Trihalomethanes: from precursors to management strategies

EngD

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A Thesis submitted to Newcastle University in partial fulfilment of the requirements for the degree of Doctor of Engineering in the Faculty of Science, Agriculture and Engineering

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Cassie Building

2017

Declaration

I hereby certify that the work presented in this thesis is my original research work, with the exception of collected data presented in Chapter 3 which were performed at Scottish Water Scientific Services. The experiment set up and subsequent all analytical work was carried out at the research laboratories in Cassie, Devonshire and Drummond Buildings, School of Civil Engineering and Geosciences, Newcastle University. Excitation emission fluorescence analysis was performed in the School of Geography at Newcastle University. However, all interpretation and statistical calculations of the data are my own work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions. All work in chapter 3 has been already published. All results from chapters 4, 5 and 6 have not been published in any scientific journals or for a degree at this or any other university.

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Abstract

Investigation and characterisation of dissolved organic carbon (DOC) in raw and treated water from six case study sites located across Scotland identified the main aspects that influenced the formation of trihalomethanes (THMs) during and after disinfection. DOC and temperature were the main drivers of THMs found in this research. However, other variables such as bromide also played an important role in driving reactions towards brominated species of THMs. DOC quality, essentially of humic and fulvic origin remained constant along the year, but quantity affected THMs yields due to seasonal changes. Further DOC characterisation showed that treatment by coagulation or membrane filtration successfully removed hydrophobic DOC leaving a larger proportion of hydrophilic DOC in treated waters. This investigation identified two main groups of organic substances that corresponded to the hydrophilic fraction of DOC: phenolics and carboxylic acids. The final stage of the experimental work lead to the application of adsorption with activated carbon (AC) to remove these compounds from the treatment although at large doses. This work also presents a cost benefit analysis of two potential strategies to manage THMs precursors: the use of Ultraviolet (UV) scan sensors and AC adsorption. These technologies contribute to the enhancement of the industrial sponsors’ processes by improving compliance with regulatory quality and public health standards.

Acknowledgements

I would like to thank firstly to my academic supervisor Dr David Werner for his continuous support, advice and encouragement throughout these years of study. I would also like to thank to my industrial supervisors Paul Weir and Mark Haffey at Scottish Water who helped me with logistic and technical support. Many thanks as well to the kind and cheerful people of the Process Science Team at Scottish Water.

I am also very grateful to all the technical team at the School of Civil Engineering and Geosciences especially to David Race, Berni Bowler, Phil Green and Graham Patterson for their advice and assistance over the last 4 years in the laboratories and office that made my work there ran smoothly.

Thank you to all my friends in the postgraduate suit at Cassie Building who made my postgraduate life easier with their company, advice and fun times. I learnt so much from them.

And finally, thanks to my parents for their emotional support and encouragement throughout my years of study and working abroad.

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List of Abbreviations

AC Activated Carbon

Ag-AC Silver Activated Carbon

ANOVA Analysis Of Variance

AOM Algogenic Organic Matter

AWTP Amlaird Water Treatment Plant

BDOC Biodegradable Dissolved Organic Carbon

BWTP Broadford Water Treatment Plant

CA Carboxylic Acids

CAPEX Capital Expenditure

COC Colloidal Organic Matter

DBPs Disinfection by Products

DEFRA Department of the Environment Fisheries and Agriculture

DOC Dissolved Organic Carbon

DWI Drinking Water Inspectorate

DWQR Drinking Water Quality Regulator in Scotland

DWD Drinking Water Directive

EEM Excitation Emission Matrix

EU European Union

ESI Electron Spray Ionization

FTIR Fourier Transform Infrared analysis

FWTP Forehill Water Treatment Plant

GAC Granular Activated Carbon

GIS Geographical Information System

GC-ECD Gas Chromatography Electron Capture Detector

GC-MS Gas chromatography Mass Spectrometry

GWTP Gigha Water Treatment Plant

HAA Haloacetic acids

HPI Hydrophilic

HPO Hydrophobic

HIWATE Health Impact of long term exposure to disinfection by products in drinking water

HPSEC High Pressure Size Exclusion Chromatography

ICP-OES Inductively Coupled Plasma Optical Emission Spectroscopy

LIMS Laboratory Information Management System

MF Micro Filtration

MIEX Magnetic Ion Exchange

MW Molecular Weight

MWCO Molecular Weight Cut Off

MS Mass Spectrometry

NF Nano Filtration

NOM Natural Organic Matter

OFWAT The Water Services Regulation Authority

OPEX Operational Expenditure

PAC Powdered Activated Carbon

PCV Prescribed Concentration Value

PCWTP Port Charlotte Water Treatment Plant

POC Particulate Organic Matter

SNH Scottish Natural Heritage

RE Relative Error

RO Reverse Osmosis

SEC Size Exclusion Chromatography

SEPA Scottish Environment Protection Agency

SLM Sustainable Land Management

SSKIB Scottish Soils Knowledge and Information Base

SUVA Specific Ultraviolet Absorbance

SW Scottish Water

SWTP Stornoway Water Treatment Plant

THM trihalomethane

THMs Trihalomethanes

THMFP Trihalomethanes Formation Potential

TPI Transphilic

UF Ultra Filtration

UK United Kingdom

USEPA United States Environmental Agency

UV Ultraviolet

UV/Vis Ultraviolet Visible

WTP Water Treatment Plants

Chapter 1

INTRODUCTION

1.1 Background

Due to the continuous development of technology and industry around the world health concerns related to exposure of chemicals by diverse routes has increased in the recent years. Many of these chemicals are used in our foods as artificial flavours and colours but are also present in toiletries, etc. This exposure to a wide variety of chemicals is intrinsically linked to other substances we often assume as safe, such as potable water (1, 2).

When we use tap water for sustenance and our daily routines we are also exposed to the plethora of chemicals contained therein. Not all of these are harmless, some, such as disinfectants react with other organic compounds dissolved in water forming disinfection by-products. This forms a major contradiction of potable water supply. Chemicals, such as disinfectants, are used in water treatment to protect us from pathogens and water borne diseases but are also causing other potentially carcinogenic toxic compounds. More than 600 types of disinfection by products (DBPs) have been discovered and reported in drinking water supplies (3, 4), but the most important group due to its abundance, toxicity and potential carcinogenicity are trihalomethanes (THMs).

THMs were discovered in 1974 (5) and since then, companies and quality regulators have attempted to control their levels in water through understanding of their formation by characterising its precursor natural organic matter (NOM) measured as dissolved organic carbon (DOC), its diverse mechanisms of reaction, and modifying the water treatment process or disinfection practices. DBP formation will depend on the disinfectant used, the organics present in water (precursors) and the reaction conditions for example temperature and pH, provide many different combinations and possibilities. Chlorinated disinfectants are cheap and efficient at eliminating pathogens, and provide residuals protecting water in distribution networks. Removing them from the drinking water network could increase the risk of getting waterborne diseases – which constitutes a greater risk than getting cancer by DBPs exposure for example. There is no clear evidence of cancer incidences linked to DBPs in drinking water and epidemiological studies of THMs have been limited to a few studies in Europe (6-9), however, carcinogenicity evidence exits from in-vitro studies (10-12). In this context, the World Health Organisation (WHO) establishes the international standards for drinking water and states that primary consideration should be given to ensure that water disinfection is never compromised, but has nonetheless defined guidance values for individual THM compounds and are 300 μg/L for chloroform, 100 μg/L for dibromochloromethane and bromoform, and 60 μg/L for bromodichloromethane (13).

For total THMs, the WHO recommends a fractionation approach to account for additive toxicity. Based on WHO guidelines and the opinion of the European Commission's Scientific Advisory Committee, the 1998 European Union Drinking Water Directive defines 100 μg/L as the allowable maximum concentration of total THMs (comprising chloroform, bromodichloromethane, dibromochloromethane and bromoform) in drinking water (14). The US EPA regulates THMs at a maximum allowable annual average level of 80 μg/L. The US EPA additionally regulates another group of DBPs called haloacetic acids (HAAs) at a maximum permissible level of 60 μg/L (15) for five compounds (HAA5).

Scotland follows measures implemented by the European Union and internal regulators such Drinking Water Quality Regulator for Scotland (DWQR) which establishes maximum permissible levels at 100μg/L for total THMs. In the past four years, the public water supply company in Scotland: Scottish Water, has experienced high levels of THMs in their water supplies forcing the development of methods to minimize or eliminate THMs from their water supplies.

One of the main approaches to understand THMs formation was to identify: What caused THMs in Scotland and was it catchment specific? What is the origin of THMs precursors in surface waters? Are there any climatic factors affecting THMs formation directly or indirectly, and what are the implications of these in the context of global change? Thus, to comply with regulations, Scottish Water has been working to understand and reduce the risks of THMs failures in regulatory samples (Innovation, Regulation, Public Health, Catchment Management; and Process Optimization and Operations teams).

Although the number of failures had reduced considerably, as explained in further chapters, since 2012, it is still necessary to prevent future failures. This project was created to understand whether the treatment process or external factors such catchment influences had a significant effect on THMs formation. This work also presents detailed analysis of THMs precursors from source origins through treatment process and suggests possible management strategies for their reduction.

1.2 Aims and objectives

Aim

The aim of this work was to first review available data and then select five case study sites from more than 200 drinking water plants located around Scotland that could provide a clearer understanding of the main treatment types, size (water supply) and geographical locations that determine THMs formation, as well as a detailed chemical characterisation of their precursors to ultimately identify effective strategies to reduce and/or minimize THMs in drinking water supplies.

Objectives

- i) To review regulatory monitoring data to identify geographic, climatic and operational determinants of THM formation in Scottish Water treatment works.
- ii) To identify five case study sites around Scotland that represent the majority of drinking water sites for detailed monitoring of THMs and factors underpinning their formation, and to characterise DOC in surface and treated water samples through two distinctive sampling monitoring programmes.
- iii) To verify reactivity towards THMs of abundant types of DOC which make up residuals in treated water at the point of disinfection, and to determine the best strategy to reduce or minimize these THM precursors.
- iv) To propose the use of a new or existing technology as aids to control and minimise THMs formation based on a cost-benefit analysis

1.3 Thesis organisation

This research project was based on existing work performed at Scottish Water. Historical data was compiled from their database for detailed statistical analysis. This preliminary work was carried out at Scottish Water Offices in Glasgow for a period of 15 months. Complementary information for soil analysis was collected from James Hutton Institute during this period. Sampling for quarterly monitoring was performed by Scottish Water sampling teams and delivered to Newcastle University for characterisation analysis. Monthly monitoring sampling was performed entirely by Scottish Water Scientific Services in Edinburgh. Experimental work of surface and treated water samples during quarterly monitoring, reactivity experiments with model DOC compounds, and the evaluation of different sorbent materials, was performed entirely at the Department of Civil Engineering and Geosciences, Newcastle University.

1.4 Research contribution

1.4.1 Evaluating seasonal, geographical and operational factors in Scotland that influence THMs formation

One of the main contributions of this work is the construction of a simple THMs prediction tool based on the analysis of three main predictors: DOC, temperature and chloride as a proxy for bromide. This investigation is described in detail in chapter 3 and currently published online (16), and constitutes one of the largest assessments ever performed on water systems, especially related to THM formation as a function of geographic, operational, and climatic factors. Data showed that DOC varies by location and regional weather (e.g., precipitation). Chloride and especially ambient temperature conditions also relate to THMs formed during water treatment across the Scottish network. The importance of such factors has been observed previously in many studies (17-20) but in this work, factors are at a country-scale. The most important contribution of this research is the suggestion that ambient temperature plays a crucial role in THM formation, implying that THMs formation may increase as a result of global warming. Further investigations performed at laboratory scale and detailed in Chapter 4 confirmed the direct influence of temperature as well as DOC quantity and quality on THMs formation. If we consider projected increases in temperature of 2-3°C in the next 40 years, then treatment adaptations, such changing disinfection practices or applying enhanced DOC removal processes, may be needed to reduce impact of global warming on THMs formation and the associated health issues.

1.4.2 Dissolved organic carbon characterisation

Characterisation of surface and treated waters provided insight into the nature of DOC in Scotland. At the point of disinfection, two main groups of DOC compounds were identified as contributing a substantial part of the residual hydrophilic and hydrophobic portions of DOC still present in treated water: carboxylic and phenolic acids. These compounds constitute an important percentage of the total DOC found in treated water before the point of disinfection that represents 28%. These compounds showed a particular reactivity towards THMs formation potential, particularly phenolic acids which were more reactive towards THMs formation compared to carboxylic acids, although present at lower concentration. This information is crucial for drinking water treatment processes that show similar DOC character (of humic and fulvic nature) and could target phenolic and carboxylic acids to control and minimize THMs formation. The use of activated carbon (AC) as an option to adsorb THMs precursors and application of online monitoring sensors for DOC detection as alternative technologies for THMs control were evaluated, with the latter having better cost-benefits, and these lessons could be applied in other countries with similar geography and geology to Scotland.

1.5 Thesis structure

The Thesis is structured in seven chapters. All chapters, except Chapter 2, include discussion of results, conclusions and references following a research paper format. Figures and Tables with additional supplementary information have been also included in each chapter. A brief summary of the following chapters is shown as follows:

Chapter 2: Literature review

This chapter presents a comprehensive analysis of the literature on past and current investigations related to sources, nature and external influences of NOM that determine the chemical character of DOC in Scottish surface waters. This chapter also mentions the implications of residual DOC present in treated water that causes disinfection by-products and current strategies to minimise their presence in drinking water treatment sites.

Chapter 3: Climatic, geographic and operational determinants of trihalomethanes (THMs) in drinking water systems

This chapter focuses in summarizing an extensive statistical analysis of existing operational data collected from 93 drinking water sites around Scotland that show how THMs formation is rooted in geographic, operational and climatic factors. Correlation analysis showed that ambient temperature was the primary THMs formation predictor in potable water and water distribution systems while dissolved organic carbon and chloride, indicating that marine influence, also affected THMs formation. This finding was confirmed with Geographical Information System (GIS) mapping of median THMs levels that indicated that brominated THMs were most prevalent in coastal areas and on islands. This real-world dataset confirms both geographic and climatic factors are key to THMs formation. If ambient temperatures increase, THMs control will become more challenging, substantiating concerns about the impact of global warming on water quality.

Chapter 4: Root causes of seasonal trends in trihalomethanes (THMs) formation in drinking water treatment sites

Findings from the previous chapter were confirmed by looking at actual data collected monthly and quarterly for a year to identify factors underpinning the observed seasonality in THMs formation. THMs formation potential (THMFP) experiments confirmed that THMs increased or decreased due to temperature changes by maintaining constant DOC and chlorine levels and altering only temperature. Seasonality affected other water quality parameters such as Ultraviolet (UV) absorbance, DOC and chloride. It was established that quality of DOC remains constant across the year by not changing its character but only its abundance. DOC quantity and temperature then appear to influence THMs formation more effectively than any other investigated factors which again confirm that climatic factors have an important impact on THMs formation.

Chapter 5: Natural organic matter compounds in Scottish water, their THMs formation potential and treatability by activated carbon adsorption

Due to elucidation of DOC in the previous Chapter, reactivity of phenolic and carboxylic acids towards THMs was investigated in more detail which of the two produced more THMs. Phenolic compounds were found as the most reactive, especially those with methoxy groups. An evaluated strategy to reduce or minimise THMs in treated water was the use of activated carbon (AC) to adsorb these compounds. Silver impregnated AC and other charcoal based materials were used for sorption experiments leading to the final conclusion that at the selected pH conditions adsorption of phenolic acids was possible, but only for very high AC doses, and further work is needed to optimise removal efficiencies.

Chapter 6: Business case for the installation of UV/Vis online monitoring sensors at drinking water sites

This chapter evaluates the use of two technologies that can aid in controlling THMs formation in real scale drinking water treatment plants. The two technologies were: silver impregnated AC bed in existing filtration units for adsorption of phenolic compounds, and, ultraviolet (UV)/visible online monitoring sensors. Cost-benefit analysis was applied to both technologies to choosing the best application that will aid to control THMs formation to enhance drinking water processes, and it was concluded that silver impregnated AC is too costly, whilst enhanced online monitoring is comparatively inexpensive with substantial anticipated benefits.

Chapter 7: Final conclusions

This chapter summarises all key findings from this work and to recommend their application in the company and potentially to other water utilities that have experienced similar problems related to THMs and their management. Lessons learnt from experimentation and other additional studies that are needed for future work are also commented for final consideration.

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Chapter 2

LITERATURE REVIEW

2.1. Introduction

2.1.1 Water Sources in Scotland

Scotland is an area rich in natural resources which provide to the region a vast biodiversity as well as maintaining many industries that influence the life of its population. Fresh water resources in Scotland are vast and include lochs, rivers, ground water boreholes and estuaries that provide water to its inhabitants as well as hydropower (1). These resources are also important for the regional economy by supporting industries such as salmon, shellfish farming, distilleries and tourism (available at www.snh.gov.uk). Therefore, the Scottish authorities are advocated to protect them for future generations and in 2003 they established the Water Environment and Water Services Act (www.legislation.gov.uk/asp/2003/3/pdfs/asp_20030003_en.pdf) which aims to protect and improve the water environment and implementing sustainable development in the region.

The typical Scottish scenery shows pristine lakes and rivers that are well known to visitors from all over the world, but these water bodies differ in water quality which is affected by climate, geology, soils, topography and human intervention. According to the Scottish National Heritage 2% of the land in Scotland is fresh water that represents 90% of the total surface water volume in the United Kingdom (available at www.snh.gov.uk).

The particular geography of Scotland gives fresh water sources a diverse chemical composition. For example, the uplands areas have hard rock, poor soils and scarce grassland providing to most of the upland lochs and rivers an acidic nature, making them soft (2), whereas in the lowlands, fresh water bodies are alkaline and rich in nutrients that originated in forested peatland and vegetation decay (3). The particular brown to yellow coloration in some rivers and lochs has been attributed to peaty soils (4, 5). Peatland is known for its high content of carbon and its contribution to carbon sequestration in the terrestrial environment, and it covers 15% of the UK, with 75 % of the UK's peatland being located in Scotland (6). Located at the north of the British Isles, Scotland is surrounded by the sea and a great percentage of its territory is formed by islands. Surface waters located in coastal areas will be affected by easterly or westerly winds and rain adding salts of marine origin to freshwater thus altering its chemical composition.

Seasonal changes such as drought or intense rain will also affect the release of organic and inorganic compounds from soils to water systems or to the atmosphere. There is clear evidence for example that natural organic matter (NOM) concentrations in the form of dissolved organic carbon (DOC) are increasing in surface waters across Europe (7, 8), the US and Canada (5, 9, 10) and the causes for these observations are still under investigation.

In a previous study, positive correlation between seasonal temperature changes and levels of DOC in soils and water was found to be present (11). Climatic changes that induce an increase of temperature produce drought which causes increments of DOC and colour in water. Drought affects the decomposition processes of organic material by aerating ordinarily anaerobic peats increasing DOC release, which during periods of elevated rainfall is then transported to streams draining from organo-mineral soils (12).

Due to climatic changes, future projection studies have concluded that temperature will increase and therefore likely cause an increase on DOC making its removal more problematic during drinking water processes (7, 13-15). This increase of DOC in raw and treated water is interfering with drinking water disinfection processes by increasing the concentrations of disinfection by-products (DBPs). These compounds are formed by the reaction of natural organic carbon in raw water with a disinfectant. In Scotland, only four DBPs are regulated: chloroform ($CHCl_3$), bromoform ($CHBr_3$), dichlorobromomethane ($CHCl_2Br$) and dibromochloromethane ($CHBr_2Cl$) known as trihalomethanes (THMs).

2.2. Disinfection by-products (DBPs)

2.2.1 Trihalomethanes as a disinfection by-product

Due to its low cost, chlorine has been widely used as an oxidant in drinking water disinfection, but chlorine and its various species (e.g. HOCl, ClO^-, Cl_2) have the main disadvantage of reacting with many water matrix components including organic and inorganic substances such iron, nitrate, phenols, pharmaceuticals, hydrocarbons, etc. The chemical reaction between natural organic carbon present in raw water sources and disinfectants has proven to be the origin of DBPs such as trihalomethanes (16, 17). Trihalomethanes (THMs) are represented by the chemical structure of CHX_3 where X can be any or a mixture of chlorine or bromine bonded to the methane including bromoform chloroform, bromodichloromethane and dibromochloromethane.

Chlorine can be used at different points during drinking water treatment, i.e. for pre-chlorination, which is nowadays discouraged, or as primary disinfection and post-treatment adding disinfectant at distribution networks to keep the residual chlorine levels adequate which enables favourable bacteriological control (18). The main disadvantages of chlorination are: pH dependency (leading to formation of various chlorine species) which influences their chemical reactivity, NOM interaction, chemical interaction with numerous organic micro pollutants and formation of bromine by chlorination of bromide–

containing waters (19). During water treatment conditions at the pH range from 6 to 8 the main chlorine species are hypochlorous acid (HOCl) and hypochlorite (ClO^-), since at pH > 4 hydrolysis of Cl_2 is almost complete. HOCl is a stronger oxidant than ClO^- and its formation depends on pH control, its pKa is 7.5, therefore pH control at this value is crucial to maintain an effective and lasting chlorination. However, other chlorine species (Cl_3^- and Cl_2O) can be formed but due to their very low concentrations in solution are not considered. At pH value of 8, THMs and other DBPs such haloacetic acids (HAA) can be formed, therefore chlorination at this pH value should be avoided (20). The chlorination reaction between hypochlorous acid (pK = 7.54) and B (organic or inorganic compounds) is shown in the reactions:

$$\mathrm{HOCl} + \mathrm{B} \rightarrow \text{products}$$
$$\mathrm{HOCl} \leftrightarrow \mathrm{ClO^-} + \mathrm{H^+}, \quad pK_{\mathrm{HOCl},\,25^{0}\mathrm{C}} = 7.54 \qquad (19)$$

In general chlorination reactions are still under much scrutiny due to the chemical complexity of NOM as well as the variable stability of chlorinated compounds (21). Three reactions can be originated by the polar nature of Cl-O bonds ($Cl^{\delta+} \rightarrow OH^{\delta-}$): oxidation; addition to unsaturated bonds and nucleophilic substitution at nucleophilic sites. These reactions will lead to a series of interactions between chlorine species and other compounds in water. For example, oxidation of metals and other inorganics (ammonia, bromide, iodide, nitrate, manganese, iron, etc.) occur via HOCl; addition reactions typically occur at alkaline conditions between HOCl and unsaturated aliphatic compounds (fatty acids, terpenes, chlorohydrin, etc.) and in the case of nucleophilic substitution, it typically occurs in aromatic compounds including aromatic hydrocarbons and phenols (19, 22). Early studies showed that chloroform (120 µg/L) was formed by chlorination of natural water containing 12 mg of organic precursor at pH 7.5 and similar yield of $CHCl_3$

was obtained with humic like substances (23). The oxidation of bromide in water sources yields hypobromous acid and hypobromite ions (HOBr and OBr^-) that are the reactive forms of bromine. Bromide naturally occurs in water sources located nearby coastal areas and chlorination and chloramination of these waters containing bromide cause a shift from chlorinated to brominated DBPs (24). NOM from fulvic acids has also been reported to produce high concentrations of bromoform and dibromoacetic acid after chlorination due to the presence of bromide bonded to fulvic acid (25).

Bromide reactions with NOM

$HOBr/OBr^- + NOM \rightarrow Br - NOM$

$HOBr/OBr^- + NOM \rightarrow NOM_{ox} + Br^-$ (26)

THMs formation has also been linked to the type of disinfection treatment. Goslan et al. (2009) found that THMs formation is increased when chlorination is used whereas lower levels were obtained when chloramination was used. Chloramination takes place after chlorine has been added to the disinfection vessel and ammonia is added subsequently. Chlorination alone takes place first allowing 26 min. contact time for primary disinfection before ammonium is added for best results. However, this contact time allows the formation of DBPs at treatment works. When looking at THM formation in the distribution systems, the addition of chlorine contributes to more THM formation compared to chloramination sites that showed lower THMs concentrations (27, 28).

2.2.2 Health risks and THMs

From the first time that THMs were identified in 1974 by Rook (23), many studies have been performed regarding the toxicity levels of these compounds in drinking water and its relationship with cancer (29-32). More than 600 DBPs have been identified and new emerging compounds are being investigated, but only few of these are regulated by the authorities due to their toxicity levels. Direct contact with these compounds can occur at the point of use of potable water network. Humans are exposed to THMs through oral, dermal contact and by inhalation, for instance when taking showers. These compounds have been related to growth retardation, cancer, spontaneous abortion and congenital cardiac defects, thus, THMs and other DBPs potentially pose a risk of toxicity in the population and therefore it is important to reduce or control their formation in water supplies (33).

Health risks of long term exposure to THMs are important, but there are generally accepted to be smaller in comparison with risks associated with poor disinfection. The risk of illness and death resulting from exposure to pathogens in drinking water is much greater than the risks from disinfectants and DBPs, in other words disinfection should not be compromised by trying to reduce THMs concentrations (13).

The strict regulations adopted in the UK towards THMs are due to the evidence from toxicology and epidemiological studies reviewed by the World Health Organization (WHO) that took place in US and Europe over a 70 year period (34). The results of this report created awareness regarding short and long term exposure of THMs in drinking water. The WHO reported associations between long term exposure of humans to drinking water with low concentrations of THMs and cancer, especially to the bladder than any other type. However, the report is not conclusive in finding evidence of associations between chlorinated DBPs and cardiovascular diseases or adverse pregnancy outcomes for example.

In a recent study, reported data from the HIWATE Project (35) showed that there was no conclusive evidence on THMs concentrations in drinking water monitored in various countries around Europe and adverse pregnancies as initially reported by the WHO in 2004 (34). However, the results were not definitive and more studies are recommended to prevent health risks in the future. More recent in vivo studies where high doses of THMs were incorporated to drinking water, induced eye defects and polyuria in new born rats (36). Other studies, urge attention to the importance of detection and control of other emerging DBPs in drinking water due to their toxicity such nitrosamines or nitrogen containing DBPs (N-DBPs) and haloacetic acids (HAAs). In the case of N-DBPs (haloacetonitriles, halonitromethanes and cyanogen halides) levels of toxicity are much higher than THMs and manifests the need of toxicology studies in vivo that will indicate the risks related to exposure to these compounds (37, 38).

HAAs are currently regulated in the US being 60 µg/L the maximum annual permissible concentration at the consumers tap but they are not yet regulated in the UK despite of recommendations by the WHO (see table 2.2). Researchers in the UK are also advocating to introduce not just HAA but also N-DBPs such nitrosodimethylamine (NDMA) within the drinking water quality regulations to minimize health risks to the population, although there is not much evidence on toxicological studies for these compounds, but the potential hazard still persist (24, 39).

Table 2.1 Disinfection by-product guidelines and regulations (US EPA, 2002; WHO, 2004; SEPA, 2009) with maximum contaminant level

Disinfection By-Product	Guidelines for US Protection Agency Regulations (2002)	World Health Organization Guidelines (2008)	European Union Standards	Scottish Environmental Protection Agency (2009)
****Total Trihalomethanes as ratio***	≤0.8	≤1	≤1	≤1
Total Trihalomethanes	80 µg/L	300 µg/L	100 µg/L	100 µg/L
Chloroform	80µg/L	80 µg/L		
Bromodichloromethane	80µg/L	60 µg/L		
Dibromochloromethane	60µg/L	100 µg/L		
Bromoform	80µg/L	100 µg/L		
Haloacetic acids (HAA5)	60 µg/L	none	none	none
Monochloroacetic acid		70 µg/L	none	none
Dichloroacetic acid	60µg/L	60 µg/L	none	none
Trichloroacetic acid	30µg/L	100 µg/L	none	none
Monobromoacetic acid		None	none	none
Dibromoacetic acid		None	none	none
Bromoacetic acid		None	none	none
Bromate	10 µg/L	10 µg/L	10 µg/L	10 µg/L
Chlorite	80 µg/L	1000 µg/L	none	none
Chlorate		700 µg/L	none	none
Fluoride	1500µg/L	1500 µg/L	1500µg/L	1500µg/L

* The sum of the ratio of the concentration of each compound to its respective guideline value should not exceed 1

2.3 NOM: Precursor of disinfection by-products

2.3.1 NOM Sources

For a comprehensive reduction of THMs precursors such NOM, it is also important to understand hydrological processes such diffusion runoffs and infiltration to investigate carbon release mechanisms from soils to water sources through the catchments, and seasonal changes could be an important factor determining these releases. Therefore, a detailed characterisation of NOM species in water would be crucial to understand its treatability in water treatment works and mechanisms of reaction between NOM and disinfectants. NOM is difficult to characterise due to its complex composition and many possible routes of DBPs formation have been reported involving chemical oxidation of these substances (40, 41). Fresh surface water contains many components of organic and inorganic origin. Inorganic materials present in water can be found in the form of suspended solids, salts, oxides, metal complexes, etc. In the case of organic compounds, the range of molecules is vast: from small molecular weight compounds such amino acids, lipid acids, proteins and carbohydrates to more complex molecules such fulvic and humic acids. The majority of organic carbon in water is found as DOC and only about 10% is in colloidal or particulate form known as COC and POC respectively (40, 41).

Organic carbon has been classified into allochthonous and autochthonous forms according to their sources (40). Allochthonous refers to external sources and carbon that has been introduced into water bodies from soils and plants. The majority of organic carbon in streams, rivers and small lakes is of allochthonous origin. Fresh plant litter decomposes and produces DOC that is transported to surface waters (streams) through leaching.

This leachate typically contains water and carbohydrates or oligomers with a DOC content of 500 mg/L (40). Other components of leachate are smaller molecules of less than 1000 molecular weight (MW) similar to fulvic acids and also coloured, usually small MW organic acids (42). The amount of organic carbon produced by plant degradation from crops and leaves through leaching can be also an important contributor of DOC levels in water bodies. In the case of organic matter from soil origin leached to water, its characteristics depend on the depth at which it formed. For example, in the surface layer (0 to 30cm), carbon sources originate from plant decay caused by microorganisms such fungi and bacteria, metabolising cellulose, lignin, amino acids, carbohydrates and fatty acids. In this layer the organic matter is actively decomposing and carbon content is much higher and at the same time of much younger age (40). However, plant decomposition can occur over a long period of time (in some cases for hundreds of years) and carbon is accumulated and transported deeper within the soil. In deeper layers (more than 100 cm) the organic matter has degraded and humified and is much older.

Carbon 14 analysis had established that the age of soils rich in carbon at deeper layers (>100cm) is between hundreds to thousands of years (14). The organic matter is subsequently absorbed by clay minerals, iron and aluminium oxides and persists as humic and fulvic substances for long periods of time. Humic substances are found in deeper layers of soil than fulvic substances (> 100cm) and are reported to be dated 1400 years old according to radioisotope analysis (14) whereas fulvic substances are only a few hundred years old and found between 30-100cm soil depth.

In the UK, the majority of carbon is found in peatlands of which Scotland comprises a total area of 17,789 Km^2 (43). In peat, decomposition of plants such the *Sphagnum sp*. occurs over long periods of time and this decay allows carbon to accumulate in the form of peat itself. It would be important to understand the interaction between plant degradation and carbon accumulation as well as the complex hydrology of the terrain to understand transport of carbon into water sources. Other allochthonous source of carbon is from human input. Agricultural and industrial activities have a considerable input of carbon as well as other contaminants. Unmanaged livestock grazing contribute to a high organic matter content introduced to water sources through rainfall. The removal of forest land to be converted into grassland also alters the carbon balance in the area. Burning of grassland and peatland contribute to release of inorganic carbon into the atmosphere (44).

Autochthonous organic carbon originates inside large aquatic systems such as lakes and it derives from algae and microorganism degradation. Lakes that are fed by rivers contain organic matter of allochthonous origin but in smaller amounts. The larger the lake the less allochthonous organic carbon is present as these substances dilute in large water volumes. Therefore autochthonous organic carbon is most commonly found in large rivers and lakes. Other attributes such depth and temperature within lakes also have a direct effect in the proliferation of algae and bacteria (45).

Carbon from algae or algogenic organic matter (AOM) is released from cell lysis or intracellular excretions in the forms of glycolic acids, amino acids, sterols, pigments, polysaccharides, vitamins, polymeric organic acids and fatty acids (40), but polysaccharides constitute 90% of the excreted compounds (46, 47). Polysaccharides are a type of carbohydrates that are easily hydrolysed into sugars by enzymatic bacterial reactions. Carbohydrate concentrations correlate to algal population but they also decrease with depth as algal population decreases at greater depth due to reduction of nutrients, light and temperature (40).

The increase of algal populations in lakes or reservoirs have a negative effect in coagulation and flocculation processes during drinking water treatment and it causes membrane fouling (48), but it depends in the type of algae, physiological and environmental conditions where these organisms develop. AOM then constitutes an important percentage of the hydrophilic character of NOM (57%) and its removal is facilitated at negative zeta potential value (-15mV) and low specific ultraviolet absorbance (49). The loading of autochthonous NOM in a water supply can be controlled by reducing algal growth. Algal populations thrive in phosphorous and nitrogen rich conditions and the sources of these compounds are mainly from human input (50). Algae also proliferate during summer when temperatures are higher. A way to control the nutrient concentrations would be by minimising and limiting the influx of waste streams aided by catchment management and better wastewater treatment.

Microbial populations in water sources are vast and difficult to isolate. Characteristics of the water sources such as size, temperature and location influence the growth and development of the microbiological population (42). Many of these species are harmless and ubiquitous in water bodies. This is the case of cyanobacteria and planktonic species, but some pathogen microorganisms are introduced by hydrological interaction of contaminated land in un-managed catchment areas with large livestock population (51).

Microorganism that are common pathogens related to waterborne diseases include: viruses, enteric protozoan (*Cryptosporidium* and *Gardia lamblia*) and enteric bacteria such *Salmonella* spp., *Shigella* spp. and *Escherichia coli* (52). These bacteria are subject to strict regulation by the drinking water regulators and the World Health Organisation (WHO) due to the health risks that they pose to the populations (34).

In the case of algal and heterotrophic bacterial populations, these could live in symbiosis in water bodies where algae excrete carbon in the form of DOC and bacteria will consume it (40). Humic substances in water favour the development of planktonic communities by providing the necessary nutrients and energy, but at the same time some species can be harmed or stressed due to the low molecular masses of the building blocks of humic substances that can pass across their bio-membrane (53, 54). An interesting question therefore arises: Could it be possible to say that excess of organic matter in the form of humic substances can have an effect to the micro- ecology in water sources?

2.3.2 Factors affecting NOM in water sources

a) NOM in lochs, rivers and streams

NOM comprises a large number of substances that also differ largely in size that can range between 0.45um to 1nm (colloidal range) and at the same time this composition can vary according to the source type and location. For example, NOM can be found in the form of DOC concentrations of up to 1000 mg/L in ground water associated with oil-fields to very low levels found in rock aquifers of only 0.5 mg/L. Interstitial waters contain DOC ranging from 2 to 30 mg/L, whereas river water DOC can vary depending on many factors such as climate, vegetation and season being most common in the range from 2 to 5 mg/L. However, this concentration can increase up to 25 mg/L (or more) if the river has drained swamps or bogs (40).

Lochs and reservoirs represent an important source of fresh water for Scotland. According to the Drinking Water Quality Regulator, Scotland has 243 lochs and reservoirs, 198 river sources and 84 spring and boreholes (55). But, from all these water bodies the most important are lochs and reservoirs. NOM of autochthonous origin in lochs depends on algal populations, oxygen, phosphorus and nitrogen concentration which define their trophic level.

Thus, oligotrophic and mesotrophic lakes contain carbon as DOC between 1 to 4 mg/L whereas dystrophic lakes have the highest range between 20-50 mg/L. These lakes are related to bogs and marshes and contain yellow organic acids (fulvic acids). Although, the algal productivity in a lake is an important source of carbon, the depth layers (stratified zones) also contribute to variation in the chemical composition due to density and temperature. Higher amounts of NOM will be found in the upper layers where temperature is higher and light favours algal photosynthesis and bacterial development whereas the lower layers at very low temperatures will show lower concentrations of carbon and other nutrients. This environment will affect the chemistry of the Lochs, the top layer being in constant contact with the atmosphere and well oxygenated whereas the deeper layers are sometimes anoxic (40).

At specific conditions, temperature variations due to seasonal changes cause lakes to overturn (dimictic lakes) where the bottom water containing organic acids and methane from the sediment at low temperatures (1-4 °C) is carried toward the surface where temperatures are much higher (20 °C) and likewise oxygenated water is carried to the bottom making chemical composition in these layers change (40). In lakes, 90% of the carbon is found as DOC and 10% is POC (available at www.snh.org.uk).

b) Climate change and hydrological pathways

Climatic changes that are taking place not just in Europe and UK but also around the world are having an impact in the chemistry of water and therefore an increase of carbon as DOC (3, 9, 12, 13, 56-58). Changes in temperature that cause events such as heavy rainfall and drought alter the hydrological cycle and modify the transport of nutrients and other compounds from soil to water (40). The increase in freshwater DOC indicates depletion of terrestrial carbon stores by the influence of temperature increase, rainfall and CO_2 release. A positive relationship between temperature increments and DOC levels was found in peat core warming experiments and rainfall events also induce DOC increments in streams draining from organo-mineral soils. Also high concentrations of DOC have been associated with long periods of rainfall through stream flow deposition (12). However, the majority of DOC increases have been related to depletion of SO_2 pollution and related soil acidification but these mechanisms require further investigation (12). Sulphate deposition decreases in soils is due to acidity reduction in soils and in consequence increases DOC in surface waters (59).

In a different experiment, deposition of nitrate in soils (NO_3^-) in a forested area in the US was shown to increase leachate DOC in lakes (58). This experiment showed that nitrogen deposition has a role on DOC export from soils as well but mechanisms have not yet been elucidated. Due to the chemical composition of the soil in Scotland (peaty and high in carbon content) research is taking place to evaluate whether these climatic events are the cause of the release of carbon from soil to water bodies and/or into the atmosphere (4, 5).

Many studies in the UK are measuring the 'fluvial flux' of carbon from a peatland that occur through DOC, POC, dissolved inorganic carbon and dissolved CO_2 (5, 14, 60). However, due to climatic changes combined with extraction, drainage and burning, peatlands are no longer storing carbon but releasing it to the atmosphere and into water in the forms of CO_2 and CH_4 and DOC (8, 44, 61, 62).

In Scotland, wetlands are mostly of two types: those that receive water from soil, rock and rainfall such as fens and those that receive all water from rainfall such as raised bogs (63). Bogs and fens are peatlands that differ in the type of water input: bogs depend on precipitation whereas fens depend on groundwater (61). Fens tend to be basic and supplied by larger amounts of water with DOC concentrations range from 5 to 15 mg/L. Bogs, in contrast contain between 30 to 400 mg/L DOC (40) and are high in organic acid content due to plant decomposition which provides the characteristic yellow colour (pH<4). Continuous rainfall during spring and summer introduce water into the peatlands and during winter the already saturated peatlands will cause runoffs. Rainfall thus causes flooding when the peatlands are saturated. The amount of carbon exported from peatlands also depends on how water flows through it. These hydrological processes vary from catchment to catchment due to soil composition, vegetation, land use and seasonal changes (61, 64). Infiltration (through macro pores such as root channels) and diffusion processes produced by runoffs contribute to the release of carbon as DOC from peatland into underground waters and streams through soil pipes networks (65). Particulate organic carbon (POC) is also transported within peatlands and released into rivers during rainfall (66). Thus, organic carbon leached into water systems will change its quality in terms of colour, taste, pH balance and metal complexation properties (61).

c) Rainfall, runoff and land use

Rainfall events such the one recorded during the months of April to September 2012, affecting towns and agriculture had a great impact not just in England and Wales but in the whole of the United Kingdom (available data at www.gov.uk/goverment/statistics/uk-floods). Scotland has also experienced climatic changes and these circumstances are being addressed by the government. In January 2012, the Government issued the Climate Change Risk Assessment where it states that adaptability measurements have to be applied to the inevitable changes in the climate that have an impact in the economy, ecosystems, food, water, infrastructure, health and trade in the whole country (67). Peatland areas have been affected by drainage, afforestation, extraction and agriculture (44) and the government has promoted restoration of these areas to minimise the carbon release through a more sustainable catchment management especially around peat deposits (1). Positive correlations between DOC and colour in upland catchments have been found in previous studies (64). This coloration is typically due to the presence of fulvic acids that provide discoloration to streams and rivers, hence highly coloured surface water can be transported by rainfall and runoff.

Climatic events and the direct/indirect human intervention have an effect in the hydrology of peatland. There are structural (growth of soil pipes) and chemical changes (oxygen increase enhances mineralization of carbon-bound nitrogen, phosphorous and sulphur) involved. Global increase in temperature enhances evapotranspiration of CO_2 and CH_4 (10, 61), draught, rainfall and runoff events. In the case of peatlands, the amount of stored carbon is quite vast and decomposition of just 2mm of peat can yield 1.6 billion tonnes of CO_2 by oxidation per year (61).

Another event caused by the rise of temperature is the decrease of water table depth in peatlands where the water levels decrease and expose organic soils to the atmosphere accelerating the oxidative processes of the organic material (58). At these aerobic conditions, the microbial phenol oxidation will be activated and will induce decomposition of peat and phenolic compounds from plants such lignin, cutin and tannin (68). Hydrology then, plays an important part in the transport of organic matter fractions into water bodies.

Humic substances contribute to the increase of discoloration and transport of other inorganic materials which have been reported to be directly related to increased precipitation. The excess rainfall will consequently cause runoff events as well as potentially transporting natural organic matter and other contaminants of human origin (pesticides, herbicides, industrial chemicals, oils, etc.) through the catchment area into surface waters if not well managed.

In Scotland, soil type is defined by topography, climate, temperature and rainfall. In the uplands, annual rainfall is approximately 2000 mm and the majority of this area is used for low intensity sheep-grazing and the soil is of peaty nature whereas the Eastern Coast and Central part of Scotland are the agricultural areas with lower annual average rainfall of approximately 1000 mm (69). These particular characteristics may also help to identify areas where high natural organic matter inputs will induce THM formation in water treatment works that are located in nearby areas.

Studies related to climate change explain discrepancies in whether natural organic matter in the form of DOC increase or decrease during rainfall and runoff. During drought DOC decreases in river catchments (12), but considers that drought increases aeration and therefore DOC levels in a peatland catchment. Reduced levels in SO_4^{2-} contribute to depletion of DOC during dry seasons. Overall, climate changes such increase of temperature will influence excess or depletion of rainfall and runoff and consequently will have a direct impact in transport of organic matter to aquatic bodies (60).

In a recent climate simulation experiments where draught, rainfall and runoff were monitored to better understand DOC release from peat soil and litter, it was demonstrated that short term draught events will have greater impact rather than long term temperature increase (11). These experiments also showed that DOC release from vegetation litter is greater than from peat as corroborated by identifying its carbon age as being less than 40 years as well as the difficulty to remove carbon by coagulation which was more challenging indicating its hydrophilic nature particular to plant decay (10).

Another driver of natural organic matter contribution to water resources is land use. Excessive land use and deforestation reduce carbon sequestration by vegetation and fires release it to the atmosphere as CO_2. The dynamics of DOC varies by changing organic matter introduction, substrate quality and microbiological degradation pathways (58). The soil carbon declines after long term conversion of pasture lands to arable lands, drainage, tourism, overgrazing and wildfire (62).

Carbon losses in many areas around the UK and especially in Scotland have been affected by land use changes which also shows a positive relationship between total NO_3 leaching and increase of DOC in lochs due to wrongly managed land use (70). Forestry is also a driver for increase in pH of surface waters that leads to denitrification of soils and carbon losses (71, 72).

d) Catchment nature and mineralogy

Carbon is not only stored in soils but also in the vegetation around the catchment. Forest and woodlands contain carbon stock in the UK in an estimated amount of 113.8 ± 25.6 Tg (63). Plant matter is the most important source of carbon input to soils. The total amount of soil carbon in the UK is of 9.8 billion of tonnes from which 6.8 billion are in Scotland and peatlands (upland blanket, raised bogs and fen peats) and constitute a total 4.5 billion tonnes. Distribution of soil types in Scotland are shown in Fig. 2.1 showing high mineral soils in the midland region of Scotland whereas the Highlands and Southern areas are dominated by peaty soils especially in the west.

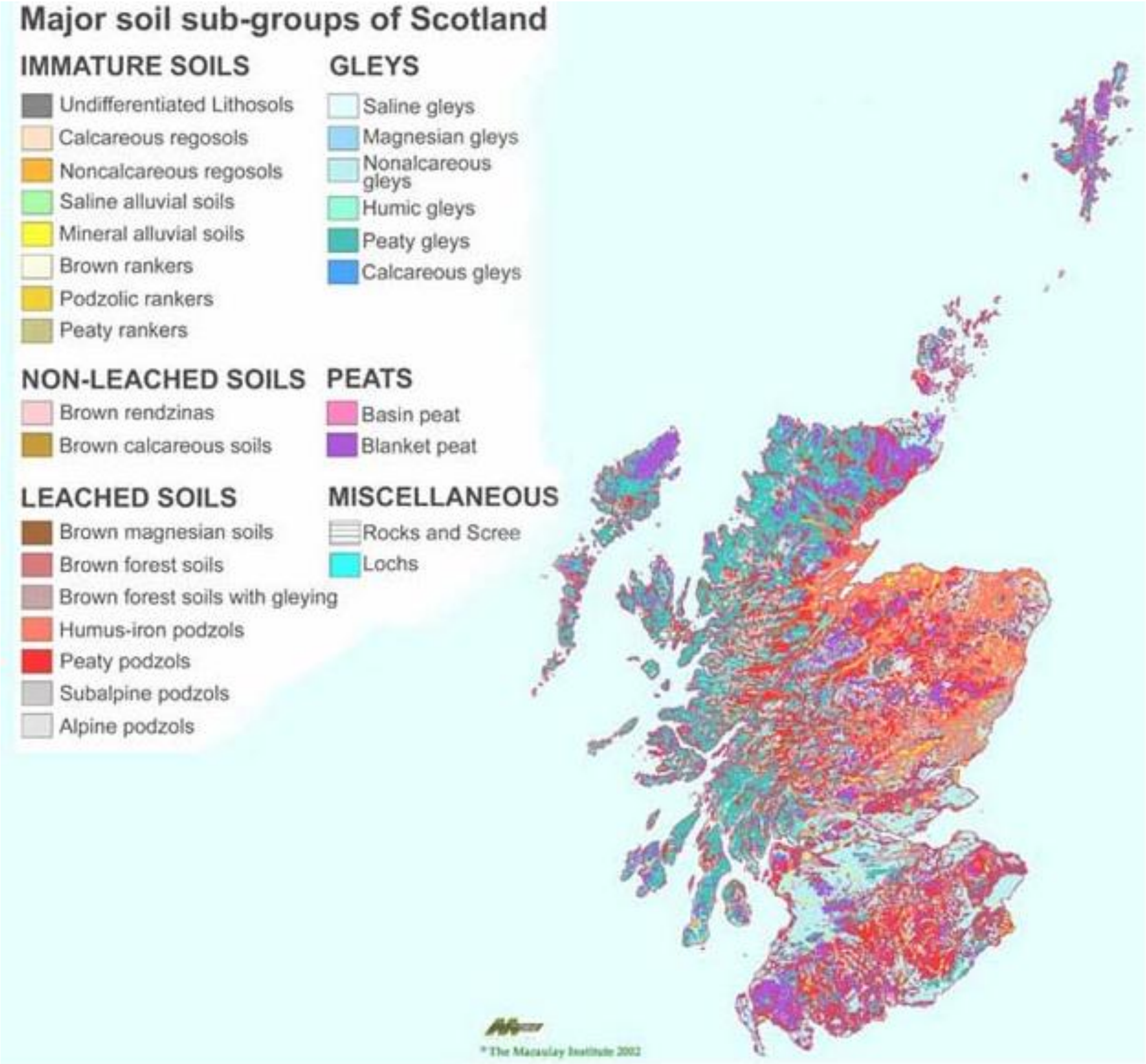


Figure 2.1 Major soil groups of Scotland (extracted from Scotland's Soil Resources,The Macaulay Institute, 2002)

Negative effects in land use such as conversion of grassland and woodlands to crops are evident by soil carbon losses and alteration of ecosystems. Climate change effects such as a rise in temperature will be in the long term, but the most vulnerable type of soils to be affected are of peaty origin, as any reduction on soil humidity with drought can release significant amounts of soil carbon (71). An appropriate land management and reforestation programs could be implemented by more strict land use policies to protect carbon stocks. Interactions of natural organic matter as DOC with metals can be also altered by climatic changes. DOC binds to metals by organic complexation reactions and it is regulated by pH. Acidity in surface water enhances photochemical degradation of DOC and as a result it releases bound metals such Fe and Al and nutrients such P, S and N. Metals are then released into their toxic forms such Cu^{2+} which is in particular toxic to phytoplankton and algae (73) modifying then the local ecosystem whereas the release of P and N will generate trophic conditions by excessive nutrient production including CO_2 evasion. At neutral and high pH, metals will remain bound to DOC and will sediment in the form of POC, thus the release of nutrients will be kept balanced.

e) Natural sources of bromide and chloride

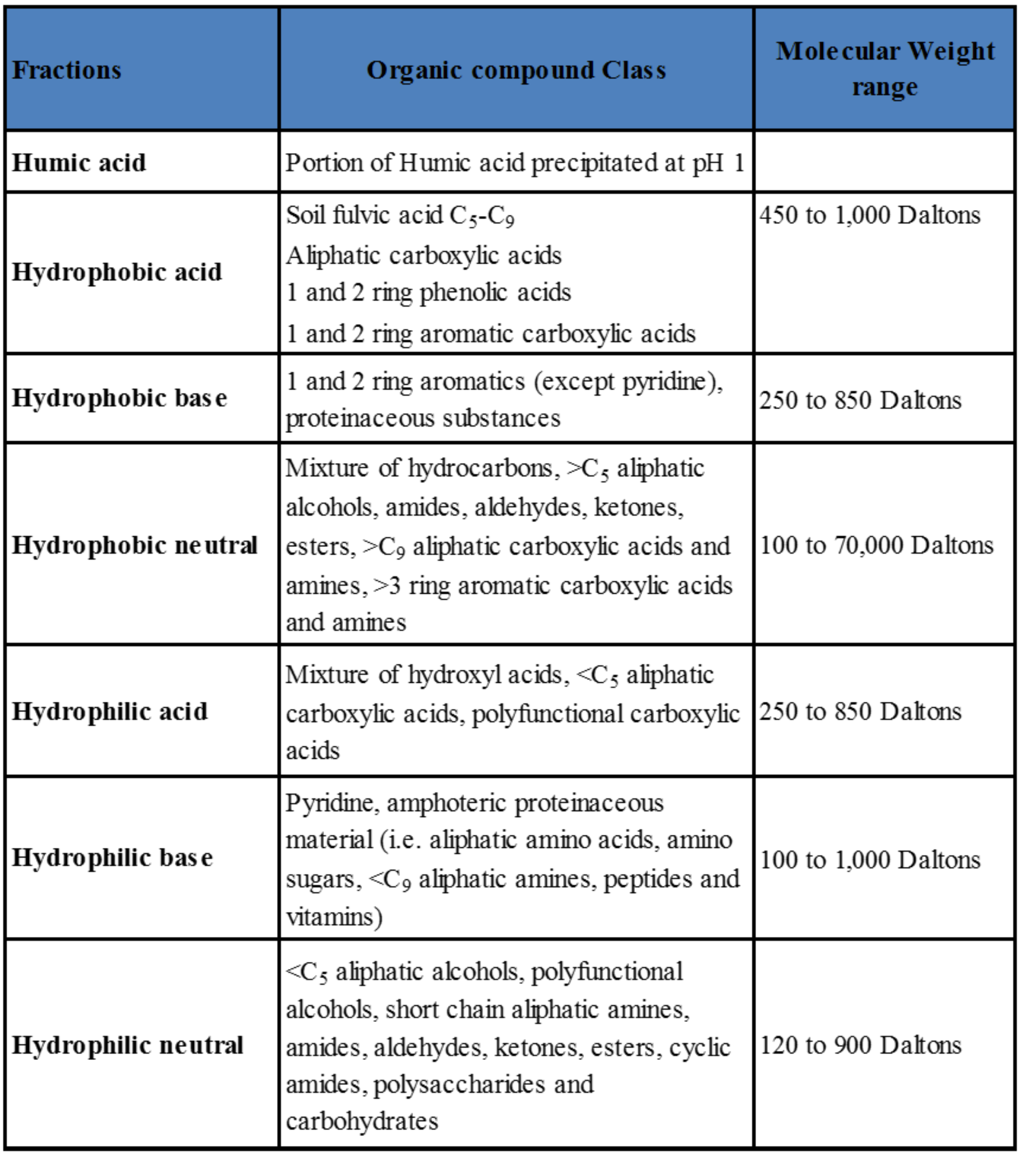
Bromide (Br^-) and chloride (Cl^-) are as ubiquitous in nature as NOM and can be found in minerals such halides, oxides and hydroxides. Chloride concentrations in sea water can be as high as 19,000 mg/L (74) and surface and groundwater can be affected by estuarine infiltration or coastal location with concentrations for surface water up to 90 mg/L and boreholes with 250 mg/L (74). Bromide concentrations in seawater range from 65-71 mg/L and high concentrations have also been found in soils and aquifers located in coastal areas. Intrusion from seawater, dissolution of geological sources and human intervention (75) contribute to the increase of halogen compounds in water resources. Island ground water in Scotland for example shows elevated concentrations of chloride (East Lothian, Arbroath, Morayshire and Northwest of Fife) with an average of 65 mg/L as compared to the inland areas (25 mg/L) and uplands (10 mg/L). Iodide and bromide in raw water sources will form iodated and brominated DBPs which have been reported to be more toxic than chlorinated analogous (76). A study performed in seven sites around Scotland, found concentrations of bromide range from 32 - 259 µg/L where variability can be attributed to seasonal changes. In the case of iodide, the concentrations found for these seven sites range from 1.5 - 12 µg/L (67). Organic halogens present in surface water samples from lakes, rivers and bogs at the south of the Sweden for example showed concentrations between 10-100 µg/L where a direct a relationship between humic substances and naturally occurring organo-halogen compounds was found (77). More recent studies stated that natural organo-halogen compounds have been found in plants that undergo degradation by halo peroxidase enzymes (chloro and bromo peroxidases) in bromination reactions on the forest floor (78) which can also contribute to the increase of bromide in soils. Bromide is subsequently transported bound to humic substances from surface water to drinking water processes and transformed by oxidation to toxic forms. Bromide (Br^-) can be oxidised to $OHBr^-$, OBr^- and Br_2 by OH radicals present during ozonation, chlorination or chloramination of drinking water (21). The resulting $BrO^\cdot$ radical will lead to the formation of bromite BrO_2^- that can be further oxidised to bromate BrO_3^- which is also a highly toxic and regulated DBP.

