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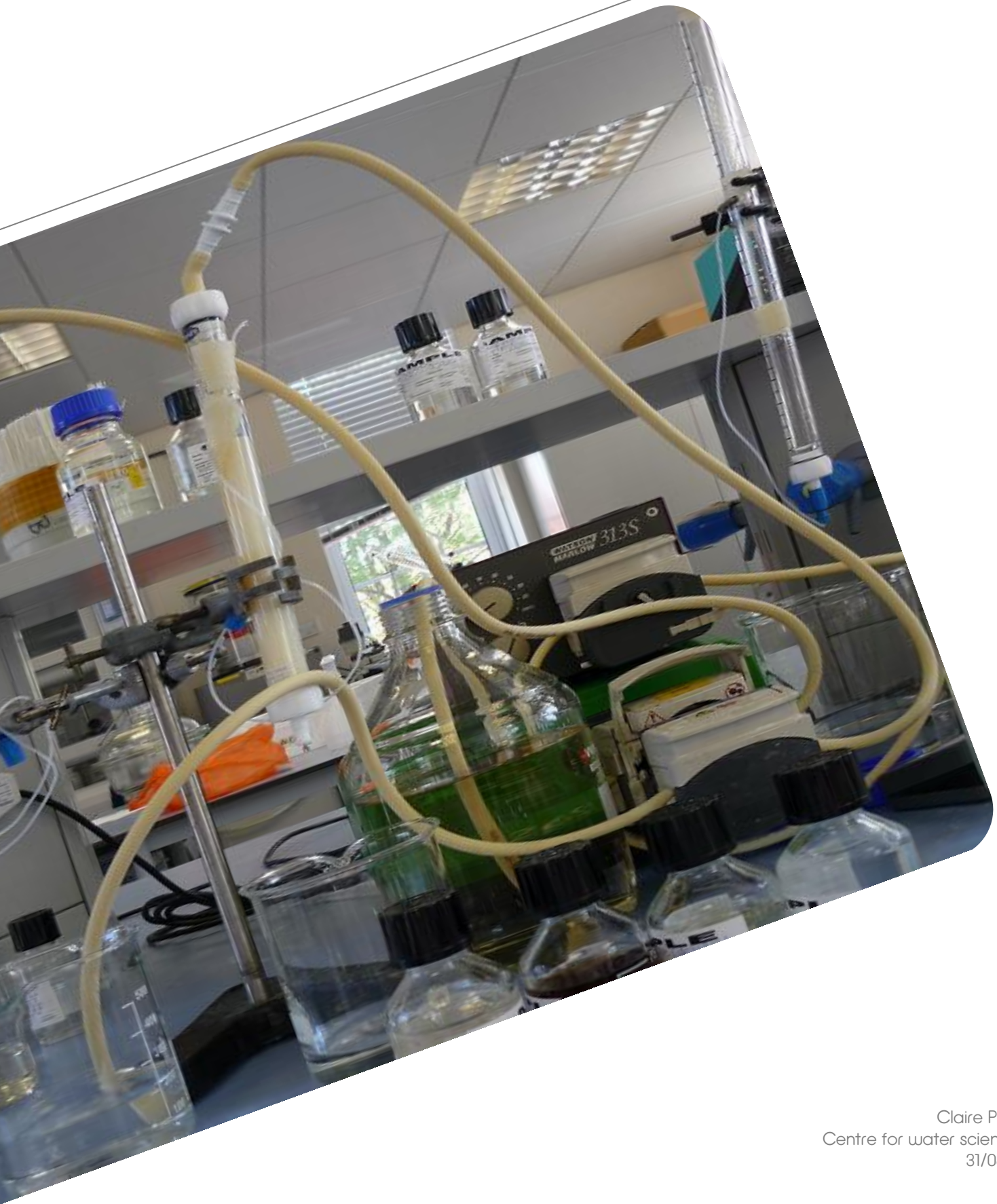
Development of a rapid fractionation tool for natural organic matter



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31/08/10

Development of a rapid fractionation tool for natural organic matter

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This project was carried out by Cranfield University for Yorkshire Water and United Utilities

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Abstract

A rapid natural organic matter (NOM) fractionation tool was developed to enable NOM to be classified by hydrophobicity at the water treatment works and in the catchment. This fractionation method uses XAD adsorption resins to remove hydrophobic (HPO) NOM from solution in 6 minutes. A review of fractionation literature identified the need for this tool, as the information provided by onsite UV_{254} monitors does not identify the seasonal changes in NOM type. This is needed to enhance effluent quality whilst optimising chemical dosage. The rapid tool was used to fractionate model compounds and natural waters, with the fractions produced compared against the traditional column fractionation procedure.

Both fractionation tools recognised the hydrophobicity of the model compounds to be tannic acid>1,3 acetonedicarboxylic acid>d-xylose which agreed with their log K_{OW} values. However, the rapid tool isolated a greater proportion of the model compound with intermediate hydrophobicity due to a higher resin concentration than in the traditional method. Both tools identified the same seasonal trend in the hydrophobicity of Butterley Reservoir, but rapid fractionations produced a lower average % HPO fraction (measured as dissolved organic carbon (DOC) removal from the solution). This was investigated by comparing the relationship between DOC and UV_{254} for control tannic acid solutions and solutions after prolonged mixing with resin. DOC leaching from the resin was confirmed by DOC concentrations of over 9mgC/L when 10mL resin was mixed with 1L ultra pure water for 72 hours. Resin leaching caused the HPO and transphilic (TPH) fractions to be overestimated in column fractionation with back elution but underestimated in rapid fractionation with mass analysis.

Keywords

NOM, XAD fractionation, rapid, adsorption isotherms, model compounds

Acknowledgements

I have been incredibly fortunate in working alongside so many fantastic individual here at Cranfield. Firstly, I would like to thank my supervisors; Dr. Peter Jarvis and Dr Bruce Jefferson, for always listening and offering sound advice whenever I popped in for a quick chat. Project discussions with Pete always led to new idea, developments and renewed enthusiasm for the project. In particular, I would like to recognise the time he has spent checking reports, presentations and results for me, despite having a million and one other pressures on his time. And to Bruce for taking a personnel interest in me, and never showing his bad cop side!

In the lab, two people have, in particularly, been vital to this work. Dr Emma Goslan, 'the fractionation queen', has trained me in XAD fractionation and has always been a friendly ear for some of my more unusual questions. Also, Emma kindly provided her results for the column fractionations of four natural waters in the Longwood WTW catchment, which have been compared against rapid fractionations within this work. A big thank you to Jane Hubble, 'the TOC queen', for the countless time she has spent, fixing and gently persuading the TOC 5000A, along with calls to engineers and all the training.

I would also like to thank my sponsors Yorkshire water and United Utilities for providing the financial support which allowed this project to go ahead. Then to everyone who has come and gone from Phd room 3, for the laughs, camaraderie, the yoga and the biscuits. And also to all those who have been a part of Tuesday meals, CSA drinks and weekend trips.

To the Pipers: my Dad and David for proof reading, and all their interest in my project; and my Granny for fortnightly packets, our long phone calls and for still being who I want to be when I grow up. Finally to Gareth, for making my world a magical place. I love you all.

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Abbreviations

AMW – Apparent molecular weights
CHA – Hydrophilic charged
C_i – Background concentration
C_o – Influent concentration
C_e – Equilbria concentration
DBP – Disinfection by product
DEAE - Diethylaminoethylcellulose
DOC – Dissolved organic carbon
DWI – Drinking water inspectorate
FA – Fulvic acids
GAC – Granular activated carbon
HAA – Haloacetic acids
HA – Humic acids
HPI – Hydrophilic
HPIA- Hydrophilic acids
HPINA – Hydrophilic non-acids
HPO – Hydrophobic
HPON – Hydrophobic neutrals
IC – Inorganic carbon
k' – Column capacity factor
K_{OW} – Octanol-Water partition coefficient
MW – Molecular weight
MWCO – Molecular weight cut off
NEU – Hydrophilic neutrals
NF- Nanofiltration
NOM – Natural organic matter
NMR – Nuclear magnetic resonance
PAC – Powdered activated carbon
TOC – Total organic carbon
TC – Total carbon
TPH - Transphilic
THM – Trihalomethane
SHA – Slightly hydrophobic acids
SUVA – Specific ultraviolet absorbance
UF - Ultrafiltration
UV_{254} – Ultraviolet light at 254nm wavelength
VHA – Very Hydrophobic acids
WTW – Water treatment works
X – Amount of solute adsorbed per unit weight of adsorbent
X_m – Monolayer capacity of an adsorbent for an adsorbate

1. Introduction

The complex mixtures of aquatic and terrestrially derived organic material, which are found in all source waters, are known as natural organic matter (NOM) (Leenheer and Croue, 2003). NOM causes a variety of problems in drinking water treatment, which include an increased coagulant demand and the residual NOM producing disinfection by products (DBPs). These problems are exacerbated by spatial and seasonal variations in NOM type and concentration (Sharp et al., 2005), and increasing NOM concentrations caused by climate change (Fabris et al., 2008).

The complexity of NOM prevents the identification of chemical and physical attributes of individual molecules, and it is instead split into molecular groups of similar NOM types (Bolto et al., 2002). Classifications based on molecular hydrophobicity are, arguably, the more useful, (Kim and Yu, 2005) as they represent the ease of separation from the aqueous phase and therefore the treatment potential at the water treatment works (WTWs). Hydrophobic (HPO) NOM is more easily removed by conventional treatments (Bolto et al., 1999) whilst hydrophilic (HPI) NOM is more likely to pass through to the final effluent (Collins et al., 1986).

In the traditional fractionation technique, acidified raw water is passed through columns containing macroporous resins, which adsorb HPO NOM, and leave HPI NOM in the effluent. This method has been successfully used to identify temporal (Goslan et al., 2002) and spatial (Wei et al., 2008) variations in NOM. However column fractionation is a non-portable and time consuming technique (taking hours per fractionation). In addition, XAD column fractionation can only be performed by trained personnel, making it unavailable for use in the catchment or at the WTWs. WTWs currently rely on UV_{254} meters to estimate NOM concentrations. However, the relationship between NOM concentration and UV_{254} absorbance is dependent on NOM type as it is the aromatic NOM species that have the greatest UV_{254} absorbance (Parsons et al., 2004). As a result, there is a need for a tool that can rapidly fractionate NOM by hydrophobicity in order to allow WTWs optimisation based on raw water NOM type and concentration.

In this study, the need for onsite NOM fractionation is addressed by using a four staged method development beginning with the traditional column fractionation and ending in a single sample rapid fractionation tool. The key differences between the two fractionation methods include the use of a batch mixed rather than plug flow resin/solution contact, and an increased resin concentration from 15mL/L to 250mL/L.

The sorption of three model compounds to three macroporous resins was assessed using the mass analysis of dissolved organic carbon (DOC) for each method development stage. The fractions created are then used to evaluate the rapid fractionation tool with respect to the column fractionation procedure, which has already proved to be a useful indicator of NOM treatability. The fractions produced using tradition column fractionation with back elution and the rapid fractionation techniques are then compared for a variety of natural waters samples to assess the ability of each technique to identify temporal and spatial NOM variability.

Finally, adsorption isotherms are used to provide information on the adsorption process. This will include identifying which adsorption model the data correlates with, and allow informed comparisons to be made between each resin.

2. Aims and Objectives

The aim of this study was to develop a rapid fractionation tool to characterise NOM based on hydrophobicity, using XAD adsorption resins. This will improve the real time monitoring of water quality with respect to NOM. Success was measured using the following objectives:

- Examine the effects of resin/solution contact method and resin concentration in order to develop a portable, rapid fractionation tool.
- Compare the fractions produced using the rapid tool with column fractionation using mass analysis for model compounds with different log K_{OW} values.
- Compare the fractions produced using the rapid tool and column fractionation with back elution for natural waters to assess their ability to monitor temporal and spatial variability.
- Explore the adsorption processes that govern the removal of HPO DOC onto macroporous resins to assess the resins fitness for purpose.

3. Literature Review: Advances and challenges in the use of XAD fractionation for NOM characterisation

3.1. Introduction

Aqueous natural organic matter (NOM) is derived from the degradation of both microbial organic material within the water itself (autochthonous) and terrestrially derived organic matter leached from soil within the catchment (allochthonous) (Croue et al., 2003; Goslan, 2003). Organic matter type is dependent upon the catchment's climate, topological features, vegetation and geological features, which control the dominant functional groups, sub-structures and molecular weight distributions of the NOM (Aoustin et al., 2001). However, the constant degradation and synthesis of NOM over time results in a near infinite variety of NOM molecules (Filella, 2009) and causes bulk samples of NOM to have no readily identifiable structure (Kukkonen et al., 1990).

In the treatment of natural waters to provide potable water that is acceptable to consumers, water treatment works (WTW) must remove NOM. If left untreated NOM can produce waters of 160 hazen units (Sharp et al., 2006a) along with taste and odour problems (Cornelissen et al., 2008). It also acts as a food source for bacteria, leading to favourable conditions for more diverse populations to develop. During the disinfection of drinking water, untreated NOM reacts with chlorine disinfectants to form disinfection by products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are probable human carcinogens (Aoustin et al., 2001; Kitis et al., 2002; Wigle and Lanphear, 2005). As a result, DPB levels are now regulated in many countries (for example the USA regulates THMs and HAA, to 80µg/l and 60µg/L respectively (Singer, 1999)) and there has been increased research into the types and concentrations of DBPs created by different types of NOM (Galland et al., 2002; Liang and Singer, 2003) and disinfectants (Goslan et al., 2009). A recently published report produced for the Drinking Water Inspectorate (DWI) stated that if England and Wales (who currently regulate THMs at 100µg/L and do not regulate HAAs) had a similar standard to the US, that they would expect a high number of exceedences (DEFRA, 2008; Goslan et al., 2009).

The presence of NOM is also problematic within the WTW. It has a high coagulant demand and causes flocculation problems due to the fragile, open structures of the complexation flocs formed after charge neutralisation of the NOM (Jarvis et al., 2005). This increases the required coagulant dose and creates flocs, which are more difficult to remove using conventional floc removal processes. If membrane technology is used in water treatment, NOM can cause membrane fouling (Hong and Elimelech, 1997; Lee et al., 2004; Zularisam et al., 2006). All of the above increase the costs of water treatment. These problems are not caused uniformly for all NOM. Molecular size, structure and NOM hydrophobicity all alter: the ease of removal from solution; coagulant demand; membrane fouling potential; the DBP formation potential. Therefore NOM type, as well as concentration, must be determined to allow treatment to be maximised at a minimised cost.

3.2. Aims and Objectives

With infinite variations in the type of NOM molecules present in a water sample, successful monitoring of NOM removal capabilities can only be established for groups of similar (either physically or chemically) NOM molecules as opposed to individual molecules. Various characterisation procedures have been developed to achieve this, including membrane separation (reverse osmosis, ultrafiltration and nanofiltration), adsorption resins and ion exchange resins. After treatment, NOM concentration is monitored by analysis of dissolved organic carbon (DOC) content. This review will concentrate on the use of macroporous adsorption resins (collectively termed XAD adsorption resins), which rely on their high surface areas and active sorption sites to remove NOM from the aqueous phase, deemed the current state of the art method for NOM fractionation by Kim and Yu (2005).

The fractionation of NOM using XAD adsorption resins has been developed over the past three decades and as a result, researchers have developed different approaches all based on the original methods established by Leenheer and Huffman (1976) and Malcolm and MacCarthy (1992). While the usefulness of the technique is in part due to its versatility, the lack of a clear unambiguous method reduces comparability between studies as altering experimental parameters produces different fractions. It also leads to the potential for errors in the choice of the method selected and the

experimental conditions. In an attempt to overcome this, the objectives of this review are to:

- Examine the need for characterisation of NOM and the usefulness of fractions.
- Provide an overview of the different fractionation techniques.
- Identify the sorption process gaps of XAD fractionation.
- Detail the variations in methods used for XAD fractionation.
- Allow selection of the best methods for analysis to provide fractions most useful for purpose.

3.3. NOM at the WTWs

3.3.i. Treating NOM

The conventional drinking water treatment procedures of coagulation (with alum or ferric) and flocculation or filtration successfully remove a range of pollutants and are often all that is required to remove NOM to below the discharge consent levels. If the required NOM removal cannot be achieved, coagulation may be enhanced. This may include the strengthening of NOM floc structures with the addition of synthetic polymers (Jarvis et al., 2006). When increased NOM loading occurs, an increased coagulant dose and improved pH control of the raw water are commonly used in efforts to maintain effluent quality. However, increased coagulant and chemical usage increases treatment costs whilst lower coagulant pH increases the water's corrosive nature (Yan et al., 2009).

Coagulation does not treat all NOM to the same extent and considerable variations in DOC removal by coagulants are seen in laboratory and plant scale facilities due to variations within the NOM (Collins et al., 1986). Allochthonous material is dominated by non-polar hydrophobic humics, which have large molecular weight, a more aromatic structure, and a low nitrogen content (Croue et al., 2003). These generally show greatest removal by coagulation (Collins et al., 1986; Bolto et al., 1999) and when this type of NOM dominates source waters, coagulation alone may be sufficient to limit problems such as DBP formation (Bond, 2009). However, autochthonous NOM (which tends to have a lower molecular weight, increased polarity, nitrogen and carboxyl groups (Croue et al., 2003; Goslan, 2003)) has a greater affinity for water (hydrophilic) making its removal at WTW's more difficult.

Bursill et al. (2002) reports that even with careful optimisation of enhanced coagulation, NOM removal in excess of 60% is difficult to achieve in typical South Australian waters.

In order to assess the feasibility of alternative NOM removal techniques, Bolto et al., (2002) tested the removal of NOM fractions from a variety of water types using alum coagulation, anion exchange resins and cationic polymers. In agreement with other studies (Collins et al., 1986; Matilainen et al., 2002; Mesdaghinia et al., 2006; Pivokonska et al., 2008; Soh et al., 2008) water fractions containing NOM of a higher molecular weight, and high humic content were treated most effectively by conventional alum coagulation. In contrast, the more hydrophilic, smaller NOM was treated more effectively by ion exchange resins (Bolto et al., 2002). In another study the use of powdered activated carbon (PAC) alongside enhanced coagulation increased NOM removal from 45% to 76%, compared with sole use of enhanced coagulation (Uyak and Toroz, 2007). The PAC was able to remove more of the lower weight and neutral NOM that was untreated by enhanced coagulation.

Therefore, by combining treatments a wider variety of NOM types can be removed, reducing final effluent concentrations. For this reason add on treatments such as MIEX (Mergen et al., 2008; Singer and Bilyk, 2002), activated carbon (Cheng et al., 2005), membranes (Siddiqui et al., 2000) and advanced oxidation (Ho et al., 2002), are often employed to coagulation sites when this alone cannot meet removal demands. The most suitable add-on treatment can only be selected if NOM type and variability of the individual WTWs is fully understood. Tertiary treatments also act to reduce coagulant requirements thereby limiting chemical use important on economic, environmental and health grounds (Fabris et al., 2008).

3.3.ii. Monitoring NOM

For treatment to be successful and to identify the limits of coagulation, the raw water concentration of NOM to a WTW must first be identified. NOM concentrations in natural waters are often below 10mgC/L (Bolto et al., 2002), but vary both spatially and temporally and peaks over 20mgC/L are not uncommon (Figure 1). Increasing concentrations of NOM over the last two decades have been recorded worldwide due to more extreme weather events caused by global warming (Fabris et al., 2008). Whilst no rapid measure of NOM concentration is available, UV absorbance at

254nm (UV_{254}) has been shown to be a good surrogate measure for DOC (Figure 1) (Goslan, 2003; Mesdaghinia et al., 2006) and UV_{254} monitors are widely used onsite to estimate raw and treated NOM levels and thus determine site operation requirements.

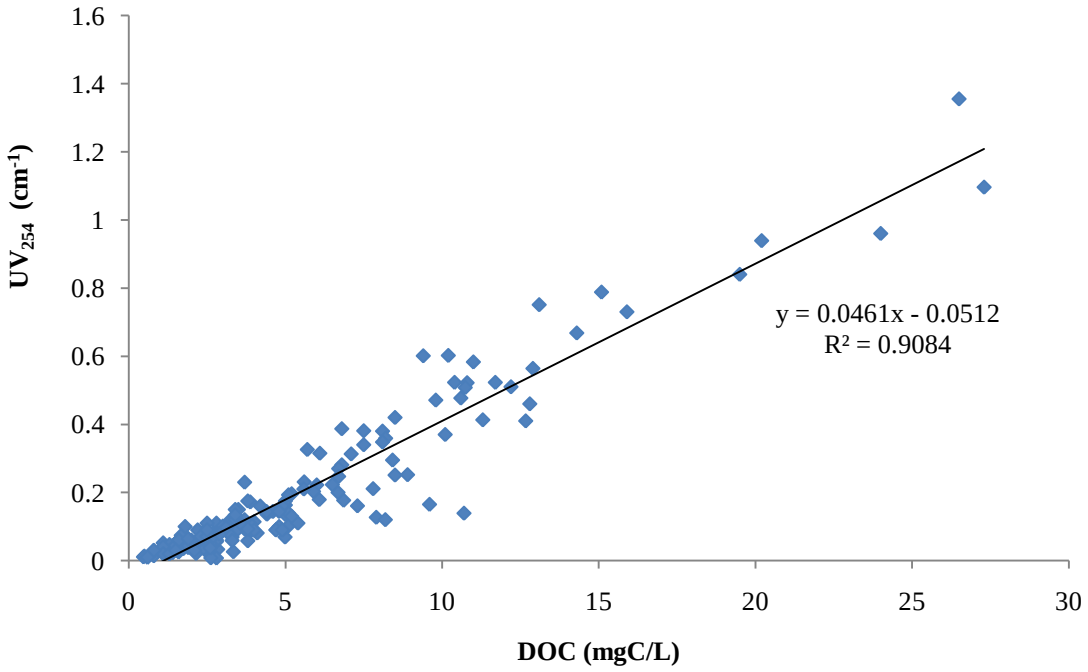


Figure 1: A comparison of UV and DOC data from 171 natural water samples with varying NOM types. UV shows strong correlation with DOC and can therefore be used as a surrogate for DOC measurements. Adapted from (Goslan, 2003)(Kitis et al., 2002; Lee et al., 2004; Fabris et al., 2008; Allpike et al., 2005; Boyer and Singer, 2005; Kim et al., 2006; Uyak and Toroz, 2007; Cho et al., 1998; Fearing et al., 2004; Gallard and Von Gunten, 2002

-Ritter et al., 1999; Volk et al., 2000; White et al., 1997; Pivokonska et al., 2008; Soh et al., 2008; Singer and Bilyk, 2002; Gjessing et al., 1999).

Variation in the UV_{254} absorbance of different NOM types

UV_{254} absorbance is largely the result of the aromatic functional groups within NOM of a more hydrophobic (HPO) nature. It can therefore underestimate NOM content when the water has a higher proportion of lower aromatic, more hydrophilic (HPI) NOM. 96 natural waters were fractionated into HPO NOM and HPI NOM using XAD adsorption resins (Figure 2). In general, waters with a higher total DOC content (above 11mg/L) were at least 50% HPO in nature. This corroborates previous research which suggests peaks in NOM concentrations are caused by storm run off of allochothonous (HPO) material (Scott et al., 2001). Interestingly, the results showed a different correlation between DOC (mgC/L) and UV_{254} absorbance for waters which

were over 50% HPO to waters ≤50% HPO. The DOC concentration of water with over 50% HPO DOC can be estimated using UV_{254} (r^2 = 0.95) (Figure 2). However, in waters of a lower HPO content, the relationship with UV was weaker (r^2 = 0.59). If NOM type is unknown, an incorrect conversion between UV_{254} and DOC may be used resulting in the underestimation of DOC concentrations for HPI waters. This underlines the importance of the need for improved onsite monitoring of NOM type.

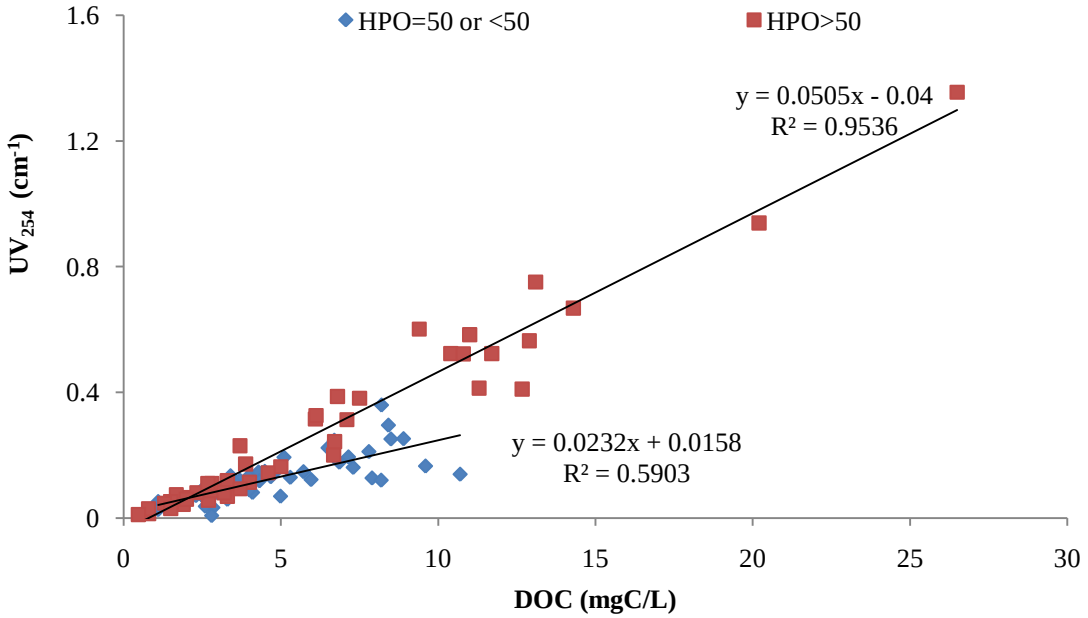


Figure 2: DOC and UV data from 96 source waters. Two data sets are created showing waters with predominate HPO fraction (>50%) (45 natural waters) and those of a lower HPO NOM (51 natural waters) complied from 17 sources (Croue et al., 2003; Kitis et al., 2002; Lee et al., 2004; Boyer and Singer, 2005; Cho et al., 1998; Fearing et al., 2004; Goslan et al., 2004; Hua and Reckhow, 2007; Liang and Singer, 2003; Mergen et al., 2008; Song et al., 2009; Zazouli et al., 2007; Imai et al., 2001; Siddiqui et al., 2000; White et al., 1997; Pivokonska et al., 2008; Roe et al., 2008)

SUVA (specific ultra violet absorbance) (expressed as the ratio of UV_{254} and DOC in $m^{-1}L\ mg^{-1}$ C) is a measure of the UV_{254} absorbance of a molecule or group of molecules and was shown by Edzwald and Tobiason (1999) to correlate well with the nature of the organic matter and aromatic content of NOM (Parsons et al., 2004). A comparison of the SUVA with the % DOC within the HPO fraction has been completed for 96 natural waters (Figure 3). Edzwald et al. (1999) suggests SUVA values greater than 4 represent a dominance of HPO NOM whilst values below 3 indicate the predominance of HPI NOM (Volk et al., 2000; Edzwald and Tobiason, 1999), which is in agreement with the data shown in Figure 3. As the % DOC in the HPO fraction increases, so does the SUVA (r^2=0.47). Species with a SUVA value of

3<x<4 have an intermediate hydrophobicity and are termed transphilic (TPH). While SUVA provides a crude estimate of NOM type, data shows a wide variability from the line of best fit. It therefore has limited value in providing an accurate assessment of NOM type.

