CRANFIELD UNIVERSITY

Tom Bond

TREATMENT OF DISINFECTION BYPRODUCT PRECURSORS

SCHOOL OF APPLIED SCIENCES

PhD THESIS

CRANFIELD UNIVERSITY

CENTRE FOR WATER SCIENCE

DEPARTMENT OF SUSTAINABLE SYSTEMS

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TREATMENT OF DISINFECTION BYPRODUCT PRECURSORS

March 2009

Supervisor: Dr. Bruce Jefferson

This thesis is submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy.

ABSTRACT

Natural organic matter (NOM) in drinking water forms disinfection byproducts (DBPs) through reactions with disinfectants, typically chlorine. Many DBPs are harmful to human health. Potentially the most effective means of controlling DBPs is to remove NOM precursors before disinfection. However, both DBP formation and removal of precursors in natural waters are variable and unpredictable, reflecting the diverse and variable nature of NOM. To better understand the relationships between DBP formation, compound character and treatment, experiments were undertaken with a range of NOM surrogates, assessing both DBP formation and treatability. Activated aromatics, β-dicarbonyls, masked β-dicarbonyls and amino acids were indentified as reactive precursor categories. No correlations were found between compound physicochemical properties and DBP formation. This indicates reliable bulk predictors of DBP formation are unlikely to exist in natural waters. In contrast, treatability was explicable in terms of compound physicochemical properties. Levels of removal by coagulation and anion exchange were controlled by amount of anionic charge, while molecular weight and hydrophobicity also affect removal by activated carbon and nanofiltration. Advanced oxidation processes (AOPs) at high doses was able to completely mineralise all NOM surrogates, however at lower doses DBP formation can be increased, dramatically in the case of two amino acids. Biotreatment is effective in removing amino acids but can cause moderate increases in DBP levels. A DBP control strategy is outlined based on this information. Where a high proportion of DBP precursors are highly-anionic aromatic compounds, coagulation may be sufficient for DBP control. Where reactive precursors are moderately-anionic carboxylic acids, ion exchange should be considered. In waters where less-treatable NOM has a high DBP

generating capacity, activated carbon should be investigated for removal of neutral or weakly-charged aromatic precursors and a (hydrophobic) nanofiltration membrane for neutral or weakly-charged amino acids or carbohydrates.

ACKNOWLEDGEMENTS

Thanks are due to a range of people who gave advice, offered comments or helped in other ways during this thesis. Firstly, these have been my supervisors, especially Bruce Jefferson for his constructive comments during writing-up. The help of Emma Goslan, for many questions answered, and of Simon Parsons, for input at important moments, is also appreciated. Felicity Roddick was very supportive during my time in Melbourne and also offered useful comments after my return.

Then are the people who I worked with while undertaking experiments and who showed me new techniques or equipment. At Cranfield Cynthia Bougeard from the HAA Project helped on many occasions. Olivier Henriet did a highly proficient job of his MSc thesis and his hard work is much appreciated. Max Mergen showed me his method for MIEX experiments and helped out in various other ways as did Rita, Karine and others. In Melbourne, Wee Hong, David, Jonothan and Meivy all made my time in the RMIT labs much smoother, while Linhua Fan kindly did some follow-up work.

Barrie Holden and Craig Tarft of Anglian Water, Jenny Banks of Yorkshire Water, Andy Campbell of United Utilities, Julie Hart of Severn Trent Water, and Stewart Waugh of Northumbrian Water all gave useful advice, help or comments. I hope this thesis contains useful information.

Then there are those people who are appreciated for more social reasons. Principally Elisa, particularly for her efforts to keep me balanced during thesis writing. Then there are those who I spent time with during my PhD, often over a beer or two, and who made the time enjoyable. Finally, thanks to anyone else who I may have forgotten to mention by name.

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ABBREVIATIONS AND NOTATION

α – polarisability
γ – surface tension
ρ – density
·OH – hydroxyl radical
1,1,1-TCP – 1,1,1-trichloropropanone
1,1-DCP – 1,1-dichloroprpanone
AC – activated carbon
AOM – algal organic matter
AOP – advanced oxidation process
AWQC – Australian Water Quality Centre
AWWA – American Water Works Association
AwwaRF – American Water Works Association Research Foundation
BCAN – bromochloroacetonitrile
CD – constant diffusivity
CD-RSSCT – constant-diffusivity rapid small-scale column test
C_e – aqueous phase concentration of substance at equilibrium
D – carbon dose
DBAN – dibromoacetonitrile
DBNM – dibromonitromethane
DBP – disinfection byproduct
DCA – dichloroacetaldehyde
DCAA – dichloroacetic acid
DCAAFP – dichloroacetic acid formation potential
DCAN – dichloroacetonitrile
Defra – Department for Environment, Food and Rural Affairs
DOC – dissolved organic carbon
DWI – Drinking Water Inspectorate
DXAA – dihaloacetic acid
DXAAFP – dihaloacetic acid formation potential
EBCT – empty bed contact time
FAF – fulvic acid fraction
FTIR - Fourier transform infrared spectroscopy
GAC – granular activated carbon
GC-ECD – gas-chromatography electron capture detector
GC-MS – gas-chromatography mass-spectrometry
HAA – haloacetic acid
HAAFP – haloacetic acid formation potential
HAF – humic acid fraction
HPI – hydrophilic fraction
HPIA – hydrophilic acid

HPIA+N – hydrophilic acid and neutral
HPIB – hydrophilic base
HPINA – hydrophilic non-acid
HPOA – hydrophobic acid
HPLC – high performance liquid chromatography
HPON – hydrophobic neutral
IoR – index of refraction
K_F – Freundlich adsorption capacity parameter
LC – large column
log K_{OC} – log (soil-water partition coefficient)
log K_{OW} – log (octanol-water partition coefficient)
MF – microfiltration
M radius – molecular radius
MIEX® – magnetic ion exchange
MTBE – methyl tert butyl ether
MR – molar refractivity
MV – molar volume
MW – molecular weight
MWCO – molecular weight cut-off
n – Freundlich adsorption intensity parameter
N-DBP – nitrogenous disinfection byproduct
NDMA – nitrosodimethylamine
NF – nanofiltration
NF270 – NF270 membrane (Dow-Filmtec)
NF90 – NF90 membrane (Dow-Filmtec)
NOM – natural organic matter
Nr-DBP – non-regulated disinfection byproduct
PAC – powdered activated carbon
PD – proportional diffusivity
PD-RSSCT – proportional-diffusivity rapid small-scale column test
pK_a – acid dissociation constant
r – Pearson moment correlation coefficient
polyDADMAC – polydiallyldimethylammonium chloride
PSA – polar surface area
q_e – amount adsorbed per g of carbon
R – carbon particle radius
RMIT – Royal Melbourne Institute of Technology
RO – reverse osmosis
RSSCT – rapid small-scale column test
SC – small column
SHA – slightly hydrophobic acid
Sol – water solubility

SUVA – specific ultraviolet absorbance
TCA – trichloroacetaldehyde
TCNM – trichloronitromethane
THM – trihalomethane
THMFP – trihalomethane formation potential
TOC – total organic carbon
TOXFP – total organic halide formation potential
TPHA – transphilic acid
TPI –transphilic
TXAA – trihaloacetic acid
TXAAFP – trihaloacetic acid formation potential
UF – ultrfiltration
UP – ultrapure
USEPA –United States Environmental Protection Agency
UV/H_2O_2 – ultraviolet/hydrogen peroxide
UV_{254} – ultraviolet (254 nm) absorbance
UV-C – ultraviolet-C irradiation
VHA – very hydrophobic acid
VUV – vacuum ultraviolet
WTW – water treatment works

CHAPTER 1: INTRODUCTION

INTRODUCTION

1.1 Background

Disinfection byproducts (DBPs) are an unwanted result of reactions between organic matter and disinfectants during potable water production. Since chlorine is the most commonly used disinfectant in water treatment (*1*), chlorinated DBPs have received most research attention. Two groups – the trihalomethanes (THMs) and haloacetic acids (HAAs) – are considered to be the dominant DBPs on a mass basis in drinking water (*2*). Many DBPs are known or suspected mutagens or carcinogens (*3*). The THMs were the first DBPs to be identified in drinking water (*4*), and have been regulated since 1979 in the USA to limit the risk they pose to human health. Since 1998 the HAAs have also been regulated, and current consents in the USA are 80 and 60 µg L^{-1} for the THMs and HAAs respectively (*5*). The THMs are also regulated in the UK at 100 µg L^{-1}, and the drinking water inspectorate (DWI) have been investigating the effect that implementing a HAA standard would have in the UK (*6*).

As a result the UK water industry has been actively exploring HAA levels present within drinking water throughout the country and possible control strategies. As an antecedent to this project Cranfield University carried out a wide-ranging survey of HAA and THM levels present in a variety of UK water treatment works (WTWs) (*7*). It was found not only were DBP levels unpredictable and variable, but further that wide seasonal fluctuations could occur at the same site. As a consequence five water companies – Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water – decided to fund a follow-up study in which HAA formation chemistry and mitigation strategies were to be investigated in more detail. This is one of

the two resulting PhD projects, the other being Cynthia Bougeard's thesis on *Haloacetic Acids and other Disinfection By-Products in UK Treated Waters: Occurrence, Formation and Precursor Investigation*. Thus the focus of this thesis was to be treatment of HAA precursors: a comparison of technologies to assess their utility for precursor removal. Literature shows both DBP formation and removal in natural waters to be unpredictable; features related to the complex, variable and incompletely resolved identity of aqueous natural organic matter (NOM). Moreover, while model compounds have an established history in DBP formation studies (*8*), their use to simulate NOM in water treatment work is more limited. Hence, any relationships between compound physicochemical properties, DBP formation and treatability are incompletely understood. Because of this uncertainty it was decided to represent NOM with model compounds for both treatment and DBP formation studies. It was anticipated this approach would bridge a knowledge gap between these areas (Figure 1.1). Soon it became apparent that it was impracticable to study HAA precursors in isolation from precursors of other DBP groups. This was because the same precursor molecule can produce not only HAAs, but also THMs and other DBP groups upon chlorination. Furthermore, due to limited knowledge of precursor identity in natural water, control strategies for one DBP group are often applicable to others.

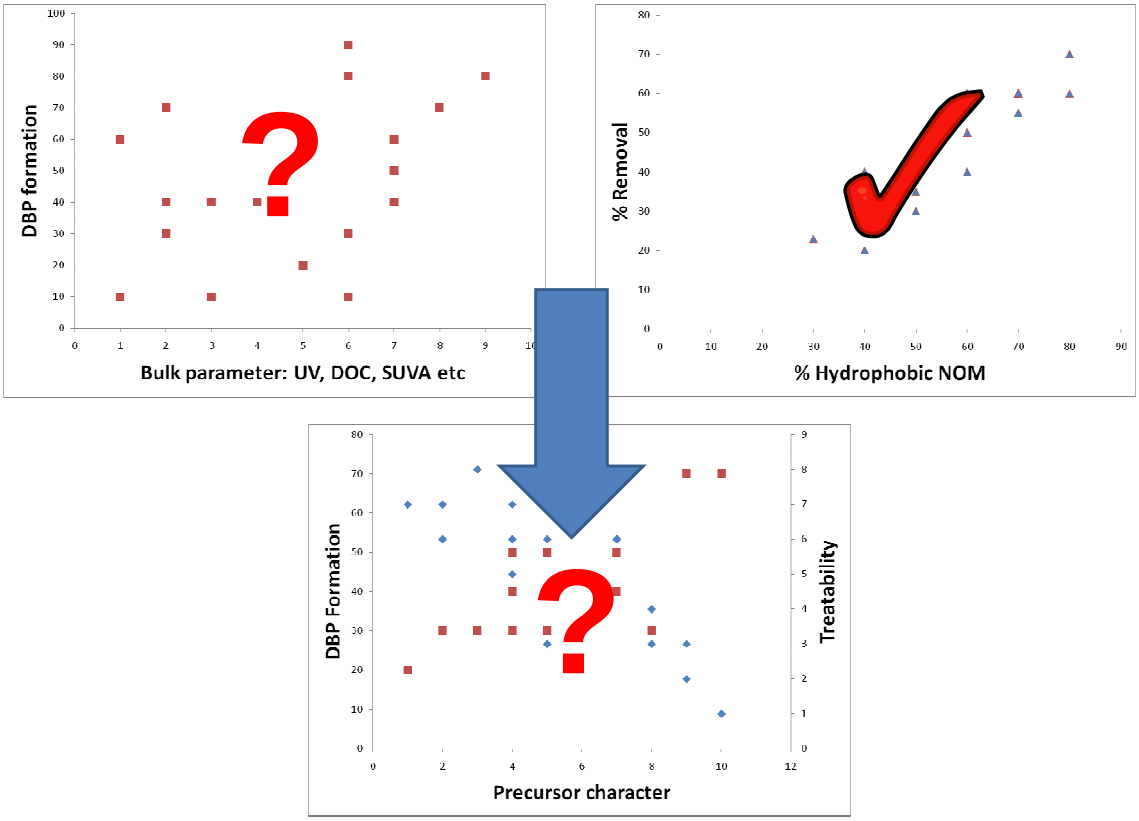

Figure 1.1: Schematic representation of project objectives

1.2 Objectives

It was hypothesised that relationships between compound physicochemical properties, treatability and DBP formation could be probed by use of NOM surrogates. Accordingly the main objectives of this thesis were as follows:

(1) To identify relationships between physicochemical properties of NOM and removal by major classes of water treatment process

(2) To determine the identity of important DBP precursors and whether they can be measured in drinking water

(3) To determine links between physicochemical properties of NOM and DBP formation

(4) To determine whether DBP precursors can be selectively removed from drinking water through knowledge of their physicochemical properties

(5) To recommend appropriate strategies for removal of DBP precursors

1.3 Thesis Structure

This thesis takes the form of a series of chapters formatted as papers for publication. All papers were written by the first author, Tom Bond and have been edited by Dr Bruce Jefferson. Chapter 6 comes from a placement at the Royal Melbourne Institute of Technology (RMIT), with the remaining experiments at Cranfield University. All experimental work was undertaken by Tom Bond with the following exceptions. Chapter 4: fractionation experiments, HAA formation potential (HAAFP) and THM formation potential (THMFP) tests carried out by Olivier Henriet as part of his MSc thesis. Chapter 6: preparation of UV-C and UV/H_2O_2 treated samples for HAAFP

testing at the Australian Water Quality Centre (AWQC) carried out by Dr Linhua Fan at the RMIT. Chapter 5: MIEX® experiments for five compounds carried out by Max Mergen. Chapter 7: fractionation of two natural waters undertaken by Cynthia Bougeard.

The focus of Chapter 2 is the relationships between NOM and DBP formation. It comprises a review of literature from over 30 years of investigation into formation of DBPs during water treatment, with particular focus on NOM surrogates: *Disinfection Byproduct Formation from Natural Organic Matter* by T. Bond, E.H. Goslan, S.A. Parsons and B. Jefferson, submitted to *Chemical Reviews*. Model compound properties and THM formation data were collated to ascertain whether any correlations existed between compound physicochemical properties and THM formation. Additionally, DBP formation from model compounds and natural waters was analysed to identify reactive precursors found in aqueous systems.

Chapter 3 examines the links between character of NOM and its susceptibility to removal by different treatment processes. Literature data regarding removal of NOM and DBP precursors by the main categories of water treatment process were examined mechanistically. The chapter, entitled *Treatment of Disinfection Byproduct Precursors* by T. Bond, E.H. Goslan, S.A. Parsons and B. Jefferson, has been submitted to the journal *Environmental Technology*. In order to complement Chapter 2, the treatability of different chemical groups in NOM was assessed, to determine circumstances in which various treatments are most effective for precursor removal.

In Chapter 4, *Disinfection Byproduct Formation and Fractionation Behaviour of Natural Organic Matter Surrogates* by T. Bond, O. Henriet, E.H. Goslan, S.A. Parsons

and B. Jefferson, has been submitted to the journal *Environmental Science and Technology*. To provide direct linkage between model compound and drinking water studies, a diverse range of model compounds were fractionated using standard drinking water characterisation methodology. The formation of HAAs, THMs and non-regulated DBPs including haloketones, haloacetonitriles and haloacetaldehydes from the same surrogates was measured, many for the first time. To quantify relationships amongst and between compound physicochemical properties and DBP formation, correlations were computed.

The treatment of model compounds representative of species found in drinking water is studied in the following three chapters. Chapter 5, *Disinfection Byproduct Formation of Natural Organic Matter Surrogates and Treatment by Coagulation, MIEX® and Nanofiltration* by T. Bond, E.H. Goslan, S.A. Parsons and B. Jefferson, has been submitted to the journal *Water Research.* The chapter compares treatment of surrogates by coagulation, the standard water treatment process, MIEX® a novel anion exchange treatment, and two nanofiltration (NF) membranes. Results are discussed with reference to precursor control strategies.

Chapter 6 is *Chemical and Biological Oxidation of NOM surrogates and effect on HAA Formation* by T. Bond, E.H. Goslan, B. Jefferson, F. Roddick, L. Fan, and S.A. Parsons is in press in the journal *Water Research*. It is a comparison of biodegradation, ultraviolet (UV) irradiation and two advanced oxidation processes (AOPs): vacuum UV (VUV) and UV/H_2O_2 for NOM treatment. Formation of HAAs before and after treatment was measured to monitor the efficacy of these treatments for precursor removal.

The final research chapter, *Granular Activated Carbon for the Treatment of Disinfection Byproduct Precursors* by T. Bond, C.M.M. Bougeard, E.H. Goslan, S.A. Parsons and B. Jefferson has been submitted to the journal *Chemosphere*. It examines activated carbon for removal of precursor material by comparing isotherm tests carried out with NOM surrogates and two natural waters with rapid small-scale tests (RSSCTs) using the natural waters. In this way the success of the process for precursor removal is analysed with reference to the physicochemical properties of NOM.

Within Chapter 8, *Discussion: Implications for Drinking Water Production* the objectives of this study are presented as questions and answered to highlight findings and recommendations relevant for water treatment.

Finally, *Conclusions and Future Work*, Chapter 9, lists the key results of the study and makes recommendations how future investigations can expand current knowledge of DBP precursor treatment.

Table 1.1: Thesis Structure

Chapter	Objective/s addressed	Focus	Journal	Status
2	2, 3	Literature DBP formation	*Chemical Reviews*	Submitted
3	1, 4, 5	Literature DBP precursor treatment	*Environmental Technology*	Submitted
4	2, 3	DBP formation and fractionation behaviour of NOM surrogates	*Environmental Science and Technology*	In press
5	1, 4, 5	Coagulation, MIEX®, nanofiltration	*Water Research*	Submitted
6	1, 4, 5	AOPs, UV treatment, biodegradation	*Water Research*	Published
7	1, 4, 5	Precursor removal by activated carbon	*Chemosphere*	Submitted
8	1, 2, 3, 4, 5	Implications for water treatment		

Conference Papers

Bond, T., Goslan, E., Jefferson, B., Roddick, F. and Parsons, S.A., *Model compounds to elucidate natural organic matter treatability and haloacetic acid formation*, IWA NOM: from Source to Tap conference, September 2008, Bath, UK.

Bond, T., Goslan, E., Jefferson, B., Roddick, F. and Parsons, S.A., *Removal of HAA precursors*, Emerging Issues in Disinfection Byproducts conference, April 2008, Cranfield University, UK

1.4 References

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(4) Rook, J. J. Formation of halogens during the chlorination of natural water. *Water Treatment and Examination*, **1974,** 23, 234-243.

(5) USEPA. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule, 2006, available at: http://www.epa.gov/fedrgstr/EPA-WATER/2006/January/Day-04/w03.pdf (accessed June/08).

(6) Defra/DWI; Jackson, P.; Hall, T.; Young, W.; Rumsby, P. *A Review of Different National Approaches to the Regulation of THMs in Drinking Water*; Report Defra7831, WRc plc.: Swindon, 2008.

(7) Goslan, E. H.; Parsons, S. A. *Survey of the Disinfection By-Product Formation Potential of UK Waters*; Cranfield University: UK, 2006.

(8) Dickenson, E. R.; Summers, R. S.; Croué, J.-P.; Gallard. H. Haloacetic acid and trihalomethane formation from the chlorination and bromination of aliphatic β-dicarbonyl acid model compounds. *Environ. Sci. Technol.* **2008**, 42, 3226

CHAPTER 2: FORMATION OF HALOGENATED DISINFECTION BYPRODUCTS FROM NATURAL ORGANIC MATTER SURROGATES

CHAPTER 2: FORMATION OF HALOGENATED DISINFECTION BYPRODUCTS FROM NATURAL ORGANIC MATTER SURROGATES

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2.1 Abstract

Disinfection byproducts (DBPs) in drinking water, including trihalomethanes (THMs) and haloacetic acids (HAAs), arise from reactions of natural organic matter with chlorine. While formation of THMs correlates strongly with chlorine substitution, no meaningful relationships exist between compound physicochemical properties and DBP formation. Thus reliable predictors of DBP formation are unlikely in natural waters. Activated aromatic compounds are known to be reactive precursors, in addition DBP formation from β-dicarbonyl, amino acid and carbohydrate precursors can be significant. Therefore effective DBP control strategies need to encompass both hydrophobic and hydrophilic NOM components.

2.2 Introduction

The main reason for water disinfection is to prevent the spread of waterborne disease through the inactivation of microbial pathogens. Partly due to its low cost chlorine is the commonest chemical disinfectant used in the production of drinking water (*1*). Another

beneficial feature is its stability, which means a disinfectant residual is maintained in the distribution system, thus preventing bacterial re-growth. In addition to its activity as a disinfectant chlorine also reacts with organic and inorganic molecules present in water. Reactions with organic molecules can give rise to disinfection byproducts (DBPs), many of which are harmful or potentially harmful to human health (*2)*.

The earliest published identification of disinfection byproducts in potable water came in 1974 (*3)*. Prior to this time, although it was appreciated that reactions of chlorine with organic material could produce chlorinated products, their identification was stymied by an absence of analytical methods. By the early 1970s headspace gas chromatography (GC) was being utilised for the analysis of trihalomethanes (THMs), particularly chloroform (*4)*. These techniques were used to demonstrate the link between amount of organic material in water (as measured by colour) and levels of chloroform formed upon chlorination (*3)*. This breakthrough prompted the US Environmental Protection Agency (USEPA) to initiate a survey of four THMs and two other volatile organic chemicals in 80 waters across the country. THMs were detected in all 79 tap waters where chlorine or chloramine was the practised disinfectant (*5*). Soon after the USEPA began investigating the health impact of THMs and reported chloroform could act as a carcinogen in animal studies (*6)*.

From this point onwards there has been much research dedicated to elucidating the formation, control and health risks of DBPs. With growing interest and analytical sophistication has come the realisation that many different products can arise from the reactions between organics and chemical disinfectants. Hence, the focus has moved from solely THMs to incorporate other classes of DBPs. By 1980 it was appreciated that another group of DBPs, the haloacetic acids (HAAs) could occur in drinking water at

levels similar to, or above those of THMs (*7).* In 1987, analysis of treated water from ten utilities in the USA found 196 compounds thought to be produced from chlorination (*8*). In addition to THMs and HAAs those DBPs present in significant amounts included haloacetonitriles, haloaldehydes, haloketones and halonitromethanes (Table 2.1).

Water providers have several available routes to minimise DBP formation. Altering disinfection practice or position or removing DBP precursors before disinfection have received most attention. At the same time the risk from DBPs has to be balanced against that arising from microbial infection due to incomplete disinfection. However, even allowing for this caution it is likely that DBP regulations will in the future become more stringent and encompass additional DBPs as the health risk becomes less ambiguous (Table 2.2). More recently it has been appreciated that non-chlorine disinfectants produce their own DBPs. In total some 600-700 DBPs have been reported not only for chlorine but also for alternative disinfectants such as chloramine, ozone and chlorine dioxide (*9).* Yet of this total only a small percentage have been quantified in drinking water. N-Nitrosodimethylamine (NDMA) is one DBP of particular current concern and is suspected of being a human carcinogen (*10).* It follows that the identity of formed DBPs is affected by the disinfectant used, disinfection conditions and nature of precursors present in any water. Of all the identified DBPs, the THMs and HAAs are still considered to be the dominant groups on a weight basis in potable water (*9).*

NOM is an ill-defined mixture of many chemical groups that varies both temporally and spatially (*11, 12).* A consequence of this variability is that specific DBP precursor identity in natural waters is limited. The major chemical groups in NOM are listed as humic species, carboxylic acids, amino acids, proteins and carbohydrates (*13),* though other chemicals may also be present. While most NOM is of autochtonous (derived

from biota in water) or allochthonous (from the terrestrial watershed) origin, characterisation is typically achieved by fractionation into categories grouped by hydrophobicity (*13)*. These techniques employ adsorption columns (with ion-exchange or non-ionic resins) to isolate NOM into operationally-defined fractions. Humic acids are contained within the hydrophobic fractions, while carbohydrates, amino acids and carboxylic acids comprise much of the hydrophilic material (Figure 2.1, Table 2.3). Furthermore, terrestrial NOM is commonly lignin-derived and with high aromatic content, whereas microbial derived substances (from algae and bacteria) tend to have low aromatic and high nitrogen content (*14)*. Hence allochthonous NOM is often described as humic or non-polar and tends to be hydrophobic in character (*15)*, whereas autochtonous NOM is often termed non-humic or polar and tends to be more hydrophilic. Thus catchment characteristics affect both fractional and chemical composition of NOM. Since NOM classification rarely extends to a molecular level, there is uncertainty about identity of reactive DBP precursors in drinking water.

Model compounds have been used as surrogates of NOM since the early days of DBP research (*16)*. They allow for more specific investigation of formation mechanisms and kinetics than the use of natural waters. Further, and in contrast to NOM, model compounds have well-defined physicochemical properties. In general most important DBP precursors identified have been aromatic compounds and in this respect the recent discovery that several aliphatic β-dicarbonyl acid species generate high amounts of THMs and HAAs was notable (*17)*. Most work has studied THM formation, with limited studies examining HAAs or other DBP groups. Important DBP precursors identified from over thirty years of DBP research are shown in Table 2.4.

The objectives of this review were to investigate relationships between the identity and properties of NOM and DBP formation and further to highlight the prevalence of different NOM classes as DBP precursors. This approach entailed complementary use of literature model compound and drinking water data. Correlations between model compound physicochemical properties and DBP formation are discussed with regard to drinking water studies.

Table 2.1: Important DBPs

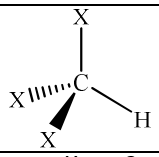
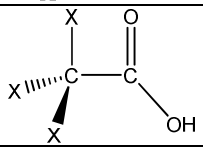
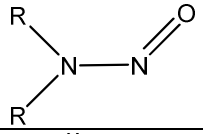
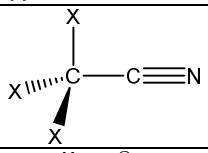
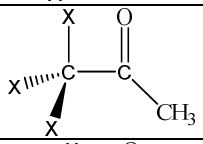
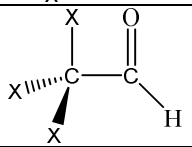
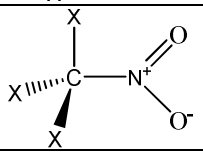
Class	Structure	Important DBPs
Trihalomethanes (THMs)		Chloroform ($CHCl_3$) Bromoform ($CHBr_3$)
Haloacetic acids (HAAs)		Dichloroacetic acid (DCAA) Trichloroacetic acid (TCAA)
Nitrosamines		N-Nitrosodimethylamine (NDMA) N-nitrosodiethylamine (NDEA)
Haloacetonitriles (HANs)		Dichloroacetonitrile (DCAN) Trichloroacetonitrile (TCAN)
Haloketones		
Haloaldehydes		Dichloroacetaldehyde (DCA) Trichloroacetaldehyde (TCA)
Halonitromethanes		Trichloronitromethane (TCNM)

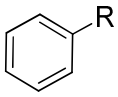
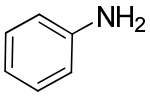
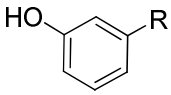
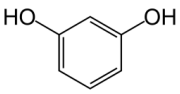
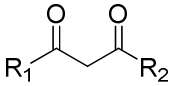
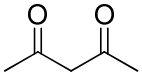
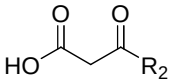
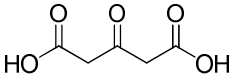
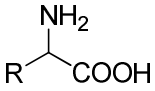
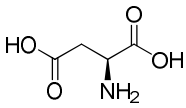
Table 2.2: Milestones in DBP History

Year	Milestone	Reference
1974	Chlorination of organic matter in drinking water linked to chloroform formation	3
1975	USEPA survey of THMs in drinking water across USA	5
1976	National Cancer Institute classify chloroform as suspected human carcinogen	
1976	USEPA investigation into health impact of THMs	
1977	THMFP test developed	A
1979	HAAs indentified in drinking water at levels similar to THMs	7
1979	THMs regulated at 100 $\mu g.L^{-1}$ by USEPA	
1986	DCAA and TCAA linked to liver tumours in mice and rats	B
1989	UK regulations: THMs 100 $\mu g.L^{-1}$	
1990	196 chlorination products identified in treated waters	8
1993	WHO Guidelines: DCAA 50 $\mu g.L^{-1}$, TCAA 100 $\mu g.L^{-1}$	
1998	First stage of USEPA D/DBP rule: THMs 80 $\mu g.L^{-1}$, HAA_5 60 $\mu g.L^{-1}$, based on annual average	
2006	600-700 DBPs reported for chlorine, chloramines, ozone and chlorine dioxide	9
2006	Second stage of USEPA D/DBP rule: THMs 80 $\mu g.L^{-1}$, HAA_5 60 $\mu g.L^{-1}$, based on locational running annual average (LRAA)	

Table 2.3: Chemical Composition of NOM and Significance for DBP Formation (adapted from Croué, 2000)

Chemical group	Impact on DBP formation		Additional references
	THM formation	HAA formation	
Humic species	Primary source	Primary source	23
Carbohydrates	Important at pH 8	Probably minor	30
Amino acids	Minor (except for tryptophan and tyrosine)	Important for : aspartic acid, histidine, asparagine, tryptophan	21, 31
Proteins	Important during algal blooms	Not known, may be significant	21, 27
Carboxylic acids	β-dicarbonyl acids important precursors	β-dicarbonyl acids important precursors	17

Table 2.4: Important DBP Precursors

Chemical group		**Model compound**			**Reference**
Name	**Structure**	**Name**	**Structure**	**DBPFP (µg mgC^{-1})**	
Aromatic					
Substituted benzene		Aniline		THM: 400	18
Substituted phenol		Resorcinol		THM: 1456	23
Aliphatic					
β-diketone		2,4-pentanedione		THM: 1892	24
β-ketoacid		3-oxopentanedioic acid		THM: 1414 HAA: 1500	17
Amino acid		L-aspartic acid		HAA: 387	31

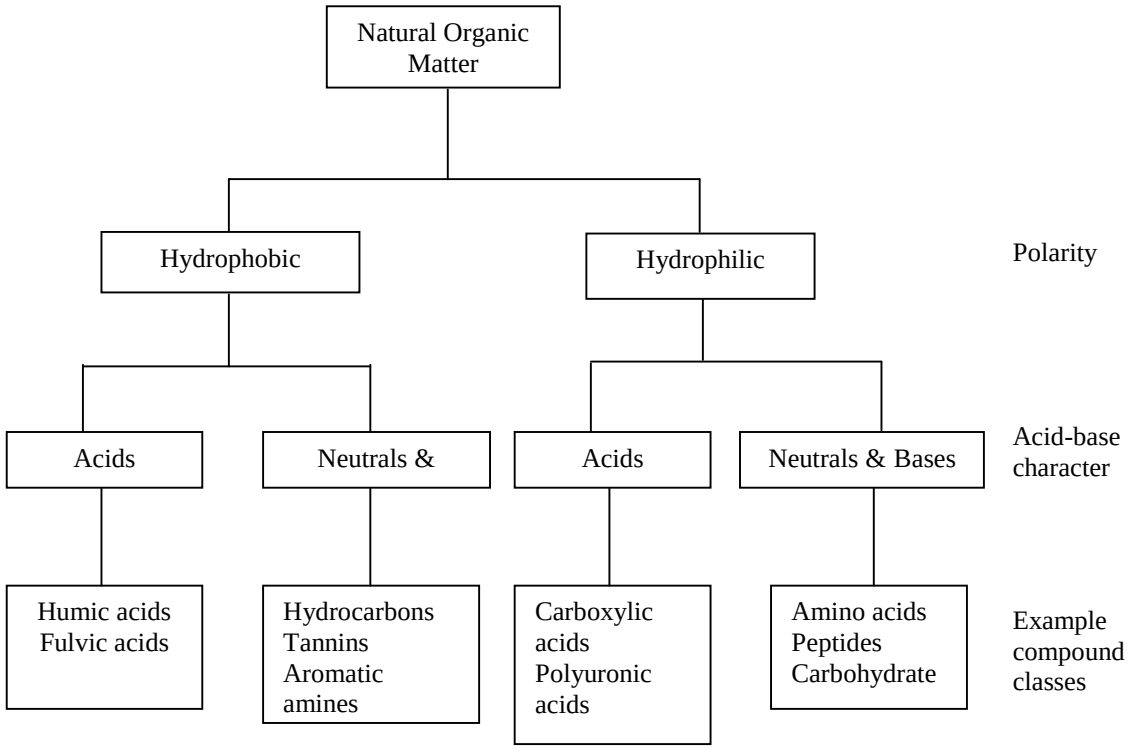


Figure 2.1: Classification of NOM (based on Leenheer and Croué, 2003)

2.3 Methods

To elucidate relationships between THM formation and compound physicochemical properties correlations were calculated for 176 compounds taken from 15 studies (*17-30)*. For 9 compounds THM data appears in multiple studies, where available the value recorded at pH 7 was included; if THMFP was recorded under similar conditions in multiple studies, the mean was taken. All THM data was converted in to units of µg mgC^{-1} to facilitate data comparison. HAA data for a subset of 26 compounds was available (*17, 19, 31)*, with DCAA data only for the latter study (*31)*. Properties collated were: chlorine demand, molecular weight (MW), octanol-water partition coefficient (log K_{OW}), pKa, molar volume (MV), surface tension (γ), polar surface area (PSA), polarizability (α), density, soil-water partition coefficient (log K_{OC}) and aqueous hydroxyl rate constant ($k_{\cdot OH}$). Chlorine substitution efficiency (% mol Cl substituted in THMs/mol Cl_2 consumed) was determined from THMFP and chlorine demand data where available. log K_{OC} values were estimated using two different models: the Sabljic molecular connectivity method with improved correction factors; and the traditional method based on log K_{OW} (*32)*. Remaining properties were taken from various chemical databases (*32-36)*, with experimental values were used wherever available. Relationships were evaluated using the Pearson product-moment correlation coefficient (r) calculated with Minitab 15™. This coefficient is a dimensionless index used to measure the degree of linear relationship between two variables, and assumes a value between −1 and +1.

2.4 Factors Affecting DBP Formation

Traditionally there has been a perception that humic substances are the major source of DBP precursor sites (*37)*. This partly stems from the early studies of THM formation from aromatic structures, notably resorcinol (*16)* and the preponderance of aromatics used in model compound studies. More recently this perception has been weakened due to the high DBP formation being found from aliphatic model compounds, notably high DCAA formation from a small number of amino acids (*31)* and high THM and DCAA formation from β-dicarbonyl acids (*17)*. Similarly, significant DBP formation has been reported from hydrophilic fractions of natural waters (*13, 16)*. To illustrate this point, $CHCl_3$ formation from the hydrophobic neutral (HPON), hydrophobic acid (HPOA), hydrophilic acid (HPIA) and hydrophilic base (HPIB) fractions of the Suwannee River (USA) were observed to be 51, 55, 36 and 29 µg mgC^{-1} (*13)*. There are conflicting reports about the identity of THM and HAA precursors in natural waters. For example one study concluded that HAA precursors have a higher aromatic content than THM precursors (*38)*. Supporting this, it has been suggested that hydrophilic NOM is a more significant precursor of THMs than HAAs (*12)*. Conversely, other research proposes that the hydrophilic fraction produces a higher proportion of HAAs relative to THMs than the hydrophobic fraction (*16, 39)*. It has been proposed that waters which produce high THM levels may also have a propensity to generate trichloroacetic acid (TCAA), and further that dichloroacetic acid (DCAA) precursors are overall less hydrophobic than TCAA precursors (*38),* which correlates with high DCAA formation from aliphatic model compounds (*17, 31)*. It is proposed that DCAA and TCAA may be produced as a result of differing mechanistic pathways (*40)*. Raised DCAA levels have been linked to the presence of diketones then aldehydes after oxidation (*28)*. Conversely TCAA

formation has been likened to THM formation and may proceed through common intermediates (*28).*

Changes in chlorine dose can affect the identity of formed DBPs. In general an increase in chlorine dose will shift DBP speciation to the less brominated-species (*41).* Further, it has been observed that with an increase in chlorine dose the levels of TCAA increased more than DCAA (*28*) and that high doses favour HAA formation over THM formation (*42*). A decrease in formation of 1,1,1-trichloroacetaldehyde (TCA) and dichloroacetonitrile (DCAN) at higher chlorine doses (*28*) may reflect the subsequent formation of $CHCl_3$ and DCAA respectively from these intermediate DBPs (*40, 43*).

In general, the presence of bromide (Br^-) increases levels of halogenated DBPs. The active species regarding DBP formation is hypobromous acid (HOBr), which is formed from oxidation of bromide by hypochlorous acid. Hypobromous acid is a more efficient substitution agent than hypochlorous acid. For example THM formation from glucose chlorination increased by 100% in the presence of 300 µg L^{-1} bromide, relative to no bromide, from 44 to 89 µg mgC^{-1} (*30*). While at bromide concentrations under 100 $\mu g.L^{-1}$, complete incorporation of bromide into THMs was observed during carbohydrate chlorination (*30*). Similarly in natural water studies, it has been observed that 5-10% of HOCl typically became incorporated into THMs, while bromine incorporation levels were higher at around 50% (*44*). The higher reactivity of bromine than chlorine in HAA formation has also been reported (*45).* The reactivity of HOBr becomes more significant in high bromide waters. Concentrations of up to 450 $\mu g.L^{-1}$ are not unusual in surface waters (*46),* while much higher levels are possible, for instance 2500 $\mu g.L^{-1}$ in a Greek river (*47).* In high bromide waters it is typical for mixed chlorinated-brominated DBPs to be the commonest species formed. With respect to

DBP control, since regulations are reported on a mass basis, not only is the higher reactivity of bromine than chlorine a problem, but also its higher mass, at 2.25 times heavier than chlorine. However, it has been reported that with high chlorine doses, as in laboratory THMFP tests, the excess chlorine can "out compete" bromine (*48*), with bromine incorporation in THMs found to decrease with an increase in the Cl/Br ratio (*41).*

The effect of pH on DBP formation is complicated and can favour formation of certain products over others (Table 2.5). Generally any effects occur because acidic or basic conditions increase the speed of a rate-determining reaction step. The higher THM formation from carbohydrates at pH 8 compared with pH 5 has been explained by basic conditions promoting the rate-determining hydrolysis of the halogenated leaving group (Figure 2.3). For DCAA, the effect of pH is contradictory (Table 2.5), with an increase in pH having been variously reported to increase and have no impact on its formation in natural waters (Table 2.5), while for 3-oxopentanedioic acid an increase was found with a fall in pH from 8 to pH 5.5 (Table 2.5). In natural waters higher pH levels have been reported to increase THM levels, have no effect on DCAA levels and decrease TCAA levels (Table 2.5). These differences may be explained by THM and TCAA precursors being similar (*40*) and higher pH levels favouring base-catalysed hydrolysis of the halogenated leaving group. This route produces chloroform, while electron-pair donation gives rise to TCAA formation (Figure 2.2). Both mechanisms are possible in postulated models (*16, 28).* The instability of DCAN and 1,1,1-trichloropropanone (TCP) at pH 7 and 8 (Table 2.5) is likely to translate to increased DCAA and $CHCl_3$ formation respectively from these intermediate DBPs (*40, 43).*

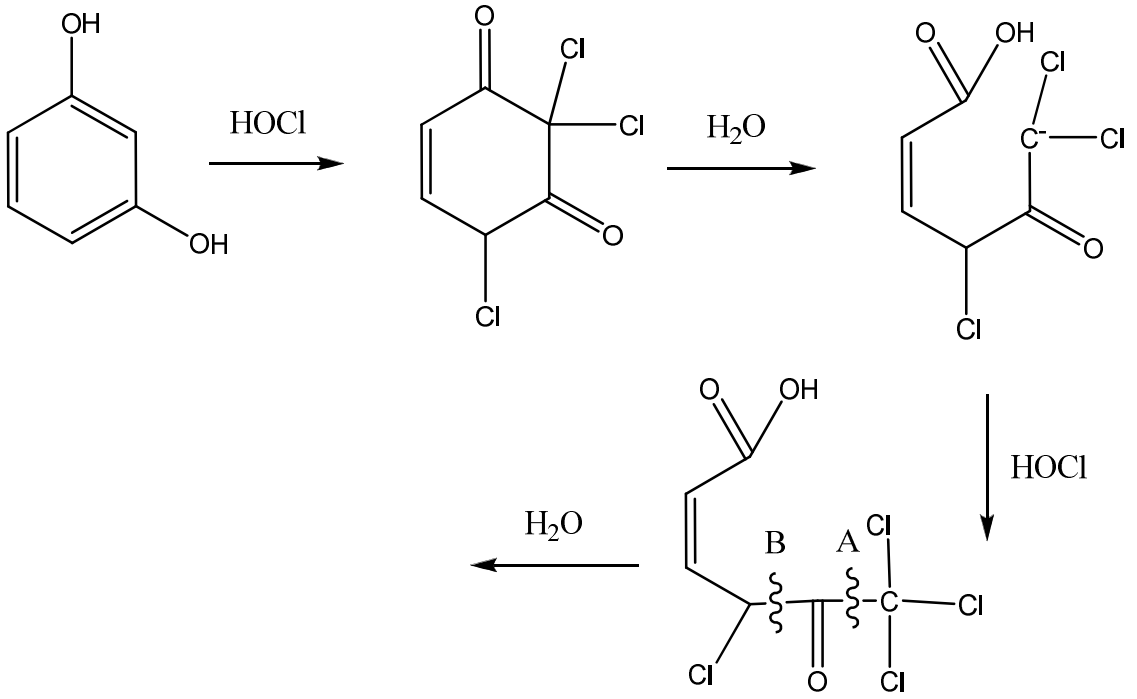


Figure 2.2: Chlorination of resorcinol. Cleavage at A will result in the production of $CHCl_3$ and cleavage at B will form TCAA (adapted from Rook, 1977)

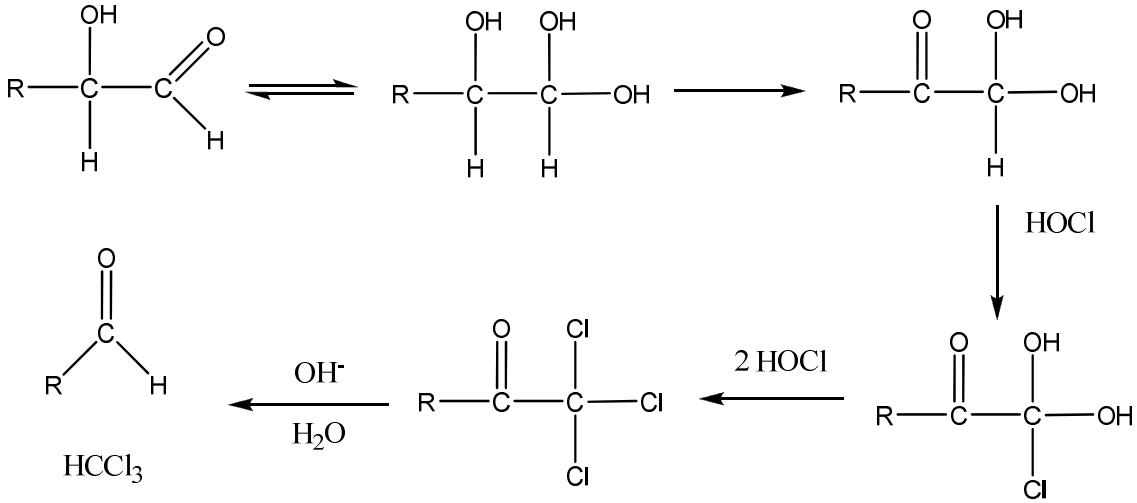


Figure 2.3: Chlorination of carbohydrates. Based on Navalon et al., 2008

Table 2.5: Effect of pH on DBP Formation

Precursor	DBP/s	Effect	Reference/s
3-oxopentanedioic acid	DCAA	Increase from pH 8 to pH 5.5	17
Citric acid	THMs	High levels at pH 7. compared with pH 5.5, 8 and 9.3	17, 22, 26
Amino acids	DCAN/ DCAA	Increase in hydrolysis of DCAN to DCAA at alkaline pH	43, 71
Amino acids	TCA	Increase from pH 7 to 8	64
Natural water	THMs	Increase at pH 9.4	C
Natural water	TCAA	Decrease at pH 9.4	C
Natural water	DCAA	No significant change with pH	C
Natural water	DCAN	Higher formation at pH 5	C
Natural water	TCA	Higher formation at pH 5	C
Natural water	DCAA	Increase at higher pH	47
Natural water	TCAA	Decrease at higher pH	47
Carbohydrates	THMs	Increase from pH 5 to pH 8	17
Natural water	TCP, DCAN	TCP and DCAN unstable at pH 7 and 8, stable at pH 6	69
Natural water	TCAA	Decrease at higher pH	69
Natural water	DCAA	Insensitive to pH	69

2.5 Chlorination of NOM

While chlorine is dosed as a gas or as sodium hypochlorite, it is hypochlorous acid (HOCl) which is the major reactive form during water treatment. Since hypochlorous acid is an electrophile it tends to react with electron-rich moieties in NOM. Oxidation, addition and electrophilic substitution reactions are all possible pathways. Normally only electrophilic attack is significant in reactions with organics, based on kinetic analysis (*49)*. Second order rate constants for reactions of chlorine and organics vary widely, from 0.1 – 10^9 $M^{-1}s^{-1}$ (*49)* and chlorine reacts selectively with certain chemical functionalities. Amines, reduced sulphur moieties and activated aromatic functionalities are all highly reactive towards chlorine and have rate constants towards the upper end of the range listed, for example the apparent rate constant for the reaction between chlorine and the amino acid cysteine is ~6.2 x10^7 at pH 7, due to the reactivity of a sulphur-containing side group (*50)*. Hypochlorous acid also reacts rapidly with amines to produce chloramines. For the less reactive moieties, reactions with chlorine can be too slow to impact during the time span of water disinfection. For instance, reactions of HOCl with alkenes are typically too slow to be relevant during water treatment, as illustrated by the negligible apparent rate constant for reaction with the steroid progesterone (*51)*. The speed of chlorine addition to alkenes can increase if the double bond is activated by electron-donor groups. Similarly reactions with alcohols are very slow e.g., the apparent rate constant of ~0 at pH 7 for reaction with the monosaccharide ribose, but can lead to oxidation to ketones and aldehydes (*52)*. Likely reaction sites can be predicted based on the following order of reactivity, bearing in mind nearby electron-donor or –withdrawing groups will also have an effect: reduced sulphur groups >

primary and secondary amines > phenols, tertiary amines >> double bonds, other aromatics, carbonyls, amides (*49).*

2.5.1 Chlorination of Humic Substances

Humic substances, including humic and fulvic acids are major constituents of soil organic matter humus. They are generally derived from terrestrial vegetation and have high lignin content. Since lignin is aromatic, humic substances also tend to be aromatic in character (*53*). This aromaticity confers high UV absorption and often colour, and the ability form supramolecular aggregates. Much of the hydrophobic fraction of NOM is comprised of humic substances. This fraction/s typically comprises around 50% of the NOM of an average river (*54*) and up to 76% for a moorland catchment (*55).*

Chlorine reacts with aromatic compounds by electrophilic substitution. In the presence of an electron-donating and ortho-para directing group, for example phenol, stepwise chlorination occurs at the 2, 4, and 6 positions respectively, to give THM formation of 154 µg mgC^{-1} (Table 2.6). The major reactive sites within fulvic acids are reported to be the carbon between two hydroxyl groups or one hydroxyl and one O-glucoside group (*16*), with resorcinol being the most important THM precursor at 1410 µg mgC^{-1} (Table 2.6). Boyce and Hornig (*29)* proposed a reaction mechanism for resorcinol whereby electrophilic substitution of chlorine and a complex series of hydrolysis and decarboxylation reactions lead to chloroform formation. A simplified version is shown in Figure 2.2. Resorcinol-type structures were classified as fast-reacting THM precursors, while more slowly reacting THM precursors may consist of phenolic compounds (*56).* This is also seen by comparison of rate constants for reaction with chlorine: 0.36 and ~4 x 10^3 M^{-1} s^{-1} for phenol and resorcinol respectively (*56, 59).* Resorcinol structures are thought to be commonly contained within macromolecular

humic species found in natural waters (*58)*. However, there is still limited information about the concentration they and similar compounds reach in drinking water. The reactivity of aromatic compounds can be explained in terms of the electron-donating or electron-withdrawing influence of substituents (*49)*. The high reactivity of resorcinol is thus ascribable to having two activating ortho-para hydroxyl groups in the one and three positions.