Similar mechanism occur for $HOCl^-$ and OCl^-, where the reaction between bromide and chlorine favours the formation of $OHBr^-$ at a very fast rate (1.5×10^3 $Mol^{-1}s^{-1}$) and in presence of NOM it will yield more brominated than chlorinated THMs (76), thus naturally occurring halogens such bromide present in surface waters can also lead to the formation of brominated THM species (19, 25, 79). Successful bromide removal (including other halides such as F, Cl and I) has been performed in a range of 93%-99% by using aromatic polyamide reverse osmosis membranes for example (76).

2.2.3 NOM Classification

The total concentration of NOM is generally measured as total organic carbon (TOC) or dissolved organic carbon (DOC) and particulate natural organic matter (POC) by using a

0.45 µm membrane to separate POC from DOC. The portion that passes through the membrane contains DOC and what remains in the membrane is POC. But, these straight forward analyses do not differentiate between size and structures of the specific compounds that constitute NOM. Some substances behave similarly to others, thus there is a need to classify them according to their reactivity. The main fractions of NOM are shown in table 2.1 and the most common analytical techniques to differentiate between fractions and detection of chemical structures are explained below.



Fractions	**Organic compound Class**	**Molecular Weight range**
Humic acid	Portion of Humic acid precipitated at pH 1	
Hydrophobic acid	Soil fulvic acid C_5-C_9 Aliphatic carboxylic acids 1 and 2 ring phenolic acids 1 and 2 ring aromatic carboxylic acids	450 to 1,000 Daltons
Hydrophobic base	1 and 2 ring aromatics (except pyridine), proteinaceous substances	250 to 850 Daltons
Hydrophobic neutral	Mixture of hydrocarbons, $>C_5$ aliphatic alcohols, amides, aldehydes, ketones, esters, $>C_9$ aliphatic carboxylic acids and amines, >3 ring aromatic carboxylic acids and amines	100 to 70,000 Daltons
Hydrophilic acid	Mixture of hydroxyl acids, $<C_5$ aliphatic carboxylic acids, polyfunctional carboxylic acids	250 to 850 Daltons
Hydrophilic base	Pyridine, amphoteric proteinaceous material (i.e. aliphatic amino acids, amino sugars, $<C_9$ aliphatic amines, peptides and vitamins)	100 to 1,000 Daltons
Hydrophilic neutral	$<C_5$ aliphatic alcohols, polyfunctional alcohols, short chain aliphatic amines, amides, aldehydes, ketones, esters, cyclic amides, polysaccharides and carbohydrates	120 to 900 Daltons

Table 2.2 Classification of Dissolved Organic Carbon Fractionation (Adapted from Matilainen & Sillanpaa, 2010)

2.2.4 NOM characterisation

The composition of NOM is varied and contains a wide range of chemical substances that are either suspended or in dissolved form. The following pages will briefly describe the most available methods that aid in identifying NOM fractions, functional groups and molecular structures.

a) Total organic carbon (TOC)/dissolved organic carbon (DOC)

NOM is typically measured in laboratories as total organic carbon (TOC) that includes the sum of the particulate and dissolved organic carbon forms. It usually involves the use of 0.45 µm filter where the filtrate contains the DOC portion and the particulate part remains in the filter (27). TOC analysers are currently used to measure TOC using an oxidant reagent and infrared spectroscopy enabling fast and high through put analyses.

b) Ultraviolet (UV) absorbance

NOM can be measured by the absorbance response at specific wavelengths which are typically 220nm and 254nm at the UV absorbance side of the spectrum and the operation of the instrument is based on the Beer Lambert Law were concentration of the analyte can be measured according to its absorbance at a specific wavelength. Absorbance at any wavelength between 220 to 280nm is the most adequate for NOM measurements. For example absorbance at 220nm is associated to carboxylic and aromatic chromophores but also strong absorbances have been found for anions such bromide, nitrite and nitrate and at 254nm only aromatic groups can be detected (80).

c) Specific ultraviolet absorbance (SUVA)

This is a common measurement at water treatment works and it represents the ratio between the absorbance at 254 nm by a given sample and the DOC concentration and it is represented by L mg^{-1} m^{-1} (81). This ratio defines the nature of NOM in terms of its hydrophilic and hydrophobic fractions. SUVA ratios above 4 indicate hydrophobic material especially aromatic compounds and SUVA values below 3 indicate hydrophilic material (17). SUVA can be associated with charge or zeta potential (mV) and treatability for NOM removal by coagulation. In waters with low anionic charge or neutral, coagulation will have no effect in their removal and will be considered as residual NOM (21, 82). The high SUVA values and high responses for specific hydrophobic fractions such phenols has been shown positively correlated with THM potential formation (83).

d) Fluorescence

This technique is more sensitive and selective than UV-vis methods (84, 85) and it is widely used for estimating biodegradable NOM due to strong correlations between fluorescence and biological oxygen demand (56). A new technique: 3-D fluorescence excitation-emission matrix EMM (85-87) has been developed to visualise fluorophores covering excitation and emission ranges from 200nm to 500nm. Very specific emission and excitation wavelengths values will provide information on chemical groups (80). Typical raw water will contain two main fluorescence peaks as humic and protein maxima; and also three peaks specifically for tryptophan, fulvic and humic like fluorophores. Extensive study by Chen et al. used fluorescence to identify aromatic double bonds and methoxyl functional groups in soil humic samples; phenolic groups in hydrophilic fractions and aliphatic compounds rich in oxygen bonds as OH corresponding to sugars (88).

e) Biological test

Two tests measure organic carbon based on microbial interaction: 1) Biodegradable dissolved organic carbon (BDOC) measures the amount of DOC that is consumed by heterotrophic microorganisms and 2) assimilable organic carbon (AOC) is constituted by degradable low molecular weight compounds which are very difficult to remove during treatment and consequently transported to distribution systems (89).

f) Fractionation with resins

This method differentiates hydrophobic and hydrophilic character of NOM and it can be performed by NOM adsorption to Amberlite XAD resins (90, 91). NOM is separated into four fractions: very hydrophobic acids, slightly hydrophobic acids, charged and neutral hydrophilic compounds (56). Hydrophilic fractions do not absorb into these resins, only the hydrophobic fractions (compounds of humic origin). The XAD method involves the use of XAD-8 resins for hydrophobic compounds of large molecular weight and XAD-4 for weak hydrophobic acid fractions (91, 92). Although, these methods are very common and widely used, they have disadvantages due to pH alterations during fractionation, contamination from resin bleeding, irreversible adsorption of NOM compounds and size exclusion effects and most importantly they are time consuming (56).

g) Fractionation with Size Exclusion Chromatography (SEC)

In this method, the fractionation is based on molecular size where larger molecules are retained for shorter times. SEC is used as a hyphenated technique with high performance liquid chromatography (HPSEC) which has improved the separation by increasing specificity (93, 94). Numerous detectors have been also used in combination with HPSEC that add variability to this technique such fluorescence and UV absorbance (95). This technique has the disadvantage that it can only detect compounds at a specific wavelength. However, by using hyphenated instrumentation, detection can be enhanced. For example by using a HPSEC with a mass spectrometer, a UV-Vis and fluorimeter detectors, selective quantitative and qualitative separation can be achieved as well as obtaining molecular weight information. The addition of substances that mimic humic acid chemical structure such polystyrene sulphonate or polyethylene glycol can aid to determine molecular weight distributions. Fourier transform infrared analysis has also been used coupled with electron spray ionisation (ESI) mass spectrometry (MS) to detect iodine interactions with natural organic matter (96).

h) Elemental composition of NOM

These methods are used to calculate atomic ratios such O/C, H/C and N/C and to aid to determine chemical structure of NOM fractions which have been previously separated through SEC or resins. These include: gas and liquid chromatography separation techniques complemented with single and triple quadrupoles mass spectrometers (97-99); pyrolysis gas chromatography mass spectrometry (py-GC-MS) (80); micro scale sealed vessel pyrolysis mass spectrometry MSSV-py-MS (100); nuclear magnetic resonance (NMR) including ^{1}H, ^{13}C, ^{15}N and ^{31}P experiments widely used for structural carbon, nitrogen and phosphorous elucidation in NOM fractions for both liquid and solid state samples (80, 101). One of the latest applications of NMR combines the use of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry to characterise insoluble fractions of NOM (102); Fourier transform infrared analysis (FTIR) is used to determine functional groups (80) and coupled with mass spectrometry (FTIR-MS) it can simultaneously determine functional groups and masses, as can the most recent FTICR-

MS application to determine molecular composition that uses an ion cyclotron resonance devise coupled to the mass spectrometer (22, 97).

2.4. Current strategies to minimize THMs formation

In 2010, the Drinking Water Inspectorate amended regulation 26 which applies to England and Wales and introduces the DBP rule (available at www.dwi.gov.uk). This rule states that DBPs should be kept as low as possible without compromising disinfection and this should be done by identifying and removing DBPs precursors. The most conventional strategies to remove NOM have been sedimentation, GAC, sand filtration, ion exchange and coagulation.

Although, these processes have been successful in eliminating a high percentage of NOM especially hydrophobic fractions, the problem of DBPs formation during disinfection still remains an issue. Extensive studies have reported new technologies applied at laboratory scale to eliminate NOM. Some of these applications are nano-membranes and advanced oxidation processes which had proven to reduce up to 95% DBPs formation in drinking water systems.

2.4.1 Water Treatment Processes for NOM removal

a) Coagulation

At the preliminary stages of drinking water treatments, natural sedimentation aids to reduce suspended particles being transported towards drinking treatment works as well as reduction of bacterial activity due to the action of natural UV light. Larger humic particulate substances can be deposited at the bottom of lakes and reservoirs for example. The next stage of most drinking treatment processes is coagulation and flocculation.

Factors such pH, temperature and charge densities have shown also an important effect on coagulation by choosing the correct type and amount of coagulant (17, 21) and when all these factors are taking into consideration the process is called enhanced coagulation. Optimum pH values for coagulation are between 4.5 and 6 (48, 103) otherwise it requires addition of lime or soda ash. Ferric sulphate ($FeSO_4$) and aluminium sulphate or alum ($Al_2(SO_4)_3.14H_2O$) are commonly used coagulants in the UK and proven to be the most adequate for NOM removal (48). Addition of the right coagulant depends on physico-chemical characteristics of surface water and consequently will affect NOM removal efficiencies. For example the use of alum is adequate for alkaline waters which will induce NOM removal whereas the use of iron based coagulants favours NOM removal at low pH (104).

During coagulation positively charged chemicals are added to raw water usually ferric and/or aluminium salts in the forms of chlorides and sulphates that hydrolyse and neutralize the negatively charged suspended or dissolved particles in water by binding them together (27). The larger and heavier bound particles or flocs start to sediment and after filtration it can be removed as particulate NOM.

High MW hydrophobic organic substances (humic and fulvic acids) constitute 75% of NOM and this major source of DBPs (including THMs and HAAs) can be removed by coagulation. Hydrophilic fractions can be also removed but to a lesser extent between 14% and 17% (21). During many years, the use of sedimentation, coagulation, flocculation and settling followed by filtration was considered as ‘conventional coagulation’ as it was widely used in treatment works around the world.

Coagulation removes the hydrophobic and large MW fractions of NOM at the right pH range and temperature, but if water sources precursors show hydrophilic or neutral character, it will have little effect. This issue is being considered by researchers to search for alternatives coagulants to remove NOM or other alternatives solutions. Hydrophobic fractions have been also related to specific ultraviolet absorbance (SUVA), when raw waters show high SUVA values of 4 L mg^{-1} m^{-1} facilitate the treatability by coagulation.

Another important characteristic of water is its electrostatic charge or zeta potential which indicate the amount of charged groups such carboxylic acids and oxides (27). This parameter is pH dependant and very useful to determine the adequate amount of coagulant. The higher the zeta potential value (mV) the more difficult to remove are NOM and algae for which an optimum value range is -10 mV to +5 mV to successfully remove NOM and -12mV to +12mV to remove algal material (46). A narrower window for NOM removal between -10 mV to +3 mV at acidic conditions pH 4.5-6 has also proven to be successful (21).

A new technology is the use of graphene oxide as one of the newest coagulants to remove NOM (105). The advantages of this nano compound are its large surface area; large number of activated functional groups and affinity for aromatic double bonds compounds and hydrogen bonding; and its potential biodegradability by enzymatic reactions. However, environmental repercussions of sludge disposal containing nanoparticles has not been investigated yet and it may be an issue as well as high costs of the technology if applied at industrial scale (105). Other new applications that proved to remove DOC include Zirconium coagulants (106) and poly-aluminium chloride chitosan composites (107).

b) Activated Carbon (AC)

Many materials have been reported to be used for the production of activated carbon including coal, wood or coconut shells (17). The most used form of activated carbon in the water industry is granular activated carbon (GAC). This adsorbent is used packed as a filter bed which has been used to remove most of the hydrophobic fraction of NOM especially large MW compounds whilst non humic and low MW fractions tend to pass through the filter. Adsorption is faster when carbon particles are smaller (108). Usually, GAC is applied after coagulation-filtration and sedimentation stages and before disinfection. GAC before membrane filtration minimizes membrane fouling and removes NOM fractions. A downside of GAC systems is the need for regeneration of the carbon bed over time (108).

c) Ion exchange

The principle behind ion exchange is the interaction between covalently charged (positive or negatively) functional groups in a polymeric resin with charged substances in water. Ion exchange columns or vessels operate a set pressure that hold the resins and facilitate rapid adsorption. Resins can be regenerated periodically to improve efficiency of removal usually with salt solutions. In the recent years, MIEX (magnetic ion exchange) resins have been used for the efficient removal of hydrophobic fractions of NOM, UV absorbing compounds, colour and as alternative to the use of coagulants (109). In this case, the resin allows ion exchange with raw water after rapid clarification and recycled back to then be regenerated in brine (110). Removal efficiencies of 80% for hydrophobic fractions of NOM with molecular weight < 1,000 Da have been reported (103). But, MIEX showed even higher removal efficiencies for transphilic fractions of NOM than the hydrophobic fractions (70-89% removal efficiency). Removal of fractions with molecular weight between 5,000 - 10,000 Da showed 95% efficiency. A particular advantage about MIEX resins is that it can also remove bromide, although removal can be affected by alkalinity (104). Ion exchange is most effective for the removal of hydrophobic fractions of NOM and low molecular weight anionic material.

d) Membranes technologies to eliminate NOM

Four types of membranes are currently used for the removal of NOM: ultrafiltration (UF), microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) which mainly differ in pore size. MF and UF are considered as low pressure membrane filters where pressure will enable size exclusion and any particle or molecules larger than the pores will be retained allowing only water and smaller molecules to pass through the membrane.

UF can separate bacteria, algae, viruses, cysts, polar compounds and NOM with separation range between 10^{-5} to 10^{-7} m. MF can separate particulates, bacteria, cysts, algae, clays and colloids with a separation range between 10^{-5} to 10^{-8} m (27). Efficacies for removal of NOM using membranes has showed that ultrafiltration is limited for the removal of NOM at 44% efficiency where the membrane cut off was 60,000 Da (21). A recent study at laboratory scale mentions the use of Ag-TiO_2 and hydroxiapiate composite coupled with photocatalysis for microfiltration to oxidise microorganisms and to degrade NOM simultaneously (111).

TiO_2 has shown promising photocatalytic and oxidative properties that degrade organic contaminants including humic acid, pesticides, herbicides and halophenols; and in combination with noble metals such silver has shown bactericidal properties (112, 113). This promising technology combines the use of microfiltration with advance oxidative process such photocatalysis. Another similar technology, but applied to UF has shown similar results on excellent NOM removals up to 95% and minimization of membrane fouling (114).

NF has shown higher NOM removal efficiencies than conventional MF and UF but it uses high pressure due to the small pore size in the membrane. The molecular weight cut off (MWCO) for these membranes can be as low as 100 Da with removal of DOC up to 99%. NF also favours the removal of hydrophilic NOM fractions more so than hydrophobic due to columbic repulsion between acids and the membrane surface (104). One of the main disadvantages of NF is fouling by algae, NOM and some inorganics such as calcium and manganese which increases costs by frequent cleaning. Usually pre-treatment is required to remove turbidity, iron and manganese and there are plants that use the combination of UF and NF to successfully reduce DOC.

Although this process has proven to be the most effective in removing DOC fractions, the costs implicated in the maintenance and operation of these systems is elevated (115). Innovative applications of NF are the use of carbon nanotubes. These nanoparticles can be engineered on their surfaces or embedded into the matrices to specifically bind to contaminants or catalyse degradation reactions. Similar to UF and MF, some examples include the incorporation of TiO_2 to degrade organic materials and microorganisms (116). Reverse osmosis (RO) membranes can also retain some hardness in the permeate making it a desirable property for many municipal applications, since this makes the water less aggressive to distribution piping materials, but this technology is very costly.

e) Oxidation Processes

Ozonation is one of the strongest oxidant gases used in drinking water and constitutes one of the most important oxidative processes. There are a reported 1000 Ozone plants around the world and the numbers will continue to increase (117). The mechanism of reaction involves the introduction of O_3 gas into water to produce hydroxyl radicals (·OH) which are highly reactive and non-selective meaning that will react with any substance in water. OH radical is considered as the most oxidative substance known (118).

Doses of ozone have shown some implication in the removal of DOC. Naturally, NOM and ozone react to produce OH radicals, but for optimal oxidation higher doses are required. For example by adding ozone doses of 0.85 mg mg DOC^{-1} removals of DOC, UV and THM were 5%, 47% and 6% respectively, but dosing 3 mg mg DOC^{-1} increased removal to 16%, 72% and 43% (118). This also indicates that the process is selective for UV absorbing species (21). Large hydrophobic NOM fractions can be degraded into smaller and more biodegradable ones through oxidation. This reaction then favours the formation of smaller hydrophilic fractions. The reaction rates of NOM and OH radical are of the second order rate ranging from 1 to 10 x 10^8 M^{-1} s^1 (21, 119).

Hydroxyl radicals form by spontaneous ozone decomposition, but catalysts such as H_2O_2 and TiO_2 can be added to aid decomposition. Other methods to produce hydroxyl radicals in water are: UV light radiation with hydrogen peroxide (UV/H_2O_2), Fenton's reactants and photolysis. These treatments which are based on a second or third reaction are known as advanced oxidation process AOPs (120). UV/H_2O_2 eliminates the use of ozone completely and uses the direct interaction of natural or artificial light. Photolysis depends on the ability of compounds to adsorb light. The addition of H_2O_2 enhances the production of OH radicals facilitating NOM degradation. The elimination of NOM is favoured by optimal doses of UV radiation at of 500 mJ cm^{-2} at 254nm and 0.0032 M to 0.0163 M for H_2O_2 during treatment of surface water (117). Although, by removing successfully NOM and subsequently reducing chlorinated THMs, excess peroxide could induce formation of brominated compound and therefore brominated THMs (20).

When ozone is used in combination with ultraviolet radiation, doses of 0.5-3.0 J cm^{-2} and hydrogen peroxide of 10-20 mg/l have shown reductions of DOC, UV, THM formation potential and HAA formation potential where highest UV radiation doses removed up to 20% DOC, but the increased costs associated with high energy input mean that UV radiation could be only partially applied (21).

The ozone process in combination with peroxide O_3/H_2O_2 aims to decrease O_3 demand by increasing its conversion to OH radicals; $O_3/H_2O_2/TiO_2$ showed the best results in terms of NOM removal by using titanium oxide as semiconductor. Other AOP are Fenton and photo Fenton processes which are still being investigated at the laboratory scale, but were proven to remove NOM successfully up to 99%. Humic substances are sensitive to light and generate oxidative conditions through a series of reactions that aid to generate $HO_2\cdot/O_2\cdot$ and further oxidation will produce more $\cdot OH$ as showed in the series of reactions below (121):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^\bullet OH \qquad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH + H^+ \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^\bullet + H^+ \qquad (3)$$

$$NOM + O_2 + h\nu \rightarrow NOM_{ox} + HO_2{}^\bullet/O_2{}^{\bullet -}$$

Ozonation can be affected by the presence of high levels of carbonate and bicarbonate in water sources (alkalinity above 200mg/l as $CaCO_3$) by scavenging of ·OH radicals (21). Disadvantages of the technology are the need to use expensive equipment for piping and housing due to its corrosive properties to organic materials, and ozone is very toxic if inhaled and strict safety measurements have to be applied. If released into the environment as gas it can be easily dissipated, but in water sources that contain bromide it can convert it to bromate or in the presence of bromide tend to increase THMs (118).

2.4.2 Sustainable options for NOM mitigation in water sources

One of the main drivers for water quality degradation derives from human input. The uses of land for agricultural purposes, urbanization, wind farms installations, livestock grazing, peatland burning, etc. alters the local ecosystems and contribute to stress aquatic ecosystems by altering the local hydrology and geomorphology (122). Climate causes change in water source quality such increase of DOC, algal and microbiological population increase, colour and turbidity will have a direct impact on drinking water processes. Conventional treatment will have to be adapted or modified in order to remove recalcitrant NOM fractions and the implications in costs for adaptability, maintenance and operation will be much greater.

The high quality and quantity of water resources in Scotland make them vulnerable to climate change. Organic carbon release from peatlands to water sources is one of the mayor contributors of DOC. Restoration and mitigation strategies are taking place in Scotland and other locations in the UK where peatlands are within the catchment areas to minimize the flux of carbon to water sources (61). One of the strategies to restore peatlands is ditch blocking. Drainage causes water table levels to drop facilitating the release not only of carbon but other nutrients such nitrogen, sulphur, phosphorous and metals (123). The mechanism behind these processes is related to aerobic microbial activity and physical leaching from deeper peat layers that become exposed (61).

A recent study by Wilson et al. monitored the impact of ditch blocking on an upland blanket bog in Wales and collected data prior and post restoration that showed strong evidence that DOC, POC, pH and conductivity from peat decreased in streams one year after restoration (124). Blocking takes place using dams of different materials including wood and plastic. Another blocking technique is called infilling where dams are built and compressed to destroy any soil pipes beneath the ditch (125).

Another study performed in the north of England reveals that not only DOC levels are reduced in streams after ditch blocking but it also improves biodiversity (123). More extensive work by Peacock et al. monitored the introduction of peat forming vegetation such *Sphagnum sp*. into 60 bogs. The results showed reduction of CH_4 fluxes to the atmosphere, but had no effect on DOC levels (125).

2.5 Thesis objectives and knowledge gap

2.5.1 Evaluating seasonal, geographical and operational factors in Scotland that influence THMs formation

Stored quality variables from Scottish drinking water sites can provide relevant information on whether climatic effects, geographical location and/or treatment processes influence THMs formation. Location can influence the quality and quantity of DOC, for example the West of Scotland has higher rainfall levels and peatland compared to the East which can contribute to an excess of DOC (of peaty origin) released after rainfall events.

However, seasonal change in terms of increase or decrease of temperature can also influence THMs precursor characteristics. Despite of the climatic and geographical influences, THMs incidences could also be due to treatment performance which includes disinfection practices.

Hypothesis 1:

Climatic variables such as temperature and rainfall correlate positively with THMs formation

Hypothesis 2:

Catchment characteristics influence the nature of DOC in Scottish surface waters

Hypothesis 3:

THMs incidences in Scottish Water depend on treatment processes and disinfection practices

Hypothesis 4:

Coagulation and direct filtration are more successful in removing THMs precursors than membrane filtration

Hypothesis 5:

DOC, halides and temperature are the most important precursors of THMs

2.5.2 Characterisation of DOC to establish a relationship with the catchment area

The particular geography of Scotland allows a vast possibility of DOC compounds in surface water; it leads to the hypothesis that characteristics of the catchments are an important factor that determines the organic load into them. In the case of water sources located by coastal areas, the presence of halides will be crucial for monitoring; WTWs located by woodland will have NOM contribution from plant decay and bacteriological degradation (typically phenolic); peatland areas will release organic carbon from humic and fulvic nature into streams by leaching; and microbial and algal populations will provide a diverse organic load after degradation including carbohydrates. At the same time, DOC quality and quantity can be affected by seasonal changes

Hypothesis 1:

Quality and quantity of DOC in surface water varies by seasons and according to catchment characteristics

Hypothesis 2:

Residual DOC in treated water before the point of disinfection is primarily of humic and fulvic nature

Hypothesis 3:

Residual DOC in treated water before the point of disinfection is of plant and algal degradation character

Hypothesis 4:

Hydrophilic (or small molecular weight compounds) DOC is the main residual in Scottish surface waters

Hypothesis 5:

Halides contribute to whether chlorinated or brominated THMs species will be formed after chlorination

Hypothesis 6:

Carboxylic acids are more abundant than phenolic compounds in terms of residual DOC

Hypothesis 7:

Carboxylic acids are more reactive than phenolic compounds towards THM formation

Hypothesis 8:

Is quality of DOC more relevant than quantity for THM formation?

2.5.3 Management strategies for THMs control based on DOC character found at drinking water sources.

Location influences chemical composition in water sources in Scotland and strategies can be built in order to reduce or minimize THMs formation potential based on DOC sources geographical characteristics of the catchment, physico-chemical composition and type of treatment. According to:

Hypothesis 1:

A THM prediction model that uses a small number of quality variables could be easily monitored and interpreted by operators

Hypothesis 2:

THM reduction could be obtained by modifying or changing steps during the process (such incorporation of adsorption units or changing disinfection practices)

Hypothesis 3:

More frequent monitoring of quality variables in source water could aid in predicting earlier potential surges of THMs

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Chapter 3

CLIMATIC, GEOGRAPHIC AND OPERATIONAL DETERMINANTS OF TRIHALOMETHANES (THMS) IN DRINKING WATER SYSTEMS

3.1 Introduction

Chlorine disinfection is the most common and inexpensive way of eliminating pathogens from water to avoid serious water borne diseases such as diarrhoea, typhoid and cholera. However, chlorine-based disinfectants produce undesirable disinfection by-products (DBPs) such as trihalomethanes (THMs): chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$), which are closely monitored due to their suspected adverse human health effects (1, 2). In this context, the World Health Organisation (WHO) recommends the international standards for drinking water and states that primary consideration should be given to ensure that water disinfection is never compromised, but has nonetheless defined guidance values for individual THM compounds. These values are based on health criteria such as 10^{-5} excess lifetime cancer risks, and tolerable daily intakes for threshold effects, and are 300 μg/L for chloroform, 100 μg/L for dibromochloromethane and bromoform, and 60 μg/L for bromodichloromethane (3). For total THMs, the WHO recommends a fractionation approach to account for additive toxicity. Based on WHO guidelines and the opinion of the European Commission's Scientific Advisory Committee, the 1998 European Union Drinking Water Directive defines 100 μg/L as the allowable maximum concentration of total THMs (comprising chloroform, bromodichloromethane, dibromochloromethane and bromoform) in drinking water (4). The US EPA regulates THMs at a maximum allowable annual average level of 80 μg/L. The US EPA additionally regulates another group of DBPs called haloacetic acids (HAAs) at a maximum permissible level of 60 μg/L (5) for five compounds (HAA5). Other, unregulated DBPs may be formed in water disinfection, but it is generally accepted that measures taken to reduce organic THM precursors through multistep water treatment before disinfection should also reduce the formation of other DBPs (6, 7).

THMs form through the reaction between chlorine disinfectants and a pool of natural organic matter (NOM) present in water, often quantified as dissolved organic carbon (DOC). Therefore, in locations where the raw water source is rich in NOM (i.e., DBPs precursors), minimization of THM formation during water treatment and distribution can be a challenge. Scotland is a case in point. The total volume of water abstracted for drinking water is 1600 ML/d, with 87% coming from surface water sources (lochs, reservoirs, rivers and springs) and 13% from groundwater (http://www.gov.scot/Publications/2004/04/19262/36053). Scotland has 75% of the peatland in the UK, is surrounded by marine waters, and a great percentage of its territory are islands(8). Scottish geography provides raw waters of diverse chemical composition. For example in the Highlands, granitic parent soil and scarce grassland makes soils organic-rich and soft, whereas in the lowlands, fresh water bodies are often alkaline and higher in nutrients originating from forested peatland and vegetative decay. The diversity of organic compounds present in surface water is vast and dependent on the sources where they originate (9-11). An important characteristic of surface waters in Scotland is discolouration. Brown to yellow colours are common in rivers and lochs, which is attributed to soils rich in humic and fulvic acids. Similarly, phenolic compounds produced by vegetation decay are also released by rainfall and runoff events into surface waters (12, 13).

Within this context, climate change projections have suggested Scottish temperatures will increase and precipitation will become more variable in the future, increasing microbial and chemical reaction rates, potentially altering DOC levels in surface waters, and bringing new challenges in drinking water treatment (8, 14-16). Hydrological changes such as water table level fluctuations, produced by rainfall or drought can increase or decrease in situ DOC levels. When water table levels drop during summer due to natural water evaporation, microbial activity increases producing higher levels of DOC in soil layers (17). Rainfall may then contribute to the release of larger quantities of carbon compounds from organic rich soils, whereas this is less likely from granite, mudstone and sandstone soils, which will release mainly inorganic compounds (17, 18). Organic and organo-mineral soils will release compounds with lower molecular weight as a result of microbial degradation (19). Further, freshwater bodies near coastal areas will be affected by easterly or westerly winds, with impacted rainwater adding marine salts, altering freshwater composition (18). Dissolved halides (bromide, chloride and iodide) from marine sources have been previously correlated with THMs formation (20-22), creating particular problems in water treatment on marine islands.

The array of possible causes of THMs formation is diverse. Therefore, this work was performed to identify “best predictors” of THMs levels in final potable water and distribution networks, and determine how THM formation rates might change in the future. Specifically, large regulatory monitoring datasets were assessed from 93 full-scale drinking WTPs in Scotland to distinguish among geographical, large-scale anthropogenic and operational factors on THMs formation on a country-scale. The ultimate goal here was to quantify relationships between detected THMs levels, and the seasonality and diversity of DOC across the region, and translate those observations to a deeper understanding how climate change will impact THMs formation and treated water quality in the future.

3.2 Methods

3.2.1 Sampling Methodology

Exploratory statistical analysis, multi-linear regression and data mining was applied to water quality parameters measured in Scottish Water Laboratories at different sampling points across their water network (i.e., raw water is surface water at the inlet of each WTP, final potable water refers to disinfected water at the treatment site; and distribution water refers to potable water samples taken at randomised customer taps) between January 2011 to January 2013. All monitored quality data were archived and then drawn from Scottish Water's Laboratory Information Management System (LIMS). A summary of the data used in the statistical analyses appears in **Table 3.1**. As background, Scotland is divided into 16 geographical regions. The number of sites used in the analysis varied among regions, being allocated in a stratified manner to make resulting analyses representative. One-third (n = 93) of the total number of drinking water treatment sites (n = 270) was used to make the analysis workable. The actual number of sites per region is given by n_i (**Table 3.2)**.

Water samples were collected and analysed following a scheduled sampling programme and certified analytical protocols approved by the Drinking Water Quality Regulator (DWQR) for Scotland and the United Kingdom Accreditation Service (UKAS). THMs were measured using a modified in house method based on EPA Method 524.2 for purgeable organic compounds in water by capillary column gas chromatography mass spectrometry (23, 24). Soil data, used to describe background soil type and horizon data across Scotland, were provided by the James Hutton Institute (Aberdeen, Scotland). Rainfall and temperature data were collected from nine Meteorological Stations located across Scotland (Paisley, Dunstaffanage, Tiree, Stornoway, Lerwick, Wick, Nairn, Braemar and Leuchars), including data from January 2011 to January 2013 (historical data available from http://www.metoffice.gov.uk).

Using these data, average and standard deviations for monthly rainfall and temperature were calculated. Larger WTPs in Scotland's main cities have more wider-scoped sampling strategies than rural locations, which meant available data density varied from WTP to WTP across the country.

Raw Water	*Mean*	*Median*	*STDV*	*CV*	*1st Quartile*	*3rd Quartile*	*n*
Alkalinity (mg HCO_3^-/L)	**29.3**	20.0	29.3	1.0	10.0	45.0	411
Ammonium (mg NH_4^{2-}/L)	**0.03**	0.03	0.01	2.60	0.03	0.03	164
Chloride (mg Cl^-/L)	**81.3**	104.5	50.8	1.6	24.3	119.7	16
Colour (mg Pt/Co /L)	**57.0**	42.0	51.2	1.1	23.0	76.0	2643
Conductivity (µS/cm at 20°C)	**80.3**	43.0	117.2	0.7	33.0	75.0	93
pH	**7.0**	7.2	0.6	11.9	6.7	7.4	2643
DOC (mg C/L)	**6.6**	5.4	5.2	1.3	3.3	8.3	1233
Turbidity (NTU)	**2.6**	1.0	14.0	0.2	0.5	1.8	2643
UV Transmittance (%)	**54.5**	58.4	15.6	3.5	46.5	65.2	88
Bromide (µg/L)	**64.1**	30.0	96.3	0.7	15.3	68.9	96

Final Potable Water	*Mean*	*Median*	*STDV*	*CV*	*1st Quartile*	*3rd Quartile*	*n*
Alkalinity (mg HCO_3^-/L)	**33.6**	25.0	32.3	1.0	16	41	795
Ammonium (mg NH_4^+/L)	**0.3**	0.2	0.1	3.3	0.2	0.3	1638
Colour (mg Pt/Co /L)	**3.2**	2.0	2.4	1.3	2	4	2850
Conductivity (µS/cm at 20°C)	**182.1**	199.0	69.3	2.6	136.8	222	512
pH	**7.9**	7.9	0.5	15.7	7.6	8.3	2986
DOC (mg C/L)	**1.8**	1.6	1.1	1.7	1	2.3	2402
Turbidity (NTU)	**0.3**	0.3	0.3	0.9	0.2	0.3	7759
Bromodichloromethane (µg/L)	**9.7**	7.1	8.4	1.2	3.9	13.5	2496
Bromoform (µg/L)	**2.6**	0.3	8.0	0.3	0.3	0.6	2497
Chloroform (µg/L)	**29.7**	21.3	27.4	1.1	8.8	44.1	2496
Dibromochloromethane (µg/L)	**6.2**	2.7	8.7	0.7	0.3	9.3	2497
Total THM (µg/L)	**48.0**	42.0	32.2	1.5	24.2	66.7	2493
Chlorine free (mg/L)	**0.5**	0.6	0.3	1.6	0.3	0.8	24901
Chlorine total(mg/L)	**0.9**	0.9	0.3	3.1	0.7	1.1	24892

Distribution Networks	*Mean*	*Median*	*STDV*	*CV*	*1st Quartile*	*3rd Quartile*	*n*
Ammonium (mg NH_4^+/L)	**0.1**	0.0	0.8	0.1	0.0	0.0	3088
Chloride(mg/L)	**17.8**	11.4	17.4	1.0	7.6	20.9	1079
Colour (mg Pt/Co /L)	**3.1**	2.0	6.1	0.5	2.0	3.0	3440
Conductivity (µS/cm at 20°C)	**125.7**	96.0	81.6	1.5	78.0	155.0	3423
pH	**8.0**	7.9	0.5	15.6	7.7	8.2	3463
Sulphate(mg SO_4^{2-}/L)	**17.1**	11.5	17.0	1.0	2.8	28.3	1079
DOC (mg C/L)	**1.7**	1.5	1.0	1.7	1.0	2.1	1809
Turbidity (NTU)	**0.3**	0.3	0.5	0.6	0.2	0.3	3449
Bromodichloromethane (µg/L)	**9.6**	7.1	8.5	1.1	3.9	12.1	1955
Bromoform (µg/L)	**2.0**	0.3	7.1	0.3	0.3	0.3	1958
Chloroform (µg/L)	**34.5**	25.9	31.3	1.1	11.2	50.8	1955
Dibromochloromethane (µg/L)	**4.8**	0.9	7.7	0.6	0.3	6.0	1959
Total THM (µg/L)	**50.5**	43.6	36.4	1.4	23.7	70.6	1954
Chlorine free (mg/L)	**0.3**	0.3	0.3	1.2	0.1	0.5	8781
Chlorine total(mg/L)	**0.6**	0.5	0.3	1.8	0.3	0.8	8780

Table 3.1 Quality variables data monitored at Scottish Water (Jan 2011-Jan 2013). STDV: Standard deviation; CV: Coefficient of Variation; n: number of entries. All parameters were measured according to modified in house analytical standard methods stablished by the United Kingdom Accreditation Service (UKAS)

Regions in Scotland (strata)	Level	Group size, N_i	$n_i = (N_i/2.9)$
Clyde	1	6	2
Caithness	2	8	3
Orkney	3	11	4
Inverness	4	12	4
Ayr	5	13	4
Tay	5	13	4
Shetlands	5	16	6
North East Mainland	6	19	7
Nith	6	19	7
Western Isles	7	20	7
Fort William	8	21	7
Tweed	8	21	7
Skye & Lochalsh	8	21	7
West Coast	9	22	8
Forth	10	23	8
Argyll	11	25	9
Total	=	**270**	**93**

N_i : number of water treatment plants per region
n_i : selected water treatment plants per region

Table 3.2 Stratified sampling to determine the number of sites selected per region

3.2.2 Exploratory Statistics

The median values for quality variables in raw water, final potable water and distribution networks sampling points at the 93 WTPs were plotted using ArcMap 10.1 (ArcGIS, Environmental Systems Research Institute, CA, 2011) over a soil type layer based on the carbon richness grouped in six categories (25). A data set that included median values for quality parameters measured at the 93 WTPs from January 2011 to January 2013 (at noted sampling points) was used to compare and visualize spatial distributions. Analysis of means and errors were calculated using Minitab 17 (Leadtools Technologies Inc, version 17.1.0, 2014) and reported with 95% confidence limits by showing plus minus standard errors of the mean.

3.2.3 Correlations and multilinear regressions

Pearson correlations and multilinear regressions were calculated using Matlab R2015a (MathWorks, version 8.5, 2015). Bivariate correlations between measured variables in raw water, final potable water and distribution networks were performed using Minitab 17. Correlation analysis was also performed between bromide data measured from raw water and chloride in distribution network samples with a maximum threshold of three days between sampling dates. Finally, comprehensive multilinear regressions were performed using two data sub-sets from the original database that did not contain missing values: data from WTPs that used chlorine disinfection ($n = 502$) and WTPs that used chloramination ($n = 64$). In multilinear regressions for individual and total THMs (dependent variables), using a robust linear fit function (linfit, RobustOpts), only the predictors with high p-value were retained. The robust method option was chosen because it is less influenced by outliers than conventional least-square fit and transformation analysis, especially for non-normally distributed data. Annual average values were subtracted from correlation data to obtain a multilinear regression intercept corresponding to a representative THM concentration.

3.3 Results

3.3.1 Spatial analysis

Soils across Scotland are highly varied, ranging from organic carbon-rich soils that form peatlands, bogs and marshes that predominate in the west of Scotland, to brown earths and humous iron podzols that include agricultural land often more located in eastern Scotland. Using these data, plots describing median THMs concentrations in water distribution networks associated with the 93 WTPs were overlaid onto a map of soil types across Scotland (**Fig. 3.1**).

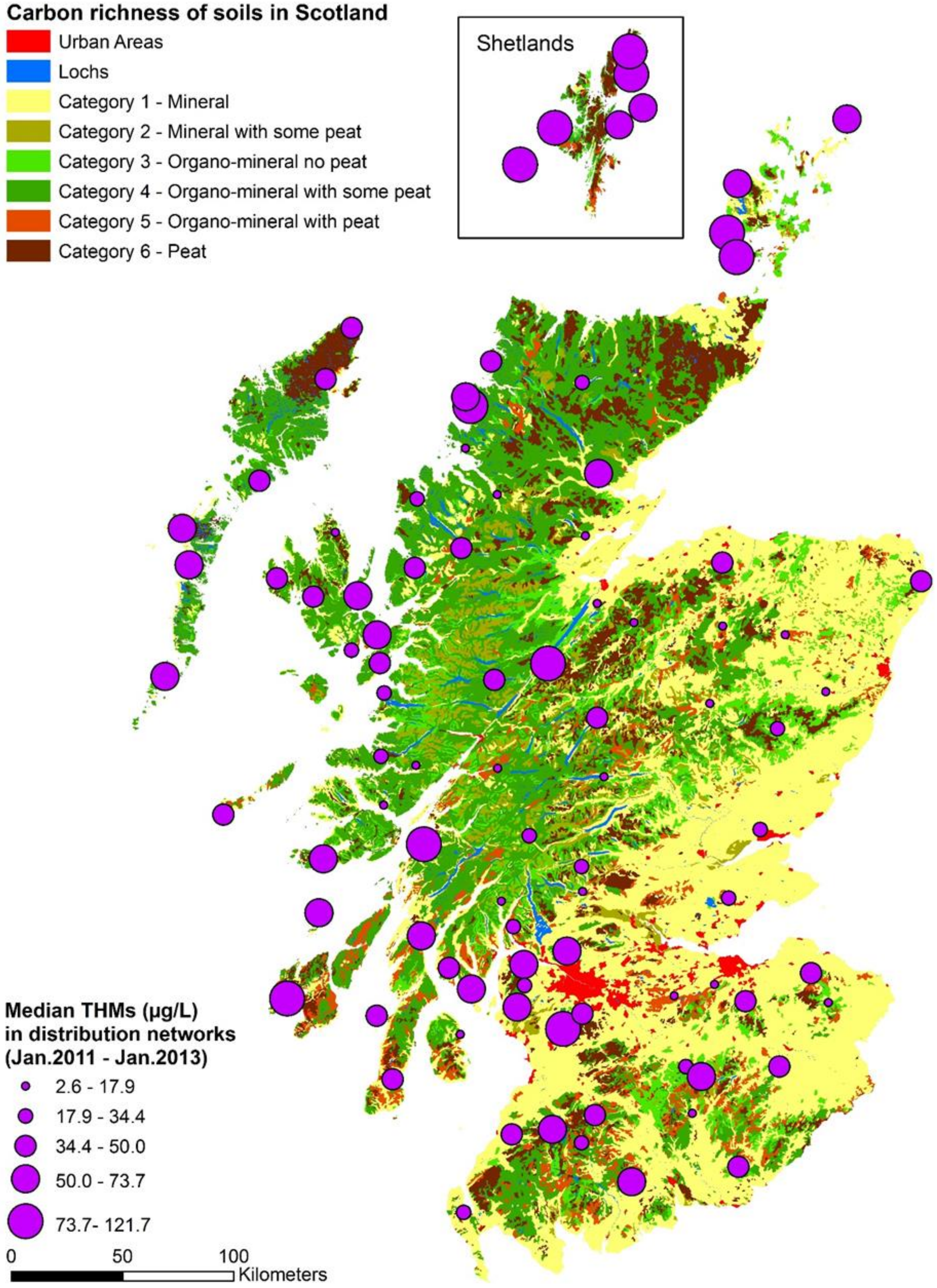

Figure 3.1 Spatial distribution of median total THMs on 93 drinking water plants around Scotland on a carbon richness soil layer (Jan. 2011-Jan.2013) (Obtained using http://www.esri.com/news/arcnews/spring12articles/introducing-arcgis-101.html; version ArcMap 10.1)

The largest median THMs levels were most often found in coastal proximities and in the west (**Figure 3.1**) where peat is abundant and precipitation is high (**Fig. 3.2**), whereas lower THMs levels were found in the Eastern Mainland. The most obvious spatial pattern was for brominated THMs compounds such dibromochloromethane **(Fig. 3.3a**), which were primarily found on islands and associated with WTPs sites near the coast, which implies a strong influence of marine halides on associated THMs formation in distribution systems. Specifically, the spatial distribution of dibromochloromethane shows a clear link between brominated THMs and high levels of marine chloride found at coastal sites (**Figure 3.3a and 3.3b**). The presence of rich organic soils and peatland with halides from marine influence provide a perfect precursor combination for THMs formation.

Median DOC values for each drinking WTP were also overlaid on the soil type distribution map, allowing visualization of spatial trends between soil types, DOC in raw water and DOC in distribution networks (**Figure 3.3c and 3.3d**), but the relationships are not as clear as between coastal proximity, chloride levels and brominated THMs formation.

3.3.2 Temporal trends

Mean DOC and THMs levels across potable water and distribution networks displayed similar seasonal changes with ambient temperature and local rainfall (**Fig. 3.4**). Based on Meteorological Station data from across Scotland, the highest recorded monthly temperatures were in July, 2011 and August, 2012 with 16.5 ± s.e.0.69°C and 17.4 ± s.e.0.56°C, respectively. In terms of rainfall, highest mean levels were found in December 2011 and 2012 with 189.8 ± s.e.39.3mm and 145.1 ± s.e.16.2 mm, respectively.