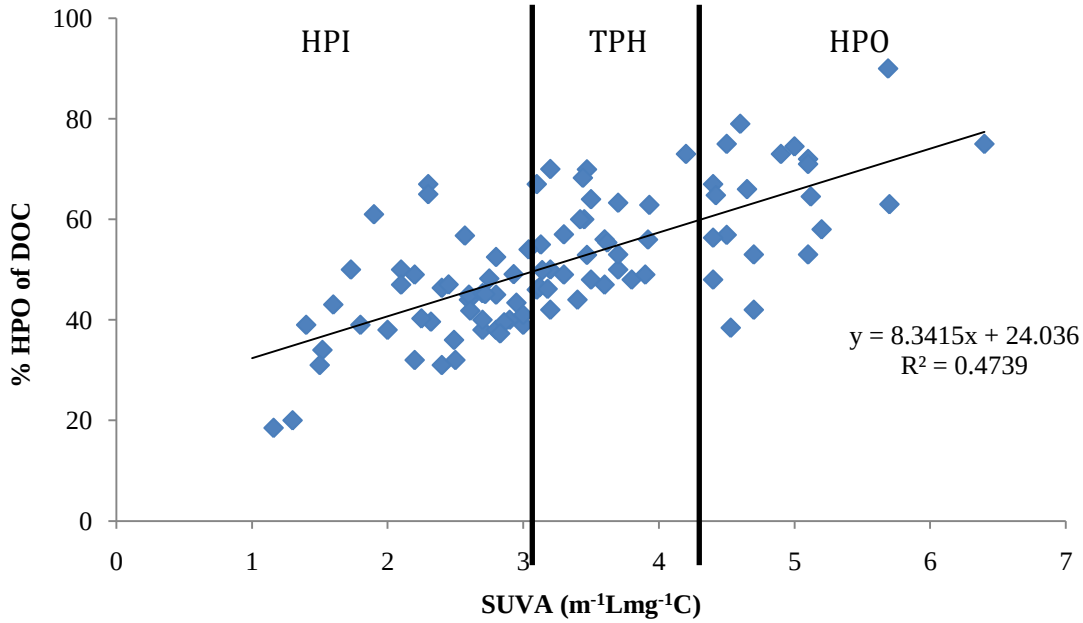


Figure 3: As the % HPO content of water increases so does the SUVA. This shows the dominance of aromatic compounds within the HPO fraction. Data compiled from 17 sources (Croue et al., 2003; Kitis et al., 2002; Lee et al., 2004; Fabris et al., 2008; Boyer and Singer, 2005; Cho et al., 1998; Fearing et al., 2004; Goslan et al., 2004; Hua and Reckhow, 2007; Liang and Singer, 2003; Mergen et al., 2008; Song et al., 2009; Zazouli et al., 2007; Imai et al., 2001; White et al., 1997; Pivokonska et al., 2008; Roe et al., 2008).

If UV_{254} is used as the only measure of NOM entering a WTW, changes in the type, treatment potential and concentration of NOM may not be detected, leading to a reduction in plant optimisation and potentially effluent quality. For example raw water samples from Draycote WTW (Mergen et al., 2008) and Silver Lake, Colorado (Siddiqui et al., 2000) have similar UV_{254} absorbance ($0.139cm^{-1}$ and $0.23cm^{-1}$ respectively) but very different DOC concentrations (10.7mgC/L compared to 3.7mgC/L) that would not be recognised using UV_{254} measurements. Analysis of the HPO fraction content of the raw water (20% and 65%) was able to pick up this difference between the water qualities. Therefore, UV_{254} cannot be used to give a reliable estimation of NOM concentration or the coagulant dose required to give a good quality final effluent unless NOM type is already known.

3.4. Adsorption Methods for Characterising NOM

Given the limitations of UV_{254} and bulk DOC analysis of raw waters in assisting with coagulant dose control, other techniques are required to classify NOM by type. Ideally these would include the rapid isolation and purification of each chemical species within NOM without a reduction in recovery (Serkiz and Perdue, 1990) or a change in the original state of the NOM (Peuravuori and Pihlaja, 1998b). This is an unobtainable ideal due to the amount of NOM species and as all isolation processes are also concentration processes (Croué et al., 1999). Instead, NOM is commonly fractionated and isolated into groups of different chemical or physical characteristics (Bolto et al., 2002). The fractions produced are dependent upon the method used. Choice of method must be dictated by the ability of the fractions produced to answer the research question with the fewest drawbacks. However, method repeatability and the ability to perform inter-study comparisons must also be considered.

The most commonly used NOM fractionation techniques are based on adsorption resins. Adsorption techniques are all based on similar theories. They aim to isolate NOM from the aqueous solution onto a variety of different, high surface area media. This is generally achieved by controlling the pH of the solute, thereby altering the solubility (or hydrophobicity) of different NOM compounds allowing preferential sorption and concentration onto the media dependent on the conditions used.

3.4.i. Types of adsorbents

Granular activated carbon (GAC) is commonly used as an adsorbent of NOM at the WTWs (Parsons and Jefferson, 2006). However, when the motivation of NOM adsorption is for classification purposes, not water purification, resins are often used as the adsorption media. These resins can remove both smaller NOM molecules than GAC (Gusler et al., 1993) and can be manufactured to produce NOM fractions most useful for specific requirements (Faust and Aly, 1987). Other advantages of the use of resins for analytical purposes include a low energy process in which selective adsorption can be achieved on a homogenous surface with a high surface area (Leenheer and Huffman, 1976).

Resins include macroporous resins (such as the XAD adsorption resins) in which NOM is held to the surface using weak partial bonds (dipole, Van der Waal) and ion exchange resins (stronger ionic bonds) (Table 1). In general, both resin types are

based on either a styrene (XAD-4, Bio-Rad AG-MP-50) or acrylic (DAX-8, XAD-7HP) structure (Figure 4), and this material choice affects the chemical properties of the resin. Acrylic resins tend to have greater hydrophilicity than styrene structures (Aiken et al., 1992) whereas styrene structured anionic exchange resins show a greater affinity for aromatic NOM than those of an acrylic structure (Cornelissen et al., 2008; Humbert et al., 2005).

Table 1: A comparison of properties and fractions produced for XAD and ion exchange resins.

Resin type	Resin Name	Resin properties	Fraction Sorbed	Reference
Macroporous adsorption XAD resins	XAD-8	Acrylic ester of slight polarity, surface area = 140m^2/g	HPO	Malcolm and McCarthy (1992)
	DAX-8	Acrylic ester of moderate polarity, surface area=160m^2/g	HPO	Bolto et al., (1999)
	XAD-7HP	Acrylic ester of weak polarity, surface area=380m^2/g	HPO	Goslan et al., (2002)
	XAD-4	Styrene-divinylbenzene Aromatic polymer, non-polar, Surface area=725m^2/g	TPH/HPI acids	Croue et al., (2000)
Ion exchange resins	BioRad AG-MP-50	Strong acid sulphonated polystyrene, cation exchange resin	HPI bases	Leenheer (1981)
	Duolite A-7	Weak base phenol-formaldehyde condensation product, anion-exchange macroporous resin	HPI acids	Leenheer (1981)
	Diaion WA 10	Weak anion exchange resin (alkylamine) on polystyrene, gel matrix	HPI acids	Mahaba et al., (2003)
	IRA-958	Macroreticular, Strong anion exchange on polystyrene	HPI charged fraction	Bolto et al., (1999)
	Dowex 50W X-8	Strong cation exchanger resin, gel matrix on polystyrene	HPI bases	Peuravuori and Pihlaja, (1998)
	DEAE cellulose	Diethylaminoethylcellulose, weakly basic anion exchanger	HPO & HPI	Peuravuori and Pihlaja, (1998b)

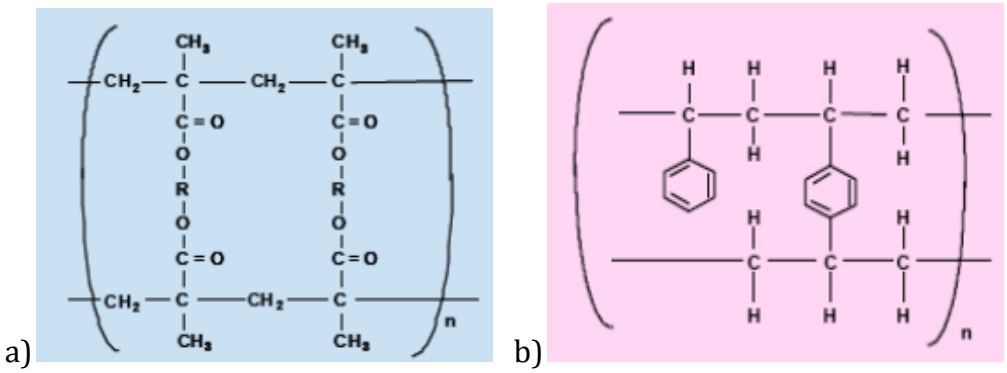


Figure 4: Chemical structure of a) Amberlite XAD-7HP and b) Amberlite XAD-4. Adapted from Rohm and Haas specification sheets

Macroporous XAD adsorption resins

All macroporous XAD adsorption resins (such as those outlined in Table 1) rely on hydrophobic/hydrophilic interactions between the resin and solute (Peuravuori and Pihlaja, 1998b). As previously identified, the hydrophobicity of NOM has a major control on water treatability at the WTWs. Therefore, the use of adsorption resins is particular suited to identifying removal potential.

XAD adsorption resin fractionation exploits differences in polarity, and therefore aqueous solubility, of NOM. As water is a polar solvent it forms strong hydrogen bonds with polar orgaincs, which are thus referred to as hydrophilic (HPI). Non-polar organics (termed hydrophobic (HPO)) are unable to interact in this way causing them to be partially separated from the aqueous phase. For HPO molecules Van der Waal forces then become the dominant attraction force, enabling non-polar molecules to adsorb to resins with large surface areas. Disassociation tendencies within NOM functional groups can be controlled by pH. Van der Waal forces dominate in acidic conditions (causing adsorption to the resin), whilst stronger dipole forces prevail in alkaline conditions, increasing NOM preference for the aqueous phase. These basic principals control the separation of NOM onto XAD resins.

Ion exchange resins

The key differences between ion exchange resins and other macroporous adsorption resins are in the forces controlling adsorption. Whereas Van der Waal and dipole forces drive resin interactions in the XAD adsorption resins, ion exchange resins target groups of molecules within the NOM and result in a transfer of charge that causes the NOM (and accompanying inorganic salts) to bind to the resin with ionic bonding. These fractions are then eluted using solvents and pH reversal (Marhaba et al, 2003) to create fractions of acidic and basic characteristics. The major drawback to the use of ion exchange resins is that inorganic salts will sorb to the resin as well as NOM (Aiken et al., 1992). This can reduce % NOM removed to the resin and the reusability of the resin, as the inorganic salts compete for sorption sites and may not be desorbed from the resin as easily as NOM species. In brackish water these salts were shown to interfere with the retention of smaller NOM molecules onto DEAE (Peuravuori and Pihlaja, 1998b). Due to their different adsorption process, XAD resins do not adsorb these smaller molecular weight inorganic salts.

Choosing resins for characterisation purpose

NOM sorption to resins is influenced by surface area (controlling the number of adsorption sites), pore sizes (only NOM able to enter the pore spaces has access to all sorption sites) and the number of cross links (Gusler et al., 1993). XAD adsorption and ion exchange resins can be used in isolation or in series in numerous resin combinations. Each resin will separate NOM into two unique fractions (the sorbed and desorbed fraction). For example, after initially splitting NOM into a HPO and HPI fraction using XAD-8, ion exchange resins can further classify each fraction into acid, basic and neutral components (Leenheer, 1981). By carefully controlling operational parameters, the versatility of adsorption resins can be fully realised to investigate multiple hypotheses.

Choice of adsorption resin is a key factor in controlling species isolation. The level of adsorption is partially controlled by resin particle size, as this affects the adsorbate's access to adsorption sites. As resin particle size increases, there is a reduction in exchange capacity with the solution, leading to a reduction in breakthrough time (the time taken for a substance to be present in the column effluent) (Cornelissen et al., 2008). A higher water content causes the resin to have a more open structure, thus allowing larger NOM particles more access to sorption sites and enhancing NOM adsorption (Cornelissen et al., 2008). Therefore, in general, fully wetted resins are used through absorption procedures. For example, the pore size of hydrated XAD-8 resin is in excess of 250A, allowing NOM complete access to its surface area (Malcolm, 1989) as most NOM molecules are much smaller than 250A. In contrast, XAD-4 is shown to exhibit problems in uptake of larger NOM, which are thought to block pore spaces (Malcolm and MacCarthy, 1992).

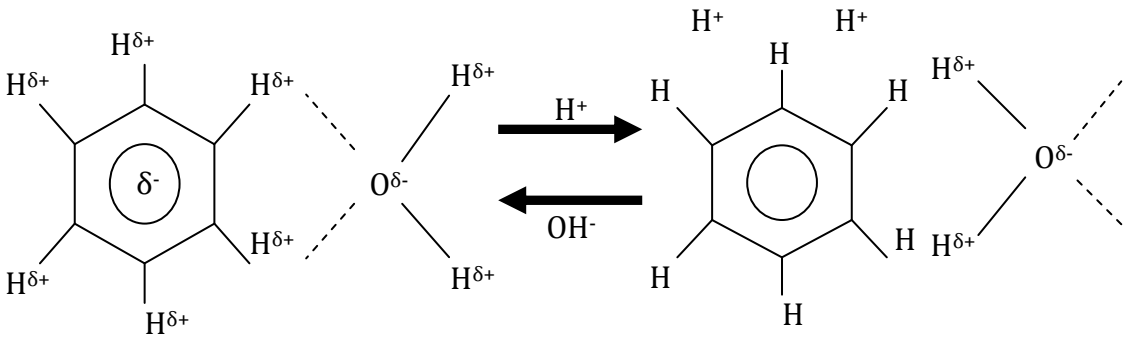
Resin structures may be customised to create preferential adsorption under different conditions (Gusler et al., 1993). For example, the addition of an acetyl group onto XAD-4 increased its equilibrium adsorption capacity for phenols by 20% (Li et al., 2001). XAD-8 is specific for hydrophobic solutes and showed no measureable adsorption of hydrophilic solutes (Leenheer and Huffman, 1976).

3.4.ii. The sorption of NOM to XAD adsorption resins

NOM can exhibit hydrophobic or hydrophilic tendencies depending upon the experimental conditions, with only those molecules hydrophobic enough relative to

the sorbing resin at the chosen pH and contact time (or flow rate) able to adsorb (Peuravuori and Pihlaja, 1998b). As a consequence, the fractions produced by adsorption resins are operationally defined (Chow et al., 2005). Contact time is commonly controlled by placing a known volume of resin in a glass column and passing the NOM solution through it at a constant flow rate. With resin type also constant, pH is the variable used to control sorption.

At raw water pH, NOM species of varying solubility are held in solution due to hydrogen bonding and dipole forces between the partially charged water molecules and NOM surfaces (Figure 5). When the pH of the solute is lowered, (generally using 0.1M HCl) the degree of ionization of acidic groups in NOM (such as humics and fulvics) decreases, and the overall charge of the molecule becomes less negative or neutral (Croué et al., 1999) (Figure 5). These uncharged conjugate species are now non-polar and therefore hydrophobic substances (Malcolm, 1989). From contact angle theory (of which a full review is given in Good (1992)), polar water will then favour reactions with itself (hydrogen bonds), reaching a system of maximum entropy when there is a minimal interface between the water and the non-charged species, known as phase separation.



Phenol is soluble in water at higher pH due to the partial dissociation of its H atoms allowing it to interact with water molecules to form hydrogen bonds

At lower pH, phenol no longer dissociates due to the higher concentration of H^+ ions in the solution. It can no longer form hydrogen bonds with the water and its relative hydrophobicity increases.

Figure 5: Phenol in its dissociated and conjugate states. Phenol is used to represent a simple NOM molecule

In its conjugate state the NOM molecule becomes more compact, as previous electrostatic repulsion between ionized functional groups are minimized (Croué et al., 1999) and this acts to increase apparent sorption capacity of the resin. Adsorption is the primary binding mechanism in the removal of NOM onto XAD adsorption resins

(Leenheer and Huffman, 1976) and is controlled by three steps: the transport of the NOM from bulk solution to the exterior of the resin; solute diffusion into pores of the adsorbent; adsorption of the solute onto the internal pore surface (Faust and Aly, 1987). The first step is generally considered to be the result of Van der Waal forces (Leenheer and Huffman, 1976) although for resins with polar surfaces (such as XAD-12) hydrogen bonding and aromatic π-electron bonds may also be important (Croué et al., 1999). The second step can be considered as molecular diffusion into the stagnant film of liquid surrounding an adsorbent particle (Cooney, 1998). The final step is rapid and therefore does not influence the overall kinetics of adsorption (Faust and Aly, 1987).

The adsorption of NOM onto a resin column is best understood by considering a model compound solution. Adsorption is first concentrated at the top of the resin column, but as sorption sites fill, this portion of the column can be considered exhausted and the adsorption zone (Cooney, 1998) or mass transfer zone (Faust and Aly, 1987) moves down the column (Figure 6). In this way maximum loading of the resin is achieved, and the system can be considered as a series of layers in contact with solution of decreasing concentration with height in column (Faust and Aly, 1987).

When the adsorption zone reaches the bottom of the resin column the maximum capacity of the resin to sorb the compound is reached, and the effluent concentration begins to rise (Croué et al., 1999). This is known as column breakthrough. Breakthrough time is dependent on the affinity of the compound for the resin, the amount of resin, and the flow rate. The shape of the breakthrough curve is controlled by the sorption kinetics, with steeper slopes indicating rapid film transfer or internal diffusion, and flatter adsorption isotherms (Faust and Aly, 1987). When the effluent concentration is equal to the influent concentration (C_o) the column is in equilibrium and sorption and desorption occur at the same rate. The breakthrough curves become much more complex when mixed compounds are considered, due to different adsorption rates for different molecules and competition between molecules for adsorption sites.

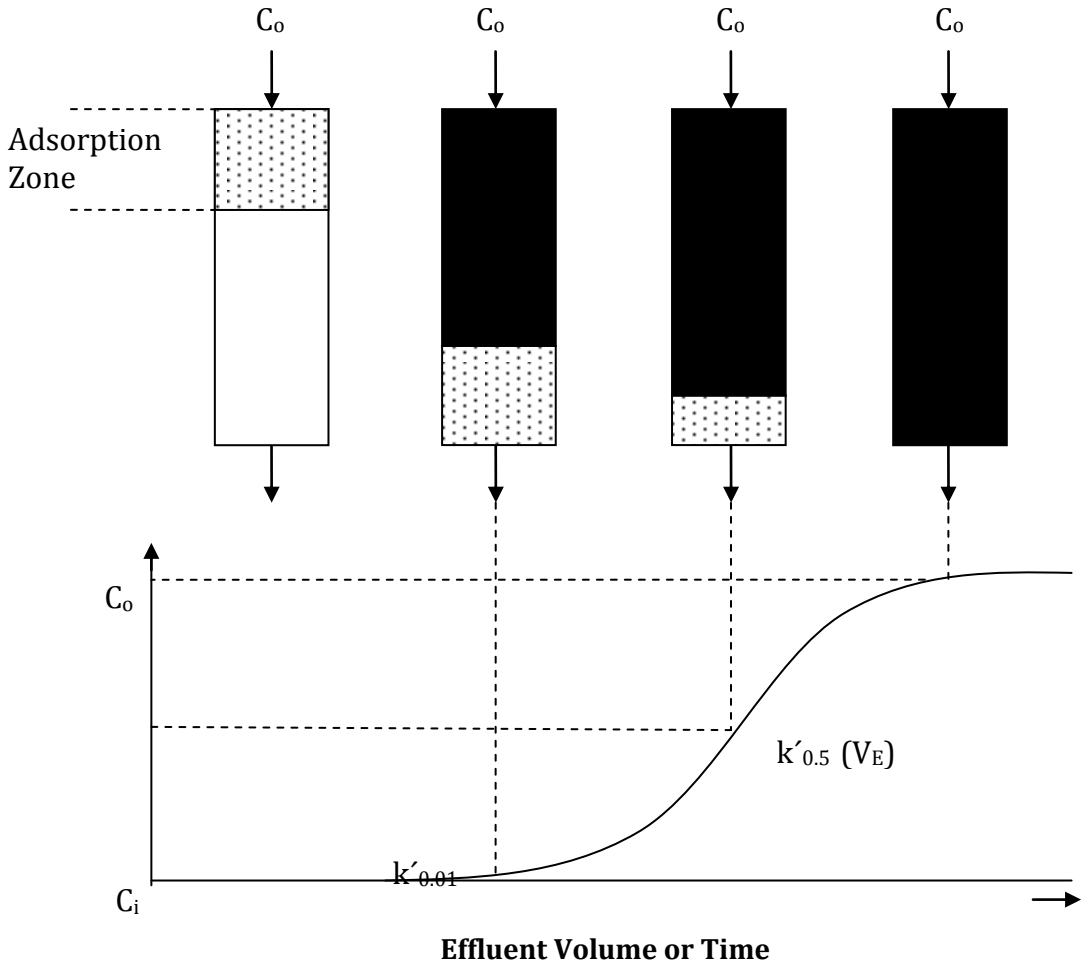


Figure 6: The effect on the effluent concentration of model compound as the adsorption zone passes through the column. Adapted from Malcolm and MacCarthy (1992) and Cooney (1998). $k'_{0.01}$ refers to the initial breakthrough of the solution, above background concentration (C_i). V_E refers to the point at which the effluent of the model compound reaches an undesirable level and the process is stopped. Each NOM compound produces a concentration curve of differing gradient, dependent on the compounds affinity for the resin.

Column capacity factor (k´)

In XAD resin adsorption studies, the ability of the resin column to adsorb the influent solution is defined by the column capacity factor k´:

k´ = (mass of solute sorbed on resin) / (mass of solute dissolved in water) **Eq. 1**
Leenheer, (1981)

At $k'_{0.5}$ the effluent concentration is at 50% of the influent concentration (after subtracting the background concentration (C_0-C_i). In the separation of the HPO fraction of NOM the value $k'_{0.5}$ is generally accepted to be the column capacity for humic adsorption, as at this point more than 95% of humics are adsorbed to the resin (Leenheer, 1981; Malcolm, 1989; Malcolm and MacCarthy, 1992). Resin column and

flow rates are generally controlled to maintain this k´ value with the assumption that the solution to be tested is 50% HPO (Goslan, 2003; Leenheer, 1981). The capacity factor at $k'_{0.5}$ was calculated for 20 different model organic solutions by Thurman and Malcolm (1978) and used to compare their sorption to XAD-8 resin. The results suggested XAD-8 resin favours different functional groups in the order: $-CH_3$>-CO_2H>-CHO>-OH$\geq$$NH_2$ which is an inverse solubility trend (Thurman, 1978).

3.4.iii. Resin regeneration

Backwashing of the resin with a high pH solution (such as 0.1M NaOH) favours the reverse reaction of dissolution causing an increase in polarity of the NOM species. As a result, the sorbed NOM becomes more hydrophilic with resulting dipole and hydrogen bonding able to overcome the Van der Waals forces between the NOM and resin surface, causing elution from the resin. The resin may then be returned to a low pH, to regenerate it for further use. This method will not remove 100% of the sorbed NOM as a small portion of NOM, termed the hydrophobic neutral fraction (Goslan et al., 2002), will remains on the resin as is none polar regardless of pH. Also, if NOM is fractionated directly onto XAD-4, the larger humic molecules interact strongly with XAD-4 even at pH 13 and can therefore not be desorbed easily (Aiken et al., 1992). Complete NOM removal and resin regeneration can be achieved using Soxhlet extraction as in Leenheer, (1981).

3.4.iv. Adsorption isotherms

The NOM removed by the resin at equilibrium sorption (C_o) can be calculated for different solution concentrations and used to plot an adsorption isotherm. The shape of this isotherm gives important information on the surface coverage of the adsorbent by the adsorbate (Faust and Aly, 1987). Adsorption in aqueous systems is commonly modelled using the Langmuir or Freundlich equations:

The Langmuir adsorption isotherms is expressed as: $$X = \frac{X_m b C_e}{1 + bC_e}$$ **Eq. 2**

The Freundlich adsorption isotherm by: $$X = KC_e^{1/n}$$ **Eq. 3**

The modified Freundlich equation by: $$X = K(C_e/D)^{1/n}$$ **Eq. 4**

(Faust and Aly, 1987)

Where X = the amount of solute adsorbed (x) per unit weight of adsorbent (m); C_e = equilibrium concentration of the solute; X_m = monolayer capacity; and b, D, K, and n represent constants.

The main difference between the models is that whereas the Langmuir model assumes a monolayer adsorption in which the specific adsorption sites have equal adsorption energy, the Freundlich model is an empirical model that allows for heterogeneity in adsorption sites and multi-layer adsorption (Parsons and Jefferson, 2006). In the modified form of the Freundlich equation, equilibrium concentration is normalised against adsorbent dose and this allows comparisons of different experimental conditions or solution mixtures (Bond, 2009). In general, studies of organic molecule adsorption onto both macroporous resins and activated carbon show similar adsorption mechanisms with a best fit with Freundlich models with multi-component systems (such as NOM) fitting the modified Freundlich model well (Ucer et al., 2005; Sun et al., 2008; Wand et al., 2010). There is some evidence of a more complex sorption mechanism for some resins, with resin swelling suggestive of some absorption into the resin polymer matrix in cross linked resins XAD-12 and Reillex-425 of lower surface areas (Gusler et al., 1993).

3.5. The Development of Adsorption Fractionation

Macroporous resin adsorption was first utilised for NOM fractionation by Leenheer and Huffman (1976) (Figure 7) in an effort to monitor changes in water quality caused by increased fossil fuel consumption. A series of XAD adsorption resins and ion exchange resins were evaluated for adsorption characteristics using model compound solutions. A stratified column containing XAD-8 and XAD-2 was also used to successfully fractionate three natural waters into HPO acid, neutral and basic fractions and a HPI fraction (Leenheer and Huffman, 1976). The classification scheme proposed in this study was developed further by Leenheer (1981) using XAD-8, Bio-Rad AG-MP-50 and Duolite A-7 resins in series to produce six NOM fractions named (HPO/HPI acids, bases or neutrals) according to the predominant property of the fraction (Leenheer and Croué, 2003). Isolation of different and more meaningful NOM groups was a major purpose of the study by Leenheer (1981) and this was achieved, with only strongly hydrophilic, neutral, simple structures remaining in the effluent of all three columns (Peuravuori and Pihlaja, 1998b).