Table 2.6: THMFP, HAAFP and properties of model compounds

Model compound	THMFP ***HAAFP***	Cl_2 demand	$logK_{OW}$	pKa_1	MW	MV	γ	PSA	α	Density	log K_{OC}	$k_{\cdot OH}$
	µg mgC^{-1}	mol/mol			Da	cm^3	dyne/cm	$Å^2$	10^{-24} cm^3	g/cm^3		10^{-8} $molL^{-1}s^{-1}$
1,2,3-trihydroxy-benzene	2	6.9	0.97	9.0	126	84.7	78.6	60.69	12.64	1.488	n.a	n.a
1,2,4-trihydroxy-benzene	257	3.9	0.55	n.a.	126	84.7	78.6	27.69	12.64	1.488	n.a	n.a
1,2-dihydroxybenzene	7	4.1	0.88	9.5	110	86.2	57.1	40.46	11.89	1.275	2.65	n.a
1,3,5-trihydroxy-benzene	1544	9.1	0.16	8.5	126	84.7	78.6	27.69	12.64	1.488	2.85	n.a
1,3-dihydroxy-4-chloro-benzene	1627	6.1	1.80	n.a.	145	98.2	59.7	18.46	13.83	1.471	n.a	n.a
1,3-dimethoxy-benzene	0	n.a.	2.21	n.a	138	137.4	29.6	18.46	15.70	1.005	1.93	72
1,3-propanedioic acid	2	1.6	-0.81	2.9	104	67.3	70.5	52.60	7.56	1.546	0.53	n.a
1,4-dihydroxy-benzene	7	3.3	0.59	10.9	110	86.2	57.1	18.46	11.89	1.275	2.64	n.a
1-hydroxy-3-methoxybenzen	142	n.a.	1.34	9.7	124	111.8	38.6	18.46	13.80	1.109	n.a	n.a
1-naphthol	14	7.2	2.85	9.3	144	121.9	51.0	9.23	18.22	1.181	n.a	130
2,3,6-trichloro-phenol	657	6.9	3.77	5.8	197	123.7	50.5	9.23	16.97	1.596	3.08	n.a
2,3-dichloro-phenol	596	8.0	2.84	7.7	163	111.7	47.8	9.23	15.03	1.450	2.86	n.a
2,4,6-trichloro-phenol	58	6.8	3.69	6.2	198	123.7	50.5	20.23	16.97	1.596	3.07	120
2,4-dichloro-phenol	78	8.1	2.92	7.9	163	111.7	47.8	9.23	15.03	1.458	2.86	n.a
2,4-dihydroxy-benzoic acid	1039	7.5	1.63	3.1	154	98.8	84.2	44.76	14.64	1.559	1.59	160
2,4-pentane-dione	1892	n.a.	0.40	8.9	100	105.3	27.5	34.14	10.01	0.950	0.00	99
2,6-dihydroxy-benzoic acid	1636	n.a.	2.20	1.1	154	98.8	84.2	44.76	14.64	1.559	n.a	100
2,6-dihydroxy-toluene	100	n.a.	1.58	n.a.	124	102.5	51.6	18.46	13.81	1.210	n.a	n.a

Model compound	THMFP ***HAAFP***	Cl_2 demand	$logK_{OW}$	pKa_1	MW	MV	γ	PSA	α	Density	$logK_{OC}$	$k_{\cdot OH}$
2-butanone	2	n.a.	0.29	14.7	72	91.6	21.0	17.07	8.17	0.786	0.58	6.6
2-Ethyltoluene	12	n.a.	3.53	n.a.	120	138.5	29.0	0.00	16.10	0.867	2.92	n.a
2-naphthol	3	4.4	2.70	9.5	144	121.9	51.0	9.23	18.22	1.181	n.a	120
2-oxobutyric acid	2 ***128***	1.1	-0.75	n.a	102	86	40.8	43.4	8.79	1.18	n.a	n.a
2-oxo-pentanedioic acid	4 ***123***	1.4	-1.10	n.a.	146	97.4	67.9	69.67	11.24	1.499	1.00	n.a
2-pentanone	2	n.a.	0.91	n.a.	86	108.1	22.6	17.07	10.00	0.796	0.85	19
3,4,5-trichloro-phenol	1129	5.2	4.01	7.8	197	123.7	50.5	9.23	16.97	1.596	3.07	n.a
3,5-dichloro-phenol	1190	7.6	3.62	8.2	163	111.7	47.8	9.23	15.03	1.458	2.85	n.a
3,5-dihydroxy-benzoic acid	996	7.1	0.86	4.0	154	98.8	84.2	44.76	14.64	1.559	1.58	n.a
3,5-dihydroxy-toluene	726	7.9	1.58	n.a.	124	102.5	51.6	40.46	13.81	1.210	n.a	n.a
3,5-dimethoxy- benzoic acid	5	1.9	2.19	4.0	182	149.9	42.4	44.76	18.44	1.214	1.00	70
3,5-dimethoxy-4-hydroxy-cinnamic acid	21	6.1	1.30	n.a.	224	171.4	51.9	53.99	23.36	1.307	n.a	n.a
3,5-heptanedione	14	n.a.	1.12	n.a.	128	138.3	28.9	34.14	13.69	0.926	0.36	n.a
3-hydroxybenzoic acid	44 ***479***	7.6	1.50	4.3	138	100.3	64.4	35.53	13.90	1.375	1.37	n.a
3-hydroxy-butyric acid	72 ***187***	1.2	-0.47	4.4	104	87.0	46.3	35.53	9.37	1.195	0.00	n.a
3-nitroaniline	1	8.5	1.37	2.5	138	103.5	60.3	49.06	14.68	1.333	1.71	n.a
3-nitrobenzoic acid	1	0.1	1.83	3.5	167	113.8	66.4	72.12	15.74	1.468	1.22	n.a
3-oxo-butanedioic acid	15 ***506***	3.8	-2.58	n.a.	132	80.9	77.2	69.67	9.41	1.631	n.a	n.a
3-oxo-hexanedioic acid	1378 **25**	5.8	-1.82	n.a.	160	113.9	61.8	69.67	13.08	1.405	n.a	n.a
3-oxo-pentanedioic acid	1414 ***1500***	5.3	-0.30	n.a.	146	97.4	67.9	69.67	11.24	1.499	1.00	n.a

Model compound	THMFP ***HAAFP***	Cl_2 demand	$logK_{OW}$	pKa_1	MW	MV	γ	PSA	α	Density	$logK_{OC}$	$k_{\cdot OH}$
4-(4-hydroxy-phenyl)phenol	12	10.5	2.80	n.a.	186	151.5	53.8	18.46	21.64	1.228	n.a	n.a
4,6-dichloro-1,3-dihydroxy-benzene	1593	5.0	2.32	n.a.	179	110.1	61.8	18.46	15.78	1.624	n.a	n.a
4,6-dioxo-heptanoic acid	1223 ***30***	4.8	-0.20	n.a.	158	132.9	44.0	60.44	14.31	1.189	n.a	n.a
4-chlorobenzoic acid	1	0.1	2.65	4.0	157	113.9	51.5	26.30	15.09	1.374	1.37	50
4-hydroxybenzoic acid	23 ***570***	8.2	1.58	4.5	138	100.3	64.4	35.53	13.90	1.375	1.37	60
4-oxo-heptanedioic acid	7 ***5***	1.3	-1.33	n.a.	174	130.4	57.5	69.67	14.92	1.334	n.a	n.a
5,7-dioxooctanoic acid	1133 ***22***	6.0	0.29	n.a.	172	149.4	42.8	60.44	16.14	1.152	n.a	n.a
Acetamide	2	0.5	-1.26	0.6	59	62.3	29.9	20.31	5.89	0.947	0.73	1.9
Acetic acid	2	0.1	-0.17	4.8	60	56.1	31.9	26.30	5.10	1.068	0.00	0.17
Acetone	564	n.a.	-0.24	20.0	58	75.1	18.8	17.07	6.33	0.772	0.30	1.3
Acetophenone	124	0.5	1.58	21.6	120	120.9	34.1	17.07	14.38	0.993	1.66	54
Acetylacetone	169	4.0	0.40	8.9	100	105.3	27.5	34.14	10.01	0.950	0.00	n.a
Aniline	410	n.a.	0.90	4.6	93	91.7	41.7	3.24	12.08	1.015	1.65	170
Anisole	6	1.0	2.11	-6.5	108	113.4	29.3	9.23	13.05	0.953	2.07	54
Asparagine	1	4.1	-3.82	8.8	132	94.0	71.6	49.80	11.57	1.404	0.08	0.49
Benzaldehyde	1	0.1	1.48	n.a.	106	101.0	38.8	17.07	13.08	1.049	1.51	44
Benzene	12	n.a.	2.13		78	89.4	28.8	0.00	10.40	0.873	2.22	79
Benzoic acid	9	n.a.	1.87	4.2	122	101.9	48.7	26.30	13.15	1.197	1.16	18
beta-(3,5-dimethoxy-4-hydroxyphenyl)-propionic acid	34	6.1	1.00	n.a.	226	179.8	48.2	53.99	22.69	1.258	n.a	n.a
BSA	43	n.a.	n.a.	n.a.	66000	n.a	n.a	n.a	n.a	n.a	n.a	n.a
Catechol	8	n.a.	0.88	9.5	110	86.2	57.1	40.46	11.89	1.275	n.a	110

Model compound	THMFP ***HAAFP***	Cl_2 demand	$logK_{OW}$	pKa_1	MW	MV	γ	PSA	α	Density	$logK_{OC}$	$k_{\cdot OH}$
Chlorophyll	9	9.7	n.a.	n.a.	894	n.a	n.a	127.03	n.a	n.a	13.04	n.a
Chloroxylenol	12	4.7	3.27	9.7	157	132.3	40.2	20.23	16.91	1.183	3.07	n.a
Citraconic acid	8 ***11***	0.1	0.60	n.a.	130	93.7	57.4	52.60	11.19	1.387	1.02	n.a
Citric acid	1293	n.a.	-1.64	2.8	192	109.0	103.9	88.13	14.28	1.762	2.02	3.2
Cytochrome	41	n.a.	n.a.	n.a.	12500	n.a	n.a	n.a	n.a	n.a	n.a	n.a
Diacetic ether	3	2.0	0.25	n.a.	130	128.1	30.2	43.37	12.54	1.015	n.a	n.a
Diethylaniline	94	8.3	3.31	6.6	149	160.4	34.5	3.24	19.75	0.930	2.46	n.a
DL-Isoleucine	1	2.6	-1.70	n.a.	131	126.6	39.0	29.54	13.82	1.035	0.92	18
DL-Leucine	1	2.6	-1.52	2.3	131	126.6	39.0	29.54	13.82	1.035	0.89	18
DL-Threonine	6	5.6	-2.94	n.a.	119	91.1	60.0	38.77	10.75	1.307	0.00	5.1
Erythrulose	42	1.4	-3.90	n.a	120	84.5	69.1	44.76	9.97	1.420	n.a	n.a
Ethanol	2	0.1	-0.31	15.9	46	59.0	22.3	9.23	5.09	0.780	0.00	19
Ethyl acetoacetate	3	1.7	0.70	n.a.	130	128.1	30.2	43.37	12.54	1.015	0.28	n.a
Ethylbenzene	33	n.a.	3.15		106	122.2	29.0	0.00	14.19	0.868	2.71	75
Ferulic acid	10	7.6	1.51	4.6	194	147.4	56.1	44.76	20.72	1.316	1.75	n.a
Fructose	43	1.1	-1.55	12.1	180	113.3	92.6	63.22	14.83	1.589	1.00	16
Fumaric acid	573	n.a.	0.46	3.0	116	77.4	67.6	74.60	9.42	1.499	0.80	60
Galactose	53	0.8	-2.43	12.9	180	104.0	81.7	55.38	14.76	1.732	1.00	20
Glucose	44	0.8	-3.24	12.9	180	104.0	81.7	55.38	14.76	1.732	1.00	15
Glyceraldehyde	53	0.8	-1.07	n.a	90	70.7	53.3	35.53	7.59	1.272	0.00	n.a
Glyoxalic acid	2	1.1	-1.40	3.3	74	53.4	50.2	43.37	5.17	1.384	0.00	12
Hesperetin	349	n.a.	2.60	n.a.	302	207.2	67.4	63.22	30.49	1.458	3.67	n.a

Model compound	THMFP **HAAFP**	Cl_2 demand	$logK_{OW}$	pKa_1	MW	MV	γ	PSA	α	Density	$logK_{OC}$	$k_{\cdot OH}$
Hesperidin	114	n.a.	-0.72	n.a.	611	369.3	98.0	146.29	56.29	1.650	n.a	n.a
Hexane	18	n.a.	3.90	-	86	127.5	20.3	0.00	11.83	0.675	2.17	66
Humic acid	77	n.a.	n.a.	n.a.	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
Hydroquinone	25	n.a.	0.59	10.9	110	86.2	57.1	18.46	11.89	1.275	2.64	52
Isocitric acid	17	n.a.	-2.01	n.a.	192	109.7	100.9	88.13	14.26	1.751	n.a	n.a
Isopropanol	147	n.a.	0.05	17.1	60	75.9	22.6	9.23	6.91	0.791	0.03	n.a
L-Alanine	1	2.8	-2.96	2.3	89	76.7	45.8	29.54	8.32	1.161	0.15	0.52
L-Arginine	2	8.2	-4.20	2.2	174	118.7	66.1	48.38	16.13	1.460	1.32	35
L-Asparagine	***2*** 5	5.6	-3.82	2.0	132	n.a	n.a	49.85	n.a	n.a	n.a	n.a
L-Aspartic acid	***115*** 7	5.5	-3.89	2.0	133	87.8	78.2	55.84	10.78	1.514	0.89	n.a
L-Cysteine	***387*** 0	6.2	-2.49	1.7	121	90.7	58.9	54.84	11.45	1.334	0.44	190
L-Glutamic acid	***9*** 1	2.4	-3.69	2.2	147	104.3	69.2	55.84	12.62	1.409	1.16	1.6
L-Glutamine	0	3.8	-3.46	2.2	146	110.5	64.5	49.85	13.41	1.321	1.00	5.4
L-Glycine	***5*** 0	5.6	-3.21	2.4	75	n.a	n.a.	26.30	n.a.	n.a.	0.00	0.17
L-Histidine	13	12.0	-3.32	2.8	155	108.9	79.6	47.36	15.07	1.423	1.00	48
L-Lysine	***89*** 3	3.8	-3.05	3.1	146	129.9	51.5	32.78	15.23	1.125	1.11	3.5
L-Methionine	***2*** 0	6.0	-1.87	2.3	149	123.7	50.5	54.84	15.17	1.206	0.97	74
L-Ornithine chlorohydrate	***3*** 2	4.6	-4.22	n.a.	132	113.4	54.5	32.78	13.40	1.165	0.85	n.a
L-Phenylalanine	0	2.7	-1.44	1.2	165	137.4	53.5	29.54	18.03	1.201	1.78	65
L-Proline	***2*** 0	5.4	-2.54	n.a.	115	96.9	43.4	29.54	11.06	1.186	0.65	3.1

Model compound	THMFP **HAAFP**	Cl_2 demand	$logK_{OW}$	pKa_1	MW	MV	γ	PSA	α	Density	$logK_{OC}$	$k_{\cdot OH}$
L-Serine	3	5.3	-3.07	2.2	105	74.2	72.2	38.77	8.93	1.415	0.00	3.2
L-Tryptophan	209 ***59***	16.0	-1.06	7.4	204	149.8	71.1	34.47	22.90	1.362	2.57	130
L-Tyrosine	128 ***34***	13.4	-2.04	2.2	181	135.8	65.7	38.77	18.78	1.333	1.99	130
L-Valine	0	2.7	-2.26	2.3	117	110.1	39.8	29.54	11.98	1.063	0.64	8.5
Maleic acid	2	0.5	0.46	1.8	116	113.9	61.8	69.67	13.08	1.405	0.80	60
Malic acid	27	n.a.	-1.26	3.4	134	81.6	86.2	61.83	9.99	1.641	0.00	8.2
Malonic acid	2	1.8	-0.81	2.9	104	67.3	70.5	52.60	7.56	1.546	0.54	0.16
Maltopentaose	63	5.1	-10.20	n.a	829	455.4	126.0	247.82	68.43	1.810	n.a	n.a
Maltose	53	1.7	-5.03	n.a	342	193.6	110.8	101.53	28.06	1.760	1.00	23
Maltotriose	65	3.0	-6.30	n.a	504	278.7	119.1	147.68	41.43	1.800	n.a	n.a
m-aminophenol	161	7.7	0.21	4.4	109	90.1	57.4	12.47	12.83	1.210	1.86	n.a
m-chlorophenol	598	8.8	2.50	9.1	129	99.8	44.7	20.23	13.09	1.287	2.64	72
m-Cresol	157	n.a.	1.96	10.1	108	104.1	38.8	20.23	13.06	1.038	2.64	n.a
Methoxyacetic acid	3 ***13***	0.8	-0.68	n.a.	90	79.0	35.5	35.53	7.63	1.139	0.00	6.1
m-hydroxy-acetophenone	560	11.0	1.39	9.3	136	119.3	43.9	26.30	15.12	1.140	1.88	n.a
m-hydroxy-benzaldehyde	121	9.8	1.29	9.0	122	99.5	52.0	37.30	13.83	1.226	1.72	n.a
m-hydroxy-benzoic acid	88	9.1	1.50	4.3	138	100.3	64.4	35.53	13.90	1.375	1.37	n.a
m-methoxy-phenol	48	8.1	1.34	9.7	124	111.8	38.6	18.46	13.80	1.109	2.28	320
m-methylphenol	83	8.7	1.96	10.1	108	104.1	38.8	20.23	13.06	1.038	n.a	n.a
m-nitrophenol	173	9.2	2.00	8.4	139	99.7	60.2	55.05	13.74	1.395	2.49	n.a
m-Xylene	60	n.a.	3.20	-	106	121.9	28.7	0.00	14.23	0.870	2.64	75

Model compound	THMFP ***HAAFP***	Cl_2 demand	log K_{OW}	pKa_1	MW	MV	γ	PSA	α	Density	logK_{OC}	$k_{\cdot OH}$
N-acetyl-neuraminic acid	5 ***60***	2.9	-5.16	n.a.	309	188.0	95.7	101.99	26.03	1.640	n.a	n.a
Naphthalene	29	n.a.	3.30	-	128	123.5	40.2	0.00	17.48	1.037	1.30	94
Naphtho-resorcinol	259	3.4	1.97	n.a.	160	120.4	64.4	18.46	18.97	1.330	n.a	n.a
n-butyraldehyde	1	0.2	0.88	n.a.	72	91.8	22.5	17.07	8.23	0.784	0.71	39
Nitrobenzene	21	n.a.	1.85	-	123	101.2	45.3	45.82	13.00	1.215	2.28	39
o-aminophenol	10	3.9	0.62	4.8	109	90.1	57.4	12.47	12.83	1.210	1.87	n.a
o-chlorophenol	56	8.9	2.15	8.6	129	99.8	44.7	20.23	13.09	1.287	2.65	120
o-Cresol	143	n.a.	1.95	10.3	108	104.1	38.8	20.23	13.06	1.038	2.65	110
o-hydroxy-acetophenone	129	9.9	1.92	n.a.	136	119.3	43.9	37.30	15.12	1.140	1.88	n.a
o-hydroxy-benzaldehyde	81	9.7	1.81	n.a.	122	99.5	52.0	37.30	13.83	1.226	1.73	n.a
o-hydroxy-benzoic acid	54	6.0	2.26	3.0	138	100.3	64.4	35.53	13.90	1.375	1.38	n.a
o-methoxy-phenol	65	7.7	1.32	10.0	124	111.8	38.6	18.46	13.80	1.109	2.29	200
o-methylphenol	61	7.5	1.95	10.3	108	104.1	38.8	20.23	13.06	1.038	2.65	n.a
o-nitrophenol	18	9.6	1.79	7.2	139	99.7	60.2	66.05	13.74	1.395	2.50	n.a
Orcinol	1212	6.3	1.58	n.a.	124	102.5	51.6	40.46	13.81	1.210	2.85	n.a
Oxalic acid	2	0.3	-2.22	1.3	90	50.8	87.3	52.60	5.72	1.772	0.28	0.014
Oxaloacetic acid	42	n.a.	-2.58	n.a.	132	80.9	77.2	69.67	9.41	1.631	0.00	n.a
p-aminophenol	2	5.4	0.04	5.5	109	90.1	57.4	12.47	12.83	1.210	1.86	n.a
p-chlorophenol	75	8.7	2.39	9.4	129	99.8	44.7	20.23	13.09	1.287	2.64	93
p-cresol	43	n.a.	1.94	10.3	108	104.1	38.8	20.23	13.06	1.038	2.64	120
Pepsin	51	n.a.	n.a.	n.a.	30000	n.a	n.a	n.a	n.a	n.a	n.a	n.a
Phenol	154	n.a.	1.46	10.0	94	87.8	40.9	9.23	11.15	1.071	2.43	66

Model compound	THMFP	Cl_2 demand	log K_{OW}	pKa_1	MW	MV	γ	PSA	α	Density	logK_{OC}	$k_{\cdot OH}$
Phenylacetic acid	1	0.1	1.41	4.3	136	116.8	46.7	37.30	14.81	1.164	1.42	79
Phenylalanine	2	2.0	-1.38	1.2	165	137.4	53.5	29.54	18.03	1.201	1.78	65
Phenylthiourea	269	12.4	0.71	n.a.	152	117.5	71.4	38.57	18.50	1.294	1.29	38
Phlorizin	446	n.a.	0.72	n.a	436	280.5	80.1	100.14	42.32	1.555	n.a	n.a
Phloroglucinol	332 ***700***	9.0	0.16	8.5	126	84.7	78.6	27.69	12.64	1.488	2.85	100
p-hydroxy-acetophenone	336	9.8	1.35	8.1	136	119.3	43.9	26.30	15.12	1.140	1.87	n.a
p-hydroxy-benzaldehyde	57	8.8	1.35	7.6	122	99.5	52.0	37.30	13.83	1.226	1.72	n.a
p-hydroxy-benzoic acid	61	9.4	1.58	4.5	138	100.3	64.4	35.53	13.90	1.375	1.37	60
p-methoxy-phenol	6	3.4	1.58	n.a.	124	111.8	38.6	18.46	13.80	1.109	2.28	260
p-methylphenol	11	5.5	1.94	10.3	108	104.1	38.8	20.23	13.06	1.038	2.64	n.a
p-nitrophenol	17	7.6	1.91	7.2	139	99.7	60.2	55.05	13.74	1.395	2.49	38
Propionaldehyde	2	0.2	0.59	n.a.	58	75.3	20.5	17.07	6.39	0.770	0.44	22
Pyrogallol	0	n.a.	0.97	9.0	126	84.7	78.6	60.69	12.64	1.488	2.86	n.a
Pyruvic acid	56	1.0	-1.24	2.5	88	69.8	42.6	43.37	6.95	1.261	0.00	0.31
Quercetin	199	8.5	1.48	n.a.	302	167.9	114	72.45	29.06	1.799	2.73	150
Quinone	33	n.a.	0.20	n.a	108	86.0	47.8	34.14	10.75	1.256	0.14	n.a
Rennin	17	n.a.	n.a.	n.a.	30000	n.a	n.a	n.a	n.a	n.a	n.a	n.a
Resorcinol	1456	6.6	0.80	9.3	110	86.2	57.1	18.46	11.89	1.275	2.64	120
Ribose	51	0.7	-2.32	n.a	150	99.5	81.4	53.99	12.45	1.508	1.00	16
Rutin	258	n.a.	-2.02	n.a.	611	334.1	125.2	155.52	54.77	1.820	1.47	n.a
Salicylic acid	30	n.a.	2.26	3.0	138	100.3	64.4	35.53	13.90	1.375	1.38	120
Sinapic acid	6	5.2	0.25	n.a.	184	148.3	51.6	53.99	19.19	1.335	1.62	n.a

Model compound	THMFP	Cl_2 demand	log K_{OW}	pKa_1	MW	MV	γ	PSA	α	Density	logK_{OC}	$k_{\cdot OH}$
Styrene	44	n.a.	2.95	-	104	115.3	30.9	0.00	14.73	0.902	2.71	60
Succinic acid	1	0.1	-0.59	4.2	118	83.8	61.6	52.60	9.39	1.408	0.80	3.1
Syringic acid	5	4.6	0.25	4.3	184	148.3	51.6	53.99	19.19	1.335	1.13	n.a
Thioacetamide	2	4.2	-0.26	13.4	75	70.2	50.6	35.33	8.77	1.070	0.44	n.a
Thiourea	5	3.9	-1.08	2.0	76	57.3	89.5	38.57	8.34	1.326	0.44	98
Toluene	23	n.a.	2.73	-	92	105.7	28.8	0.00	12.32	0.871	2.43	51
Uracil	7	1.2	-1.07	9.5	112	84.8	41.3	40.62	9.91	1.321	n.a	57
Urea	5	3.8	-2.11	0.1	60	49.5	55.3	23.55	5.46	1.212	0.69	0.0079
Vanillic acid	136	5.4	1.43	4.5	168	124.3	56.5	44.76	16.54	1.351	1.23	n.a
Xylose	46	0.6	-1.98	12.1	150	85.4	75.3	46.15	12.29	1.757	1.00	22
β-Alanine	3	2.8	-3.05	3.6	89	76.7	45.8	29.54	8.32	2.161	0.22	1.1

Notation: THMFP = THM formation potential (µg mgC^{-1}) , HAAFP = HAA formation potential (µg mgC^{-1}), Cl_2 demand = chlorine demand (mol/mol), log K_{OW} = log (octanol/water partition coefficient), pKa = acid dissociation constant, MW = molecular weight (Da), MV = molar volume (cm^3), γ = surface tension (dyne/cm^2), PSA = polar surface area ($Å^2$), α = polarisability (10^{-24} cm^3), Density (g/cm^3), log K_{OC} = log (soil/water partition coefficient), $k_{\cdot OH}$ = aqueous hydroxyl radical rate constant (10^{-8} mol L^{-1} s^{-1}).

2.5.2 Chlorination of Carboxylic Acids

In general simple carboxylic acids moieties are not reactive with chlorine, as shown by apparent rate constant of 2.3 M^{-1} s^{-1} at pH 7.2 for reaction with sorbic acid (*59)*, which also contains an alkene functionality. A corollary is the low DBP formation from simple carboxylic acids, as shown by a THMFP of 2 µg mgC^{-1} for acetic acid (Table 2.6). An exception is the high chlorine reactivity and DBP formation found for certain β-dicarbonyl acids, illustrated by respective THM and HAA formation of 1414 and 1500 µg mgC^{-1} for 3-oxopentanedioic acid (Table 2.5). There is limited data about the occurrence of carboxylic acids in drinking water. This partly because carboxylic acid functionality in NOM is associated with other categories, including humic substances and amino acids, groups with higher reactivity towards chlorine. In fact NOM is primarily organic acids rich in oxygenated functionalities (*12)*, and under natural pH conditions is anionic. The high charge density associated with hydrophobic and transphilic (TPI) fractions of NOM (*13, 60)* is a reflection of high carboxylic acid functionality. In particular the transphilic fraction, with its high proportion of carboxylic acid functionality (*61*) may be an important precursor pool. As with carboxylic acids, simple carbonyl groups react slowly, as shown by the negligible apparent negligible rate constant for reaction of chlorine with the steroid progesterone (*49)*. Reaction with carbonyl groups normally proceeds through initial chlorine substitution at the α-carbon to the carbonyl group. With β-dicarbonyl species the electron-withdrawing effect of both carbonyls makes the hydrogen groups attached to the α-carbon more acidic. Both acid- and base-catalysed enolisation can lead to DBP formation (Figure 2.4). The higher TCA formation of fulvic acid isolates than humic acid isolates (*40)*, was linked to higher methyl ketone content, which could include β-dicarbonyl species. Base-catalysed

halogenation of β-dicarbonyls is dominant above pH 5 and kinetically controlled by keto-enolisation (*49)*. Thus it may be expected that DBP formation from β-dicarbonyl species would increase with pH. However, the higher DBP formation reported for 3-oxopentanedioic acid (a β-dicarbonyl acid), at pH 5.5 compared with pH 8, with DCAA formation 2062 and 1462 µg mgC^{-1} respectively (*17),* indicates keto-enolisation is not always the rate-determining step. THM formation from citric acid is also highly pH dependent, with high levels at pH 7 but not pH 8 explained by neutral pH being optimum for the rate-determining oxidative decarboxylation step (Table 2.5). While chlorination proceeds through enolisation and chlorination at the α-carbon, the exact route by which HAAs and THMs are liberated, and also any pH dependence, has still to be elucidated. A route by which β-keto acids can give rise to DCAA is shown for 3-oxopropanoic acid (Figure 2.4). However formation of THMs is more complex. Figure 2.5 shows a possible route by which 5, 7-dioxooctanoic acid could give rise to both DCAA and $CHCl_3$.

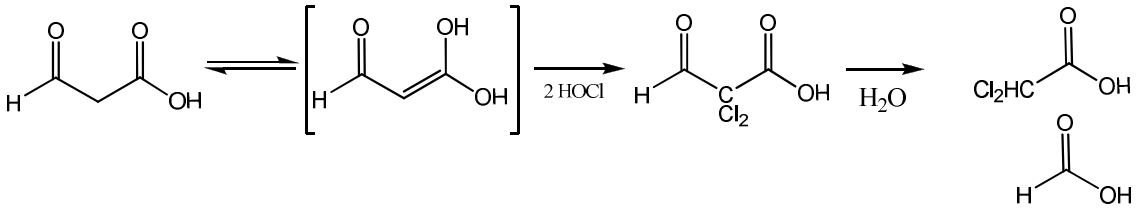


Figure 2.4: Chlorination of 3-oxopropanoic acid

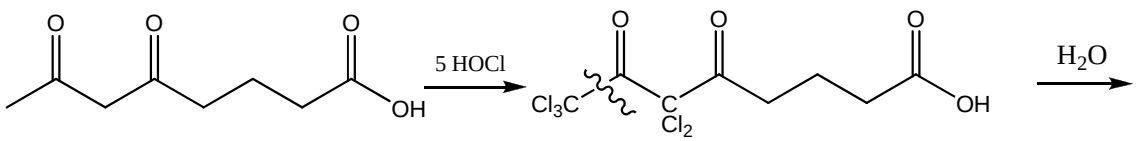


Figure 2.5: Chlorination of 5,7-dioxooctanoic acid. Adapted from Dickenson et al., 2008

Evidence from natural water research suggests DCAA precursors are more hydrophilic than TCAA precursors (*38)* and that TCAA formation proceeds through intermediates common to THM formation (*40)*. The explanation is thought to be that TCAA does not readily form from direct chlorine substitution of DCAA. Meanwhile, formation of TCAA over $CHCl_3$ from a trichloroacetyl precursor structure is thought to be favoured by the presence of conjugation capable of stabilising the formed carbonium ion (*28*). This information could suggest that DCAA precursors themselves are different to TCAA and THM precursors. At the same time model compound work has identified a small number of precursors which produce high levels of both DCAA and THMs. The most striking example is 3-oxopentandioic acid, found to produce $CHCl_3$ at 1414 µg mgC^{-1} and DCAA at 1500 µg mgC^{-1} (Table 2.6). The most likely explanation for this is that various possible degradation pathways after chlorine substitution can liberate both DCAA and $CHCl_3$ (Figure 2.5).

2.5.3 Chlorination of Amino Acids and Proteins

Amino acids are typically present at mean levels of 0.3 mg L^{-1} in surface waters (*54*), representing some 2-5% of the total DOC, though values can be higher in waters with algal or wastewater influence. Concentrations of total amino acids between 1.35- 2.74 mg L^{-1} have been recorded in coastal plain rivers of the South-eastern USA (*62)*. Glutamic acid, glycine, serine and aspartic acid are considered the most abundant species (*54*). These four species all have low THMFP (0-5 µg mgC^{-1}, Table 2.6) and are relatively hydrophilic (log K_{OW} = -3.07 to -3.89, Table 2.6), hence they are assumed to lie within hydrophilic fractions of NOM. The concentration of proteins and amino acids is linked to levels of microbially-derived NOM, specifically algae and wastewater

effluent. It has been reported that levels of total dissolved amino nitrogen, presumed to mainly comprise proteinaceous material, in a lake water rose between 0.1-3 mg L^{-1} to 1.0 mg L^{-1}during algal blooms (*27*). From the algal bloom a THMFP of 115 µg L^{-1} was reported, with proteinaceous material thought to account for 8-11% THM formation from ultrafiltrate fractions (*27*). The highest THMFP recorded from four model proteins was 51 µg mgC^{-1} for pepsin (Table 2.6). Combined amino acids are thought to be 4-5 times commoner than free amino acids (*21)*, which is significant as amide groups involved in peptide links are unavailable for reaction with chlorine. The chlorine demand of linked amino acids can be theoretically calculated from the demand of constituent parts, bearing in mind that the amide/peptide bond and also glycine and aspartic acid are unavailable for reaction with chlorine (*21)*. Reactivity of chlorine with amino acids is high, with chlorine demand as high as 13 and 16 mol/mol for tyrosine and tryptophan respectively (Table 2.6). The respective THMFP for these amino acids is 128 and 209 and µg mgC^{-1} (Table 2.6), higher than other amino acids and like their chlorine demand linked to the presence of aromatic or cyclic unsaturated side groups (*21*). Similarly, side groups including amine, sulphur or activated aromatic groups are presumed to be the main precursor sites of linked amino acids. For simpler amino acids high chlorine demand does not translate into high THM formation, for example the chlorine demand and THMFP of glycine were measured as 5.6 mol/mol and 0 µg mgC^{-1} respectively (Table 2.6). This can be explained by oxidation pathways and/or formation of alternative groups of DBPs. For α-amino acids initial chloramination followed by decarboxylation and deamination can produce carbonyl or nitrile compounds (Figure 2.6). For L-aspartic acid it has been proposed that this can lead to the predominant formation of 3-oxopropanoic acid, a β-keto acid, as a reaction intermediate at pH 8

(Figure 2.7, (*21*)). This significance of this became apparent when the high DBP formation of several β-keto acids was reported (*17)* followed by the high DCAA formation of L-aspartic acid (387 µg mgC^{-1}) itself and of L-asparagine (115 µg mgC^{-1}) (Table 2.6). L-asparagine is thought to be another amino acid which can generate a β-keto acid from chlorine oxidation (*17).* For this to occur the amino acid must have two terminal oxygenated groups and a four carbon backbone, which can become a β-keto acid through loss of the alpha carboxylic group. Aspartic acid and asparagine are the only common amino acids where this can occur and are unusual in being represented by low chlorine demand at but high DBP formation (*21*). Nitrile formation could also give rise to DCAA and TCAA based on the classical mechanism of amino acid chlorination. However given the unfavourable kinetics of chlorination of single carboxylic groups, it is more likely that DCAA formation proceeds through the β-keto acid intermediate. In addition, levels of nitrogen containing NOM, of which amino acids and proteins are important components, have been linked to those of nitrogen containing DBPs (*63*). It has also been noted that DCAN results from the chlorination of amino acids, polypeptides and hydrophobic substances with amino acid moieties (*64*). L-aspartic acid is also an important DCAN precursor, producing 158 µg mgC^{-1} at pH 6.4, plus 91 µg mgC^{-1} of TCA (*64*). In view of the importance of aspartic acid as a DBP precursor its quantification at an average concentration of 0.27 mg L^{-1} (0.097 mgC L^{-1}) in rivers of the South-eastern USA (*62)* is relevant. Based on this concentration and the above DBPFP data, this indicates it could be responsible for the formation of 38 µg L^{-1} of DCAA, 15 µg L^{-1} of DCAN and 9 µg L^{-1} of TCA, i.e. significant levels of all three DBPs.

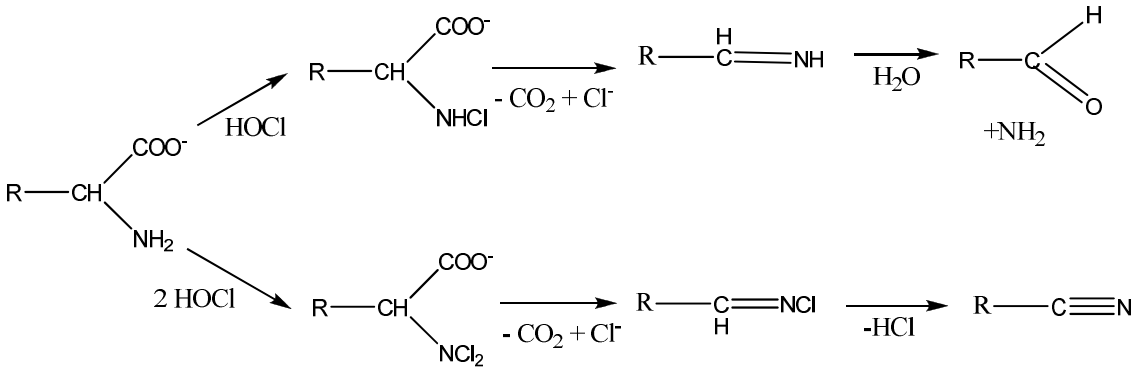


Figure 2.6: Chlorination of amino acids. Based on Deborde and von Gunten, 2008

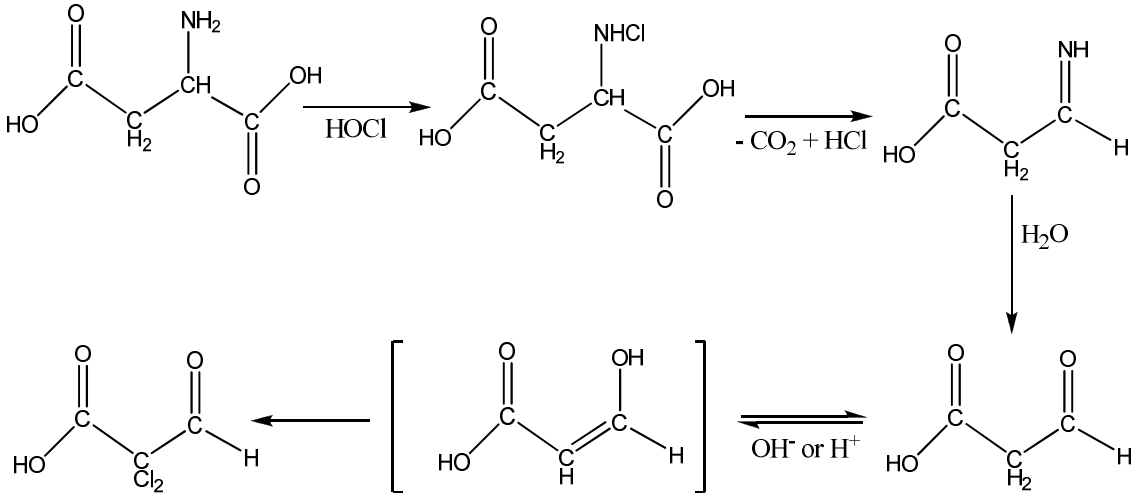


Figure 2.7: Chlorination of aspartic acid. Based on Hureiki et al., 1994

2.5.4 Chlorination of Carbohydrates

Total dissolved carbohydrates are typically present in surface waters at mean concentrations of 0.5 mg.L^{-1} (*54*), comprising 5-10% of the total DOC, while a recent study found concentrations of 1 mg L^{-1}, or 50% of the DOC in a Spanish river (*30*). Glucose is considered the commonest carbohydrate in surface waters (*54)* while arabinose and mannose are also thought to be widespread (*65*). Like similar carbohydrates, glucose is hydrophilic (log K_{OW} = -3.24, Table 2.6), which indicates carbohydrates are likely to belong to hydrophilic NOM fractions. As noted,

functionalities contained within carbohydrates are slow to react with chlorine, illustrated by the negligible apparent rate constant for the monosaccharide ribose (*59)*. Navalon and co-workers (*30)* found pH to have a strong affect on the THM formation. At pH 5 only small amounts of THMs were observed, though this became significant at pH 8, for example from glucose 44 µg mgC^{-1} and from maltotriose 65 µg mgC^{-1} (Table 2.6). After 72 hours it was thought reactions had still not reached completion, revealing the slow kinetics of carbohydrate chlorination. Though these THM values are still much lower than from more reactive precursors, they become significant given the ubiquity of carbohydrates in surface waters. The presence of bromide increases THMs still further, with complete incorporation of bromide into THMs recorded at bromide concentrations under 100 µg L^{-1}. Most of the chlorine substituted at pH 8 can be accounted for by THMs, indicating formation of other DBPs is not significant. The proposed mechanism proceeds through chlorine substitution of the α-hydroxy aldehyde moiety (Figure 2.3). The pH dependence has been ascribed to the basic conditions promoting the rate determining hydrolysis of the halogenated leaving group.

2.6 Correlations between Model Compound Properties and THM Formation

Model compound THMFP was positively correlated (r = 0.879) with the chlorine substitution efficiency (Table 2.7). The number of data points used for this correlation was 121, with a linear relationship observed between these two parameters (Figure 2.8). This underlines the importance of the chlorine substitution step to formation of DBPs. Conversely there is only a weak correlation of 0.258 between THMFP and chlorine

demand, which indicates most chlorine consumed is involved in oxidation rather than substitution reactions, as previously noted (*49*). This trend is clearly illustrated by many of the aliphatic amino acids, such as L-glycine, which have significant chlorine demand but low THMFP, in this case 5.6 mol/mol and 0 μg mgC^{-1} respectively (Table 2.6). There are no meaningful relationships between any of the physicochemical properties and THM formation. This can be explained by compounds with similar physicochemical properties having disparate THM formation potential. In most cases this is due to the position of activating or deactivating groups. To illustrate such a pair is 2-oxobutyric and 3-hydroxybutyric acids. Here shifting the position of an oxygenated group to a neighbouring carbon increases the THMFP by 36 times from former to latter, from 2 to 72 (Table 2.6). Another well-studied example is phenol and resorcinol, which differ by the latter compound having an extra hydroxyl group, and have respective THMFP of 154 and 1456 μg mgC^{-1} (Table 2.6). Although HAA formation data is scanter, equivalent examples exist, including the amino acids L-glutamine and L-aspartic acids, where chemical functionality is similar, MW comparable at 146 and 133 Da, yet with HAAFP 5 and 387 μg mgC^{-1} respectively (Table 2.6).

Table 2.7: Correlations between Compound Properties and THMFP

	THMFP	HAAFP	Cl_2 demand	Cl_2 substn	log K_{OW}	pKa	MW	MV	γ	PSA	α	Density	log K_{OC}
	both µg mgC^{-1}		mol/mol	mol Cl/mol			Da	cm^3	dyne cm^{-1}	$Å^2$	10^{-24} cm^3	g cm^{-3}	
HAAFP	0.345												
Cl_2 demand	0.258	0.097											
Cl_2 substn	**0.879**	0.325	0.007										
MW	0.141	-0.175	0.296	0.174									
log K_{OW}	0.049	0.325	0.086	0.409	0.253								
pKa	-0.052	0.606	0.166	0.045	-0.319	-0.159							
MV	-0.007	-0.377	0.153	0.039	-0.196	-0.056	0.945						
γ	0.113	0.312	0.088	0.082	-0.507	-0.316	0.629	0.389					
PSA	0.020	0.040	-0.092	-0.005	-0.608	-0.302	0.779	0.663					
α	0.011	-0.270	0.25	0.049	-0.179	-0.074	0.969	0.976	0.677				
Density	0.18	0.432	0.029	0.188	-0.397	-0.285	0.502	0.24	0.623	0.359			
log K_{OC}	0.11	0.146	0.454	0.112	0.647	0.196	0.649	0.344	0.045	0.42	-0.007	0.713	
$k_{\cdot OH}$ (10^{-8} $M^{-1}s^{-1}$)	0.184	0.115	0.479	0.076	0.479	0.095	0.184	-0.295	0.239	0.377	-0.089	0.034	0.566

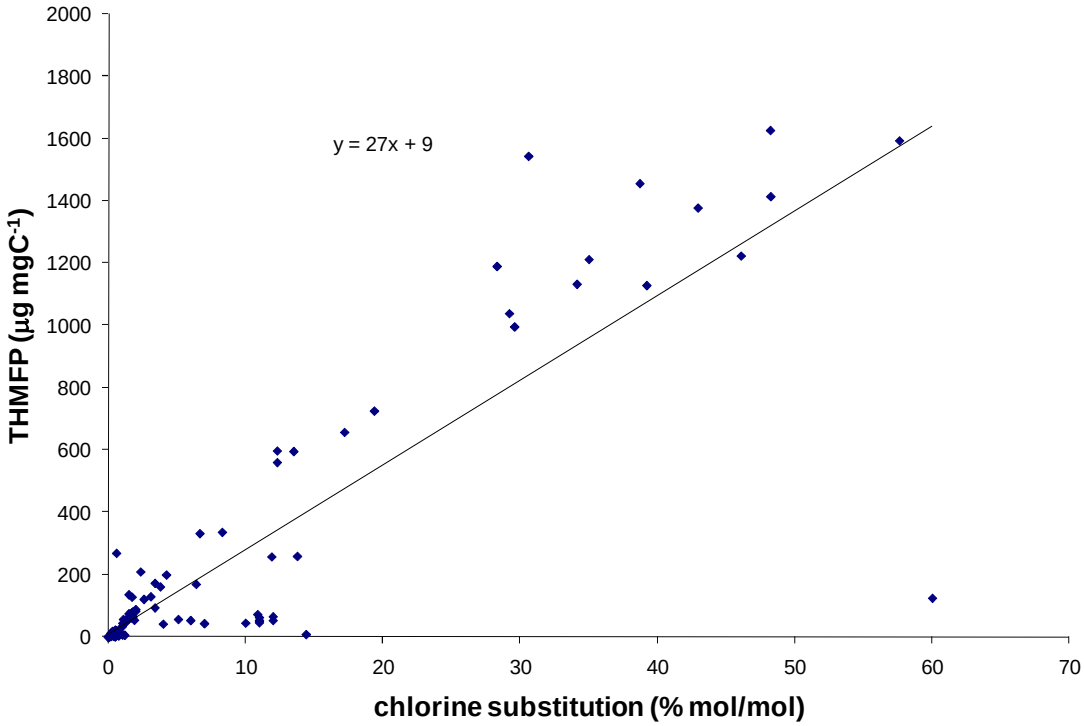


Figure 2.8: Relationship between THMFP and chlorine substitution yield

There is only a modest relationship between HAA formation and THM formation, r = 0.362 (25 data pairs) (Table 2.7). This indicates that reactive DBP precursors often form high amounts of either THMs or HAAs but not both. One example of such a compound is 3-oxohexanedioic acid, with a THMFP of 1378 µg mgC^{-1} and HAAFP of 25 µg mgC^{-1} (Table 2.6). A converse example is L-aspartic acid, with DCAA formation of 387 µg mgC^{-1} and THMFP of 7 µg mgC^{-1} (Table 2.6). It worth stressing that many studies have measured only THMs but not HAAs, thus the HAA formation of some reactive THM precursors is unknown. Examples include orcinol and m-hydroxyacetophenone, with THMFP of 1212 and 560 µg mgC^{-1} respectively (Table 2.6).

There is a modest correlation of 0.325 between HAAFP and log K_{OW} (26 data pairs) (Table 2.7), while data is not comprehensive enough to make meaningful correlations

between log K_{OW}, DCAA and TCAA formation. However, research using natural waters has found DCAA precursors to be overall more hydrophilic than TCAA precursors and also HAA precursors to be overall more hydrophobic than THM precursors (*38)*. Model compound research has also identified several reactive HAA precursors which are β-keto acids or molecules which can be oxidised to β-keto acids, form predominantly DCAA and are hydrophilic (Table 2.6) (*17, 31)*, with few hydrophobic HAA precursors identified (*19)*. Therefore, there may be hydrophobic TCAA precursors awaiting discovery. An alternative explanation, as discussed above, is that THM and TCAA precursors are the same or similar and that neutral or basic pH favours formation of the former over the latter.

To determine whether any correlations between physical properties and THM formation might exist between chemically-similar subsets of compounds the same statistical analysis was undertaken for aliphatic compounds, non-halogenated aromatics and amino acids, with selected correlations presented (Table 2.8). In general and with a few exceptions, the same lack of correlations is apparent for these groups. For the aliphatic compounds there is similar positive correlation between chlorine substitution and THMFP as for the complete set of compounds, 0.797 and 0.879 respectively (number of data pairs 55 and 121). The correlation of 0.412 between THMFP and HAAFP for the aliphatic compounds (data pairs = 21) indicates a proportionately higher number of compounds which form significant amounts of both DBP groups, several being β-keto acids (*17)*.

Table 2.8: Correlations between Compound Properties and DBPFP for aliphatic compounds, non-halogenated aromatic compounds and amino acids

	Aliphatic compounds		Non-halogenated aromatic compounds	Amino acids	
	THMFP	**HAAFP**	**THMFP**	**THMFP**	**HAAFP**
	both µg mgC $^{-1}$		µg mgC $^{-1}$	both µg mgC $^{-1}$	
HAAFP	0.412			-0.031	
Cl_2 demand	0.276	0.077	0.17	0.815	0.003
Cl_2 substn	0.797	0.413	0.977	0.994	0.010
MW	0.156	-0.088	-0.069	0.449	-0.280
log K_{OW}	0.132	0.170	-0.107	0.772	-0.383
pKa	0.032	0.173	0.034	0.623	-0.014
MV	0.042	-0.269	-0.077	0.518	-0.510
γ	-0.005	0.242	0.317	0.33	0.650
PSA	0.135	0.223	0.053	-0.079	0.378
α	0.004	-0.241	-0.016	0.708	-0.385
Density	0.018	0.382	0.33	0.071	0.626
log K_{OC}	0.136	0.063	0.195	0.708	-0.148
k_{OH} (10^{-8} $M^{-1}s^{-1}$)	0.212	0.044	0.146	0.559	0.189

Note: HAA data excluded for non-halogenated aromatic compounds due to small number of data points.

For the non-halogenated aromatic compounds there are again no strong relationships between THMFP and physical properties, other than the one with chlorine substitution (r = 0.977, data pairs =55). Regarding the amino acids the positive relationships between THMFP and chlorine demand, log K_{OW} and log K_{OC}, respectively 0.815, 0.772 and 0.708 for 22, 22 and 21 data pairs (Table 2.8), indicate the importance of electrophilic side groups in heightened THM formation and chlorine demand. This is especially the case for L-tryptophan and L-tyrosine, both relatively reactive THM precursors and with higher chlorine demand than the other amino acids (*21)*. For HAA formation of amino acids, similar positive correlations are not present. Instead, there is a negative correlation of -0.383 between HAAFP and log K_{OW} (Table 2.8), linked to the high HAA formation of the hydrophilic L-aspartic acid and L-asparagine, which have log KOW of -3.89 and -3.82 respectively (Table 2.6). The presence of "masked" β-diketo acid structures appears to be key in HAA formation from amino acids, rather than the identity of any side chains.