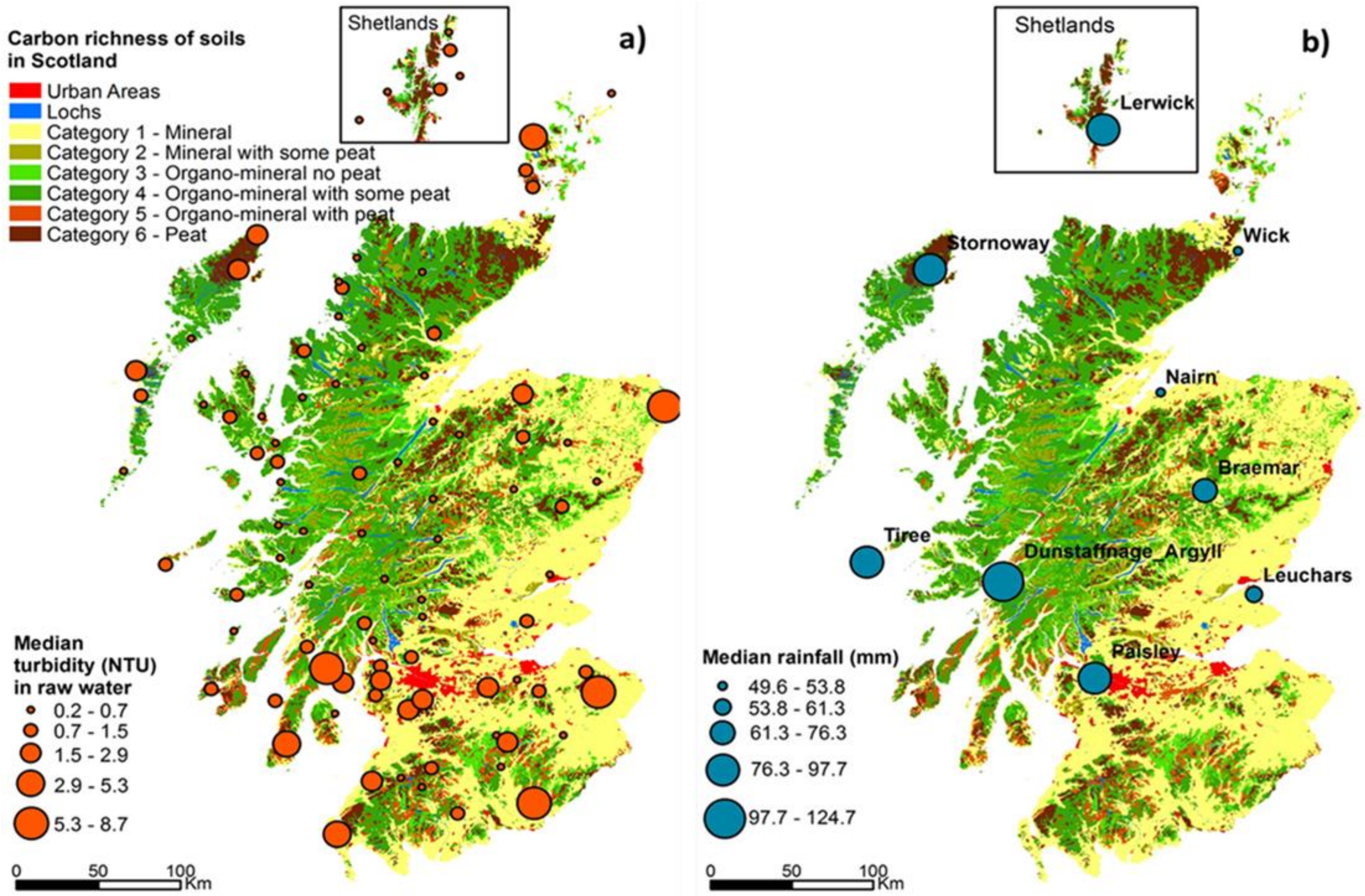

Figure 3.2 a) Spatial distribution of median turbidity (NTU) in raw water on soil types (Jan. 2011-Jan.2013) and b) rainfall values at nine meteorological stations around Scotland (Obtained using http://www.esri.com/news/arcnews/spring12articles/introducing-arcgis-101.html; version ArcMap 10.1)

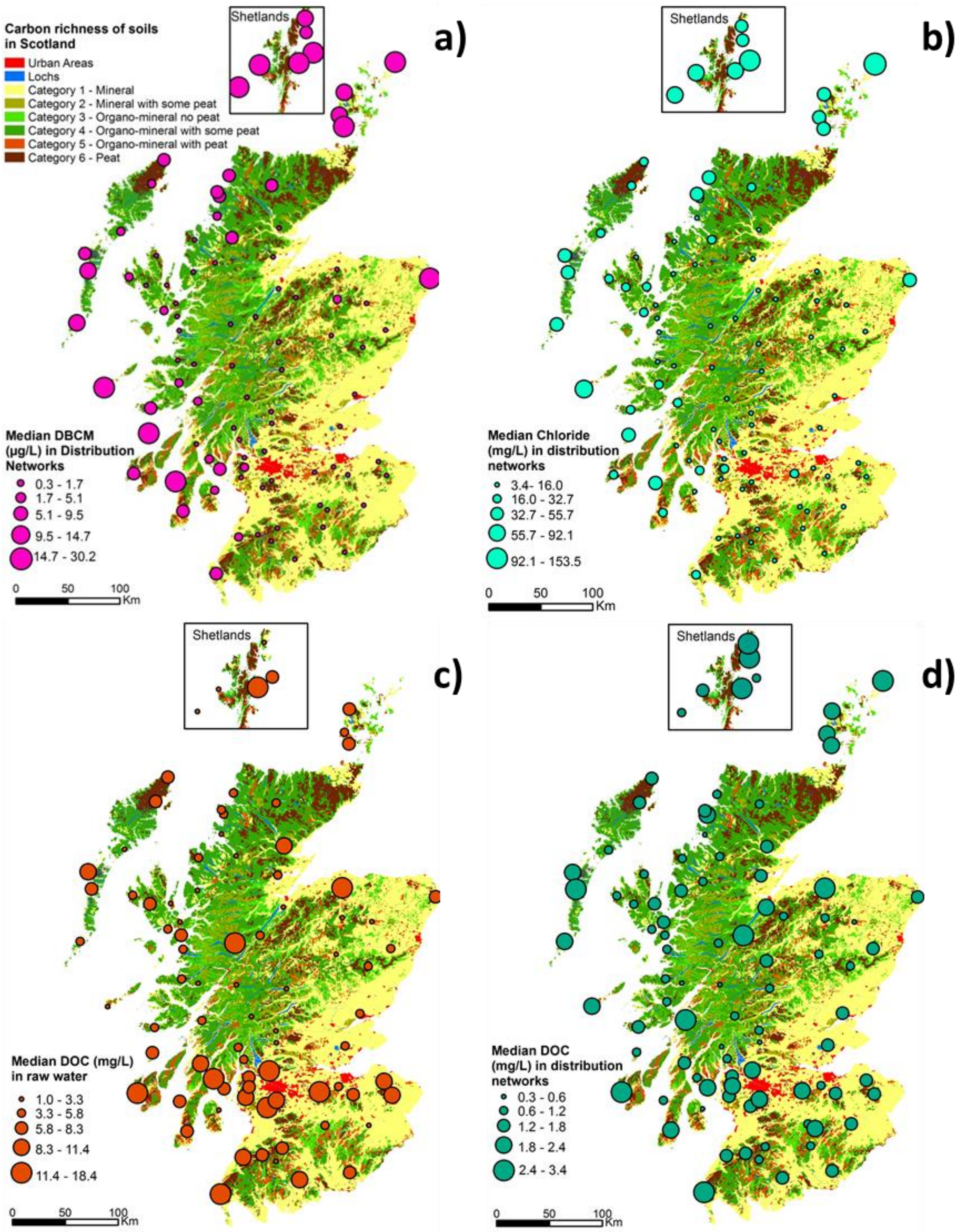

Figure 3.3 Median values for a) Dibromochloromethane (DBCM), b) chloride, c) DOC (raw water) and d) DOC (distribution networks) at 93 drinking water treatment plants in Scotland (Jan.2011-Jan.2013) (Obtained using http://www.esri.com/news/arcnews/spring12articles/introducing-arcgis-101.html; version ArcMap 10.1)

For example, the strongest seasonal influence on total THMs in potable water is ambient temperature (**Fig. 3.4a)**, although the seasonal temperature maxima in July precedes the median total THMs maxima in September (i.e., by about 2 months). This can be explained by DOC levels in potable water, which also influence THMs levels, but peak in September (**Fig. 3.4b**), suggesting higher temperatures associated with elevated DOC levels results in higher THMs levels. In contrast, the combination of lower ambient temperatures from Jan-April and lower potable water DOC explain lower total THMs levels observed in distribution networks in the first third of the calendar year. Raw water DOC (**Fig. 3.4c**) generally follows seasonal rainfall levels, with higher median values being recorded in the second half of the year. As the water table drops during summer months the microbial activity increases, elevating DOC production which is flushed out of the system by rainfall events and continues to do so until the water table increases again in the winter (17, 26).

Ambient temperature plays an important role in chemical reaction kinetics and disinfection practice. Chlorine consumption in distribution networks is accelerated by high temperatures, and during summer months excess chlorine is sometimes added to maintain minimum residual levels. This additional chlorine dosing will result in more THMs formation, which may partially explain the observed seasonal trends. However, temperature dependency of THMs formation and also decay in distribution networks is very complex (27, 28). For example, a temperature-dependant kinetic effect is seen in the marked increase of THMs in distribution networks relative to final potable water THMs in December. This is potentially because lower temperatures slow down the rates of THM formation during primary disinfection, which then increase from reactions with residual chlorine during transport in the distribution systems. Temperature effects on THM formation were less evident in WTPs using chloramines instead of chlorine as disinfectant residual, as will be discussed in more detail later. Regardless of the exact mechanism, the observed relationship with ambient temperature suggests that global warming may exacerbate the THM formation potential in WTPs.

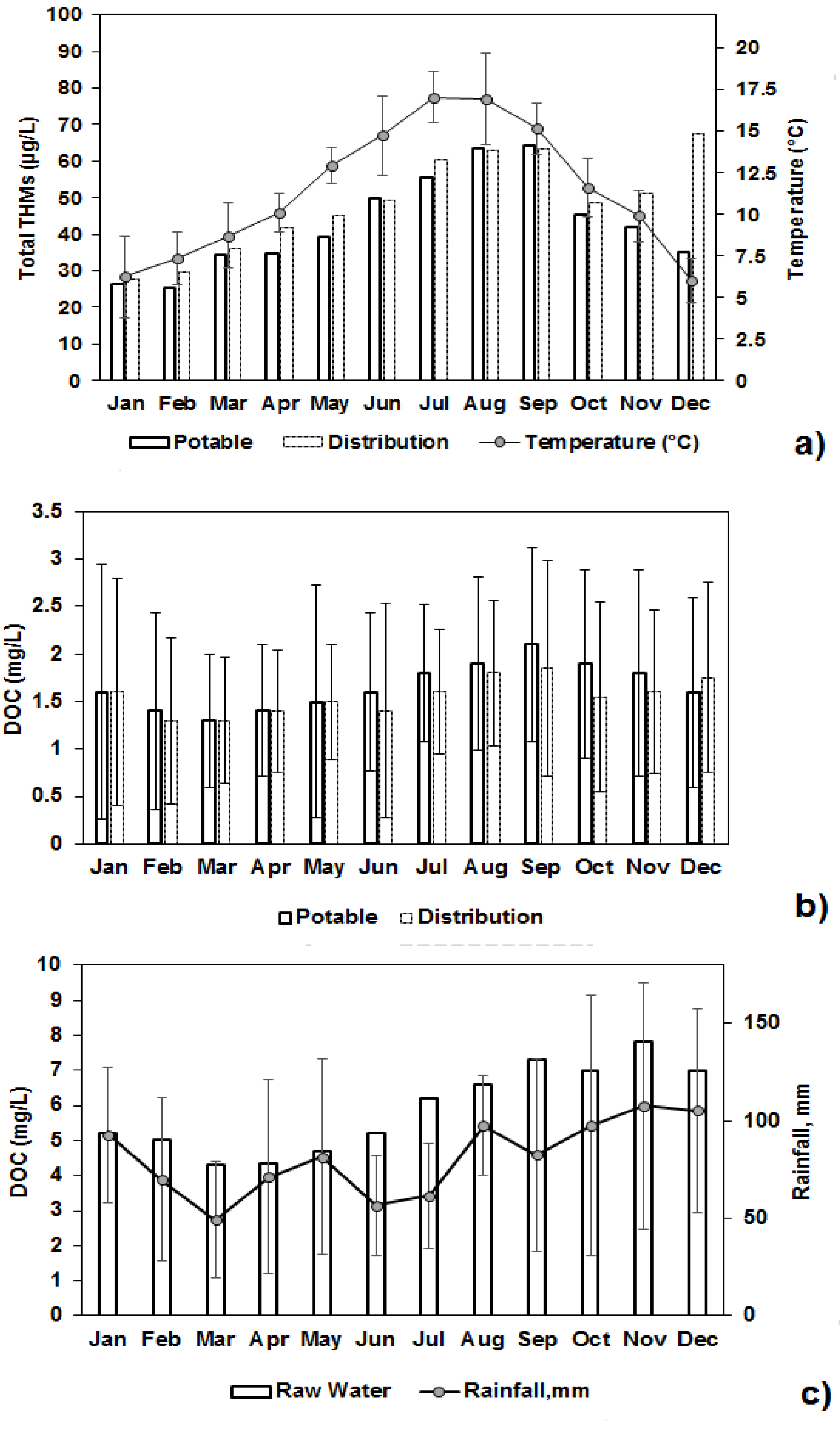

Figure 3.4 Bar plots with standard errors for: a) median total THMs in potable and distribution samples with ambient temperature (error bars not shown for better visibility but typical ranges appear in Table 1), b) median DOC in potable and distribution samples, c) median DOC in raw water with rainfall levels (Jan. 2011 to Jan. 2013)

3.3.3 Pearson's bivariate correlation analysis for THMs and other water quality parameters in potable water and distribution systems

Pearson's correlation analysis was applied to all measured data, and confirmed that ambient temperature, DOC and chloride were most influential to THMs formation across Scottish WTPs (**Table 3.3**).

	Final potable water			***Distribution networks***		
Quality Variables	r^2	*p*	*n*	r^2	*p*	*n*
Alkalinity (mg HCO_3^-/L)	**0.17**	0.06	125	**n.a**	n.a	n.a
Ammonium (mg NH_4^+/L)	**-0.39**	0.00	114	**0.01**	0.87	924
Colour (mg Pt/Co)	**0.39**	0.00	1187	**0.25**	0.00	954
pH	**0.02**	0.61	1187	**0.00**	0.90	939
DOC (mg C/L)	**0.47**	0.00	2320	**0.55**	0.00	1740
Turbidity (NTU)	**0.06**	0.02	1373	**0.09**	0.00	940
Free chlorine (mg/L)	**0.02**	0.32	2317	**-0.14**	0.00	1669
Total chlorine (mg/L)	**-0.08**	0.00	2317	**-0.36**	0.00	1669
Chloride (mg Cl^-/L)	**n.a**	n.a	n.a	**0.41**	0.00	583
Sulphate (mgSO_4^{2-}/L)	**n.a**	n.a	n.a	**0.21**	0.00	294
Conductivity (µS/cm at 20°C)	**n.a**	n.a	n.a	**0.24**	0.00	925
Fluoride (µg F^-/L)	**n.a**	n.a	n.a	**0.10**	0.08	293
****Ambient Temperature (°C)***	**0.66**	0.00	24	**0.43**	0.04	24
****Rainfall (mm)***	**0.18**	0.40	24	**0.33**	0.26	24

** Ambient temperature and rainfall correlations were performed using monthly average values taken from nine meteorological station (Data available online from http://www.metoffice.gov.uk/public/weather/climate-historic/)*

Table 3.3 Bivariate Pearson correlations between quality variables in potable and distribution water samples with THMs. All parameters were measured according to modified in house analytical standard methods stablished by the United Kingdom Accreditation Service (UKAS) and collected from Jan.2011 to Jan. 2013.

Verifying the findings of seasonal trends, monthly average temperatures showed a significant correlation with monthly average THMs in potable water (r^2 = 0.66, $p < 0.05$) and distribution systems (r^2 = 0.43 p = 0.04) (**Fig. 3.5a)**. Greater correlation between THMs and ambient temperature in potable water than distribution networks can be due to the immediate reaction kinetics with chlorine. As contact time in distribution networks increases, the dependency of THMs formation in the networks relies on residual chlorine, DOC and temperature. Rainfall was not significantly correlated with THMs in potable water ($r^2 = 0.18$, $p = 0.397$) (**Fig. 3.5b**) or distribution networks ($r^2 = 0.33$, $p = 0.256$) **(Fig. 3.5b**). In the case of rainfall and DOC, no significant correlations were found between DOC in raw water ($r^2 = 0.33$, $p = 0.11$), potable water ($r^2 = 0.4$, $p = 0.06$) or water in distribution networks ($r^2 = 0.4$, $p = 0.052$) (**Fig. 3.5c**). Similarly, a local survey of water treatment plants in Beijing, China, reported weaker, but still positive, Pearson correlations between THMs with water temperature ($r = 0.253$, $p < 0.05$) and TOC ($r = 0.176$, $p > 0.05$), respectively (29).

Unfortunately, bromide levels are not measured regularly, except at a few sites in the raw water ($n = 30$), but for the available measurements, chloride and bromide levels significantly correlate ($r^2 = 0.87$, $p < 0.05$) (**Fig. 3.5d**). This observation is consistent with other studies where chloride and bromide also were correlated, such as in Australian surface waters where chloride is being used as a proxy for bromide in coastal areas (30). This is relevant because, even at low concentrations, bromide promotes THMs formation as a first-order rate reaction (31).

Therefore, the presence of both halides during disinfection can increase reaction rates with DOC. One of the conclusions from our study is to routinely measure both ions as well as temperature in raw waters and distribution networks, especially in coastal areas, and also to consider alternative treatment technologies, including filtration (e.g. GAC) and-or ion exchange resins in such situations that can remove halides as THMs precursors prior to disinfection (22).

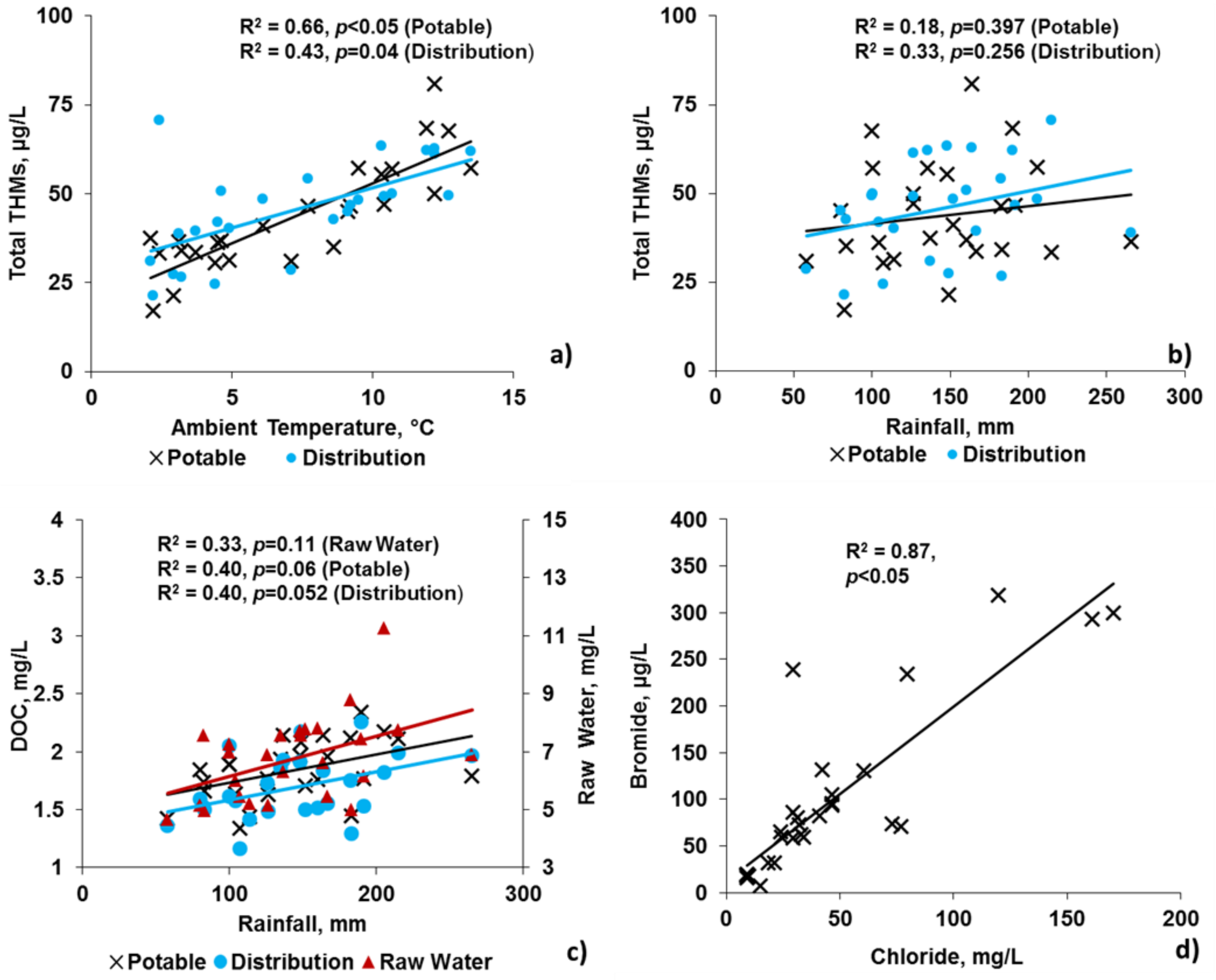

Figure 3.5 Correlation plots between monthly average concentrations (Jan.2011-Jan.2013) for a) THMs and ambient temperature, b) THMs and rainfall and c) DOC and rainfall. d) Correlations between bromide and chloride concentrations (Jan. 2011-Jan.2013)

Other weak, but statistically significant, correlations with total THMs in distribution networks, were observed with colour, conductivity and turbidity (**Table 3.3**). Due to the effectiveness of conventional treatment steps, such as coagulation, sand filtration, GAC, and membrane filtration, turbidity and colour are usually very low in most WTPs (80-95% removal). However, colour and DOC in raw water showed a strong correlation between each other ($r^2 = 0.78$, $p < 0.001$, n = 994) and colour also correlated weakly but significantly with THMs in distribution samples ($r^2 = 0.25$, $p < 0.001$, n = 954) and in potable water samples ($r^2 = 0.39$, p

< 0.001, n = 1187). We suspect the correlation between colour and DOC in raw water is primarily related to the presence of coloured phenolic compounds typically abundant in organic soils (32, 33).

3.3.4 Similarities with haloacetic acids (HAAs) formation

No guidance parameter value has been set for HAAs in the European Union Drinking Water Directive, and these DBPs are therefore not as widely monitored as THMs, but available data suggests strong correlations of HAAs and THMs formation. Monthly average concentrations collected in 2014 for five haloacetic acids (HAA5) taken from distribution networks in one drinking water treatment plant in the West of Scotland also showed a strong and significant positive Pearson correlation with ambient temperature ($r^2 = 0.61$, n = 12, $p = 0.034$) and DOC ($r^2 = 0.66$, n = 12, $p = 0.018$). A strong and significant correlation was also found between THMs and HAAs monthly average values for this particular site during the same period ($r^2 = 0.68$, n = 12, $p = 0.015$). In line with the findings of studies in China(34), Canada(6), England and Wales(35, 36), these correlations substantiate that the formation of THMs and other DBPs in water disinfection with chlorine have similar underlying causes.

3.3.5 DOC removal efficiency

The mean DOC concentration in raw waters, potable waters and within distribution systems across Scotland were 6.6 ± s.e.0.48 mg/L (n = 1233); 1.8 ± s.e.0.02 mg/L (n = 2402) and 1.7 ± s.e.0.02 mg/L (n =1809), respectively (**Table 3.1**). Overall, DOC removal efficiencies across all WTPs was typically 65 to 75%, which was lower than colour (87%) and turbidity (77%) removal. In general, water treatment removes colour more effectively than DOC, leaving less coloured DOC residuals (typically lower molecular weight). This residual DOC fraction, often found in potable and distribution networks, might sustain microbial communities in water lines and potentially react in combination with chlorine and halides to form THMs.

3.3.6 Treatment effects for groundwater

Fourteen of the 93 WTPs in this study abstracted groundwater as their primary source water. Three of these sites used additional GAC filtration for treatment, whilst the other 11 used chlorination only because of good raw water quality in terms of turbidity (0.4 NTU) and colour (16 mg Pt/Co) which are values very close to drinking water. Average total THMs levels in distribution networks associated with these sites were significantly lower (mean 36.7 ± s.e.1.7 µg/L) than sites with surface water sources (51.2 ± s.e.0.5 µg/L; $t = -8.1$, $p < 0.001$). The mean total THMs levels from WTPs that use disinfection only in distribution networks (36.2 ± s.e.3.6 µg/L) vs disinfection plus GAC units (38.9 ± s.e.3.6 µg/L) were not significantly different ($t = -0.52$, $p < 0.601$). GAC is typically only used at sites with poorer quality raw water. However, data here indicate GAC has limited additional benefit to reducing THMs levels. It should be noted that inclusion of GAC filtration can improve THMs precursor removal (37, 38) but the specific adsorbent must be chosen carefully (22). Further work needs to be done to better understand the choice of GAC utilized at these groundwater sites and their efficacy for THMs precursor removal.

3.3.7 Treatment effects for surface water

Coagulation is one of the most common treatment methods employed to produce potable water in Scotland and is included in ~50% of the WTPs in this study. The common coagulant is aluminium sulphate supplemented with polyelectrolyte (0.1 mg/L polyacrylamide) and coupled pH adjustment to between 5.8 and 6.3 which is then raised to 8 as water leaves the WTPs to prevent network corrosion. In reviewing THM levels from WTPs with coagulation, the lowest THMs values were observed at WTPs with coagulation followed by ultrafiltration which produced total THMs levels of 21.1 ± s.e.3.1 µg/l (n = 40) and 16.0 ± s.e.1.1 µg/L (n = 41) in potable and distribution water, respectively (**Table 3.4**).

Coagulation with dissolved air flotation (DAF) and rapid gravity sand filters (RGF) produced similar THMs levels to WTPs with coagulation and pressure filtration, but sites that combine coagulation with RGF and GAC tended to have much higher THMs levels across all potable water and distribution system samples. For example, two-sample t-tests showed that sites using coagulation with GAC had a significantly higher mean THMs in distribution samples at 83.3 ± s.e.5.3µg/L ($t = -8.9$, $p < 0.001$) compared with all other WTPs with coagulation (mean 48.8 ± s.e.0.9µg/L). Similar to groundwater sources, our results show THMs precursor removal is not necessarily substantially enhanced by an additional GAC treatment step which reinforces the requirement of further study around this area.

When evaluating WTPs with membrane filtration, sites with hollow fibre ultrafiltration (UF) membranes performed much better than other WTPs, producing the lowest THMs levels (**Table 3.4**), which may, however, be due to the low raw water DOC of the hollow fibre UF plants. Of membrane options, spiral UF had the highest THMs levels (51.3-55.9 µg/L) in potable and distribution water samples which relates to their higher molecular weight cut-off (MWCO). However, total THMs levels were not significantly different between membrane and coagulation plants (including GAC filtration) ($t = 0.99$, $p = 0.33$) which again will be influenced by inlet DOC loadings. In the case of less common treatment options, ozone with GAC treatment and coagulation with Inverness (up-flow) filters yielded significantly higher total THMs levels in distribution networks (100.0 ± s.e.2.8 µg/L) than traditional coagulation or membrane WTPs (46.6 ± s.e.0.82 µg/L) ($t = 18.5$, $p < 0.001$). Total THMs in potable water

		Dissolved Organic Carbon, mg C/L									DOC R. Efficiency%		Total trihalomethanes µg/L					
		Raw			Potable			Dist			Potable	Dist	Potable			Dist		
Treatment	**Additional Treatments**	**Mean**	***sd***	***n***	**Mean**	***sd***	***n***	**Mean**	***sd***	***n***	**%**	**%**	**Mean**	***sd***	***n***	**Mean**	***sd***	***n***
	Dissolved Air Flotation_RGF	**6.8**	3.1	95	**1.66**	0.67	153	**1.47**	0.59	233	**75.6**	**78.4**	**41.2**	26.3	149	**38.1**	24.7	233
	Pressure Filtration	**11.2**	4.7	41	**1.84**	0.82	88	**1.82**	0.53	82	**83.6**	**83.7**	**39.1**	19.5	94	**39.9**	20.2	81
Coagulation	**Rapid Gravity Filtration**	**8.9**	4.9	318	**2.12**	1.30	539	**1.94**	0.92	530	**76.2**	**78.2**	**44.8**	25.4	589	**56.2**	28.4	619
	Rapid Gravity Filtration_GAC	**4.8**	1.8	52	**1.87**	0.87	167	**2.06**	0.78	56	**61.1**	**57.1**	**64.9**	35.5	169	**83.3**	40.5	58
	Ultrafiltration	**4.6**	1.4	25	**1.58**	0.56	40	**1.55**	0.35	41	**65.6**	**66.3**	**21.1**	19.9	40	**16.0**	7.0	41
	Spiral_UF	**7.5**	6.7	104	**1.47**	0.59	337	**1.34**	0.58	145	**80.3**	**82.1**	**51.3**	26.4	334	**55.9**	34.4	154
Membranes	**Multi tubular_NF**	**5.8**	3.6	303	**1.40**	1.21	327	**1.05**	0.89	279	**75.9**	**81.9**	**46.1**	36.9	348	**36.9**	35.5	283
	Hollow fibre_UF	**2.3**	0.8	20	**1.95**	0.58	20	**2.26**	1.47	39	**15.2**	**1.9**	**18.0**	17.1	20	**25.6**	23.3	39
	Coagulation & DynaSand	**7.2**	11	77	**2.13**	0.76	202	**1.83**	1.24	104	**70.4**	**74.5**	**45.0**	28.1	201	**54.4**	33.2	108
Unconventional	**Coagulation_Inverness Filter**	**3.3**	3.8	42	**2.22**	1.05	153	**2.44**	1.21	61	**32.6**	**25.9**	**78.3**	34.1	159	**94.2**	36.3	67
	Ozone & GAC	**3.7**	0.8	77	**3.08**	0.67	59	**2.98**	0.69	26	**16.8**	**19.4**	**68.1**	20.4	69	**100.0**	21.2	58
No treatment	**Disinfection only**	**3.06**	3.2	79	**1.45**	1.11	288	**1.36**	1.17	177	**52.5**	**55.4**	**36.9**	37.5	291	**36.2**	47.5	179
	Disinfection_GAC	**1.8**	0.5	4	**1.59**	0.63	29	**1.53**	0.67	36	**11.5**	**15.1**	**35.4**	19.7	30	**38.9**	20.8	34

UF: Ultrafiltration (MWCO 8,000Da)
NF: Nanofiltration (MWCO 2,000Da)
Inverness Filter: Sand filtration unit with upward flow direction
DynaSand® Sand filter backwash continuously
R. Efficiency%: Removal Efficiency; **RGF**: Rapid Gravity Filtration; **GAC**: granulated activated carbon; **Dist**: Distribution networks; **sd**: standard deviation

Table 3.4 Total THMs and DOC per treatment type in 93 Scottish Water sites found in DynaSand®-based WTPs (45.0 ± s.e.2.0 µg/L) were evaluated against all other sand filtration treatments (47.1 ± s.e.0.8 µg/L) and no significant difference were found in potable (t = -0.98, p = 0.328) or distribution water samples (t = 0.67, p = 0.502). These results show that conventional coagulation and membrane filtration systems are generally better options than non-conventional treatment options in terms of THMs formation trends for Scottish drinking water systems.

3.3.8 Chlorination versus chloramination plants; Potable water versus distribution water

Scottish Water uses both chlorination and chloramination for disinfection. Eleven of the 93 WTPs within the network use chloramine as the disinfectant, whereas the remaining WTPs use chlorination. Chlorination and chloramination sites do not differ significantly in terms of total THMs levels in their final potable water, but THMs levels are significantly higher in water distribution networks with chlorination (53.5 ± s.e.0.88 µg/L, n = 1716) vs chloramination (28.7 ± s.e.3.8 µg/L, n =238) (t = 11.96, p < 0.001). These results are partially explained by the loss of free chlorine on the addition of ammonia at the WTPs in the production of chloramine and the need for extra chlorine doses within networks with chlorination systems (e.g., in service reservoirs), which ensure isolated households have acceptable chlorine residuals (0.2-0.3 to 1 mg/L as free chlorine). It should be noted that this practice is performed more often in summer months when higher temperatures can cause more rapid depletion of chlorine (39). In the case of chloramination WTPs, the higher stability of mono- and di-chloramines results in lower rates of disinfectant decay, which causes longer lasting residuals, considerably lower THMs formation, and less need for additional disinfectant in the distribution networks. This statement is corroborated by a very important finding of this study which is that the relationship found between ambient temperature and total THMs differs according to the type of disinfection. The data was separated into two sets one containing sites that use chlorination and another using chloramination (**Fig. 3.6**). For the chlorination dataset a strong and significant correlation was found between THMs and ambient temperature monthly average values (n = 24) in potable water ($r^2 = 0.71$, $p < 0.05$), and also in distribution networks ($r^2 = 0.48$, $p < 0.05$). However, no such correlation was found between these two variables in the chloramination dataset. The finding indicates that WTPs using chlorination will be most affected by changes in ambient temperature.

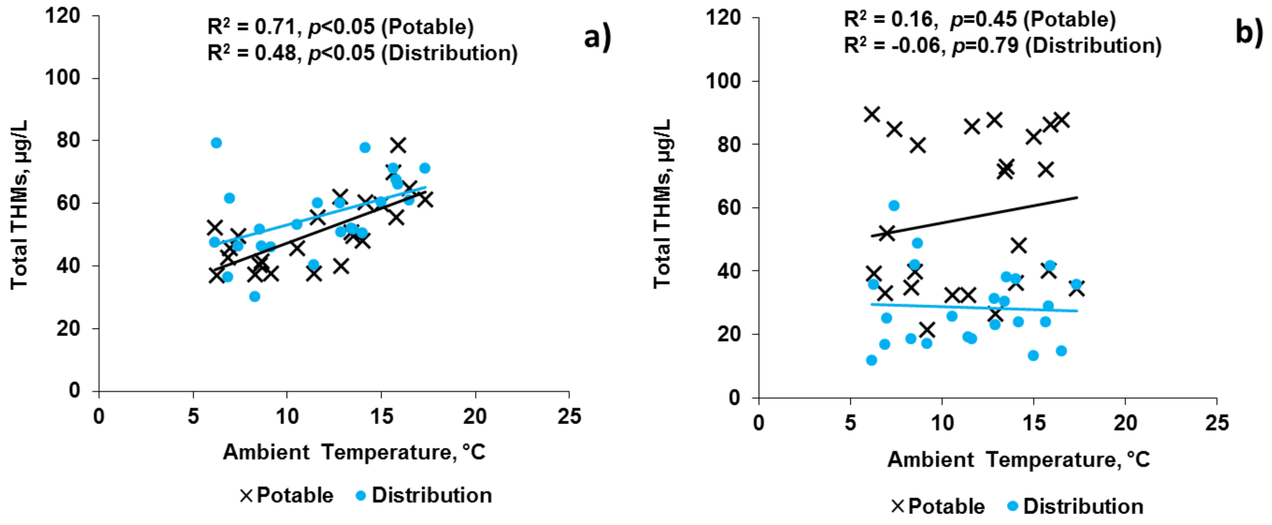

Figure 3.6 Correlations between monthly average total THMs concentrations and ambient temperature (Jan.2011-Jan.2013) in a) chlorination and b) chloramination WTPs (n = 24)

Overall, these above results indicate THMs formation control also must consider phenomena in the distribution networks. In fact, 79% of the WTP systems (73 of 93) had statistically significant higher total THMs ($t = -2.4$, $p < 0.001$) in their distribution networks (51 ± s.e.0.8 µg/L) than in their treated potable water (48 ± s.e.0.6µg/L). This implies net THMs formation reactions continue outside of the WTP itself and managing such reactions in the distribution system is key to minimizing THMs levels at the tap.

3.3.9 Multilinear regression models for individual THMs compounds

Chlorination-based WTP systems display much stronger multivariate regression correlations for total THMs levels ($r^2 = 0.76$, $p < 0.05$) than chloramination systems ($r^2 = 0.37$, $p < 0.05$) with the main predictors being ambient temperature, chloride and DOC in chlorination sites and chloride and DOC for sites that use chloramination. Relative to specific THM compounds, chloroform and bromodichloromethane are most associated with ambient temperature, chloride and DOC, whereas bromoform was only correlated with temperature and chloride in chlorination systems (**Table 3.5**).

THMs prediction models indicate, for example, that concentrations higher than the annual average for each of the predictors will yield higher THMs. These models will facilitate the interpretation of results at the treatment sites and help operators and managers to control the process by setting temperature-dependant targets for residual DOC and halide concentrations in order to minimize THMs formation. We believe the negative correlation of chloroform with chloride is due to the preferential formation of brominated THMs from waters with high halide levels. Bromoform formation was often below 0.5 µg/L, which appeared to skew regression analysis, therefore below-detection limit bromoform data (0.3 µg/L) were not included in the regression analysis for the chlorination dataset.

Elimination of such low values was not performed for chloramination sites due to small number of data entries and hence no correlation could be established for bromoform data (**Table 3.5**). It is then of great importance to identify bromide concentrations at the raw water and in the distribution networks in the future and thus to produce an improved prediction model for THMs formation. Previously THMs studies also have used other predictors, including pH, UV, fluorescence, and C/N ratios, which can provide useful information on characteristics of THMs precursors (39). However, this current investigation relied on monitoring data typically available to water utilities (a pragmatic approach), and we found that chloride and DOC, consistently predicted THMs levels, which we suspect is valuable to water companies for THMs management. Multilinear regression models are based on current treatment practice which may change in the future due to further process optimisation. However, ambient temperature data was incorporated into the multilinear regression model due to the evidence of seasonal changes affecting levels of THMs in chlorination plants which was corroborated with positive and strong associations. Such findings are very important because they bring into the attention that not just DOC and halide residuals at the disinfection point of water treatment are causing THMs formation, but external factors such as ambient temperature are also influential. Thus, rising temperatures caused by global warming will have an immediate effect on THMs formation and the economics of water treatment in the future.

Linear Regression models for trihalomethanes using Chlorination (*p*<0.05)			**r^2**	**n**
total THMs (µg/L)	=	52.0 + 1.4[T-8.8](°C) + 0.4[Cl^- -17.8](mg/L) + 26.9[DOC - 1.7](mg/L)	**0.76**	**502**
Chloroform (µg/L)	=	36.3 + 0.7[T - 8.8](°C) - 0.4[Cl^- - 17.8](mg/L) + 24.0[DOC - 1.7](mg/L)	**0.73**	**502**
Bromodichloromethane (µg/L)	=	10 + 0.2[T - 8.8](°C) + 0.3[Cl^- 17.8](mg/L) + 4.3[DOC - 1.7](mg/L)	**0.80**	**502**
Dibromochloromethane (µg/L)	=	3.3 + 0.06[T - 8.8](°C) + 0.3[Cl^- - 17.8](mg/L) - 0.4[DOC - 1.7](mg/L)	**0.84**	**502**
*Bromoform (µg/L)	=	18.3 + 1.1[T - 8.8](mg/L) + 1.2[Cl^- - 17.8](mg/L)	**0.66**	**144**

* Lowest limit of detection for bromoform (0.3µg/L) eliminated for this model

Linear Regression models for trihalomethanes using Chloramination (*p*<0.05)			**r^2**	**n**
total THMs (µg/L)	=	13 -0.5[Cl^- - 17.8](mg/L) + 18.0[DOC - 1.7](mg/L)	**0.37**	**64**
Chloroform (µg/L)	=	8.2 -0.9[Cl^- - 17.8](mg/L) + 13.7[DOC - 1.7](mg/L)	**0.38**	**64**
Bromodichloromethane (µg/L)	=	4.8 + 0.5[Cl^- - 17.8](mg/L) + 2.2[DOC - 1.7](mg/L)	**0.73**	**64**
Dibromochloromethane (µg/L)	=	N.A	**-**	**-**
Bromoform (µg/L)	=	N.A	**-**	**-**

Table 3.5 Linear regression models for THMs in distribution networks during chlorination and chloramination (Jan. 2011 – Jan.2013)

3.4 Conclusions

THMs are conditionally carcinogenic compounds that are formed during chlorine disinfection. THM formation has been known for many years (40), but most studies on THMs have been based upon local or laboratory assessments, which limits the scope of bigger picture predictions based on multiple real-world observations. For example, it is suspected water quality may decline as climate changes (41), but it is very tenuous to make specific predictions without stronger and more extensive field data that confirm speculation. This is especially critical to the water industry, which must make major infrastructural decisions about future water systems and there is uncertainty about the climate within which they will operate.

Within this context, we assembled an extensive database that contained operating data from 93 full-scale WTP systems, including 46,999 data entries from across Scotland. To our knowledge, this is one of the largest assessments ever performed on water systems, especially related to THM formation as a function of geographic, operational, and climatic factors. Although the sampling frequency varied between WTPs and the data for some parameters were less complete than others, the dataset is still extensive and allows statistical comparisons among factors that impact THMs at a rigorous level. Overall, data show that DOC, which varies by location and regional weather (e.g., precipitation), chloride and especially ambient temperature conditions all significantly relate to THMs formed during water treatment across the Scottish network. The importance of such factors to THM formation has been observed previously (22, 37, 42), but here we show such factors are manifestly important at a country-scale, which becomes very significant when one considers the possible impacts of climate change on the water industry. Scottish data specifically show that warming temperatures and-or more variable precipitation will very likely change or exacerbate THM formation potential in regional WTPs. However, such observations have global implications, especially in countries that use regularly chlorination in water treatment, such as the United Kingdom or United States. For example, we observe much higher THMs levels in potable water systems with higher seasonal temperatures, which we suspect is related to accelerated formation kinetics and also altered DOC release from organic rich soils. If one considers projected increases in temperature of 2-3°C within the next 40 years (43) (which is within the Scottish temperature range), treatment adaptations, such as moving away from chlorination or applying enhanced DOC removal processes, may be needed to reduce impact of global warming on THMs formation and its possible health consequences. Although this has considerable operational implications to companies, we provide here a template for addressing this prospective problem, including implications of catchment management, different treatment options and infrastructural upgrades, which we hope will assist water companies with similar decisions around the world.

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Chapter 4

ROOT CAUSES OF SEASONAL TRENDS IN TRIHALOMETHANES (THMs) FORMATION IN DRINKING WATER TREATMENT SITES

4.1 Introduction

Addition of chlorine or chloramine as disinfectants are a worldwide practice due to its efficacy to eliminate pathogens and low cost (1). If natural organic matter (NOM) in the form of dissolved organic carbon (DOC) is still present prior to the point of disinfection it will react and form disinfection by products (DBPs). The mechanisms or reaction between the diverse chemical species that form NOM create an incredibly vast variety of potential halogenated analogous of which trihalomethanes (THMs) are the most regulated and documented due to their potential carcinogenic effects (1).

Thus, one of the main research interest in the drinking water field for the past forty years since chloroform was identified in potable water by Rook in 1974 (1) has been to identify root causes of DBPs formation to aid in reducing the occurrence of DBPs such trihalomethanes in potable water supplies. However, not just the amount of DOC determines THMs, but also external factors such geographical location and seasonality for example, as discussed in chapter 3. THMs formation at a country scale in Scotland data showed seasonal trends with peak THM concentrations in late summer and early autumn, which coincided with high raw water DOC and ambient temperature. It was also speculated, that seasonal changes in microbial activities affect DOC release and quality, and changes in rainfall patterns over the year, as well as changes in disinfection practice to assure residual chlorine concentrations within distribution networks.

These could all be factors contributing to the observed seasonality in THMs formation. This chapter seeks to more reliably establish the relative contribution of these factors to seasonality in THM formation. To this end, five full-scale drinking water treatment plants were selected as case study sites for the monthly monitoring of raw and treated water quality so that the effect of seasonal changes and operational factors could be studied more closely during a period of one year for each individual site. In addition, quarterly samples were taken from each of the case study sites to study THM formation potential under well controlled laboratory conditions, where individual factors could be isolated. The main objective was to identify more reliably what factors caused the seasonal trends in THMs in drinking water observed in chapter 3 at the country scale.

4.2 Methods

4.2.1 Selection of six case study sites

Case study sites were selected from a total of 93 sites to identify six which will represent the majority of drinking water sites around Scotland. Cluster analysis was performed to achieve this objective using K-means algorithm by R Studio free software (Integrated Development for R. R Studio, Inc., Boston, MA. Version: 3.3.1). Preliminary exploratory analysis of data involved the division of water treatment plants (WTPs) sizes into three categories: small, medium and large. Size was defined by applying a histogram of frequency for size (ML/day) using also R Studio software. Minimum size was allocated at 0.006 ML/day and maximum at 110 ML/day. Frequency plots showed that the majority of WTWs from the selected 93 sites were small (n = 47, 51.6%) ranging from 0.006 ML/day to 0.838 ML/day, medium size WTWs (n = 26, 28.6%) from 0.838 ML/day to 13.5 ML/day and large WTWs (n = 18, 19.8%) from 13.5 ML/day to 110 Ml/day. Twenty centroids were used for K-means with maximum number of 100 iterations. The K groups were plotted against the following quality variables: total THMs (distribution and potable water), TOC (raw water, final potable and distribution networks), colour (raw water), chloride (distribution networks) and bromide (raw water) to determine outliers (anomalies).

This approach selected a preliminary set of 21 drinking treatment plants which were grouped per regions from which the final selection of six case study sites was narrowed down according to accessibility, type of treatment (conventional coagulation and membrane filtration) and geographical location. The selected six case study sites were: Forehill, Amlaird, Stornoway, Port Charlotte, Gigha and Broadford (all flow diagrams appear in Appendices for chapter 4, Figures 4.1-4.6).

However, due to problems with sampling accessibility and delivery, the monthly monitoring programme included only five case study sites (Amlaird, Stornoway, Forehill, Broadford and Gigha) during a one year period starting in November 2014 until September 2015. Port Charlotte WTP was eliminated as many samples were missing, but included in the quarterly monitoring programme

4.2.2 Case Study Sites description

a) Forehill Water Treatment Plant (FWTP)

The River Ugie supplies raw water to Forehill WTP which is pumped to an impounding reservoir located at the site. Forehill supplies water to 24,415 inhabitants by distributing treated water into nine service reservoirs with a total length of 281.87 Km of mains. Average flow rate processed at the site is 20 ML/day. Raw water is dosed with lime. Ferric sulphate and polyacrylamide are added for coagulation at pH 5-5.5 and the clarified water is pH re-adjusted with lime to pH 8.5 to aid manganese removal. Rapid gravity filters (seven single media sand filters) filter the clarified water and backwash every 72 hours. Filtrate water passes through two granulated activated carbon (GAC) units before is chlorinated in a contact tank for a minimum of 10 minutes and pH adjusted to approximately 8-8.5. Due to the different residence times in the reservoirs different doses of chlorine are added to maintain disinfection residuals.

b) Amlaird Water Treatment plant (AWTP)

Raw water is abstracted from Craigendunton Reservoir located 4 Km north east of the treatment site which is supplemented by Loch Goin and four other burns. Supply to the local distribution systems is carried out by three service reservoirs located within the boundaries of the AWTP to a population size of 34,800 and covering a total main length of 200 Km. The average flow rate of the works is 13.9 ML/day and it functions under automatic remote control (telemetry) with minimum operator intervention.

Raw water is automatically monitored for colour, turbidity and pH (adjusted with lime prior to coagulation to reach pH values between 8-8.5 using ferric sulphate and polyacrylamide (0.1%). The flocculated water passes through six dissolved air flotation (DAFs) units, then it is clarified and filtered by pressure sand filtration (sand beds with 10% manganese dioxide) to finally being chlorinated and pH adjusted below 8.5. The soils surrounding AWTP are formed by peat and peaty gleys and surrounded by manmade forests with bracken vegetation. Sheep grazing or agricultural activities are not typical in this catchment area.

c) *Stornoway Water Treatment Plant (SWTP)*

Raw water is abstracted from Loch Mor A Stairr located at 5 km north west of Stornoway. Treated water is stored into four service reservoirs to be distributed to six supply zones for a total population of 9630 and a total main length of 125 Km. Average flow rate is 5 ML/day. Aluminium sulphate is added for coagulation and polyacrylamide (0.1%) for coagulation and flocculation and water is distributed to four clarifiers. Clarified water is treated with sodium carbonate and chlorine for manganese removal and passes through 12 pressure filters. Stornoway is controlled by telemetry and functions with very little human intervention except for filters backwash. The catchment area is formed by mainly undisturbed bog peatland and covered by sphagnum vegetation.

d) Port Charlotte Water Treatment plant (PCWTP)

Raw water flows by gravitation from Loch Gearach located 2 Km away of the WTPC to supply a population of 757 using eight storage service reservoirs and a total main length of 50 Km with average flow demand of 0.44 ML/day. Raw water is mixed with sodium carbonate and aluminium sulphate (17%) simultaneously to achieve pH between 8-8.4 and continues to a coagulation tank where polyacrylamide (0.1%) is added immediately. The clarified water is divided into three pressure filters (PF) followed by three manganese contact tanks (MCTs). The treated water reaches a baffled contact tank for final chlorination at final concentration of 1 mg/L for a minimum of 20 minutes contact time.