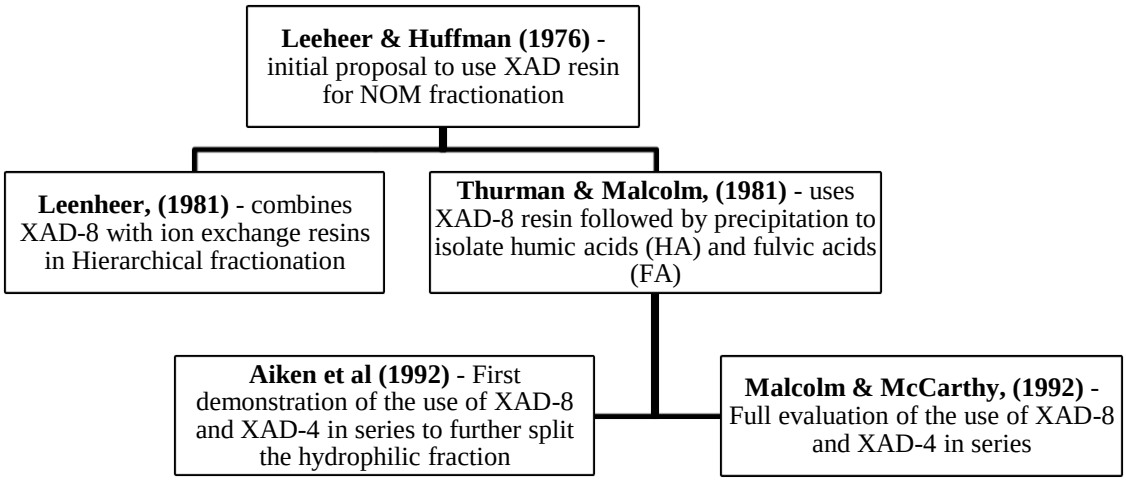


Figure 7: The development of the XAD adsorption resin fractionation procedure

The use of XAD-8 in isolating the HPO fraction has been accepted as the preferred method and is successfully used throughout the literature (Kitis et al., 2002; Gadmar et al., 2005). Adsorption at different pHs can be used to produce fractions with a range of hydrophobicities. However, in NOM fractionations, solutions are commonly acidified to pH2, as this maximises hydrophobicity without causing precipitation of the humic material. After fractionation with XAD-8 the HPO fraction can be further classified into humic acids (HA) and fulvic acids (FA), with HA precipitating when the pH is lowered to 1 (Thurman and Malcolm, 1981). The US Geological Survey and the International Humic Substances Society have adopted this method to produce international standards and reference material of fulvic and humic acids (Town and Powell, 1993; Ma et al., 2001; Gadmar et al., 2005).

In contrast, the isolation of the hydrophilic (HPI) materials is more challenging due to its preference for the aqueous phase, and as a result a wider range of methods have been developed. These include alternative ion exchange resins (Peuravuori and Pihlaja, 1998b; Imai et al., 2001; Marhaba et al., 2003), gel chromatography (Thurman and Malcolm, 1981) and the increasingly preferred use of XAD-4. This was first utilized by Aiken et al., (1992) with a subsequent thorough evaluation by Malcolm and MacCarthy (1992). The use of XAD-8 and XAD-4 in series produce three distinct fractions (Figure 8) which are referred to as the hydrophobic (HPO), transphilic (TPH), and hydrophilic (HPI) fractions throughout the remainder of this review. The term transphilic originates from Croué et al. (1999) and includes those

species of intermediate polarity (Croue et al., 2003; Liang and Singer, 2003), which pass through the first column but are sorbed to XAD-4 at pH2. Due to the discontinuation of production of XAD-8 resin, it is substituted for XAD-7HP (Goslan et al., 2002) or DAX-8 (Croué et al., 1999) in the production of the HPO fraction.

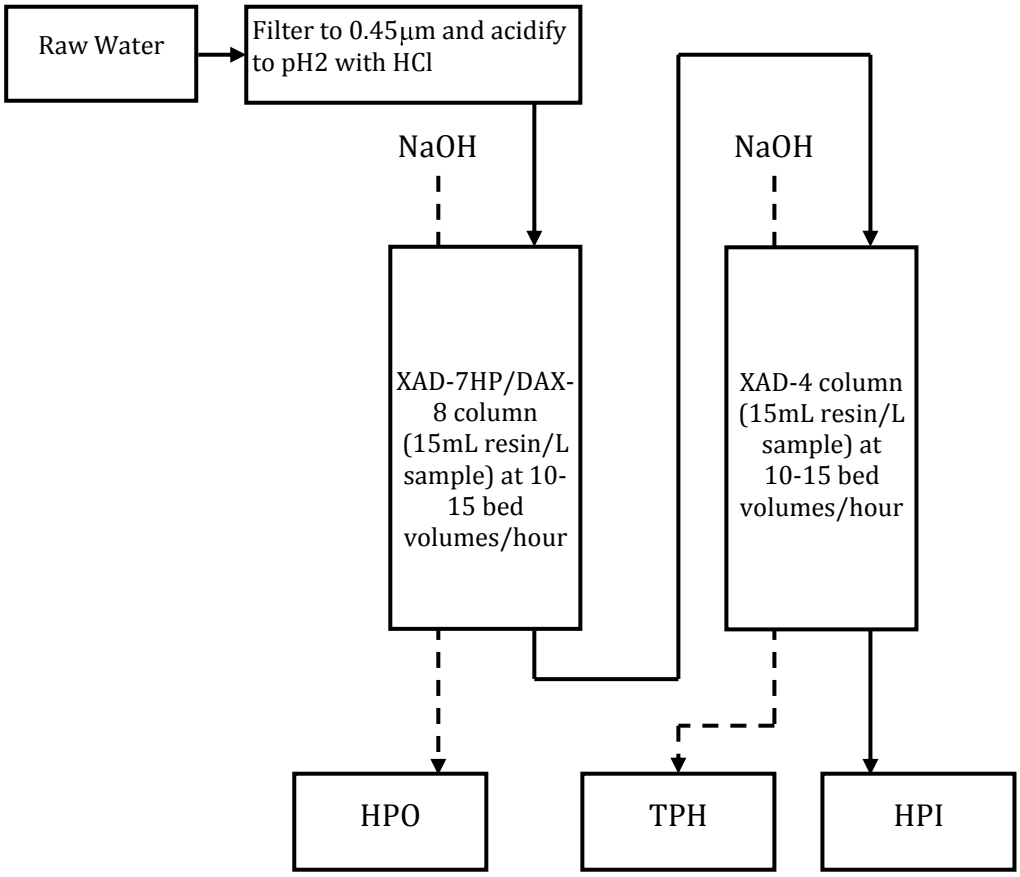


Figure 8: Schematic of the fractionation method, adapted from Goslan et al. (2002). An acrylic based XAD resin first removes larger, more aromatic HPO NOM, before the solution is passed through the styrene based XAD-4 for removal of TPH NOM.

This technique relies on the back elution of NOM fractions from the resin, which are then analysed for DOC to determine the character of the raw NOM. This process acts to concentrate the NOM, which was particularly important as the dilute nature of NOM within natural water hindered historical characterisations due to insufficient sensitivity of analysis techniques , 2004). Analytical advancements have enabled some researchers to use a mass analysis technique instead of back elution in which the fractions sorbed to each column are calculated as the difference between the column's influent and effluent. This was successfully used by Lee et al. (2004) and Chow et al. (2004), removing the back elution step. The traditional fractionation method using back elution is still the more widely used technique, in part because

concentrated fractions can be further analysed, such as identifying their THM formation potential. However, the mass analysis technique appears to be gaining popularity, particularly when the sole purpose of fractionation is for NOM classification of a water sample.

3.5.i. The fractions created

The terms HPO, TPH and HPI are not absolute as the fractions produced do not consist of discrete molecules, but instead a molecule range that overlaps with other fractions to different degrees, dependent upon the column capacity factor (k') for each NOM compound (as shown in Figure 9). For example in column fractionations of 21 different model compound solutions by Bond (2009), even the most hydrophobic model compound tested, tannic acid, was present in all three fractions (HPO (90%), TPH (3%) and HPI (7%). Due the near infinite number of NOM molecules (Filella, 2009), it is impossible to directly calculate the hydrophobicity of each compound, particularly as hydrophobicity will also vary in mixed compound systems and with NOM concentration due to competition for sorption sites. While no NOM functional groups can be defined as purely hydrophobic or hydrophilic, trends in the concentration of functional groups in each fraction (Figure 9) show strong agreement between studies and can be used to estimate a molecule's hydrophobicity.

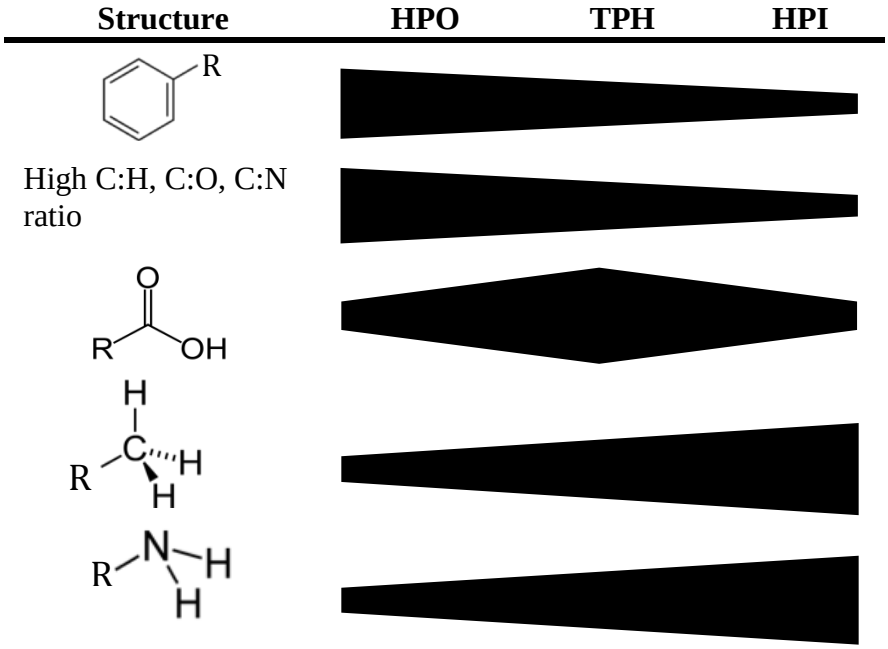


Figure 9: Hydrophobicity of NOM due to the prevalence of different functional groups. Adapted from Croué et al., (1999) and Leenheer (2004).

In general, a 6:1 (or greater) ratio of carbon atoms per hydrophilic functional group is associated with the HPO fraction (Malcolm, 1990). This fraction includes both humic acids (HA) and fulvic acids (FA) which are complex large molecules containing many aromatic phenol groups and conjugated double bonds (which reduces the available sites for bonding with non carbon molecules). The main difference between HA and FA is identified by Peuravuori and Pihlaja, (1998b) to be a higher aliphatic content in FA resulting from substitutions in the benzene ring functional groups and a correspondingly greater unsaturation in HA ((Peuravuori and Pihlaja, 1998a). The TPH fraction commonly has the highest proportion of carboxylic acid groups (Bond, 2009) and carbohydrates (Croué et al., 2003). The HPI fraction contains more aliphatic and carboxyl carbons and nitrogenous compounds (such as low molecular weight carbohydrates, proteins and amino acids) (Peuravuori and Pihlaja, 1998b; Marhaba et al., 2003; Hua and Reckhow, 2007).

These trends are confirmed by elemental and molecular weight analysis (Aiken et al., 1992) and ^{13}C NMR (nuclear magnetic resonance) spectrum absorbance band analysis , 2004) of the three fractions and are independent of source water. Bond (2009) successfully demonstrates that log K_{ow} can be used as an alternate assessment of an organic model compound's affinity for each fraction. Negative values are associated with a predominance of the HPI fraction and values above 0.67 indicate a more HPO nature (Bond, 2009).

3.6. Versatility of XAD fractionation and its use in assessing NOM variability

3.6.i. Changing motivations for XAD fractionation

The development of XAD fractionation was originally motivated by the need to isolate different NOM species based on chemical attributes (Leenheer, 1981) and the limitations of other characterisation schemes at the time (Leenheer and Huffman, 1976). As a result, the early years of the research were concentrated on maximising the usefulness of the NOM fractions produced and NOM species identification (Figure 10). NOM characterisation has remained an important driver for XAD fractionation throughout the 1990's and early 21st century. This is, in part, due to continued analytical advances increasing the ability to investigate NOM structure.

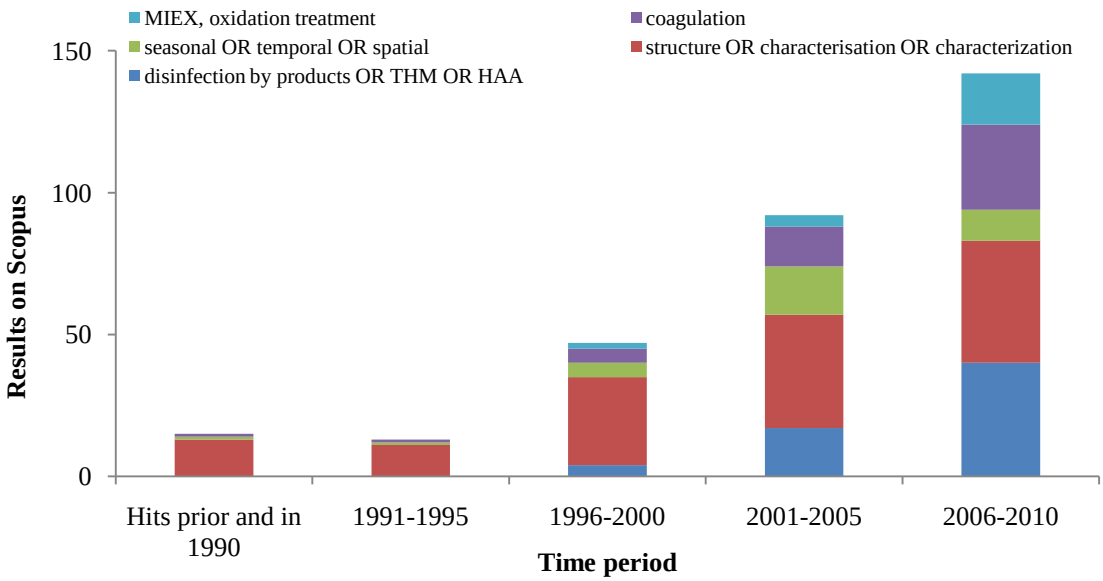


Figure 10: Research into NOM over time. Search was conducted in Scopus, and limited to life science and physical science. Search term to include fractionation AND NOM OR DOC along with the above.

In the last 15 years, NOM fractionations have been used to investigate an increasingly wide range research questions. The production of DBPs from NOM reacting with chlorine was first identified by Rook (1977), and research on their effects on human health, their chemistry, and NOM removal began in earnest in the early 1990's with a three day symposium entitled 'Disinfection By-Products in Water Treatment: The chemistry of their Formation and Control' in August 1993 (Miller, 1993). This has continued into the 21st century with the recognition of DBPs as probable human carcinogens (Wigle and Lanphear, 2005; Singer, 1999). Over the same time period, climate change has become a 'hot topic'. The water industry is increasingly encouraged to find lower carbon and chemical intensive processes to treat water to increasingly stringent discharge consents. Meanwhile, NOM concentrations have been rising worldwide as a result of climate change and changes in land use.

NOM fractionation provides important information on water treatability and residual NOM levels. It is therefore identified as an important tool in meeting these challenges. As a result, over the last 15 years research into NOM fractionation has risen sharply, driven by a need to understand fluctuations in NOM type and concentration, advanced technologies for NOM removal and limiting DBP formation (Figure 10). NOM fractionation using XAD adsorption resins can be successfully used to identify both spatial and temporal variations in NOM character. This

information can be often combined with WTW NOM treatment capabilities (Fearing et al., 2004; Sharp et al., 2006b) or analysis of THM and HAA precursor formation (Goslan et al., 2002; Hua and Reckhow, 2007) to indicate which NOM fractions are more problematic for different locations and treatment methods.

3.6.ii. Using XAD adsorption resins to understand NOM variability

Spatial variations

The NOM within natural water is site specific; a consequence of the soil type, land use, climate and other physical catchment characteristics (Aoustin et al., 2001; Sulaymon et al., 2009). No single treatment technique exists that can give the most effective NOM removal for all water types. For example, HPI waters cause greater membrane fouling (Lee et al., 2004), whilst HPO waters have higher coagulant demands (Sharp, 2005). Increased understanding of these differences in NOM allows the most appropriate treatment techniques to be selected. A collection of different water types which vary by NOM type (from 79% HPO Albert water to the 37% HPO Severn Trent catchment 3 water) and concentration (from 11mgC/L at Myrtle Beach to 0.8mgC/L at Greenville) are presented in Figure 11.

Variation between water bodies

A study of four French water types (Lee et al., 2004) concludes that lake and reservoir waters (Cazau lake and Bultiere reservoir) have a greater hydrophilic content than river waters (Marne and Yffiniac) (Figure 11). This is a result of the domination of autochthonous material (i.e. algae) in low flowing water bodies such as lakes (Leenheer, 2004), whilst rivers have greater erosion potential increasing HPO allochthonous material. Similar trends are identified by Wei et al. (2008) (who found Mayan reservoir (Beijing) to be more HPI than both rivers (the Huanghe and Pearl) sampled) and Song et al. (2009) (who found influent water to Myrtle Beach treatment works to be more HPO (73%) than influents to Greenville (61%) and Spartanburg (67%), which were both supplied by reservoirs). Imai et al. (2001) found forest streams and river water to exhibit a greater hydrophobicity than lake water from the same catchment.

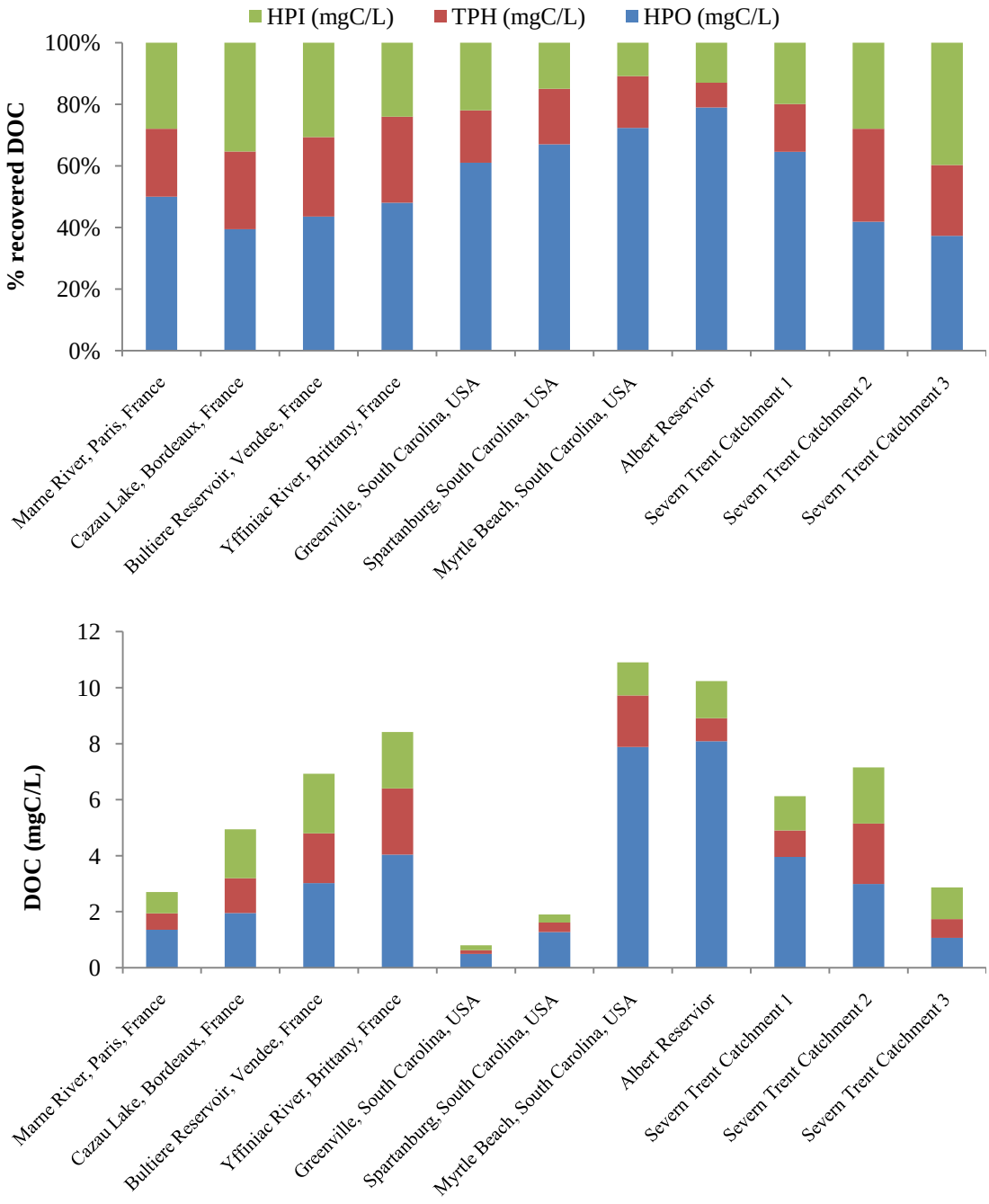


Figure 11: A selection of XAD fractionation results, adapted from Sharp et al. (2006b); Lee et al. (2004); Song et al. (2009); Roe et al. (2008).

Therefore XAD fractionation identifies a higher hydrophilicity in waters from lakes and reservoirs, likely to be the result of greater amount of autochthonous material. In contrast, NOM concentration does not appear to be related to water body type of the water samples given in Figure 11. Greenville water (supplied by a reservoir) and Albert reservoir have the lowest and second highest NOM concentrations

respectively, whilst Marne River and Yffiniac River also have widely varying concentrations (Figure 11).

Catchment variations

Water samples taken from similar catchments have been previously shown to exhibit more similar NOM types (Fabris et al., 2008; Roe et al., 2008; Wei et al., 2008). For example, while total NOM concentrations for three Norwegian raw waters with similar catchment characteristics (natural lakes with granite bedrock and coniferous forests vegetation) varied from 4.9-15.9mgC/L, they show very similar NOM fractions (70-79% HPO) (Fabris et al., 2008).

In a study of sixteen UK WTWs within Severn Trent's operational area, Roe et al. (2008) identified three distinct water types with an example of each presented in Figure 11 (Severn Trent catchment 1-3). Water type 1 is of a high HPO content and found within moorland catchments whilst water type 3 has a higher HPI content and is generally found within lowland, urbanised catchments (Roe et al., 2008). Water type 2 is an intermediate classification. The other waters presented in Figure 11 agree with this classification, with the HPO waters Myrtle Beach and Albert WTW (Sharp et al., 2006b; Song et al., 2009) described as wetland and moorland catchment respectively (type 1 water) whilst Marne River, near Paris, fits with the type 3 classification.

Temporal variations

Seasonal and long term variations in climate and land use can act to vary NOM type and concentration. There are many examples of seasonally changing NOM concentrations within the literature (Maurice and Namjesnik-Dejanovic, 1999; Ratnaweera et al., 1999; Chang et al., 2000; Goslan et al., 2002; Leenheer, 2004; Sharp et al., 2006b; Sulaymon et al., 2009). For example, in the catchment study by Imai et al. (2001) all four rivers discharging to Lake Kasumigaura had maximum DOC concentration in May, due to irrigation of the surrounding paddy fields. As a consequence WTWs optimised for catchment type may need further alterations of operating conditions seasonally or over longer time periods to maximise NOM removal performance.

Albert Reservoir has a typical moorland water type, being both HPO and highly coloured. XAD fractionations, completed between November 2000 and September

2003, show the majority of variation in NOM concentration to be caused by variation in the HPO fraction (Figure 12), or more particularly, the FA fraction (Sharp et al, 2006b). This seasonal variation is suggested to be the result of higher soil microbe activity in the warm, but dry, summer leading to a flush through of organics during autumn storms (Sharp et al, 2006b; Scott et al., 2001). The relationship between NOM concentration and rainfall is highlight in a study by Maurice et al. (2002) of the McDonalds Branch freshwater fen, where NOM concentration rose from 3.4mgC/L during autumn drought conditions to 9.9mgC/L the following spring. A higher NOM concentration was also identified by Leenheer (2004) under high flow condition of the Santa Ana River, California (increased from 3.42-5.14mgC/L), with the HPO and colloidal fraction causing the majority of the increase in NOM concentration. In high flow condition, increased run off leads to greater allochthonous NOM content. Of the sixteen waters investigated by Roe et al. (2008), moorland waters types with a high HPO content experienced the greatest seasonal variation.

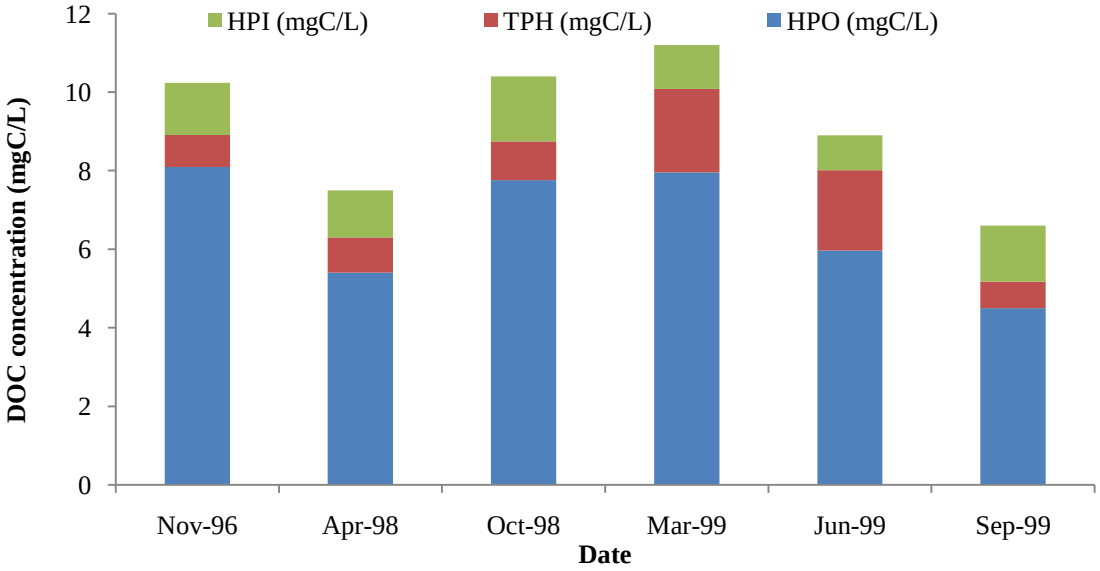


Figure 12: Temporal variations at Albert WTW. Adapted from Sharp et al. (2006b).

