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Catchment Influences on Dissolved Organic Carbon Concentration and Character; Implications for Potable Water Treatment and Trihalomethane Control

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Catchment Influences on Dissolved Organic Carbon Concentration and Character; Implications for Potable Water Treatment and Trihalomethane Control

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Abstract

The presence of dissolved organic carbon (DOC) in raw water can cause a number of issues in potable water treatment due to its effect on aesthetic, chemical and biological water quality parameters. Of particular concern is the role of DOC as a precursor to potentially harmful disinfection by-products (DBPs), most notably haloacetic acids (HAAs) and trihalomethanes (THMs), which are formed during the chlorination of natural waters. Rising concentrations of DOC in surface waters draining upland catchments have been reported in the past few decades. This is a major concern for drinking water companies in these areas given the regulatory requirement to maintain THM concentrations below maximum permissible levels. Coagulation-flocculation is recognised as the most effective means of removing DOC from raw water during potable water treatment and controlling the formation of THMs in finished water.

The present study is focussed on upland drinking water reservoir catchments in the North Wales area. In this area many catchments comprise extensive areas of forest and peatland coverage, both of which have been associated with high DOC loading of surface waters. In this study the concentration and character of leachable DOC was compared in soils derived from different habitats in order to assess the effect of habitat type (beech, spruce, larch and pine forests and blanket peat) on DOC treatability and THM formation potential (THMFP). Significant differences were identified between different habitats, with the beech habitat identified as most appropriate for drinking water catchments due to it having relatively low leachate DOC concentration, THMFP and colour.

In the 20th century many peatland areas were drained for agriculture, game and forestry, resulting in the destabilisation of their vast carbon stores, and an increase in the export of DOC to surface waters. In this study the effect of peatland restoration *via* ditch blocking on pore water DOC treatability and THMFP was simulated using a water table manipulation experiment. Overall there was little evidence of differences in THMFP or DOC treatability between different water table regimes. There was also no evidence of variation in microbial activity, based on CO_2 flux and enzyme activity measurements, between different treatments. The results suggest that in the short term at least, ditch blocking may have little or no effect on DOC export from peatlands, though this could be the result of a delay in the microbial response to a change in water table regime.

A number of catchment characteristics, including geological, pedological and ecological features are known to exert an influence on surface water quality. In this study GIS mapping was used to display and quantify the spatial extent of ecological and pedological features in two upland drinking water catchments and the subcatchments of their main input streams. Contrasting surface water quality in the two reservoirs could be explained by differences in catchment characteristics, with greater coniferous forest coverage, deeper soils and shallower mean catchment slope explaining higher DOC loading in Reservoir A. UV absorbance measurements (A_{253}:A_{203}, and to a lesser extent, SUVA) were also shown to provide a proxy for standardised THMFP (STHMFP), suggesting they may be useful as a means of monitoring THMFP.

Seasonal variations in DOC concentration and character were observed in fluvial and reservoir samples, including THMFP and THM formation rate, indicating temporal variations in THM yields. However, mixing of waters in large reservoirs was found to temper this variability, resulting in a more consistent supply to water treatment works (WTWs). Seasonal variations in DOC character were found to be partly the result of a seasonal increase in algogenic DOC inputs. A laboratory based experiment was set up to examine the effect of an algal bloom on the treatability and STHMFP of DOC in a water source formerly dominated by terrigenous DOC. Though the algal bloom was associated with a shift towards lower STHMFP and a slower rate of THM formation, it was also associated with an increase in brominated THMs (BrTHMs; thought to be more carcinogenic) and a decrease in treatability due to it being dominated by hydrophilic, aliphatic DOC. Characterisation of algogenic DOC using high pressure size exclusion chromatography (HPSEC) also showed that DOC produced during different growth phases of an algal bloom can be identified by peaks in specific regions of the HPSEC chromatogram.

The contribution of individual treatment processes to DOC and THM precursor removal was assessed over a 12 month period at the WTW located at Reservoir A. DOC concentration and STHMFP decreased significantly following coagulation-flocculation. However, selectivity in the removal of DOC also resulted in an increase in the proportion of BrTHMs. The precipitation-filtration process designed to remove manganese also resulted in a shift in DOC character.

A jar testing experiment demonstrated the benefits, in terms of DOC and THM precursor removal, of switching the chemical coagulant used at WTWs. However, with all three coagulants included in the study, low molecular weight, hydrophilic, aliphatic DOC was found to be recalcitrant to removal. Enhanced removal of this DOC fraction will be important for THM amelioration if DOC concentrations in surface waters continue to rise.

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List of abbreviations

AOD	Above Ordnance Datum
AOM	Algogenic Organic Matter
BAT	Best Available Technology
BrTHMs	Brominated trihalomethanes
DAF	Dissolved Air Floatation
DBPs	Disinfection By-Products
DCWW	Dŵr Cymru Welsh Water
DICQ	3-dihydroindole-5,6-quinone-2-carboxylate
DI-SPME	Direct Immersion Solid Phase Microextraction
DNA	Deoxyribonucleic Acid
DOC	Dissolved Organic Carbon
DyDOC	Dynamic DOC model
DWI	Drinking Water Inspectorate
EEM	Excitation-Emission Matrix
EOM	Extracellular Organic Matter
GIS	Geographical Information System
HAAs	Haloacetic Acids
HANs	Haloacetonitriles
INCA-C	Integrated Catchments Model for Carbon
IOM	Intracellular Organic Matter
HMW	High Molecular Weight
HPIN	Hydrophilic Neutral
HPIA	Hydrophilic Acid
HPIB	Hydrophilic Base
HPOA	Hydrophobic Acid
HPOB	Hydrophobic Base
HPSEC	High Pressure Size Exclusion Chromatography
L-DOPA	L-3,4-dihydroxyphenylalanine
LMW	Low Molecular Weight

LOQ	Limit of Quantification
MUF	methylumbelliferone
MWD	Molecular Weight Distribution
NDBPs	Nitrogenous Disinfection By-Products
NICA-Donnan	Non-ideal Competitive Adsorption-Donnan model
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
PAX-18	polyaluminium chloride ($Al_n(OH)_mCl_{3n-m(aq)}$)
PIX-322	ferric sulphate ($Fe_2(SO_4)_{3(aq)}$)
POC	Particulate Organic Carbon
RGF	Rapid Gravity Filter
RNA	Ribonucleic Acid
SPME	Solid Phase Microextraction
STHMFP	Standardised Trihalomethane Formation Potential
SUVA	Specific UV Absorbance
THMs	Trihalomethanes
THMFP	Trihalomethane Formation Potential
TOX	Total Organic Halide
t_R	Retention time
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
WTW	Water Treatment Works

Chapter 1: Introduction

1.1. General Introduction

The quality of drinking water is one of the most powerful determinants of human health and the provision of a safe, reliable drinking water supply, a prerequisite for social and economic development (WHO & UNICEF, 2012). Industrial-scale potable water treatment involves a series of treatment stages designed to control aesthetic, chemical and biological water quality parameters whose levels are strictly regulated. However, illness caused by chemical contamination is negligible compared with that caused by microbial pathogens (Galbraith, *et al*. 1987; Herwaldt, *et al*. 1992). Disinfection, a process designed to minimise the risk of infection from water-borne pathogenic or disease-causing microorganisms, is therefore essential in potable water treatment. Chlorine dosing is the most widely-used method of disinfection and has been described as one of the most effective public health measures ever undertaken (Bull, *et al*. 1995). Indeed, for UK-based drinking water companies, dosing with chlorine prior to distribution is a regulatory requirement (DWI, 2010). In the 1970s however, it was discovered that chlorination resulted in the formation of potentially harmful halogenated by-products (so-called disinfection by-products; DBPs), due to chlorine reacting with natural organic matter (NOM) present in raw water (Rook, 1974; Symons, *et al*. 1975). Of particular concern is the formation of trihalomethanes (THMs), which have been found to have carcinogenic properties (Richardson, *et al*. 2007) and are now subject to regulatory limits in the UK (DWI, 2010). The removal of NOM prior to disinfection is therefore a priority in contemporary potable water treatment and is recognised as the most effective means of minimising THM levels in finished water (US EPA, 1999). In practice NOM is typically expressed by the measurement of total organic carbon (TOC), and according to its most simple classification, may be partitioned into dissolved organic carbon (DOC) and particulate organic carbon (POC) (Thurman, 1985). Virtually complete removal of POC can typically be achieved during conventional potable water treatment, whereas DOC is more recalcitrant and its removal incomplete (Shorney, *et al*. 1999). In practice therefore, DOC is the main THM precursor of concern. A rising trend in DOC concentrations in surface waters draining upland catchments has been reported in the last few years, affecting many areas in Central and Northern Europe and North America (Freeman, *et al*. 2001a; Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Worrall, *et al*. 2003; Skjelkvåle, *et al*. 2005; Monteith, *et al*. 2007). Climate change is also predicted to alter the concentration and character of DOC in surface waters with consequences for treatability and DBP formation potentials (Ritson, *et al*. 2014).

1.2. Disinfection by-products

In the 1970s it was discovered that THMs were formed during the chlorination of drinking water (Rook, 1974; Symons, *et al*. 1975). Since then more than 600 species of DBP have been identified, with THMs and haloacetic acids (HAAs) representing the dominant fraction (Boorman, *et al*. 1999; Krasner, *et al*. 2006). However, it is also reported that over 50% of the total organic halide (TOX) consists of unidentified species (Hua & Reckhow, 2007). Though currently in the UK, only THMs are subject to regulation, in the US, maximum permissible concentrations are also given for five HAA species (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromate and chlorite) (US EPA, 2009). As information on the molecular structures and toxicological properties of so-called emerging DBPs increases, it is likely that additional regulatory limits for specific DBPs will be introduced.

1.2.1. THM formation

THMs are a group of compounds with the general formula CHX_3, where X may be any halogen (F, Cl, Br or I) or a combination of these. $CHCl_3$ is the dominant THM species formed during chlorination (Figure 1.01), with $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ also formed if bromine is present (Peters, *et al*. 1980). During potable water treatment, a disinfection stage is required to reduce the risk of infection from water-borne viruses, bacteria and protozoa (Gray, 1999). Although other methods of disinfection are available, such as ozonation and UV radiation, chlorine is by far the most widely used (White, 1999). Commonly the chlorine is delivered under pressure as liquefied gas (Cl_2), but may also be dosed as NaOCl or $Ca(OCl)_2$ (Parsons & Jefferson, 2006). In aqueous solution chlorine exists as hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) which can act as halogenating agents. Although it is now widely accepted that NOM, and in particular humic substances, are the main reaction precursors in the formation of THMs during chlorination, the precise reaction mechanism involved remains elusive.

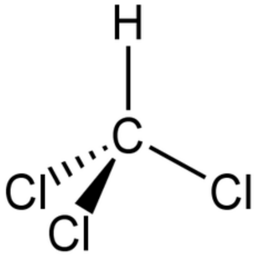

Figure 1.01. The chemical structure of chloroform.

Due to the complexity and poorly-defined nature of NOM, research into THM formation mechanisms has focussed on the reaction of chlorine with simpler model compounds. Aliphatic carboxylic acids, hydroxybenzoic acids and phenols have all been reported to act as precursors for $CHCl_3$ formation (Larson & Rockwell, 1979). Christman & Ghassemi, (1966) investigated the reaction between chlorine and various derivatives of vanillic acid, syringic acid and 3,5-dihydroxybenzoic acid. Chemical degradation experiments suggested that these compounds could be representative of the phenolic polymer core of humic substances. These workers found that structures relating to 3,5-dihydroxybenzoic acid, namely resorcinol and orcinol, were the dominant precursors to $CHCl_3$ under alkaline conditions. The proposed mechanism for the conversion of these precursors to $CHCl_3$ involved the initial incorporation of a halogen from the hypochlorous molecule *via* electrophilic substitution and addition, followed by hydrolysis and oxidative bond cleavage about the C_2 aromatic ring (Boyce & Hornig, 1983). More recently, differences in the reactivity of model compounds with chlorine have led to the development of a two-phase model of THM formation involving fast- and slow-reacting DOC precursors. Resorcinol-type structures, it is suggested, act as fast-reacting THM precursors with other phenolic compounds acting as slow-reacting THM precursors (Gallard & von Gunten, 2002).

1.2.2. Measurement of trihalomethane formation potential (THMFP)

The propensity of the DOC contained in a water sample to form THMs upon chlorination can be assessed by measuring THM formation potential (THMFP) (Standing Committee of Analysts, 1981). This is a standard measurement representing the total yield of THMs formed following chlorination of a water sample with excess chlorine for a given temperature and incubation period (typically 25°C and 7 days, respectively) and is generally expressed in $\mu g\ L^{-1}$. The THMFP of a water sample will depend both on the concentration of DOC present, and its reactivity with chlorine. A standardised THMFP (STHMFP) measurement can be obtained by dividing THMFP by DOC concentration and represents the concentration of THMs formed after chlorination of a water sample, per unit of DOC. STHMFP, which represents the reactivity of DOC with chlorine is typically expressed as $\mu g\ L^{-1}$ mg DOC^{-1}.

1.2.3. Factors affecting THM yield and speciation

Though the reaction mechanism in THM formation is complex, various factors are known to affect THM yield and speciation, including temperature, pH, contact time, chlorine dose, bromide concentration and DOC concentration and character. These factors are discussed in turn below.

In common with many reactions under kinetic control, the rate of THM formation is reported to increase with temperature (Peters, *et al*. 1980). As such, higher THM yields are often reported during the summer months when ambient temperatures are higher.

pH is reported to exert a strong influence on the reaction kinetics involved in THM formation with a three-fold increase in reaction rate per unit increase in pH reported (Adin, *et al*. 1991). However, an inverse relationship between pH and HAA formation potential (HAAFP) has also been found, suggesting a trade-off between THMFP and HAAFP (Kim, *et al*. 2003).

THM yield increases with increasing contact time. To ensure effective disinfection, in the UK, a minimum period of contact with free chlorine is required prior to distribution (30 min at pH < 8.0 after which $\geq$ 0.5 mg L^{-1} of free chlorine should still be present), in accordance with WHO recommendations (WHO, 2011). In addition, a minimum free chlorine residual of 0.2 mg L^{-1} is required at the point of delivery (consumers' taps) (DWI, 2010). As such, a free chlorine residual is maintained between the water treatment works (WTW) and the point of delivery and chlorine is available to react with NOM throughout the distribution system. The period of contact between free chlorine and THM precursors will therefore depend on the residence time of water in the distribution system (i.e. the length of the distribution system). Where high THM yields have been identified, some water treatment companies have opted to introduce a system of chloramination. This involves converting most of the free chlorine to combined available chlorine by dosing with NH_3 prior to distribution. Though chloramination has been effective in reducing THM levels at the point of delivery, it also increases the yield of nitrogenous DBPs (NDBPs) such as haloacetonitriles (HANs) (Yang, *et al*. 2008). Though not currently subject to regulation in the UK, these are reported to have higher toxicity than carbon-based DBPs (Muellner, *et al*. 2007).

Since a free chlorine residual is maintained between the WTW and the point of delivery, THM formation is under first order kinetic control with respect to DOC (Lee, *et al*. 2007). However, the precise concentration of free chlorine present, which will vary between WTWs depending on the chlorine dosing system and the presence/absence of a chloramination stage, will affect the rate of THM formation. This is significant since it will affect the concentration of THMs at the point of delivery.

Trace levels of bromide occur in surface waters and as a production impurity (*ca*. 1%) in chlorine used at potable WTWs (Winchester & Duce, 1966; Bond, *et al*. 2014). In the presence of aqueous chlorine, bromide is rapidly oxidised to bromine (HOBr and OBr^-) which is a more powerful halogenating agent than chlorine (Morris, 1978). Thus, depending on DOC characteristics, the presence of bromide may increase the rate of THM formation (Nokes, *et al*. 1999). A shift towards more brominated THM species (BrTHMs) will also occur as bromine concentration increases. This will be disproportionate to the increase in $Br^-:Cl_2$ ratio due to the preferential incorporation of bromine relative to chlorine (Hua, *et al*. 2006). For example, at similar initial molar concentrations, kinetic studies have indicated that bromine substitution with NOM was approximately an order of magnitude greater than chlorine substitution (Westerhoff, *et al*. 2004; Hua, *et al*. 2006).

For a given DOC type and providing chlorine is in excess, increased DOC concentration will result in a proportional increase in the concentration of THMs (Liang & Singer, 2003). However, DOC characteristics are also reported to influence both the total yield and speciation of THMs. These factors are discussed in section 1.6.

1.2.4. THM toxicology

Both epidemiological and laboratory-based research has indicated a slight increased incidence in various types of cancer with exposure to THMs. For example, population-based case control studies suggest a weak association between lifetime consumption of chlorinated drinking water and incidence of rectal, colon and bladder cancer (Cantor, *et al*. 1998; Hildesheim, *et al*. 1998). At high doses, individual THM species ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) were also found to be carcinogenic in rodent bioassays (National Cancer Institute, 1976; Dunnick, *et al*. 1985; George, *et al*. 2002). In general, BrTHMs are considered more toxic due to a higher carcinogenic risk associated with long-term exposure (WHO, 2005). Consumption of drinking water with high THM concentrations has also been associated with adverse effects on male reproductive health and miscarriage (Borzelleca & Carchman, 1982; Waller, *et al*. 1998; Bielmeier, *et al*. 2001; Luben, *et al*. 2007). It should be emphasized however that the health risks associated with ingestion of THMs, even over a lifetime, are extremely small (Bull, *et al*. 1995).

1.2.5. THM regulation

Drinking water companies have a responsibility to provide a safe and reliable potable water supply for domestic and commercial consumers. The Drinking Water Inspectorate (DWI) is responsible for setting and enforcing standards for drinking water quality in the UK. These include bulk parameters such as pH, turbidity and conductivity, bacterial counts, aesthetic parameters including odour, colour and taste, as well as concentrations of individual contaminants including metals and DBPs. The Water Supply (Water Quality) Regulations (2010) which apply in England and Wales, set maximum permissible limits for regulated parameters as well as specifying the point of compliance (e.g.

consumers' taps, service reservoirs or WTWs) and the required sampling frequency (DWI, 2010). In addition to adhering to DWI regulations, Dŵr Cymru Welsh Water (DCWW), who supply drinking water to most of Wales, and co-sponsor the present study, have an internal framework of water quality standards which are based on industry best practice and include more stringent targets for various contaminants.

In response to the reported link between THM consumption and adverse health effects, regulatory limits for THM levels have been introduced. The DWI specify a maximum total THMs concentration of 100 µg L^{-1}, measured at the end of the distribution system (i.e. consumers' taps) (DWI, 2010). Should this level be exceeded, then the drinking water company responsible is liable to receive a financial penalty. DCWW has set a more stringent target of maintaining THM concentrations below 70 µg L^{-1} at the end of the distribution system. Depending on specific circumstances, exceedance of this level prompts either a short-term mitigation response e.g. adjustment in coagulation conditions, or a long-term remedial solution such as installation of an additional treatment process. The World Health Organization (WHO) guidelines include maximum values for individual THM species, reflecting the higher toxicity associated with brominated species (60 µg L^{-1} for $CHCl_2Br$, 100 µg L^{-1} for $CHClBr_2$ and $CHBr_3$ and 300 µg L^{-1} for $CHCl_3$) (WHO, 2011), though currently, in the UK, there are no regulatory limits for individual THM species.

It should be noted that WHO guidelines for THM levels in drinking water are rigorous, since they are based on a 10^{-5} excess lifetime cancer risk. In addition, the risks associated with exposure to THMs should be balanced against the health benefits of chlorination. In a review of the toxicological evidence conducted by Bull, *et al*. (1995), it was concluded that the health risks associated with DBPs are insignificant compared to those associated with microbial contamination of the water supply. The WHO advise that where a choice must be made between adhering to microbiological guidelines and guidelines for DBPs, that microbiological quality must always take precedence and that efficient disinfection must never be compromised (WHO, 2011).

1.3. Potable water treatment and NOM removal

A number of different treatment processes are employed to remove different size fractions of organic matter from raw water (Figure 1.02). Gross solids such as floating vegetation are generally removed from raw water by coarse and fine screens at the intake of WTWs. Suspended solids which contribute to turbidity, including silt, clay, fine particles of organic and inorganic matter, plankton and other microorganisms are kept in suspension by turbulence and can be removed prior to coagulation using settling tanks (Gray, 1999). Suspended solids including POC are also removed during subsequent coagulation-flocculation and clarification stages. Virtually complete removal of POC is achieved by these methods (Shorney, *et al*. 1999). DOC removal is also achieved during coagulation-flocculation, typically using iron or aluminium salts allied with pH control, followed by clarification using dissolved air floatation (DAF) or sedimentation and sand filtration (Matilainen, *et al*. 2010). However, DOC removal is not a complete process. Removal rates reported in previous studies range between 29-70% using iron-based coagulants and 25-67% using aluminium sulphate in a range of raw water types (Matilainen, *et al*. 2010).

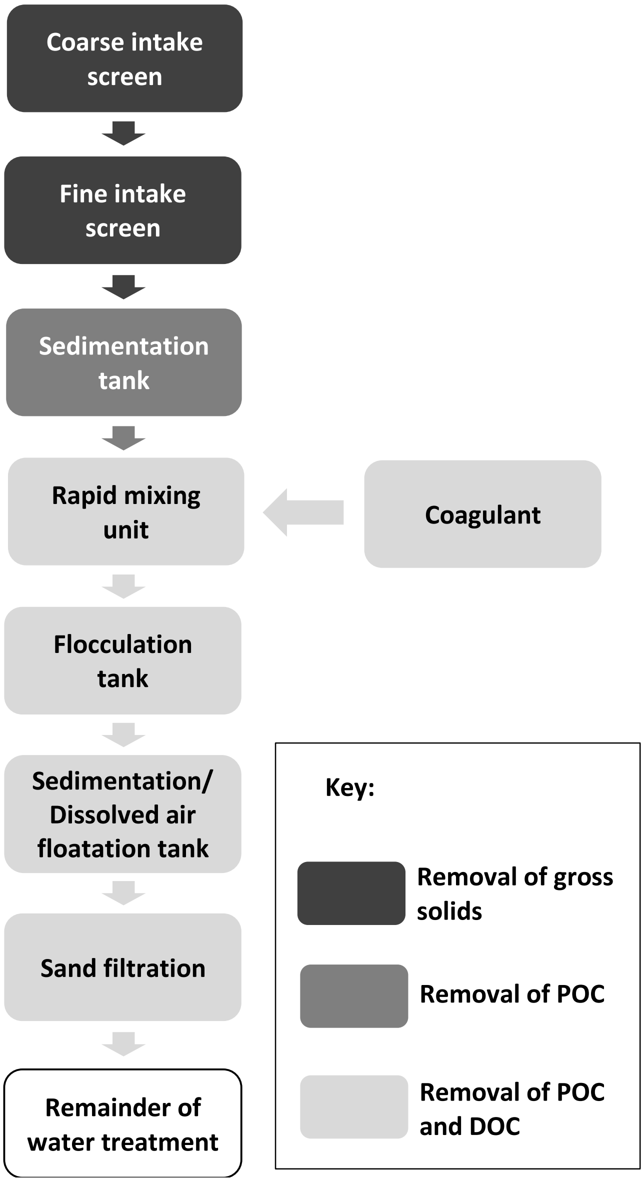

Figure 1.02. Flow diagram showing treatment stages designed to remove organic matter during conventional potable water treatment.

Although not regulated directly, the DWI recommend that TOC levels be monitored in case of any abnormal change in concentration (DWI,2010), reflecting the role of TOC in affecting other water quality parameters. Since virtually complete removal of gross solids and POC can be achieved during conventional potable water treatment (Shorney, *et al*. 1999), the dissolved organic fraction generally represents the main concern for drinking water companies. In addition to its role as a reaction precursor in the formation of DBPs (Rook, 1974; Symons, *et al*. 1975; Adin, *et al*. 1991; Owen, et al. 1995), DOC can compromise the aesthetic quality of drinking water, contributing colour, odour and taste (Davies, *et al*. 2004; WHO, 2011). It can also be responsible for the transport of regulated organic and inorganic micro-pollutants such as pesticides and metal contaminants (Gao, *et al*. 1998; Rothwell, *et al*. 2007). Biodegradable DOC in finished water can also lead to bacterial regrowth within water distribution systems (Prévost, *et al*. 1998).

1.3.1. THM amelioration

A number of options are available to water treatment companies concerned with minimising concentrations of THMs in the water supply. These can be summarised as follows:

- Removal of THM precursors prior to chlorination;
- Use of alternative chemical disinfectants;
- Use of non-chemical disinfection;
- Removal of THMs prior to distribution (WHO, 2011).

Removal of THM precursors prior to chlorination is by far the most attractive THM control strategy in terms of efficacy and cost and may be enhanced by optimising the coagulation-flocculation process (US EPA, 1999). This is discussed in more detail in section 1.3.2.

Alternative chemical disinfectants include ozonation, dosing with chlorine dioxide, and chloramination. Though ozone is an effective disinfectant, if used in isolation, it provides no residual disinfection in the distribution system. Furthermore, if dosed prior to chlorine, ozone can increase the THMFP of the water by producing a shift towards lower molecular weight (MW) DOC (Gang, *et al*. 2003). Switching from chlorine to chlorine dioxide has been associated with a decrease in THM yield but also the formation of chlorite and chlorate as by-products (Craun, 1993), whose toxicology is largely unknown. Chloramination has become a popular alternative to chlorination as a strategy for minimising THM formation, though in the UK, where a period of contact with free chlorine is a regulatory requirement (DWI, 2010), it is used as a secondary disinfection stage. This involves dosing with NH_3 after chlorination, removing most of the free chlorine from solution by forming chloramine species (NH_2Cl, $NHCl_2$ and NCl_3), whilst maintaining a disinfection residual within the distribution system (Guay, *et al*. 2005). Though chloramination has produced impressive results both in terms of TOX and THM reduction (Kristiana, *et al*. 2009), the fraction of TOX comprising unidentifiable species of unknown toxicity is increased (Hua & Reckhow, 2007) in addition to the formation of NDBPs (Bond, *et al*. 2011).

The use of non-chemical disinfection would prevent THM formation. However, as stated earlier, substituting chlorination is not an option available to drinking water companies in the UK. Instead, UV irradiation can be used prior to chlorination to provide a disinfection pre-treatment. UV radiation at wavelengths between 200 and 280 nm can kill or inactivate viruses and bacteria by damaging RNA and DNA, thus preventing replication (Wacker, 1963). However, viruses and bacteria can be protected from UV disinfection by attachment to, or enmeshment within colloidal organic matter (Emerick, *et al*. 2000; Templeton, *et al*. 2005).

The removal of THMs prior to distribution is technically feasible but is the least attractive option for controlling THM concentrations. Techniques such activated carbon filtration-adsorption, air stripping, UV radiation and advanced oxidation can be used either to remove or degrade THMs (WHO, 2011). However, in the UK, these processes would need to be followed by an additional chemical disinfection stage to provide residual disinfection in the distribution system, which may negate the preceding THM reduction.

1.3.2 Coagulation-flocculation

The removal of NOM by coagulation-flocculation, followed by clarification, is the main strategy for THM control in potable water treatment. This is typically achieved using iron- or aluminium-based coagulants (O'Melia, *et al*. 1999). NOM is kept in suspension due to electrostatic repulsion between neighbouring anionic particles which inhibits their collision under the influence of Brownian motion and van der Waals forces. Negative surface charges on NOM are acquired due to the ionisation of carboxyl groups on their surface (Duan & Gregory, 2003). Successful coagulation depends on overcoming the electrostatic repulsion between particles in order to destabilize the colloidal system and enable the agglomeration of NOM. The agglomeration of NOM is necessary to ensure its subsequent removal by dissolved air floatation or sedimentation. Two principal mechanisms are responsible for the removal of NOM from water by aluminium and iron salts: charge neutralisation by cationic hydrolysis products and incorporation of impurities in a hydroxide precipitate (so-called sweep flocculation) (Matilainen, *et al*. 2010). In the presence of water, aqueous Al(III) and Fe(III) salts rapidly dissolve yielding their respective trivalent ions, Al^{3+} and Fe^{3+}. These metal cations are readily hydrolysed in water (Edzwald & Tobiason, 1999). The relative concentrations of the hydrolysed products change with pH. Charge neutralisation is reported to take place where the doubly-charged cationic species ($Me(OH)^{2+}$) dominates. Sweep flocculation tends to occur where conditions favour the formation of the insoluble metal hydroxide ($Me(OH)_3$). The insoluble hydroxide precipitate is preferentially formed at higher pH values where the solubility limit is lowered and/or at high coagulant doses which overcome the solubility limit (Yan, *et al*. 2008).

Traditionally, coagulation-flocculation was designed to attain target levels of colour and turbidity (Iriarte-Velasco, *et al*. 2007). Enhanced coagulation refers to the optimisation of coagulation conditions to achieve maximum DOC removal and may involve higher coagulant doses or lower coagulation pH than is conventionally applied (WHO, 2011). Enhanced coagulation has been recognised as the best available technology (BAT) for minimising THM and other DBP formation in chlorinated drinking water (US EPA, 1999).

A number of factors affect the efficiency of DOC removal by coagulation. In addition to coagulation pH and dose, temperature, coagulant type (Uyak & Toroz, 2007), raw water alkalinity and pH (Yan, *et al*. 2008), concentration of electrolytes in solution (Runkana, *et al*. 2006) and DOC characteristics are also significant. The effect of DOC character on DOC removal efficiency is discussed in section 1.6. At potable WTWs the optimal conditions (pH, coagulant dose and sequence of chemical addition) for DOC removal are established experimentally using jar test experiments. These must be carried out on a regular basis due to fluctuations in the quality of the raw water entering the WTW.

1.4. Natural organic matter (NOM)

NOM is a ubiquitous constituent or natural surface and ground waters and comprises biogenic materials and substances at various stages of chemical and biological degradation (Hope, *et al*. 1994). The origins of NOM include plant, microbial and animal products both in the form of metabolised (excreted) or egested waste products and their decomposing remains (Wetzel, 2001). NOM may be leached into the hydrosphere from external (allochthonous) sources *via* runoff and percolation during rainfall events. Alternatively it may be produced *in situ* in the water body from aquatic plants, plankton and higher organisms (autochthonous NOM) (Hope, *et al*. 1994; Kalbitz, *et al*. 2000). It plays a significant role in the functioning of aquatic ecosystems and is an important component of the carbon cycle (Schnitzer & Khan, 1972; Evans, *et al*. 2012).

As mentioned earlier, in practice NOM is typically expressed by the measurement of TOC, and according to its most simple classification, may be partitioned into DOC and POC (Figure 1.03). DOC is operationally defined as the organic carbon in a water sample which passes through a 0.45 µm porosity membrane and POC is the fraction retained on the membrane (Thurman, 1985). However a significant portion of organic matter below the 0.45 µm size threshold is known to be colloidal in nature (Chow, *et al*. 2005a). DOC may be further sub-divided into humic and non-humic constituents as described below.

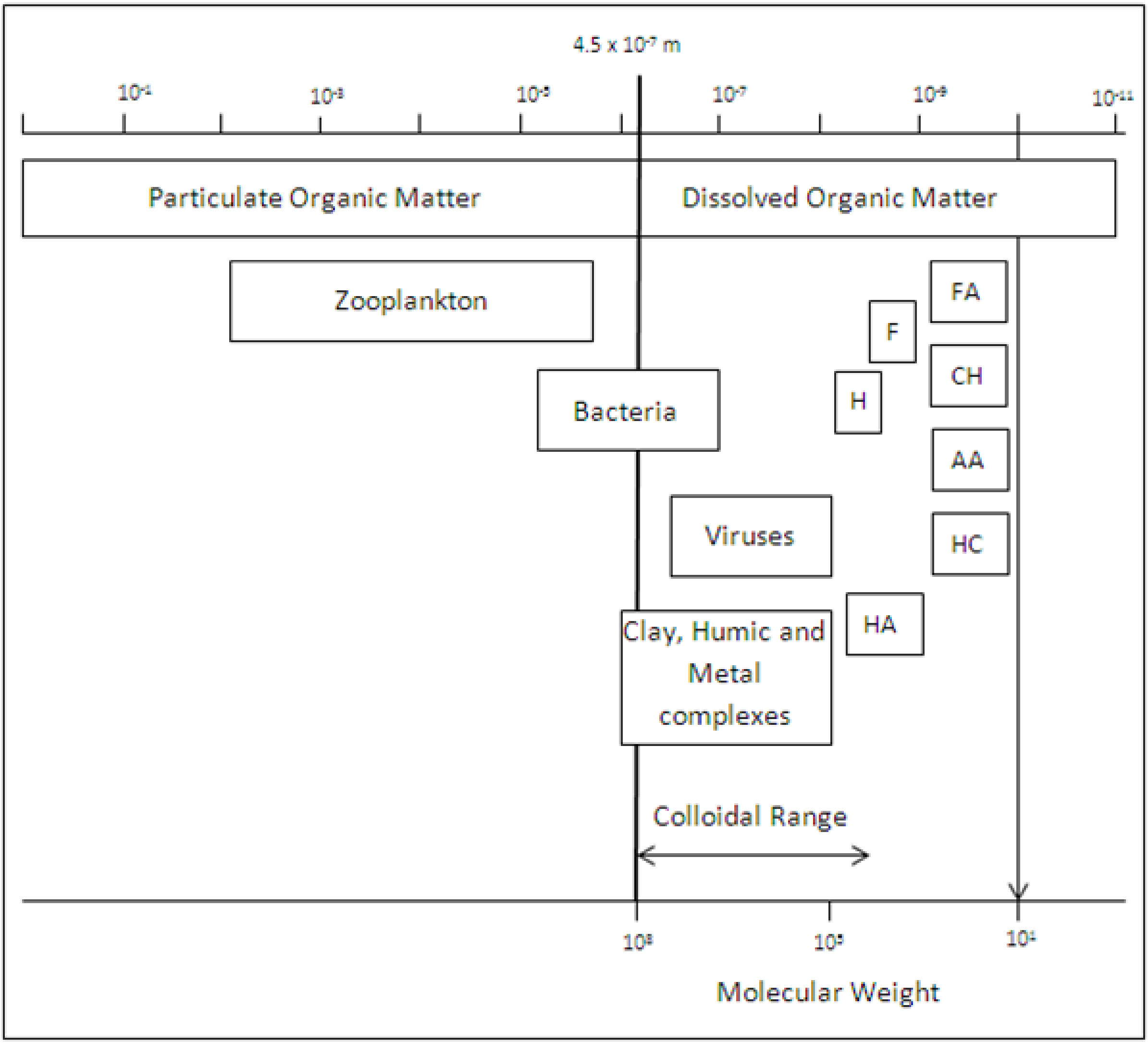

Figure 1.03. Size range of various organic compounds in natural waters. F: Fulvic acid, H: Humic acid, FA: Fatty acid, CH: Carbohydrate, AA: Amino acids, HA: Hydrophilic acids, HC: Hydrocarbons (adapted fromThurman, 1985).

1.4.1. Humic substances

Humic substances, which tend to represent the dominant DOC fraction in surface waters (50-75%) (Thurman, 1985), are produced largely as a result of the microbial degradation of structural plant materials and animal tissues. They comprise amorphous hydrophobic acids of high MW (HMW) and high aromatic content (Schnitzer & Khan, 1972). Humic substances can be partitioned into humic and fulvic acids based on differing solubility; humic acids are reported to form precipitates at low pH, whereas fulvic acids remain in solution (Kononova, 1961; Malcolm & MacCarthy, 1992). Humic acids are characterised by a black-brown colour and fulvic acids, which have a lower MW and a higher content of oxygen-containing functional groups, range in colour from light yellow to yellow-brown (Kononova, 1961; Hope, *et al*. 1994). Humic substances are relatively recalcitrant to biodegradation (Fukushima, *et al*. 1996) and can persist, unchanged in the aquatic environment for several years.

1.4.2. Non-humic substances

Non-humic substances include carbohydrates, proteins, peptides, amino acids, waxes and lipids (Schnitzer & Khan, 1972). Hydrophilic DOC is commonly referred to as the non-humic fraction (Croue, 2004). Other defining characteristics are their low MW (LMW) and low UV-absorption properties. In the aquatic environment they are highly susceptible to biodegradation and hence exhibit high flux rates (Schnitzer & Khan, 1972). On a seasonal basis algogenic organic matter (AOM) may represent an important non-humic DOC source (Wetzel, 2001), consisting of extracellular organic matter (EOM; released from algal cells by diffusion) and intracellular organic matter (IOM; released from senescent algal cells during cell lysis) (Li, *et al*. 2012). Though relatively transitory, they can cause a profound shift in raw water quality and treatability (Bernhardt, *et al*. 1991).

1.5. Functions and cycling of DOC in surface waters

As well as providing an important pathway for carbon transfer between terrestrial and aquatic environments (Battin, *et al*. 2009; Evans, *et al*. 2012), NOM including DOC is an important energy source, directly supporting the aquatic food chain; as Wetzel, (2001) describes, "*The metabolism of detrital organic matter results in a complex carbon cycle that dominates both the structure and function of lake and river ecosystems*" (pp. 759). Furthermore, DOC can perform a range of functions in aquatic systems which influence the physical and biogeochemical conditions. For instance, humic substances can buffer against acidification or contribute acidity, depending on the ionic strength of the water (Wetzel, 2001) and also play an important role in the transport of metals (Schnitzer & Khan, 1972; Driscoll, *et al*. 1995). DOC can also affect the bioavailability of phosphorus to phytoplankton (Tranvik, 1988). Due to the presence of chromophoric functional groups, DOC influences the physical properties of surface waters through its effect on the light regime (Evans, *et al*. 2012) and consequently, thermocline depth (Pérez-Fuentetaja, *et al*. 1999). DOC also undergoes a number of environmentally significant transformations in aquatic systems. For example, DOC can undergo complexation reactions with inorganic compounds such as chelation (McColl & Pohlman, 1986). DOC also interacts with other organic compounds including forming complexes with enzymes (Münster & De Haan, 1998) and bonding to carbohydrates and proteins to form macromolecular structures (Münster, 1985).

The loss of DOC from freshwater systems occurs *via* a number of routes but can be summarised in terms of conversion to CO_2 or conversion to POC. Losses to the atmosphere as CO_2 include biological routes *via* heterotrophic microbial metabolism and respiration and chemical routes, most notably, photochemical oxidation (Waiser & Robarts, 2004). Alternatively, DOC may be incorporated into POC in the form of microbial biomass or biofilms (Kuserk, *et al*. 1984). However, the tendency of HMW polyphenolic molecules to act as complexing and chelating agents has been found to inhibit biofilm growth by limiting the supply of metal ions (Freeman, *et al*. 1990). DOC is also susceptible to precipitation in the presence of iron and aluminium oxides resulting in its transfer to lake and river sediments (Pokrovsky & Schott, 2002).

1.6. Characterisation of natural organic matter

The important role of DOC in the biogeochemical processes of aquatic systems and its significance in potable water treatment has motivated a substantial amount of research into its molecular structure and physio-chemical properties. However, its heterogeneity and structural complexity has hindered efforts to define the molecular structures of DOC. Instead, various analytical techniques have been used to help define the character and properties of DOC indirectly, advancing, in particular, our understanding of variations in DOC properties with origin and the implications of this for treatability and DBP formation potential. Descriptions of the main characterisation techniques are provided below, in addition to their application in terms of the present research and their limitations.

1.6.1. Fractionation

As described above, membrane filtration can be used to separate NOM into operationally defined size fractions such as DOC (< 0.45 µm) and POC (> 0.45 µm). Early application of the technique provided evidence that NOM is composed of a range of molecular sizes (Aiken, 1984). Subsequently, membrane filtration has been developed into more sophisticated pressure-driven techniques such as ultrafiltration and reverse osmosis which are capable of processing samples more rapidly than conventional techniques (Kitis, *et al*. 2002).

Basic characterisation of DOC according to hydrophobicity/hydrophilicity and acidity/basicity can be achieved by fractionation using Amberlite™ XAD™ resins. The method, which has been developed and adapted by a number of researchers (e.g. Leenheer, 1981; Thurman & Malcolm, 1981; Malcolm

& MacCarthy, 1992; Marhaba, *et al*. 2003) involves the separation of hydrophobic acid/base (HPOA/HPOB; XAD-8 absorbable), hydrophilic acid/base (HPIA/HPOB; XAD-4 absorbable) and hydrophilic neutral (HPIN; neither XAD-8 nor XAD-4 absorbable) fractions within a DOC sample. The acidic/basic partition is achieved by desorption using NaOH and HCl, respectively. By measuring the DOC concentration in each fraction, it is possible to assess the overall character of DOC in the original sample, i.e., the relative contribution of HPOA, HPIA, HPIN, HPOB and HPIB molecules. However it should be noted that these definitions are not absolute but represent qualitative indicators of DOC character since many DOC molecules are amphoteric and amphipathic. Nonetheless, by using standardised procedures, XAD-fractionation can provide a useful estimate of DOC hydrophobicity and allows comparison of DOC character between different source waters (Her, *et al*. 2008). In addition, fractional character is reported to provide an indication of STHMFP; the HPOA fraction is generally associated with the highest STHMFP (Galapate, *et al*. 1999; Chow, *et al*. 2005b; Chow, *et al*. 2006), although exceptions have been observed (Imai, *et al*. 2003; Lu, *et al*. 2009) suggesting that the association may be site specific. Research has also shown that the hydrophilic DOC fraction produces a higher proportion of BrTHMs (Teksoy, *et al*. 2008) and that the HPIN fraction is least amenable to removal by coagulation (Sharp, *et al*. 2006).

The use of high pressure size exclusion chromatography (HPSEC) in the characterisation of DOC is a relatively new application. The technique utilises a column packed with porous beads as the stationary phase, and a liquid phase which is typically phosphate buffered. The apparatus is usually equipped with a UV-vis detector which is typically set to $\lambda = 254$ nm though other types such as fluorescence and organic carbon detectors may also be used (Matilainen, *et al*. 2011). The separation mechanism in HPSEC is based solely on the size of DOC molecules thus, by using calibration standards of known MW, HPSEC can be used to assess the MW distribution (MWD) of DOC. The technique can provide both a qualitative representation of DOC MWD in the form of a chromatogram which can be overlain and compared with other DOC samples, and a quantitative representation of the MWD in the form of MW averages (M_p: peak MW, M_n: number average MW and M_w: weight-average MW). HPSEC has been particularly useful in assessing the removal of different DOC fractions during potable water treatment (Fabris, *et al*. 2008; Zhao, *et al*. 2009). In addition, HPSEC technology has helped to identify an inverse relationship between DOC MW and STHMFP (Oliver & Visser, 1980; Gang, *et al*. 2003) and between DOC MW and its removal efficiency by coagulation (Chow, *et al*. 2008; Korshin, *et al*. 2009).

1.6.2. Optical properties

UV-vis absorption spectroscopy has become another widely used method for characterising DOC with different wavelengths thought to identify different chromophoric functional groups on the DOC molecule. Absorbance at λ = 254 nm has been used as a proxy for DOC concentration (Edzwald, *et al*. 1985). However, this relies on the dominance of aromatic humic substances since this wavelength specifically detects the C=C double bonds associated with condensed aromatic structures. Absorbance at λ = 400 nm has been used as a proxy for the brown colour associated with humic substances (Mitchell & McDonald, 1992).

Specific UV absorbance (SUVA), defined as absorbance at λ = 254 nm (cm^{-1}) * 100/DOC concentration (mg L^{-1}) has been widely used in the study of natural waters with research showing that it provides a qualitative indication of DOC MW, hydrophobicity and % aromaticity (Edzwald & Tobiason, 1999; Weishaar, *et al*. 2003). SUVA has been found to correlate positively with STHMFP (Edzwald, *et al*. 1985). Furthermore, aliphatic DOC, associated with low SUVA values, is reported to form a higher proportion of BrTHMs than aromatic DOC (Heller-Grossman, *et al*. 1993). SUVA can also provide a proxy for DOC treatability since the HMW, aromatic (high SUVA) DOC fraction is reported to be more amenable to removal by coagulation-flocculation than the LMW, aliphatic (low SUVA) DOC (Sharp, *et al*. 2006). Ratios between two different wavelengths (spectral slope ratios) such as E4:E6, E2:E3 and A_{253}:A_{203} have also been used to infer DOC character and origin. For example, E4:E6 (absorbance at λ = 465:665 nm) is reported to be inversely proportional to MW (Chen, *et al*. 1977) and correlates negatively with age or degree of humification (Campbell, *et al*. 1967; Thurman, 1985). E2:E3 (absorbance at λ = 250:365 nm) has been negatively correlated with the aromaticity and MW of aquatic humic substances (Peuravuori & Pihlaja, 1997; Wang, *et al*. 2009). A_{253}:A_{203} (absorbance at λ = 253:203 nm) is reported to correlate with the proportion of hydroxyl-, carboxyl-, ester- and carbonyl-substituted aromatic rings (Korshin, *et al*. 1997) which have been implicated in reactions generating DBPs (Kim & Yu, 2007). Although UV-vis measurements provide only a qualitative indication of DOC character, their low cost and potential for use as proxies for STHMFP and treatability suggest they may have useful application in potable water treatment industry as a monitoring technique.

1.6.3. Fluorescence spectroscopy

Fluorescence spectroscopy represents an emerging technique in the characterisation of DOC, offering enhanced sensitivity relative to UV-vis and the potential for identifying specific structural components of DOC. The technique involves the excitation of molecules within a sample by irradiation and the measurement of emitted radiation at a different wavelength (Matilainen, *et al*. 2011). The intensity of peaks in different regions of the fluorescence excitation-emission matrix (EEM) can indicate the relative abundance of protein-, humic- and fulvic-like components (Coble, 1996; Spencer, *et al*. 2007) and therefore confers information as to the origin of DOC.

1.6.4. Nuclear magnetic resonance

Nuclear magnetic resonance (NMR), both liquid and solid phase, can be used to provide structural information on DOC. ^{1}H NMR for example may provide basic information such as aromaticity and degree of humification (Kim, *et al*. 2006). The chemical shift regions associated with ^{13}C NMR spectra can be assigned to more specific structures such as carboxylic/phenolic moieties (Chen, *et al*. 2002), though for natural samples, the low abundance of ^{13}C can lead to a lack of sensitivity. Practical application of NMR techniques may also be limited by the complexity and heterogeneity of DOC (Matilainen, *et al*. 2011).

1.7. Temporal variation in DOC concentration

In the UK, typical fluvial DOC trends show a peak in late summer/early autumn and a trough in winter/early spring (Dawson, *et al*. 2004; Neal, *et al*. 2005). The DOC peak generally occurs towards the end of the growing season when DOC which has accumulated in the soil matrix under warm aerobic conditions is flushed from the catchment (Hope, *et al*. 1994). A trough in DOC concentration generally occurs after the catchment has been purged of readily leachable DOC and when colder, waterlogged conditions inhibit microbial degradation, which further limits DOC production in the winter months (Halliday, *et al*. 2012). Increases in algal populations in surface waters, which in the UK tends to occur in spring, may also result in seasonal elevations in DOC concentration (Wetzel, 2001).

Antecedent conditions are reported to affect fluvial DOC concentrations. Thus DOC concentrations are reduced following prolonged periods of high rainfall due to the depletion of the terrestrial DOC pool (Tate & Meyer, 1983). Conversely, high DOC concentrations are often observed following periods of dry weather (Edwards, *et al*. 1985; Grieve, 1991; Tipping, *et al*. 1999). This can be explained by reduced microbial utilisation of DOC in dry periods (Lundquist, *et al*. 1999) in addition to the flushing of accumulated DOC following rewetting (Kalbitz, *et al*. 2000).

On shorter timescales, distinctive trends in stream DOC concentration have been observed during rainfall events. Many studies have reported a flushing effect during storm events resulting in a substantial increase in stream DOC concentration during the rising limb of the storm hydrograph and a return to lower concentrations as discharge returns to base flow (Thurman, 1985; Scott, *et al*. 1998). DOC concentrations also show a diurnal pattern, with elevated concentrations reported during daylight hours as a result of increased photosynthetic production and the phototransformation of recalcitrant DOC into more bioavailable forms (Lindell, *et al*. 1996; Parker, *et al*. 2010).

1.8. Spatial variation in DOC concentration

A number of geographical factors are reported to influence surface water DOC concentration including climate, topography, geology, soil type, habitat, hydrology (flow paths/pattern of water storage/residence times (Soulsby, *et al*. 2006)), catchment size (Cohen, 2009; Clair, *et al*. 1994) and anthropogenic influence. Fluvial DOC concentrations are also reported to decrease with increasing stream order (Lock & Ford, 1986). Variations in DOC concentration with climate are controlled principally by primary production and decomposition rates (Meybeck, 1981) and are strongly related to the development of distinct habitat types according to climatic conditions (Thurman, 1985).

Since many of these spatial characteristics are interrelated, understanding their relative importance in affecting surface water quality is complex. However, since soil type integrates a number of these factors, it has been argued that this represents the dominant control on surface water composition and quality (Aitkenhead, *et al*. 1999; Soulsby, *et al*. 2006; Stutter, *et al*. 2006). Furthermore, certain habitats are reported to exert a disproportionately strong influence DOC concentration. For example wetland and forested catchments are often associated with high DOC loading (Hope, *et al*. 1994; Hope, *et al*. 1997; Gergel, *et al*. 1999; Cohen, 2009). High DOC flux from forested catchments is partly due to high DOC loading as rainwater passes through above ground biomass (Stevens, *et al*. 1989; Kawasaki, *et al*. 2005) as well as the large source of leachable carbon in the litter layer (Hongve, 1999). In North Wales, where the present study is focussed, many drinking water catchments include extensive forested areas. Although the concentration and character of DOC in forest floor leachates is understood to vary according to tree species (Hongve, 1999; Pizzeghello, *et al*. 2006; Fröberg, *et al*. 2011), relatively little is known about the effects of different tree species on DOC removal efficiency during coagulation, and THMFP.

DOC concentrations in waters draining wetland habitats are particularly high (*ca.* 25 mg L^{-1} (Thurman, 1985)) and dominated by HMW humic substances (Scott, *et al*. 2001). A combination of high primary productivity and low decomposition rates causes the accumulation of deep layers of peat in wetland environments (Mitsch & Gosselink, 2000). The considerable depth of organic material in such environments provides a large pool of available carbon (Thurman, 1985). In addition, the absence of a mineral layer in many wetland areas, which would normally contribute to DOC adsorption as it passes through the soil profile, also leads to high DOC loading (Tipping, *et al*. 1999). A negative correlation is reported between slope and DOC loading due to its effect on residence times as well as being a predictor of wetland abundance and soil depth (Rasmussen, *et al*. 1989; Clair, *et al*. 1994; Sobek, *et al*. 2007). In the UK many peatland areas were drained during the 20th century for agriculture, forestry and game (Holden, *et al*. 2004). The consequent water table drawdown reportedly led to an increase in DOC concentration in surface waters draining these sites (Clausen, 1980) and in recent years peatland restoration *via* ditch blocking and other techniques is increasingly being considered as a means of improving surface water quality. At present there is a lack of consensus as to the effects of peatland restoration on DOC concentration, with some research reporting a decrease (Wallage, *et al*. 2006; Turner, *et al*. 2013) and others reporting no significant difference or an increase in DOC concentration following ditch blocking (Armstrong, *et al*. 2010; Peacock, 2013). Furthermore, within the existing research there is limited consideration of the effects of ditch blocking on DOC character and in particular, potential changes in THMFP. This is particularly important in North Wales where ditch blocking is being considered as a strategy for mitigating against rising DOC concentrations and controlling THM levels.

1.9. DOC and climate change

1.9.1. Changing DOC concentrations

DOC concentrations have been reported to be increasing in waters draining upland catchments in the UK over the last few decades (Freeman, *et al*. 2001a; Worrall, *et al*. 2003), with similar trends observed in Central and Northern Europe and North America (Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Skjelkvåle, *et al*. 2005; Monteith, *et al*. 2007) (Figure 1.04). In the UK, measurements undertaken at 22 upland sites showed a mean increase in DOC concentration of 91% between 1988 and 2003 (Evans, *et al*. 2005). Various hypotheses have been proposed to explain this phenomenon, many of which relate either directly or indirectly to climate change.

Proposed explanations for increased surface water DOC loading include an enzymatic response to increased drought (Freeman, *et al*. 2001b), changes in hydrological flow paths in response in increased precipitation (Hejzlar, *et al*. 2003; Hongve, *et al*. 2004) and the effect of increased temperature and atmospheric CO_2 concentrations on primary productivity and microbial processing (Evans, *et al*. 2005; Freeman, *et al*. 2004). Land management practices have also been implicated in rising DOC levels, specifically increased peat erosion resulting from controlled moorland burning (Yallop, *et al*. 2010), enhanced aerobic decomposition and solubilisation of DOC resulting from peatland drainage (Holden, *et al*. 2004; Wallage, *et al*. 2006) and the disturbance and change in hydrological regime associated with afforestation (Holden, *et al*. 2007). In addition, increased DOC production has been linked to a soil microbial response to enhanced atmospheric nitrogen deposition (Pregitzer, *et al*. 2004; Findlay, 2005). Alternatively, declining sulphur and sea salt deposition has been linked with rising DOC export. The associated decrease in the acidity and ionic strength of soil water solutions is reported to increase organic matter solubility (Evans, *et al*. 2006; Monteith, *et al*. 2007; Evans, *et al*. 2012).

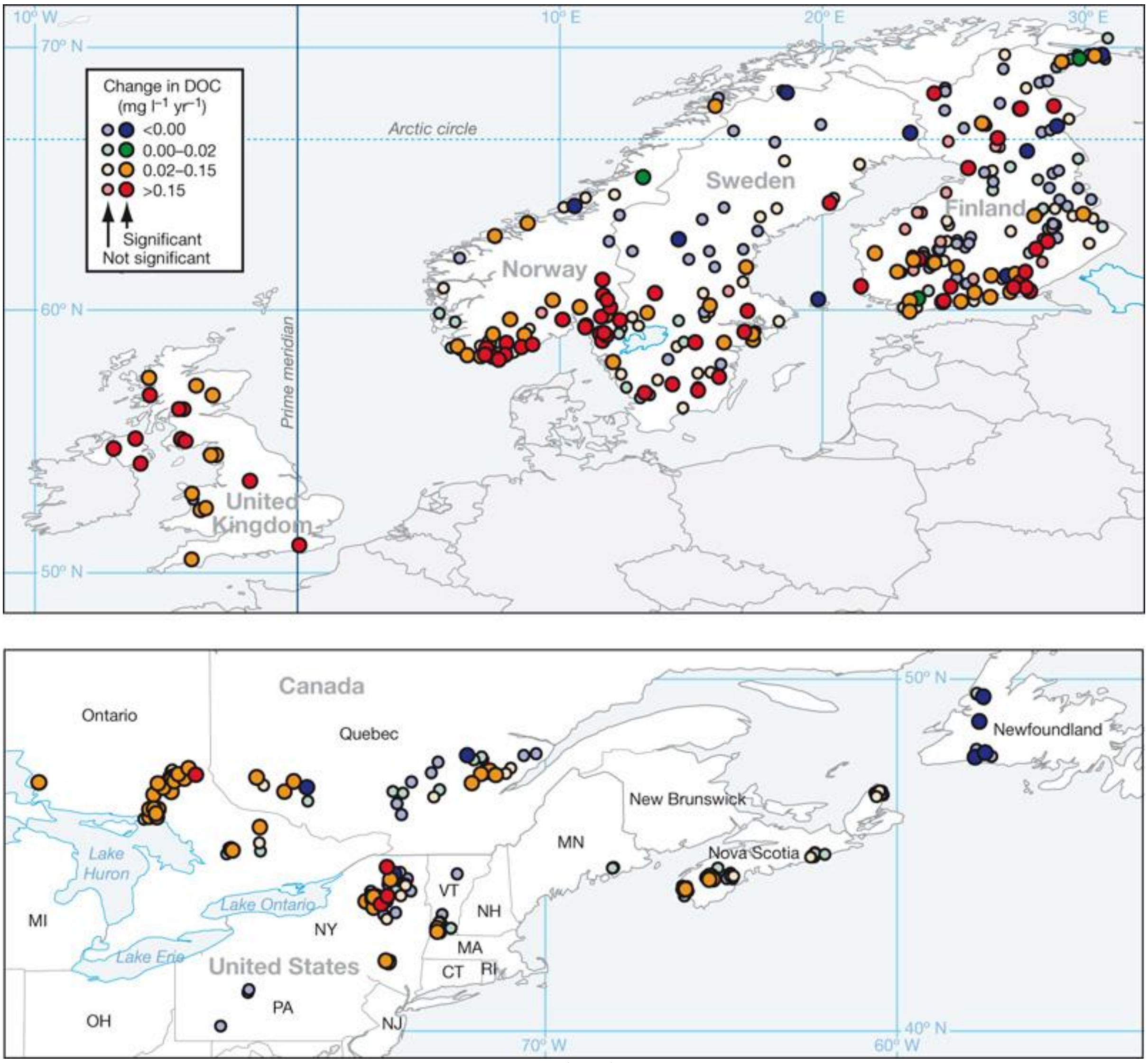

Figure 1.04. Trends in DOC concentration (mg L^{-1} yr^{-1}) observed in Europe (upper pane) and North America (lower pane) for the period 1990-2004 (Monteith, *et al*. 2007).

UK Climate Projections (UKCP09) provides a set of climate change projections for the UK under different greenhouse gas emission scenarios. Under the "*medium emissions*" scenario to the 2080s, an increase in mean daily temperatures, particularly in the summer, is predicted, with the smallest change for Scotland (+ 2.5°C) and the largest increase for southern England (+ 4.2°C). Precipitation is predicted to increase in winter and decrease in the summer. In addition, the severity and frequency of extreme weather events including storm events and drought is predicted to increase (Jenkins, *et al*. 2009).

Higher temperatures are likely to increase DOC production by increasing microbial and invertebrate populations and consequently, the rate of organic matter decomposition in soils (Freeman, *et al*. 2001b; Cole, *et al*. 2002). Longer growing seasons may also increase the supply of DOC by increasing the terrestrial carbon pool (Holden & Adamson, 2002). The supply of DOC from autochthonous sources is also predicted to increase as a result of the higher surface water temperatures and consequent reduced mixing increasing the occurrence and duration of algal blooms (George, *et al*. 2007). Periods of drought are commonly followed by a flush of DOC from the catchment into surface waters when rainfall occurs (Evans, *et al*. 2005). Thus increases in the duration and frequency of droughts may result in more frequent and more pronounced fluctuations in surface water DOC concentrations. UKCP09 projections for the UK indicate a decrease in summer precipitation of up to 40% and an increase in winter precipitation of between 10% and 30% (Jenkins, *et al*. 2009). These changes suggest an increase in the seasonality of DOC export and an increase in the magnitude of the late summer/autumn DOC peak (Ritson, *et al*. 2014).

1.9.2. Changing DOC character

Looking at thermal effects first, increased temperatures are likely to impact on the character of DOC as a result of changes in soil microbial processes. For instance, simulated temperature increase in peat substrates has been found to result in an increase in phenol oxidase activity and hence release of phenolic compounds (Freeman, *et al*. 2001a). Enhanced microbial activity under warmer conditions has also been associated with the production of more degraded hydrophilic DOC (Lumsdon, *et al*. 2005). By contrast, recovery from acidification is predicted to result in an increase in more coloured, hydrophobic DOC as solubility increases (Worrall & Burt, 2010). Thus predicting changes in the character of DOC released from terrestrial sources is complex. An increase in the contribution of proteinateous DOC is expected to result in a shift towards more AOM in surface waters (Ritson, *et al*. 2014).

With regard to rainfall, an increase in the frequency of extreme weather conditions such as drought and rainfall events may result in more dramatic fluctuations in the character of DOC entering water bodies since under drought conditions the ratio of hydrophilic:hydrophobic DOC is reported to increase whilst upon rewetting the ratio decreases as the hydrophobic fraction is solubilised (Scott, *et al*. 1998; Watts, *et al*. 2001). In addition, during storm events, the relative importance of allochthonous inputs, which tend to be dominated by hydrophobic DOC, would be expected to increase, exacerbating the temporal shifts in DOC character.

1.9.3 Implications for potable water treatment

Overall, changes in surface water DOC character in response to climatic forcing are likely to be complex. However, increased seasonality in DOC concentration and character generally suggest that WTWs may need to adopt a more season-specific approach to DOC treatment. Increased short-term fluctuations in DOC character relating to extreme weather events may also require new mitigation strategies. For example, Tang, *et al*. (2012) recommend more frequent jar tests to optimise coagulation conditions particularly during periods of high rainfall following drought. Improved understanding of temporal variability in DOC concentration and character with respect to treatability and THMFP will be crucial to informing mitigation strategies. In addition, understanding the role of individual treatment processes in DOC and THM precursor removal is crucial for optimising THM amelioration. Although coagulation-flocculation is known to be the most effective strategy from removing THM precursors (US EPA, 1999), little is known about the effect of subsequent physical and chemical treatment processes in affecting DOC character and its reactivity with chlorine.

The potential for increasing contributions of algogenic DOC is particularly important since previous studies suggest that algogenic DOC is characterised by LMW (Fang, *et al*. 2010) and comprises a high proportion of HPIN, aliphatic DOC (Her, *et al*. 2004; Leloup, *et al*. 2013), characteristics which tend to confer poor removal efficiency during coagulation (Sharp, *et al*. 2006; Chow, *et al*. 2008; Korshin, *et al*. 2009). Although studies have shown that algogenic DOC tends to be associated with lower STHMFP than DOC of terrigenous origin (Fang, *et al*. 2010), little research has been conducted into DOC reactivity during different growth phases of an algal bloom, during which different types of DOC are reported to be produced (Huang, *et al*. 2009).