Chlorinated water is stored in the service reservoir and pH adjusted to values between 7.5 -8. PCWTP has a backwash sequence of PFs and MCTs which is performed once a month where rinsed water is recycled back to the coagulation tank. PCWTP is located in Islay at the West of Scotland. Loch Gearach receives water from three stream tributaries influenced by manmade forestry and low sheep and cattle grazing activities. The soils surrounding the catchment area of PCWTP are mainly peaty with bracken vegetation.

e) Gigha Water Treatment plant (GWTP)

Raw water is abstracted from Mill Loch located 100 m away from the site and has one service reservoir for a small distribution zone that serves to a population of 110 with a total main length of 49 Km. Mill Loch has a measurement gauge to measure depth levels and an inlet flow rate of 0.26 ML/day. Raw water pass through basket strainers (2mm) at 3 bars until it reaches the stack of 36 tubular membrane modules. Each module has 72 straws made of cellulose acetate. The permeate passes through a granular activated carbon (GAC) filter then chlorine is dosed as sodium hypochlorite before continuing through a limestone contact tank for pH adjustment (7.5-7.9) and manganese removal. GWTP is located in the island of the same name at the West of Scotland. The main activities of the island are sheep grazing, very small scale of barley and wheat production and tourism during summer. The Loch has no tributaries and it is only fed by an aquifer and runoff as a result of rainfall and the catchment area has peatland and bracken vegetation. Although, this Loch has experienced blooms of bog bean in the past now it is controlled and its waters provide a good habitat for local birds.

f) Broadford Water Treatment Plant (BWTP)

The site abstracts raw water from river Allt A’Mhuilinn which is screened prior to entering the site. Treated water is stored into one service reservoir to be distributed to two supply zones for a total population of 1023 and a total main length of 17.25 Km with average flow rate of 0.257 ML/day. Raw water at pH 8-8.5 passes through a 25 µm micro strainer washable filter. Microfiltration is achieved with 12 modules containing spiral membranes made of cellulose acetate.

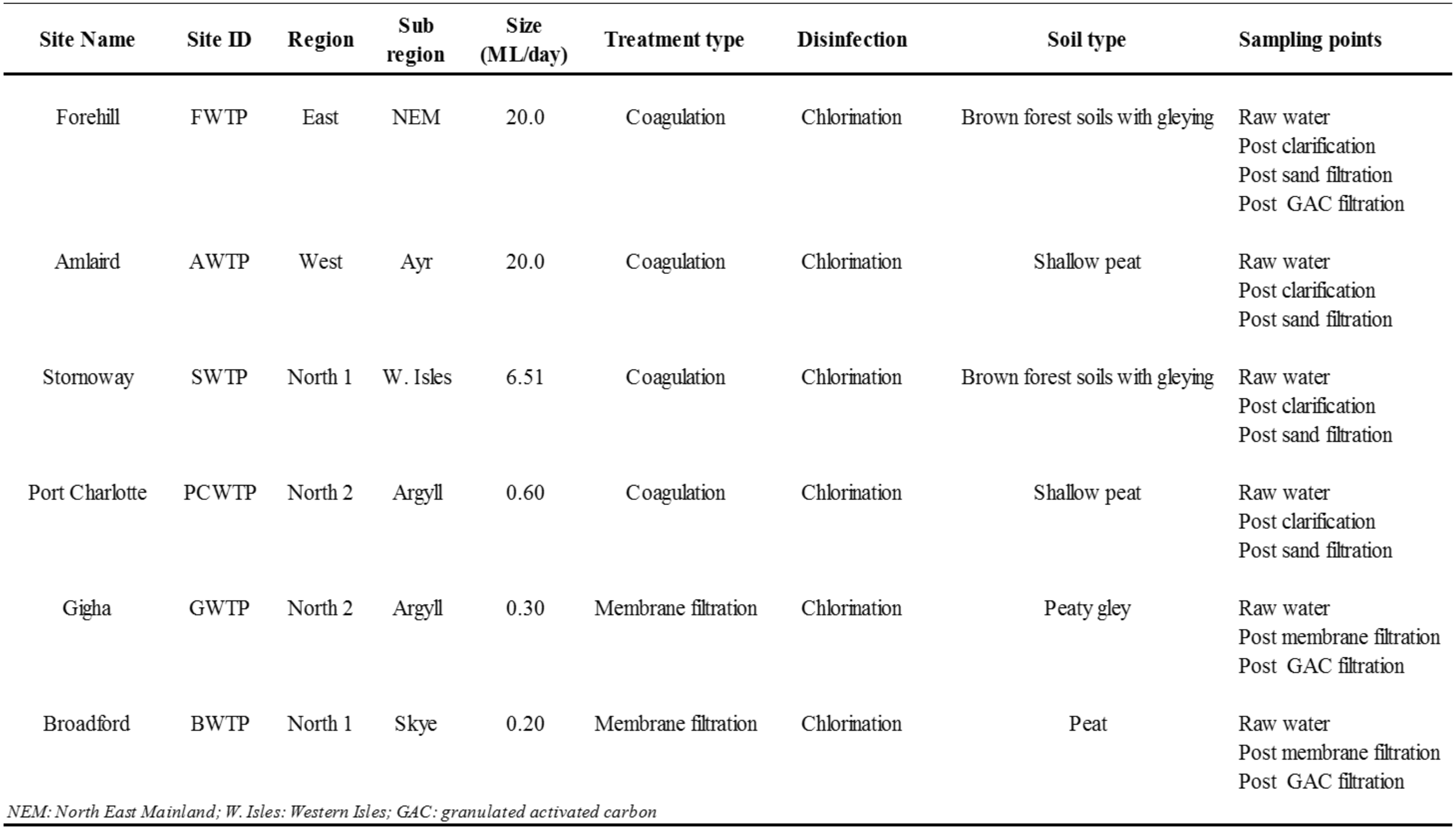
Disinfection is achieved by adding sodium hypochlorite solution after 20 minutes contact time, the clear water passes through a GAC filter and after this through a limestone bed rich in magnesium oxide used also for manganese control. BWTP is controlled by telemetry and functions with very little human intervention. The catchment area around Broadford is dedicated mainly to forestry and sheep grazing. The land nearby is not used for other agricultural purposes and peatland is the predominant type of soil in this area.

4.2.3 Sampling monitoring strategy

During the monthly monitoring, samples were collected and analysed by Scottish Water Scientific Services after each step of the process including final potable water (**Table 4.1**) following a scheduled sampling programme and certified analytical protocols approved by the Drinking Water Quality Regulator (DWQR) for Scotland and the United Kingdom Accreditation Service (UKAS).

All data was extracted and processed for statistical analysis from Scottish Water Laboratory Information Management System (LIMS). THMs were measured using a modified in house method based on EPA Method 524.2 for purgeable organic compounds in water by capillary column gas chromatography mass spectrometry (2, 3). Rainfall and temperature data were collected from nine Meteorological Stations located across Scotland (Paisley, Dunstaffanage, Tiree, Stornoway, Lerwick, Wick, Nairn, Braemar and Leuchars), including data from November 2014 to September 2015 (historical data available from http://www.metoffice.gov.uk). Using these data, average and standard deviations for monthly rainfall and temperature were calculated.

A quarterly monitoring programme that covered each season was also set up for a period of one year starting in November 2014 to September 2015 from six drinking water treatment plants (Amlaird, Stornoway, Port Charlotte, Forehill, Broadford and Gigha). Samples were collected after each step of the process before the point of disinfection (**Table 4.1**) in 5 L high density polyethylene containers with caps purchased from VWR, Poole, England. Samples were delivered to the research laboratories at the School of Civil Engineering and Geosciences (Newcastle University) where samples were filtered through glass fibre pre filters (Millipore, Cork, Ireland) to remove larger particulates and then through 0.45µm polyamide membrane



Site Name	Site ID	Region	Sub region	Size (ML/day)	Treatment type	Disinfection	Soil type	Sampling points
Forehill	FWTP	East	NEM	20.0	Coagulation	Chlorination	Brown forest soils with gleying	Raw water Post clarification Post sand filtration Post GAC filtration
Amlaird	AWTP	West	Ayr	20.0	Coagulation	Chlorination	Shallow peat	Raw water Post clarification Post sand filtration
Stornoway	SWTP	North 1	W. Isles	6.51	Coagulation	Chlorination	Brown forest soils with gleying	Raw water Post clarification Post sand filtration
Port Charlotte	PCWTP	North 2	Argyll	0.60	Coagulation	Chlorination	Shallow peat	Raw water Post clarification Post sand filtration
Gigha	GWTP	North 2	Argyll	0.30	Membrane filtration	Chlorination	Peaty gley	Raw water Post membrane filtration Post GAC filtration
Broadford	BWTP	North 1	Skye	0.20	Membrane filtration	Chlorination	Peat	Raw water Post membrane filtration Post GAC filtration

NEM: North East Mainland; W. Isles: Western Isles; GAC: granulated activated carbon

Table 4.1 Case study drinking water plants located around Scotland

(Sartorius, Goettingen, Germany) to be stored at 4°C until for further use. THMs analysed in Newcastle University followed modified methods from McNeal and Munch (2, 3).

4.2.4 Analytical methods applied to quarterly and monthly monitoring sampling

a) Analyses of water quality

DOC was determined using a total organic carbon analyser TOC-5050A coupled with an autosampler ASI-5000A (Shimadzu, Japan). UV-Visible scans were performed in a UV-Vis spectrophotometer SpectraMaxM3 (Molecular Devices, Sunnyvale, California, USA); pH and conductivity were monitored with a HQ40d Hach-Lange pH meter (Loveland, Colorado, USA). Samples for anion determination were filtered through 0.2 µm cellulose acetate syringe filters (VWR, Poole, England) prior to injection into a ICS-1000 Ion Chromatography System (Dionex, USA). Metals were analysed by Inductively Coupled Plasma Optical Emission Spectroscopy (Vista MPX CCD, Simultaneous ICP-OES, Varian, Middlesburgh, Australia).

b) Fluorescence Excitation Emission analysis

Fluorescence excitation emission analysis were performed in a Varian Cary Eclipse Fluorescence spectrophotometer using Cary Eclipse Software version 7.1 (Middleburgh, Australia). Scans were carried out in filtered samples using the synchronous method and exciting a Xenon lamp from 280 to 500nm. Excitation and emission slits widths were 5nm. Excitation emission matrix 3D plots (3D-EEM) were obtained measuring spectra ranging from 200 to 500 nm at 5 nm increments in the fastest control scan. Each set of data for every sample was imported to Matlab R2015a (Math Works, version 8.5, 2015) to produce 3D contour plots with all dimensions at the same range. Raman and water calibration tests were performed every time prior to analysis. Glucose, albumin, benzoic acid, algogenic and humic acid standards all 99% purity grade were purchased from Sigma Aldrich (Bellefonte, USA) to produce standard stocks at 5 mg C/L which were used to verify fluorescence peaks locations.

c) Trihalomethanes formation potential (THMFP)

Ammonium chloride, sodium hydroxide, sodium thiosulphate, sodium chloride, potassium bromide, potassium chloride, aluminium oxide, mono and di potassium phosphate, disodium hydrogen phosphate, sodium bicarbonate, iron sulphate heptahydrate, sodium hypochlorite (12%) and manganese sulphate hydrate salts were purchased from BDH (Poole, England) with 99% purity. Sodium sulphate, magnesium carbonate, orthophosphoric acid, pentane (pesticide residue analysis grade) and 1,2-dibromopropane were also purchased from Sigma-Aldrich (St. Louis, USA) with 99% purity. A trihalomethanes calibration mix with 2000 µg/mL for each compound in methanol was purchased from Supelco (Bellefonte, USA). DOC concentrations were measured in each raw and treated water samples from each case study site in order to be able to dilute them to 1 mg/L (4). A set of samples without dilution maintaining their original DOC content was also used for THMFP experiments and incubated at the same conditions than diluted samples. Samples with DOC values higher than 1 mg/L were diluted with a solution that mimicked typical Scottish surface water (**Table 4.2**).

Water solutions with DOC content of 1 mg/L (270mL) where transferred into amber glass bottles with glass caps and buffered with 2.74 mL phosphate buffer solution (34g $KHPO_4$ and 5.85g NaOH in 250mL deionised water) and immediately chlorinated with 1.4 mL of a 1000 mg/L sodium hypochlorite solution previously standardised with 0.1M sodium thiosulphate according to APHA methods and filled to the brim with deionised water to avoid any oxygen to enter into the reaction vessel.

Anions and Cations	Synthetic surface water buffer (mg/L)
Na^+	15.2
K^+	2.5
Ca^{2+}	149.8
Mg^{2+}	6.9
Fe^{2+}	1.23
Mn^{2+}	0.14
Al^{3+}	0.1
HCO_3^-	400
SO_4^{2-}	3.3
Cl^-	44.5
pH	6.9-7.1
PO_4^{2-}	0.6
Br-	0.09
P	0.055
TOC	0

Table 4.2 Synthetic surface water buffer with salts content used in THMFP tests

Each sample was prepared in triplicate and incubated at 5°C, 15°C and 25°C. The reaction was stopped after seven days (+/- 4 hours) with 40 mg of ammonium chloride (NH_4Cl) crystals to quench free chlorine and 1 g of buffer salt mix (97.5% by weight KH_2PO_4 and 2.5% Na_2HPO_4) to adjust pH. These chemicals were added to 40 mL clear glass vials (VWR, Poole, England) and once the sample was added it was immediately tightly capped with a Teflon lined rubber seal cap (VWR, Poole, England) avoiding inclusion of air bubbles and shaken to dissolve the salts. Samples were stored at 3ºC for no longer than seven days (±4 hours) before THMs extraction. Pesticide residue analysis grade pentane amended with 300 µg/L of 1,2-dibromopropane internal standard was used for THMs extraction from water samples. First, 2g of sodium sulphate were added to a new 40 mL glass vial and 20 mL of the preserved water sample were then quickly combined with 4 mL of the internal standard containing pentane and the vial was sealed with a Teflon-lined cap. After 1 min of intensive mixing by hand and 15 minutes of mixing at 200 rounds per minute on an orbital shaker, the water-pentane mixture in the vials was allowed to density-separate into two layers, before 1 mL of the pentane layer was transferred into glass vials capped with Teflon liners for GC analysis.

THMs were analysed on an Agilent gas chromatograph equipped with an electron capture detector (GC-ECD). Sample injection (1 µL) in splitless mode using a 60 m HP-5 capillary column with the following temperature programme: 30ºC for 10 min; 3ºC per min to 41ºC, 6 min hold; 5ºC per min to 81ºC; 25ºC per min to 180ºC, 10 min hold. The carrier gas was hydrogen at a constant flow of 1 mL per min. Nitrogen was used as make-up gas for the ECD (30 mL per min) and the detector temperature was 300ºC. Calibration standards were prepared fresh for each GC run by diluting the THMs calibration mix in internal standard amended pentane for a four point instrument calibration.

d) Size Exclusion Chromatography

Polyethylenglycol (PEG) solutions with MW 10,000; 4,000; 1,000; 400 and 200 were used as standards for size exclusion chromatography and were supplied by Sigma Aldrich with > 99% purity (St. Louis, USA). Di sodium phosphate, sodium dihydrogen phosphate and sodium sulphate were purchased from BDH (Poole, England) with > 99% purity. PEG standards were diluted with deionized water to obtain solutions with final concentrations of 10 mg/L. Standards run through a SuperMultipore PW-N size exclusion chromatography column TOSOH Bioscience (Stuttgart, Germany) with 4 µm pore size, 6 mm internal diameter and 150 mm length coupled with a guard column of the same type (20 mm length) in a Shimadzu liquid chromatography system LC-10AD with a SPD-10A UV-Vis detector

(Kyoto, Japan) using 20µL injection volume and total running time of 15 minutes and monitoring at 254 nm wavelength.

Aqueous solution containing final concentrations of disodium phosphate 0.0016 M, sodium hydrogen phosphate and sodium sulphate 0.025 M were used as separation buffer (pH 7.1-7.5) in an isocratic separation at 0.6 mL/min flow rate. Approximated molecular weight in Daltons was obtained by using a linear calibration curve of a logarithmic transformation of retention time (min) and molecular weight (Daltons) of PEG standards at 200, 400, 1000, 4000 and 10,000 Daltons ($r^2 = 0.998$, n = 3).

e) DOC characterisation by resin fractionation

This test was performed at Scientific Services Laboratories (Scottish Water): treated and untreated water samples (2L) were previously filtrated through 0.45 µm cellulose membranes and pumped through two columns packed with Amberlite XAD 7HP and XAD 4 resins. Hydrophilic fraction was eluted directly after passing consecutively through resins XAD 7HP and XAD 4 and collected for further analysis. Hydrophobic fraction was eluted from the XAD 7HP column with 0.1M NaOH solution and transphilic fraction (TPI) was eluted from the XAD 4 column also with 0.1M NaOH. Cleaning and rinsing of the columns are performed with deionised water and 0.1M HCl following standard in house procedures (Scientific Services UKAS accredited in house method: IC044).

4.2.5 Exploratory statistics and Pearson bivariate correlations

All results obtained from the monthly and quarterly sampling programmes were used for exploratory statistical analysis that included: analysis of means, 2 sample t-test, variances and Pearson correlation analysis were calculated using Minitab 17 (Leadtools Technologies

Inc, version 17.1.0, 2014) and reported with 95% confidence limits by showing plus minus standard errors of the mean.

4.3 Results and discussion

4.3.1 THMs from monthly monitoring data

In line with the earlier findings (chapter 3), results from the monthly monitoring programme combined with data collected from Scottish Water LIMS database showed the clear influence of the seasons on total THMs concentrations for samples taken at the five case study sites during a period of three years (Jan.2013 - Dec.2015). Lowest THMs levels were generally found in March and then gradually increased to September for Amlaird, Stornoway, Broadford and Gigha WTPs. In year 2014, Broadford, a tubular membrane plant, did not show the characteristic trend of ambient temperature and total THMs shown in chapter 3. Ambient temperature in May 2014 and June 2014 were lower (less than 15°C) for those months compared to values found during the same period in 2013 and 2015 (**Figure 4.1d**). Small changes in maintenance practice such as an increase in the frequency of cleaning the membranes could have contributed to the variation of THMs concentrations during these months for the Broadford WTP. Overall, though the four WTPs showed the same seasonal trend observed in chapter 3 for the median THM value of 93 treatment plants, with THMs broadly following the trend in ambient temperature.

Forehill WTP showed a different trend (**Figure 4.1b**) that did not follow the ambient temperature pattern. The installation of a new granulated activated carbon (GAC) filtration system with Filtrasorb 400 (charcoal based material) in 2014, improved the reduction of organic content including THMs precursors. Concentrations of total THMs in Forehill reached their lowest level for months following the installation in April 2014 to values below

5 µg/L and gradually increased in 2015, still within permissible levels, to values below 30 µg/L.

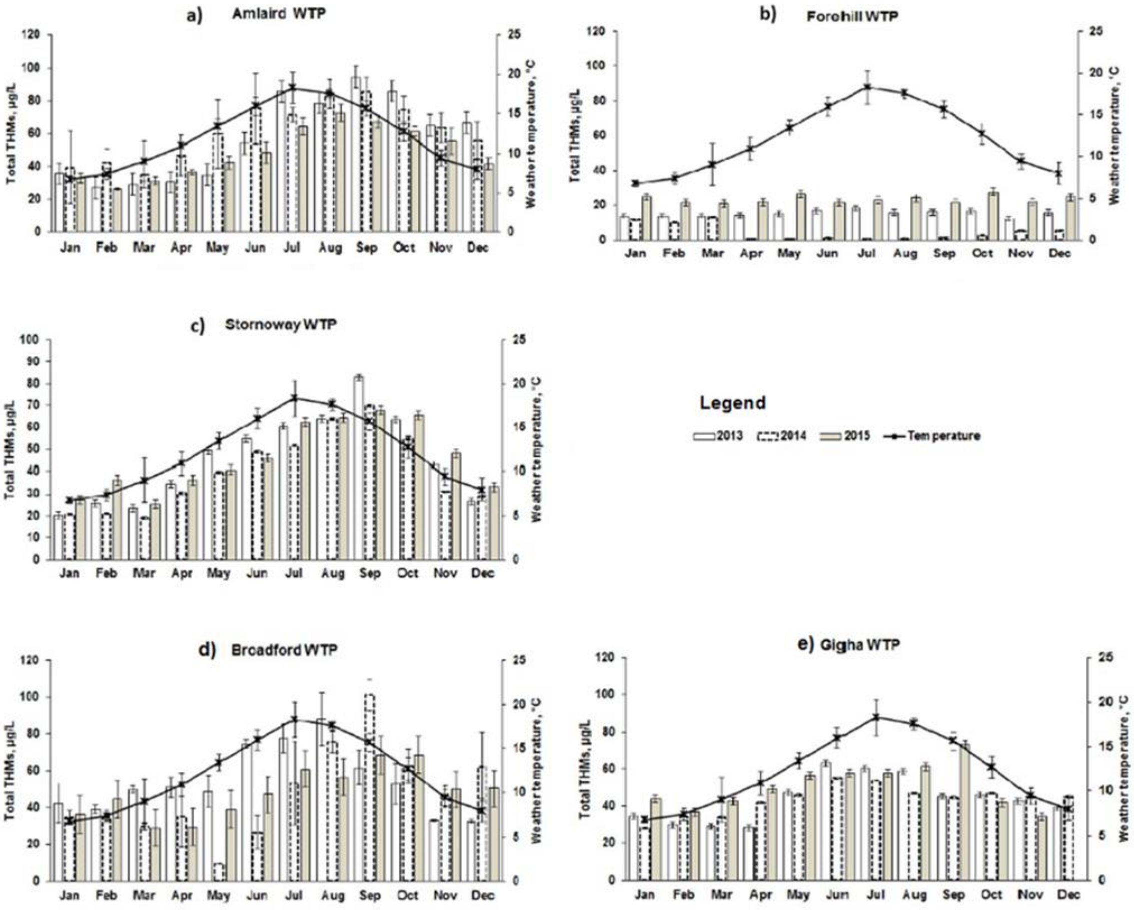


Figure 4.1 Seasonal trends for total THMs and monthly ambient temperatures at six case study sites

The case of Forehill WTWs is also particular due to high levels of bromide found in treated water. Despite of its estuarine location, bromide is also incorporated in excess to the treatment by being contained in chloride salts used for chlorine formation currently used as disinfectant in the site. In the previous chapter, it was also shown that brominated THMs were more present in coastal areas due to the propensity of bromide to shift chlorination of DOC towards brominated THMs (5, 6).

The amounts observed for bromoform and dibromochloromethane at this site were higher than any other case study site but it did not compromise total THMs levels (further discussion in section 4.3.3). Therefore, the inclusion of GAC filtration at this site, although primarily to control pesticides, also improved the control of residual DOC bringing THMs to very low levels, demonstrating the potential of GAC filtration as a control strategy to minimize THMs in drinking water supplies, although it appears THMs returned to the levels before GAC installation when then DOC sorption capacity of the GAC had been exhausted after about nine months. From these monthly results we could also say, that although temperature appears to be a crucial determinant of THMs, each drinking water treatment site is undergoing variation in their processes over time that will influence THMs control and formation. This motivates well-controlled laboratory experiments, where such co-factors can be eliminated.

4.3.2 Other quality parameters from monthly monitoring data

After corroborating the previously observed alignment in trends for temperature and THMs formation in the selected case study sites during the monthly monitoring, other quality parameters were also evaluated in order to identify those with similar seasonal changes, which could potentially also explain the observed trends in THMs. Only a few raw water variables showed an apparent trends similar to THMs in terms of seasonality: colour, bromide and TOC. These parameters showed peak values in September and lowest in March (**Figure 4.2**). Colour as a proxy for tannins, bromide and TOC are well-known THM precursors, and could therefore be root causes of the observed THM seasonality. Increased alkalinity may result from respiration and organic matter decomposition processes releasing CO_2, and hence may correlated with trends in DOC ($r^2 = 0.4$, $p < 0.05$). However, monthly total THMs in distribution networks only correlated with raw water variables weakly: colour ($r^2 = 0.4$, $p = 0.000$), TOC ($r^2 = 0.3$, $p = 0.01$) demonstrating the importance of treatment.

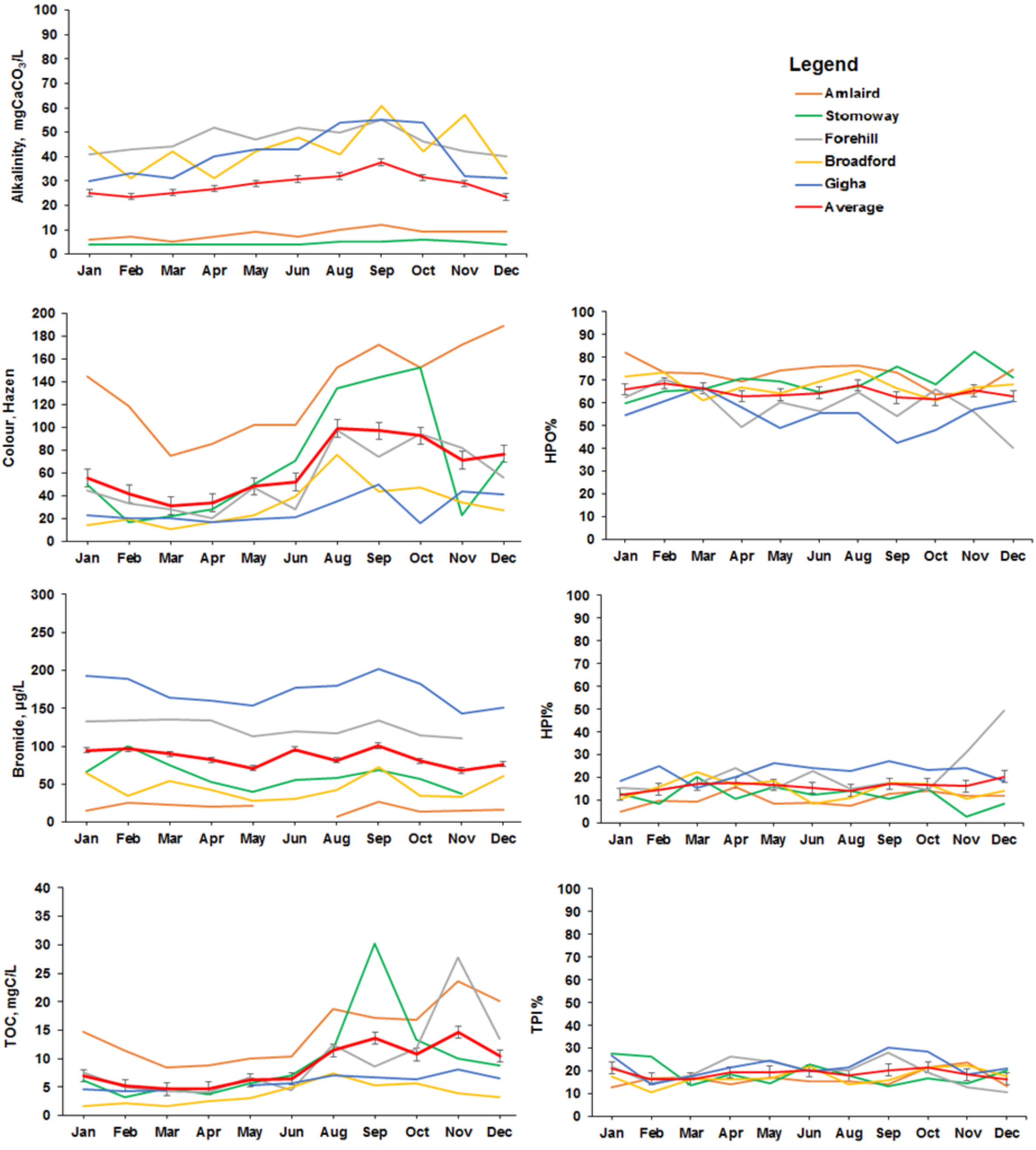


Figure 4.2 Seasonal trends for quality variables in raw water at five treatment sites with their average values from monthly sampling monitoring (November 2014-September 2015)

In contrast, DOC fractions in raw water: hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) expressed in % do not appear to be influenced by changes of temperature or the seasons. Each particular fraction had a similar behaviour in all site. For example, monthly average of HPO fraction in percentage appeared significantly higher in raw water at 64.7% ± s.e.0.69 compared to HPI at 16.3% ± s.e.0.62 (*t*-test = 52.2, *p* = 0.000) and TPI at 18.9% ± s.e.0.56 (*t*-test = 51.6, *p* = 0.000) fractions. These values appeared to be constant along the year, showing no DOC quality change related to the observed temperature trends. However, percentages of DOC fractions changed with treatment, as discussed below. Looking at DOC quality variables in treated water samples taken just before the point of disinfection, UV absorbance at 254nm and TOC both showed maximum values in October (**Figure 4.3**). No other water quality parameters showed seasonal changes similar to trends in THMs and concentrations of these parameters were fairly constant (detailed values appear in supporting information for this chapter).

Looking more closely at the effect of treatment on DOC fractions for example, there was a change in DOC quality compared to that found in raw water. Firstly, HPO percentages reduced significantly (*t*-test = 14.8, *p* = 0.000) from raw at 64.7% ± s.e.0.69 to treated water at 46.7% ± s.e.1.0 corroborating the general wisdom that hydrophobic compounds are removed more successfully by coagulation and membrane treatments than hydrophilic compounds (7). However, 46.7% of DOC is still substantial, indicating that an important percentage in terms of HPO compounds remain dissolved in treated water. In the case of HPI fractions, the percentages were different. Treated water showed significantly higher (*t*-test = -15.6, *p* = 0.000) percentages of hydrophilic DOC fraction at 34.1% ± s.e.0.96 compared to the amounts found in raw water with 16.3% ± s.e.0.62. Whereas, for the transphilic fraction, there was not significant change (*t*-test = -0.38, *p* = 0.706) in the percentages remaining more or less constant in raw water 18.9% ± s.e.0.56 and after treatment 19.2% ± s.e.0.45 indicating that this portion of DOC was neither preferentially, nor particularly poorly removed in the treatment.

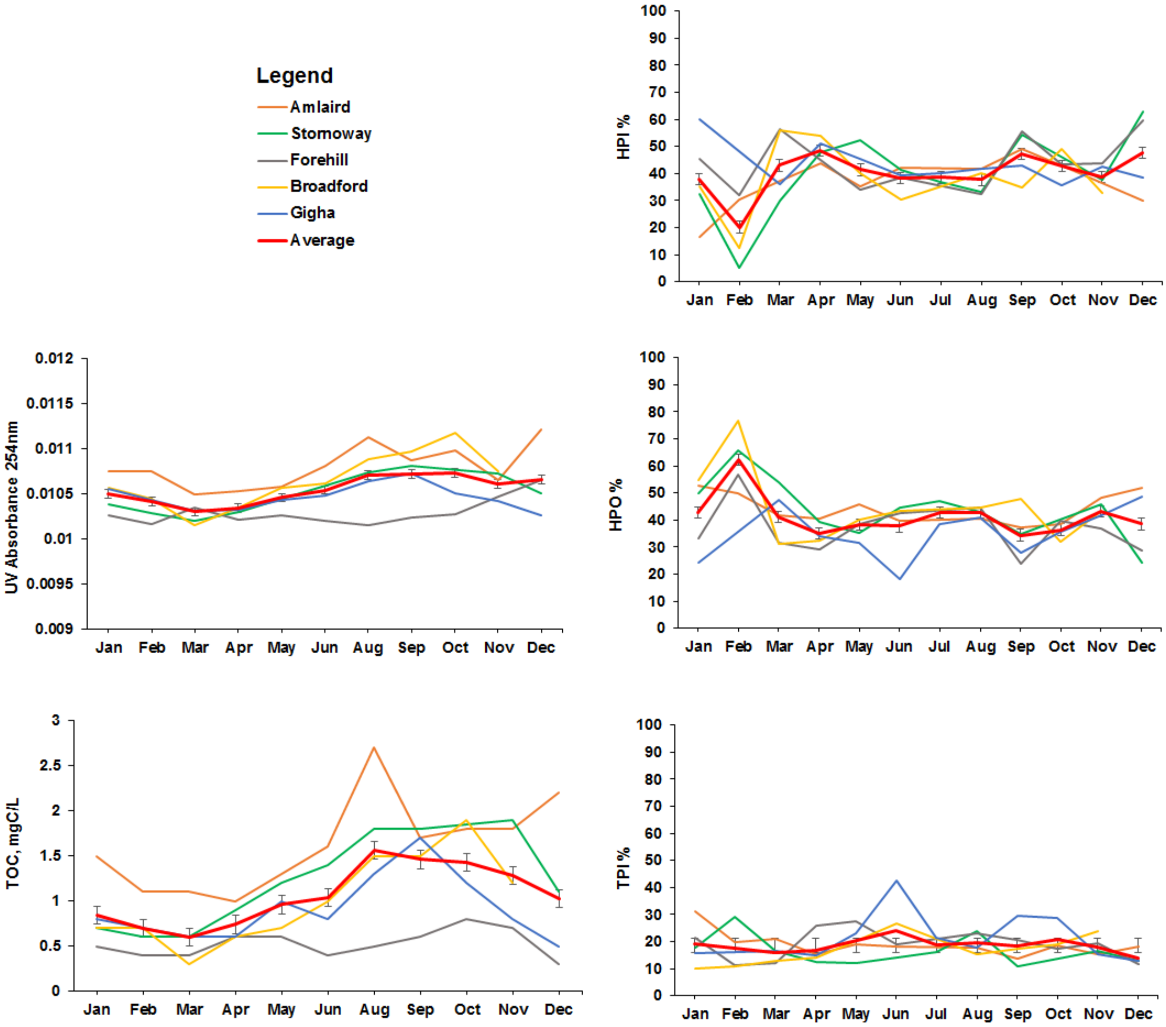


Figure 4.3 Seasonal trends for quality variables in treated water at five treatment sites with average values obtained from monthly sampling monitoring (November 2014-September 2015)

The amount and reactivity of these various compounds are evaluated and discussed in further sections of this chapter. Looking at the value of DOC content normalised (absorbance divided by DOC mg/L) UV absorbance at 220nm, 254nm, 270nm and 350nm (**Figure 4.4**), it can be seen that there is no evident seasonal change in DOC quality during the period of one year. Another plot shows a clear influence of the seasons when looking at only absorbance values

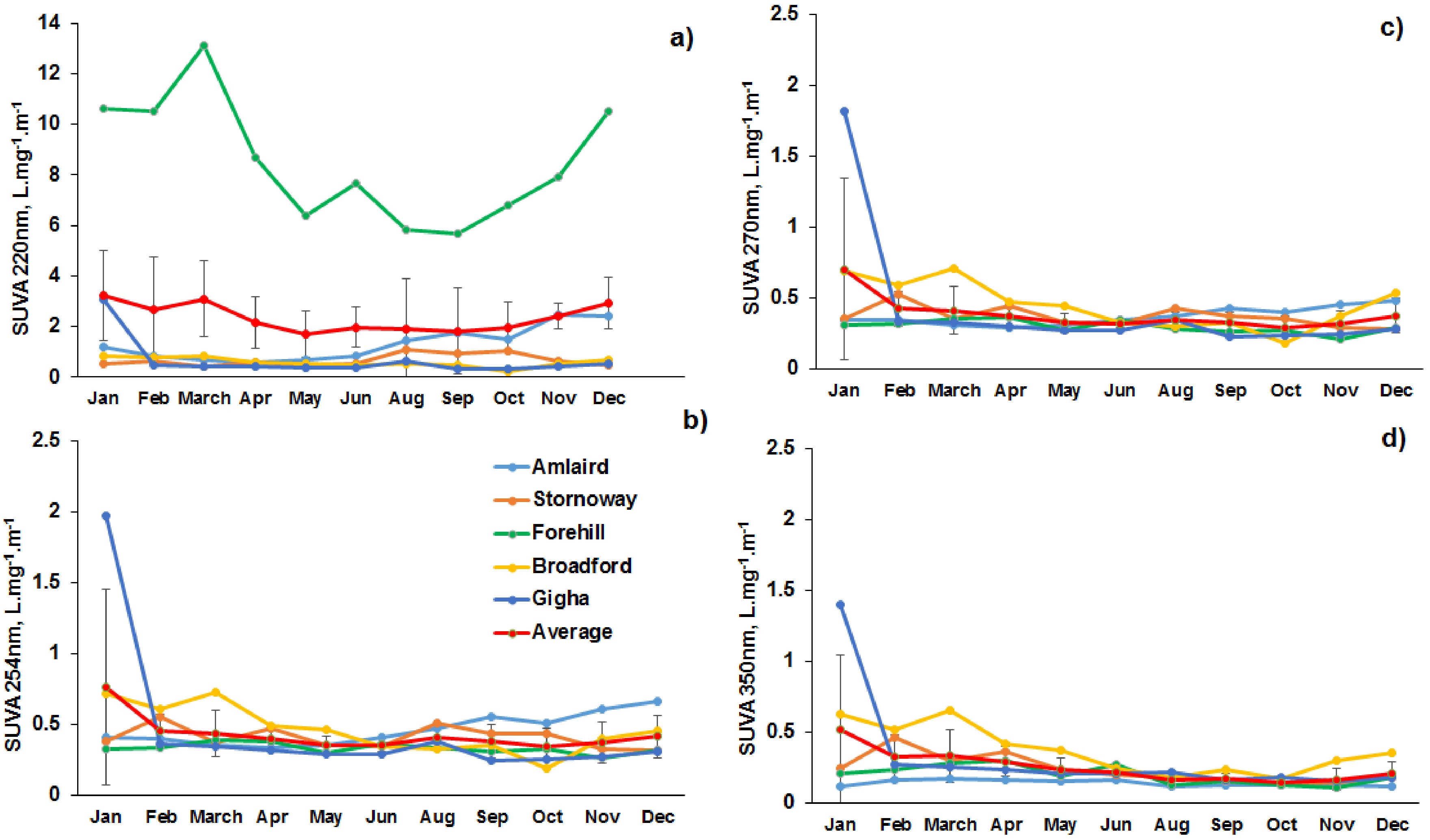


Figure 4.4 Normalised UV absorbances per mg DOC/L values (SUVA) in raw water at five WTPs at a) 220nm, b) 254nm, c) 270nm and d) 350nm

without normalisation (**Figure 4.5**), but these apparent variations were eliminated after normalisation, showing that, while DOC is seasonably variable, with greater DOC concentrations, and hence greater UV absorbance, in the summer, DOC quality remains fairly constant. The term normalisation follows the same concept of SUVA (specific ultraviolet absorbance) in which the typical absorbance at 254nm is associated with aromatic compounds (8, 9) and more specifically, SUVA differentiate between hydrophobic or hydrophilic character of DOC (10). The reduction of absorbance values from raw water and further along the process is positive in the sense that treatment does perform in removing DOC compounds with UV absorbance. As Scottish surface water have rich organic soils from humic and fulvic origin, then the presence of aromatic and phenolic compounds is potentially high. The investigation of DOC fractions and absorbances was performed in order to find an indication of the nature of residual DOC. Percentages of DOC fractions and normalisation of UV absorbances showed a constant trend indicating that quality of THMs precursors remained constant along the year, but treatment affected the amounts of residual DOC at the point of disinfection.

4.3.3 THMs and other quality parameters in quarterly monitoring data

a) THMFP

In previous sections, monthly monitoring identified temperature, colour and TOC as parameters with similar seasonal trends as THMs. Another sampling monitoring programme collected water from the same sites in quarterly periods starting in November 2014 until September 2015 to evaluate and verify root causes of seasonal changes in THMs formation, and also for a more detailed investigation of DOC character.

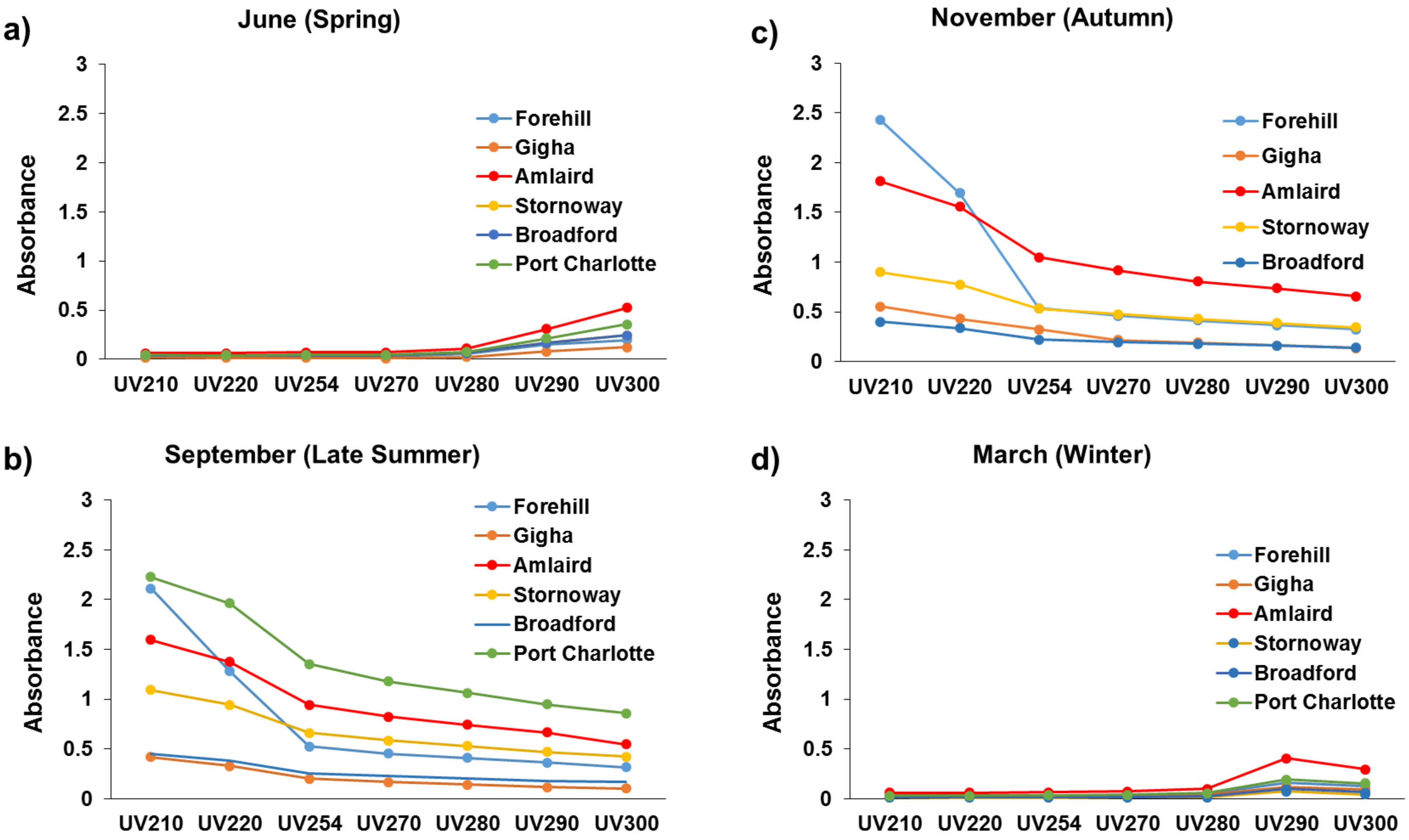


Figure 4.5 Raw water ultraviolet (UV) absorbances measured quarterly in six drinking treatment plants (November 2014-September 2015)

Looking at THMs formed in a controlled experiment with a constant amount of DOC (DOC = 1 mg/L) and at constant incubation temperature (15°C), chloroform yielded the highest concentration of the trihalomethanes in all case study sites, followed by bromodichloromethane, dichlorobromomethane and bromoform as shown in **Figure 4.6**. With temperature and DOC kept constant, there was no clear and consistent trend of THMs formation with the seasons.

THMFP experiments involving the reaction of only 1 mg C/L DOC contained in each sample with chlorine, keeping DOC concentration and quality and chlorine dose constant, was also evaluated at 5ºC, 15ºC and 25ºC to study the temperature effect on THM formation. In **Figure 4.7**, raw water taken from all sites showed a clear and positive effect of temperature on THMs formation, corroborating ambient (or water) temperature as a root cause of the THMs seasonality in Scottish WTPs. The lowest levels of THMs were consistently found at 5°C and gradually increased after incubation at 15°C and further at 25°C (**Appendix Table 4.1**).

As a general rule, THMs levels increased strongly and consistently with the increase of temperature (**Figure 4.7**) in all sites. Higher THMs concentrations were also obtained from the reaction of undiluted raw water samples that contained a much higher portion of DOC, as compared to the same samples diluted to a concentration of 1 mg/L DOC and incubated at the same temperature, which confirms that the level of DOC is also positively correlated with THMs formation, corroborating seasonal trends in DOC as another root cause of the seasonality in THM concentrations (**Figure 4.8)**

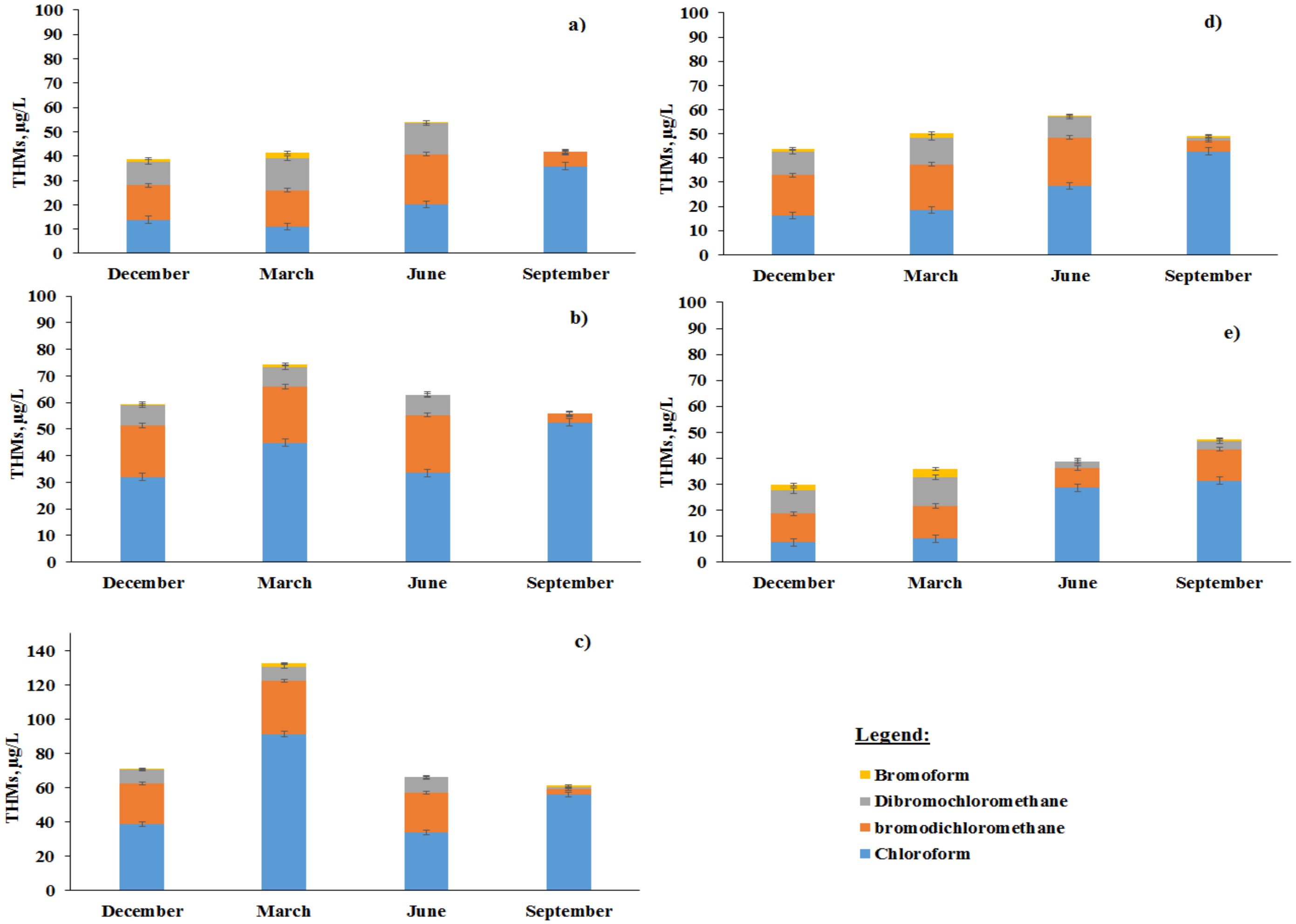


Figure 4.6 Trihalomethanes formation potential (THMFP) in raw water samples (1mg DOC/L) incubated at 15°C from 5 WTPs: a) Forehill, b) Amlaird, c) Stornoway, d) Broadford and e) Gigha

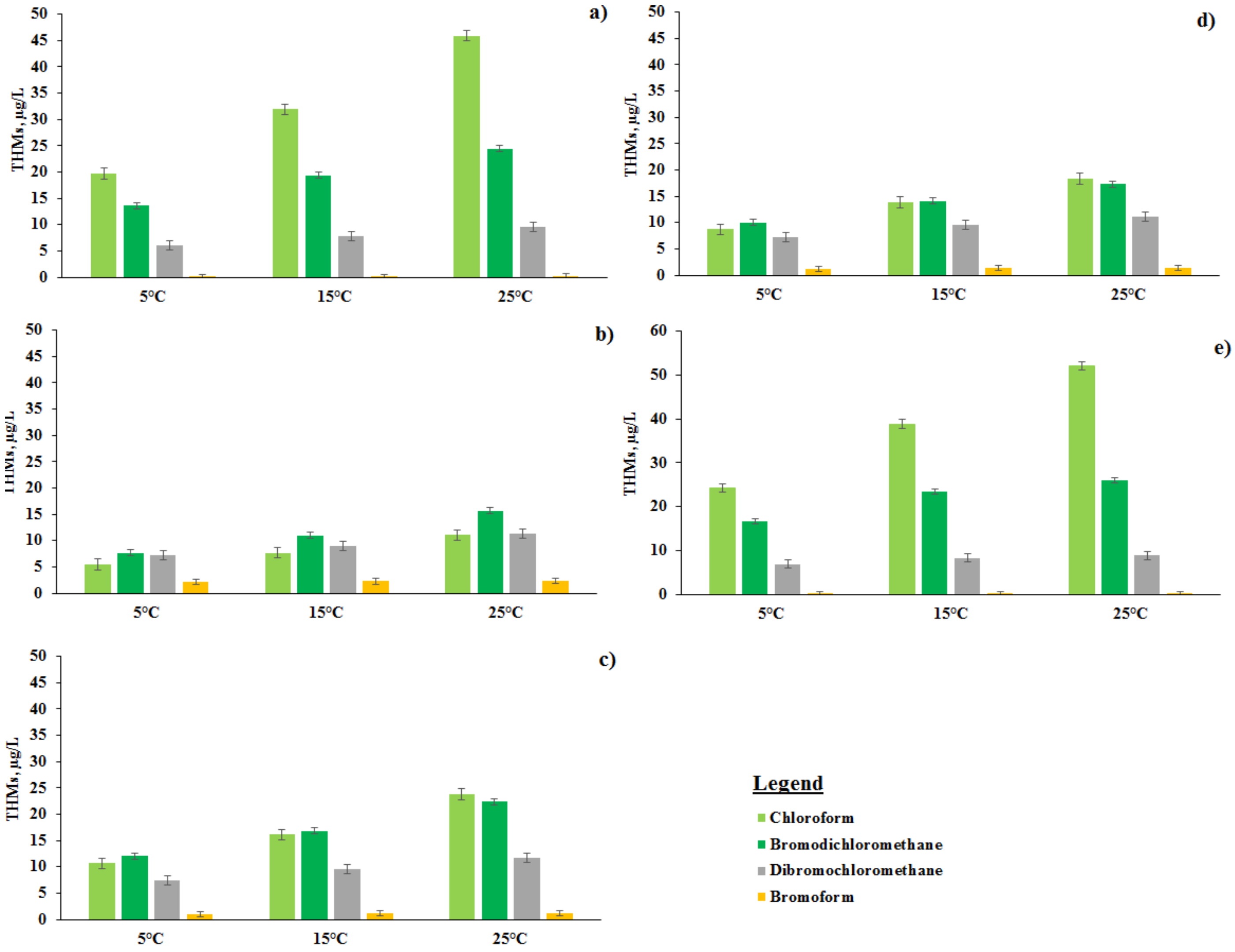


Figure 4.7 Effects of temperature for THMFP in raw water (DOC = 1mg/L) for samples taken from: a) Amlaird WTP and b) Gigha WTP c) Broadford WTP d) Forehill and e) Stornoway at 5°C, 15°C and 25°C

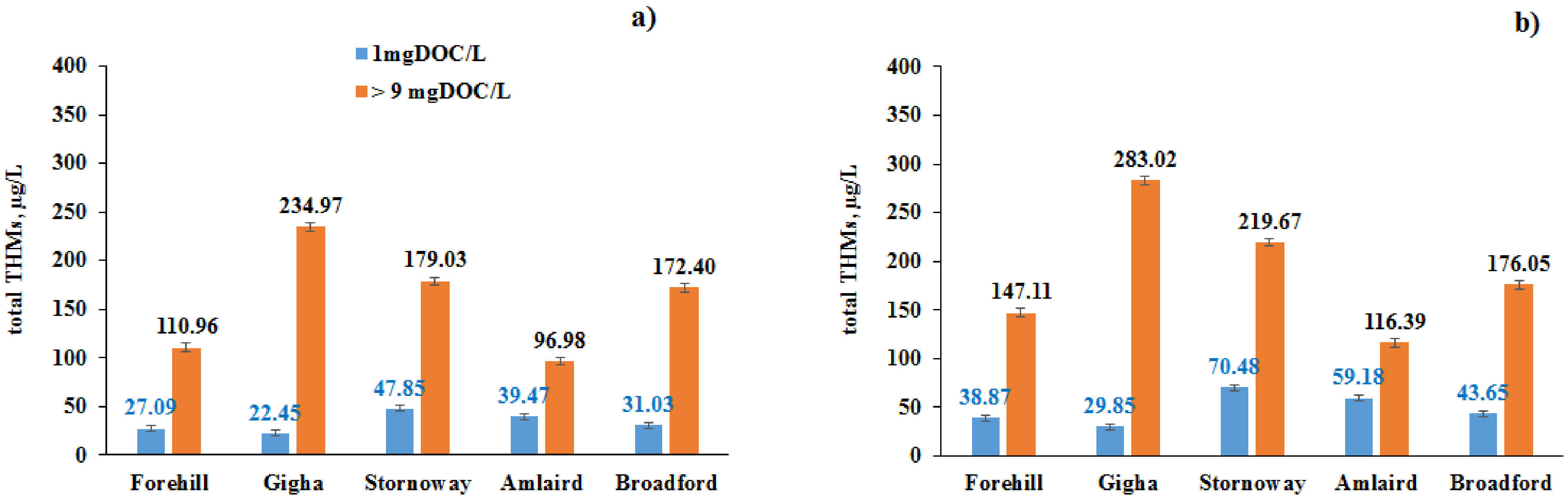


Figure 4.8 THMFP for diluted (1mgDOC/L) and undiluted (>9mgDOC/L) raw water samples at five WTPs (quarterly monitoring) incubated at a) 5°C and b) 15°C

THMFP experiments further confirmed that reductions in DOC with treatment considerably decreased THMs formation after every step of the treatment process, since post sand filtration and post GAC were the samples that formed the lowest THMs levels. However, variable DOC reactivity was evident when comparing raw water samples from different sites, especially for sites that have high organic content from peaty origin such as is the case of Amlaird. Concentrations of THMs were lower for raw water samples taken from Gigha WTP (28.1± s.e.4.6μg/L) as compared to Amlaird (39.3 ± s.e.5.6μg/L), even though DOC concentration was maintained constant as in Amlaird at 1mg/L. Gigha is located by the coast and its catchment is not similar to Amlaird's which is particularly peaty. It seems then, that external influences such type of soil or geographical location still has some impact on THM formation via DOC quality.