Monthly XAD-fractionation data were complied for Tehranpars WTP, Iran between August 2006 and January 2007 (Zazouli et al., 2007) (Figure 13) and showed a peak of 2.8mgC/L in August which drops through the time period to a minimum of 1.1mgC/L in January. Fractionation data indicate an increased HPO fraction is predominately responsible for the higher NOM concentrations (Zazouli et al., 2007), which is in agreement with the conclusions of Sharp et al. (2006b). The same pattern

was seen for the Tigris river, Iraq between August 2004 and July 2005 (Sulaymon et al., 2009) with both total DOC concentration and THM formation potential dropping approximately 50%, from a maximum in August to a minimum in December, before returning to maximum levels in the following July. However, NOM fractionation was not completed for this study and so it cannot be certain that this seasonal variation was the result of the HPO fraction.

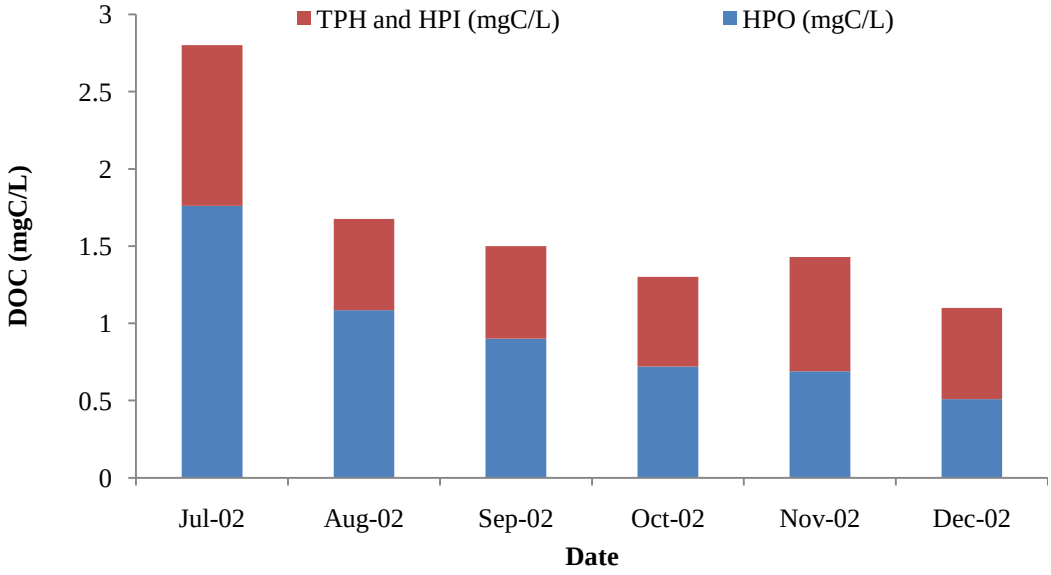


Figure 13: Raw water XAD fractionation data from Tehranpars WTP (Zazouli et al., 2007).

DBP precursor variation

The variations in the formation of the major DBP species, THMs and HAAs, in natural waters, have received increased attention within the scientific community in an effort to control effluent concentrations and minimize health risks. XAD fractionation can be used to identify the effect of each fraction on DBP production, allowing WTW's to concentrate NOM removal efforts on the most problematic fractions within a catchment.

In a study by Hua and Reckhow (2007) DBP precursor formation was studied for NOM fractions from five individual natural waters. In waters with a higher HPO content, a higher concentration of both THM and tri-HAA was produced (Hua and Reckhow, 2007). This was in agreement with a previous investigation by Singer (1999) who found the production of halogenated DBP to be directly proportional to the aromatic carbon content (HPO) of the organic constituents in the water and it is also in line with the traditional perception that humic substances are the major source

of DBP precursor sites (Leenheer and Croué, 2003). Roe et al. (2008) find a positive relationship between HPO content and THM formation for waters of a high HPO content (type 1). Seasonal variations in the relative % of each NOM fraction within natural water could therefore alter the concentration and type of DBP, without a change in the overall concentration of NOM. However, DBP precursor levels did not show significant seasonal variance in studies by Goslan et al. (2009) and Gallard and Von Gunten (2002), although a higher chlorine demand was observed during summer in the latter.

In waters of a high % HPI fraction, Hua and Reckhow (2007) found the DBP formation potential of the HPI fraction to be proportionally higher than in waters of a lower % HPI fraction. This confirms previous evidence that the ability of the HPI fraction to produce DBPs increases in water of a more HPI nature (Liang and Singer, 2003) and is in agreement with well cited data from the Colorado river in which 65% of the DOC is HPI, contributing 56% of the THM formation potential (Collins et al., 1986). Bond (2009) suggest this variation in the HPI fractions DBP formation potential could be a result of varying reaction kinetics between chlorine and different NOM functional groups. Unsaturated HPO functional groups such as arenes react more rapidly with chlorine than carboxylic structures (more dominate in the TPH fraction) (Bond, 2009). In a HPI water type with minimal HPO functional groups, the slower reaction between carboxylic and chlorine may increase in importance leading to a higher relative DBP formation potential for the HPI fraction in these waters.

3.6.iii. Summarising the usefulness of XAD adsorption resins in assessing NOM variability

The information provided by fractionating NOM with XAD adsorption resins can be used to highlight the differences in NOM between water bodies and catchments, its seasonally and in its production of DBP precursors. It is therefore a vital tool in achieving the challenging targets facing the water industries. Waters of a high HPO content show strong seasonal variation in NOM type and concentration, with the HPO fraction most important in DBP formation potential. In waters with a more dominant HPI fraction (such as lakes and catchments with a drier climate), seasonal variations are less pronounced and concentration spikes are less common. This compliments Figure 2 in which no water with a HPI fraction over 50% of total NOM had a concentration above 10.7mgC/l. However, in these waters the HPI fraction (which is

most difficult to remove using conventional treatments) has an increased DBP formation potential than waters of a higher HPO content.

3.7. Comparison of Fractionation techniques

Ion exchange and XAD fractionation are by no means the only methods of NOM separation. The use of granular activated carbon (GAC) (Cheng et al., 2005), liquid extraction procedures (McDonald et al., 2004), gel permeation chromatography (Thurman and Malcolm, 1981; Hesse et al., 1999), and size exclusion chromatography (Matilainen et al., 2002; Allpike et al., 2005) are just a few examples of alternative separation methods which are summarised in Croué et al. (1999) and Goslan (2003). More recently the development of the polarity rapid assessment method (PRAM) allows NOM to be characterised by polarity using seven solid phase extraction cartridges (Rosario-Ortiz et al., 2004) (Rosario-Ortiz et al., 2004). However, this technique is still in the early stages of development and its use is currently hindered by excessive carbon bleeding and a limiting trialled concentration range (8-10mgC/L) (Rosario-Ortiz et al., 2007).

3.7.i. Ultrafiltration / Nanofiltration

Whilst adsorption procedures fractionate NOM based on chemical variations such as hydrophobicity, an alternative approach is to fractionate NOM according to physical attributes such as molecular size. Separation by molecular size is most commonly completed by the pressure-driven membrane processes of ultrafiltration and nanofiltration (UF/NF). Dissolved solutes are separated according to their molecular sizes, with molecular weight cut off (MWCO) values generally ranging between 30,000–500 Daltons (Goslan et al., 2004; Collins et al., 1986; Chow et al., 2005; Wei et al., 2008).

Comparisons between UF/NF and XAD fractionation in the classification of NOM are common throughout the literature (Kitis et al., 2002; Goslan et al., 2004; Chow et al., 2006) and the advantages and disadvantages of the two techniques are highlighted in Table 2. In general, UF/NF produces a higher DOC recovery (reported at 77-96% compared to 60-75% for XAD-8/4 with back elution by Croué et al. (1999). It also has a shorter processing time and does not require chemical reagents, which allows

the nature of the DOC to be maintained in original state , 2004; Chow et al., 2005; Wei et al., 2008).

Table 2: A comparison of XAD resins and UF/NF membranes in NOM fractionation

XAD Fractionation		UF/NF Fractionation	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**
Splits based on Polarity (and size)	Currently takes a long time	Provides a quick separation method	Polarity not considered
NOM fractions representative of raw water treatability	Can never reach 100% recovery - generally <90%	DOC recovery often over 90%	Molecule selectivity due to aggregation and trapping within membrane
Desalting achieved during fractionation procedure	Harsh conditions of low pH may alter NOM	No extreme conditions required	Desalting pre-treatment may be required
Concentration alongside fractionation	HPO/HPI split changes temporally due to NOM build up on resin	Concentration alongside fractionation	Membrane fouling
Operational specific - can tailor conditions to suit objectives	Wrong method may be chosen	Superior to other methods at retaining NOM reactivity	Membrane pore sizes vary so can only give AMW
Good representation of WTW treatability	Sensitive to method alterations		Arguably less useful fractions produced
	Difficulties in comparing different methods results		

Disadvantages of UF/NF include a non-isotropic membrane pore size. Instead membrane weight cut off (MWCO) values are established as the size for which greater than 90% of the particles are retained (Chow et al., 2005). As NOM has widely varying structural characteristics, UF/NF produces a wider distribution of molecular weight, which cannot be directly related to manufacturer MWCO values (Kitis et al., 2002; Goslan et al., 2004). Instead, apparent molecular weights (AMW) are used within UF literature (Collins et al., 1986) that are affected by chemical composition (Chow et al., 2005). Other problems include: the aggregation of the molecules when NOM is concentrated on the membrane (Goslan et al., 2004); the concentration of salts alongside NOM (Croué et al., 1999); pore adsorption and plugging by the HPO NOM (Aoustin et al., 2001); membrane fouling from HPI NOM (Hong and Elimelech, 1997; Lee et al., 2004).

Perhaps the biggest disadvantage of UF/NF is in its fitness for purpose. As seen in Figure 10, the majority of NOM research involves its removal at the WTW's, particularly in respect to DBP formation potential. As already seen, XAD fractionation based on chemical attributes such as hydrophobicity shows a strong relationship to the treatment potential for the natural water. HPO compounds, account

for a large proportion of the SUVA of natural waters (Croué et al., 1999) and DBP formation potential (Singer, 1999). However, as a polydispersed mixture the HPO fraction is often split into various fractions during UF/NF (Aoustin et al., 2001). Whilst most studies indicate maximum THMFP generally occurs for AMW size classes between 1 and 10 kDa (Chow et al., 2005), a study by Kitis et al. (2002) did not find consistent trends between DBP yields and MW. In contrast, molecular size was reported as the most important characteristic affecting DOC removal with ferric sulphate (Goslan et al., 2004).

In designing NOM separation research, decisions must be made on what the best fractionation method is based on the requirements of the study. Each technique has strengths and weaknesses and these should be compared in assessment of the ideal techniques. To compensate for weaknesses and limitations in each technique Chow et al. (2005) suggest that two fractionation techniques (UF and XAD) should be used together to validate isolation and characterisation of DOM in terms of THM formation potential.

3.8. Analysis of the Variations within XAD fractionation

As a result of the historic development of XAD fractionation, the varying motivations for NOM research and the number of research teams, a wide variety in the methods used to produce each NOM fraction are seen throughout the literature (Table 3). This is important as it allows the technique both to be modified to suit purpose and to improve the accuracy and robustness of the procedure as new materials and techniques are developed. However, a lack of a consistent fractionation method can lead to problems by causing uncontrolled variations to the operational defined fractions.

3.8.i. Changes in the fractionation technique

A variety of studies using XAD fractionation are outlined in Table 3 to show the variations in method and research motivations. Whilst these method alterations are generally crucial to improve the technique and fill gaps in research knowledge, in some cases method alterations are not fully documented which leads to problems in comparisons between research. It is consistently stated throughout the literature (Malcolm and MacCarthy, 1992; Gadmar et al., 2005) that XAD fractionation is an

'operationally defined method' of separating NOM. Therefore any change to accepted methodologies must be carefully researched to ensure unanticipated alterations in the fractions produced do not occur. The following sections will describe some of the key method alteration within the XAD fractionation literature.

Table 3: The variety of research questions that rely on NOM XAD fractionation data and the different methods that are used to create each fraction

Reference	Motivation of Study	Fractionation Method Summary	Conclusions
XAD fractionation with back elution			
Leenheer, 1981	Improve DOC isolation and fractionation recoveries. Create meaningful fractions	XAD-8 and ion exchange resins (Bio-Rad AG-MP-50 and Duolite-A-7) with back elution and controlled pH to produce 6 fractions	Showed excellent recovery (other than hydrophilic bases) and greater accuracy due to concentration. Fractions have several distinguishing infrared features therefore meaningful
Malcolm and McCarthy, 1992	Further development of the procedure to maximise accuracy and precision of resin fractionation to map long term change	XAD-8 and XAD-4 (with back elution) in series to produce four fractions (including HA and FA)	Good precision, over 85% recovery of organics, but low recovery of XAD-4 acids (possibly due to pi-pi bonding)
Collins et al., 1986	The effect of NOM character on treatability at WTW's to reduce of THM formation	XAD-8 fractionation of treated and untreated NOM into HPO and HPI fractions	Identified key attributes of NOM that affect treatability. THM precursors are preferentially removed
Goslan et al., 2002	Monitor the effect of seasonal changes on NOM with regards to THM-FP	As in Malcolm and McCarthy (1992) but with XAD-7HP substituted for XAD-8	Increase in hydrophobic fraction during autumn which corresponds with increase in THM-FP
Kim & Yu, 2005	To characterise NOM for selection of treatment processes for DBP	The use of XAD-7HP and A-21 resin to produce 3 fractions	DBPs produced were influenced by chemical and structural characteristics such as aromaticity and functionality
Kitis et al., 2002	Investigate reactivity of NOM for DBP with comparison of resin fractionation and ultrafiltration	The use of XAD-8 to produce two fractions (HPO and HPI)	UF and fractionation both give similar results and show same relationships between SUVA and THM and HAA.
Imai et al., 2001	Investigate increasing DOM concentrations in Japanese lakes and characterise incoming DOM from different catchment sources	As in Leenheer (1981) but with Duolite-A-7 substituted for Bio-Rad-MP-1	DOM fractions produced very useful for character evaluation and were significantly different dependent upon sample origin,
Bolto et al., 1999	Comparing NOM removal and DBP formation of residual NOM for alum coagulation and cationic polymers	DAX-8, XAD-4 and Amberlite IRA-958 in series to produce four fractions	Different NOM fractions show greatest removal with different treatment. Alum coagulation is best for HPOs whilst polymers generally remove more HPIs
Croue et al., 2003	NOM characterisation to investigate metal binding capacities	The use of XAD-8 and XAD-4 in series (k'=100) to produce three fractions (HPO, TPH and HPI)	The HPO fraction is dominated with copper binding with the nitrogen rich TPH fraction also important. Changes in a rivers physiochemical environment can remove metal ions by preferential sorption

Mergan et al., 2008	Investigate the ability of MIEX technology to remove waters of different hydrophobicity, and it's performance with consecutive resin use	As in Malcolm and MacCarthy (1992)	Single use of resin resulted in an increasing % removal as hydrophobicity increased, but this trend reverses during continuous resin use. Therefore for WTWs use MIEX provides a good option for HPI waters

Reference	Motivation of Study	Fractionation Method Summary	Conclusions
XAD fractionation with mass analysis (rapid fractionation)			
Chow et al., 2004	Introduction of a rapid fractionation technique, specifically designed to study WTW processes. Variation in alum dosing is compared for a high DOC water.	DAX-8, XAD-4 and Amberlite IRA- 958 in series to produce four fractions.	Rapid fractionation is successfully used to compare treatability of different fractions with varying alum dosage.
Lee et al., 2004	Identify the impact of hydrophobicity on low pressure membrane fouling, for four different membranes.	XAD-8 and XAD-4 in series to identify the three fractions.	High HPI contents produced a greater flux decline in membranes. The hydrophobicity of the membrane did not appear significant in altering flux decline. Both size and shape of molecules are important in fouling. Ultrafiltration membranes show less fouling than microfiltration membranes.
Jegatheesan et al., 2008	Modelling chlorine decay kinetics and THM formation in treated water and in XAD fractions.	DAX-8, XAD-4 and Amberlite IRA- 958 in series to produce four fractions.	The more HPO fractions contain the highest % THM formation potential. THM formation in treated water is mostly due to slow reacting agents.
Pivokonska et al., 2008	Identification of the removal efficiency of NOM fractions using different alum dosing to optimise chemical use.	DAX-8, XAD-4 and Amberlite IRA- 958 in series to produce four fractions.	NOM removal efficiency depends on the NOM character and on the operating conditions during water treatment. The HPI neutral fraction is most difficult to remove with alum coagulation.

Choice of resin

One of the major alterations in the XAD fractionation method is in the choice of resin. This is a result of:

- *Product discontinuation* - XAD-8 (discontinued) is substituted for DAX-8 (Croué et al., 1999; Marhaba et al., 2003; Jegatheesan et al., 2008) or XAD-7HP (Kim and Yu, 2005; Goslan et al., 2002; Bond, 2009).
- *Maximising elution recovery* - the substitution of Duolite A-7 with XAD-4 (Malcolm and MacCarthy, 1992) or Diaion WA 10 (Marhaba et al., 2003).

- *Alternate fraction production* - the use of Amberlyst A-21 to split the HPO fraction into phenolic and carboxylic groups (Kim and Yu, 2005).

The properties of XAD-8 and its two substitutes were previously shown in Table 1 to be similar, although XAD-7HP has a much larger surface area ($380m^2/g$ compared to $160m^2/g$ for DAX-8 and $140m^2/g$ for XAD-8) and DAX-8 has a better wetting ability than XAD-8 (Peuravuori et al., 2002). The fractions produced using both DAX-8 and XAD-8 were compared using solid-state ^{13}C NMR spectroscopy and pyrolysis gas chromatography and shown to produce similar humic isolation with a higher aliphatic carbon content in the DAX-8 isolate the main difference (Peuravuori et al., 2001; Peuravuori et al., 2002) and a speculated minor difference in the fraction's THM precursor content (Chow et al., 2005). Other differences include a higher % isolation of humic solute (Peuravuori et al., 2002; Farnworth, 1995) and a more precise HPO/HPI sorption/desorption mechanism in DAX-8 (Peuravuori et al., 2001).

After the discontinuation of XAD-8 resin, its producer (Rohm and Haas) suggested XAD-7HP as an alternative product. However, as resin surface area is a key control of adsorption rate (Aiken et al., 1992), the resin's properties would suggest DAX-8 is more compatible to XAD-8. No research comparing XAD-7HP to either DAX-8 or XAD-8 could be found by the author. This is seen as a major oversight in the literature and a key area for further work. Comparison of the resins may reveal one resin to be of more use than the other, thus unifying these two methodologies, and would certainly be useful to allow comparison between historic results.

If ion exchange resins are to be used in place of (or as well as) XAD-4 then unless there is a valid research reason for the use of alternate resin, the use of well researched resins such as Bio Rad AG-MP-50 (Leenheer, 1981) and Amberlite IRA-958 (Bolto et al., 1999; Chow et al., 2004) is advised, to maintain comparability between studies.

Back elution or mass analysis

XAD fractionation with mass analysis was initially developed as a substitute for the more time-consuming back elution technique, when the fractionation need is to characterise NOM to monitor WTW's processes (Chow et al., 2004). By this means the performance of treatment processes has been successfully assessed for different water types (Lee et al., 2004), and optimised based on water composition (Pivokonska

et al., 2008) providing a more rapid alternative to the techniques used by Bolto et al. (1999) and Mergen et al. (2008) in similar process performance studies.

The disadvantage of the mass analysis technique is that the sorbed fractions are not available themselves for further analysis. Therefore in NOM characterisation studies such as Croué et al. (2003) or when further fractions (HA and FA) are required (Malcolm and MacCarthy, 1992) the back elution process is necessary. However, in a recent development, use of the mass analysis technique has been extended to DBP formation studies (Wei et al., 2008; Jegatheesan et al., 2008).

In a study by Soh et al. (2008), XAD fractionation with both back elution (following Bolto et al., 1999) and mass analysis (Chow et al., 2004) were compared for DOC, UV_{254} absorbance and colour. The fractions produced in both procedures were similar with the greatest difference seen for the charged HPI fraction (effluent from XAD-4) (with DOC of 1.65mgC/L and 1.81mgC/L and UV_{254} absorbance of 0.049cm^{-1} and 0.028cm^{-1} for mass analysis and back elution respectively) (Soh et al., 2008). In both procedures DOC, UV_{254} and colour were at maximum levels in the most HPO charged fraction, reducing to minimum levels in the HPI neutral fraction (Soh et al., 2008). This indicates that when NOM isolates are not needed for further direct analyses, the use of mass analysis can reduce the analysis time of NOM fractionation without a reduction in fraction usefulness.

Number of fractions produced

The number of fractions collected in each XAD fractionation clearly varies between studies (Tables 3 & 4) and choice of the number of isolates should be based on the aim of the study. For example, whilst Leenheer (1981) aims to create more meaningful fractions for characterisation purposes (thus producing six fractions), NOM is commonly fractionated into three fractions (HPO, TPH, HPI) in studies of NOM treatability at WTWs. Increasing the amount of fractions characterises NOM to a greater degree and forms more homogenous solutions but it is also more time consuming and more expensive (Leenheer, 2004) and increasing NOM losses occur with increasing fractions. Whilst additional steps can be employed to collect more of the NOM, isolation need must be weighed against increased workload, cost and diminishing returns (Croué et al., 1999).

Naming of fractions

When literature comparisons are made for XAD fractionations, the variety of names and acronyms used for equivalent NOM isolates (and different terms for NOM itself), reduces the clarity of the data (Goslan, 2003; Filella, 2009). Table 4 presents some of the more common terms for each NOM isolate. However, a variety of other less common nomenclatures exists, such as those used by Wei et al. (2008) and Imai et al. (2001). The variety in is in part a result of the variation in the fractionation procedures used. For example, the use of the term hydrophilic fraction include effluent from XAD-8 (Kitis et al., 2002), effluent from XAD-8/XAD-4 (Bond et al., 2009) and effluent from XAD-8 which then sorbs to XAD-4 at pH 4 at $5<k'<50$ (Croué et al., 1999). The greatest inconsistency in nomenclature is seen for that fraction which passes through the XAD-8 (or alternative) column but is sorbed to the XAD-4 column (Table 4). This intermediate fraction acts as both a HPI (on XAD-8) and a HPO (on XAD-4) compound during the procedure, making it difficult to name this fraction as its hydrophobicity varies with the sorbant. The use of the term TPH (Croué et al., 1999) is identified by this review to provide the greatest clarity over the organics within this fraction and appears to be dominating in present research. It is therefore used throughout the rest of this work.

Variations in experiment conditions

As XAD fractionation is operationally defined, any alteration in the methods used may cause a difference in the arbitrary HPO/HPI designation (Leenheer, 1981) and reduce research comparability. For example in the production of the HA and FA fractions, Ma et al. (2001) split HA and FA before use of XAD-8 whilst Goslan et al. (2002), Peuravuori and Pihlaja (1998b) and Malcolm and MacCarthy (1992) use XAD-8 prior to precipitation of HA. Common method deviations such as filter size, flow rate and pH can be easily controlled and consistency between studies should be maintained when possible. A lack of comprehensive method reporting is often seen throughout XAD fractionation literature (for example Cho et al. (1998) and Siddiqui et al. (2000) failed to report full fractionation method) and this may reduce the value of the results.

Filter size

In the majority of XAD fractionation studies, NOM is first filtered at 0.45μm (0.45-0.22μm (Filella, 2009)) to remove particulate organic carbon. However, the difference between particulate and dissolved organic carbon (DOC) is arbitrary (Filella, 2009) and has been extended in research by Leenheer (2004) to include the colloidal fraction, redefining DOC as <1μm filter, to improve total DOC recovery rates. Changes in the filter size prior to fractionations impacts the NOM fractions produced, in particularly the HPO fraction. As larger NOM molecules are generally associated with the HPO fraction (Kitis et al., 2002), a smaller filter size acts both to reduce the % HPO fraction, and alter the type of NOM found within this fraction.

Table 4: The different terminologies used to describe XAD fractions

<table>
<tr><td></td><td colspan="5">Fraction Names</td></tr>
<tr><td>Fraction Production Method</td><td>Malcolm and MacCarthy, 1992</td><td>Goslan et al., 2002; Fearing et al., 2004; Sharp et al., 2005</td><td>Croue et al, 2003; Chow et al., 2006; Bond et al.,2009</td><td>Bolto et al., 1999; Jegatheesan et al., 2008; Fabris et al., 2008</td><td>Gadmar et al., 2004; Kitis et al., 2002; Kim et al., 2006</td></tr>
<tr><td>Absorbed to XAD-8 (or alterative) at pH2, eluted at pH13 and precipitates at pH1</td><td>Humic Acid</td><td>Humic acid fraction (HAF)</td><td rowspan="2">Hydrophobics (HPO)</td><td rowspan="2">Very Hydrophobic acids (VHA)</td><td rowspan="2">Hydrophobic acids (HPOA)</td></tr>
<tr><td>Absorbed to XAD-8, eluted at pH 13 and soluble at pH1</td><td>Fulvic Acid</td><td>Fulvic acid fraction (FAF)</td></tr>
<tr><td>Material remaining upon XAD-8 after desorb procedure (determined either by Soxhlet extraction or mass balance)</td><td>HPO Neutrals</td><td>Hydrophobic neutrals (HPON)</td><td>Hydrophobic neutrals (HPON)</td><td></td><td>Hydrophobic neutrals (HPON) (not always collected)</td></tr>
<tr><td>Elute of XAD-8 which then adsorbs to XAD-4 at pH2</td><td>XAD-4 acids</td><td>Hydrophilic acids (HPIA)</td><td>Transphilic acids (TPHA)</td><td>Slightly Hydrophobic acids (SHA)</td><td rowspan="2">Hydrophilic (HPI)</td></tr>
<tr><td>Material remaining upon XAD-4 during desorption at pH13</td><td colspan="2"></td><td>Transphilic neutrals (TPHN) (not always collected)</td><td></td></tr>
</table>

Elute from both columns in series at pH2	Hydrophilic	Hydrophilic non-acids (HPINA)	Hydrophilic (HPI)	Further split into Hydrophilic charged (CHA) and Hydrophilic neutrals (NEU) using an IRA-958 column	

Flow rate

Variations in flow rates impact the column capacity factor (k´) (the ability of the column to adsorb NOM). Flow rates beyond 20 bed volumes per hour (10-15 bed volumes per hour (Malcolm, 1989)) reduce the columns adsorption capacity, with an equilibrium between adsorption and desorption not reached during the contact time (Thurman and Malcolm, 1978). Flow rates are not always taken into consideration or reported when designing XAD fractionations.