1.10. Scope of study

The experimental work presented in this thesis was undertaken at upland drinking water catchments in North Wales and their associated WTWs. Reported increases in DOC concentrations affecting upland areas, and the potential for changes in DOC concentration and character under future climate scenarios are a concern for WTWs in this area, in particular due to the potential for increased THM levels in treated water. This thesis was motivated by the need to better understand the nature and drivers of spatial and temporal variations in DOC concentration and character relating to THMFP and DOC treatability. In addition this project examines the role of potable water treatment processes in THM amelioration. The main aims of this thesis are as follows:

- To examine the effect of habitat type and ditch blocking on DOC concentration and character in order to inform catchment management strategies.
- To assess spatial and temporal variations in DOC concentration and character, and their relationship to catchment characteristics.
- To examine the effect of algal blooms on THMFP and DOC treatability.
- To investigate the role of individual treatment processes in DOC and THM precursor removal.
- To assess the efficacy of different types of coagulant for DOC and THM precursor removal in a high-DOC, upland water source.

1.11. Thesis structure

Chapter 2 investigates potential differences in the concentration and character of leachable carbon in soils derived from different habitat types (beech, spruce, larch and pine forests and blanket peat). XAD-fractionation and THMFP measurements were used to compare DOC treatability and THMFP associated with leachates derived from these different soil types.

Chapter 3 presents the results of a water table manipulation experiment conducted using peat cores collected from two drained peatland sites. Quantification and characterisation of pore water DOC was conducted over a 12 month period to investigate the potential effects of ditch blocking on pore water chemistry including THMFP.

Chapter 4 investigates spatial and temporal variations in DOC concentration and character in fluvial and reservoir samples in two upland drinking water catchments with respect to treatability and THMFP. GIS mapping was used to measure the spatial extent of ecological and pedological features in stream subcatchments and investigate potential relationships between catchment characteristics and surface water quality.

Chapter 5 presents the results of a laboratory based experiment designed to investigate changes in DOC concentration and character over the course of an algal bloom. XAD-fractionation and HPSEC measurements were undertaken to investigate whether algogenic DOC was responsible for seasonal variations in DOC character observed in surface waters from Chapter 4. STHMFP measurements were also undertaken to compare the reactivity of DOC with chlorine during different growth phases of the algal bloom.

Chapter 6 examines the efficiency of DOC and THM precursor removal at an upland WTW employing coagulation-flocculation over a 12 month period. The contribution of individual treatment processes to THM amelioration were assessed and correlations between raw water quality and treatment efficiency investigated.

Chapter 7 presents the results of a bench-scale jar testing experiment designed to examine DOC and THM precursor removal during coagulation-flocculation using 3 commercially available coagulants. XAD-fractionation, HPSEC and THMFP measurements were undertaken on raw and treated water in order to compare the efficacy of each coagulant under optimised conditions for DOC removal.

The chapters in this thesis have been written in the format of research papers. Several have already been submitted to peer-reviewed journals (Chapters 2, 6 and 7). Two have been published (Chapters 2 and 6), with a third having been re-submitted for review following revisions (Chapter 7). The contributions of co-authors are detailed at the beginning of each chapter. As a result of this thesis format, some repetition in the introduction and methods sections between chapters was unavoidable. At the request of the project co-sponsor DCWW, study site locations have been omitted. Details of published and submitted papers are given below.

1.12. Dissemination of research

1.12.1. Published articles

Chapter 2: Gough, R., Holliman, P.J., Willis, N., Jones, T.G. and Freeman, C., 2012. Influence of habitat on the quantity and composition of leachable carbon in the O2 horizon: Potential implications for potable water treatment. *Lake and Reservoir Management,* **28**(4), pp. 282-292.

Chapter 6: Gough, R., Holliman, P.J., Willis, N., and Freeman, C., 2013. Dissolved organic carbon and THM precursor removal at a UK upland water treatment works. *Science of the Total Environment*, **468-469**, pp. 228-239.

Peacock, M., Burden, A., Cooper, M., Dunn, C., Evans, C.D., Fenner, N., Freeman, C., Gough, R., Hughes, D., Hughes, S., Jones, T., Lebron, I., West, M., and Zielinski, P., 2013. Quantifying dissolved organic carbon concentrations in upland catchments using phenolic proxy measurements. *Journal of Hydrology*, **477**, pp. 251-260.

Ritson, J.P., Graham, N.J.D., Templeton, M.R., Clark, J.M., Gough, R., and Freeman, C., 2014. The impact of climate change on the treatability of dissolved organic matter (DOM) in upland water supplies: a UK perspective. *Science of the Total Environment*, **473–474**, pp. 714-730, doi: 10.1016/j.scitotenv.2013.12.095.

1.12.2. Articles re-submitted following revisions

Chapter 7: Gough, R., Holliman, P.J., Heard, T.R., and Freeman, C., 2012. DOC and THMFP removal following coagulation of a typical UK upland water with alum, PAX-18 and PIX-322. *Manuscript submitted for publication*.

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Chapter 2: The influence of habitat on the quantity and composition of leachable carbon in the O2 horizon: Potential implications for potable water treatment

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2.1. Abstract

Organic material leached from the organic (O) horizon of soils is a major source of natural organic matter (NOM) in surface waters. Dissolved organic carbon (DOC) is a known precursor for the formation of disinfection by-products (DBPs) including trihalomethanes (THMs), formed during chlorination. In this study the concentration and composition of leachable O2 horizon DOC from five habitats within a UK upland reservoir catchment (beech, spruce, larch and pine forests and blanket peat) were compared with an emphasis on potential treatment implications. XAD-fractionation and THM formation potential (THMFP) tests were carried out to this end. Statistically significant differences were found between habitats, with pine and larch leachates yielding particularly high DOC concentrations (mean 19.3 and 13.4 mg L^{-1}, respectively) and $THMFP_{7d}$ values (mean 1306 and 1527 µg L^{-1}, respectively). The inter-species variation observed suggests that the typical distinction made between deciduous and coniferous species in previous studies is over-simplistic. Interestingly, peat leachate exhibited a surprisingly low DOC concentration (mean 9.0 mg L^{-1}) suggesting that the high DOC flux associated with these habitats may be the result of other factors such as depth of organic matter and mineral content. Averaged across all habitats, mean standardised THMFP (STHMFP) was highest in the hydrophobic acid (HPOA) fraction, although substantial differences in the relative reactivities of fractions were found between habitats. Synergistic effects are also likely to complicate the relationship between fractional character and STHMFP.

2.2. Introduction

Natural organic matter (NOM) is a ubiquitous constituent of natural surface and ground waters. It is present in dissolved, colloidal and particulate form and is derived from both internal and external sources of biological material including leaf litter and soil humus, terrestrial and aquatic plants, and plankton (Hope, *et al*. 1994). Partially-decomposed organic material in the organic (O) horizon of soils, leached from the substrate during rainfall events, represents a major source of NOM in surface waters (Cronan & Aiken, 1985; Michalzik, *et al*. 2001; Buckingham, *et al*. 2008). Elevated NOM concentrations in raw waters entering treatment works can contribute undesirable taste, colour and odour in potable water and encourage bacterial growth within distribution systems. Furthermore dissolved organic carbon (DOC), operationally defined as NOM which passes through a 0.45 µm filter (Kitis, *et al*. 2001), is widely reported to be the main precursor to potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), formed during the chlorination of natural waters (Rook, 1974; Symons, *et al*. 1975).

These issues are exacerbated by the current trend towards increasing DOC concentrations in freshwaters draining upland catchments in Northern and Western Europe and North America (Bouchard, 1997; Freeman, *et al*. 2001; Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Worrall, *et al*. 2003). Climate change (Forsberg, 1992; Freeman, *et al*. 2004; Worrall, *et al*. 2004; Evans, *et al*. 2005), recovery from acidification (Monteith, *et al*. 2007; Evans, *et al*. 2012) and changes in land use (Wallage, *et al*. 2006) have all been proposed as explanations for this phenomenon. As a result of this deterioration in raw water quality, drinking water companies have been forced to develop mitigation strategies to comply with regulatory limits for THMs and other regulated water quality parameters. Whilst one approach has been to modify or enhance the treatment processes (Keeley, *et al*. 2012), improved catchment management is increasingly being investigated as a means of improving raw water quality before it reaches the treatment plant.

On a continental/global scale, climatic parameters including precipitation and temperature have been identified as crucial determinants of DOC loading to surface waters (Scott, *et al*. 1998). Seasonal variations and sudden weather events are also critical in explaining temporal variations in DOC flux and concentration (McDowell & Likens, 1988; Clark, *et al*. 2007). At a local scale, soil properties including moisture content and pH, and topography affect DOC concentrations due to their impact on decomposition rates/solubility and hydrological regimes, respectively (Andersson, *et al*. 2000; Blodau, *et al*. 2004; Worrall & Burt, 2005).

A number of studies have identified variations in the quantity of DOC leached from different types of habitat. For instance, DOC export from peatland catchments has received substantial coverage in the literature and % wetland coverage in a catchment has been cited as a key parameter affecting DOC export (Creed, *et al*. 2008). In addition, a number of studies have identified the type of forest coverage (e.g. deciduous *versus* coniferous) as an influence on DOC composition and quantity. Leaching of DOC from deciduous leaf litter has been proposed as an explanation for seasonality in DOC concentration in discharge from forested catchments (Hongve, 1999). Modelled annual DOC flux, calculated from soil solution DOC concentrations, has also been shown to vary between soils derived from different tree species, with Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) stands associated with a higher flux (38 g m^{-2} y^{-1} and 37 g m^{-2} y^{-1}, respectively) than birch (*Betula pendula/Betula pubescens*) (21 g m^{-2} y^{-1}) (Fröberg, *et al*. 2011). Chow, *et al.* (2009) also report differences in DOC flux and standardised THM formation potential (STHMFP) between Live oak (*Quercus wislizenii*), Blue oak (*Quercus douglasii*), Foothill pine (*Pinus sabiniana*) and annual grass leachates. Studies have explored differences in UV absorbance indices and proportions of compound classes in DOC derived from different tree species stands (Park, *et al*. 2002; Pizzeghello, *et al*. 2006;

Fröberg, *et al*. 2011). However only a limited number of studies have employed more exploratory methods of DOC characterisation such as XAD-fractionation in this context (Kaiser, *et al*. 2001) and a detailed understanding of DOC differences between tree species remains absent from the literature.

DOC can be partitioned according to polarity and acidity/basicity using macroporous DAX-8™ and XAD-4™ resins (Thurman & Malcolm, 1981; Marhaba, *et al*. 2003) typically into five fractions: Hydrophobic acids (HPOA), hydrophobic bases (HPOB), hydrophilic acids (HPIA), hydrophilic bases (HPIB) and hydrophilic neutrals (HPIN). Importantly, the relative proportions of these different fractions are thought to provide a useful indication of DOC treatability since the coagulation stage of the treatment process preferentially removes the high molecular weight (HMW) humic and fulvic acids which constitute the HPOA DOC fraction (Krasner & Amy, 1995). In the context of rising DOC concentrations, and given the growing emphasis in the water treatment industry on catchment management approaches, greater knowledge of the characteristics and treatability of DOC derived from different tree species may prove valuable for decision makers. Hence, this study was designed to evaluate variations in the composition and quantity of leachable DOC in soils derived from different types of habitat within an upland catchment. The influence of four different tree species, as well as blanket peat, was investigated. In particular, this study focused on a comparison of DOC characteristics relating to treatability and DBP formation using fractionation and chlorination procedures, respectively. By selecting sites within a single catchment, variations in leachable carbon characteristics relating to climatic factors were controlled for. The standardised method of DOC extraction employed is a departure from lysimeter-based experiments published previously (Hongve, 1999; Kaiser, *et al*. 2001; Fröberg, *et al*. 2011) and is designed to enable a direct comparison of leachable carbon between habitat types.

2.3. Study site

Soil samples were collected from the catchment of an upland reservoir (name withheld for reasons of security) which covers an area of 24.8 km^2. Mean annual air temperature is 8.6°C and mean annual precipitation 1.434 m (1961-1990, UKPC Met Office gridded climate data). Thirty-eight to forty ML of water is abstracted daily from the 1.5 km^2 reservoir for drinking water treatment. DOC removal is achieved by coagulation ($Al_2(SO_4)_3$) and flocculation followed by dissolved air floatation (DAF) for clarification and filtration using rapid gravity sand filters (RGF). The parent material in the catchment is Denbigh Grits and Devensian Till deposits. Afforestation of the catchment has taken place since the 1950s with woodland plantations now covering 30% of the catchment and flanking most of the perimeter of the reservoir. Of the afforested area, monospecific stands of Sitka (*Picea* *sitchensis*) and Norway spruce (*Picea abies*) account for approximately 85%, Scots pine (*Pinus sylvestris*) 8%, Japanese larch (*Larix kaempferi*) 5% and European beech (*Fagus sylvatica*) 2%. The remainder of the catchment comprises grassland (38%) and peatland (32%) habitat (Cohen, 2009). The experimental design included stands of four different tree species (European beech, Norway spruce, Japanese larch and Scots pine) and an area of blanket peat. The blanket peat habitat is dominated by *Sphagnum* with some *Calluna vulgaris* and *Eriophorum*. Soils in the four afforested habitats were classified as seasonally wet loam with peaty surface, according to the national survey of soil types within England and Wales (NSRI, 2005). Typical abstracted reservoir water quality comprises low turbidity (0.6-0.9 NTU), high colour (80-120 Hazen), relatively high DOC content (8-14 mg L^{-1}) and slight acidity (pH 5.5-6.5).

2.4. Materials and methods

Samples were collected in October 2011 from the five contrasting vegetative environments. Leaf litter (or sphagnum in the case of peat samples) was removed by hand and 10 cm-deep cores of substrate extracted using 10 cm diameter plastic tubing. Five replicate cores were collected along a 15 m transect at each location. Samples were transported to the laboratory and stored at 4°C until analysis.

The quantity of water-extractable (leachable) carbon in each of the five soils was assessed according to a method adapted from Jones, (2006). All cores except beech were comprised entirely of O2 horizon material (Table 2.01). For the beech cores the O2 horizon was retained and the remainder of the core discarded. Each core was then homogenised by hand and any coarse material removed. A 10 cm^3 subsample of O2 horizon material was placed in a stomacher bag with 90 mL of Milli Q water before being homogenised for 1 min using a Seward Stomacher 80 Laboratory Blender. The solution was then centrifuged at 10,000 RPM for 5 min in a Beckman Coulter Avanti J-26 XP centrifuge to separate particulate matter from the supernatant. Finally the solution was filtered through a 0.45 µm nylon membrane (Whatman). Five subsamples were taken from each core and the leachates combined in order to obtain a sufficient volume of sample to perform the analyses. DOC concentration was determined using a Thermalox TOC/TN analyser (Analytical Sciences Ltd) equipped with a non-dispersive infrared CO_2 detector. pH was measured for each of the leachate samples (5 per habitat). Phenolics concentration was determined using a version of the spectraphotometric method developed by Box, (1983), adapted for 0.3 mL micro-plate wells. Absorbance at $\lambda = 400$ nm (used as a proxy for colour (Mitchell & McDonald, 1992)) and specific UV absorbance at $\lambda = 254$ nm (SUVA) were also determined for each sample. The latter index is calculated by dividing the absorbance at λ = 254 nm by DOC concentration (mg L^{-1}) and multiplying by 100. A positive relationship is thought to exist between SUVA and DOC hydrophobicity and MW (Edzwald & Tobiason, 1999). SUVA has also been found to correlate strongly with DOC % aromaticity (Weishaar, *et al*. 2003). Finally, the profile of THM formation following chlorination of the samples was measured over a 7 d period and the samples fractionated using macroporous resins.

2.4.1. Trihalomethane formation potential

THMFP analyses were conducted on composite samples, made by combining equal volumes of the five replicate leachates obtained for each habitat. $THMFP_{7d}$ represents the quantity of THMs formed (µg L^{-1}) after chlorination of a water sample over a 7 d incubation period. The method used was adapted from the Standing Committee of Analysts, (1981) procedure. In this study samples were diluted to 1 mg L^{-1} DOC in order to derive a standardised $THMFP_{7d}$ value ($STHMFP_{7d}$) which provides a measure of DOC reactivity. A $THMFP_{7d}$ value was then calculated by multiplying $STHMFP_{7d}$ by DOC concentration. It should be noted that this chlorine dose is substantially higher than that applied at water treatment works and may encourage the formation of chlorinated THMs over brominated species. 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5M $KH_2PO_{4(aq)}$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $NaOCl_{(aq)}$ to provide 5 mg of free Cl per mg of DOC. After 7 d incubation in the dark at 25°C, the reaction was quenched using 0.4 mL of 0.8M $Na_2SO_{3(aq)}$. Extraction of the four chlorinated and brominated THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) was achieved using direct immersion SPME (DI-SPME) followed by quantification using a Varian 450 GC coupled with an electron capture detector. In addition to the standard 7 d THMFP analysis, THM concentrations were also measured at 1 h, 1 d and 3 d in order to profile the formation of THMs over time.

2.4.2. XAD-fractionation

Fractionation of DOC was achieved by resin adsorption using a method adapted from Thurman & Malcolm, (1981) and Marhaba, *et al*. (2003). Samples were separated into five fractions: hydrophobic acids (HPOA), hydrophobic bases (HPOB), hydrophilic acids (HPIA), hydrophilic bases (HPIB) and hydrophilic neutrals (HPIN) according to their adsorption onto a series of macroporous resins. A column packed with Superlite™ DAX-8™ resin and a second packed with Amberlite™ XAD-4™ resin (both Supelco) were connected in series using PEEK™ tubing. Water samples (1 L) were pumped through the system, loading DOC fractions sequentially onto the resins using a Cecil 1100 Series liquid chromatography pump (4 mL min^{-1}) and the effluent (HPIN) fraction collected. The HPOA fraction was then eluted by passing 60 mL of 0.1M NaOH through the DAX-8 column followed by 40 mL of Milli Q water, (both at 2 mL min^{-1}). This was repeated for the XAD-4 column to obtain the HPIA fraction. The HPOB fraction was eluted by passing 60 mL of 0.1M HCl through the DAX-8 column followed by 40 mL of Milli Q water, (both at 2 mL min^{-1}). The HPIB fraction was obtained by repeating this process with the XAD-4 column. As was for the THMFP analyses, fractionation was carried out on composite samples.

2.4.3. Statistical analysis

Where conditions were satisfied by the data, Analysis of Variance (ANOVA) and Kruskal-Wallis tests were performed to investigate differences in water quality parameters between habitat types (beech, spruce, larch, pine and peat) and between different fractions. The HPOB and HPIB fractions were omitted from these analyses since their concentrations were consistently below the limit of quantification (LOQ). Where significant results for ANOVA and Kruskal-Wallis tests were found, Tukey HSD and Nemenyi post-hoc tests, respectively, were carried out in order to identify where the differences between groups lay. The F-ratio, degrees of freedom (in parentheses) and significance (p) are reported for ANOVA analyses. For Kruskal-Wallis analyses the test statistic (H), degrees of freedom and significance are reported. In this case the Monte Carlo significance value is used due to small sample sizes. Significance level (< 0.01/< 0.05) is reported for post-hoc tests. Statistical analysis was carried out using version 18 of the SPSS Statistics package (PASW).

2.5. Results

2.5.1. Influence of habitat coverage

Mean leachate DOC concentration ranged from 7.3 mg L^{-1} in the spruce leachate to 19.3 mg L^{-1} in the pine leachate (Table 2.01). One-way ANOVA revealed that DOC concentration differed significantly as a function of habitat, F (4,20) = 21.6, $p = 0.000$. Post-hoc comparisons using the Tukey HSD test indicated that pine leachate had significantly higher DOC concentration than the other four groups ($p < 0.01$). The DOC concentration for larch leachate was significantly higher than spruce ($p < 0.01$) and significantly higher than beech ($p < 0.05$). All other comparisons were not significant ($p < 0.05$) (Table 2.01).

Mean phenolics concentration per mg DOC was highest in the larch leachate (0.124 mg phen. mg DOC^{-1}) and lowest in the beech leachate (0.072 mg phen. mg DOC^{-1}) (Table 2.01). A Kruskal-Wallis analysis revealed that phenolics per mg DOC did not vary significantly as a function of habitat type, H (4) = 7.8, $p = 0.1$.

Mean SUVA values showed a considerable range from 1.2 L mg^{-1} m^{-1} in the larch leachate to 7.0 L mg^{-1} m^{-1} in the spruce leachate (Table 2.01). A Kruskal-Wallis analysis revealed that SUVA differed significantly as a function of habitat, H (4) = 21.1, p = 0.000. Post-hoc comparisons using the Nemenyi test show that spruce, which had the highest mean SUVA value differed significantly from all groups (all $p < 0.01$) except peat. The larch leachate mean SUVA value was significantly lower than beech, spruce and peat (all $p < 0.01$). All other comparisons were not significant ($p < 0.05$) (Table 2.01).

Table 2.01. Results of leachate DOC quantity and composition analyses of beech, spruce, larch, pine and peat samples showing statistically significant differences identified by ANOVA and Kruskal-Wallis analysis.

	Beech (a)	**Spruce (b)**	**Larch (c)**	**Pine (d)**	**Peat (e)**
O2 horizon depth (cm)	9.8 ± 0.7	39.2 ± 1.2	32.8 ± 1.0	38.8 ± 1.6	> 300
DOC concentration (mg L^{-1})	8.1 ± 0.55 cd	7.3 ± 1.3 cd	13.4 ± 1.0 abd	19.3 ± 1.5 abce	9.0 ± 0.83 d
pH (SU)	6.1 ± 0.23	4.5 ± 0.51	5.1 ± 0.38	4.7 ± 0.13	6.0 ± 0.12
Phenolics (mg phen. mg DOC^{-1})	0.072 ± 0.011	0.098 ± 0.022	0.124 ± 0.007	0.115 ± 0.008	0.119 ± 0.004
SUVA (L mg^{-1} m^{-1})	2.8 ± 0.12 bc	7.0 ± 0.99 acd	1.2 ± 0.36 abe	2.4 ± 0.19 b	3.3 ± 0.17 c
Colour (Abs_{400}) (UV a.u.)	0.039 ± 0.003 b	0.060 ± 0.006 ac	0.023 ± 0.008 bde	0.051 ± 0.005 c	0.049 ± 0.005 c

Results given as mean ± standard error (n = 5). Letter annotations denote significantly different means ($p < 0.05$). e.g. beech (a) has a significantly different DOC concentration to larch and pine, but not to spruce and peat.

Mean colour, indicated by absorbance at λ = 400 nm, ranged from 0.023 UV a.u. in the larch leachate to 0.060 UV a.u. in the spruce leachate (Table 2.01). A Kruskal-Wallis analysis revealed that colour differed significantly as a function of habitat, H (4) = 13.8, p = 0.008. Post-hoc comparisons using the Nemenyi test identified a number of significant differences. Beech leachate showed significantly lower colour than spruce ($p < 0.01$), and larch had significantly lower colour than spruce, pine and peat (all $p < 0.01$). All other comparisons were not significant ($p < 0.05$) (Table 2.01).

STHMFP was measured at intervals over a 7 d period for each habitat type (Figure 2.01). For all measurements $CHCl_3$ accounted for > 95% of total measured THMs. All samples showed a rapid initial rate of THM formation in the early stages of the reaction which gradually slowed over the 7 d incubation period. Larch showed the highest $STHMFP_{3d}$ and $STHMFP_{7d}$ (84 and 114 µg THM mg DOC^{-1}, respectively). THM formation in the peat and spruce leachates followed a similar profile throughout with an $STHMFP_{7d}$ of 87 and 85 µg THM mg DOC^{-1}, respectively. Beech and pine exhibited the lowest reaction rates and $STHMFP_{7d}$ with 75 and 68 µg THM mg DOC^{-1}, respectively.

THMFP (Figure 2.02) was also calculated by multiplying STHMFP (Figure 2.01) by DOC concentration. For this parameter also, larch showed the highest $THMFP_{3d}$ and $THMFP_{7d}$ (1118 and 1527 µg L^{-1}, respectively). Pine exhibited the second highest $THMFP_{3d}$ and $THMFP_{7d}$ (828 and 1306 µg L^{-1}, respectively) followed, after some margin by peat (626 and 778 µg L^{-1} for $THMFP_{3d}$ and $THMFP_{7d}$, respectively) and finally spruce and beech which showed very similar $THMFP_{7d}$ values (622 and 609 µg L^{-1}, respectively).

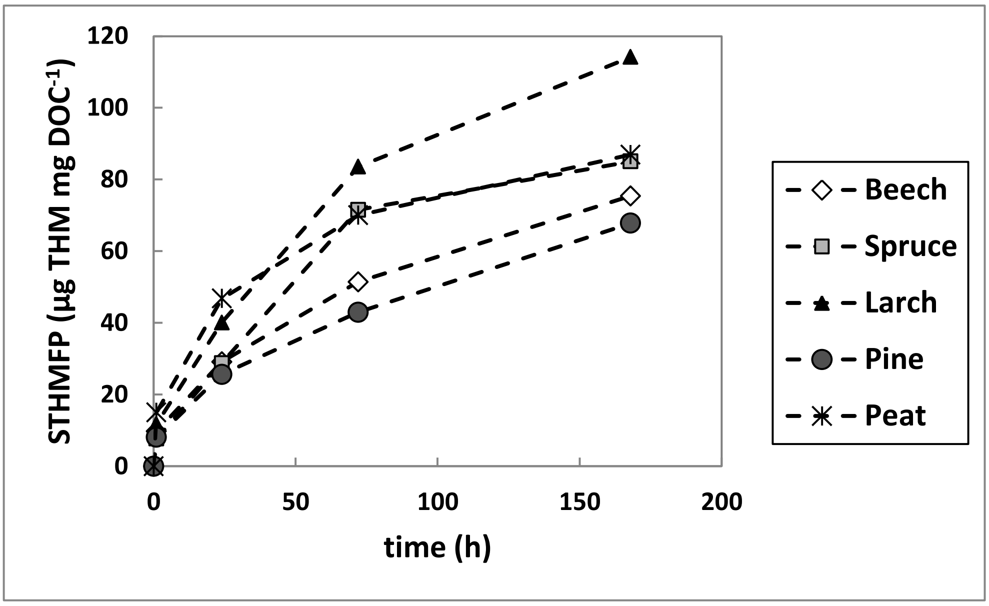

Figure 2.01. Profile of STHMFP over a 7 d incubation period following chlorination of beech, spruce, larch, pine and peat leachates.

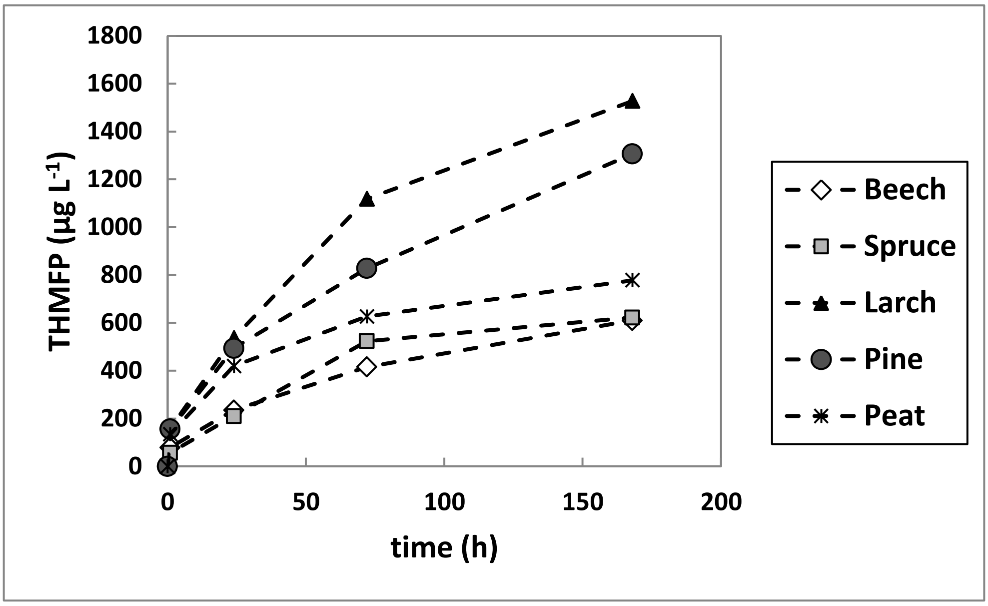

Figure 2.02. Profile of THMFP over a 7 d incubation period following chlorination of beech, spruce, larch, pine and peat leachates.

2.5.2. Fractional character

For all soil types, the basic fractions (HPIB and HPOB) showed minimal contribution to the total recovered DOC and were consistently below the LOQ for DOC concentration (Figure 2.03). With the exception of spruce, HPOA was the dominant DOC fraction across the samples in percentage terms. Larch exhibited the highest HPOA fraction (50% of total DOC) followed by peat, pine, beech and finally spruce with 38%. The HPIA and HPIN fractions represented the remainder of the DOC. Their relative proportions were variable across the habitat types.

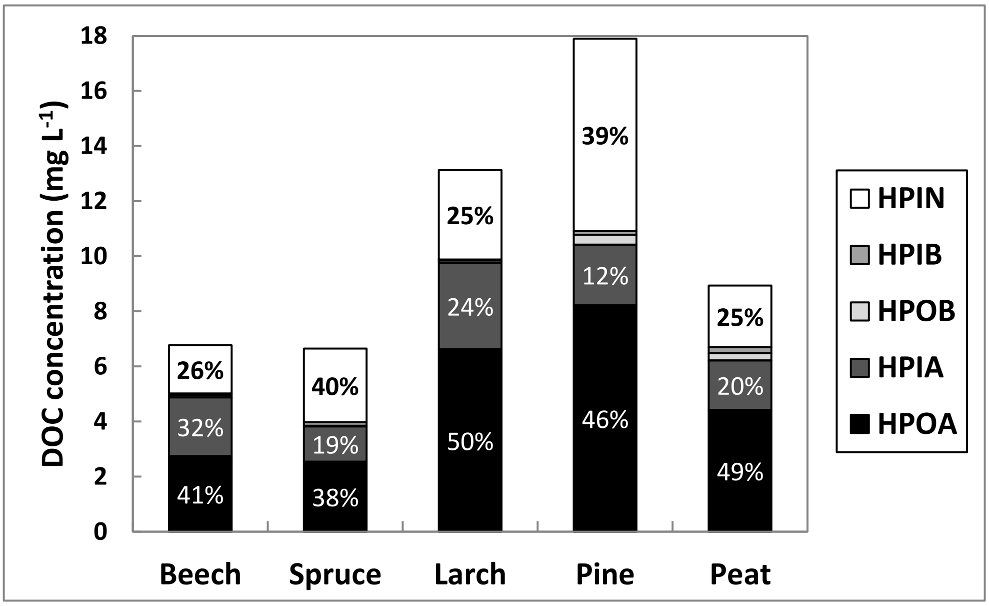

Figure 2.03. % contributions of HPIN, HPIB, HPIA, HPOB and HPOA fractions to total recovered DOC following fractionation.

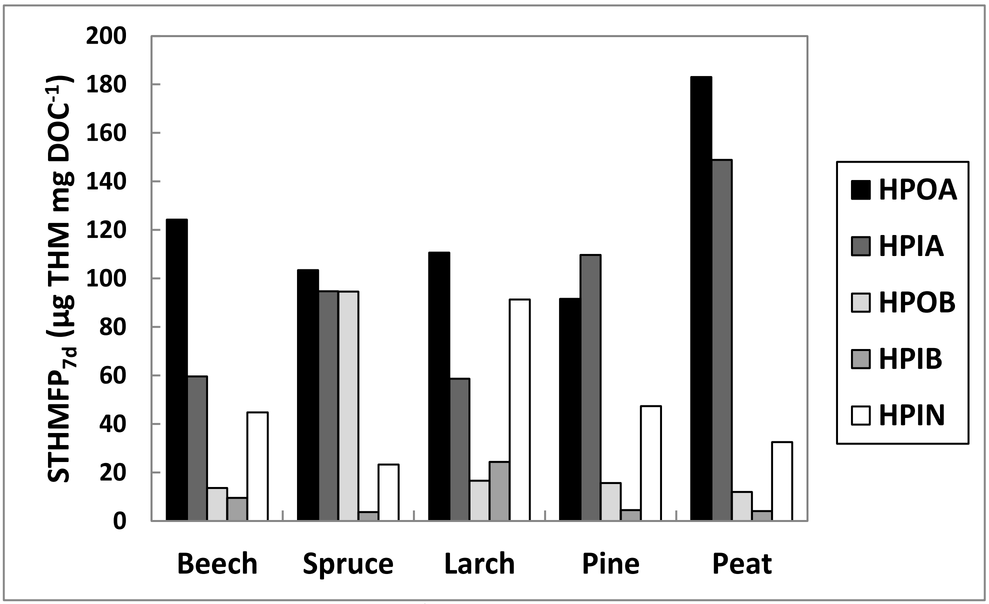

Figure 2.04. STHMFP$_{7d}$ (µg THM mg DOC^{-1}) of individual fractions (HPIN, HPIB, HPIA, HPOA and HPOB) associated with beech, spruce, larch, pine and peat leachates.

$STHMFP_{7d}$ was calculated for each of the five fractions derived from each habitat type (Figure 2.04). These data were averaged to derive mean $STHMFP_{7d}$ values for each DOC fraction (Figure 2.05). For all measurements $CHCl_3$ accounted for > 95% of total measured THMs. Mean $STHMFP_{7d}$ ranged from 48 µg THM mg DOC^{-1} in the HPIN fraction to 123 µg THM mg DOC^{-1} in the HPOA fraction. One-way ANOVA revealed that $STHMFP_{7d}$ differed significantly as a function of DOC fraction, *F* (2,12) = 6.3, *p* = 0.013. Post-hoc comparisons using the Tukey HSD test indicated that the HPOA fraction had significantly higher $STHMFP_{7d}$ than the HPIN fraction (*p* < 0.05). The HPIA fraction, which had an intermediate mean $STHMFP_{7d}$, did not differ significantly from the other two fractions (*p* < 0.05) (Table 2.02).

Table 2.02. Results of DOC composition analyses for HPIN, HPOA and HPIA fractions showing statistically significant differences identified by ANOVA and Kruskal-Wallis analyses.

	HPIN (a)	**HPOA (b)**	**HPIA (c)**
$STHMFP_{7d}$ (µg THM/mg DOC)	48 ± 12 b	123 ± 16 a	94 ± 17
$THMFP_{7d}$ (µg/L)	168 ± 60 b	642 ± 85 ac	188 ± 29 b
Colour (Abs_{400}) (UV a.u.)	0.011 ± 0.005	0.024 ± 0.005 c	0.004 ± 0.001 b

Results given as mean ± standard error (*n* = 5). Letter annotations denote significantly different means (p < 0.05).

These $STHMFP_{7d}$ data were multiplied with DOC concentration to derive $THMFP_{7d}$ for each of the five fractions (Figure 2.06). The HPOA fraction consistently contributed the highest $THMFP_{7d}$ of all the fractions. $THMFP_{7d}$ ranged from 168 µg L^{-1} in the HPIN fraction to 642 µg L^{-1} in the HPOA fraction (Figure 2.06). Kruskal-Wallis analysis showed that $THMFP_{7d}$ differed significantly as a function of DOC fraction, *H* (2) = 12.0, *p* = 0.009. Post-hoc comparisons using the Nemenyi test showed that the mean $THMFP_{7d}$ concentration in the HPOA fraction differed significantly from both the HPIA and HPIN fractions (both *p* < 0.01) but that the HPIA/HPIN comparison was not significant (*p* < 0.05) (Table 2.02).

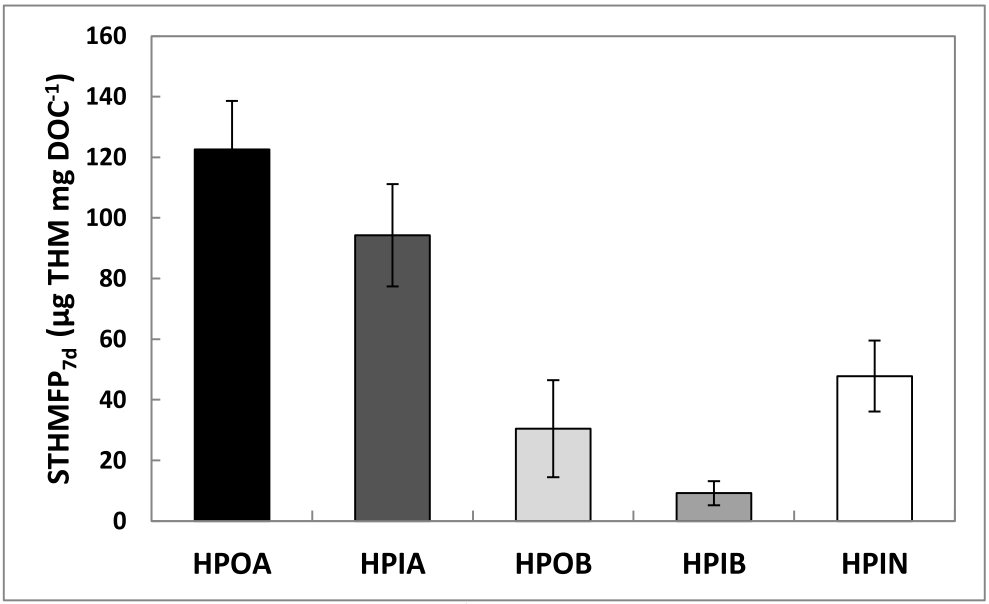

Figure 2.05. Mean STHMFP$_{7d}$ (µg THM mg DOC^{-1}) associated with HPIN, HPIB, HPIA, HPOA and HPOB fractions from the soil leachates. Error bars represent the standard error of the mean, (*n* = 5).

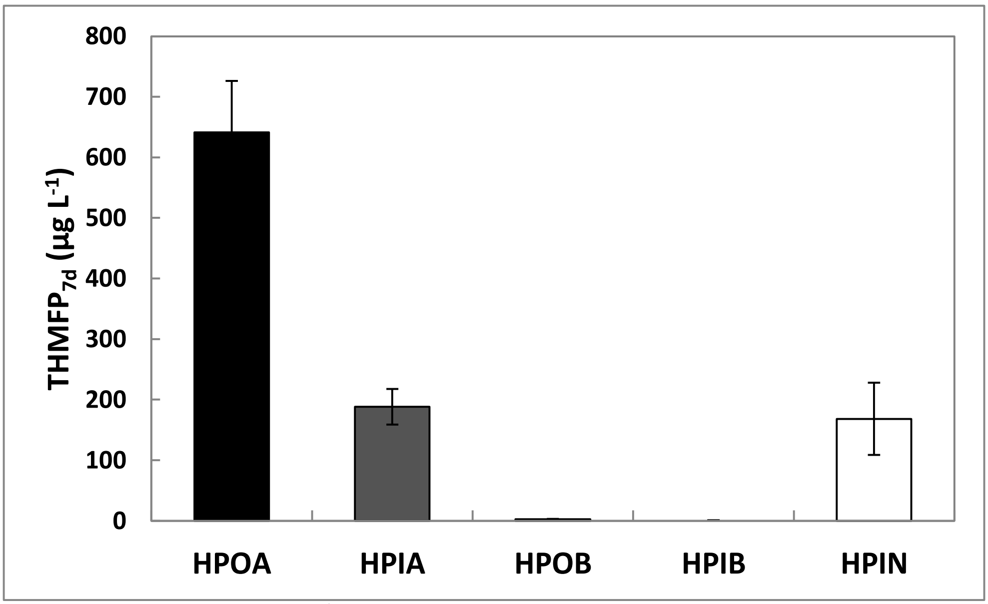

Figure 2.06. Mean THMFP$_{7d}$ (µg L^{-1}) associated with HPIN, HPIB, HPIA, HPOA and HPOB fractions from the soil leachates. Error bars represent the standard error of the mean, (*n* = 5).

Mean colour, (absorbance at λ = 400 nm), ranged from 0.004 UV a.u. in the HPIA fraction to 0.024 UV a.u. in the HPOA fraction (Table 2.02). A Kruskal-Wallis analysis revealed that colour differed significantly as a function of DOC fraction, *H* (2) = 9.3, *p* = 0.01. Post-hoc comparisons using the Nemenyi test indicated that the mean colour for the HPOA fraction differed significantly from the HPIA fraction ($p < 0.01$). All other comparisons were not significant ($p < 0.05$) (Table 2.02).

2.6. Discussion

2.6.1. DOC

These results indicate that DOC concentration varies significantly as a function of forest type with pine (mean 19.3 mg L^{-1}) exhibiting significantly higher DOC concentration than the remaining groups and larch (mean 13.4 mg L^{-1}) significantly higher than spruce (mean 7.3 mg L^{-1}) and beech (mean 8.1 mg L^{-1}). A number of studies have identified differences in the DOC concentration of forest leachates between deciduous and coniferous types (Kaiser, *et al*. 2001; Pizzeghello, *et al*. 2006; Fröberg, *et al*. 2011) with coniferous soils associated with highest DOC concentrations. Recently, Fröberg, *et al.* (2011) identified significantly higher fluxes of DOC in spruce and pine stands compared with birch stands in Sweden. Lindroos, *et al*. (2011) also reported significantly higher DOC concentrations in pine leachates compared with birch leachates, with an intermediate concentration obtained for spruce. This present study supports the view that pine soils are responsible for high DOC loading of leached water but suggests that larch soils may also be associated with large quantities of leachable carbon. Larch leachate was associated with particularly low SUVA (mean 1.2 L mg^{-1} m^{-1}) suggesting that a high concentration of fresh DOC from litter was present (Beggs & Summers, 2011). This can be explained by the timing of sampling during the litter-fall period. Our data also highlight the presence of between-species variations within the broader category of coniferous forest since the DOC concentrations for each of the three coniferous species were significantly different (pine > larch > spruce). By comparing sites within the same catchment, and therefore minimising variations in soil characteristics resulting from climatic conditions, this study also provides a useful comparison of peatland *versus* forest coverage in terms of its influence on DOC quantity and composition. DOC in peat leachate was of an intermediate concentration (mean 9.0 mg L^{-1}) compared to the other habitats and was significantly lower than pine (mean 19.3 mg L^{-1}). Previous studies have cited peatlands as accounting for significantly higher DOC export than forest soils (Aitkenhead & McDowell, 2000; Clark, *et al*. 2008). The results of this present study suggest that higher DOC fluxes from peatlands may not be the result of higher concentrations of potentially-mobile organic matter within the O2 horizon. Instead factors such as greater depth of organic matter and the absence of a mineral layer which may partition DOC during its passage through the soil profile may account for this difference (Tipping, *et al*. 1999).

2.6.2. Trihalomethane formation potential

The main objective of this study was to compare leachable DOC composition and quantity between habitats in terms of likely treatability and its propensity to form THMs. It is known that different natural waters vary significantly in terms of STHMFP (Gallard & von Gunten, 2002). Studies have also shown that significant differences in STHMFP occur between leachates derived from different habitats (Chow, *et al*. 2009). However, relatively few studies have examined differences between coniferous species and variations between forested and peat-covered catchments in this respect. STHMFP analyses showed that larch leachate contained the most THM precursors per mg of DOC ($STHMFP_{7d}$: 114 µg THM mg DOC^{-1}) whilst XAD-fractionation revealed that larch leachate also had the highest HPOA fraction (50% of DOC), generally considered to be the fraction with the highest STHMFP (Chow, *et al*. 2005; Zhang, *et al*. 2009). In addition, mean phenolic concentration per mg of DOC was highest in the larch leachate (0.124 mg phen. mg DOC^{-1}), although no statistical difference in phenolic content was found between habitats. Model compound studies have shown that phenolic structures may be responsible for THM formation upon chlorination (Norwood, *et al*. 1980). However, a lack of consensus remains regarding the potential relationship between the phenolic content of DOC and STHMFP.

In general, the $STHMFP_{7d}$ of the soil leachates (Figure 2.01) did not mirror their respective proportions of HPOA DOC (Figure 2.03). This is perhaps unsurprising given the variability in the relative reactivities ($STHMFP_{7d}$) of fractions observed between the different soils (Figure 2.04). No relationship was found between SUVA and $STHMFP_{7d}$. This supports the findings of a study by Weishaar, *et al*. (2003) which concludes that, although a useful indicator of DOC aromaticity, SUVA does not provide an indication of the relative reactivity (STHMFP) of DOC from different sources. However, a direct evaluation of actual THM yield was derived by multiplying $STHMFP_{7d}$ by DOC concentration from different leachates to give a $THMFP_{7d}$ value. Larch and pine showed relatively high $THMFP_{7d}$ values (mean 1527 and 1306 µg L^{-1}, respectively), largely reflecting their high DOC concentrations. Conversely peat, spruce and beech produced relatively lower $THMFP_{7d}$ values (mean 778, 622 and 609 µg L^{-1}, respectively). These $THMFP_{7d}$ values are likely to be substantially higher than the THM concentrations observed in drinking water since the residence time of water in distribution systems is likely to be significantly less than the 7 d incubation period used here.

2.6.3. Fractional character

Relatively few studies have explored differences in the fractional character of DOC from different tree species beyond the coniferous/deciduous distinction. Hongve, (1999) found that lysimeter leachates from coniferous (Norway spruce) soil cores contained a higher proportion of HPOA DOC than deciduous (mixed-species) cores. Kaiser, *et al*. (2001) reported higher proportions of HPOA in pine leachates compared with beech, as well as variations in the relative proportions of DOC fractions seasonally for both species. The study reported highest HPOA proportions in the three-month period June-August, corresponding with the growing season. HPOA concentrations were also high for the September-November period which corresponds to the litter-fall period. Increased concentrations of HPIA DOC have been associated with changes in environmental conditions such as warming, drying or freezing (Christ & David, 1996; Tipping, *et al*. 1999). This supports the observation of relatively higher proportions of HPIA DOC in spring and winter (Kaiser, *et al*. 2001). The higher proportions of HPOA DOC in the larch and peat leachates (50% and 49%, respectively) observed in this study could be explained by the addition of dead litter material to the system during the autumn months when sampling took place. However this does not explain the relatively high proportion of HPOA DOC in the pine sample (46%), and the relatively low HPOA proportion in the beech sample (41%). These findings do however indicate that a simple distinction between coniferous and deciduous forests in terms of their DOC-forming processes may be over-simplified, and that differences between individual species of conifers should also be considered in the examination of the fractional character of soil leachates. Future work should also consider the seasonality of DOC production and flux which will necessarily vary between species. It should also be noted that seasonal changes in flow paths will affect downstream DOC composition and quantity (Kraus & Anderson, 2010).

Previous studies have identified differences in the reactivity (STHMFP) of XAD-derived DOC fractions. The highly charged, HMW HPOA fraction has been reported as having the highest STHMFP (Galapate, *et al*. 1999; Chow, *et al*. 2005; Chow, *et al*. 2006; Zhang, *et al*. 2009) although exceptions have been observed. Imai, *et al*. (2003) for example report comparable reactivities for what they term aquatic humic substances (equivalent to HPOA) and hydrophilic fractions (equivalent to HPIA, HPIN and HPIB combined) from a shallow eutrophic lake, with 0.176 and 0.195 µmol THM mg C^{-1}, respectively. Lu, *et al*. (2009) report higher $STHMFP_{48h}$ in the HPIA fraction (~150 µg mg C^{-1}) than the HPOA fraction (~130 µg mg C^{-1}) of river water DOC. Averaged across all DOC sources, the present study identified the following order in $STHMFP_{7d}$: HPOA > HPIA > HPIN (Figure 2.05) with the HPOA/HPIN comparison statistically significantly ($p < 0.05$) (Table 2.02). However substantial variations in the relative reactivities of DOC fractions were observed between different habitats (Figure 2.04) suggesting biological origin may be an important factor influencing fraction $STHMFP_{7d}$. Also, considerable disparities were observed between leachate $STHMFP_{7d}$ (Figure 2.02) and the total $STHMFP_{7d}$ calculated by addition of their individual fractions (Figure 2.04). This suggests that synergistic effects further complicate the relationship between fractional character and STHMFP.

Colour was found to vary significantly as a function of DOC fraction with the HPOA fraction associated with the highest colour (0.024 UV a.u.). This is consistent with the findings of previous studies (Oliver, *et al*. 1983; Thurman, 1985). Given this characteristic distinction, these data suggest that monitoring of intake water colour (standardised for DOC concentration) could provide a practical means of detecting changes in the fractional character of the DOC which may impact upon the coagulation process.

The ability of conventional coagulation methods to remove low MW (LMW) HPIA and HPIN fractions is known to be poor whilst the HPOA fraction is generally believed to be the most amenable to removal (Randtke, 1988; Edwards, 1997; Sharp, *et al*. 2006). This preferential removal has been attributed to the higher charge densities associated with the HPOA fraction (Sharp, *et al*. 2006). On this basis, the leachates could be divided into two groups in terms of the predicted % removal of DOC by coagulation, with larch, pine and peat characterised by the highest % DOC removal and beech and spruce the lowest. However, given the variation in DOC concentration from different leachates, the likely concentration of recalcitrant DOC and the coagulant dose required to achieve optimum DOC removal should also be considered. On this basis, pine and larch leachates would likely be associated with highest concentration of recalcitrant DOC, coagulant demand and sludge production, followed by peat, with beech and spruce substantially lower. Future work should include a direct assessment of coagulation efficiency for the different leachates *via* bench-scale jar testing in order to provide confirmation of these differences for practitioners in the field.

2.7. Summary and conclusions

In summary, this study has compared the influence of different types of vegetative environment on the quantity and composition of leachable carbon in the O2 horizon. The main aim was to assess the potential implications of different types of habitat coverage for potable water treatment both in terms of the THMFP of the leachable DOC and the likely removal efficiency by coagulation. Though transformations of the DOC will occur during its transit through the catchment, knowledge of the role of different habitats as sources of DOC is important in a water treatment context. The concentration of leachable carbon varied significantly as a function of habitat type, with larch and pine soils yielding particularly high DOC concentrations. Significant inter-species variation was found in DOC quantity and composition suggesting that a simple coniferous/deciduous distinction is too general for investigations into soil leachates. Our results suggest that the higher DOC flux from peatland environments, widely reported in the literature, may not be the result of higher concentrations of potentially-mobile organic matter in the O2 horizon. Rather, greater O2 horizon depth, and the absence of an adsorbent mineral layer may be more likely explanations (Tipping, *et al*. 1999). Although the results of this present study support the general view that the HPOA fraction is associated with the highest reactivity upon chlorination, this was not the case for all samples. Large discrepancies between leachate $STHMFP_{7d}$ and the total derived by combining the individual fraction $STHMFP_{7d}$ values also suggest that synergistic effects may complicate the relationship between fractional character and STHMFP. Despite having relatively low $STHMFP_{7d}$, their high DOC concentrations mean that larch and pine leachates are associated with the highest $THMFP_{7d}$. These two types of leachate would also be likely to exert the highest coagulant demand and contain the largest quantity of potentially-recalcitrant (HPIA/HPIN) DOC. Monitoring the colour of abstracted water and standardising for DOC concentration could help to identify temporal changes in DOC fractional character likely to impact upon coagulation efficiency. Peat, spruce and beech leachates all have relatively low DOC concentrations and $THMFP_{7d}$ values. However, given the volume of organic substrate associated with the peatland habitat, the actual THM yield is likely to be significantly greater. Spruce samples were also associated with particularly high colour which is undesirable in treatment works intake water. Of the habitats investigated in this study therefore, beech may provide a good option for drinking water catchments given its relatively low leachate DOC concentration, THMFP and colour, although the role of intermediate carbon modifications make predicting downstream DOC characteristics difficult. An investigation into seasonal variability in DOC composition and quantity, as well as bench-scale coagulation experiments could also help to inform decision makers.

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Chapter 3: Influence of water table depth on pore water chemistry and trihalomethane formation potential in peatlands

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3.1. Abstract

During the 20th century, many UK peatland areas were drained for forestry, game, and in an attempt to increase their agricultural value. This led to widespread water table drawdown and the consequent destabilization of vast carbon stores. In addition, drained catchments were found to produce more coloured, dissolved organic carbon (DOC)-rich water, presenting problems for potable water treatment. The blocking of peatland drainage ditches in order to restore the water table is increasingly being considered as a strategy to address this deterioration in water quality. However, studies investigating the effect of peatland restoration on DOC concentration have yielded mixed results and few studies have considered the impact of ditch blocking on DOC characteristics relevant to potable water treatment. In particular, the effect of ditch blocking on the potential of DOC to form trihalomethanes (THMs), a potentially harmful disinfection by-product (DBP), has not been assessed. In this study, the impact of peat rewetting on DOC concentration and characteristics (including THM formation potential; THMFP) was assessed over a 12 month period using peat cores collected from 2 drained peatland sites. Phenol oxidase and β-glucosidase activity and CO_2 flux measurements were also made to assess any changes in microbial processing resulting from differences in water table regime. There was little evidence of differences in DOC concentration or characteristics between the different treatments. The absence of any difference in the standardised THMFP (STHMFP) of DOC between treatments suggests that, in the short term at least, ditch blocking may not impact on the THMFP of waters draining peatland catchments.

3.2. Introduction

Intact peatlands are net sinks of carbon with rates of organic matter production exceeding its decomposition (Moore & Bellamy, 1974). The accumulation of deep layers of peat is the result of very low decomposition rates (Kang & Freeman, 1999). This is reported to result from the inhibitory effects of low nutrient, highly acidic, anaerobic (waterlogged) conditions, on microbial metabolism. In particular, the activity of the phenol oxidase enzyme is limited under anaerobic conditions due to its requirement for biomolecular oxygen (Freeman, *et al*. 2001), resulting in an accumulation of phenolic compounds. In turn these phenolic substances are reported to inhibit the activity of hydrolase enzymes (Freeman, *et al*. 1990; Freeman, *et al*. 2001; Wetzel, 2001).

Broadly speaking, current research into the effect of water table on the hydrochemistry of pore water and waters draining peatland areas has been motivated by two separate issues; drought-induced water table drawdown under changing climatic conditions and the question of peatland restoration (ditch blocking) following artificial drainage of wetlands for agriculture, forestry and game, particularly in the 20th century (Holden, *et al*. 2004). Indeed water table depth has been identified as the single most important factor controlling DOC production and loss from peatlands due to its importance in governing wetland properties in general (Boddy, *et al*. 2008; Fenner, *et al*. 2009).

Field studies comparing dissolved organic carbon (DOC) concentrations of ditch and pore waters from drained and restored peatlands have yielded conflicting results. Some studies have observed decreased DOC concentrations following ditch blocking (Wallage, *et al*. 2006; Gibson, *et al*. 2009; Armstrong, *et al*. 2010; Turner, *et al*. 2013). Other studies report no significant difference in DOC concentrations or increased DOC concentration following restoration (Armstrong, *et al*. 2010; Peacock, 2013). In addition to differences in DOC concentration, previous studies have also identified changes in DOC character in response to changing water table regime including increased phenolic content (Toberman, *et al*. 2008), increased UV absorption properties (Worrall, *et al*. 2007) and changing molecular weight distributions (MWDs) (Fenner, *et al*. 2001). The effect of water table adjustment on DOC dynamics is reported to depend on the response of numerous biological and chemical processes controlling DOC production, mineralisation and solubility. In turn, these processes will depend on the particular relationship between peat composition and chemistry, and vegetation and microbial communities under the modified conditions (Laiho, 2006). The interpretation of results is also complicated by the fact that drained and restored peatlands may not simply be characterised by a stable high water table, but are more prone to fluctuations in water table than intact peatlands (Holden, *et al*. 2011) and therefore , alternating aerobic and anaerobic conditions.

In the UK, where a significant proportion of potable water is derived from upland sources, the issue of peatland restoration is particularly important. Specifically, the effect of peatland rewetting by means of ditch blocking on the concentration and characteristics of DOC in waters supplying drinking water reservoirs has important implications. DOC can cause undesirable colour, odour and taste in drinking water (Davies, *et al*. 2004; WHO, 2011), lead to bacterial regrowth within water distribution systems (Prévost, *et al*. 1998; Liu, *et al*. 2002) and transport organic and inorganic micro-pollutants (Gao, *et al*. 1998; Rothwell, *et al*. 2007). Perhaps most importantly from a public health perspective, it can also act as a reaction precursor in the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) during chlorination (Rook, 1974; Symons, *et al*. 1975; Adin, *et al*. 1991; Owen, *et al*. 1995). To date however, the effect of adjusting the water table in peatlands on the THM formation potential (THMFP) of DOC has not been explored.

In this experiment the effect of water table level on the concentration and characteristics of pore water DOC was investigated including the reactivity of DOC with chlorine *via* THMFP measurements. In order to determine the effects of different water table regimes on microbial processes, enzyme activity was measured at the end of the experiment and CO_2 flux measured periodically. Peat cores were collected from 2 drained peatland sites and subjected to water table manipulation over a 12 month period. Low water table was maintained in one set of cores to provide a control group, with fluctuating and high water table treatments designed to represent two possible hydrological outcomes under a rewetting scenario.

3.3. Methods

3.3.1. Site description and core extraction

Fifteen intact peat cores were collected in September 2011 from 2 upland sites. Site A is characterised as H-13 habitat (*Calluna vulgaris* – *Cladonia arbuscula* heath). At this site, drainage ditches were dug in the 1960s to support low-intensity sheep grazing. At the time of sampling, the water table was between 6 and 12 cm below the ground surface. Site B is a *Sphagnum*-rich M-19 habitat (*Calluna vulgaris* – *Eriophorum vaginatum* blanket mire). Drainage ditches were dug between the 1930s and 1970s leading to widespread water table draw-down. The site was formerly managed as a grouse moor and now supports low-intensity sheep grazing. At the time of sampling, the water table was between 8 and 13 cm below the ground surface.

Open-ended 40 cm-long sections of 10 cm diameter plastic PVC tubing were used for peat core collection. To minimise disturbance and compaction of the peat core, the collection procedure of Freeman, *et al*. (1993) was followed. First, the base of the tubing was used as a template to cut through the top 15 cm of peat. Next, the tubing, whose bottom edge had been chamfered, was eased over the pre-cut peat. With the tubing *in situ*, a trench was then excavated around the outside of the tubing to allow space for the second section of peat to be cut. This process was repeated until the surface of the peat was 5 cm from the top of the tubing. Next a plastic end cap was fitted to the bottom of the tubing before lifting the intact core from the excavated pit. The cores were then transported immediately to the laboratory.

3.3.2. Water table manipulation

In the laboratory a 7 mm diameter transparent reservoir tube was attached to the exterior of the plastic tubing with lateral drainage tubes at 10 cm intervals connecting it to the peat core. The cores were kept outside and were therefore exposed to ambient conditions. Loss of moisture from the cores occurred as a result of evapotranspiration. The water table within each core was controlled by the addition of distilled water at the top of the core and monitored by inspecting the height of the water in the transparent external reservoir tubing. Three different water table regimes were applied to the cores from each site (*n* = 5). For the low water table cores (henceforth AL and BL for sites A and B, respectively), the water table was maintained at – 15 cm by disconnecting the reservoir tubing at this depth. For the high water table cores (AH and BH) the water table was maintained at the surface. For the fluctuating water table cores (AF and BF) the water table was adjusted between – 15 cm and 0 cm. Oscillations of high-low-high water occurred at a frequency of 7 days.

3.3.3. Sample collection and analysis

Water samples were collected monthly by attaching a 30 mL plastic syringe to the top of the reservoir tubing on each core. The sample was drawn into the syringe slowly so as to minimise disturbance of the peat. The first 5 mL of sample was discarded, and the following 10 mL collected for analysis. The lateral drainage tubes connecting the reservoir tubing to the peat core allowed for the collection of a sample representing the entire peat core, accounting for variation in hydraulic conductivity with depth. Analysis of water samples was focussed on the determination of DOC concentration and character. A suite of analyses were performed on a monthly basis (see Table 3.01), with other analyses conducted on a biannual basis or at the end of the experiment.

Table 3.01. Sampling frequency for different analyses

Analysis	**Minimum sampling frequency**		
	Monthly	**Every 6 months**	**End of experiment**
pH	√		
Conductivity	√		
DOC concentration	√		
SUVA	√		
Phenolics concentration	√		
$THMFP_{7d}$/$STHMFP_{7d}$		√	
CO_2 flux		√	
Phenol oxidase activity			√
Β-glucosidase activity			√
Sulphate concentration			√
HPSEC			√

pH and conductivity were measured on un-filtered samples. pH was measured using a Mettler Toledo S20 pH meter calibrated daily with pH 4 and pH 7 reference standards (Sigma). Conductivity was measured using a Primo 5 handheld conductivity meter calibrated daily with a 1413 µs cm^{-1} calibration solution (Hanna Instruments).

For determination of DOC concentration samples were filtered through a 0.45 µm membrane filter (Whatman) and acidified before measurement using a Thermalox TOC/TN analyser equipped with a non-dispersive infrared CO_2 detector.

UV absorbance measurements were made using a Molecular Devices SpecraMax M2e multi-detection reader (spectrophotometer) with aliquots of samples pipetted into a 96-well clear micro-plate. Absorbance at λ = 254 nm was measured to derive a standard UV absorbance (SUVA) value, calculated using the following formula: UV Abs. 254 (cm^{-1}) * 100/DOC (mg L^{-1}). Phenolic concentration was measured using the photometric method described by the Box, (1983), adapted for 0.3 mL micro-plate wells.

$THMFP_{7d}$ denotes the quantity of THMs formed (µg L^{-1}) following chlorination of a water sample for a 7 d incubation period at 25°C. The method used was adapted from the Standing Committee of Analysts, (1981) procedure. Samples were diluted to 1 mg L^{-1} DOC to derive a standardised $THMFP_{7d}$ ($STHMFP_{7d}$) value which provides a measure of DOC reactivity. $THMFP_{7d}$ was calculated by multiplying $STHMFP_{7d}$ by DOC concentration. For chlorination, 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5M $KH_2PO_{4(aq)}$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $NaOCl_{(aq)}$ to provide 5 mg of free Cl per mg of DOC. After a 7 d incubation in the dark at 25°C, the reaction was quenched using 0.4 mL of 0.8M $Na_2SO_{3(aq)}$. Extraction of the four chlorinated and brominated THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) was achieved using direct immersion SPME followed by quantification using a Varian 450 GC coupled with an electron capture detector.

CO_2 flux, which provided an estimate of soil respiration, was measured using a PP Systems portable EGM-4 Environmental Gas Monitor for CO_2 (Hansatech) equipped with a SRC-1 Soil Respiration Chamber which was sealed onto the top of the peat core housing. CO_2 measurement was achieved using a non-dispersive infrared CO_2 detector.