This controlled experiment confirms that temperature is crucial for THMs formation but also DOC character can be influenced by the catchment and modified by the treatment. Thanks to the successful reduction of THMs in sites such Forehill, reactivity of residual DOC can be minimised by optimizing coagulation or membrane filtration (7, 11, 12). Also, incorporation of further steps in the process, such adequate GAC, can aid to reduce DOC even more efficiently to minimize THMs formation.

b) SUVA in quarterly samples

DOC and specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) results showed a clear DOC hydrophobicity ranging from 3.3 to 5.8 L/m-mg in raw water samples during summer and a mixture of hydrophobic and hydrophilic character with 2.3 to 4.7 L/m-mg during autumn (9, 13). In contrast, $SUVA_{254}$ values for winter and spring in raw and treated water samples ranged from 0.1 to 0.6 L/m-mg which indicates the presence of hydrophilic compounds at very low levels (**Appendix Table 4.2**). The highest $SUVA_{254}$ values in the last stage of the process before the point of disinfection were found similarly during summer at 0.3-3.9 L/m-mg disregarding the type of process, which indicates that both conventional coagulation and membrane drinking water processes struggle to remove all hydrophobic DOC material. Hence, in terms of the process, it is very difficult to determine whether coagulation or membrane filtration is the most efficient process in terms of DOC reduction in water treatment, as both maintained a hydrophobic and hydrophilic residual DOC before the disinfection step.

c) UV scans

Raw water DOC values ranged from 10-26 mg/L with particular yellow discoloration whereas treated water samples presented very low levels of DOC values lower than 5 mg/L and in some cases undetected by our instruments (limit of detection 1mg/L) as shown in (**Appendix Table 4.2)**. Raw water samples collected during late summer and autumn months showed larger absorbances for all monitored wavelengths but more specifically for shorter wavelengths from 210-254 nm (**Figure 4.5b and 4.5c**). Low absorbances in the UV visible region (210-230nm) have been linked to anions such nitrate, nitrite and chloride and to very small MW organic compounds such alcohols, carboxylic acids, ketones and aldehydes (14). Coincidentally, higher levels of rainfall happen during these months which can explain the possibility of these salts and inorganics carried to surface water by rainfall and runoff events (15). Absorbance at 254 nm has been considered as a general indicator of DOC and is widely reported in DOC characterisation studies (16, 17). Organic compounds absorbing at 254 nm usually contain aromatic rings with conjugated or aliphatic groups in their chemical structure. However, the presence of keto, methoxy, carboxyl or hydroxyl groups into the aromatic rings will shift absorbance to longer wavelengths such 280-300 nm (18). These compounds are usually derived from either lignin, plant material, humic or fulvic acids or from microbial and algae degradation (9). At the same time, aromatic methoxylated organic compounds have been shown to be quite reactive with chlorine to produce THMs (19). Our results showed that stronger absorbances at longer wavelengths were found during spring and winter months (**Figure 4.5a and 4.5d**) when absorbances at other wavelengths were almost undetectable. Although, absorbance responses at 280-300 nm were not as high and obvious as for shorter wavelengths 210-230 nm (**Appendix Table 4.2**), these findings suggest some changes in DOC character during the seasons and the longer absorbances seen in winter and spring represent the residual DOC in raw and treated water and therefore is likely responsible of producing THMs during these months. There is some disagreement between our quarterly analysis, which shows changes in UV absorbance for different seasons, and the monthly data measured at Scottish Water, which does not show these changes, and it is not clear what could have caused these discrepancies. Longer absorbances 280-300 nm may be valuable to enhance DOC monitoring. However, normalisation of UV absorbance values with DOC similar to SUVA for the values obtained from the monthly data indicated a more constant trend, while characterisation of the water used for the THMFP experiments show that there is some seasonal influence on DOC quality.

d) Excitation Emission Fluorescence Analysis

Fluorescence excitation emission matrix (EEM) contour plots showed two very distinctive peaks for all samples taken quarterly from the six case study sites during a one year period (November 2014 – September 2015) with excitation/emission values in the range from 220-250/350-440nm and 300-380/350-425nm respectively (**Table 4.3**). Despite catchment areas differences and geographical locations between all sites, samples presented a clear homogeneity with a strong humic and fulvic like influence. However, fluorescence intensity diminished from raw water samples to treated samples in the evaluated sites. This effect demonstrates the direct relationship between amount of DOC and intensity of fluorescence peaks (13, 20). As all raw water samples showed discoloration, dilution was applied to allow clearer scans and to improve the response of emitted energies which could cause a slight shift of the emission bands (10-20 nm) if not applied otherwise. This effect has been previously referred as the fluctuation of unsaturated aromatic compounds of fulvic and humic nature (21) that occurs when the solution contains large amount of these compounds and it was observed particularly during summer and autumn months where intensities of response were much higher and above the threshold of detection. Also, vibrational energies produced by conjugated bonds present in the aromatic and condensed portions of humic and fulvic acids will induce stronger intensity of fluorescence (22). Then again, seasonality plays an important role in DOC quantity, and perhaps also quality.

Peaks with excitation/emission values of 220-250/300-380 and 350-440, 350-425 correspond to humic like and fulvic fluorophores respectively (22, 23). These results show that Scottish surface waters have great humic and fulvic influence all year around. Gigha WTP presented a third peak in raw water samples for summer and autumn periods with excitation/emission 220-230/300-350 that corresponds to saccharides (**Figure 4.9a**). During summer months higher temperatures promote the growth not of only bacteria but also of other microorganisms and aquatic plants. This particular site showed blooms of bog bean (aquatic plant) in the past which could be contributing to the release of this type of organic compounds. However, this peak seems to overlap the typical location for tyrosine 225-237/309-321 and tryptophan 225-237/340-380 (24, 25) which indicate the presence of high nitrogen content typically found in proteinic residuals from algal blooms (25). It is possible then to say that this site presents three influences: humic and fulvic acids, sugars and protein material which makes its DOC

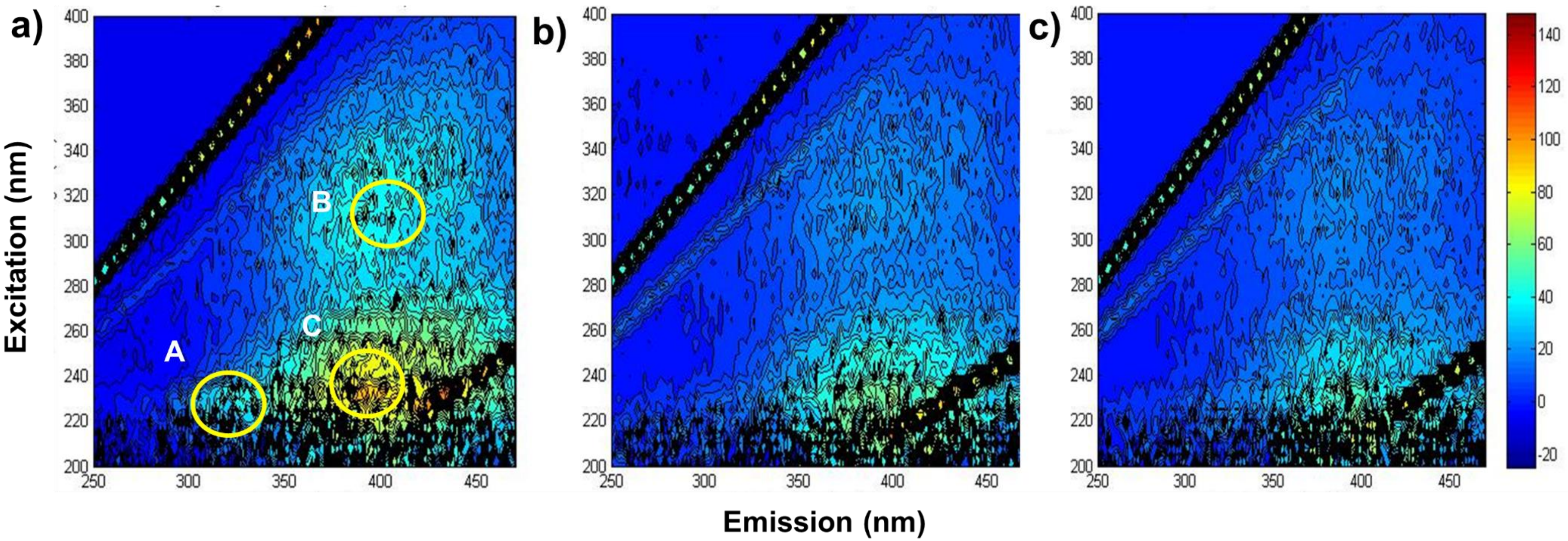


Figure 4.9 Typical fluorescence excitation emission matrix (EEM) plots for Gigha WTP (September 2015) at: a) raw water (A: proteinaceous material; B: humic acids; C) fulvic acids); b) post membrane filtration; c) post granulated activated carbon filtration

		First (nm)		Second (nm)		Third (nm)	
Site name	**Sample type**	**Excitation,**	**Emission**	**Excitation,**	**Emission**	**Excitation,**	**Emission**
Amlaird	Raw water	230-240	360-420	320-360	400-440	None	None
	Post clarification	230-240	360-420	320-360	375-410	250-260	375-425
	Post sand filtration	220-240	360-420	340-380	375-410	None	None
Forehill	Raw water	230-250	375-440	320-350	375-425	None	None
	Post clarification	230-250	375-440	320-350	375-425	None	None
	Post sand filtration	230-250	350-425	320-350	375-425	None	None
	Post GAC	None	None	None	None	None	None
Stornoway	Raw water	230-250	370-425	320-350	400-440	None	None
	Post clarification	220-230	370-400	300-340	375-425	None	None
	Post sand filtration	220-230	370-400	300-340	375-425	None	None
Port Charlotte	Raw water	220-230	380-410	300-340	375-425	None	None
	Post clarification	220-240	380-410	300-340	360-400	None	None
	Post sand filtration	220-240	380-410	300-400	360-400	None	None
Gigha	Raw water	220-230	380-420	300-340	360-400	None	None
	Post membrane filtration	220-230	380-400	300-340	350-400	None	None
	Post GAC	220-230	380-400	300-340	360-400	None	None
Broadford	Raw water	220-240	380-425	300-340	375-425	None	None
	Post membrane filtration	220-240	380-425	300-340	375-425	None	None
	Post GAC	220-240	380-425	300-340	375-425	None	None

GAC: Granulated activated carbon

Table 4.3 Fluorescence excitation emission wavelengths pairs (nm) found in water samples at different sampling points in six drinking water treatment sites (December 2014 – September 2015

character very complex. The location of these peaks was corroborated by using two types of sugars: lactose and glucose at 5 mg C/L as standards (**Table 4.4**). Other pure standards were used to identify typical fluorescence peak locations for proteins and organic aromatics at low DOC concentrations (5 mg C/L) such albumin, benzoic acid and humic acid at specific excitation emission values (**Figure 4.10)**. Overall, fluorescence EEM application for DOC characterisation was advantageous due to its not invasive approach which maintained DOC quality unaltered, in contrast to fractionation techniques. Thus, EEMs plots gave a general interpretation of the DOC quality present in Scottish waters as being of humic and fulvic origin in its majority. From the six sites only one presented sugars and protein like material which indicates that, fingerprint like peak areas can provide a general information on the nature of DOC samples. However, more detailed structural information about their chemical character such identifying its molecular weight and chemical groups will be even more beneficial.

Standards (5 mgC/L)	Excitation (nm)	Emission (nm)	Excitation (nm)	Emission (nm)
Glucose	220-230	290-325	275-280	300-325
Lactose	220-230	290-325	275-280	300-325
Albumin	220-230	300-310	275-285	300-310
Algogenic acid	220-230	300-310	275-280	375-450
Humic acid	275-280	375-450		
Benzoic acid	275-290	275-300		

Table 4.4 Standards for EEM plots

e) High Pressure Size Exclusion Chromatography

High pressure size exclusion chromatography (HPSEC) has been used to determine nominal and relative molecular weight of NOM in surface, treated and waste water samples (16, 21, 23, 26). By applying HPSEC to raw and treated water samples in six WTPs, nominal molecular weight (MW) in Daltons was identified in four seasonal sampling periods (**Table 4.5**). Molecular weight ranging from 3797 to 2495 Daltons were found in raw water samples whereas treated water samples presented relatively smaller molecular weights ranging from 2495 to 105 Daltons. A maximum of three well defined peaks were separated in treated water from Gigha WTP during all seasons while the other treatment sites showed one or two peaks in the treated water samples (**Figure 4.11**). Post clarification, post sand filtration post membrane and post GAC samples showed DOC compounds ranging from 2647 to 1737 which indicates that still a small portion of the larger DOC compounds (hydrophobic) remain after treatment disregarding its type. Three sites: Forehill, Gigha and Amlaird showed MW < 1000 Da in the treated samples. These peaks eluted much later during the chromatographic separation and were also present in raw water samples with a very small response signal. The presence of peaks below 500 Daltons may indicate the presence of aliphatic organic compounds of hydrophilic nature. The small differences between MW found in the different seasons is due to small shifts in chromatographic separation rather than DOC quality. The intensity of response in raw water samples was usually ten times larger than treated water samples indicating again, as in the previous fluorescence EEM experiments, the efficacy of the treatment processes to remove DOC, especially of large molecular weight. It would be very difficult to isolated specific types of compounds or chemical species from the information obtained from HPSEC experiments. As a general overview, some studies have identified as the most characteristic compounds found below 5000 Daltons saccharides, small polyphenols and carboxylated species from humic and fulvic nature and aromatic amino acids rather than peptides, proteins or polysaccharide materials (23, 27).

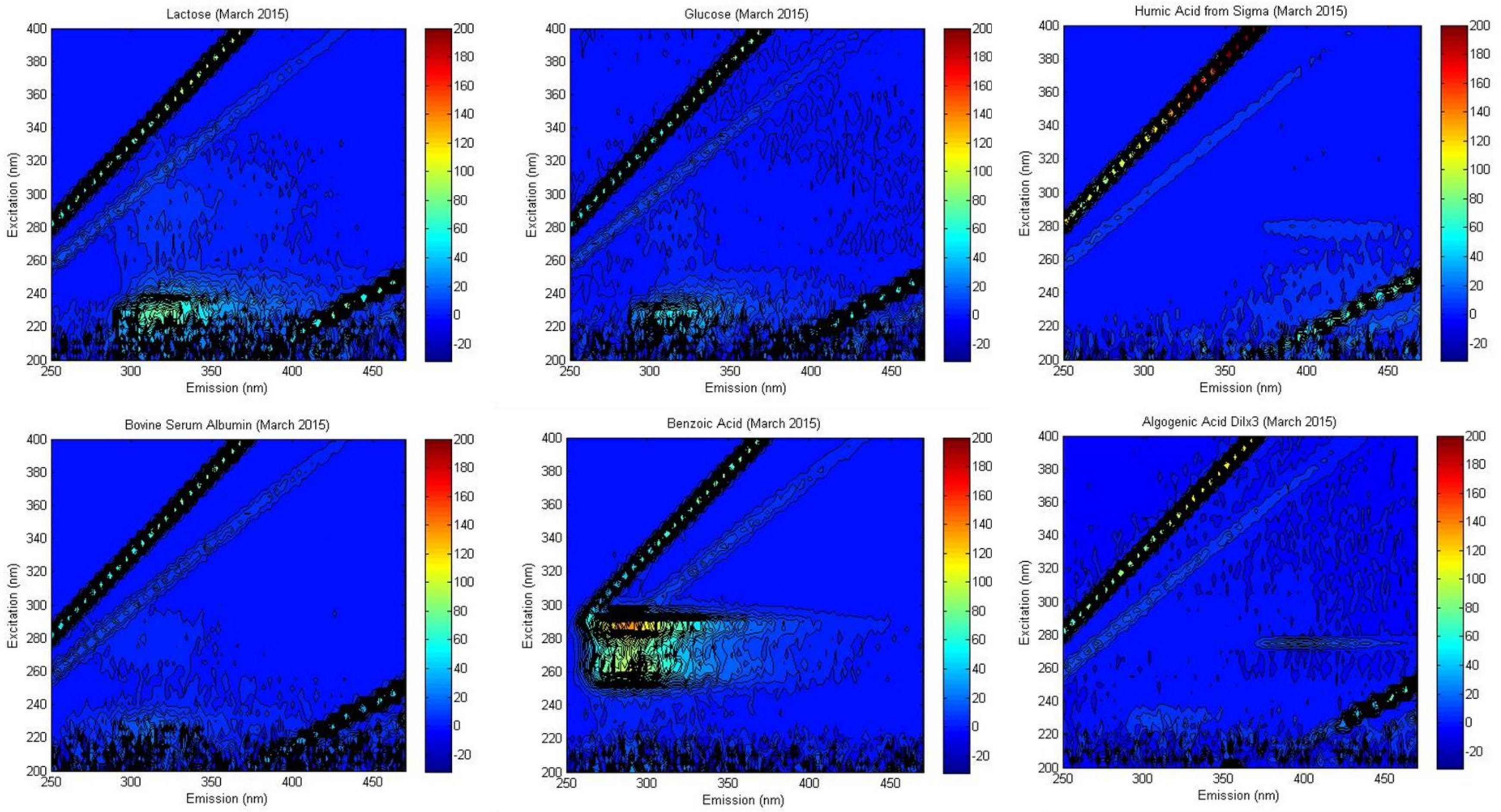


Figure 4.10 Fluorescence Excitation Emissions plots for pure standards at 5mgC/L (March 2015)

		November-14	March-15	June-15	September-15
Site	**Sampling point**	**MW (Da)**	**MW (Da)**	**MW (Da)**	**MW (Da)**
Amlaird	**Raw water**	3797	2904	2864	3101
		955	935	866	855
	Post clarification	1906	1913	2064	2037
	Post sand filtration	1906	2064	1975	1888
Gigha	**Raw Water**	3294	2986	2625	2736
		645	649	642	619
		111	105	107	110
	Post Membrane	2495	2363	2121	2029
		775	798	795	859
		109	103	106	105
	Post GAC	2495	2340	2121	2002
Forehill	**Raw water**	2864	3341	2625	2647
		551	543	577	563
	Post clarification	1906	1839	1848	1923
		551	545	569	539
	Post sand filtration	1906	1880	1873	1831
		551	564	569	551
	Forehill Post GAC	1906	2002	1923	1863
		551	553	566	551
Broadford	**Raw water**	2864	2876	2825	3041
	Post Membrane	1906	2589	2699	2647
	Post GAC	1906	2299	2710	2428
Stornoway	**Raw water**	2495	2540	3145	2732
	Post clarification	1906	1839	1795	1737
	Post sand filtration	1906	1856	1839	1913
Port Charlotte	**Raw water**	2864	2786	2632	2953
	Post clarification	1906	1856	1873	1913
	Post sand filtration	1906	1839	1863	1885

Table 4.5 HPSEC results showing molecular weight (Daltons) for DOC compounds found in raw and treated water samples at six WTPs in Scotland

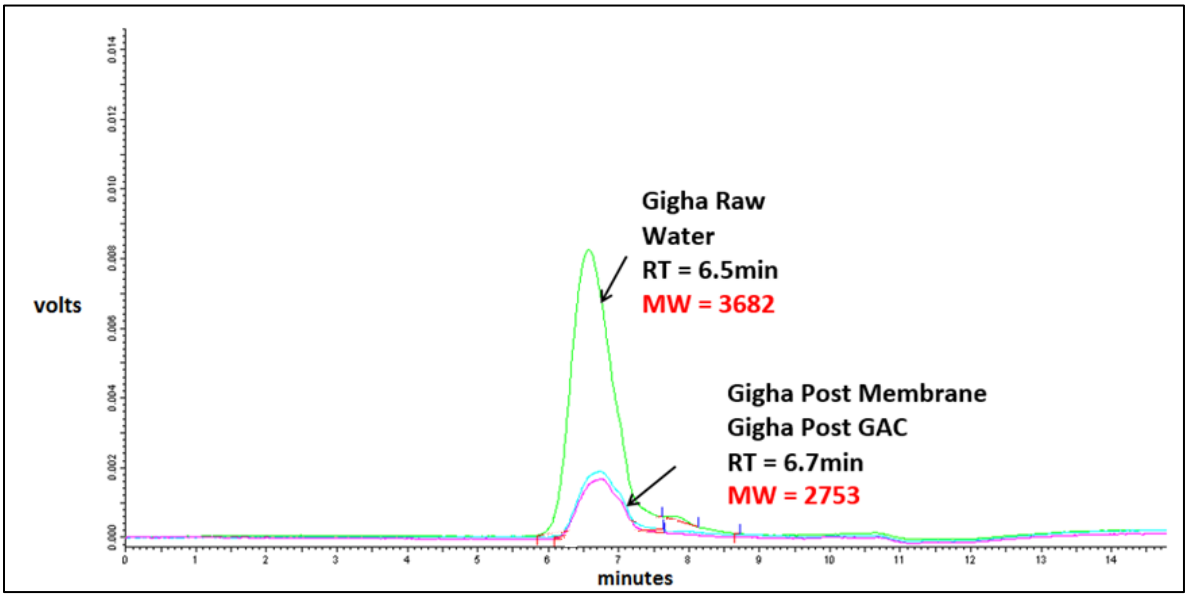


Figure 4.11 High Performance Size Exclusion (HPSEC) traces for raw and treated water samples taken from Gigha WTP in March 2015

f) Cations and anions

Metal speciation in raw water samples differed per treatment site and per season (**Appendix Table 4.3**). Highest levels of metals were observed during autumn months which coincides with the rainy season and high rainfall levels which will carry mineral deposition from soils to surface water bodies. The majority of metals present in raw waters is greatly reduced due to the efficiency of the coagulation processes and in the case of alkaline metals its levels are usually maintained constant along the process or with slight increase of calcium for example due to the addition of lime for pH correction. Sites that use coagulation also incorporate iron, aluminium and sulphate to the treated water which could slightly increase the levels found in raw water inlet flows, but by maintaining a correct coagulation control, iron and aluminium will be kept below the permissible levels in the final potable water. Overall, there was not an evident influence of cations or anions on THMs formation. However, further investigation using Pearson correlation analysis showed that only aluminium and iron had a strong and statistically significant relationship with DOC in the raw water sampling point ($r^2 = 0.8$, $p <$

0.001). Iron content for Amlaird, Stornoway and Port Charlotte showed values greater than 0.5 mg/L in December and September 2015. Usually, high iron and aluminium content have been reported in ground waters, but its presence in surface water such in the case of these Lochs could be attributed to the strong influence of peat. A recent study by Emsens mentions the ability of wet peatlands or fens to release high quantities of iron which highly correlate with inorganic and organic carbon (28).

In the case of anions, surface raw water from these sites showed undetectable levels of nitrate, nitrite, (values below 50 mg/L for nitrate and nitrite) sulphate and phosphate which indicates their pristine condition. Sites located by the coast showed the highest levels of chloride and bromide such Forehill (45.5 mg/L ± s.e.1.42 and 124.4 µg/L ± s.e.3.1) and Gigha (63.4 mg/L ± s.e.3.77 and 172.14 µg/L ± s.e.5.7). These two halides showed strong and significant correlations between each other (29), at the same time chloride has shown also positive and strong relationship with total THMs (see chapter 3). The high levels of bromide (above 50 µg/L) will shift the reaction mechanisms to brominated THMs.

All heavy metal analysis were lower than 0.001mg/L and complied with quality regulations. Although, the levels of anions and cations in the samples changed along the year, its influence could be disregarded in terms of THMs formation except for the presence of halides. High levels of chloride were found in January and February whereas the lowest values were in November for all sites. This effect could be due to high rainfall levels that began in autumn and wash out salt content from soils which appears in winter months. Sites located by the coast will require a more rigorous monitoring for both chloride and bromide. However, its elimination or reduction of the process will also require further study and potentially further investment to apply the best strategy to eliminate them from the treatment.

4.4 Conclusions

Seasonal changes have a very important impact in the quantity of DOC in raw and therefore treated water. The highest surges of THMs were observed during September for example compared to low concentrations found in winter months. However, based on monthly monitoring data, quality of DOC is maintained largely unaltered along the seasons, whilst quarterly sampling indicated some variability. Results obtained from the quarterly monitoring data allowed a more detailed DOC characterisation which included UV scans, fluorescence EMM plots and HPSEC that provided a general view of potentially most abundant DOC compounds present in surface and treated water at the selected sites being mainly of hydrophilic origin.

Seasonal influence is observed during rainy periods for example that exacerbate the levels of DOC that are introduced into surface water bodies. In the previous chapter, halides such chloride and bromide showed a positive and direct relationship with THMs. These relationships combined with the increases of DOC and changes in DOC quality due to seasonal influences promote the formation of THMs along the year. However, due to the complexity of the sites under investigation, each will have its own particular issues that will influence changes towards THMs formation. Therefore, a THMs prediction model should be site specific for example to minimize these variabilities.

The results from THMFP experiments have clearly established temperature as being positively correlated with THMs formation in raw and treated water. DOC quantity was identified as a second root cause of seasonality in THM formation, as it correlated positively with THMs in the monthly monitoring, and there was also reduced THMFP with reduced levels of DOC at a fixed temperature in laboratory experiments. Quantity is affected by the change of seasons (rainy or dry periods for example, but also temperature dependant microbial activities) which imply an increase or reduction of THMs. The influence of quality of DOC on THMs appears to be less clear, as it was generally more constant along the year according to the monthly monitoring data as shown by the results from normalised UV absorbances as well as by looking into DOC fractions. Residual hydrophobic, hydrophilic and transphilic DOC is, however, definitely altered by water treatment, with HPO being more successfully removed than the other fractions. The residual fractions may cause THMs formation despite their low concentrations through diverse reaction mechanisms which are exacerbated at higher water temperature. In consequence, improvements in treatment practices could minimize and control THMs precursors.

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Chapter 5

NATURAL ORGANIC MATTER COMPOUNDS IN SCOTTISH WATERS, THEIR THM FORMATION POTENTIALS, AND TREATABILITY BY ACTIVATED CARBON ADSORPTION

5.1 Introduction

Natural organic matter (NOM) present in surface water is one of the main precursors of disinfection by products (DBPs) in drinking water treatment due to its reactivity with disinfectants. The mechanisms of reaction between the diverse chemical species that form part of NOM, including many large molecular weight compounds, create a vast variety of halogenated analogous from which trihalomethanes (THMs) are one of the most regulated and documented types due to their potential carcinogenic effects to the population (1-3).

The addition of chlorine as a disinfectant in chlorination or chloramination is a worldwide practice due to its efficacy to eliminate pathogens, its ability to provide disinfectant residuals in distribution networks and its low cost and therefore its use will continue unless other disinfection alternatives are incorporated. Soil characteristics play an important role in influencing DOC quality in surface water as well as ambient temperature and geographical location. Scotland has a considerable percentage of its territory covered by peatland which has a high organic content, that when disrupted or influenced by run off or rainfall, releases large amounts of DOC to surface waters (4, 5).

Disturbance of peatland, marine influence, plants and leaves degradation will provide surface waters with a diverse chemical composition (6-8). The typical discoloration present in Scottish surface waters is usually due to humic and fulvic acids. These acids present in soils are compounds of large molecular weight (polymeric phenolic compounds) and constitute a portion of the hydrophobic fraction (HPO) of DOC (9, 10). This fraction also includes polymers of polyhydroxybenzenes, polyhydrobenzoic acids, benzene polycarboxylic acids, sugars, nitrogenated bases and terpenoids (11). Degradation of both humic and fulvic acids produce similar monomeric units that contain hydroxylated aromatic rings (phenolics). Other relatively smaller molecular weight compounds are lignin residuals from plant degradation and polypeptides, fatty acids and proteins from algal and microbiological metabolic activities (12, 13). These compounds can be of small molecular weight such as carboxylic acids, small aliphatic compounds (C1-C5), aldehydes, ketones, sugars and amino acids that constitute the hydrophilic fraction (HPI) of DOC (10).

Grouping DOC compounds according to their molecular size and physical properties has been a convenient way to classify and potentially identify THMs precursors. In the previous chapter, residual DOC before the point of disinfection was shown to be primarily of humic and fulvic nature due to results obtained from the excitation emission fluorescence experiments which showed peaks corresponding to these substances that reduced intensity at each step of the treatment process. However, there was no clear distinction between coagulation and membrane plants in terms of their effectiveness to remove more efficiently humic and fulvic compounds.

In chapter 4, HPSEC experiments also showed that larger MW compounds were found most abundantly in raw water and gradually diminished further in the treatment process leaving small MW compounds in treated water (See Figure 4.11 in page 129).

As shown in chapter 4, hydrophobic compounds are usually easier to remove during enhanced coagulation treatment and membrane filtration due to their larger molecular weight (12, 13). On the other hand, hydrophilic compounds, such carbohydrates, peptides and proteins and small molecular weight compounds (less than 6 carbons) such as alcohols, ethers, aldehydes and carboxylic acids are also known to be present in surface water but in low concentrations and due to their high water solubility are more difficult to remove by either coagulation and membrane treatments (14). These results lead to the hypothesis that residual DOC of hydrophilic nature in water prior to the point of disinfection could be the main cause of THM formation. However, reactivity of the most likely compounds to be found in Scottish waters after treatment needed to be evaluated. Early studies by Rook proved for example that highly reactive free meta-positioned OH-groups were the most reactive when chlorinated to form halogenated analogous including THMs and haloacetic acids (15, 16).

As the residual DOC contents found in Scottish surface waters have shown mostly humic and fulvic influence, one can hypothesize that organic compounds of hydrophilic nature, including small aromatic species, tend to remain in drinking water treatments to the point of disinfection and then contribute to THMs formation. Therefore, in this chapter two main groups of organic compounds were quantified and then selected for further experimentation to determine their reactivity towards THMs.

These substances were a group of phenolic and carboxylic compounds that are typically found in peaty soils (17) and in drinking water supplies (18). Evaluation of silver granulated activated carbon and other activated carbons was conducted to evaluate options to remove these hydrophilic DOC compounds as well as other negatively charged inorganic anions as it was proven successful in other studies (19).

5.2 Methods

5.2.1 Analytical Methods

a) Quantification of carboxylic acids and total phenols

Carboxylic acids (35) in raw and treated water were measured at the Department of Chemical Engineering of University of Jaen (Spain) using solid phase extraction and gas chromatography coupled with mass spectrometry (GC-MS) using a previously developed method at their facilities (20, 21).

The analysis was performed in duplicate for samples collected in June and September 2015, i.e. during the summer months when THM formation tends to be the highest, at each step of the process from the six case study sites. Samples were previously filtered through 1.6µm glass fiber membranes (Millipore, Cork, Ireland) to remove larger particulates and then through 0.45µm polyamide membranes (Sartorius, Goettingen, Germany) and stored in Duran® bottles at 4°C for further use. Total phenols were measured using Hach-Lange cuvette test kit LCK345 with ranges from 0.05-5mg/L using a portable UV spectrophotometer DR1900 (Hach-Lange, Loveland, Colorado, USA).

b) Trihalomethanes formation potential (THMFP) of phenolic compounds and carboxylic working solutions

Pyruvic, glycolic, propionic, butyric, isovaleric, hexanoic, stearic, oleic, linoleic, phthalic, hexanoic, benzoic, 3- hydroxybenzoic and 3,4-dihydrobenzoic acids were selected for THMFP experiments based on results obtained from the quantification of 35 carboxylic acids as these compounds were amongst the most abundant found in Scottish raw and treated water samples. Similarly, eight phenolic acids found typically in peaty soils (22) were also selected for THMFP: gallic, phenylacetic, syringic, cinnamic, salicylic, vanillic, ferulic and caffeic acids. All standard solutions were prepared using 99% purity chemicals from Sigma Aldrich (Bellefonte, USA). Standard solutions were all diluted individually using artificial surface water buffer (Table S3 in chapter 3) in deionized water to final DOC concentration of 1 mg C/L for each compound, chlorine concentration (5 mg/L) and pH (7-7.2) were the initial conditions of the experiment. Incubation temperatures were 5°C, 15°C and 25°C for the standard seven days THMFP experiment. THMs were analysed on an Agilent gas chromatograph (Santa Clara, California, USA) equipped with an electron capture detector (GC-ECD) as described in chapter 4 (23, 24).

c) Silver impregnated activated carbon (Ag-AC) batch experiments for pyruvic, syringic and ferulic acid

Coconut shell based granulated activated carbon was obtained from Chemviron (Feluy, Belgium) at 0.05% and 0.1% concentration of silver impregnation. The carbon was pulverized through a vibration pulveriser device and passed through a 500 µm sieve and a second 200 µm sieve then baked at 60°C for 2 hours and left to cool at room temperature in ceramic containers until further use to reduce potential for bacteriological contamination.

The final fraction selected for the experiments was less than 200 µm. Amounts at 20 mg, 40 mg, 80 mg and 160 mg for each Ag-AC type were added to 1L glass Duran® bottles containing 400 mL solutions (ferulic, syringic and vanillic acid) prepared separately and diluted in artificial surface water buffer (pH 7-7.2) to final concentrations of 2 mgC/L as DOC for each compound and left at room temperature on IKA KS4000 orbital shakers (Stuart Scientific, United Kingdom) for 24 hours. The solutions were filtered through 0.45 µm polyamide membranes (Sartorius, Goettingen, Germany) to eliminate any residual Ag-AC and 270mL aliquots of each filtrated were used for measuring THMFP (25). Controls were prepared using the same phenolic and carboxylic acid solutions without the addition of Ag-AC for THMFP and removal efficiencies calculations.

d) Batch granulated activated carbon experiments for ferulic acid removal

Ferulic acid solution at 2 mg DOC/L was prepared fresh for batch adsorption experiments in deionized water, buffered with phosphate buffer (pH 7-7.2) and mixed with sodium chloride (40 mg Cl^-/L) and potassium bromide (300 µg Br^-/L). The solutions (400mL) were transferred to clean Duran 1L bottles. Amounts of powdered activated carbon: 20, 40, 80 and 160mg were added to each bottle for the five different types: 0.05% Ag-AC and 0.1% Ag-AC (Chemviron, Feluy, Belgium), Filtrasorb400 (Calgon Carbon, Pittsburgh, USA), Aquacarb208 (Calgon Carbon, Pittsburgh, USA), Norit (Sigma-Aldrich, Bellefonte, USA) and Brimac Bonechar (Brimac Environmental Services, Greenock, UK). Batch experiments were carried out in an orbital shaker at 15°C for 24 hours. Filtrated samples were used immediately for THMFP at pH 7-7.2, and final concentration of chlorine at 5mg/L.

e) Analyses of water quality

DOC was determined using a total organic carbon analyser TOC-5050A coupled with autosampler ASI-5000A (Shimadzu, Japan). UV-Visible scans were performed in a UV-Vis spectrophotometer SpectraMaxM3 (Molecular Devices, Sunnyvale, California, USA); pH and conductivity were monitored with a HQ40d Hach-Lange pH meter (Loveland, Colorado, USA). Samples for anion determination were filtered through 0.2 µm cellulose acetate syringe filters (VWR, Poole, England) prior to injection into a ICS-1000 Ion Chromatography System (Dionex, USA).

5.2.2 Exploratory Statistics

Statistical analysis included: analysis of means, 2 sample t-test, variances and Pearson correlation analysis were calculated using Minitab 17 (Leadtools Technologies Inc, version

17.1.0, 2014) and reported with 95% confidence limits by showing plus minus standard errors of the mean.

5.3 Results and discussion

5.3.1 Carboxylic acids and total phenols

Seasonality was important when looking at carboxylic acids concentrations found in June and September. Analytical tests were performed only during these two seasons. Concentrations for 35 carboxylic acids in raw water were significantly higher (*t*-test = -4.78, $p < 0.001$) in September (56.9µg/L ± s.e.6.8) compared to concentrations found in June (20.6µg/L ± s.e.3.3), in line with earlier observations for total DOC reported in Chapter 3 and 4 results (**Table 5.1**).

However, there was no significant difference between carboxylic acids concentrations found in raw and treated water during the same season. For example carboxylic acids in raw water (20.5µg/L ± s.e.3.3) were not significantly different (*t*-test = 0.57, $p = 0.572$) to concentrations found in the treated water (18.0 µg/L ± s.e.3.2) during the month of June. Similarly, there was no significant difference (*t*-test = 0.08, $p = 0.94$) between concentrations found in samples taken in September for raw water (56.9 µg/L ± s.e.6.8) and final potable water (56.2µg/L ± s.e.6.1). These results show that seasonality plays an important role in the total abundance of these particular THMs precursors in raw water, which are then very difficult to remove in treatment works. In the previous chapter, seasonality influenced the formation of THMs, due to both changes in temperature and raw water DOC. In this case, carboxylic acid content is also higher during September months when higher temperatures are more evident, but evaluation of these results showed that the treatment process does not result in a reduction or increase in concentrations of these compounds.

Site	Sample Point	Total CA mg/L		DOC, mg/L		%CA/mg DOC		Total Phenols, mg/L		%Phenols/mgDO	
		June	Sep	June	Sep	June	Sep	June	Sep	June	Sep
Forehill	Raw Water	0.71	1.43	8.3	12.5	8.5	11.4	0.32	0.53	3.8	4.2
	Post Clarification	0.62	1.34	3.9	3.0	15.7	44.3	0.08	0.08	2.0	2.8
	Post Filtration	0.55	1.28	4.0	3.4	13.7	37.5	0.06	0.08	1.6	2.4
	Post GAC	0.74	1.46	3.0	2.7	24.7	53.3	0.07	0.06	2.3	2.2
Gigha	Raw Water	0.60	0.98	6.7	5.2	9.0	19.0	0.29	0.19	4.4	3.6
	Post Membrane	0.43	1.53	4.0	1.2	10.6		0.09	0.08	2.2	6.9
	Post GAC	0.43	1.15	2.4	1.0	18.1		0.09	0.08	3.5	8.0
Amlaird	Raw Water	0.79	1.98	12.1	17.7	6.5	11.2	0.68	1.42	5.6	8.0
	Post Clarification	0.69	1.68	3.3	4.1	21.0	41.4	0.09	0.13	2.8	3.2
	Post Filtration	0.64	1.93	3.0	4.4	21.3	43.9	0.07	0.08	2.3	1.9
Stornoway	Raw Water	0.58	1.91	7.1	12.8	8.1	14.9	0.47	1.06	6.5	8.3
	Post Clarification	0.47	1.62	3.3	3.9	14.4	41.8	0.09	0.11	2.9	2.7
	Post Filtration	0.45	1.12	3.0	3.8	15.1	29.4	0.08	0.11	2.8	2.8
Broadford	Raw Water	0.49	1.41	4.1	6.0	12.0	23.5	0.21	0.37	5.1	6.1
	Post Membrane	0.57	1.31	2.0	3.2	28.4	40.4	0.13	0.15	6.3	4.7
	Post GAC	0.55	1.12	1.0	3.8	54.5	29.6	0.09	0.12	9.0	3.2
Port Charlotte	Raw Water	0.61	1.78	9.4	23.5	6.5	7.6	0.45	1.53	4.8	6.5
	Post Clarification	0.82	2.00	3.3	5.9	24.6	34.0	0.12	0.18	3.6	3.1
	Post Filtration	0.65	1.70	3.4	5.2	19.0	32.9	0.11	0.17	3.3	3.3

CA: Carboxylic acids; DOC: Dissolved organic carbon

Table 5.1 Total carboxylic acids (mg/L) and total phenols (mg/L) per sampling point at each case study site (June and September 2015)

A Spanish study where carboxylic acids were monitored at different stages of a drinking water treatment site, explains that increase of carboxylic acids in treated potable water after chlorination are due to further oxidation reaction of larger organic compounds for example (18). In raw, treated and in distribution networks, the presence of these compounds can support growth of microbial populations as a carbon substrate, for example pyruvic acid which is one of the most abundant carboxylic acids found in surface water is present due to microbial degradation which then can be further used as substrate (26).

Raw water showed the presence of the majority of the 35 monitored carboxylic acids at variable concentrations, which were highest during the month of September **(Figure 5.1).** The most abundant carboxylic acids in raw and treated water (>100µg/L) were isovaleric, hexanoic, myristic, pyruvic, 2-nitrobenzoic and 3-nitrobenzoic found during September. Structurally, there was no clear evidence that Scottish surface water samples showed a signature type of carboxylic acids. Only two aromatic carboxylic acids were found abundantly in treated water for example during June (phthalic and 3-hydroxybenzenic acids). However, the vast possibilities of potential carboxylic acids in surface water could be more abundant than measured, as our quantitation was limited to 35 compounds (see appendix for chapter 5).

In terms of the carboxylic acids contribution to DOC, results found in June were significantly lower (*t*-test = -4.13, $p = 0.001$) in raw water at 8.45 ±s.e.0.83 (%CA/mg DOC) compared to treated water at 21.6 ±s.e.3.1 (%CA/mg DOC). Similarly, analysis performed in September showed statistically significant differences (*t*-test = -7.56, $p < 0.001$) for raw 14.6 ±s.e.2.4 (%/mg DOC) and treated 39.0 ±s.e.2.2 (%/mg DOC) water. Regardless of the type of treatment, these results show that total carboxylic acids in treated water in terms of percentage of residual

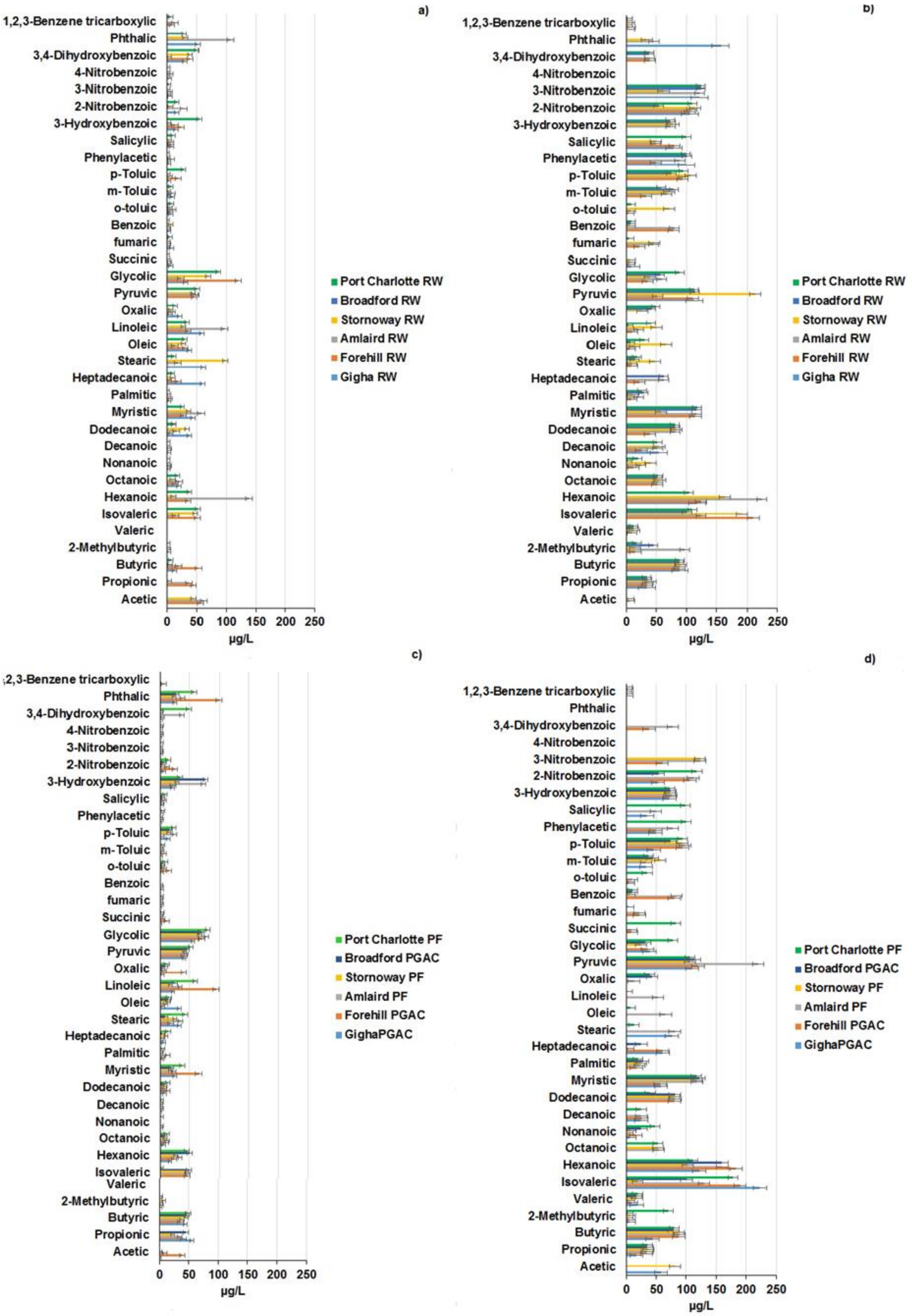

Figure 5.1 Carboxylic acids (35) average concentrations (µg/L) in a) raw water (June); b) raw water (September); c) treated water (June) and d) treated water (September)

DOC are much higher than in raw water samples, i.e. they are more difficult to remove from water than other DOC constituents due to their hydrophilicity.