Column capacity factor (k´)

The column capacity factor (k´) of a mixed solution is the uncontrolled variable, which provides the unique HPO/HPI spilt for that solution. The k´ value is impacted by solution concentration so when model compound are investigated, equal solution concentrations should be used. For example, Gadmar et al. (2005) tested concentrations of 0-40mgC/L, and showed the relative proportion of the HPI fraction increased for samples of higher concentrations. In natural waters, this causes the same organic matter type retained by the XAD-8 resin in low $SUVA_{254}$ water to pass through the XAD-8 column in higher $SUVA_{254}$ waters (Chow et al., 2005). This led to differing amounts of THM precursors present in each fraction from different waters (Chow et al., 2005). As a result the THM formation potential and XAD fractionation data are most useful for comparing samples from similar sources or treatment studies (Chow et al., 2005). The k´ values is also controlled by the amount of resin used with a rearrangement of the equation for column breakthrough volume (Leenheer, 1981) gives:

k´ = ((column breakthrough volume of solution)/(resin void volume)) -1 **Eq. 5**

The amount of resin is generally calculated based on an idealised solution that is 50% retained and 50% eluted ($k´_{0.5retained}$=50). Based on a 65% void volume of XAD-8 this results in 15mL of resin/ L of solution (Leenheer, 1981; Goslan et al, 2002), which is

commonly used in the literature (Croué et al., 1999; Thurman and Malcolm, 1981; Marhaba et al., 2003). The equation indicates that k' can be controlled by varying the amount of resin, or concentration of a model compound solution. The affect of k´ on the HPO/HPI spilt is investigated by Kitis et al. (2002) and Song et al. (2008) with the fraction retained to the resin increasing with a decreasing k´ value. This has been deliberately employed by Croué et al. (1999) who reduced k´ to 5 in the XAD-4 column in order to isolate HPI (redefined in this study as NOM which does not sorb to a XAD-4 column at a k′ of 50 but will sorb to a XAD-4 column at a k′ of 5) from ultra-HPI (does not sorb to a column of XAD-4 at a k′ of 5) NOM.

pH of sorption and desorption

A pH of 2 is commonly used in XAD fractionation literature as this maximises the HPO/HPI split based on 99+% of HA and FA having a k´ over 50 at this pH (Malcolm, 1989). However, Town and Powell (1993) suggest a pH of 2.5 is more appropriate due to the low solubility (0.01mg/L) of humic acids at pH2 giving rise to possible precipitation of humic acid within the resin pores and consequential unavailability for desorption. The pH of desorption is also important and shows less agreement between studies varying between pH10 (Marhaba et al., 2003), pH11 (Kitis et al., 2002) and pH13 (Kim and Yu, 2005; Leenheer, 1981; Malcolm and MacCarthy, 1992) and is not always reported. Finally, whilst the majority of studies use HCl to acidify samples, Liang and Singer, (2003) use H_2SO_4.

Sample collection

Originally presented theoretically by Malcolm and MacCarthy (1992), Gadmar et al. (2005) showed the DOC content of the column effluent to vary as the XAD fractionation progressed with increasing DOC content over time. These results indicate a variation in column sorption capacity as the fractionation progresses due to a reduction in free sorption sites leading to increased competition between NOM molecules for adsorption sites, identified previously by (Croué et al., 2000). When a mass analysis technique is employed it is therefore important if sub-samples during fractionation, or samples from the fully collected sample, are used in analysis of DOC content (Gadmar et al., 2005).

3.9. Conclusions

NOM is a complex mix of organic species, which react in different ways during water treatment processes. The hydrophobicity of these species is the most important determinant of removal potential. HPO species are readily removed from solution by the traditional coagulation method, whilst HPI species remain in solution and pass through to the final effluent. Variations in absolute NOM concentration and type cannot be easily measured directly at WTW's and UV_{254} is often used as a surrogate measure. However, UV_{254} is predominately a measure of aromaticity and therefore does not show the same relationship for different NOM species. A combination of more stringent EU regulations on the concentration of DBP in WTWs effluents, and international targets to reduce carbon footprints and chemical use are driving the need to further characterise NOM.

XAD adsorption resins can be used to fractionate NOM based on hydrophobicity and can be chosen or modified to preferentially adsorb different organics. Adsorption is controlled by pH, with low pH's promoting sorption to the resin, and high pH's promoting desorption and resin regeneration. The use of XAD-8 (substituted by DAX-8 or XAD-7HP since discontinuation) and XAD-4 is the most popular NOM fractionation procedure and creates three fractions termed HPO, TPH and HPI which can be analysed for DOC using either back elution or mass analysis. Investigations with model compounds indicate these fractions are not discrete, with overlaps between the molecules contained in each fraction. However, different functional groups within NOM are shown to dominate different fractions. Aromatic groups are more commonly associated with the HPO fraction; carboxylic acids are associated with the TPH fraction and carbohydrates with the HPI fraction.

Whilst originally used purely as a NOM characterisation tool, XAD fractionation is increasingly used to assess temporal and spatial variation in NOM type, predict residual DBP formation potential and identify treatment solutions. As XAD fractionation is an operationally defined procedure, the affect of any method alteration on the fractions produced must be assessed and reported to maintain consistency in study comparisons. This is currently lacking within the literature (for example no comparison between DAX-8 and XAD-7HP could be found by the author).

4. Materials and Methods

4.1. Material selection

4.1.i. Sorbents

In the traditional column fractionation method, outlined by Malcolm and McCarthy (1992), the acrylic based macroporous resin XAD-8 (Amberlite^{TM}) is used as the HPO sorbent followed by the styrene based XAD-4 (Amberlite^{TM}) as the TPH sorbent. Since the discontinuation of XAD-8, two similar resins have been used as substitutes, DAX-8 (Superlite^{TM}) (Croué et al., 1999; Marhaba et al., 2003; Jegatheesan et al., 2008) and XAD-7HP (Amberlite^{TM}) (Kim and Yu, 2005; Goslan et al., 2002; Bond, 2009). No previous comparative study of these two resin's sorption capacity for DOC was found in the literature.

As a consequence, the three macroporous resins chosen for trials throughout all method development stages were DAX-8, XAD-7HP and XAD-4. DAX-8, obtained from Sigma Aldrich, is an acrylic based macroporous resin of slight polarity. XAD-7HP, obtained from Rohm and Haas, is an acrylic based macroporous resin of weak polarity. XAD-4, also obtained from Rohm and Haas, is a styrene based, non-polar, macroporous resin. The selection of these three resins enabled a comparison of these three resins' sorption capacities for DOC and the identification of the most useful resin or paired resins in the rapid DOC fractionation.

4.1.ii. Sorbates

Model compounds

Three model compound solutions were selected to best represent the three NOM fractions (HPO, TPH and HPI) produced during the traditional column fractionation technique. Selection of compound was based on work by Bond (2009) who identified a positive relationship between log K_{ow} (a measure of the hydrophilic tendency of a substance) and sorption to XAD-7HP followed by XAD-4 macroporous resins using column fractionation with back elution method (see section 3.5). From the 21 model compounds investigated, tannic acid, 1,3 acetonedicarboxlyic acid (also known as 3-oxopentanedioic acid) and d-xylose were selected as compounds with HPO, TPH and HPI tendencies respectively. None of the 21 model compounds tested by Bond (2009) was present in the TPH fraction (HPI to XAD-7HP but HPO to XAD-4) by

more than 50%. For this reason a further model compound, citric acid, which was not trialled by Bond (2009), was also analysed using the column fractionation procedure due to its intermediate log K_{OW} (-1.64) value and high carboxylic acid group content, both of which indicated transphilic properties.

Natural water

Characterisation of NOM using XAD absorption resins were shown in section 3.6.ii. to be an important analytical tool in the identification of seasonal and spatial variations in NOM type and concentration, to improve treatment at the WTWs. In order to both investigate NOM variability and test the rapid fractionation tool developed in this research against the tradition column fractionation procedure, a section of natural waters were collected for analysis using both these fractionation techniques.

13 natural water samples were obtained from Butterley reservoir, Marsden, West Yorkshire between the 8th October 2009 and the 31st May 2010 to investigate NOM seasonality. On the 23rd April 2010 further samples were taken from the same water catchment, from Eastergates intake, Scammonden reservoir, and a raw and treated sample from Longwood WTW (Figure 14). Longwood WTW often struggles to treat incoming NOM due to the variability caused by these different source waters (Figure 15), which can be identified in fractionations with XAD adsorption resins. Samples of approximately 7L were stored in 10L plastic containers at 5^{O}C prior to use. Finally, in order to compare the NOM type and concentration of water from a different catchment, a raw sample stored in a 25L plastic container, and 2L treated sample stored in a 2L glass bottle, were collected from Oswestry WTW, Shropshire, UK on the 12th May 2010 and stored at 5^{O}C.

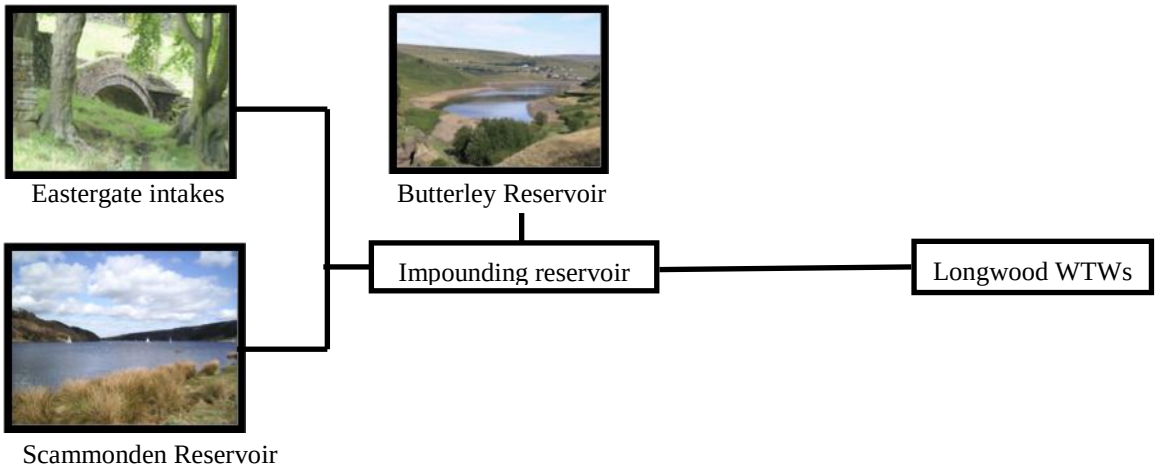


Figure 14: A schematic of the connected water pathways of the three source waters for Longwood WTW's.

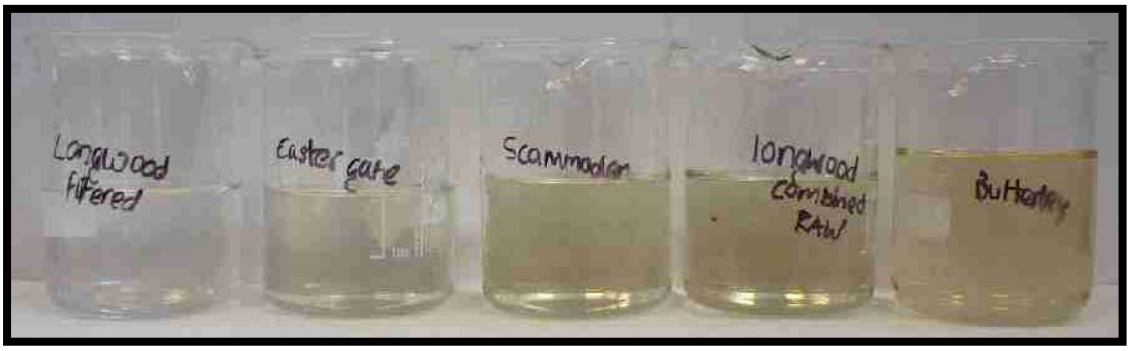


Figure 15: Natural water samples taken 23/04/2010 from the Longwood WTW catchment, filtered at 0.7μm and acidified to pH2. Variations in NOM type and concentrations create visibly different waters.

4.2. Material Preparation

4.2.i. Soxhlet cleaning of macroporous resin

Prior to use, each macroporous resin was cleaned using the Soxhlet procedure outlined in Goslan (2003). Approximately 800mL of resin was slurried with 1.5L of 0.1M NaOH for one hour before the resin was stored for 24 hours in methanol. The resin was then placed in cellulose extraction thimbles, and covered with glass wool to reduce resin leakage. These were placed inside the Soxhlet chamber (Figure 16) and Soxhlet extracted with at least 1.8L of methanol, then acetonitrile and finally methanol, for 48 hours each.

Before being used, resin was placed in a glass column and at least 6L of ultra pure water passed through at a flow rate of 10-12 bed volumes/hour until a run off DOC of

below 0.5mgC/L was achieved[1]. 2.5 bed volumes of 0.1M NaOH was subsequently passed through the resin to remove any impurities, followed by ultra pure water to return the column to a neutral pH. The resin was stored in 0.1M HCl, in a sealed glass bottle for a maximum of two weeks before use.

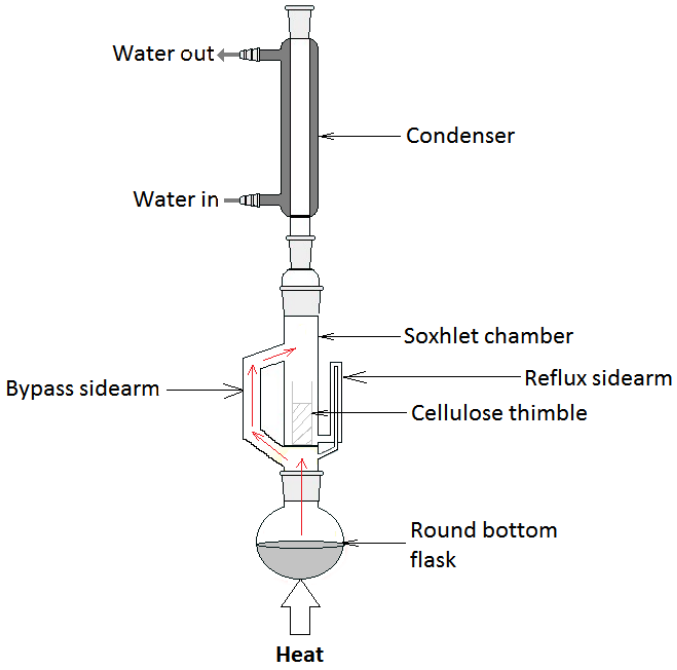


Figure 16: Soxhlet extraction apparatus set up. Approximately 16 thimbles, each containing 50mL resin could be placed in the Soxhlet chamber.

4.2.ii. Sorbate

Model compound

Model compound solutions of approximately 20mgC/L were created to represent the maximum concentrations of DOC commonly present in natural waters from within the Butterley reservoir catchment. This therefore simulated the maximum DOC loading of resin that would be expected in fractionation of natural water. The weight of each model compound to provide 1L of 20mgC/L solution was established using:

(20 (mgC/L) x MW) / MW (Carbon) = Model compound (mg/L) **Eq. 6**
MW = molecular weight

For example, tannic acid ($C_{76}H_{52}O_{46}$) has a molecular weight of 1701.22.

(20 x 1701.22) / (76 x 12) = 37.3mg/L tannic acid (3.s.f)

[1] Resin run off results are reported but were not deducted from any residual DOC measurements.

The model compound was added to 1L of ultrapure water which was then acidified to $1.95<pH\leq2.04$ using concentrated HCl (10M). The pH was measured using a Jenway 3310, which was calibrated using pH7 and pH4 standard solutions prior to use. Each model compound solution was prepared on the day of use.

Natural water

Natural water was filtered at 0.7μm and acidified to $1.95<pH\leq2.04$ using concentrated HCl (10M) on the day of use[2]. A 75mL sample was collected for DOC analysis and stored at $5^{o}C$.

4.3. Method development stages

The development of a rapid fractionation tool was completed using a four-step procedure (Figure 17), with each method detailed in the following section. In the first development stage, the contact method between resin and solution (which facilitates the sorption of HPO DOC) is transformed from the tradition plug flow, used in column fractionation, to a batch mixed system. All other variables (resin/solution ratio, DOC concentration, pH, temperature) remained unchanged. All four method development stages were trialled with each model compound solution to test the impact of method alterations on the fractions produced. All experiments outlined below were completed at room temperature ($20^{o}C$) at $1.95>pH\geq2.04$. In the following method development stages, the resin/solution ratio was increased and a scale down in the sample size was carried out. This cumulated in the final rapid fractionation tool: a single shaken sample.

After rapid fractionation had been developed and tested with model compounds, both rapid batch mixing and the single sample shake test were used to fractionate the natural water samples. Results were compared against fractionations of the same natural water samples using traditional column fractionation with back elution (see section 4.3.iii), which has been previously shown to provide a good estimation for residual NOM at the WTWs.

[2] The common convention for fractionation with macroporous resin is to filter at 0.45μm. However, the column fractionations of the natural waters completed for this work were part of a catchment wide column fractionation programme which had already begun to use a 0.7μm filter pore size and this was maintained for consistency purposes.

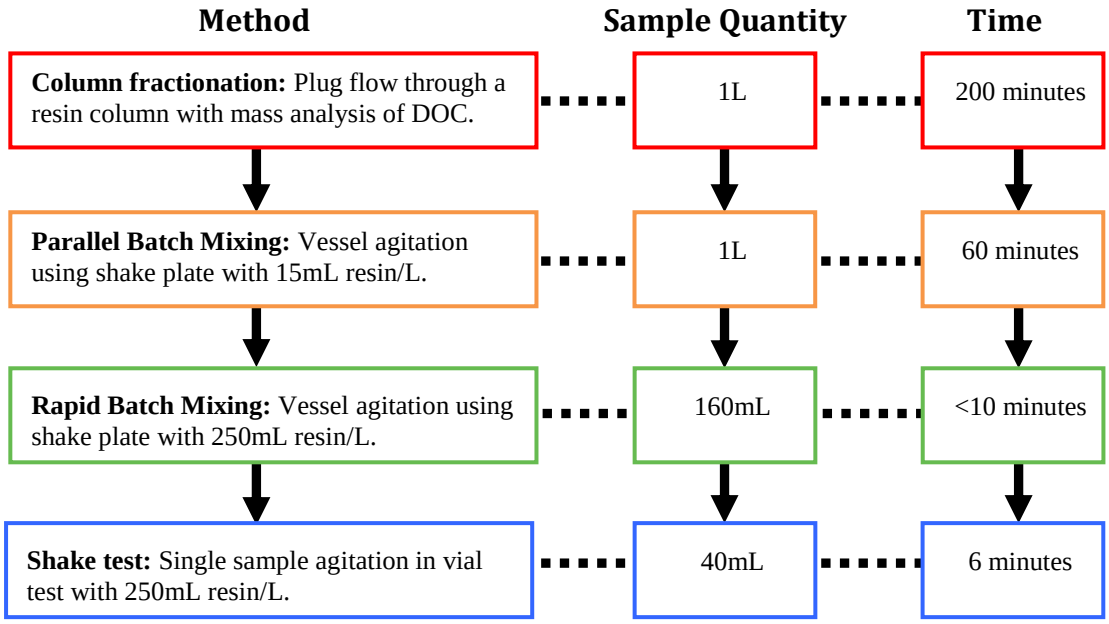


Figure 17: A schematic of the development of the rapid fractionation tool. Time of procedure indicates the point at which DOC removal equilibrium is established.

4.3.i. Column fractionation of model compounds with XAD adsorption resins

In order to assess the hydrophobicity of each model compound and to determine which out of 1,3 acetonedicarboxylic acid and citric acid would best represent a TPH solution, column fractionation with mass analysis was completed following methods outlined in Chow (2004) (see sections 3.5 & 3.8.i) (Figure 18). Mass analysis has been shown to provide a faster assessment of DOC fractionation to the traditional back elution technique, and was therefore seen as an important consideration in the development of a rapid fractionation tool.

15mL resin was used to fractionate each 1L model compound solution. This resin volume maintains a column capacity factor (k') of 50 (assuming a resin volume of 65% the column volume) (Goslan, 2003) and is commonly used throughout the literature. Each column fractionation (completed with both DAX-8/XAD-4 in series and XAD-7HP/XAD-4 in series) was carried out three times onto the same resin, which was desorbed with NaOH (0.1M), returned to neutral pH with ultrapure water, and re-acidified with 0.1M HCl between fractionations.

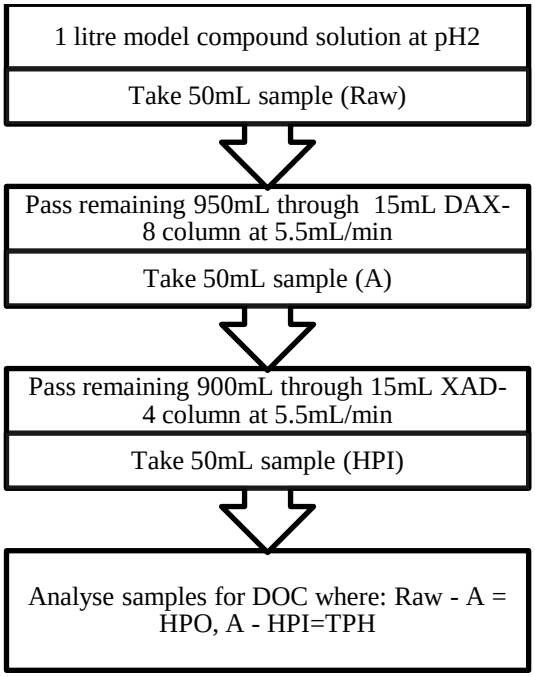


Figure 18: Procedure used for model compound column fractionation with mass analysis.

Three replica fractionations were completed to give the average HPO, TPH and HPI fractions for each of the four model compounds. The three model compounds best representative of a HPO, TPH and HPI solution were then used in all further model compound investigations. The direct sorption to XAD-4 resin was also analysed for these three model compounds following the procedure outlined above. This was to identify the difference between direct and secondary use of XAD-4.

4.3.ii. Batch mixing with XAD adsorption resins

Parallel batch mixing of model compounds

The first 15mL of cleaned DAX-8/XAD-7HP/XAD-4 resin was measured out using a 25mL glass measuring cylinder and transferred to a 2L glass beaker using 25mL HCl. This was placed on a SSL1 orbital shake plate and rotated at 150rpm (a speed previously used by Yu et al. (2009) in batch sorption experiments with activated carbon and anion-exchange resins), which gave full vertical mixing of the resin[3] (Figure 19). A 1L model compound solution was prepared and added to the rotating beaker (with approximately 50mL reserved as a raw sample). Samples of approximately 25mL were taken at every 2 minutes for the first 10 minutes, then every 10 minutes in the first hour, and then hourly for the next six hours and a final

[3] Due to the centrifuge effect, resin concentration was observed to be greater in the centre of the beaker.

sample is taken after 24 hours. Samples were left to settle momentarily, (to avoid blockage of the syringe nozzle) and then passed through a syringe and 0.45μm filter to isolate the solution from the resin. By this method, the sample was isolated in approximately 30 seconds whilst the resin/solution ratio was maintained within the reaction beaker. Each experiment was replicated three times, with Soxhlet cleaned resin.

a)  b) 

Figure 19: a) vertical mixing of DAX-8 resin b) plan view of parallel batch fractionation procedure.

Rapid batch mixing of model compounds and natural waters

A rapid test was trialled using 250mL resin/L (a 1:4 ratio) of model compound or natural water. 40mL of cleaned and wetted resin (in 0.1HCl) was placed in a 400mL glass beaker, with excess solution decanted. 160mL of the model compound or natural water solution was added to initiate the reaction, which followed the parallel batch fractionation methods. Samples of approximately 15mL were taken over an hour period at the same time increments used during the parallel batch fractionation, with a further sample taken after one minute of mixing. Experiments using the model compounds and one natural water sample (taken from Butterley reservoir on 3rd December 2009) were completed three times, whilst singular experiments were completed for the remaining natural waters. Soxhlet cleaned resin was used throughout all experiments with model compounds. However, a combination of Soxhlet cleaned resin and used resin (which had been desorbed by rinsing with 0.1M NaOH and returned to neutral pH with ultrapure water, before re-acidification with 0.1M HCl) was used for natural water, to maintain consistency with the column fractionation procedure.

Single sample shake test for model compounds and natural waters

In a final stage of method development, 10mL of cleaned DAX-8/XAD-7HP/XAD-4 resin in 0.1M HCl was placed into a 50mL glass sample bottle with the excess HCl decanted. This can be achieved for both the DAX-8 and XAD-7HP but was more difficult for the XAD-4 resin (Figure 20), which maintained a more fluid consistency due to a slight excess of HCl and the more buoyant nature of the styrene based XAD-4. 40mL of model compound solution or filtered, acidified natural water was added to the resin, giving the same resin/solution ratio achieved in the rapid batch mixing procedure. The bottle was sealed and the vessel was immediately agitated using a Heidolph Multireax vial shaker at speed 8, which simulated a hand shaking agitation and allowed full mixing of the resin and solution (Figure 21). Using the vial shaker allowed three replicas to be completed simultaneously. After six minutes the resin/solution mixture was left momentarily to separate and was decanted into a sample bottle using the method described in the previous sections[4].

In a second stage, a 20mL sample of each of the solutions treated with DAX-8 or XAD-7HP resin was added to 5mL of XAD-4 resin (maintaining the same 1:4 resin:solution ratio) and again agitated for six minutes and filtered into sample bottles. By this means samples could be analysed to give HPO, TPH and HPI fractions for each of the model compounds and natural waters.

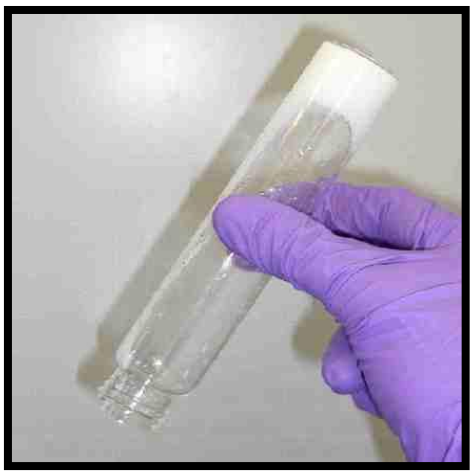
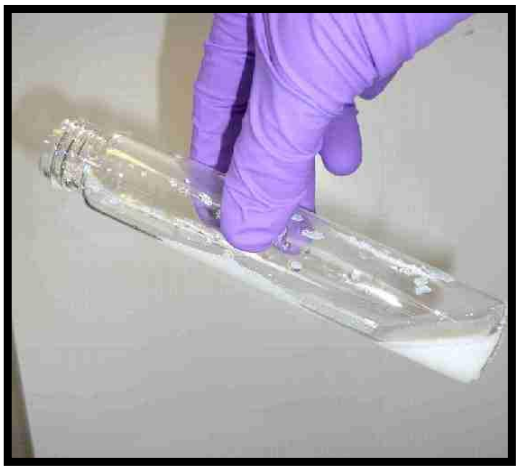
a)  b) 

Figure 20: a) XAD-7HP b) XAD-4 in single sample glass bottle.