Soil enzyme analyses took place at the end of the experiment so as to avoid disturbing the peat during pore water sampling. A 10 cm-deep core of peat was collected from the top 10 cm of each peat core and homogenised by hand. Phenol oxidase activity was measured using a method adapted from Pind, *et al*. (1994) and Dunn, *et al*. (2013) for 1.5 mL vials. The method is based on the measurement of the breakdown product 3-dihydroindole-5,6-quinone-2-carboxylate (DICQ). 1 g of peat was weighed and placed in a stomacher bag with 9 mL of Milli Q water. This was homogenized for 30 s using a Seward Stomacher 80. Six replicates of 0.5 mL of homogenate were pipetted into separate 1.5 mL centrifuge vials. To three of these vials, 0.5 mL of Milli Q water was added for blanks. 0.5 mL of 10 mM L-3,4-dihydroxyphenylalanine (L-DOPA) (Sigma), which in the presence of phenol oxidase is rapidly converted to DICQ, was added to the remaining three vials. The vials were incubated at field temperature for 9 min before centrifuging at 10,000 RPM for 5 min. 0.3 mL of the supernatant from each vial was pipetted into separate wells on a clear micro-plate and absorbance measured at $\lambda =$ 460 nm using a Molecular Devices SpecraMax M2e spectrophotometer. The mean absorbance of the blanks was subtracted from the mean absorbance of the L-DOPA-containing samples. Phenol oxidase activity was calculated according to the Beer-Lambert Law, using the molar absorption coefficient of DICQ (3,700) and expressed as µmol DICQ g^{-1} min^{-1}.

β-gucosidase activity was measured using a method adapted from Freeman, *et al*. (1995) and Dunn, *et al*. (2013) for 1.5 mL vials. The method is based on the measurement of the breakdown product methylumbelliferone (MUF). 1 g of peat was weighed and placed in a stomacher bag with 7 mL of 400 µM 4-MUF β-D-glucopyranoside substrate. This was homogenized for 30 s using a Seward Stomacher 80. In addition, a stomacher bag containing 1 g of peat and 7 mL of Milli Q water was homogenised by the same method. The stomacher bags were then incubated at field temperature for 60 min before pipetting 1.5 mL of homogenate from each stomacher bag into a 1.5 mL centrifuge vial and centrifuging at 10,000 RPM for 5 min. 0.3 mL of the supernatant from the substrate-containing solution was then pipetted into a micro-plate well. 5 x 0.25 mL of the blank supernatant were also pipetted into 5 separate micro-plate wells. To make the standard curve, 50 µL of 0, 10, 20, 50 and 100 µM MUF-free acid solutions were then added to these wells. Fluorescence was measured at 450 nm emission and 330 nm excitation with a slit setting of 2.5 nm using a Molecular Devices SpectraMax M2e spectrophotometer. β-gucosidase activity is expressed as µmol MUF g^{-1} min^{-1}.

Sulphate concentration was measured using a Metrohm 850 Professional Ion Chromatograph equipped with a Dionex AS14A column. Concentrations were determined using a five point calibration with two sets of check standards in the sample run (Fluka). The eluent was a 4.5 mM $NaCO_3$/1.4 mM $NaHCO_3$ solution made using Milli Q water.

High pressure size exclusion chromatography (HPSEC) was conducted using a Varian PL-GPC-50 DataStream unit detecting at $\lambda = 254$ nm. The HPSEC unit was interfaced to Cirrus software and equipped with a Bio Sep 2000 column. Calibration standards were sodium polystyrene sulfonate polymers with MWs of 150,000, 77,000, 32,000, 13,000 and 4,300 Da (Fluka) and cyanocobalamin (1,340 Da). The mobile phase was Milli Q water buffered with phosphate (0.002 M KH_2PO_4 + 0.002 M $K_2PO_4.3H_2O$) to pH 6.8. HPSEC analysis was performed at the end of the experiment on composite samples, derived by combining equal volumes of the five replicates.

3.3.4. Statistical analysis

Statistical analysis was performed on data using version 20 of the SPSS Statistics package (PASW). Analyses were performed on five different occasions over the course of the experiment; pre-treatment (August 2012), winter (December 2012), spring (March 2013), summer (June 2013) and autumn (September 2013). Where conditions were satisfied by the data, analysis of variance (ANOVA) and Kruskal-Wallis tests were performed to investigate differences between treatment groups, and between the two sites. For significant ANOVA and Kruskal-Wallis results, Tukey HSD and Nemenyi post-hoc tests were performed, respectively. The significance level (< 0.01 or < 0.05) is reported for post-hoc tests.

3.4. Results

Pore water remained acidic throughout the experiment for all treatment groups, with little temporal variation in mean pH values which ranged between 4.1 and 4.7 (Figure 3.01a). The only statistically significant difference in mean pH identified was the AH/BF comparison ($p < 0.05$) in December 2012. Though mean pore water conductivity for individual treatment groups varied over the course of the experiment, there appeared to be little synchronicity between treatments over time (Figure 3.01b). Conductivity ranged between 26 µs cm^{-1} (AH; March 2013) and 63 µs cm^{-1} (BL; August 2013). No statistically significant differences were identified between treatments (Table 3.02).

Mean DOC concentrations of the different treatment groups were similar for the pre-treatment samples and in the first post-treatment sample (October 2012) but over subsequent months varied more considerably (Figure 3.01c). In general DOC concentrations were lowest in the pre-treatment samples (16-28 mg L^{-1}) and show a prominent peak in November 2012 (40-96 mg L^{-1}) before decreasing towards February 2013. Concentrations then appear to show a general increase until the end of the experiment in September 2013. Although the AH and AF groups appear to show relatively low DOC concentrations compared with the other treatment groups, no statistically significant differences in DOC concentration were found.

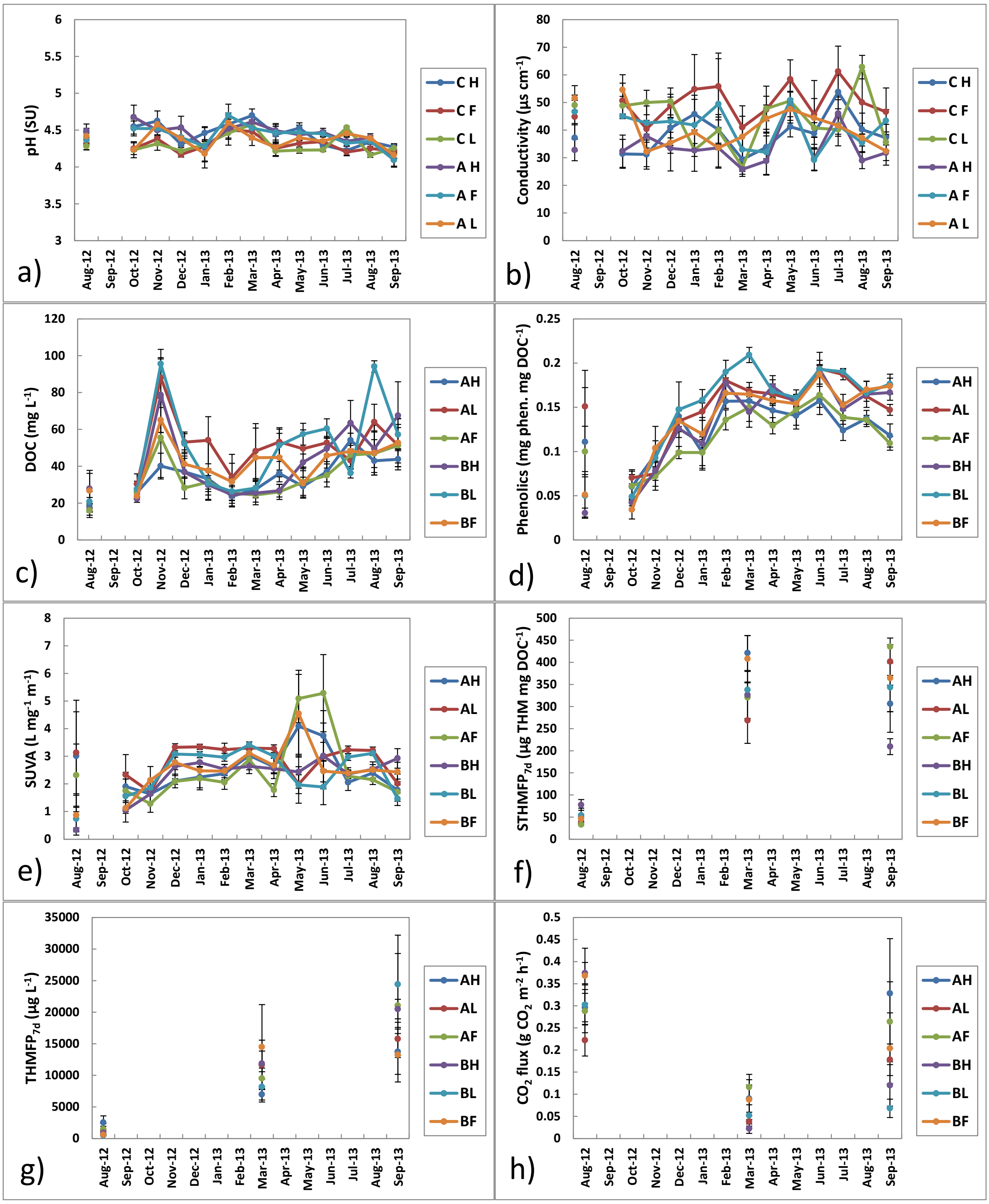

Figure 3.01. Pore water measurements between August 2012 and September 2013 including pH (a), conductivity (b), DOC concentration (c), standardised phenolics concentration (d), SUVA (e), STHMFP$_{7d}$ (f) and THMFP$_{7d}$ (g) and CO$_2$ flux (h) for AH, AL, AF, BH, BL and BF treatment groups. Error bars represent the standard error of the mean (*n* = 5).

In contrast to the DOC concentration results, mean standardised phenolics measurements for the different treatment groups showed considerable differences at the pre-treatment stage and were more similar during the remainder of the experiment (Figure 3.01d). A high degree of variation within groups however, resulted in there being no statistically significant difference between groups in the pre-treatment samples. Following a minimum in October 2012 (0.03-0.07 mg phen. mg DOC^{-1}), phenolics measurements for all groups showed a dramatic increase until March 2013 (0.14-0.21 mg phen. mg DOC^{-1}) after which they appeared to stabilise before a slight decrease in the final 2 months of sampling. In March 2013 standardised phenolics in the BL treatment was significantly higher than the AH and AF treatments (both $p < 0.01$). A number of statistically significant differences were also identified between groups in September 2013 (Table 3.02). However, with the exception of the AL/AF ($p < 0.05$) comparison, these differences were all between the two sites.

Table 3.02. Statistically significant differences between treatment groups identified by ANOVA and Kryskal-Wallis analysis.

	pre-treatment (Aug 2012)	**winter (Dec 2012)**	**spring (Mar 2013)**	**summer (Jun 2013)**	**autumn (Sep 2013)**
pH		AH/BF ($p < 0.05$)			
Conductivity					
DOC concentration					
SUVA		AH/AL ($p < 0.01$) AL/AF ($p < 0.01$)			
Standardised phenolic concentration			AH/BL ($p < 0.01$) AF/BL ($p < 0.01$)		AH/BH ($p < 0.01$) AH/BL ($p < 0.01$) AH/BF ($p < 0.01$) AL/AF ($p < 0.05$) AF/BH ($p < 0.01$) AF/BL ($p < 0.01$) AF/BF ($p < 0.01$)
STHMFP$_{7d}$		▨		▨	AH/AF ($p < 0.05$) AL/BH ($p < 0.05$) AF/BH ($p < 0.01$) BH/BL ($p < 0.01$)
THMFP$_{7d}$		▨		▨	
CO$_2$ flux		▨		▨	
Phenol oxidase activity	▨	▨	▨	▨	
β-glucosidase activity	▨	▨	▨	▨	
Sulphate concentration	▨	▨	▨	▨	

White cells indicate where statistical analyses were carried out and shaded cells where no statistical analysis was performed.

Variability in mean SUVA measurements between treatment groups was high in the pre-treatment samples and in May and June 2013 although the large error bars for these measurements also indicate a high degree of variability within groups (Figure 3.01e). Indeed the only statistically significant differences between treatments occurred in December 2012 when mean SUVA measurements were very similar but variability within groups also appeared to be very low (Table 3.02). For this month the AL measurement was significantly higher than AH and AF measurements (both $p < 0.01$). Between October and December 2012 SUVA measurements showed a general increase before stabilising between December 2012 and April 2013. The minimum mean SUVA measurement (0.3 L mg^{-1} m^{-1}) was recorded for the BH sample at the pre-treatment stage and the maximum (5.3 L mg^{-1} m^{-1}) for the AF sample in June 2013. In general however, measurements tended to vary between 2.0 and 3.5 L mg^{-1} m^{-1}.

$STHMFP_{7d}$ was measured on the pre-treatment samples and subsequently at a six month interval (in March 2013 and September 2013). A substantial increase in mean $STHMFP_{7d}$ values and variability between treatment groups was observed between the pre-treatment samples (33-77 µg THM mg DOC^{-1}) and the March 2013 samples (268-421 µg THM mg DOC^{-1}) (Figure 3.01f). $STHMFP_{7d}$ values and variability in September 2013 (209-435 µg THM mg DOC^{-1}) were comparable to March 2013. However there appeared to be no consistency in the relative $STHMFP_{7d}$ measurements of different treatment groups over time. The only statistically significant difference in mean $STHMFP_{7d}$ values between treatment groups occurred in September 2013; the BH group was found to have a lower mean $STHMFP_{7d}$ than the AL ($p < 0.05$), AF ($p < 0.01$) and BL ($p < 0.01$) groups and mean $STHMFP_{7d}$ for the AH group was significantly lower than the AF group ($p < 0.05$) (Table 3.02).

$THMFP_{7d}$, calculated by multiplying $STHMFP_{7d}$ by DOC concentration, represents the total yield of THMs associated with the chlorination of a sample. As was the case with $STHMFP_{7d}$, $THMFP_{7d}$ increased considerably between the pre-treatment samples (465-1,454 µg L^{-1}) and the March 2013 samples (6,975-14,470 µg L^{-1}) (Figure 3.01g). This was largely the result of increased DOC reactivity ($STHMFP_{7d}$) and to a lesser extent, increased mean DOC concentration in some groups. In contrast to $STHMFP_{7d}$, mean $THMFP_{7d}$ for most groups also increased between March 2013 and September 2013 when they ranged between 13,254 and 24,387 µg L^{-1}. This increase was due to increased DOC concentration. No significant differences between the mean $THMFP_{7d}$ values of the different groups were identified.

In the pre-treatment samples, mean CO_2 flux rates ranged between 0.22 and 0.37 g CO_2 m^{-2} h^{-1}. Flux rates were reduced in March 2013 to between 0.02 and 0.33 g CO_2 m^{-2} h^{-1} and recovered in September 2013 when they ranged between 0.07 and 0.33 g CO_2 m^{-2} h^{-1} (Figure 3.01h). There appeared to be no consistency in the relative CO_2 flux rates of different groups over time and no significant differences were found between different treatment groups.

Soil enzyme activity was measured at the end of the experiment in September 2013. Mean phenol oxidase activity was lowest for the BH treatment (6.8 nmol DIQC g^{-1} min^{-1}) and highest for the BF treatment (14.7 nmol DIQC g^{-1} min^{-1}) (Figure 3.02). However, no significant differences were found between treatment groups. Mean β-glucosidase activity was lowest for the BH treatment (23.6 nmol MUF g^{-1} min^{-1}) and highest for the AL treatment (38.4 nmol MUF g^{-1} min^{-1}) (Figure 3.03). Although mean values for Site A treatments were consistently higher than Site B, no significant differences were found between treatment groups.

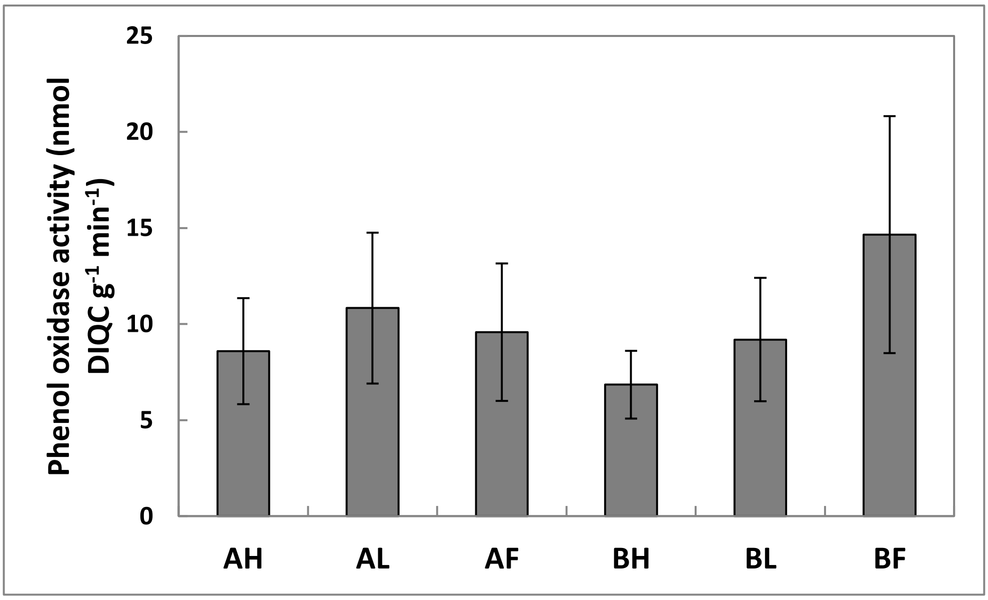

Figure 3.02. Soil phenol oxidase activity in September 2013 for AH, AL, AF, BH, BL and BF treatment groups. Error bars represent the standard error (*n* = 5).

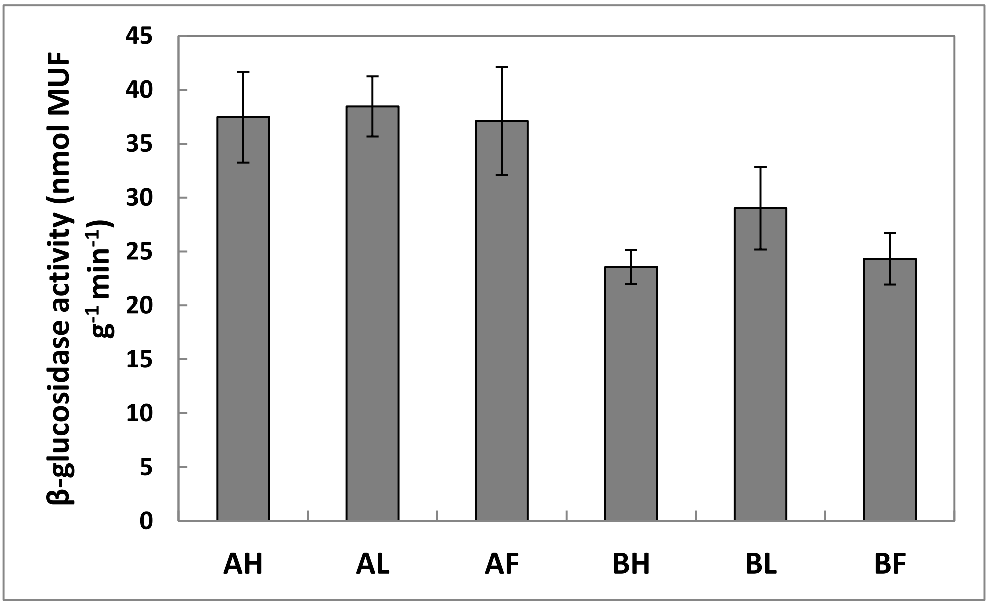

Figure 3.03. Soil β-glucosidase activity in September 2013 for AH, AL, AF, BH, BL and BF treatment groups. Error bars represent the standard error (*n* = 5).

Mean sulphate concentrations, measured in September 2013, ranged from 4.0 mg L^{-1} in the BF treatment group to 11.7 mg L^{-1} in the BL group (Figure 3.04). However, no significant differences were found between treatment groups.

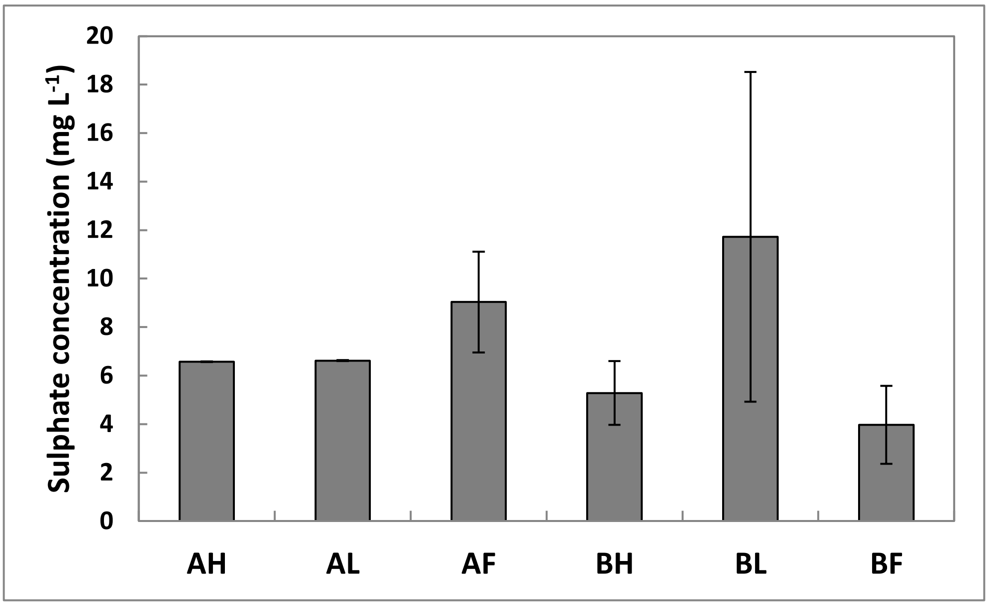

Figure 3.04. Pore water sulphate concentration in September 2013 for AH, AL, AF, BH, BL and BF treatment groups. Error bars represent the standard error of the mean (*n* = 5).

The MWDs for amalgamated samples from each treatment group in September 2013 all appear similar (Figure 3.05). All show a small peak at retention time (t_R) ≈ 4.5 min representing high MW (HMW) molecules that are too large to interact with the pores of the stationary phase (Huber, *et al*. 2011). The dominant peak occurs at t_R ≈ 8.5 min (~ 3.5 kDa) with an overlapping peak at t_R ≈ 9.7 min. All samples were dominated by HMW (> 1.0 kDa) DOC which varied between 88 and 92 % of the sample.

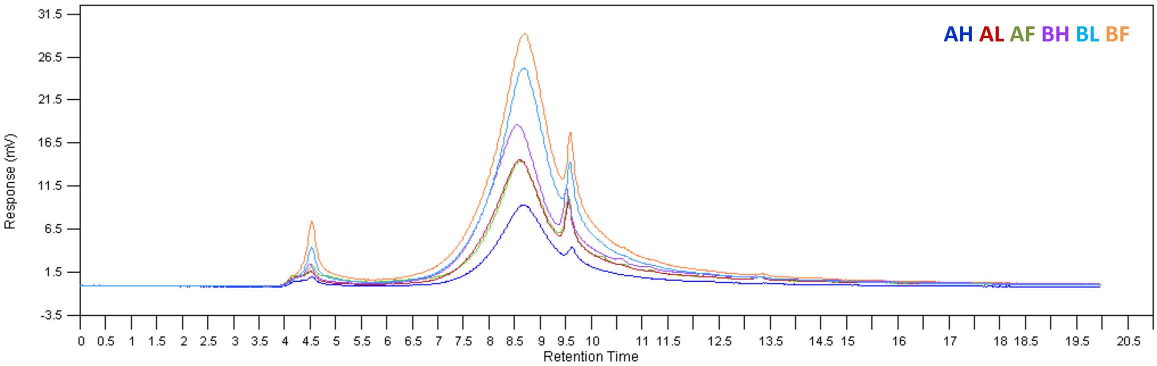

Figure 3.05. HPSEC chromatograms for amalgamated samples from AH, AL, AF, BH, BL and BF treatment groups in September 2013.

3.5. Discussion

3.5.1. Pore water DOC concentration and controlling factors

The DOC concentrations reported here are within the range of peat pore water concentrations reported previously both from piezometers installed in the field (Wallage, *et al*. 2006; Evans, *et al*. 2012; Peacock, 2013) and mesocosm (peat core) experiments (Pastor, *et al*. 2003; Clark, *et al*. 2006). With increasing depth, pore water DOC concentration is reported to increase (Freeman, *et al*. 1993) and hydraulic conductivity to decrease (Mathur & Levesque, 1985). Thus our DOC measurements represent the average DOC concentration for the peat core, incorporating natural variations in DOC concentration and hydraulic conductivity.

Mean DOC concentrations for all treatment groups showed considerable temporal fluctuations. Seasonal variations in DOC production have been associated with temperature- and moisture-driven changes in the rate of microbial processing of organic matter (Halliday, *et al*. 2012). Higher DOC concentrations have been reported in the summer than in winter (Kalbitz, *et al*. 2000), though Evans, *et al*. (1996) report that soil solution DOC peaks can occur throughout the year. Fluctuations in soil conditions caused by shorter-term weather events such as episodic warming and freeze-thaw events have also been shown to increase pore water DOC concentrations (Tipping, *et al*. 1999; Kaiser, *et al*. 2001). Since moisture conditions were controlled in the present study and there were no statistically significant differences between treatment groups, it appears that temperature is the main driver of temporal changes in DOC concentration. The increase in DOC concentration observed in November 2012 may have been caused by some agitation of the peat resulting from commencement of sampling since physical disturbance has been reported to increase DOC production (Blodau & Moore, 2003).

Most field-based studies comparing DOC concentrations between drained and restored peatlands present results for ditch waters. In a parallel control study conducted by Turner, *et al*. (2013) involving two drained catchments and the blocking of ditches in one, a decrease in ditch water DOC concentration of 2.5 % in the year following ditch blocking was observed. In a similar study, Gibson, *et al*. (2009) report a slight (0.3 mg L^{-1}) but statistically significant decrease in ditch DOC concentration following ditch blocking. Armstrong, *et al*. (2010), who present findings from a UK survey of 32 restoration sites report significantly lower mean DOC concentration for waters sampled from blocked ditches compared with unblocked ditches. However, in an intensively monitored site they report no difference in DOC concentration 7 years after ditch blocking. Similarly, Peacock, (2013) reports no difference in ditch water DOC concentration between unblocked ditches and ditches blocked using 2 different methods (reprofiling and damming) 20 months after ditch blocking. Chapman, *et al*. (1999) on the other hand reported significantly lower stream DOC concentrations in peaty podzols drained for forestry compared with intact moorland. Comparisons of pore water DOC concentrations between drained and restored peatlands have also yielded contradictory results. Wallage, *et al*. (2006) report that pore water concentrations were 60-70% lower following restoration, compared with a nearby drained area and a nearby intact site. Peacock, (2013) on the other hand found no difference in pore water DOC concentrations between drained and restored sites.

Water table manipulation experiments have also been undertaken at a laboratory scale using peat mesocosms. Freeman, *et al*. (1993) used 60 cm peat monoliths to investigate the effect of severe drought on pore water chemistry. For the drought simulation the water table was gradually lowered over a period of 10 weeks to a depth of 20 cm, maintained at this depth for a further 6 weeks before returning to the surface. A significant decrease in DOC concentration was observed in the simulated drought cores compared with the control group at a depth of 10 cm. Toberman, *et al*. (2008) compared pore water soluble phenolics concentrations and extracellular phenol oxidase activity in peat cores under three water table regimes. In the “impeded drainage” cores the water table was maintained at the surface for the duration of the 60 day treatment period. “Transient impeded drainage” cores were kept saturated for 20 days before free-drainage was applied for the remainder of the experiment. A control group comprised “free-draining” cores from which water was allowed to drain and was not replenished. Unexpectedly, an increase in phenol oxidase activity in the impeded drainage cores was observed, with a simultaneous increase in the concentration of soluble phenolics. This was attributed to the stimulating effect of a rise in pH on DOC solubility and extracellular phenol oxidase activity. Concurrently, Guggenberger, *et al*. (1994) observed decreased DOC mobilisation under lower pH conditions accompanied by reduced carbon mineralisation and by implication, reduced microbial activity.

The effect of the introduction of aerobic conditions on DOC concentrations in peatlands as a result of drought or artificial drainage depends to a large extent on the response of microbial processes (i.e. DOC production). The activity of extracellular enzymes in general would be expected to increase under aerobic conditions, provided the peat substrate is not so dry that moisture constraints limit activity (Toberman, *et al*. 2008). In addition, according to the enzyme latch theory, the enhanced degradation of phenolic compounds by phenol oxidase will reduce the inhibition of hydrolase enzymes (Freeman, *et al*. 2001). However, there is disagreement in the discussion of the role of phenol oxidase in DOC processing. Whereas in some cases the action of phenol oxidase is considered to result in the full mineralization of phenolic compounds (Worrall, *et al*. 2004; Evans, *et al*. 2006), in other cases it is assumed to cause the mobilization of soluble compounds from insoluble organic matter, thereby contributing to the DOC pool (Fenner, *et al*. 2005; Toberman, *et al*. 2008). However, it should be noted that phenolic compounds comprise only a fraction of pore water DOC (in this study ranging between ~ 5 and 20%) and their inhibitory effect on DOC production *via* hydrolase enzymes may outweigh their own contribution to the DOC pool (Freeman, *et al*. 1990). Though there were no statistically significant differences in phenol oxidase activity between treatments, mean activity measurements for the high water table treatments were the lowest for both sites, consistent with these cores having the lowest oxygen availability. The lack of any statistically significant differences in CO_2 flux between treatment groups suggests that the rate of organic matter mineralisation was not affected by differences in water table regime.

In addition to production, the solubility of DOC is a crucial determinant of pore water DOC concentrations. A positive relationship is reported between DOC solubility in peat pore water and pH and temperature, and an inverse relationship with ionic strength (Lofts, *et al*. 2001; Fenner, *et al*. 2005; Lumsdon, *et al*. 2005). In the present study, only pH and ionic strength were potentially variable between treatment groups. Whereas in anaerobic conditions, anaerobic bacteria reduce SO_4^{2-} to largely undissociated H_2S, under aerobic conditions, H_2S is oxidised to dissociated H_2SO_4 resulting in increased concentrations of SO_4^{2-} and H^+ (Freeman, *et al*. 1993; Adamson, *et al*. 2001). The solubility of DOC is diminished by the high degree of protonation resulting from low pH (Tipping & Hurley, 1988). The explanation for diminished solubility resulting from higher ionic strength is less clear but is thought to relate to the reduced charge density of organic substances, leading to coagulation (Kalbitz, *et al*. 2000).

Enhanced solubilisation of DOC upon rewetting of peat following ditch blocking has been proposed as the cause of short-term increases in DOC concentration (Toberman, *et al*. 2008; Clark, *et al*. 2006). In the present study there is little evidence of variations in sulphate concentrations, pH or ionic strength (conductivity) between treatments. Thus variations in pore water DOC concentration resulting from differences in solubility between treatments is likely to be minimal. The interpretation of results in peatland restoration experiments is also complicated by the physical disturbance that occurs during ditch blocking which can lead to a temporary increase in DOC loading (Armstrong, *et al*. 2010). Even in controlled laboratory-based experiments, raising the water table may agitate the peat structure leading to enhanced mobilisation of DOC (Clark, *et al*. 2006). In addition, field experiments have demonstrated the potential for long lag-periods following rewetting when DOC production remains high. This has been explained by a legacy of high enzyme activity from previously aerated peat (Worrall, *et al*. 2007; Peacock, 2013).

Since ditch blocking can lead to oscillations in the water table rather than a return to the steady high water table associated with intact peatlands (Holden, *et al*. 2011), a fluctuating water table treatment was included in this study. Fenner & Freeman, (2011) showed that alternating wet and dry conditions associated with frequent drought events can confound the destabilisation of peatland carbon stocks. They observed that enhanced microbial activity and alkalinity generation during drought led to more favourable pH conditions for anaerobic enzyme activity upon rewetting. This is significant because anaerobic decomposition shifts metabolic end products towards DOC, CH_4 and CO_2, rather than primarily CO_2 under aerobic decomposition (Boddy, *et al*. 2008; Fenner, *et al*. 2009).

The absence of any statistically significant differences in pore water DOC concentrations in the present study may be the result of a delay in the microbial response to changing water table regime which has been previously reported (Worrall, *et al*. 2007; Peacock, 2013). Alternatively, variations in the response of peat cores under different water table regimes to ambient temperature fluctuations may have overridden moisture-driven differences in DOC dynamics.

3.5.2. DOC character

The differences in production and solubility mechanisms in peat subjected to different hydrological conditions (described above) would imply a difference in DOC composition. Indeed enhanced phenol oxidase activity under waterlogged conditions is reported to cause an increase in phenolic DOC concentrations following impeded drainage in peat mesocosms (Toberman, *et al*. 2008). Worrall, *et al*. (2007) also report a significant increase in SUVA, suggesting an increased contribution of aromatic DOC following ditch blocking in an upland peat catchment. An increase in the contribution of phenolic DOC relative to other DOC species in waterlogged conditions may also relate to the enhance solubility of phenolic compounds relative to other DOC resulting from their hydrophilic hydroxyl content (Bond, *et al*. 2009). In this study, statistically significant differences in standardised phenolic concentrations between groups tended only to occur in the comparison between the two peatland sites with only the AL/AF within-site comparison in September 2013 statistically significant. This outcome is consistent with the absence of any statistically significant differences in phenol oxidase activity between treatment groups. Furthermore, no significant differences in pH or ionic strength, which may have modified DOC character, were observed between treatments.

Little evidence of differences in SUVA values between treatments was observed. Indeed the only significant result was observed in December 2012 when AL showed significantly higher SUVA than AH or AF (both $p < 0.01$) and mean SUVA values were nonetheless very similar. The SUVA values reported here, which tended to range between 2 and 3.5 L mg^{-1} m^{-1} are lower than expected since pore water DOC in peatland systems is assumed to be dominated by HMW humic structures with high aromaticity and UV-absorbing properties. However, since our samples included a portion of DOC from the surface of the peat core close to the vegetation, it is possible that the presence of fresh DOC from this source may have lowered the overall UV absorption of the sample. Previous studies have found that SUVA values for fresh leachates are lower than older, more biodegraded DOC (Beggs & Summers, 2011).

HPSEC results show that pore water DOC was dominated by HMW molecules in all treatment groups. This is consistent with the view that peatlands produce DOC rich in HMW humic compounds (Scott, *et al*. 2001). HPSEC chromatograms were also very similar to those of fluvial and reservoir samples (Chapter 4) though a low MW (LMW) peak associated with algogenic DOC (Chapter 5) was absent. It should be noted however that the HPSEC analysis used UV detection at $\lambda = 254$ nm, potentially underestimating the proportion of LMW hydrophilic DOC molecules (Leenheer & Croue, 2003). Nonetheless the similarity in the chromatograms of different treatment groups indicates that there were no major differences in the MWDs of DOC between different treatments. This result is in contrast to the findings of Fenner, *et al*. (2001) who report selective enrichment of the 5-90 kDa DOC fraction in pore water following rewetting.

Given that there is little evidence of significant differences in DOC characteristics between treatment groups, it is perhaps unsurprising that no significant difference in reactivity ($STHMFP_{7d}$) was observed. However, the increase in mean $STHMFP_{7d}$ between pre-treatment samples and the March 2013 and September 2013 samples is striking. This increase is difficult to interpret since it is not accompanied by comparable changes in other DOC characteristics. However, it may be significant that, in a number of cases, the standardised phenolic content was higher in the latter samples, since a positive relationship is reported to exist between % aromaticity and STHMFP (Weishaar, *et al*. 2003) and structures relating to the phenolic polymer core of humic substances are reported to act as THM precursors (Christman & Ghassemi, 1966). In future, measurement of pore water Br^- concentrations would be useful in order to assess the potential impact of water table regime on brominated DBP formation potentials. Previous research suggests that rewetting drained peat can cause an increase in Br^- concentration (Hughes, *et al*. 1998).

3.6. Conclusions

The impact of ditch blocking on peatland hydrochemistry, and in particular its effect on the concentration and characteristics of exported DOC, has important implications for potable water treatment. Not only does DOC compromise the aesthetic quality of water and increase treatment costs, but it may also present a public health issue, in particular due to its role as a reaction precursor in the formation of THMs.

Impeded decomposition under waterlogged conditions in intact peatlands is understood to limit the export of DOC. Indeed water table drawdown under changing climatic conditions has been implicated in the widespread increase in DOC levels in waters draining upland catchments. It would seem intuitive therefore, that the restoration of wetlands previously drained for agriculture and other purposes, would lead to a decrease in DOC concentrations. However, field-based studies investigating the impacts of drain blocking on pore water and ditch water DOC concentrations have yielded conflicting results. Furthermore, to date no studies have considered the impact of ditch blocking on DOC reactivity with chlorine (STHMFP).

No significant differences in DOC concentrations were observed between different water table regimes in the present study based on seasonal comparisons over a 12 month period. Importantly, there was also no indication of differences in biological activity based on enzyme activity and CO_2 flux measurements, or differences in solubility controls based on pH, conductivity and sulphate measurements. However, the effect of water table changes on DOC dynamics is known to be complex, involving numerous interrelated biological and chemical responses over various timescales. It is possible that the absence of a treatment effect in the present study was due to a delay in the microbial response to adjusted water tables, which has been reported previously.

The lack of any differences in the THMFP of DOC between different treatments, which in the present experiment were simulated at 2 different upland sites, suggests that in the short term, ditch blocking may not increase the THMFP associated with waters draining upland catchments. However, it should be noted that previous studies have identified changes in DOC character upon rewetting (e.g. increased SUVA and dissolved phenolic concentrations) which are consistent with an increase in DOC reactivity with chlorine. Future experiments on this subject should also consider the longer-term effects of rewetting on the STHMFP of DOC given evidence suggesting a delay in the microbial response.

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Chapter 4: Assessing spatial and temporal variability in surface water quality in two upland sites in relation to catchment characteristics

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This chapter was written by Rachel Gough. Jennifer Williamson carried out stream sampling in Catchment A between June 2012 and November 2012 and conducted DOC concentration, UV absorbance and phenolics measurements on these samples. Peter Holliman and Christopher Freeman provided advice on experimental design and editorial suggestions.

4.1. Abstract

The composition and character of water abstracted from drinking water reservoirs impacts both treatment efficacy and final water quality. Surface water quality is influenced by a range of catchment characteristics including habitat and land use, soil type, parent material and topography and also shows distinctive seasonal variations. The concentration and character of dissolved organic carbon (DOC) is particularly significant in a water treatment context. Not only does it affect the aesthetic quality of water, but it can also react with chlorine during disinfection to form potentially harmful disinfection by-products (DBPs) including trihalomethanes (THMs). The widely-reported increase in DOC export from upland areas is therefore a major concern for drinking water companies who rely on upland reservoirs to meet potable water demands. Improved understanding of the nature and drivers of spatial and temporal variations in DOC and THM formation potential (THMFP) is necessary to inform future catchment management practices and optimise treatment processes. This study presents water quality data for two upland reservoirs and their main input streams. Stream DOC concentration, character and flux were measured over a 14 month period in Catchment A in order to investigate seasonality in water quality and identify potential sources of high THMFP. The spatial extent of ecological and pedological features in the two reservoir catchments and their respective stream subcatchments were also calculated to investigate potential relationships between catchment characteristics and DOC concentration and quality. Fluvial DOC concentration showed a late summer maximum but DOC export appeared to be mainly controlled by stream discharge. Extensive coniferous forest plantations, shallower mean catchment slope and deeper soils in Catchment A appear to be responsible for higher DOC loading in this catchment. Peatland coverage in both catchments is likely to be the cause of high THMFP. UV absorbance data (A_{253}:A_{203} and SUVA) may provide a means of monitoring seasonal variations in THMFP though fractional character was less useful as a predictive tool. Chemical or biological transformation in large reservoirs may reduce DOC concentration and temper seasonal fluctuations in water quality before entering the water treatment works (WTWs).

4.2. Introduction

The chemical and biological properties of surface water are acquired, to a large extent, during the passage of water through the catchment due to the interaction of water with vegetation, soils and mineral layers. Various organic and inorganic compounds will be solubilised and transported downstream during runoff, influencing solute concentrations, pH and ionic strength (Stutter, *et al*. 2006). Conversely, soils also have an adsorption capacity, which varies depending on its composition and chemistry (Hope, *et al*. 1994). Runoff also results in erosion and transport of particulates, which may be solubilised or degraded during in-stream chemical and biological processing or deposited as sediment (Wallace, *et al*. 1995). Physical catchment characteristics including topography, geology, soil and vegetation type affect catchment runoff processes by influencing both the distribution of water flowpaths and the pattern of water storage (Soulsby, *et al*. 2006). Since soil type integrates a number of these catchment characteristics, it is argued that this represents the dominant control on surface water composition and quality (Aitkenhead, *et al*. 1999; Soulsby, *et al*. 2006; Stutter, *et al*. 2006). Primary productivity and microbial processing of organic matter in soils, controlled by habitat and soil type, will determine the pool of available leachable organic matter (Freeman, *et al*. 2004; Fenner, *et al*. 2009). In turn, the development of particular habitat and soil types will be determined to a large extent by climate, topography and parent material (Billett, *et al*. 1992), with biological processes also fluctuating on a seasonal basis (Fenner, *et al*. 2005). Relationships between catchment characteristics and surface water quality are therefore complex. Geographical Information Systems (GIS) are increasingly being used in the study of catchment influences on hydrochemistry (Soulsby, *et al*. 2006; Cohen, 2009), offering an effective means of visualising and measuring landscape features and modelling runoff.

The importance of catchment characteristics in affecting the quality of drinking water supplies is recognised by the UK drinking water regulator, the drinking water inspectorate (DWI) who recommend that *"catchment and raw water source protection"* is included in the drinking water safety plans of drinking water providers (DWI, 2005). In the UK many drinking water sources are located in upland areas which confer a unique set of challenges for water treatment companies. In particular, these areas are often associated with deep, acidic, peaty soils which can export large amounts of highly-coloured humic material (Tipping, *et al*. 1999). In addition, wetland habitats, also common in these locations, are reported to exert a disproportionally large influence on surface water DOC concentration (Aitkenhead, *et al*. 1999; Gergel, *et al*. 1999; Cohen, 2009). Indeed in upland headwater catchments, the proportion of peatland cover was identified as the most important predictor of fluvial DOC flux (Hope, *et al*. 1997).

DOC can cause undesirable colour, odour and taste in drinking water (Davies, *et al*. 2004; WHO, 2011) and lead to bacterial regrowth within water distribution systems (Prévost, *et al*. 1998; Liu, *et al*. 2012). It can also transport organic and inorganic micro-pollutants (Gao, *et al*. 1998; Rothwell, *et al*. 2007) and may act as a reaction precursor in the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) (Rook, 1974; Symons, *et al*. 1975; Adin, *et al*. 1991; Owen, *et al*. 1995).

Importantly, it has been reported that carbon stores in upland soils are destabilising. A nationwide survey of carbon losses showed that peat soils and bog habitats have lost carbon at a much higher rate than other soil and habitat categories (Bellamy, *et al*. 2005). Though losses to the atmosphere and *via* leaching to deeper soils layers will be partly responsible, a rise in DOC concentrations draining upland catchments in the UK, as well as further afield; in Northern and Western Europe and North America, shows that leaching to surface waters is also a factor (Bouchard, 1997; Freeman, *et al*. 2001; Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Worrall, *et al*. 2003).

This study focusses on 2 upland drinking water reservoir catchments; Catchment A and Catchment C. Though the catchments are geographically close (23 km distance), and at a similar elevation, there are distinct differences in surface water quality and hence unique challenges associated with water treatment at these two sites. This study aims to assess seasonal and spatial variations in surface water quality (input stream and reservoir water) within and between these catchments, focussing on DOC concentration and character. The main input streams for each reservoir were identified and discharge measurements used to calculate DOC flux. Monthly sampling of the main input streams was undertaken at Catchment A over a 14 month period. Biannual sampling of input streams and abstracted reservoir water was also undertaken at both catchments. In addition to the quantification and characterisation of DOC, THM yield was assessed using THM formation potential (THMFP) measurements. Correlations between THMFP and UV absorbance properties were investigated to assess their utility as predictors of THM yield. Finally, GIS mapping was used to measure the spatial extent of ecological and pedological features in each catchment and investigate potential relationships between catchment characteristics and surface water quality. Understanding the role of catchment characteristics in affecting DOC flux and character will help to inform future catchment management practices. Identifying important DOC inputs will also help water treatment companies target monitoring programmes and mitigation strategies. Improved understanding of seasonality in DOC inputs to drinking water reservoirs will enable better optimization of treatment processes.

4.3. Methods

4.3.1. Site description and sampling regime

Two UK upland reservoir catchments were chosen for this study (see Table 4.01 for key reservoir and catchment descriptors). Both reservoirs supply potable water treatment works (WTWs) and are associated with unique treatment issues. Thirty-eight to forty ML of water is abstracted daily from Reservoir A. Its 24.8 km^2 catchment comprises extensive areas of coniferous plantations, grassland and peatland. Reservoir water quality during the study period comprised low turbidity (0.21-0.62

FTU), high colour (52-117 Hazen), high DOC content (9.0-16.2 mg L^{-1}) and slight acidity (pH 5.6-6.0). The main supply for Reservoir A is a headwater lake, which drains a 5.9 km^2 area of grassland and wetland, connected to the reservoir *via* stream 1 (Figure 4.01). On average 25 ML of water is abstracted daily from Reservoir C. Its catchment is larger than Catchment A at 33.9 km^2 and its topography steeper. The catchment is comprised mainly of peatland and grassland. Reservoir water quality during the study period included relatively high turbidity (0.37-1.50 FTU), low colour (17-24 Hazen), low DOC concentration (2.5-5.3 mg L^{-1}) and slight acidity (pH 6.2-6.9). Reservoir C is supplied by 4 lakes, connected by a network of tunnels and leats. The main inputs are stream 1, whose 20.8 km^2 subcatchment contains 3 of the 4 supply lakes and enters the reservoir *via* a tunnel, and stream 4 (subcatchment: 8.6 km^2) which drains the remaining supply lake (Figure 4.02). See Figures 1-4 in appendix for maps showing spatial extent of Phase 1 habitat and soil types for stream subcatchments in Catchment A and C.

Table 4.01. Reservoir and catchment descriptors.

	Catchment A	**Catchment C**
Reservoir elevation AOD (m)	431	355
Catchment area (km^2)	24.8	33.9
Mean catchment slope (degrees)	4.5	17.0
Reservoir area (km^2)	1.5	1.1
Reservoir depth (m)	Mean 11.2, max 32.2	Mean 25.8, max 80.1
Reservoir volume (ML)	13,932	37,864
Mean annual air temp (°C)	8.6	9.7
Mean annual rainfall (m)	1.434	0.978
Reservoir water colour (Hazen)	52-117	17-24
Reservoir turbidity (FTU)	0.21-0.62	0.37-1.5
Reservoir DOC concentration (mg L^{-1})	9.0-16.2	2.5-5.3
pH (SU)	5.6-6.0	6.2-6.9
Treatment issues	Colour, algae (seasonal)	THMs, cryptosporidium
Treatment processes	Coagulation-flocculation, DAF, RGF	Ozonation, GAC filtration/adsorption, UV

The six main input streams for each reservoir were identified during a preliminary field survey. The streams in Catchment A were sampled on a monthly basis (excluding November 2011) between October 2011 and November 2012. A more comprehensive stream survey which included additional water quality analyses (7 d THMFP profiles, XAD-fractionation and high pressure size exclusion chromatography; HPSEC) was carried out on a biannual basis; in October 2011 and May 2012 for both catchments. Abstracted reservoir water was also analysed during biannual sampling. Stream discharge was calculated using channel cross-section area and flow velocity measurements made using a Geopacks flow meter (Map Marketing).

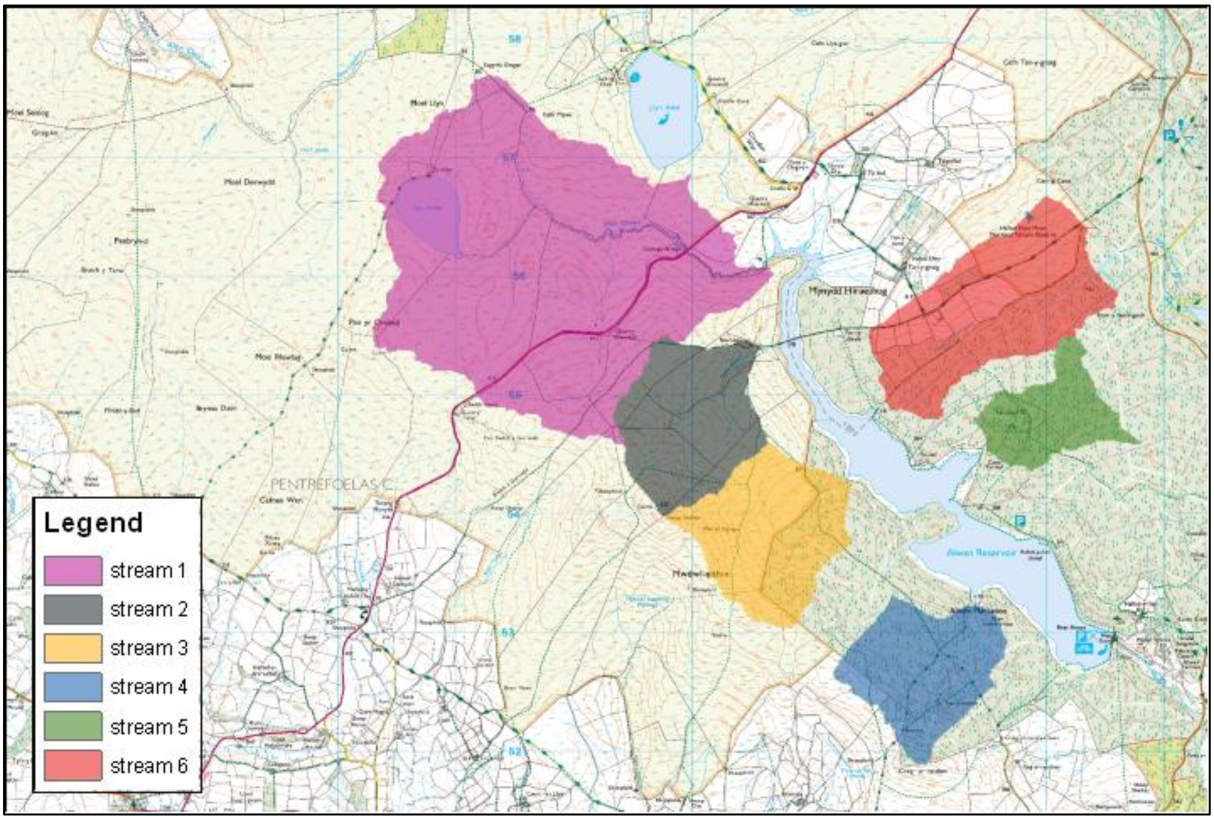


Figure 4.01. Map showing location and spatial extent of stream subcatchments in Catchment A. Distance between grid lines represents 1 km.

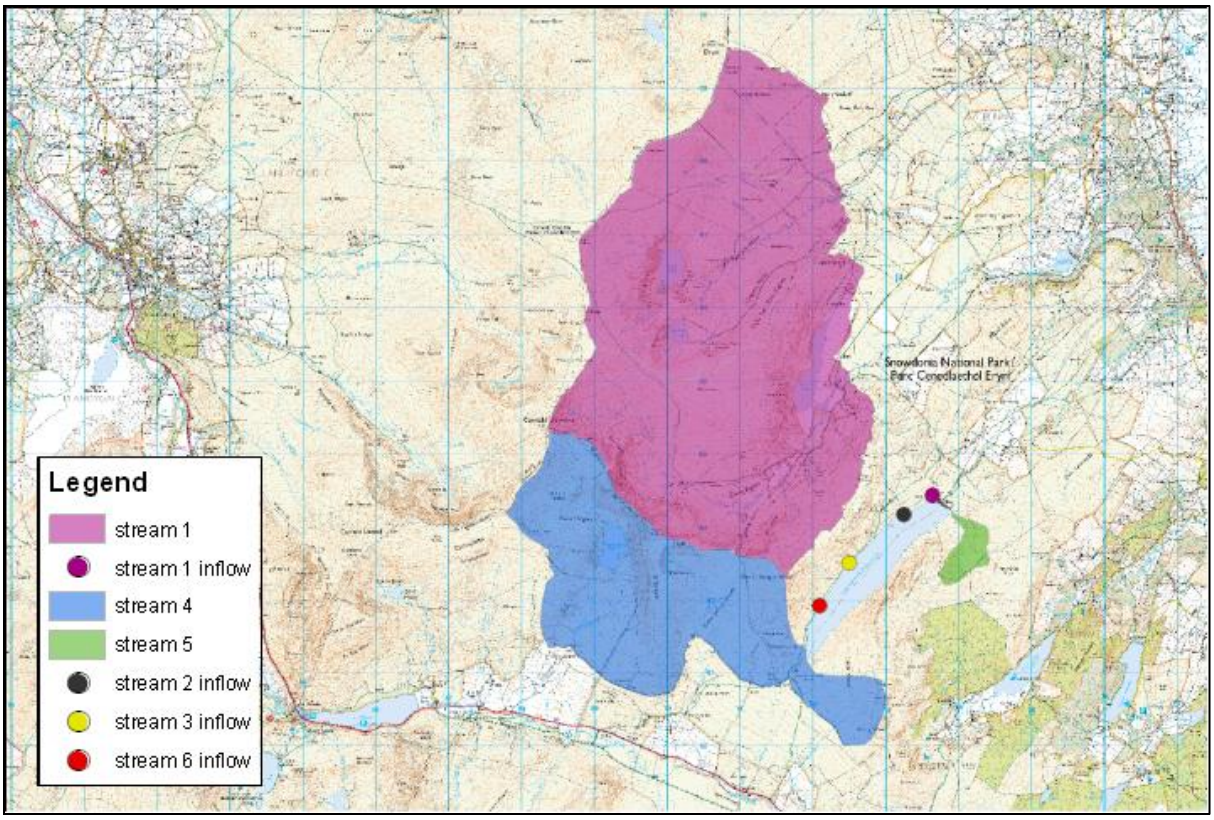


Figure 4.02. Map showing location and spatial extent of stream subcatchments in Catchment C. Distance between grid lines represents 1 km.

Analysis of samples was focussed on measurement and characterisation of DOC. DOC measurement was carried out using a Thermalox TOC/TN analyser equipped with a non-dispersive infrared CO_2 detector. UV analyses including absorbance at λ = 400 nm (used as a proxy for colour (Mitchell & McDonald, 1992)) and at λ = 254 nm were made using a Molecular Devices SpecraMax M2e multi-detection spectrophotometer with aliquots of samples pipetted into a 96-well clear micro-plate. SUVA measurements were derived from the following formula: UV Abs. 254 (cm^{-1}) * 100/DOC (mg L^{-1}). UV measurements were also used to derive the A_{253}:A_{203} ratio (absorbance at λ = 253:203 nm). A_{253}:A_{203} is reported to correlate with the proportion of hydroxyl-, carboxyl-, ester- and carbonyl-substituted aromatic rings (Korshin, *et al*. 1997) which have been implicated in reactions generating DBPs (Kim & Yu, 2007). Phenolic concentration was measured using the Box, (1983) method adapted for 0.3 mL micro-plate wells.

4.3.2. High pressure size exclusion chromatography

HPSEC was conducted using a Varian PL-GPC-50 DataStream unit detecting at λ = 254 nm. The HPSEC unit was interfaced to Cirrus software and equipped with a Bio Sep 2000 column. Calibration standards were sodium polystyrene sulfonate polymers with molecular weights (MWs) of 150,000, 77,000, 32,000, 13,000 and 4,300 Da (Fluka) and cyanocobalamin (1,340 Da). The mobile phase was Milli Q water buffered with phosphate (2 mM KH_2PO_4 + 2 mM $K_2PO_4.3H_2O$) to pH 6.8.

4.3.3. XAD-fractionation

Fractionation of DOC was achieved by resin adsorption using a method adapted from Thurman & Malcolm, (1981) and Marhaba, *et al.* (2003). Samples were separated into five fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophilic neutral (HPIN) according to their adsorption onto a series of macroporous resin adsorbents (Superlite™ DAX-8™ resin and Amberlite™ XAD-4™ resin, both Supelco).

4.3.4. Trihalomethane formation potential

$THMFP_{7d}$ denotes the quantity of THMs formed (µg L^{-1}) following chlorination of a water sample after a 7 d incubation period at 25 °C. The method used was adapted from the Standing Committee of Analysts, (1981) procedure. In this study samples were diluted to 1 mg L^{-1} DOC in order to derive a standardised $THMFP_{7d}$ ($STHMFP_{7d}$) value which provides a measure of DOC reactivity. A $THMFP_{7d}$ value was then calculated by multiplying $STHMFP_{7d}$ by DOC concentration. For the chlorination procedure, 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5M $KH_2PO_{4(aq)}$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $NaOCl_{(aq)}$ to provide 5 mg of free Cl per mg of DOC. After a 7 d incubation in the dark at 25 °C, the reaction was quenched using 0.4 mL of 0.8M $Na_2SO_{3(aq)}$. Extraction of the four chlorinated and brominated THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) was achieved using direct immersion SPME followed by quantification using a Varian 450 GC coupled with an electron capture detector. In this study stream samples were chlorinated according to this procedure on a biannual basis and THM concentrations also measured at 1 h, 1 d and 3 d in order to profile the formation of THMs over time.

4.3.5. Geographical Information Systems (GIS) analysis

Version 9 of the ArcGIS package (ESRI UK) was used to display and quantify the spatial extent of ecological and pedological features within different catchments and subcatchments. To do this, it was first necessary to map the watersheds associated with each reservoir and their input streams. This was achieved using the *Hydrology* functions in the *Spatial Analyst* extension and a digital elevation model (DEM) downloaded from Digimap (EDINA, 2013) (10 m resolution). Defined watersheds were then clipped to other GIS layers displaying habitat and soil type. Habitat information was displayed using the digitised version of the England and Wales 1997-2003 Phase 1 Habitat Survey supplied by the Countryside Council for Wales (CCW, 2005) and soil information using the National Soil Research Institute NATMAP series data (NSRI, 2005). An Ordnance Survey map, also downloaded from Digimap (EDINA, 2013), was used to display reservoirs, streams and other surface features.

Phase 1 habitat categories were organized into the more generalised groupings proposed by Cohen, (2009) and into the broader classifications of *wetland*, *non-wetland*, *coniferous woodland* and *other*. Soil types were classified according to the groups defined by Yallop & Clutterbuck, (2009), namely *blanket bog*, *fen peat*, *peaty topsoil*, *peat to loam* and *non-peat*.

4.3.6. Statistical analysis

Statistical analysis was performed using version 20 of the SPSS Statistics package (PASW). Friedman's ANOVA was conducted to investigate potential differences in water quality parameters between different streams in Catchment A ($n = 13$). Post-hoc analysis employed the Wilcoxon signed-rank test incorporating a Bonferroni correction. Spearman's correlation analysis was performed to test for significant correlations between the spatial extent of habitat and soil types and stream water quality parameters (mean of 13 monthly samples) in Catchment A. Spearman's correlation analysis was also employed to test for significant correlations between DOC characteristics (SUVA and A_{253}:A_{203}) and $STHMFP_{7d}$ in the biannual data from both catchments (*n* = 28).

4.4. Results

4.4.1. Catchment A 14 month stream data

Typically, variations in stream water DOC concentration, characteristics and flux, exhibited a similar temporal trend across the 6 streams (Figure 4.03a). The DOC concentration maximum was observed for all streams in August 2012 (mean 37.6 mg L^{-1}) and the minimum in March 2012 (mean 10.0 mg L^{-1}). Significant differences were identified between streams in terms of DOC concentration (Table 4.02). Stream 4 which showed the lowest mean DOC concentration (13.7 mg L^{-1}) was significantly lower than Streams 2, 5 and 6. Stream 5 which had the highest mean DOC concentration (22.6 mg L^{-1}) was significantly higher than all streams except Stream 1. Mean DOC flux varied substantially during the course of sampling between a mean of 1.0 g s^{-1} in March 2012 and 23.8 g s^{-1} in April 2012 (Figure 4.03b). This closely followed the trend in stream discharge (Figure 4.03c). Stream 1, which exhibited by far the highest DOC flux (mean 26.5 g s^{-1}), was significantly higher than all other streams in this respect (Table 4.03). This was partly due to relatively high DOC concentration, but predominantly due to being the main input stream in terms of discharge. Colour (absorbance at λ = 400 nm), showed a similar temporal trend to that of DOC concentration (Figure 4.03d), with a maximum in August 2012 (mean 0.228 UV a.u.) and a minimum in March 2012 (mean 0.041 UV a.u.). A second large peak was observed in June 2012 (mean 0.219 UV a.u.), which was not accompanied by a comparable increase in DOC concentration, indicating a shift in DOC character for this month. Significant differences between streams were the same as for DOC concentration except for an additional significant result for the Stream 4/Stream 1 comparison (Table 4.03). The colour peak in June 2012 coincides with a substantial increase in SUVA for all streams (Figure 4.03e) where mean SUVA reached 6.0 L mg^{-1} m^{-1} in contrast to mean measurements between 3.5 and 4.4 L mg^{-1} m^{-1} during the rest of the sampling period. Throughout the sampling period, SUVA values for all streams indicate relatively high hydrophobicity and MW (Edzwald & Tobiason, 1999; Volk, *et al*. 2002), and therefore high humic content. No significant differences in stream SUVA measurements were observed between streams.