Degradation of larger molecular weight carboxylic acids by oxidation and formation of smaller molecules could be attributed to microbiological activity rather than chlorination for example at this stage. It could be assumed that at the raw water sampling point, the total DOC consists of a varied and large pool of organic compounds from which only a small percentage constitutes carboxylic acids, but these are amongst the most difficult DOC compounds to remove in the treatment, hence contribute significantly to DOC in treated water.

After coagulation, sand filtration and membrane filtration, the amount of residual DOC is significantly reduced leaving DOC constituents to which carboxylic acids contribute 39%. Carboxylic acids correspond to the hydrophilic portion of DOC which corroborates previous statements about the difficulty to remove this fraction in the treatment (27, 28). In terms of what type of treatment is able to remove more carboxylic acids, there is no significant difference (t-test = -0.69, p = 0.506) between carboxylic acid percentage per mg DOC 32.5 ±s.e.5.6 (%CA/mg DOC) found in permeate samples (post membrane) compared to sites that applied coagulation and sand filtration at 28.1 ±s.e.2.8 (%CA/mg DOC).

In contrast, total phenols in terms of their relative content per mg DOC, did not show a significant difference (t-test = -1.24, p = 0.256) between average raw water values found in June 5.1 ±s.e.0.39 (%/mg DOC) and September 6.13 ±s.e.0.78 (%/mg DOC). Similarly, no difference (t-test = -0.26, p =0.798) was found in results from treated water either in June 3.42 ±s.e.0.57 (%/mg DOC) or September 3.62 ±s.e.0.51 (%/mg DOC). In the case of phenolic compounds, percentage per mg DOC appears reduced from raw to treated water for both seasons. Samples taken in June showed total phenols percentages in terms of mg DOC from raw 5.1 ±s.e.0.39 (%/mg DOC) to treated water 3.42 ±s.e.0.57 (%/mg DOC) reduced significantly (*t*-test = 2.37, *p* = 0.031) as well as in samples collected during September from raw 6.13 ±s.e.0.78 (%/mg DOC) and treated water 3.62 ±s.e.0.51 (%/mg DOC) also reduced significantly (*t*-test = 2.68, *p* = 0.028). In terms of total phenols content in mg/L for all sites during the quarterly sampling, there was a significant (*t*-value = 5.3, $p < 0.000$) reduction from raw water 0.57 ± s.e.0.09mg/L to treated water 0.097 ± s.e.0.004mg/L for example in all sites.

Enhanced coagulation and sand filtration as conventional treatment have been successfully used for the removal of phenolic compounds in previous studies (29-31). 2-sample t-test showed that total phenols concentration were significantly lower (*t*-value = 2.61, *p*-values = 0.028) in sites that used enhanced coagulation (2.7 %/mg DOC ± s.e.0.14) compared to membrane sites (4.81 %/mg DOC ± s.e.0.81) in terms of normalised values as percentage per mg DOC.

In terms of treatment, carboxylic acids appear to significantly increase as percentage of DOC from raw to treated water, but in the case of phenolic compounds, coagulation sites removed them better that membrane sites for example. The increase of carboxylic acids in treated water might be caused by diverse factors.

The influence of seasons is directly related with temperature increase as mentioned in previous chapters. In this study, only two seasons were sampled (spring and summer) which cannot be compared to results from a similar study that took place in Spain, where higher carboxylic acid concentrations were found in winter (18); but it is known that temperature changes affect directly microbial and enzymatic activity which may increase typical carboxylic acids formed as part of metabolic activities such pyruvic, valeric and isovaleric acids for example, which can occur not just in surface water but also in soils (26).

Temperature changes, exacerbate microbial and enzymatic reactions that degrade humic and fulvic acids, which contribute to the addition of these compounds in water, but phenolic species are more successfully removed by coagulation treatment whereas carboxylic acids will conservatively remain in the treated water as residual DOC due to their hydrophilicity which makes them difficult to remove. Specific residual carboxylic acids and phenolic compounds could also be of very small molecular weight and of high solubility which makes them very difficult to remove using the described treatments.

The next stage of this work will define in terms of chlorine reactivity which group of the identified compounds contributing to DOC residuals at the disinfection point leads to higher THMs formation potential, either carboxylic acids or phenolic compounds, in order to then apply the best mitigation strategies.

5.3.2 THMFP from carboxylic acids and phenolic compounds

DOC characterisation experiments lead to the preliminary hypothesis that residual DOC components in Scottish surface waters show a residual portion of hydrophobic and hydrophilic DOC which structurally could be formed by aromatic compounds from humic and fulvic origin. As these substances are primordially released by peaty soils through different degradation mechanisms, experimentation with typical carboxylic acids and phenolic compounds found in these rich organic soils was the next step to verify their reactivity towards THMs formation.

Carboxylic acids can be found in raw water as small aliphatic (C1-C6) and benzene-carboxylic acids due to oxidation and biological degradation of humic and fulvic acids (32). Larger aliphatic and aromatic molecular weight carboxylic acids could be present in surface water due to human activity such oil and hydrocarbon spills and the winery industry (1, 33). Carboxylic acids can be also present in raw and drinking water and have been reported as disinfection by products due to different oxidative mechanisms of DOC during disinfection by chlorination, chloramination or ozone treatment (18).

Four carboxylic acids: pyruvic, butyric, hexanoic and benzoic acids were selected from the 35 carboxylic acids monitored in June and September as these showed higher concentrations than any other in the analysed samples (**Figure 5.2**). THMs formation potential reactions applied to standard solutions of each compound at constant pH (7-7.2) and DOC concentration (1 mg/L) showed no measurable reactivity after incubation at 5°C. However, the highest yield was obtained from pyruvic acid chlorination at 15 and 25°C. Samples incubated at 25°C showed measurable concentrations of chloroform with 4.12 µg/L ± stdv.0.3 and bromodichloromethane 1.23 µg/L ± stdv.0.07. The other carboxylic acids produced chloroform and bromodichloromethane below 1 µg/L at both temperatures. Looking at phenolic compounds such 2-methoxyphenol, it produced approximately 25 times higher concentrations of chloroform at 25°C (107.21 µg/L± stdv.0.08) and twice the amount of bromodichloromethane (2.16 µg/L± stdv.0.04) compared to concentrations obtained by chlorinating pyruvic acid. In the case of chlorination of 3,5-dimethoxyphenol, similar high yield was observed for chloroform as well (102.82 µg/L± stdv.4.94), but bromodichloromethane was five times higher (5.72 µg/L± stdv.0.15) than the yield obtained from pyruvic acid.

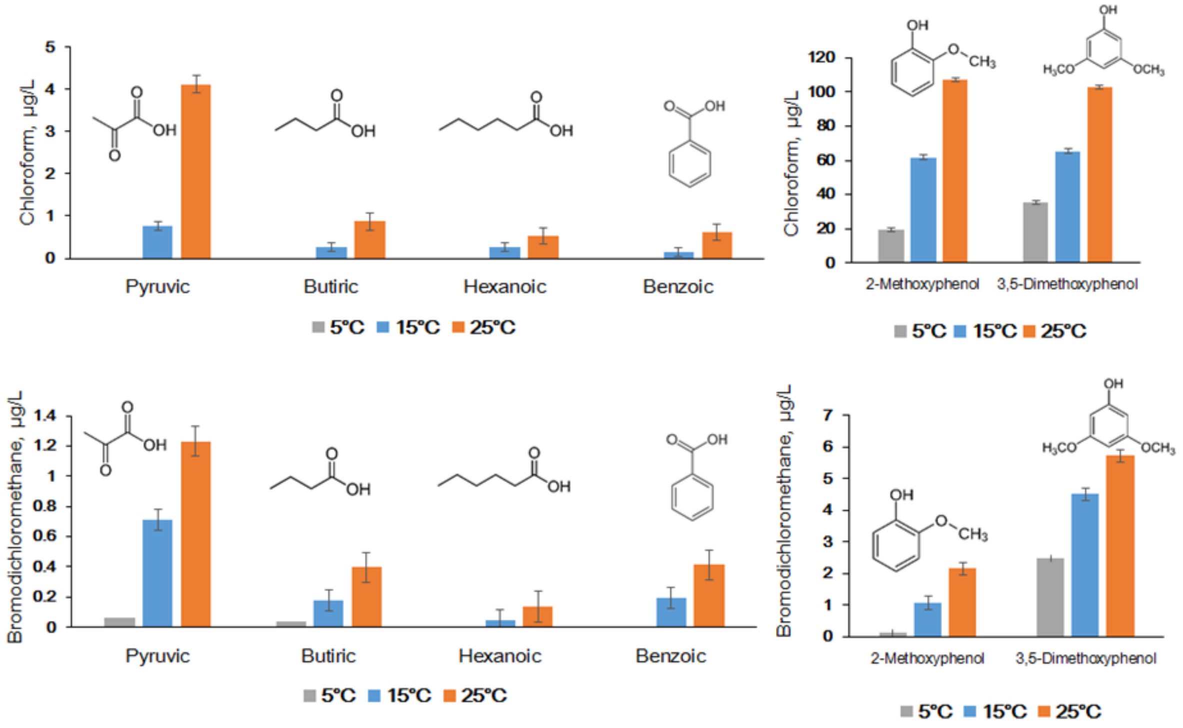

Figure 5.2 Chloroform and bromodichloromethane concentrations from chlorination of four carboxylic acids (pyruvic, butyric, hexanoic and benzoic acids) and two phenolic compounds (2-methoxyphenol and 3,5-dimethoxyphenol), measured as THMFP. Note the differences in the scaling of the y-axes.

Chlorinated THMs concentrations steadily increased with the increase of temperature corroborating that temperature is a crucial factor for THMs formation as demonstrated under controlled conditions. The incubation reaction occurred at constant pH levels (7.0-7.2) that maintained HOCl distribution in equilibrium (*pKa* = 7.52) favouring formation of chloroform from phenolic compounds as stated by Deborde et al. (34).

In addition, the methoxylated groups located in the aromatic ring also favour the electrophilic substitution reaction between HOCl and the aromatic ring for subsequent formation of phenoxide ions that have much faster oxidation rates to produce chloroform (35) as opposed to carboxylic acids which lack on electrophilic carbon in their molecule due to their saturated aliphatic structure.

The fast reaction mechanisms will primarily form chloroform followed by bromodichloromethane and the formation rates will be determined by the number of methoxylated groups present in the aromatic ring. In this case, 3,5-dimethoxyphenol produced the highest amounts of both chlorinated THMs. Although, total phenolic compounds in the residual DOC portion found in treated water prior to disinfection, represent a lesser percentage of DOC compared to carboxylic acids, the rate of measured THMs formation was much higher from phenolic compounds for the same reaction conditions (**Figure 5.2**). However, the two selected phenolic compounds for the experimental work were not measured directly from original samples but used as reference from pure standard solutions prepared in the laboratory. For this purpose, eight typical phenolic acids found in peaty soils in Scotland (17) were used as reference compounds for THMFP analysis.

All the selected phenolic compounds were in fact phenolic acids showing carboxyl, hydroxyl and methoxy chemical groups located at different positions within the aromatic ring, which would make them hydrophilic. Chemical structures and THMFP (chloroform and bromodichloromethane) yield of these compounds are shown in **Figure 5.3.**

The three compounds that showed higher yield of chloroform contained methoxylated chemical groups in their structure: syringic, vanillic and ferulic acids. Chloroform concentration at 25°C incubation temperature showed the highest values at 12.5 µg/L ± stdv.0.6; 37.0 µg/L ± stdv.0.19 and 62.6 µg/L± stdv1.0 for each of these phenolic acids respectively.

Bromodichloromethane concentrations were found between 1.19µg/L and 2.39µg/L for all incubated phenolic acids showing no preference for any particular compound. THMFP

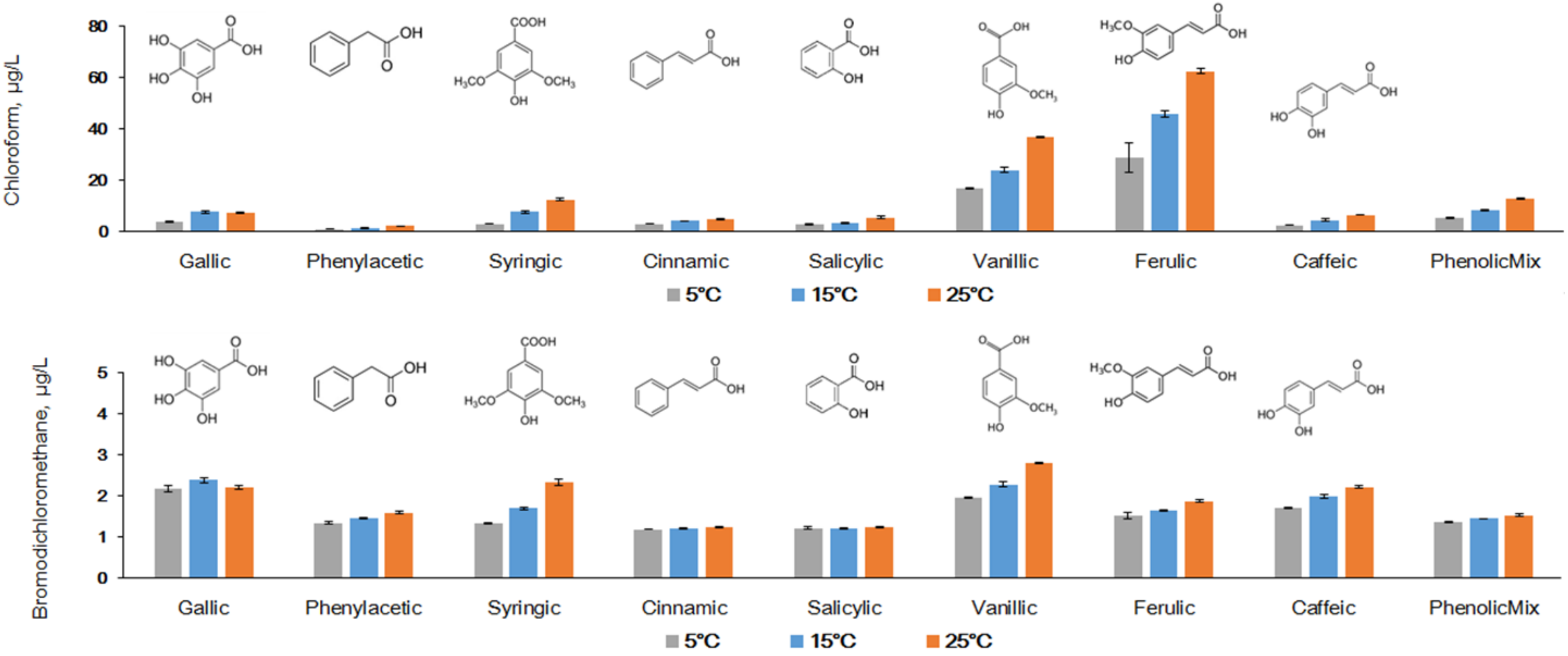

Figure 5.3 Chlorination of eight phenolic acids to obtain chloroform and bromodichloromethane (DOC = 1 mg/L, pH = 7, Cl_2 = 5 mg/L), measured as THMFP

experiments did not show any of the brominated species: bromoform or dibromochloromethane which indicates that formation of brominated THMs only occurs when halides are present in the solution which was not the case at this stage.

Interestingly, by mixing all eight compounds in one solution and maintaining the same final concentration of 1 mg/L as DOC, the results show that chloroform concentration was below 20 μg/L for the three temperatures used during incubation, indicating possible competition in reaction kinetics between carboxylated groups rather than hydroxyl and methoxy groups alone that react much faster (15) and potentially producing other DBPs. To illustrate this effect, the amount of chloroform obtained by reacting just syringic acid (1 mg DOC/L) at 5°C produced 3.0 μg/L of chloroform and each phenolic compound produced different amounts at the same DOC concentration and temperature conditions.

The sum of chloroform concentrations estimated to be produced by the eight phenolic acids using a DOC normalized THMFP from the single compound experiments yielded a total 7.7 μg/L (each chloroform concentration was divided by eight to account for their reduced contribution to total DOC in the mixture before adding the individual contributions) at the incubation temperature of 5°C. However, chloroform concentrations produced by the mixture of eight compounds was 5.2 μg/L also at the same incubation temperature, showing a reduction of 32% as compared to the value predicted from the separate measurements.

Applying the same experiment at 15°C, the sum of each concentration of phenolic compounds produced 8.2 μg/L of chloroform and the total mix solution produced 12.3 μg/L in this case, the mixture produced more chloroform than anticipated, an excess of 33.3%. At 25°C, the sum of each compound yielded 12.8 μg/L whilst the mixture produced 17.34 μg/L chloroform also in an excess of 26.2%. These experiments show that the THMFP of a mixture of compounds can be roughly predicted (within ±33%) from the THMFP measured for each of the compounds separately, by accounting for their relative contribution to the DOC.

However, there was always a difference between the amount of chloroform produced by each individual compounds compared to the mixture of the eight, that could be related to sample preparation issues rather than reaction mechanisms. Although, the different reaction paths during chlorination when many organic compounds remain in solution, can lead to the formation of other products that are not necessarily chloroform and therefore cannot be quantitated.

In general terms, methoxylated groups in phenolic compounds influence the reaction kinetics at high temperatures producing primordially chlorinated THMs species. The most reactive DOC compounds were phenolic compounds with methoxyl groups. The next stage in the experimentation will investigate how to remove this type of compounds specifically by applying enhanced treatment processes such GAC. Although, reactivity from carboxylic acids towards THMs was not as evident as with phenolic compounds, these could produce other DBPs within treated water.

5.3.3 Activated carbon adsorption experiments

Preliminary batch adsorptivity experiments using standard solutions of ferulic, syringic and pyruvic acids at 2 mg/L as final DOC prepared separately as adsorbates, showed that THMPF was reduced gradually from lower to higher doses of Ag-AC, for either amount of silver impregnation (0.05% and 0.1%). As a controlled experiment, initial concentrations as mg DOC/L for each compound and incubation temperature at 15°C were maintained constant; also no halide salts were present in the solution during chlorination, in consequence only chlorinated THMs species were produced: chloroform and bromodichloromethane.

In fact, there was no crucial difference between THMFP obtained after adsorption using either type of Ag-AC for each of the three chlorinated solutions, but there was a significant difference between the removal efficiencies obtained from the two phenolic compounds syringic and ferulic acid compared to pyruvic acid (carboxylic acid) as appears in **Figure 5.4**. The lowest adsorption values were obtained in terms of THMFP removal efficiencies percentages for pyruvic acid at 50 mg/L Ag-AC at 0.05% and 0.1% Ag-AC, with 9.6% and 14% removal respectively (**Figure 5.4a**). The efficiencies gradually increased up to the maximum dose of 400 mg/L for both silver impregnated AC, albeit only to 20-22%. These are very low removal efficiencies even for very high AC doses. Removal efficiencies for ferulic acid however, were higher using 50 mg/L Ag-AC 0.05% and 0.1% with 21.0% and 23.5% respectively (**Figure 5.4b**), but syringic acid showed the best removal efficiencies of 34.9% and 43.9% (**Figure 5.4c**). The removal efficiencies gradually increased to the maximum dose of 400 mg/L where syringic acid was removed 60.6% and 63.2% for 0.05% and 0.1% Ag-AC types respectively.

Adsorption mechanisms work in different ways for different types of compounds. One factor that influences adsorption is the optimum pH value to enable anionic activation. Adsorption mechanisms on AC are therefore dependent on optimum pH control (36). Low molecular weight carboxylic acids such pyruvic acid have a *pKa* = 2.5. With this low pKa value, the predominant speciation is the pyruvate anion, and when the solution is maintained at pH 7 then, adsorption would be compromised due to the high water solubility of the anion, and possibly also electrostatic repulsion from negative charges on the AC surface, which will, however, depend on AC point of zero charge.

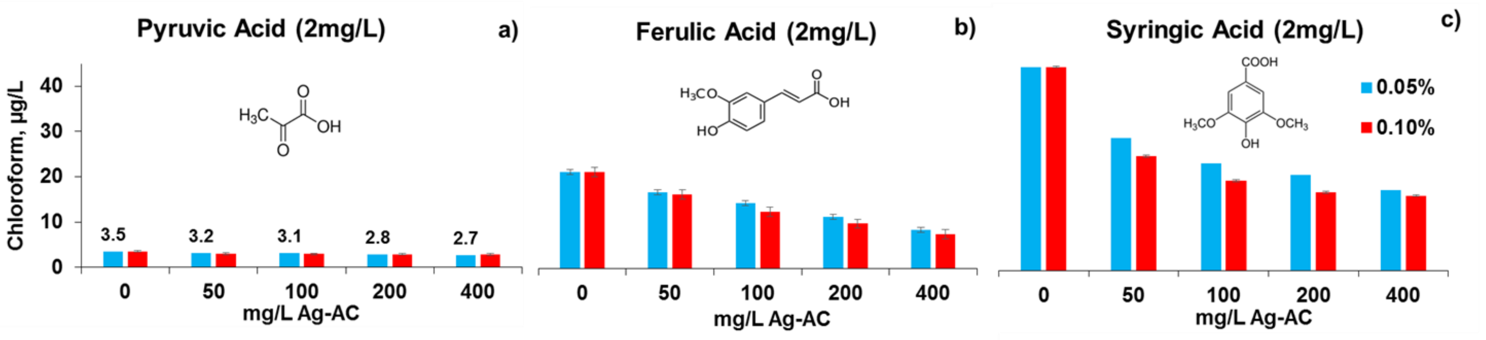

Figure 5.4 THMFP for pyruvic, ferulic and syringic acid using 0.05% and 0.1% Ag-GAC (DOC = 1mg/L, pH = 7, Cl_2 = 5mg/L

The neutral pH 7 value is widely used in the majority of WTPs in Scotland which adjust pH to enable enhanced coagulation and in many cases it is maintained higher than 8 up to the point of disinfection. Due to this practice, solutions were maintained buffered at this pH value to mimic real like treatment sites. In the case of ferulic acid (*pKa* = 3.46) and syringic acid (*pKa* = 3.93) as selected adsorbates, adsorption is more successfully achieved for the phenolic acid that has additional methoxylated groups such is the case of syringic acid.

The powdered activated carbon used in these experiments seems to be more adequate for larger compounds rather than smaller such pyruvic acid, which is due to the well-known fact that water solubility generally decreases with increasing molecular size, hence favouring adsorption (37). For comparison with the silver impregnated AC, four other granulated activated carbon (Norit, Filtrasorb 400, Aquacarb 208 and Brimac Bonechar) converted into PAC were used to perform adsorption experiments using as adsorbate ferulic acid solution (2 mg DOC/L) containing also chloride (40 mg/L) and bromide salts (300 µg/L).

Halides such chloride and bromide were established as one of the main drivers for THMs formation in previous chapters consequently these salts were added to form brominated THMs and to investigate whether these species could be also removed by the selected GAC. THMFP for the controlled ferulic acid solution produced initial concentrations of chloroform (2 µg/L ± stdv.6.8e^{-17}), bromodichloromethane (12.6 µg/L ± stdv.1.3), dibromochloromethane (44.7 µg/L ± stdv.5.6) and bromoform (34.7 µg/L ± 4.1) which indicated clearly the influence of salt content with a shift towards brominated THMs, especially dibromochloromethane, caused primarily by the fast kinetic rates of bromide radicals in the presence of chloride (34, 38, 39).

The adsorption batch experiments showed a more efficient reduction of THMs when doses of activated carbon were increased from 50 mg/L to 400 mg/L. Applying one way ANOVA tests to the six types of carbon used in the experimentation, there is no significant difference between the mean values ($p = 0.283$) for all groups (**Figure 5.5**) indicating that each type of carbon can adsorb ferulic acid with similar effectiveness.

Removal efficiencies for silver activated carbons showed no statistically difference (*t*-test = 0.31, $p = 0.756$) between the mean removal efficiency obtained for 0.05% (73.6% ± s.e.4.5) and 0.1% (71.5% ± s.e.4.6) impregnation when using the four different doses. These two types were available during experimentation but higher silver impregnation percentages are also commercially available such 0.2% and 0.4% which could be tested in the future to verify whether they can improve removal efficiencies. Overall, best adsorption in terms of THMs reduction were obtained at 400 mg/L for all types of activated carbon, but at 200 mg/L Filtrasorb400, Aquacarb208 and Norit 0.1% Ag-AC removal efficiencies were complete for chloroform and for the other three THMs between 78-85%. It is interesting to note, though, that while reductions in THMFP generally increase with higher AC dose, there appears to be a limit to what can be achieved by increasing AC dose, i.e. THMFP removal efficiency appears to level off at a value of less than 100%. Brimac Bonechar was the most effective in terms of

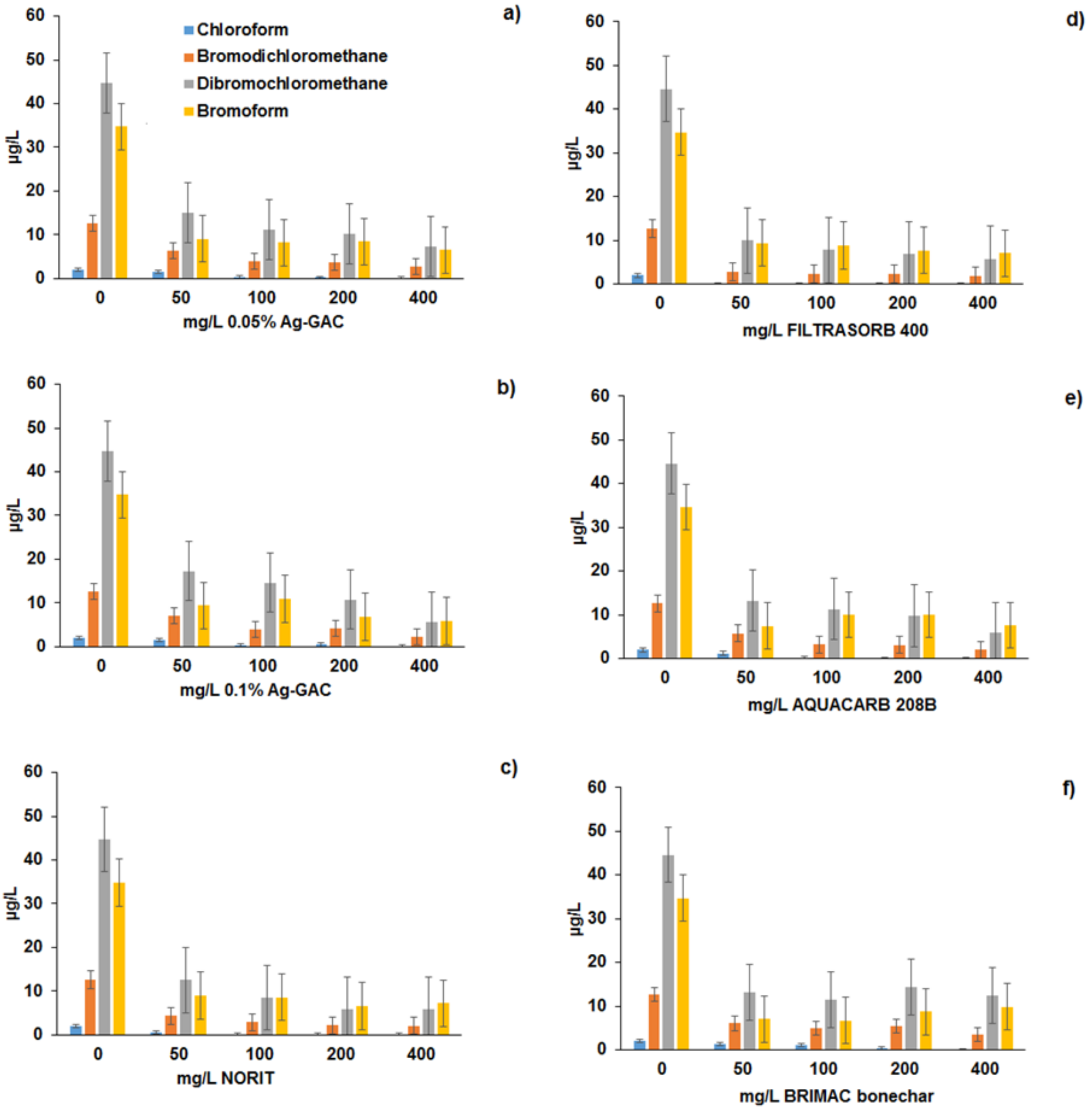

Figure 5.5 Adsorption of trihalomethanes by six types of AC at four doses (mg/L) in batch experiments at 25°C

performance compared to any other carbon type by reducing THMFP between 71%-72% (higher dose) when looking at removal of brominated species. When looking at chloroform and bromodichloromethane concentrations it appears that increasing PAC dose improves THMs control, but brominated compounds show a residual concentration that cannot be reduced even when PAC dose is increased (**Figure 5.5**).

All carbon types removed THMs precursors to some extent based on the results of their formation potential, but there also appeared to always be a residual THMFP which was not readily removed by PAC even at large doses. The potential causes for this persistent residual could not be unambiguously established with the methods used in the experiments, showing a need for more study around this area. In any case, a 400 mg/L PAC dose equivalent to 400 g PAC per m^3 would be a very large amount to use in water treatment, where recommended ranges are typically between 1-20 mg/L (37), indicating that THM precursors are difficult to effectively be removed by activated carbon adsorption, in line with earlier findings from water treatment works as explained in chapter 3, although case study data from Forehill WTP in chapter 4 demonstrated a time-limited benefit of GAC filtration in terms of reduced THMs in disinfected water.

5.4 Conclusions

Organic dissolved compounds of small molecular weight considered as the hydrophilic portion of DOC have shown their preponderance in treated water samples for all the monitored sites. The reactivity of these groups of chemicals was confirmed when THMFP reactions were performed using a group of 35 carboxylic acids and eight phenolic acids. The experiments maintained the same levels of chlorine, pH and DOC and only temperature changed. Disregarding the group of DOC precursors that was monitored, THMs were always produced at higher concentrations at higher temperatures. Comparisons between the two selected groups of THMs precursors showed a clear difference between carboxylic acids and phenolic compounds, phenolic acids being the compounds that produced more THMs, specifically chloroform and dichlorobromomethane. Although DOC quality in Scottish surface waters remained the same along the year, in terms of humic and fulvic acids constitution (verified by fluorescence excitation emission analysis in the previous chapter) the concentrations of carboxylic acids in the treated water before the point of disinfection in each of the selected case study sites represented a higher percentage of the DOC compared to phenolic acids.

However, due to the reactivity experiments it can be said that, although present at lower concentrations, some phenolic acids tend to yield more chloroform than others such is the case of vanillic and ferulic acids. Particularly due to their chemical structure which possess methoxylated groups, mechanism of reaction drive formation of chloroform and dichlorobromomethane, exacerbated by addition of chlorine excess and high temperatures.
Due to the highest yield of THMs produced by phenolic compounds, granulated activated carbon was selected for adsorption of the most reactive compounds (containing methoxylated groups in their structure) with and without silver impregnation in 24 hours batch experiments. Experiments showed that some adsorption of THMs precursors was achieved by all selected PAC types. However, large doses of carbon (200 mg/L and 400 mg/L) were needed for effective THM precursor adsorption. Thus, optimisation for the removal of these compounds could be improved by investigating what may explain residual THMFP which cannot be removed by AC adsorption.

The high doses needed to achieve moderate or poor removal efficiency of all the AC types investigated for phenolic compounds with high THMFP suggesting that GAC filtration will have limited effectiveness for the removal of these THM precursors in line with observations from real treatment sites (chapter 3), although there is also evidence for a temporary benefit until GAC becomes exhausted (chapter 4, Forehill WTP). Experimentation with excess addition of chloride and bromide salts lead to the obvious formation of brominated THMs species, but anionic adsorption of halides was not achieved due to their small molecular weight and high hydrophilicity. It appears that silver impregnation did not consistently improve

THMFP removal efficiency, as some ACs without silver impregnation performed as well as the silver impregnated AC types. Further experimentation is required with continuous flow to monitor the best alternative for adsorption of either phenolic compounds or carboxylic acids, but findings are unlikely to differ substantially from those obtained in the batch experiments, and a wider range of adsorbent types should be considered.

This work identified a large portion of the DOC present in treated waters from Scottish water sites and their reactivity towards THMs formation. The influence of temperature is also evident in these laboratory experiments and raises concerns about climate change making THM control even more challenging in the future. In the case of Scotland, the presence of phenolic compounds that naturally occur in high organic content soils exacerbate the problem. It would be more applicable to modify treatment processes to reduce THMs precursor that specifically target phenolic acids and halides for example. The AC types investigated had limited removal effectiveness for these compounds. On the other hand, the changes in DOC composition resulting from different treatment steps suggest that coagulation to some extent preferentially removes phenolic compounds, and hence, enhanced coagulation could be an area to be explored further in future research, since phenolic compounds had significant THMFP.

Also, the application of other strategies such modifications or disturbances within the catchment can contribute to reduced DOC release from soil. Overall, the introduction or modification of steps of the process will imply addition of costs but the benefits for the future would be more rewarding as health concerns for the population will be highly diminished with the reduction of disinfection by products from drinking water supplies.

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Chapter 6

BUSINESS CASE FOR THE INSTALLATION OF UV/VIS ONLINE MONITORING SENSORS AT DRINKING WATER SITES

6.1 Introduction

According to STREAM requirements to obtain an EngD degree it is necessary to add a complementary section to a Doctoral Thesis that applies an economical evaluation of a relevant part of the knowledge generated by the research project that can be of benefit to the industrial sponsor. The aspects that could be included in the evaluation can be related to marketing, investment, economic, technology management, cost benefit or legal analysis of any of the findings obtained from the main research topic as suggested per STREAM guidelines.

Two important findings obtained from the experimental work lead to propose, firstly the use of granulated activated carbon with silver impregnation as an alternative media to remove DOC compounds in treated water prior to disinfection and secondly, the use of ultraviolet/visible (UV/Vis) online sensors to monitor spectral wavelengths which indicate different types of DOC for coagulation enhancement and THMs control.

Investigation on DOC removal from Scottish surface waters in drinking water treatment plants explained in Chapter 3 lead to batch adsorption experiments in Chapter 5 to evaluate the suitability of GAC in the drinking water processes as a strategy to control and minimise THMs formation. The installation of new GAC filtration units in some sites with historical recurrences of elevated THMs and residual DOC is currently taking place as part of a larger project within the company.

Silver impregnated GAC was investigated in this thesis (chapter 5) as a potential alternative due to its strong and positively charged sites (1-3) that could adsorb negatively charged hydrophilic DOC and other inorganic species from raw and treated waters. However, a simultaneous column study at Newcastle University (4) showed that GAC containing higher impregnation of silver reduced THMFP significantly in the short-term, but by no more than 20% in the longer term, and in addition to this limited benefit, the costs of the quantities of GAC needed for installation and maintenance need to also be considered in comparison with alternatives technologies (**Figure 6.1**).

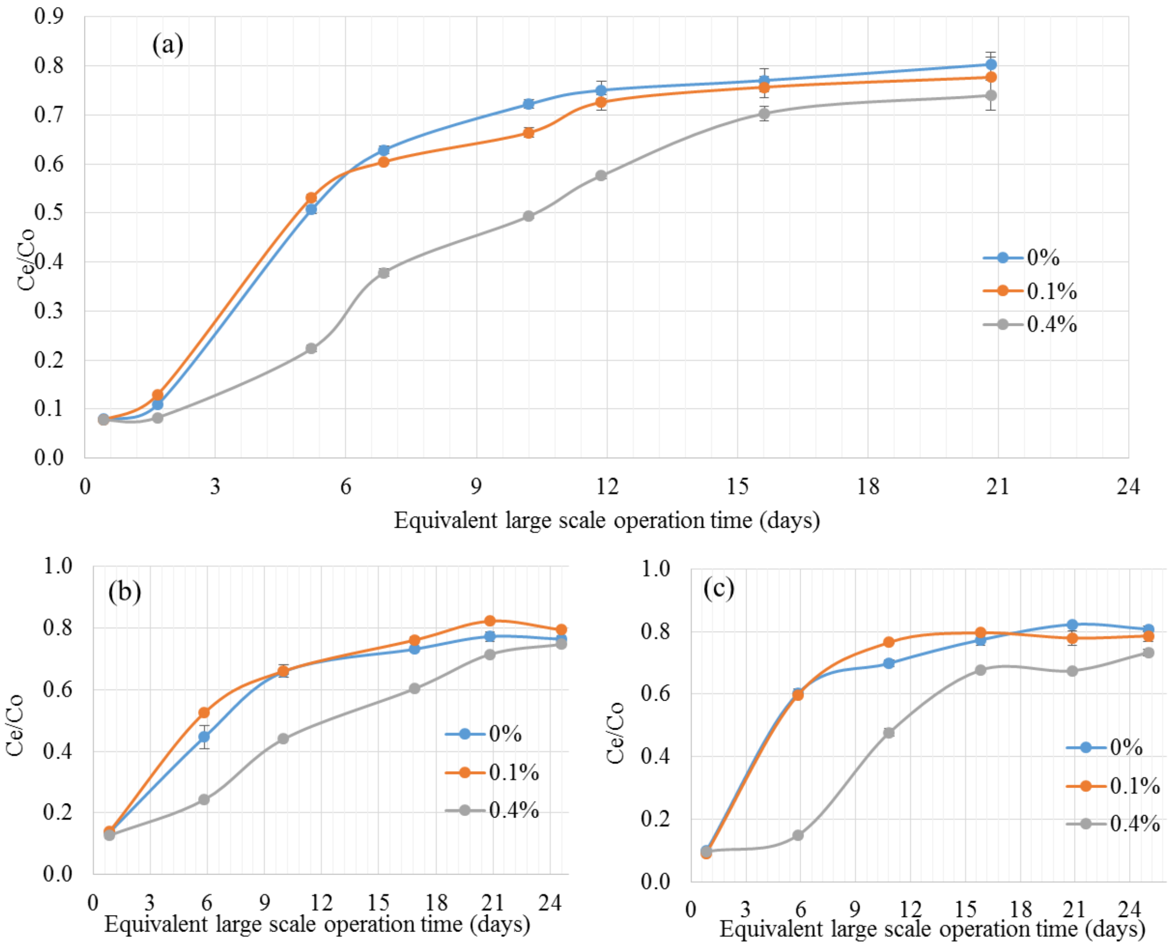


Figure extracted from Sani et al (4)
Ce: THMFP of the GAC filter effluent; Co: THMFP of the GAC influent

Figure 6.1: THMFP breakthrough predicted from column studies for GAC filtered water from three drinking water treatment plants in Scotland: a) Auchneel, b) Bracadale and c) Broadford. Figure extracted with permission from THMs report by Sani, 2017 (4).

In the case of the second option, experimental work related to characterisation of DOC to control THMs was primarily performed to understand mechanisms and formation rates of THMs in the selected case study sites. In chapter 4, detailed UV measurements in raw and treated water samples proved to be an important parameter well correlated with THMs that also helped to better understand the nature of DOC present in the selected sites. UV absorbances, along with fluorescence measurements, indicated that DOC quality remained fairly constant throughout the year. However, its abundance fluctuated according to the seasons. In summer and autumn, absorbance values are higher for the most typical wavelengths such 230 nm, 254 nm and 280 nm and during winter and spring the most predominant wavelengths were obtained from 270-290 nm and the lower wavelengths were near the detection limit (chapter 4).

A more in depth investigation in chapter 4 showed that absorbance at particular wavelengths can, in principle, be related to a group of chemicals that showed great reactivity towards THMs formation. Absorbance at lower wavelengths (230 nm) was related to hydrophilic DOC fractions of very small molecular weight such carboxylic acids, ketones and alcohols, whereas 254 nm corresponded to the typical aromatic DOC of humic and fulvic origin; and finally larger wavelengths ranging from 270-290 nm were associated to aromatic moieties with carboxylic and phenolic functional groups. This information can potentially provide better insight into the nature of DOC and its relation to THMs formation specifically for surface water in Scotland. Although the pool of organic compounds in raw water during summer and autumn was quite vast, absorbances at 280 nm during spring and winter time proved to be the most reactive towards THMs formation despite of the low absorbance values obtained during these months as stated in chapter 4, section 4.3.2.

As high reactivity towards THM formation was particularly found from low concentrations of DOC with high absorbance values at 280 nm, then monitoring absorbances at this wavelength throughout the year is crucial and would help process scientists and operators to predict THMs formation to apply the best strategies to minimize their presence. One strategy would be modifying coagulant dose when DOC levels change, for example, and more particularly at the specified wavelengths that will help to differentiate DOC quality.

In terms of estimated costs for implementing the second option: installing a sensor unit that could scan water in a wider UV/Vis wavelengths range would be a most suitable alternative as a business case for this project due to its commercial availability. Such a monitor would provide information on absorbances at specific wavelengths to differentiate DOC quality in real time, sensor maintenance and operational costs are minimal, interpretation of results is straight forward and overall it will help reduce the potential risks of THMs failures in the future by improving understanding of DOC quality for optimization of existing treatment processes.

This chapter will thus evaluate the cost-benefits of a project associated with installation, maintenance and operational costs of online monitoring UV/Vis sensor probes for the simultaneous monitoring of absorbances at different wavelengths (230 nm, 254 nm and 280 nm) in a drinking water treatment site at the raw water sampling point. Although, monitoring UV absorbance has been extensively studied and focused on 254 nm worldwide as DOC quality indicator, it is important to consider that the existence of large amounts of compounds with phenolic nature is particular to the nature of Scottish soils that surround the catchment areas and makes it quite unique. The incorporation of additional wavelengths such as 230 nm and 280 nm will provide more accurate information about DOC quality changes throughout the seasons.

Introduction of these probes into drinking water processes will enable more extensive data collection to monitor DOC fluctuations in diverse geographical regions across Scotland and the possibility to transfer knowledge with other teams within the company and external institutions. As these investigations are new and innovative, the final goal will be to provide a continued progression to analyse, understand, plan and implement solutions for the management of THMs formation and hence significantly minimize THMs formation and failure identification.

As Scottish Water faces significant challenges in increasing its reputation as an organisation leading in customer service and water quality, this proposal can benefit the company in helping it meet and exceed its regulatory objectives.

This chapter has the following structure:

- 6.2 Silver impregnated GAC as an sorbent alternative material to remove DOC
  Cost Benefit analysis for new GAC materials
- 6.3 Online monitoring UV/Vis sensors in drinking water
  Business case of online water quality monitoring sensors
  Cost-benefit analysis for the installation of UV/Vis online monitoring sensors
- 6.4 Conclusions

6.2 Silver impregnated GAC as an alternative material to remove DOC

Many membrane and coagulation sites around Scotland have as a final step in their treatment process GAC filtration units which are usually installed to remove bad odours and organic micro pollutants including DOC. In chapter 3 it is explained that current GAC systems did not perform very effectively in terms of DOC removal, however, some benefits lasting for about nine months following installation of a new GAC filter were documented for the Forehill WTP case study site in chapter 5. On the other hand, some sites that use coagulation complemented with GAC had a significantly higher mean THMs in distribution samples at 83.3 ± s.e.5.3µg/L (t = -8.9, p < 0.001) compared with WTPs that apply coagulation alone (mean 48.8 ± s.e.0.9µg/L) indicating that the implementation of GAC units did not obviously favour reduction of THMs precursors. Overall, our results show THMs precursor removal is not necessarily substantially enhanced by an additional GAC treatment step which reinforces the requirement of further study around this area (5).

In a more specific case study site, Forehill showed pesticides and herbicides levels in the raw water due to heavy agricultural activities in the River Ugie catchment. This situation encouraged the installation of a GAC system that target mainly these pollutants. THMs levels in this site have always been low, but elevated concentrations of brominated THMs species were noticed and required further investigation.

It was found that high levels of bromide in chlorine (120 mg/Kg) may be the origin of bromide in the system due to contamination of raw material rather than natural causes such estuarine water, for example, which was the main cause for bromide in sites located by the coast and Islands. High bromide levels will increase the risk of producing brominated THMs in sites with these characteristics, causing concern about these inorganic species in water and whether these could be minimized from the system along with DOC. In chapter 5, detailed characterisation of DOC indicated that the most reactive forms of DOC found in Scottish surface waters were: carboxylic acids and phenolic compounds. The current process conditions that maintain pH levels between 8-8.5 after coagulation, do not favour the adsorption mechanisms of carboxylic acids due to their acidic nature, which implies they are present in anionic form, very water soluble, and not readily adsorbed to GAC. At the same time, halides in their soluble form are also not readily sorbed by GAC, and it was initially thought that halides could be better controlled by silver impregnated granulated activated carbon Ag-GAC as trialled by Watson et al. where 91-95% halides removal was achieved, depending on the halide, at pH = 5 (6, 7).

However, our own results in chapter 5, showed no evidence of significant chloride or bromide adsorption during batch experimentation at different Ag-GAC doses, perhaps due to the high pH values used in the experiments as mentioned above. In terms of THMFP reduction in column studies, a parallel study at Newcastle University showed after a relatively short-lived higher effectiveness, Ag-GAC showed a very moderate removal efficiency (~20%) at the highest impregnation concentration of 0.4%, demonstrating that this material is not suitable for long term use for either halides or DOC removal and a constant regeneration would be necessary, increasing operational and maintenance costs (4). Also, the long-term removal efficiency of Ag-GAC of ~ 20% was no better than that observed for the GAC without silver impregnation.

6.2.1 Cost Benefit analysis for new GAC materials

Scaling up the doses of Ag-GAC from bench studies to a real size filter the required sorbent mass was calculated using standard filter bed and sorbent packing measurements (volume = 1.77m^3, δ = 1,480kg/m^3) which showed that the mass of Ag-GAC required for installation is 2.6 tonnes for an existing unit (location: Broadford WTW, Skye; flow rate: 27 m^3/h; tank size: 2.5 m^3; empty bed contact time: EBCT = 3.9 min). Capital investment and installation costs (**Tables 6.1 and 6.2**) were calculated for one such filtration unit. Yearly total costs for the replacement of GAC material which includes capital, operational and maintenance costs are shown in **Table 6.2,** for instance the total installation and operational yearly costs per unit is

£13,950. This value is the base to calculate total costs per silver impregnation percentage calculated as it appears in **Table 6.1**.

% of silver impregnation	Cost(£)/tonne	Cost(£)/unit (volume = 1.77m^3)
0	440	1,148
0.05	800	2,088
0.1	1,500	3,915
0.2	3,000	7,830
0.4	6,000	15,660

Table 6.1 Costs of Ag-GAC material per tonne and per filtration unit (Volume of GAC=1.77m^3)

Installation Costs for a New Silver impregnated granulated activated carbon (Ag-GAC) bed in a Filtration System	Qty	Cost, £
Change of old GAC material for the new Ag-GAC system, labour		
Basic labour to install and change GAC bed in a filter system with favourable site conditions. Dismount unit. Change old material and disposal. Install new material and assembly of filter unit. Install water supply line. Verify operation. Includes planning, equipment and material acquisition, area preparartion and protection, setup and cleanup	5h	**1,250**
New system job supplies		
Cost of related materials and supplies typically required to install new GAC beds in filtration systems including: connectors, fittings and mounting hardware	1 unit	**1,500**
Extra allowance costs		
Job related costs of especiality equipment and tools used for job quality and efficiency. Including: daily rental and extra consumables	1 unit	**1,500**
Old GAC bed disposal		
Costs associated to transport and disposal fees of old GAC bed and other materials	1 unit	**1,500**
Total installation costs for a new Ag-GAC bed in a Filtration System	1 unit	**5,750**
Operational and Maintenance Costs for one filtration unit per year	**Qty**	**Cost, £**
Regeneration costs (yearly)		
Including use and disposal of chemicals for regeneration	**1 unit**	**5,000**
Maintenance and Operational costs (yearly)		
Maintenance and operational Labour	**1 unit**	**2,400**
Total Operational and Maintenance Costs for one Ag-GAC filtration unit	**1 unit**	**7,400**
Total Installation Costs for a new Ag-GAC bed in a Filtration System	**1 unit**	**5,750**
Total Installation and Operational costs	**1 unit**	**13,150**

Table 6.2 Total Installation and Operational Costs for the installation of a new Ag-GAC bed in a filtration unit

A filtration unit with GAC at 0.05% silver impregnation for example has a total cost of £15,238 (total installation and maintenance costs: £13,150 and cost per unit at each silver impregnation percentage values obtained from table 1: £2,088) and the most expensive unit with 0.4% silver impregnation costs £28,810 (total installation and maintenance costs: £13,150 and cost per unit at each silver impregnation percentage values obtained from table 1: £15,660). GAC replacement costs appear to be elevated compared to conventional GAC (at much lower cost for the same bed size at £1,148). However, the benefit of replacing the existing GAC for Ag-GAC could potentially improve DOC removal. However, apart from a very short initial benefit, GAC has about the same capability to reduce THMFP with or without silver impregnation as shown in a report by Sani et al. (4).
Sani et al. also mentions that GACs did not have a satisfactory performance in the control of THMFP, since breakthrough was observed in two to three weeks of operation. One of the downsides of using Ag-GAC during experimentation is the very short lived breakthrough time. This situation will cause extra cost for chemicals used in filter regeneration and for more frequent chemical disposal and licensing as well as overall increase of maintenance and operational costs than a more conventional unit will not normally produce, due to the high Ag-GAC costs compared to ordinary GAC materials. For example 0.4% Ag-GAC showed the highest THMFP removal percentage, but only for a short period estimated to last less than two weeks (4), and it is also the most expensive (**Table 6.1**), making this option the most adequate in terms of short-term removal efficiencies but not in terms of costs.