[4] It was apparent that natural water samples, which were originally filtered at 0.7μm would obtain further treatment due to the 0.45μm filter used to isolate the solution from the resin. In order to quantify this error, each raw natural water sample was also filtered at 0.45μm and analysed for TOC.

a)  b) 

Figure 21: a) Single sample test set up, b) showing complete mixing between resin and solution.

4.3.iii. Hydrophobicity of natural waters: Column fractionation with back elution

The ability of both rapid batch fractionation and the single sample shake test to identify the hydrophobicity of natural water samples was identified in comparisons of the two techniques against traditional column fractionations with back elution. 75mL of each raw water sample was taken for analysis of DOC content. 2L samples of each filtered and acidified natural water were passed through two columns containing 30mL of XAD-7HP and XAD-4 resin in series (Figure 22) using a modified version of the fractionation procedure outlined by Malcolm, (1989), (described in section 3.5). Flow speeds were maintained using a peristaltic pump at 5.5mL/min for XAD-7HP and XAD-4. Column fractionations (with back elution) of natural waters were not replicated.

The acidified sample was first passed through the XAD-7HP resin, wasting the first 1.5 bed volumes. After approximately 1L of sample had passed through both the XAD-7HP and XAD-4 columns, 75mL of effluent was collected as the HPI fraction. Once the 2L raw sample had passed through both columns, ultrapure water was then pumped through each column until a neutral pH was observed in the column effluent. 2.5 bed volumes of 0.1M NaOH (75mL) were then passed through, in the same direction, to desorb the HPO (from XAD-7HP) and TPH (from XAD-4) NOM remaining on each resin column. This was collected as the HPO and TPH fractions. Ultrapure water was again passed through the columns to return them to neutral pH before 3 bed volumes 0.1M HCl, re-acidified the columns for the next procedure.

Resin was reused for further fractionations until resin run off with ultrapure water was in excess of 2mgC/L. In-between fractionations the resin was left in 0.1M HCl.

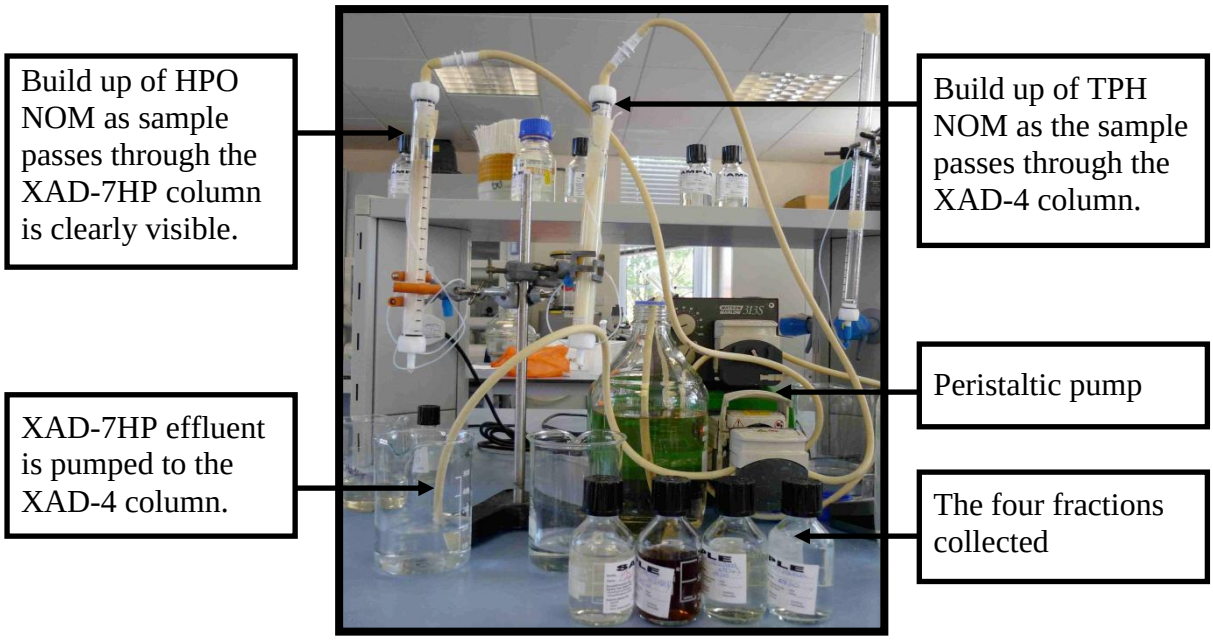


Figure 22: Column fractionation with back elution procedure, with the four fractions shown in the bottom right (from left to right: Raw, HPO, TPH and HPI).

4.3.iv. Establishing adsorption isotherms

A variety of resin/solution concentrations were used to establish adsorption isotherms, which provide information regarding the adsorption mechanisms governing this DOC sorption process. As the macroporous resin shows a high affinity for DOC, low resin concentrations ranging from 0.5-10mL resin/L of model compound solution were required. The weight of 10mL of each of the three wetted resins was calculated (to 0.01g) and used to determine the weight of resin required to achieve these concentrations of 0.5, 2, 4, 6, 8, and 10mg resin/L for 200mL model compound solutions. The resin was added to 400ml glass beakers with the reaction initiated upon the addition of 200mL of model compound solution. Samples of approximately 10mL were taken at 10 minutes, 60 minutes and 3, 6, 24, 30, 48 and 72 hours. Experiments were replicated three times for each resin and the mean average taken.

In a separate control experiment, the use of acidified ultrapure water in place of the model compound solution allowed the evaluation of the effect of experimental conditions on the resin/solution mixture.

4.4. Analytical techniques

4.4.i. DOC

The Shimadzu 5000A TOC analyser was used to analyse DOC of each sample at a 0-10mgC/L calibration[5]. When necessary, samples were diluted using acidified ultrapure water. The machine was adjusted to its most precise settings by maximising the amount of sample it used. For parallel batch fractionations and column fractionations, three 7mL vials (sealed with parafilm to avoid the emission of VOCs) of each sample were analysed in the TOC and the mean average taken. However, for the remaining tests only one sample of each could be analysed due to the reduction in initial solution volume as part of the method development.

Quality assurance

Analysis for organic carbon can be performed using either a TC-IC method (the difference between total carbon (TC) and inorganic carbon (IC)) or a NPOC method (non purgable organic carbon which requires acidification of samples to below pH3). Initial quality assurance experiments with dilutions of a 1000ppm carbon standard solution, equally spaced across the calibration range at 0, 2.5, 5, 7.5 and 10mgC/L, were completed to identify the working range and accuracy of each method.

Each solution was placed in ten 7mL vials sealed with parafilm, one as a machine calibration and the remaining nine as 'unknown' samples. Analysis of the results identified a lower limit of detection for the NPOC analytical method (see Appendix I), which was thus employed, for all DOC analysis of model compound solutions. The results also highlighted an error in the machine's analysis of the initial calibration points, which were statistically different to all other samples[6], causing two calibrations sets to be completed for all sample analysis throughout this research, and only accepted at $r^2>0.985$. However, natural water fractions, created using the traditional column fractionation with back elution were analysed using the TC-IC method to maintain consistency across a wider catchment sampling programme.

[5] Due to sporadic malfunctions of the Shimadzu TOC 5000A, some column fractionation samples were instead analysed using a Shimadzu TOC-V analyser.
[6] 99% certainty (as outside three standard deviations) of a difference between the samples used for the 0-10 NPOC calibration and the other samples.

4.4.ii. UV adsorption

UV_{254} was analysed using a Spectramax Plus 384 for both model compounds and natural waters samples from the rapid batch and single sample fractionations. For model compounds, the occurrence of a direct relationship between DOC and UV acted as a further quality assurance of the TOC analysis. UV adsorption data was obtained using a 4cm x $1cm^2$ vial with the machine calibrated, before use, with a sample of ultrapure water. Each sample was measured once, at room temperature (20^oC). UV absorbance data could not be collected for the HPI model compound, which showed no UV absorbance even at raw concentrations.

4.4.iii. Significance

Unless stated otherwise, significance was calculated at both the 95% (p=0.05) and 99% (p=0.01) confidence intervals and based on the standard deviation (σ) of each data point. This method has been used to calculate the significance of the variation in absorbance, with normal distribution assumed. As three replicas were performed for each test, a t-distribution with two degrees of freedom (n-1) predicts 95% of the data lie within 4.303 standard deviations, and 99% of the data within 9.925 standard deviations (Fowler and Cohen, 1995). These limits have been used in assessment of significance at p=0.05 and p=0.01.

5. Result I: The Development of a single sample rapid NOM fractionation tool for model compounds

The traditional NOM characterisation method, known as XAD column fractionation with back elution, takes over 3 hours to produce each fraction, and can only be used by trained personnel in a laboratory environment. As a result it cannot be easily used to optimise WTW processes according to raw water NOM. Four method development steps were used to transform this procedure into a single sample rapid fractionation device, capable of onsite NOM fractionations. Three model compounds, which varied in hydrophobicity were used to assess the fractions produced in each method development stage.

5.1. Modifying the contact mechanism: A comparison of column plug flow and batch mixing fractionation

The removal of model compounds onto three different macroporous resins (DAX-8, XAD-7HP and XAD-4), were compared for both plug flow column fractionation, modified from Malcolm and McCarthy (1992), and a parallel batch mixed fractionation as the first two stages in the development of a rapid and robust fractionation tool. DOC removal was assessed using mass analysis (Chow et al, 2004; Lee et al, 2004) for both rapid and column fractionations.

5.1.i. First method development stage: Column fractionations

Model compound identification

The three model compounds, which were used throughout this research to represent HPO, TPH and HPI NOM, were selected based on their log K_{OW} values, which is a measure of their aqueous solubility or hydrophobicity. Column fractionations with mass analysis were performed for four 20mgC/L compound solutions onto DAX-8 followed by XAD-4 (Figure 23) and XAD-7HP followed by XAD-4 (Figure 24). Results are presented as % DOC as this removes any variations in total TOC concentrations resulting from the calibration standards used in the TOC analysis and precision of model compound solution production.

The amount of sorption to XAD-7HP and DAX-8 for each of the four model compounds was of the order: tannic acid>1,3 acetonedicarboxylic acid>citric acid> d-

xylose. The high sorption of tannic acid onto XAD-7HP (88%) and DAX-8 (99%), along with its high log K_{OW} value (13.3) confirms it to be a very hydrophobic compound. In contrast, less than 1% of d-xylose adsorbed to any of the three resins. This, combined with the very negative K_{OW} value (-1.98) indicated that d-xylose was very hydrophilic in nature. Of the two compounds investigated for intermediate hydrophobicities, 1,3 acetonedicarboxylic acid (K_{OW}=-1.13) shows a greater TPH fraction for both XAD-7HP/XAD-4 (18%) and DAX-8/XAD-4 (18%) than the citric acid of which 97% was HPI in respect to both macroporous resins for both column fractionations. This was despite a high carboxylic acid group content being suggestive of a TPH nature. Consequentially, 1,3 acetonedicarboxylic acid was used in all following investigations to model the sorption of TPH NOM in each method development stage whilst tannic acid and d-xylose were used to model HPO and HPI NOM compounds respectively.

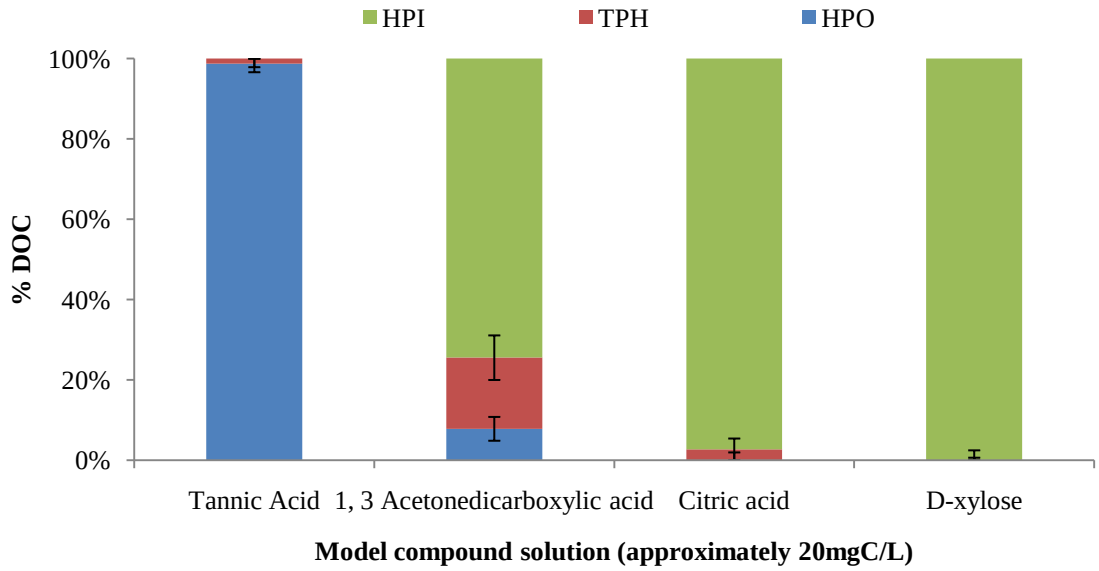


Figure 23: The fractionation of model compounds using DAX-8 to produce the HPO fraction followed by XAD-4 to produce the TPH fraction[7]. The DOC remaining in the solution was the HPI fraction.

[7] Error bars were not extended below 0% or above 100% for any of the column fractionation results.

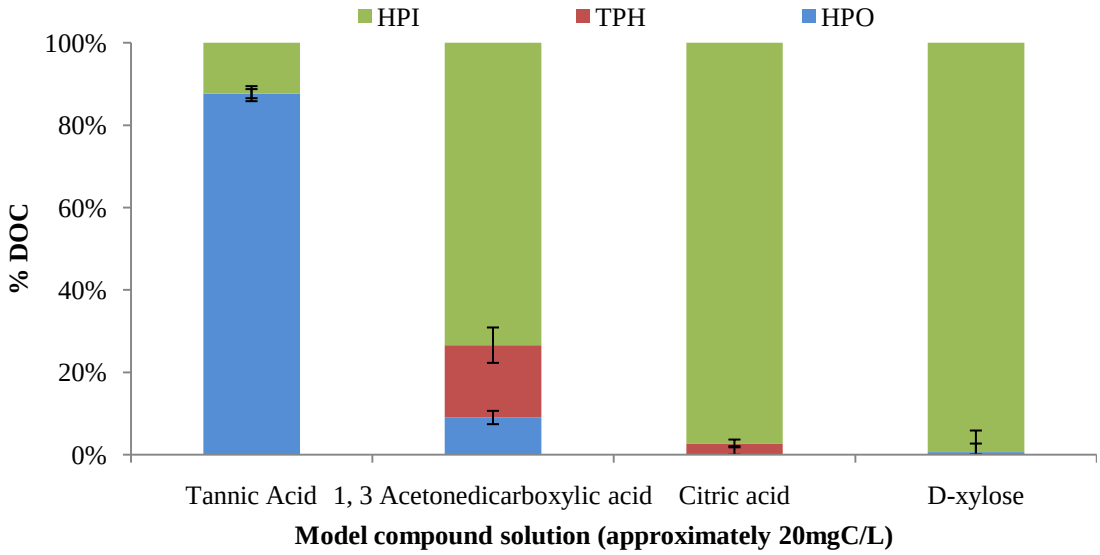


Figure 24: The fractionation of model compounds using XAD-7HP to produce the HPO fraction followed by XAD-4 to produce the TPH fraction. The DOC remaining in the solution was the HPI fraction.

The three selected model compounds were also directly fractionated onto 15mL of cleaned XAD-4 resin (Figure 25). In conventional fractionation, this resin is used to separate the TPH fraction after HPO material has been removed onto XAD-7HP or DAX-8. The same order of hydrophobicities (from HPO to HPI: tannic acid>1,3-acetonedicarboxylic acid>d-xylose) was observed for the model compounds onto XAD-4. Therefore, despite being typically used to remove TPH material, XAD-4 was also able to remove HPO compounds. However, a significant reduction in total DOC sorption of over 12%, for both 1,3 acetonedicarboxylic acid (the TPH model compound) and the tannic acid (the HPO model compound), occurred when the XAD-4 resin was used in isolation, instead of as a secondary sorbent, following either the DAX-8 or XAD-7HP. This suggests XAD-4 has a lower affinity for HPO molecules than the other two resins.

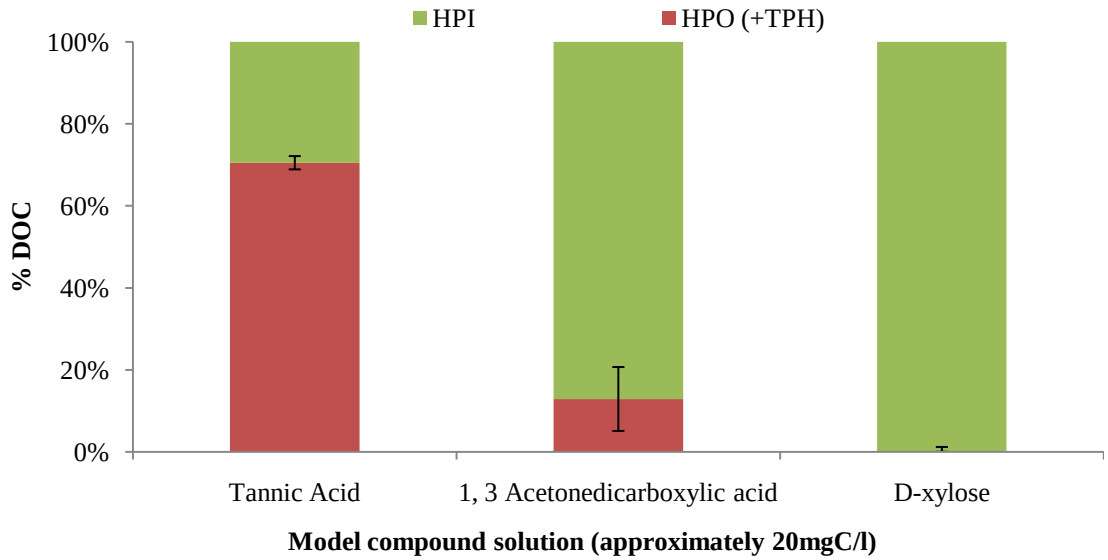


Figure 25: The fractionation of model compounds into HPO (+TPH) and HPI using XAD-4 only. The fraction sorbed to the XAD-4 is referred to as HPO (+ TPH) because it is HPO with respect to the XAD-4 but it includes the substances referred to as TPH with regards to DAX-8 and XAD-7HP.

In all column fractionations, despite the deliberate selection of compounds of HPO, TPH and HPI natures as predicted by their log K_{OW} values, only d-xylose was 100% contained within one fraction. This is in line with previous fractionations of model compounds by Bond (2009) and highlights the indistinct nature of each operationally defined fraction. The probability of absorption to the resin occurring is partially controlled by number of free adsorption sites. This reduces over time as DOC concentration on the resin increases and therefore the chance of adsorption to the resin decreases. This means that molecules contained within one fraction at the start of the procedure, can be found in other fractions as the procedure progresses.

Variations between column fractionation

The error for each fractionation is expressed as one standard deviation from the average % DOC removal (based on three fractionations) onto each resin[8]. Standard deviations range from 0.65% (for the TPH fraction of d-xylose in the DAX/XAD-4 fractionation) to 7.79% (in the fractionation of 1,3 acetonedicarboxylic acid by XAD-4 in isolation), and for all resins the greatest deviation of results occurred for 1,3

[8] Any negative DOC removal calculated during the mass analysis was given the value of 0. Negative values could arise as a result of leaching from the resin.

acetonedicarboxylic acid, the TPH model compound. For each model compound, the variation in the solution starting concentration was below 2mgC/L[9].

DAX-8 and XAD-7HP, which are both used as a replacement to XAD-8 for the fractionation of HPO material, gave similar sorption of all model compounds, with no significant difference in adsorption (as calculated using a t-test). Adsorption of the HPO model compound to the XAD-4 was significantly lower (p=0.05) than sorption to the DAX-8, and 17% lower than sorption to XAD-7HP (not significant). For XAD-4, sorption of the TPH model compound was higher than both the other resins (although this was not significant due to the higher deviation seen between results for the TPH model compound). This indicates that XAD-4 has a greater affinity for TPH NOM than the other resins.

The three model compounds selected to represent HPO, TPH and HPI solutions were previously fractionated by Bond (2009)[10] using column fractionation with back elution onto XAD-7HP followed by XAD-4 (Table 5). The HPO fraction results obtained by Bond (2009) were similar to the results obtained in this research for all model compounds. However, Bond (2009) reports a significantly higher TPH fraction for tannic acid (p=0.01), 1,3 acetonedicarboxylic acid (p=0.05) and d-xylose (p=0.01). This difference may have been the result of a reduced DOC loading on the resins used in Bond (2009) as 10mgC/L solutions were used rather than the 20mgC/L used in this study. Also a back elution technique was used to collect the fraction instead of the mass analysis technique used in this study, which may have led to differences in fraction recovery (section 8.3.ii.).

Table 5: The % DOC recovered in each fraction by Bond (2009), with the results from this study given in ( ).

	Tannic acid	1,3 Acetondicarboxylic acid	D-xylose
% HPO	90 (88)	8 (9)	1 (1)
% TPH	7 (0)	44 (18)	6 (0)
% HPI	3 (12)	46 (73)	93 (99)

[9] Average raw compound concentrations were 17.8mgC/L (tannic acid), 18.0mgC/L (citric acid) and 18.7mgC/L (d-xylose). The average concentration of raw 1,3 acetondicarboxylic acid was lower at 10.9mgC/L, thought to be a result of an error in the TOC5000A calibration during analysis.

[10] 2L of each 10mgC/L model compound solution was passed through columns containing 30mL of XAD-7HP and XAD-4 resin in series, with DOC analysed using back elution followed by a TC-IC calculation of TOC using the TOC5000A.

5.1.ii. Second method development stage: Parallel Batch fractionation

Results for the removal of 1L model compound solutions onto 15mL DAX-8, XAD-7HP and XAD-4 using a batch mixing procedure are presented in Figures 26-28. For all resins the sorption of each model compound was of the order of hydrophobicity tannic acid>1,3 acetonedicarboxylic acid>d-xylose, which was also seen in column fractionations. For each experiment replicate, the variation in initial model compound concentration was below 2mgC/L[11].

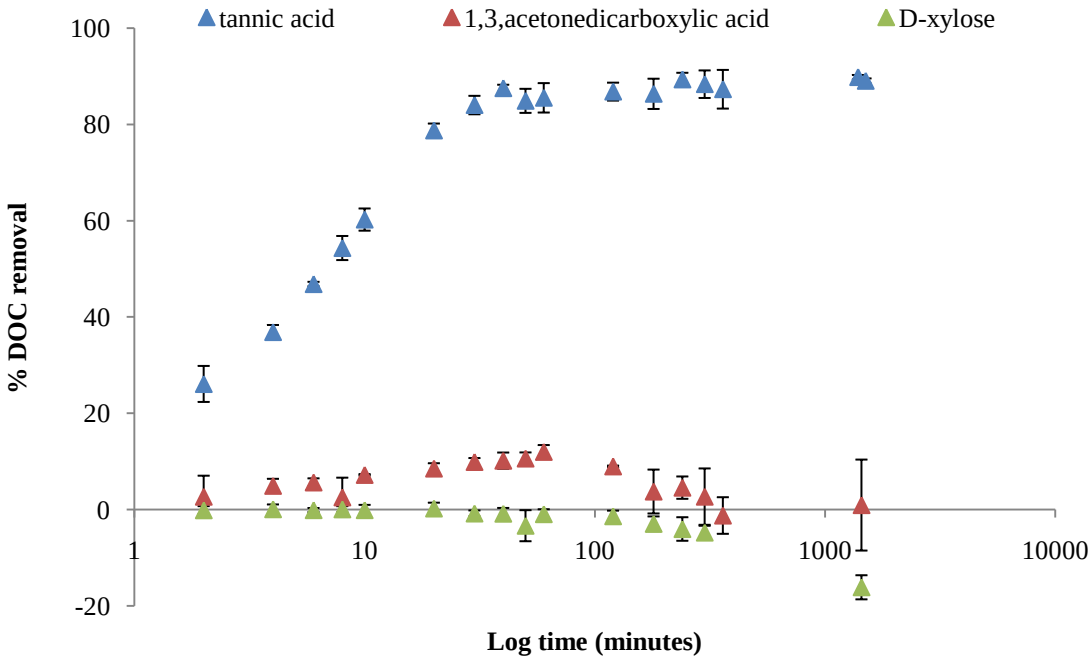


Figure 26: The sorption of 20mgC/L model compound solutions to DAX-8 resin using 1L of solution and 15mL of resin.

[11] In one case (in the sorption of tannic acid to XAD-7HP), the TOC5000A calibration was replaced for the calibration used on the following day.

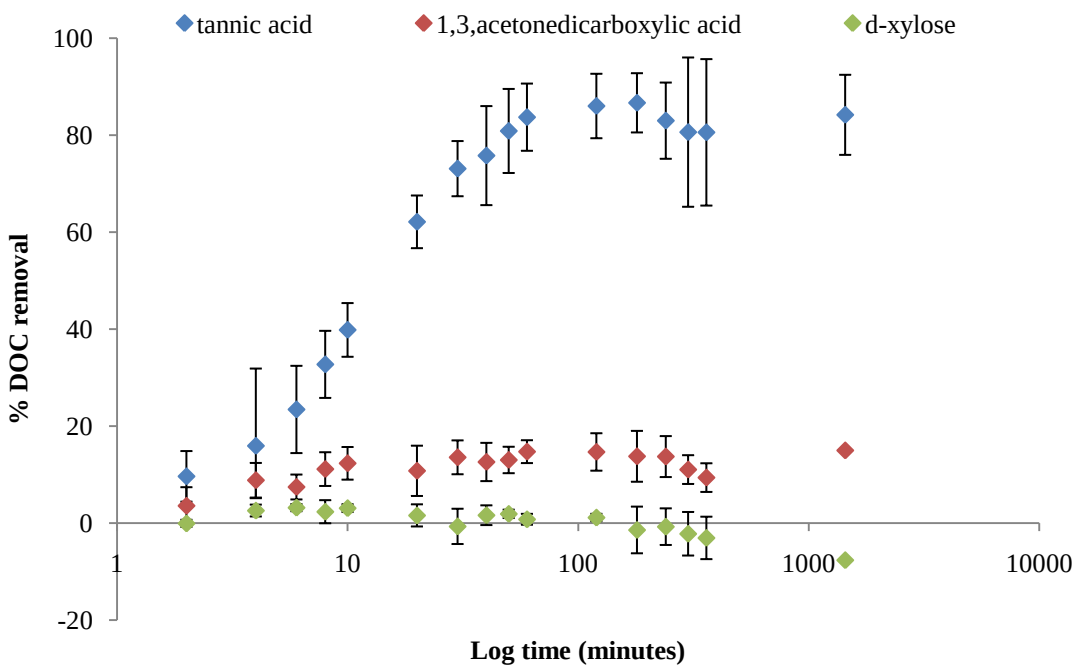


Figure 27: The sorption of 20mgC/L model compound solutions to XAD-7HP resin using 1L of solution and 15mL of resin.