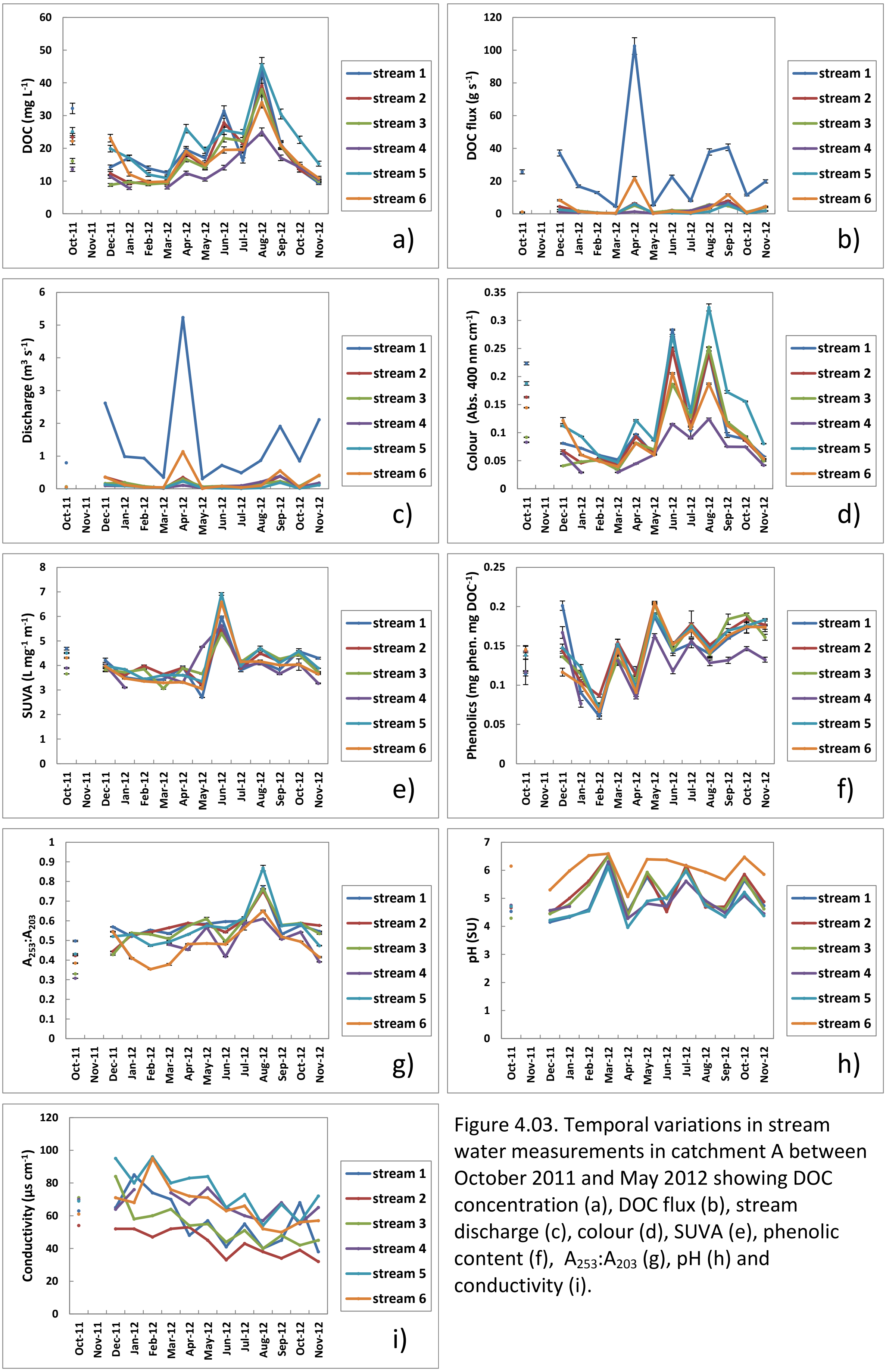


Figure 4.03. Temporal variations in stream water measurements in catchment A between October 2011 and May 2012 showing DOC concentration (a), DOC flux (b), stream discharge (c), colour (d), SUVA (e), phenolic content (f), A_{253}:A_{203} (g), pH (h) and conductivity (i).

Table 4.02. Mean results of Catchment A stream water DOC quantity and composition analysis showing statistically significant results identified by Friedman's ANOVA analysis.

Stream	**1 (a)**	**2 (b)**	**3 (c)**	**4 (d)**	**5 (e)**	**6 (f)**
DOC concentration (mg L^{-1})	20.2 ± 2.7	17.6 ± 2.5 de	16.3 ± 2.3 E	13.7 ± 1.4 bEF	22.6 ± 2.5 bCDf	17.8 ± 1.9 De
DOC flux (g s^{-1})	26.5 ± 7.2 BCDEF	2.4 ± 0.7 A	2.3 ± 0.5 A	1.8 ± 0.6 A	1.7 ± 0.5 A	4.3 ± 1.7 A
Discharge (m^3 s^{-1})	1.40	0.14	0.15	0.12	0.07	0.23
Colour (Abs$_{400}$) (UV a.u.)	0.116 ± 0.022 D	0.106 ± 0.020 DE	0.064 ± 0.018 E	0.069 ± 0.009 ABEf	0.082 ± 0.023 BCDf	0.053 ± 0.015 de
SUVA (L mg^{-1} m^{-1})	4.0 ± 0.2	4.1 ± 0.2	4.0 ± 0.2	3.9 ± 0.2	4.2 ± 0.3	4.0 ± 0.2
Phenolics per mg DOC (mg phen. mg DOC^{-1})	0.14 ± 0.01 D	0.15 ±.0.01 Df	0.14 ± 0.01	0.13 ± 0.01 Abe	0.15 ±.0.01 D	0.14 ± 0.01 b
A_{253}:A_{203}	0.57 ± 0.02 DF	0.56 ± 0.02	0.54 ± 0.03	0.48 ± 0.03 A	0.56 ± 0.03 F	0.47 ± 0.02 AE
pH (SU)	5.0 ± 0.2 F	5.2 ± 0.2 F	5.1 ± 0.2 F	4.9 ± 0.2 F	4.8 ± 0.2 F	6.0 ± 0.1 ABCDE
Conductivity (µs cm^{-1})	57.6 ± 4.1 Be	44.2 ± 2.3 aCDEF	55.1 ± 3.5 BE	66.5 ± 2.0 B	74.9 ± 3.6 aBCF	66.0 ± 3.3 BE

Results given as mean ± standard error ($n = 13$). Letter annotations denote significantly different means (lower case: $p < 0.05$, upper case: $p < 0.01$).

Fluctuations in standardised phenolic content were largely synchronous across all streams (Figure 4.03f). Lowest mean phenolics measurement occurred in February 2012 (0.07 mg phen. mg DOC^{-1}) and the maximum in May 2012 (0.19 mg phen. mg DOC^{-1}). Mean values for individual streams were similar, ranging between 0.13 and 0.15 mg phen. mg DOC^{-1}, although significant differences were identified. Stream 4, which had the lowest mean concentration (0.13 mg phen. mg DOC^{-1}), was significantly lower than Streams 1, 2 and 5. In addition, phenolic content in Stream 2 (mean 0.15 mg phen. mg DOC^{-1}) was found to be significantly higher than Stream 6 (mean 0.14 mg phen. mg DOC^{-1}) (Table 4.03).

The mean A_{253}:A_{203} ratio varied between 0.39 in October 2011 and 0.74 in August 2012 when most streams showed a prominent peak (Figure 4.03g), coinciding with peak DOC concentration (Figure 4.03a). Stream 1, which showed the highest mean A_{253}:A_{203} value (0.57), was significantly higher than Stream 4 and Stream 6, which had the lowest mean A_{253}:A_{203} value (0.47), and was also significantly lower than Stream 5 (Table 4.03).

Most pH measurements showed slight acidity throughout the sampling period though fluctuations in pH did occur (Figure 4.03h). In general these fluctuations were synchronous between streams. The pH of Stream 6 (mean pH: 6.0) was found to be significantly higher than all other streams (Table 4.03).

A general trend of decreasing conductivity was apparent for all streams between December 2011 and November 2012 (Figure 4.03i). Significant differences in stream conductivity were identified between Stream 2, which exhibited the lowest conductivity (mean: 44.2 µs cm^{-1}), and all other streams. Stream 5, which exhibited the highest conductivity (mean: 74.9 µs cm^{-1}) also had significantly higher conductivity than all other streams except Stream 6 (Table 4.03).

4.4.2. Catchments A and C biannual stream and reservoir data

The DOC concentration in Catchment A stream samples was consistently lower in May 2012 than in October 2011 (Figure 4.04a) which coincides with the descending flank of a late summer peak (Figure 4.03a). DOC concentrations for Catchment C stream samples were similar on both sampling dates, as were reservoir DOC measurements in both catchments. However, 12 month data for Reservoir A showed that DOC concentrations did fluctuate over time (Chapter 6). The DOC concentration of Catchment C samples were consistently lower than Catchment A samples, with the lowest DOC concentration observed in the three streams with the smallest subcatchments and the lowest discharge (C2,C3 and C6).

Discharge measurements showed that C1 and C4 are the main input streams in Catchment C, and are comparable in size to A1 in Catchment A (Figure 4.04b). In both catchments, lower stream discharge was observed in May 2012, except for C4 which showed an increase. In October 2011 total DOC flux for all streams was substantially higher (29.9 g s^{-1}) in Catchment A compared with Catchment C (5.6 g s^{-1}), mostly as a result of the high flux from A1 in Catchment A (Figure 4.04c). However, in May 2012 total DOC flux was similar (5.2 and 4.6 g s^{-1} in Catchments A and C, respectively).

Standardised phenolic content in stream samples were lower in May 2012 compared with October 2011 in both catchments (Figure 4.04d). By contrast, phenolics measurements for both reservoirs were very similar for both sampling dates but slightly higher in May 2012. Though relatively little variation in Catchment A measurements was apparent between October 2012 and May 2011, the monthly data shows that temporal variations in the standardised phenolic content of the streams did occur (Figure 4.03f).

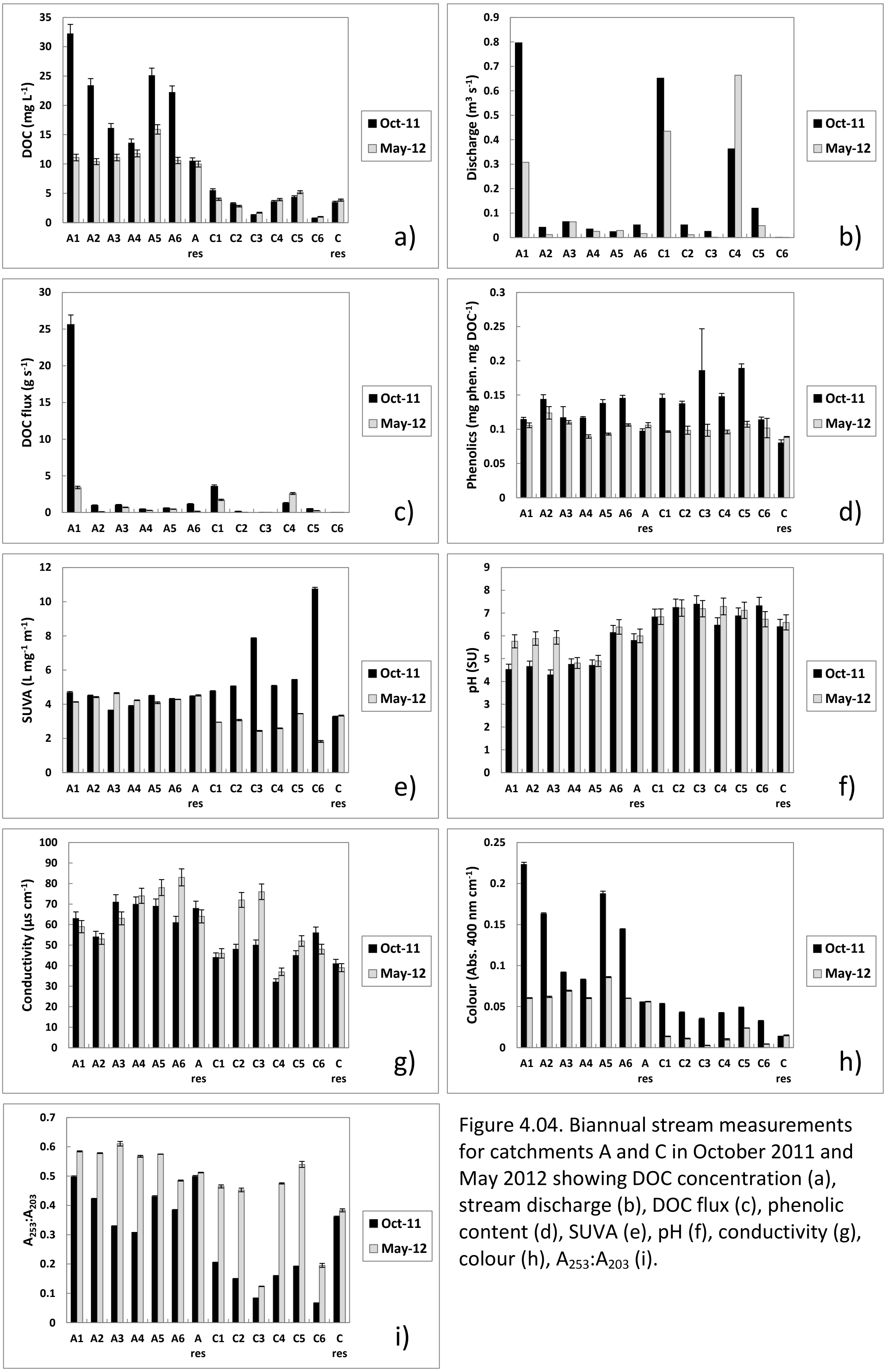


Figure 4.04. Biannual stream measurements for catchments A and C in October 2011 and May 2012 showing DOC concentration (a), stream discharge (b), DOC flux (c), phenolic content (d), SUVA (e), pH (f), conductivity (g), colour (h), A_{253}:A_{203} (i).

Catchment C SUVA measurements were more variable than Catchment A measurements, both between samples and between sampling dates (Figure 4.04e). SUVA measurements in Catchment C stream samples were higher in October 2011 than May 2012, with C3 and C6 showing particularly high SUVA in October 2011 (7.9 and 10.7 L mg^{-1} m^{-1}, respectively). However, Reservoir C samples showed similar SUVA values in October 2011 and May 2012 (3.3 L mg^{-1} m^{-1} in both cases). Reservoir A samples, which showed higher SUVA than Reservoir C, were also similar on both sampling dates (4.5 mg^{-1} m^{-1} in both cases). pH measurements show that Catchment A streams are more acidic than those in Catchment C (Figure 4.04f). Reservoir C pH was also higher than Reservoir A both in October 2011 and May 2012. In general stream sample conductivity was lower in Catchment C than Catchment A (Figure 4.04g). Reservoir C also showed lower conductivity than Reservoir A on both sampling dates (41 and 39 µs cm^{-1} in October 2011 and May 2012, respectively, compared with 68 and 64 µs cm^{-1} for Reservoir A).

Colour measurements (absorbance at $\lambda = 400$ nm) in Catchment A (Figure 4.04h) appear to correspond closely with DOC concentration (Figure 4.04a), with lower colour observed in stream samples in May 2012. Stream colour measurements were also lower in May 2012 in Catchment C samples despite similar DOC concentration for both sampling dates. This, along with increased standardised phenolic concentration and SUVA, indicates a change in DOC character. Reservoir colour measurements at both sites were similar in October 2011 and May 2012 but substantially lower in Reservoir C compared with Reservoir A.

In all samples A_{253}:A_{203} was higher in May 2012, though for reservoir samples the difference was small (Figure 4.04i). The increase in May 2012 was most pronounced in C1, C2, C3 C4 and C5. In October 2011 A_{253}:A_{203} for Catchment C streams were much lower than Catchment A streams but the difference was less stark in May 2012. A_{253}:A_{203} for Reservoir C samples was lower than Reservoir A on both sampling dates. Spearman's correlation analysis showed a significant positive correlation between A_{253}:A_{203} and $STHMFP_{7d}$ across all biannual samples ($n = 28$), $r_s = 0.770$, $p < 0.01$ (Figure 4.05). A weaker positive correlation was identified between SUVA and $STHMFP_{7d}$ ($n = 26$), $r_s = 0.351$, $p < 0.05$ (Figure 4.06).

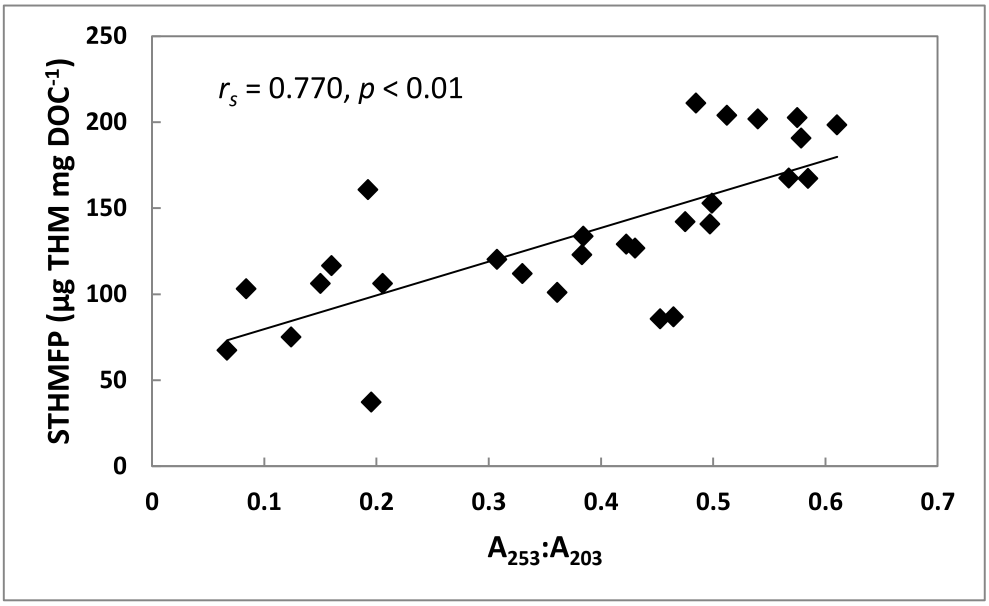


Figure 4.05. Correlation between A_{253}:A_{203} and STHMFP7d for biannual stream and reservoir samples (n = 28).

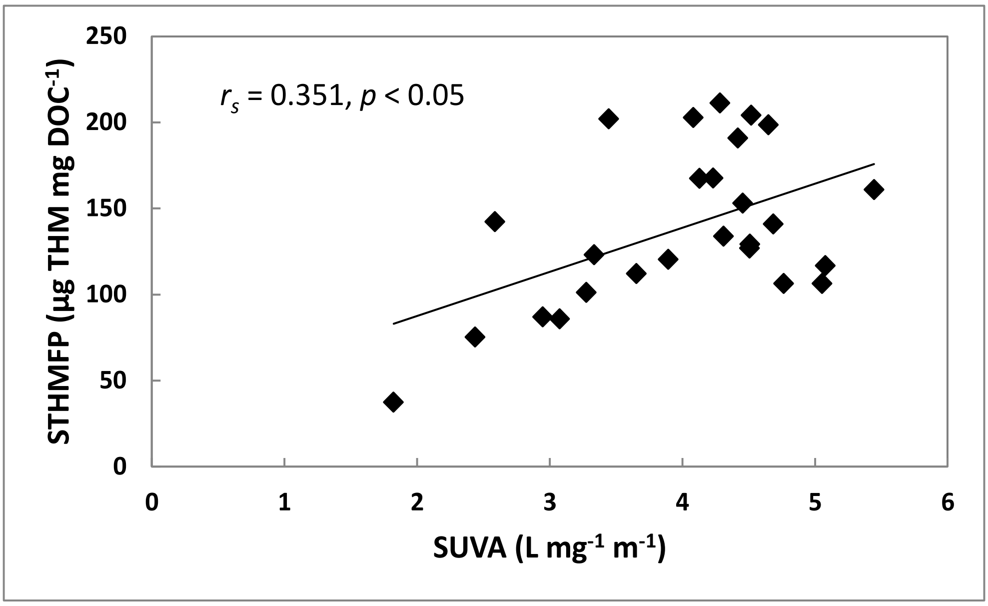


Figure 4.06. Correlation between SUVA and $STHMFP_{7d}$ for biannual stream and reservoir samples (n = 26).

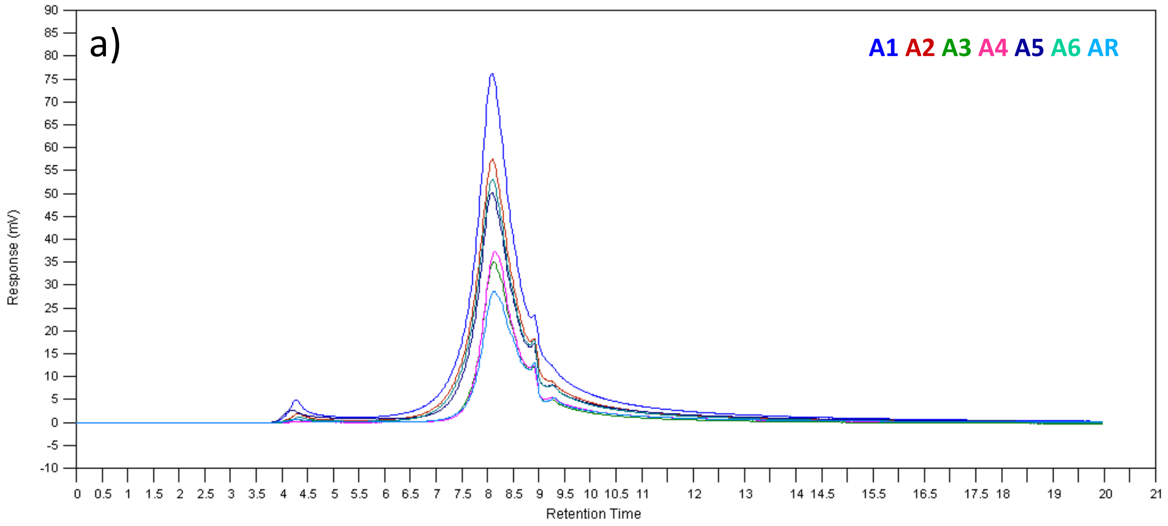
High pressure size exclusion chromatography

Stream and reservoir samples from both catchments and both sampling dates displayed similar MW distribution (MWDs) with the retention time (t_R) of MW peaks remaining constant (Figures 4.07a-4.07d). These included a small peak at $t_R \approx 4.2$ min which represents the high MW (HMW) molecules that are too large to interact with the pores of the stationary phase (Huber, *et al*. 2011), followed by a dominant peak at $t_R \approx 8.2$ min with two overlapping peaks as $t_R \approx 9.0$ and 9.4 min.

The height of the peaks is determined predominantly by DOC concentration (Figure 4.07). Comparison of Figures 4.07a and 4.07c, representing MWDs of DOC in Catchment A samples in October 2011 and May 2012, shows subtle differences in the relative size of the different peaks; the HMW peak at t_R ≈ 4.2 min was slightly smaller and the lower MW peaks at t_R ≈ 9.0 and 9.4 min were more prominent in May 2012, indicating a slight shift to lower MW molecules for all samples. An increase in the height of the lower MW peaks (t_R ≈ 9.0 and 9.4 min) in May 2012 was also apparent in Catchment C samples but was more substantial (Figures 4.07b and 4.07d).

Comparison of samples from the two catchments showed several key differences; the Catchment C samples were characterised by a smaller HMW peak at t_R ≈ 4.2 min and larger lower MW peaks at t_R ≈ 9.0 and 9.4 min, relative to the dominant peak at t_R ≈ 8.2 min. These differences indicate a higher proportion of lower MW molecules in Catchment C samples.

The differences in MWDs between catchments and sampling dates described here did not significantly affect the relative proportions of HMW and LMW molecules (separated by the 1.0 kDa MW boundary (Zou, *et al*. 2004)) which remained similar (mean LMW%: 6.5-8.5) and indicate the consistent dominance of HMW molecules in all samples.



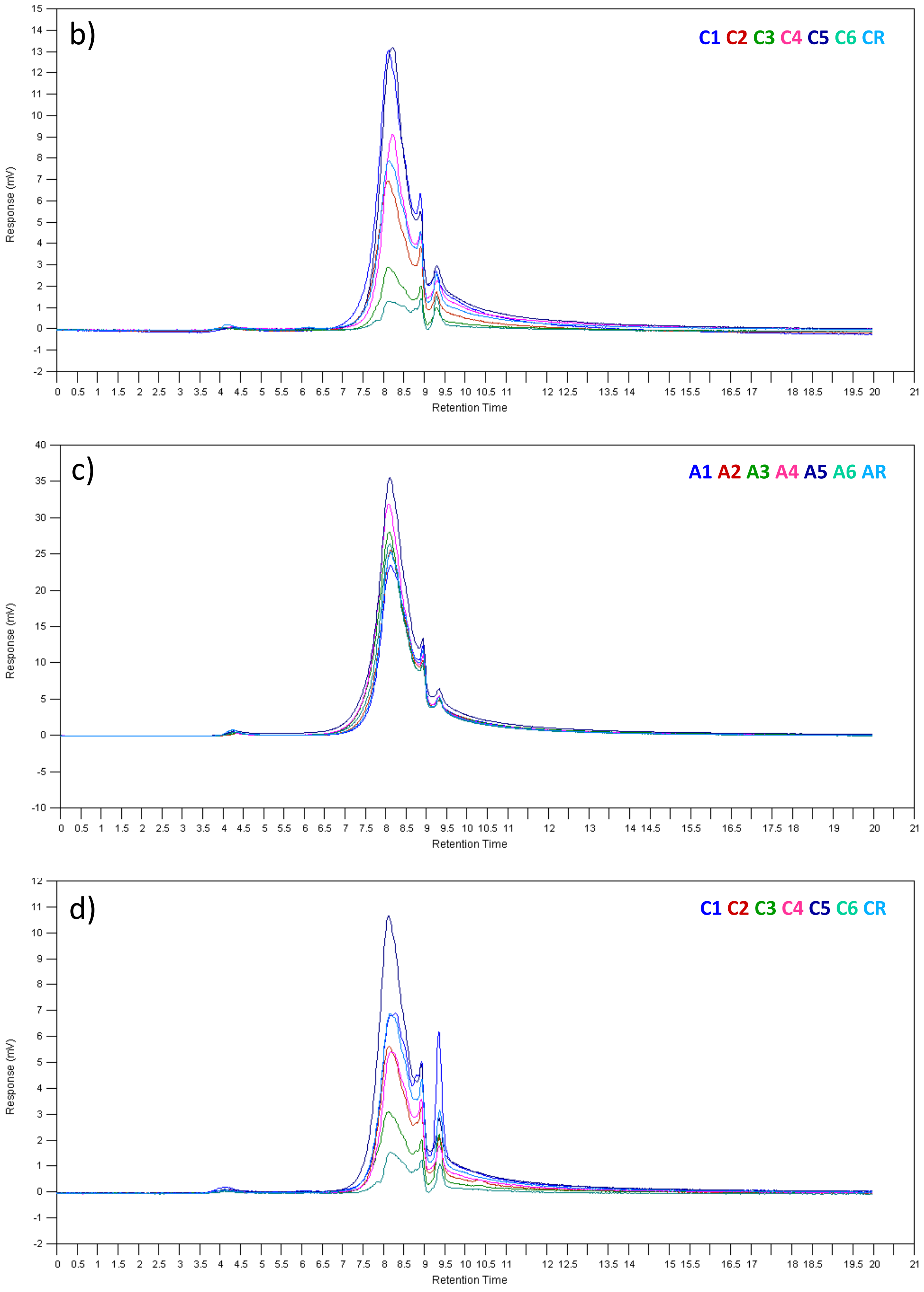


Figure 4.07. HPSEC chromatograms for catchment A (a and c) and catchment C samples (b and d) in October 2011 (a and b) and May 2012 (c and d).

Trihalomethane formation potential

All Catchment A samples showed higher $STHMFP_{7d}$ in May 2012 (167 to 211 µg THM mg DOC^{-1}; $STHMFP_{7d}$) compared with October 2011 (112 and 141 µg THM mg DOC^{-1}) (Figures 4.08a and 4.09a). The reservoir sample had a higher $STHMFP_{7d}$ than any stream in October 2011 (153 µg THM mg DOC^{-1}) and was exceeded only by A6 in May 2012 (204 µg THM mg DOC^{-1} compared with 211 µg THM mg DOC^{-1} for A6).

Lower DOC concentrations for all samples in May 2012 dampened the effect of higher $STHMFP_{7d}$ values on $THMFP_{7d}$ measurements, although an increase in $THMFP_{7d}$ was observed in the A1, A2 and A4 samples as well as the reservoir sample (Figures 4.08b and 4.09b). Variability in $THMFP_{7d}$ between samples was reduced in May 2012 due to DOC concentrations being more similar. $THMFP_{7d}$ ranged between 1605 and 4529 µg L^{-1} in October 2011 and between 1857 and 3222 µg L^{-1} in May 2012.

On average, Catchment C stream samples had lower $STHMFP_{7d}$ than Catchment A stream samples, and reservoir $STHMFP_{7d}$ was lower for Catchment C both in October 2011 and May 2012 (Figures 4.08c and 4.09c). In percentage terms, a larger variation in $STHMFP_{7d}$ was observed in Catchment C stream samples which ranged between 67 and 161 µg THM mg DOC^{-1} in October 2011 and between 37 and 202 µg THM mg DOC^{-1} in May 2012. In contrast to Catchment A samples, only 4 of the 7 Catchment C samples showed an increase in $STHMFP_{7d}$ in May 2012 (C1, C2, C3 and C6), whilst the remaining samples showed a decrease.

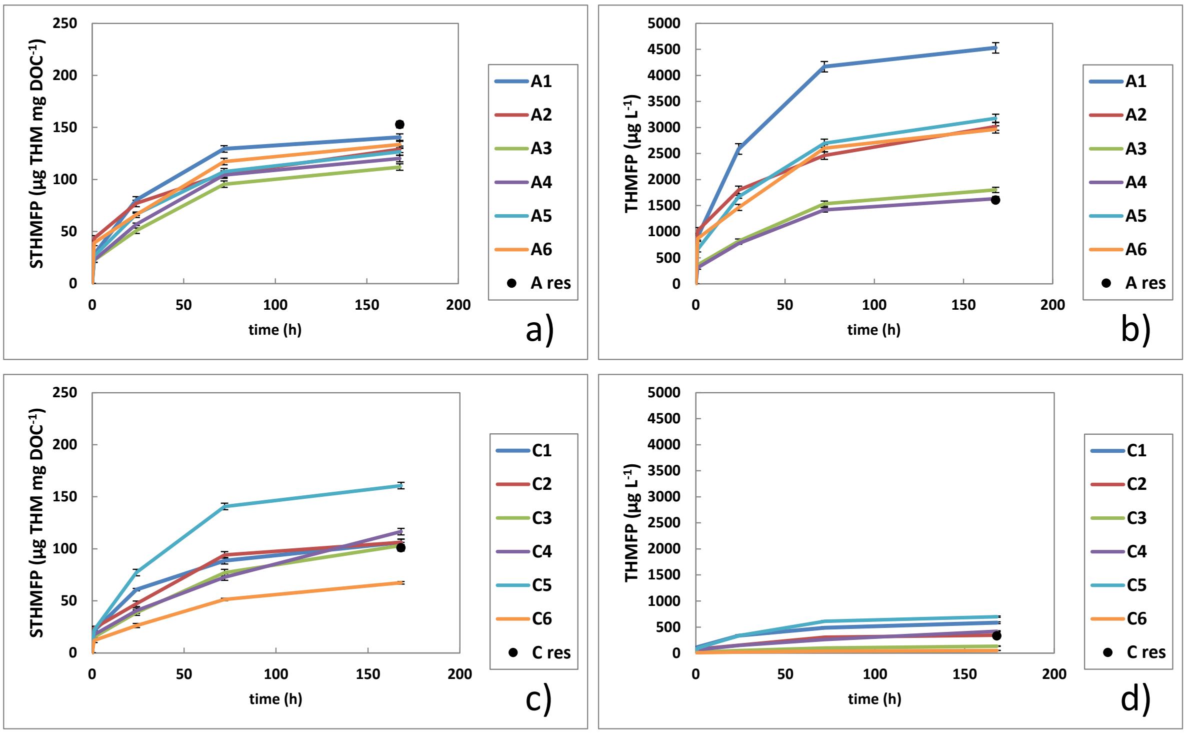


Figure 4.08. Profile of STHMFP (a and c) and THMFP (b and d) over a 7 d incubation period following chlorination of stream and reservoir samples for Catchment A (a and b) and Catchment C (c and d) collected in October 2011. Error bars represent the standard error of the mean derived from a detection repeatability experiment.

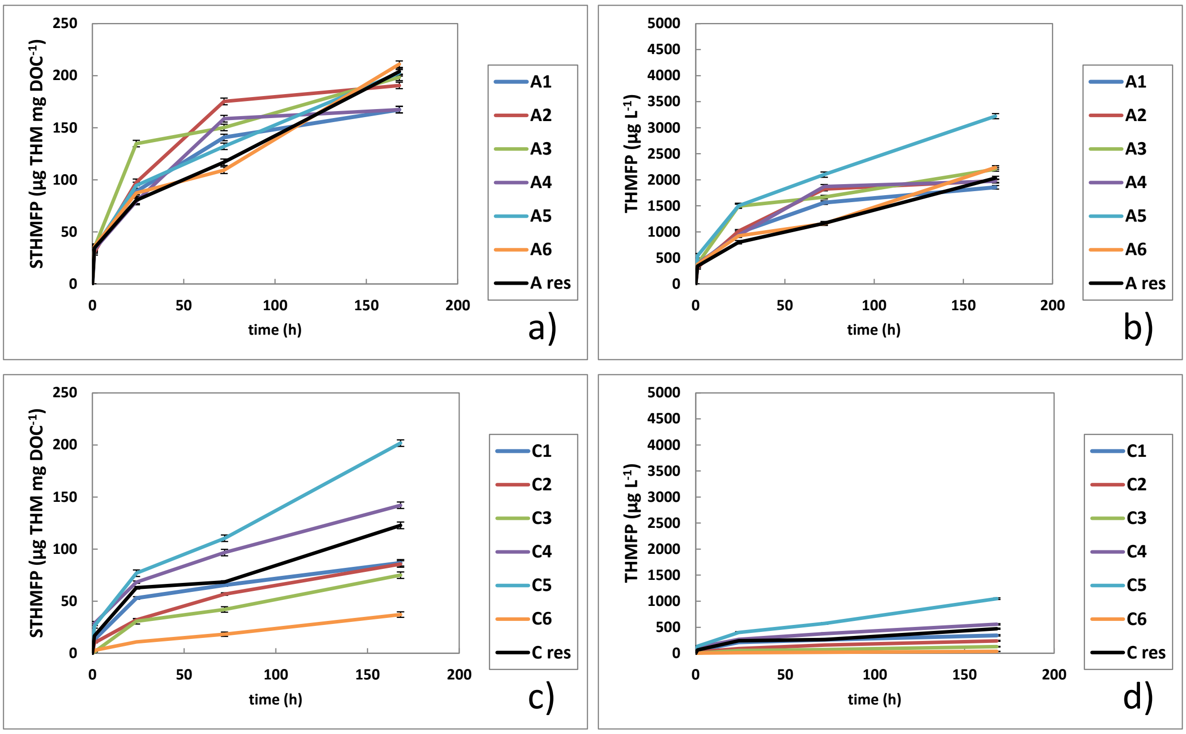


Figure 4.09. Profile of STHMFP (a and c) and THMFP (b and d) over a 7 d incubation period following chlorination of stream and reservoir samples for Catchment A (a and b) and Catchment C (c and d) collected in May 2012. Error bars represent the standard error of the mean derived from a detection repeatability experiment.

Lower DOC concentrations in Catchment C samples meant that $THMFP_{7d}$ measurements were substantially lower than in Catchment A. However, a higher degree of variability in $STHMFP_{7d}$ between samples meant that $THMFP_{7d}$ measurements were more variable than in Catchment A and showed a particularly large range in May 2012 (36 to 1049 µg L^{-1}) (Figures 4.08d and 4.09d).

The rate of THM formation, as indicated by the percentage of THMs formed within the first 24 h of the reaction varied both between sites and between sampling dates. On average, lower reaction rates were observed in May 2012 in both Catchments. Catchment A samples showed a higher reaction rate both in October 2011 and May 2012, with $STHMFP_{1d}$ as a percentage of $STHMFP_{7d}$ 24% and 18%, respectively, compared with 17% and 12% in Catchment C.

Fractional character

In October 2011 Catchment A stream samples displayed similar fractional character (Figure 4.10a). HPIN and HPOA were the dominant fractions, with the HPIA fraction representing a smaller proportion (16-28%). In comparison, the reservoir sample had a larger HPOA fraction (48%) and smaller HPIN fraction (23%). In May 2012 the stream samples displayed similar fractional character to the October 2011 samples (Figure 4.10c), though in all cases except A3 the HPIA fraction was slightly larger. Compared with October 2011 the reservoir sample had a smaller HPOA fraction (28%) and a larger HPIN fraction (40%).

Catchment C samples were distinct from Catchment A and showed greater variability. In October 2011, with the exception of C3 and C6, which had very low DOC concentration, the HPOA fraction was dominant (57-60%) and the HPIN fraction substantially lower (0-16%) (Figure 4.10b). For C3 and C6 the relative contributions of the HPOA and HPIN fractions were roughly reversed. In May 2012 all samples showed a dramatic increase in the contribution of the HPIN fraction (Figure 4.10d). C3 and C6 remained distinct from the other stream samples, with HPIN the dominant fraction. The reservoir sample for May 2012 had a relatively large HPOA fraction (45%), with smaller HPIN (28%) and HPIA (19%) fractions.

For most samples the contribution of the HPOB and HPIB fractions combined was minimal, but was higher in the Catchment C samples, particularly in May 2012. This is likely to be an artefact of XAD-fractionation of samples with low DOC concentrations.

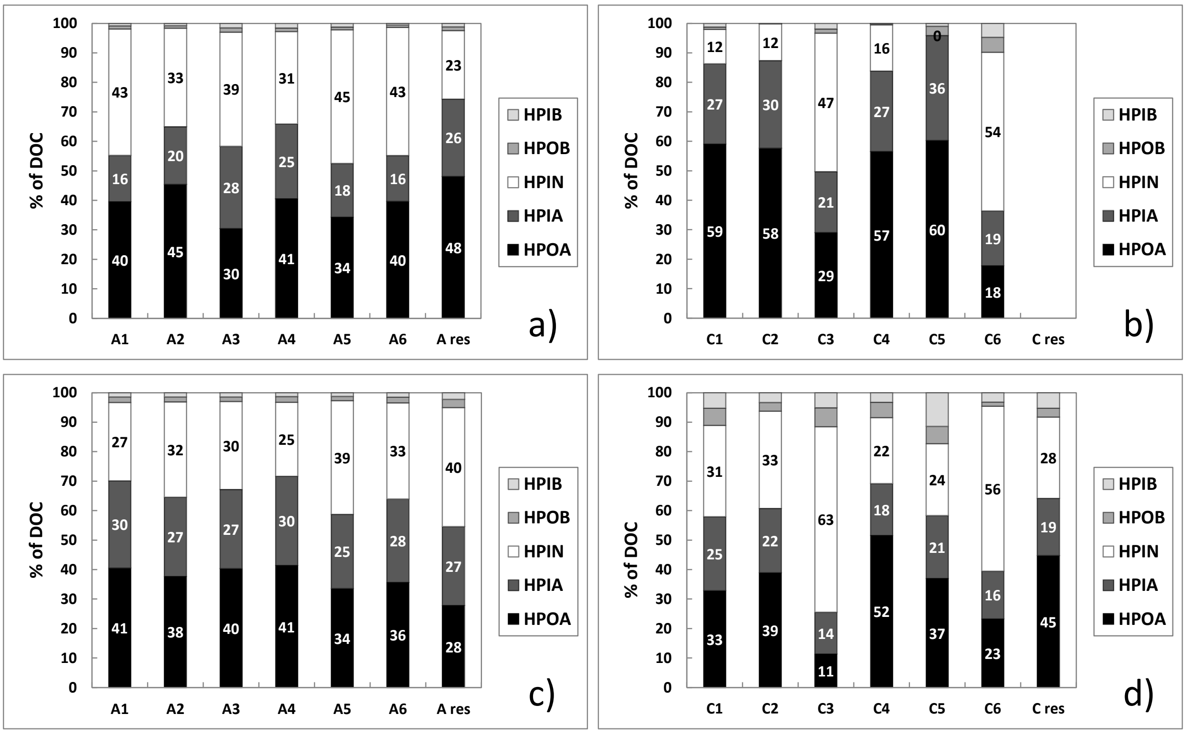


Figure 4.10. % contribution of HPOA, HPIA, HPIN, HPOB and HPIB fractions to the total recovered DOC following fractionation for stream and reservoir samples for Catchment A (a and c) and Catchment C (b and d) in October 2011 (a and b) and May 2012 (c and d).

4.4.3. Catchment and subcatchment characteristics

In Catchment A the subcatchments of A4 and A5 are dominated, almost exclusively, by woodland/dense scrub habitat, of which the vast majority is coniferous plantations (Figure 4.11a). This habitat also represents a large portion of the subcatchments of A3 and A6 (35% and 44%, respectively) but is absent from subcatchments of A1 and A2 where unimproved grassland occupies most area. Bog habitat occupies a substantial area in the subcatchments of A1 and A2 (17% and 24%, respectively) and is also present in the subcatchments of A3 and A6 (12% and 3%, respectively). Flush and spring habitat also occurs in these 4 subcatchments, occupying between 9% and 15%. Heath habitats are represented in all subcatchments except that of A5, occupying most area in the subcatchments of A3 and A6 (29% and 23%, respectively).

The subcatchment areas for Streams C2, C3 and C6 in Catchment C were too small to be delineated using the digital elevation model and hence their habitat/soil characteristics could not be precisely quantified, although GIS maps suggest these subcatchments are dominated by heath habitat and peaty topsoil/peat to loam soils. Of the remaining subcatchments, C1 and C4 are dominated by unimproved grassland (59% and 52%, respectively) (Figure 4.11b). The subcatchment of C5 is almost exclusively occupied by heath habitat (95%) which is also present in C1 and C4 (17% and 32%, respectively). Bog habitat is present in all three subcatchments but only in significant quantity in the subcatchment of C1 (17%).

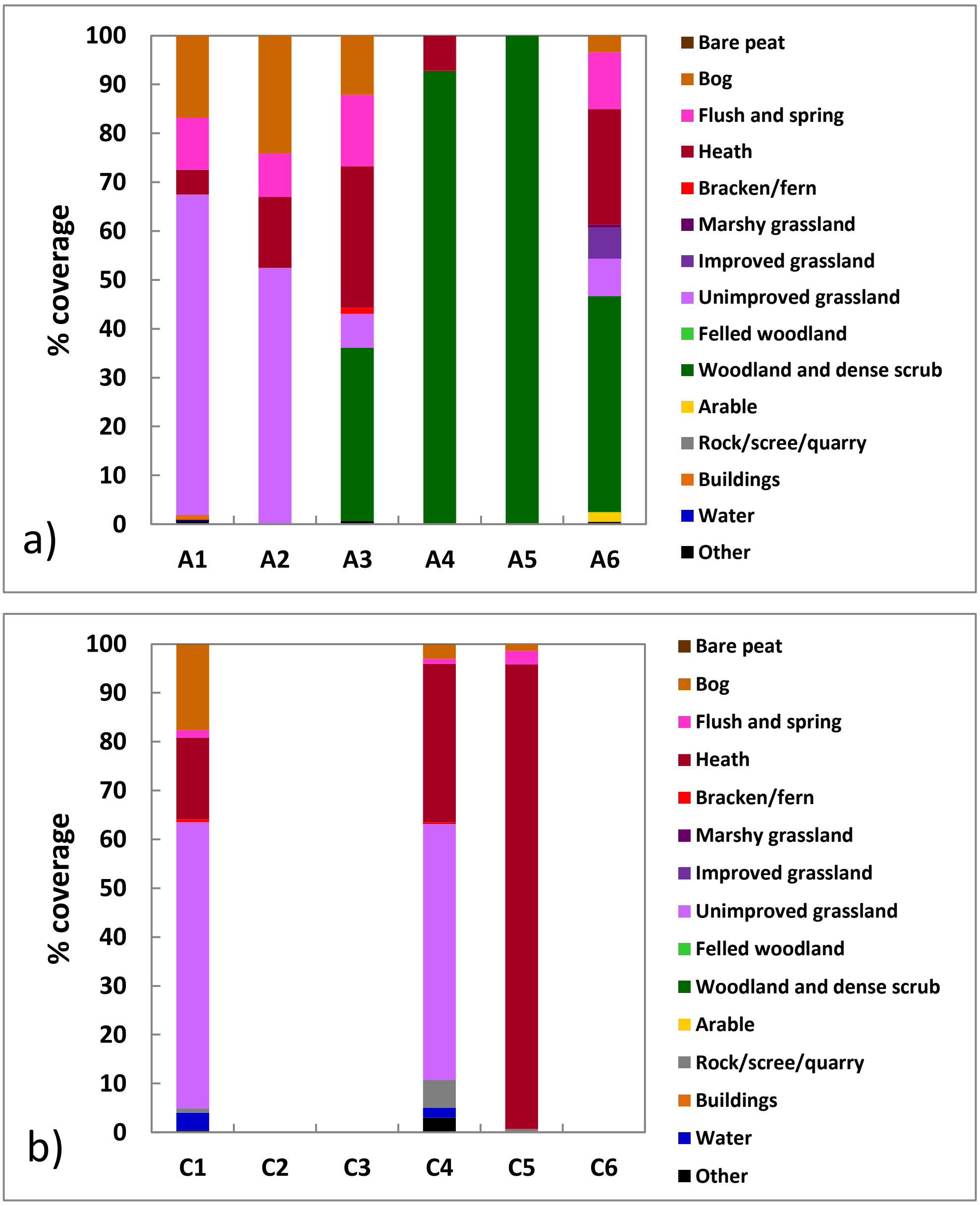


Figure 4.11. Extent of Phase 1 habitat types in Catchment A stream subcatchments (a) and Catchment C stream subcatchments (b).

Catchment A stream subcatchments were comprised entirely of peat to loam and blanket bog soils, though the subcatchments of A3 and A5 showed more extensive blanket bog coverage than the other subcatchments (61% and 46%, respectively) (Figure 4.12a). Though similarly dominated by peat to loam soils, in Catchment C the subcatchments of C1, C2, C3, C4 and C6 also include areas of peaty topsoil though in the case of C2, C3 and C6 these areas could not be precisely determined (Figure 4.12b).

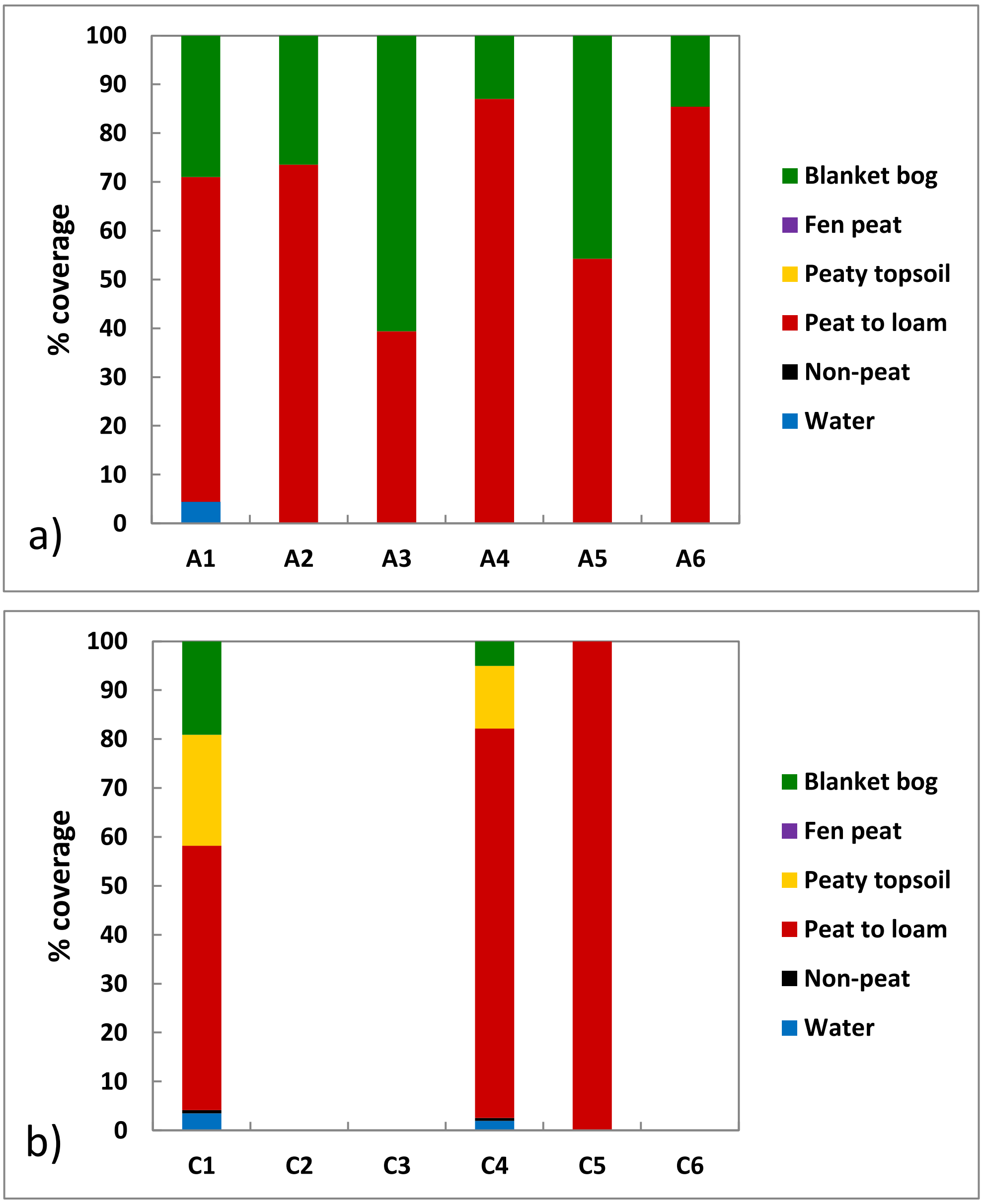


Figure 4.12. Extent of different soil types in Catchment A stream subcatchments (a) and Catchment C stream subcatchments (b).

Only two statistically significant correlations were identified between subcatchment characteristics (habitat and soil type) and mean stream water quality measurements in Catchment A. A strong negative correlation was identified between % bog habitat and stream water conductivity (r_s = -.928, $p < 0.01$). A strong positive relationship was found between % woodland/dense scrub habitat and stream water conductivity (r_s = .899, $p < 0.05$).

The two reservoir catchments appear fairly similar in terms of the relative coverage of different habitats, however a number of important differences can be identified (Figure 4.13). The first main difference is the larger heath coverage in Catchment C (26%) compared with Catchment A (10%). Secondly, woodland and dense scrub represents 27% of Catchment A but is absent from Catchment

C. Thirdly, wetland habitats (marshy grassland, bog, flush and spring, swamp and bare peat) occupy a larger proportion of Catchment A (20%) than Catchment C (13%) (Figure 4.14).

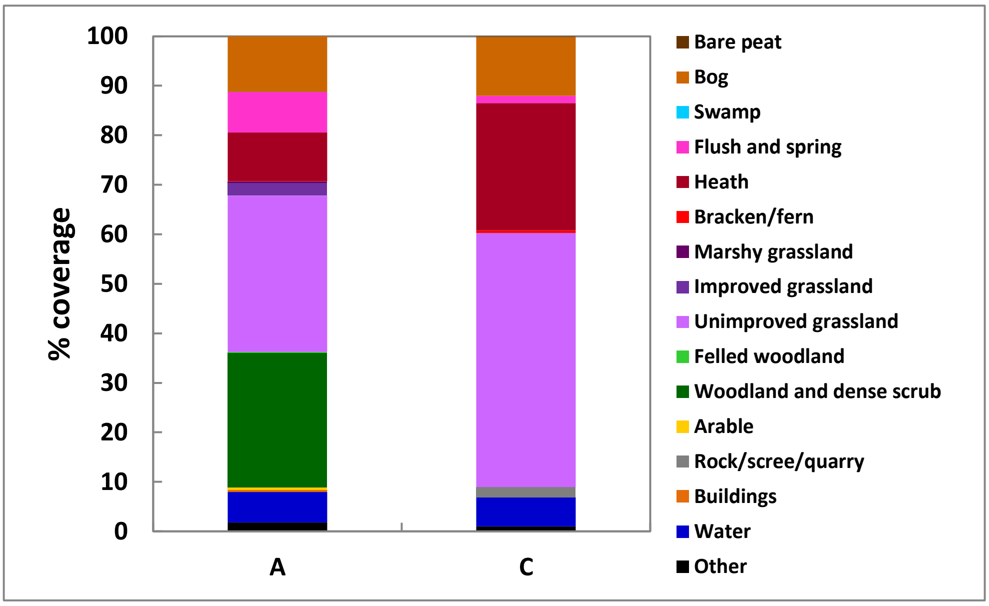


Figure 4.13. Extent of Phase 1 habitat types in Catchments A and C.

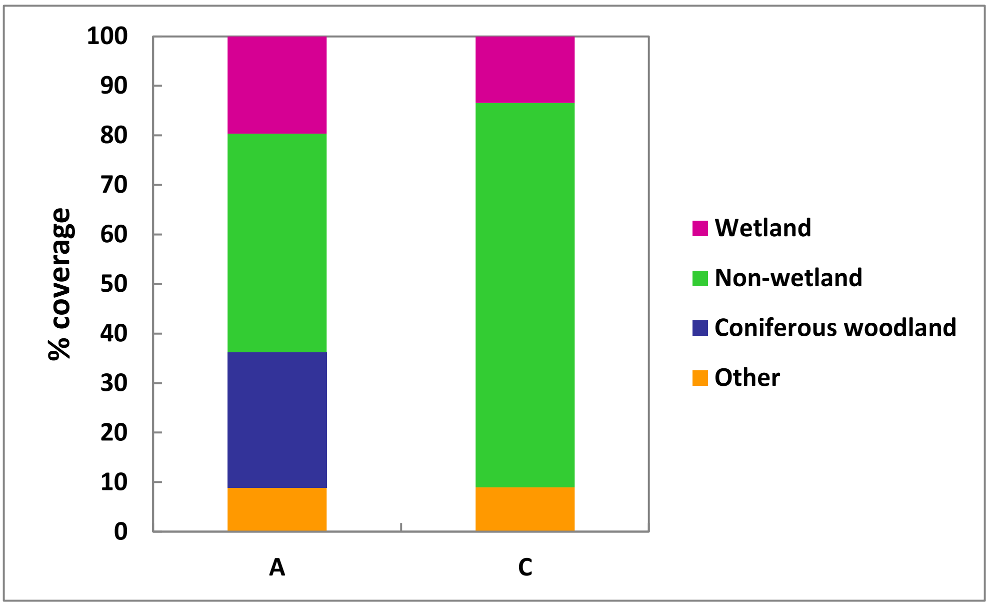


Figure 4.14. Extent of generalised habitat types in Catchments A and C.

In terms of soil type Catchment A and C are fairly similar; both dominated by peat to loam soil and both < 1% non-peat soils (Figure 4.15). The most important difference in terms of its potential influence on surface water quality is that Catchment A has almost double (24%) the blanket bog coverage of Catchment C (13%).

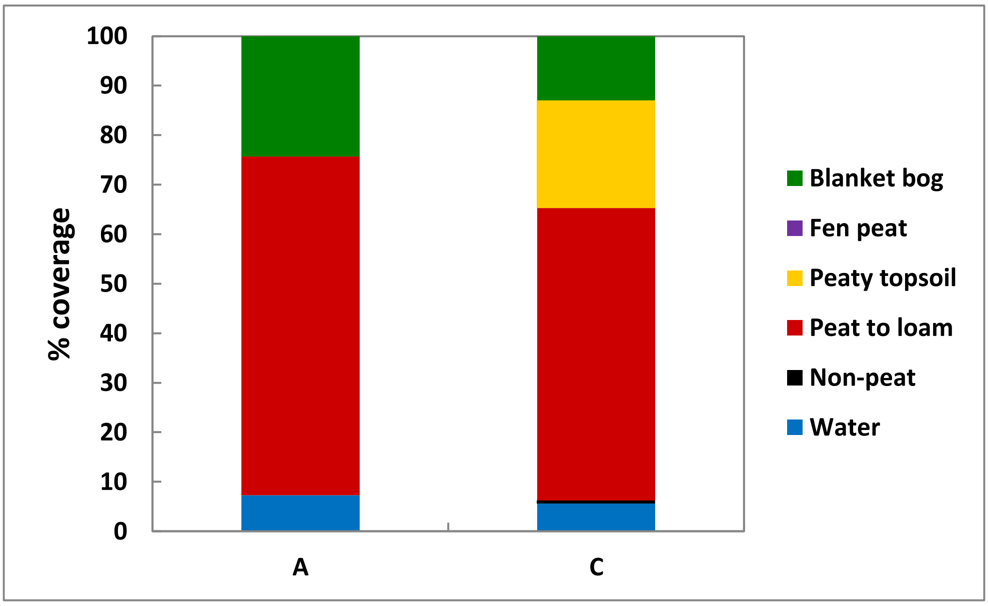


Figure 4.15. Extent of different soil types in Catchments A and C.

4.5. Discussion

4.5.1. Catchment A 14 month stream data – seasonality

The synchronicity of fluctuations in DOC concentration and character between streams highlights the importance of seasonal drivers in DOC production and export. In addition, in this catchment, a close association between stream discharge and DOC flux was observed, suggesting that antecedent rainfall may be the dominant driver of temporal variations in DOC flux. A strong association between stream discharge and DOC flux has been reported previously (Hope, *et al*. 1994).

The trend in DOC concentration observed here shows a similar seasonal pattern to those reported previously with a peak in late summer/early autumn and a trough in winter/early spring (Dawson, *et al*. 2004; Neal, *et al*. 2005). The DOC peak generally occurs towards the end of the growing season when DOC which accumulates in the soil matrix under warm aerobic conditions is flushed from the catchment (Hope, *et al*. 1994). The trough occurs after the catchment has been purged of readily leachable DOC and when colder, waterlogged conditions inhibit microbial degradation, thus limiting DOC production (Halliday, *et al*. 2012). Interestingly, comparing fluvial data with Reservoir A data from Chapter 6 suggests that DOC levels are reduced in the reservoir, possibly due to microbial processing, photo-degradation and/or precipitation (Parks & Baker, 1997; Pokrovsky & Schott, 2002; Waiser & Robarts, 2004).

The data indicate a shift in DOC characteristics in June 2012. For this month a moderate peak in DOC was observed, ahead of the DOC maximum in August with the simultaneous occurrence of peak

SUVA values, as well as a peak in colour which appeared disproportionate to the increase in DOC for this month. These results are consistent with a flush of HMW, aromatic (humic) DOC (Edzwald & Tobiason, 1999; Weishaar, *et al*. 2003; Chow, *et al*. 2006). Though stream discharge, which has been positively correlated with SUVA in a previous study (Volk, *et al*. 2002), was not particularly high at the time of sampling, rainfall in June 2012 was unusually high (appendix Figure 5). This may have led to the inundation of dormant hydrological pathways, mobilising older, more humified material relative to more labile, lower MW organic matter (USGS, 2013).

August 2012 was also an exceptional month for stream water DOC measurements. The DOC maximum occurred in this month as did the colour maximum, most likely a product of DOC concentration. The lower stream SUVA values for this month compared with June 2012 may be the result an unusually wet summer and the enhanced leaching of HMW, aromatic DOC in June, leaving the soil depleted in this fraction. A_{253}:A_{203}, which previous studies (Korshin, *et al*. 1997; Kim & Yu, 2007; Chapter 6) and the present chapter suggest correlates positively with STHMFP, also peaked in August, suggesting that stream water may have particularly high $THMFP_{7d}$ in this month. Knowledge of seasonal variations in stream water inputs could help drinking water suppliers anticipate changes in raw water quality and optimise treatment processes accordingly.

4.5.2. Catchment A 14 month stream data – differences between streams and correlations with catchment characteristics

Few statistically significant correlations were found between subcatchment characteristics and mean stream water quality parameters in this study. This may be due to the small sample size, and/or the fact that such relationships have been reported to be season-specific (Gergel, *et al*. 1999; Cohen, 2009). A strong negative correlation was found between % bog habitat and stream water conductivity (r_s = -.928, $p < 0.01$). Conductivity is an indicator of mineral groundwater influence, the absence of which is a defining feature of bog habitats (Mitsch & Gosselink, 2000). In contrast, a strong positive correlation was identified between conductivity and woodland/dense scrub (r_s = .899, $p < 0.05$). This supports the findings of Eisalou, *et al.* (2013) who observed that the conductivity of rainwater increases substantially during throughfall as well as during leaching through the litter material of forest floors in both coniferous and deciduous stands.

A positive correlation has been reported between catchment size and surface water DOC concentration (Clair, *et al*. 1994; Cohen, 2009) since an increase in catchment size represents an increase in the pool of available carbon. No relationship was observed in this study. In fact the stream with the smallest catchment (Stream 5) also showed the highest mean DOC concentration, perhaps emphasizing the important role of other catchment characteristics. A positive correlation between SUVA and % peatland and forest coverage has also been reported (Piirsoo, *et al*. 2012) although no correlation was found in this study.