Looking at the potential benefits that could be obtained by adding Ag-GAC to a water treatment train an important question arises: would the use of such costly technology to remove THMs precursors be justified? In this context, it is important to consider that even a fairly small 20% reduction in THMFP can potentially make a significant difference in terms of regulatory fails, as many failures are just slightly exceeding drinking water quality standards. To answer this question, 89 WTPs selected from 239, represent coagulation processes with sand filtration. Data collected in 2016 from coagulation sites (n =17) had 76 THMs values between 80 µg/L and 100 µg/L and 19 over 100 µg/L. By incorporating the new GAC beds into the treatment process, assuming it reduces THMFP by about 20% as indicated by the experiments (**Figure 6.1**), all of the THM concentrations exceeding 100 µg/L, and 79% of the THM concentrations exceeding 80 µg/L, which is a company internal target, could have been avoided.

Other process technologies could be applied to improve DOC and halides removal efficiencies such ion exchange resins (MIEX) or reverse osmosis (RO) membranes (6, 8, 9) that will minimize THMs precursors and potentially halides, but the costs of these technologies are much higher than GAC filtration and the justification of their application in Scottish Water could be assessed in more detail in the future. To summarize, the analysis demonstrates that addition of GAC filtration to treatment trains may be beneficial at WTPs with THM levels near the regulatory limit, but there is no treatment benefit from the use of silver-impregnated as compared to ordinary GAC, which could justify the higher cost of the former.

6.3 Online monitoring UV/Vis sensors in drinking water

From our previous investigations, sites that successfully removed DOC were the ones that applied coagulation (10-12). In this sense, enhanced coagulation could be tailored according to specific sites for example by monitoring UV wavelengths at an early stage, adjust chemical dosing accordingly, and thus reduce THMs precursors further in the treatment.

Online water quality monitoring has been widely implemented in water utilities around the world, but this activity has been always limited to a fixed number of parameters that have been established by local authorities and regulators mainly at the raw water and in the final potable water to maintain the best quality standards.

The ingress of organic substances of natural origin and pollutants into surface bodies is generally due to rainfall or runoff events. Human interventions from chemical, biochemical, agricultural and other industrial activities also incorporate organic pollutants through many different pathways. Monitoring these chemical substances at the raw and source water, as well as in the final potable water, would be unsustainable for water companies due to their large number and costs implicated in sampling, chemical analysis and interpretation of results.

Thus, only the most relevant and important parameters are monitored on a daily basis. Typically, analyses of these parameters are performed off-site and reported a few days after the moment the sample was taken originally, which does not provide the best representation of what is happening at the treatment plant in real time. If any parameter shows abnormal fluctuations in concentrations, it cannot be detected immediately but until it has reached the final potable water, been sampled, analysed and reported through LIMS.

Due to potential adversities and unexpected changes in the quality of raw water, online monitoring systems have been incorporated in drinking water utilities worldwide to control sudden changes in quality and prevent potential failures, non-compliance regulatory samples and customer complaints. This type of technology has also been applied at Scottish Water. At the moment, the main online water quality parameters that are currently monitored at the raw water sampling point are:

- UV absorbance monitors at 254 nm
- colour,

- turbidity and
- pH

In the final potable water:

- Free and total chlorine,
- Turbidity
- pH
- UV online monitor sensors (report TOC in mg/L)
- Metals (iron, aluminium)

Many water utilities with particular identified vulnerabilities, use other surrogate parameters or contaminant-specific analysers. Water quality sensors can monitor parameters that can be present in water due to its source characteristics or resulting from treatment rather than from contamination and most importantly in real time, providing a much faster information on the actual state of water to apply corrective measures.

As a specific example, nitrification may occur in drinking water when excess ammonia is available from chloramination process or from the breakdown of chloramines. Early detection of impending nitrification is a worthwhile operational benefit and monitoring nitrification is usually included in online monitoring systems for utilities that use chloramination as disinfectant in the distribution systems. The potential and degree of nitrification can be determined by evaluating nitrite, nitrate, ammonia and assimilable organic carbon levels in the distribution systems.

Similarly to the previous example, wavelength measurements can provide an indication of the characteristics of different organic compounds present in water by differentiating absorbances at the three selected wavelengths considered as surrogate of DOC. UV/Vis sensors can provide this information by obtaining a system with light absorption in the continuous broadband spectral analysis from 200 nm to 700 nm. Depending on the manufacturer, this option can be limited to only few selected wavelengths or the whole spectral range. Many companies provide this type of sensors and the selection process can be narrowed down to costs associated to capital investment and operational costs.

6.3.1 Online water quality monitoring sensors as a business case

At the moment, Scottish Water has twenty five sites with online UV absorbance monitors at 254 nm that report DOC values in real time, representing 10% of all drinking water treatment sites. These instruments have been installed in the past three years and are currently fully functioning and located at the raw water and post filtration sampling points. The price of these sensors was £10,500 each including installation. These sensors read absorbance at 254nm which provide information in one type of DOC (of fulvic and humic acid origin) and calculate DOC in mg/L thanks to an internal algorithm which calibrates the relationship between UV absorbance and DOC. It is important to mention that online "DOC" monitoring systems were installed initially to control DOC surges in sites that showed discolouration and their main purpose is to optimize coagulation. There are no regulatory values for DOC levels at the raw water or in the final potable water at the moment because DOC per se is not considered harmful. However, strong correlations have been found between DOC and THMs at final potable water and distribution networks as stated in chapters 3, 4 and 5. As this evidence is corroborated by many studies around the world (10, 13, 14), Scottish Water has established its internal quality values to prevent and control THMs formation for example.

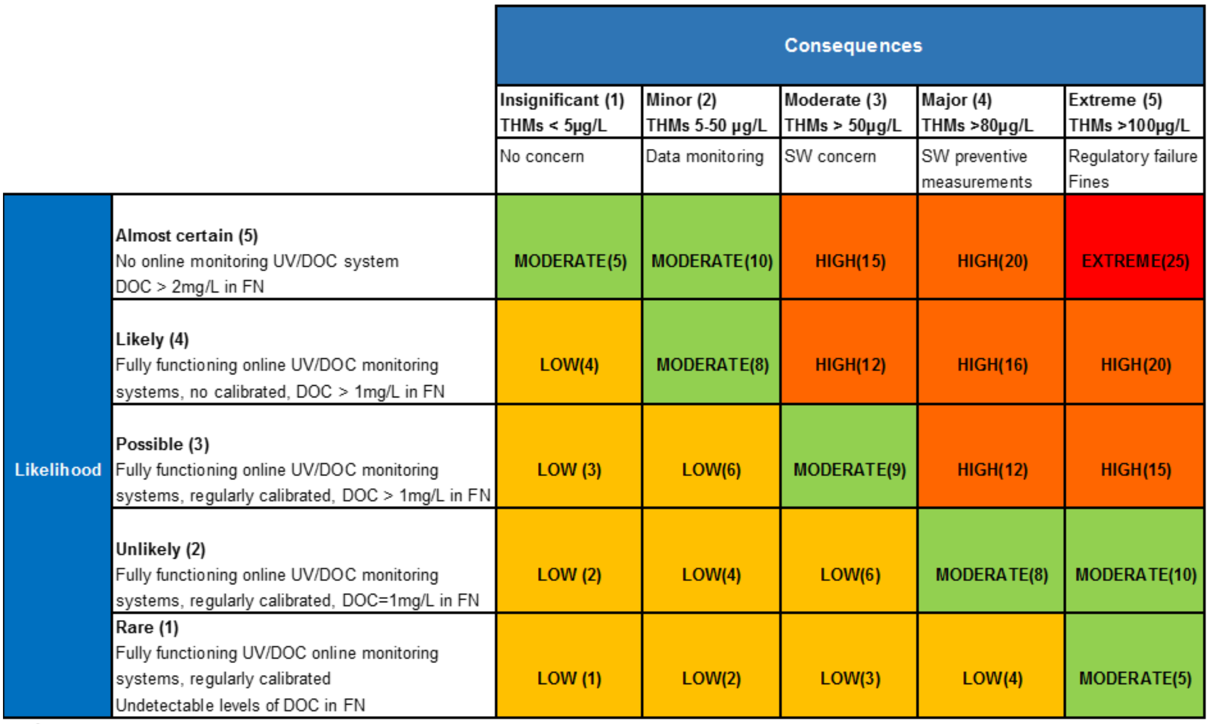
The treatment process has shown robustness in the sense that DOC is removed from the raw water (removal efficiencies >75%) leaving a residual DOC in final treated water that ranges from undetectable limits below 0.2 mg/L to mean values of 0.89±s.e.0.01 mg/L (n=14,094, data collected from LIMS found in final potable for the period Jan. 2015- Oct. 2016 for all 239 drinking water treatment plants around Scotland) which is within the internal operational target value for TOC at 1 mg/L. However, Scottish Water aims to reduce this value even lower to 0.5 mg/L in the following years.

The installation of UV/Vis scanning sensors has to be justified from a technical and economical point of view. Therefore, another interesting question arises: how is this new technology any better than the current “TOC” monitors or UV 254 nm sensors? And what would be the benefits to the company of installing or replacing new systems? One of the main advantages of the new technology compared to the existing one is the real time analysis of DOC concentrations and the simultaneous measurement of absorbances at three wavelengths, which may indicate shifts in DOC quality. Also, these new sensors are faster and more reliable data can be gathered in order to apply corrective measures sooner.

By preventing possible quality change in water, the company will be ahead of possible regulatory failures and customer complaints in the future. Hence, if the current UV 254 nm online monitoring systems have provided an improvement in THM formation control, then the new proposed units that show information on three different wavelengths can benefit DOC understanding even further in terms of control and process modification. The additional wavelengths will give an unprecedented level of information for lesser costs compared to the installed units that measure only one wavelength as mentioned before.

These wavelengths provided specific insight on DOC quality in Scottish surface waters where the typical UV absorbance at 254 nm was found to be the closest indicative to natural organic matter (NOM) quality and directly linked to DOC, but also other wavelengths such as 280 nm and 230 nm showed strong correlations with DOC. Absorbances ratios such (A280/A254 and A230/A254) may indicate DOC character (15) and aid to improve coagulation for example by reducing or increasing coagulant dose according to DOC levels and quality. A crucial finding in chapter 4, where wavelengths at 280 nm were related to phenolic compounds with carboxyl groups in much higher abundance during winter months, indicated that although ambient temperature during those months was low still THMs were formed. Absorbances at 230nm indicated the presence of small compounds such carboxylic acids for example. Both types of DOC compounds were investigated further in chapter 5 by testing their reactivity, it was found that phenolic compounds produced more THMs than carboxylic acids. Then, distinction between these groups and their abundance by using UV absorbances will benefit process control by differentiating between DOC types.

To answer the second question, a risk assessment matrix was proposed to provide a scoring criteria to select treatment sites at a higher risk. Highest scoring values were given to sites that showed historical evidence of THMs failures, high TOC levels and no current UV monitoring, whereas as a contrast the lowest scoring values were given to sites with no evidence of THMs failures and undetectable levels of TOC in final potable water (**Table 6.3**).



		Consequences				
		Insignificant (1) **THMs < 5µg/L**	**Minor (2)** **THMs 5-50 µg/L**	**Moderate (3)** **THMs > 50µg/L**	**Major (4)** **THMs >80µg/L**	**Extreme (5)** **THMs >100µg/L**
		No concern	Data monitoring	SW concern	SW preventive measurements	Regulatory failure Fines
Likelihood	**Almost certain (5)** No online monitoring UV/DOC system DOC > 2mg/L in FN	MODERATE(5)	MODERATE(10)	HIGH(15)	HIGH(20)	EXTREME(25)
	Likely (4) Fully functioning online UV/DOC monitoring systems, no calibrated, DOC > 1mg/L in FN	LOW(4)	MODERATE(8)	HIGH(12)	HIGH(16)	HIGH(20)
	Possible (3) Fully functioning online UV/DOC monitoring systems, regularly calibrated, DOC > 1mg/L in FN	LOW (3)	LOW(6)	MODERATE(9)	HIGH(12)	HIGH(15)
	Unlikely (2) Fully functioning online UV/DOC monitoring systems, regularly calibrated, DOC=1mg/L in FN	LOW (2)	LOW(4)	LOW(6)	MODERATE(8)	MODERATE(10)
	Rare (1) Fully functioning UV/DOC online monitoring systems, regularly calibrated Undetectable levels of DOC in FN	LOW (1)	LOW(2)	LOW(3)	LOW(4)	MODERATE(5)

UV/DOC: Ultraviolet and dissolved organic carbon
FN: Final potable water

Table 6.3 Risk assessment matrix to select drinking water treatment sites with higher risk of THMs failures that will benefit from the installation of new monitoring technology. Numbers indicate scoring rates for selection of most vulnerable sites.

Final potable water (FN) TOC and THMs data was collected from LIMS covering the period from Jan. 2015 to Oct. 2016 from 239 drinking water sites. Sites with high scoring values were selected according to the number of THMs failures, TOC values above 1 mg/L as well as UV online monitors systems already installed and fully operative. The next criteria in the selection process were treatment type and population size population that these sites supply (**Table 6.4**).

Treatment sites that have coagulation treatment were given priority over membrane plants, as coagulation can be optimized by linking chemical dosing to UV monitoring. Another important consideration was the size of the population they supply. In consequence greater risks might develop from larger sites in terms of potential THMs failures in their water supply.

Site name	TOC$^{\&}$ (>1mg/L)	THMs* (>50µg/L)	Type of Treatment	Size, MLD	UV 254nm sensor	RISK
Achmelvich	23	31	Membrane	3.84		Moderate
Afton	73	48	Coagulation	25	yes	Low
Amlaird	113	81	Coagulation	20	yes	Low
Ardfern	25	1	Membrane	0.2		Low
Ardrishaig	46	18	Coagulation	8	yes	Low
Ascog 1&2	44	22	Spruce	4.5		High
Assynt	18		Coagulation	18.2		High
Auchneel	26	1	Coagulation	5.6		High
Badentinan	17		Membrane	18		Low
Ballygrant	16	4	Membrane	0.4		Low
Barra New	36	9	Coagulation	0.913		High
Bayhead	29		Coagulation	0.838		Moderate
Benbecula	38		Coagulation	2.351		Moderate
Black Esk	28	1	Coagulation	20.5	yes	Low
Boardhouse	49	2	Coagulation	3		High
Bonar Bridge	117	1	Membrane	1.25		High
Bracadale	62	1	Membrane	0.2		High
Bradan	80	17	Coagulation	110	yes	Moderate
Broadford	122	60	Membrane	0.65		High
Bunessan	57	9	Membrane	0.3		High
Burncrooks 1&2	92	29	Coagulation	21	yes	Low
Campbeltown	26	3	Coagulation	4		High
Camphill	33	22	Coagulation	45.5	yes	Low
Carradale	27	2	Membrane	0.3		Low
Carron Valley	46	16	Coagulation	129		High
Carsphairn	18		Membrane	1.034		Low
Castle Moffat	24		Coagulation	32	yes	Low
Corsehouse	81	27	Coagulation	4.75		High
Dougliehill Low	76	39	Coagulation	6	yes	Low
Fort Augustus	98	49	Membrane	11.4		High
Gigha	77	29	Membrane	0.3		High
Glenfarg	43		Coagulation	85		High
Glenlatterach	31	17	Coagulation	9		High
Howdenhaugh	111	7	Membrane	15		High
Invercannie	44	3	Membrane	60		Low
Inverness Loch Ashie	117		Membrane	38.5		Moderate
Kaim	35	22	Coagulation	6	yes	Low
Kirbister	55	14	Coagulation	3		Moderate
Kirkmichael	67	1	Membrane	0.28		Moderate
Kyle of Lochalsh	144	9	Membrane	2.2		Moderate
Lochenkit	35	12	Coagulation	1.4	yes	Low
Lochinvar	31	13	Coagulation	6.5		High
Lochinver	105	4	Membrane	12.96		Moderate
Lochmaddy	42	5	Coagulation	0.939		Moderate
North Hoy	34		Membrane	0.04		Low
Osedale	32	4	Membrane	0.4		Low
Papa Stour	40	20	Coagulation	0.004		High
Penwhapple	66	12	Coagulation	9	yes	Low
Picketlaw	57		Coagulation	7.8	yes	Low
Port Charlotte	40	2	Coagulation	0.6	yes	Low
Savalbeg	48	9	Coagulation	12	yes	Low
Skerries	30	48	Membrane	0.016		High
Stornoway	60	45	Coagulation	6.513		High
Tarbert Argyll No 1	55		Coagulation	1		Moderate
Tarbert Western Isles	85	43	Membrane	1.058		High
Teangue	110	26	Membrane	0.5		High
Tiree	48		Membrane	0.5		Moderate
Tullich	83	19	Ozone	10		High
Westray	158	1	Coagulation	0.032		High
Whalsay	86	54	Coagulation	0.302		High
Yell	84		Membrane	0.203		Moderate

TOC$^{\&}$: number of TOC measurements with values over 1mg/L
THMs: number of THMs measurements with values over 50µg/L*

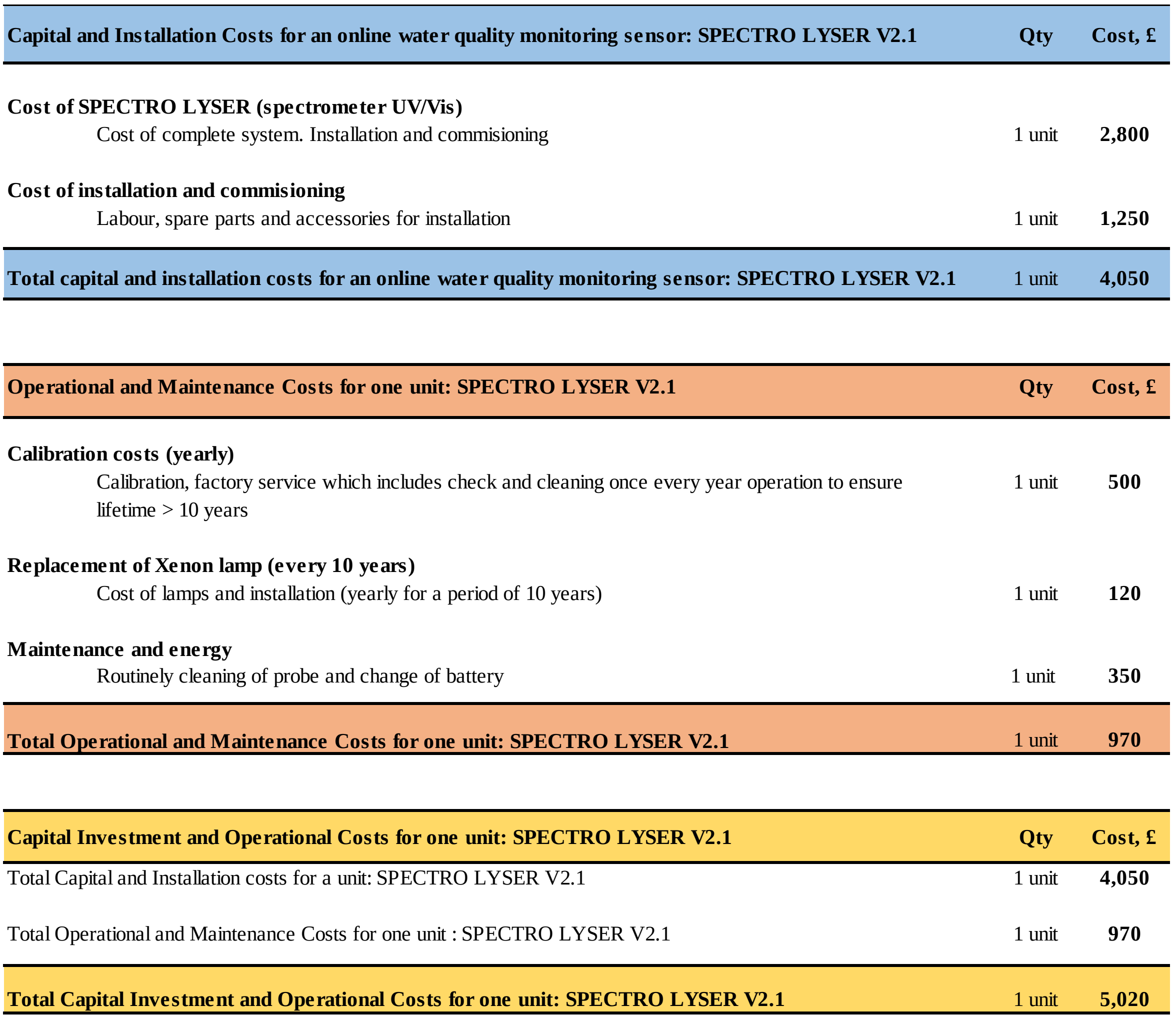
Table 6.4 THMs risk in drinking water treatment sites with high, medium and low

As Scottish Water aims to satisfy all customers irrespective of location or accessibility to their properties, smaller sites have been also taken into account. Sixty drinking water sites (**Table 6.4**) were given scores of high, moderate or low risks for THMs failures. Some of them already have installation of UV 254 nm monitors. Finally, whilst the old DOC sensors measure only one wavelength and are costly, the new sensors measure three wavelengths and are cheaper, as discussed in the next section.

6.3.2 Capital investment and operational costs for the installation of UV/Vis monitoring sensors

Capital investment includes the cost of the actual equipment, installation and commissioning up to the point the system was provided by the supplier and handed over. The total costs for a single unit is £5,020 (**Table 6.5**) as compared to a typical DOC sensor at UV 254 nm at £7,800 (ABB Ltd). The supplier can provide discounts of up to 20% for each unit if the project goes ahead and installation is approved for more than twenty sites. Results from risk assessment evaluation showed a list with sixty sites with higher, moderate and low risk for THMs failures. Sites with high and moderate scoring will benefit with the introduction of the new sensors and change their status to low risk sites. However, only coagulation sites with high and moderate scoring have been selected for the installation of UV/Vis sensors in the first instance (**Table 6.6**).

The final number of selected sites totals twenty one (**Table 6.6)** based on a minimum of 50 values above 1 mg/L DOC during a year, evidence of THMs values above 80 µg/L and whether there is a UV sensor already installed. The total investment for the installation of these sensors arises to £85,050 for the 21 sites with an annual investment of £20,370 for the maintenance and operation of all units. At the discount rate of 20% due to the number of selected units, the final investment arises to £68,040 but maintenance and operational costs will remain the same.



Capital and Installation Costs for an online water quality monitoring sensor: SPECTRO LYSER V2.1	Qty	Cost, £
Cost of SPECTRO LYSER (spectrometer UV/Vis)		
Cost of complete system. Installation and commisioning	1 unit	**2,800**
Cost of installation and commisioning		
Labour, spare parts and accessories for installation	1 unit	**1,250**
Total capital and installation costs for an online water quality monitoring sensor: SPECTRO LYSER V2.1	1 unit	**4,050**

Operational and Maintenance Costs for one unit: SPECTRO LYSER V2.1	Qty	Cost, £
Calibration costs (yearly)		
Calibration, factory service which includes check and cleaning once every year operation to ensure lifetime > 10 years	1 unit	**500**
Replacement of Xenon lamp (every 10 years)		
Cost of lamps and installation (yearly for a period of 10 years)	1 unit	**120**
Maintenance and energy		
Routinely cleaning of probe and change of battery	1 unit	**350**
Total Operational and Maintenance Costs for one unit: SPECTRO LYSER V2.1	1 unit	**970**

Capital Investment and Operational Costs for one unit: SPECTRO LYSER V2.1	Qty	Cost, £
Total Capital and Installation costs for a unit: SPECTRO LYSER V2.1	1 unit	**4,050**
Total Operational and Maintenance Costs for one unit : SPECTRO LYSER V2.1	1 unit	**970**
Total Capital Investment and Operational Costs for one unit: SPECTRO LYSER V2.1	1 unit	**5,020**

Table 6.5 Total Capital and Operational Costs for online monitoring UV/Vis sensors

This cost is subject to change yearly according to annual inflation rates for a total period of 10 years when the instruments will require replacement. These costs are low and can be introduced in annual investment plans carried out within the company and reviewed annually. At this point, 25 sites were selected previously in Scottish Water in 2015 that showed historical high levels of THMs and TOC. These sites have benefited with the installation of UV 254 nm online sensors in terms of THMs control to enhance process performance. To illustrate this improvement, total THMs data taken from potable water from three sites Amlaird, Afton and Bradan WTPs during 2014, 2015 and 2016 (**Figure 6.2a, 6.2b and 2c**) showed evident improvement by reporting no concentrations above 100 µg/L in 2015 and 2016 after the installation of online sensors compared to results in year 2014 were the number of values above 100 µg/L was 31 for Amlaird, 11 for Bradan and one for Afton.

Site name	TOC& (>1mg/L)	THMs* (>50µg/L)	Type of Treatment	Size, MLD	UV 254nm sensor	RISK	SCORE
Assynt	18		Coagulation	18.2		Moderate	8
Auchneel	26	1	Coagulation	5.6		High	12
Barra New	36		Coagulation	0.913		Moderate	8
Bayhead	29		Coagulation	0.838		Moderate	8
Benbecula	38		Coagulation	2.351		Moderate	8
Boardhouse	49		Coagulation	3		Moderate	8
Campbeltown	26	3	Coagulation	4		High	12
Corsehouse	81	27	Coagulation	4.75		High	12
Glenfarg	43	1	Coagulation	85		High	12
Glenlatterach	31	17	Coagulation	9		High	12
Kirbister	55	14	Coagulation	3		High	12
Lochinvar	31	13	Coagulation	6.5		High	12
Papa Stour	40	20	Coagulation	0.004		High	12
Stornoway	60	45	Coagulation	6.513		High	12
Tarbert Argyll No 1	55	43	Coagulation	1		High	12
Tullich	83	19	Ozone	10		Moderate	8
Westray	158	1	Coagulation	0.032		High	12
Whalsay	86	54	Coagulation	0.302		High	12
Broadford	122	60	Membrane	0.65		Moderate	8
Kyle of Lochalsh	144	9	Membrane	2.2		Moderate	8
Inverness Loch Ashie	117		Membrane	38.5		Moderate	8

TOC&: number of TOC measurements with values over 1mg/L
THMs: number of THMs measurements with values over 50µg/L*

Table 6.6 Selected sites for installation of UV/Vis online monitoring sensors

Overall, the number of values for THMs concentrations above 80 µg/L reduced from 31 in 2014 to four and seven in 2015 and 2016 in Amlaird WTP indicating an improvement of 77% and 87% respectively. Similarly, Bradan and Afton also reduced THMs values above 80 µg/L and increased the number of THMs values below 50 µg/L after installation of sensors in 2015 and 2016 as seen in **Figures 2b and 2c**. These results show that the introduction of these monitors will control THMs and benefit Scottish Water in the future by maintaining regulatory sample levels accordingly at substantially less costs than previous units and providing more information on DOC character.

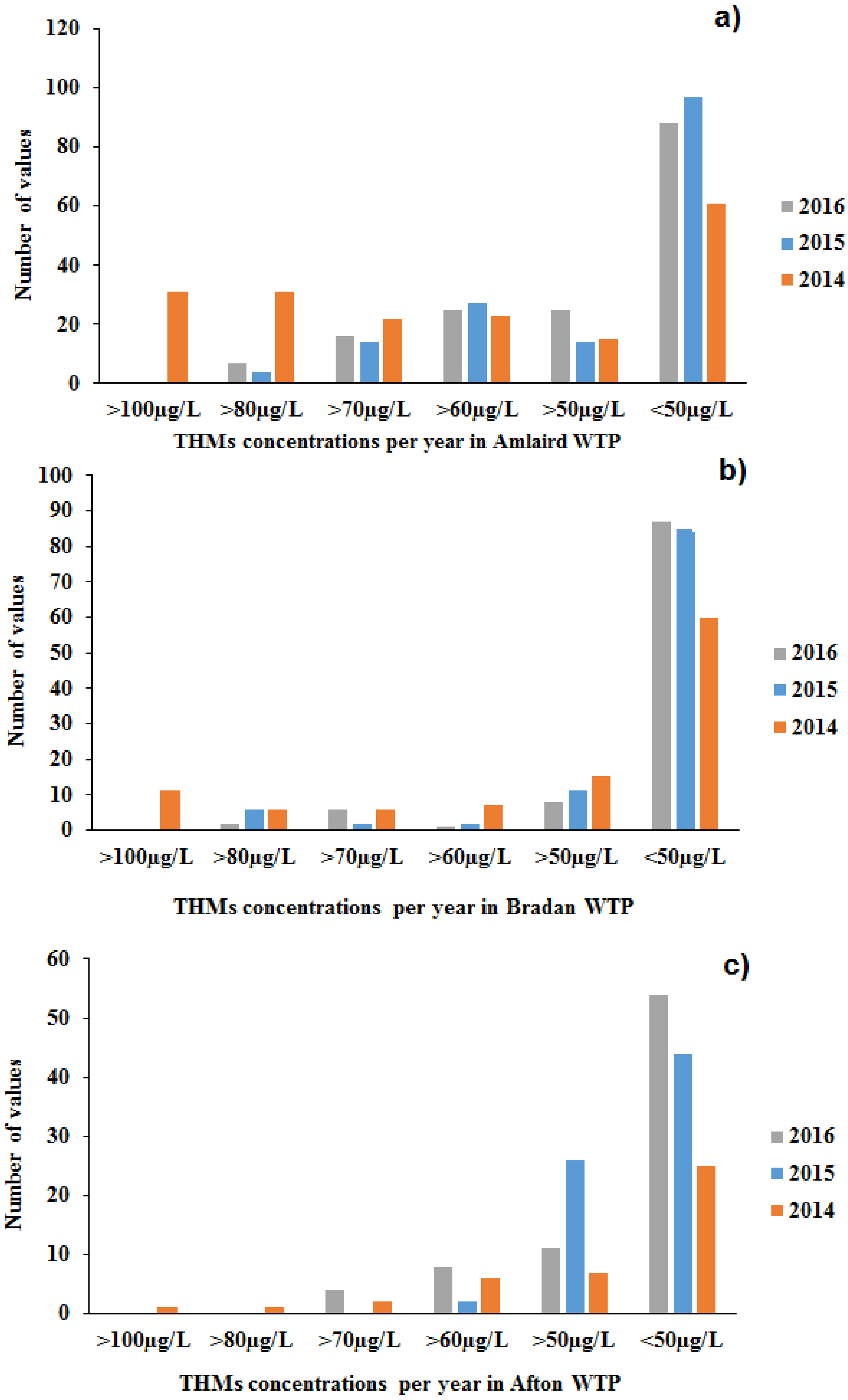


Figure 6.2 Number of counts of THMs concentrations per year in: Amlaird a), Bradan b) and Afton c) WTPs before (2014) and after (2015, 2016) installation of UV 254 nm online monitor

6.4 Conclusions

This chapter has economically evaluated investment plans for two strategies that can minimize THMs precursors in drinking water around Scotland. Two distinct strategies, installation of silver impregnated GAC filtration units and enhanced DOC monitoring, were selected after three years of research that provided invaluable insights on DOC character which helped to evaluate the best ways to eliminate THMs from drinking water supplies. Comparative analysis of costs implicated in the installation of Ag-GAC materials in existing filtration units and UV/Vis online monitoring sensors showed that the second option is cheaper and suitable for monitoring DOC and, in consequence, hopefully reducing THMs. Some assumptions were applied to costs related to installation of the units which may vary accordingly if a formal quote was requested from vendors and some hidden costs on labour by personal involved in the investigation of failures if these occurred were also not included. Disinfection by products in drinking water are still an ongoing problem that requires attention. Although, Scottish Water is engaged in reducing these compounds by many approaches (chloramination, incorporation of new GAC systems and membranes, aeration in service reservoirs, cleaning of distribution networks and flushing, etc.), high DOC persists and THMs as well. Installation of UV/Vis online sensors, as a potential solution to this problem in terms of process delivery, will enable early detection of DOC levels, improve coagulation processes, thus reducing TOC levels in final potable water, preventing THMs formation in the future and improve overall drinking water quality. Process optimisation will consequently benefit the company in reducing the risk of THMs failures, improve quality standards in final drinking potable water, to comply with regulatory demands and public health by supplying the best water quality. Process optimization is particularly important for enhancing water infrastructure resilience in a changing environment, as indications are that global warming will exacerbate the THM control challenge in the future.

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Chapter 7

FINAL CONCLUSIONS

The aim of this work was to investigate the main characteristics of dissolved organic compounds to understand the formation of disinfection by products in particular THMs. This work was solely prepared with samples taken from surface and treated water from different areas around Scotland which aided in providing a general view of diverse factors that can influence the formation of these compounds in drinking water, ranging from natural and climatic factors through chemical processes.

The most important contribution of this research is the suggestion that ambient temperature plays a crucial role in THM formation, implying that THMs formation may increase as a result of global warming. The particular geography of Scotland and the influence of temperature as well as DOC quantity and quality on THMs. Seasonal changes have a very important impact in the quantity of DOC in raw and therefore treated water. The highest surges of THMs were observed during September for example compared to low concentrations found in winter months. However, based on monthly monitoring data, quality of DOC is maintained largely unaltered along the seasons, whilst quarterly sampling indicated some variability.

Results obtained from the quarterly monitoring data allowed a more detailed DOC characterisation which included UV scans, fluorescence EMM plots and HPSEC that provided a general view of potentially most abundant DOC compounds present in surface and treated water at the selected sites being mainly of hydrophilic origin. The results from THMFP experiments have clearly established temperature as being positively correlated with THMs formation in raw and treated water. DOC quantity was identified as a second root cause of seasonality in THM formation, as it correlated positively with THMs in the monthly monitoring, and there was also reduced THMFP with reduced levels of DOC at a fixed temperature in laboratory experiments. At the point of disinfection, two main groups of DOC compounds were identified as contributing a substantial part of the residual hydrophilic and hydrophobic portions of DOC still present in treated water: carboxylic and phenolic acids.

Comparisons between the two selected groups of THMs precursors showed a clear difference between carboxylic acids and phenolic compounds, phenolic acids being the compounds that produced more THMs, specifically chloroform and dichlorobromomethane. Due to the highest yield of THMs produced by phenolic compounds, granulated activated carbon was selected for adsorption of the most reactive compounds (containing methoxylated groups in their structure) with and without silver impregnation in 24 hours batch experiments.

Experiments showed that some adsorption of THMs precursors was achieved by all selected PAC types. However, large doses of carbon (200 mg/L and 400 mg/L) were needed for effective THM precursor adsorption. Thus, optimisation for the removal of these compounds could be improved by investigating what may explain residual THMFP which cannot be removed by AC adsorption.

This work identified a large portion of the DOC present in treated waters from Scottish water sites and their reactivity towards THMs formation. The AC types investigated had limited removal effectiveness for these compounds. On the other hand, the changes in DOC composition resulting from different treatment steps suggest that coagulation to some extent preferentially removes phenolic compounds, and hence, enhanced coagulation could be an area to be explored further in future research, since phenolic compounds had significant THMFP.

This information is crucial for drinking water treatment processes that show similar DOC character (of humic and fulvic nature) and could target phenolic and carboxylic acids to control and minimize THMs formation. The use of activated carbon (AC) as an option to adsorb THMs precursors and application of online monitoring sensors for DOC detection as alternative technologies for THMs control were also evaluated, with the latter having better cost-benefits, and these lessons could be applied in other countries with similar geography and geology to Scotland.

Appendices

CHAPTER 4

Figure 4.1 Flow Process Diagram for Forehill WTP

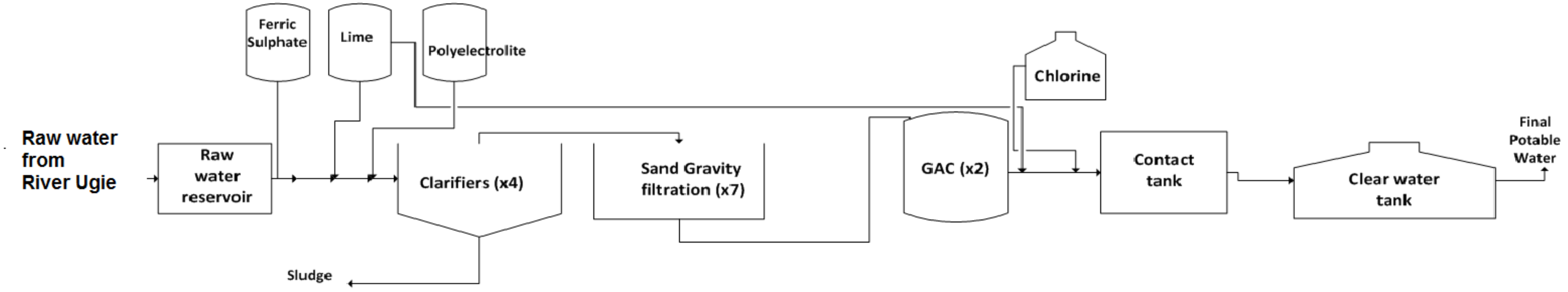


Figure 4.2 Flow Process Diagram for Amlaird WTP

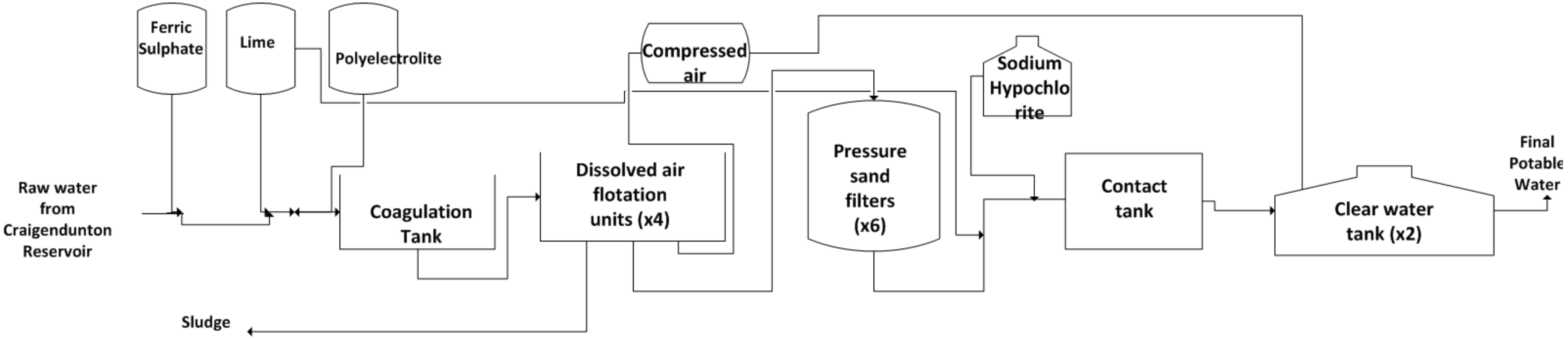


Figure 4.3 Flow Process Diagram for Stornoway WTP

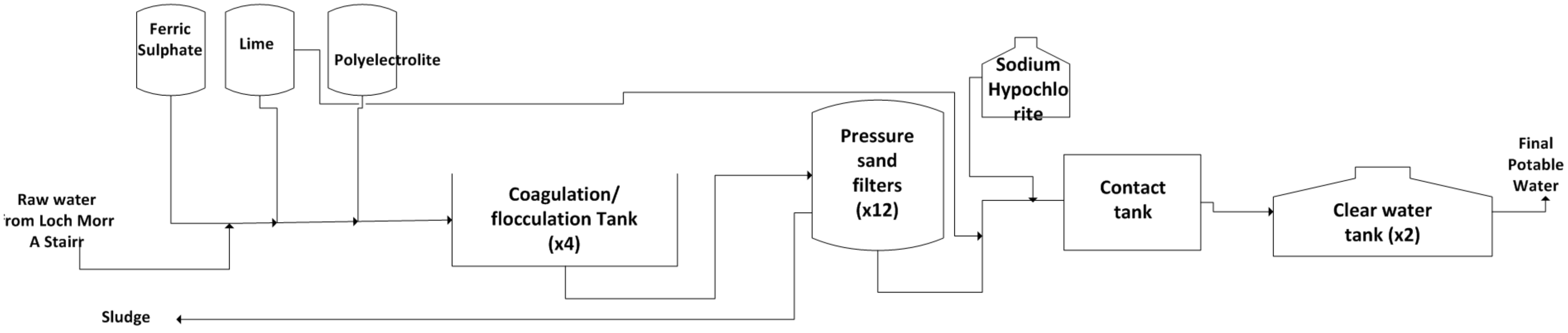


Figure 4.4 Flow Process Diagram for Port Charlotte WTP

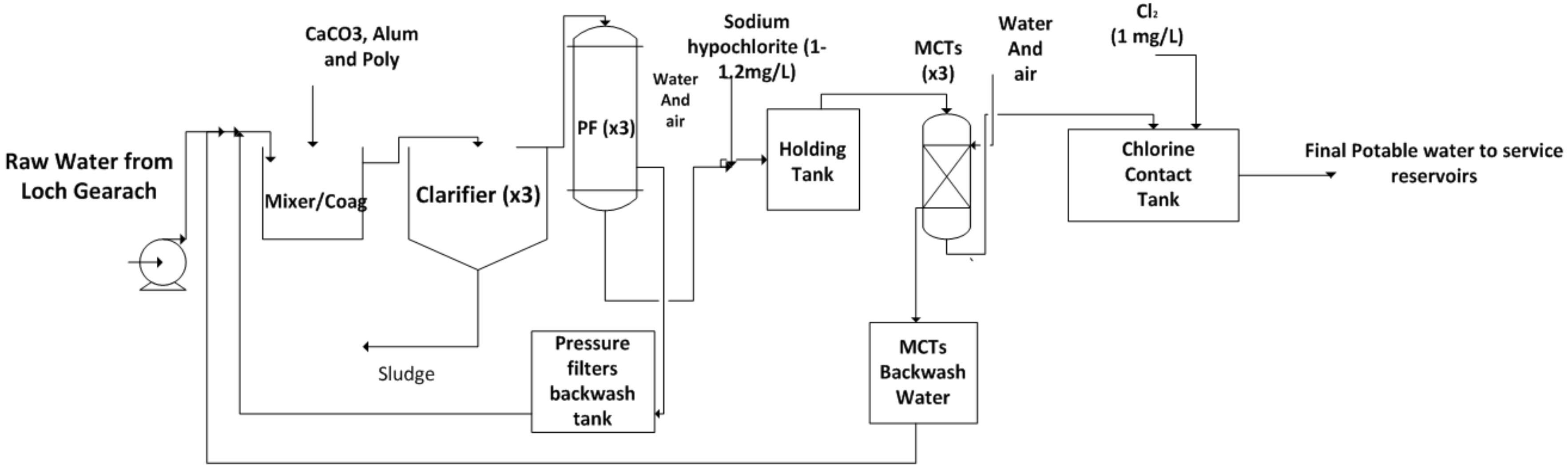


Figure 4.5 Flow Process Diagram for Gigha WTP

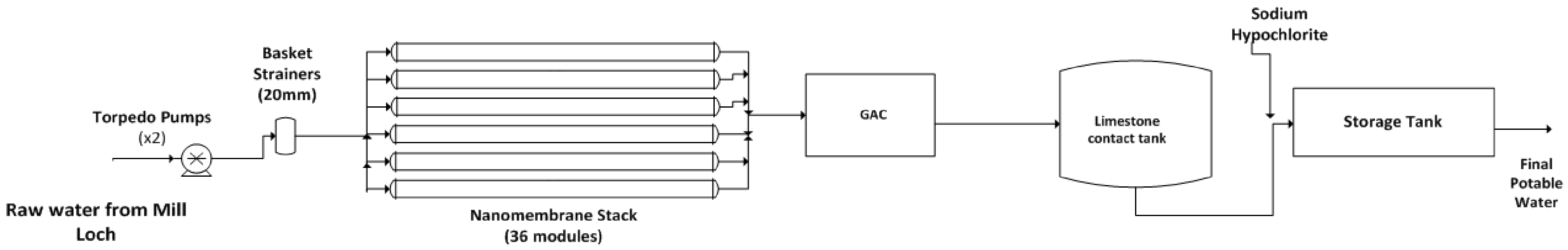


Figure 4.6 Flow Process Diagram for Broadford WTP

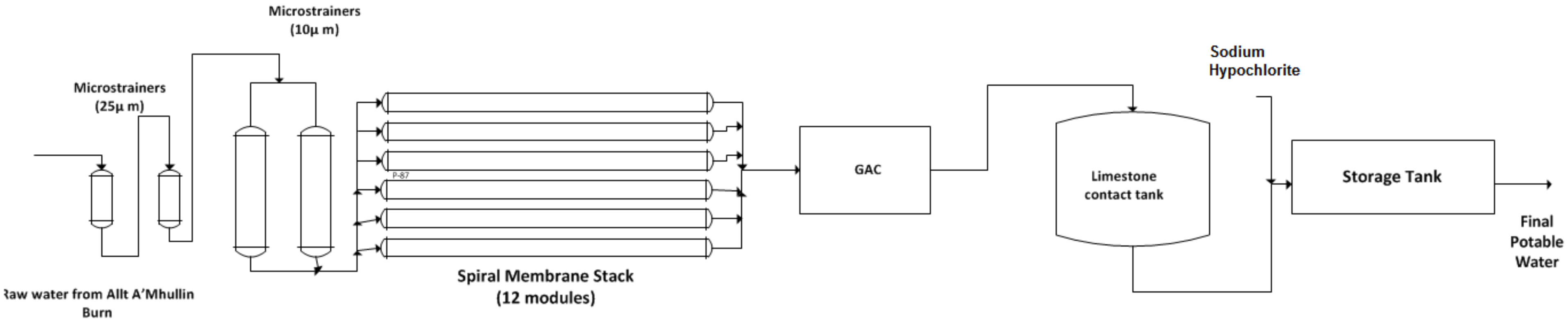


Table 4.1 THMFP from quarterly monitoring sampling

			December					March					June					September				
site	**sample.point**	**T, °C**	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**	**Total THMs**	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**	**Total THMs**	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**	**Total THMs**	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**	**Total THMs**
Forehill	Raw Water	5	8.73	9.99	7.27	1.11	27.09	6.04	9.25	9.29	1.90	26.47	12.50	14.82	10.24	0.10	37.66	27.73	4.59	0.00	0.00	32.32
	Post Clarification	5	3.52	4.95	4.92	1.27	14.67	1.72	3.40	3.27	1.29	9.69	1.43	3.52	3.68	0.21	8.84	6.30	3.79	0.36	0.00	10.44
	Post Filtration	5	3.34	4.80	4.95	1.99	15.08	1.41	3.25	3.15	1.25	9.07	1.19	2.43	2.97	3.46	10.05	3.14	2.91	0.36	0.00	6.41
	Post GAC	5	2.03	2.59	3.33	4.08	12.03	0.62	2.27	3.27	4.95	11.11	0.17	2.31	3.39	5.23	11.10	0.81	0.76	2.52	1.25	5.35
	Raw Water	15	13.83	14.11	9.64	1.30	38.87	11.06	14.87	13.10	2.27	41.31	20.06	20.65	12.80	0.32	53.83	35.84	5.76	0.00	0.00	41.60
	Post Clarification	15	4.94	7.15	6.18	1.47	19.74	3.04	4.96	4.55	1.61	14.15	1.67	5.25	4.75	0.55	12.22	11.74	6.16	0.63	0.00	18.53
	Post Filtration	15	4.43	6.45	5.95	2.18	19.01	2.61	4.67	4.23	1.54	13.06	1.92	2.68	3.40	3.37	11.37	6.03	4.95	0.78	0.00	11.76
	Post GAC	15	2.07	2.72	3.18	3.71	11.68	0.76	2.73	3.58	5.10	12.18	1.07	3.80	3.90	5.24	14.00	1.38	1.45	2.62	1.07	6.52
	Raw Water	25	18.35	17.27	11.14	1.38	48.14	17.88	19.80	15.30	2.40	55.38	24.64	24.97	14.99	0.57	65.16	45.88	6.59	0.00	0.00	52.47
	Post Clarification	25	6.83	9.71	7.77	1.72	26.04	4.60	7.05	6.07	1.94	19.66	4.57	8.59	7.46	1.00	21.62	15.89	8.20	0.83	0.00	24.93
	Post Filtration	25	5.78	8.73	7.84	2.53	24.88	5.21	7.82	7.07	2.13	22.23	4.90	10.99	6.68	5.06	27.63	8.30	6.68	1.28	0.00	16.25
	Post GAC	25	2.43	3.23	3.80	4.27	13.73	1.44	3.38	4.14	5.31	14.26	1.40	5.43	4.64	5.55	17.03	1.68	1.79	2.68	0.93	7.09
Gigha	Raw Water	5	5.46	7.65	7.25	2.09	22.45	6.16	9.06	8.70	2.81	26.74	18.23	6.45	2.43	0.00	27.12	20.86	9.67	2.59	0.72	33.84
	Post Membrane	5	1.37	3.78	4.59	1.08	10.82	3.89	5.68	6.39	2.82	18.79	4.49	5.17	3.88	0.27	13.80	12.35	23.19	21.26	4.04	60.85
	Post GAC	5	2.09	3.99	4.71	1.06	11.84	3.64	5.39	6.00	2.75	17.79	8.05	14.60	16.15	4.98	43.77	9.10	17.95	18.36	4.16	49.58
	Raw Water	15	7.65	10.96	8.97	2.26	29.85	9.05	12.49	11.10	3.11	35.76	28.66	7.64	2.57	0.00	38.87	31.26	12.25	3.01	0.80	47.32
	Post Membrane	15	2.89	5.28	5.57	1.47	15.22	5.08	7.69	8.12	3.16	24.06	10.83	8.08	4.78	0.43	24.11	21.32	36.01	27.60	4.50	89.44
	Post GAC	15	2.04	4.38	5.01	1.17	12.60	4.72	7.10	7.68	3.12	22.63	13.64	21.80	21.31	6.27	63.02	11.80	21.66	20.41	4.27	58.14
	Raw Water	25	11.09	15.68	11.31	2.41	40.49	11.45	15.74	12.98	3.27	43.44	44.78	9.73	2.90	0.00	57.42	45.19	15.09	3.50	0.83	64.61
	Post Membrane	25	4.49	8.00	7.04	1.44	20.97	5.72	8.78	9.30	3.36	27.16	21.21	11.10	5.44	0.50	38.25	25.28	38.86	27.82	4.43	96.39
	Post GAC	25	25.42	25.20	17.81	2.26	70.68	5.05	7.73	8.40	3.28	24.45	24.24	30.08	26.01	7.04	87.37	22.85	38.24	32.38	5.46	98.93
Amlaird	Raw Water	5	19.69	13.62	6.13	0.02	39.47	29.15	16.38	6.27	0.94	52.75	20.52	15.54	5.83	0.00	41.89	39.42	2.37	0.00	0.00	41.79
	Post Clarification	5	52.97	4.70	1.76	0.00	59.42	26.23	4.75	1.45	0.69	33.11	4.87	6.76	5.26	0.09	16.97	10.02	1.79	0.00	0.00	11.81
	Post Filtration	5	66.17	5.61	1.85	0.00	73.63	41.73	6.46	1.80	0.69	50.68	32.21	5.99	1.46	1.72	41.38	8.00	0.95	0.00	0.00	8.95
	Raw Water	15	31.89	19.38	7.83	0.08	59.18	44.82	21.16	7.32	0.98	74.27	33.60	21.70	7.57	0.00	62.87	52.56	3.16	0.00	0.00	55.72
	Post Clarification	15	96.83	5.77	1.81	0.00	104.41	49.58	6.70	1.60	0.69	58.56	7.28	9.87	7.06	0.37	24.57	13.65	2.32	0.00	0.00	15.97
	Post Filtration	15	106.29	6.45	1.88	0.00	114.62	53.44	7.67	2.49	0.84	64.43	44.11	6.70	1.53	1.72	54.05	10.65	1.19	0.00	0.00	11.84
	Raw Water	25	45.91	24.39	9.56	0.16	80.01	65.87	26.16	9.15	1.02	102.20	42.11	25.91	8.98	0.00	77.00	66.55	3.87	0.00	0.00	70.42
	Post Clarification	25	128.72	6.19	1.81	0.00	136.72	78.86	7.59	1.67	0.69	88.81	9.36	11.84	8.04	0.42	29.66	18.70	3.03	0.00	0.00	21.73
	Post Filtration	25	131.03	6.35	1.88	0.00	139.26	79.08	8.79	2.54	0.84	91.25	54.15	7.01	1.48	1.50	64.14	13.98	1.31	0.00	0.00	15.29
Stornoway	Raw Water	5	24.27	16.67	6.87	0.03	47.85	50.40	24.80	7.04	1.95	84.19	26.84	18.51	7.24	0.00	52.60	44.93	3.19	1.04	0.64	49.81
	Post Clarification	5	21.32	9.98	3.89	0.35	35.54	6.12	11.48	16.31	7.71	41.63	2.92	5.51	4.09	0.02	12.55	4.45	3.63	2.35	0.80	11.24
	Post Filtration	5	21.46	6.23	1.87	0.20	29.76	5.90	8.27	10.49	4.97	29.64	22.17	10.53	3.66	0.00	36.37	7.02	2.87	1.59	0.91	12.40
	Raw Water	15	38.79	23.36	8.24	0.08	70.48	91.23	30.89	8.53	1.99	132.64	33.93	23.13	8.93	0.00	66.00	55.82	3.56	1.07	0.64	61.09
	Post Clarification	15	42.83	15.59	4.69	0.38	63.49	8.53	15.98	19.55	8.16	52.22	3.81	7.34	5.28	0.13	16.56	6.57	5.60	3.17	0.88	16.22
	Post Filtration	15	42.80	8.78	2.14	0.20	53.92	9.59	11.22	11.88	5.08	37.78	33.07	13.39	4.21	0.00	50.68	11.06	3.75	1.75	0.95	17.50
	Raw Water	25	52.05	26.05	8.85	0.10	87.05	121.81	37.81	9.40	1.99	171.02	45.77	30.15	11.11	0.00	87.03	71.50	3.86	1.08	0.64	77.09
	Post Clarification	25	67.88	19.83	5.12	0.40	93.24	10.32	20.34	22.03	8.22	60.92	10.53	12.79	9.24	0.75	33.31	9.80	7.79	3.62	0.91	22.12
	Post Filtration	25	54.13	10.54	3.17	0.00	67.84	12.49	12.81	12.25	4.99	42.54	46.65	17.47	5.07	0.00	69.19	17.26	4.72	1.79	0.96	24.73
Broadford	Raw Water	5	10.64	12.05	7.37	0.97	31.03	12.26	13.96	9.47	1.60	37.28	19.63	15.16	6.77	0.15	41.71	30.00	3.85	1.14	0.64	35.64
	Post Membrane	5	5.58	8.07	6.75	1.12	21.52	24.74	8.76	3.62	1.21	38.33	35.08	10.25	1.75	0.00	47.08	9.78	2.83	1.24	0.64	14.49
	Post GAC	5	3.76	6.07	5.57	1.19	16.60	35.25	10.22	3.35	0.84	49.66	17.21	8.18	2.33	0.00	27.72	17.81	4.71	0.89	0.72	24.14
	Raw Water	15	16.13	16.80	9.60	1.12	43.65	18.43	18.87	11.21	1.67	50.18	28.36	20.09	8.59	0.24	57.28	42.77	4.46	1.18	0.64	49.05
	Post Membrane	15	9.06	11.82	9.03	1.32	31.23	37.58	10.78	3.93	1.19	53.48	51.49	13.49	2.11	0.00	67.09	12.40	3.05	1.26	0.64	17.35
	Post GAC	15	6.21	8.83	7.29	1.33	23.67	53.44	7.67	2.49	0.84	64.43	24.89	10.13	2.67	0.00	37.69	24.19	5.65	1.01	0.72	31.58
	Raw Water	25	23.81	22.34	11.72	1.20	59.08	24.32	20.46	13.39	1.80	59.97	39.07	26.08	10.40	0.24	75.79	56.10	5.00	1.21	0.64	62.96
	Post Membrane	25	12.93	14.89	10.67	1.41	39.91	59.69	14.65	4.40	1.21	79.94	72.08	16.53	2.50	0.00	91.11	17.16	3.75	1.35	0.73	23.00
	Post GAC	25	8.39	11.96	10.32	1.67	32.34	59.89	12.83	3.54	0.84	77.10	39.18	14.96	3.72	0.00	57.86	31.92	6.84	1.21	0.72	40.70