The removal rates, and removal equilibrium obtained for all three model compounds onto the DAX-8 and XAD-7HP show strong similarity. DOC removal equilibrium of the HPO model compound occurred after 40 minutes (87% removal) for DAX-8 and after 60 minutes (84% removal) for XAD-7HP. For the TPH model compound equilibria occurred after approximately 30 minutes for both the DAX-8 (10%) and XAD-7HP (14%). As expected from the low log K_{OW} of the HPI model compound, d-xylose, no significant removal was observed throughout the time period for either resin (p=0.05). Instead, after 24 hours mixing with DAX-8[12] DOC concentration of the solution had significantly risen (p=0.05) from initial model compound DOC concentrations (the cause of this is investigated in section 7.2). Batch mixing fractionations with DAX-8 showed excellent repeatability, with a slightly higher deviation observed in batch mixing with XAD-7HP, in particular for the HPO model compound. A slight reduction in DOC removal onto DAX-8 and XAD-7HP was also observed for the TPH model compound, although this was not significant (p=0.05).

As with the DAX-8 and XAD-7HP, no significant adsorption of DOC occurred for the HPI model compound onto XAD-4 (at p=0.05). However, whilst a negative % DOC removal was also observed after 180 minutes, this was not significant at p=0.05

[12] No significance test was possible for the XAD-7HP sorption of d-xylose due to a power cut in the second and third replica tests between 360 minutes and 24 hours.

for the XAD-4 due to a higher standard deviation of the results. Variation in DOC removal between test repetitions was noticeably greater for the removal of the HPO model compounds onto XAD-4[13] (with a standard deviation of over 20% after 120 and 180 minutes of mixing) than with the DAX-8 or XAD-7HP.

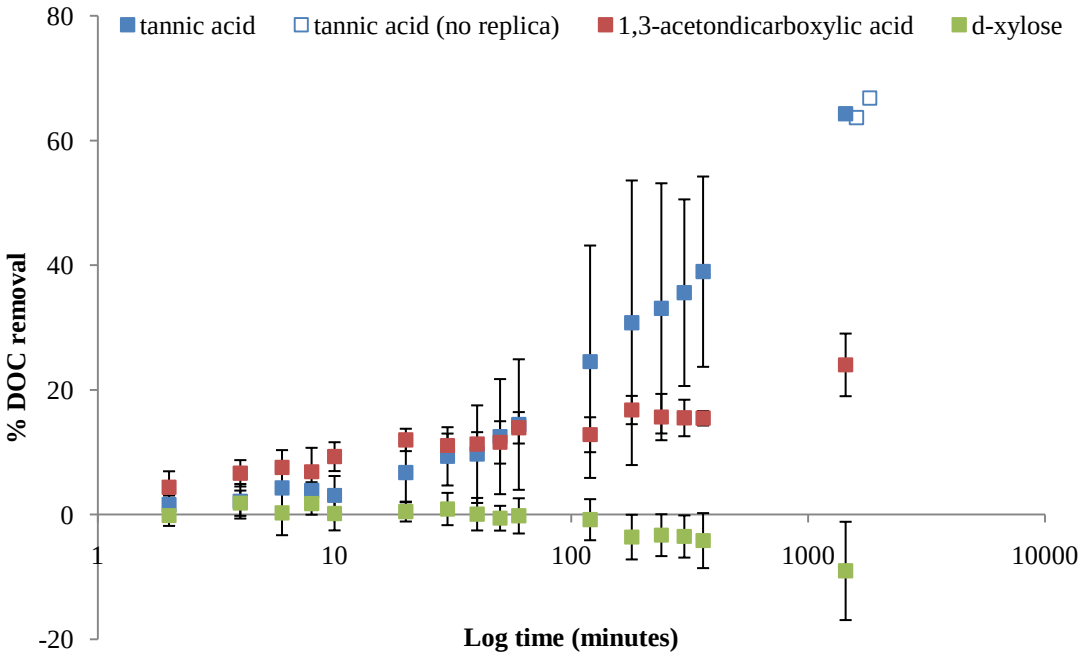


Figure 28: The sorption of 20mgC/L model compound solutions to XAD-4 resin using 1L of solution and 15mL of resin.

Unlike the HPO sorption resins XAD-7HP and DAX-8, equilibrium DOC removal onto XAD-4 resin was not achieved during the 24 hour contact time between resin and solution. This was confirmed by an increased DOC removal observed after 30 hours of mixing for tannic acid. However, even with an increased mixing time, it was unlikely that the DOC removal of the HPO model compound would have reached the level of removal obtained with DAX-8 or XAD-7HP. As seen for column fractionations, XAD-4 showed a lower affinity for HPO DOC than the other two resins. DOC removal equilibrium was also not confirmed for the TPH model compound over the 24 hour test period, but was consistently in excess of the removal achieved by DAX-8 or XAD-7HP, after 60 minutes of mixing. In contrast to the results for DAX-8 and XAD-7HP, during the first 40 minutes of resin/solution contact, a higher % DOC removal occurred for 1,3 acetonedicarboxylic acid, the TPH

[13] This high standard deviation was the result of one of the three test repetitions reaching removal equilibrium (of approximately 57%) after 180 minutes, at a much faster rate than in the other two experiments. The cause of this is unknown.

model compound, than the HPO model compound, tannic acid, although this was not significant at p=0.05.

5.1.iii. A comparison of Column fractionation and Batch mixing

The % DOC removal achieved after treating approximately 1L of model compound solution with 15mL of macroporous resin using both a plug flow column and batch mixing contact procedure are presented in Table 6. In all cases the order of hydrophobicity of the model compounds was tannic acid>1,3 acetonedicarboxylic acid>d-xylose.

Table 6: the % DOC removal onto macroporous resins for three model compounds using column fractionation and parallel batch mixing fractionations.

Model compound	Fractionation type	DAX-8	XAD-7HP	XAD-4
Tannic acid	*Column*	99	88	71
(HPO)	*Batch*	87	86	64**
1,3 Acetonedicarboxylic acid	*Column*	8	9	13
(TPH)	*Batch*	10*	15	24**
D-xylose	*Column*	0	1	0
(HPI)	*Batch*	0*	2*	1*

* Results used are the DOC removal prior to a reduction DOC removal after continued mixing.
** After 24 hour of mixing equilibrium had not yet been observed.

XAD-7HP shows the strongest correlation between the different resin/solution contact methods; with no significant difference between the % DOC removal for any model compound solution (at p=0.05). Similarly, results for DOC removal onto DAX-8 showed no significant difference between the column plug flow and parallel batch mixing fractionations (at p=0.05). As no removal equilibrium was obtained for the sorption of tannic acid and 1,3 acetonedicarboxylic acid onto XAD-4 over 24 hours it was not possible to state, with any certainty, if the results were significantly different. However, due to the high variation in the sorption of 1,3 acetonedicarboxylic to XAD-4 (particularly in column fractionation) and the continuing increase in tannic acid sorption to XAD-4 after 24 hours, it seemed likely that the final % DOC removal onto XAD-4 for the different resin/solution contact methods would not be significantly different[14].

[14] Even with a standard deviation of zero, the DOC removal at equilibrium for batch mixing would have to be in excess of 46% to be significantly different to the column fractionation results.

The time taken to pass 1L of model compound solution through a 15mL resin column was approximately 200 minutes (based on a flow rate of 5.5mL/minute). In comparison, for DAX-8 and XAD-7HP the time required to achieve a similar DOC removal (or to produce the HPO fraction) was reduced to within 60 minutes. For XAD-4, the DOC removal achieved in column fraction of the HPO model compound was not achieved during a 24 hour period. However, the 13% sorption of the TPH model compound observed after the 200 minutes column fractionation was achieved within 60 minutes using the batch mixing procedure. Therefore, by altering the resin/solution contact method from a plug flow column to a batch mixed system the time to achieve comparable DOC removal was reduced by at least 70% for all resins and model compounds except the sorption of the HPO model compound onto XAD-4.

5.2. Rapid fractionation using an increased resin/solution ratio.

5.2.i. Introduction

The speed at which DOC is removed from a solution is, in part, governed by the amount of resin surface area available for sorption and the number of adsorption sites. Therefore, in order to produce a rapid fractionation tool, the resin/solution ratio was increased from 15mL/L to 250mL/L, and tested for each model compound and macroporous resin. Samples were analysed for both DOC and UV_{254} to assess if UV_{254} could be used as a rapid onsite surrogate to DOC.

5.2.ii. Third method development stage: Rapid batch fractionation

Equilibrium DOC removal and UV_{254} was achieved in less than 10 minutes for all model compound and resin mixtures (Figures 29-34). The three model compounds show significantly different % DOC removal from each other after 1 minute for DAX-8, 2 minutes for XAD-7HP and 4 minutes for XAD-4 ($p=0.05$). In all cases, the % DOC removal of model compounds was (from highest to lowest) tannic acid>1,3 acetonedicarboxylic acid>d-xylose and the % reduction in UV_{254} absorbance was greater for tannic acid than 1,3 acetonedicarboxylic acid[15]. At equilibrium, the % reduction in UV_{254} absorbance was approximately 20% higher than the % DOC removal for all model compound solutions. This was unexpected as, due to the use of

[15] UV_{254} could not be analysed for d-xylose as, even at raw model compound concentrations, it showed no absorption of UV_{254}.

the single model compound solution, the reduction in DOC (mgC/L) and UV_{254} (cm^{-1}) should be identical (discussed in section 7.2).

The results obtained for rapid fractionation show no statistically significant difference between DAX-8 and XAD-7HP for % DOC removal or UV_{254} absorbance for all model compounds. After 4 minutes of mixing, DOC removal onto DAX-8 was 83%, 38% and 3%, for the HPO, TPH and HPI model compounds respectively (Figure 29), and 86%, 43% and 2% DOC removal onto XAD-7HP (Figure 31). For the HPO and TPH model compounds the UV_{254} absorption was, on average, 99% and 58% for both DAX-8 and XAD-7HP after 4 minutes. In general, UV_{254} absorption data show less variance than % DOC removal for both DAX-8 and XAD-7HP.

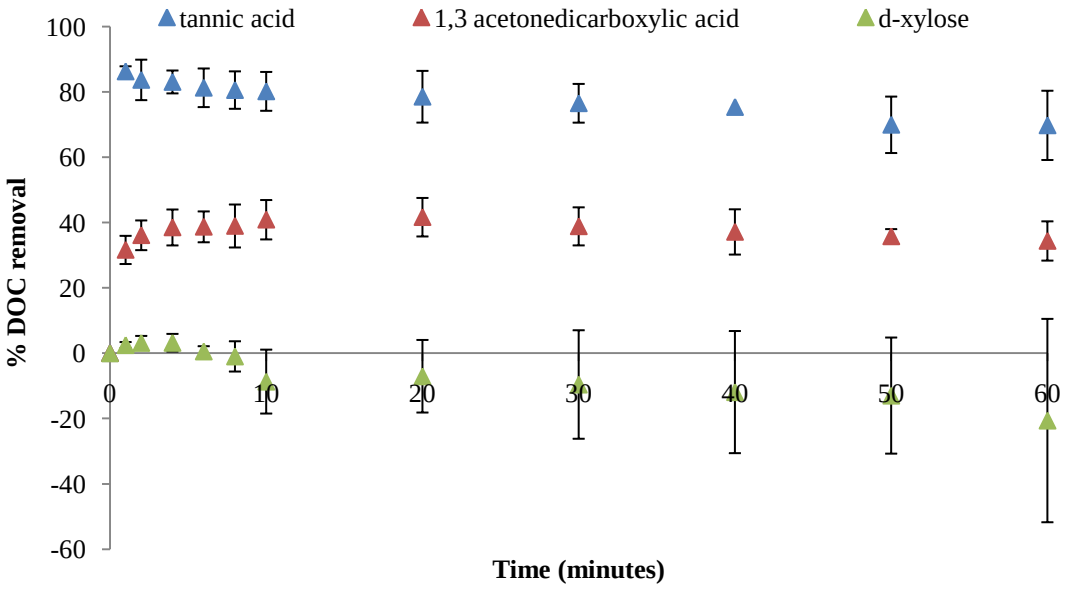


Figure 29: The sorption of 20mgC/L model compound solutions to DAX-8 resin using 160mL of solution and 40mL of resin.

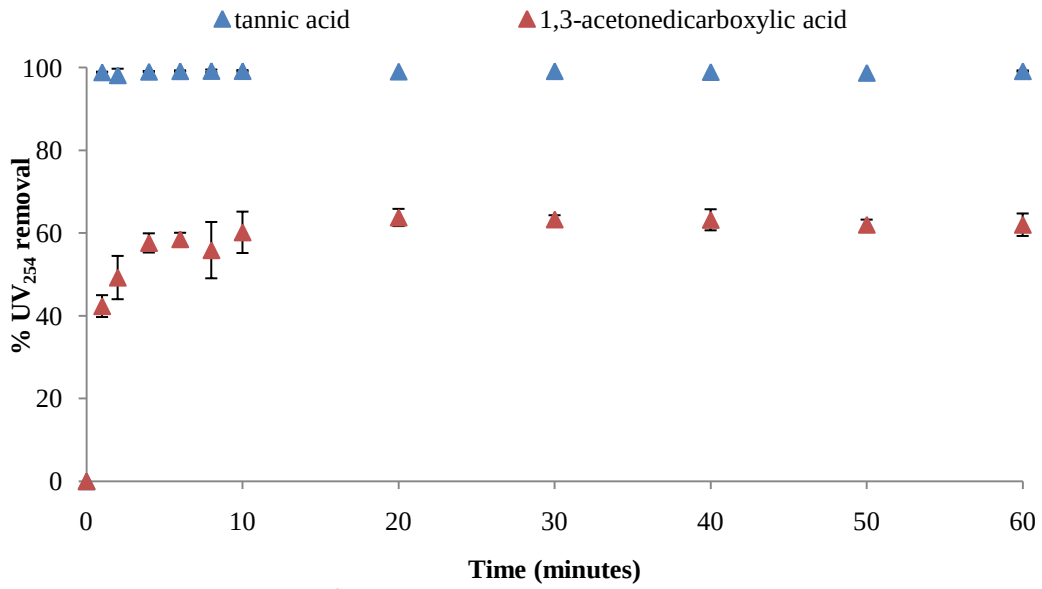


Figure 30: The % UV_{254} (cm^{-1}) removal 20mgC/L model compound solutions to DAX-8 resin using 160mL of solution and 40mL of resin.

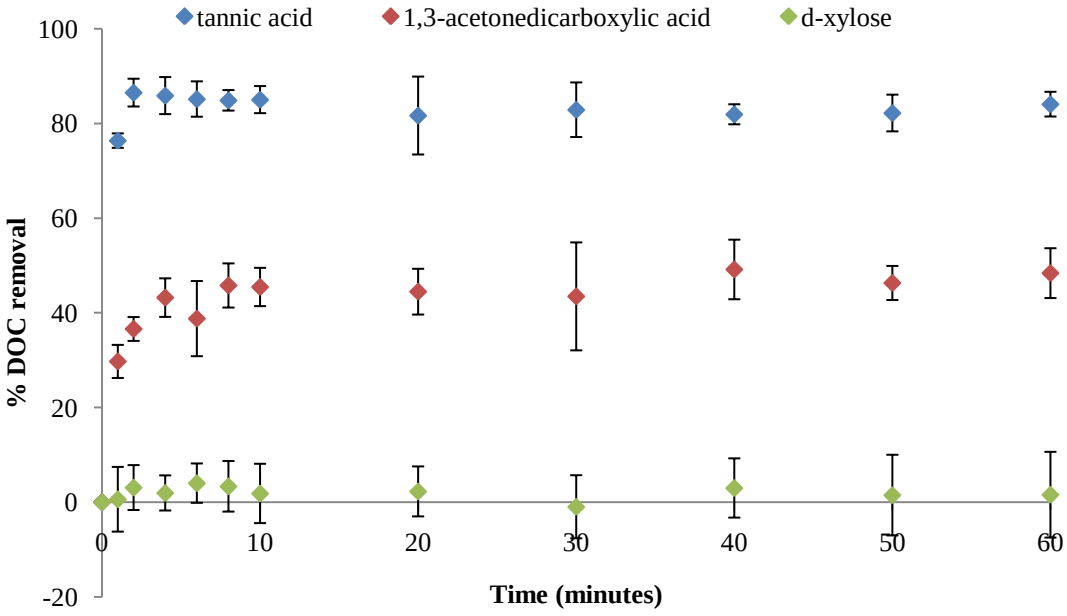


Figure 31: The sorption of 20mgC/L model compound solutions to XAD-7HP resin using 160mL of solution and 40mL of resin.

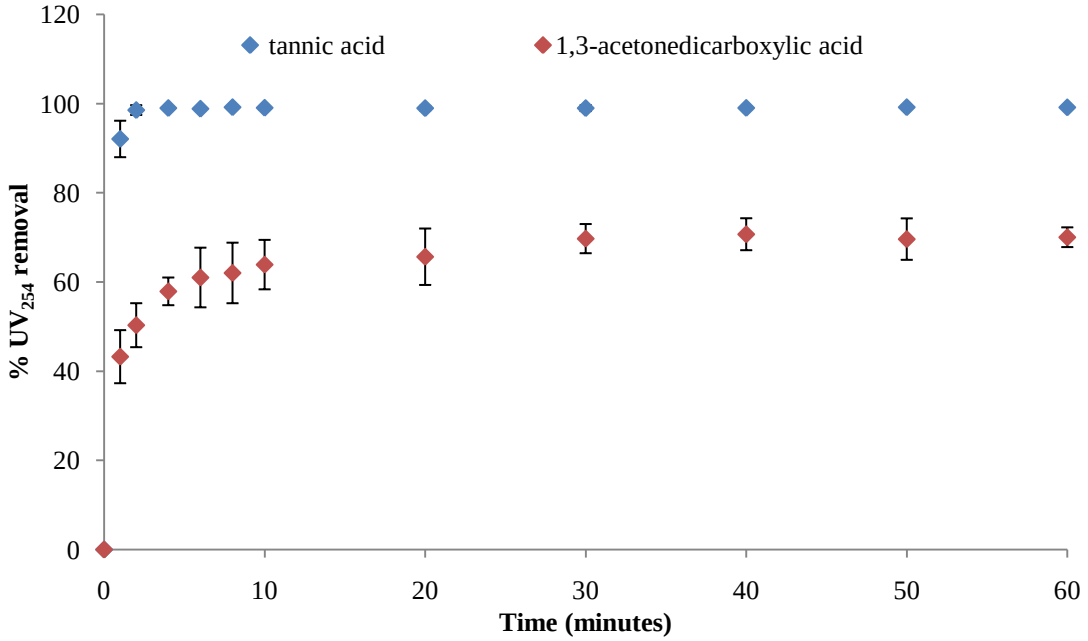


Figure 32: The % UV_{254} (cm^{-1}) removal 20mgC/L model compound solutions to XAD-7HP resin using 160mL of solution and 40mL of resin.

Unlike XAD-7HP, which maintained an equilibrium % DOC removal over the 60 minute time period (Figure 31), all three model compounds showed a reduction in DOC removal onto DAX-8 after 60 minutes (Figure 29). The % DOC removal dropped by a total of 16%, 8% and 24% for the HPO, TPH and HPI model compounds respectively, causing a negative removal of the HPI model compound, d-xylose, after 8 minutes (Figure 29). However, due to the high standard deviation, particularly for the HPI model compound, none of the reductions in DOC removal were significant at p=0.05. No reduction in UV_{254} absorbance occurred for either resin during the 60 minutes sample period.

After 4 minutes of mixing with XAD-4 resin, 79%, 53% and 9% of DOC removal was achieved for the HPO, TPH and HPI model compounds respectively (Figure 33), and 96% and 77% UV_{254} absorbance for the HPO and TPH model compounds (Figure 34). XAD-4 removed 17% more DOC from the TPH model compound solution, and 10% and 7% more DOC from the HPI model compound than either DAX-8 or XAD-7HP respectively, but removed less DOC from the HPO model compound. However, these differences in removal were not significant at p=0.05. After 60 minutes the % DOC sorption to XAD-4 decreased by 9% for the HPO model compound and 17% for the HPI model compound (Figure 33). However neither decrease was significant at

p=0.05. As see previously with DAX-8 and XAD-7HP resins, UV_{254} removal did not reduce over the 60 minute sampling period.

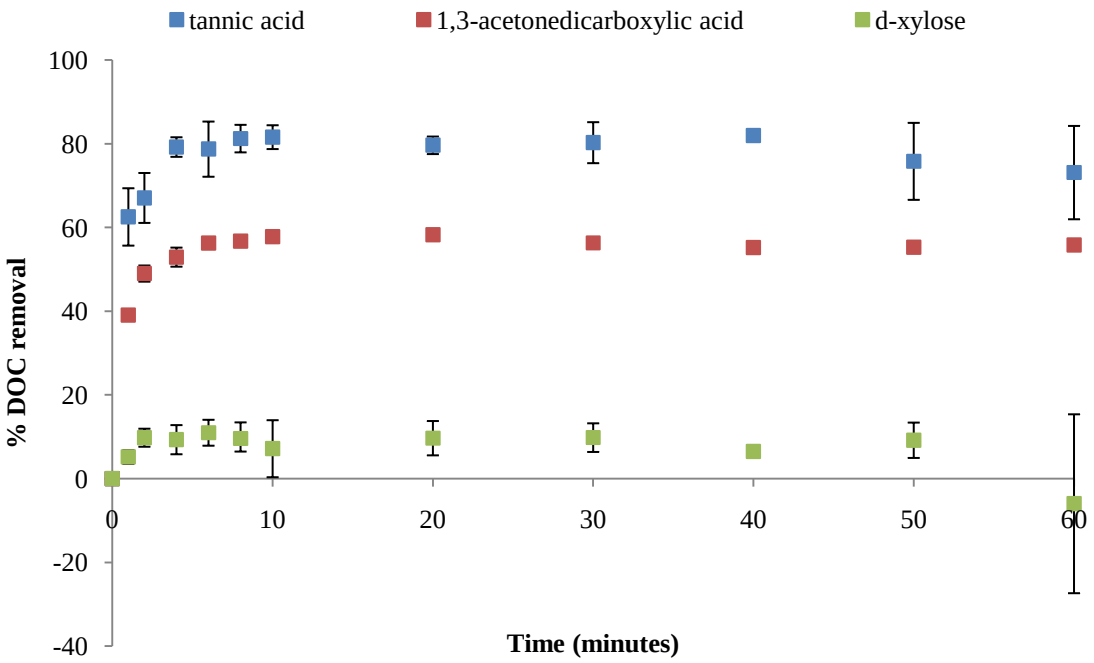


Figure 33: The sorption of 20mgC/L model compound solutions to XAD-4 resin using 160mL of solution and 40mL of resin.

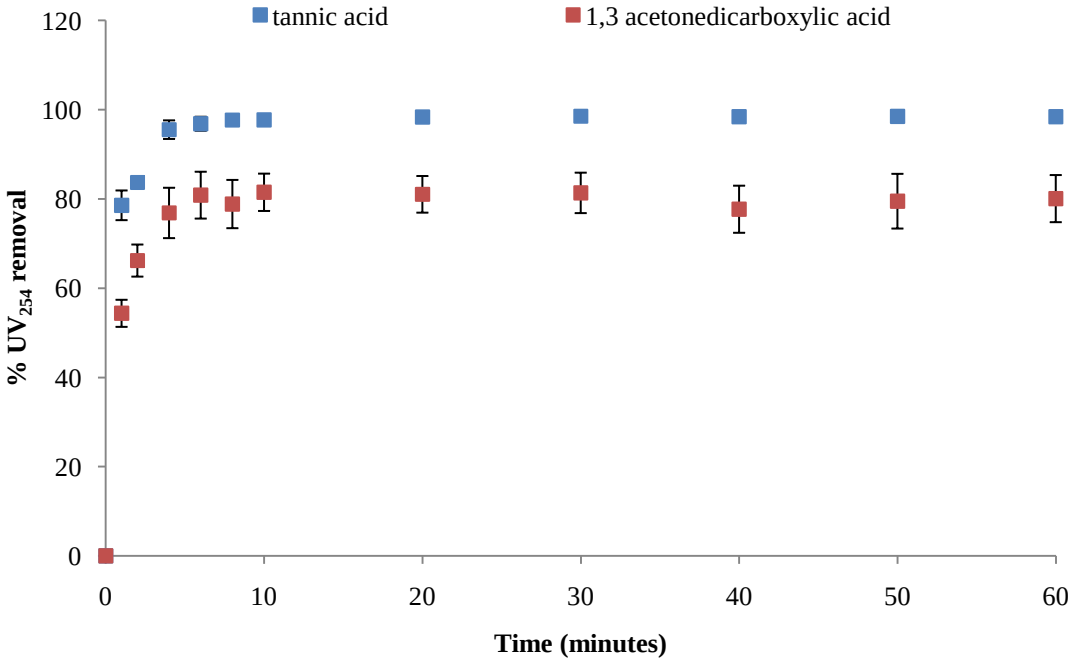


Figure 34: The % UV_{254} (cm^{-1}) removal 20mgC/L model compound solutions to XAD-4 resin using 160mL of solution and 40mL of resin.

A comparison of UV_{254} and DOC

The relationships between DOC and UV_{254} are presented for both tannic acid (Figure 35) and 1,3 acetonedicarboxylic acid (Figure 36) for all three resins. The significance of each regression line (all significant at p=0.01) is calculated according to Fowler and Cohen, (1995). As expected (due to the presences of only one chemical structure in each solution), both tannic acid and 1,3 acetonedicarboxylic acid show strong relationships between DOC and UV_{254} ($0.84<r^2<0.98$) throughout the sorption reactions onto all three resins. However, for XAD-4 and DAX-8 there were some data points in which a higher level of DOC occurred (9.1mgC/L and 5.6mgC/L respectively) than would be expected by the low UV_{254} absorbance ($0.014cm^{-1}$ and $0.008cm^{-1}$ respectively). These data points were all produced after at least 40 minutes of contact between the resin and the model compound solution, when a reduction in DOC removal had occurred. The data for XAD-7HP did not show such a large variation in the relationship between DOC and UV_{254}, and did not show the same level of reduction in DOC removal after 40 minutes of mixing.