2.7 Discussion: Importance of NOM Groups to DBP formation

It has been demonstrated how other than chlorine substitution, no compound physicochemical properties correlate with formation of THMs or HAAs. This lack of relationships indicates there is no reliable predictor of DBP formation likely to be found in drinking waters. Relationships exist between bulk parameters and DBP formation in individual waters, but they are believed to be site specific. Positive correlations have been found between total organic carbon (TOC) and THM formation (*66)* and between SUVA (specific ultraviolet absorbance) and THM formation of NOM isolates and bulk

water (*67)*. Relationships with SUVA or UV absorbance implicate hydrophobic/humic NOM as the principal precursor pool (*68)*. One strong correlation with DBP formation that has been identified in drinking water is with differential absorbance at 272nm (Δ272) (*69)*. This technique compares absorbance at 272 nm before and after chlorination, and so is not a predictive technique. Since absorbance decreases upon chlorination, values are invariably negative. In contrast to predictive bulk parameters, Δ272 has been found to correlate strongly (R^2 commonly 0.99) with formation of both total organic halides (TOX) and individual DBP species (*69)*. Thus these correlations show remarkable linearity when compared to bulk predictive parameters. In contrast, conventional absorbance spectra of NOM, both before and after chlorination, have no identifiable peaks. Since activated aromatic species, including resorcinol, show an absorbance peak at 272 nm, this evidence strongly implicates activated aromatic compounds as a key precursor pool in different water sources.

It has been observed that TCAA precursors are more hydrophobic than THM and DCAA precursors (*38)*, and similarly that the TCAA/THM ratio increases with SUVA (*40*). Hence formation of TCAA from hydrophobic NOM is likely to be a particular concern. The formation of TCAA can be mitigated by chlorinating at alkaline pH (Table 2.5), although this is likely to promote THM formation (Table 2.5), so this is likely only to be beneficial where TCAA is of more concern than THMs. Since hydrophobic NOM is the fraction most treatable by coagulation (*13)*, in hydrophobic-rich waters this is an effective strategy for hydrophobic precursors, notably those of TCAA and THMs (*38)*. However, in waters where hydrophilic NOM moieties are a significant precursor source UV absorbance or SUVA are unlikely to correlate to DBP formation. In these waters there is a greater analytical challenge to assign DBP formation to chemical NOM

groups. Furthermore, as hydrophilic NOM is the main constituent of a post-coagulation residual, in these waters additional treatment may be needed to suppress DBP formation by precursor removal. Amongst carboxylic acids, β-dicarbonyl species are presumed to be the primary group of reactive precursors. Charge density measurements suggest carboxylic acid functionality is associated with hydrophobic and transphilic NOM fractions rather than hydrophilic (*13, 60)*. Humic species with carboxylic acid functionality are the likely location of charge in hydrophobic fractions, whereas in the transphilic fraction more hydrophilic species are implicated (*61)*. Whether the transphilic fraction contains β-dicarbonyl species is unknown on current knowledge, but high DBPFP arising from that fraction could indicate the presence of reactive β-dicarbonyl acid precursors. β-dicarbonyls, or groups oxidisable to that functionality, in fulvic acid pseudo-structures have been postulated as DBP precursor sites using a mechanistic approach (*28)*. Moreover, ^{13}C nuclear magnetic resonance (NMR) analysis also supports the existence of β-dicarbonyl moieties within fulvic acid structures (*70)*. The presence of β-hydroxy acids in hydrophilic NOM has been supported by ^{13}C NMR, and the detection of mixed aliphatic alcohols and carboxylic acids by pyrolysis then gas chromatography with mass spectroscopy (GC-MS) (*16)*. There is limited data from model compound work that DCAA formation from β-dicarbonyls, specifically 3-oxopentanedioic acid, increased at pH 5.5 as opposed to pH 8, whereas for citric acid pH 7 appears optimum for THM formation (Table 2.5). In summary, further work is needed both to clarify the occurrence and fractional behaviour of β-dicarbonyls and further to determine the effect of pH on DBP formation.

Levels of nitrogenous NOM, of which proteins and amino acids are important components, have been linked to the formation of nitrogen containing DBPs (*63)*, while

model compound work has highlighted the formation of DCAA, haloacetonitrile and TCA from a small number of amino acids (*31, 64, 71)*. Further, research suggests the hydrolysis of dichloroacetonitrile (DCAN) to DCAA and TCA formation both increase at alkaline pH (Table 2.5). However, since for L-aspartic acid and L-asparagine DCAA formation is thought to proceed through β-dicarbonyl intermediates (*17, 21)*, whether DCAA might also increase at acidic pH, as with 3-oxopentanedioic acid (Table 2.5) requires further investigation. Moreover, there is still a need to conclusively quantify the importance of specific amino acids to the formation of the aforementioned DBPs.

Kinetic work suggests chlorination of carbohydrates is slow and unlikely to be significant during the timescale of drinking water disinfection. Meanwhile, model compound studies indicate THMs are the predominant DBPs from carbohydrate precursors and amounts become significant at alkaline pH and 72 h chlorination. This information indicates the combination of high carbohydrate concentrations, chlorination at alkaline pH and lengthy distribution systems have the potential to generate substantial THMs in customers' drinking water. Conversely, DBP formation is not likely to be important at neutral or acidic pH and short contact times. Further, the sampling location of DBP samples is likely to be important. Typical chlorination contact times are ~30-60 mins (*72)*. For a fast-reacting precursor such as resorcinol, where the majority of chloroform forms within 5 mins (*56)*, THM formation is rapid enough for peak levels to be recorded at a water treatment works (WTW). However, for less reactive species such as carbohydrates this is unlikely to be the case. As a final point, kinetic analysis suggests a limited number of functionalities present in NOM are reactive towards chlorine, the most noteworthy being activated aromatics, amines and β-dicarbonyl

species. Thus it is anticipated that while undiscovered reactive precursors undoubtedly exist, they are likely to occur within these reactive categories.

2.8 Acknowledgements

Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water are gratefully acknowledged for their financial support.

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CHAPTER 3: TREATMENT OF DISINFECTION BYPRODUCT PRECURSORS

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3.1 Abstract

Formation of harmful disinfection byproducts (DBPs), of which trihalomethanes (THMs) and haloacetic acids (HAAs) are the major groups, can be controlled by removal of natural organic matter (NOM) before disinfection. Literature removal of precursors is variable, even with the same treatment. The treatment of DBP precursors and NOM was examined with the intention of outlining precursor removal strategies for various water types. Literature Freundlich adsorption parameters and hydroxyl rate constants were collated to link treatability by activated carbon and advanced oxidation processes (AOPs) respectively, to physicochemical properties. While hydroxyl rate constants did not correlate meaningfully with any property, a moderate correlation was found between Freundlich parameters and log K_{OW}, indicating activated carbon will preferentially adsorb hydrophobic NOM. Humic components of NOM are effectively removed by coagulation and where they are the principal precursor source, coagulation may be sufficient to control DBPs. Where humic species remaining post-coagulation retain significant DBP formation potential (DBPFP), activated carbon is deemed a suitable process selection. Anion exchange is an effective treatment for transphilic (TPI) species, known for high carboxylic acid functionality and consequently is recommended for carboxylic acid precursors. Amino acids have been linked to HAA formation and are

important constituents of algal organic matter (AOM). They are predicted to be effectively removed by biotreatment and nanofiltration. Carbohydrates have been found to reach 50% of NOM in river waters. Should they pose a barrier to successful DBP control, additional treatment stages such as nanofiltration are likely to be required to reduce their occurrence.

3.2 Introduction

While disinfection of drinking water is necessary to suppress microbial activity, a significant associated risk is the formation of disinfection byproducts (DBPs) through reactions of disinfectants with natural organic matter (NOM). Many DBPs pose a health risk to humans (*1*), and consequently two halogenated groups – the trihalomethanes (THMs) and haloacetic acids (HAAs) - are regulated in the USA, at 80 µg L^{-1} and 60 µg L^{-1} for total THMs and five HAA species respectively. Total THMs are also legislated in the UK at 100 µg L^{-1}. In chlorinated drinking water, the dominant THM species is typically chloroform ($CHCl_3$), with dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) the prevalent HAA species (*2*). At high bromide concentration the formation of mixed brominated and chlorinated DBPs is typical (*2*). There are several approaches to control disinfection byproducts (DBPs), including removal of precursor material before disinfection and altering disinfectant dose, type or dosing location (*3*). However, reducing disinfectant doses is limited by the need to provide sufficient residuals for distribution. Moreover, switching disinfectant can result in formation of alternative DBPs, as illustrated by links between chloramines and N-nitrosodimethylamine (NDMA) and dichloroacetonitrile (DCAN) formation (*4*).

Therefore in several ways the removal of NOM, including precursor material, is more satisfactory. Not only is the production of alternative DBPs avoided, but precursor removal can often be attained through utilisation of existing technology. Many studies have examined DBP precursor removal, particularly THM precursors, with limited research encompassing HAA precursor removal. There is wide geographical and seasonal variation in NOM composition (*5, 6*), which is reflected in variable removal of NOM, even by the same treatment. NOM is typically characterised with adsorption chromatography into fractions of varying hydrophobicity (*5, 7*). Such procedures can be used to provide data about the relative importance of operationally-defined fractions to DBP formation. Although humic species, which comprise much of the hydrophobic NOM fractions, are thought to be the major source of DBP precursors (*8*), a range of NOM species can be involved. This conclusion is supported by model compound work, where both hydrophobic and hydrophilic molecules, notably activated aromatic species, β-dicarbonyl compounds and a small number of amino acids, have been identified as reactive DBP precursors (*9-11*). In a recent review no meaningful correlations were found between compound physicochemical properties and THM formation, indicating reliable predictors of DBP formation in natural waters are unlikely to exist (*12*). Since the majority of water treatment research uses natural waters rather than model compounds, links between DBP formation and treatability are incompletely resolved. This is compounded by very limited knowledge about specific chemical identity of DBP precursors in drinking water and the unpredictability of DBP formation. Consequently, there is uncertainty about how to operate NOM removal processes for targeted precursor removal. The objectives of this review were therefore to analyse literature data regarding removal of NOM, THM precursors and HAA precursors and consequently

highlight circumstances in which various treatment processes can be effectively deployed for precursor removal.

3.3 Precursor Removal by Coagulation

Coagulation followed by clarification and/or filtration is the standard process used to remove particulate matter and NOM from surface waters and is normally the first step of conventional water treatment (*13*). Coagulants are typically iron or aluminium salts which hydrolyse rapidly to form positively-charged insoluble precipitates in water, removing NOM through a variety of principally electrostatic mechanisms (Table 3.1). There is a wide range of efficacy associated with coagulation, with total organic carbon (TOC) removal ranging from 7-76% and removal of THM and HAA precursors from 7-76% and 15-78% respectively (Table 3.2, (*14-16*)). The respective removals of TOC, ultraviolet absorption (UV), THM formation potential (THMFP), dihaloacetic acid formation potential (DXAAFP) and trihalacetic acid formation potential (TXAAFP) of 8%, 73%, 10%, 12% and 22% in a water with 1.1 mg L^{-1} dissolved organic carbon (DOC) illustrates the lower end of treatability (Table 3.2, (*14*)). Two key points arise from comparison of this data: the higher removal of UV absorbing material compared with other parameters, and higher removal of TXAAFP relative to DXAAFP. Both are features of literature, as illustrated by a more treatable water, where removal of UV, TOC, THMFP, DXAAFP and TXAAFP were 52%, 74%, 62%, 65% and 75% respectively (Table 3.2, (*14*)). The higher susceptibility of TCAA precursors to coagulation than DCAA precursors is linked to the former's more hydrophobic nature (*14*). High removal of high molecular weight (MW), hydrophobic organics is typical during coagulation of drinking water. This is shown by respective removals of 84%,

64%, 14% and 17% for the humic acid (HAF), fulvic acid (FAF) hydrophilic acid (HPIA), and hydrophilic non-acid (HPINA) fractions of an upland water (*17*). Note the hydrophobic acid fraction (HPOA) is comprised of the HAF and the FAF. In addition HPIA and HPINA are respectively equivalent to transphilic acid (TPHA) and hydrophilic (HPI) fractions (Chapters 4, 7 and 8). This data also correlates to charge, since high anionic charge is a feature associated with hydrophobic fractions of drinking water; as shown by charge densities of 6.8, 4.2 and 0.006 meq $gDOC^{-1}$ for the HAF, FAF and HPIA fractions respectively of an upland water (*6*). A consequence of this selectivity for hydrophobic NOM is that the levels of HPINA in the raw water indicate the residual post-coagulation (*17*). Similar reasoning explains the positive relationship between SUVA and treatability (Figure 3.1), since high SUVA values indicate a high proportion of hydrophobic material in a water (*7*). The charge-driven nature of NOM coagulation means that electrophoretic monitoring is appropriate, for example it has been demonstrated how optimum removal can be achieved by operating within a zeta potential window of -10 to 3 mV (*17*). However, NOM removal is often indirectly controlled through coagulating between pH 4.5 – 6, or by using coagulant doses above those required for particle removal, termed enhanced coagulation (*13*). The effect of coagulating at acidic pH on downstream disinfection should also be considered, since chlorination at acidic pH has been reported to increase DCAA levels (*18*). However, as THMs have been found to increase and TCAA to decrease at higher pH downstream consequences are complicated (*19*), and would require empirical verification. The same applies to choice of coagulant. While it is thought that generally higher removals of precursors can be obtained with iron salts rather than aluminium salts, the latter may be more effective at low coagulant doses (*20*). Thus coagulation can be expected to be

successful for removal of DBP precursors which are anionic in character, which will typically also be hydrophobic and of high MW. However, in waters where reactive precursors are of low anionic charge or neutral, coagulation will have little impact upon their removal, and they will comprise part of the post-coagulation NOM residual. Such waters are likely to have a high proportion on HPINA species and are also likely to be of low SUVA.

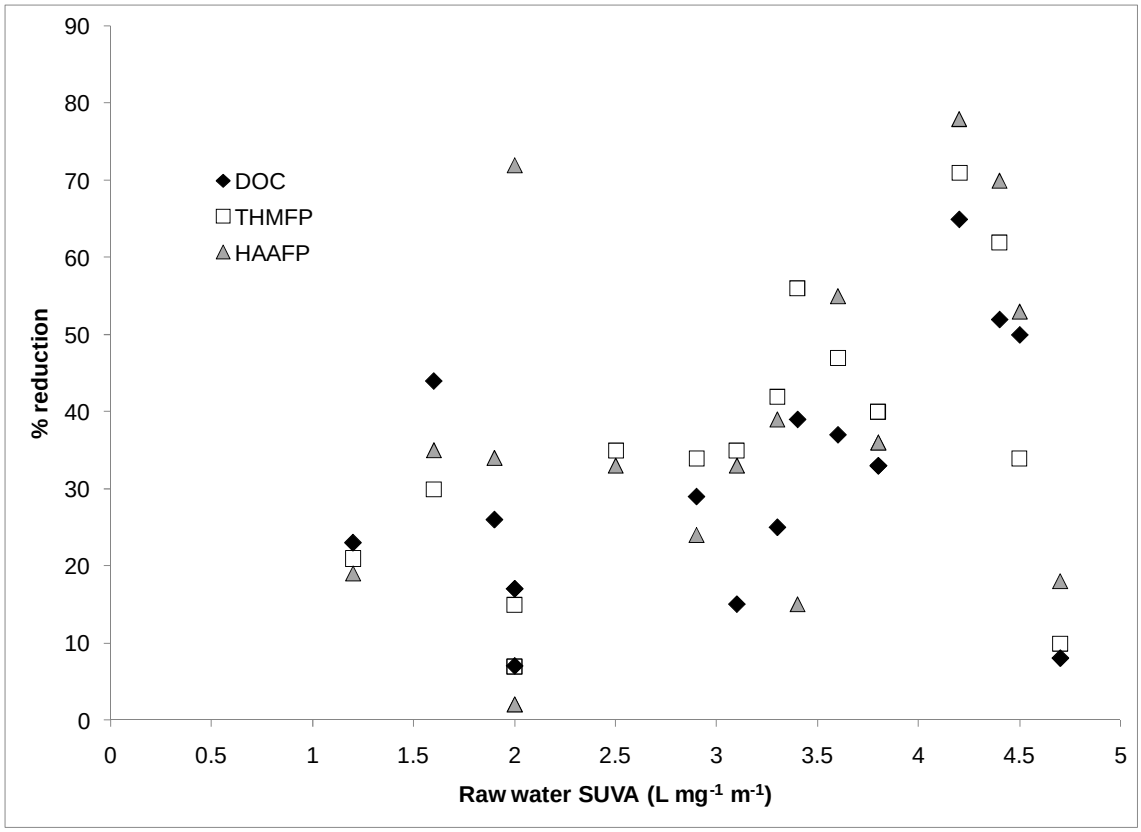

Figure 3.1: Relationships between raw water SUVA and removal of bulk NOM, THM precursors and HAA precursors by coagulation

Table 3.1: Selectivity of NOM Removal Processes

Process	Mechanism/s	Selectivity	Least treatable
Coagulation	Adsorption onto flocs and charge neutralisation/ colloid destabilisation. Sweep flocculation.	Large, anionic molecules	Neutral molecules
Anion exchange	Ion exchange (electrostatic), also adsorption (hydrophobic) and hydrogen-bonding	Small, anionic molecules	Neutral molecules
Membranes	Size exclusion, differing diffusion rates across membrane. Electrostatics for charged membranes	Species >MWCO	Hydrophobic molecules <MWCO
Activated Carbon	Reversible physical adsorption by non-specific forces	Small, neutral, hydropobic molecules	Hydrophilic charged molecules
Biotreatment	Enzyme controlled microbial degradation and adsorption	Low MW polar molecules (e.g. amino acids, aldehydes)	Large & hydrophobic molecules
AOPs	·OH reactions: electron transfer, H abstraction and OH addition	Relatively unselective	
Ozone	Electrophilic addition: oxidation and bond cleavage. Also OH radical reactions	Aromatic compounds and amines	Saturated compounds

Table 3.2: NOM and DBP Precursor Removal by coagulation and MIEX®

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1})	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Coagulation	pH 6. Alum. Optimised dose	Indianapolis Water DOC 2.8, SUVA 3.1 67% hydrophilic, 33% hydrophobic	TOC 15% UV 28%	35 %	DXAA 30% TXAA 32%	(*14*)
Coagulation	pH 6. Alum. Optimised dose	East St. Louis Water DOC 5.0, SUVA 3.3 57% hydrophilic, 43% hydrophobic	TOC 25% UV 37%	42 %	DXAA 32% TXAA 43%	(*14*)
Coagulation	pH 6. Alum. Optimised dose	Groton Water DOC 3.3, SUVA 3.6 56% hydrophilic, 44% hydrophobic	TOC 37% UV 70%	47 %	DXAA 50% TXAA 59%	(*14*)
Coagulation	pH 6. Alum. Optimised dose	Manatee Water DOC 8.2, SUVA 4.4 48% hydrophilic, 52% hydrophobic	TOC 52% UV 74%	62 %	DXAA 65% TXAA 75%	(*14*)
Coagulation	pH 6. Alum. Optimised dose	Tolt Water DOC 1.1, SUVA 4.7 42% hydrophilic, 58% hydrophobic	TOC 8% UV 73%	10 %	DXAA 12% TXAA 22%	(*14*)
Coagulation	60 mg L^{-1} Alum	NBA Water: DOC 5.1, SUVA 3.8	DOC 33%, UV 38%	40%	36%	(*15*)
MIEX	5 mL L^{-1} MIEX	NBA Water, as above	DOC 75%, UV 84%	69%	71%	(*15*)
MIEX + Coagulation	5 ml L^{-1} MIEX + 16 mg L^{-1} Alum	NBA Water, as above	DOC 76%, UV 85%	76%	73%	(*15*)
Coagulation	40 mg L^{-1} Alum	SL Water: DOC 5.2, SUVA 2.0	DOC 17%, UV 22%	7%	20%	(*15*)
MIEX	4 mL L^{-1} MIEX	SL Water, as above	DOC 42%, UV 54%	25%	52%	(*15*)
MIEX + Coagulation	4 ml L^{-1} MIEX + 20 mg L^{-1} Alum	SL Water, as above	DOC 42%, UV 58%	27%	52%	(*15*)

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1})	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Coagulation	30 mg L^{-1} Alum	Durham Water TOC = 5.1, SUVA = 3.4	TOC 39 %, UV 76%	56%	15%	(*16*)
MIEX + Coagulation	6 ml L^{-1} MIEX + 7 mg L^{-1} Alum	Durham Water, as above	TOC 76%, UV 92%	81%	nr	(*16*)
Coagulation	60 mg L^{-1} Alum	Manatee Water TOC = 10.6, SUVA = 4.5	TOC 50%, UV 78%	34%	53%	(*16*)
MIEX + Coagulation	8 ml L^{-1} MIEX + 10 mg L^{-1} Alum	Manatee Water, as above	TOC 87%, UV 94%	nr	nr	(*16*)
Coagulation	30 mg L^{-1} Alum	Indianapolis Water TOC = 4.6, SUVA = 1.9	TOC 26%, UV 23%	nr	34%	(*16*)
MIEX + Coagulation	6 ml L^{-1} MIEX + 12 mg L^{-1} Alum	Indianapolis Water, as above	TOC nr, UV 34%	nr	nr	(*16*)
Coagulation	40 mg L^{-1} Alum	Hackensack Water TOC = 4.3, SUVA = 2.5	TOC nr, UV 45%	35%	33%	(*16*)
MIEX + Coagulation	4 ml L^{-1} MIEX + 12 mg L^{-1} Alum	Hackensack Water, as above	UV 81%	82%	nr	(*16*)
Coagulation	10 mg L^{-1} Alum	Manchester Water TOC = 2.6, SUVA = 1.2	TOC 23%, UV 3%	21%	19%	(*16*)
MIEX + Coagulation	2 ml L^{-1} MIEX + 10 mg L^{-1} Alum	Manchester Water, as above	TOC 46%, UV 47%	60%	58%	(*16*)
Coagulation	45 mg L^{-1} Alum	Sioux Falls Water TOC = 8.7, SUVA = 1.6	TOC 44%, UV 26%	30%	35%	(*16*)
MIEX + Coagulation	6 ml L^{-1} MIEX + 20 mg L^{-1} Alum	Sioux Falls Water, as above	TOC 72%, UV 76%	66%	59%	(*16*)
Coagulation	30 mg L^{-1} Alum	MWD Water TOC = 2.8, SUVA = 2.9	TOC 29%, UV 41%	34%	24%	(*16*)
MIEX + Coagulation	6 ml L^{-1} MIEX + 10 mg L^{-1} Alum	MWD Water, as above	TOC 61%, UV 80%	79%	79%	(*16*)

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1})	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Coagulation	20 mg L^{-1} Alum	Austin Water TOC = 2.8, SUVA = 2.0	TOC 7%, UV 27%	15%	72%	(*16*)
MIEX + Coagulation	6 ml L^{-1} MIEX + 10 mg L^{-1} Alum	Austin Water, as above	TOC 54%, UV 79%	79%	80%	(*16*)
Coagulation	150 mg L^{-1} Alum	Tampa Water TOC = 26.4, SUVA = 4.2	TOC 65%, UV 80%	71%	78%	(*16*)
MIEX + Coagulation	8 ml L^{-1} MIEX + 45 mg L^{-1} Alum	Tampa Water, as above	TOC 89%, UV 96%	88%	nr	(*16*)

nr = not recorded

3.4 Precursor Removal by Ion Exchange

Ion exchange removal mechanisms relate to the exchange an ion in the aqueous phase for one in the solid phase attached to the ion exchanger (Table 3.1). For example, the MIEX® anion exchange resin developed for NOM removal works by exchanging anionic NOM for a chloride ion attached to the cationic resin surface (*21*). MIEX® is a relatively novel process used as an alternative to coagulation or as an adjunct to reduce coagulant doses. Reports on its use have shown improved removal of NOM and THM precursors relative to coagulation (*22*). For instance, coagulation of one water water with 60 mg L^{-1} Alum attained respective removals of DOC, UV, THMFP and HAAFP at 33%, 38%, 40% and 36% (Table 3.2, (*15*)). Equivalent values with 5 mL L^{-1} MIEX® were 75%, 84%, 69% and 71%. Combined treatment, with 5 mL L^{-1} MIEX® then 16 mg L^{-1} Alum was still more effective, with equivalent values of 76%, 85%, 76% and 73% (Table 3.2), indicating synergistic benefits of combined treatment, and that MIEX® pre-treatment can reduce coagulant doses. Whilst there is still debate regarding the type of NOM which MIEX® treats more effectively than coagulation, evidence suggests transphilic NOM is involved. Lee and co-workers (21) found MIEX® removed between 63-75%, 70-89% and 2-67% of the hydrophobic, transphilic and hydrophilic fractions respectively in three waters. The transphilic acid fraction was also found to have higher affinity for MIEX® than other fractions (*23*), this being explained by its higher charge density. While the exact chemical identity of transphilic acids is unknown, they are assumed to be more hydrophilic than the hydrophobic acids and with a high proportion of carboxylic acid functionality (*24*). In a recent study, uptake of a water of hydrophobic-character deteriorated from 65 - 25% with consecutive MIEX® use designed to simulate full-scale operation; whereas removal of two waters of hydrophilic

and algogenic-character were more consistent at ~60% and ~30% respectively (*22*). These differences were explained by the hydrophobic-character water containing more high MW species capable of blocking resin exchange sites, and the algogenic water containing a higher proportion of neutral species. Thus as with coagulation, NOM composition has a strong influence on treatability, although it appears with anion exchange the amount of hydrophobic species is not the determining factor. An added benefit of MIEX® is that it offers some removal of bromide, although this decreases with increasing alkalinity and bromide concentration (*25*). This is significant as bromine, formed by the oxidation of bromide in the presence of chlorine, is a more effective substitution agent than chlorine and has been found to increase DBP levels (*2*). However, removal is inconsistent: in one water with alkalinity 20 mg L^{-1} as $CaCO_3$, MIEX® effected as reduction in bromide from 163 to <10 µg L^{-1}, contrasting with another water with alkalinity 155 mg L^{-1} as $CaCO_3$ and bromide 38 µg L^{-1}, where no bromide reduction was observed (*16*). This variability was rationalised by increasing competition for ion exchange sites by bicarbonate ions in the higher alkalinity water. Residual NOM remaining after ion exchange is thought to be mainly comprised of neutral compounds (26). Thus ion exchange is likely to be most effective for treatment of hydrophobic and especially transphilic DBP precursors, but also offers removal of low molecular-weight anionic material. As with coagulation, residual NOM remaining post-treatment will be neutral and low charge species, properties associated with the hydrophilic components of NOM (*6*).

3.5 Analysis Methods for Activated Carbon and Advanced Oxidation Processes

To elucidate relationships between compound properties and removal by activated carbon (AC) and advanced oxidation processes (AOPs), Freundlich adsorption parameters (log K_F (capacity parameter) and 1/n (intensity parameter)) and aqueous hydroxyl rate constants ($k_{\cdot OH}$) were collated (*27-30*) for 158 compounds (Table 3.3). The following compound physicochemical properties were also assembled: molecular weight (MW), octanol-water partition coefficient (log K_{OW}), molar volume (MV), surface tension (γ), polar surface area (PSA), polarizability (α), density and the soil-water partition coefficient (log K_{OC}) (Table 3.3). Properties were taken from (*31-34*), with experimental values were used wherever available. log K_{OC} values were estimated with (*31*) using two different models. Literature THM formation data was included where available (*35, 36*). The Pearson product-moment correlation coefficient (r) calculated with Minitab 15™ was used to assess relationships between adsorption parameters and compound physicochemical properties (Table 3.4 and 3.5). This coefficient is used to measure the degree of linear relationship between two variables and can assume a value from $^{-}1$ to +1.

Table 3.3: Literature Freundlich adsorption parameters and physicochemical properties

Compound	log K_F	1/n	log K_{OC}	THMFP	log K_{OW}	MW	MV	γ	PSA	α 10^{-24}	ρ	$k_{\cdot OH}$
				µg mgC^{-1}		Da	cm^3	dyne/cm	$Å^2$	10^{-24} cm^3	g/cm^3	10^{-8} $M^{-1}s^{-1}$
1,1,1-Trichloroethane	0.35	0.34	1.69		2.49	133	96	28.9	0.0	10.2	1.39	1
1,1,2,2-Tetrachloroethane	1.04	0.37	2.03		2.39	168	108	33.9	0.0	12.1	1.56	
1,1,2-Trichloroethane	0.76	0.6	1.83		1.89	133	96	29.7	0.0	10.2	1.44	3
1,1-Dichloroethane	0.26	0.53	1.54		1.79	99	85	23.2	0.0	8.3	1.18	1.3
1,1-Dichloroethylene	0.69	0.54	1.54		1.77	97	79	23.1	0.0	8.2	1.22	
1,1-Diphenylhydrazine	2.13	0.16	3.50		2.8	184	161	52	6.5	23.5	1.14	
1,2,3,4-Tetrahydronaphthalene (tetralin)	1.87	0.81	3.26		3.49	132	136	35.8	0.0	17.1	0.97	
1,2,4-trichlorobenzene	2.20	0.31	2.86		2.97	181	125	39.9	0.0	16.2	1.45	
1,2-cis-Dichloroethylene	1.08	0.59	1.64		1.86	97	78	25.9	0.0	8.4	1.24	38
1,2-Dibromoethane	1.70	0.48	1.64		1.96	188	88	36.4	0.0	10.6	2.17	
1,2-Dibromoethene	1.34	0.46	1.64		1.76	186	82	38.5	0.0	10.6	2.28	
1,2-Dichlorobenzene	2.42	0.38	2.65		3.28	147	113	36.7	0.0	14.3	1.30	25
1,2-Dichloroethane	0.56	0.83	1.64		1.41	99	84	25	0.0	8.3	1.17	7.9
1,2-Dichloropropane	1.28	0.59	1.83		1.98	113	101	24.7	0.0	10.2	1.16	4
1,2-Dichloropropene	0.91	0.46	1.83		2.3	111	94	25.5	0.0	10.1	1.18	
1,2-trans-Dichloroethene	0.49	0.51	1.64		1.86	97	78	25.9	0.0	8.4	1.25	50
1,3-Dichlorobenzene	2.07	0.45	2.64		3.42	147	113	36.7	0.0	14.3	1.30	22
1,4-Dichlorobenzene	2.08	0.47	2.64		3.34	147	113	36.7	0.0	14.3	1.30	53
1,4-Dimethylbenzene (p-xylene)	1.93	0.19	2.64		3.15	106	122	28.7	0.0	14.2	0.87	70
1-Chloro-2-nitrobenzene	2.11	0.46	2.50		2.34	158	113	48.3	45.8	14.9	1.39	
2,4,6-Trichlorophenol	2.11	0.39	3.07	58	3.69	198	124	50.5	20.2	17.0	1.60	120
2,4-D	1.83	0.27	1.47		2.81	221	148	51.2	35.5	19.4	1.57	
2,4-Dichlorophenol	2.20	0.15	2.86	78	2.92	163	112	47.8	9.2	15.0	1.46	
2,4-Dimethylphenol	1.89	0.44	2.86		2.4	122	120	37.2	20.2	15.0	1.01	

Compound	log K_F	1/n	log K_{OC}	THMFP	log K_{OW}	MW	MV	γ	PSA	α 10^{-24}	ρ	k_{OH}
2,4-Dinitrophenol	1.52	0.61	2.56		1.67	184	112	79.6	100.9	16.3	1.65	
2,4-Dinitrotoluene	2.16	0.31	2.56		2.08	182	129	57.2	91.6	17.5	1.52	
2,6-Dinitrotoluene	2.16	0.32	2.57		2.08	182	129	57.2	91.6	17.5	1.41	
2-Acetylaminoflourene	2.50	0.12			3.03	223	181	53.4	20.3	27.0	1.23	
2-Chloro-5-hydroxy-toluene	2.00	0.42			2.89	143	116	42.1	20.2	15.0	1.37	
2-Chloroethyl vinyl ether	0.59	0.8	0.91		1.04	107	107	24.2	9.2	10.7	0.99	
2-Chloronapthalene	2.45	0.46	3.47		4.14	162	136	42.9	0.0	19.4	1.20	
2-Chlorophenol	1.71	0.41	2.65		2.04	129	100	44.7	20.2	13.1	1.28	120
2-Methoxyaniline	1.70	0.34	1.51		1.09	123	116	39.3	35.3	14.7	1.06	
2-Nitrophenol	2.00	0.34	2.50		1.71	139	100	60.2	66.1	13.7	1.40	
2-Phenyl-2-propanol	2.32	0.34	1.55		1.73	136	137	34.4	9.2	16.5	0.97	46
3,3-Dichloro-4,4-diamino-diphenylmethane	2.28	0.64			1.46	269	204	55	52.0	29.2	1.31	
3,3-dichlorobenzidine	2.48	0.2	3.87		1.28	255	187	57.4	52.0	27.3	1.36	
3,4-Benzofluoranthene	1.76	0.37			6.23	252	196	63.4	0.0	35.8	1.29	
3,4-Dinitrotoluene	2.43	0.17	2.56		2.2	182	129	57.2	91.6	17.5	1.41	
3,5-Dinitro-6-hydroxytoluene	1.63	0.9			2.13	198	128	70.8	100.9	18.3	1.55	
4,4-Diamino-3,3-dichlorobiphenyl	2.48	0.2			3.51	253	183	57.3	6.5	27.4	1.38	
4,4-Methylene-bis-(2-chloroaniline)	2.28	0.64	4.13		3.91	267	197	56.8	6.5	29.3	1.44	
4,6-Dinitro-o-cresol	2.23	0.27	2.78		2.13	198	128	70.8	100.9	18.3	1.55	
4-Aminobiphenyl	2.30	0.26	3.23		2.86	169	157	44.9	3.2	21.8	1.16	
4-Bromophenyl phenyl ether	2.16	0.68	3.62		5.11	249	176	42.1	9.2	23.9	1.42	
4-Chlorophenyl phenyl ether	2.05	0.26	3.62		4.7	204	172	40.6	9.2	22.8	1.19	
4-Dimethylaminoazobenzene	2.40	0.24	2.96		4.58	225	219	37.7	28.0	28.4	1.02	
4-Nitrobiphenyl	2.57	0.27	3.86		3.59	199	167	47	45.8	22.8	1.20	
4-Nitrophenol	1.88	0.25	2.49		1.91	139	100	60.2	55.1	13.7	1.40	38
4-Nonylphenol	2.40	0.37	4.78		5.76	220	236	35.6	9.2	27.8	0.94	
5-Bromouracil	0.60	0.47	0.93		-0.21	191	97	54.6	40.6	13.0	1.97	52
5-Chlorouracil	1.40	0.58	0.93		-0.35	147	91	57.3	40.6	12.1	1.61	55

Compound	log K_F	1/n	log K_{OC}	THMFP	log K_{OW}	MW	MV	γ	PSA	α 10^{-24}	ρ	k_{OH}
5-Fluorouracil	0.74	1	0.93		-0.89	130	85	46.1	40.6	10.2	1.53	52
6-Amino-purine	1.85	0.38			-0.09	135	84	122.7	46.8	14.7	1.61	
Acenaphthene	2.28	0.36	3.79		3.92	154	135	49.2	0.0	20.5	1.15	
Acenaphthylene	2.06	0.37	3.79		3.94	152	128	54.7	0.0	20.3	0.90	
Acetamino-fluorene	2.50	0.12			2.8	239	181	63.3	29.5	27.6	1.32	
Acetophenone	1.87	0.44	1.66	124	1.58	120	121	34.1	17.1	14.4	0.99	54
Acridine orange	2.26	0.29			3.62	302			19.4			90
Acridine yellow	2.36	0.12	5.45		2.02	274			19.4			
Acrolein	0.08	0.65	0.44		-0.01	70	20	17.07	6.3	0.8		70
Acrylonitrile	0.15	0.51	0.92		0.25	53	67	25	23.8	6.2	0.81	53
Adenine	1.85	0.38	1.29		-0.09	135	84	122.7	46.8	14.7	1.61	58
Adipic acid		0	1.33		0.08	146	117	52.4	52.6	13.1	1.36	20
Alachlorh	2.68	0.26	2.27		3.52	270	241	39.8	29.5	30.0	1.12	
Aldicarb	2.12	0.4	1.51		1.13	190	175	34.3	67.2	20.1	1.08	
Aldrin	2.81	0.92	5.02		6.5	365	211	55.3	0.0	30.8	1.60	
alpha-BHC	2.48	0.43	3.53		3.72	291	183	41	0.0	22.5	1.59	
alpha-Endosulfan	2.29	0.5	4.34		3.83	407	209	74.9	54.7	31.1	1.74	
alpha-Naphthol	2.26	0.32	3.48		2.85	144	122	51	9.2	18.2	1.28	130
alpha-Napthylamine	2.20	0.34			2.25	143	126	51.4	3.2	19.2	1.12	
Anethole	2.48	0.42	2.83		3.17	148	154	31.8	9.2	48.8	0.96	
Anthracene	2.58	0.7	4.31		4.45	178	158	47.9	0.0	24.6	1.25	
Atrazine	2.26	0.18	2.36		2.61	216	170	53.8	45.2	23.2	1.19	
Benzene	0.00	2.3	2.22	12	2.13	78	89	28.8	0.0	10.4	0.87	79
Benzidine dihydrochloride	2.34	0.37	2.22		1.56	257			6.5			
Benzo(alpha)pyrene	1.53	0.44			6.4	252	196	63.4	0.0	35.8	1.29	
Benzo(b)fluoranthene	1.76	0.37	6.44		5.78	252	196	63.4	0.0	35.8	1.29	
Benzo(g,h,i)perylene	1.04	0.37			6.89	276	200	74.2	0.0	40.0	1.38	
Benzo(k)fluoranthene	2.26	0.57			6.11	252	196	63.4	0.0	35.8	1.29	

Compound	log K_F	1/n	log K_{OC}	THMFP	log K_{OW}	MW	MV	γ	PSA	α 10^{-24}	ρ	k_{OH}
Benzoic acid	-0.12	1.8	1.16	9	1.87	122	102	48.7	26.3	13.2	1.20	18
Benzothiazole	2.08	0.27	3.00		2.01	135	106	54.2	41.1	16.1	1.27	
beta-BHC	2.34	0.49			3.72	291	183	41	0.0	22.5	1.59	
beta-Endosulfan	2.79	0.83	4.34		3.83	407	209	74.9	54.7	31.1	1.94	
beta-Naphthylamine	2.18	0.3	3.47		2.25	143	126	51.4	3.2	19.2	1.12	
beta-Napthol	2.30	0.26	3.47		2.7	144	122	51	9.2	18.2	1.28	120
Bis(2-Chloroethoxy) methane	1.04	0.65			1.28	172	147	31.5	18.5	15.2	1.18	
Bis(2-Chloroisopropyl) ether	1.38	0.57	1.33		2.48	171	157	27.9	9.2	16.3	1.09	
Bis(2-ethylhexyl phthalate)	4.05	1.5	5.22		8.1	391	396	36.4	52.6	45.5	0.98	
Bromoform	1.29	0.52	1.54		2.4	253	85	49.8		11.8	2.89	1
Butylbenzyl phthalate	3.18	1.26	1.54		9.29	459	418	43.3	52.6	54.1	1.10	
Carbofuran	2.42	0.41	1.85		2.32	221	194	40.5	38.8	23.7	1.18	32
Carbon tetrachloride	1.04	0.83	1.69		2.83	154	91	35.2	0.0	10.3	1.59	
Chlordane	2.28	0.33	1.69		6.1	410	226	54.1		31.8	1.80	
Chlorobenzene	1.96	0.99	2.43		2.84	113	101	33	0.0	12.3	1.11	56
Chlorodibromoethane	1.65	0.517			2.55	222	99	39.8	0.0	12.5	2.24	
Chloroethane	-0.23	0.95	2.43		1.43	65	73	17.9	0.0	6.4	0.92	
Chloroform	0.41	0.73	1.38		1.97	119	80	28.9	0.0	8.4	1.49	0.5
Cyclohexanone	0.79	0.75	1.54		0.81	98	103	32.5	17.1	11.0	0.95	
Cytosine	0.04	1.6	2.39		-2.29	111	72	69.2	35.9	10.8	1.55	63
DDE	2.37	0.37	5.18		6.51	318	227	45.7	0.0	31.7	1.40	
DDT	2.51	0.5			6.91	355	244	46.8	0.0	33.5	0.99	
Diamino-biphenyl-dihydrochloride	2.34	0.37			1.56	257			6.5			
Dibenzo(a,h)anthracene	1.83	0.75	5.34		6.75	278	226	57.7	0.0	38.7	1.23	
Dibenzo(a,h)anthrazene	1.84	0.75	5.34									
Dibromochloromethane	0.68	0.34	1.54		2.16	208	83	42.2	0.0	10.7	2.42	
Dibromochloropropane	2.35	0.51	1.54		2.96	236	116	39.6	0.0	14.4	2.05	
Dichlorobromomethane	0.90	0.61			2	164	81	35.3	0.0	9.5	1.98	
Dieldrin	2.78	0.51	4.03		5.4	381	206	60.2	12.5	30.7	1.75	

Compound	log K_F	1/n	log K_{OC}	THMFP	log K_{OW}	MW	MV	γ	PSA	α 10^{-24}	ρ	$k_{\cdot OH}$
Diethyl phthalate	2.04	0.27	2.10		2.7	222	198	39.3	52.6	23.4	1.12	
Dimethyl phthalate	1.99	0.41	1.57		1.64	194	165	40.5	52.6	19.7	1.18	
Dimethylphenylcarbinol	2.32	0.34			1.73	136	137	34.4	9.2	16.5	0.97	
Diphenylamine	2.08	0.31	3.28		3.5	169	155	44	3.2	22.1	1.16	100
Endosulfan sulphate	2.84	0.81	4.51		3.66	423	218	65.9	61.0	31.1	1.94	
Endothall	1.34	0.329	1.00		1.91	186	121	68.8	61.8	15.7	1.54	15
Endrin	2.82	0.8	4.03		5.4	381	206	60.2	12.5	30.7	1.75	3
Ethylbenzene	1.72	0.79	2.71		3.15	106	122	29	0.0	14.2	0.87	75
Ethylenediaminetetraacetic acid	-0.07	1.5	3.02		-0.43	292	187	86.1	111.7	24.6	1.57	20
Fluorene	2.52	0.28	4.05		4.18	166	148	46.2	0.0	21.3	1.20	
gamma-BHC (lindane)	2.45	0.43	3.53		3.72	291	183	41	0.0	22.5	1.59	
Guanine	2.08	0.4	1.01		-0.98	151	69	124	53.7	14.1	2.19	92
Heptachlor	3.09	0.95	4.72		5.47	373	208	54.7	0.0	29.9	1.66	
Heptachlor epoxide	3.33	0.75	4.72		4.98	389	203	59.6	12.5	29.8	1.91	
Hexachlorobenzene	2.65	0.6	3.53		5.73	285	161	47.2	0.0	22.1	1.77	
Hexachlorobutadiene	2.41	0.45	3.00		4.78	261	149	42.4	0.0	19.5	1.68	
Hexachloroethane	1.98	0.38	2.35		4.14	237	130	42.8	0.0	16.0	2.09	
Isophorone	1.51	0.39	2.35		1.7	138	153	26.4	17.1	16.4	0.92	
Methoxychlor	2.06	0.36	4.63		5.08	346	268	41.3	18.5	34.9	1.41	
Methyl ethyl ketone	1.29	0.295	0.58		0.29	72	92	21	17.1	8.2	0.81	
Methylene chloride	0.11	1.16	1.38		1.25	85	68	23.1	0.0	6.5	1.22	
m-Xylene	2.36	0.75	2.64	60	3.2	106	122	28.7	0.0	14.2	0.87	75
Naphthalene	2.12	0.42	3.26	29	3.3	128	124	40.2	0.0	17.5	1.04	94
n-Butylphthalate	2.34	0.45	3.16		2.86	220			80.2			
N-Dimethylnitrosamine	-4.17	6.6	1.58		-0.57	74	75	30.4	32.7	19.2	1.01	
Nitrobenzene	1.83	0.43	2.28		1.95	123	101	45.3	45.8	13.0	1.20	39
N-Nitrosodi-n-propylamine	1.38	0.26	2.69		1.36	130	140	31.1	32.7	14.9	0.93	
n-Nitrosodiphenylamine	2.34	0.37	3.75		3.13	198	182	44	32.7	24.0	1.09	
o-Anisidine	1.70	0.34	1.51		1.18	123	116	39.3	35.3	14.7	1.10	

Compound	log K_F	1/n	log K_{OC}	THMFP	log K_{OW}	MW	MV	γ	PSA	α 10^{-24}	ρ	$k_{\cdot OH}$
o-Xylene	2.24	0.47	2.65		3.12	106	122	28.7	0.0	14.2	0.88	67
PCB	4.15	1.03			6.29	292	203	44.8	0.0	27.9	1.44	
p-Chlorometacresol	2.09	0.16			2.89	143	116	42.1	20.2	15.0	1.37	
Pentachlorophenol	2.64	0.34	3.53		5.12	266	148	54.7	9.2	20.9	1.98	
Phenanthrene	2.33	0.44	4.32		4.46	178	158	47.9	0.0	24.6	1.18	
Phenol	1.32	0.54	2.43	154	1.46	94	88	40.9	9.2	11.2	1.07	66
Phenyl mercuric acetate	2.43	0.44	2.43		-0.38	44			12.0			
p-Nitroaniline	2.15	0.27	1.71		1.39	138	104	60.3	71.8	14.7	1.33	140
p-Nonylphenol	2.40	0.37	4.78		5.76	220	236	35.6	9.2	27.8	0.94	
Silvex	2.33	0.38	1.91		3.8	270	177	49.5	35.5	23.2	1.52	
Styrene	2.51	0.48	2.71	44	2.95	104	115	30.9	0.0	14.7	0.90	60
Tetrachloroethylene	1.71	0.56	2.03		2.95	166	100	35.6	0.0		12.07	20
Tetraline	1.87	0.81			3.49	132	136	35.8	0.0	17.1	0.97	
Thymine	1.43	0.51	0.93		-0.62	126	103	35.7	40.6	11.8	1.23	64
Toluene	1.42	0.44	2.03	23	2.73	92	106	28.8	0.0	12.3	0.87	51
Toxaphene	2.98	0.74	5.00		6.37	412	246	47.4	0.0	32.7	1.65	5
Tribromomethane	1.71	0.6889			2.29	253	85	49.8	0.0	11.8	2.97	
Trichloroethylene	1.45	0.62	2.43		2.26	131	89	31	0.0	10.2	1.47	29
Trichlorofluoromethane	0.75	0.24	1.69		2.53	137	85	26.3	0.0	8.5	1.47	
Uracil	1.04	0.63	1.83		-1.07	112	85	41.3	40.6	9.9	1.32	57

Notation: log K_F = Freundlich capacity parameter, 1/n = Freundlich intensity parameter (dimensionless), log K_{OC} = log (soil/water partition coefficient), THMFP = THM formation potential (µg mgC^{-1}), log K_{OW} = log (octanol/water partition coefficient), molecular weight (MW), molar volume (MV), γ = surface tension (dyne/cm^2), PSA = polar surface area ($Å^2$), α = polarisability (10^{-24} cm^3), ρ = density (g cm^{-3}), , $k_{\cdot OH}$ = aqueous hydroxyl radical rate constant (10^{-8} mol L^{-1} s^{-1}).

Table 3.4: Correlations between Compound Properties and log K_F for all compounds

	log K_F	**1/n**	**log K_{OC}**	**THMFP**	**log K_{OW}**	**MW**	**MV**	**γ**	**PSA**	**α**	**Density**
				µg mgC^{-1}		Da	cm^3	dyne/cm	Å^2	10^{-24} cm^3	g/cm^3
1/n	**-0.574**										
log K_{OC}	**0.546**	-0.07									
THMFP	0.347	-0.501	0.058								
log K_{OW}	**0.568**	-0.107	**0.69**	-0.424							
MW	**0.557**	-0.057	**0.574**	0.074	**0.676**						
MV	**0.609**	-0.044	**0.622**	-0.055	**0.765**	0.818					
γ	0.26	-0.097	0.242	0.117	0.006	0.371	0.165				
PSA	0.038	0.022	-0.128	0.189	-0.318	0.116	0.097	0.501			
α	**0.556**	0.005	**0.686**	-0.073	**0.753**	0.787	0.91	0.329	0.073		
Density	0.018	-0.026	-0.044	0.137	0.002	0.147	-0.095	0.116	-0.024	-0.04	
k_{-OH} (10^{-8} $M^{-1}s^{-1}$)	0.309	-0.154	0.187	0.07	-0.048	-0.21	-0.107	0.169	0.08	0.033	-0.168

Table 3.5: Correlations between Compound Properties and log K_F for non-halogenated compounds

	log K_F	**1/n**	**log K_{OC}**	**THMFP**	**log K_{OW}**	**MW**	**MV**	**γ**	**PSA**	**α**	**Density**
				µg mgC^{-1}		Da	cm^3	dyne/cm	$Å^2$	10^{-24} cm^3	g/cm^3
1/n	**-0.763**										
log K_{OC}	0.384	-0.112									
THMFP	0.335	-0.499	0.024								
log K_{OW}	**0.473**	-0.129	**0.655**	-0.541							
MW	**0.4**	-0.091	0.462	0.023	**0.68**						
MV	**0.483**	-0.046	0.485	-0.068	**0.798**	0.908					
γ	0.049	-0.111	0.026	0.079	-0.138	0.258	-0.076				
PSA	-0.036	0.031	-0.288	0.203	-0.338	0.219	-0.013	0.419			
α	0.358	0.018	**0.56**	-0.116	**0.795**	0.853	0.858	0.105	-0.109		
Density	-0.009	-0.095	-0.114	0.149	-0.268	0.233	-0.159	0.888	0.599	-0.002	
k_{OH} (10^{-8} $M^{-1}s^{-1}$)	0.396	-0.193	0.412	0.088	0.264	-0.1	-0.145	-0.019	-0.342	0.04	-0.022

3.6 Precursor Removal by Activated Carbon Adsorption

The primary adsorbent used for water treatment is activated carbon (AC), which can be applied as powdered activated carbon (PAC) or granular activated carbon (GAC). While PAC can be applied at various stages of water treatment, GAC is typically utilised after coagulation-filtration/sedimentation but before post-disinfection (*7*). Activated carbon is variously employed for removal of specific contaminants such as pesticides as well as taste and odour causing compounds, and bulk NOM. GAC can offer preferential removal of DBP precursors over bulk NOM (Table 3.6, (*37*-*39*)). After 50 days operation, removal of DOC, THM precursors and HAA precursors were high at 80%, 95% and 89% respectively (Table 3.6, (*39*)). After 250 days respective removals were 42%, 40% and 71%. This data is from a full-scale trial with empty bed contact time (EBCT) 21 mins and illustrates how initially high removal levels declines over the bed life of the GAC. A minimum EBCT of 10-15 is generally recommended for DBP precursor removal (*39*). Reversible physical adsorption caused by non-specific mechanisms such as van der Waals forces dipole interactions and hydrophobic interactions are considered the commonest means of sorption (Table 3.1, (*40*)). In the presence of oxygen it is thought that AC can act as a catalyst for oxidative coupling reactions between phenolic compounds, which can affect the degree of sorption (*41*).