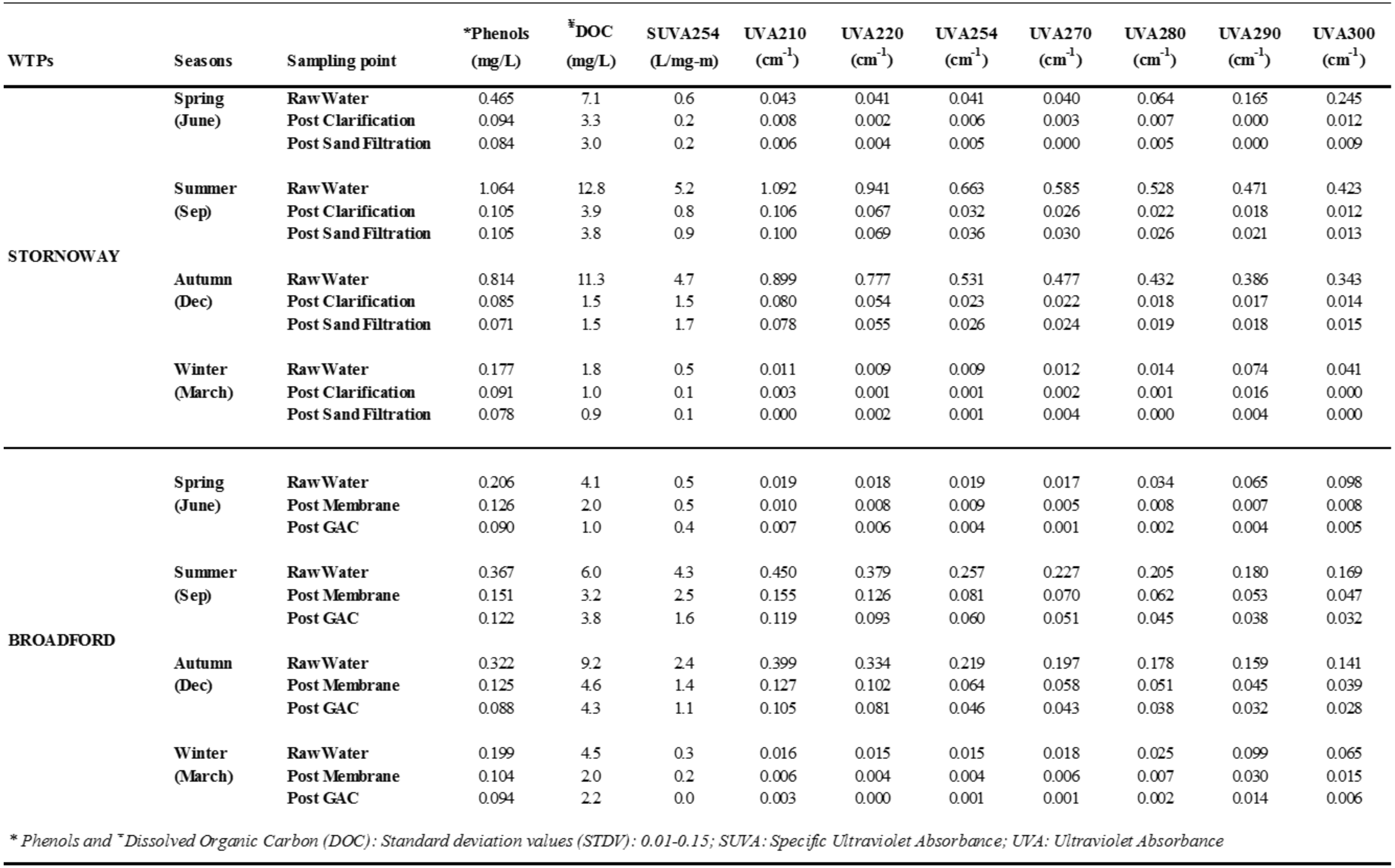
All results showed standard deviations: 0.1-5.5

Table 4.2 Phenols, DOC, SUVA and Absorbances in six WTPs around Scotland (December 2014 – September 2015)

WTPs	Seasons	Sampling point	*Phenols (mg/L)	¥DOC (mg/L)	SUVA254 (L/mg-m)	UVA210 (cm^{-1})	UVA220 (cm^{-1})	UVA254 (cm^{-1})	UVA270 (cm^{-1})	UVA280 (cm^{-1})	UVA290 (cm^{-1})	UVA300 (cm^{-1})
AMLAIRD	Spring (June)	Raw Water	0.683	12.1	0.6	0.064	0.063	0.071	0.073	0.112	0.307	0.523
		Post Clarification	0.091	3.3	0.1	0.004	0.006	0.004	0.000	0.001	0.002	0.012
		Post Sand Filtration	0.068	3.0	0.2	0.006	0.003	0.005	0.000	0.004	0.001	0.010
	Summer (Sep)	Raw Water	1.417	17.7	5.3	1.598	1.373	0.945	0.825	0.744	0.664	0.545
		Post Clarification	0.132	4.1	1.3	0.169	0.111	0.054	0.046	0.040	0.033	0.029
		Post Sand Filtration	0.082	4.4	0.7	0.140	0.083	0.030	0.021	0.017	0.014	0.012
	Autumn (Dec)	Raw Water	1.475	26.5	4.0	1.815	1.559	1.047	0.916	0.807	0.739	0.657
		Post Clarification	0.153	1.5	3.9	0.210	0.133	0.059	0.052	0.045	0.038	0.032
		Post Sand Filtration	0.087	1.5	2.5	0.189	0.114	0.037	0.029	0.023	0.020	0.016
	Winter (March)	Raw Water	0.749	10.8	0.6	0.060	0.058	0.063	0.072	0.098	0.406	0.295
		Post Clarification	0.146	0.8	0.7	0.006	0.003	0.006	0.008	0.003	0.023	0.014
		Post Sand Filtration	0.084	0.9	0.1	0.004	0.002	0.001	0.004	0.003	0.013	0.007
FOREHILL	Spring (June)	Raw Water	0.318	8.3	0.3	0.038	0.033	0.029	0.031	0.054	0.155	0.198
		Post Clarification	0.078	3.9	0.0	0.005	0.004	0.001	0.000	0.001	0.000	0.002
		Post Sand Filtration	0.064	4.0	0.0	0.003	0.003	0.002	0.000	0.000	0.000	0.001
		Post GAC	0.070	3.0	0.1	0.005	0.002	0.002	0.000	0.000	0.000	0.001
	Summer (Sep)	Raw Water	0.528	12.5	4.2	2.112	1.281	0.524	0.454	0.410	0.363	0.314
		Post Clarification	0.084	3.0	1.4	1.672	0.710	0.043	0.035	0.031	0.027	0.023
		Post Sand Filtration	0.081	3.4	1.0	1.816	0.780	0.033	0.003	0.023	0.020	0.016
		Post GAC	0.060	2.7	0.3	1.583	0.640	0.008	0.005	0.005	0.004	0.001
	Autumn (Dec)	Raw Water	0.621	19.7	2.7	2.428	1.694	0.537	0.460	0.414	0.367	0.325
		Post Clarification	0.140	6.2	1.0	1.976	0.983	0.062	0.055	0.046	0.414	0.367
		Post Sand Filtration	0.125	4.6	0.9	1.948	0.951	0.042	0.034	0.030	0.026	0.023
		Post GAC	0.080	2.9	0.1	1.829	0.839	0.003	0.005	0.005	0.004	0.004
	Winter (March)	Raw Water	0.256	9.8	0.3	0.026	0.023	0.027	0.029	0.046	0.161	0.125
		Post Clarification	0.083	4.7	0.1	0.004	0.003	0.003	0.003	0.005	0.030	0.011
		Post Sand Filtration	0.096	4.8	0.1	0.005	0.004	0.006	0.005	0.006	0.017	0.012
		Post GAC	0.080	3.9	0.1	0.003	0.000	0.003	0.002	0.000	0.005	0.003

** Phenols and ¥Dissolved Organic Carbon (DOC): Standard deviation values (STDV): 0.01-0.15; SUVA: Specific Ultraviolet Absorbance; UVA: Ultraviolet Absorbance*

Table 4.2 Phenols, DOC, SUVA and Absorbances in six WTPs around Scotland (December 2014 – September 2015)



WTPs	Seasons	Sampling point	*Phenols (mg/L)	¥DOC (mg/L)	SUVA254 (L/mg-m)	UVA210 (cm^{-1})	UVA220 (cm^{-1})	UVA254 (cm^{-1})	UVA270 (cm^{-1})	UVA280 (cm^{-1})	UVA290 (cm^{-1})	UVA300 (cm^{-1})
STORNOWAY	Spring (June)	Raw Water	0.465	7.1	0.6	0.043	0.041	0.041	0.040	0.064	0.165	0.245
		Post Clarification	0.094	3.3	0.2	0.008	0.002	0.006	0.003	0.007	0.000	0.012
		Post Sand Filtration	0.084	3.0	0.2	0.006	0.004	0.005	0.000	0.005	0.000	0.009
	Summer (Sep)	Raw Water	1.064	12.8	5.2	1.092	0.941	0.663	0.585	0.528	0.471	0.423
		Post Clarification	0.105	3.9	0.8	0.106	0.067	0.032	0.026	0.022	0.018	0.012
		Post Sand Filtration	0.105	3.8	0.9	0.100	0.069	0.036	0.030	0.026	0.021	0.013
	Autumn (Dec)	Raw Water	0.814	11.3	4.7	0.899	0.777	0.531	0.477	0.432	0.386	0.343
		Post Clarification	0.085	1.5	1.5	0.080	0.054	0.023	0.022	0.018	0.017	0.014
		Post Sand Filtration	0.071	1.5	1.7	0.078	0.055	0.026	0.024	0.019	0.018	0.015
	Winter (March)	Raw Water	0.177	1.8	0.5	0.011	0.009	0.009	0.012	0.014	0.074	0.041
		Post Clarification	0.091	1.0	0.1	0.003	0.001	0.001	0.002	0.001	0.016	0.000
		Post Sand Filtration	0.078	0.9	0.1	0.000	0.002	0.001	0.004	0.000	0.004	0.000
BROADFORD	Spring (June)	Raw Water	0.206	4.1	0.5	0.019	0.018	0.019	0.017	0.034	0.065	0.098
		Post Membrane	0.126	2.0	0.5	0.010	0.008	0.009	0.005	0.008	0.007	0.008
		Post GAC	0.090	1.0	0.4	0.007	0.006	0.004	0.001	0.002	0.004	0.005
	Summer (Sep)	Raw Water	0.367	6.0	4.3	0.450	0.379	0.257	0.227	0.205	0.180	0.169
		Post Membrane	0.151	3.2	2.5	0.155	0.126	0.081	0.070	0.062	0.053	0.047
		Post GAC	0.122	3.8	1.6	0.119	0.093	0.060	0.051	0.045	0.038	0.032
	Autumn (Dec)	Raw Water	0.322	9.2	2.4	0.399	0.334	0.219	0.197	0.178	0.159	0.141
		Post Membrane	0.125	4.6	1.4	0.127	0.102	0.064	0.058	0.051	0.045	0.039
		Post GAC	0.088	4.3	1.1	0.105	0.081	0.046	0.043	0.038	0.032	0.028
	Winter (March)	Raw Water	0.199	4.5	0.3	0.016	0.015	0.015	0.018	0.025	0.099	0.065
		Post Membrane	0.104	2.0	0.2	0.006	0.004	0.004	0.006	0.007	0.030	0.015
		Post GAC	0.094	2.2	0.0	0.003	0.000	0.001	0.001	0.002	0.014	0.006

** Phenols and ¥Dissolved Organic Carbon (DOC): Standard deviation values (STDV): 0.01-0.15; SUVA: Specific Ultraviolet Absorbance; UVA: Ultraviolet Absorbance*

Table 4.2 Phenols, DOC, SUVA and Absorbances in six WTPs around Scotland (December 2014 – September 2015)

WTPs	Seasons	Sampling point	Phenols (mg/L)	DOC (mg/L)	SUVA254 (L/mg-m)	UVA210 (cm-1)	UVA220 (cm-1)	UVA254 (cm-1)	UVA270 (cm-1)	UVA280 (cm-1)	UVA290 (cm-1)	UVA300 (cm-1)
GIGHA	**Spring (June)**	**Raw Water**	0.294	6.7	0.2	0.019	0.013	0.014	0.012	0.022	0.081	0.122
		Post Membrane	0.089	4.0	0.1	0.009	0.007	0.003	0.002	0.003	0.001	0.001
		Post GAC	0.085	2.4	0.0	0.009	0.004	0.001	0.000	0.000	0.000	0.000
	Summer (Sep)	**Raw Water**	0.186	5.2	3.9	0.419	0.329	0.199	0.165	0.140	0.116	0.101
		Post Membrane	0.085	1.2	3.1	0.101	0.069	0.038	0.031	0.026	0.020	0.015
		Post GAC	0.079	1.0	3.4	0.084	0.058	0.033	0.027	0.022	0.017	0.013
	Autumn (Dec)	**Raw Water**	0.293	14.1	2.3	0.554	0.431	0.324	0.216	0.190	0.161	0.137
		Post Membrane	0.114	5.4	0.7	0.151	0.089	0.035	0.029	0.025	0.020	0.016
		Post GAC	0.113	5.2	0.6	0.139	0.082	0.029	0.026	0.021	0.018	0.015
	Winter (March)	**Raw Water**	0.226	8.5	0.2	0.016	0.017	0.016	0.021	0.036	0.120	0.095
		Post Membrane	0.104	4.8	0.0	0.005	0.006	0.002	0.002	0.009	0.023	0.019
		Post GAC	0.101	4.6	0.1	0.005	0.005	0.004	0.005	0.009	0.021	0.017
PORT CHARLOTTE	**Spring (June)**	**Raw Water**	0.452	9.4	0.5	0.045	0.043	0.047	0.046	0.074	0.215	0.358
		Post Clarification	0.120	3.3	0.2	0.006	0.005	0.007	0.002	0.006	0.010	0.009
		Post Sand Filtration	0.113	3.4	0.1	0.005	0.004	0.004	0.000	0.008	0.010	0.007
	Summer (Sep)	**Raw Water**	1.528	23.5	5.7	2.227	1.964	1.352	1.177	1.064	0.947	0.858
		Post Clarification	0.183	5.9	1.8	0.237	0.175	0.105	0.087	0.075	0.062	0.055
		Post Sand Filtration	0.170	5.2	2.0	0.239	0.174	0.103	0.086	0.073	0.061	0.053
	Autumn (Dec)	**Raw Water**	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
		Post Clarification	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
		Post Sand Filtration	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A	N.A
	Winter (March)	**Raw Water**	0.389	7.3	0.5	0.030	0.031	0.034	0.039	0.054	0.190	0.155
		Post Clarification	0.131	1.0	0.4	0.003	0.006	0.004	0.006	0.005	0.025	0.012
		Post Sand Filtration	0.131	1.0	0.4	0.004	0.001	0.004	0.005	0.000	0.022	0.011

** Phenols and ¥Dissolved Organic Carbon (DOC): Standard deviation values (STDV): 0.01-0.15; SUVA: Specific Ultraviolet Absorbance; UVA: Ultraviolet Absorbance*

Table 4.3 Typical metal content for raw and treated water in six WTPs around Scotland (December 2014 – September 2015)

			Spring June			Summer Sept			Autumn December			Winter March		
Site Name	**Element**	**Units**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Raw Water**	**Post Clarification**	**Post Filtration**
Amlaird	**Ca**	**mg/L**	2.9	18.6	18.2	3.1	28.2	28.6	3.2	25.0	25.4	2.6	18.1	19.1
	Mg	**mg/L**	1.3	1.7	1.7	1.4	2.1	2.1	1.5	2.0	2.0	1.4	1.8	1.8
	Na	**mg/L**	5.9	5.9	5.9	4.4	4.6	4.7	4.3	4.6	4.7	6.0	6.2	6.2
	K	**µg/L**	340.9	328.5	331.9	197.7	216.0	219.1	486.1	1706.5	1197.4	410.1	412.2	430.6
	Zn	**µg/L**	17.1	8.8	1.8	13.2	1.7	3.1	15.1	2.4	3.1	22.5	12.0	9.3
	Al	**µg/L**	52.5	15.1	17.2	101.9	33.2	15.9	127.3	14.8	23.6	67.0	20.1	38.3
	Fe	**µg/L**	360.1	6.4	1.1	789.8	2.2	2.3	1221.5	35.7	15.7	332.6	8.8	0.9
	Mn	**µg/L**	2.2	2.9	0.6	7.0	4.6	6.0	15.5	30.7	1.2	5.7	2.0	0.6
	Cu	**µg/L**	24.4	5.3	3.5	3.4	1.0	1.4	4.7	1.5	1.2	2.9	0.0	1.5
	Si	**mg/L**	0.1	0.1	0.1	0.7	0.6	0.6	1.0	0.9	0.8	0.9	0.8	0.8
	S	**mg/L**	4.4	16.8	16.7	4.2	25.8	26.0	0.9	16.8	16.9	4.4	16.8	16.9
Stornoway	**Ca**	**mg/L**	1.0	1.0	1.0	0.8	0.8	0.8	0.7	0.8	0.7	2.1	2.1	2.1
	Mg	**mg/L**	1.7	1.6	1.7	1.3	1.3	1.3	1.2	1.2	1.1	4.6	4.5	4.6
	Na	**mg/L**	12.8	24.9	25.0	9.5	24.0	24.0	8.8	26.6	28.7	24.9	36.4	35.9
	K	**µg/L**	527.5	568.8	584.7	299.0	349.3	345.5	733.2	565.6	900.4	884.6	930.4	900.9
	Zn	**µg/L**	17.5	17.2	2.9	15.3	12.9	2.2	16.7	5.3	2.2	43.5	15.3	6.6
	Al	**µg/L**	24.7	4.9	6.4	62.2	3.7	15.0	56.4	24.8	29.0	12.8	22.2	24.2
	Fe	**µg/L**	245.5	1.4	6.8	562.9	1.5	0.5	499.9	2.9	4.5	63.8	0.9	0.6
	Mn	**µg/L**	6.0	15.3	1.0	1.3	18.1	4.3	12.1	23.0	9.0	56.4	71.1	1.5
	Cu	**µg/L**	13.5	3.0	3.7	15.0	1.6	1.6	26.8	0.0	1.9	22.7	3.3	3.2
	Si	**mg/L**	0.4	0.4	0.4	0.6	0.6	0.6	0.4	0.4	0.4	0.5	0.5	0.5
	S	**mg/L**	4.2	9.9	10.0	3.9	12.1	12.1	1.0	9.6	10.4	6.0	9.8	9.9
Port Charlotte	**Ca**	**mg/L**	4.5	4.5	4.5	5.5	5.3	5.3	-	-	-	4.3	4.7	4.3
	Mg	**mg/L**	3.3	3.3	3.3	3.6	3.4	3.4	-	-	-	3.8	3.8	3.7
	Na	**mg/L**	22.6	37.7	37.4	18.9	60.9	60.6	-	-	-	25.5	41.2	41.6
	K	**µg/L**	915.1	788.4	788.8	504.3	600.3	608.4	-	-	-	1340.0	1104.5	1277.4
	Zn	**µg/L**	42.2	10.3	13.1	4.4	13.1	3.6	-	-	-	17.4	16.5	10.1
	Al	**µg/L**	44.6	11.5	10.3	116.7	16.8	17.5	-	-	-	35.6	11.4	5.8
	Fe	**µg/L**	361.7	0.4	0.5	1461.0	2.2	1.3	-	-	-	150.1	0.6	0.4
	Mn	**µg/L**	4.5	4.5	4.5	9.5	33.3	41.1	-	-	-	8.1	11.5	7.6
	Cu	**µg/L**	4.0	3.4	0.9	2.7	3.0	0.7	-	-	-	1.4	2.6	3.2
	Si	**mg/L**	0.2	0.2	0.2	0.3	1.1	1.0	-	-	-	1.1	1.0	1.0
	S	**mg/L**	4.6	16.7	16.9	4.3	35.9	35.0	-	-	-	5.5	16.6	16.8

Table 4.3 Typical metal content for raw and treated water in six WTPs around Scotland (December 2014 – September 2015)

			Spring June				**Summer Sept**				**Autumn December**				**Winter March**			
Site Name	**Element**	**Units**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Post GAC**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Post GAC**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Post GAC**	**Raw Water**	**Post Clarification**	**Post Filtration**	**Post GAC**
Forehill	**Ca**	**mg/L**	19.4	31.6	32.4	31.7	18.6	35.1	34.5	36.7	13.9	10.6	10.1	19.4	12.9	11.9	11.8	19.1
	Mg	**mg/L**	6.6	7.0	7.0	7.1	6.2	6.8	7.3	6.9	4.7	3.7	4.0	6.2	5.1	4.9	4.9	6.6
	Na	**mg/L**	21.6	22.0	24.0	24.2	20.7	21.1	22.1	23.4	23.1	20.7	20.8	20.6	28.7	27.3	27.3	23.4
	K	**µg/L**	2497.7	2517.3	2576.4	2480.5	3250.4	3446.4	3441.0	3575.6	4029.3	3423.8	4442.7	4858.9	3005.0	2711.2	2683.5	3031.4
	Zn	**µg/L**	4.4	2.5	8.6	1.8	2.6	1.8	4.2	4.7	9.2	7.4	5.8	5.1	19.3	12.4	7.4	14.0
	Al	**µg/L**	23.2	23.8	24.7	13.7	41.4	12.0	12.2	22.6	21.8	9.3	13.7	63.1	12.2	11.5	12.0	28.5
	Fe	**µg/L**	208.6	0.9	5.3	1.0	331.2	0.5	0.4	0.3	95.8	12.2	7.2	396.3	14.6	1.0	1.1	187.3
	Mn	**µg/L**	0.5	0.2	0.2	0.3	5.2	0.0	1.4	0.3	1.1	6.7	2.1	3.5	0.3	1.4	0.0	2.9
	Cu	**µg/L**	9.2	3.1	4.5	1.3	5.0	2.2	1.6	1.5	8.6	614.6	616.2	11.8	7.4	2.9	2.3	4.4
	Si	**mg/L**	5.2	5.0	5.1	5.2	2.1	6.0	7.7	6.0	1.2	0.6	0.6	7.2	0.3	0.3	0.3	7.4
	S	**mg/L**	9.2	24.1	24.2	23.5	9.5	27.8	27.0	28.4	5.4	21.5	21.8	21.5	6.5	5.7	5.7	9.3
Broadford	**Ca**	**mg/L**	13.4	12.4	-	13.1	16.6	15.2	-	15.1	10.8	9.2	-	9.2	10.2	9.5	-	10.3
	Mg	**mg/L**	2.5	2.5	-	2.5	2.7	2.5	-	2.6	1.8	1.7	-	1.7	2.3	2.2	-	2.9
	Na	**mg/L**	10.4	9.9	-	9.9	7.9	7.5	-	7.4	6.0	5.6	-	5.6	10.5	10.0	-	10.9
	K	**µg/L**	342.3	304.8	-	297.8	255.7	247.8	-	234.9	988.5	941.6	-	695.4	347.5	307.8	-	297.8
	Zn	**µg/L**	13.5	7.3	-	0.4	3.8	4.8	-	1.3	2.5	3.2	-	0.9	10.7	15.6	-	14.8
	Al	**µg/L**	11.4	10.2	-	8.1	19.1	14.0	-	118.3	24.9	8.9	-	7.0	18.8	9.2	-	8.5
	Fe	**µg/L**	60.9	2.9	-	2.0	150.5	8.8	-	5.6	102.1	11.7	-	5.4	42.4	6.0	-	4.8
	Mn	**µg/L**	0.2	0.0	-	0.0	1.0	0.4	-	0.1	1.0	1.6	-	0.2	6.3	5.3	-	2.2
	Cu	**µg/L**	12.3	2.9	-	1.7	3.4	1.9	-	1.6	2.1	2.7	-	2.6	3.8	0.0	-	4.7
	Si	**mg/L**	0.4	0.4	-	0.4	0.6	0.6	-	0.6	0.5	0.5	-	0.5	0.5	0.5	-	0.5
	S	**mg/L**	4.5	4.1	-	4.1	4.1	4.0	-	3.9	0.8	0.5	-	0.5	4.5	4.2	-	4.2
Gigha	**Ca**	**mg/L**	13.9	12.4	-	12.6	15.9	13.5	-	13.6	44.5	38.1	-	37.8	30.0	31.2	-	31.4
	Mg	**mg/L**	5.2	4.8	-	4.9	5.8	5.2	-	5.3	7.0	6.6	-	6.6	7.0	6.8	-	7.0
	Na	**mg/L**	28.0	26.3	-	26.5	27.3	25.0	-	25.2	21.3	21.0	-	22.3	23.5	23.5	-	26.1
	K	**µg/L**	2042.8	1803.4	-	1799.8	1475.4	1284.4	-	1303.2	5099.3	5305.7	-	4918.7	3062.3	3102.6	-	3117.1
	Zn	**µg/L**	3.0	5.7	-	1.4	56.0	33.4	-	16.5	1.6	11.7	-	1.9	10.3	4.6	-	5.1
	Al	**µg/L**	11.5	5.7	-	6.9	8.7	4.8	-	7.7	12.7	6.9	-	7.7	21.6	14.5	-	13.6
	Fe	**µg/L**	13.6	0.6	-	0.0	54.7	1.2	-	0.6	50.5	21.2	-	10.5	1.6	0.6	-	0.5
	Mn	**µg/L**	0.4	3.6	-	0.0	1.0	9.9	-	0.0	2.0	1.0	-	0.7	44.6	0.3	-	0.4
	Cu	**µg/L**	6.8	6.7	-	0.9	52.9	31.6	-	3.8	2.6	3.2	-	2.7	4.5	1.5	-	4.1
	Si	**mg/L**	0.2	0.2	-	0.2	0.2	0.1	-	0.1	6.3	6.6	-	6.5	7.1	7.0	-	7.0
	S	**mg/L**	5.0	4.4	-	4.4	4.4	3.8	-	3.9	3.8	2.2	-	2.2	21.2	21.0	-	21.1

Table 5.1 Average values for individual carboxylic acids (35) taken in June and September 2015 from six case study sites around Scotland

Site name	Sampling Point		Acetic	Propionic	Butyric	2-Methyl butyric	Valeric	Isovaleric	Hexanoic	Octanoic	Nonanoic	Decanoic	Dodecanoic	Myristic	Palmitic
Gigha	Raw Water	Mean	**-**	**34.0**	**51.0**	**-**	**-**	**-**	**118.0**	**20.0**	**1.5**	**28.2**	**38.0**	**44.0**	**2.9**
		STDV	-	-	53.7	-	-	-	-	-	-	36.5	-	-	-
	Post Membrane	Mean	**39.0**	**40.5**	**66.0**	**5.1**	**-**	**51.0**	**39.0**	**30.0**	**2.9**	**0.4**	**44.3**	**38.0**	**13.0**
		STDV	55.1	0.7	31.1	6.1	-	-	29.7	29.8	-	-	50.5	28.3	-
	Post GAC	Mean	**29.1**	**36.0**	**44.0**	**2.7**	**18.0**	**223.0**	**69.5**	**6.4**	**3.3**	**12.6**	**7.0**	**41.5**	**3.1**
		STDV	40.9	26.9	0.0	2.5	-	-	74.2	-	3.5	17.5	-	23.3	-
Forehill	Raw Water	Mean	**56.0**	**39.5**	**70.5**	**8.2**	**-**	**130.5**	**80.0**	**32.5**	**6.6**	**13.2**	**22.2**	**71.5**	**6.1**
		STDV	-	7.8	24.7	9.6	-	112.4	62.2	26.2	7.6	16.8	23.8	61.5	2.7
	Post Clarification	Mean	**91.0**	**39.0**	**-**	**4.4**	**-**	**89.0**	**98.0**	**34.0**	**4.6**	**26.3**	**24.9**	**47.5**	**6.0**
		STDV	-	-	-	2.8	-	46.7	52.3	29.7	-	36.4	21.4	14.8	3.0
	Post Filtration	Mean	**48.0**	**40.0**	**67.0**	**7.9**	**9.1**	**75.0**	**85.0**	**17.0**	**18.0**	**18.7**	**25.5**	**42.5**	**0.8**
		STDV	-	7.1	33.9	10.0	-	38.2	87.7	14.2	-	24.5	22.0	23.3	-
	Post GAC	Mean	**39.0**	**37.5**	**62.0**	**3.9**	**8.3**	**118.0**	**103.5**	**9.8**	**8.2**	**13.4**	**46.0**	**61.0**	**10.1**
		STDV	-	4.9	36.8	1.8	-	101.8	112.4	-	11.0	17.9	48.1	5.7	9.8
Amlaird	Raw Water	Mean	**33.3**	**36.5**	**54.5**	**48.9**	**9.3**	**69.0**	**181.0**	**37.0**	**12.9**	**27.2**	**48.5**	**87.5**	**10.9**
		STDV	39.2	0.7	48.8	68.1	-	77.8	60.8	22.6	15.8	35.1	46.0	41.7	14.2
	Post Clarification	Mean	**30.0**	**37.0**	**67.5**	**8.0**	**6.3**	**104.0**	**95.0**	**18.5**	**9.1**	**27.1**	**44.4**	**43.0**	**10.4**
		STDV	-	2.8	29.0	2.1	-	79.2	107.5	9.2	-	35.3	50.4	21.2	10.7
	Post Filtration	Mean	**9.1**	**35.0**	**63.5**	**1.6**	**4.5**	**88.5**	**97.0**	**33.0**	**1.6**	**12.7**	**44.5**	**70.5**	**17.5**
		STDV	-	0.0	36.1	0.3	-	58.7	89.1	29.7	-	17.4	53.1	67.2	6.4
Stornoway	Raw Water	Mean	**24.4**	**21.7**	**48.0**	**7.8**	**13.0**	**119.5**	**86.5**	**32.8**	**20.5**	**27.9**	**58.5**	**47.5**	**6.7**
		STDV	29.1	26.0	60.9	10.2	-	101.1	106.8	32.8	27.6	38.4	34.6	14.8	6.2
	Post Clarification	Mean	**0.1**	**43.5**	**65.0**	**9.5**	**10.0**	**97.0**	**68.5**	**29.9**	**18.0**	**26.3**	**43.5**	**66.5**	**14.9**
		STDV	-	9.2	33.9	12.1	-	75.0	54.4	32.7	-	36.4	53.0	72.8	20.0
	Post Filtration	Mean	**41.4**	**29.5**	**66.5**	**6.5**	**18.0**	**32.0**	**64.0**	**31.1**	**7.7**	**0.9**	**44.4**	**67.5**	**12.9**
		STDV	57.4	10.6	30.4	1.2	-	18.4	53.7	31.0	-	-	50.3	70.0	17.1
Broadford	Raw Water	Mean	**-**	**38.5**	**67.5**	**45.0**	**12.0**	**75.0**	**42.0**	**31.5**	**1.9**	**1.3**	**44.7**	**67.0**	**14.9**
		STDV	-	4.9	29.0	-	-	36.8	-	29.0	-	-	51.4	70.7	20.0
	Post Membrane	Mean	**2.0**	**41.0**	**41.0**	**5.1**	**18.0**	**116.5**	**71.0**	**16.1**	**13.0**	**0.3**	**44.2**	**71.5**	**9.7**
		STDV	0.8	9.9	-	6.3	-	99.7	45.3	12.7	-	-	50.6	62.9	13.1
	Post GAC	Mean	**-**	**40.0**	**63.0**	**1.1**	**17.0**	**75.0**	**105.0**	**8.3**	**25.0**	**1.4**	**44.2**	**70.5**	**14.5**
		STDV	-	7.1	22.6	0.8	-	36.8	77.8	-	-	-	52.0	72.8	19.1
Port Charlotte	Raw Water	Mean	**-**	**34.0**	**48.0**	**9.1**	**12.0**	**81.0**	**71.0**	**35.5**	**10.2**	**26.5**	**46.0**	**72.0**	**13.3**
		STDV	-	-	58.1	11.2	-	41.0	46.7	24.7	12.5	36.1	49.5	65.1	18.0
	Post Clarification	Mean	**54.0**	**30.5**	**66.0**	**33.5**	**14.0**	**97.5**	**102.5**	**34.5**	**21.8**	**1.2**	**46.5**	**83.0**	**14.1**
		STDV	-	7.8	35.4	44.6	-	70.0	84.1	23.3	28.6	-	48.8	49.5	19.6
	Post Filtration	Mean	**-**	**-**	**49.0**	**1.5**	**-**	**1.9**	**45.0**	**11.0**	**0.9**	**1.8**	**13.0**	**38.0**	**3.6**
		STDV	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 5.1 Average values for individual carboxylic acids (35) taken in June and September 2015 from six case study sites around Scotland

Site name	Sampling Point		Hepta decanoic	Stearic	Oleic	Linoleic	Oxalic	Pyruvic	Glycolic	Succinic	fumaric	Benzoic	o-toluic	m-Toluic	p-Toluic
Gigha	Raw Water	Mean	**59.0**	**61.0**	**38.0**	**58.0**	**21.0**	**113.0**	**32.0**	**7.3**	**7.5**	**2.8**	**6.9**	**9.5**	**2.7**
		STDV	-	-	-	-	-	-	-	1.6	-	-	-	-	-
	Post Membrane	Mean	**10.3**	**49.0**	**46.0**	**51.2**	**24.0**	**73.5**	**39.0**	**8.3**	**22.0**	**39.7**	**9.1**	**17.4**	**52.0**
		STDV	5.2	32.5	26.9	70.5	14.1	46.0	32.5	8.1	-	55.6	-	22.1	56.6
	Post GAC	Mean	**33.8**	**54.5**	**33.0**	**22.0**	**3.5**	**75.5**	**47.5**	**0.4**	**0.3**	**2.5**	**2.8**	**17.1**	**30.0**
		STDV	38.5	30.4	-	-	-	48.8	12.0	-	-	-	0.9	22.5	22.6
Forehill	Raw Water	Mean	**20.5**	**8.9**	**18.2**	**22.7**	**3.6**	**78.5**	**77.5**	**3.1**	**11.2**	**39.9**	**4.4**	**17.5**	**56.0**
		STDV	2.1	-	18.1	18.9	-	46.0	60.1	1.4	15.3	55.3	1.9	21.9	52.3
	Post Clarification	Mean	**34.6**	**43.0**	**8.3**	**26.4**	**7.4**	**77.5**	**56.5**	**3.7**	**22.3**	**40.3**	**3.8**	**34.2**	**55.5**
		STDV	37.3	-	6.6	30.5	-	41.7	33.2	0.8	30.7	54.7	3.1	45.0	53.0
	Post Filtration	Mean	**13.0**	**31.0**	**40.5**	**39.5**	**5.9**	**74.5**	**40.0**	**2.5**	**12.1**	**82.0**	**19.6**	**1.8**	**29.5**
		STDV	-	18.4	37.5	16.3	-	44.5	25.5	-	15.4	-	24.7	-	24.7
	Post GAC	Mean	**31.1**	**18.0**	**3.7**	**94.0**	**40.0**	**80.5**	**53.0**	**9.7**	**11.2**	**40.4**	**9.7**	**5.5**	**47.8**
		STDV	42.3	-	-	-	-	55.9	24.0	1.9	15.3	56.0	7.6	-	65.3
Amlaird	Raw Water	Mean	**31.9**	**14.1**	**13.5**	**59.0**	**7.8**	**50.0**	**41.0**	**4.9**	**22.8**	**40.3**	**8.5**	**37.7**	**48.9**
		STDV	42.6	7.0	0.7	53.7	-	2.8	25.5	3.2	31.4	56.2	2.1	41.5	65.2
	Post Clarification	Mean	**6.4**	**24.0**	**11.2**	**21.5**	**46.6**	**93.5**	**54.0**	**3.1**	**22.9**	**41.2**	**7.1**	**34.6**	**57.5**
		STDV	0.4	22.6	12.5	20.6	55.8	62.9	26.9	-	29.9	57.7	0.1	44.5	51.6
	Post Filtration	Mean	**3.7**	**58.0**	**37.9**	**43.5**	**9.7**	**132.0**	**77.0**	**6.5**	**11.3**	**42.6**	**8.3**	**18.1**	**61.0**
		STDV	0.7	32.5	39.7	13.4	4.7	124.5	-	2.8	15.1	58.6	2.1	21.1	52.3
Stornoway	Raw Water	Mean	**9.5**	**73.0**	**47.0**	**39.0**	**16.9**	**128.5**	**54.0**	**3.2**	**24.0**	**5.7**	**37.9**	**36.5**	**53.9**
		STDV	-	35.4	26.9	15.6	14.4	119.5	21.2	3.2	32.6	0.6	46.8	48.8	75.1
	Post Clarification	Mean	**33.1**	**25.6**	**34.6**	**35.5**	**20.1**	**76.0**	**41.0**	**1.8**	**0.5**	**8.2**	**2.9**	**18.5**	**50.0**
		STDV	42.3	26.1	45.9	23.3	21.1	50.9	22.6	-	-	-	-	24.8	50.9
	Post Filtration	Mean	**9.4**	**25.0**	**14.0**	**18.0**	**5.5**	**74.0**	**46.0**	**1.5**	**1.3**	**6.2**	**4.3**	**28.9**	**54.5**
		STDV	-	-	-	-	-	45.3	29.7	-	-	-	-	39.7	55.9
Broadford	Raw Water	Mean	**34.0**	**11.6**	**7.6**	**11.2**	**24.1**	**82.0**	**65.5**	**1.8**	**1.2**	**7.3**	**4.8**	**40.3**	**45.5**
		STDV	39.6	3.5	1.5	11.1	23.9	45.3	13.4	-	-	-	-	54.8	41.7
	Post Membrane	Mean	**13.4**	**34.0**	**8.4**	**44.0**	**20.9**	**74.5**	**63.0**	**4.5**	**0.7**	**8.1**	**3.9**	**28.9**	**51.0**
		STDV	6.5	-	9.3	-	24.3	43.1	4.2	-	-	-	-	38.4	45.3
	Post GAC	Mean	**14.6**	**9.1**	**14.0**	**25.0**	**25.9**	**80.0**	**50.5**	**1.7**	**0.9**	**9.5**	**3.3**	**22.8**	**45.0**
		STDV	14.7	-	-	-	24.3	48.1	26.2	-	-	-	-	30.0	41.0
Port Charlotte	Raw Water	Mean	**9.6**	**15.0**	**30.0**	**37.5**	**31.5**	**82.0**	**87.5**	**0.4**	**5.0**	**4.3**	**7.6**	**32.4**	**61.5**
		STDV	-	4.2	0.0	4.9	24.7	43.8	2.1	-	0.1	5.5	0.1	36.3	47.4
	Post Clarification	Mean	**13.8**	**40.5**	**21.0**	**61.5**	**51.6**	**78.5**	**76.0**	**4.4**	**7.8**	**18.0**	**39.3**	**36.0**	**62.0**
		STDV	5.9	12.0	5.7	23.3	62.8	44.5	11.3	0.6	10.2	-	43.4	45.3	53.7
	Post Filtration	Mean	**14.0**	**43.0**	**15.0**	**60.0**	**11.0**	**52.0**	**80.0**	**2.8**	**1.6**	**-**	**8.8**	**3.7**	**23.0**
		STDV	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 5.1 Average values for individual carboxylic acids (35) taken in June and September 2015 from six case study sites around Scotland

Site name	Sampling Point		Phenyl acetic	Salicylic	3-Hydroxy benzoic	2-Nitro benzoic	3-Nitro benzoic	4-Nitro benzoic	3,4-Dihydroxy benzoic	Phthalic	1,2,3-Benzene tricarboxylic
Gigha	Raw Water	Mean	**51.6**	**43.5**	**15.0**	**61.0**	**63.6**	**3.3**	**30.0**	**104.0**	**0.6**
		STDV	68.5	50.2	-	63.6	82.6	-	-	73.5	-
	Post Membrane	Mean	**49.7**	**26.7**	**13.0**	**6.2**	**1.5**	-	**39.2**	**89.5**	**0.4**
		STDV	69.7	33.0	-	-	-	-	53.5	92.6	-
	Post GAC	Mean	**24.8**	**19.1**	**46.5**	**29.7**	**1.8**	**0.2**	**1.2**	**25.0**	-
		STDV	34.3	22.6	36.1	33.0	-	-	-	-	-
Forehill	Raw Water	Mean	**25.5**	**43.2**	**24.0**	**106.0**	**1.4**	**0.2**	**39.0**	-	**6.6**
		STDV	33.2	52.0	-	-	-	-	0.0	-	2.1
	Post Clarification	Mean	**50.1**	**23.1**	**82.0**	**13.0**	**30.8**	**1.0**	**19.9**	**47.0**	-
		STDV	69.2	22.6	-	-	41.3	-	25.6	-	-
	Post Filtration	Mean	**25.3**	**19.9**	**25.0**	**32.5**	**32.2**	**0.3**	**20.2**	**32.0**	**3.7**
		STDV	34.9	24.2	-	31.9	43.6	-	26.6	-	-
	Post GAC	Mean	**24.9**	**2.6**	**47.5**	**65.5**	**30.6**	**0.8**	**20.2**	**99.0**	**3.6**
		STDV	34.2	-	36.1	57.3	41.6	-	25.2	-	3.3
Amlaird	Raw Water	Mean	**48.2**	**27.5**	**43.5**	**68.5**	**62.6**	**4.8**	**20.5**	**76.5**	**7.7**
		STDV	57.8	30.5	43.1	57.3	84.1	-	26.2	43.1	7.5
	Post Clarification	Mean	**0.8**	**51.9**	**78.5**	**58.5**	**61.2**	**1.3**	**41.0**	**34.0**	**1.6**
		STDV	-	66.6	7.8	67.2	84.6	-	-	-	-
	Post Filtration	Mean	**39.5**	**27.7**	**73.5**	**62.0**	**61.9**	**0.2**	**57.5**	**38.0**	**2.4**
		STDV	54.4	30.2	2.1	70.7	86.5	-	29.0	-	-
Stornoway	Raw Water	Mean	**0.5**	**26.3**	**40.4**	**59.9**	**31.4**	**1.0**	**39.0**	**32.5**	**5.1**
		STDV	-	32.1	53.2	76.6	43.2	-	-	2.1	-
	Post Clarification	Mean	**0.7**	**26.9**	**64.0**	**56.1**	**30.9**	-	**36.5**	**23.0**	**2.2**
		STDV	-	32.7	14.1	73.5	42.5	-	3.5	-	-
	Post Filtration	Mean	-	**5.4**	**51.0**	**4.7**	**62.1**	-	**0.9**	**24.0**	**0.4**
		STDV	-	-	31.1	-	86.2	-	-	-	-
Broadford	Raw Water	Mean	**101.0**	**5.9**	**52.0**	**30.3**	**124.0**	-	**19.9**	**26.0**	**2.5**
		STDV	-	-	31.1	33.5	-	-	25.7	-	-
	Post Membrane	Mean	**0.9**	**26.0**	**54.0**	**60.5**	**61.0**	-	**19.7**	**46.0**	**2.4**
		STDV	-	32.5	26.9	64.3	-	-	25.9	-	-
	Post GAC	Mean	**0.9**	**3.6**	**75.0**	**30.3**	-	**0.5**	**1.6**	**28.0**	**2.2**
		STDV	-	-	1.4	33.5	-	-	-	-	-
Port Charlotte	Raw Water	Mean	**49.7**	**54.9**	**63.5**	**63.5**	**63.5**	**1.3**	**44.5**	**29.0**	**4.3**
		STDV	69.7	63.8	13.4	65.8	85.6	-	7.8	-	2.8
	Post Clarification	Mean	**0.9**	**54.3**	**67.0**	**63.5**	**31.2**	**1.5**	**39.5**	**81.0**	**3.8**
		STDV	-	63.3	9.9	64.3	42.2	-	53.1	1.4	1.9
	Post Filtration	Mean	**3.4**	**8.2**	**34.0**	**14.0**	**1.4**	**0.9**	**49.0**	**58.0**	-
		STDV	-	-	-	-	-	-	-	-	-