Surprisingly, the subcatchments of Stream 4 and 5, which represented the lowest and highest DOC concentration, respectively, had very similar habitat coverage (both > 90% woodland/dense scrub habitat). The difference in DOC concentration may be due to the higher proportion of larch stands in the subcatchment of Stream 5, whose soils have been associated with comparatively high leachable DOC content, and which form deep layers of litter, increasing the available DOC pool (Chapter 2). Streams 4 and 5 also have the lowest mean pH. This can be explained by the dominance of coniferous forest coverage in both subcatchments. A significant decrease in pH has been reported as rainwater passes through coniferous canopies and litter (Eisalou, *et al*. 2013), due to the high exchangeable acidity of coniferous litter and the fact that coniferous litter is readily leached of organic acids (Nykvist, 1963; Alfredsson, *et al*. 1998). The higher pH of Stream 6 may be associated with the arable land-use (2%) in its subcatchment, often associated with lime application (Bradley & Ormerod, 2002).

Stream 4 appears to exhibit distinct DOC characteristics including lowest mean DOC concentration (13.7 mg L^{-1}), SUVA (3.9 L mg^{-1} m^{-1}) and phenolic content (0.13 mg phen. mg DOC^{-1}). These results are consistent with the presence of relatively lower MW, more aliphatic DOC. Microbial processing as soil pore water moves downwards through the soil profile has been proposed as an explanation for the selective depletion of hydrophobic acids relative to hydrophilic acids and decreased DOC concentration observed in forested catchments (Cronan & Aiken, 1985). Thus differences in hydrological flowpaths, though beyond the scope of this study, may explain why Stream 4 shows distinct DOC concentration and quality, despite having very similar subcatchment habitat to Stream 5.

Despite the fact that few correlations between subcatchment characteristics and stream water quality parameters were found, a number of statistically significant differences were identified between streams. Such comparisons may provide a useful means of identifying source waters likely to compromise drinking water quality. The high DOC flux of Stream 1 suggests that it will exert a strong influence on reservoir DOC concentration and character. The high flux is partly due to relatively high DOC concentration, but predominantly due to its high discharge, resulting from its large associated subcatchment which includes the 0.3 km^2 headwater lake. In addition, high A_{253}:A_{203} (indicating high STHMFP) suggests in may also represent a high THMFP which could justify continued monitoring.

4.5.3. Catchments A and C biannual stream and reservoir data

Markedly higher DOC concentration and colour measurements observed in Catchment A stream and reservoir samples compared with Catchment C represent a significant issue for water treatment at this site. Though no statistically significant correlation between DOC/colour and ecological/pedological characteristics was found in this study, differences in catchment characteristics may still have contributed to this difference. In general Catchment A stream subcatchments were characterised by a higher proportion of wetland and/or forested (coniferous) habitats, both of which are reported to correlate positively with DOC loading (Hope, *et al*. 1994; Hope, *et al*. 1997; Gergel, *et al*. 1999; Cohen, 2009). High DOC flux from forested catchments is partly due to high DOC loading as rainwater passes through above ground biomass (Stevens, *et al*. 1989; Kawasaki, *et al*. 2005) as well as the large source of leachable carbon in the litter layer (Hongve, 1999). A combination of high primary productivity and low decomposition rates cause the accumulation of deep layers of peat in wetland environments (Mitsch & Gosselink, 2000) providing a large pool of available carbon (Thurman, 1985). At a catchment scale, the proportion of wetland coverage is similar but Catchment A includes a significant area of coniferous forest habitat, lowering the overall coverage of non-wetland habitat which is likely to increase the DOC loading of Reservoir A. Another contributing factor is likely to be the deeper soils in Catchment A, as indicated by the absence of the *shallow very acid peaty soils over rock* soil category, as well as field observations. This effectively increases the pool of leachable DOC in the catchment (Aitkenhead, *et al*. 1999). Finally, the shallower slope in Catchment A may have increased DOC concentration. A negative correlation is reported between slope and DOC loading due to its effect on residence times as well as being a predictor of wetland abundance and soil depth (Rasmussen, *et al*. 1989; Clair, *et al*. 1994; Sobek, *et al*. 2007). These factors appear to have overridden the potential influence of Catchment C's larger area on DOC loading (Clair, *et al*. 1994; Cohen, 2009).

Stream pH is related to a variety of factors including climate and catchment characteristics. In this case the lower pH of Catchment A samples is likely to be caused by the dominance of peatland and coniferous habitats. The peaty soils which predominate in this catchment are rich in organic acids which participate in cation exchange reactions, releasing H^+ ions into the surrounding solution, thus lowering pH (Urban, *et al*. 1995). In addition, the substantial depth of organic soils in this catchment is likely to isolate soil water from the neutralising capacity of mineral groundwater which tends to have a higher pH (Wetzel, 2001). As described earlier, coniferous forests are also likely to impart acidity.

Between biannual sampling dates, Catchment C stream SUVA measurements showed greater variability. This may be due to greater temporal variability in SUVA generally, or because the timing of seasonal fluctuations in SUVA differed between catchments. The SUVA values of samples from both catchments indicate relatively high hydrophobicity, HMW DOC, consistent with high humic content (Edzwald & Tobiason, 1999; Volk, *et al*. 2002), most likely due to high peatland coverage in both catchments, and the large forested coverage in Catchment A (Piirsoo, *et al*. 2012). STHMFP has been reported to correlate positively with SUVA in previous studies (Edzwald, *et al*. 1985; Chow, et al. 2003; Chapter 6). With the removal of C3 and C6 October 2011 measurements, a positive correlation between SUVA and $STHMFP_{7d}$ was found (r_s = .351, $p < 0.05$, n = 26), although A_{253}:A_{203} was a more accurate predictor of $STHMFP_{7d}$ (r_s = .770, $p < 0.01$, n = 28). The exceptionally high SUVA values for C3 and C6 may have been caused by very low DOC concentrations and potential interference from other UV-absorbing compounds such as nitrate (Carter, *et al*. 2012).

A comparison of stream and reservoir data in both catchments seems to indicate much greater temporal stability in reservoir DOC concentration and character compared with stream samples. Though temporal variations in water quality in Reservoir A have been observed (Chapter 6), the similarity in reservoir SUVA measurements between sampling dates, along with DOC concentration, phenolics, colour and A_{253}:A_{203} in both catchments is striking. This suggests that both reservoirs act to temper the seasonal variations in DOC concentration and character in the streams, allowing greater temporal stability in water quality entering the WTWs.

Fractional character

The consistency in the fractional character of stream samples in Catchment A in October 2011 and May 2012 individually is surprising given the differences in subcatchment characteristics. The similarity in the fractional character of samples between sampling dates is also interesting considering the substantial increase in the $STHMFP_{7d}$ values in May 2012. Several studies have reported differences in STHMFP associated with different DOC fractions (Galapate, *et al*. 1999; Chow, *et al*. 2005; Zhang, *et al*. 2009). However this study indicates that large variations in $STHMFP_{7d}$ can occur in the absence of a significant change in DOC fractional character and therefore, that fractional character it is not an effective predictor of $STHMFP_{7d}$.

A different seasonal trend was observed in the fractional character of Catchment A reservoir and Catchment C stream samples, with an increase in the proportion of HPIN observed in May 2012. This may be the result of the presence of algogenic DOC which is reported to have a high hydrophilic DOC content (Her, *et al*. 2004).

High pressure size exclusion chromatography

The increase in the proportion of lower MW DOC evident in May 2012 for Catchment C, and to a lesser extent, Catchment A samples may be indicative of an increase in the contribution of algogenic DOC (Fang, *et al*. 2010). This is supported by the decrease in SUVA and standardised phenolic content of Catchment C stream samples since algogenic organic matter (AOM) is reported to be dominated by proteinateous compounds with low aromaticity and low SUVA (Li, *et al*. 2012). In temperate zones, algal biomass tends to show a spring maximum (Wetzel, 2001). The change in DOC character appeared slight in Catchment A stream samples compared with Catchment C. This may reflect higher allochthonous inputs of humic DOC due to higher rainfall in Catchment A during this month (appendix Figure 5).

Trihalomethane formation potential

Average stream $STHMFP_{7d}$ and reservoir $STHMFP_{7d}$ were lower in Catchment C than in Catchment A on both sampling dates. Overall, THM yield is likely to be lower in Catchment C due to lower DOC reactivity ($STHMFP_{7d}$), concentration and THM reaction rate. Differences in the rate of THM formation may have been caused by variations in the proportions of fast- and slow-reacting THM precursors, which have been identified in previous studies (Gallard & von Gunten, 2002; Dickenson, *et al*. 2008). Given the evidence of an increase in contribution of AOM in May 2012, it is possible that the decrease in THM reaction rate observed in Catchment A and Catchment C samples in May 2012 was also linked to increased algal populations. However, further research would be required to confirm this.

Though DOC reactivity ($STHMFP_{7d}$) increased for Catchment A samples in May 2012, its effect on THM yield was offset by decreased DOC concentration and decreased THM reaction rate. The higher $STHMFP_{7d}$ measurements in Catchment A samples compared with Catchment C are likely to be related to DOC functionality. Indeed A_{253}:A_{203}, which is reported to indicate the proportion of hydroxyl-, carboxyl-, ester- and carbonyl-substituted aromatic rings (Korshin, *et al*. 1997), was higher in Catchment A samples. These moieties are reported to be involved in THM-forming reactions with a positive correlation between $STHMFP_{7d}$ and A_{253}:A_{203} reported previously (Kim & Yu, 2007; Chapter 6) and in the present chapter. A_{253}:A_{203} measurements may therefore be a useful tool for monitoring temporal fluctuations in THM yield.

Comparing STHMFP values with other studies is complicated by procedural inconsistencies including different incubation periods and temperatures. Notwithstanding these potential differences, the $STHMFP_{7d}$ values in this study are substantially higher than values reported elsewhere for various surface water sources (Uchiyama, *et al*. 1986; Page, *et al*. 2002; Rizzo, *et al*. 2005; Iriarte-Velasco, *et al*. 2007; Uyak & Toroz, 2007). This is likely to be connected to the upland location of Catchments A and C and their extensive peatland habitat coverage which produces and exports large amounts of aromatic humic substances (Thurman, 1985) as indicated by high SUVA measurements. A positive correlation between SUVA and STHMFP was identified in this study and has been reported previously (Edzwald, *et al*. 1985).

4.6. Conclusions

Seasonal fluctuations in stream and reservoir water quality were assessed in Catchment A. This information could help water suppliers anticipate changes in raw water quality and optimise treatment processes accordingly. The synchronicity of temporal variations in stream DOC concentration and quality highlights the importance of seasonal drivers of DOC production and export. Monitoring of input streams also showed that DOC flux was closely related to stream discharge.

Significant differences in DOC flux, concentration and character were identified between streams in Catchment A and allowed for the identification of inputs likely to significantly influence reservoir water quality. GIS mapping enabled the accurate estimation of the spatial extent of catchment and subcatchment ecological and pedological features. Few statistically significant correlations between subcatchment characteristics and stream water quality were identified. These related to the influence of habitat type on conductivity. However, explanations for differences in stream and reservoir water quality relating to catchment characteristics were discussed. Large areas of coniferous forest are likely to be responsible for higher acidity and DOC loading in Catchment A surface waters compared with Catchment C. Shallower catchment slope and greater soil depth may also have contributed to higher DOC concentrations. High STHMFP measurements in stream and reservoir samples in both catchments are likely to be connected to the extent of peatland coverage which exports large amounts of aromatic humic material.

A_{253}:A_{203} and, to a lesser extent SUVA, may be useful parameters for monitoring temporal fluctuations in $STHMFP_{7d}$ and therefore predicting THM yield. Though fractional character has been correlated with STHMFP in previous studies, the present study showed that STHMFP may vary despite the fractional character of DOC remaining stable. THM yield was found to vary seasonally in response to changes in DOC reactivity and concentration. Overall Catchment A was associated with higher THM yield due to higher DOC concentration, DOC reactivity ($STHMFP_{7d}$) and THM formation rate.

A shift in DOC character in May 2012 including decreased DOC MW and THM reaction rate and increased HPIN DOC, may indicate a seasonal increase in algogenic DOC, though further study would be required to confirm this. Algal blooms are an important issue in potable water treatment since they can present a public health risk, affect treatment efficiency and increase nitrogenous DBP formation potentials.

Reservoir DOC concentrations were lower than stream concentrations, possibly due to microbial processing, photo-degradation and/or precipitation of DOC. In addition, reservoir DOC concentration and quality appears to show more temporal stability suggesting that mixing in large reservoirs may act to temper seasonal fluctuations in raw water quality at treatment works.

4.7. Acknowledgements

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4.8. References

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Chapter 5: Characterisation of algogenic organic matter during an algal bloom

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5.1. Abstract

Seasonal increases in algogenic organic matter (AOM) in surface waters supplying potable water treatment works (WTWs) can cause a number of treatment issues. Previous studies show that AOM is distinct from terrigenous, humic-dominated organic matter. However limited information exists relating to changes in the character of AOM during different algal growth phases. In this study, reservoir water containing DOC dominated by humic material was enriched with nutrient medium to create an algal bloom which was monitored using chlorophyll-*a* measurements. Over the course of the algal bloom, DOC was characterised using various methods including XAD-fractionation, high pressure size exclusion chromatography (HPSEC) and UV absorbance measurements. In addition, the reactivity of DOC with chlorine both before and after fractionation was assessed using trihalomethane formation potential (THMFP) and bromine incorporation measurements to monitor whether THM yield varied between different growth phases. Characterisation of DOC during the algal bloom indicated a shift towards more hydrophilic, low molecular weight (LMW), aliphatic (low SUVA) DOC with the release of extracellular organic matter (EOM) and later intracellular organic matter (IOM) during cell lysis. XAD-fractionation results suggest that algae produce predominantly hydrophilic neutral (HPIN) DOC. Algogenic DOC was also distinct from humic-dominated DOC in terms of THM formation properties. A reduction in standardised THMFP (STHMFP) and the rate of THM formation was observed as the algal bloom progressed. However bromine incorporation increased with culture age. This is significant since brominated THMs are reported to be more carcinogenic. Thus a mixed picture emerged with regard to the relative risks associated with AOM versus humic DOC in terms of their role as THM precursors.

5.2. Introduction

Algogenic organic matter (AOM), consisting of cells, extracellular organic matter (EOM; released from algal cells by diffusion) and intracellular organic matter (IOM; released from senescent algal cells during cell lysis), causes a number of issues in potable water treatment. These substances may contribute taste and odour, elevate total organic carbon (TOC) levels, increase coagulant and chlorine demand, cause membrane fouling and lead to an increase in disinfection by-products (DBPs) such as trihalomethanes (THMs) (Bernhardt, *et al*. 1991; Nguyen, *et al*. 2005; Li, *et al*. 2012). Some species of algae also produce toxic metabolites which present a public health risk (Žegura, *et al*. 2011).

Within the DOC pool, AOM shows a number of differences from natural organic matter (NOM) of terrigenous origin. Firstly, AOM has a higher nitrogen content than humic material due to its proteinateous origin; TOC/TON ratios are reported as follows: NOM >> EOM > IOM ≈ algal cells (Fang, *et al*. 2010; Li, *et al*. 2012). In addition, AOM is more biodegradable and is characterised by lower molecular weights (MWs) (Leenheer & Croue, 2003; Nguyen, *et al*. 2005; Fang, *et al*. 2010). XAD-fractionation and SUVA measurements indicate that AOM contains more hydrophilic and less aromatic carbon (Her, *et al*. 2004; Leloup, *et al*. 2013). AOM characteristics also change as an algal bloom progresses through a series of growth phases (typically: lag phase, exponential growth phase, stationary phase and death phase). EOM is mostly released during the exponential growth phase and is composed of lower MW compounds such as glycolic and amino acids. IOM, released from senescent cells, mostly during the death phase is composed of higher MW products such as polysaccharides (Huang, *et al*. 2009).

Though algal cells tend to be associated with higher THM formation potential (THMFP), standardised for carbon content (STHMFP) than IOM and EOM (Yang, *et al*. 2011), coagulation-flocculation is generally effective in removing algal cells during treatment. Therefore EOM and IOM represent the main algogenic THM precursors in potable water treatment. Under standardised chlorination conditions, the STHMFP of AOM varies between algae species though contradictory results have been reported with regard to the relative reactivity of blue-green vs. green algae vs. diatoms (Plummer & Edzwald, 2001; Nguyen, *et al*. 2005). Few studies have compared STHMFP values during different algal growth phases and contradictory results have been reported with regard to the reactivity of AOM as an algal bloom progresses. Nguyen, *et al*. (2005) and Huang, *et al*. (2009) conclude that DOC reactivity (STHMFP) does not vary significantly as a function of growth phase but only Huang, *et al*. (2009) measured STHMFP during the death phase when large amounts of IOM are released into solution. Conversely, Yang, *et al*. (2011) report TOC and THMFP data that suggest a peak in STHMFP during the exponential growth phase. Furthermore there are very limited data available for THM formation rates during different growth phases - an important consideration in a potable water treatment context since residence times of water in distribution systems is generally much shorter than the 7 d incubation periods typically used in the measurement of STHMFP. The speciation of THMs and specifically, the percentage of brominated THMs (BrTHMs) formed, is also reported to vary between species of algae and according to growth phase as a result of changing AOM character (Huang, *et al*. 2009; Yang, *et al*. 2011). However, changes in bromine incorporation in dissolved AOM (EOM and IOM) have received very little attention. This is important since BrTHMs are reported to be more carcinogenic than $CHCl_3$ (US EPA, 1975). To our knowledge bromine incorporation of individual XAD fractions upon chlorination has not been assessed.

In this study an algal bloom was generated in the laboratory using Reservoir A water by enriching with nutrient medium. Quantification and characterisation of DOC including XAD-fractionation, high pressure size exclusion chromatography (HPSEC) and THMFP measurements were undertaken during the different growth phases. In particular the data was used to assess how STHMFP, THM formation rate and bromine incorporation varied with growth phase and compared with the raw reservoir water. In addition, characterisation of the DOC produced during the algal bloom was used to assess whether increased algal biomass was responsible for the change in DOC character observed in May 2012 (12 months prior to this experiment) in Catchment A and C surface waters (Chapter 4), specifically, an increase in the proportion of hydrophilic neutral (HPIN) DOC, decreased THM formation rate and more prominent HPSEC low MW (LMW) peaks.

5.3. Methods

5.3.1. Site description and sample collection

The water used in the study was collected from a UK upland drinking water reservoir (Reservoir A). Its catchment comprises extensive areas of peatland (32%) and grassland (38%) as well as mainly-coniferous forest plantations (30%) (Cohen, 2009). Each day 38-40 ML of water is abstracted from the reservoir for treatment at the adjacent potable water treatment works (WTW). Treatment consists of coagulation ($Al_2(SO_4)_3$) and flocculation followed by dissolved air floatation (DAF) for clarification, primary filtration using rapid gravity sand filters (RGF), secondary RGF for manganese removal and finally chlorine dosing for disinfection. Though algal populations are normally low in this reservoir, the drinking water provider has reported increased algal biomass in late spring/early summer. For this study, 10 L of water was collected from the surface (0-1 m depth) of Reservoir A in May 2013 and transported immediately to the laboratory.

5.3.2. Cultivation and measurement of algae

A 30 % Bold Basal medium with three-fold nitrogen and vitamins (3N-BBM+V) (CCAP, UK) was made using 10 L of reservoir water. During a preliminary study, chlorophyll-*a* measurements indicated that this nutrient concentration was sufficient to produce an algal bloom. The solution was transferred to a 15 L glass jar, placed in a naturally-lit area of the laboratory and provided with aeration *via* an air pump connected to an air stone.

Algal population density was monitored by measuring chlorophyll-*a* concentration. These measurements were plotted over time and used to decide on the timing of the collection of larger sub-samples to represent distinct growth phases. For chlorophyll-*a* measurement, a 20 mL sub-sample was filtered through a Whatman GF/C filter which was then placed in a 15 mL centrifuge tube with 90% acetone. After refrigerating for 24 h at 4°C, 1.5 mL of the supernatant was pipetted into a 1.5 mL centrifuge vial. The solution was centrifuged at 1,800 g for 1 min and 347.5 µL pipetted into a 96-well clear micro-plate. Absorbance at λ = 665 and 750 nm was measured using a Molecular Devices SpecraMax M2e multi-detection spectrophotometer. Chlorophyll-*a* concentration was calculated using the following formula:

$$\text{Chlorophyll-}a\ (\text{mg L}^{-1}) = 11.9\ (\text{Abs}_{665} - \text{Abs}_{750})\,\frac{v}{Vp}$$

Here V is the volume filtered (mL), v is the volume of extract (mL), p is the pathlength (cm) and 11.9 the specific absorbance coefficient of chlorophyll-*a* in 90% acetone (Golterman, 1969).

5.3.3 Routine analyses

For the measurement of DOC concentration and characteristics, samples were filtered through a 0.45 µm membrane filter (Whatman). DOC measurement was carried out following acidification (to remove inorganic carbon) using a Thermalox TOC/TN analyser equipped with a non-dispersive infrared CO_2 detector. UV absorbance measurements were made using a Molecular Devices SpecraMax M2e multi-detection spectrophotometer with aliquots of samples pipetted into a 96-well clear micro-plate. SUVA values were derived from the following formula: UV Abs_{254} (cm^{-1}) * 100/DOC (mg L^{-1}).

5.3.4 Growth phase analyses

In addition the measurements described above, raw, exponential growth phase and death phase samples (Figure 5.01) underwent further analyses including HPSEC, XAD-fractionation and THMFP and STHMFP measurements. THMFP and STHMFP were also measured for XAD fractions obtained from these three samples.

High pressure size exclusion chromatography

High pressure size exclusion chromatography (HPSEC) was conducted using a Varian PL-GPC-50 DataStream unit detecting at λ = 254 nm. The HPSEC unit was interfaced to Cirrus software and equipped with a Bio Sep 2000 column. Calibration standards were sodium polystyrene sulfonate polymers with MWs of 150,000, 77,000, 32,000, 13,000 and 4,300 Da (Fluka) and cyanocobalamin

(1,340 Da). The mobile phase was Milli Q water buffered with phosphate (0.002 M KH_2PO_4 + 0.002 M $K_2PO_4.3H_2O$) to pH 6.8.

XAD-fractionation

Fractionation of DOC was achieved by resin adsorption using a method adapted from Thurman & Malcolm, (1981) and Marhaba, *et al.* (2003). Samples were separated into five fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophilic neutral (HPIN) according to their adsorption onto macroporous resins; Superlite™ DAX-8™ resin and Amberlite™ XAD-4™ resin (both Supelco).

Trihalomethane formation potential

$THMFP_{7d}$ denotes the quantity of THMs formed (µg L^{-1}) following chlorination of a water sample for a 7 d incubation period at 25 °C. The method used was adapted from the Standing Committee of Analysts, (1981) procedure. Samples were diluted to 1 mg L^{-1} DOC to derive a standardised $THMFP_{7d}$ ($STHMFP_{7d}$) value which provides a measure of DOC reactivity. $THMFP_{7d}$ was calculated by multiplying $STHMFP_{7d}$ by DOC concentration. For chlorination, 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5M $KH_2PO_{4(aq)}$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $NaOCl_{(aq)}$ to provide 5 mg of free Cl per mg of DOC. After a 7 d incubation in the dark at 25 °C, the reaction was quenched using 0.4 mL of 0.8M $Na_2SO_{3(aq)}$. Extraction of the four chlorinated and brominated THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) was achieved using direct immersion SPME followed by quantification using a Varian 450 GC coupled with an electron capture detector. THM concentrations were also measured after 1 d in order to compare the rate of THM formation between samples. The bromine incorporation factor (BIF) was calculated using the following formula:

$\mathrm{BIF} = \frac{CHCl_2Br \ + 2\ CHClBr_2 \ + 3[CHBr_3]}{[total\ THM]}$ (concentrations in µmol L^{-1}) (Yang, *et al*. 2011).

5.4. Results

5.4.1. Algal growth

The raw water chlorophyll-*a* concentration was 51 µg L^{-1}. This began to increase sharply around day 13 and peaked at day 20 with 635 µg L^{-1} (Figure 5.01). Almost immediately the concentration began to fall again, returning to a chlorophyll-*a* concentration similar to the raw water (70 µg L^{-1} on day 30). The profile of chlorophyll-*a* concentration over time indicates three distinct growth phases in the algal bloom: a lag phase between days 0 and 14, an exponential growth phase between days 14 and 20 and a death phase between days 20 and 30. The green alga *Ankistrodesmus* sp. was found to dominate the algal bloom. The timing of sample collection for each growth phase is highlighted in Figure 5.01 in orange.

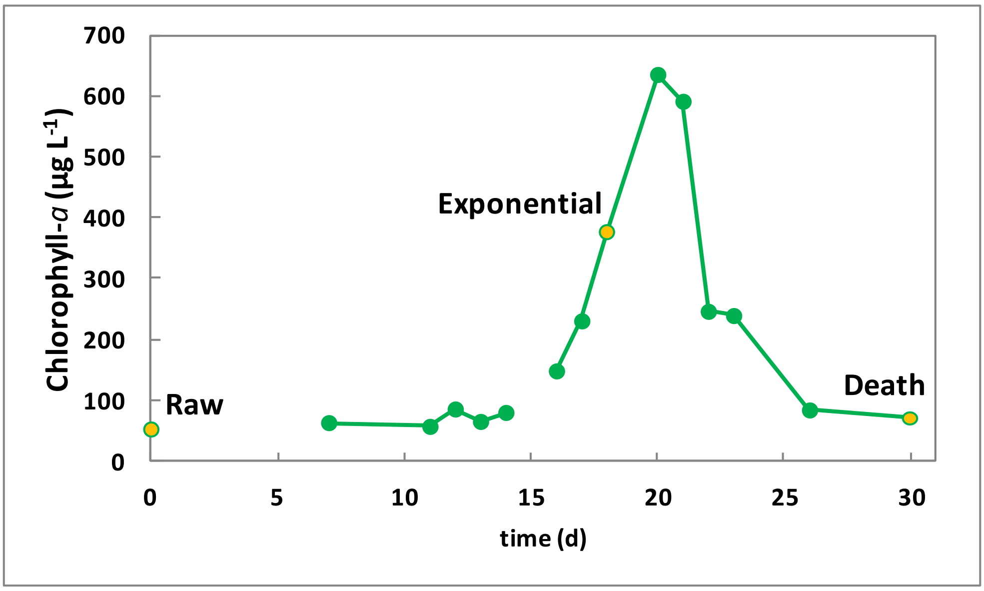

Figure 5.01. Chlorophyll-*a* concentration plotted over time showing timing of collection of raw, exponential growth phase and death phase samples.

5.4.2. Routine analyses

Raw water DOC concentration measured 11.1 mg L^{-1}. DOC concentration remained fairly stable during the lag phase of the algal bloom but showed a sudden increase to 14.3 mg L^{-1} at the beginning of the exponential growth phase (day 15) (Figure 5.02). The concentration then decreased to slightly below raw water concentration as the exponential growth phase proceeded. Around day 23, during the death phase, DOC concentration then increased dramatically, reaching a final concentration of 19.5 mg L^{-1} at day 30.

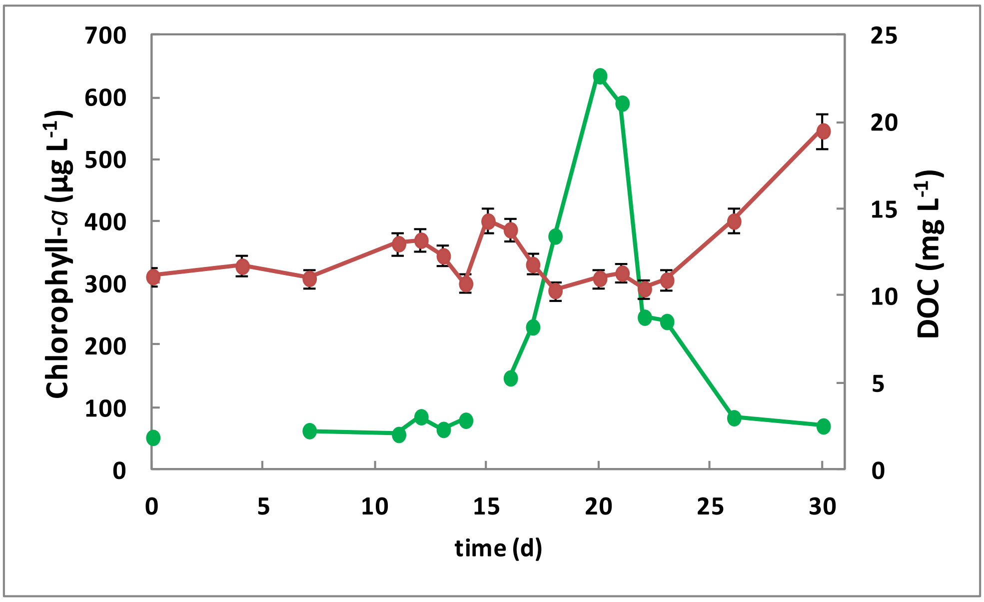

Figure 5.02. Chlorophyll-*a* concentration (green) plotted with DOC concentration (red) over the course of the algal bloom. Error bars represent 5% CV%.

At day 0, SUVA measured 3.3 L mg^{-1} m^{-1}. This decreased during the lag phase to 2.3 L mg^{-1} m^{-1} at day 15. SUVA then increased slightly during the exponential growth phase to 3.1 L mg^{-1} m^{-1} at day 18 before decreasing steadily to a low of 1.2 L mg^{-1} m^{-1} at day 30 (Figure 5.03).

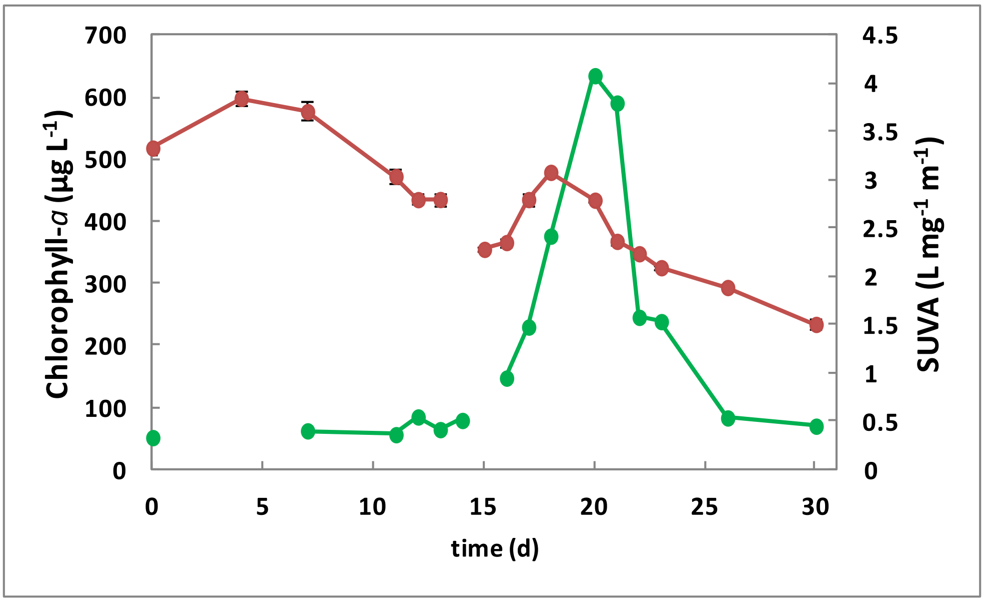

Figure 5.03. Chlorophyll-*a* concentration (green) plotted with SUVA (red) over the course of the algal bloom.

5.4.3. High pressure size exclusion chromatography

The MW distribution (MWD) of the raw sample (Figure 5.04a) is typical of reservoir samples collected from this site; it shows a small peak at a retention time (t_R) ≈ 4.5 min (peak 1; M_p ~ 69 kDa) representing high MW (HMW) molecules that are too large to interact with the pores of the stationary phase (Huber, *et al*. 2011). The dominant peak occurs at $t_R \approx 8.5$ min (peak 2; $M_p \sim 3.5$ kDa) with two overlapping peaks at $t_R \approx 9.4$ (peak 3; $M_p \sim 2.2$ kDa) and 9.8 min (peak 4; $M_p \sim 1.6$ kDa). A number of changes in the MWD are evident when comparing the raw sample with the exponential growth phase (Figure 5.04b) and death phase samples (Figure 5.04c). Firstly, peak 1 is diminished in the exponential growth phase and remains minimal in the death phase. Secondly, during the death phase, the contribution of peak 2 decreases. Thirdly, the contribution of peak 3 increases very slightly during the exponential growth phase before decreasing again in the death phase. Fourthly, a new low MW (LMW) peak appears during the exponential growth phase at $t_R \approx$ 10.3 min (peak 5; $M_p \sim 1.0$ kDa) but disappears during the death phase. Finally, the prominence of peak 4 is increased in the exponential growth phase and shows a more dramatic increase in the death phase. Figure 5.04d shows the MWD of Reservoir A water in May 2012 (Chapter 4). It was observed that, compared with the corresponding October 2011 sample, peaks 3 and 4 were more pronounced. The same was true for a number of stream samples in Catchment A, as well as reservoir and stream samples in Catchment C (Chapter 4).

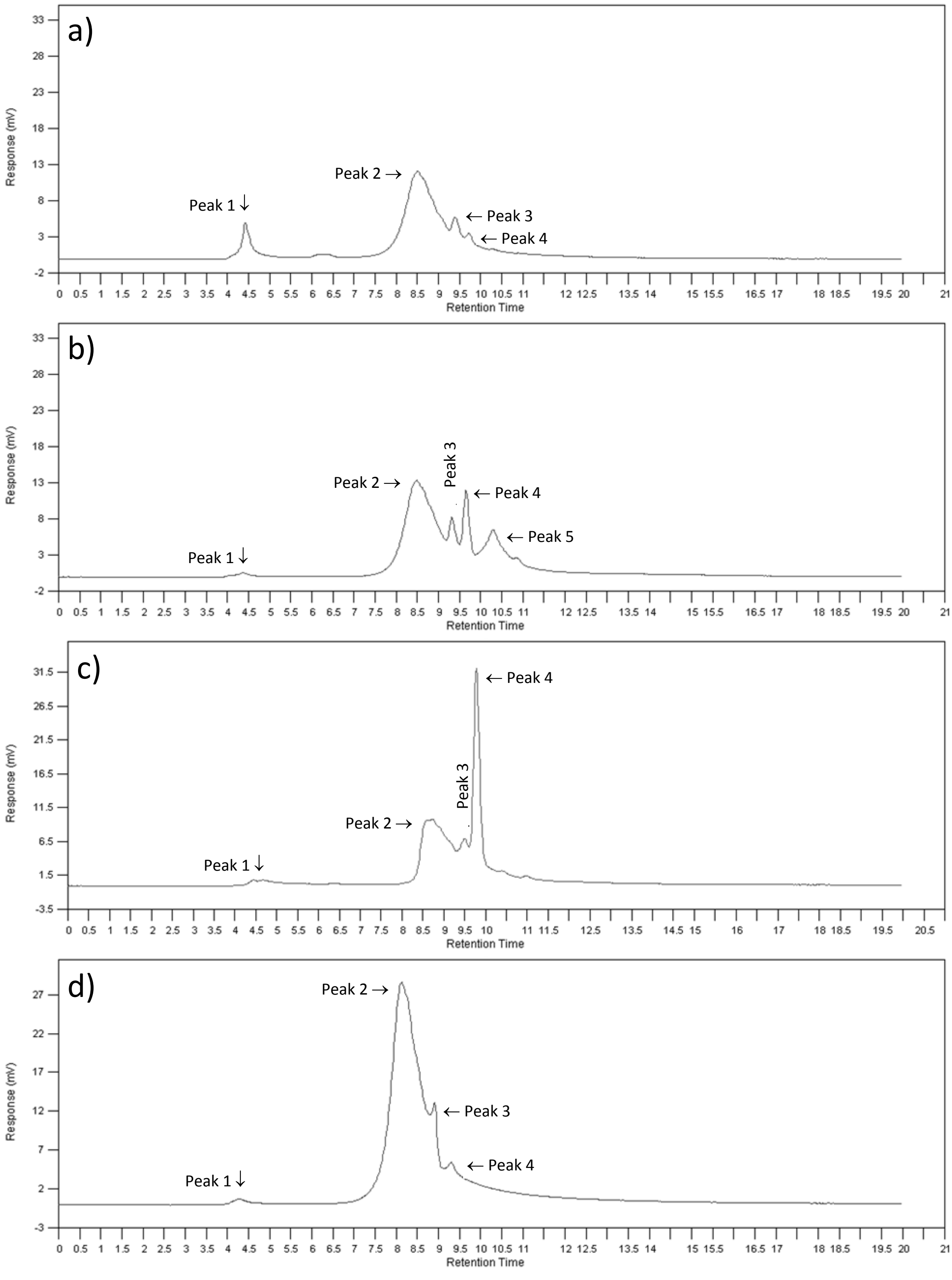

Figure 5.04. HPSEC chromatograms for raw (a), exponential growth phase (b) and death phase (c) samples and for May 2012 Reservoir A water (d), also shown in Chapter 4.

5.4.4. XAD-fractionation

For raw, exponential growth phase and death phase samples, the HPOB and HPIB fractions combined represented < 5% of DOC although their % contribution increased with culture age (Figure

5.05). The raw sample was dominated by HPOA DOC (57%) with the HPIA fraction representing approximately one quarter (24%) of the DOC and the HPIN fraction 17%. The exponential growth phase sample was also dominated by the HPOA fraction (49%) but showed a reduction in HPOA and HPIA compared with the raw sample and an increase in the HPIN fraction to 29%. The death phase sample showed a dramatic difference in fractional character compared with the previous samples with the HPIN fraction becoming dominant (55%), a further slight reduction in the HPIA fraction (to 14%) and a more substantial reduction in the HPOA fraction (to 27%).

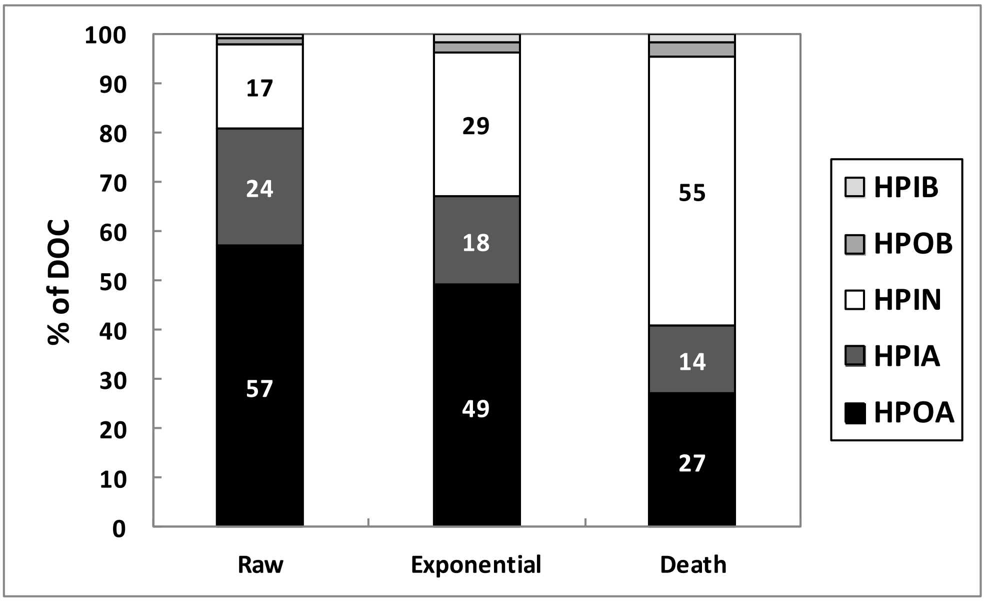

Figure 5.05. % contribution of HPOA, HPIA, HPIN, HPOB and HPIB fractions to the total recovered DOC following fractionation of raw, exponential growth phase and death phase samples.

5.4.5. Trihalomethane formation potential

STHMFP

Since the $STHMFP_{7d}$ measurement is standardised for DOC concentration it can be used to compare DOC reactivity with chlorine between samples. For the un-fractionated samples highest $STHMFP_{7d}$ was observed for the raw sample (81 µg THM mg DOC^{-1}) followed by the exponential growth phase (66 µg THM mg DOC^{-1}) and death phase sample (31 µg THM mg DOC^{-1}) (Figure 5.06a). Interestingly, for all samples analysed, including the un-fractionated samples and their constituent fractions (HPOA, HPIA and HPIN), $STHMFP_{7d}$ showed the following sequence: raw > exponential > death (Figures 5.06a-5.06d). Highest $STHMFP_{7d}$ was recorded for the HPIA fraction of the raw water (122 µg THM mg DOC^{-1}) (Figure 5.06c) and lowest $STHMFP_{7d}$ for the HPIN fraction of the death phase sample (17 µg THM mg DOC^{-1}) (Figure 5.06d).

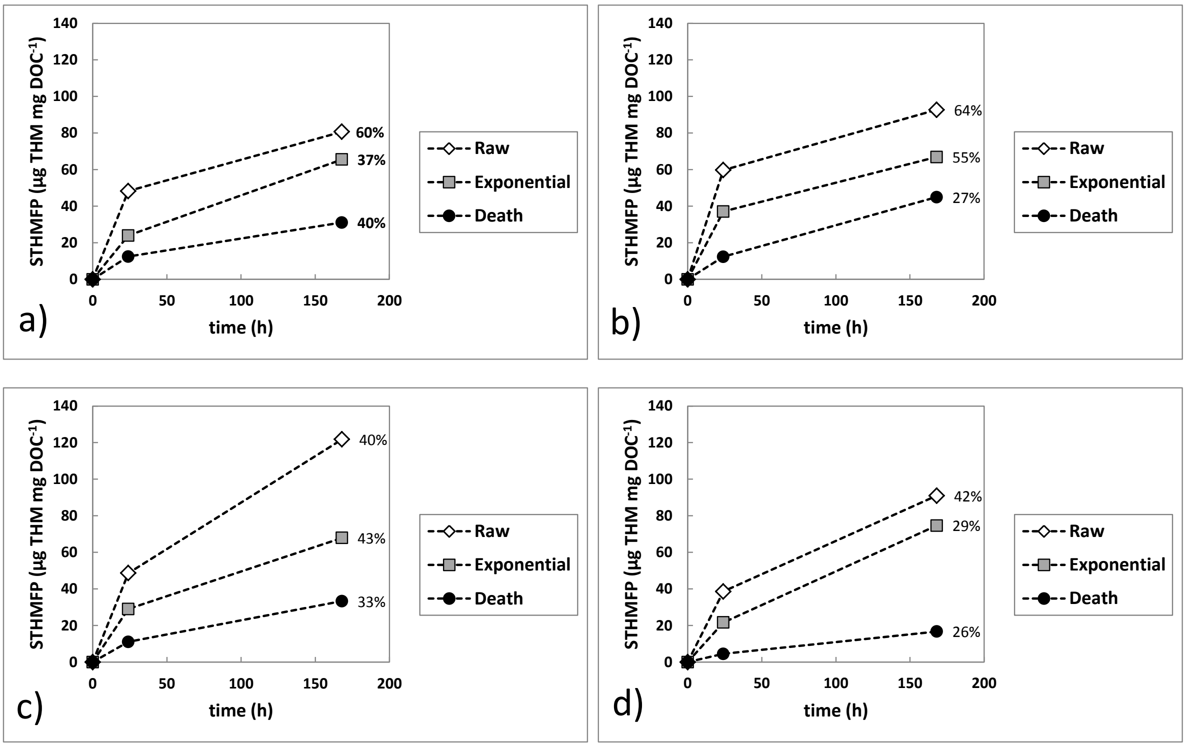

Figure 5.06. Profile of STHMFP over a 7d incubation period following chlorination of the raw, exponential growth phase and death phase samples including in their unfractionated state (a) and their constituent fractions; HPOA (b), HPIA (c) and HPIN (d). $STHMFP_{1d}$ as a percentage of $STHMFP_{7d}$ is also shown.

Rate of THM formation

Of the un-fractionated samples (Figure 5.06a), the raw sample showed a higher reaction rate ($STHMFP_{1d}$ as a percentage of $STHMFP_{7d}$) than the exponential growth phase and death phase samples (60% compared with 37% and 44%, respectively). The fractionated samples, particularly the HPIA and HPIN fractions showed a greater range of reaction rates than the un-fractionated samples. The raw HPOA sample (Figure 5.06b) showed the highest reaction rate (64%) and the death phase HPOA and HPIN fractions the lowest reaction rates (27% and 26%, respectively) (Figures 5.06b and 5.06d).

Bromine incorporation

Bromine incorporation into THMs increased with culture age from a bromine incorporation factor (BIF) of 0.02 in the raw sample, to 0.03 in the exponential growth phase sample and 0.06 in the death phase sample (Figure 5.07). On average BIF values for fractions showed the following trend: HPOA < HPIA < HPIN. However, there was substantial variation in BIF values for individual fractions between different samples (raw, exponential and death). The death phase HPIN sample showed the highest BIF value (0.19), more than double any of the other samples.

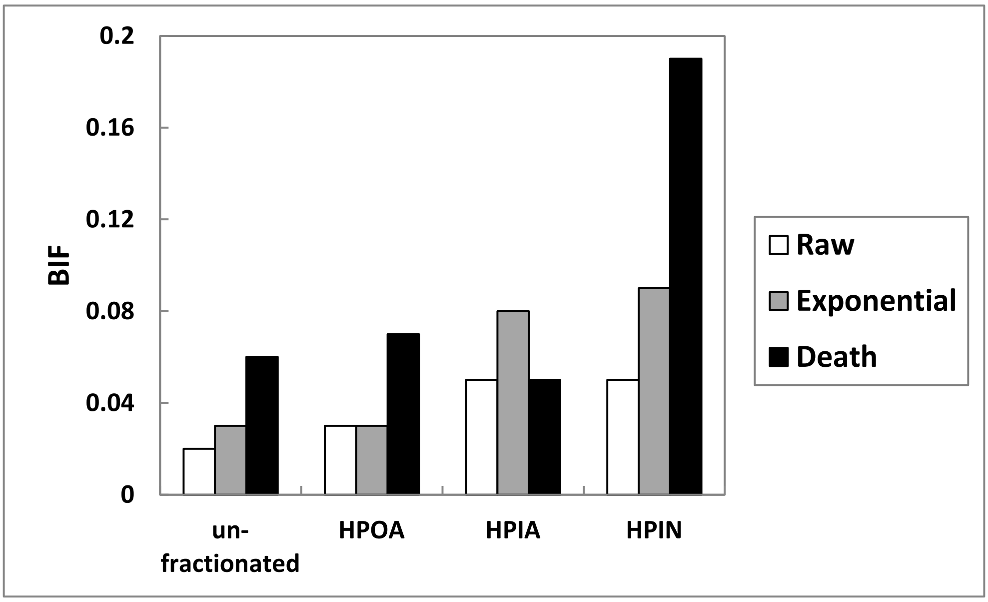

Figure 5.07. Bromine incorporation factor (BIF) for unfractionated and HPOA, HPIA and HPIN fractions associated with the raw, exponential growth phase and death phase samples.

5.5. Discussion

5.5.1. Algal growth

Chlorophyll-*a* measurements indicate low algal biomass in the raw water taken from Reservoir A. Following nutrient enrichment and favourable light and temperature conditions in the laboratory, an algal bloom was generated resulting in a maximum chlorophyll-*a* concentration of 635 µg L^{-1}. This was substantially lower than the peak chlorophyll-*a* concentrations reported for laboratory-based algal blooms cultivated by Huang, *et al*. (2009) which showed approximately 2,700 µg L^{-1} and 2,100 µg L^{-1} for *Anabaena flos-aquae* and *Microcystis aeruginosa*, respectively. This enhanced growth can be explained by a difference in culture conditions since Huang, *et al*. (2009) used inoculated algae stock cultures and un-diluted nutrient growth media. Typically, four growth phases can be identified during an algal bloom. During the lag phase, indicated by static chlorophyll-*a* concentrations, algal cells use the newly-available nutrients to replenish internal nitrogen and phosphorus constituents. The exponential growth phase, characterised by a rapid increase in chlorophyll-*a* concentration, involves rapid cell division and a dramatic increase in algal biomass. During this phase, significant amounts of EOM are released. The stationary phase, characterised once again by static chlorophyll-*a* concentrations, occurs when the nutrient pool has been exhausted and cell division stops. Finally, the death phase, when chlorophyll-*a* concentration declines occurs as a result of cell death. During the death phase large amounts of IOM are released due to widespread cell lysis. Our data did not show an identifiable stationary phase, which normally occurs between the exponential and death phase and is characterised by stable chlorophyll-a concentration (Yang, *et al*. 2011), although previous studies have also reported the absence of a distinct stationary phase such as the *Anabaena flos-aquae* culture in Huang, *et al*. (2009).

5.5.2. DOC concentration

Our DOC concentration data show a more erratic trend than those reported for inoculated algal cultures where DOC concentration has tended to increase steadily with culture age (Huang, *et al*. 2009; Yang, *et al*. 2011). We suggest that this is due to the competing effects of microbial degradation of DOC and algal DOC production during the algal bloom, which more accurately reflects conditions in the field. Thus, the increase in DOC concentration during the early-exponential growth phase may reflect a significant release of EOM and the subsequent fall in DOC concentration during the late-exponential growth phase by an increase in microbial population and the consequent degradation of EOM. The dramatic increase in DOC concentration during the late-death phase is likely to be caused by the release of IOM during cell lysis overwhelming the loss of DOC by microbial activity.

5.5.3. Specific UV absorbance

SUVA is reported to correlate positively with DOC hydrophobicity and MW (Edzwald & Tobiason, 1999) and % DOC aromaticity (Weishaar, *et al*. 2003). Thus, the general reduction in SUVA during the course of the algal bloom is consistent with an increase in the relative contribution of low UV-absorbing, hydrophilic, aliphatic compounds typical of algogenic DOC, and a decrease in the relative contribution of humic constituents (Her, *et al*. 2004; Yang, *et al*. 2011; Huang, *et al*. 2012). In addition, IOM is reported to be associated with lower SUVA values than EOM (Fang, *et al*. 2010) the release of which may have contributed to the reduction in SUVA during the death phase. The slight recovery of SUVA during the exponential growth phase coincides with a decrease in DOC concentration. This may be explained by the preferential removal of low-SUVA algogenic DOC by microbial degradation since AOM is reported to be more biodegradable than humic material (Nguyen, *et al*. 2005).

5.5.4. High pressure size exclusion chromatography

Since the raw water chlorophyll-*a* concentration was minimal, the raw water HPSEC chromatogram can be said to represent predominantly non-algal DOC. The exponential growth phase chromatogram represents the introduction of algogenic DOC – predominantly EOM to the system, which is released into solution *via* diffusion through algae cell walls. The death phase chromatogram then shows the additional effect of the release of IOM into solution due to cell lysis. The likely presence of bacteria and the exposure of the solution to direct sunlight in the laboratory also introduce the possibility of bio- and photo-degradation processes.

The decrease in the contribution of HMW DOC represented by peaks 1 and 2 during the course of the algal bloom indicates the degradation of the humic DOC present in the original raw sample (Figure 5.04). The appearance of a novel LMW peak (peak 5) in the exponential growth phase is likely to be related to the release of EOM. Its absence in the death phase sample can be explained by its biodegradable nature which confers a rapid removal rate. EOM may also be responsible for the slight increase in peak 3 since this appears to decrease during the death phase.

A unique feature of the death phase HPSEC chromatogram is the substantial increase in the contribution of peak 4, suggesting that the release of IOM during cell lysis may be responsible. As such, our data suggest that the IOM (peak 4) has a higher MW than the main fraction of EOM (peak 5). This is in contrast to the findings of Fang, *et al*. (2010) who identify IOM as having slightly lower MW than EOM based on HPSEC coupled with a fluorescence detector.

Comparison of the raw HPSEC chromatogram with the chromatograms for stream and reservoir samples collected in May 2012 (Chapter 4) suggests that algae may indeed have been responsible for the increased contribution of lower MW DOC, specifically the increase in peaks 3 and 4. Furthermore, our data suggest that the higher MW peak (peak 3) is likely to be related to the release of EOM and the lower MW peak (peak 4) to the release of IOM during cell lysis. Additional evidence for this theory can be seen in the HPSEC results of Her, *et al*. (2004) which shows the presence of a number of distinct MW peaks in algogenic DOC versus a single smooth peak for Suwannee River humic acid.

5.5.5. XAD-fractionation

The XAD-fractionation data reported here, showing a higher contribution of the HPIN fraction in the exponential and death phase samples compared with the raw sample, suggest that the increase in the contribution of the HPIN fraction in Reservoir A water in May 2012 (Chapter 4) may have been due to increased abundance of algae. Her, *et al*. (2004) analysed AOM extracted from algal cells (IOM; species unknown) and report similar fractional character to our death phase result with 57.3% HPIN, 25.9% HPOA and 16.8% HPIA. Similar proportions were reported by Henderson, *et al*. (2008) for EOM derived from four species (*Chlorella vulgaris*, *Microcystis aeruginosa*, *Asterionella formosa* and *Melosia* sp.); in the stationary phase, HPIN represented 57% or more and HPIA varied between

8% and 17%. However, data presented in Leloup, *et al*. (2013) for *Euglena gracilis* indicate that the HPIN fraction dominates AOM during the exponential and stationary growth phases (75% and 69%, respectively) and that the HPOA and HPIA fractions correlate with increased cell mortality and release of IOM during later phases. They proposed that the HPIN fraction initially formed may be transformed to HPOA and HPIA according to Stevenson's (1982) theory of polyphenols. By contrast, our data suggest that the contribution of HPIN increases with cell mortality and that the contribution of HPOA and HPIA decreases with culture age. This difference may be due to the different algae species involved, however, a comparison of IOM from different species cultured under standardised conditions would be necessary to confirm this.

5.5.6. Trihalomethane formation potential

STHMFP

Our STHMFP$_{7d}$ data, which show a marked decrease as the algal bloom progressed, conflicts with the results of previous studies indicating that STHMFP does not vary as a function of growth phase (Nguyen, *et al*. 2005; Huang, *et al*. 2009). This may be due to the presence of different algal species in our culture. Alternatively, differences in culture conditions may be responsible. Indeed Nguyen, *et al*. (2005) show that STHMFP for the same species may vary depending on the conditions in which the algae are cultured.

High STHMFP$_{7d}$ in the un-fractionated raw water sample (81 µg THM mg DOC^{-1}) can be explained by the dominance of allochthonous humic material which is reported to react more readily to form THMs than algogenic DOC (Fang, *et al*. 2010). This enhanced reactivity has been linked to its high hydrophobicity and aromaticity (and hence high SUVA) (Chow, *et al*. 2003; Zhang, *et al*. 2009). Reduced reactivity in the un-fractionated samples with culture age may be due to microbial degradation of humic DOC and an increased contribution from hydrophilic, aliphatic, low SUVA DOC with the release of EOM, and later IOM, into the DOC pool. Reduced STHMFP$_{7d}$ between the exponential and death phase samples can also be explained by the release of IOM from senescent cells in the death phase. Indeed, Li, *et al*. (2012) report lower STHMFP for IOM (21.46 µg THM mg DOC^{-1}) compared with EOM (32.44 µg THM mg DOC^{-1}) extracted from *Microcystis aeruginosa* during the exponential growth phase. However, our exponential and death phase samples also show much higher STHMFP$_{7d}$ values (66 and 31 µg THM mg DOC^{-1}, respectively) than those reported previously (Table 5.01), possibly due to the presence of residual humic material from the original raw water sample. The consistency in the STHMFP$_{7d}$ results in terms of the relative reactivity of raw, exponential and death phase samples (raw > exponential > death) suggests that the reduced reactivity of the un-fractionated samples with culture age is partly due to reduced reactivity in all three of their main constituent fractions, rather than merely the result of a change in the proportions of the different fractions.

Table 5.01. Summary of STHMFP results obtained following chlorination of AOM, adapted from Yang, *et al*. (2011).

	Growth phase	**STHMFP (µmol mmol C^{-1})**	**STHMFP (µg THM mg DOC^{-1})**	**Chlorination conditions**	**Reference**
Blue-green algae (EOM)					
A. flos-aquae	Stationary	2.61		pH 7, 21°C, 7 d reaction	(Hoffman, *et al*. 2008)
M. aeruginosa	Stationary	2.81		pH 7, 21°C, 7 d reaction	(Hoffman, *et al*. 2008)
M. aeruginosa	Stationary	1.41		pH 7, 21±1°C, 3 d reaction	(Fang, *et al*. 2010)
M. aeruginosa	Exponential	1.31		pH 7.2, 22±1°C, 3 d reaction	(Yang, *et al*. 2011)
M. aeruginosa	Stationary	1.21		pH 7.2, 22±1°C, 3 d reaction	(Yang, *et al*. 2011)
M. aeruginosa	Exponential		32.44	pH 6.8, 25±1°C, 7 d reaction	(Li, *et al*. 2012)
O. prolifera	Stationary		30±4	pH 7, 20°C, 7 d reaction	(Nguyen, *et al*. 2005)
Blue-green algae (IOM)					
M. aeruginosa	Exponential		21.46	pH 6.8, 25±1°C, 7 d reaction	(Li, *et al*. 2012)
Green algae (EOM)					
S. quadricanda	Exponential		~22	pH 7, 21°C, 7 d reaction	(Plummer & Edzwald, 2001)
C. vulgaris	Exponential	1.51		pH 7.2, 22±1°C, 3 d reaction	(Yang, *et al*. 2011)
C. vulgaris	Stationary	1.31		pH 7.2, 22±1°C, 3 d reaction	(Yang, *et al*. 2011)
S. quadricauda	Stationary		48 ± 12 or 63 ± 14 depending on culturing regime	pH 7, 20°C, 7 d reaction	(Nguyen, *et al*. 2005)
Diatom (EOM)					
C. mulleri	Stationary		29±6	pH 7, 20°C, 7 d reaction	(Nguyen, *et al*. 2005)
Cyclotella sp.	Exponential		~49	pH 7, 21°C, 7 d reaction	(Plummer & Edzwald, 2001)
NOM					
Suwannee River NOM		7.04		pH 7, 21±1°C, 3 d reaction	(Fang, *et al*. 2010)
Present study					
	Raw	8.02	81	pH 6.8, 25°C, 7 d reaction	
	Exponential	6.49	66	pH 6.8, 25°C, 7 d reaction	
	Death	3.02	31	pH 6.8, 25°C, 7 d reaction	

Although lower STHMFP$_{7d}$ was observed for algogenic DOC compared with humic DOC in this study, it should be noted that, whereas DOC with high hydrophobicity, HMW and high SUVA such as humic material is reported to be amenable to removal by coagulation, LMW hydrophilic, low SUVA DOC is reported to be relatively more recalcitrant (Sharp, *et al*. 2006; Chow, *et al*. 2009). In addition algogenic DOC is reported to be associated with higher nitrogenous DBP (NDBP) production than humic DOC (Bond, *et al*. 2011). Thus the relationship between DOC origin and THM yield is not straightforward.

Rate of THM formation

In the present study, the rate of THM formation was found to decrease as the algal bloom progressed and DOC origin shifted from predominantly humic to predominantly algogenic. This suggests that AOM was responsible for the decrease in the THM formation rate in Reservoir A water observed in May 2012 (Chapter 4). In terms of THM concentrations at the point of delivery to the consumer, it appears that chlorination of AOM may be less problematic than chlorination of humic material in this reservoir water due to its slower reaction rate. Previous studies have identified fast- and slow-reacting THM precursors based on DOC functionality (Gallard & von Gunten, 2002; Dickenson, *et al*. 2008). Thus, the algogenic DOC in this study appears to contain relatively more slow-reacting THM precursors than humic DOC. In the fractionated samples, the death phase HPOA and HPIN fractions showed particularly low reaction rates; $STHMFP_{1d}$ as a percentage of $STHMFP_{7d}$ was 27% and 26%, respectively, which corresponds with the low reaction rate of the un-fractionated death phase sample.

Bromine incorporation

The increased bromine incorporation in the un-fractionated samples with culture age in this study can be explained by shifting DOC character during successive growth phases. Previous studies have shown a negative relationship between bromine incorporation and SUVA, hydrophobicity and aromaticity (Heller-Grossman, *et al*. 1993; Kitis, *et al*. 2002; Teksoy, *et al*. 2008). XAD-fractional character and SUVA measurements indicate a shift towards lower SUVA, aromaticity and hydrophobicity as the algal bloom progressed due to the release of EOM during the exponential growth phase, and IOM during the death phase. This is important because brominated THMs are reported to more carcinogenic than $CHCl_3$ (US EPA, 1975). Our data suggests therefore, that changing speciation of THMs with culture age increases the potential health risks associated with chlorination of dissolved AOM. The BIF data reported here contrasts with that of Huang, *et al*. (2009) who found that the BIF of dissolved AOM for *Anabaena flos-aquae* remained fairly stable throughout the algal bloom but for *Microcystis aeruginosa* fell as the bloom progressed and made a slight recovery during the death phase. This trend, it was suggested, was due to a decrease in hydrophilic content with culture age.

To our knowledge bromine incorporation for XAD fractions of AOM has not been studied previously. The high BIF values associated with the HPIN fraction can be explained by its low SUVA, hydrophobicity and aromaticity. The variation in BIF values within the same fraction over time suggests that variation in BIF in the un-fractionated samples were not simply the result of changes in the fractional character, but also relate to changes in the reactivity of DOC within individual fractions. The BIF values reported in this study (0.02-0.19) are very low compared with those reported previously (Table 5.01). For example Yang, *et al*. (2011) report median BIF values of 1.4 and 1.3 for dissolved AOM associated with *Chlorella vulgaris* and *Microcystis aeruginosa*, respectively. Those reported by Huang, *et al*. (2009) varied between ~ 1.1 and ~ 1.8. Kitis, *et al*. (2002) report BIF values of ~ 0.9 and ~ 1.7 for a high SUVA water (Myrtle Beach, California) and a low-SUVA water (Tomhannock reservoir, New York). However, all of these measurements involved spiking with bromine, whereas in the present study, bromine was derived from the ambient bromide level in the samples and from the *ca*. 1% Br_2 as a production impurity in NaOCl. Bromine incorporation in a real treatment scenario is likely to be higher due to the lower chlorine residuals involved and as a result, higher $Br^-:Cl_2$ ratio (Bond, *et al*. 2014).