Many literature Freundlich parameters are for toxic and halogenated compounds, thus to more accurately reflect the nature of NOM correlations for non-halogenated compounds are also presented (Table 3.5). For both sets of compounds log K_F shows moderate correlations with log K_{OW}, molecular weight and molecular volume. For the complete set of compounds these relationships have correlations of 0.568 (Figure 3.2), 0.557 and

0.609 (157, 157 and 151 data pairs) respectively (Table 3.4). For the non-halogenated compounds the equivalent correlations are 0.473, 0.4 and 0.483 (81, 81 and 77 data pairs) respectively (Table 3.5). In addition for all compounds log K_F exhibits positive correlations with log K_{OC} and polarisability, at 0.546 and 0.556 (134 and 150 data pairs) respectively. These trends indicate adsorbability increases with compound size and hydrophobicity, but that while MW and log K_{OW} provide an indication of adsorption performance, these relationships are not strong enough to be used as accurate predictors. Correlations with MW and α are in accordance with Traube's rule, which states adsorbability increases with size for a series of homologous organic compounds, corresponding to increasing polarisability. Part of the reason for weakness of correlations is the very wide range of values exhibited for log K_F: from -4.17 for N-dimethylnitrosamine to 4.14 for PCB, which equate to K_F values ranging from 6.8×10^{-5} to 1.41×10^{4} (Figure 3.2). In contrast the other properties examined do not vary by such a magnitude. THM formation does not correlate with any physiochemical property (Table 3.4 and 3.5), in accordance with a more extensive study of model compound DBP formation (*12*).

However, literature suggests that for NOM adsorption these correlations are complicated by size exclusion and electrostatic effects. It has been reported that smaller humic acids were preferentially removed by an activated carbon (*42*), this being explained by size exclusion, with smaller GAC pores being less accessible to high MW components of NOM molecules. While average NOM size is thought to be in the range 4-40 Å, the mean pore radius of F400 carbon commonly used in water treatment is 12 Å (42). This is the likely explanation for carbons with larger pore size having been found

to perform more effectively in regard to NOM uptake (*43*), while a more recent study recommended selection of a carbon with pores > 1 nm (*44*). Increased NOM uptake, particularly of HAA precursors has been observed for a steam-treated carbon with increased mesopores, relative to non-modified carbon, although for a more hydrophilic water differences were negligible (*44*). However, since there is limited knowledge about DBP precursor size, assessing the benefits of using a carbon with increased mesopores for precursor uptake requires empirical investigation and is site specific. Electrostatics also affect adsorption, with coulombic repulsion between anionic solutes and acidic groups on the carbon surface being the most relevant interactions (*43*). The same study recommended selection of a carbon with a basic point of zero charge (pH_{pzc}) to facilitate coulombic attraction between NOM and AC. As most molecules listed in Table 3.3 are neutral, pK_a values were not included as a compound property. Overall, while the correlation of 0.557 between log K_F and MW (Table 3.4) is influenced by the carbon pore size distribution and electrostatic interactions are affected by the charge of the carbon surface; hydrophobic molecules are more treatable than hydrophilic (Figure 3.2). Activated carbon will be most successful when reactive precursors belong to this category.

Table 3.6: NOM and DBP precursor removal by AOPs and activated carbon

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1}, alkalinity mg L^{-1} as $CaCO_3$)	Bulk removal	THM precursor removal	HAA precursor removal	Reference
UV/H_2O_2	UV: 500 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}	DOC 1.4 - 2.0. SUVA 3.2 – 5.1	DOC -11% UV 24%	8%	DCAAFP: -35% TCAAFP: 8%	(*37*)
UV/H_2O_2	UV: 550 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}	As above	DOC -6% UV 20%	44%	DCAAFP: -11% TCAAFP: 6%	(*37*)
UV/H_2O_2	UV: 1300 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}	As above	DOC -8% UV 32%	48%	DCAAFP: -197% TCAAFP: 11%	(*37*)
UV/H_2O_2	UV: 3000 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}	As above	DOC 20% UV 59%	73%	DCAAFP: -74% TCAAFP: 69%	(*37*)
BAC	3 days contact, EBCT 8.2 mins	As above	DOC 28% UV 22%	11%	DCAAFP: -11% TCAAFP: 8%	(*37*)
BAC	3 days contact, EBCT 8.2 mins	As above	DOC 15% UV 23%	-9%	DCAAFP: 29% TCAAFP: 46%	(*37*)
BAC	3 days contact, EBCT 8.2 mins	As above	DOC 13% UV 11%	6%	DCAAFP: -4% TCAAFP: 32%	(*37*)
BAC	3 days contact, EBCT 8.2 mins	As above	DOC 26% UV 28%	14%	DCAAFP: -1% TCAAFP: 2%	(*37*)
UV/H_2O_2 - BAC	UV: 500 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}, BAC as above	As above	DOC 51% UV 60%	42%	DCAAFP: 37% TCAAFP: 50%	(*37*)
UV/H_2O_2 - BAC	UV: 550 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}, BAC as above	As above	DOC 38% UV 45%	56%	DCAAFP: 3% TCAAFP: 42%	(*37*)
UV/H_2O_2 - BAC	UV: 1300 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}, BAC as above	As above	DOC 67% UV 70%	58%	DCAAFP: 40% TCAAFP: 71%	(*37*)
UV/H_2O_2 - BAC	UV: 3000 mJ cm^{-2}, H_2O_2: 10-20 mg L^{-1}, BAC as above	As above	DOC 80% UV 81%	85%	DCAAFP: 63% TCAAFP: 85%	(*37*)
O_3-UV	UV: 0.13 W s cm^{-2}, ozone consumption 0.004 mg mL^{-1}	TOC: 1.8, alkalinity 4, pH 6.6, SUVA 4.	DOC 17% UV: 90%	48%	48%	(*38*)

Process/es	Process parameters	Water characteristics	Bulk removal	THM precursor removal	HAA precursor removal	Reference
O_3-UV	UV: 0.27 W s cm^{-2}, ozone consumption 0.008 mg mL^{-1}	As above	DOC 19% UV: 91%	50%	54%	(*38*)
O_3-UV	UV: 0.81 W s cm^{-2}, ozone consumption 0.026 mg mL^{-1}	As above	DOC 39% UV: 94%	80%	74%	(*38*)
O_3-UV	UV: 1.61 W s cm^{-2}, ozone consumption 0.062 mg mL^{-1}	As above	DOC 56% UV: 91%	89%	83%	(*38*)
GAC	EBCT 21 mins, full-scale, 0 days	DOC variable	DOC 87%	97%	73%	(*39*)
GAC	EBCT 21 mins, full-scale, 50 days	DOC variable	DOC 80%	95%	89%	(*39*)
GAC	EBCT 21 mins, full-scale, 100 days	DOC variable	DOC 77%	90%	91%	(*39*)
GAC	EBCT 21 mins, full-scale, 150 days	DOC variable	DOC 50%	90%	60%	(*39*)
GAC	EBCT 21 mins, full-scale, 200 days	DOC variable	DOC 46%	62%	80%	(*39*)
GAC	EBCT 21 mins, full-scale, 250 days	DOC variable	DOC 42%	40%	71%	(*39*)

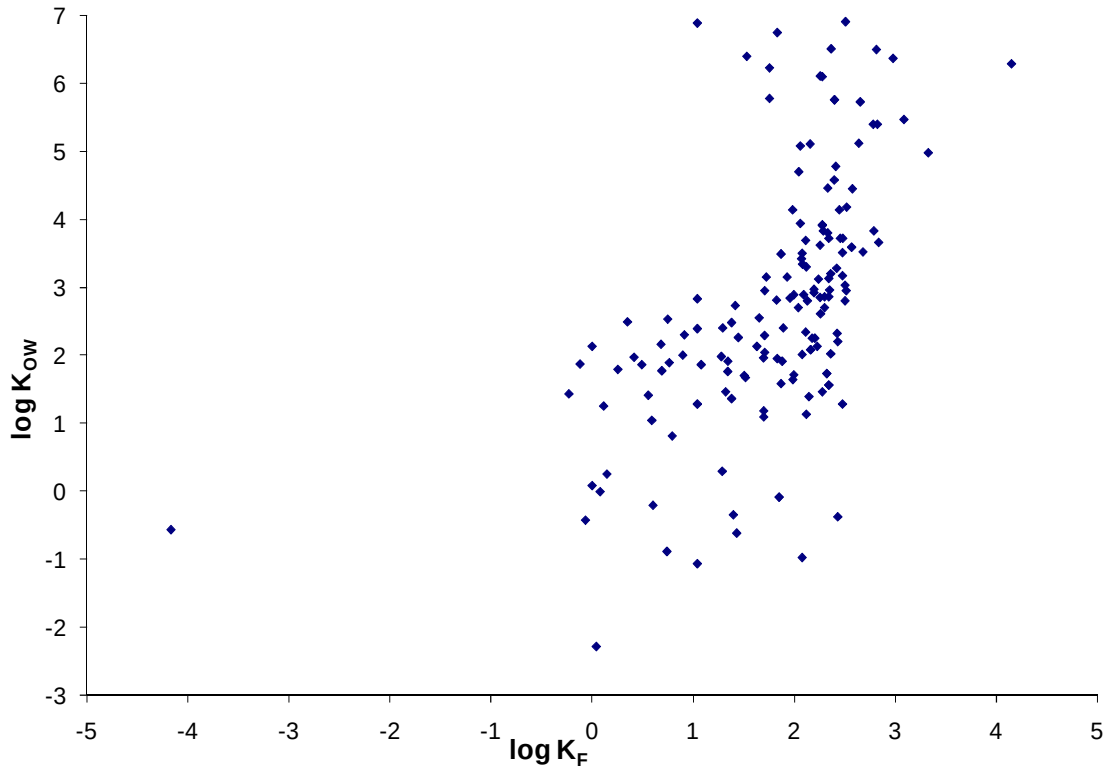

Figure 3.2: Relationship between log K_F and log K_{OW} for all compounds

3.7 Precursor Removal by Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are characterised by the in situ generation of hydroxyl radicals (·OH) and are currently considered an advanced water treatment. There are various ways of generating AOPs, among them ozone/UV, ozone/H_2O_2, UV/H_2O_2, vacuum UV and Fenton's reactions (*45*). Although the means of ·OH production varies, all these processes share the same method of degrading NOM (Table 3.1), through fast and non-selective reactions with organic compounds (*29*). The average second-order rate constants for reactions between NOM and ·OH in seventeen waters was 3.9 x 10^8 $M^{-1}s^{-1}$ (*46*), with values determined by competition kinetics. More recently rate constants were directly measured at 1-5 x 10^8 $M^{-1}s^{-1}$ for ·OH and NOM reactions (*47*). These values are typical for organics and are 3-4 orders of magnitude higher than for other oxidants used in water treatment (*29*).

For the complete set of compounds there is r = 0.309 for the relationship between $k_{\cdot OH}$ and log K_{OC} (51 data pairs) (Table 3.4). All others correlations were between -0.168 and 0.187 (Table 3.4), which is in accordance with the non-selective nature of ·OH reactions. For the non-halogenated compounds, the correlations of 0.396 for the relationship between $k_{\cdot OH}$ and log K_F (30 data pairs) and 0.412 for the relationship between $k_{\cdot OH}$ and log K_F (29 data pairs) were the highest recorded (Table 3.5).

UV doses of 0.5 – 3 J cm^{-2} and H_2O_2 doses of 10-20 mg L^{-1} for UV/H_2O_2 treatment are typical of those employed for NOM oxidation (*37*). At 0.5 J cm^{-2} reductions in DOC, UV, THMFP, DCAAFP and TCAAFP of -11%, 24%, 8%, -35% and 8% were recorded (*37*). With 3 J cm^{-2} equivalent values were 20%, 59%, 73%, -74% and 69%, thus AOPs

can increase formation of DBPs and DCAA in particular across a range of UV fluence values. Note the similarity in behaviour between TCAA and THM precursors and disparate nature of DCAA precursors, as noted elsewhere (*48*). Such increases occur through formation of reactive DCAA precursors on oxidation. The specific identity of these precursors is uncertain but a rise in DCAA has been linked to formation of diketones and then aldehydes (*49*). Higher respective removals of DOC, UV, THMFP and HAAFP at 56%, 91%, 89% and 83% with a similar water source and an ozone-UV AOP (UV: 1.61 W s cm^{-2}, ozone 0.062 mg mL^{-1}), shows what can be achieved with higher energy and chemical input (*38*). However, while AOPs can completely mineralise NOM to carbon dioxide the high costs involved mean that partial oxidation is the more feasible means of operation. Since AOP products, including aldehydes and carboxylic acids tend to be biodegradable (*45*), there has been interest in applying AOPs in synergy with biodegradation. Thus in contrast to UV/H_2O_2 alone (UV: 3 J cm^{-2}; H_2O_2 10-20 mg L^{-1}), the same AOP dose combined with biological activated carbon (BAC) achieved reductions in DOC, UV, THMFP, DCAAFP and TCAAFP of 80%, 81%, 85%, 63% and 85% respectively (Table 3.6, (*37*)), and thus effected significant DCAAFP removal. Finally, the presence of carbonate and bicarbonate ions can scavenge ·OH and suppress the success of AOPs. Thus, while AOPs are an effective technology for removing a variety of NOM, careful assessment of downstream DBP formation is advised before they are utilised for DBP control.

3.8 Precursor Removal by Ozone

Compared with AOPs, ozone is an established part of water treatment, with well over 1000 ozone water treatment plants worldwide (*28*). Ozone is typically employed for disinfection, taste and odour control and degradation of target organic contaminants, rather than bulk DOC removal. This is partly because rate constants for reactions of ozone with organics are much lower than with ·OH. For example apparent rate constants range from 3 x 10^{-5} M^{-1} s^{-1} for acetic acid to 20 x 10^{3} M^{-1} s^{-1} for dimethylamine to 18 x10^{6} M^{-1} s^{-1} for phenol (*29*). Ozone can be operated as an AOP by adding UV or H_2O_2 to generate ·OH. In fact, ·OH is also produced naturally through reactions between NOM and ozone, and this is thought to be the major degradation route for target compounds (*46*). There is a consensus that ozone alone, under typical water treatment conditions, which involve doses of ~1 mg O_3/mg DOC, is relatively ineffective for DBP precursor removal, though higher doses may enable improved performance (*50*). To illustrate, in one reservoir water at an ozone dose of 0.85 mg mgDOC^{-1} removals of DOC, UV and THM precursors were 5%, 47% and 6% respectively (Table 3.7, (*51-54*)). At an ozone dose of 3 mg mgDOC^{-1} removal of these parameters had increased to 16%, 72% and 43%, which also illustrates the selectivity for UV absorbing species typical of the process. Particularly at high doses, ozone has the potential to increase HAA and THM levels, though these effects are unpredictable. For example, in one study, with a high ozone dose of 5 mg mgDOC^{-1} an increase in HAA formation of 50% was observed, contrasting with a 12% decrease at 0.5 mg mgDOC^{-1} and a 12% increase at 1.0 mg mgDOC^{-1}. Elsewhere, 5% and 4% increases in THMFP and HAAFP were observed with combined ozone (2.0 mg mgDOC^{-1}) and biotreatment (Table 3.7, (54)). Increased levels of bicarbonate concentration during ozonation have been reported to

decrease subsequent HAA formation (55). Since bicarbonate reduces the formation of hydroxyl radicals through scavenging reactions, this indicates that ozone may more be effective at reacting with precursor sites than hydroxyl radicals. In one water with SUVA 2.5 L mg^{-1} m^{-1}, mean removals of THMFP and HAAFP for ozone-coagulation were respectively 57% and 66%, and consequently similar to coagulation-ozone, where equivalent values of 54% and 71% were observed (*51*). As intimated by the rate constants listed, ozone reacts preferentially with activated aromatic compounds. Although nucleophilic reactions are possible, they are slow and electrophilic addition to unsaturated bonds is the main reaction route (*56*). Hence, as shown by the generally higher reduction in UV absorbing species than other parameters (Table 3.7), ozone primarily reacts with humic species, with the main products groups being aldehydes, ketones and carboxylic acids (56). As such compounds are typically biodegradable; using ozone upstream of biodegradation can improve precursor removal. Values of -5-54% and -4-70% removal for THM and HAA precursors respectively have been reported for combined ozone-biofiltration (Table 3.7, (*50, 53, 54*)). Given the propensity for ozone to react selectively with aromatics the effectiveness even of combined ozone-biofiltration for precursor removal may be limited by the amount of aromatic/humic material. This idea is supported by Wricke and co-workers (*57*), who found the maximum production of biodegradable DOC was only around 30% of the total DOC. Ozone can also form bromate, a suspected human carcinogen and inorganic DBP, through reactions with bromide in drinking water (*58*). Bromate is currently regulated in the USA at 10 µg L^{-1} and while its formation is most acute in high bromide waters, its presence can be mitigated by ozonating at acidic pH (*58-59*).

Table 3.7: NOM and DBP precursor removal by ozone and biotreatment

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1}, alkalinity mg L^{-1} as $CaCO_3$)	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Preozone-coagulation	Ozone dose: 1.1 mg L^{-1} Coagulant: Alum 42 mg L^{-1} pH: 7.8-8.0	TOC: 3.1, SUVA: 2.5, alkalinity >200, bromide 25 µg L^{-1}	DOC: 30%, UV:56%	nr	76%	(*51*)
Preozone-coagulation	Ozone dose: 0.7 mg L^{-1} Coagulant: Alum 29 mg L^{-1}, pH: 6.5	As above	DOC: 19%, UV: 42%	54%	48%	(*51*)
Preozone-coagulation	Ozone dose: 2.8 mg L^{-1} Coagulant: Alum 23 mg L^{-1}, pH: 6.3-6.4	As above	DOC: 0%, UV: 66%	58%	70%	(*51*)
Preozone-coagulation	Ozone dose: 2.4 mg L^{-1} Coagulant: Alum 21 mg L^{-1} pH: 6.3-6.5, bromide spike 200 µg L^{-1}	As above	DOC: 4%, UV: 59%	54%	na	(*51*)
Preozone-coagulation	Ozone dose: 2.5 mg L^{-1} Coagulant: Alum 44 mg L^{-1}, pH: 7.1-7.7	As above	DOC: 21%, UV: 69%	66%	66	(*51*)
Preozone-coagulation	Ozone dose: 3.0 mg L^{-1} Coagulant: Alum 37 mg L^{-1} pH: 7.4-7.8, bromide spike 200 µg L^{-1}	As above	DOC: 18%, UV: 68%	51%	69	(*51*)
Coagulation-ozone	Ozone dose: 0.8 mg L^{-1} Coagulant: Alum 26 mg L^{-1}, pH: 7.7-7.9	As above	DOC: 16%, UV: 49%	47%	60	(*51*)
Coagulation-ozone	Ozone dose: 2.6 mg L^{-1} Coagulant: Alum 30 mg L^{-1}, pH: 7.6-7.9	As above	DOC: 19%, UV: 69%	58%	73	(*51*)
Coagulation-ozone	Ozone dose: 2.3 mg L^{-1} Coagulant: Alum 30 mg L^{-1} pH: 7.8-8.1, bromide spike 200 µg L^{-1}	As above	DOC: 34%, UV: 64%	48%	81	(*51*)

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1}, alkalinity mg L^{-1} as $CaCO_3$)	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Mean for preozone		As above	DOC: 15%, UV: 60%	57%	66%	(*51*)
Mean for intermediate ozone		As above	DOC: 23%, UV: 61%	54%	71%	(*51*)
Ozone	Dose: 0.85 mgO_3 $mgDOC^{-1}$	Minaga Reservoir water, DOC concentrated to 5	DOC: 5%, UV: 47%	6%	nr	(*52*)
Ozone	Dose: 1.49 mgO_3 $mgDOC^{-1}$	As above	DOC: 8%, UV: 60%	10%	nr	(*52*)
Ozone	Dose: 3 mgO_3 $mgDOC^{-1}$	As above	DOC: 16%, UV: 72%	43%	nr	(*52*)
Ozone	Dose: 0.2 mgO_3 $mgDOC^{-1}$	TOC 1.4-1.5	UV: 28%	14%	5%	(*53*)
Ozone	Dose: 0.4 mgO_3 $mgDOC^{-1}$	As above	UV: 50%	0%	18%	(*53*)
Ozone	Dose: 0.8 mgO_3 $mgDOC^{-1}$	As above	UV: 50%	12%	15%	(*53*)
Ozone	Dose: 1.4 mgO_3 $mgDOC^{-1}$	As above	UV: 57%	7%	18%	(*53*)
Ozone	Dose: 2.2 mgO_3 $mgDOC^{-1}$	As above	UV: 68%	5%	13%	(*53*)
Ozone	Dose: 2.8 mgO_3 $mgDOC^{-1}$	As above	UV: 77%	25%	20%	(*53*)
Biotreament	Bioactive sand	DOC 2.66		37%	62%	(*53*)
Ozone-biotreatment	Dose: 0.4 mgO_3 $mgDOC^{-1}$ Bioactive sand	DOC 2.66		50%	62%	(*53*)
Ozone-biotreatment	Dose: 0.8 mgO_3 $mgDOC^{-1}$ Bioactive sand	DOC 2.66		54%	68%	(*53*)
Ozone-biotreatment	Dose: 1.6 mgO_3 $mgDOC^{-1}$ Bioactive sand	DOC 2.66		51%	65%	(*53*)
Ozone-biotreatment	Dose: 2.0 mgO_3 $mgDOC^{-1}$ Bioactive sand	DOC 3.7, pH 7, alkalinity 12-20		-5%	-4%	(*54*)
Ozone-biotreatment	Dose: 2.0 mgO_3 $mgDOC^{-1}$ Bioactive sand	As above		45%	44%	(*54*)
Ozone	Dose: 0.5 mgO_3 $mgDOC^{-1}$	Lake Houston: DOC 3.3, alkalinity 8		17%		(*50*)
Ozone	Dose: 1.0 mgO_3 $mgDOC^{-1}$	As above		10%		(*50*)

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1}, alkalinity mg L^{-1} as $CaCO_3$)	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Ozone	Dose: 2.0 mgO_3 $mgDOC^{-1}$	As above		14%		(*50*)
Ozone	Dose: 3.0 mgO_3 $mgDOC^{-1}$	As above		12%		(*50*)
Ozone	Dose: 5.0 mgO_3 $mgDOC^{-1}$	As above		7%		(*50*)
Ozone-biotreatment	Dose: 0.5 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above		34%		(*50*)
Ozone-biotreatment	Dose: 1.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above		31%		(*50*)
Ozone-biotreatment	Dose: 2.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above		32%		(*50*)
Ozone-biotreatment	Dose: 3.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above		41%		(*50*)
Ozone-biotreatment	Dose: 5.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above		50%		(*50*)
Ozone	Dose: 0.5 mgO_3 $mgDOC^{-1}$	Lake Austin: DOC 2.3, alkalinity 61			12%	(*50*)
Ozone	Dose: 1.0 mgO_3 $mgDOC^{-1}$	As above			-12%	(*50*)
Ozone	Dose: 2.0 mgO_3 $mgDOC^{-1}$	As above			0%	(*50*)
Ozone	Dose: 5.0 mgO_3 $mgDOC^{-1}$	As above			-50%	(*50*)

Process/es	Process parameters	Water characteristics (TOC/DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1}, alkalinity mg L^{-1} as $CaCO_3$)	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Ozone-biotreatment	Dose: 0.5 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above			37%	(*50*)
Ozone-biotreatment	Dose: 1.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above			12%	(*50*)
Ozone-biotreatment	Dose: 2.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above			56%	(*50*)
Ozone-biotreatment	Dose: 3.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above			70%	(*50*)
Ozone-biotreatment	Dose: 5.0 mgO_3 $mgDOC^{-1}$ Bioactive gravel	As above			55%	(*50*)

nr = not recorded
na = not available

3.9 Precursor Removal by Biotreatment

Biological processes in water treatment typically entail development of a biofilm on a sand or activated carbon filter and are more widely employed in Europe than the USA (*60*). Biotreatment can remove NOM through enzyme-controlled microbial degradation, as well as adsorption (Table 3.1). The rate of biodegradation is controlled by substrate mass transport and biodegradation kinetics (*61*). NOM can be divided into easily biodegradable and recalcitrant material (*62*), while typical EBCT for NOM removal are 19-36 min and 5-10 min for activated carbon and sand filters respectively (*61, 62*). Small non-UV absorbing molecules tend to be biodegradable (*63*). In general, small compounds are more biodegradable due to increased ease of transport across the cell membrane (*64*). For example, aldehydes were found to be readily biodegradable (*53*), with average removal of 70% found for various amino acids (*65*). Lower biodegradation of amino acids has been reported elsewhere, such as 46% removal by Prévost et al. (*66*). These values were interpreted as indicating either aggregation to humic structures or the lower biodegradability of specific amino acids. The amount of biodegradable material in a water is linked to characteristics of the catchment. Waters with a higher proportion of biologically-derived NOM are likely to be low in aromaticity, with high nitrogen content and relatively biodegradable (*67*). Amounts of biodegradable NOM in rivers in Europe and the USA were found to vary from a few percent to around 40% (*67*). Despite this higher removal of HAA precursors in particular are found in the literature, with reductions of 37% and 62% for THM and HAA precursors respectively by bioactive sand (Table 3.7, (*53*)). These values indicate that at least in certain waters, reactive HAA precursors can belong to a readily biodegradable group, possibly aldehydes or amino acids. More moderate reduction of precursor concentration is found

in other studies, and DBP levels can even increase slightly post-treatment. This is demonstrated by one study using 3 days contact with BAC, where increases in THMFP and DCAAFP up to 9% and 11% were measured (Table 3.6, (*37*)). Interestingly, TCAA precursors proved more biodegradable than DCAA precursors, with respective maximum removal of 29% and 46% (Table 3.6, (*37*)). This is the opposite of what would be predicted based on the overall more hydrophilic character of DCAA precursors than TCAA precursors (*14*), and high biodegradability of low MW, aliphatic molecules (*63*), and highlights the uncertain identity of aquatic precursors. To summarise, biotreatment will only have a significant impact on precursor removal where reactive precursors are readily biodegradable. Such situations are more probable in waters with high amounts of biologically-derived NOM, and are likely to involve HAA precursors. As discussed above, oxidative pre-treatment can also be used to increase the amount of biodegradable material.

3.10 Precursor Removal by Membranes

Membrane processes are an increasingly common feature of water treatment (*7*). Four types are utilised: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), listed in order of decreasing pore size and size of molecules rejected, though there is overlap between these classifications (*68*). Rejection of molecules occurs through size exclusion and electrostatic repulsion for charged membranes, while for tighter membranes differing diffusion rates of various solutes across the membrane also participate (*68*). Thus, the properties of the membrane surface affect the type of molecules removed. In general, due to the small size of DBP precursors NF membranes are required for successful precursor removal. UF has been

found to have only limited efficacy for DBP control: with removals up to 44%, 50% and 32% found for bulk DOC, THM precursors and HAA precursors respectively by a membrane with molecular weight cut-off (MWCO) 60,000 Da (Table 3.8, (*69-71*)). These values are higher than other work using UF membranes, where respective retentions as low as 17%, 10% and 13% have been recorded (*69, 70, 72*). It is feasible the former higher values (*69*), relate to increased high MW species in the particular water, which had a high SUVA of 6.2 L mg^{-1} m^{-1}. Elsewhere SUVA has been found to positively correlate with MW (*73, 74*). In contrast, while requiring higher operating pressures NF has proved extremely effective for precursor removal (Table 3.8, (*69-71*)). The maximum retention achievable with NF is represented by a study using four different membranes of MWCO 100 – 300 Da, where with one water of DOC 3.8 mg L^{-1}, removals of 93%, 98% and 99% respectively were recorded for DOC, THM and HAA precursors (Table 3.8, (*69*)). Minimum retention from a study using five waters and a thin film composite (TFC), negative membrane of MWCO 200 Da were 67%, 66% and 67% (Table 3.8, (*71*)), values presumed to correspond to a large proportion of low MW NOM. Several studies have suggested that optimum precursor removal is obtained with a membrane of molecular weight cut-off around 200 Daltons (*75*), at which pore size rejection of THMs and HAAs themselves can also be expected.

In addition to studies using natural waters, model compounds have also been used to assess membrane performance, with removal found to be affected by properties other than size. Hydrophilic model compounds were found to be preferentially removed compared with hydrophobic compounds for three different NF membranes (*76, 77*). The latter study found that for a group of neutral molecules, of MW 146 – 154 Da, retention varied from 0 - 91% and 0 - 82% for two NF membranes with membrane molecular

weight cut-off (MWCO) 180 and 150-300 Da respectively (*77*). There was found to be a linear relationship between log K_{OW} and retention. The preferential rejection of acids by a negatively charged membrane (*78*) can be explained by coulombic repulsion between solute acids and membrane surface. One potential problem with NF is the low removal of bromide, which can cause a shift towards brominated DBPs upon chlorination of the permeate stream (*70*). Despite this NF is still highly effective for DBP precursor removal and may perhaps be used to best effect for removal of low MW, hydrophilic precursors recalcitrant to other treatment processes.

Table 3.8: NOM and DBP precursor removal by membrane processes

Process/es	Process parameters (MWCO = Da)	Water characteristics (DOC = mg L^{-1}, SUVA = L mg^{-1} m^{-1})	Bulk removal	THM precursor removal	HAA precursor removal	Reference
Four NF membranes (mean retention reported)	Membranes thin-film composite (TFC), or PVC, MWCO 100-300 Da	SLW Water. DOC: 3.8, SUVA: 6.2	DOC 93% UV 99%	98%	99%	(*69*)
As above	As above	BLW Water. DOC: 2.2, SUVA: 3	DOC 87% UV 97%	96%	94%	(*69*)
As above	As above	BRW Water. DOC: 3.2, SUVA: 2.5	DOC 92% UV 98%	96%	95%	(*69*)
As above	As above	BRW/F Water. DOC: 1.6, SUVA: 3	DOC 86% UV 89%	86%	88%	(*69*)
UF membrane	TFC, MWCO 60,000	SLW Water. DOC: 3.8, SUVA: 6.2	DOC 44%	50%	32%	(*69*)
NF membrane	polysulfone, MWCO 600-800, hydrophobic, negative	6 waters, TOC: 3.3 – 13.1; SUVA: 1.6 – 4.4. Median retention reported at 70% recovery.	TOC 71%	77%	75%	(*70*)
NF membrane	polamide, MWCO 300, slightly negative	As above	94%	96%	92%	(*70*)
NF membrane	polysulfone, MWCO 200-400, hydrophilic, highly negative	As above	91%	94%	81%	(*70*)
NF membrane	TFC, 200 Da, negative	5 waters: DOC: 1.31 – 9.76	67 – 94%	66 – 93%	67 – 97%	(*71*)

3.11 Physical Properties of NOM Groups

Analysis of removal mechanisms shows treatability of NOM is largely determined by physical properties, especially size, charge and hydrophobicity (Table 3.1). Thus to assess the treatability of NOM groups by different treatment processes it was necessary to assign these properties. Several assumptions were made while compiling Table 3.9 (*79-83*), due to the uncertainty about precise characteristics of NOM. This ambiguity is complicated by aggregation and overlap in functionality between the listed groups. For example amino acids and humic species can have carboxylic acid functionality, while amino acids may be associated with humic substances in natural waters (*84*). It is proposed humic species are the largest, most hydrophobic and highly charged of the NOM groups. This is because charge is primarily a feature of hydrophobic fractions (*6*), while MW and aromaticity have been reported be directly proportional to specific ultra violet absorbance ($SUVA_{254}$) (*73, 74*). Although fragmentation of large humic species may occur naturally, it is assumed fragments will retain character of the whole. Carboxylic acids in NOM are assumed to be smaller and more hydrophilic than humic species, properties consistent with the transphilic fraction of NOM known for high carboxylic acid functionality (*23*). One specific example would be citric acid (*67*), other mixed keto-acid compounds (*10*), or more simply still fatty acids. Thurman considered glutamic acid, glycine, serine and aspartic acid to be the most abundant aqueous amino acids (*83*). These species are relatively small (MW 75-147 g mol^{-1}) and hydrophilic (log K_{OW} -3.21 to -3.89), while only glutamic and aspartic acid have a single negative charge based on pK_a values. However, combined amino acids are considered 4-5 commoner than free species (*79*), hence amino acids are considered of intermediate MW (Table 3.9). Proteins in water often originate from algae or phytoplankton and based on

pyrolysis data can include phenol, pyridine, toluene and styrene groups (*8*). Glucose is considered the commonest sugar in drinking water (*83*), while arabinose and mannose are also thought to be widespread (*85*). These three carbohydrates are neutral, relatively hydrophilic (log K_{OW} -2.39 to -3.24) and relatively small (MW 150-180 g mol^{-1}) and are taken as representative of species found in aquatic environments.

Table 3.9: Proposed DBP formation, physical properties and treatability of NOM Groups

Group	Humic species	Carboxylic acids	Amino acids	Proteins	Carbohydrates	Reference/s
Abundance	50-76% of DOC	Uncertain	2-5%	Variable. 1 mg L^{-1} during algal bloom	5-50% of DOC	(*6*, *81*, *82*, *83*)
THMFP	Major source	β-dicarbonyl species	Low	Variable	Significant at pH 8	(*8*, *10*, *11 79*, *80*, *82*)
HAAFP	Major source	important for THMs and HAAs	Significant	Uncertain	Low	
Physical Property						
Charge	***	***	*	*		
Size	***	**	**	***	*	
Hydrophobicity	***	*	*	*	*	
Treatability						
Coagulation	***	**	*	*		
Ion Exchange	***	***	*	*		
Ozone	***	*	*	*	*	
Biotreatment	*	**	***	**	**	
Activated Carbon	***	**	**	**	**	
Membranes	**	**	***	***	***	
AOPs	***	***	***	***	***	

3.12 Discussion: Implications for DBP Control

Due to the difficulty of identifying precursor material, characterising waters to predict DBP formation is more complicated than predicting treatability. DBP formation is not straightforward to predict from bulk characters, except where a majority of precursors belong to a group which correlates to a bulk property, as has been observed for humic species and UV absorbance (*48*). Since the treatability of NOM groups can be predicted, assuming their physical characteristics are understood, guidance can be provided for their targeted removal. The high DBPFP of humic species is well known (Table 3.9), while they can represent up to ~75% of NOM in temperate upland catchments (Table 3.9). Fortunately, due their charge and size, humic substances are the NOM group most treatable by coagulation (Table 3.9). Therefore well-optimised coagulation may be sufficient for DBP control where humic species contain the bulk of precursor material. There are precedents for high precursor removal by coagulation in hydrophobic rich waters, for example the maximum removals of 71% and 78% for THM and HAA precursors respectively reported by Singer and Bilyk (*16*). There is also evidence TCAA precursors are more treatable than DCAA and THM precursors by coagulation (*14*). Residual humic substances remaining after coagulation are perhaps most likely fragments of lower size and charge. Owing to their hydrophobicity, in situations where they retain significant DBPFP, activated carbon adsorption is recommended for their removal. Anion exchange or oxidation by ozone/an AOP followed by biofiltration may also be successful. Such situations will be indicated by hydrophobic fractions of a post-coagulation holding relatively high DBPFP.

The variety, identity and amount of carboxylic acids present in NOM have not been fully elucidated (Table 3.9). Assuming carboxylic acids are generally smaller and

consequently with less charged groups than humic substances, their removal by coagulation is also presumed to be lower (Table 3.9). The transphilic fraction of NOM having high DBPFP is hypothesised to coincide with carboxylic acids being an important source of precursors. Ion exchange is proposed to be an effective choice for their treatment, given its efficiency in treating the transphilic fraction of NOM. Otherwise activated carbon, biotreatment, membranes and AOPs can all be expected to have some success, depending on the nature of the acids present. Due to electrostatic repulsion lower removal by activated carbon and charged membranes can be expected than for neutral analogues.

Amino acids and proteins are particularly important constituents of NOM in waters with high algal activity, wastewater influence, or more generally high amounts of biologically derived NOM. Where amino acids and proteins are reactive precursors it is feasible that concentration of nitrogen containing NOM will correlate to DBP formation, in particular non-regulated nitrogen containing DBPs (*4*). Further, L-aspartic acid and L-asparagine are known to be reactive HAA precursors (*11*), and are probably significant DBP precursors in such waters. Coagulation and ion exchange may provide uptake of the charged amino acids, but due to the low charge of the commonest aquatic species high removal is not expected for these two processes (Table 3.9). Since amino acids are known to be readily biodegradable, biotreatment is a recommended process option, while nanofiltration is also likely to be effective. The efficacy of adsorption would depend on other NOM present, since owing to their low hydrophobicity they will be less adsorbable than similar hydrophobic NOM components. Because of their relatively non-selective nature, AOPs are proposed to be a suitable process selection across the range of NOM, including amino acids (Table 3.9). It is predicted that larger

size of proteins than amino acids, plus any hydrophobic and/or charged side groups will make them relatively more responsive to all treatments bar biodegradation (Table 3.9). This observation is in accordance with the successful removal of algae by coagulation previously reported (*86*). Finally, carbohydrates have been found to comprise 50% of NOM in river waters and to form significant THM levels at pH 8 (Table 3.9). On current knowledge the predominant carbohydrates in water are small, neutral and relatively hydrophilic. Thus they are not expected to be treatable by either coagulation or ion exchange. Instead additional treatment may be necessary in waters where there are important sources of precursors. Nanofiltration may perhaps be most effective, while activated carbon, biotreatment and AOPs may also meet with success. In summary, more effective process selection criteria for precursor removal would come with increased knowledge of precursor identity in an individual water. This would facilitate choice of appropriate technologies for precursor treatment. Depending on the nature of reactive precursors present, optimised coagulation treatment may be prove sufficient for precursor control in hydrophobic waters. Where the post-coagulation residual remains reactive regarding DBP formation, the deployment of MIEX®, for carboxylic acid precursors, and/or GAC for hydrophobic precursors, and/or NF for hydrophilic precursors is recommended.

3.13 Acknowledgements

Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water are gratefully acknowledged for their financial support.

3.14 References

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CHAPTER 4: DISINFECTION BYPRODUCT FORMATION AND FRACTIONATION BEHAVIOUR OF NATURAL ORGANIC MATTER SURROGATES

DISINFECTION BYPRODUCT FORMATION AND FRACTIONATION BEHAVIOUR OF NATURAL ORGANIC MATTER SURROGATES

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4.1 Abstract

While NOM surrogates are established in disinfection byproduct (DBP) research, their use in fractionation studies is rare. To understand how surrogates relate to drinking waters a range of natural organic matter (NOM) surrogates were fractionated with XAD resins. Their trihalomethane (THM), haloacetic acid (HAA), haloacetaldehyde, haloacetonitrile and haloketone formation after chlorination was recorded. While compounds with higher log K_{OW} values behaved as hydrophobic acids, fractionation of the more hydrophilic compounds did not clearly correlate to log K_{OW}. High HAA formation from ferulic and aspartic acids and 1,1,1-trichloropropanone (1,1,1-TCP) formation from 3-oxopropanoic acid were notable. Three amino acids – asparagine, aspartic acid and tryptophan - formed significant levels of dichloroacetonitrile (DCAN) and trichloroacetaldehyde (TCA). Formation of DBPs did not correlate to any compound physical property; however there were several correlations between DBP groups. The most significant were between dichloroacetic acid (DCAA) and dichloroacetonitrile (DCAN); DCAN and TCA and dichloroacetaldehyde (DCA) and trichloroacetaldehyde, indicating the possibility of similar relationships in natural waters.

Keywords: DBPs, non-regulated DBPs, fractionation, NOM, model compounds.

4.2 Introduction

Soon after chlorination of natural organic matter (NOM) in water was linked to trihalomethane (THM) production by Rook in 1974 (*1*) the same author found resorcinol to be a major THM precursor (*2*), with resorcinol-type structures recognized as reactive sites for THM formation in fulvic acids. Most subsequent DBP research had focused on the THMs and to a lesser extent the haloacetic acids (HAAs); groups considered the dominant DBPs on a mass-basis in potable water (*3*). Both are regulated in the USA, with limits of 80 µg L^{-1} and 60 µg L^{-1} for THMs and HAA_5 respectively (*4*). In recent years many other DBPs have been indentified in drinking water, including haloketones, haloaldehydes, haloacetonitriles and nitrosamines. There is a concern that non-regulated DBPs, including nitrogen containing DBPs (N-DBPs), may be more toxic than the regulated species (*5*). Overall some 600-700 DBPs have been identified in drinking water from various disinfectants (*6*).

Diversity of DBPs is reflected in NOM, which acts as precursor to DBPs. The five main chemical groups of NOM are listed as humic substances, carboxylic acids, carbohydrates, amino acids and proteins (*7*). There is a view that humic substances, which tend to be aromatic and hydrophobic, contain the bulk of DBP precursors (*7*). However, the high HAA and THM formation of several aliphatic β-diketones and β-diketoacids (*8*) indicates certain hydrophilic structures are also significant DBP precursors.

Characterization of natural waters is often achieved through separation into fractions of varying hydrophobicity with adsorption resins (*9*). While characterization rarely extends to specific chemical identity, research indicates both hydrophobic and hydrophilic

fractions can have significant DBPFP. For example total organic halogen formation potential (TOXFP) yields from hydrophobic acid (HPOA) and hydrophilic acid (HPIA) fractions isolated from the South Platte River (USA) were 122 and 98 µgCl mgC^{-1} respectively (7). Furthermore, since hydrophobic fractions are more amenable to removal by coagulation, this suggests hydrophilic moieties can determine final DBP formation (*10*). The objective of this study was to identify significant precursors of regulated and non-regulated DBPs from a range of structurally-diverse NOM surrogates (Table 4.1). The surrogates were also fractionated with XAD resins, thus providing a direct link to drinking water work. Surrogates were chlorinated both with and without bromide for THM and HAA measurements. This approach is relevant to drinking water as bromide in the presence of chlorine becomes oxidized to bromine, forming brominated DBPs. While bromide rather than bromine has been used in natural water studies (*11*) to the authors' knowledge it is employed for the first time here with NOM surrogates.

Table 4.1: Properties of NOM Surrogates (following page)

Model compound	Classification	log K_{OW}	pKa	MW	n	MV	γ	PSA	log K_{OC}	α	Density	WSol
				Da		cm^3	dyne/ cm	A^2		10^{-24} cm^3	g/cm^3	10^{-3} ppm
Tannic acid[b]	Phenolic	13.33	3.2	1701	1.927	799.0	203.1	502.98	n/a	150.48	2.120	n.a.
p-coumaric acid[a]	Phenolic	1.79	4.4	164	1.660	123.4	62.4	35.53	1.893	18.07	1.329	18.3
Ferulic acid[a]	Phenolic	1.51	4.6	194	1.626	147.4	56.1	44.76	1.755	20.72	1.316	5.97
Sinapic acid[a]	Phenolic	1.29	4.4	184	1.566	148.3	51.6	53.99	1.616	19.19	1.335	5.78
Resorcinol[a]	Phenolic	0.80	9.3	110	1.612	86.2	57.1	18.46	2.638	11.89	1.275	717
5-methylfurfural	Furan	0.67	n.a	110	1.513	100.1	35.1	30.21	1.458	11.94	1.099	29.1
Acetic acid	Carboxylic acid	-0.17	4.8	60	1.375	56.1	31.9	26.30	0	5.10	1.068	1000
L-tryptophan	Amino acid	-1.06	2.4	204	1.697	149.8	71.1	34.47	2.567	22.90	1.362	13.4
3-oxopentanedioic acid	Carboxylic acid	-1.13	n.a.	146	1.494	97.4	67.9	69.67	1	11.24	1.499	1000
Oxalic acid	Carboxylic acid	-1.19	1.3	90	1.480	50.8	87.3	52.60	.278	5.72	1.772	220
Acetamide	Amide	-1.26	0.6	59	1.392	62.3	29.9	20.31	.733	5.89	0.947	2250
L-leucine	Amino acid	-1.52	2.4	131	1.462	126.6	39.0	29.54	.894	13.82	1.035	21.5
D-xylose	Carbohydrate	-1.98	12.1	150	1.646	85.4	75.3	46.15	1	12.29	1.757	555
L-tyrosine	Amino acid	-2.04	2.2	181	1.614	135.8	65.7	38.77	1.987	18.78	1.333	.479
Arabinose	Carbohydrate	-2.39	12.3	150	1.543	99.5	81.4	53.99	1	12.45	1.508	500
L-serine	Amino acid	-3.07	2.2	105	1.519	74.2	72.2	38.77	0	8.93	1.415	425
Glycine	Amino acid	-3.21	2.3	75	1.460	59.8	54.4	26.30	0	6.50	1.254	249
D-mannose	Carbohydrate	-3.24	12.9	180	1.573	113.9	92.0	63.22	1	14.88	1.581	713
L-glutamic acid	Amino acid	-3.69	2.2	147	1.522	104.3	69.2	55.84	1.16	12.62	1.409	8.88
L-asparagine	Amino acid	-3.82	2.0	132	1.533	94.0	71.6	49.80	.083	11.57	1.404	29.4
L-aspartic acid	Amino acid	-3.89	2.1	133	1.531	87.8	78.2	55.84	.894	10.78	1.514	5.39

Experimental conditions: [a] 1.5 µM compound, [b] 0.3 µM compound.

4.3 Methods and Materials

4.3.1 Selection of NOM Surrogates

Surrogates (Sigma Aldrich, UK) were selected to represent the main chemical groups found within NOM (*5*). Relatively hydrophobic compounds of phenolic character are resorcinol, tannic acid and the lignin monomers ferulic and *p*-coumaric acids (*12*), while sinapic acid is another naturally occurring cinnamic acid derivative. Carbohydrates and amino acids are important groups within NOM and represented by various surrogates of principally hydrophilic nature, though tryptophan is more hydrophobic (Table 4.1). Carboxylic acids are represented by the monoprotic acetic and oxalic acids, both ozonation byproducts (*13*), the β-dicarbonyl 3-oxopentanedioic acid, as well as within various amino acid and phenolic species. Finally acetamide has been detected after the pyrolysis of NOM (*7*).

4.3.2 Halogenation Method

Experiments were carried out in duplicate with solutions prepared with ultrapure (UP) water. Surrogates were halogenated for 24 h at 20°C ± 2°C and pH 7 (phosphate buffer). The chlorine/compound ratio was 35 M/M to provide an excess for all compounds (*8*). The concentration of surrogate was 15 µM, unless otherwise stated (Table 4.1). Compounds (Sigma Aldrich or Fisher Scientific) were of analytical purity or higher. Chlorine stock solution was prepared from concentrated sodium hypochlorite (>8%, Fisher). A bromide concentration of 0.45 mg L^{-1} was used for bromination tests; as observed in high-bromide natural waters (*14*). Bromide stock solution was obtained by diluting potassium bromide (>99%, BDH). Two procedural blanks were included for each halogenation batch with results adjusted according to any peaks in the blanks.

Chlorine demand was measured with samples from the same source as for DBP determinations.

4.3.3 Chlorine and DBP quantification

Extra detail of the chlorine and DBP quantification procedures are provided in the supporting information. Chlorine concentration was determined by iodometric titration (*15*), which measures combined chlorine and bromine concentration. The concentration of the chlorine stock solution was determined at least in triplicate on the day of use. Chlorine demand was obtained by titration of excess chlorine after 24 h.

Chlorinated samples for THM analysis were quenched by sodium sulphite then extracted into methyl tert butyl ether (MTBE) (*16*). HAA samples were quenched with ammonium chloride, acidified to pH 1.5, extracted into MTBE and derivatized with 10% acidic methanol for 2 h at 50°C (*17*). Non-regulated DBP samples were acidified to pH 3.5 then extracted into MTBE (*18*) immediately after 24 h and analyzed the same day. Since there is uncertainty over the stability of non-regulated DBPs in the presence of different quenching agents (*18*), no quenching agent was used. DBPs quantified were dichloroacetaldehyde (DCA), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), trichloroacetaldehyde (chloral hydrate) (TCA), 1,1-dichloropropanone (1,1-DCP), trichloronitromethane (chloropicrin) (TCNM), and 1,1,1-trichloropropanone (1,1,1-TCP). Mean average deviations for duplicate samples of non-regulated DBPs ranged from 0.02 µg L^{-1} for TCAN to 1.1 µg L^{-1} for TCA (n = 21 pairs). Due to the limited availability of relevant standards, chlorination with the addition of bromide was not undertaken for analysis of non-regulated DBPs. DBPs were analyzed using capillary gas chromatography with an electron capture detector (Agilent 6890).

4.3.4 Fractionation Method

Fractionation was performed using the method of Croué et al. with modification (*7*). Two liters of solution (calculated concentration from dilution: 10 mg C L^{-1}) was acidified to pH 2 and passed through tandem XAD-7HP and XAD-4 columns (Rohm and Haas, Germany). Each column (resin volume: 60 mL) was back-eluted with NaOH (0.1 M, ~800 mL) and cleaned with UP water followed by HCl (0.5 %). The column distribution coefficient (k') was 100. The dissolved organic carbon (DOC) of the initial solution and 3 fractions was measured using a Shimadzu TOC-5000A analyzer. Prior to each run, blanks were collected before and after both columns. Results were accepted when recovery was between 85 and 115%. This procedure used separates operationally-defined hydrophobic acids (HPOA) and transphilic acids (TPHA), substances not retained by either resin are classified as hydrophilic (HPI). The abundance of the hydrophobic neutral fraction (HPON) was obtained by mass balance as the portion which did not elute off the XAD-7HP resin.