5.6. Conclusions

In this study an algal bloom, dominated by the green alga *Ankistrodesmus* sp., was generated using Reservoir A water and monitored using chlorophyll-*a* measurements. Three distinct growth phases were identifiable (lag, exponential and death) during which sub-samples were collected. These were analysed to compare DOC concentration and character between growth phases. In particular, we investigated the reactivity of these samples with chlorine to assess the impact of algogenic DOC on THM yield in potable water. Potential variations in AOM reactivity between growth phases has received limited attention in the literature.

Our data support the findings of previous studies showing the lower STHMFP of algogenic DOC compared with humic DOC. However, in contrast to some previous studies, the present experiment also found that STHMFP varied markedly between different growth phases. STHMFP was found to decrease as the algal bloom progressed consistent with the following order of reactivity: IOM < EOM < NOM. In addition, it was found that algogenic DOC produced both during the exponential and death phases formed THMs at a lower rate than humic DOC, as indicated by the % of $THMFP_{7d}$ formed within the first 24 h. These data suggest that algogenic DOC has a lower THM yield than humic DOC. However, when assessing the relative risks associated with AOM and humic DOC in terms of THM formation, the more recalcitrant nature of algogenic DOC should be considered.

In addition, our data show that formation of BrTHMs, considered to be more carcinogenic, varies as follows: IOM > EOM > NOM. Measurement of bromine incorporation for different XAD fractions was carried out for the first time in this study. The results suggest that increased bromine incorporation with culture age results not only from a change in XAD fractional character but also from a change in the reactivity of individual fractions over time.

Though several previous studies have considered the fractional character of AOM, by analysing AOM during both the exponential growth phase and the death phase, our results provide a more detailed assessment of the impact of algae on the fractional character of the DOC pool. Whilst our data support the findings of previous research showing the dominance of the HPIN fraction in algogenic DOC, it disagrees with the suggestion of a correlation between cell mortality and the release of HPOA and HPIA fractions. Instead, this study indicates that senescent algal cells predominantly contribute HPIN material to the DOC pool.

Although the interpretation of our HPSEC data is complicated by the possibility for microbial and photo-degradation processes in our culture, our results showed several clear differences between the MWDs of raw, exponential and death phase DOC. Our data suggest that algogenic DOC represents distinct peaks in the HPSEC chromatogram and, in contrast to previous findings, indicate that IOM may be characterised by a lower MW than EOM.

This study also investigated whether the changes in reservoir and stream DOC character observed in May 2012 compared with October 2011 in Catchments A and C (Chapter 4) were the result of a seasonal increase in the abundance in algogenic DOC. Our results suggest that algae may indeed have been responsible for the shift towards lower MW DOC and the increase in the HPIN fraction, as well as a decrease in THM formation rate in the May 2012 samples.

5.7. Acknowledgements

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Chapter 6: Dissolved organic carbon and trihalomethane precursor removal at a UK upland water treatment works

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6.1. Abstract

The removal of dissolved organic carbon (DOC) during potable water treatment is important for maintaining aesthetic water quality standards, minimising concentrations of micro-pollutants, controlling bacterial regrowth within distribution systems and, crucially, because it contains a sub-component that can act as trihalomethane (THM) precursors. In this study, the concentration and characteristics of raw water DOC and THM formation potential (THMFP) entering an upland potable water treatment works were analysed over 12 months. Correlations between raw water DOC characteristics, standardised THMFP (STHMFP) and % DOC removal were also investigated. DOC and THM precursor removal during a series of treatment stages was examined over this period, as well as potential selectivity in the removal of DOC fractions, to assess the importance of different treatment stages for DOC removal and THM amelioration. Though THMFP removal remained high and fairly stable throughout the study period (83-89 %), the data suggest that this was mostly the result of high DOC removal rates rather than the selective removal of THM precursors. Whilst this chemical agnosticism makes DOC removal more robust, it may make the overall process more vulnerable to exceeding permissible THM concentrations under changing climatic conditions. The kinetics of the reaction between DOC and chlorine appeared to vary seasonally, indicating temporal changes in the proportions of fast- and slow-reacting precursors with implications for THM concentrations at the point of delivery to the consumer. The initial treatment stages, comprising coagulation-flocculation and dissolved air floatation (DAF) were by far the most important in terms of bulk DOC removal and the preferential removal of THM precursors, though, surprisingly, DOC quality was also modified following chlorination and secondary rapid gravity filtration (RGF). Though net THM concentration decreased following initial treatment stages, a doubling in the proportion of brominated THMs (BrTHMs), which are reported to be more carcinogenic, was also observed.

6.2. Introduction

Although there is no regulatory standard for total organic carbon (TOC), the Water Supply (Water Quality) Regulations, (2010), which apply in England and Wales, recommend that potable water TOC concentration should be monitored, reflecting its relationship to other water quality parameters (DWI, 2010). The removal of dissolved organic carbon (DOC), operationally defined as organic matter which can pass through a 0.45 µm filter (Kitis, *et al*. 2001; Thurman, 1985), is often necessary under the general requirement that drinking water be acceptable to the majority of consumers in terms of its aesthetic properties (colour, odour and taste) (Davies, *et al*. 2004; WHO, 2011). DOC can also be responsible for the transport of regulated organic and inorganic micro-pollutants such as pesticides and metal contaminants (Gao, *et al*. 1998; Rothwell, *et al*. 2007). Biodegradable DOC in finished water can also be responsible for bacterial regrowth within water distribution systems (Liu, *et al*. 2002; Prévost, *et al*. 1998). Perhaps most significant from a public health perspective, is the role of DOC, and humic substances in particular, as reaction precursor in the formation of disinfection by-products (DBPs); particularly trihalomethanes (THMs) during chlorination (Adin, *et al*. 1991; Owen, *et al*. 1995; Rook, 1974; Symons, *et al*. 1975).

The Water Supply (Water Quality) Regulations, (2010) specify a maximum total THMs concentration of 100 µg L^{-1}, measured at the end of the distribution system (i.e. consumers' taps) (DWI, 2010). World Health Organisation (WHO) guidelines include maximum values for individual THM species, reflecting the higher toxicity associated with brominated species (60 µg L^{-1} for $CHCl_2Br$ and 100 µg L^{-1} for $CHClBr_2$ and $CHBr_3$ compared with 300 µg L^{-1} for $CHCl_3$) (WHO, 2011). Chloramination, an alternative method of disinfection, has been introduced at some water treatment works (WTWs) to reduce THM levels in finished water. This involves dosing with NH_3 after chlorination which effectively removes free chlorine from solution by forming chloramine species (NH_2Cl, $NHCl_2$ and NCl_3), whilst maintaining a disinfection residual within the distribution system (Guay, *et al*. 2005).

Coagulation using Al or Fe salts, followed by flocculation and clarification by sedimentation or dissolved air floatation (DAF), is the most widely-used method of DOC removal (Matilainen, *et al*. 2010). Other methods are available, including membrane filtration, ion exchange, activated carbon filtration/adsorption, ozonation and biodegradation, but coagulation tends to offer a preferable balance between cost and DOC removal efficiency (Sharp, *et al*. 2006c). Used in combination with metal coagulants, synthetic and natural polyelectrolytes may improve coagulation efficiency and floc characteristics. Prehydrolysed coagulants such as PACl are reported to be effective over a wider range of raw water conditions than conventional coagulants (Bolto & Gregory, 2007; Yan, *et al*. 2009). Enhanced coagulation, which refers to the optimisation of coagulation conditions for DOC removal, is recognised as the best available technology (BAT) for controlling DBP levels in chlorinated drinking water (US EPA, 1999).

Reported DOC removal rates by coagulation vary substantially (Matilainen, *et al*. 2010), reflecting the range of impacting factors, including raw water and DOC characteristics, and coagulation conditions such as pH, coagulant type and dose, temperature and sequence of chemical addition (Letterman & Vanderbrook, 1983; Runkana, *et al*. 2006; Uyak & Toroz, 2007; Yan, *et al*. 2008). The fractional character of DOC has been identified as an important factor affecting bulk DOC removal during coagulation, with higher molecular weight (MW), more hydrophobic acids relatively amenable to removal, and the lower MW, more hydrophilic DOC more recalcitrant (Gu, *et al*. 1995;

Krasner & Amy, 1995; Huang & Shiu, 1996; Edwards, 1997; White, *et al*. 1997; Sharp, *et al*. 2006b; Chow, *et al*. 2009b).

DOC characteristics are also reported to influence DBP formation. THMs, which are the main DBP of concern in potable water treatment, vary both in terms of total yield and speciation as a result of DOC characteristics. For example, the hydrophobic acid fraction is reported to be associated with the highest standardised THM formation potential (STHMFP) (Galapate, *et al*. 1999; Chow, *et al*. 2005; Chow, *et al*. 2006a; Zhang, *et al*. 2009), although exceptions have been observed (Imai, *et al*. 2003; Lu, *et al*. 2009) suggesting that the association is site specific. Specific UV absorbance (SUVA), which provides a qualitative indication of DOC MW, hydrophobicity and % aromaticity (Edzwald & Tobiason, 1999; Weishaar, *et al*. 2003), is also reported to correlate positively with STHMFP (Edzwald, *et al*. 1985; Chow, *et al*. 2003). An inverse relationship is reported to exist between DOC MW and STHMFP (Gang, *et al*. 2003). Interestingly, aliphatic DOC has been found to produce a higher proportion of brominated THMs (BrTHMs) upon chlorination (Heller-Grossman, *et al*. 1993; Teksoy, *et al*. 2008). This suggests that the relationship between DOC and THMs is complex.

Upland catchments are often associated with deep, acidic, peaty soils which can export large amounts of highly-coloured humic material (Tipping, *et al*. 1999). Understanding the role of different treatment processes in DOC and THM precursor removal has become increasingly important since, for a number of decades, a rising trend in DOC concentrations in surface waters draining upland catchments in Northern and Western Europe and North America has been observed (Bouchard, 1997; Freeman, *et al*. 2001; Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Worrall, *et al*. 2003; Monteith, *et al*. 2007). Increased seasonal variation and shorter-term fluctuations in DOC concentration and quality due to extreme weather events also present a challenge for maintaining finished water standards including THM levels (Elliott, *et al*. 2005; Eimers, *et al*. 2008).

This study comprised three main aims: (1) to investigate temporal variations in raw water DOC concentration and characteristics including THMFP over a 12 month period, (2) to investigate potential relationships between % DOC removal, STHMFP and selected raw water parameters, and (3) to assess the role of different treatment processes in terms of DOC and THM precursor removal and any selectivity in the removal of different DOC fractions.

6.3. Methods

6.3.1. Works description and sampling regime

Sampling was undertaken at a potable WTW in an upland area of the UK where raw water is abstracted from an adjacent 24.8 km^2 reservoir. The catchment comprises mainly coniferous woodland plantation (30%) flanking much of the perimeter of the reservoir, grassland (38%) and peatland habitat (32%) (Cohen, 2009). During the sampling period, raw water comprised high DOC concentration (9.0-16.2 mg L^{-1}), high colour (52-117 Hazen), relatively low turbidity (0.21-0.62 FTU), low alkalinity (~3 mg L^{-1} as $CaCO_3$) and slight acidity (pH 5.6-6.0).

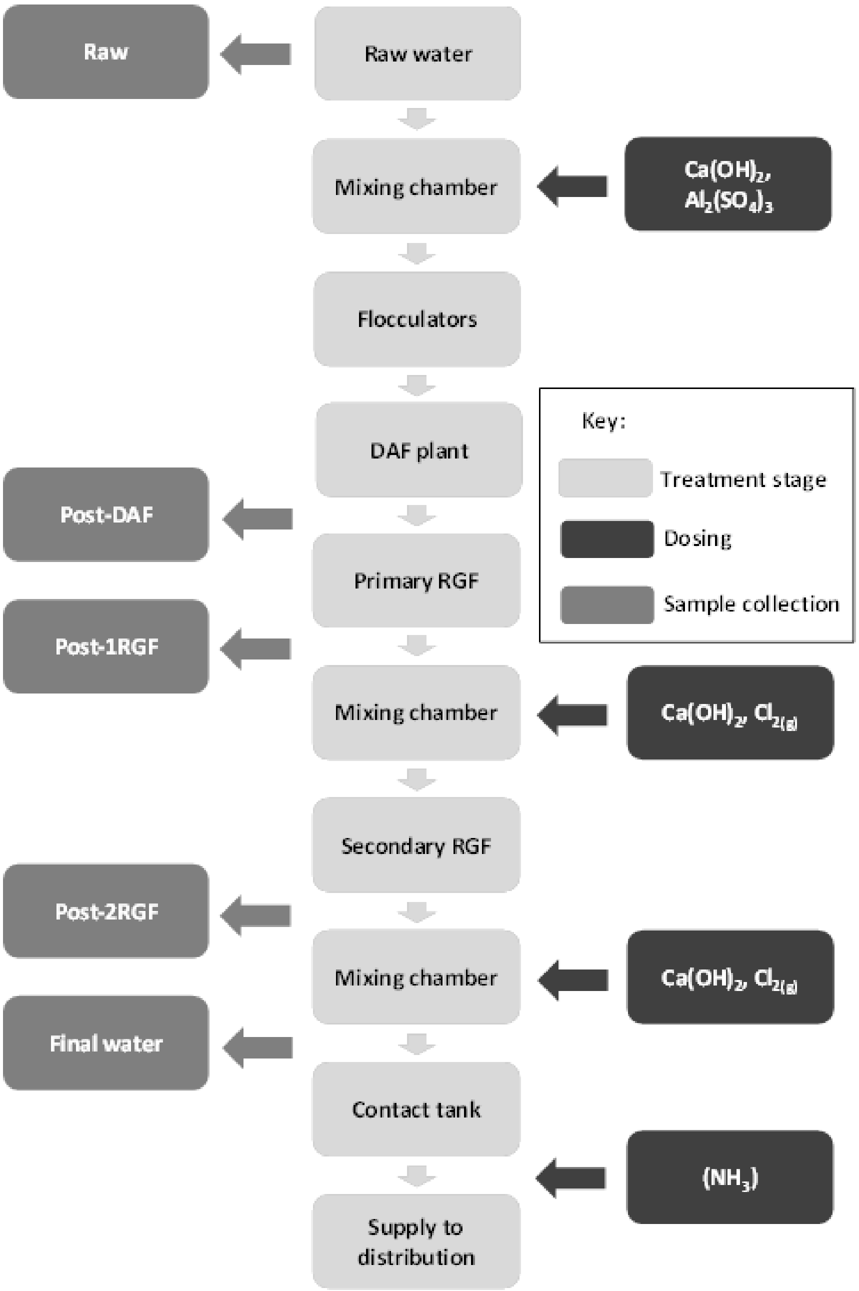

Figure 6.01. Diagram showing treatment stages, chemical dosing and sampling points.

During normal operation the WTW receives 38-40 ML of water per day from the reservoir. A works flow diagram is shown in Figure 6.01. The raw water passes into a rapid mixing chamber where it is dosed with lime (0.15% w/v $Ca(OH)_2$) for pH correction and coagulant (8% w/v $Al_2(SO_4)_{3(aq)}$). Dosed water passes under gravity to four mechanical flocculators, arranged in parallel where pin-flocs formed during the rapid mixing aggregate into macro-flocs. During subsequent DAF, the flocs are captured by ascending micro-bubbles and buoyed to the surface to form a sludge layer. This layer is removed by a continuously rotating paddle. Though sedimentation is more commonly used for clarification, DAF may be a more appropriate process where flocculation produces smaller, low density flocs or in waters rich in algae, since algal cells have a tendency to float (Teixeira & João, 2006).

The DAF stage is followed by the first set of rapid gravity filters (primary RGF) which are designed to prevent floc carry-over. Following clarification the water is dosed with lime and chlorine for primary disinfection and manganese oxidation. The water then enters secondary RGFs for manganese removal *via* a process of precipitation-filtration. This is followed by final pH adjustment and a second chlorine dose to achieve a free chlorine residual of 1.5 mg L^{-1}. The contact tank prior to distribution provides a period of contact with free chlorine to ensure adequate disinfection, which is a priority during potable water treatment (WHO, 2011). The option of dosing with NH_3 for chloramination is also available prior to distribution if required for THM control. Chemical dosing is adjusted based on raw water quality which is assessed using on line monitors. Jar testing is used to verify that coagulation conditions (coagulant and lime dose) are optimised.

Samples were collected from sampling points along the treatment chain as shown in Figure 6.01. By comparing the post-DAF sample with the raw water sample, the combined effect of coagulation, flocculation and clarification (DAF) can be assessed. The post-1RGF sample incorporates an additional filtration step and represents the culmination of all the treatment steps designed to reduce DOC concentration, since the primary filters prevent floc carry-over from the DAF stage. The post-2RGF sample was collected to assess whether this additional filtration step, which is designed to remove manganese by precipitation-filtration, affects DOC concentration and/or characteristics. The final water sample represents the total effect of all the physical and chemical treatments employed at the WTW.

For consistency the final water sample was collected before the NH_3 dosing point, since this treatment was only applied periodically. Samples were collected on a monthly basis over a 12 month period between September 2011 and August 2012. A more comprehensive analysis of raw water and post-1RGF samples, including XAD-fractionation and 7 d THMFP profiles was conducted on a seasonal basis; autumn (September 2011), winter (December 2012), spring (March 2012) and summer (June 2012). Samples were collected in amber glass bottles so as to leave no headspace, transported immediately to the laboratory and stored at 4°C until analysis which took place approximately 24 h after sample collection. The samples were not de-chlorinated before analysis.

6.3.2. Analyses

Analysis of samples was focussed on measurement and characterisation of DOC and determination of THMFP. Raw water turbidity (FTU) and colour (Hazen) were recorded at the WTW from on line monitors. All samples were filtered through a 0.45 µm nylon membrane filter (Whatman) before analysis. DOC measurement was carried out using a Thermalox TOC/TN analyser equipped with a non-dispersive infrared CO_2 detector. UV analyses including absorbance at λ = 400 nm (used as a proxy for colour (Mitchell & McDonald, 1992)) and at λ = 254 nm were made using a Molecular Devices SpecraMax M2e multi-detection reader (spectrophotometer) with aliquots of samples pipetted into a 96-well clear micro-plate. SUVA values were derived from the following formula: UV Abs. 254 (cm^{-1}) * 100/DOC (mg L^{-1})). Absorbance was also measured at λ = 253 nm and λ = 203 nm to derive the A_{253}:A_{203} ratio which is reported to correlate with the proportion of hydroxyl-, carboxyl-, ester- and carbonyl-substituted aromatic rings (Korshin, *et al*. 1997). These functional groups have been implicated in reactions generating DBPs (Kim & Yu, 2007). Phenolic concentration was measured using the Box, (1983) method adapted for 0.3 mL micro-plate wells. High pressure size exclusion chromatography (HPSEC) was conducted using a Varian PL-GPC-50 DataStream unit detecting at λ = 254 nm. The HPSEC unit was interfaced to Cirrus software and equipped with a Bio Sep 2000 column. Calibration standards were sodium polystyrene sulfonate polymers with MWs of 150,000, 77,000, 32,000, 13,000 and 4,300 Da (Fluka) and cyanocobalamin (1,340 Da). The mobile phase was Milli Q water buffered with phosphate (2 mM KH_2PO_4 + 2 mM $K_2PO_4.3H_2O$) to pH 6.8. From the MW distributions (MWDs) the following MW indices were calculated:

M_p: peak MW

M_n: number-average MW (Equation 1) - the value at which there are equal numbers of molecules on each side

$$M_n = \frac{\sum_i h_i}{\sum_i {}^{h_i}/_{M_i}} \qquad (1)$$

M_w: weight-average MW (Equation 2) - the value at which there are equal masses of molecules on each side

$$M_w = \frac{\sum_i h_i \, M_i}{\sum_i M_i} \qquad (2)$$

Here h_i is the height (from the baseline) of the HPSEC curve at the i^{th} increment and M_i is the MW of the species eluting at this increment (obtained *via* calibration with standards).

XAD-fractionation

Fractionation of DOC, which was carried out on a seasonal basis, was achieved by resin adsorption using a method adapted from Thurman & Malcolm, (1981) and Marhaba, *et al.* (2003). Samples were separated into five fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophilic neutral (HPIN) according to their adsorption onto macroporous resins. A column packed with Superlite™ DAX-8™ resin and a second packed with Amberlite™ XAD-4™ resin (both Supelco) were connected using PEEK™ tubing. The system was connected to a Cecil 1100 Series liquid chromatography pump to control the elution rate. The HPIN fraction was retrieved by passing the sample through both columns at a rate of 4 mL min^{-1} and collecting the eluent. This process also loaded the resins with the remaining fractions. The HPOA fraction was eluted by passing 60 mL of 0.1M NaOH through the DAX-8 column followed by 40 mL of Milli Q water, (both at 2 mL min^{-1}). This was repeated for the XAD-4 column to obtain the HPIA fraction. The HPOB fraction was eluted by passing the 60 mL of 0.1M HCl through the DAX-8 column followed by 40 mL of Milli Q water, (both at 2 mL min^{-1}). The HPIB fraction was obtained by repeating this process with the XAD-4 column.

Trihalomethane formation potential

THMFP$_{7d}$ denotes the quantity of THMs formed (µg L^{-1}) following chlorination of a water sample for a 7 d incubation period at 25 °C. The method used was adapted from the Standing Committee of Analysts, (1981) procedure. Samples were diluted to 1 mg L^{-1} DOC to derive a standardised THMFP$_{7d}$ (STHMFP$_{7d}$) value which provides a measure of DOC reactivity. THMFP$_{7d}$ was calculated by multiplying STHMFP$_{7d}$ by DOC concentration. For chlorination, 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5M $KH_2PO_{4(aq)}$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $NaOCl_{(aq)}$ to provide 5 mg of free Cl per mg of DOC. After a 7 d incubation in the dark at 25 °C, the reaction was quenched using 0.4 mL of 0.8M $Na_2SO_{3(aq)}$. Extraction of the four chlorinated and brominated THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) was achieved using direct immersion

SPME followed by quantification using a Varian 450 GC coupled with an electron capture detector. For the seasonal samples, THM concentrations were also measured at 1 h, 1 d and 3 d in order to profile THMFP with reaction time.

Statistical analysis

Statistical analysis was performed using version 20 of the SPSS Statistics package (PASW). Friedman's ANOVA was conducted to investigate selectivity in the removal of DOC and THM precursors during successive treatment stages. Post-hoc analysis employed the Wilcoxon signed-rank test incorporating a Bonferroni correction (Bonferroni, 1936). Spearman's correlation was performed to test for significant correlations between raw water quality parameters, in particular between DOC removal rates, raw water $THMFP_{7d}$ and raw water DOC characteristics.

6.4. Results

6.4.1. Temporal variations in raw water DOC characteristics, THMFP and DOC removal rates

Within the 12 month sampling period, maximum raw water DOC concentration was observed in January 2012 (16.2 mg L^{-1}) and the minimum in August 2012 (9.0 mg L^{-1}) (Figure 6.02a). This seasonal trend in DOC is broadly in agreement with Dŵr Cymru Welsh Water (DCWW) raw water data for preceding years, though the August minimum is comparatively late, and normally occurs between May and June. DOC removal rates averaged 76% for the 12 month period with a low of 62% in March 2012 and a high of 83% in November 2011 (Figure 6.02b). Colour (absorbance at λ = 400 nm), which is affected by both DOC quantity and quality, varied between 0.084 a.u. in November 2011 and 0.050 a.u. in January 2012 (Figure 6.02c).

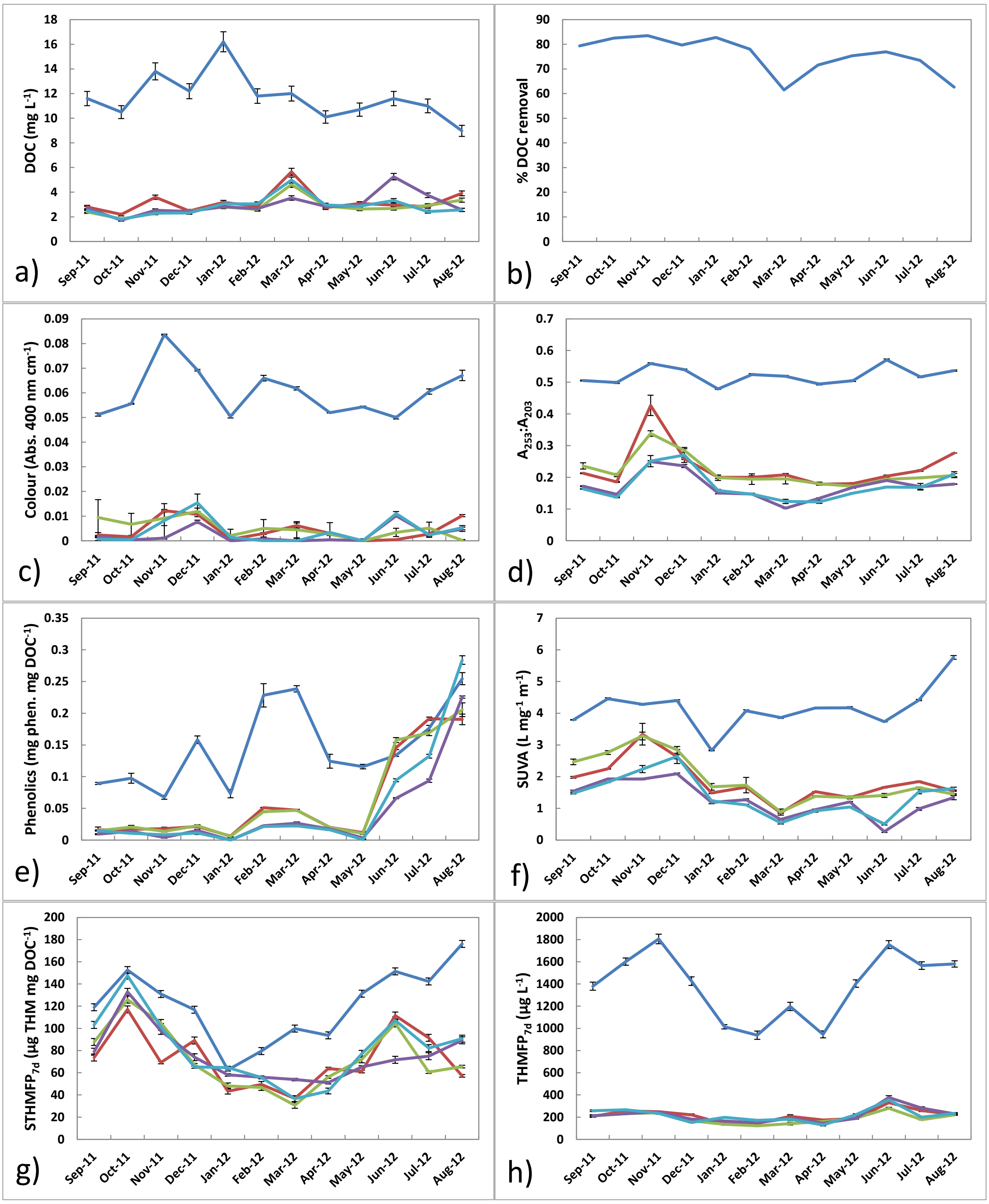

Figure 6.02. Analyses for treatment chain samples between September 2011 and August 2012; raw (dark blue), post-DAF (red), post-1RGF (green), post-2RGF (purple) and final water (light blue) including DOC concentration (a), % DOC removal (b), colour (c), A_{253}:A_{203} (d), standardised phenolic concentration (e), SUVA (f), $STHMFP_{7d}$ (g) and $THMFP_{7d}$ (h). Error bars represent 5% covariance (a), the standard error (*n* = 3) (c, d, e and f) and the standard error derived from a detection repeatability experiment (g and h).

Little variation occurred in the A_{253}:A_{203} ratio which showed a minimum in January 2012 (0.48) and a maximum in June 2012 (0.57) (Figure 6.02d). Raw water phenolics concentration, standardised for

DOC concentration, ranged between 0.07 mg phen. mg DOC^{-1} in November to 0.25 mg phen. mg DOC^{-1} in August (Figure 6.02e). Although variable, raw water SUVA values, which provide a broad indication of hydrophobicity, MW and % aromaticity, remained high during the sampling period (Figure 6.02f). The minimum SUVA (2.8 L mg^{-1} m^{-1}) in January 2012, coincided with peak DOC concentration and the maximum (5.8 L mg^{-1} m^{-1}) in August, coincided with the minimum DOC concentration. STHMFP$_{7d}$ broadly follows the same seasonal trend exhibited by SUVA. Coinciding with the SUVA maximum and minimum, lowest STHMFP$_{7d}$ was observed in January (63 µg THM mg DOC^{-1}) and the highest in August (176 µg THM mg DOC^{-1}) (Figure 6.02g).

Raw water THMFP$_{7d}$ was highest in November (1806 µg L^{-1}), with a second peak in June (1755 µg L^{-1}), and was lowest in February (938 µg L^{-1}), though the whole period January 2012 – April 2012 was characterised by relatively low THMFP$_{7d}$ (Figure 6.02h). Comparing the two measurements influencing THMFP$_{7d}$, variability in raw water STHMFP$_{7d}$ (CV: 27%) was considerably higher than the variability in DOC concentration (CV: 16%). Percentage STHMFP$_{7d}$ removal (and therefore the preferential removal of THM precursors) during treatment varied considerably, ranging from 17% in October 2011 to 69% in March 2012. In contrast to its contributing factors (STHMFP$_{7d}$ and DOC concentration), % THMFP$_{7d}$ removal remained fairly stable (CV: 2%), ranging between 83% in April 2012 and 89% in July 2012.

Monthly raw water HPSEC data for this sampling period indicate that variations in DOC MWDs were minimal (Figure 6.03). The raw water MWDs include a small peak at retention time (t_R) ≈ 4.2 min which represents high MW (HMW) molecules that are too large to interact with the pores of the stationary phase (Huber, *et al*. 2011). This is followed by a dominant peak at t_R ≈ 8.0 min with two overlapping peaks at t_R ≈ 8.9 and 9.3 min. These data were converted to MW ranges with HMW characterised as > 1.0 kDa and low MW (LMW) as < 1.0 kDa (Zou, *et al*. 2004). According to these definitions, raw water DOC consistently comprised > 94% HMW molecules.

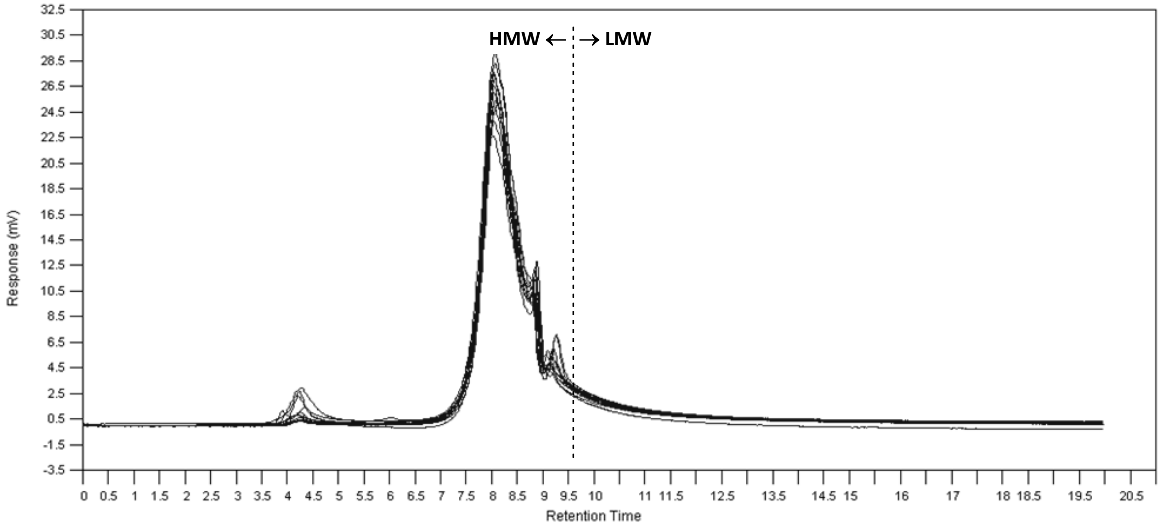

Figure 6.03. HPSEC chromatograms for all raw water samples between September 2011 and August 2012.

6.4.2. Relationships between raw water characteristics, % DOC removal and STHMFP

The relationship between % DOC removal rate and various DOC characteristics was investigated using Spearman's correlation coefficient. The only statistically significant relationship was found to be with standardised phenolics concentration, r_s = -0.778, $p < 0.01$, suggesting that phenolic compounds are more recalcitrant. $STHMFP_{7d}$ was found to vary as a function of DOC concentration, r_s = -0.588, $p < 0.05$, suggesting that as raw water DOC concentration increases, its relative reactivity with chlorine decreases. $STHMFP_{7d}$ also varied positively with SUVA, r_s = 0.615, $p < 0.05$, suggesting that more hydrophobic DOC has a higher reactivity with chlorine. Finally, a significant positive correlation was found between $STHMFP_{7d}$ and A_{253}:A_{203}, r_s = 0.755, $p < 0.01$.

6.4.3. Selectivity in DOC and THM precursor removal during successive treatment stages

Friedman's ANOVA was used to investigate changes in water quality resulting from different treatment processes (Table 6.01), including selectivity in DOC and THM precursor removal. Unsurprisingly a substantial and statistically significant decrease in DOC concentration occurred during the early treatment stages (coagulation-flocculation and DAF) ($p < 0.05$). A statistically significant reduction in SUVA from 4.2 L mg^{-1} m^{-1} in the raw water to 1.8 L mg^{-1} m^{-1} following DAF treatment ($p < 0.05$) also occurred as a result of these early treatments, indicating the preferential removal of hydrophobic, HMW DOC during coagulation-flocculation and DAF. A smaller but significant reduction in SUVA also occurred after secondary RGF. A_{253}:A_{203} also fell substantially following the DAF stage ($p < 0.05$) (from 0.52 to 0.23 UV a.u.) and showed a smaller reduction following secondary RGF ($p < 0.05$). Colour showed a substantial and statistically significant reduction following the DAF stage ($p < 0.05$) in line with reduced DOC concentration. Standardised phenolic concentration increased following the DAF stage ($p < 0.05$), supporting the view that phenolic compounds are more recalcitrant. % HMW DOC (> 1.0 kDa) was higher in the raw sample compared with all subsequent samples ($p < 0.05$) and no statistical difference between stages thereafter. A comparison of the MW averages (M_p, M_n and M_w) support this result, each showing statistically higher values in raw water compared with the samples collected further along the treatment chain ($p < 0.05$), and again, no significant difference between these subsequent samples.

Table 6.01. DOC quality and THMFP results for process chain samples collected between September 2011 and August 2012 showing statistically significant differences identified by Friedman's ANOVA analysis.

	Raw (a)	**Post-DAF (b)**	**Post-1RGF (c)**	**Post-2RGF (d)**	**Final water (e)**
DOC concentration (mg L^{-1})	11.7 ± 0.5 bcde	3.2 ± 0.2 a	2.8 ± 0.2 a	3.0 ± 0.2 a	2.8 ± 0.2 a
SUVA (L mg^{-1} m^{-1})	4.2 ± 0.2 bcde	1.8 ± 0.2 ad	1.9 ± 0.2 ade	1.3 ± 0.2 abc	1.4 ± 0.2 ac
Colour (Abs$_{400}$) (UV a.u.)	0.060 ± 0.003 bcde	0.004 ± 0.001 a	0.005 ± 0.001 a	0.002 ± 0.001 a	0.004 ± 0.001 a
A_{253}:A_{203}	0.52 ± 0.01 bcde	0.23 ± 0.02 a	0.22 ± 0.01 Ad	0.17 ± 0.01 ac	0.17 ± 0.01 a
Phenolics per mg DOC (mg phen. mg DOC^{-1})	0.15 ± 0.02 bcde	0.25 ± 0.06 a	0.19 ± 0.06 a	0.24 ± 0.02 a	0.22 ± 0.05 a
% HMW DOC	96.6 ± 0.2 bcde	94.5 ± 0.4 a	93.4 ± 0.5 a	91.8 ± 0.9 a	92.1 ± 0.8 a
Mp (Da)	5267 ± 25 bcde	3156 ± 120 a	3161 ± 118 a	2990 ± 23 a	3139 ± 140 a
Mn (Da)	3180 ± 54 bcde	2385 ± 54 a	2246 ± 55 a	2113 ± 88 a	2133 ± 82 a
Mw (Da)	4401 ± 27 bcde	3219 ± 44 a	3075 ± 21 A	3038 ± 40 a	3070 ± 31 a
STHMFP$_{7d}$ (µg THM mg DOC^{-1})	121 ± 10 bcde	72 ± 7 a	72 ± 8 a	75 ± 7 a	81 ± 9 a
THMFP$_{7d}$ (µg L^{-1})	1384 ± 87 bcde	216 ± 16 a	190 ± 14 a	216 ± 19 a	217 ± 17 a
% BrTHMs	4.8 ± 1.4 bcde	11.8 ± 3.4 a	10.0 ± 2.9 ad	8.4 ± 2.4 ac	9.8 ± 2.8 a

Results given as mean ± standard error ($n = 12$). Letter annotations denote significantly different means ($p < 0.05$).

An example of the MWDs for samples collected along the treatment chain is shown in Figure 6.04. The first peak ($t_R \approx 4.2$ min) which appears in the raw sample is absent from all subsequent samples. A dramatic reduction in the area of the second peak between the raw water and post-DAF stage and a further slight reduction between the two RGF stages is seen for this month but not all, in line with reduced DOC concentration. A shift towards lower MW molecules is also apparent in treated water compared with raw.

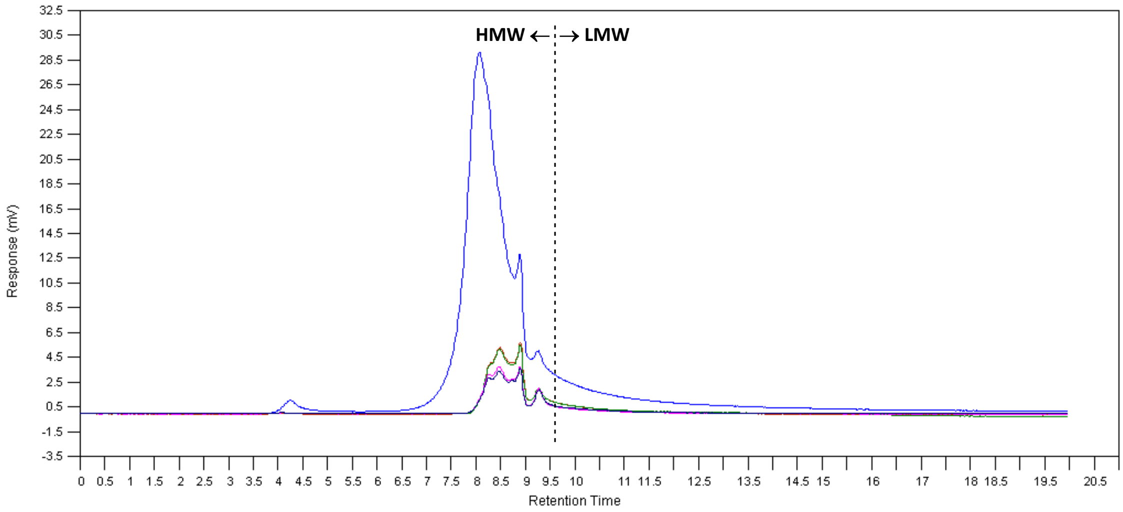

Figure 6.04. HPSEC chromatograms for process chain samples in November 2011 (raw: blue, post-DAF: red, post-1RGF: green, post-2RGF: pink, final water: dark blue).

$THMFP_{7d}$ and $STHMFP_{7d}$ showed a dramatic and statistically significant reduction in the post-DAF sample compared with the raw water ($p < 0.05$) and no significant change thereafter, suggesting that THM precursors were preferentially removed during these early treatment stages (coagulation-flocculation and DAF). Comparing THM speciation, % BrTHMs was found to increase significantly following the early treatment stages ($p < 0.05$) (Figure 6.05). A slight but statistically significant reduction in %BrTHMs was also observed following secondary RGF ($p < 0.05$).

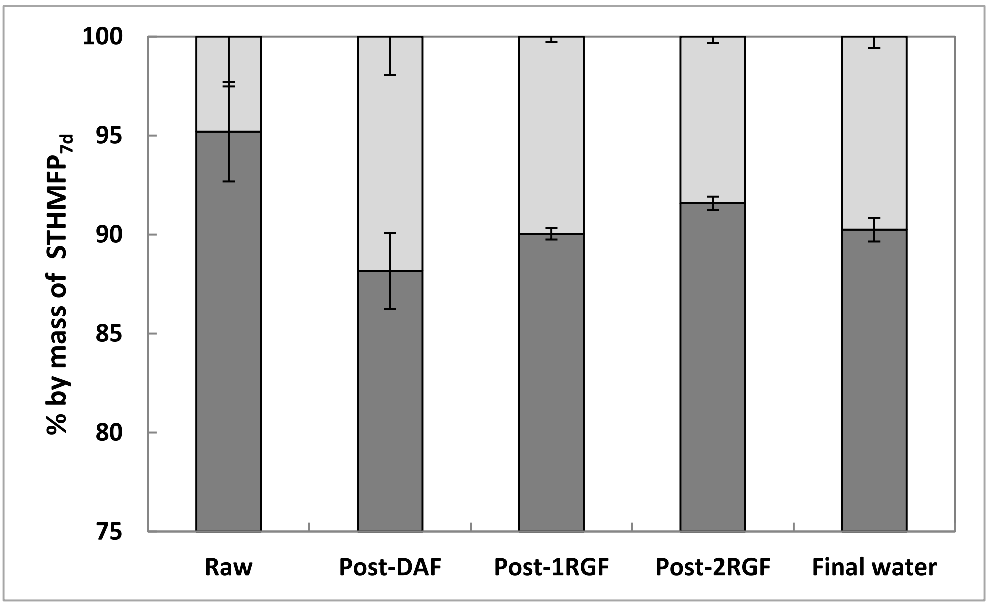

Figure 6.05. Mean % contribution of THM species ($CHCl_3$: dark grey, BrTHMs: light grey) to $STHMFP_{7d}$ for treatment chain samples. Error bars represent the standard error (n = 12).

6.4.4. Seasonal analysis of fractional character and THMFP profiles

Fractional character and 7 d THMFP profiles for raw and post-1RGF samples were investigated on a seasonal basis. Post-1RGF samples represent the culmination of all the treatments designed to reduce DOC. In the raw water samples, the HPOA fraction dominated, varying between 36% in winter to 51% in spring (Figure 6.06). This fraction consistently represented the dominant fraction in percentage terms. The HPIA fraction varied between 16% in summer to 28% in spring, HPIN from 35% in winter to 18% in spring whilst the HPOB and HPIB fractions combined consistently represented < 10% of total DOC. Compared to the raw water samples, the contribution of the HPOA fraction in the post-1RGF samples was less in all cases except in the summer, where the fractional character of the DOC in the post-1RGF sample remained very similar to that of the raw water.

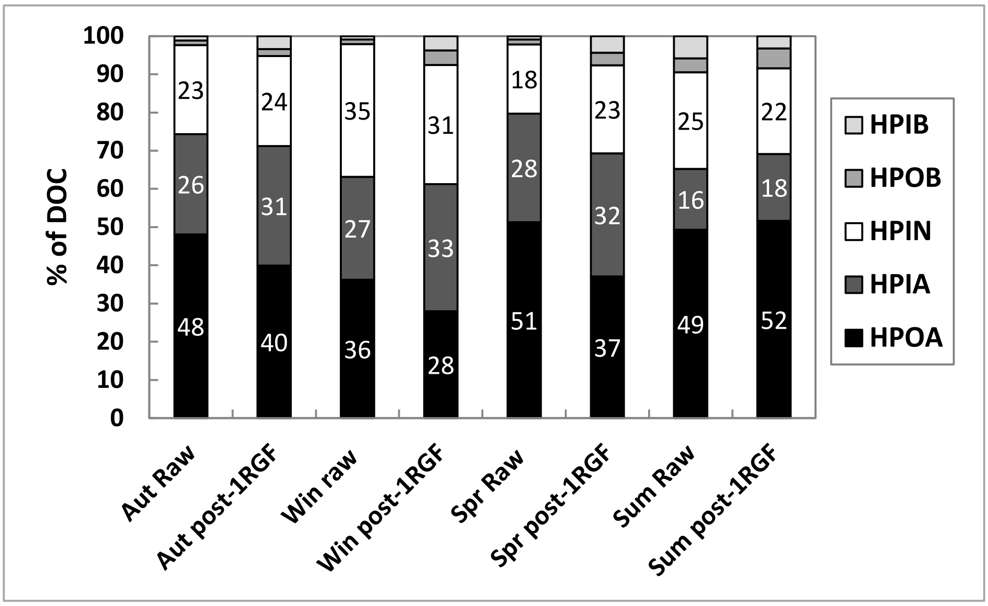

Figure 6.06. % contribution of the HPOA, HPIA, HPIN, HPOB and HPIB fractions to the total recovered DOC following fractionation for raw and post-1RGF samples in autumn, winter, spring and summer.

The 7 d STHMFP profiles (Figure 6.07) show that the kinetics of the reaction, and specifically the % of THMs formed within the first 24 h, varied seasonally. In the raw water $STHMFP_{1d}$ as a percentage of $STHMFP_{7d}$ ranged from 39% in winter to 68% in autumn. In the post-1RGF sample the $STHMFP_{1d}$ percentage was also highest in autumn (56%) but was lowest in summer (38%). The 7 d THMFP profiles (Figure 6.08) confirm that THMFP reduction during treatment remained high throughout the sampling period. Though temperature fluctuations and other conditions within the distribution system such as the role of biofilms could not be replicated, the post-1RGF profiles provide an approximate model of THM concentrations at different points in the distribution system. Estimated post-1RGF THMFP at 36 h, which is the maximum residence time for water in the distribution system, exceeded the regulatory limit of 100 µg L^{-1} in autumn (127 µg L^{-1}) and summer (131 µg L^{-1}).

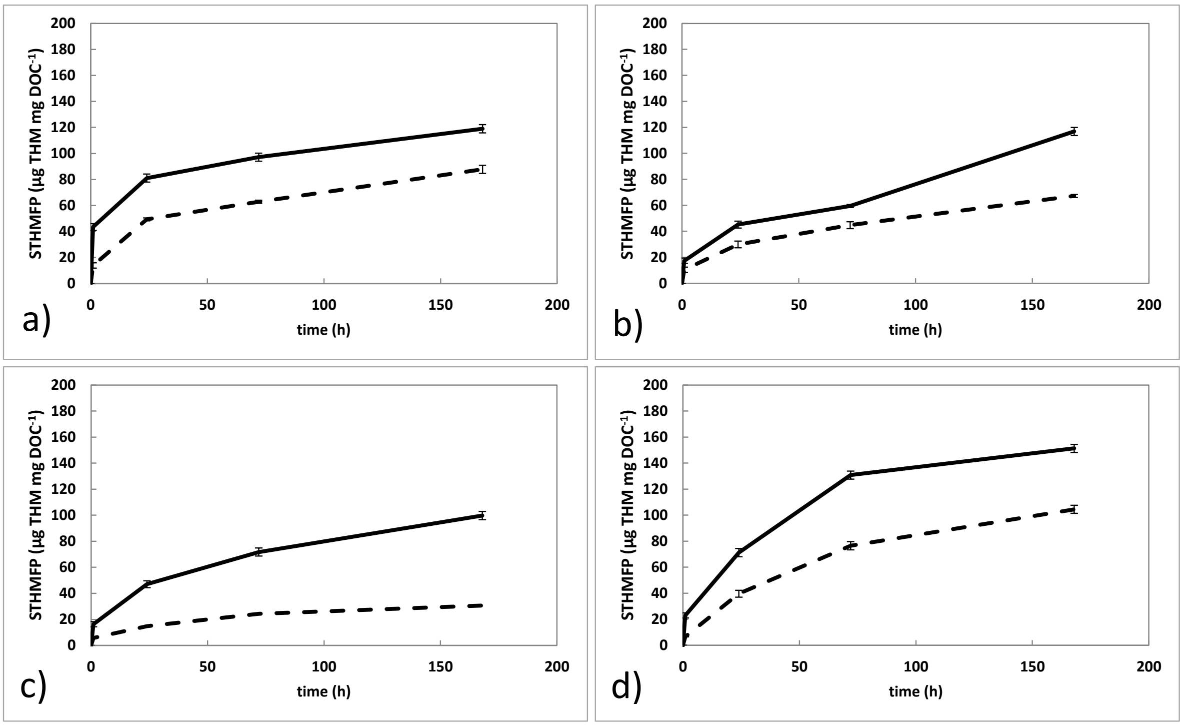

Figure 6.07. Profile of STHMFP over a 7 d incubation period following chlorination of raw (solid line) and post-1RGF (dashed line) samples in autumn (a), winter (b), spring (c) and summer (d). Error bars represent the standard error derived from a detection repeatability experiment.

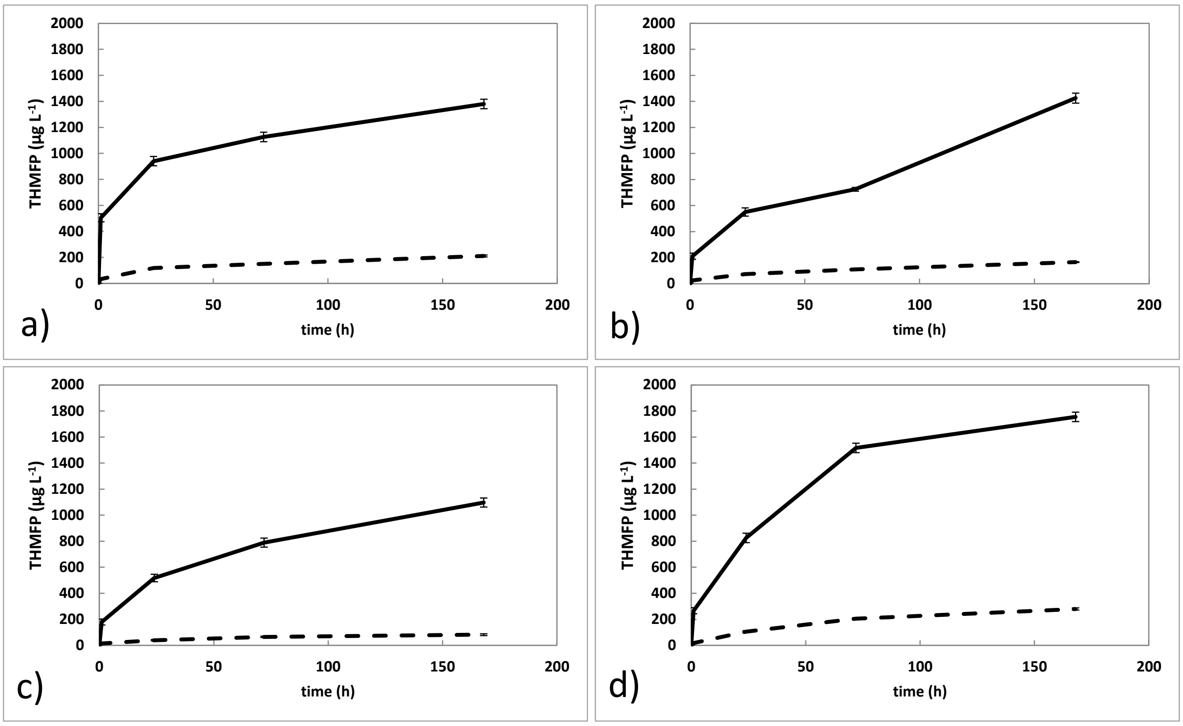

Figure 6.08. Profile of THMFP over a 7 d incubation period following chlorination of raw (solid line) and post-1RGF (dashed line) samples in autumn (a), winter (b), spring (c) and summer (d). Error bars represent the standard error derived from a detection repeatability experiment.

6.5. Discussion

6.5.1. Raw water quality and DOC removal rates

Compared with the global average for lake DOC concentrations (median: 5.71 mg L^{-1}), the reservoir water analysed in this study exhibits relatively high DOC concentration throughout the year (Sobek, *et al*. 2007). Algal assemblages analysed for this water source suggest that the reservoir is oligotrophic; a trophic state associated with low levels of primary production (Wetzel, 2001). Allochthonous DOC sources are therefore likely to account for this high DOC loading. Both peatland and coniferous forestry plantations, which cover extensive areas of this catchment, have been associated with high DOC flux; predominantly humic acids (Kaiser, *et al*. 2001; Clark, *et al*. 2008; Creed, *et al*. 2008; Lindroos, *et al*. 2011). The seasonal trend in DOC concentration observed in this study conforms with data from previous years showing a maximum in late autumn/early winter and a minimum in late spring/early summer (DCWW data), though in this case the minimum occurred later than normal; in August. Fluvial DOC concentrations have been found to peak in late summer/ autumn as DOC which accumulates in the soil matrix during the summer months due to warm, aerobic conditions is flushed from the catchment (Hope, *et al*. 1994; Neal, *et al*. 2005). This peak may also be influenced by litter-fall from deciduous tree species in the autumn (Chow, *et al*. 2009a). Lower stream DOC concentrations are generally observed in late winter/spring when the soil tends to be more waterlogged and cold conditions inhibit microbial degradation (Halliday, *et al*. 2012). This trend has been observed in the inflow streams of this reservoir (Chapter 4). The lag between this and the reservoir DOC trend may be the result of relatively long residence times in the reservoir.

% DOC removal rates remained high throughout the sampling period (mean 76%) compared with previous studies where 29-70% average DOC removal rates are reported for iron-based coagulants and 25-67% for aluminium sulphate in a range of raw water types (Matilainen, *et al*. 2010). This is important given the rising trend in DOC concentration for surface waters in many upland catchments (Bouchard, 1997; Freeman, *et al*. 2001; Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Worrall, *et al*. 2003; Monteith, *et al*. 2007). Reports suggest DOC removal rates during coagulation depend on many factors, including DOC and raw water characteristics, and coagulation conditions (Letterman & Vanderbrook, 1983; Runkana, *et al*. 2006; Sharp, *et al*. 2006a; Uyak & Toroz, 2007; Yan, *et al*. 2008). The high removal rates reported in this study are likely due to the high proportion of HMW, hydrophobic humic substances in the raw water, which have been found to be easily removed by conventional coagulation-flocculation (Randtke, 1988; Edwards, 1997; Sharp, *et al*. 2006b), allied to the higher charge densities associated with this DOC fraction (Edzwald, 1993; Sharp, *et al*. 2006b).

The only statistically significant relationship between % DOC removal and raw water characteristics was a negative correlation with standardised phenolic content ($p < 0.05$). The difficulty of removing phenolic compounds by conventional coagulation methods has been reported previously (Tomaszewska, *et al*. 2004). This relates to the enhanced aqueous solubility of phenolic compounds relative to other DOC due to their hydrophilic hydroxyl content (Bond, *et al*. 2009) and, because the coagulation process is under kinetic control within a competitive precipitation process so the least soluble material will be removed first. Although phenolic content has been correlated positively with $STHMFP_{7d}$ in previous studies (Harrington, *et al*. 1996; Imai, *et al*. 2003) no relationship was found in this study. The positive relationship between $STHMFP_{7d}$ and A_{253}:A_{203} ($p < 0.05$), which has been reported previously, is likely due to the fact that the functional groups identified by the A_{253}:A_{203} index (e.g. esters and ketones) react *via* haloform-like reactions during chlorination (Korshin, *et al*. 1997; Kim & Yu, 2007).

SUVA values for raw water indicate relatively high DOC hydrophobicity and MW throughout the year (mean 4.2 L mg^{-1} m^{-1}) (Edzwald & Tobiason, 1999; Volk, *et al*. 2002) suggesting high humic content. The high SUVA values in this reservoir are likely due to the high proportion of peatland and forested area in the catchment, both of which have been found to correlate positively with surface water SUVA (Piirsoo, *et al*. 2012). Interestingly, peak SUVA in August (5.8 L mg^{-1} m^{-1}) coincided with the DOC minimum (9.0 mg L^{-1}), and lowest SUVA in January (2.8 L mg^{-1} m^{-1}) with the DOC maximum (16.2 mg L^{-1}). Environmental conditions are reported to cause temporal variations in SUVA; a positive relationship is reported between soil water content and SUVA (HPOA proportion) in pore water (Christ & David, 1996; Chow, *et al*. 2006b) and increased stream water SUVA has also been found to correlate with rainfall events (Volk, *et al*. 2002). However, understanding variations in SUVA where long residence times are involved, such as in lakes and reservoirs, is complicated due to the likelihood that a number of chemical and microbial transformations will affect DOC quality and quantity. It has been proposed that the aromatic DOC fraction is relatively stable (Kalbitz, *et al*. 2003) and therefore consumption of microbially labile DOC by microorganisms could increase the relative proportion of aromatic carbon (Chow, *et al*. 2006b). Conversely microbial activity has been linked to an increase in the proportion of HPIA DOC due to acceleration of the microbial degradation of HPOA to HPIA DOC (Christ & David, 1996). Transformations of DOC may also be driven by photo-degradation, which is reported to cause an increase in the proportion of LMW hydrophilic DOC (Waiser & Robarts, 2004), and precipitation which can cause partitioning of DOC fractions. Precipitation of DOC is common in acidic waters containing high concentrations of iron or aluminium; features consistent with the reservoir in the present study (Parks & Baker, 1997; Pokrovsky & Schott, 2002). Precipitation and settling out of DOC in the reservoir may also explain the substantial decrease in DOC concentration in the reservoir compared with its input streams (Chapter 4). Though microbial populations are likely to be low in this reservoir due to oligotrophic conditions, the coincidence of the SUVA maximum with the DOC minimum in August may be the result of enhanced microbial processing of labile LMW HPIA DOC under higher water temperature conditions. Conversely, the suppression of microbial activity due to low water temperature in January may have contributed both to the higher DOC pool overall (DOC maximum) and the relatively large pool of labile LMW HPIA DOC (indicated by the SUVA minimum).

A statistically significant correlation between raw water $STHMFP_{7d}$ and SUVA was observed ($p < 0.05$). A positive relationship between SUVA and $STHMFP_{7d}$ has been reported previously with SUVA even having been used as a surrogate for STHMFP (Edzwald, *et al*. 1985; Chow, *et al*. 2003) although it has been suggested that SUVA is not a useful indicator of DOC reactivity from distinct sources due to the relationship being site specific (Weishaar, *et al*. 2003). It is perhaps unsurprising therefore that the seasonal pattern of $STHMFP_{7d}$ in the raw water is visually similar to that of SUVA (Figures 6.02f and 6.02g). During the study period, the reactivity of the DOC ($STHMFP_{7d}$) was more variable (CV: 27%) than DOC concentration (CV: 16%), suggesting that variations in raw water THMFP over time are controlled mostly by variations in the character of DOC. This also highlights the importance of the selective removal of THM precursors during treatment as opposed to merely bulk DOC removal. The overall reactivity of the raw water ($STHMFP_{7d}$) was highest in August 2012 (176 µg THM mg DOC^{-1}) and the lowest in January 2012 (63 µg THM mg DOC^{-1}). The rate of halogenation in the early stages of the reaction also varied seasonally, with the proportion of THMs formed in the first 24 h of reaction 39% in winter, compared with 68% in autumn. This suggests that summer presents the highest risk for THMFP. THM precursors are known to vary in reactivity according to DOC functionality, with fast- and slow-reacting THM precursors having been identified in previous studies; Gallard & von Gunten, (2002) report that resorcinol-type structures and phenolic compounds act as fast- and slow-reacting THM precursors, respectively whilst Dickenson, *et al*. (2008) identified β-diketone-acids and β-keto acids, as fast- and slow-reacting THM precursors. Though the broad hydrophobic/hydrophilic DOC descriptors used in this study are insufficient for identifying compounds likely to influence the rate of THM formation, it is likely that temporal changes in the proportions of fast- and slow-reacting precursors are responsible for the seasonality in reaction kinetics observed. Interestingly, a negative correlation was identified between $STHMFP_{7d}$ and DOC concentration ($p < 0.05$), indicating that as DOC concentration increases, the relative proportion of THM precursors decreases. This further emphasizes the importance of STHMFP as well as DOC concentration in affecting raw water THMFP. The first $THMFP_{7d}$ peak in November 2011 was the result of higher than average DOC and $STHMFP_{7d}$ whereas higher than average $STHMFP_{7d}$ was solely responsible for the second peak in June 2012. The lowest raw water $THMFP_{7d}$ occurred between January and April, predominantly due to low $STHMFP_{7d,}$ despite the DOC concentration maximum in January.

The 7 d THMFP profiles (Figure 6.08) provide a useful visual indication of bulk THMFP removal during treatment. % reduction in $THMFP_{7d}$ between the raw and post-1RGF stages remained stable, ranging between 83% and 89% over the 12 month period (Figure 6.02h). These removal rates are high compared to reports in the literature. Iriarte-Velasco, *et al*. (2007) report 31-48% bulk removal of THMFP for a low DOC surface water under different alkalinity conditions using alum and polyaluminium chloride coagulants. Page, *et al*. (2002) report 55% THMFP removal on average across a range of reservoir waters and DOC concentrations using alum. Similarly Uyak & Toroz, (2007) report an average 56% precursor removal under optimum conditions averaged across three surface water sources using ferric chloride and alum coagulants. The coagulation system employed at this WTW is therefore well-optimised for DOC removal. However, the 7 d THMFP post-1RGF profiles, which are an approximate model for THM concentrations along the distribution system, suggest that the system may still be vulnerable to exceeding the regulatory limit of 100 µg L^{-1} at the extremities of the distribution system (36 h after water leaves the WTW) in autumn and summer. The majority of the reduction in THMFP is due to bulk DOC removal (Figure 6.02a), with the coagulation system less successful in selectively removing THM precursors (Figure 6.02g). As a result of mainly climatically-driven changes in DOC production and processing, the quality of both allochthonous and autochthonous DOC is expected to change in the future (Ritson, *et al*. 2014). Though the precise nature of these changes is difficult to predict, it is likely that WTWs will need to respond to increased seasonality as well as shorter-term changes in DOC quality resulting from increasingly frequent and severe extreme weather events (Elliott, *et al*. 2005; Eimers, *et al*. 2008; Jenkins, *et al*. 2009). As a result it may be necessary to adopt a season-specific approach to coagulation optimisation focussed on the selective removal of THM precursors. In this context Tang, *et al*. (2013) recommend more frequent jar tests to optimise coagulation conditions particularly during periods of high rainfall following drought. Introducing additional treatment processes may be necessary to enhance the removal of recalcitrant THM precursors. For example, anion exchange and granular activated carbon (GAC) can be successful in removing more recalcitrant LMW hydrophilic and neutral DOC (Bond, *et al*. 2011). Finally, controlling THM levels may require switching to a chloramination system, which has been associated with a substantial decrease in THM formation (Kristiana, *et al*. 2009), though this strategy is also associated with an increase in nitrogenous DBPs such as N-nitrosodimethylamine (Choi & Valentine, 2002), as well as currently unidentifiable chlorinated by-products (Hua & Reckhow, 2007).