4.3.5 Correlation coefficients

The Pearson product-moment correlation coefficient (r) calculated with Minitab 15™ was used to define linear relationships between compound physicochemical properties and DBPFP. Properties used were: molecular weight (MW), log K_{OW} (partitioning in octanol/water), pKa , index of refraction (n), molar volume (MV), surface tension (γ), polar surface area (PSA), polarizability (α), density (ρ) and water solubility (WSol) (*19, 20, 21*) with experimental values used where available. Also included was log K_{OC} (partitioning in soil/water) estimated using (*20*).

4.4 Results

4.4.1 Fractionation

Fractionation of even the most hydrophobic or hydrophilic compounds resulted in material being assigned into multiple operationally-defined fractions (Figure 4.1). To illustrate the most hydrophobic compound, tannic acid (log K_{OW} = 13.33 at pH 7, Table 4.1) had 90%, 3% and 7% recovery in the HPOA, TPHA and HPI fractions respectively; while equivalent values for the most hydrophilic compound, aspartic acid (log K_{OW} = -3.89 at pH 7) were 5%, 4% and 91%. Overlap between fractions was most striking for 3-oxopentanedioic acid and L-tryptophan, which both had over 33% in two separate fractions. This indicates different fractions are not sharply delineated, which should be considered when testing natural waters. A possible implication would be that reported DBP formation of HPI is partly due to residual hydrophobic material not retained by the XAD-7HP resin. Previously it has been thought that bleeding of hydrophobic acids into hydrophilic fractions should not occur during properly operated fractionation (*9*).

Analysis of fractionation behavior revealed three main groups: the first being compounds designated as hydrophobic acids. This category comprised tannic, p-coumaric, ferulic and sinapic acids, as well as resorcinol (Figure 4.1), with 73-97% HPOA recovery. They are the five most hydrophobic compounds, with log K_{OW} ranging from 0.8 – 13.33 (Table 4.1). The second category was the hydrophobic neutrals: 5-methylfurfural and L-tryptophan, where 75% and 62% respectively behaved as HPON (Figure 4.1). The remaining compounds behaved as HPI to a greater or lesser extent, with 48-93% of material belonging to this fraction. Apart from acetic acid, with log K_{OW} = -0.17 (Table 4.1) all these compounds (log K_{OW} -1.13 to -3.89) are more

hydrophilic than the HPOA and HPON compounds (log K_{OW} -1.06 to 13.33). Note the arrow indicating log K_{OW} in Figure 4.1 is to show order of hydrophobicity, rather than as a scale. Thus no compounds were defined as TPHA, with 3-oxopentanedioic acid having the highest TPHA proportion at 44%, followed by ferulic and sinapic acids, both with 27% respectively. Adsorption onto XAD-resins occurs through hydrogen bonding, aromatic Π-electron and hydrophobic interactions (*7*), of which only hydrogen bonding is likely to apply for the hydrophilic compounds. Figure 4.1 therefore indicates adsorption is controlled by hydrophobic/aromatic interactions rather than hydrogen bonding, which corresponds to the poor adsorption of small, aliphatic polar compounds reported for XAD resins (*22*). The XAD-4 resin is uncharged and non-polar (*9*) and paradoxically more hydrophobic than XAD-7HP resin. As such it is hypothesized the hydrophilic compounds were too hydrophilic to be retained. They therefore belong to the 15-30% of NOM not retained by the fractionation protocol (*9*). While the most hydrophobic and hydrophilic surrogates behaved as HPOA and HPI respectively; identity of compounds comprising TPHA is uncertain. It should be considered that aggregation could lead to differing fractionation behavior in natural waters compared with individual compounds. For example amino acids can be associated with hydrophobic NOM fractions (*7*).

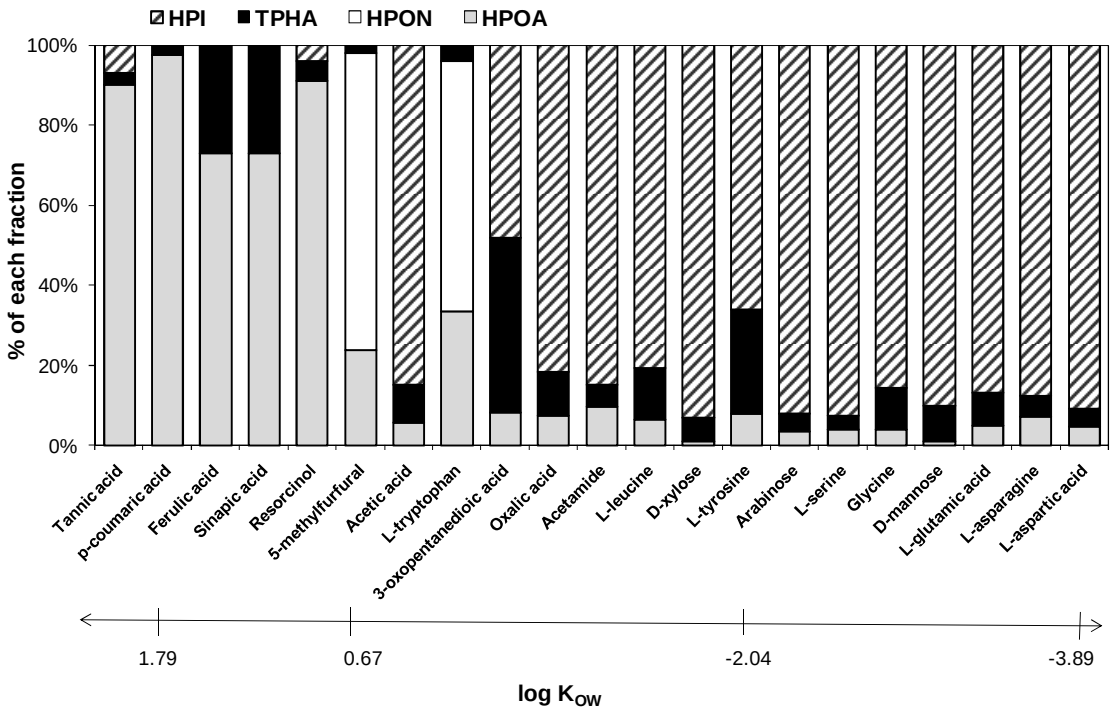

Figure 4.1: Fractionation behaviour of NOM surrogates

4.4.2 Chlorine Demand and Halogen Substitution Efficiency

The surrogates were observed to fit into four groups according to the combination of high/low levels for both chlorine demand and DBP substitution (Table 4.2). Ferulic acid, L-tryptophan and resorcinol were characterized by both high chlorine demand from 7.2 - 13.8 mol/mol (mean demand for chlorination with and without bromide) and high DBP substitution efficiency, from 12.7 - 44.9 % molCl/molCl_2 (total measured DBPs). Such behavior correlates with structure as they are activated aromatics, towards which chlorine has high reactivity (*23*). The remaining aromatic compounds: tannic, p-coumaric and sinapic acids and L-tyrosine comprise the second group, with high chlorine demand between 7.9 and 32.9 M M^{-1}, but low DBP substitution efficiency from 0.5 - 5.0 % molCl/molCl_2. Tannic acid had the highest chlorine demand of any compound, but its low DBP substitution efficiency (0.5 % molCl/molCl_2) indicates

chlorine was consumed oxidizing its complex structure and/or in the formation of non-detected DBPs. Higher HAA formation for the compound has been reported under chlorination at higher temperature (*24*), thus it is probable HAA formation follows full oxidation and/or degradation of larger non-detected DBPs. The chlorine demand of tyrosine and tryptophan has been reported as 13 and 16 mol/mol respectively (*25*), data consistent with this study. The third group was the structurally-disparate 5-methylfurfural, acetic acid, 3-oxopentanedioic acid and aspartic acid, defined by low chlorine demand between 0.6 and 5.35 mol/mol, yet high DBP substitution efficiency from 10.2 - 80.3, % molCl/molCl_2 and hence effective precursors. 3-oxopentanedioic acid was the most efficient DBP precursor, with 80% of consumed chlorine converted into measured DBPs, mainly chloroform and 1,1,1-TCP (Table 4.2, Figures 4.2 and 4.4). Its DBP formation has previously been studied: at pH 8, 57% and 41% of chlorine consumed was converted to $CHCl_3$ and DCAA respectively (*8*). Based on these data it appears pH strongly affects the identity of DBPs, with pH 7 promoting formation of 1,1,1-TCP over that of DCAA in particular. However, it is also thought 1,1,1-TCP acts an intermediate in the formation of other DBPs at pH 7 and 8 and reaction times over 24 h (*26*), consequently over longer time periods hydrolysis to $CHCl_3$ may occur (Figure 4-SI-1). The final group was comprised of compounds with low chlorine demand ($\leq$ 7.0 mol/mol) and DBPFP and comprises the bulk of hydrophilic compounds (Table 4.2). Even within this group there was wide variation in chlorine demand. The carbohydrates (arabinose, mannose and xylose) had mean chlorine demand from 0.1-1.1 mol/mol, explained by the low reactivity of aliphatic and alcohol groups towards chlorine (*23*). Aliphatic amino acids (leucine, serine, glycine, asparagine and glutamic acid) had mean chlorine demand from 2.65-7.0 mol/mol, comparable to other groups and related to the

reactivity of the amine functionality. Comparison values for the chlorine demand of xylose, glycine and glutamic acid of 0.6, 5.6 and 2.4 mol/mol respectively (*25*, *27*) compare well with this study. In the classical mechanism of amino acid chlorination two moles of chlorine are consumed in dichloramine formation, with higher chlorine demand indicative of further oxidation, which at least for glycine can result in CO_2 and N_2 liberation (*25*). This mechanism could also occur for 5-methylfurfural, which also has an amine group and similar chlorine demand to glycine. For most compounds consumed chlorine was similar with and without bromide. Small increases were observed with Br^- present for ferulic acid, resorcinol, tyrosine, 3-oxopentanedioic acid and D-xylose. Since bromine is a more effective substitution agent but less effective oxidant than chlorine (*8*) similar demand with Br^- present indicates halogenation was not the rate-determining step and/or the high chlorine dose meant it was able to out-compete bromine during substitution as previously noted (*28*). 3-oxopentanedioic acid exhibited different behavior as THMFP and HAAFP were lower with Br^- present. Superficially this seems surprising given the properties of bromine. However, Dickenson et al. (*8*) found that with bromine present dihaloacetic acid (DXAA) formation was much lower at 19% substitution efficiency, compared with 41% for chlorination alone. This was explained by the formation of unidentified brominated byproducts, a situation also thought to apply here. Based on the high 1,1,1-TCP yield these species are expected to be brominated haloketones, which were not analyzed in the current study, but were found in high-bromide natural waters (*3*).

Table 4.2: Chlorine demand and halogen substitution efficiency into DBPs

	Chlorination				Chlorination with bromide				
Category/ Compound	**Chlorine demand (mol/mol)**	**Chlorine substitution (% mol Cl/mol Cl_2)**			**Chlorine demand (mol/mol)**	**Chlorine substitution (% mol Cl/mol Cl_2)**		**Bromide substitution (% mol/mol)**	
		THM4	**HAA9**	**Nr DBPs**		**THM4**	**HAA9**	**THM4**	**HAA9**
High chlorine demand + high substitution efficiency									
Ferulic acid	8.9	1.6	10.1	1.0	10.2	0.9	6.9	6.4	51.9
L-tryptophan	13.5	5.6	1.1	7.4	14.0	6.1	0.7	66.4	4.7
Resorcinol	6.7	43.0	1.1	0.8	7.7	35.8	0.4	14.6	2.8
High chlorine demand + low substitution efficiency									
Tannic acid	32.4	0.4	0.1	<0.1	33.3	0.2	0.2	<0.1	<0.1
p-coumaric acid	8.5	0.6	1.1	1.4	7.3	0.2	0.8	1.7	3.8
Sinapic acid	9.4	1.0	2.6	1.4	9.8	0.7	1.0	26.5	15.7
L-tyrosine	11.7	2.4	0.7	0.2	13.3	1.6	0.5	19.6	5.2
Low chlorine demand + high substitution efficiency									
5-methylfurfural	0.8	14.0	0.6	12.5	0.9	4.1	0.4	21.4	0.3
Acetic acid	0.1	0.0	1.2	9.0	1.1	3.3	0.1	0.1	0.1
3-oxopentanedioic acid	3.3	44.2	1.3	34.8	4.7	8.4	0.4	17.3	3.0
L-aspartic acid	5.7	1.2	9.1	3.6	5.0	0.8	7.1	2.1	25.4
Low chlorine demand + low substitution efficiency									
Oxalic acid	0.6	8.3	<0.1	0.6	1.1	5.2	<0.1	<0.1	<0.1
Acetamide	6.4	<0.1	<0.1	0.1	4.7	0.3	<0.1	<0.1	<0.1
L-leucine	2.8	<0.1	<0.1	0.4	2.5	<0.1	<0.1	<0.1	<0.1
D-xylose	<0.1	29.2	2.0	13.8	0.1	<0.1	<0.1	<0.1	<0.1
Arabinose	0.4	4.1	<0.1	3.4	0.4	<0.1	<0.1	<0.1	<0.1
L-serine	8.8	<0.1	<0.1	0.2	5.2	<0.1	<0.1	<0.1	<0.1
Glycine	5.7	0.3	<0.1	0.2	5.5	0.2	<0.1	<0.1	<0.1
D-mannose	1.3	<0.1	0.2	1.0	0.9	3.1	0.2	0.3	<0.1
L-glutamic acid	3.1	<0.1	<0.1	0.7	2.5	<0.1	0.1	<0.1	0.3
L-asparagine	5.7	<0.1	0.4	3.0	5.9	0.1	0.4	<0.1	1.0

Nr DBPs = sum of non-regulated DBPs

4.4.3 THMFP Results

Ten compounds formed over 0.015 mol THMs/mol compound (Figure 4.2), with resorcinol the most reactive, forming 0.96 and 0.94 mol/mol with and without Br^- respectively. The compound is well-studied and the value without Br^-, which equates to 1588 µg mgC^{-1}, compares well with literature values of 1544 and 1456 µg mgC^{-1} (*29, 30*). This potency over other activated aromatic species, including p-courmaric, ferulic and sinapic acids is conferred by the electron donating influence of OH groups in the meta configuration (*2*). The next most significant precursor was 3-oxopentanedioic acid, with chlorination THMFP of 0.49 mol/mol. Values for tryptophan and tyrosine of 228 and 103 µg mgC^{-1} (0.25 and 0.09 mol/mol respectively) after chlorination respectively compare well with previous values of ~210 and ~128 µg mg C^{-1} (*25*). The higher THMFP for tryptophan of 0.37 mol/mol in the presence of bromide indicates halogen substitution was the rate-determining step. Speciation analysis revealed $CHCl_3$, $CHCl_2Br$ and $CHBr_2Cl$ were the predominant DBPs in the presence of Br^- (Figure 4.2), while 5-methylfurfural was unusual in forming $CHBr_3$. With Br^- present resorcinol still formed mainly $CHCl_3$, attributed to the speed of chlorination: resorcinol has been classified as a fast-reacting THM precursor, with the bulk forming inside 5 min (*8*).

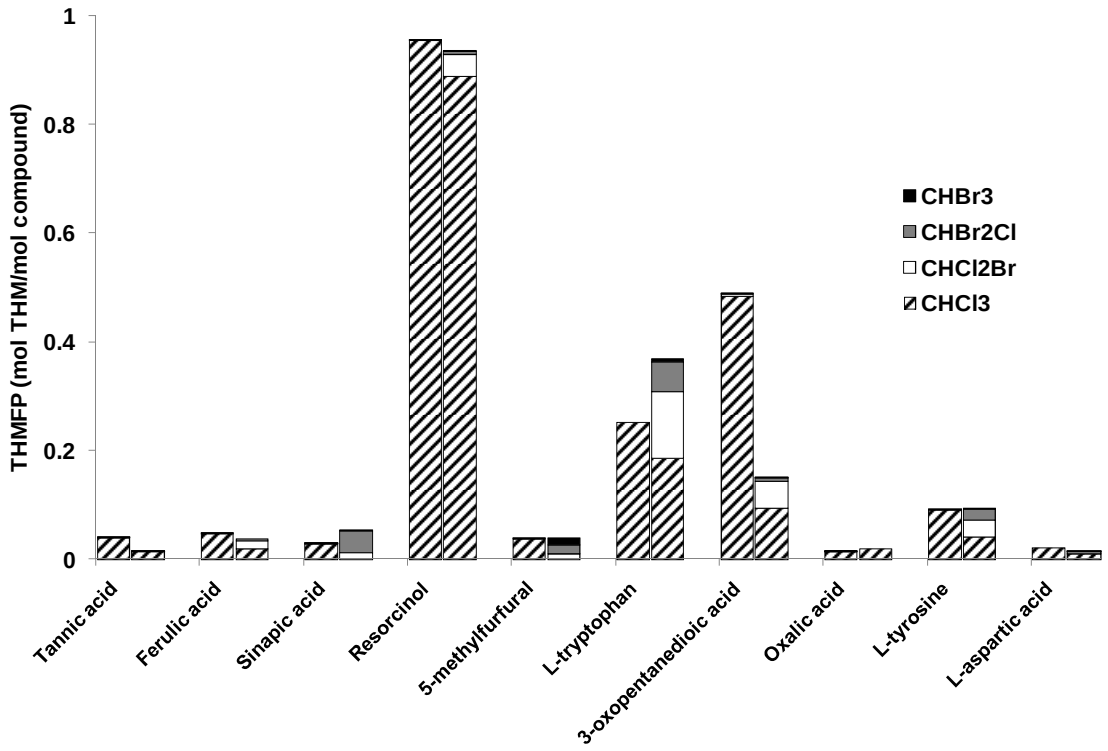

Figure 4.2: Significant THM precursors. For each compound the left bar represents chlorination and the right chlorination with bromide

4.4.4 HAAFP Results

Ferulic acid, which formed 0.37 and 0.40 mol HAAs/mol compound without and with Br^- respectively, was the most reactive precursor (Figure 4.3). Upon chlorination the lignin monomer p-coumaric acid formed 0.04 mol/mol and the related sinapic acid 0.09 mol/mol of HAAs respectively. To the authors' knowledge, the HAAFP of these three precursors is reported here for the first time. As lignin structures they are predicted to be contained within humic substances found in freshwater and behaved primarily as hydrophobic acids (Figure 4.1). Hence ferulic acid structures in particular are envisaged to represent part of the DXAA and trihaloacetic acid (TXAA) formation of hydrophobic fractions. Their relative HAA formation can be explained by the presence of one methoxy (ferulic acid) or two methoxy (sinapic acid) groups increasing reactivity

relative to the parent structure (p-coumaric acid). This is analogous to THMFP work involving resorcinol, where the meta configuration is more reactive (*29*). Aspartic acid was the second most reactive HAA precursor, forming 0.26 and 0.22 mol/mol in the absence and presence of Br^- respectively (Figure 4.3). The former value equates to 693 µg mgC^{-1}, higher than the 387 µg mgC^{-1} DCAA found by Reckhow and Kim (*31*). Its reactivity is believed to result from formation of a β-keto acid intermediate upon chlorination, a moiety known to have high DCAAFP (*8*, *25*). Analysis of HAA speciation revealed differences relating to surrogate hydrophobicity, though these were not absolute. The HPI or TPHA surrogates aspartic acid, asparagine and 3-oxopentanedioic acid formed predominantly DCAA on chlorination, over 93% for all. In contrast the HPOA and HPON surrogates sinapic acid, resorcinol, tryptophan and tyrosine formed mainly TCAA upon chlorination, over 70% for all. Ferulic acid and p-coumaric acid formed approximately equal amounts of DCAA and TCAA upon chlorination. This pattern correlates to drinking water research, where overall TXAA precursors were found to be more hydrophobic than DXAA precursors (*10*).

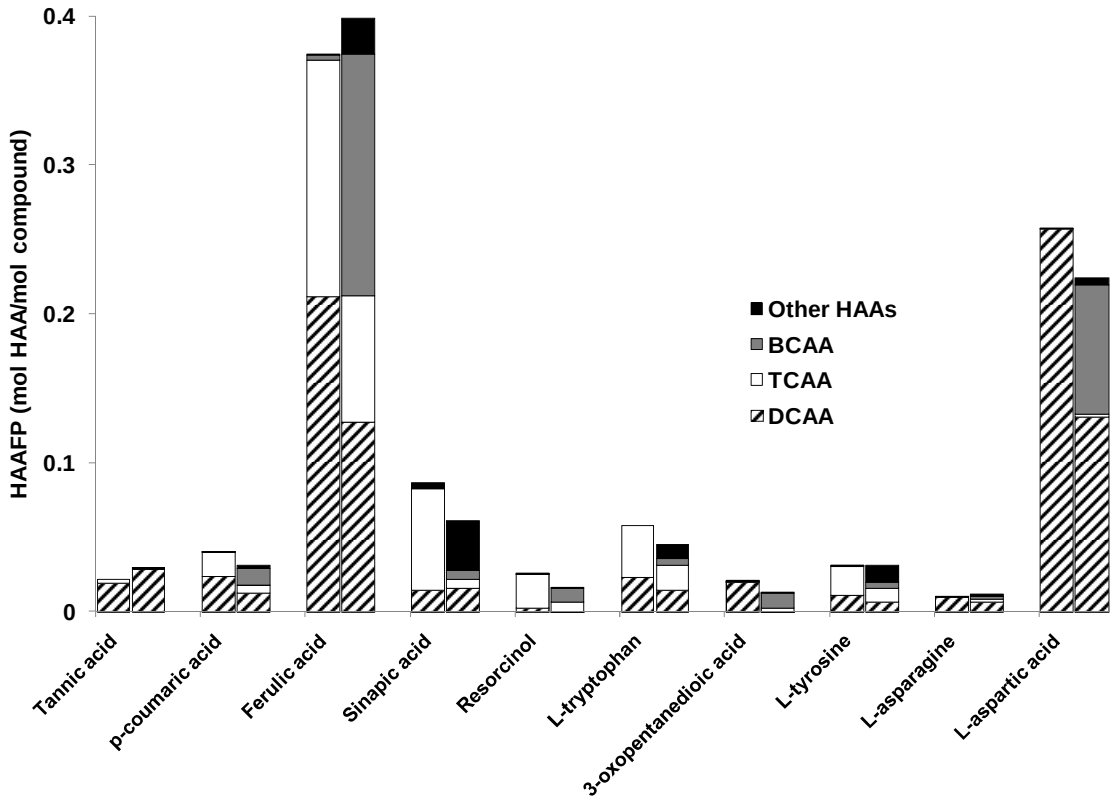

Figure 4.3: Significant HAA precursors. For each compound the left bar represents chlorination and the right chlorination with bromide

4.4.5 Non-regulated DBPs

Nine compounds formed over 0.015 mol/mol of non-regulated DBPs (Figure 4.4). Similar to THM and HAA formation, the majority of hydrophilic surrogates formed insignificant levels of non-regulated DBPs. Three amino acids were among the four most important precursors. Tryptophan, the most reactive, formed 0.20 mol/mol of TCA, with DCA and DCAN formation at 0.11 and 0.09 mol/mol respectively. Aspartic acid and asparagine formed mainly DXAA amongst the regulated DBPs, and had similar formation patterns amongst the non-regulated DBPs: mainly DCAN at 0.06 and 0.04 mol/mol, with significant TCA at 0.02 and 0.01 mol/mol respectively. This is in agreement with the finding that DCAN resulted from the chlorination of amino acids,

polypeptides and hydrophobic substances with amino acid moieties (*32*), while high DCA formation from tryptophan is noteworthy given the limited studies encompassing this DBP. Aspartic acid has previously been found to produce 158 µg mgC^{-1} DCAN and 91 µg mgC^{-1} TCA at pH 6.4 (*33*), data consistent with values of 130 and 76 µg mgC^{-1} in this study. The second most reactive precursor was 3-oxopentanedioic acid (Figure 4.1), which formed 0.37 mol/mol of 1,1,1-TCP plus minor amounts of 1,1-DCP and DCA. The HPOA or HPON surrogates coumaric, sinapic and ferulic acids, as well as resorcinol, formed mainly TCA with values from 0.01 – 0.03 mol/mol. Amongst the regulated DBPs all these compounds formed significant levels of TCAA (Figure 4.3), while resorcinol was also a major THM precursor. Finally, 5-methyfurfural formed 0.02 mol/mol of 1,1,1-TCP and 0.01 mol/mol of both TCA and DCA.

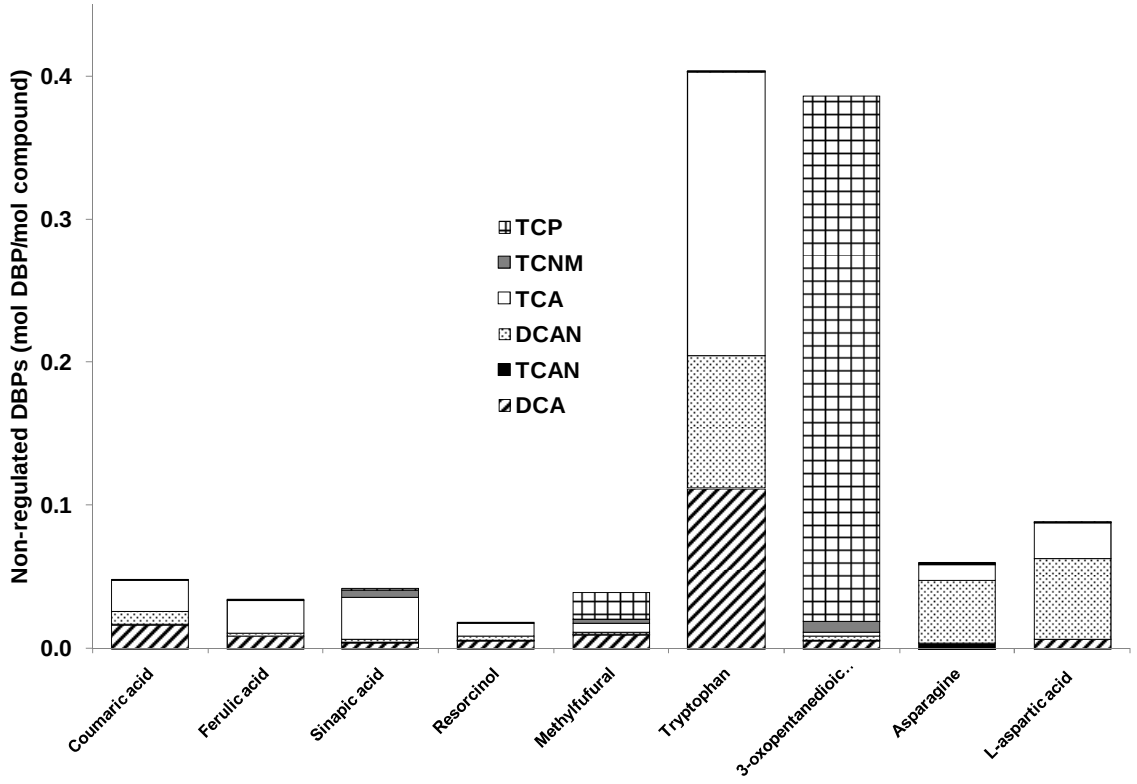

Figure 4.4: Significant precursors of non-regulated DBPs

4.5 Discussion

There were no significant relationships found between physical properties and formation of any DBP groups (Table 4-SI-1). This is explained by chemical functionality not reflected in physical properties having the key impact on DBP formation. Another articulation of this finding is that compounds can have similar physicochemical properties but divergent DBP formation, as with glutamic and aspartic acid, which have very similar log K_{OW}, pk_a and MW, yet upon chlorination aspartic acid formed DCAA, TCA and DCAN at 0.26, 0.02 and 0.06 mol/mol respectively, whereas equivalent values for glutamic acid were all 0.00 mol/mol (Table 4.1, Figure 4.3, Figure 4.4). The only parameter to effectively correlate with DBPFP was chlorine substitution, with correlation coefficients of 0.844, 0.827 and 0.842 between substitution into THMs, HAAs and non-regulated DBPs and formation of THMs, DCAA and non-regulated DBPs respectively (Table 4-SI-1). This signifies the importance of the chlorine substitution step to final DBP formation. Conversely, the lack of correlation between chlorine demand and DBPFP, illustrated by correlation of -0.024 between chlorine demand and THMFP, indicates the majority of chlorine was consumed in oxidation reactions. Analysis of correlations between DBP species indicated relationships between DCAA and DCAN (r = 0.678) and DCAN and TCA (r = 0.697) (Table 4-SI-1). Therefore waters which produce high concentrations of DCAA are also likely to form TCA and particularly DCAN. The former correlation is explained by DCAA being produced from the hydrolysis of DCAN, a process which occurs via the slow formation of dichloroacetamide in the presence of free chlorine (*34*). Since tryptophan, asparagine and aspartic acid were the most significant DCAN precursors and as DCAN is also known to be unstable at pH 7 and 8 (*26*), it would be interesting to investigate whether

DCAN might decrease concurrent to an increase in DXAA over longer contact times for these amino acids. It has been proposed that pathways leading to DCAA formation are different to those for TCAA formation and that the latter may be more similar to THM formation (*35*). However, no significant correlations were observed between these groups and it is notable ferulic acid formed significant levels of both DCAA and TCAA: 0.21 and 0.16 mol/mol respectively (Figure 4.3) upon chlorination. Correlations amongst the non-regulated DBPs involve DCA and TCA (r = 0.914), 1,1,1-TCP and 1,1-DCP (r = 0.703) and TCNM and 1,1-DCP (r = 0.769). Again it is probable similar correlations occur in drinking waters. These correlations are conveniently explained by one DBP being the precursor to another, as for DCAA and DCAN. However further mechanistic investigation is needed to confirm this explanation for many of the listed correlations. In addition there was also a correlation of r = 0.620 (n = 9 pairs) for the relationship between DCAA/TCAA and DCA/TCA (Figure 4-SI-2), indicating compounds have a propensity to form either the di- or tri-halogenated DBPs of these pairs. Overall this study has shown activated aromatic compounds, β-dicarbonyl species and amino acids to be key precursor groups, and clarified the DBPs resulting from their halogenation. Conversely, many hydrophilic surrogates had low chlorine demand and formed insignificant DBP levels, which illustrates the low reactivity of many NOM moieties towards chlorine (*23*). It is worth noting there is uncertainty about the size and behavior of NOM in natural waters as opposed to the selected surrogates. Specifically, peptide linking decreases chlorine demand of amino acids (*25*), while this group can associate with hydrophobic fractions (*7*). However, knowledge of individual surrogates is a prerequisite to understanding more complex systems. The most reactive activated-aromatic precursors, resorcinol and ferulic acid, were defined by HPOA behavior. The

high THMFP of resorcinol is established, whereas ferulic acid differed in forming predominantly DXAA and TXAA. Based on 3-oxopentanedioic acid, β-dicarbonyl species are expected to belong to TPHA and HPI fractions of drinking water. The high 1,1,1-TCP formation of this precursor is likely to be an antecedent to higher THM formation over longer time periods. Aspartic acid was the most reactive DXAA precursor, also forming lesser amounts of DCAN and TCA, whereas tryptophan formed a variety of DBPs, notably DCAN, DCA, TCA and $CHCl_3$. Thus single compounds can give rise to various DBPs, with their identity affected by contact time and pH, as well as chlorine and bromide levels. While the latter was found in both HPOA and HPON fractions, aspartic acid behaved as a HPI surrogate. DBP control strategies therefore need to consider HPOA, TPHA and HPI fractions. Increased efficacy is predicted to follow better knowledge of the relative occurrence and contribution to overall DBP formation of these reactive precursor groups in different water sources.

4.6 Acknowledgments

Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water are all gratefully acknowledged for their financial support of this project. Thanks also to Imran Janmohamed for help with the GC-ECD analysis.

4.7 References

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4.8 Supporting Information

4.8.1 Chlorine and DBP quantification extended version

Chlorine concentration was determined by iodometric titration (*15*), which measures combined chlorine and bromine concentration. The concentration of the chlorine stock solution was determined at least in triplicate on the day of use. Chlorine demand was obtained by titration of excess chlorine after 24 h.

Chlorinated samples were quenched by sodium sulphite, with THMs extracted into methyl tert butyl ether (MTBE) containing the internal standard (bromofluorobenzene, 1µg mL^{-1}) (*16*). HAA samples were quenched with ammonium chloride, acidified to pH 1.5 with sulfuric acid (Fisher), extracted into MTBE and derivatized with 10% acidic methanol for 2 h at 50°C (*17*). Non-regulated DBPs were extracted using Krasner et al. (2001) with modifications. Standards were obtained from Sigma-Aldrich Ltd (UK), apart from DCA (TCI Europe, Belgium). 30 mL sample was adjusted to a pH of 3.5, then DBPs extracted into 3 mL of MTBE, with separation aided by addition of 10 g of sodium sulphate and 1 g copper sulphate. Then each sample was shaken manually for 4 minutes. Since there is uncertainty over the stability of non-regulated DBPs in the presence of different quenching agents (*18*), no quenching agent was used. Instead samples were extracted immediately after 24 h and analysed the same day (*18*). DBPs quantified were dichloroacetaldehyde (DCA), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), trichloroacetaldehyde (chloral hydrate) (TCA), 1,1-dichloropropanone (1,1-DCP), trichloronitromethane (chloropicrin) (TCNM), and 1,1,1-trichloropropanone (1,1,1-TCP). Retention times of each non-regulated DBP were recorded individually and together, with no co-elution observed. Mean average deviations for duplicate samples of non-regulated DBPs ranged from 0.02 µg L^{-1} for

TCAN to 1.1 µg L^{-1} for TCA (n = 21 pairs). Due to the limited availability of relevant standards chlorination with bromide was not undertaken for analysis of non-regulated DBPs. DBPs were analysed using capillary gas chromatography with micro electron capture detector (Agilent 6890). For the HAA analysis, a capillary column (DB 1701 – 30 m × 0.25 mm id × 0.25 µm, Agilent UK) was used with helium carrier gas at a constant linear velocity of 1.1 mL min^{-1}. The split ratio was set at 5:1. A volume of 1 µL was injected. The initial oven temperature was 35 °C held for 2 minutes followed by a 5 °C per minute temperature ramp to 125 °C. The temperature was increased to 220 °C at a rate of 25°C min^{-1}. The temperature of the injector was set at 200 °C and the detector at 230 °C. For the THM analysis, a capillary column (DP5.625 – 30 m × 0.25 mm id × 0.25 µm, Agilent UK) was used with helium carrier gas at a constant linear velocity of 1.0 mL min^{-1}. The split ratio was set at 10:1. A volume of 1 µL was injected. The initial oven temperature of was 35 °C held for 2 min, followed by a 5 °C min^{-1} temperature ramp to 90 °C. The temperature was then increased to 260 °C at a rate of 30°C min^{-1}. The temperature of the injector was set at 200°C and the detector at 290°C.

For the non-regulated DBPs, a ZB-1ms column (30 m × 0.25 mm × 0.25 µm, Phenomenex UK) was used with helium carrier gas at a column flow rate of 1.0 mL min^{-1}. A volume of 1 µL sample was injected splitless. The initial oven temperature of 35°C was held for 22 min, followed by a 10 °C per min increase to 145 °C, a value held for 2 min, before a final ramp of 20°C min^{-1} to 225 °C, with this maximum held for 10 min. The total run time was 49 minutes. The temperature of the injector was set at 200 °C and the detector at 290 °C. For all DBPs data was collected at a rate of 20 Hz.

4.8.2 Figures and Tables

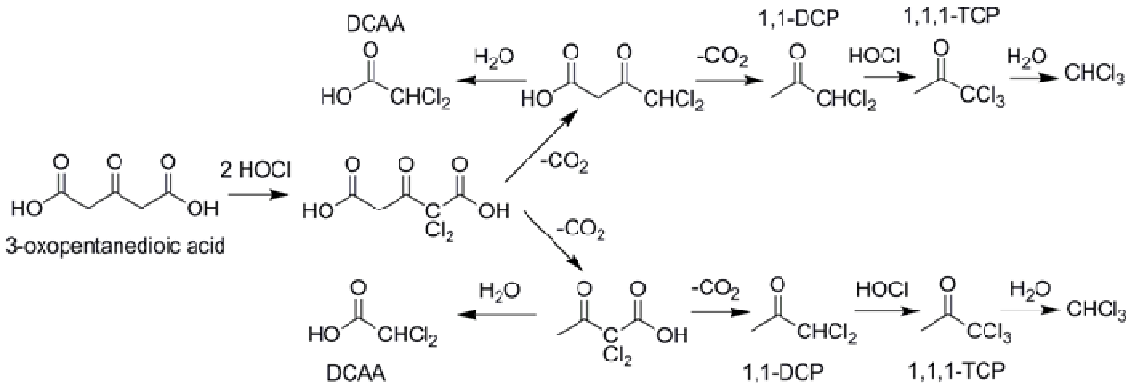

Figure 4-SI-1: chlorination of 3-oxopentanedioic acid

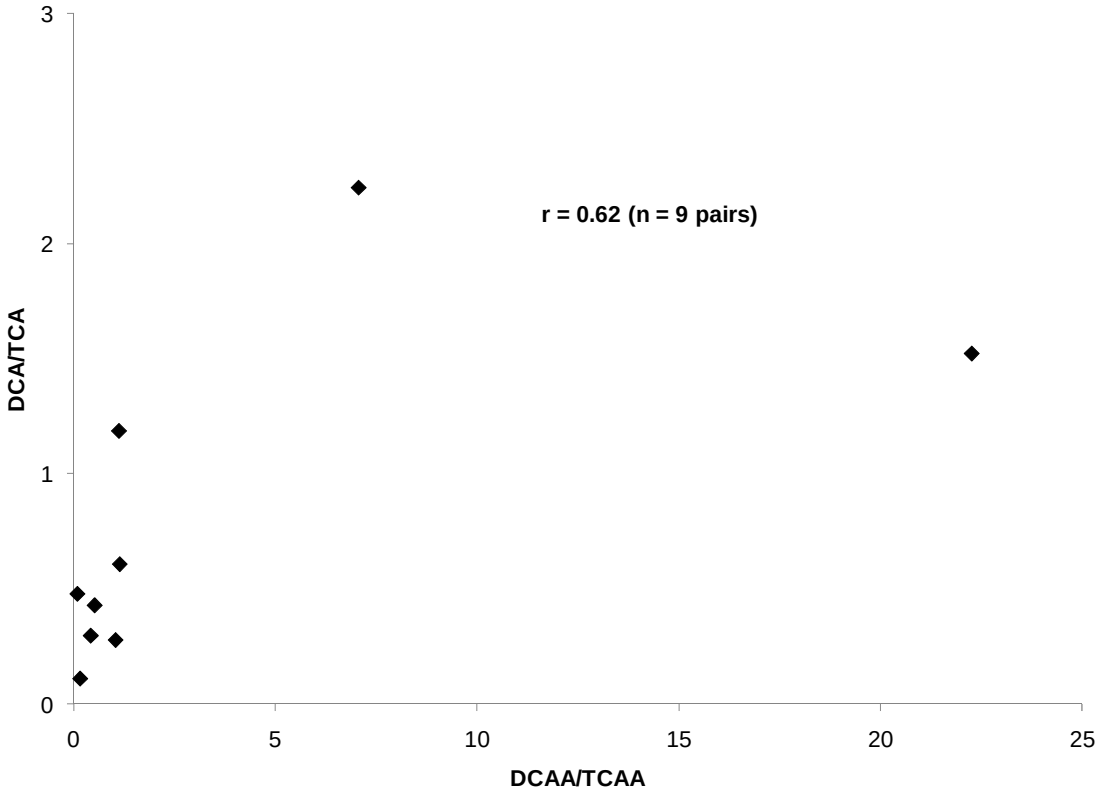

Figure 4-SI-2: Formation of DCAA/TCAA versus DCA/TCA. DBP formation in µg mgC^{-1}.

Table 4-SI-1: Correlations between physical properties and DBP formation of NOM surrogates. Note: DBPs in µg. mgC^{-1} (following page)

	THMs	DCAA	TCAA	Nr DBPs	DCA	TCA	DCAN	TCAN	1,1-DCP	1,1,1-TCP	TCNM	Cl_2 demand	Cl_2 subn in THMs	Cl_2 subn in HAAs	Cl_2 subn in Nr DBPs
DCAA	-0.052														
TCAA	0.101	0.188													
Nr DBPs	0.46	0.149	-0.058												
DCA	0.112	0.08	0.123	0.365											
TCA	0.037	0.26	0.168	0.32	0.914										
DCAN	-0.061	0.678	-0.09	0.267	0.433	0.697									
TCAN	-0.077	-0.052	-0.092	0.096	-0.006	0.272	0.538								
1,1-DCP	0.227	-0.066	-0.147	0.597	-0.043	-0.222	-0.169	-0.108							
1,1,1-TCP	0.48	-0.018	-0.095	0.912	0.018	-0.085	-0.082	-0.058	0.703						
TCNM	0.497	-0.146	0.017	0.43	-0.097	-0.144	-0.091	0.135	0.769	0.495					
Cl_2 demand	-0.024	0.009	0.181	-0.039	0.183	0.202	0.058	-0.003	-0.202	-0.111	-0.126				
Cl_2 subn: THMs	0.844	-0.107	-0.021	0.539	0.041	-0.079	-0.154	-0.12	0.349	0.614	0.428	-0.203			
Cl_2 subn: HAAs	-0.021	0.827	0.671	0.089	0.076	0.217	0.402	-0.108	-0.082	-0.026	-0.096	0.032	-0.034		
Cl_2 subn: Nr DBPs	0.375	-0.015	-0.153	0.842	0.173	0.047	-0.002	-0.04	0.631	0.869	0.37	-0.261	0.678	0.01	
log K_{OW}	0.06	-0.151	0.197	-0.096	-0.026	-0.118	-0.281	-0.198	-0.002	-0.025	0.008	0.779	0.016	-0.003	-0.064
pK_a	0.25	-0.163	0.012	-0.252	-0.162	-0.208	-0.279	-0.17	-0.115	0.045	0.097	-0.32	0.497	-0.031	0.391
MW	-0.091	-0.058	-0.037	-0.083	-0.068	-0.065	-0.085	-0.06	-0.208	-0.047	-0.223	0.854	-0.118	-0.073	-0.122
n	0.056	-0.003	0.233	-0.052	0.23	0.229	0.041	-0.023	-0.252	-0.131	-0.137	0.784	0.052	0.102	-0.124
MV	-0.096	-0.062	0.016	-0.084	-0.038	-0.035	-0.088	-0.063	-0.218	-0.057	-0.217	0.874	-0.14	-0.054	-0.137
γ	-0.077	0.026	-0.145	-0.028	-0.073	-0.022	0.044	0.007	-0.241	-0.018	-0.259	0.709	-0.067	-0.075	-0.116
PSA	-0.102	-0.038	-0.099	-0.047	-0.131	-0.117	-0.077	-0.049	-0.169	0.008	-0.213	0.806	-0.107	-0.084	-0.079
log K_{OC}	0.45	0.022	0.479	0.095	0.476	0.384	-0.014	-0.241	-0.107	-0.025	0.098	0.507	0.318	0.21	-0.004
α	-0.087	-0.063	0.001	-0.09	-0.034	-0.035	-0.084	-0.063	-0.216	-0.065	-0.218	0.875	-0.127	-0.061	-0.138
ρ	-0.043	0.074	-0.127	0.055	-0.107	-0.045	0.052	-0.007	-0.146	0.076	-0.192	0.423	0.121	0.014	0.053
WSol	0.213	-0.212	-0.248	0.119	-0.165	-0.286	-0.283	-0.172	0.267	0.252	0.197	-0.239	0.237	-0.249	0.212

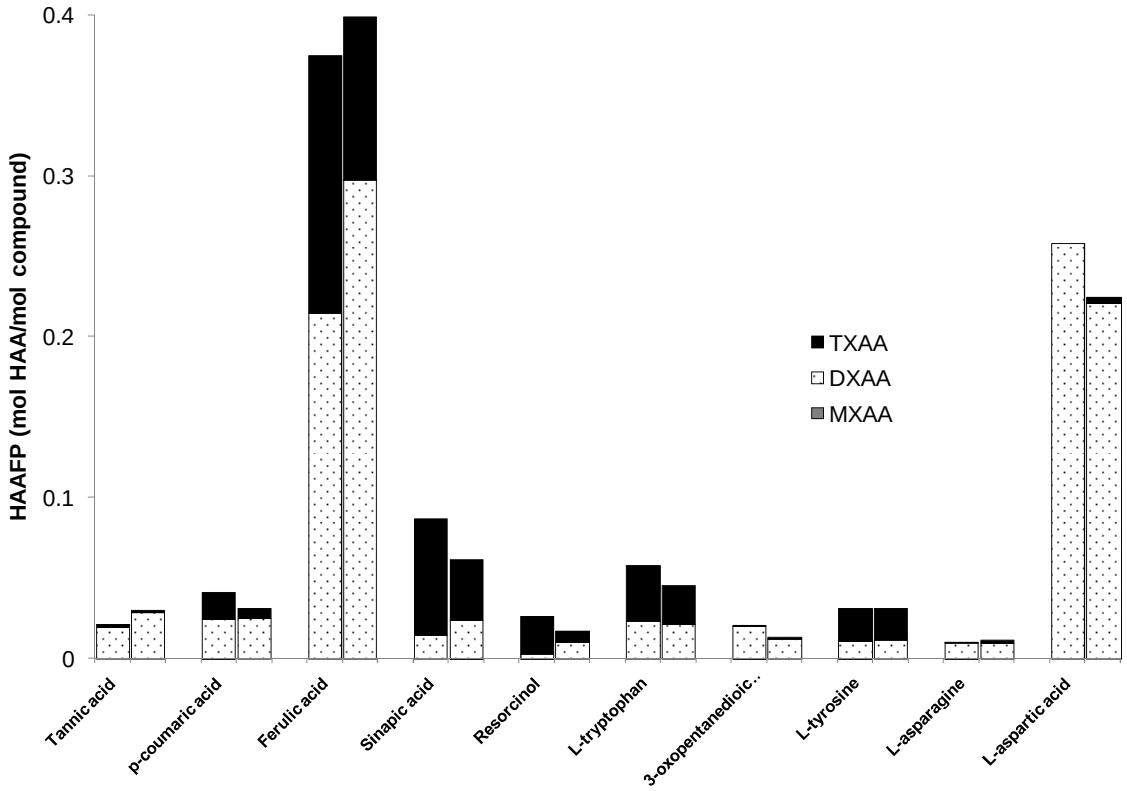

Figure 4-SI-3: Formation of MXAA, DXAA and TXAA

CHAPTER 5: DISINFECTION BYPRODUCT FORMATION OF NATURAL ORGANIC MATTER SURROGATES AND TREATMENT BY COAGULATION, MIEX® AND NANOFILTRATION

DISINFECTION BYPRODUCT FORMATION OF NATURAL ORGANIC MATTER SURROGATES AND TREATMENT BY COAGULATION, MIEX® AND NANOFILTRATION

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5.1 Abstract

Potentially the most effective means of controlling disinfection byproducts (DBPs) is to remove precursors before disinfection. To understand relationships between physical properties, treatability and DBP formation nine NOM surrogates were studied. Their DBP formation and removal by coagulation, MIEX® anion exchange resin and two nanofiltration membranes was measured. Whereas treatability of NOM surrogates was explained in terms of their physicochemical properties, the same was not true of DBP formation. Hence it was not possible to selectively remove reactive precursors. Instead precursor removal should be targeted at groups defined by physicochemical properties. Coagulation and MIEX® offered effective removal of highly-charged anionic species and where a high proportion of DBP precursors belong to this group may be sufficient for DBP control. In waters where less-treatable NOM has a high DBP generating capacity a (hydrophobic) nanofiltration membrane is particularly suitable for removal of neutral, hydrophilic precursors.

Key Words NOM, treatability, coagulation, MIEX®, nanofiltration, DBPs

5.2 Introduction

Natural organic matter acts as a precursor to disinfection byproducts (DBPs), amongst which the trihalomethanes (THMs) and haloacetic acids (HAAs), products of chlorination, are considered to be dominant on a mass-basis in natural waters (*1*). Since these DBPs present a health risk to humans, their levels in drinking water are regulated to limit exposure: in the UK, THMs 100 µg L^{-1}, in the USA: THMs 80 µg L^{-1} and HAA_5 60 µg L^{-1}. It is anticipated future DBP regulations in the UK may encompass the HAAs (*2*) and perhaps further DBPs.

A number of approaches exist for reducing DBP formation including catchment management, altering the disinfection process and/or removal of precursors (*3*). While the second option is desirable, evidence suggests that changing disinfectant produces alternative DBPs which also pose a health risk, for example chloramines have been linked to N-nitrosodimethylamine (NDMA) formation (*4*). Further, the capability to reduce disinfectant doses is limited by the need to supply adequate disinfection. Thus it is a limited option over the longer term. Meanwhile, precursor removal does not generate alternative DBPs, as well as often utilising existing technology and hence much research practice is focussed on this area (*3*). For instance, the following removals of bulk NOM, THM precursors and HAA precursors respectively have been reported: coagulation (7-44%, 15-34% and19-72%; (*5*)), coagulation and MIEX® anion exchange resin (46-72%, 60-79% and 58-80%; (*5*)) , nanofiltration (67-94%, 66-92% and 66-97%; (*6*)).

Thus preferential removal of DBP precursors over bulk NOM have been reported, as well as improved removal using MIEX® and coagulation in comparison with

coagulation alone. The reasons for these differences are unclear, but they presumably relate to differences in physicochemical properties between precursors and bulk NOM. The principal characterisation is related to hydrophobicity where water is fractionated into hydrophobic and hydrophilic components by use of resins (*7*). While there is a perception that hydrophobic NOM is the major source of DBP precursors (*8*), hydrophilic NOM can also generate high DBP levels, and thus contain reactive precursors. For example, in NOM from the South Platte River (USA), THM formation potential (THMFP) for the hydrophobic acid (HPOA) and hydrophilic acid (HPIA) fractions were comparable, at 46 and 35 µg $CHCl_3$ mgC^{-1} respectively (*7*). Moreover, there is evidence that since hydrophilic NOM is less treatable by coagulation, it is this group which can determine post-coagulation NOM levels (*9*), and in turn final DBP formation, at least where chlorination is the final treatment step.

Although information exists regarding the chemical groups contained within operationally-defined fractions (*7*), rarely does this classification extend to a molecular level. To address this research into DBP formation also involves model compounds to act as surrogates for the main chemical groups found in NOM: humic substances, carboxylic acids, amino acids, proteins and carbohydrates (*7*). However, equivalent work in terms of treatability is limited and this makes connection between the understanding of DBP formation and strategies to control their formation difficult. Further the selection and operation of technologies in relation to DBP precursor removal rather than bulk NOM remains uncertain. Our aim was to understand whether selective removal of DBP precursors is feasible through testing NOM surrogates, and in so doing inform process selection for precursor removal. The treatments selected were coagulation, anion exchange (MIEX®) and nanofiltration. Coagulation is the standard

NOM removal process at water treatment works (WTW) (*3*) and can be considered the benchmark against which to compare other treatments. MIEX® is a relatively novel process which has been used as an adjunct or alternative to coagulation and has shown improved removal of NOM and DBP precursors relative to coagulation (*10*). Finally, nanofiltration is becoming a realistic option for NOM removal, with high rejection of DBP precursors achievable dependent on operating conditions and membrane (*6*).

5.2 Methods and Materials

5.2.1 NOM Surrogates

Compounds were chosen from the main chemical groups of NOM (*7*) with emphasis on hydrophilic NOM. Amongst the chosen compounds were amino acids and carbohydrates, which are important constituents of NOM and of hydrophilic nature (Figure 5.1, Table 5.1). Surrogates were classified as hydrophobic or hydrophilic based on their log K_{OW} (*11, 12*) values being above or below zero respectively, and as anionic or neutral at pH 7 based on their pK_a values (*11-13*) (Table 5. 1). Experimental log K_{OW} values were used where available. Surrogates were obtained from Fisher Scientific (Loughborough, UK) or Sigma Aldrich (Dorset, UK) at analytical purity or above. Concentration was determined by measuring dissolved organic carbon (DOC) with a Shimadzu 5000A TOC analyser (Milton Keynes, UK). Initial concentration of NOM surrogates was 10 mg L^{-1} as DOC in deionised water. For all processes except nanofiltration samples were filtered (0.45 µm) before analysis.

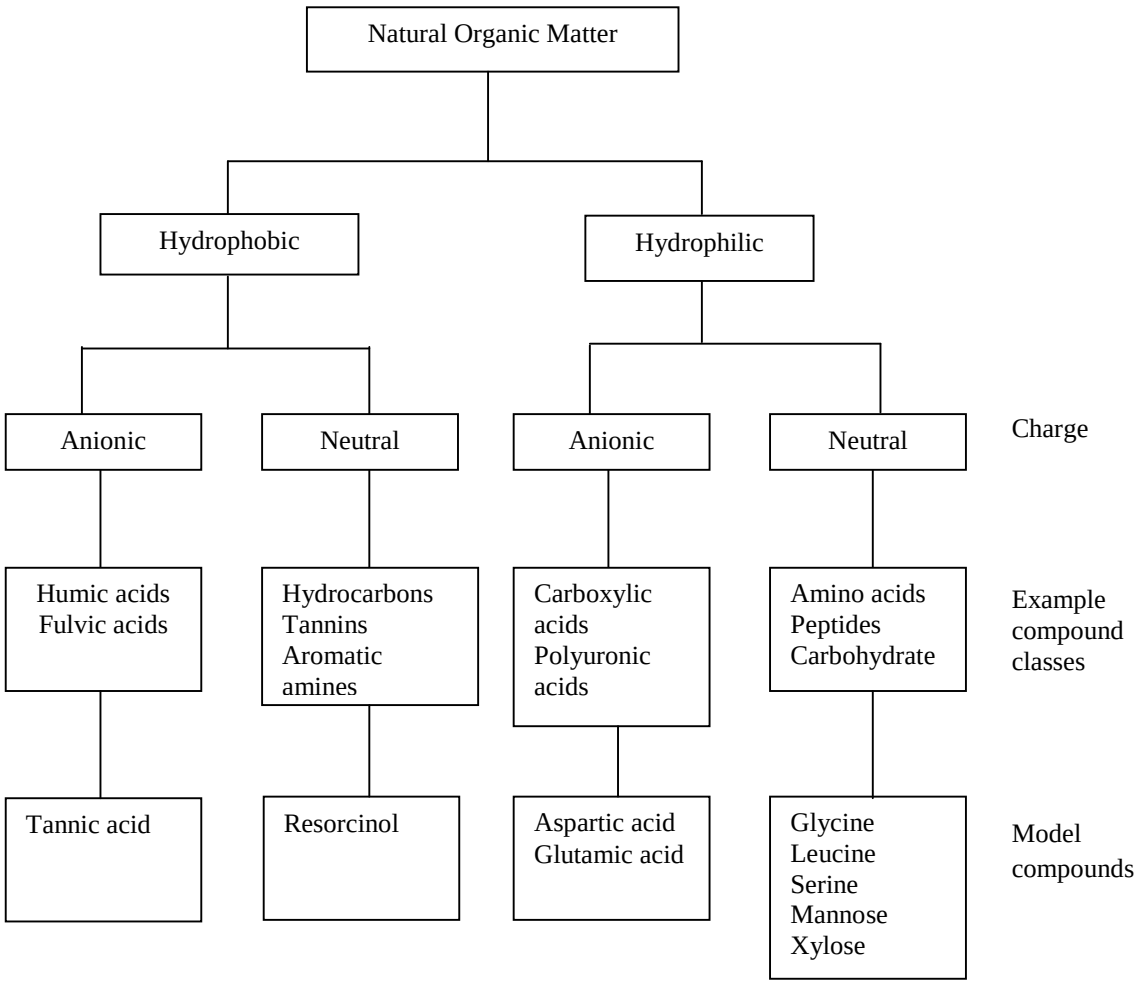
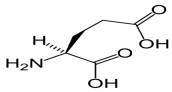
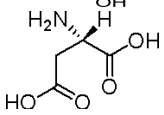
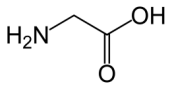
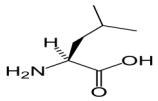
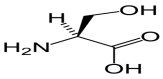
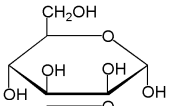
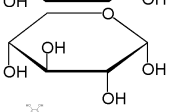
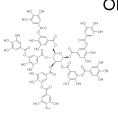
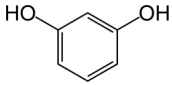


Figure 5.1: NOM Classification, adapted from Leenheer and Croué, 2003

Table 5.1: Properties of NOM Surrogates

Compound	Structure	log K_{OW}	MW g mol^{-1}	pK_a pK_b pK_{c2}	Classification	Chemical group
L-Glutamic acid		-3.69	147	2.16 9.58 4.15	Hydrophilic anionic	Amino acid
L-Aspartic acid		-3.89	133	1.95 9.66 3.71	Hydrophilic anionic	Amino acid
Glycine		-3.21	75	2.34 9.58 NA	Hydrophilic neutral	Amino acid
L-Leucine		-1.52	131	2.32 9.58 NA	Hydrophilic neutral	Amino acid
L-Serine		-3.07	105	2.13 9.05 NA	Hydrophilic neutral	Amino acid
D-Mannose		-3.24	180	12.08 NA NA	Hydrophilic neutral	Carbohydrate
D-Xylose		-2.39	150	12.14 NA NA	Hydrophilic neutral	Carbohydrate
Tannic Acid		13.3	1701	3.2 NA 8.7	Hydrophobic anionic	Phenolic
Resorcinol		0.80	110	9.32 NA 11.1	Hydrophobic neutral	Phenolic

Note: pK_a and pK_{a2} = first and second acid dissociation constants respectively, pK_b = base dissociation constant, N/A = not applicable

5.2.2 Coagulation Experiments

Experiments were undertaken using a Phipps and Bird 902B jar tester (Virginia, USA). The coagulant was ferric sulphate (Ferripol XL, EA West). Jar tests covered a Fe/DOC ratio of 0.3 – 3.0 and pH range of 3-11. Zeta potential was measured using a Zetasizer 2000HSA (Malvern Instruments, UK), with extra jar tests if required to obtain samples with zeta potential around zero. The rapid mix phase of jar tests lasted for 90 seconds at 200 rpm, during which the coagulant was added and pH adjusted with dilute NaOH or HCl. This was followed 15 minutes of slow stirring at 30 rpm then 15 minutes of settling.

5.2.3 MIEX® Experiments

Experiments were undertaken using a Phipps and Bird 902B jar tester and the method of Mergen et al. (*10*). In short the resin dose was 10 mL L^{-1} and the same MIEX® resin (Orica Watercare, UK) was used for 15 consecutive jar tests in a 1 L beaker, i.e. 0 to 1500 bed volumes. After each jar test 900 mL of supernatant was decanted, 100 mL of which was collected for analysis and the remainder stored in a combined sample container. Samples were analysed from each separate jar test and the combined supernatant after alternate jar tests. This protocol was designed to replicate full scale operation.

5.2.4 Nanofiltration Experiments

Experiments were carried out in an Amicon 8200 200 mL dead-end filtration cell (Millipore UK) under 2 bar of nitrogen pressure. Membranes were soaked overnight in deionised water before being rinsed to remove preservation liquids and the pure water permeability recorded. A different membrane was used for each experiment and 120 mL of permeate was collected, with the pure water permeability also being recorded after

every experiment. Two different membranes were used, of similar molecular weight cut-off (MWCO), both supplied by Dow-Filmtec, the NF270 and NF90.

5.2.5 DBPFP Tests

The HAA formation potential (HAAFP) and THMFP of NOM surrogates were recorded on a gas chromatograph with a micro electron capture detector (Agilent 6890 GC-μECD). Samples were diluted in ultrapure (UP) water (18.2 MΩ) to 15 μM (moles L^{-1}) and buffered at pH 7 with phosphate buffer. The chlorination conditions were 24 h at 20°C ± 2°C with a chlorine/compound dose of 35 M/M. Chlorine stock solution was prepared from concentrated sodium hypochlorite (>8%, Fisher) by dilution in UP water. All samples were prepared in duplicate. THMs were extracted according to USEPA Method 551.1 and HAAs by USEPA Method 552.3. The internal standard was bromofluorobenzene at 1μg mL^{-1}.

5.3 Results

5.3.1 Coagulation

The hydrophobic anionic tannic acid was the most treatable compound by coagulation, with a maximum removal of 89 ± 5% (Figure 5.2, Table 5.2). Results for four surrogates over the pH and dose range are shown in Figure 5.2 to illustrate patterns of coagulation behaviour, with optimum removal conditions for all compounds in Table 5.2. . The two hydrophilic anionic species, glutamic and aspartic acid showed moderate removal maxima of 31 ± 5% and 27 ± 5%, respectively. The hydrophilic neutral and hydrophobic neutral compounds showed no significant removal, with values ranging from 0-8 ± 5% (Figure 5.2, Table 5.2). These results can be explained in terms of

compound charge. The two hydrophilic anionic surrogates have a single negative charge at pH 7 based on their pK_a values (Table 5.1) Tannic acid has multiple strongly acidic carboxyl groups, presumed to occur because some digallic acid moieties are linked to the central glucose via phenolic rather carboxyl groups (*13*). If this interpretation is correct, a maximum of five carboxyl groups could provide negative charge. All other compounds are neutral under ambient pH conditions.

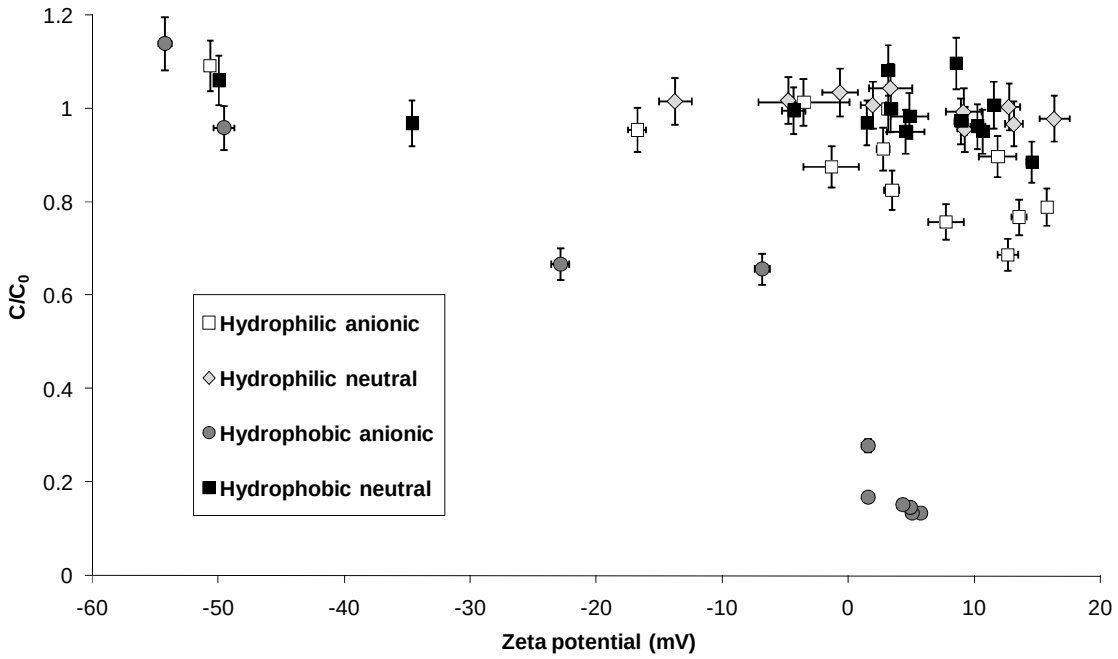


Figure 5.2: Coagulation of glutamic acid, leucine, tannic acid and resorcinol

Table 5.2: Results Summary

Compound	Coagulation % removal Max (pH, Fe/DOC dose)	MIEX % removal Min	MIEX % removal Max	NF270 % removal	NF90 % removal	DBPFP (µg mgC^{-1}) $CHCl_3$	DBPFP (µg mgC^{-1}) DCAA	DBPFP (µg mgC^{-1}) TCAA
L-Glutamic acid	31 ± 5 (pH 4.5, dose 3.6)	12 ± 5	54 ± 5	70 ± 5	73 ± 5	0	1	0
L-Aspartic acid	27 ± 5(pH 4.5, dose 3.0)	14 ± 5	48 ± 5	70 ± 5	53 ± 5	54	693	0
Glycine	2 ± 5(pH 9, dose 1.3)	0 ± 5	6 ± 5	24 ± 5	45 ± 5	23	1	0
L-Leucine	6 ± 5(pH 4.5, dose 0.9)	0 ± 5	9 ± 5	65 ± 5	83 ± 5	0	0	0
L-Serine	8 ± 5(pH 4.5, dose 1.2)	0 ± 5	1 ± 5	31 ± 5	86 ± 5	0	2	0
D-Mannose	8 ± 5(pH 4.5, dose 2.0)	2 ± 5	12 ± 5	72 ± 5	86 ± 5	0	1	0
D-Xylose	7 ± 5(pH 4.5, dose 3.0)	0 ± 5	14 ± 5	51 ± 5	83 ± 5	16	1	0
Tannic acid	89 ± 5(pH 4.5, dose 1.9)	56 ± 5	92 ± 5	92 ± 5	62 ± 5	5	3	0
Resorcinol	5 ± 5(pH 4.5, dose 0.9)	0 ± 5	6 ± 5	N/A	N/A	1588	5	52

The observed data correlates with previous findings (*9*) where coagulation preferentially removed high MW hydrophobic organics, which are typically highly charged. To illustrate, reported maximum removals by fraction were humic acid fraction (84%); fulvic acid fraction (64%); hydrophilic acid fraction (14%) and hydrophilic non-acid fraction (17%) (*9*). Note the hydrophobic acid fraction (HPOA) is comprised of the humic acid fraction (HAF) and the fulvic acid fraction (FAF), and further that HPINA and HPIA are respectively equivalent to transphilic acid (TPHA) and hydrophilic (HPI) fractions (Chapters 4, 7 and 8). In relation to the current work, tannic acid behaved as a hydrophobic acid in terms of its treatability by coagulation and glutamic and aspartic acids as hydrophilic acids. Being unaffected by coagulation, the remaining compounds are representative of those molecules comprising a post-coagulation residual, which is likely to be rich in amino acids and carbohydrates.

The removal mechanisms of coagulation have been described as charge complexation/precipitation and adsorption onto precipitated flocs and metal hydroxides (*14*). While maximum removal of tannic acid occurred at pH 4.5, with a dose of Fe/DOC 1.9 and zeta potential 5.1 ± 0.3 mV, minimum removal was at pH 9 with a Fe/DOC dose of 1.9 and zeta potential -54.2 ± 0.7 mV (Figure 5.2). For glutamic acid maximum and minimum removal was at pH 4.5 (Fe/DOC 3.6, zeta potential 12.7 ± 0.8 mV) and pH 11 (Fe/DOC 2.9, zeta potential -50.6 ± 0.1 mV) respectively. Thus these anionic compounds demonstrate that, as with natural waters, optimum removal can be expected in a zeta potential window centred around zero (Figure 5.2) (*9*). These data also demonstrate how zeta potential control can be utilised for systems with relatively low anionic charge. These data also demonstrate how zeta potential control can be utilised for systems with relatively low anionic charge. Previously it has been shown

how zeta potential can effectively be used to achieve low NOM residuals with varying source waters and coagulation conditions, including those with relatively low NOM concentrations and coagulant doses (*15*). Regarding pH, removal by a charge neutralisation mechanism can only be expected when coagulant particles are positively charged and NOM anionic. Ferric hydroxide has an iso-electric point around pH 7-8 (*16*) and as the pH rises beyond this value the increasingly negative charge of coagulant particles makes destabilisation less likely. This becomes more likely, given that as seen from their pK_a or pK_b values tannic, aspartic and glutamic acids also become more negative as the pH rises above 9. It also appears that any other possible removal mechanisms such as adsorption to iron hydroxide particles or sweep flocculation were not operative, noting that flocs were observed for all compounds at pH 4.5 and the higher coagulant doses. The results are consistent with coagulation being a charge driven process. This agrees with literature, where the electrical character of NOM was noted as the key defining factor in the efficacy of coagulation (*9*), and charge neutralisation is believed to be the dominant removal mechanism for natural organic matter (*16*).

5.3.2 MIEX®

The removal of NOM surrogates by MIEX® mirrors the coagulation data, with results explicable in terms of charge. The hydrophobic anionic tannic acid was effectively treated, with maximum removal of 92 ± 5% after 100 bed volumes declining to 56 ± 5% after 1500 bed volumes (Figure 5.3, Table 5.2). The two hydrophilic anionic surrogates showed moderate and similar treatability: for glutamic acid removal varies from 53 ± 5% (100 bed volumes) to 12 ± 5% (1500 bed volumes) and for aspartic acid the respective values were 48 ± 5% and 14 ± 5%. The combined value after 1500 bed

volumes was considered most representative of operation on a full-scale water treatment plant (*10*) and for tannic, glutamic and aspartic acids the respective values were 77 ± 5%, 25 ± 5% and 22 ± 5%. Therefore while MIEX® did show improved removal of glutamic and aspartic acids at low bed volumes compared with coagulation, this difference was not maintained under conditions more typical of full-scale ion exchange. The remaining neutral compounds showed no significant removal (0-7 ± 5% in combined 1500 bed volumes sample).

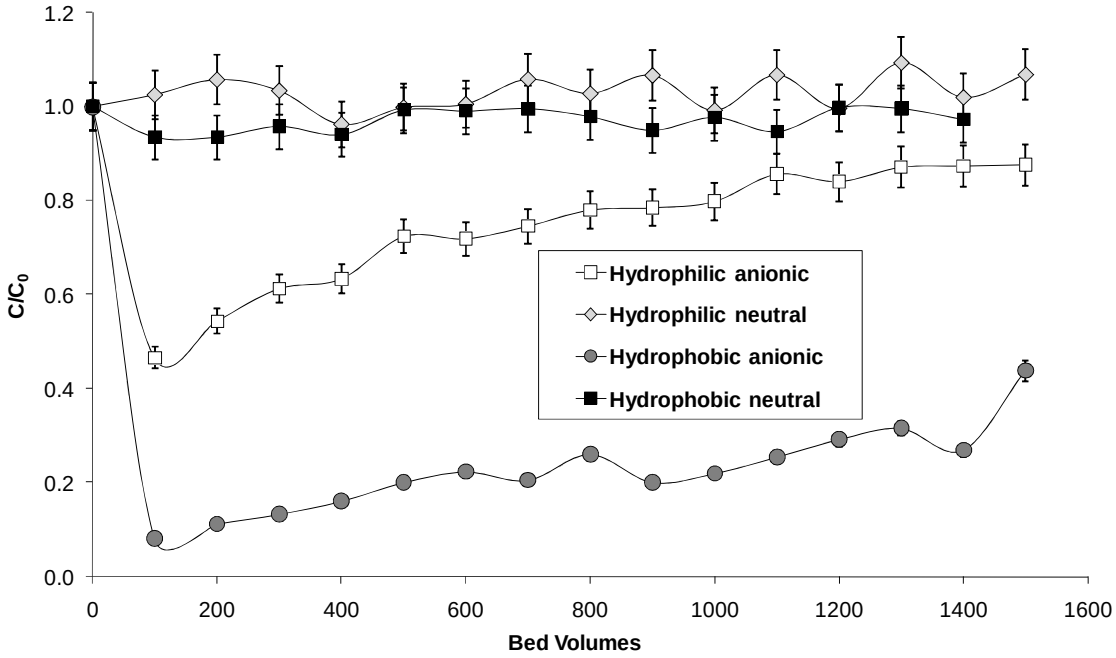


Figure 5.3: MIEX treatment of glutamic acid, leucine, tannic acid and resorcinol

Based on the literature it is expected any improved performance of MIEX® over coagulation is due to higher removal of transphilic acids. The range of removal for NOM fractions has been recorded as 63-75% for the hydrophobic fraction, 70-89% for

the transphilic fraction and 2-67% for the hydrophilic fraction (*17*). The transphilic acid fraction was also found to have higher affinity for MIEX® than other fractions (*18*), this being explained by its higher charge density. While the exact chemical identity of transphilic acids is unknown, they are assumed to be more hydrophilic than the hydrophobic acids and with a high proportion of carboxylic acid functionality (*19*). The two hydrophilic anionic species in this study were hydrophilic acids both in terms of their physical properties and treatability by MIEX® and coagulation and have only a single negative charge. It can be expected that multiple dissociated carboxylic acid groups are necessary for the high removals reported for transphilic acids. However, as previously noted much research has been conducted with only single usage of MIEX® resin, and thus may overestimate removal compared with continuous testing (*10*). During that study a water of hydrophobic character showed 65% removal after the first resin use, declining to 25% by 15 consecutive resin uses (*10*). This removal range is similar to the ranges observed for tannic, aspartic and glutamic acids, which were 33, 34 and 42% respectively (Table 5.2). In contrast two waters of hydrophilic character showed consistent removal between first and last resin use (*10*). This distinction was thought to be due to the hydrophobic water containing higher molecular weight NOM capable of blocking ion exchange sites. Whereas, in the current investigation the low MW and hydrophilic aspartic and glutamic acids showed similar declines in removal as the larger and hydrophobic tannic acid. Note removal declined steadily from first to last resin use for all 3 acids (Figure 5.3), therefore it does not appear that a specific surface coverage was necessary before removal deteriorated. A similar conclusion is drawn if concentration of compounds and resin are compared in meq L^{-1}. An exchange capacity of 0.52 meq mL^{-1} for MIEX® (*20*) equates to 5.2 meq L^{-1} in this study. The initial

concentration of aspartic and glutamic acid was 0.21 and 0.17 meq L^{-1} respectively, with a total of respectively 2.86 and 2.31 meq L^{-1} added by the final jar test, of which 22% and 25% respectively had been removed. Thus there was unused exchange capacity even during the final test. For tannic acid the amount of anionic charge is ill-defined (*13*) and so concentration has not been converted to meq L^{-1}. Thus the mechanism by which ion exchange declines is not thought related to surface coverage or exchange site saturation. Instead the involvement of more complex mass transfer phenomena is likely.

Information regarding removal mechanism can also be elucidated from these results. As with coagulation there has been some debate about the exact mechanism/s responsible for NOM removal. Magnetic ion exchange resin is a strong base anion resin with ammonium functional groups. Recently it has been shown that anion exchange was indeed the removal mechanism for a range of NOM isolates by MIEX® at ~pH 8 (*20*). At the same time the existence of other mechanisms has been postulated for various anion exchange resins. Hydrophobic interactions were thought to be responsible for a small amount of NOM uptake by strong base resins, up to 7% for a lake water (*21*). A non-electrostatic mechanism involving hydrogen bonding has also been postulated for weak base resins (*22*). A maximum 6 ± 5% (100, 200 and 400 bed volumes separate samples) uptake was recorded for the hydrophobic neutral resorcinol (Table 5.2), which could be partly explained by experimental error, as no removal in the 1500 bed volumes combined sample was recorded. Similar results were recorded for the hydrophilic neutral species (Table 5.2). If hydrogen bonding were a factor, some removal might be expected for both hydrophilic and hydrophobic neutral species, as all were capable of hydrogen bonding. That this was not observed again indicates the

absence of hydrogen bonding with MIEX®. Non-electrostatic mechanisms may still operate in other ion exchange resins of differing chemical design.

In the current investigation MIEX® testing was undertaken without addition of salt/s. Literature suggests the presence of sodium bicarbonate has little effect on uptake of NOM. In a recent study it was found the separation factor for Suwannee River Fulvic Acid (SRFA) over chloride was ~8 times greater than for bicarbonate over chloride (*20*). Further, separation factors remained relatively constant over a range of resin loadings. It was found that SRFA removal was not adversely affected by the presence of bicarbonate, in fact it was slightly promoted.

5.3.3 Nanofiltration

With the NF270 membrane removal generally increased with molecular weight from glycine (MW 75 g mol^{-1}; 24 ± 5% removal) to tannic acid (1701 g mol^{-1}; 92 ± 5% removal) (Figure 5.4, Table 5.2). With the NF90 membrane the relationship between MW and removal was less clear, glycine again exhibiting the lowest removal at 45%, with mannose (180 g mol^{-1}) the maximum at 86 ± 5%. Average removal with the NF90 (mean 71 ± 5%) was higher than with NF270 membrane (59 ± 5%). The exceptions to this pattern were aspartic (NF270 70 ± 5%; NF90: 53 ± 5%) and tannic acids (NF270 92 ± 5%; NF90: 62 ± 5%), where removal with NF270 was higher than with NF90. Under the experimental conditions used flux decline was not observed. Resorcinol was found to dissolve the surface of both membranes at the concentration of these tests and thus results for the compound are not included. Removal was affected by compound MW and hydrophobicity, with MW alone not being a good predictor of removal. These trends can be explained with reference to the membrane surface properties. While the two membranes have similar MWCOs (NF270: 150-430 Da; NF90 200-400 Da ; *23, 24*Nyström et al., 2004, Amy et al., 2005) the NF90 was classified as hydrophobic (contact angle 60°) with a higher surface charge (-25 mV at pH 7) than the more hydrophilic (contact angle 25°) NF270 membrane (-16 mV at pH 7.7). It is evident that the NF90 showed particularly improved removal of the hydrophilic, neutral species (average removal: 76%), over the NF270 membrane (average removal: 49%). Lower retention of more hydrophobic model compounds than more hydrophilic compounds was also found for three different NF membranes previously (*24, 25*). The increased retention of hydrophilic species was explained by their higher affinity for water due to hydrogen-bonding (*25*). The hydrophilic surrogates have log K_{OW} values ranging from -

1.52 to -3.89 (Table 5.1) which would appear to lead to a preference for the aqueous phase over the hydrophobic NF90 surface. For tannic acid the opposite applies, its highly hydrophobic log K_{OW} of 13.3 and affinity for the hydrophobic NF90 membrane surface leads to lower rejection relative to the NF270. It is expected that negatively charged solutes are rejected more effectively than similar neutral compounds by a negatively charged membrane due to electrostatic repulsion (*25*). However, tannic acid's lower removal with the NF90 indicates that for strongly-hydrophobic compounds non-electrostatic interactions can overwhelm coulombic repulsion. It is known that hydrophobic solutes can adsorb onto and partition into hydrophobic membranes, thus facilitating transport and giving lower rejections than expected by size exclusion alone (*26*). This is consistent with the retention of tannic acid, which is known to aggregate with proteins and polymers and has been described as "molecular glue" (*13*). Hydrophobic interactions were thought to be an important part of these associations. In summary while NF is effective at removing a range of NOM, membrane properties are important regarding preferential removal. If the intention is primarily to remove hydrophilic NOM then a hydrophobic membrane such as the NF90 should be used, whereas a hydrophilic membrane like the NF270 is more suitable for removal of hydrophobic molecules.

Again NF experiments were carried out without salt/s addition. It has been reported that the presence of divalent ions can lead to a decrease in rejection of negatively charged ions by a negatively charged membrane surface through shielding of the membrane surface charge. In a recent study on the rejection of pharmaceuticals by NF in the presence of 0 - 10 mM of Ca^{2+}, a small decrease in rejection for negatively charged solutes was observed with increased Ca^{2+}, while neutral solutes were unaffected (*26*).

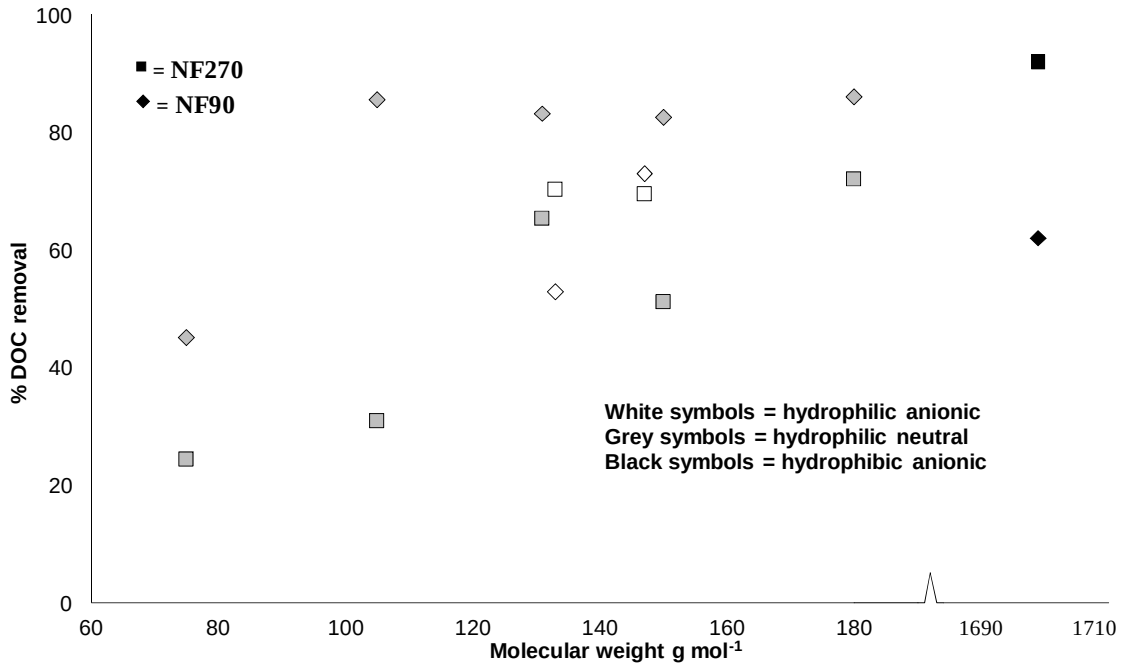


Figure 5.4: Treatment of NOM Surrogates by Nanofiltration

5.3.4 DBPFP

The hydrophobic neutral resorcinol had the highest THMFP, forming 1588 µg mgC^{-1} of $CHCl_3$ (Table 5.2), which compares well with a literature value of 1544 µg mgC^{-1} (*27*). The next highest $CHCl_3$ former was the hydrophilic anionic aspartic acid at 54 µg mgC^{-1}, with the remaining species all forming moderate to negligible amounts of $CHCl_3$ (0-23 µg mgC^{-1}). Aspartic acid was found to be the most important HAA precursor, with an HAAFP of 693 µg mgC^{-1}, with DCAA accounting for this entire total. Resorcinol was the next most reactive HAA precursor, though in contrast to aspartic acid, TCAA was the dominant HAA at 52 µg mgC^{-1}. The remaining surrogates had combined DCAA and TCAA formation potential between 0-3 µg mgC^{-1}. The high DCAA formation of aspartic acid has previously been noted as 387 µg mg C^{-1} (*28*). The

reactivity of aspartic acid is explained by the formation of a β-dicarbonyl intermediate upon chlorination (*29, 30*). Amino acid chlorination can lead to formation of either a nitrile or carbonyl product. For aspartic acid the latter pathway was thought to be dominant at pH 8 and leads to 3-oxopropanoic acid (*29*). The high DBPFP of several similar aliphatic β-dicarbonyl acid species has been reported (*30*), with β-keto acid structures in particular acting as DCAA precursors. Enolisation is thought to rapidly lead to chlorine substitution in these species. In contrast for remaining amino acids, including glutamic acid, while the same reaction route can occur it does not lead to formation of a β-dicarbonyl compound, thus explaining their low HAA and THM formation.

5.4 Discussion

It can be seen how model compound treatability (and hence that of NOM) was determined by compound physical properties. In the case of coagulation and MIEX® the degree of anionic charge was the key factor in removal. For NF retention can be explained by principally compound size, while hydrophobicity also affects transport through the membrane. However formation of DBPs cannot be predicted by the same physical properties. This is shown clearly by the case study of aspartic and glutamic acid. The two are amino acids and share similar chemical functionality, as well as pK_a values, MW and log K_{OW} (Table 5.1). They therefore behave very similarly when treated by coagulation and MIEX®, while the larger size of glutamic acid, mean removal 72% for both membranes, confers slightly better removal by NF than for aspartic acid, mean 62% (Figure 5.5). Concurrently aspartic acid had a DCAA formation potential (DCAAFP) of 693 µg mg C^{-1} , while for glutamic acid the value was 1 µg mg C^{-1} (Table

5.2). This discrepancy is due to subtle differences in the location of chemical groups (Table 5.1). The implications of this are that it is impracticable to selectively remove reactive DBP precursors (aspartic acid) over non-reactive precursors (glutamic acid). Furthermore, this issue is confused by a lack of knowledge about specific reactive DBP precursors in natural waters. Instead a pragmatic precursor removal strategy targeted at groups which, as defined by their treatability, are thought to contain the bulk of reactive DBP precursors is recommended. Empirical measurement of the effect of treatment options on DBPFP may derive this information. Where a high proportion of DBP precursors belong to the hydrophobic acid fraction, which is also highly charged and represented here by tannic acid, then optimised coagulation and/or MIEX® treatment may be sufficient to mitigate DBP levels. There are literature precedents of high precursor removal by coagulation in hydrophobic rich waters, for instance the maximum removals of 71% and 78% for THM and HAA precursors respectively (*5*). Hydrophilic anionic molecules of low charge, such as aspartic and glutamic acids were less treatable by coagulation and MIEX®, with up to ~30% and ~50% removal achievable respectively. However, optimised treatment may remove sufficient precursors to control DBP levels. Zeta potential was an effective control parameter for coagulation, with anionic surrogates behaving as natural waters and exhibiting maximum removal in the zeta potential window centred around zero. Literature suggests that MIEX® can offer improved treatment of transphilic acids compared with coagulation (*10*). It is inferred from our study that such compounds are likely to have multiple dissociated carboxylic acid groups. Anion exchange is therefore predicted to be a good process selection option for DBP control where highly charged carboxylic acids contain precursor material. In waters where the post-coagulation residual retains the

capacity for generation of high DBP levels then additional treatment may be required. This is most likely when hydrophobic neutrals like resorcinol or hydrophilic groups including amino acids and carbohydrates contain reactive DBP precursors. NF has been shown to be a successful process for removing a range of NOM and therefore also for DBP control. As well as operational issues such as membrane fouling, operating pressure and permeability, consideration should be given to membrane surface properties, with selection of a specific membrane possible with knowledge of target precursor groups and/or empirical testing. A hydrophobic NF membrane has been shown to be particularly effective for retention of hydrophilic species capable of hydrogen-bonding. A NF membrane with a hydrophilic surface is proposed to be more efficient where residual NOM has proportionately higher hydrophobic content.

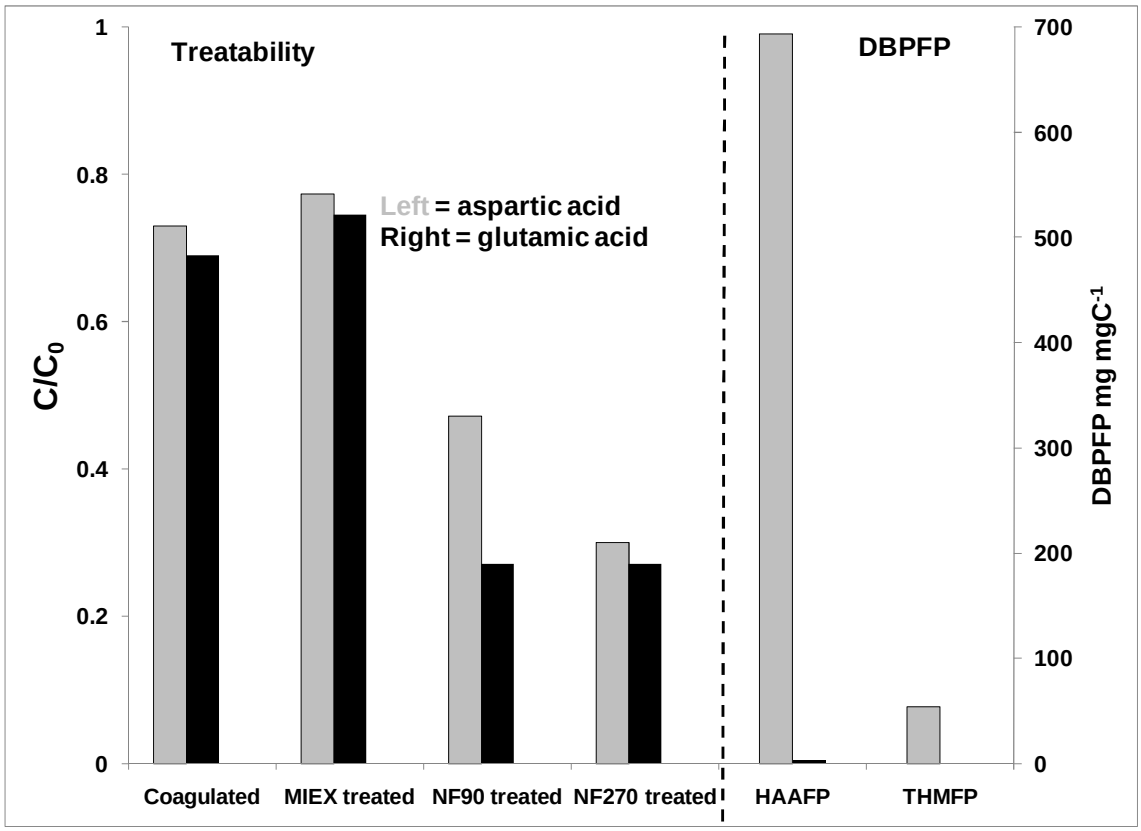


Figure 5.5: Comparison of treatability and DBPFP of aspartic and glutamic acids

5.5 Conclusions

1. Treatability of NOM surrogates was explained in terms of compound physicochemical properties, whereas DBP formation cannot be predicted using the same properties. Hence it was not possible to selectively remove reactive precursors.
2. Under conditions representative of full-scale operation MIEX® did not provide improved removal over coagulation. Any such improved performance is likely to arise from removal of polyprotic carboxylic acids.
3. Any secondary non-electrostatic removal mechanisms were not deemed operative for coagulation and MIEX®. Highly charged anionic species were successfully treated and neutral ones unaffected.
4. A hydrophobic nanofiltration membrane was particularly effective for treating neutral, hydrophilic compounds and is a suitable process option for DBP control where precursor material is of this character.

5.6 Acknowledgements

Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water are gratefully acknowledged for their financial support. Thanks also to Max Mergen, Remi Tournier and Antoine Redoute for help with the MIEX® experiments.

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CHAPTER 6: CHEMICAL AND BIOLOGICAL OXIDATION OF NOM SURROGATES AND EFFECT ON HAA FORMATION

CHEMICAL AND BIOLOGICAL OXIDATION OF NOM SURROGATES AND EFFECT ON HAA FORMATION

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6.1 Abstract

Formation of disinfection byproducts (DBPs) can be controlled by removal of disinfection byproduct precursors before disinfection. Variable success has been reported, depending on the treatment used and water tested. Chemical and biological oxidation are candidate technologies to control DBP formation. Given the uncertainty over the identity of DBP precursors, the use of surrogates of natural organic matter (NOM) allows fundamental probing of the links between compound character, removal and DBP formation. Nine compounds were chosen to represent NOM and their removal by two advanced oxidation processes (AOPs), UV-C irradiation and biological treatment compared while haloacetic acid (HAA) formation before and after treatment was measured. Although AOPs were able to fully remove all compounds, incomplete mineralisation led to increased HAA levels, dramatically in the case of two amino acids. Biological treatment was effective in removing amino acids but also moderately increased the HAA formation potential (HAAFP) of hydrophilic compounds. These findings indicate waters with high amino acid concentrations will be susceptible to

raised HAA levels following AOP treatment and careful process selection for HAA control is required in such cases.

Key Words HAAs, AOPs, biotreatment, NOM, treatability

6.2 Introduction

The link between organic matter in drinking water and formation of disinfection byproducts (DBPs) after chlorination was first made by Rook in 1974 (*1*). Since then there has been a steady accumulation of literature on the health risks and formation of DBPs and how to minimise their presence in drinking water. Two classes of DBPs, the trihalomethanes (THMs) and haloacetic acids (HAAs), are considered to be the dominant DBPs on a weight basis in potable water (*2*). It is established that many DBPs are mutagens, carcinogens or toxicants (*3*). Some species are regulated to limit their exposure to humans, for example limits set by the US Environmental Protection Agency are 80 µg/L for THMs and 60 µg/L for HAA_5; while the UK limit for THM_4 is 100 µg/L. It is anticipated that future regulations in the UK may become more stringent and include a wider range of DBPs, including the HAAs.

Natural organic matter (NOM) acts as a precursor to DBPs. NOM is a complex and variable mix of organic compounds of biological and terrestrial origin, with a catchment-specific composition. It is often split into hydrophobic and hydrophilic fractions. There is conflicting literature regarding which NOM types are predominant as precursors of THMs and HAAs. Some researchers report that hydrophilic/polar NOM is

more prevalent in the formation of HAAs than THMs (*4*), whereas others implicate hydrophobic/non-polar NOM (*5*). Knowledge of the identity of DBP precursors would allow the selection of appropriate process/es for their removal. As large, hydrophobic NOM is more amenable to removal by conventional treatments than small, hydrophilic NOM (*6*), where the latter has a higher HAA formation potential (HAAFP) than the former minimising HAA concentrations will be more difficult.

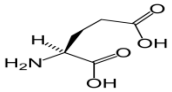
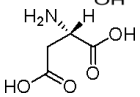
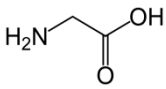
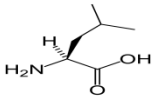
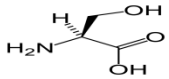
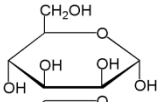
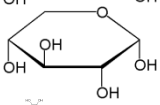
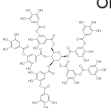
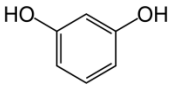
The advent of DBP regulations has motivated some water utilities to reduce chlorine doses or use alternative disinfectants in an attempt to reduce DBP levels (*7*). Of the other routes for controlling DBPs, removal of precursors before disinfection has received most attention (*7*). For example, the following reductions in HAAFP following treatment have been reported. Coagulation: 15-78% (*8*); biofiltration: -11-28% (*10*); nanofiltration: 67-97% (*10*) and advanced oxidation processes (AOPs): -74-74% (*9, 11*). Levels of removal vary widely, while biofiltration and AOPs can actually increase HAA formation. It follows that removal of DBP precursors depends on their susceptibility to different types of treatment.

While most treatments are selective for certain NOM groups, AOPs are comparatively non-discriminatory (*12*). NOM is oxidised through a complex series of reactions initiated by the hydroxyl radical (·OH). Since ·OH is a very powerful oxidant it reacts with a wide spectrum of NOM of both hydrophobic and hydrophilic character. Rate constants for reactions between ·OH and NOM have recently been directly measured at 1-5 x 10^8 M^{-1} s^{-1} (*13*), some three to four orders of magnitude higher than for other oxidants (*12*).

Since the precise identity of precursors in natural waters is largely unknown, the use of analogues is attractive as it enables the linking of explicit chemical and physical properties to treatability and formation of DBPs. The aim of this study was to compare HAA formation from nine NOM surrogates (Table 6.1) before and after treatment. The NOM surrogates were chosen from the NOM groups listed by Croué et al. (*14*), especially low molecular weight (MW) and hydrophilic NOM, which it was anticipated would be representative of a post-coagulation organic residual. Specifically, amino acids are important components of algae-rich waters (*15*). The surrogates have been classified as neutral or anionic at ambient pH based on their pK_a values and hydrophobic ($\log K_{OW}>0$) or hydrophilic ($\log K_{OW}<0$).

Two AOPs were used as treatments in comparison with UV-C oxidation and biological oxidation. The first AOP was UV/H_2O_2, where hydroxyl radicals are formed from the photolysis of H_2O_2 by UV light. The second was vacuum UV (VUV), where radiation at 185 nm is able to produce ·OH directly from water (*16*). UV-C photo-oxidation is initiated when photons are absorbed by NOM, leading to direct and/or indirect photo-transformation (*17*). The final treatment was biologically-active sand, where microbial degradation and adsorption are the principal removal mechanisms.

Table 6.1: Model compound properties

Compound	Structure	log K_{OW}	MW g/mol	pK_a, pK_b, pK_c	Classification	Chemical group	E (254 nm) cm^{-1} L mg C^{-1}
L-Glutamic acid		-3.69	147	2.16, 9.58, 4.15	Hydrophilic anionic	Amino acid	0.000
L-Aspartic acid		-3.89	133	1.95 9.66 3.71	Hydrophilic anionic	Amino acid	0.000
Glycine		-3.21	75	2.34, 9.58, NA	Hydrophilic neutral	Amino acid	0.000
L-Leucine		-1.52	131	2.32, 9.58, NA	Hydrophilic neutral	Amino acid	0.000
L-Serine		-3.07	105	2.13, 9.05 NA	Hydrophilic neutral	Amino acid	0.000
D-Mannose		-3.24	180	12.08, NA, NA	Hydrophilic neutral	Carbohydrate	0.000
D-Xylose		-1.98	150	12.14, NA, NA	Hydrophilic neutral	Carbohydrate	0.000
Tannic acid		13.3	1701	3.2, NA, 8.7	Hydrophobic anionic	Phenolic	0.045
Resorcinol		0.80	110	9.32, NA, 11.1	Hydrophobic neutral	Phenolic	0.006

6.3 Materials and Methods

Representative molecules (Table 6.1) were obtained from Fisher Scientific and Univar/Ajax Firechem at analytical purity or above.

UV-C, UV/H_2O_2 and VUV experiments were undertaken in the annular reactor detailed by Thomson et al. (*16*) and Buchanan et al. (*18*). The N-lamp used for UV-C and UV/H_2O_2 experiments emitted at 254 nm, while the H-lamp used for VUV experiments emitted at both 254 nm and 185 nm and produced ·OH from direct photolysis of water, without the need for chemical addition. Average fluence values of 12.95 mJ s^{-1} cm^{-2} for the N-lamp and 17.8 mJ s^{-1} cm^{-2} for the H-lamp were obtained by hydrogen peroxide and methanol actinometry (*19, 20*).

Dissolved organic carbon (DOC) was determined with a Sievers 820 TOC analyser. Initial concentration of representative molecules was 7.5 mg L^{-1} as compound. Mass extinction coefficients of 10 mg C L^{-1} solutions were measured with a Jenway 6505 spectrophotometer and Shimadzu TOC-5000 A analyser.

For the UV/H_2O_2 experiments H_2O_2 was added at 68 mg L^{-1} (2 mM). The concentration of hydrogen peroxide solution was determined by potassium permanganate titration, with potassium oxalate used to standardise the permanganate solution, as described by Harris (*21*).

The method of Joret and Levi (*22*) for biodegradable dissolved organic carbon (BDOC) was used to assess the susceptibility of samples to biological treatment. Duplicate samples were contacted with biologically-active sand for 7-10 days, with sodium acetate

as a positive control to verify biological activity. The sand sample came from the Yarra River, Victoria, Australia.

HAAFP of untreated and treated representative molecules was determined at the Australian Water Quality Centre, Adelaide, Australia, using gas chromatography with electron capture detection (GC-ECD). Treated samples were prepared so their DOC was approximately half the initial value, based on existing data. For the UV/H_2O_2 samples residual hydrogen peroxide was quenched with the enzyme catalase obtained from *Aspergillus niger*, at a dose of 60 µL L^{-1} (317 units L^{-1}) sample. The samples were shaken at 75 oscillations min^{-1} until visible gas generation ceased (5-6 hours). The chlorination period was 4 hours at 35°C and 7 HAAs were quantified: monobromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, monochloroacetic acid, dibromoacetic acid, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). Samples were quenched with ammonium chloride and quantified with USEPA method 552. For DCAA and TCAA, the major HAAs recorded, the limit of detection was 0.054 µg L^{-1}, the limit of reporting 1 µg L^{-1} and the precision of the method 3.4% and 3.5% relative standard deviations respectively.