HPSEC analysis indicates that raw water DOC MWDs were consistently dominated by HMW DOC (consistently > 94% contribution). Fabris, *et al*. (2009) defined this molecular weight category as HMW humics. It should be noted however that structures with few conjugated bonds exhibit low UV absorbance (Matilainen, *et al*. 2011) and so will produce little or no response from the detector (Leenheer & Croue, 2003). This poor sensitivity to these compounds which, some previous studies have shown, are more likely to form THMs (Gang, *et al*. 2003), may be the reason for the absence of a correlation between MW indices and THMFP in this study.

6.5.2. The role of successive treatments in DOC and THM precursor removal

Friedman's ANOVA revealed that the initial treatment stages (coagulation-flocculation and DAF) were responsible for the majority of DOC removal and the preferential removal of THM precursors (as evidenced by the fall in STHMFP_{7d}). These early treatment stages were also most important in modifying other DOC characteristics, causing substantial and statistically significant reductions in SUVA, A_{253}:A_{203}, colour and MW and increased standardised phenolic content. A comparison of the raw and post-1RGF fractionation results also illustrates this selective removal of DOC as the % contribution of the HPOA fraction is reduced after treatment in all cases except in the summer sample which show a slight increase (Figure 6.06).

It is the preferential removal of the HMW hydrophobic, aromatic DOC indicated by these parameters and widely reported in the literature (Randtke, 1988; Edwards, 1997; Sharp, *et al*. 2006a) that is responsible for the statistically significant reduction in STHMFP_{7d} during these treatment stages. This selectivity is thought to result from the higher charge densities associated with this DOC fraction (Sharp, *et al*. 2006a), and is important for ensuring that finished water THM levels are sufficiently low for distribution. However, as with the raw water, the rate of halogenation in the post-1RGF samples also varied seasonally with STHMFP_{1d} as a percentage of STHMFP_{7d} ranging between 38% in summer and 56% in autumn. This kind of variability may influence seasonal differences in THM levels at the point of delivery (typically 0-36 h after chlorination).

HPSEC has become a popular method for assessing DOC characteristics at different stages of water treatment, with a preferential removal of HMW DOC during coagulation consistently reported (Croue, *et al*. 1993; Chow, *et al*. 2008; Fabris, *et al*. 2008; Chow, *et al*. 2009b; Matilainen, *et al*. 2011). The MWDs in this study illustrate both the reduction in DOC concentration following initial treatment and the shift to lower MWs, a result confirmed by the statistically significant reduction in all three MW indices (M_p, M_n and M_w). However, as stated previously, there are limitations to this analysis due to the lack of sensitivity to LMW/aromatic compounds.

The secondary RGFs were the only other treatment stage associated with a statistically significant change in DOC quality. This treatment stage was associated with a slight reduction in SUVA and A_{253}:A_{203}. This did not occur during the preceding RGF stage suggesting that manganese removal chemistry may have contributed to the change. Chlorine is added prior to the secondary RGFs to oxidise Mn^{2+} to Mn^{4+}, which simultaneously results in hydrolysis of the manganese to a MnO_2-like solid. Thus, the action of chlorine would be to chlorinate more reactive (aromatic and A_{253}:A_{203}) (Edzwald, *et al*. 1985; Chow, *et al*. 2003; Kim & Yu, 2007) DOC whilst Mn precipitation would act in a similar way to coagulation, by removing some of the highly charged aromatic DOC. Other parameters, including $STHMFP_{7d}$, were less affected, although % BrTHMs decreased slightly, in line with the loss of more reactive DOC.

Interestingly, coagulation-flocculation and DAF caused a statistically significant increase in the proportion of BrTHMs. IC data confirm that this is not related to Br^- contamination during treatment, although chlorine contains *ca*. 1% Br_2 as a production impurity. However, natural Br^- from sea water is also known to transfer inland *via* aerosol particles and precipitation, resulting in the occurrence of trace levels of Br^- in natural surface waters (Winchester & Duce, 1966). Where HOCl and HOBr coexist, HOCl has been reported to react preferentially with the phenolic polymer core of humic substances to bring about oxidative bond cleavage. HOBr has been found to be a more powerful halogenating agent in the subsequent electrophilic substitution steps (Ichihashi, *et al*. 1999). DOC rich in aliphatic compounds such as ketones, indicated by low SUVA values, are therefore associated with the formation of higher proportions of BrTHMs (Heller-Grossman, *et al*. 1993; Teksoy, *et al*. 2008). Thus, the preferential removal of the aromatic DOC fraction during coagulation, which causes an increase in the relative proportion of aliphatic DOC, could be responsible for increased % BrTHMs since, under these conditions, the competitive incorporation of HOBr is likely to be enhanced. This may have implications for human health since brominated THMs are reported to be more genotoxic than their chlorinated analogues (Richardson, *et al*. 2007). This issue is particularly significant in the context of a predicted increase in sea salt deposition with rising sea surface temperatures which may increase Br^- concentration in surface waters (Hurrell, *et al*. 2004).

6.6. Conclusions

Water treatment is becoming increasingly important due to the growing global population and climate change. Chlorine-based disinfection, whose benefits include low cost, and high efficacy and lifetime, continues to be widely-used. Given the widespread trend of rising DOC levels in surface waters, the predicted increase in the seasonality of DOC loading under future climate scenarios and increasingly frequent extreme weather events, DBPs arising from chlorination are likely to become an increasing problem. In this context, our data show high DOC across the sampling period (9.0 – 16.0 mg L^{-1}) for this coniferous peatland catchment with higher DOC levels in winter and lower DOC during the summer. However the STHMFP, which correlated with SUVA as previously reported, seemed to be a more important factor in driving variations in THMFP compared with DOC level. Importantly, variations in the reaction kinetics of THM formation identified in this study, most likely driven by seasonal changes in the proportions of fast- and slow-reacting THM precursors, will also affect THM levels at the point of delivery.

Coagulation-flocculation and DAF are the first steps of water treatment at this site providing consistently effective DOC removal (mean 76%), significantly reducing THMFP from raw to post-1RGF water. However, these processes were less successful in the targeted removal of THM precursors, leading to a high THMFP in summer and autumn. Mitigation strategies, such as switching disinfection to chloramination, or the introduction of more selective DOC treatments may become necessary in the future. Interestingly, the early treatments (coagulation, flocculation and DAF) also resulted in a the doubling in the proportion of BrTHMs, it is suggested, due to the selective removal of aromatic DOC and the consequent increase in the proportion of aliphatic DOC. Brominated THMs are reported to be more carcinogenic than $CHCl_3$, and this issue is particularly significant given that climate change is predicted to result in increased sea salt (and hence Br) deposition within catchments.

Unexpectedly, the combined effect of chlorination and secondary RGFs also produced a small but statistically significant change in DOC quality, indicated by a fall in SUVA and A_{253}:A_{203}, as well as a slight reduction in the proportion of BrTHMs, possibly due to manganese removal chemistry. Future work should include measurement of Br^- along the treatment chain to investigate the potential for Br^- removal during treatment.

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Chapter 7: DOC and THMFP removal following coagulation of a typical UK upland water with alum, PAX-18 and PIX-322

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This chapter was written by Rachel Gough. Terrence Heard carried out the jar test experiments to establish optimum conditions and provided editorial suggestions. Peter Holliman and Christopher Freeman provided advice on experimental design and editorial suggestions.

7.1. Abstract

This paper considers the removal of dissolved organic carbon (DOC) from a typical UK upland reservoir water using three different coagulants (aluminium sulphate/alum ($Al_2(SO_4)_{3(aq)}$), polyaluminium chloride/PAX-18 ($Al_n(OH)_mCl_{3n-m(aq)}$) and ferric sulphate/PIX-322 ($Fe_2(SO_4)_{3(aq)}$). A comparison of DOC quality including fractional character, colour, specific UV absorbance (SUVA) and molecular weight (MW) was made between the source water and the supernatants obtained following its coagulation in each case. Trihalomethane formation potential (THMFP) was compared before and after treatment in order to assess which coagulant performed best in terms of THM amelioration. The conditions (coagulant dose and pH) required to obtain optimal DOC removal in this high DOC, low alkalinity upland drinking water source were established using bench-scale jar tests. Statistically significant differences in DOC removal rates between the different coagulants were observed. The effective THMFP removal achieved was due to a combination of high net DOC removal and the preferential removal of THM precursors. This selectivity may also be responsible for the increase in brominated THM species (BrTHMs) observed following treatment. Interestingly the standardised THMFP (STHMFP) of the DOC was found to increase substantially following fractionation and the hydrophilic neutral (HPIN) fraction was found to produce a significantly higher proportion of BrTHMs, compared with the other fractions.

7.2. Introduction

Natural organic matter (NOM) is present in all natural surface and ground waters. It occurs in dissolved, colloidal or particulate form and is derived from the degradation of biological material including soil humus, plants and plankton (Leenheer & Croue, 2003; Berthe, *et al*. 2008). Although not currently regulated as a water quality parameter, NOM can compromise the taste, colour and odour to potable water and stimulate bacterial growth within water distribution systems (Matilainen, *et al*. 2010). Furthermore dissolved organic carbon (DOC) (operationally defined as organic matter which passes through a 0.45 μm filter) (Thurman, 1985; Kitis, *et al*. 2001) can act as a precursor to potentially harmful disinfection by-products (DBPs) including trihalomethanes (THMs), formed during chlorination (Rook, 1974; Symons, *et al*. 1975). Several toxicological studies have reported links between exposure to THMs and various adverse health effects such as bladder, colon and rectal cancer (Brenniman, 1980; Cragle, 1985; Attias, *et al*. 1995; Infante-Rivard, *et al*. 2001) and even fetotoxicity and miscarrige for high exposure levels in rodents (Theiss, *et al*. 1977; WHO, 2005). In this context the World Health Organization (WHO) has published guideline maximum drinking water concentrations of 300 μg L^{-1} for $CHCl_3$, 100 μg L^{-1} for $CHBr_3$ and $CHBr_2Cl$ and 60 μg L^{-1} for

$CHBrCl_2$ (WHO, 2011). In the UK the Water Supply (Water Quality) Regulations, (2010) stipulate a stricter limit of 100 µg L^{-1} total THMs for water samples taken from consumers' taps (DWI, 2010).

Removal of DOC prior to disinfection is considered to be the most effective means of minimising THM formation although alternative strategies such as DBP removal following chlorination (Kim & Kang, 2008) or alternative disinfection methods, such as chloramination do exist (Goslan, *et al*. 2009). DOC removal is typically achieved by coagulation using iron or aluminium salts (O'Melia, *et al*. 1999). However a trend of increased DOC concentrations in water draining upland catchments in Northern and Western Europe and North America has been widely reported in recent decades (Freeman, *et al*. 2001; Hejzlar, *et al*. 2003; Stoddard, *et al*. 2003; Worrall, *et al*. 2003; Monteith, *et al*. 2007). The trend has been attributed to various factors including climate change (Forsberg, 1992; Freeman, *et al*. 2004; Worrall, *et al*. 2004; Evans, *et al*. 2005), recovery from acidification (Monteith, *et al*. 2007; Evans, *et al*. 2012) and changes in land use (Wallage, *et al*. 2006). One approach to this deterioration in raw water quality is to dose larger quantities of coagulant, however, this produces more waste and increases costs (Keeley, *et al*. 2012).

The removal of DOC at most potable water treatment works (WTW) comprises a number of stages. Firstly, in the coagulation stage, the coagulant is thoroughly dispersed in the water during rapid mixing. pH correction, if required, also occurs during the rapid mixing phase. This is followed by the flocculation stage; a period of slow stirring during which pin-flocs aggregate into macro-flocs. Removal of the floc is typically achieved by means of settling tanks or dissolved air floatation (DAF) and followed by filtration, most commonly using rapid gravity sand filters. Traditionally coagulation-flocculation is designed to attain target levels of colour and turbidity (Iriarte-Velasco, *et al*. 2007). However removal of colour/turbidity does not necessarily correlate with optimal DOC removal (Yan, *et al*. 2008a). Enhanced coagulation refers to optimised organic carbon removal beyond what would be expected if coagulation was applied solely for colour/turbidity removal (White, *et al*. 1997; Boyer & Singer, 2005). This technique has been recognised as the best available technology (BAT) for minimising THM and other DBP formation in chlorinated drinking water (US EPA, 1999).

A number of factors have been found to affect the efficiency of DOC removal by coagulation including DOC characteristics such as the relative proportions of hydrophobic/hydrophilic species (Sharp, *et al*. 2006a; Matilainen, *et al*. 2010), raw water characteristics including alkalinity and pH (Yan, *et al*. 2008b), coagulation temperature, pH, coagulant type and dose (Uyak & Toroz, 2007) and concentration of electrolyte species in solution (Runkana, *et al*. 2006). Coagulation pH is a particularly important parameter; not only does pH affect the relative proportions of hydrolysed products but it is also an important determinant of surface charge on the DOC (Letterman &

Vanderbrook, 1983). Jar testing is the industry standard method for establishing optimum coagulation conditions (pH, coagulant dose and sequence of chemical addition) to achieve the desired quality of treated water. It is necessary to establish these conditions experimentally, and on a regular basis since the quality of raw water entering many WTWs is highly variable.

The aim of this study is to compare DOC concentration and characteristics between a typical upland reservoir water and the supernatants obtained following coagulation using three commercial coagulants, (aluminium sulphate/alum ($Al_2(SO_4)_{3(aq)}$), polyaluminium chloride/PAX-18 ($Al_n(OH)_mCl_{3n-m(aq)}$) and ferric sulphate/PIX 322 ($Fe_2(SO_4)_{3(aq)}$), each widely-used in the potable water treatment industry. Bench-scale jar testing experiments were carried out in order to establish optimum conditions (coagulant dose and pH) for DOC removal using each of the three coagulants. These optimised data are also presented. SUVA, colour and molecular weight (MW) measurements were used to compare DOC character between samples. A positive relationship has been identified between SUVA and DOC hydrophobicity and MW (Edzwald & Tobiason, 1999) and between SUVA and DOC % aromaticity (Weishaar, *et al*. 2003). DOC was partitioned using XAD-fractionation to investigate potential selectivity in the removal of DOC during coagulation. Zeta-potential measurements were used to evaluate the extent of charge neutralisation. Since THM amelioration is a key objective in the coagulation process, this study also compares THMFP and THM speciation between the coagulated and raw water samples. These parameters were also compared between DOC fractions obtained following XAD-fractionation in order to investigate potential differences in reactivity relating to character.

7.3. Methods

7.3.1. Works description

The water used in was study is taken from the raw water inlet of a potable WTW in an upland area of the UK. Raw water for the works is abstracted from a reservoir whose catchment includes an extensive area of woodland plantation (30%) consisting mainly of coniferous species. The remainder of the catchment is described as grassland (38%) and peatland (32%) (Cohen, 2009). Existing treatment consists of coagulation ($Al_2(SO_4)_3$) and flocculation followed by dissolved air floatation (DAF) for clarification, primary filtration using rapid gravity sand filters (RGF), secondary RGF for manganese removal and finally chlorine dosing for disinfection. Average works output is 38-40 ML d^{-1}. During the study period raw water colour ranged from 75 to 80 Hazen, pH values ranged from 6.0 to 6.2, UV absorbance at $\lambda = 254$ nm ranged from 0.560 to 0.570 UV a.u. and typical alkalinity was 3 mg L^{-1} as $CaCO_3$. At the time of testing, raw water DOC concentration was 9.3 mg L^{-1}.

7.3.2. Reagents

The experimental design included three coagulants: aluminium sulphate/alum ($Al_2(SO_4)_{3(aq)}$), polyaluminium chloride/PAX-18 ($Al_n(OH)_mCl_{3n-m(aq)}$) and ferric sulphate/PIX-322 ($Fe_2(SO_4)_{3(aq)}$), all supplied by Kemira. Working solutions of 8.4 g L^{-1} (as Al) for alum, 0.9 g L^{-1} (as Al) for PAX-18 and 1.18 g L^{-1} (as Fe) for PIX-322 were made. These were freshly prepared before each set of jar tests in order to minimise hydrolysis prior to dosing.

7.3.3. Jar test procedure

A Stuart SW6 variable speed, programmable, six paddle flocculator was used for jar testing. 5 x 1 L aliquots of raw water were measured into 1 L beakers and placed on the flocculator. The water was dosed with lime (100% $Ca(OH)_2$) for pH adjustment followed by the coagulant while stirring at 240 RPM. pH was measured using a Mettler Toledo portable pH/conductivity meter calibrated daily with pH 4, 7 and 10 buffer solutions (Reagecon). The volume of lime required for pH adjustment had been pre-determined experimentally. Samples were then mixed at 240 RPM for 1 min after addition of the coagulant followed by 19 min at 20 RPM. Floc size at 5 and 20 min was measured by eye and recorded. The stirring paddles were removed and the floc allowed to settle for 30 min. Treated water samples were then filtered through a Whatman No 1 filter paper (11 µm pore size) to simulate the clarification stage at the WTW. These samples were analysed for colour (Hazen) using a Cecil 2020 spectrophotometer set to detect at 400 nm and residual coagulant (mg L^{-1} as total Al/Fe). Both residuals were measured using a standard Palintest® colorimetric test and a Palintest® 7100 automatic wavelength selection photometer. Eriochrome cyanide R indicator was used for the Al test and PPST in combination with a decomplexing/reducing agent was used for the Fe test. Samples were then filtered through a 0.45 µm Nylon membrane (Whatman) before off-site analyses which included determination of DOC concentration with a Thermalox TOC/TN analyser equipped with a non-dispersive infrared CO_2 detector, UV absorbance measurements using a Molecular Devices SpecraMax M2e multi-detection reader (spectrophotometer) and high pressure size exclusion chromatography (HPSEC) using a Varian PL-GPC-50 DataStream unit set to detect at a wavelength of 254 nm. The HPSEC unit was interfaced to Cirrus software and equipped with a Bio Sep 2000 column. Calibration standards consisted of sodium polystyrene sulfonate polymers with MWs of 150,000, 77,000, 32,000, 13,000 and 4,300 Da (Fluka) and cyanocobalamin (1,340 Da). For the mobile phase Milli Q water was buffered with phosphate (0.002 M KH_2PO_4 + 0.002 M $K_2PO_4.3H_2O$) to pH 6.8. XAD-fractionation and THMFP tests were also conducted.

For each coagulant under investigation, a series of sets of jar tests were conducted in order to determine the optimum coagulant dose and coagulation pH for DOC removal, as described below. A range of coagulant doses were tested initially, with pH maintained at a constant level. pH was then varied over subsequent tests by adjusting the $Ca(OH)_2$ dose in order to determine optimum pH at that coagulant dose. A final set of replicate tests were conducted using the optimum conditions (pH and coagulant dose) in order to test the repeatability of the procedure and to obtain sufficient quantities of supernatant to perform XAD-fractionation and THMFP tests. On-site analysis of supernatant colour provided an indication of degree of DOC removal but direct DOC measurements of clarified samples were used to confirm this. Where colour removal under different conditions was similar, turbidity and residual coagulant content of the clarified sample were used to decide the optimum. Satisfactory clarification was considered to have been achieved with colour measurements of < 5 Hazen. Zeta potential was measured on the supernatants derived from each optimised test. These measurements were supplied by Cranfield University with analysis conducted using a Malvern Zetasizer 2000HSA.

7.3.4. XAD-fractionation

Fractionation of DOC was achieved by resin adsorption using a method adapted from Thurman & Malcolm, (1981) and Marhaba, *et al.* (2003). Samples were separated into five fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophobic neutral (HPIN) according to their adsorption onto a series of macroporous resin adsorbents (Superlite™ DAX-8™ resin and Amberlite™ XAD-4™ resin, both Supelco).

7.3.5. Trihalomethane formation potential

THMFP analyses were conducted on composite samples, made by combining equal volumes from five replicates. $THMFP_{7d}$ denotes the quantity of THMs formed ($\mu g\ L^{-1}$) following chlorination of a water sample after a 7 d incubation period at 25 °C. The method used was adapted from the Standing Committee of Analysts, (1981) procedure. In this study samples were diluted to 1 mg L^{-1} DOC in order to derive a standardised $THMFP_{7d}$ ($STHMFP_{7d}$) value which provides a measure of DOC reactivity. A $THMFP_{7d}$ value was then calculated by multiplying $STHMFP_{7d}$ by DOC concentration. For the chlorination procedure, 97.5 mL of diluted sample was dosed with 2.0 mL of 0.5M $KH_2PO_{4(aq)}$ to buffer the solution to pH 6.8. Samples were then dosed with 0.5 mL of $NaOCl_{(aq)}$ to provide 5 mg of free Cl per mg of DOC. After 7 d incubation in the dark at 25 °C, the reaction was quenched using 0.4 mL of 0.8M $Na_2SO_{3(aq)}$. Extraction of the four chlorinated and brominated THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) was achieved using direct immersion SPME followed by quantification using a Varian 450 GC coupled with an electron capture detector. In addition to the standard 7 d THMFP analysis, THM concentrations were also measured at 1 h, 1 d and 3 d in order to profile the formation of THMs over time. In addition to analyses of raw and coagulated samples, THMFP was also determined for the isolated XAD fractions.

7.3.6. Statistical analysis

Depending on the conditions satisfied by the data, Analysis of Variance (ANOVA) and Kruskal-Wallis tests were performed to identify statistically significant differences in water quality parameters between raw water and coagulated samples using alum, PAX-18 and PIX-322 coagulants. Statistical analyses were also conducted to compare characteristics of HPOA, HPIA and HPIN fractions across all sample types. The HPOB and HPIB fractions were not included in these analyses since their contribution to total DOC was negligible. Significant results for ANOVA were further investigated using the Tukey HSD post-hoc test. Post-hoc analysis for Kruskal-Wallis was the rank-based test described by Siegel & Castellan, (1988). Here the Monte Carlo significance value was used due to small sample sizes. Arcsine transformations were carried out on percentage data before statistical analyses were undertaken. Statistical analysis was carried out using version 18 of the SPSS Statistics package (PASW).

7.4. Results

7.4.1. Optimum coagulation conditions

Optimum coagulant dose (4.2 and 4.5 mg L^{-1} as Al) and coagulation pH (6.0 and 6.1) were similar for the two aluminium-based coagulants, alum and PAX-18 (Table 7.01). Mean residual coagulant concentration was also similar (26 and 20 µg L^{-1} as Al, respectively). However the lime dose required to achieve the target pH varied more substantially with 12.3 and 7.8 mg L^{-1} of 100% $Ca(OH)_2$ required for alum and PAX-18 pH correction, respectively. Both coagulants produced a 1.50-2.25 mm diameter floc after 20 min. By contrast coagulation using PIX-322, a ferric-based coagulant, required a dose of 9.4 mg L^{-1} as Fe and more acidic conditions (mean pH 4.6) to achieve optimum DOC removal. This required a relatively high lime dose (12.5 mg L^{-1} of 100% $Ca(OH)_2$). The residual coagulant concentration observed was relatively higher than with the aluminium-based coagulants (108 µg L^{-1} as Fe) and floc size after 20 min was greater (2.25-3.00 mm diameter). Zeta potential values for supernatants treated under optimal conditions using the three coagulants were -10.9, -5.1 and -9.5 mV for alum, PAX-18 and PIX-322, respectively (Table 7.01).

Table 7.01. Optimum conditions (pH, coagulant dose and lime dose) and residual coagulant, floc size and zeta potential measurements under optimum conditions for DOC removal using alum, PAX-18 and PIX-322 coagulants.

	Optimum coagulant dose (mg L^{-1} / µmol L^{-1} as Al or Fe)	**Optimum coagulation pH**	**Lime dose (mg L^{-1} as 100% $Ca(OH)_2$**	**Residual coagulant (µg L^{-1} as Al/Fe)**	**Floc size after 20 min (mm)**	**Zeta-potential (mV)**
alum	4.2 / 156	6.0 ± 0.02	12.3	26 ± 4	1.50 – 2.25	-10.9
PAX-18	4.5 / 81	6.1 ± 0.02	7.8	20 ± 0	1.50 – 2.25	-5.1
PIX-322	9.4 / 168	4.6 ± 0.02	12.5	108 ± 6	2.25 – 3.00	-9.5

Where applicable results given as mean ± standard error (*n* = 5).

Mean DOC concentration in the raw water was 9.3 mg L^{-1}. Mean DOC concentration in samples treated with alum, PAX-18 and PIX-322 were 3.4 mg L^{-1}, 3.1 mg L^{-1} and 2.4 mg L^{-1}, respectively (Figure 7.01). These values correspond with % DOC removal levels of 63%, 67% and 74%, respectively (Table 7.02). One-way ANOVA showed that mean DOC concentration in the raw water and water treated with alum, PAX-18 and PIX-322 differed significantly, F (3,16) = 1386, $p = 0.000$. Post-hoc comparisons using the Tukey HSD test indicated that DOC concentration in the raw water samples was significantly higher than in the samples treated with each of the three coagulants ($p < 0.01$). In addition DOC concentration in samples treated with alum was significantly higher than in samples treated with PAX-18 ($p < 0.05$) and PIX-322 ($p < 0.01$) and samples treated with PAX-18 had significantly higher DOC concentrations than those treated with PIX-322 ($p < 0.01$).

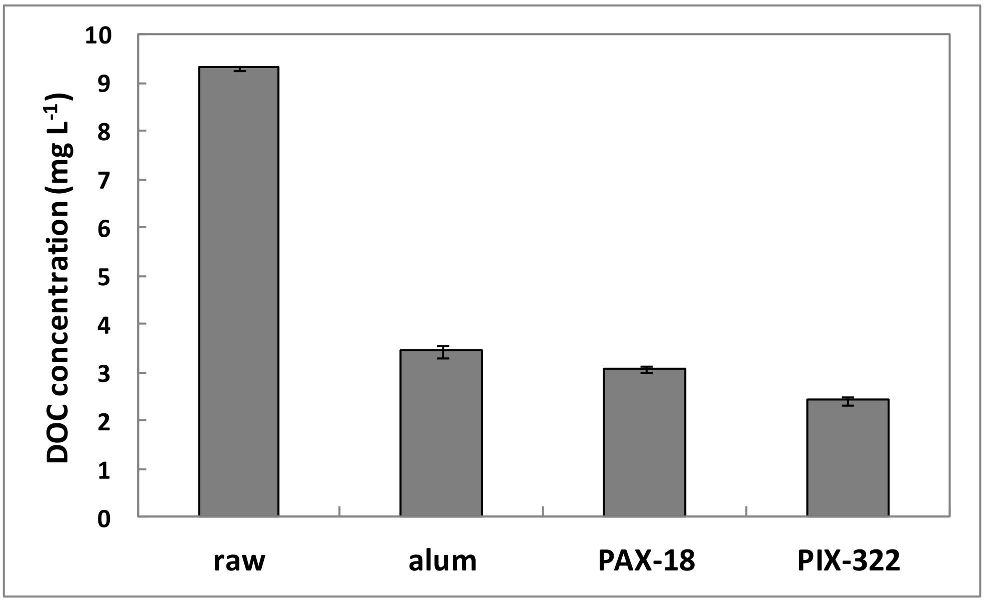

Figure 7.01. Mean DOC concentration (mg L^{-1}) for raw water and solutions derived from optimised jar tests using alum, PAX-18 and PIX-322 coagulants. Error bars represent the standard error (*n* = 5).

Mean SUVA value for the raw water was 4.1. Mean values of 2.9, 2.6 and 2.4 were calculated for samples treated with alum, PIX-18 and PAX-322 respectively (Figure 7.02), indicating a preferential removal of high aromaticity, high MW (HMW) DOC during coagulation. Differences in SUVA values in the raw water and treated samples were investigated using a Kruskal-Wallis analysis. The result revealed a significant difference between groups, *H* (3) = 15, $p = 0.000$. A rank-based post hoc test indicated that raw water SUVA was significantly higher than in samples treated with PAX-18 ($p < 0.05$) and PIX-322 ($p < 0.01$). All other comparisons were not significant.

Table 7.02. Water quality data for raw and coagulated samples (alum, PAX-18 and PIX-322).

	raw	**alum**	**PAX-18**	**PIX-322**
DOC concentration (mg L^{-1})	9.3 ± 0.1	3.4 ± 0.1	3.1 ± 0.1	2.4 ± 0.1
% DOC removal	N/A	63 ± 1	67 ± 1	74 ± 1
SUVA (L mg^{-1} m^{-1})	4.1 ± 0.03	2.9 ± 0.10	2.6 ± 0.05	2.4 ± 0.09
Colour (Abs$_{400}$) (UV a.u.)	0.037 ± 0.0003	0.002 ± 0.0006	0.001 ± 0.0007	-0.001 ± 0.0011
STHMFP$_{7d}$ (µg THM mg DOC^{-1})	86.6 ± 0.4	44.1 ± 1.4	40.9 ± 1.3	50.1 ± 1.5
THMFP$_{7d}$ (µg L^{-1})	806.6 ± 9.1	152.0 ± 10.4	125.4 ± 8.6	120.8 ± 8.2
% decrease STHMFP$_{7d}$ from raw	N/A	49.1 ± 1.9	52.8 ± 1.7	42.2 ± 2.0
% decrease THMFP$_{7d}$ from raw	N/A	81.2 ± 1.5	84.5 ± 1.2	85.0 ± 1.2
M$_p$ (Da)	5760	4824	4711	4824
M$_n$ (Da)	494	277	335	304
M$_w$ (Da)	3658	2960	2770	2709

Where applicable results given as mean ± standard error ($n = 5$), except for THM results where measurements were conducted on composite samples and the standard error derived from detection repeatability experiments.

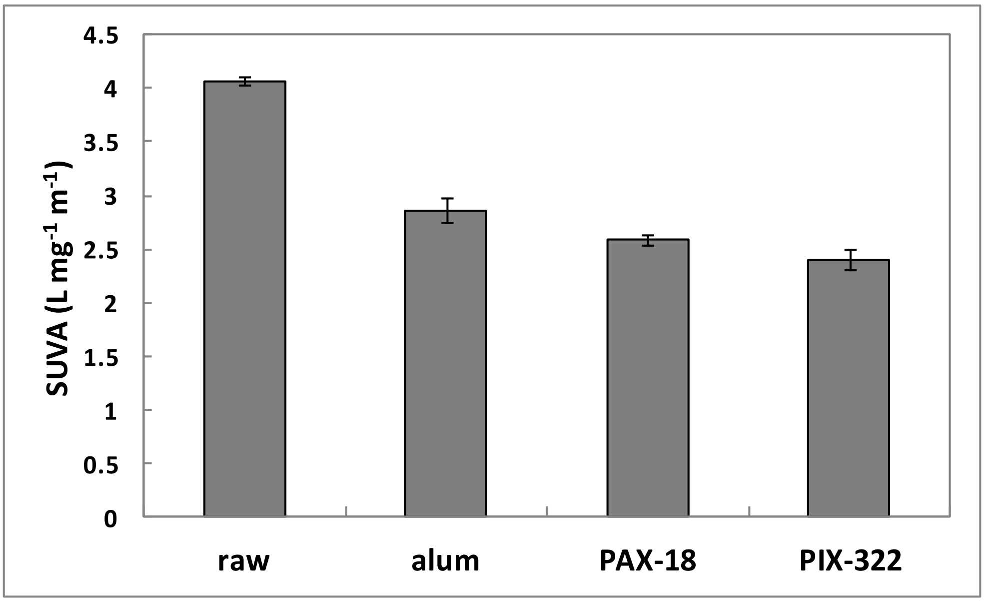

Figure 7.02. Mean SUVA values for raw water and solutions derived from optimised jar tests using alum, PAX-18 and PIX-322 coagulants. Error bars represent the standard error ($n = 5$).

A dramatic decrease in colour, indicated by absorbance at λ = 400 nm was observed following coagulation using all three coagulants (Figure 7.03). Mean raw water absorbance was 0.037 UV a.u. and mean absorbance in the coagulated samples was < 10% of this in each case (Table 7.02). One-way ANOVA revealed that mean colour in the raw water and water treated with alum, PAX-18 and PIX-322 differed significantly, $F(3,16) = 594$, $p = 0.000$. Post-hoc comparisons using the Tukey HSD test confirmed that colour in the raw water samples was significantly higher than in the samples treated with each of the three coagulants ($p < 0.01$). However comparisons between the different treatments were not found to be significant.

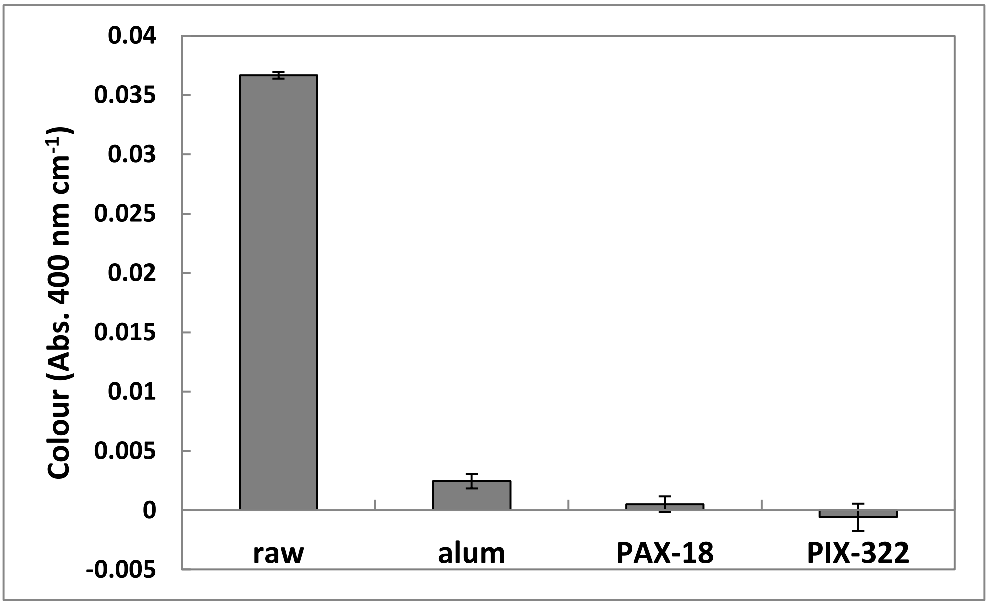

Figure 7.03. Mean absorbance values at a wavelength of 400 nm (used as a proxy for colour) for raw water and solutions derived from optimised jar tests using alum, PAX-18 and PIX-322 coagulants. Error bars represent the standard error (*n* = 5).

THMFP was determined on composite samples of raw water and water treated with alum, PAX-18 and PIX-322 coagulants, hence the samples cannot be compared statistically. However, $STHMFP_{7d}$ for the raw water (86.6 μg L^{-1}) was substantially higher than for the coagulated samples: 44.1 μg L^{-1}, 40.9 μg L^{-1} and 50.1 μg L^{-1} for alum, PAX-18 and PIX-322, respectively (Figure 7.04a). These values correspond with a 49.1%, 52.8% and 42.2% decrease in $STHMFP_{7d}$, respectively. This indicates a preferential removal of THM precursors during coagulation. Differences between the raw water and coagulated samples were even more pronounced with regard to $THMFP_{7d}$ which takes DOC concentration into account (Figure 7.04b). The $THMFP_{7d}$ for the raw water sample was 806.6 μg L^{-1} compared with 152.0 μg L^{-1}, 125.4 μg L^{-1} and 120.8 μg L^{-1} for samples treated with alum, PAX-18 and PIX-322, respectively. This corresponds to an 81.2%, 84.5% and 85.0% decrease in $THMFP_{7d}$, respectively. Though the $STHMFP_{7d}$ of the PIX-322 sample was highest (50.1 μg L^{-1}) among the coagulated waters, as a result of its comparatively low DOC concentration, its $THMFP_{7d}$ was the lowest.

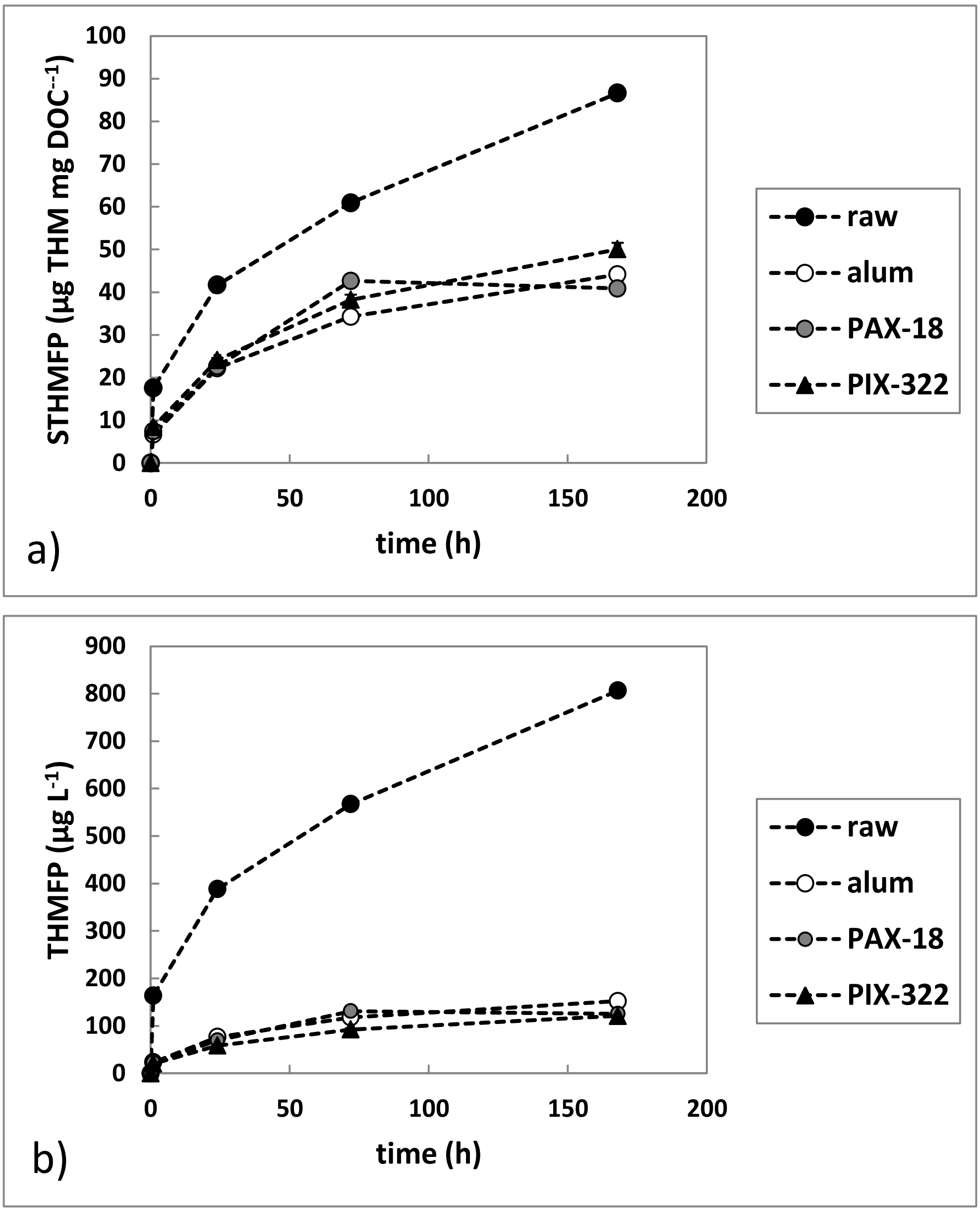

Figure 7.04. Profile of STHMFP (a) and THMFP (b) over a 7 d incubation period following chlorination of raw water and solutions derived from optimised jar tests using alum, PAX-18 and PIX-322 coagulants. Measurements were conducted on composite samples, made by combining equal volumes of the five replicates. Error bars represent the standard error and were derived from a detection repeatability experiment.

Comparing the speciation of THMs, the proportion of brominated THMs (BrTHMs) increased following coagulation from 3% in the raw water to 9%, 10% and 12% in the alum, PAX-18 and PIX-322 samples, respectively (Figure 7.05). Since $CHBr_2Cl$ and $CHBr_3$ measurements were consistently below the limit of quantification (LOQ) (1.74 and 1.09 µg L^{-1}, respectively), this increase was the result of an increase in the proportion of $CHBrCl_2$.

HPSEC analysis for the raw water and treated samples (Table 7.02) showed that peak MW (M_p) was highest in the raw water (5760 Da) and M_p values for the coagulated samples were lower and comparable to each other with 4824 Da, 4711 Da and 4824 Da for alum, PAX-18 and PIX-322, respectively. This was also the case for the number and weight-averaged MWs (M_n and M_w).

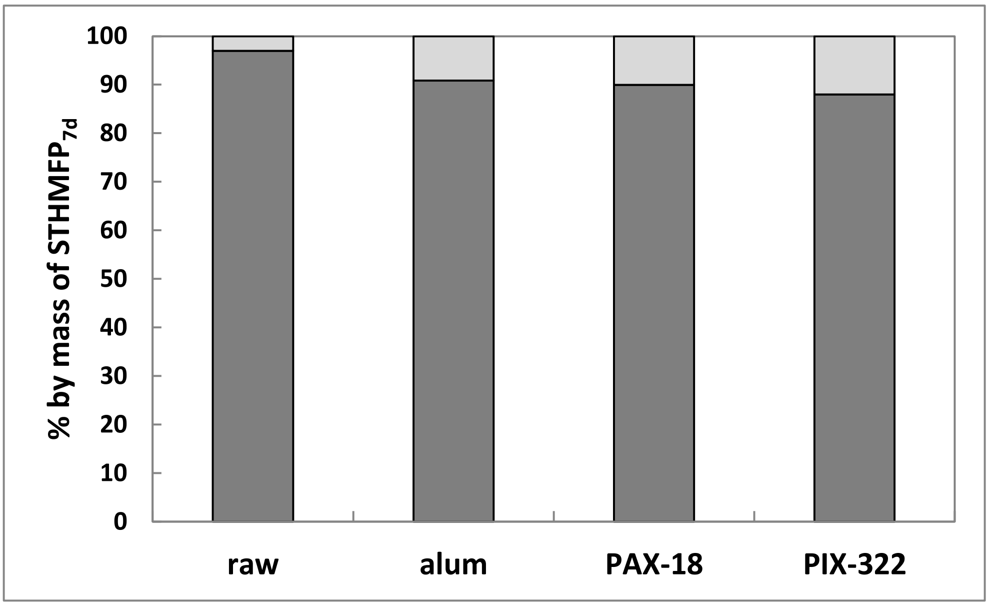

Figure 7.05. % contribution of THM species to STHMFP ($CHCl_3$: dark grey, BrTHMs: light grey) for raw water and solutions derived from optimised jar tests using alum, PAX-18 and PIX-322 coagulants.

7.4.2. XAD-fractionation

The % contribution of individual fractions (HPOA, HPIA and HPIN) to total recovered DOC concentration was compared between the raw water and the three treatments (alum, PAX-18 and PIX-322) (Figure 7.06). Kruskal-Wallis analysis showed that the % contribution of the HOPA fraction did vary significantly between the samples, H (3) = 8.2, $p = 0.014$. Rank based post-hoc analysis showed that the % of HPOA in the sample treated with alum (mean: 33.5%) was significantly lower than the % of HPOA in the raw water (mean: 49.7%) ($p < 0.05$). Comparisons between other groups were not significant. This analysis was also conducted to investigate variations in the % contribution of the HPIA fraction but revealed a non-significant result. A non-significant result was also obtained when comparing the contribution of the HPIN fraction between these samples.

A Kruskal-Wallis analysis indicated that STHMFP$_{7d}$ did not vary as a function of DOC fraction (HPOA, HPIA and HPIN). Interestingly however, when individual fractions were chlorinated to measure STHMFP$_{7d}$, it was found that the weighted sum of these values for the three prominent fractions (HPOA, HPIA, and HPIN) was consistently higher than the values of the original samples (pre-fractionation). This was the case for all four samples (raw, alum, PAX-18 and PIX-322) (Figure 7.07).

The amalgamated $STHMFP_{7d}$ values were between 41% and 106% higher than the original $STHMFP_{7d}$ values.

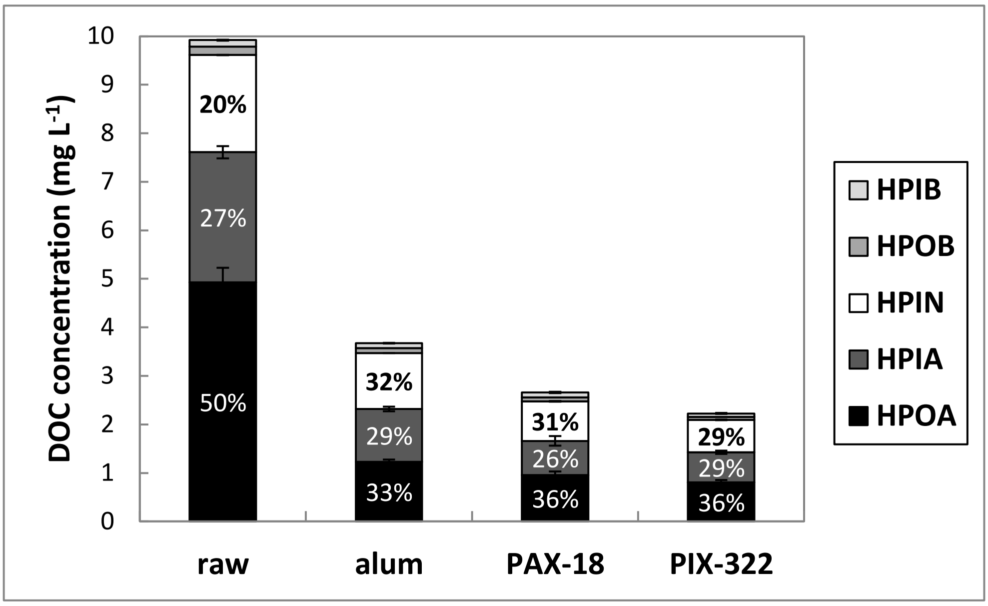

Figure 7.06. % contribution of HPOA, HPIA, HPIN, HPOB and HPIB fractions to the total recovered DOC following fractionation for raw water and supernatants from optimised jar tests using alum, PAX-18 and PIX-322 coagulants. Error bars represent the standard error (*n* = 3).

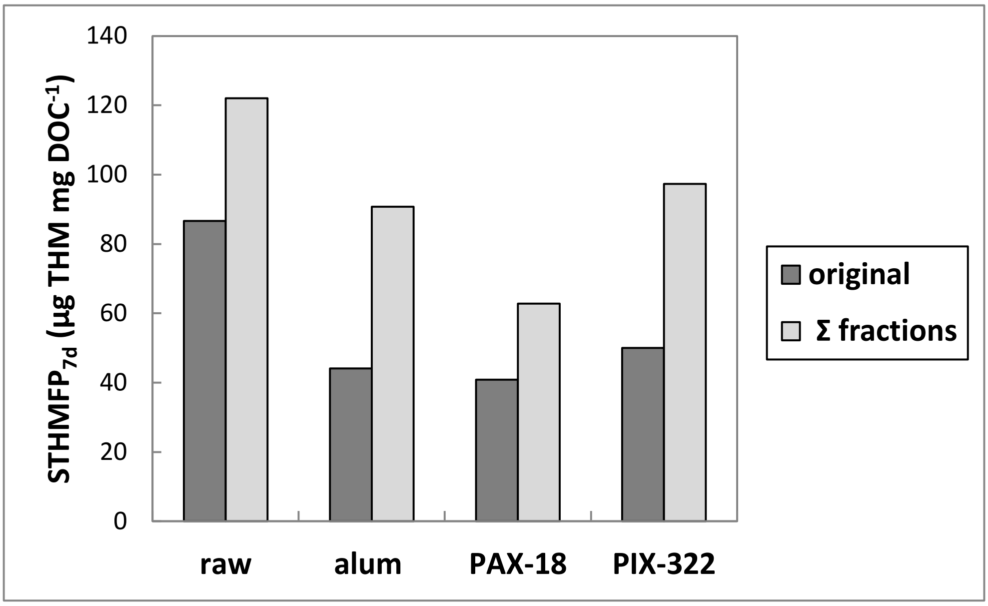

Figure 7.07. $STHMFP_{7d}$ for original, unfractionated sample and sum total $STHMFP_{7d}$ for associated fractions for raw and coagulated samples.

The contribution of the four main THM species to $STHMFP_{7d}$ in the different DOC fractions was also investigated. $CHBr_2Cl$ and $CHBr_3$ measurements were consistently below LOQ. Mean % contribution of $CHBrCl_2$ to the HPOA and HPIA fractions was < 1%. In the HPIN fraction however, the $CHBrCl_2$ species represented 17.1% of $STHMFP_{7d}$ (Figure 7.08). This relationship was tested using a Kruskal-

Wallis analysis, *H* (2) = 28.5, $p = 0.000$. Rank-based post hoc comparison indicated that the % contribution of $CHBrCl_2$ to $STHMFP_{7d}$ was significantly higher in the HPIN fraction when compared with both the HPOA and HPIA fraction ($p < 0.01$), but that the HPOA/HPIA comparison was not significant.

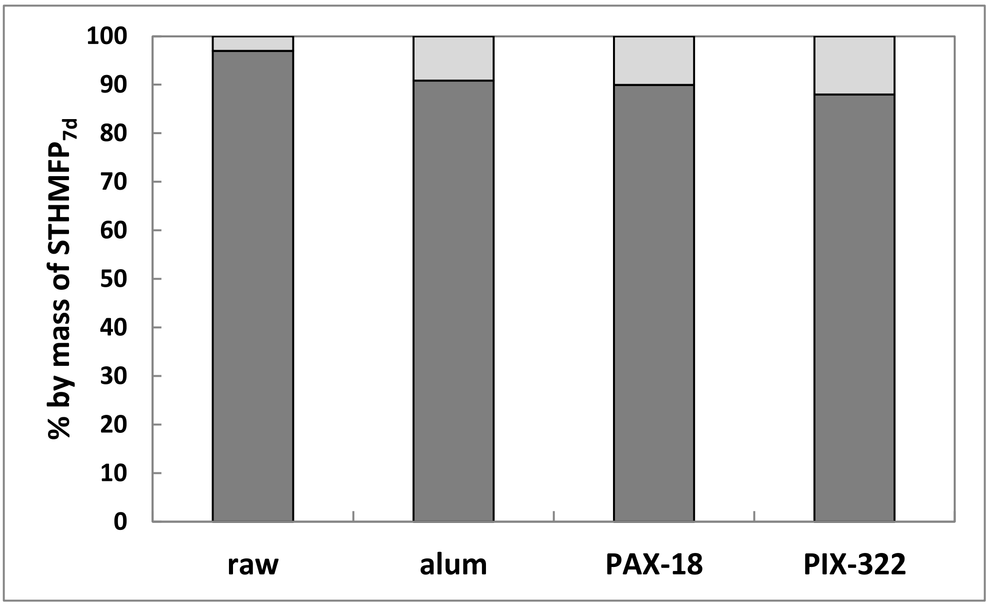

Figure 7.08. % contribution of THM species to $STHMFP_{7d}$ for HPOA, HPIA and HPIN fractions ($CHCl_3$: dark grey, BrTHMs: light grey) (the results from the raw water and supernatants from optimised jar tests using alum, PAX-18 and PIX-322 coagulants are combined in this figure). All $CHBr_2Cl$ and $CHBr_3$ measurements were below LOQ. Error bars represent the standard error ($n = 12$).

7.5. Discussion

NOM is kept in suspension (i.e. stabilized) due to electrostatic repulsion between neighbouring anionic particles which inhibits their collision under the influence of Brownian motion and van der Waals forces. NOM molecules tend to acquire a negative surface charge due to the ionisation of carboxyl groups on their surface (Duan & Gregory, 2003). Successful coagulation depends on overcoming the electrostatic repulsion between particles in order to destabilize the colloidal system and enable the agglomeration of NOM necessary to ensure its subsequent removal by physical processes. In the presence of water, aqueous Al(III) and Fe(III) salts rapidly dissolve yielding their respective trivalent ions, Al^{3+} and Fe^{3+}. These metal cations are readily hydrolysed in water when the pH is raised above a certain threshold, producing various hydroxide species (Bratby, 2006). Thus as pH is increased successive deprotonation of the hydrolysed species take place and the relative concentrations of the hydrolysed products change; the dominant species changes from left to right ($M^{3+} \rightarrow M(OH)^{2+} \rightarrow M(OH)_2^{+} \rightarrow M(OH)_3 \rightarrow M(OH)_4^{-}$) (Matilainen, *et al*. 2010; Duan & Gregory, 2003). Polymeric hydroxide products are also formed where the solubility limit is overcome leading to extensive and rapid hydroxide precipitation. This may bring about coagulation by bridging or sweep flocculation – effectively a form of co-precipitation where the NOM is trapped in an inorganic matrix. These mechanisms are reported to be most successful in the removal of particulate matter (Matilainen, *et al*. 2010).

Successful removal of DOC by hydrolysing metal coagulants is thought to involve mainly monomers or medium polymers and charge neutralisation mechanisms believed to be more important where conditions have been optimised for maximum DOC removal (Yan, *et al*. 2008a). However zeta potential at optimal coagulation conditions are reported to deviate from zero suggesting that other mechanisms such as complexation, adsorption and co-precipitation may also occur. Indeed, zeta potential values ranging from -10 to +3 mV have been cited for different source waters optimised for DOC removal (Sharp, *et al*. 2006b). The values obtained in this study for the three different coagulants (-10.9, -5.1 and -9.5 mV for alum, PAX-18 and PIX-322, respectively) are therefore comparable to those of previously reported.

The optimum coagulation pH recorded in the present study, which show more acidic conditions for the ferric-based coagulant (4.6 for PIX-322, compared with 6.0 and 6.1 for alum and PAX-18, respectively), are consistent with data reported previously (Matilainen, *et al*. 2010). This is due to the lower pH at which the preferred hydrolysed products of the coagulant are formed ($Fe(OH)_2^+$). Ferric-based coagulants are also effective over a wider pH range than aluminium-based coagulants which is advantageous in a water treatment context where coagulation conditions can be controlled less precisely than in the laboratory.

The coagulant doses established for optimum DOC removal in this study correspond to 100, 50 and 80 mg L^{-1} as neat product for alum, PAX-18 and PIX-322 respectively. The associated lime doses required for pH correction are 12.3, 7.8 and 12.5 mg L^{-1} of 100% $Ca(OH)_2$. Based solely of coagulant cost (£189, £207 and £162 per tonne of alum, PAX-18 and PIX-322, respectively), a cost saving of 45% was calculated for the replacement of alum with PAX-18, and a saving of 31% calculated for the replacement of alum with PIX-322. It should be noted however that the higher DOC removal rates associated with PAX-18 and PIX-322 will also increase sludge production and the costs associated with its de-watering and disposal. Lime dose also affects the sustainability of the coagulation process as high doses can lead to deposition within the WTW or distribution system, necessitating costly remediation. On this basis, PAX-18, which required the lowest lime dose represents the most cost-effective option for this system.

The large number of variables affecting coagulation, not least variability in raw water and DOC characteristics, mean that reported DOC removal rates tend to differ considerably. Under conditions optimised for DOC removal, Qin, *et al*. (2006) reported a removal rate of 45% at pH 5.2 using alum from a Singapore reservoir water containing 3.27-7.45 mg L^{-1} DOC. Uyak & Toroz, (2007) reported DOC removal rates of 66, 71 and 43% at pH 5.25 for three different Istanbul reservoir waters using $FeCl_3$, and 52, 67 and 34% at pH 5.25-5.50 using alum on the same three source waters. They attributed the higher removal levels observed for one water source to its higher alkalinity and DOC concentration (135 mg L^{-1} as $CaCO_3$ and 4.22 mg L^{-1}, respectively). Chow, *et al*. (2009) cited DOC removal levels of > 50% at pH 5-6 using alum for water from four reservoirs in south-eastern Australia, when optimised for DOC removal. These waters contained between 5.0 and 10.8 mg L^{-1} DOC and alkalinity between 7 and 100 mg L^{-1} as $CaCO_3$. In the present study DOC removal levels of 63, 67 and 74% were observed for alum, PAX-18 and PIX-322, respectively for this low alkalinity (3 mg L^{-1} as $CaCO_3$), high DOC (9.3 mg L^{-1}) water (Table 7.02). In the context of existing studies, these removal levels are fairly high, particularly for the ferric-based coagulant, PIX-322. These data therefore suggest that high removal rates can be achieved under optimised conditions for low alkalinity water. According to the statistical analysis carried out on mean DOC concentrations in coagulated samples, these removal rates are significantly different. Previous studies have reported improved DOC removal rates when ferric-based salts are used as opposed to aluminium-based salts (Edwards, 1997; Uyak & Toroz, 2005). This is thought to be due to the higher affinity for carboxylic groups associated with ferric ion (Sharp, *et al*. 2006c). Furthermore, the flocs formed during ferric-based coagulation are reported to be more numerous and larger (Ratnaweera, *et al*. 1999) as was observed in the present study, thus aiding their removal during clarification. The higher coagulation pH associated with the aluminium-based coagulants may also lead to lower-density, and hence less stable flocs. This has been explained by enhanced deprotonation of DOC molecules at higher pH values resulting in increased electrostatic repulsion within the floc (Slavik, *et al*. 2012) and may lead to the return of DOC into solution. Typical DOC removal rates observed at this WTW, where alum is currently being used as a coagulant, are 72-83%, i.e. higher than the DOC removal rates observed in these jar tests using alum. However, past experience at this site suggests that removal rates tend to improve significantly when conditions established during jar testing are up-scaled and applied at the WTW.

Previous studies have reported that DOC fractional character will affect the level of removal achieved by coagulation (Sharp, *et al*. 2006a; Chow, *et al*. 2009), with the hydrophilic, low MW (LMW) fraction less amenable to removal than the HMW hydrophobic acid fraction (Krasner & Amy, 1995; Edwards, 1997; White, *et al*. 1997). This has been attributed to the higher charge density associated with this fraction (Sharp, *et al*. 2006c). Similarly, in this study mean HPOA % was lower in the coagulated samples than the raw water suggesting there was a preferential removal of this fraction. However, the degree of selectivity was less pronounced than anticipated and only the alum/raw HPOA % comparison statistically significant. By contrast, Parsons, *et al*. (2004) for example report > 90% HPOA removal rate whilst the HPIN fraction was almost unchanged. In the present study, mean % contribution of the HPIA fraction to total recovered DOC was fairly stable across all samples, with no significant differences observed. The % contribution of the HPIN fraction however was approximately 10% higher in each of the coagulated samples compared to the raw water (Figure 7.06), although this was not found to be statistically significant. This may simply be an artefact of the preferential removal of the HPOA fraction during coagulation. It was also found that the coagulated samples had a lower SUVA value than the raw water, though only the PIX-18/raw and PAX-322/raw comparisons were found to be statistically significant. This outcome has been reported previously and is also thought to relate to the preferential removal of the highly aromatic, HMW HPOA DOC during coagulation (Volk, *et al*. 2000; Uyak & Toroz, 2007). This process also explains the statistically significant reduction in colour observed in all of the coagulated samples (Figure 7.03) since the HPOA fraction is reported to be associated with significantly higher colour than hydrophilic DOC (Oliver, *et al*. 1983; Thurman, 1985). The reduction in MW following coagulation, as indicated by the decrease in all three MW averages (M_p, M_n and M_w) (Table 7.02), is also consistent with a reduction in the proportion of HPOA in the coagulated water, since the hydrophobic acid DOC fraction constitutes higher MW molecules than the hydrophilic fraction (Edzwald & Tobiason, 1999).

One possible explanation for the lower HPOA removal efficiency observed here could be the very low levels of alkalinity in the raw water, a typical feature of upland water sources (Parsons, 2009). Wang, *et al.* (2009) found a positive relationship between alkalinity and humic acid removal efficiency by coagulation with aluminium salts as a result of the charge neutralising effect of the Ca^{2+} ion on the surface of humic acid molecules. OH^- species are also consumed rapidly during hydrolysing reactions (Yan, *et al*. 2008b), thus lowering the pH. Alkalinity is therefore required to buffer the solution and prevent the pH falling away from the optimum for coagulation. However, given the addition of $Ca(OH)_2$ during the jar test procedure, it is difficult to relate coagulation efficiency to raw water alkalinity. Instead, removal rates for different fractions may be related to the distinct characteristics of the DOC for this water source. The precipitation of DOC during coagulation occurs in a competitive environment. Hence if the HPIA and HPIN fractions in this water source are more amenable to removal than is normally the case, this will inhibit the removal of the HPOA fraction.

As stated previously, whilst coagulation does remove colour and taste from potable water, the major objective of DOC removal during treatment is to reduce THMFP by removing THM precursors. $THMFP_{7d}$ removal rates observed in this study were 81.2, 84.5 and 85.0% for alum, PAX-18 and PIX-322, respectively. Reported THMFP removal rates following coagulation vary widely. Iriarte-Velasco, *et al*. (2007) report 31-48% bulk removal of THMFP for a low DOC surface water under different alkalinity conditions using alum and polyaluminium chloride coagulants. Page, *et al*. (2002) report a 55% THMFP removal on average across a range of reservoir waters and DOC concentrations using alum. Similarly Uyak & Toroz, (2007) report an average 56% precursor removal under optimum conditions averaged over three surface water sources using ferric chloride and alum coagulants. The high THMFP removal shown in this study appear to be due to a combination of high bulk DOC removal levels and the selective removal of the HPOA fraction, which is generally thought to produce the highest THM yield upon chlorination (Chow, *et al*. 2005; Zhang, *et al*. 2009), though here, STHMFP was not found to vary significantly as a function of DOC fraction.