The HAAFP of oxalic acid and L-aspartic acid were measured as a follow-up study at Cranfield University, UK by GC-ECD and an adapted version of USEPA Method 552.3. The chlorination period was 24 hours at 20°C±2°C with a chlorine dose 35 M/M of compound, duplicate samples were tested and all 9 HAAs were quantified: as above plus dibromochloroacetic acid and tribromoacetic acid

6.4 Results

6.4.1 Treatment comparison

Degradation of model compounds by the two AOPs occurred far more rapidly than by UV-C, with nearly complete removal possible for the majority of compounds after 50 J cm^{-2} irradiation (Figure 6.1). To illustrate mean DOC removal for the nine compounds after the application of 47-48 J cm^{-2} was 97%, 91% and 13%, for VUV, UV/H_2O_2 and UV-C respectively (Table 6.2). Corresponding levels at a lower dose of 21 J cm^{-2} were 58%, 78% and 6% respectively, indicating that UV-C has limited treatment capacity and differences exist between VUV and UV/H_2O_2. The removal by UV/H_2O_2 compares well with Goslan et al. (*23*), who reported DOC reduction of 78% for a reservoir water at a similar UV-C dose and identical H_2O_2 dose (UV-C 22 J cm^{-2}, H_2O_2 2 mM). The UV-C data are consistent with Thomson et al. (*24*), who reported a DOC reduction of 16% for a raw water at UV-C fluence of 26 J cm^{-2}, thus underlining the similar treatability of the surrogates compared with a natural water. Overall these results illustrate the two AOPs were approximately 8 times more effective than UV-C at removing these compounds at a fluence of 47-48 J cm^{-2}. Buchanan et al. (*25*) previously found VUV to be approximately 6 times more effective than UV-C in treating a raw water.

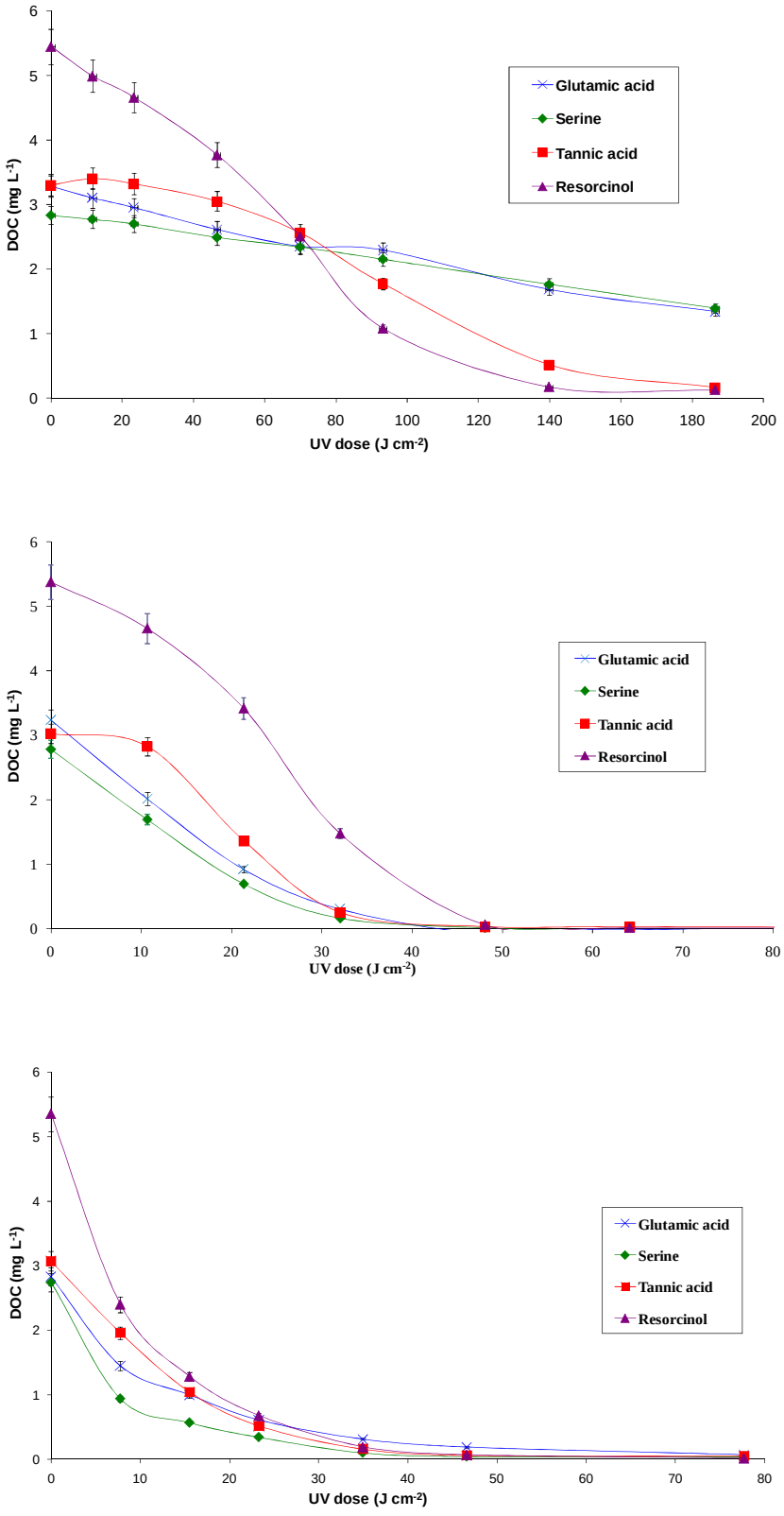


Figure 6.1 a, b, c: Degradation of selected model compounds by UV-C, VUV and UV/H_2O_2 (from top to bottom respectively).

Table 6.2: Results Summary

Compound	UV-C			VUV			UV/H_2O_2			Biodegradation
	% DOC loss		k^1	% DOC loss		k^2	% DOC loss		k^3	Max % DOC loss
	23 J cm^{-2}	186 J cm^{-2}		21 J cm^{-2}	48 J cm^{-2}		23 J cm^{-2}	47 J cm^{-2}		
L-Glutamic acid	10±5	59	0.0103	72 ± 5	102	0.0739	79±5	93	0.0576	80±3
L-Aspartic acid	11±5	61	0.0106	63 ± 5	96	0.0665	76±5	83	0.0352	N/A
Glycine	6±5	24	0.0032	47 ± 5	88	0.0425	28±5	55	0.0156	86±1
L-Leucine	4±5	31	0.0072	35 ± 5	88	0.0436	78±5	89	0.0446	87±1
L-Serine	5±5	51	0.0078	75 ± 5	99	0.1108	88±5	98	0.0871	91±0
D-Mannose	4±5	47		71 ± 5	99	0.1155	90±5	99	0.1092	56±10
D-Xylose	2±5	48		65 ± 5	98	0.094	92±5	100	0.1359	23±31
Tannic acid	-1±5	95		55 ± 5	99	0.1021	83±5	98	0.0884	5±6
Resorcinol	14±5	98		36 ± 5	99	0.0914	87±5	99	0.0941	38±2
Mean	6	57	0.0078	58	97	0.0802	78	91	0.0644	62

k^1: Zero-order rate constant, (0-186 J cm^{-2}), mg C L^{-1} min^{-1} or mg C L^{-1} J cm^{-2}. Only amino acids followed zero-order degradation behaviour
k^2: Initial first-order rate constant (0-48 J cm^{-2}), J^{-1} cm^2
k^3: Initial first-order rate constant (0-47 J cm^{-2}), J^{-1} cm^2

Removal by UV-C was linked to hydrophobicity. Tannic acid and resorcinol were the most treatable compounds, with DOC removals of 95±5% and 98±5% respectively after a dose of 186 J cm^{-2} (0.52 $kWhm^{-2}$), compared with removals of 24-59±5% for the other molecules (Table 6.2). This can be explained by the higher mass extinction coefficients of resorcinol and tannic acid: 0.006 and 0.045 cm^{-1} L mg C^{-1} respectively, compared with the other molecules, all 0.000 cm^{-1} L mg C^{-1}. It is interesting that those compounds with very limited capacity for UV-C absorption were still removed to a moderate extent, albeit at high UV-C doses. UV photo-oxidation can proceed from direct photo-transformation or indirect photo-transformation, where activated NOM can transfer energy to form excited photo-reactants such as oxygen, which in turn can react with NOM (*17*). This indicates even the hydrophilic compounds were able to absorb enough energy to initiate these types of reactions.

The biodegradability of samples as measured by removal by biologically-active sand in the BDOC test was grouped according to organic type, with the amino acids demonstrating high DOC reductions of 80-91% contrasting with 23-56% for the other

samples (Figure 6.2, Table 6.2). Similarly high removal of amino acids by biological activated carbon (BAC) has previously been reported by Jadas-Hécart (*26*), with an average removal of 70%. Supporting this view Hwang et al. (*4*) stated biodegradation is effective for removing non UV-absorbing low molecular weight acids. Given this information the aromatic character of tannic acid and resorcinol may explain their lower biodegradability; however the explanation for the two carbohydrates is less obvious. Charge does not seem to be a factor, since of the amino acids L-glutamic and L-aspartic acids were charged under ambient pH conditions (Table 6.2), instead different chemical functionality is a more likely reason. Nor does size correlate with biodegradability. It has been stated that small compounds are expected to be more biodegradable as they are more easily transported across the cell membrane (*27*), however in this study there was no such relationship, even for compounds of the same chemical type (Table 6.2).

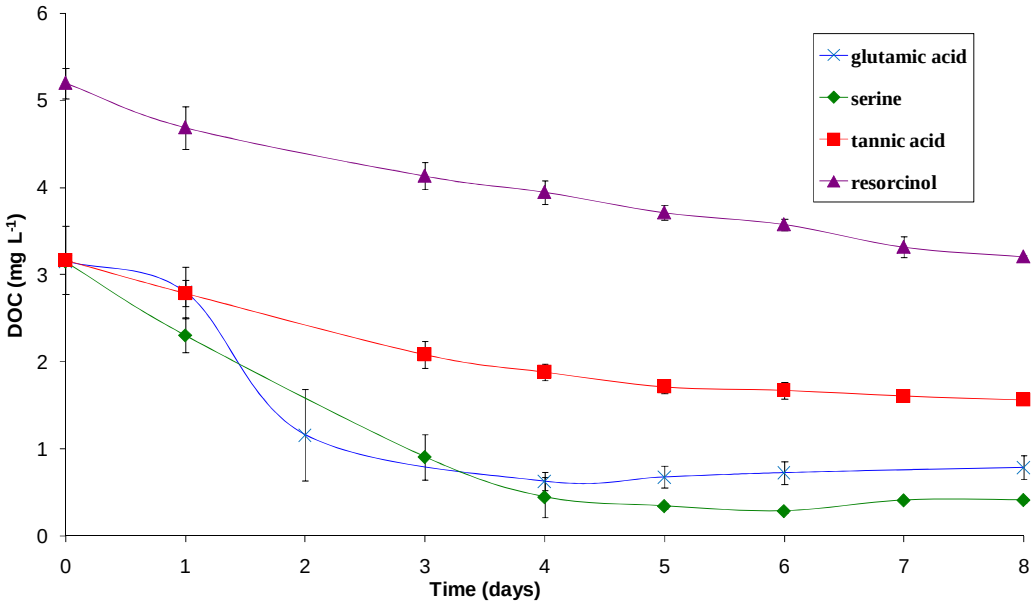


Figure 6.2: Biodegradation of selected model compounds

For the two AOPs there was no direct link between hydrophobicity and removal, which accords with Crittenden et al. (*12*) who reported AOPs were non-selective processes for removing a range of organic compounds. To illustrate, although the hydrophilic compound glycine was the slowest compound to degrade, as quantified by pseudo first-order rate constants, the hydrophobic tannic acid was also initially slow to be mineralised (0-11 J cm^{-2}), as evidenced by the convex shapes of its VUV degradation plot (Figure 6.1b and Table 6.2). It is possible the initially slow degradation of tannic acid by UV-C and VUV can be explained by its larger size, which means multiple reactions were necessary before mineralisation was attained.

After 48 J cm^{-2} of VUV irradiation, all compounds except for glycine and L-leucine, which both recorded DOC reduction of 88±5%, were degraded by over 90%. For the UV/H_2O_2 system three compounds had a DOC reduction of under 90% after 47 J cm^{-2} irradiation: L-aspartic acid in addition to L-leucine and glycine, the latter with the lowest removal of 55±5%. Kinetic analysis of the removal data revealed similar trends. Glycine was the slowest compound to degrade by VUV, with an initial pseudo first-order rate constant 0.043 J^{-1} cm^{-2}; compared with 0.044-0.116 J^{-1} cm^{-2} for the other compounds, and also by UV/H_2O_2: rate constants of 0.016 J^{-1} cm^{-2}, compared with 0.045-0.14 J^{-1} cm^{-2} respectively. The degradation of amino acids by AOPs has previously been studied in some detail by Le Lacheur and Glaze (*28*) who reported glycine to be less reactive than the other amino acids, as shown by its lower rate constant for the reaction with the hydroxyl radical of ~ 10^7 M^{-1} s^{-1} compared with serine at 3.2 x 10^8 M^{-1} s^{-1}. The first step in these reactions is H-abstraction alpha to the amino group, while reactivity is explained in terms of the stability of the radical intermediate thus formed. With the exception of glycine which forms a less stable secondary radical,

the other amino acids studied all form tertiary radicals. After 186 J cm^{-2} of UV-C exposure it was again glycine and L-leucine which were the most recalcitrant, with removals of 24±5% and 31±5% respectively. The similar ranking for the amino acid kinetic constants across the three UV-based systems, with glycine always the slowest to degrade, implies there may be common mechanistic pathways between UV-C and the AOPs, i.e., that the same or similar intermediates were formed. Since degradation by UV-C relies upon absorption of photons rather than reaction with ·OH, as is the case for AOPs, this is an interesting observation. Alternatively it may be that the slower degradation of glycine by UV-C was a result of its smaller size (Table 6.1).

6.4.2 HAA Formation

Tannic acid was the only compound to have significantly high HAAFP at 155 µg $mgDOC^{-1}$, with aspartic acid and resorcinol the next highest at 21 and 14 µg $mgDOC^{-1}$ respectively (Figure 6.3). In contrast, HAAFP of all other compounds was 0-1 µg $mgDOC^{-1}$. Resorcinol and tannic acid contain activated aromatic functionalities which react strongly with chlorine and can produce THM and HAAs (*7*).

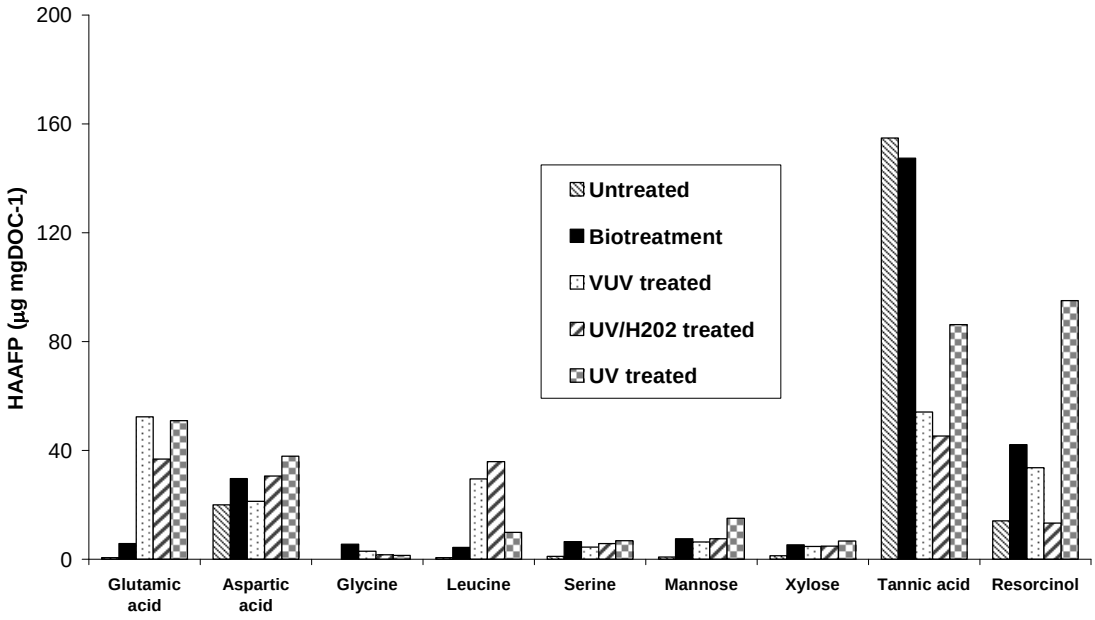


Figure 6.3: HAAFP of untreated and treated model compounds

Reckhow and Kim (*29*) found L-aspartic acid to be one of a small number of amino acids to produce high DBP levels, with DCAA formation of 387 µg $mgDOC^{-1}$. To investigate whether differences in chlorination time, between 4 h in this study and 48 h (*29*), could account for this discrepancy in HAA formation we measured the HAAs formed from L-aspartic acid after 1, 4 and 24 h chlorination. The respective values were 100±68, 82±2 and 671±30 µg $mgDOC^{-1}$, thus appearing to confirm that longer chlorination periods are necessary for L-aspartic acid to achieve maximum HAA formation. The high DCAA formation of L-aspartic acid was explained by Hureiki et al. (*30*), who proposed a mechanism where 3-oxopropanoic acid is the main intermediate resulting from chlorination. In turn 3-oxopropanoic acid is a β-keto acid structure similar to those reported as being high DBP formers by Dickenson et al. (*31*). The latter study proposes β-keto acid structures as possible slow-reacting DCAA precursors, where DCAA formation after 5 minutes is low relative to that after 24 h. Since it is

likely DCAA formation from L-aspartic acid will be slower still due to the extra steps required to form the β-keto acid intermediate, this supports the idea that higher DCAA yields require longer chlorination times.

The HAAFP of the hydrophilic compounds increases after treatment, especially by the UV based systems. Partial biodegradation increased the HAAFP of most of the representative molecules, although the increases were generally more modest. L-glutamic acid illustrates this most strikingly, from an untreated value of 1 µg $mgDOC^{-1}$ (Figure 6.3) the HAAFP rises by 5, 50, 52 and 36 µg $mgDOC^{-1}$ after biotreatment, UV-C VUV and UV/H_2O_2 respectively (Figure 6.4). Thus the UV-based systems all caused a sharp increase in HAAFP. This shift to enhanced HAA levels post-treatment has literature precedent. In their study using UV-H_2O_2 and/or biological activated carbon (BAC) to treat a raw surface water, Toor and Mohseni (*9*) found the AOP could increase DCAA formation potential (DCAAFP). UV/H_2O_2 treatment at UV fluence of 3000 mJ cm^{-2} and H_2O_2 concentration of 10-20 mg L^{-1} gave reductions in TCAA formation potential (TCAAFP) of 69% and THMFP of 73%, but DCAAFP increased by 74%. Note that all values were reported in µg L^{-1} rather than µg $mgDOC^{-1}$. BAC alone did not provide significant reduction in DCAAFP, TCAAFP or THMFP.

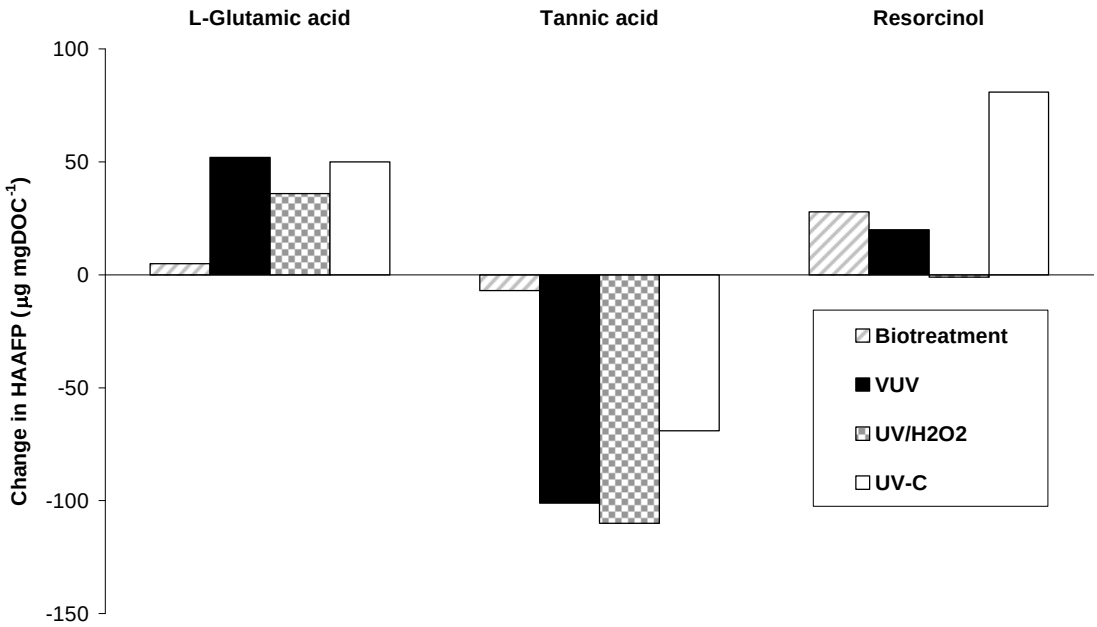
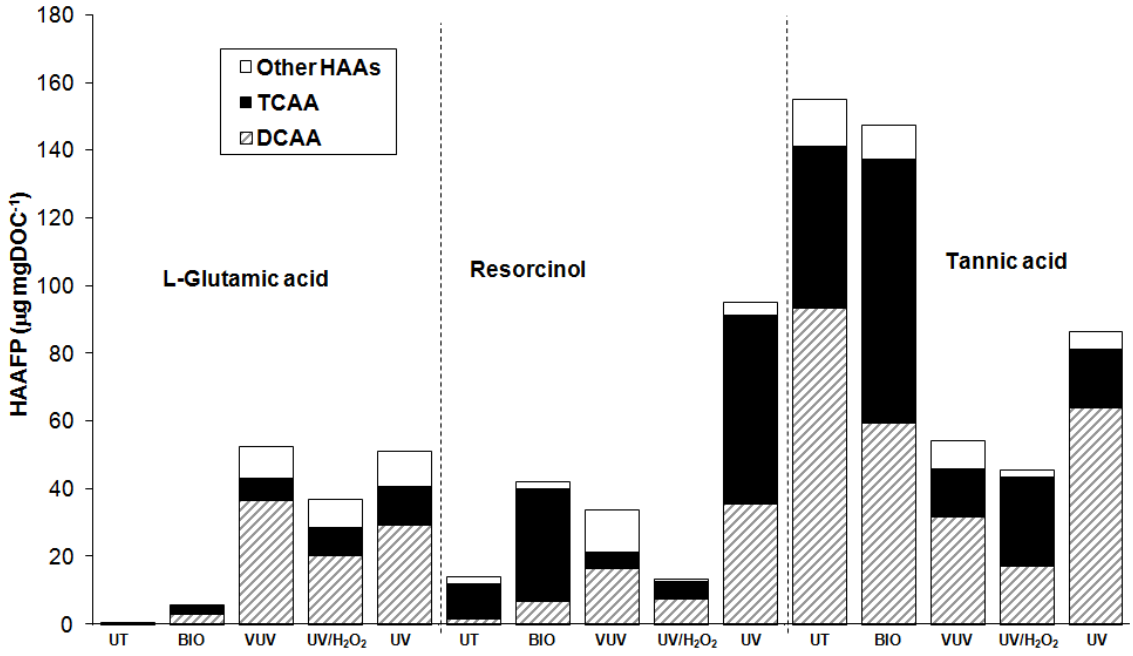


Figure 6.4: Effect of treatment on HAA formation of L-glutamic acid, resorcinol and tannic acid

For the two hydrophobic compounds the pattern was somewhat different compared with the hydrophilic compounds (Figures 6.3 and 6.4). Treatment of tannic acid caused its HAAFP to decrease from an untreated value of 155 µg mgDOC^{-1} (Figure 6.3) by 7, 69, 101 and 110 µg mgDOC^{-1} after biotreatment, UV-C, VUV and UV/H_2O_2, respectively (Figure 6.4). Thus for tannic acid AOPs caused the greatest fall in HAAFP. Resorcinol has an untreated HAAFP of 14 µg mgDOC^{-1} (Figure 6.3) which changes by 28, 81, 20 and -1 µg mgDOC^{-1} following biotreatment, UV-C VUV and UV/H_2O_2 respectively (Figure 6.4). Thus for resorcinol UV-C effected the greatest increase in HAAFP.

It has been established that DCAA and TCAA, which were the dominant HAAs in this study, have disjunct formation mechanisms (*32*). Therefore it is interesting to observe the differing effects that treatment had on formation of the two species. For the hydrophilic species DCAA was largely responsible for the increase in HAAs after

treatment. This was exemplified by L-glutamic acid (Figure 6.5). From an initial value of 1 µg mgDOC^{-1} DCAA rose to 3, 37, 20 and 29 µg mgDOC^{-1} following treatment by biodegradation, VUV, UV/H_2O_2 and UV-C, respectively. Again the behaviour of the hydrophobic molecules differs from that of the hydrophilics. For resorcinol TCAA was most common before treatment: total HAAs 14 µg mgDOC^{-1}, TCAA 10 µg mgDOC^{-1} and this dominance was maintained in the biotreated sample: total HAAs 42 µg mgDOC^{-1}, TCAA 33 µg mgDOC^{-1} and UV-C treated sample: total HAAs 95 µg mgDOC^{-1}, TCAA 56 µg mgDOC^{-1}, while in the VUV and UV/H_2O_2 treated samples DCAA was dominant: total HAAs 39 µg mgDOC^{-1}, DCAA 16 µg mgDOC^{-1} and total HAAs 13 µg mgDOC^{-1}, DCAA 7 µg mgDOC^{-1} respectively. For tannic acid DCAA was the commonest species in the untreated sample with significant amounts of DCAA and TCAA in all treated samples.



Note: UT = untreated; BIO = biodegradation

Figure 6.5: HAA speciation of untreated and treated L-glutamic acid, resorcinol and tannic acid

6.5 Discussion

A notable aspect of the results was the increase in HAAFP of the representative molecules following partial biological and chemical oxidation. In particular the untreated hydrophilic representative molecules did not form significant amounts of any HAAs, however AOP treatment increased their DCAAFP. This trend was most marked for two amino acids: L-glutamic acid and L-leucine. Since DCAA was the most problematic HAA species, effort is required to further elucidate the identity of DCAA precursors and confirm them as AOP products or intermediates. Meanwhile resorcinol, a known reactive THM precursor (*7*), behaved differently from the hydrophilic compounds by forming predominantly TCAA, both when untreated and after UV-C irradiation (Figure 6.5). There is a support for such a distinction in natural water studies: Liang and Singer (*5*) also found DCAA precursors to be less hydrophobic than TCAA precursors. Mechanistic studies have linked a rise in levels of DCAA to diketone and then aldehyde formation after oxidation (*32*). Conversely, and in agreement with the resorcinol data, TCAA formation has been likened to THM formation and may proceed through common intermediates (*33*). This information all points towards the idea that post-coagulation/hydrophilic waters can have the potential to form high levels of DCAA.

Model compounds with a known high DCAA formation are β-dicarbonyl acid species (*31*) and a small number of amino acids, notably aspartic acid and asparagine (*32*), both of which are probably oxidised to a β-dicarbonyl acid species (*30, 31*). Since both mechanistic studies and model compound work suggest β-dicarbonyl acid structures are

important in DCAA formation, it is tempting to implicate their formation through oxidation in the raised DCAA levels recorded.

Small acidic compounds are those most commonly identified as oxidation products of NOM. A range of products including mono and dibasic acids and keto acids were semi-quantitatively identified by Corin et al. (*17*) following UV irradiation of reference humic and fulvic acids and a surface water. Amongst these were β-dicarbonyl acids, including 3-hydroxypropanoic and 3-oxobutanoic acids, as well as other dicarbonyl acids of unspecified isomer. The reactions of the hydroxyl radical with glycine (*34*) and serine (*28*) have been previously studied. Both propose a reaction scheme where the initial step is hydrogen abstraction alpha to the amine group. For serine this yields mixed functional keto acids retaining the amino acid backbone, such as ketomalonic acid, 3-hydroxyoxopropanoic acid and dioxopropanoic acid. However, while these three-carbon species contain the β-keto acid moiety they also have a carbonyl group in the alpha position, and thus no hydrogen available for chlorine substitution as necessary in the mechanism of Reckhow and Singer (*32*). For glycine, which has a backbone of only two carbons, formation of β-keto acid species is not possible by this scheme. The observation that glycine only experienced minimal HAAFP increases after AOP treatment (Figure 6.3) supports the idea that β-keto acids are important. For serine the non-specific nature of radical reactions means three-carbon intermediates are unlikely to accumulate, while smaller and more inert products such as oxalic acid may do so (*28*). Oxalic acid was also tentatively identified as the major product of the glycine reaction scheme. To determine whether oxalic acid might be responsible for the enhanced HAAFP we measured its HAAFP and found it to be 0 μg mg DOC^{-1}. Thus oxalic acid was not responsible for the enhanced HAAFP reported here. More generally simple

monobasic acids cited as oxidation products of NOM do not contain functionalities thought to be reactive DBP precursors (*7*), which also indicates the involvement of other compounds. To summarise, while β-dicarbonyl acid species have been identified as UV products in natural waters, their occurrence as AOP products has still to be confirmed. Thus further work is needed to establish which compounds are key for enhanced DCAA formation and whether β-dicarbonyl acid species are involved.

In water where hydrophilic species contain a significant HAA generating capacity additional treatment may be key to controlling final HAA formation. The successful implementation of any treatment would depend on the specific composition of NOM present, and not solely on the reactive DBP precursors. Since AOPs were found to be capable of degrading both hydrophilic and hydrophobic surrogates, this makes them an attractive option for treatment of the post-coagulation residual, which is largely hydrophilic (*35*). However, based on these results AOPs carry the risk of increased HAAs, which would need to be investigated in the relevant water under varying AOP doses. It can be inferred this risk will be greater in waters with high concentration of hydrophilic species and especially amino acids. Such waters may well have a high proportion of algal organic matter (AOM) and/or a wastewater influence. Algae are known as an important source of amino acids, and it has been recorded that the protein concentration of different lake waters rose from an average of 0.1-1 mg L^{-1} during an algal bloom (*15*). Caution is advised in such cases. Using AOPs in combination with biotreatment may reduce the risk of increased DCAA. Toor and Mohseni (*9*) reported a DCAAFP reduction of 63% from combined UV/H_2O_2 and BAC treatment, contrasting with an increase of 74% for UV/H_2O_2 alone. Such a combination is analogous to the

combination of ozone-biological activated carbon, where ozone is used to generate a higher proportion of biodegradable material for removal by the BAC.

In hydrophilic-rich waters biotreatment alone is also a viable process option and has been found to be effective for amino acid removal. Since increases in HAAFP of biologically treated samples were generally less than those caused by UV based oxidation, the risk of raised HAA levels in natural waters is less. However the biologically available DOC content of untreated natural waters is typically only around 15% (*25, 36*), while amino acids only comprise up to 5% of the DOC of raw surface waters (*37*). Therefore biotreatment is only likely to reduce DBP formation in cases where highly reactive precursors belong to a readily biodegradable group such as the amino acids and/or pre-treatment has increased the bioavailable content.

The necessity of a high energy input makes UV-C treatment inefficient and expensive for DOC removal at a larger scale. This is especially true where NOM has a low UV-absorbing capacity, as the hydrophilic compounds studied here. Typical UV disinfection practice is 40 mJ cm^{-2} (*16*) so the maximum mineralisation observed here (at 186 J cm^{-2}) would not occur during microbial disinfection. Interestingly, these results indicate that exposure of natural water to sunlight (and UV-C), which can involve high energy levels, has the potential to alter the composition of DBP precursors. For example UV-C irradiation of resorcinol can increase levels of TCAA. This idea is given credence by Chow et al. (*38*), who studied the impact of simulated sunlight on DBPs. Irradiation of raw waters for 1403 and 5612 J cm^{-2} at 300-800 nm were equivalent to 1 and 4 days of clear summer weather respectively. Under these conditions HAAFP decreased by up to 50%.

6.6 Conclusions

(1) AOP treatment of L-glutamic acid and L-leucine leads to dramatically increased amounts of HAAs, specifically DCAA

(2) Biological treatment is particularly effective at removing amino acids but can also increase HAA formation of hydrophilic compounds

(3) UV-C irradiation also has the potential to increase the HAAFP of NOM surrogates

(4) Investigation is recommended before AOPs are implemented for HAA control in waters with relatively high amino acid concentrations

6.7 Acknowledgements

Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water are all gratefully acknowledged for their financial support of this project.

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CHAPTER 7: GRANULAR ACTIVATED CARBON FOR THE TREATMENT OF DISINFECTION BYPRODUCT PRECURSORS

GRANULAR ACTIVATED CARBON FOR THE TREATMENT OF DISINFECTION BYPRODUCT PRECURSORS

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7.1 Abstract

Disinfection byproducts (DBPs), the major groups of which are believed to be trihalomethanes (THMs) and haloacetic acids (HAAs), are formed through reactions between chlorine and both hydrophobic and hydrophilic natural organic matter (NOM). Activated carbon (AC) is a promising technology for DBP control though precursor removal, though there is a need to better understand selectivity of NOM adsorption by AC. Our objectives were to compare adsorption behaviour of NOM surrogates with drinking waters using isotherm methodology, and further to quantify DBP precursor removal in the drinking waters using rapid small-scale column tests (RSSCTs). It was found that for molecules smaller than the AC pore size, physicochemical interactions rather than size exclusion controlled uptake, with a phenolic molecule being the most adsorbable. Carbohydrates and amino acids were less adsorbable. The surrogates' log K_{OC} values were found to correlate well with modified Freundlich adsorption parameters. Two natural treated waters exhibited adsorbability intermediate between hydrophobic and hydrophilic surrogates, and in both HAA precursors were more adsorbable than THM precursors and bulk NOM. This can be explained by HAA precursors being on average more hydrophobic and/or of lower molecular weight than

bulk NOM. In similar waters, AC is a suitable process option for HAA precursor removal in particular.

Key Words haloacetic acids; trihalomethanes; natural organic matter

7.2 Introduction

Chlorine is the most commonly used disinfectant in potable water production (*1*). While disinfection is necessary to prevent dissemination of waterborne disease, a significant associated drawback is the creation of disinfection byproducts (DBPs), through reactions with natural organic matter (NOM). Many DBPs are considered to present a health risk to humans (*2*). Two groups – the trihalomethanes (THMs) and haloacetic acids (HAAs) – are regulated in the USA (THMs 80 µg L^{-1}, HAA_5 60 µg L^{-1}), while THMs are also regulated in the UK at 100 µg L^{-1}. One of the most promising processes investigated for removal of NOM, including DBP precursors, is activated carbon (AC) (*3*), which can applied in powdered (PAC) or granular (GAC) form. While PAC can be added at various stages of water treatment, GAC is typically introduced as a deep bed after coagulation/clarification/filtration but prior to post-disinfection (*4*). It can be designed to remove specific contaminants such as pesticides, as well as taste and odour causing compounds and bulk NOM. Since the post-coagulation residual is primarily comprised of hydrophilic material (*5*), of interest is how the relative concentration of hydrophobic and hydrophilic NOM affects the efficacy of GAC for precursor removal. While hydrophobic species are often implicated in DBP formation (*6*), it may be the less treatable hydrophilic species which determine final DBP formation (*7*). Model

compounds have found widespread use in DBP studies (*8*), though corresponding deployment to determine treatability of a spectrum of NOM is more limited.

Adsorption of NOM and NOM surrogates has previously been modelled using Freundlich methodology (*9, 10*). In the modified Freundlich equation, equilibrium concentration is normalised against adsorbent dose:

$$q_e = K_F (C_e/D)^n \quad \text{or} \quad \log q_e = \log K_F + n\log(C_e/D) \tag{1}$$

where q_e is amount adsorbed per g of carbon (mg g^{-1}), C_e is the aqueous phase concentration of substance at equilibrium (mg L^{-1}) and D is the carbon dose (g L^{-1}). K_F is the Freundlich adsorption coefficient which represents the adsorption capacity when C_e/D is equal to unity, while n relates to the magnitude of the adsorption driving force (*11*). Modified Freundlich isotherms allow comparison between tests with differing experimental conditions, and also account for the polydispersity of mixtures.

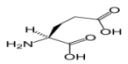
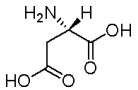
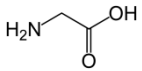
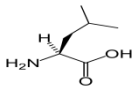
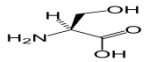
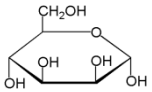
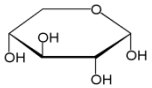
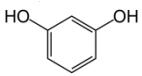
While equilibrium studies are of limited value in predicting full-scale performance, rapid small-scale column tests (RSSCTs) can be used to simulate full-scale adsorber performance. They have been shown to accurately reproduce breakthrough curves and removal of target organics (*12*). Depending on the characteristics of the target contaminants two different design equations can be used:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{R_{SC}}{R_{LC}}\right)^{2-x} = \frac{t_{SC}}{t_{LC}} \tag{2}$$

where the subscripts SC and LC represent small column and large column respectively, EBCT is empty bed contact time, R is GAC particle radius and t is operation time. The first design approach is when x = 0 and constant diffusivity is assumed (CD-RSSCT), the second proportional diffusivity, when x = 1 (PD-RSSCT). There is no clear consensus about when to use PD or CD design. To illustrate Matsui et al., (*13*) showed CD successfully predicted removal of humic substances, and Summers et al., (*14*) reported PD successfully predicted pilot column dissolved organic carbon (DOC) breakthrough.

Our objectives were to assess how the physicochemical properties and composition of NOM influence sorption, and the effect on DBP precursor treatment. This approach entailed complementary use of isotherm studies, RSSCTs, drinking waters and model compounds. Initially equilibrium studies were undertaken using NOM surrogates, which in contrast to natural waters have well-defined physicochemical properties (Table 7.1), with the intention of linking compound property to sorption behaviour. Results were compared against two well-characterised drinking waters. RSSCTs with the drinking waters were undertaken with the intention of assessing how NOM composition affects precursor removal over the carbon bed-life.

Table 7.1: Properties of NOM Surrogates

Compound	Structure	Main fraction	Chemical group	log K_{OW}	log K_{OC}	MW	MV	M radius	pK_a pK_b pK_c	IoR	MR	γ	PSA	α	ρ
						g mol^{-1}	cm^3	Å			cm^3	dyne cm^{-1}	A^2	10^{-24} cm^3	g cm^{-3}
L-Glutamic acid		HPI	Amino acid	-3.69	1.16	147	104.3	3.5	2.16 9.58 4.15	1.522	31.83	69	56	12.62	1.409
L-Aspartic acid		HPI	Amino acid	-3.89	0.894	133	87.8	3.3	1.95 9.66 3.71	1.531	27.2	78	56	10.78	1.514
Glycine		HPI	Amino acid	-3.21	0	75	59.8	2.9	2.34 9.58 NA	1.46	16.41	54	26	6.5	1.254
L-Leucine		HPI	Amino acid	-1.52	0.894	131	126.6	3.7	2.32 9.58 NA	1.462	34.86	39	30	13.82	1.035
L-Serine		HPI	Amino acid	-3.07	0	105	74.2	3.1	2.13 9.05 NA	1.519	22.54	72	39	8.93	1.415
D-Mannose		HPI	Carbohydrate	-3.24	1	180	113.9	3.6	12.08 NA NA	1.573	37.54	92	63	14.88	1.581
D-Xylose		HPI	Carbohydrate	-2.39	1	150	85.4	3.2	12.14 NA NA	1.646	31.02	75	46	12.29	1.757
Tannic acid		HPOA	Phenolic	13.3	n.a.	1701	799	6.8	3.2 NA 8.7	1.927	379.6	203	503	150.48	2.12
Resorcinol		HPOA	Phenolic	0.80	2.638	110	86.2	3.2	9.32 NA 11.1	1.612	30.01	57	18	11.89	1.275

7.3 Materials and Methods

7.3.1 Materials

NOM surrogates (Sigma Aldrich, UK) belong to key NOM chemical groups listed by Croué et al., (*6*). The following properties were collated: log K_{OW} (partitioning in octanol/water), log K_{OC} (partitioning in soil/water), molecular weight (MW), molecular volume (MV), molecular radius (M radius, calculated from molecular volume assuming spherical shape), pKa, index of refraction (IoR), molar refractivity (MR), surface tension (γ), polar surface area (PSA), polarisability (α) and density (ρ). Properties were taken from USEPA (*15*), Chemspider (*16*) and Simon et al., (*17*). Experimental values were used wherever possible. log K_{OC} values were estimated (*15*) using two different models. Relationships between physicochemical properties and adsorption parameters were examined using the Pearson product-moment correlation coefficient (r), calculated with Minitab 15™. The activated carbon was F400 (Chemviron Carbon, UK), commonly used in water treatment. The two waters tested (upland and lowland) were taken from their respective water treatments works (WTWs) prior to chlorination but post-treatment. Concentration of surrogates and waters was determined with a Shimadzu 5000A TOC analyser (Milton Keynes, UK).

7.3.2 Isotherm Tests

Powdered carbon was passed between 32 and 106 µm sieves, washed thoroughly in ultrapure water and dried overnight at 110 °C before use. Isotherms were obtained using a bottle-point method with capped 250 mL conical flasks. Model compound solutions were at 10 mg L^{-1} C (theoretical values) in deionised water. A blank and eight different carbon doses between 0.15-50 g L^{-1} were tested depending on the sample. pH of samples was between 6.3-7.0. Samples were placed in an orbital shaker at 200 rpm and

25 ±2°C for 24 h. This time was chosen after preliminary investigation showed it sufficient to reach equilibrium. Before analysis samples were filtered (0.2 µm).

7.3.3 Column Tests

Because both waters were already treated their NOM concentration was relatively low, and since coagulation typically removes high MW organics, the CD approach suitable for low MW organics was chosen (*12*). Experiments were designed based on a full-scale EBCT of 20 minutes, similar to that used previously for DBP precursor removal (*4*). Carbon was prepared in a similar manner to the isotherm tests, though with a particle size of 106-500 µm. Column tests were undertaken in a 1 cm x 50 cm glass chromatography column (Kinesis, Cambridgeshire, UK), giving a column diameter: particle size ratio of over 25 to avoid channelling effects (*18*). Carbon was heated in boiling water for 10 mins to exclude air before use. Ultraviolet (UV) absorption was measured with a Jenway 6505 spectrophotometer (Essex, UK). Duplicate DBP samples were buffered at pH 7 with phosphate buffer and chlorinated for 24 h at 20 ±2°C with chlorine dose 5 mg mgC^{-1}. THMs were extracted according to USEPA Method 551.1 and HAAs by an adapted version of USEPA Method 552.3 (*19*). DBPs were recorded on a gas chromatograph with a micro electron capture detector (Agilent 6890 GC-µECD (Agilent, West Lothian, UK)).

7.3.4 Characterisation

Surrogates (theoretical concentration: 10 mg C L^{-1}) were fractionated at pH 2 with Amberlite XAD-7HP then XAD-4 (Rohm and Haas, Germany) columns. Columns were back-eluted with NaOH (0.1 M). The portions desorbed from the XAD-7HP and XAD-4 columns are termed hydrophobic acids (HPOA) and transphilic acids (TPHA) respectively, non-absorbed material is classified as hydrophilic (HPI).

Charge density was measured by recording the point of zero charge effected by polydiallyldimethylammonium chloride (polyDADMAC, Sigma Aldrich, UK) addition with a Zetasizer 2000HSA (Malvern Instruments, UK).

Drinking waters were fractionated using Amberlite XAD-7HP then XAD-4 (Rohm and Haas, USA) columns followed by Amberlite 200 strongly acidic cation exchanger (DOWEX, Dow Chemical Co., USA). The hydrophobic neutral (HPON) fraction was that desorbed from the XAD-7HP resin with $CH_3CN:H_2O$ (3:1). After acidification to pH 2 the HPOA, transphilic (TPI) and HPIB fractions were those desorbed from the XAD-7HP, XAD-4 and cation exchange resins respectively with $CH_3CN:H_2O$ (3:1) (HPOA and TPI) and 3 molar NH_4OH (HPIB). The HPI fraction was that not retained by any column. Fractionation was undertaken with water sampled at the same point and season 2 years previously, with data presented for comparison purposes only. Inclusion is considered appropriate due to the similar bulk parameters (DOC and specific UV absorbance (SUVA)) between the sampling dates, and the observation that since coagulation preferentially removes hydrophobic material (*5*) fractional variation in treated waters is small compared to raw waters.

7.4 Results

7.4.1 Characterisation

THM formation potentials (THMFPs) were 70 µg L^{-1} and 94 µg L^{-1}, and HAA formation potentials (HAAFPs) 56 µg L^{-1} and 78 µg L^{-1} in the lowland and upland water respectively. (Figure 7.1). Associated charge density values were .0003 and .0001 meq mgC^{-1} for the lowland and upland water respectively, equivalent to values of <0.06 meq

mgC^{-1} reported for raw water HPI (5), and consistent with filtered water post-coagulation.

Although from contrasting sources, both waters were sampled post-treatment but pre-disinfection and had proportionately similar amounts of hydrophobic moieties: 25% and 23% for total HPOA and HPON in the lowland and upland water respectively. The lowland water had a relatively higher proportion of TPI at 31% and lower proportion of HPI at 40%. In the upland water respective values were 8% and 67%. Fractionation of surrogates demonstrated both tannic acid and resorcinol behaved as HPOA, with over 90% recovery from the XAD-8 resin. The remaining surrogates were all operationally defined as HPI, with 81-93% recovery in that fraction.

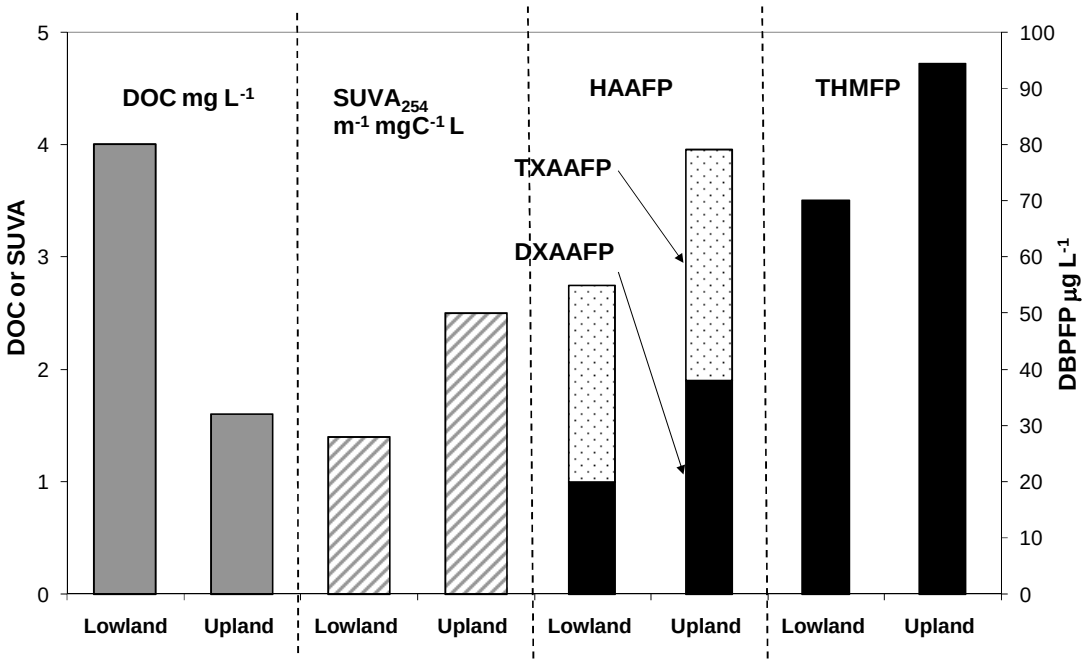


Figure 7.1: Characterisation of two drinking waters

7.4.2 Isotherm Tests

Comparison of the surrogates' isotherms revealed that the hydrophobic compounds were more adsorbable than the hydrophilic compounds (Figure 7.2, Table 7.2). Resorcinol was the most adsorbable compound as measured by modified Freundlich parameters, with both K_F ((mg/g)(g/mg)^n) and n (dimensionless) higher than the other samples at 7.11 and 0.94 respectively (Figure 7.2, Table 7.2). The lowland and upland water had the next highest capacity parameters (K_F) at 5.67 and 5.26 respectively, followed by tannic acid at 4.59. Lowest K_F values were exhibited by the 2 smaller amino acids - serine and glycine - at 0.29 and 0.33 respectively. Overall the capacity of the carbon for the different samples took the following order: resorcinol > lowland water > upland water > tannic acid > large amino acids > carbohydrates > small amino acids. The ordering of the intensity parameter (n) was similar, with the main exception that tannic acid had the second highest n value at 0.89. Thus ranking was as follows: resorcinol > tannic acid > upland water > lowland water > large amino acids > carbohydrates > small amino acids. These data compare well with modified Freundlich parameters obtained for 5 humic acids and 2 fulvic acids, where K_F values ranged from 1.83 – 8.76 and n values from 0.25 – 0.48 (*20*). The 2 natural waters had adsorbability intermediate between that of the hydrophobic and hydrophilic surrogates, which is consistent with them being a multicomponent mixture of such compounds. Traube's rule states adsorbability increases with size for a series of homologous organic compounds, in line with increasing polarisability. Theoretically large, hydrophobic molecules are more adsorbable than small, hydrophilic molecules. However, this pattern is obscured by electrostatics and size exclusion, which have been considered the main interactions controlling adsorption of NOM to AC (*3*). In water treatment coulombic

repulsion between anionic solutes and acidic groups on the carbon surface are the most relevant electrostatic interactions, while depending on the carbon pore-size larger molecules can be size-excluded. The presented results can be rationalised in terms of molecular properties, taking into account these interactions, noting that molecular radii of surrogates were 2.9 – 6.8 Å (Table 7.1), and below average F400 pore size (12 Å, (*9*)). Resorcinol is neutral and relatively small (MW = 110 g mol^{-1}) and hydrophobic (log K_{OW} = 0.8) (Table 7.1), which confers high adsorbability. In comparison tannic acid is larger (MW = 1701 g mol^{-1}) and more hydrophobic (log K_{OW} = 13.3) and has multiple anionic charge at ambient pH (*17*). Given that NOM molecules can assume varying conformations the molecular radii (Table 7.1) are an approximation, though indicate tannic acid (6.8 Å) approaches the average pore radius of the carbon, thus size exclusion effects could operate in addition to coulombic repulsion. Its high hydrophobicity is a plausible explanation for its relatively high intensity parameter. The upland water had a higher intensity parameter and lower capacity parameter relative to the lowland water. With a similar rationale to above it is hypothesised that the upland water contained proportionately more high-MW, hydrophobic NOM structures than the lowland water. This is suggested by the higher $SUVA_{254}$ of the upland water, since MW and aromaticity have been reported be directly proportional to $SUVA_{254}$ (*21*). Low K_F and n (0.094 and 0.12 respectively) values for glycine and serine compared with the other hydrophilic surrogates are linked to their smaller size, and are expected if adsorbability increases with molecular size for species able to access the majority of sorbent pores. Overall these results show that for compounds smaller than the carbon pore size, it is physicochemical interactions rather than size exclusion that drive

adsorption, and under such conditions hydrophobic compounds are more adsorbable than hydrophilic.