Comparison of the speciated THM results (Figure 7.05) shows that the proportion of BrTHMs increased following coagulation in all cases. This is significant because BrTHMs are reported to be more genotoxic than their chlorinated analogues (Richardson, *et al*. 2007). The increase in BrTHMs is likely to be caused by the preferential removal of aromatic DOC during treatment and the consequent increase in the proportion of aliphatic species which have been associated with the formation of higher proportions of BrTHMs (Heller-Grossman, *et al*. 1993; Teksoy, *et al*. 2008). Br^- occurs at trace levels in surface waters and laboratory grade chlorine contains *ca*. 1% Br_2 as a production impurity (Bond, *et al*. 2014). Interestingly, the proportion of BrTHMs also increased as DOC removal increased (alum < PAX-18 < PIX-322), most likely due to a successive increase in proportion of aliphatic DOC. Thus the enhanced removal of DOC during coagulation, whilst reducing THM precursors, may also shift their speciation towards more harmful BrTHMs.

Interestingly it was found that the reactivity of the DOC with chlorine increased following fractionation as indicated by an estimated 41-106% increase in $STHMFP_{7d}$ (Figure 7.07). This suggests that the fractionation of DOC using the resin adsorption technique described above increases the reactivity of the DOC with chlorine. It is possible that the extremes of pH used in the fractionation procedure may have hydrolysed some DOC functional groups such as esters, amides or ethers resulting in more reactive material. The potential for chemical change of DOC during fractionation has been reported previously (Gadmar, *et al*. 2005).

This study also shows that the relative proportions of different THM species formed when HPOA, HPIA and HPIN fractions are chlorinated differ significantly (Figure 7.08). The reaction of chlorine with DOC is a competitive process, thus when the HPIN fraction is chlorinated in isolation the reaction is not affected by competition from the active sites on other DOC molecules. It is possible that initial activation by chlorine makes functional groups on the HPIN DOC susceptible to bromination. In terms of its implications for the water treatment process, this result should however be treated with caution. Firstly this study has already shown that the chlorination reaction proceeds differently when DOC fractions are isolated from the original sample (Figure 7.07), which may simply be an artefact of the fractionation procedure. Secondly, when considering the chlorination of DOC, THMs represent only a fraction of total chlorinated products. Thus a fuller understanding of the nature of the reaction between chlorine and different DOC fractions would require the measurement of additional halogenated by-products.

7.6. Conclusions

This study has shown that relatively high DOC removal rates can be achieved in low alkalinity waters. Significant differences in DOC removal rates were observed under optimised coagulation conditions between alum, PAX-18 and PIX-322 coagulants (PIX-322 > PAX-18 > alum). The higher DOC removal rates for the ferric-based coagulant observed here have been reported elsewhere and are thought to be the result of the higher affinity of ferric ions for carboxylic groups in addition to their floc-forming characteristics. Though PIX-322 yielded the best results for DOC and THM precursor removal, due to its low required coagulant and lime dose, PAX-18 is likely to offer the most cost-effective solution.

Zeta-potential measurements were consistent with those reported in previous studies where optimal DOC removal was achieved. No statistically significant differences in the fractional character of the coagulated samples were found, though mean HPOA levels were lower in the coagulated samples compared with the raw water, consistent with previous studies. Colour, SUVA and MW results also indicate the selective removal of DOC with HMW and high hydrophobicity and aromaticity during coagulation. This selectivity, in combination with effective bulk DOC removal resulted in a substantial decrease in THMFP for all treatments. However, an increase in BrTHMs was also observed following coagulation, most likely due to the selective removal of aliphatic DOC. Furthermore, comparison of the different treatments suggests that BrTHMs may increase as DOC removal efficiency is improved; an important consideration given the evidence that BrTHMs are more harmful than their chlorinated analogues.

Interestingly this study has also shown that the STHMFP of DOC increases substantially following fractionation. This may be the result of the extremes of pH used during the fractionation procedure. In addition, a statistically significant difference in the proportion of $CHBrCl_2$ contributing to STHMFP was found between the HPOA, HPIA and HPIN fractions with means of < 1% calculated for the HPOA and HPIA fractions and 17% for the HPIN fraction. Broadening this comparison to include other halogenated by-products may provide insight into the cause of this phenomenon.

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Chapter 8: Synthesis and Conclusions

8.1. Introduction

The climatically driven increase in dissolved organic carbon (DOC) concentrations in surface waters draining upland catchments, and predicted changes in DOC concentration and character under future climate scenarios are a major concern for drinking water companies. To a large extent, this concern relates to the role of DOC as a reaction precursor to potentially harmful disinfection by-products (DBPs), most notably trihalomethanes (THMs) for which a maximum permissible level has been set by the Drinking Water Inspectorate (DWI, 2010). Although the mechanisms involved in the reaction between DOC and chlorine remain elusive, THM yield and speciation is known to vary according to DOC concentration and character (Oliver & Visser, 1980; Galapate, *et al*. 1999; Gang, *et al*. 2003; Chow, *et al*. 2005; Chow, *et al*. 2006). The removal of DOC prior to chlorination, typically by coagulation-flocculation, is the most effective means of controlling THM levels in treated water. However DOC removal efficiency (treatability) is also highly dependent on DOC character (Sharp, *et al*. 2006; Chow, *et al*. 2008). In this context, developing a better understanding of temporal and spatial variations in surface water DOC concentration and character, and the factors driving these variations is crucial. Such research will help drinking water companies target water quality monitoring and will inform future catchment management strategies. In the water treatment industry, where efficient DOC and THM precursor removal is becoming increasingly important, understanding the role of individual treatment processes in THM amelioration and the potential for optimising treatment processes is also a priority for current research. With these key research areas in mind, this chapter will summarise existing knowledge and describe the key findings of the present study and their relevance to the potable water treatment industry and public health. In addition, the limitations of the present study will be considered as well as important avenues for future research.

8.2. Spatial variations in DOC concentration and character

Previous research has identified various geographical controls on surface water DOC concentration at a variety of spatial scales including climate, geology, soil properties, habitat, topography and hydrological variables (Scott, *et al*. 1998; Andersson, *et al*. 2000; Blodau, *et al*. 2004; Worrall, *et al*. 2004; Soulsby, *et al*. 2006). Since the operations of drinking water companies tend to be restricted to locations chosen many decades previously, as relocating infrastructure can be financially and politically inhibitive, there is limited scope to affect many of these factors. However, where these factors relate to catchment management decisions, there is an opportunity to affect drinking water quality. Arguably, the most ubiquitous predictors of surface water DOC concentration are catchment peatland coverage and forest coverage (Hope, *et al*. 1994; Hope, *et al*. 1997; Gergel, *et al*. 1999;

Cohen, 2009). This is particularly relevant in North Wales where many drinking water catchments comprise peatland areas and extensive forestry plantations. In particular, recent research has considered the impact of peatland restoration *via* ditch blocking on DOC flux. In addition, the effect of tree species on DOC flux from forested catchments is an active area of research. In the following sections, our findings in these key research areas will be discussed in the context of potable water treatment and catchment management decisions.

8.2.1. Influence of tree species

The dominant tree species present in a catchment is reported to exert a strong influence on the quantity of leached DOC through their effects on the biological, physical and chemical properties of soils (Pizzeghello, *et al*. 2006; Hansson, *et al*. 2011). Differences in litter chemistry have also been found to drive variations in DOC leaching between different tree species (Fröberg, *et al*. 2011). Significant differences in DOC character have also been reported in soil leachates from different tree species including colour, SUVA, molecular weight (MW) and aromatic/aliphatic content (Strobel, *et al*. 2001; Pizzeghello, *et al*. 2006, Lindroos, *et al*. 2011). In a water treatment context, these differences in DOC concentration and character are significant since they imply possible variations in DOC treatability and THM formation potential (THMFP). However, relatively few studies have considered this perspective.

In the present study we compared soil leachates from European beech, Norway spruce, Japanese larch, Scots pine and peat habitats in an upland drinking water catchment. Significant differences in DOC concentration and character were observed between different forested habitats. DOC concentration in the beech leachate was relatively low (mean: 8.1 mg L^{-1}) and significantly lower than two of the three coniferous species (larch and pine). This is consistent with previous studies reporting lower DOC flux from deciduous, compared with coniferous forest stands. Higher DOC export from coniferous soils has been attributed to lower rates of organic matter turnover than in deciduous forest soils (Pizzeghello, *et al*. 2006). Elsewhere, the thinner organic soil horizons associated with deciduous stands has been proposed as an explanation (Fröberg, *et al*. 2005; Fröberg, *et al*. 2011). The standardised method used to obtain leachates in the present study meant that soil depth was controlled for. Therefore differences in DOC processing between different habitats may explain the difference in leachable DOC concentration observed. However, further analysis involving direct measurement of microbial and enzyme activity would be necessary to confirm this. Significant differences in DOC concentration and character were also observed between different coniferous species, suggesting that the partitioning of forest types into coniferous and deciduous stands may be too simplistic for investigating drivers of DOC concentration and character relating to vegetation assemblages. Marked differences in the reactivity (standardised THMFP; STHMFP) and fractional character of DOC were also observed, indicating variations in THM yield and treatability between different habitats. Given the magnitude of the differences observed, the choice of tree species planted in drinking water catchments appears important for drinking water treatment. Larch and pine leachates appeared to contain high levels of potentially-recalcitrant hydrophilic acid (HPIA)/hydrophilic neutral (HPIN) DOC. Their high overall DOC concentrations also suggested high coagulant demand and contributed to high THMFP. The lower DOC concentration associated with spruce leachates suggests that this is a preferable habitat in terms of THM yield and DOC treatability. However its high colour may confer an aesthetic issue for potable water treatment. Beech, it is suggested, may represent the best option for coverage in a drinking water catchment due to low DOC concentration, THMFP and colour. Even where replanting areas with coniferous stands is necessary due to economic considerations, our data suggest that the choice of species may be important for water quality management. However, we recommend a longer-term study involving regular sampling to confirm this given that leachate DOC concentration and character shows different seasonal trends depending on habitat type (Hongve, 1999). In addition, future research would benefit from a direct comparison of DOC treatability using jar testing experiments, since fractional character provides only a broad indication of DOC removal efficiency during coagulation.

Typically, lysimeter-based methods are used in these studies to collect pore water for analysis. However, we used a standardised method developed by Jones, (2006) to measure leachable DOC concentration per unit volume of soil. One advantage of this method is that it controls for natural variations in hydrological flowpaths. However, it does not account for soil horizon depth or adsorption processes in deeper soil horizons and therefore cannot be used to estimate catchment-scale DOC fluxes from different habitats. In future studies we recommend a combination of these two approaches to provide both a standardised comparison of leachable DOC and an actual DOC quantity which could be used to estimate catchment-scale flux. It should also be noted that our study was conducted in a single drinking water catchment. Expanding this research to include additional sites is important, particularly since drinking water catchments are rarely pristine environments and soil processes may be affected by the legacy of previous management practices.

8.2.2. Ditch blocking

Peatland drainage during the 20th century has resulted in widespread water table drawdown in many upland areas. Since waterlogged conditions in peatlands are crucial to their status as net carbon sinks, this led to the destabilisation of vast carbon stores (Holden, *et al*. 2004). As well as enhanced erosion (Robinson, 1980), drained peatland catchments are reported to be associated with higher DOC export (Clausen, 1980; Edwards, *et al*. 1987). Indeed, water table depth has been identified as the single most important factor controlling DOC production and loss from peatlands (Fenner, *et al*. 2009). Given the rising trend in surface water DOC concentration in many upland areas, and the growing emphasis on "at source" as opposed to "end of pipe" solutions (Grayson, *et al*. 2012), ditch blocking is being considered as a means of restoring peatlands and improving surface water quality. However, studies investigating the impact of peatland restoration (ditch blocking) on pore water and ditch water DOC concentrations have yielded conflicting results. In addition, very few studies have considered the effect of ditch blocking on DOC character and its implications for treatability and THMFP. Such research is crucial to enable water treatment companies to make an informed decision about ditch blocking in their catchments.

The peat cores used in our water table manipulation experiment were collected from two upland catchments (Sites A and B) which had been drained several decades previously. Their associated reservoirs, from which water is abstracted for potable water treatment, are characterised by relatively high DOC concentrations. Ditch blocking is being considered in these catchments in response to observed increases in reservoir DOC concentration. Previous research suggested that ditch blocking could result in oscillations in the water table rather than a return to the steady high water table associated with intact peatlands (Holden, *et al*. 2011). Hence a fluctuating water table treatment was included in our experiment. With regard to the effect of peatland restoration on DOC concentrations, previous studies have reported conflicting results, with some reporting no change in DOC concentration (Gibson, *et al*. 2009; Armstrong, *et al*. 2010; Peacock, 2013) and others lower DOC concentration at restored sites (Gibson, *et al*. 2009; Armstrong, *et al*. 2010; Turner, *et al*. 2013). In our study no difference in DOC concentration was observed between treatments although some differences in STHMFP were found. After 12 months, significantly lower STHMFP_{7d} was observed in the high water table treatments compared with the fluctuating water table and low water table treatments at Sites A and B, respectively. However, when DOC concentration was accounted for, no significant differences in THMFP were identified between different treatments.

SUVA and standardised phenolics measurements provided an indication of DOC treatability since a positive relationship is reported between SUVA and DOC removal efficiency during coagulation-flocculation (Sharp, *et al*. 2006a) and the inverse is the case with phenolic content (Tomaszewska, *et al*. 2004; Chapter 6). Only in peat cores collected from Site A were any significant differences in these parameters identified. The only significant differences in SUVA were identified in December 2012, with no further differences identified during subsequent quarterly analysis. During final sampling in September 2013 the low water table treatment showed higher standardised phenolic content than the fluctuating treatment, suggesting that the former produced more recalcitrant DOC. However, the magnitude of this difference was small. Overall there was little evidence of differences in THM yield or DOC treatability between different water table regimes. However, we also found no evidence of variation in microbial activity based on CO_2 flux and enzyme activity measurements. The microbial response to different hydrological conditions has been reported to be a key driver of changes in DOC flux observed in different water table simulations (Freeman, *et al*. 2001; Worrall, *et al*. 2004; Toberman, *et al*. 2008). The absence of a measurable response in the present experiment may be due to the limited duration of our experiment. Thus a longer-term study is recommended to assess the implications of water table for DOC treatability and THM yield.

It should be noted that peat core experiments, whilst offering a greater degree of control than field based studies, also have limitations. Firstly, whereas lateral flow is a key hydraulic process in intact peat, water can only percolate vertically in peat cores (Tipping, *et al*. 1999). In addition peat cores are prone to edge effects (Petersen, *et al*. 2009). For example, whereas in the field, the peat substrate is insulated from fluctuations in air temperature, in peat cores this insulating effect is reduced due to the exposure of the peat core housings. In particular this can result in higher rates of evapotranspiration than those observed in the field. In the present experiment, a significant shift in pore water quality was evident during early sample collection suggesting that peat disturbance may have been an issue. In order to validate the results obtained during this experiment, we would recommend conducting STHMFP/THMFP measurements on samples collected from experimental field sites.

8.2.3. Spatial variability in surface water quality relating to whole-catchment characteristics

Alongside our evaluation of the impact of catchment management strategies on DOC concentration and character (above), we also assessed spatial variations in surface water quality both between and within two drinking water catchments. In this study we focussed on two upland drinking water reservoirs (Reservoirs A and C) which showed distinct water quality and were therefore associated with unique treatment challenges. The aim was to improve understanding of the nature and drivers of spatial variations in DOC in relation to drinking water treatment, and THM yield in particular. In addition we aimed to investigate the causes of these differences in relation to catchment characteristics including statistical analysis of correlations between stream water quality and subcatchment characteristics in Catchment A. We used GIS mapping techniques to measure and compare catchment characteristics. The *Hydrology* functions in ArcGIS were used to delineate the watersheds associated with the two reservoir catchments and their main input streams. We then used Phase 1 Habitat Survey (CCW, 2005) and soil data (NSRI, 2005) to measure the spatial extent of ecological and pedological features in each catchment.

We identified statistically significant differences in water quality between different input streams in Catchment A including DOC concentration, A_{253}:A_{203}, colour, standardised phenolic content, pH and conductivity. We also found statistically significant differences in DOC flux. This suggests significant differences in THMFP (DOC concentration/A_{253}:A_{203}), treatability (standardised phenolic content) and aesthetic quality (colour) between input streams. We also observed variations in $THMFP_{7d}$ between different streams in both catchments, though this data could not be analysed statistically. DOC flux measurements in Catchments A and C enabled us to assess the relative importance of different streams in terms of reservoir DOC inputs. This information will help Dŵr Cymru Welsh Water (DCWW) identify the sources of high THMFP in these catchments and target water quality monitoring and catchment management solutions in these crucial areas.

In Catchment A lower DOC concentrations were observed in reservoir samples compared with stream samples. In this catchment, where high DOC loading of surface waters was observed, this reduction in DOC concentration is crucial since it reduces THMFP and pressure on the water treatment process. Various chemical and biological processes in lake and reservoir systems are reported to affect DOC concentrations and characteristics. These processes will depend on the physical and biogeochemical conditions of the aquatic system concerned. In this case, microbial processing, photo-degradation and/or precipitation (Parks & Baker, 1997; Pokrovsky & Schott, 2002; Waiser & Robarts, 2004) were proposed as possible explanations for the reduction in DOC concentration between fluvial and reservoir water. Further research is recommended in order to isolate the specific mechanisms responsible for DOC reduction in this reservoir, to ascertain whether they are climatically-linked and if they may be affected by future climate change.

We found that differences in reservoir water quality could be related to differences in ecological and pedological catchment characteristics identified by GIS mapping. The higher DOC concentrations associated with Reservoir A can be attributed to its coniferous forest coverage, a habitat absent from Catchment C. In addition, higher DOC loading may be due to the deeper soils associated with Catchment A. This is likely to be related to its shallow mean slope, a feature which may also have contributed to higher DOC loading due to longer residence times (Clair, *et al*. 1994). High SUVA in both reservoirs, indicating DOC rich in high MW (HMW), hydrophobic compounds can be related to extensive peatland coverage in both catchments. These characteristics are likely to have contributed to the high STHMFP values associated with both reservoir waters (Galapate, *et al*. 1999; Chow, *et al*. 2005; Chow, *et al*. 2006). In general Catchment A surface waters (both fluvial and reservoir) were associated with higher THM yields than Catchment C as a result of higher DOC concentration, STHMFP and THM formation rate. The higher acidity in Reservoir A can be attributed to leaching of organic acids from coniferous canopies and litter (Nykvist, 1963; Alfredsson, *et al*. 1998; Eisalou, *et al*. 2013) in addition to deeper organic soils in this catchment which can isolate soil water from the neutralising capacity of mineral groundwater (Wetzel, 2001).

We investigated correlations between surface water quality in Catchment A streams and subcatchment characteristics since previous studies have reported a link between surface water properties and landscape characteristics including correlations between DOC loading and the proportion of forest and peatland coverage (Hope, *et al*. 1994; Hope, *et al*. 1997; Gergel, *et al*. 1999; Cohen, 2009). The surface coverage of different habitat and soil types within each catchment were correlated with mean annual measurements for different water quality parameters in their respective streams (n = 6). The only significant correlations identified in our study were between stream water conductivity and habitat type. No statistically significant correlations were identified between catchment characteristics and DOC concentration or character. It may be that this was due to experimental design, i.e. an insufficient number of samples. In addition, it is possible that the monthly sampling regime was insufficient to derive representative mean values for stream water parameters given that stream hydrochemistry varies substantially as a result of antecedent conditions, including temperature and soil moisture levels (Kalbitz, *et al*. 2000), as well as during rainfall events (Thurman, 1985). Although (Cohen, 2009) identified a number of significant correlations between reservoir water quality and catchment characteristics based on one-off sampling, we have shown that reservoir water quality shows less temporal variability than stream water quality (Chapters 4 and 6).

The degree to which catchment characteristics can predict surface water DOC concentration will depend on the extent to which they provide a proxy for the controls on DOC dynamics. These include soil microbial production/assimilation, mineralization and adsorption processes, hydrological influences as well as in-stream processing (Neff & Asner, 2001). These variables have been integrated directly into mathematical models for DOC dynamics. Models such as the Integrated Catchments Model for Carbon (INCA-C), the NICA (non-ideal competitive adsorption)-Donnan model and the Dynamic DOC (DyDOC) model have been used to predict spatial and temporal variations in soil and stream water DOC concentrations according to hydrological, geochemical and biological drivers (Michalzik, *et al*. 2003; Lumsdon, *et al*. 2005; Futter, *et al*. 2007). Although these models have been found to be effective in modelling spatial and temporal variations in DOC dynamics, their commercial application may be limited due to their extensive data input requirements. Alternatively, GIS mapping has recently been used to develop a simpler predictive model for surface water colour based on correlations with catchment characteristics. This was used to develop risk-based GIS maps which were validated using field data and used to identify catchment areas likely to produce high colour (and by proxy, high DOC) levels (Grayson, *et al*. 2012). Such an approach could be feasibly adopted by water treatment companies and used to focus catchment management actions.

8.3. Temporal variations in DOC concentration and character

Various factors can drive temporal variations in DOC concentration and character in surface waters including variations in biological processing, mobilisation and transport of allochthonous DOC in response to seasonality and weather events (Tate & Meyer, 1983; Kalbitz, *et al*. 2000; Dawson, *et al*. 2004). The production and processing of autochthonous DOC also shows seasonal variations. Of particular importance is the seasonal increase in the production of algogenic organic matter (AOM) in many water bodies which can contribute to the DOC pool and cause significant problems for potable water treatment (Bernhardt, *et al*. 1991; Nguyen, *et al*. 2005; Li, *et al*. 2012). Variations in DOC concentration and character are important for potable water treatment since they result in fluctuations in treatment efficiency and ultimately, changes in finished water quality, including THM levels (Jones, 2006). Better understanding of the nature and drivers of temporal variations in surface water quality will help drinking water suppliers to anticipate potential treatment issues and adjust or optimise treatment processes accordingly.

8.3.1. Observed trends in surface water DOC concentration and character

We analysed stream water quality in Catchment A on a monthly basis during a 12 month study designed to assess temporal variation in the concentration and character of DOC inputs into Reservoir A. THMFP, high pressure size exclusion chromatography (HPSEC) and XAD-fractionation measurements were also undertaken on a biannual basis on stream and reservoir samples in Catchments A and C.

Our findings support previous research showing that stream DOC flux was predominantly controlled by temporal variations in stream discharge (Hope, *et al*. 1994). Analysis of stream water DOC concentration showed a seasonal trend similar to those reported previously where maximum DOC concentration is observed in late summer/early autumn and the minimum in winter/early spring (Dawson, *et al*. 2004; Neal, *et al*. 2005). The DOC peak generally occurs towards the end of the growing season when DOC which accumulates in the soil matrix under warm aerobic conditions is flushed from the catchment (Hope, *et al*. 1994). The trough occurs after the catchment has been purged of readily leachable DOC and when colder, waterlogged conditions inhibit microbial degradation, thus limiting DOC production (Halliday, *et al*. 2012).

DOC character also varied seasonally, with variations generally synchronous between streams, highlighting the importance of seasonal variations in DOC processing and mobilisation. Peak SUVA and colour were observed in June 2012 and were explained by the high rainfall which preceded sampling. This, we suggest, resulted in the inundation of dormant hydrological pathways, mobilising older, more humified material relative to more labile, lower MW organic matter (USGS, 2013). A_{253}:A_{203} showed a prominent peak in August 2012 indicating input of DOC with high STHMFP (Kim & Yu, 2007). Maximum DOC concentration also occurred in August 2012, further enhancing the THMFP of stream waters. The THMFP of fluvial and reservoir samples was also measured directly in October 2011 and May 2012. On average, $STHMFP_{7d}$ of fluvial samples was higher in May 2012 as were both reservoir samples. In addition, the rate of THM formation tended to be lower in May 2012. Increases in the proportion of HPIN DOC and a shift towards lower MW DOC were also observed in May 2012 in the surface waters of both catchments, but was most prominent in Catchment C. Although Reservoir C is not typically associated with high algal populations, the timing of this shift, and the synchronicity between the two catchments suggested it might be related to a seasonal increase in algal biomass.

A comparison of the temporal trend in stream (Chapter 4) and reservoir DOC concentration (Chapter 6) in Catchment A suggests a six-month time lag effect as a result of long residence times in the reservoir. Recognition of these temporal trends are important since previous studies have shown that seasonal variations in DOC concentration correlate with variations in treated water THM levels (Rodriguez, *et al*. 2003). Importantly, our data also suggest that both reservoirs (Reservoirs A and C) featured in this study act to temper seasonal variations in DOC concentration and character in input stream water. As such they appear to act as a buffer, aiding water treatment by reducing temporal variations in water quality. Quarterly depth sampling in Reservoir A (data not shown) suggested that the reservoir remained well-mixed throughout the year, with no thermal stratification or variation in DOC concentration or character with depth. However, the rise in global temperatures predicted under future climate scenarios may result in increased stratification and reduced mixing (George, *et* *al*. 2007). This could lead to increased seasonal variability in reservoir water quality and necessitate a more season-specific approach to water treatment.

8.3.2. Algogenic organic matter

Seasonal increases in the abundance of algae can represent a challenge for potable water treatment. Algal cells can produce toxic metabolites (Žegura, *et al*. 2011) and contribute undesirable taste and odour (Li, *et al*. 2012). Algal blooms also elevate total organic carbon (TOC) levels, often resulting in increased coagulant demand and DBP formation potentials (Nguyen, *et al*. 2005). Understanding the impact of algogenic organic matter (AOM) on treatment efficiency and THMFP is particularly important given the predicted increase in the frequency and duration of algal blooms resulting from climate change (Ritson, *et al*. 2014). In the present study we focussed our analysis on dissolved AOM since algal cells are typically effectively removed during coagulation-flocculation, particularly when dissolved air floatation (DAF) is employed. Thus dissolved AOM generally represent the main algogenic THM precursor in potable water treatment. Though STHMFP of AOM is known to vary as a function of algae species (Plummer & Edzwald, 2001; Nguyen, *et al*. 2005), few studies have compared STHMFP values during different algal growth phases. This is important since the character of AOM is known to shift as an algal bloom progresses, from predominantly extracellular organic matter (EOM; released from algal cells by diffusion) to predominantly intracellular organic matter (IOM; released from senescent algal cells during cell lysis).

In contrast to previous studies, our data showed that STHMFP can vary markedly between different growth phases, consistent with the following order of reactivity: IOM < EOM < NOM. To our knowledge, ours was the first study to compare the reaction rate of humic-dominated and algogenic DOC. Our results showed that algogenic DOC produced both during the exponential and death phases formed THMs at a lower rate than humic DOC, as indicated by the % of $THMFP_{7d}$ formed within the first day. These findings indicate that, in terms of overall THM yield, AOM may be less problematic than humic DOC. However, we also found that bromine incorporation during chlorination increased with culture age, probably due to the release of aliphatic HPIN DOC which has previously been associated with enhanced formation of BrTHMs (Heller-Grossman, *et al*. 1993; Teksoy, *et al*. 2008). Previous studies have noted the dominance of the HPIN fraction in algogenic DOC (Her, *et al*. 2004; Leloup, *et al*. 2013). However, whereas Her, *et al*., (2004) proposed that the proportion of HPIN correlated negatively with increased cell mortality, we found that a pronounced shift towards HPIN DOC occurred during the death phase. Since HPIN DOC is reported to be resistant to removal by coagulation (Krasner & Amy, 1995; Edwards, 1997; White, *et al*. 1997), our data suggests that DOC removal efficiency may decrease during an algal bloom, with lowest removal efficiency during the death phase. In order to improve understanding of THM risks and treatment challenges associated with algal blooms we recommend that similar experiments be repeated using different algal species and the treatability of AOM during different growth phases measured directly using jar test experiments.

Our algae experiment was motivated in part by the observed shift in DOC character and STHMFP observed during reservoir and stream sampling in May 2012 including increased HPIN, decreased THM reaction rate and more prominent HPSEC low MW (LMW) peaks (Chapter 4). The timing of this shift suggested it could be connected to a seasonal increase in the abundance of algae in surface waters. So as to more accurately reflect reservoir conditions, our algae was cultured from naturally occurring populations in Reservoir A water. In addition, the reservoir water was not filtered or inoculated. Our findings suggest that algae may indeed have been responsible for the shift towards lower MW DOC and the increase in the HPIN fraction, as well as the decrease in THM formation rate in the May 2012 samples. Importantly, our data also indicated that AOM produced during different growth phases can be identified in discrete peaks in the HPSEC chromatogram. This information will aid the interpretation of DOC HPSEC chromatograms in future research.

8.4. Potable water treatment and THM amelioration

Although effective disinfection remains a priority in potable water treatment, the issue of THMs is a growing concern as raw water quality in many upland areas deteriorates and the risk of exceeding permissible THM levels increases. The removal of DOC prior to chlorination is widely considered to be the most effective strategy for THM control. This is typically achieved by coagulation-flocculation using aluminium and iron salts (O'Melia, *et al*. 1999). Traditionally, coagulation-flocculation was optimised for colour and turbidity removal (Iriarte-Velasco, *et al*. 2007). However, increasingly, coagulation conditions are adjusted to maximise DOC removal; so-called enhanced coagulation. This has been recognised as the best available technology (BAT) for THM control (US EPA, 1999).

8.4.1. The role of different treatment processes

The mechanisms by which DOC is removed during coagulation-flocculation are generally well understood. However, relatively little data has been reported on the contribution of individual treatment stages to DOC and THM precursor removal. In addition, little is known about the effect of different chemical and physical treatment stages on THM speciation. This is important since different THM species are associated with varying levels of carcinogenicity (WHO, 2005). In the present study, DOC and THM precursor removal during a sequence of treatment processes was assessed at an upland WTW over a 12 month period. The initial treatments (coagulation-flocculation and DAF) were the only ones associated with a statistically significant decrease in DOC concentration (mean: 76% removal). STHMFP also decreased significantly during these initial treatments which can be explained by the selective removal of the hydrophobic, aromatic DOC fraction which is reported to preferentially form THMs (Galapate, *et al*. 1999; Chow, *et al*. 2005; Chow, *et al*. 2006). This selectivity during coagulation has been reported previously (Randtke, 1988; Edwards, 1997; Sharp, *et al*. 2006b) and has been attributed to the higher charge densities associated with this DOC fraction (Edzwald, 1993; Sharp, *et al*. 2006b). However, the selective removal of aromatic DOC also resulted in a significant increase in the proportion of BrTHMs. The same result was observed during bench-scale jar testing experiments using three different coagulants (Chapter 7). To our knowledge this consequence of selectivity in the removal of DOC during coagulation-flocculation has not been highlighted previously. Although individual species of THMs are not currently subject to regulation in the UK, this increase in BrTHMs is significant since brominated species are associated with higher carcinogenicity than their chlorinated analogues (Richardson, *et al*. 2007). As surface water DOC concentrations increase, it is likely that the concentration of more recalcitrant aliphatic DOC following coagulation will also rise, increasing the potential for BrTHM formation. This trend may be enhanced by the predicted increase in sea salt deposition with rising sea surface temperatures which may increase Br^- concentrations in surface waters (Hurrell, *et al*. 2004). The removal of bromide prior to disinfection is one possible solution to this issue. Effective removal has been reported during coagulation-flocculation, though removal efficiency is reduced by the presence of DOC (Ge, *et al*. 2007). Alternatively, electrolysis, granular activated carbon (GAC), ion exchange and magnetic ion exchange (MIEX) treatments have all been successful in the targeted removal of bromide (Bao, *et al*. 1999; Kimbrough & Suffet 2002; Vaaramaa & Lehto, 2003; Humbert, *et al*. 2005), though their installation would involve significant cost. Br^- can also be introduced during treatment since the chlorine used for disinfection normally contains *ca*. 1% Br_2 as a production impurity (Bond, *et al*. 2014). Therefore using purer forms of chlorine may be another means of reducing BrTHM formation.

Matilainen, *et al*. (2011) highlighted the importance of understanding changes in the concentration and characteristics of DOC at different stages in the treatment chain for optimising treatment processes. Often, assessments of treatment efficiency involve a comparison of raw and final water (Fabris, *et al*. 2008) or focus on the treatment processes designed specifically for DOC removal/THM amelioration (coagulation-flocculation and clarification). However, studies have shown that DOC MW distributions (MWDs) and chlorine demand can be altered by various physical and chemical treatment processes (Matilainen, *et al*. 2006; Zhao, *et al*. 2009). Importantly, our data showed that

DOC character may be altered during the precipitation-filtration process which is designed to remove manganese. We observed a slight but statistically significant decrease in SUVA, A_{235}:A_{203} and % BrTHMs during this treatment stage. To our knowledge, the speciation of THMs has not previously been assessed between different treatment stages. Our findings highlight the importance of considering the impact of all steps in the treatment process on THM formation potential, including those which were not designed specifically for DOC removal/THM control.

HPSEC chromatograms can provide an effective means of visualising DOC removal and shifts in the MWD of DOC during successive treatment processes. Quantification of HMW and LMW DOC using HPSEC showed that HMW DOC was preferentially removed during initial treatment processes (coagulation-flocculation and DAF) (Chapter 6 and 7), consistent with previous findings (Matilainen, *et al*. 2006; Fabris, *et al*. 2008). Typically for this type of application, HPSEC detectors are set at λ = 254 nm (Matilainen, *et al*. 2006; Fabris, *et al*. 2008; Zhao, *et al*. 2009). However structures with few conjugated bonds exhibit low UV absorbance (Matilainen, *et al*. 2011) and so will produce little or no response from the detector (Leenheer & Croue, 2003). This suggests that the chromatography will be less sensitive to aliphatic compounds. Detection of these compounds is important for treatment optimisation since they tend to be resistant to treatment (Randtke, 1988; Edwards, 1997; Sharp, *et al*. 2006b). Therefore, to ensure accurate measurement of this recalcitrant DOC fraction we suggest that the HPSEC system should be equipped with both on-line UV and DOC detectors (Leenheer & Croue, 2003).

8.4.2. Predicting THMFP

Directly monitoring THMFP in waters supplying WTWs is problematic due to the time necessary to obtain results and the short timescales within which THM formation potentials can vary. In-line UV monitors, which can record single wavelength measurements or spectral slope ratios can offer an alternative to direct THMFP measurements and are increasingly being used by drinking water companies to analyse DOC character in water supplying WTWs. SUVA (absorbance at λ = 254 nm (cm^{-1}) * 100/DOC concentration (mg L^{-1})), which has been correlated positively with DOC hydrophobicity, MW and aromaticity (Edzwald & Tobiason, 1999; Weishaar, *et al*. 2003), has been shown to have a positive relationship with STHMFP (Edzwald, *et al*. 1985). Positive correlations were also identified in the present study between $STHMFP_{7d}$ and SUVA in stream samples ($r_s = 0.351$, $p < 0.05$; Chapter 4) and in raw water entering a WTW ($r_s = 0.755$, $p < 0.05$; Chapter 6). However, A_{253}:A_{203} was found to be a more powerful predictor of $STHMFP_{7d}$ in both cases ($r_s = 0.770$, $p < 0.01$ and $r_s = 0.755$, $p < 0.05$ in Chapters 4 and 6, respectively). A_{253}:A_{203} is reported to correlate with the proportion of hydroxyl-, carboxyl-, ester- and carbonyl-substituted aromatic rings (Korshin, *et al.*

2009) and these functional groups have been implicated in reactions generating DBPs (Kim & Yu, 2007). We suggest that measurement of A_{253}:A_{203} in WTW intake water could be a useful means of monitoring THMFP.

The present study also investigated the relationship between DOC fractional character and STHMFP. Previous studies have tended to report highest STHMFP for the HPOA fraction (Galapate, *et al*. 1999; Chow, *et al*. 2005; Chow, *et al*. 2006; Zhang, *et al*. 2009) although exceptions have been observed. Imai, *et al*. (2003) for example report comparable reactivities for what they term aquatic humic substances (equivalent to HPOA) and hydrophilic fractions (equivalent to HPIA, HPIN and HPIB combined) from a shallow eutrophic lake, with 0.176 and 0.195 µmol THM mg C^{-1}, respectively. Lu, *et al*. (2009) report higher $STHMFP_{48h}$ in the HPIA fraction (~150 µg mg C^{-1}) than the HPOA fraction (~130 µg mg C^{-1}) of river water DOC. Comparing $STHMFP_{7d}$ of DOC fractions derived from soil leachates (Chapter 2), our study found that, on average, the HPOA fraction had the highest $STHMFP_{7d}$. However, a high degree of variability in the relative $STHMFP_{7d}$ measurements of different fractions was also observed between different habitats. Also, temporal variations in surface water DOC fractional character did not appear to correlate with changes in $STHMFP_{7d}$ (Chapter 4). Given the variability in the relative reactivities of different fractions reported here and elsewhere, XAD-fractionation may have limited use for the estimation of THMFP. We also found that $STHMFP_{7d}$ increased markedly following fractionation (Chapters 2 and 7), possibly due to the removal of synergistic effects, or the structural alteration of DOC moieties during the fractionation procedure. Indeed chemical changes to DOC during the XAD-fractionation procedure have been reported previously (Gadmar, *et al*. 2005). These potential artefacts are an important consideration when measuring the reactivity of isolated DOC fractions.

DOC character is also reported to affect the rate at which THMs form. This is an important determinant of THM concentrations at the point of delivery to the consumer. The present study has identified variations in THM formation rates between sites (Chapter 4) as well as on a seasonal basis (Chapters 4 and 6). In addition, it was found that algogenic DOC formed THMs at a slower rate than humic DOC (Chapter 5). Further research is required to ascertain whether distinct seasonal trends in THM formation rate can be identified. Previous studies have isolated specific DOC functional groups associated with fast- and slow-reacting THM precursors. Resorcinol-type structures and phenolic compounds are reported to act as fast- and slow-reacting THM precursors, respectively (Gallard & von Gunten, 2002). Elsewhere, the aliphatic compounds β-diketone and β-keto acids, have been identified as fast- and slow-reacting THM precursors, respectively (Dickenson, *et al*. 2008). Such detailed chemical analysis was beyond the scope of the present study. However, further research aimed at identifying fast- and slow-reacting precursors in the DOC pool may well be valuable for drinking water companies. Specifically, developing easily measured surrogate parameters for these compounds, such as UV absorption measurements, could help practitioners monitor THMFP and optimise coagulation.

8.4.3. Optimising THM amelioration

Currently many WTWs employ semi-automated adjustment of coagulation conditions in response to post-clarification colour measurements. However, our data has shown that selectivity in the removal of DOC fractions during coagulation results in colour removal measurements overestimating DOC removal (Chapters 6 and 7). Nor does colour provide an accurate proxy for THM precursor removal. The technology has not been developed for direct in-line DOC or THMFP monitoring. However, given the strong positive relationship between $STHMFP_{7d}$ and A_{253}:A_{203} found in the present study, we suggest that this would be a useful parameter to include in post-clarification water monitoring. Incorporating this measurement into automatic adjustment of coagulation conditions may help to improve THM control. Measurement of A_{253}:A_{203} in intake waters could also help to inform the timing of jar testing experiments. We also found a negative relationship between DOC removal efficiency and DOC phenolic content suggesting that phenolic moieties are recalcitrant to removal by coagulation (Chapter 6). It may therefore be useful to monitor the phenolic content of intake water DOC in order to anticipate low DOC removal efficiency and adjust other treatment stages accordingly. For example, some WTWs have the capacity to switch from chlorination and chloramination during periods of high THM yields.

It is predicted that climate change will result in increased seasonality as well as increased shorter-term fluctuations in DOC quality resulting from increasingly frequent and severe extreme weather events (Elliott, *et al*. 2005; Eimers, *et al*. 2008; Jenkins, *et al*. 2009). In this context Tang, *et al*. (2013) recommend more frequent jar tests to optimise coagulation conditions. Our jar testing experiment (Chapter 7) explored the potential for improving DOC and THM precursor removal by switching the type of coagulant used. Statistically significant differences in treated water quality were identified between different coagulants including DOC concentration and colour. STHMFP measurements also indicated differences in THM precursor removal, though these were not compared statistically. Higher DOC removal was observed for the ferric-based coagulant (PIX-322) than the aluminium-based coagulants (alum and PAX-18), consistent with previous studies (Edwards, 1997; Uyak &Toroz, 2005). This has been attributed to the higher affinity for carboxylic groups associated with ferric ion (Sharp, *et al*. 2006) as well as more numerous and larger flocs (Ratnaweera, *et al*. 1999) which aid their removal during clarification. If surface water DOC character becomes more variable in the future, as has been predicted, it may be advantageous for WTWs to routinely conduct jar test using different coagulants in order to achieve the best results for DOC and THM precursor removal. In addition, if DOC concentrations continue to rise, better removal of recalcitrant LMW aliphatic hydrophilic DOC will have to be explored, especially since these compounds are reported to form more BrTHMs (Heller-Grossman, *et al*. 1993; Teksoy, *et al*. 2008; Chapter 4, 5 and 6). The predicted increase in the seasonal contribution of algogenic DOC under future climate scenarios (Ritson, *et al*. 2014), which the present study found to be dominated by LMW aliphatic hydrophilic compounds (Chapter 5) further emphasizes the importance of such research. The jar testing experiment conducted in the present study also highlighted the fact that the coagulation strategy may be a compromise between treatment efficiency and cost which includes lime and coagulant dosing and disposal of sludge. If coagulation treatments become too expensive to be economically viable, then introduction of additional treatments may need to be considered. For example, anion exchange and granular activated carbon (GAC) can be successful in removing more recalcitrant LMW hydrophilic and neutral DOC (Bond, *et al*. 2011). Finally, controlling THM levels may require switching to a chloramination system, which has been associated with a substantial decrease in THM formation (Kristiana, *et al*. 2009), though this strategy is also associated with an increase in nitrogenous DBP such as N-nitrosodimethylamine (Choi & Valentine, 2002), as well as currently unidentifiable chlorinated by-products (Hua & Reckhow, 2007).

8.5. Final conclusions

- Our data show that the choice of tree species planted in drinking water catchments is likely to have important implications for water treatment. Significant differences in leachable DOC concentration and character were identified in soils obtained from different habitat types, suggesting differences in leachate THMFP and treatability. Our data suggest that beech habitats, whose leachates contained low DOC concentration, THMFP and colour, may represent the most appropriate forest coverage for drinking water catchments. However, we recommend further research to obtain flux measurements and to explore seasonality in DOC dynamics in order to confirm this. We also observed significant differences in DOC concentration and character in leachates derived from coniferous species, suggesting that the widely used classification of forest stands into coniferous and deciduous types is too simplistic for research into DOC export.
- Our peat core experiment was the first to investigate the impact of ditch blocking on the THMFP of pore water DOC. Although some statistically significant differences in STHMFP

were observed between treatments after 12 months, when DOC was accounted for, no significant differences in THMFP were observed. We also found little evidence of differences in DOC treatability between the control group (low water table) and the simulated ditch blocking treatments (high water table and fluctuating water table). However, we also found no evidence of a microbial response to water table adjustment after 12 months. We therefore recommend a longer-term study to allow for the potential legacy of lower microbial activity in the drained peat substrate. It is also suggested that ditch blocking studies at experimental field sites should include THMFP measurement in their suite of analyses on pore water or ditch water DOC. Such information is crucial for water treatment companies to make an informed decision about ditch blocking in their catchments.

- We have demonstrated the capability of GIS mapping for visualising and quantifying the spatial extent of catchment features likely to impact surface water quality. Although no statistically significant relationships were found between stream water DOC concentration/character and subcatchment characteristics, we were able to explain differences in reservoir water quality between two drinking water catchments by comparing the spatial extent of pedological and ecological features in each catchment. Future research should focus on the use of GIS to develop catchment risk-based maps which could be used to focus catchment management strategies in areas of high DOC flux.
- Our longitudinal study of stream water quality at Catchment A corroborates previous research identifying a late summer/autumn peak in fluvial DOC concentration and a strong relationship between DOC flux and discharge. We also identified seasonal variation in DOC fractional character and MW in stream and reservoir samples conferring changes in DOC treatability. We demonstrated that a shift towards lower MW, more hydrophilic DOC in May 2012 and a decrease in THM reaction rate is likely to have been caused by an increase in the contribution of algogenic DOC to the DOC pool. The importance of large reservoirs for tempering fluctuations in fluvial DOC inputs before reaching water treatment works was also demonstrated. The reduced mixing in reservoirs predicted under future climate scenarios is therefore a concern for drinking water companies.
- Algogenic DOC is likely to become an increasing problem for drinking water treatment with future climate change. Though previous studies have identified AOM as having lower reactivity (STHMFP) than humic DOC, ours was the first study to comprehensively profile THM formation during different algal growth phases. Differences in STHMFP, THM formation rate and bromine incorporation were identified during different growth phases. Though AOM was associated with lower STHMFP than humic DOC, as has been reported previously,

we showed that the formation of BrTHMs increased as the algal bloom progressed. This is likely to be related to the release of HPIN DOC during cell lysis, a DOC fraction which has been shown to be resistant to removal during conventional coagulation. We also showed that algogenic DOC released during different growth phases was identifiable as discrete peaks in HPSEC chromatograms. This represents an important development in the use of HPSEC for determining DOC origin.

- Our 12 month assessment of DOC and THM precursor removal at an upland WTW showed that initial treatments (coagulation-flocculation and clarification) were effective in reducing THMFP through bulk DOC removal the and selectively removing THM precursors. However, the selective removal of aromatic DOC also resulted in an increase in the proportion of BrTHMs which are more carcinogenic than their chlorinated analogues. Improving removal of the recalcitrant aliphatic, LMW DOC during coagulation should therefore be a priority for future research, particularly given the expected increase in algogenic DOC. We also recommend that the impact of all processes in the treatment chain on THMFP are considered since we have shown that processes designed to treat other water quality parameters my affect DOC reactivity with chlorine.
- A_{253}:A_{203} was found to be a more accurate predictor of STHMFP than SUVA and fractional character. We suggest that A_{253}:A_{203} should be measured at the intake of WTWs to inform the timing of jar test experiments and in post-clarification water for assessment of THM precursor removal. The development of a spectrometric proxy for THM formation rate should also be a priority for future research. The widely reported increase in DOC concentration in surface waters of upland catchments may necessitate more frequent jar testing to maintain treated water quality standards. Significant differences in DOC and THM precursor removal were observed in our jar test experiment using different coagulants. It may be therefore be prudent for WTWs to routinely conduct jar tests with a range of coagulants and develop the capability to switch dosing between different coagulants depending on intake water quality.

8.6. References

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Appendices

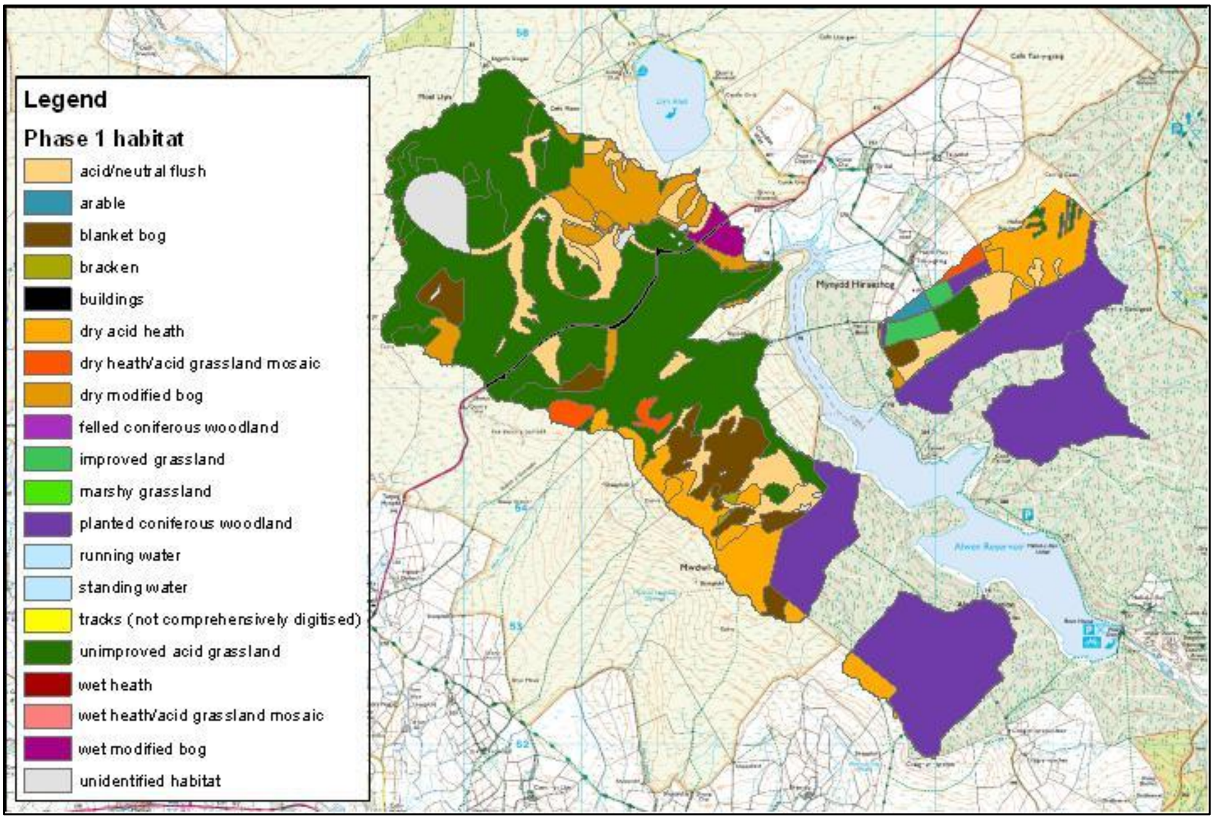

Figure 1. Map showing Phase 1 habitat coverage for stream subcatchments in Catchment A. Distance between grid lines represents 1 km.

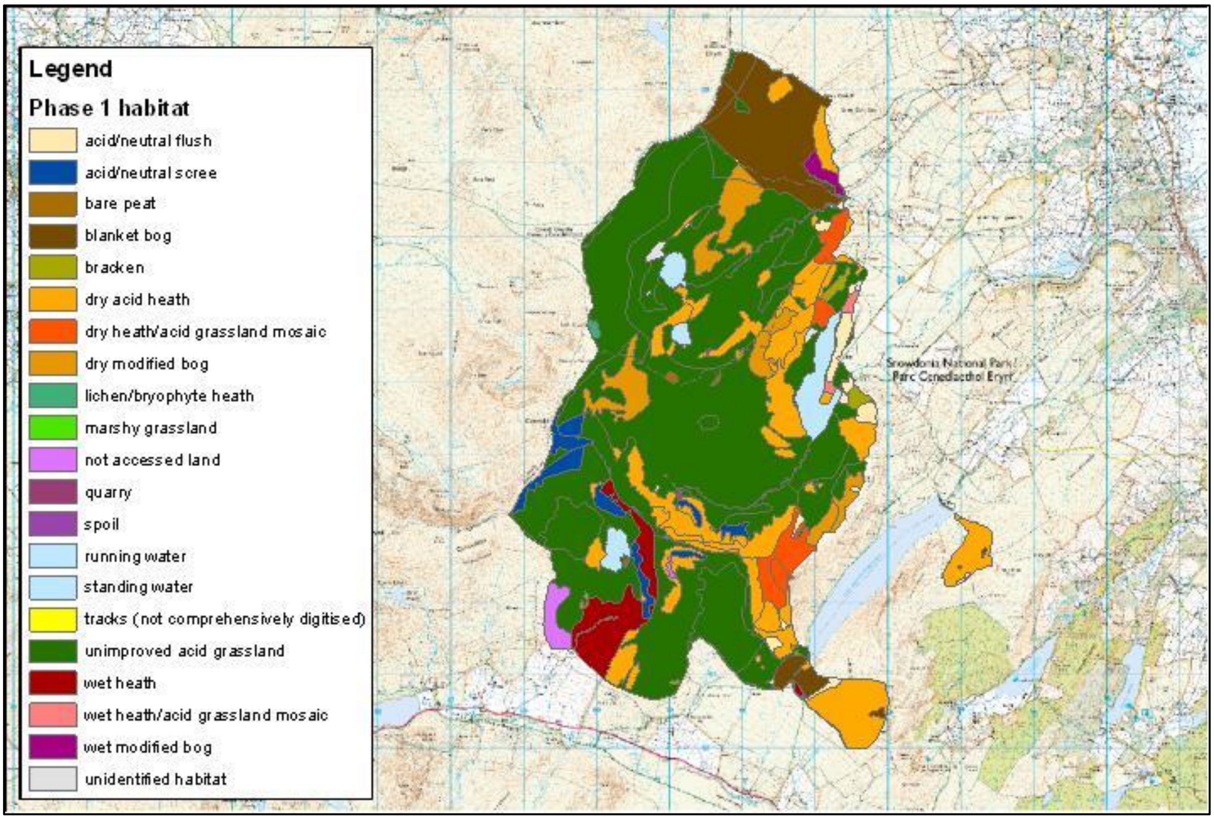

Figure 2. Map showing Phase 1 habitat coverage for stream subcatchments in Catchment C. Distance between grid lines represents 1 km.

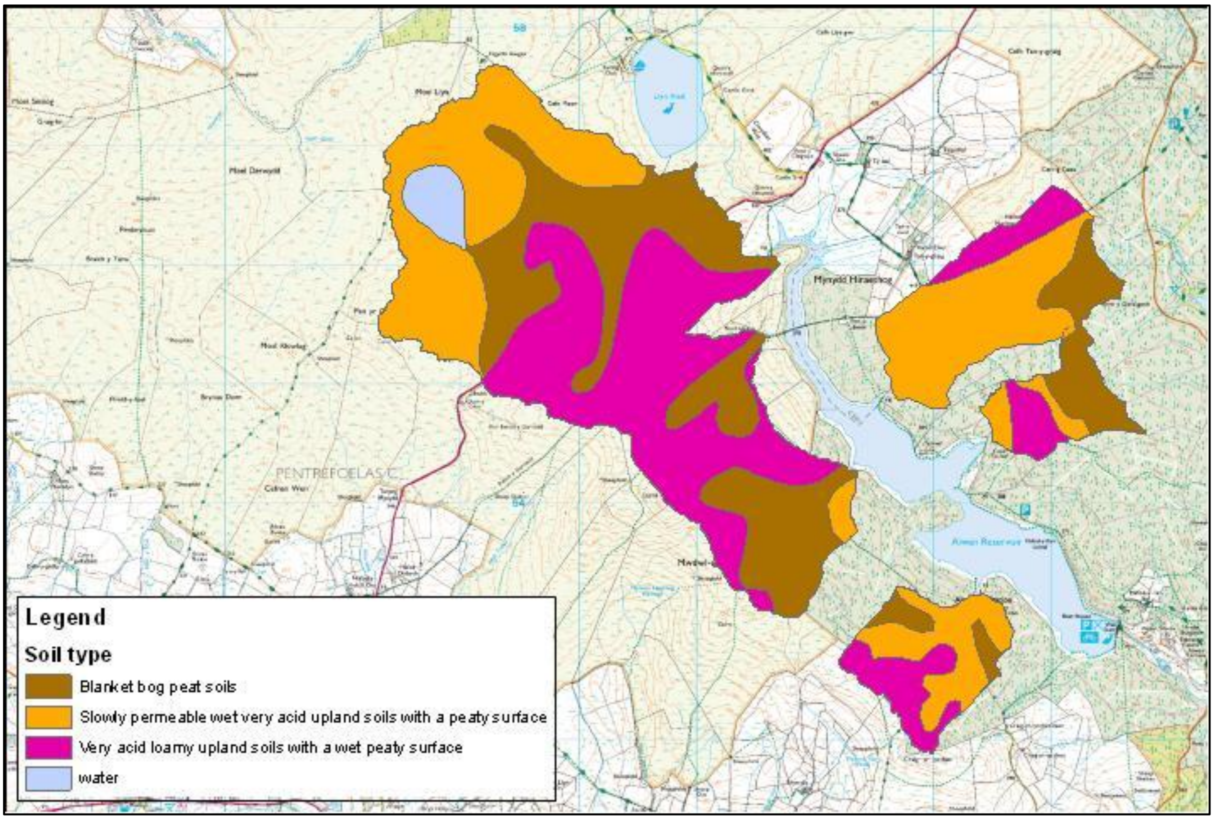

Figure 3. Map showing soil types for stream subcatchments in Catchment A. Distance between grid lines represents 1 km.

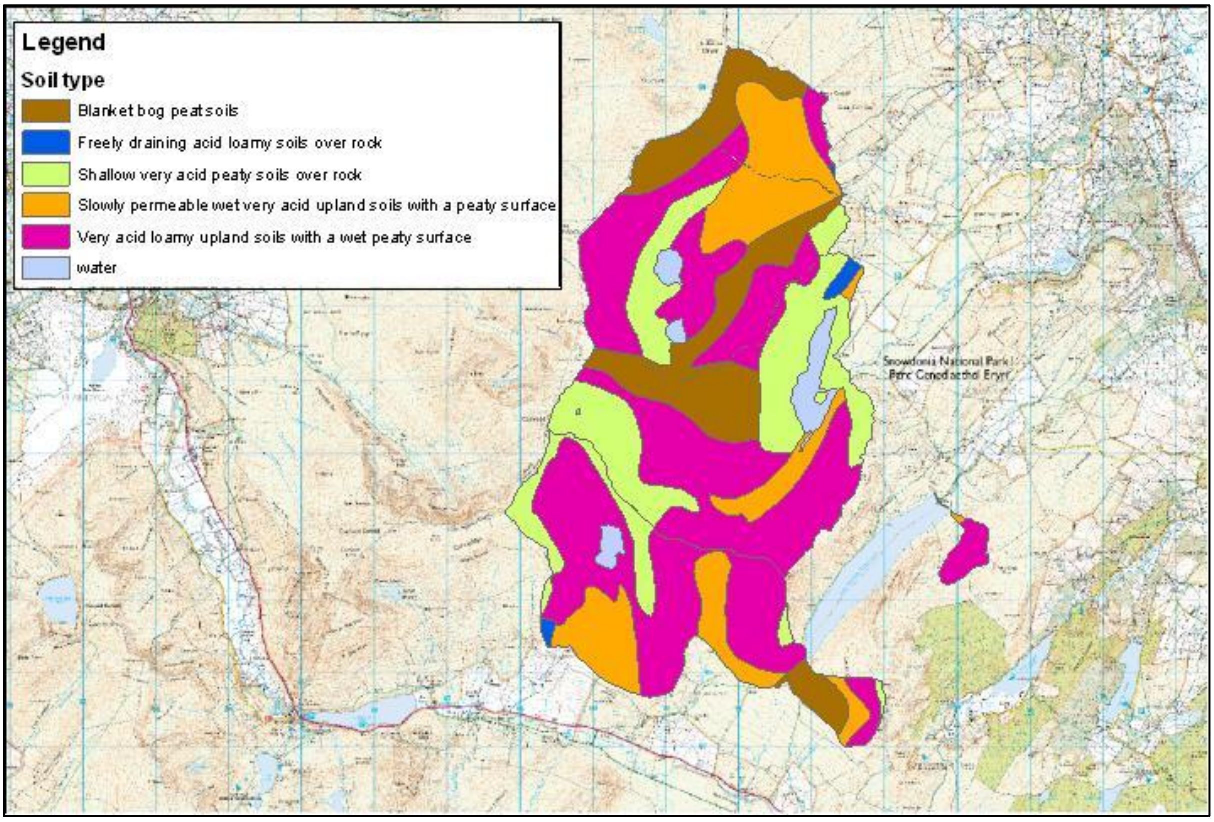

Figure 4. Map showing soil types for stream subcatchments in Catchment C. Distance between grid lines represents 1 km.

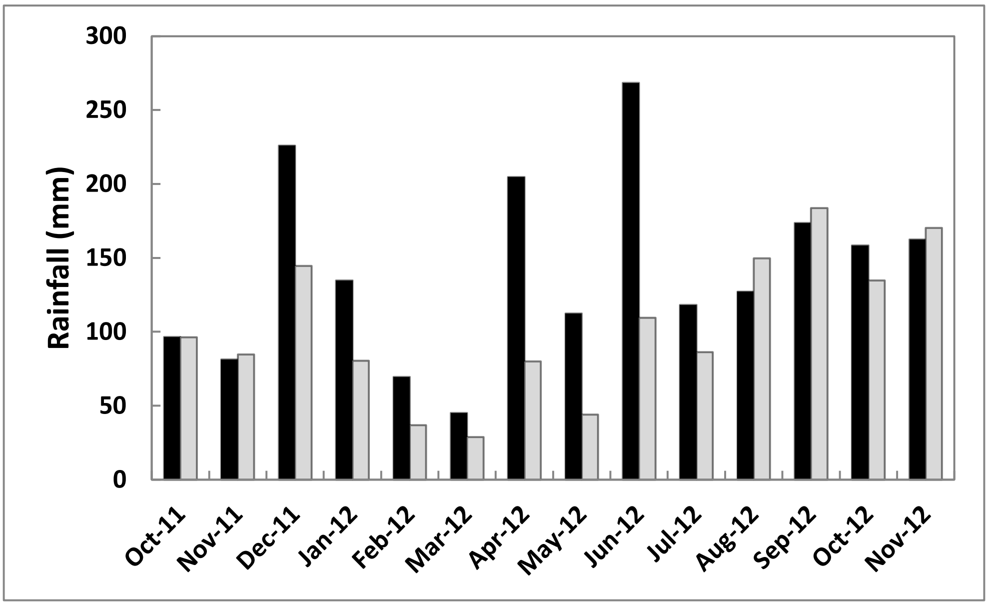

Figure 5. Monthly rainfall totals for Catchment A (black) and Catchment C (grey) between October 2011 and November 2012.