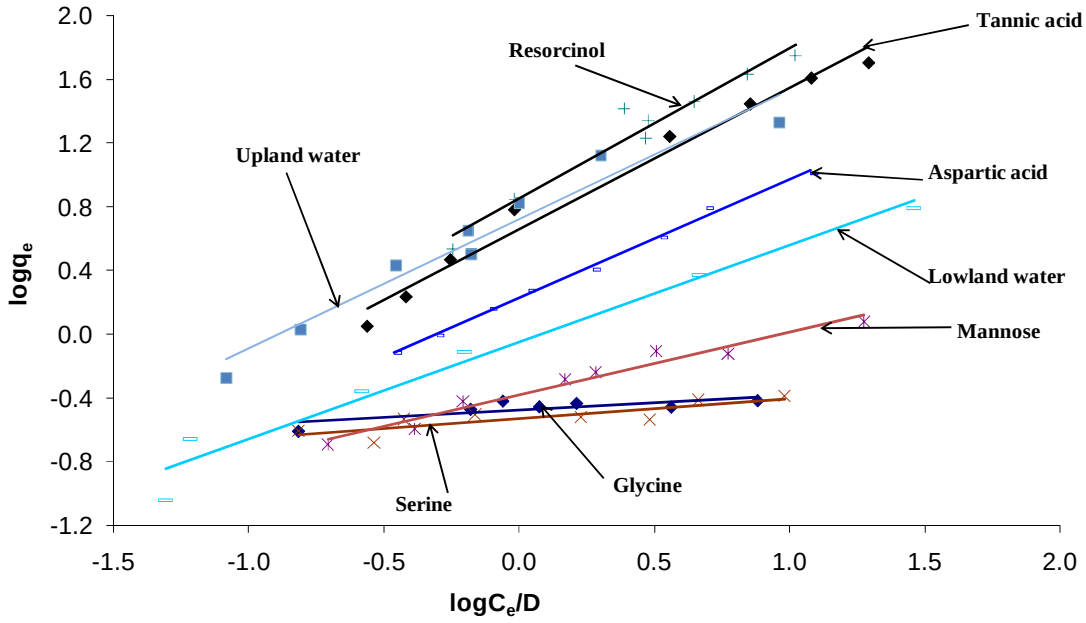


Figure 7.2: Selected modified Freundlich isotherms for NOM surrogates and 2 natural waters

Table 7.2: Modified Freundlich adsorption parameters

Sample	K_F	n	R^2
	(mg/g)(g/mg)^n	dimensionless	
Resorcinol	7.11	0.94	0.95
Lowland water	5.67	0.59	0.95
Upland water	5.26	0.81	0.95
Tannic acid	4.59	0.89	0.98
Glutamic acid	2.18	0.70	0.99
Leucine	2.11	0.67	0.98
Aspartic acid	1.69	0.75	1.00
Mannose	0.41	0.40	0.96
Xylose	0.37	0.34	0.95
Glycine	0.33	0.094	0.62
Serine	0.29	0.12	0.71

7.4.3 Correlations between Physicochemical Properties and Adsorption Parameters

Strong relationships were observed between estimated K_{OC} values and Freundlich adsorption parameters, particularly notable being the correlations between K_F and K_{OC}; log K_F and log K_{OC} and n and log K_{OC}, which had r = 0.939, 0.89 and 0.842 respectively (Table 7.3). The relationship between log K_{OC} and log K_F was represented by a straight line of equation $y = 0.51x - 0.49$. Consequently K_{OC} can be used to predict Freundlich parameters for NOM structures in lieu of isotherm tests. Previously it has also been noted that log K_{OC} correlates reasonably well to log K_{OW} (*11*). Other than those involving K_{OC}, the correlation between K_F and log K_{OW} was the strongest identified, with r = 0.58. This association stems from the higher adsorbability of operationally-defined HPOA surrogates relative to the hydrophilic. Further, it indicates that of a heterogeneous mix of sorbates, as found in aqueous environments, where carbon pore size is not limiting, hydrophobic sorbates will be adsorbed preferentially. Of properties pertaining to molecular size, molecular radius showed the highest correlation with Freundlich parameters, with r = 0.487 for relationship with log K_F. Similarly the correlation between log K_F and polarisability was 0.44. These data highlight that while molecular size, charge and polarisability all influence sorption, correlations between these properties and Freundlich parameters were weak or absent. Rather than being readily predicted by any single compound property, adsorption is a complex process influenced by multiple variables.

Table 7.3: Correlations between Freundlich adsorption parameters and compound physical properties

	K_F	n	1/n	log K_{OW}	K_{OC}	log K_{OC}	MW	MV	M radius	pk_{a1}	IoR	MR	γ	PSA	α
	$(mg/g)(g/mg)^n$						g mol^{-1}	cm^3	Å			cm^3	dyne cm^{-1}	A^2	
log K_F	0.913	0.963	-0.721	0.55	0.692	**0.814**	0.423	0.45	0.487	-0.18	0.413	0.44	0.282	0.395	0.44
K_F		0.835	-0.547	0.58	**0.939**	**0.89**	0.387	0.403	0.413	0.025	0.47	0.405	0.266	0.348	0.405
n			-0.868	0.508	0.594	**0.842**	0.42	0.444	0.498	-0.043	0.456	0.433	0.329	0.4	0.433
1/n				-0.311	-0.318	-0.746	-0.282	-0.304	-0.393	-0.248	-0.401	-0.288	-0.265	-0.273	-0.289

7.4.4 Column Tests: Removal of DBP Precursors

For both waters preferential removal of DBP precursors was observed. For the lowland water removal ranges of DOC were from 0-60% and of UV_{254} absorbing material from 23-89%. Removal of THM, dihaloacetic acid (DXAA) and trihaloacetic acid (TXAA) precursors were higher at 8-83%, 25-90% and 41-88% respectively (Figure 7.3). For the upland water DOC removal ranged from 0-77%, UV_{254} from 9-95%, DXAA formation potential (DXAAFP) from 30-89%, and TXAA formation potential (TXAAFP) from 31-97%. Again THMFP removal was lower than the other DBP precursors at 2-57% (Figure 7.4). As the lowland water RSSCT progressed the order of preferential removal became: TXAA precursors > DXAA precursors >UV_{254} > THM precursors > DOC. At the end of the tests, even when the column was exhausted with respect to DOC, some removal of DBP precursors was achieved (Figure 7.3). Such a phenomenon reflects dynamic equilibria between aqueous-phase precursors and adsorbed NOM with lower carbon affinity. These results are consistent with the preferential removal of HAA precursors observed by Jacangelo et al., (*4*), who found after 6 months' operation at full-scale GAC removed 55% of DOC, 60% of THM precursors and over 80% of HAA precursors. While TXAAFP was preferentially removed over other parameters in the lowland water, DXAAFP and TXAAFP behaved similarly in the upland water. The RSSCT with the upland water took over 3 times longer to reach DOC breakthrough than the lowland water, at 17.95 days compared with 5.31 days. The influent concentration of the upland water was 1.6 mg L^{-1}, compared with 4.0 mg L^{-1} in the lowland water (Figure 7.1), which is the major reason for this disparity, especially since the two waters had comparable capacity factors.

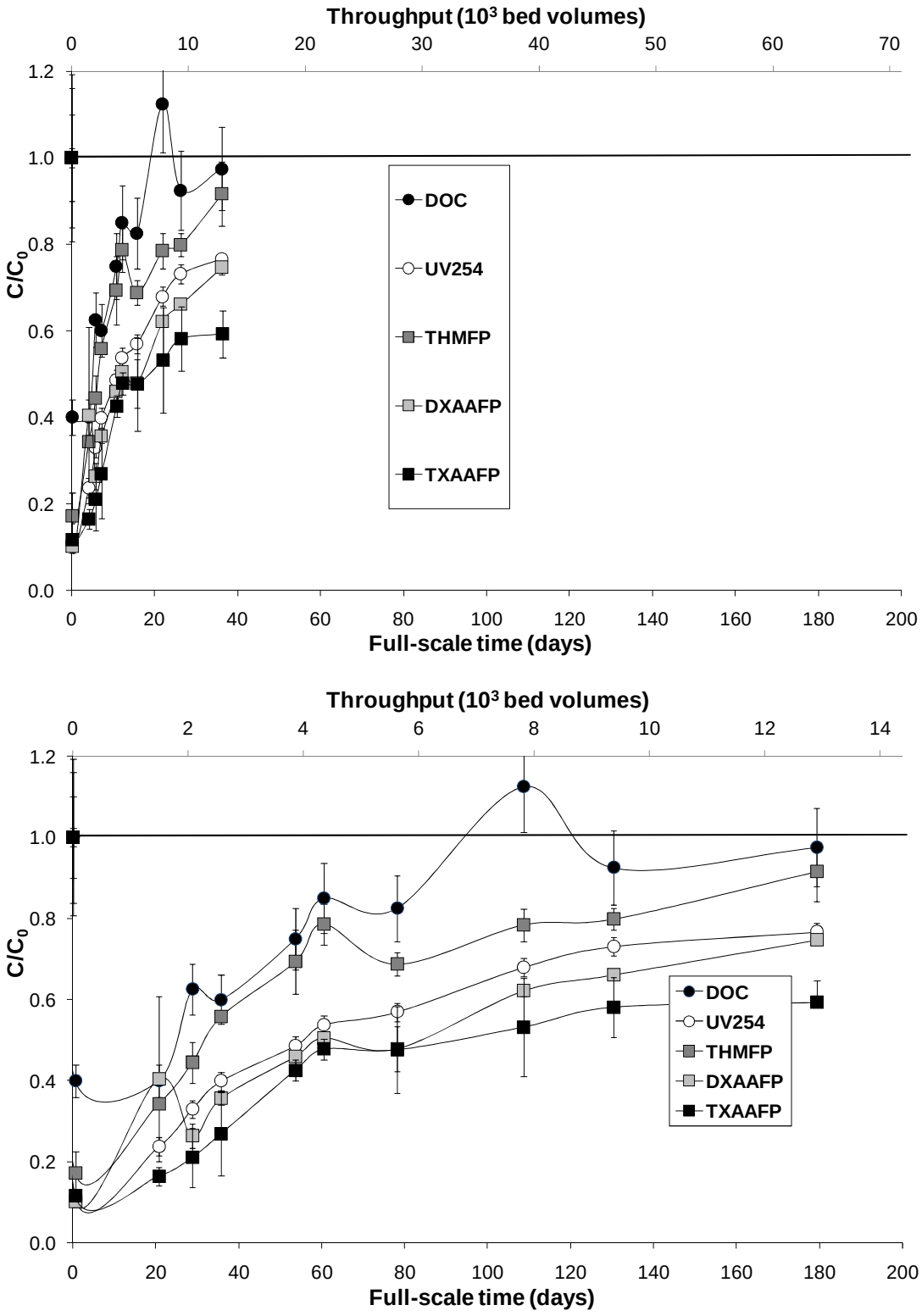


Figure 7.3a&b: RSSCT with lowland water, showing scale-up by (a) PD (above) and (b) CD (below)

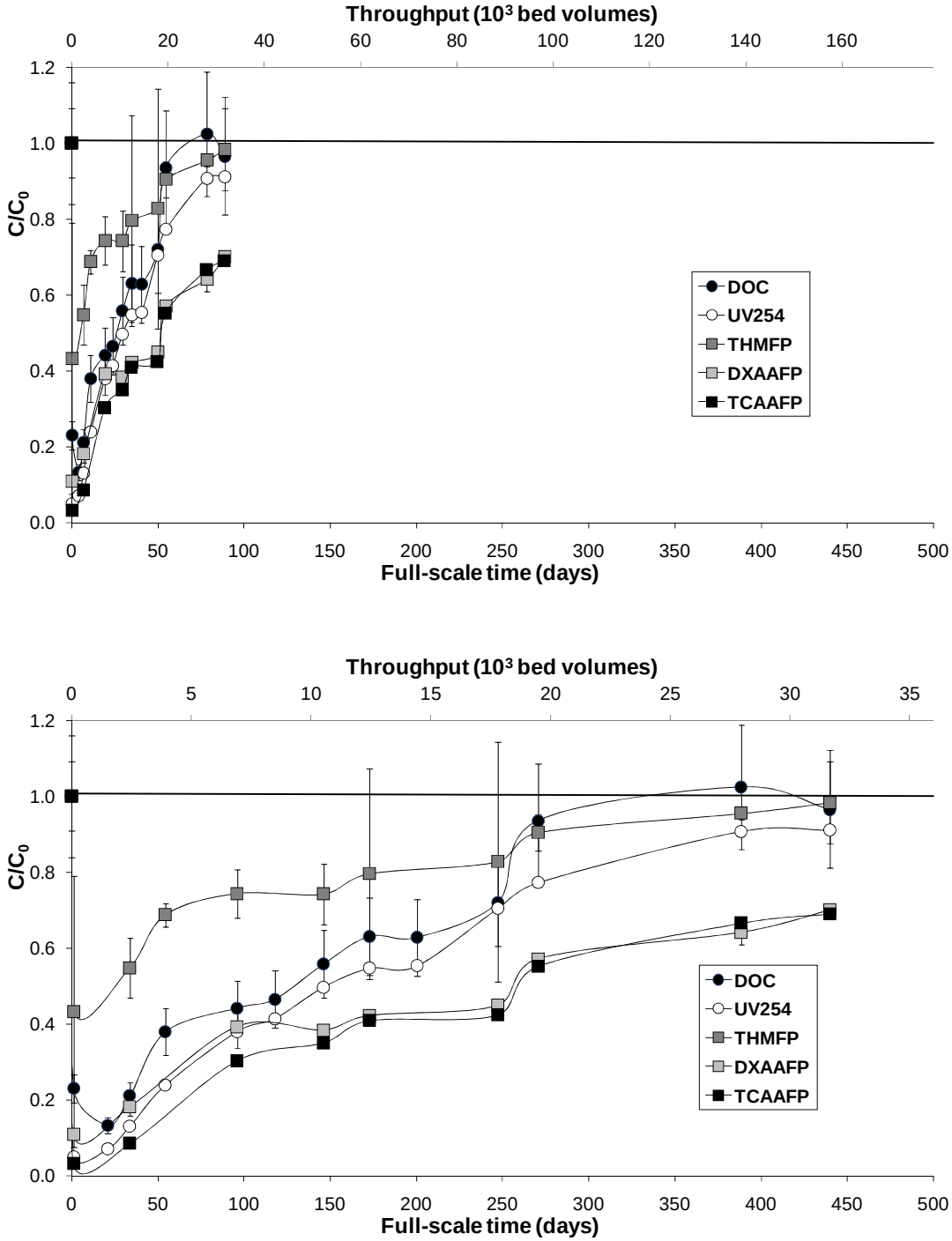


Figure 7.4a&b: RSSCT with upland water, showing scale-up by (a) PD (above) and (b) CD (below)

7.4.5 Column Tests: Comparison between RSSCT and Full-Scale Operation

For RSSCTs designed using the CD approach it is possible to retrospectively calculate predicted full-scale adsorber breakthrough using the PD equation with the experimental RSSCT run time (*22*). Then the breakthrough time as calculated by both methods can be compared. In general PD-RSSCT gives shorter breakthrough curves than the CD approach. There is a time factor difference of 4.95 in the scaled-up operation calculated using CD and PD. For the lowland water DOC breakthrough occurred after ~5.3 days. CD predicts full-scale breakthrough will occur after 130 days' operation, while PD predicts 26 days (Figure 7.3). For the upland water the equivalent times are 15.85, 440 and 89 days (Figure 7.4). Operation times for full-scale GAC adsorbers are typically in the region 100-400 days (*23*), thus the breakthrough times predicted by PD are shorter than observed in reality. At the same time CD has been observed to overestimate atrazine removal at longer operation times compared with pilot-plant performance (*24*). Thus there is evidence actual full-scale breakthrough behaviour would lie between the extremes represented by CD and PD. In certain situations, as where RSSCTs are used for a feasibility study, it is not possible to compare RSSCT performance with either pilot-plant data or full-scale operation. It such cases it is advised that both CD and PD models are used to generate breakthrough curves, with full-scale breakthrough likely to come somewhere between the two.

7.5 Discussion

The authors are unaware of the relationship between K_{OC} and adsorption of NOM structures onto AC being made previously. While this association is of utility for predicting adsorption of specific NOM structures further research is recommended to determine its applicability for other target contaminants such as pesticides. Further, since soil-water adsorption data is not available for natural waters, the positive correlations demonstrated between molecular size, hydrophobicity and modified Freundlich parameters are of more interest in drinking water production. The preferential removal of DBP precursors over bulk DOC in two waters is consistent with the occurrence of physicochemical differences between bulk NOM and DBP precursors. Both waters tested are assumed to contain similarly minor proportions of hydrophobic material, in accordance with studies showing coagulation removes mainly hydrophobic moieties (*5*). Thus coagulation effectively homogenises the fractional composition between different water sources. A key question is then whether the major pool of DBP precursors is located within either the residual hydrophobic or hydrophilic NOM, given the higher adsorbability of the hydrophobic surrogates. For both waters tested the higher adsorbability of HAA precursors in particular is thought to be most likely explained by the hydrophobic and/or transphilic fractions holding a disproportionately high DBP formation potential (DBPFP). This is consistent with the observation that hydrophobic NOM is the major source of DBPs (*6*), and that HAA precursors are more aromatic than THM precursors (*7*). Further support for this hypothesis comes from the preferential adsorption of TXAAFP over DXAAFP in the lowland water, since DXAA precursors have been found to be relatively more hydrophilic than TXAA precursors (*7*). Conversely, given the significant DBPFP recorded in hydrophilic fractions for certain

waters (*6*), it is reasonable to expect disproportionately high DBPFP among hydrophobic components of a post-coagulation residual will not prove a universal circumstance. Based on isotherms showing amino acids and carbohydrates were less absorbable than hydrophobic NOM surrogates, AC is likely to be less effective for DBP control in waters where hydrophilic compounds have high DBPFP. If DBP precursor removal strategies were extended to encompass additional DBPs more attention would need focussing on hydrophilic NOM. This is primarily because formation of nitrogen containing DBPs has been found to increase with levels of nitrogen containing NOM (*25*), of which amino acids are an important constituent.

7.6 Conclusions

- Isotherm tests using NOM surrogates found phenolic compounds to be more adsorbable than carbohydrate and amino acids, with low MW amino acids being least adsorbable.
- Preferential adsorption of HAA precursors over THM precursors in two natural waters is most likely a result of the former being more hydrophobic, though could also result from their lower relative MW.
- In waters where a majority of DBP generating capacity derives from hydrophobic and transphilic constituents of the post-coagulation residual, then AC is a suitable precursor removal option and is expected to be most effective for HAA control.

7.7 Acknowledgements

Anglian Water, Northumbrian Water, Severn Trent Water, United Utilities and Yorkshire Water are gratefully acknowledged for their financial support.

7.8 References

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CHAPTER 8: DISCUSSION

DISCUSSION: IMPLICATIONS FOR DRINKING WATER PRODUCTION

The work presented in this thesis has covered a broad range of topics. To understand the implications of this project, the work is discussed in the form of answers to questions commonly encountered during sponsors meetings and at conferences.

8.1 What is the identity and occurrence of DBP precursors in drinking water?

The key observation from this work is that chemical structure plays the defining role in a compound's DBPFP. Specifically, the following chemical structures were identified as reactive DBP precursors: activated aromatics, β-dicarbonyls, masked β-dicarbonyls and amines. The conventional viewpoint is that humic substances are the principal pool of DBP precursors found in potable water (*1*). This is shown by high measured DBP formation from certain hydrophobic-acid surrogates. Most notable were the high THM formation of resorcinol at 1588 μg mgC^{-1}, the high HAA formation of ferulic acid at 450 μg $mgC^{-1}$and the high TCA formation of L-tryptophan at 222 μg mgC^{-1} (Table 8.1). The significant TCAA formation of the lignin monomer ferulic acid and its analogue sinapic acid indicates they and similar species are an important group of TCAA precursors. The above species are activated aromatics, a class observed to have the highest chlorine demand of a range of structurally-diverse NOM surrogates (Chapter 4). High chlorine demand also correlates with fast kinetics (Chapter 2), as shown by the rate constant of ~4 x 10^3 M^{-1} s^{-1} for the reaction between chlorine and resorcinol (Chapter 2, (*2*)). Hence amongst hydrophobic material, the most important chemical

subclass is thought to be activated aromatics, including resorcinol-type and lignin-derived structures. Although postulated to occur commonly in drinking waters, the concentration of these type of structures is still uncertain, so assessing their contribution to overall DBP formation is not possible currently. Both resorcinol-structures and lignin monomers are hypothesised to be contained within macromolecular hydrophobic NOM components (Chapter 2), which would complicate any quantification. To provide an indication of reactivity using DBPFP data (Table 8.1), to produce 100 µg L^{-1} of THMs and 60 µg L^{-1} of HAAs (respectively the limits in the UK and USA) resorcinol and ferulic acid would need to be present at 0.096 and 0.22 mg L^{-1} as compound, or 0.063 and 0.13 mgC L^{-1} respectively. Since organic carbon concentrations of 4.0 mg L^{-1} are commonly found in treated waters (Chapter 7) these concentrations would represent ~1.6% and 3.3% of total DOC respectively.

However, in addition to the aforementioned hydrophobic compounds, this study has demonstrated the high DBPFP of certain hydrophilic or transphilic surrogates. The highest precursor of non-regulated DBP was 3-oxopentanedioic acid, with 1,1,1-TCP formation of 987 µg mgC^{-1} at pH 7 (24 h) (Table 8.1, Chapter 4) and with HAA formation 1500 µg mgC^{-1} and THM formation 1414 µg mgC^{-1} at pH 8 (Table 8.1, (*3*)). It is believed that 1,1,1-TCP is unstable in natural water at pH 7 and 8, though not pH 6 (*4*), and acts as a intermediate to the formation of THMs (Chapters 2 and 4). Thus 1,1,1-TCP formation may convert to THM formation over longer time periods. This compound is a β-dicarbonyl acid, and when fractionated was partially retained in both TPHA and HPI fractions, with 44% and 48% retention respectively. It had the highest TPHA composition of any surrogate. It was unusual for being characterised by having

very high DBP formation, but relatively low chlorine demand of 3.3 mol/mol (Chapter 4), comparable to that of non-reactive precursors such as L-glutamic acid (chlorine demand 3.1 mol/mol). Hence its chlorine substitution efficiency was the highest recorded, with 80% of consumed chlorine converted to measured DBPs. Knowledge about the occurrence of 3-oxopentanedioic acid and other β-dicarbonyls in aqueous environments is currently limited, however the following information is relevant. The high DCAA and THM formation of this functionality is established (*3*), while the β-dicarbonyl functionality, or groups oxidisable to that structure, have been postulated as DBP precursor sites in fulvic acid pseudo-structures using a mechanistic approach (*5*). Analysis of water with ^{13}C nuclear magnetic resonance (NMR) also supports the existence of β-dicarbonyl moieties within fulvic acid structures (*6*). Within hydrophilic NOM, β-hydroxy acid content has been supported by ^{13}C NMR, and the detection of mixed aliphatic alcohols and carboxylic acids by pyrolysis then gas chromatography with mass spectroscopy (GC-MS) (*7*). It is thought hydroxyl and dicarboxylic acids in humic waters are plant degradation products and can be derived from biochemical cycles (*8*). Also it was proposed in Chapters 2 and 5 that reactive THM precursors in the transphilic fraction may be β-dicarbonyl acids species. Of particular interest is a study measuring aqueous UV oxidation products by GC-MS (*8*). Although quantification was approximate, pentanedioic acid (isomer not identified) was identified following UV-oxidation of a humic acid reference and a fulvic acid reference, though not of a lake water. The maximum concentration was 11 μg L^{-1} after 80 h UV-irradiation of the fulvic acid reference standard. Several other dicarbonyl species were recorded, to a maximum of 120 μg L^{-1} for butanedioic acid after 80 h UV-irradiation of the fulvic acid reference standard. This is significant as it supports the idea that dicarbonyl species are

contained within larger fulvic acid structures and can be liberated by oxidation. At a concentration of 11 µg L^{-1} (5 x 10^{-3} mgC L^{-1}), 3-oxopropanoic acid would be expected to form 5 µg L^{-1} of 1,1,1-TCP. This value is insignificant alone, but would become important if other reactive β-dicarbonyl species were present, as suggested by Corin et al. (*8*). Based on the above, while β-dicarbonyl structures may be particularly prevalent within fulvic acids, they are also expected to occur within transphilic acid, TPHA and HPI fractions, with the presence of other chemical groups affecting fractional distribution. Because of this, β-dicarbonyl precursors are predicted to be a significant precursor category in fulvic-acid rich waters, typically upland waters, with further investigation required to determine occurrence in other water types including those rich in algal organic matter (AOM), or effluent organic matter (EOM). As discussed above, β-dicarbonyl species can be liberated by oxidation of other NOM structures, termed masked β-dicarbonyls in this study. This is the category assigned to L-aspartic acid, one of the common aquatic amino acids (*9*). It was the most reactive HAA precursor identified, forming DCAA at 693 µg mgC^{-1} (Table 8.1), as well as forming 130 µg mgC^{-1} of DCAN and 77 µg mgC^{-1} of TCA. This is a relatively hydrophilic species, with log K_{OW} -3.89 and HPI fractionation behaviour. Thus DCAA formation is predicted to be a feature of hydrophilic-rich waters, particularly those rich in AOM and EOM. Similar conclusions regarding the hydrophilic nature of DCAA precursors have been reached in natural water studies (*10*). Like other amino acids, it has moderate chlorine demand, at 5.7 mol/mol (Chapter 4). However its reactivity towards chlorine differs from other amino acids such as glycine (chlorine demand 5.7 mol/mol), in that high DBP formation, as well as oxidation reactions, are a feature. This is because, in contrast to most other amino acids, it becomes oxidised to a β-dicarbonyl in the presence of

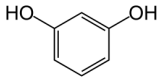
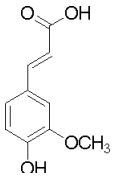
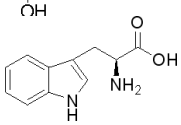
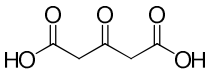
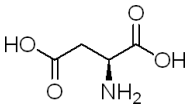
chlorine (Chapter 5). Thus, although amino acids are an important component of chlorine demand in drinking water, many species are not important DBP precursors. The exceptions are, in addition to L-aspartic acid, L-asparagine, L-tryptophan and L-tyrosine. The former two are reactive because they are masked β-dicarbonyls, and the latter two due to the presence of aromatic side groups (Chapters 4 and 5, (*11*)). Non-regulated DBPs, especially DCAN, TCA and DCA are produced from chlorination of these amino acids. To illustrate L-tryptophan formed 222, 96 and 76 μg mgC^{-1} respectively (Table 8.1, Chapter 4). In fact during this study several correlations were identified between the formation of different DBP groups. The most significant were between DCAA and DCAN; DCAN and TCA and DCA and TCA. The likelihood is that these correlations also occur in natural waters. Since the aforementioned amino acids are important precursors of these DBPs (Chapter 4), waters with high amino acids concentrations are hypothesised to have a propensity to form high levels of DCAA, DCAN, TCA and DCA.

L-aspartic acid has been quantified at 0.27 mg L^{-1} (0.097 mgC L^{-1}) in rivers of the USA (*12*). Using this concentration in conjunction with Table 8.1 implies DCAA, DCAN and TCA formation of 67, 13 and 7 μg L^{-1} respectively. Further, since the maximum removal of L-aspartic acid by coagulation was ~30% (Chapter 6), this precursor is expected to occur in post-coagulation waters. However, in should be noted that HAA formation of L-aspartic acid was low at 4 h chlorination relative to 24 h, with respective values of 82±2 and 671±30 μg mgC^{-1} (Chapter 5). Typical retention times during chlorination of water are from 30 min (*13*), thus peak DCAA formation from L-aspartic acid may not be measured in WTWs. In contrast the majority of THM formation from

resorcinol comes within 5 mins (Chapter 2, (*2*)), rapid enough to be observed in final drinking water.

The majority of hydrophilic surrogates tested were observed to be non-reactive DBP precursors (Chapter 4). These compounds included carbohydrates, aliphatic amino acids (excluding L-aspartic acid and L-aspargine) and simple carboxylic acids (Chapter 4). Although DBP formation of carbohydrates is insignificant at pH 7 (Chapter 4), there is evidence that at alkaline pH and long chlorination periods they can generate significant THM levels (Chapter 2, (*14*)). Therefore many species found within drinking water are not thought to generate significant DBP levels. This view is supported by literature, where of important functionalities found in NOM, only activated aromatic, amines and β-dicarbonyls are thought to react rapidly with chlorine (Chapter 2, (*15*)). Taken together, this suggests the number of reactive precursors found in drinking water is finite. On current knowledge, while undiscovered reactive precursors undoubtedly exist, they are likely to occur within these categories.

Table 8.1: Important DBP Precursors

Precursor Category	Structure	DBPFP µg mgC^{-1}	Main fraction	Compound	Reference
Neutral activated aromatic		$CHCl_3$ = 1588	HPOA	Resorcinol	Chapter 4
Anionic activated aromatic		$CHCl_3$ = 48 HAAs = 450	HPOA	Ferulic acid	Chapter 4
Aromatic amino acid		HAAs = 66 TCA = 222 DCA = 96 DCAN = 76	HPON	L-Tryptophan	Chapter 4
β-dicarbonyl		1,1,1-TCP = 987 THMs = 1414 (pH 8) HAAs = 1500 (pH 8)	TPHA/ HPI	3-oxopentane-dioic acid	(*3*) Chapter 4
Masked β-dicarbonyl		DCAA = 693 DCAN = 130 TCA = 77	HPI	L-aspartic acid	Chapter 4

Conditions: chlorine dose 35 M/M, pH 7 unless stated

8.2 How can key DBP precursors be measured in drinking water?

One of the key messages from this work was that no correlation could be found between physicochemical properties of NOM surrogates and DBP formation (Chapters 2 and 4). This implies standard water characterisation methods do not provide direct information about DBP precursor identity. The principal fractionation method for drinking water is adsorption chromatography, which segregates based on hydrophobicity (Chapter 4). Important observations from the fractionation work undertaken were that all surrogates had a small amount of material in minor fractions, and although fractionation is affected by hydrophobicity, boundaries between fractions are not clearly delineated. Further, fractionation did not correlate completely with physicochemical properties such as pK_a and log K_{OW} values. The implications is that while HPOA is comprised of aromatic species and HPI includes amino acids, carbohydrates, simple amides and simple carboxylic acids, the molecular identity of TPHA is uncertain. Although requiring confirmation, it is hypothesised the TPHA is likely to comprise conjugated, aromatic or relatively high MW material with hydrophobicity intermediate between HPOA and HPI compounds. The occurrence of compounds in multiple fractions indicates properties of hydrophilic and transphilic fractions, notably DBPFP, could partly arise from hydrophobic species not retained by XAD columns. In addition, future work should investigate the effect of aggregation on fractionation behaviour, especially whether compounds can appear in different fractions than they would individually. Thus, fractions are not sharply defined, and their composition may vary between different waters. As a consequence fractionation should be used to assign character to a water, rather than for direct comparison of fractional properties, including DBP formation, between different waters. Other than adsorption chromatography, membranes of varying

MWCO can be used to isolate different groups of NOM based on MW. Since neither MW nor hydrophobicity correlate to DBP formation (Chapters 2 and 4), these techniques do not provide direct information about the identity of DBP precursors. Instead, they can assess the relative contribution of operationally-defined isolates to overall DBP formation.

Another consequence of the lack of correlation between physicochemical properties and DBP formation is that reliable predictors of DBP formation in drinking are not thought to exist. While correlations may occur in individual waters, these are likely to be site specific (Chapter 2). For example, previous work has identified relationships between UV absorbance or SUVA and THM formation in certain waters (Chapter 2, (*16*)). This indicates UV-absorbing species, most likely activated aromatic compounds (Table 8.1), are the primary precursor pool (Chapter 2). One strong correlation with DBP formation that has been identified in drinking water is with differential absorbance at 272nm (Δ272) (*4*). This technique compares absorbance at 272 nm before and after chlorination, and so is not a predictive technique. Since absorbance decreases upon chlorination, values are invariably negative. In contrast to predictive bulk parameters, Δ272 has been found to correlate strongly (R^2 commonly 0.99) with formation of both total organic halides (TOX) and individual DBP species (*4*). Thus these correlations show remarkable linearity when compared to bulk predictive parameters. In contrast, conventional absorbance spectra of NOM, both before and after chlorination have no identifiable peaks. Since activated aromatic species, including resorcinol, show an absorbance peak at 272 nm, this evidence strongly implicates activated aromatic compounds as a key precursor pool in different water sources. These relationships are predicted to be strongest in humic-rich waters, with investigation required in AOM and

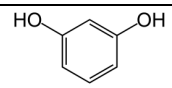
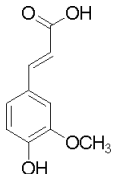
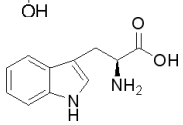
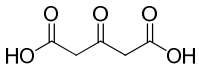
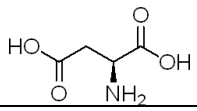
EOM influenced waters. Furthermore, the absence of correlation using conventional UV_{272} absorbance suggests the number of reactive precursors is rather small and/or their spectra overlap with those of other less reactive NOM. This explains why conventional UV_{272} absorbance does not correlate to DBP formation. Such an observation was made during GAC experiments in this study, where DBP formation did not correlate to UV_{272} absorbance, even though activated aromatic species were presumed to be a key precursor category. This underlines the difficulty of predicting DBP formation from bulk water properties. While SUVA, UV_{254} and UV_{272} measurements are a rough guide to the amount of aromatic material in a water, more sophisticated measurements involving chromatographic separation, such as GC-MS or high performance liquid chromatography (HPLC) would provide greater detail about activated aromatic precursors (Table 8.2).

Due to overlap in chemical functionality, the analysis of β-dicarbonyl species in drinking water is not straightforward, though ^{13}C NMR and GC-MS and pyrolysis GC-MS may provide information (Table 8.2, (*6*-*8*)). Fourier transform infrared spectroscopy (FTIR) may also provide information, though as with other techniques it is not straightforward to distinguish between β-dicarbonyl species and other carbonyl-containing molecules.

Another relationship identified in natural waters has been between nitrogenous NOM and non-regulated nitrogen-containing DBPs (Chapter 2, (*17*)). This is consonant with model compound work in this study, which highlights a small number of amino acids, principally L-aspartic acid and L-tryptophan, as precursors of DCAN, DCA and TCA (Chapter 4). Since amino acids are an important group of nitrogenous NOM, such correlations may be widespread, though this requires confirmation. Total dissolved

nitrogen (TDN) and dissolved organic nitrogen (DON) can be measured using available TOC analysers. Analysis of amino acids concentrations in drinking waters would allow a more direct evaluation of this hypothesis. Amino acid concentrations can be measured by a variety of methods, typically involving hydrolysis, derivatization and HPLC analysis (*17*). Alternatively, immunoassay methods are available.

Table 8.2: Properties of important precursor categories and analysis methods

Precursor Category	Structure	log K_{OW}	pKa	MW (Da)	Analysis methods
Neutral activated aromatic		0.8	9.3	110	
Anionic activated aromatic		1.51	4.6	194	SUVA, UV_{254}, UV_{272}, differential UV_{272}, pyrolysis GC-MS, GC-MS, HPLC
Aromatic amino acid		-1.06	2.4	204	amino acid analysis, DON
β-dicarbonyl		-1.13	n.a.	146	pyrolysis GC-MS, GC-MS ^{13}C-NMR
Masked β-dicarbonyl		-3.89	2.1	133	amino acid analysis, DON

8.3 Can treatment processes be selected or operated to target specific precursors?

The short answer to this question is no. This is because it has been demonstrated, both with experimental results and during a comprehensive literature review, that DBP formation does not correlate to any physicochemical property (Chapters 2 and 4). This includes MW, charge and hydrophobicity, properties which control uptake by coagulation, ion exchange, activated carbon and NF (Chapters 6 and 7). Instead DBP formation is affected by differences in chemical functionality not reflected by physicochemical properties. Subtle differences between two molecules, such as the position of activating, de-activating or stabilising groups can have a profound impact on DBP formation (Chapter 2). Thus similar compounds can have similar treatability and physicochemical properties but disparate DBPFP. This is shown clearly by L-aspartic acid and L-glutamic acid (Chapter 6), two very similar compounds with respective HAAFP of 693 and 3 µg mgC^{-1}. The log K_{OW}, MW, pKa values of L-aspartic acid are respectively -3.89, 133 Da and 2.1; while equivalent values for L-glutamic acid are -3.69, 147 Da and 2.2 (Table 8.2). The two compounds are removed to a similar degree by coagulation, ion exchange, NF, GAC and AOPs (Chapters 5, 6 and 7). Hence, it is not possible to selectively treat the reactive precursor, L-aspartic acid, over the non-reactive L-glutamic acid. Since treatability is conferred by physical properties, selective removal is only achievable where precursors have physical properties which differentiate them from other types of NOM.

Where precursors are highly charged, they will be preferentially removed by coagulation and anion exchange over weakly anionic or neutral species (Chapter 6). Such a situation is most likely in an upland water, since such catchments tend to be dominated by hydrophobic NOM (*18*), the major source of anionic charge in a water (Chapter 3). Moreover, it is likely to be most effective for large, anionic activated aromatic precursors and masked β-dicarbonyls contained within larger fulvic acids structures. The former category is represented by tannic acid. However, it is worth stressing even within hydrophobic-rich waters, the abundance of anionic activated aromatic, rather than neutral activated aromatic precursors is unknown. Neutral or weakly charged hydrophobic compounds are also likely to be degradation products of larger aromatic structures. Resorcinol represents these type of compounds, being both aromatic and neutral, and was unaffected by coagulation and MIEX® (Chapter 5). Since GAC preferentially removes hydrophobic molecules such as resorcinol (Chapters 3 and 7), where activated aromatic precursors in a post-coagulation residual retain significant DBPFP, it is proposed GAC can provide preferential precursor removal.

In Chapters 3 and 5 it is hypothesised that the explanation for the effective removal of THM precursors by MIEX® in some waters may derive from polyprotic β-dicarbonyl acids. This is because surrogates with single anionic charge (L-aspartic and L-glutamic acids), and multiple anionic charge (tannic acid) did not show increased treatability with MIEX® compared with coagulation. As discussed, fulvic acid and transphilic acid fractions are believed to be important sources of β-dicarbonyl acids. Amino acids were observed to be the most biodegradable chemical functionality (Chapter 5), therefore where they are an important precursor pool, as predicted for waters with high AOM and EOM levels, biotreatment could offer selective precursor removal. Using a hydrophobic

NF membrane, neutral hydrophilic compounds were removed preferentially over other categories. Therefore NF will be most suitable for precursor removal where reactive precursors belong to this group (Chapter 6). Based on knowledge of chemical structure of DBP precursors, such molecules are most likely to be aliphatic amino acids (specifically L-aspartic acid) or carbohydrates (Table 8.3). These precursors will be more prevalent in hydrophilic-rich waters, particularly with high levels of AOM or EOM.

8.4 What are recommended strategies to meet DBP legislation?

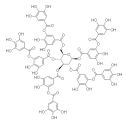
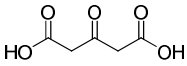
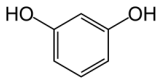
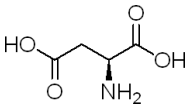
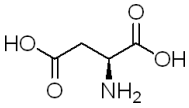
Precursor removal strategies need to be pragmatic and empirical. This is because it is not possible to selectively remove reactive DBP precursors unless their identity coincides with physical differences from bulk NOM, and moreover as NOM characterization tools do not identify reactive precursors. The first stage of a precursor removal strategy is to ensure coagulation is fully-optimised for NOM removal, as can be achieved by operating within a zeta potential window of -10 to 3 mV (Chapter 6, (*18*)). This will facilitate high removal of strongly-anionic precursor material, represented by tannic acid (Table 8.3), and moderate removal of weakly-anionic material such as L-aspartic acid (Chapter 6). Coagulation will therefore be most effective for anionic activated aromatic precursors. Since this category principally produces THMs and TCAA, it will be more effective for removal of THM and TCAA precursors, rather than more hydrophilic DCAA precursors (Chapter 3, (*10*)). Where DBP formation in post-coagulation waters remains a concern, indicating neutral and weakly anionic material contains reactive precursors, then additional treatment is required. Such precursors are believed to predominantly be neutral activated aromatics, β-dicarbonyls, masked β-dicarbonyls and amino acids. Anion exchange methods, such as MIEX®, have been observed to be more effective at removing THM precursors than coagulation, though the exact reasons remain unclear (Chapter 3). It is hypothesised this finding results from high uptake of reactive carboxylic precursors, potentially β-dicarbonyl and/or masked β-dicarbonyl species (Chapter 3). Hence, where such reactive precursors occur, MIEX® is a suitable process option (Table 8.3). Activated carbon preferentially adsorbs hydrophobic NOM over similarly-sized hydrophilic moieties (Chapter 7). Consequently, it is a recommended process where residual hydrophobic

NOM, which typically comprises ~25% of material in a post-coagulation residual (Chapter 7), has disproportionately high DBPFP. This explanation is proposed to explain the preferential removal of HAA precursors observed in an upland and lowland water (Chapter 7). Low MW, hydrophilic components of NOM, including amino acids and carbohydrates, are not removed to a high degree by the above processes (Chapters 6 and 7). When they contain a significant DBPFP, a hydrophobic NF membrane is recommended for their removal (Chapter 6). Biodegradation is effective for treating amino acids (Chapter 5), and so will prove effective where reactive precursors belong to this group, as probable in AOM and EOM influenced sources. However, in general the amount of readily-biodegradable material in drinking water is limited, which explains the often low literature precursor removal (Chapter 3, (*19*)). AOPs are not considered an effective process option. This is primarily as it has been demonstrated that treatment by AOPs can significantly increase the DBP formation of previously non-reactive amino acids (Chapter 5). Although at high doses AOPs can effectively remove all NOM, the energy requirements are uneconomic. At doses employed for water treatment, mineralisation of NOM is not recorded (Chapters 3 and 5). Finally, ozone alone is not perceived to be an effective process for precursor removal (Table 8.3, Chapter 3). It will be most effective where precursors are aromatic and ozone is used to increase their biodegradability for downstream biotreatment. This strategy will be most effective where activated aromatic precursors in a post-coagulation residual are key to controlling DBP formation, a situation most probable in humic-rich water sources.

During this study the strong pH dependence to the formation of several DBPs has become apparent. Therefore another potential route to control DBP formation is to reduce formation of problematic DBP groups through manipulation of chlorination pH.

Given the incomplete knowledge of how DBP formation from reactive precursors varies with pH, this approach would need empirical confirmation. Further, evidence does not suggest DBP formation is reduced, but that the speciation of formed DBP is altered. The formation of TCAA can be mitigated by chlorinating at alkaline pH, although this is likely to promote THM formation (Chapter 2), so this is likely only to be beneficial where TCAA is of more concern than THMs. Increased THM formation at pH 7 and above is supported by model compound and natural water research, and explained by increasing hydrolysis under alkaline conditions (Chapter 2). Any pH dependence in regards to DCAA formation is more equivocal (Chapter 2). It is thought formation of THMs and TCAA proceeds through common intermediates, notably TCA. Meanwhile, formation mechanisms of DCAA are disparate and this DBP can result from the hydrolysis of DCAN, particularly at alkaline pH (Chapter 4). This hints that particularly in AOM and EOM rich waters, where amino acids are likely to act as DCAN and DCAA precursors, chlorination at acidic pH could also reduce DCAA formation. However, this hypothesis requires investigation.

Table 8.3: Suitability of water treatment processes for precursor removal

Process	Selectivity	Good For	Example precursor	Comments
Recommended processes				
Coagulation	Highly anionic compounds	Large, anionic precursors		Process optimisation important
MIEX®	Highly and moderately anionic	β-dicarbonyl acids?		Effective for THMFP removal, putatively β-dicarbonyl acids
GAC	Hydrophobic compounds	Neutral hydrophobic species		Pore size distribution and charge of carbon surface important
NF	Effective for small, hydrophilic precursors	Amino acids, carbohydrates		Membrane surface affects selectivity
Other processes				
AOPs	Can increase DCAAFP	All precursors at high doses		Effective doses uneconomic currently
Biotreatment	Chemical functionality	Amino acids		Limited amounts of biodegradable NOM
Ozone	Selective for aromatics	Activated aromatics		Limited efficacy for precursor removal at typical doses
Ozone-biotreatment	Effective if ozone increases biodegradability of aromatic precursors			Limited by amount of aromatic precursors?

8.5 References

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CHAPTER 9: CONCLUSIONS AND FUTURE WORK

CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

Precursor Identity and Measurement

- The major classes of DBP precursor in drinking water are believed to be activated aromatics, β-dicarbonyls, masked β-dicarbonyls and amino acids. While not particularly reactive, carbohydrates can produce significant THM amounts at alkaline pH and long chlorine contact times.
- Of these listed groups, activated aromatics are believed to be the most significant group, especially in humic rich waters. They are the primary source of THMs and TCAA in such waters. β-dicarbonyl and masked β-dicarbonyl functionalities are thought to be associated with various drinking water fractions, mainly the fulvic acid and transphilic acid. They form mainly DCAA, 1,1,1-TCP and THMs. Amino acids are most prevalent in waters with algal or wastewater influence. They can form a variety of DBPs, including DCAA, DCAN, DCA, TCA and THMs.
- Several correlations were identified between formation of DBP groups. The most significant were between dichloroacetic acid (DCAA) and dichloroacetonitrile (DCAN); DCAN and TCA and dichloroacetaldehyde (DCA) and trichloroacetaldehyde, indicating similar relationships exist in natural waters.
- No compound physicochemical properties were found to correlate with formation of THMs or HAAs. This lack of relationships indicates there is no reliable predictor of DBP formation likely to be found in drinking waters.

- Instead precursor identification requires analytical techniques able to identity specific chemicals or chemical groups. The most useful are likely to include GC-MS or HPLC for activated aromatics, GC-MS for β-dicarbonyls and masked β-dicarbonyls, and amino acid analysis methods.

Precursor Treatment

- Treatability by coagulation, MIEX® and NF was controlled by physicochemical properties, while the same does not apply to DBP formation. Hence it was not possible to selectively remove reactive precursors.
- Coagulation can achieve high removal of anionic activated-aromatic precursors, particularly TCAA and THM precursors in hydrophobic-rich waters.
- In post-coagulation waters where a majority of DBP generating capacity derives from neutral or weakly anionic activated-aromatic precursors, then AC is a suitable precursor removal option and is expected to be most effective for HAA control.
- Anion exchange is an effective treatment for transphilic species, known for high carboxylic acid functionality and consequently is recommended for carboxylic acid precursors, likely to include β-dicarbonyls and masked β-dicarbonyls.
- Amino acids are effectively removed by biotreatment and nanofiltration. A hydrophobic nanofiltration membrane was particularly effective for treating neutral, hydrophilic compounds and is therefore also suitable for both amino acid and carbohydrate retention.
- Complete mineralisation of a spectrum of NOM surrogates by AOPs was achievable, but only with UV inputs much higher than used for water treatment.

At lower doses treatment of amino acids leads to dramatically increased amounts of HAAs, specifically DCAA. Hence AOPs are not recommended for HAA control in waters with relatively high amino acid concentrations

9.2 Future Work

- The deployment of analytical techniques for measurement of chemical functionality in water would enable direct assessment of the DBP formation and treatability of different chemical groups through the water treatment process stream. In particular activated aromatic species can be monitored with HPLC or GC-MS methods, while analysis of amino acid and carbohydrate concentrations are also recommended.
- Due to overlap in chemical functionality, the analysis of β-dicarbonyl species in drinking water is not straightforward, though ^{13}C NMR and pyrolysis GC-MS may provide information (*1*, *2*). Increased knowledge of the occurrence of β-dicarbonyl species would allow a more accurate judgement about their significance as DBP precursors. In particular it would facilitate an appraisal as to whether this moiety is responsible for high removal of THM precursors reported for MIEX®.
- Further it is recommended the MIEX® treatability of β-dicarbonyl acids is monitored through their use as NOM surrogates in bench-scale experiments.
- Since the molecular identity of the TPHA and TPI fractions are currently uncertain, further investigation is recommended, focussing on conjugated, carboxylic acid, β-dicarbonyl and aromatic functionalities.

- In this study surrogates have been tested individually. To determine whether aggregation affects fractionation behaviour, treatability and DBP formation future work should also involve compound mixtures.
- Investigation is recommended with a range of reactive DBP precursors to determine how changes to the chlorination pH affect the identity of formed DBPs. Such as study should encompass non-regulated DBPs, and would allow assessment of the applicability of pH strategies for DBP control in drinking waters.

9.3 References

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