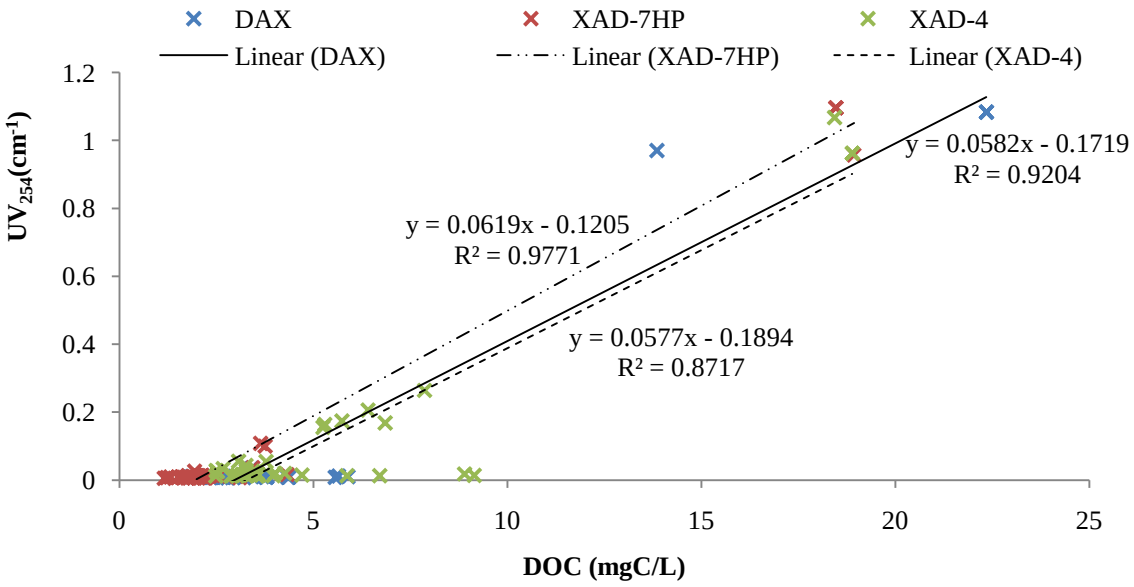


Figure 35: The relationship between UV_{254} and DOC for tannic acid. Regression lines are all significant at p=0.01.

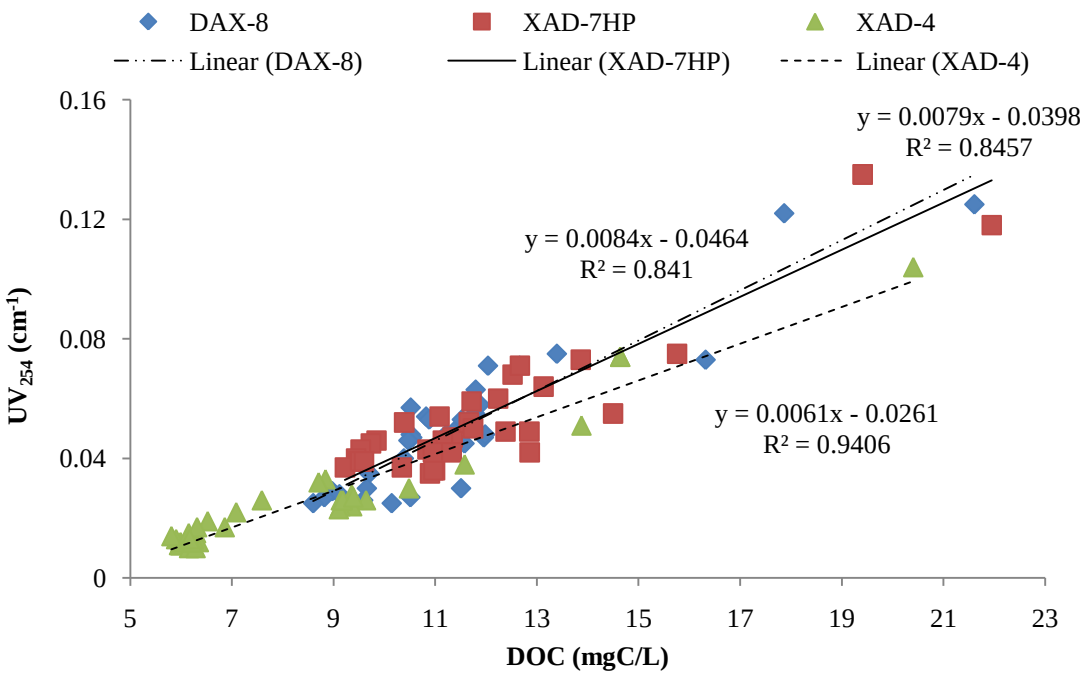


Figure 36: The relationship between DOC and UV_{254} for 1,3 acetonedicarboxylic acid. Regression lines are all significant at p=0.01.

The data presented for tannic acid lacks any DOC concentrations between 9.1 and 13.9mgC/L due to the speed of the sorption onto all resins. This could result in a skewing of the data caused by the slight differences in the initial model compound concentrations for each resin. In contrast, due to a reduced total removal of the TPH model compound, 1,3 acetondicarboxlyic acid, and a slightly slower removal rate, there was a less clustered dispersion of the data for this compound. The two model compounds show different relationships between DOC and UV_{254}, with the gradient of trend lines differing by a factor of 10. This was expected as different chemical structures have very different UV_{254} absorbance. Aromatic structures in particular have high UV_{254} absorbance, and these are prevalent within tannic acid molecules but not in 1,3 acetonedicarboxylic acid.

These results show that, for model compounds, a unique relationship exists between DOC and UV_{254} that was maintained independent of the change in adsorbent. This relationship can be utilised to identify any alterations in the type of DOC present in the solution. For example, the results taken after 40 minutes of mixing with tannic acid for both DAX-8 and XAD-4 indicate an altered relationship between DOC and UV_{254}. This is hypothesised to be due to contaminant DOC of a lower UV_{254} absorption and is investigated further in section 7.2.

5.2.iii. Final method development stage: A single sample rapid fractionation tool

The % DOC removal and % UV_{254} for 40mL model compound solutions were analysed after 6 minutes of mixing with the single sample rapid fractionation tool (Figures 37-39). As in all previous method development stages, the order of hydrophobicity (from HPO to HPI) for the three model compounds and resins was: tannic acid>1,3 acetonedicarboxylic acid>d-xylose. Other than the difference between the adsorption of tannic acid and 1,3 acetonedicarboxylic acid to DAX-8[16], each model compound has a statistically different % HPO fraction measured using both % DOC removal (p=0.05) and % removal of UV_{254} (p=0.05). As seen previously in rapid batch fractionations, the % removal of UV_{254} was significantly greater than the % DOC removal for the HPO fraction of all model compounds for all resins (p=0.05). Again, this was not expected for model compound solutions leading to further investigations (see section 7.2.).

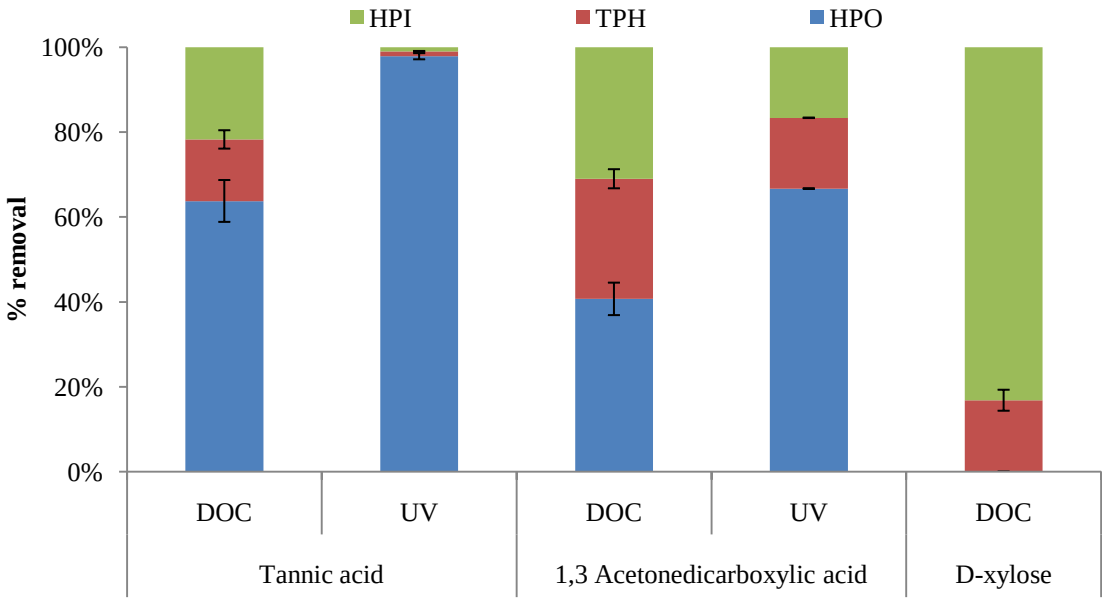


Figure 37: The % DOC removal and % removal of UV_{254} cm^{-1} after 6 minutes contact with DAX-8, followed by 6 minutes with XAD-4 resin in a single sample rapid fractionation, for the three model compounds.

[16] This was not significant for DOC due to the low sorption of tannic acid to DAX-8 for the single sample rapid fractionation, but was significant for UV_{254} (p=0.05).

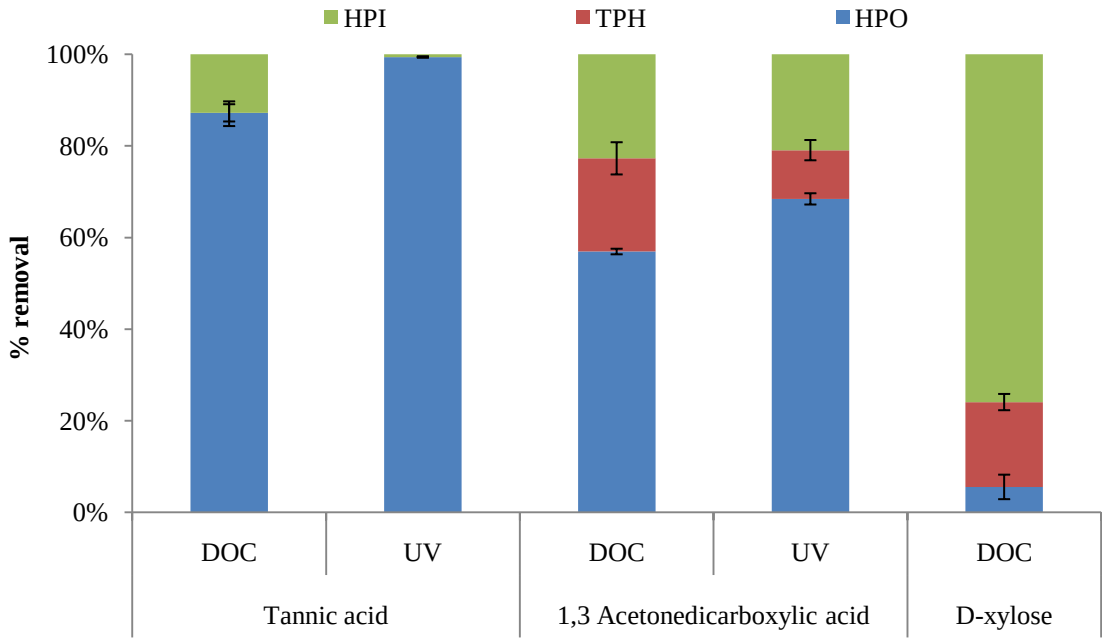


Figure 38: The % DOC removal and % removal of UV_{254} cm^{-1} after 6 minutes contact with XAD-7HP, followed by 6 minutes with XAD-4 resin in a single sample rapid fractionation, for the three model compounds.

XAD-7HP removed over 15% more DOC than DAX-8 for all model compounds in single sample rapid fractionations. While this was not significant (at p=0.05), it indicates a difference between the two resins in terms of DOC adsorption. Currently, both resins are used interchangeably as substitutes for XAD-8, to sorb the HPO fraction in traditional column fractionation. However, these results indicate XAD-7HP adsorbs a greater proportion of DOC as the HPO fraction in single sample shake tests.

XAD-4 was also used in isolation to treat the 40mL solutions of model compound. XAD-4 is commonly used as a TPH adsorbent, but these investigations show it is also capable of adsorbing high levels of HPO compounds, adsorbing a similar amount of tannic acid as XAD-7HP. However, higher levels of adsorption of the TPH compound (1,3 acetonedicarboxlyic acid) and significantly higher levels (p=0.05) of adsorption of the HPI compound (d-xylose) were possible when XAD-4 was used after either DAX-8 or XAD-7HP (p=0.05). When XAD-4 is used as a secondary resin the 40mL model compound is treated by a total of 20mL resin (10mL DAX-8 or XAD-7HP and 10mL XAD-4), instead of only 10mL of resin when XAD-4 is used in isolation. Therefore an increased resin volume (and adsorption area) causes an increased total DOC removal for TPH and HPI compounds.

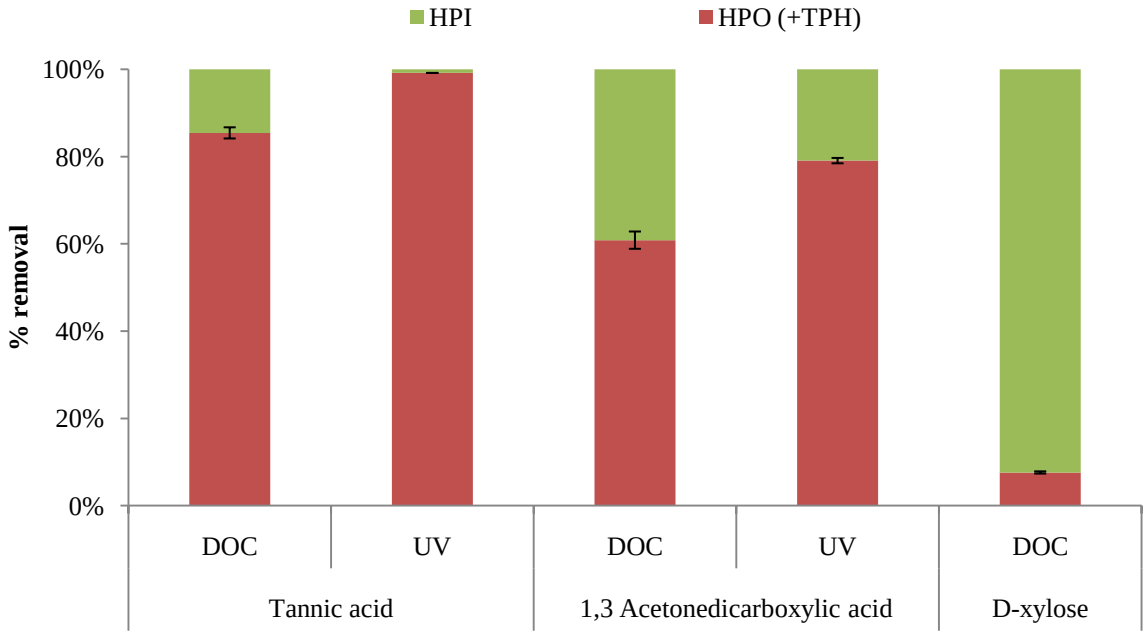


Figure 39: The % DOC and UV_{254} removal after 6 minutes contact with XAD-4 resin in a single sample rapid fractionation, for the three model compounds.

5.3. A comparison of the fractionation of model compounds achieved in each method development stage

5.3.i. The HPO fraction

The average % DOC removal achieved (the HPO fraction) using each of the method development stages is presented for each model compound with error bars showing one standard deviation (Figure 40). By altering the fractionation method from column fractionation to single sample rapid fractionation, the time to achieve the presented % DOC removal has reduced from 200 minutes to 6 minutes alongside a sample volume decrease from 1L to 40mL. Increasing the resin concentration from 15mL/L used in the parallel batch fractionation to 250mL/L used in the rapid batch fractionation, led to an increase in the DOC adsorption rate. For example, in the first 2 minutes of contact with tannic acid a 15mL/L resin concentration gave an adsorption rate of 2.4, 1.0 and 0.2mgC/min for DAX-8, XAD-7HP and XAD-4 respectively. This increased to 8.2, 8.0 and 6.3mgC/min when the resin concentration was increased to 250mL/L.

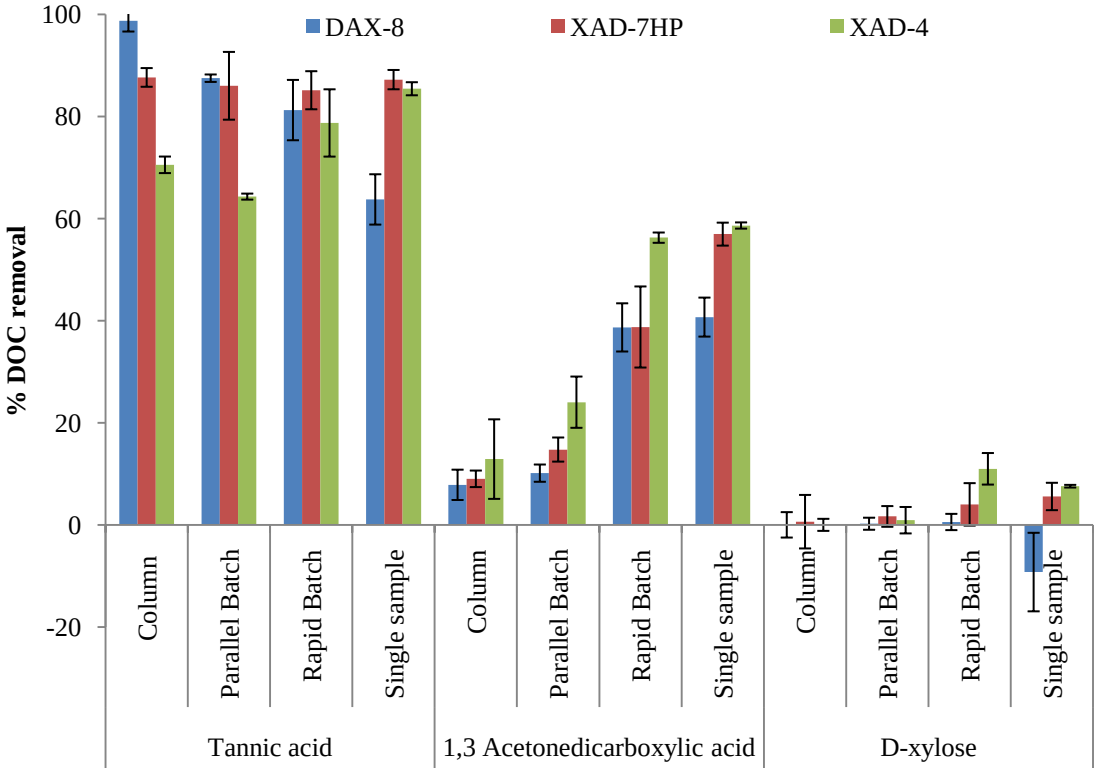


Figure 40: A summary of the average % DOC removal achieved using each method development, for the three model compounds.

For all resins and fractionation methods, the HPO model compound, tannic acid, showed the greatest % DOC removal. Removal onto DAX-8 showed the widest variation between fractionation methods, decreasing from 99% (using column fractionation) to 64% (using single sample rapid fractionation). These variations were significantly different (p=0.05). Tannic acid removal onto XAD-7HP showed strong repeatability, with the small variation not significant (88% in column fractionation to 85% in rapid batch fractionation). Removal onto XAD-4 varied from a maximum removal using the single sample rapid fractionation (85%) to a minimum removal using parallel batch fractionation (64%), although it is likely further DOC removal would have occurred had the parallel batch fractionation continued beyond 24 hours. The % DOC removal onto the single sample tool was significantly different to both parallel batch and column fractionation (p=0.05). The three macroporous resins showed the greatest variance in % DOC removal using column fractionation, with the sorption to XAD-4 significantly different to both XAD-7HP and DAX-8 at p=0.05. During the four method development stages, DOC removal of the HPO model compound tended to decrease onto DAX-8 and increase onto XAD-4.

The HPI model compound, d-xylose showed no significant deviation from zero % removal onto either XAD-7HP or DAX-8 during all of the four methods development stages (p=0.05). During the single sample rapid fractionation, a negative % DOC removal onto DAX-8 was observed for d-xylose, although this was not significant at p=0.05. There was no significant removal of d-xylose onto XAD-4 in either of the first three method development stages using 15mL resin/L model compound solution. However, when the resin/solution ratio was increased to 250mL/L, removal of d-xylose became significant for the single sample rapid fractionation (p=0.05).

The TPH model compound, 1,3 acetonedicarboxylic acid showed the greatest variation in % DOC removal, using different fractionation methods. For all three resins, the % DOC removal for each fractionation method increased in the order column<parallel batch<rapid batch<single sample. There was no significant difference, for any resin, between column fractionation and parallel batch fractionation, when the resin/solution ratio was maintained at 15mL/L, and no significant difference between rapid batch fractionation and single sample rapid fractionation, when the resin/solution ratio was maintained at 250mL/L. However, increasing the resin/solution ratio did cause a significant increase in the % DOC removal of 1,3 acetonedicarboxylic acid onto DAX-8 and XAD-4 (p=0.05)[17]. Of the three resins, DAX-8 showed the smallest total increase (between column and single sample fractionation) in % DOC removal (33%) and XAD-4 showed the greatest increase in removal (46%).

5.3.ii. The TPH fraction

The TPH fraction was collected (as % DOC removal onto XAD-4) for the traditional column fractionation and the single sample rapid fractionation tool (the final method development stage) for both DAX-8 followed by XAD-4 (Table 7) and XAD-7HP followed by XAD-4 (Table 8). Of the two procedures, XAD-7HP followed by XAD-4 showed the greatest similarity between column fractionation and single sample rapid fractionation for the TPH fraction.

[17] There was a 24% increase in the removal of 1,3 acetonedicarboxylic acid onto XAD-7HP but this was not significant due to the high standard deviation of DOC sorption in the rapid batch fractionation.

Table 7: A comparison of the % HPO, TPH and HPI fractions produced using DAX-8 followed by XAD-4.

DAX-8/XAD-4		HPO	TPH	HPI
Tannic acid	*Column*	98.74	1.26	0.00
	Single sample	63.75	14.48	21.76
1,3 Acetonedicarboxylic acid	*Column*	7.84	17.71	74.45
	Single sample	40.70	28.28	31.02
D-xylose	*Column*	0.00	0.00	100.00
	Single sample	0.00	16.83	83.17

Table 8: A comparison of the % HPO, TPH and HPI fractions produced using XAD-7HP followed by XAD-4.

XAD-7HP/XAD-4		HPO	TPH	HPI
Tannic acid	*Column*	87.65	0.00	12.35
	Single sample	87.22	0.00	12.78
1,3 Acetonedicarboxylic acid	*Column*	9.02	17.56	73.42
	Single sample	56.95	20.34	22.71
D-xylose	*Column*	0.62	0.00	99.38
	Single sample	5.56	18.52	75.92

In the fractionation of tannic acid with XAD-7HP/XAD-4, both methods produced almost identical HPO, TPH and HPI fractions. In all other fractionations, the single sample rapid fractionation produced a larger % TPH fraction than the column fractionation. However, the difference in % TPH fraction was not significant for any model compound due to the large errors associated with the TPH fraction. This is a result of the addition of the errors for the HPO/TPH boundary and TPH/HPI boundary. The TPH fraction shows the greatest variation between column and single sample fractionations for the HPI model compound, d-xylose.

5.4. A summary of model compound fractionation results

The results obtained in the fractionation of each model compound using the four method development stages can be summarised by the following:

- For all fractionation methods the order of hydrophobicity of the model compounds was from HPO to HPI: tannic acid>1,3 acetonedicarboxylic acid>d-xylose.
- Despite both DAX-8 and XAD-7HP being used by different research groups as a substitute for XAD-8, over 15% more DOC was removed using XAD-7HP than using DAX-8 for all model compounds in the single sample rapid fractionation.
- The use of XAD-7HP gave the smallest variation between fractionation method for both tannic acid and d-xylose, both when used in isolation and before XAD-4 to produce HPO, TPH and HPI fractions.
- For all model compounds, onto all resin there was a significantly greater reduction in UV_{254} absorbance than DOC (mgC/L) ($p=0.05$). As all solutions contained only one molecular type, an identical reduction in UV_{254} and DOC would be expected. The extra UV_{254} absorbance could indicate molecule dissociation in the solution or DOC leaching from the resin and is investigated further in section 7.2.
- Rapid fractionation was achieved by increasing the resin/solution ratio from 15mL/L to 250mL/L. The main difference in the fractions produced was the increased % DOC removed, by all three resins, of the TPH model compound 1,3 acetonedicarboxylic acid.

6. Results II: The analysis of NOM using column fractionation, rapid fractionation and single sample rapid fractionation for natural waters

Water from Butterley reservoir was the natural water selected to test the fractionation tools. Thirteen Butterley samples were first characterised by column fractionations using the back elution technique. Each of the waters was then fractionated using the rapid batch and single sample fractionation procedures as a means of comparing the fractionation techniques abilities to analyse differences in natural waters. The fractions created by these methods were also compared for four other water samples taken from the Longwood WTW catchment on 23/04/10. Column fractionations for these waters were completed, with thanks, by Dr E. Goslan as part of a catchment wide investigation. Raw and filtered waters from Oswestry WTW were sampled on 12/05/10 and also analysed using column and rapid fractionations. In all fractionations, XAD-7HP resin was used to desorb the HPO fraction. XAD-4 was used to desorb the TPH fraction in both column and single sample fractionations.

6.1. Seasonal variations at Butterley reservoir

Samples from Butterley reservoir were taken between 08/10/09 and 31/05/10 and analysed using column fractionation with back elution, rapid and single sample fractionation.

6.1.i. Column fractionation with back elution

The NOM fractions recovered for each 2L Butterley water sample all deviated from 100% DOC recovery (Figure 41). The % DOC recovery ranged from 65% (12/04/2010) to 151% (05/11/2009), with a mean recovery of 108%. This result was not unusual as recoveries in excess of 100% are common when analysing NOM using column fractionation with back elution, and highlight a lack of accuracy, of the procedure. A t-test was used to investigate the significance of this increased recovery:

$$\mathbf{t_{samples} = (x-x_0)/(\sigma/\sqrt{n}) \quad =1.43\ (3.sf)} \qquad \textbf{Eq. 7}$$

$\mathbf{t_{crical} = 2.179}$

x = mean of samples, x_0 = actual value

As $t_{critical} > t_{samples}$ there was no significant difference between the average recovery (108%) and the expected recovery (100%) (p=0.05), and as a result the average recovery for Butterley samples is not significantly above 100%.

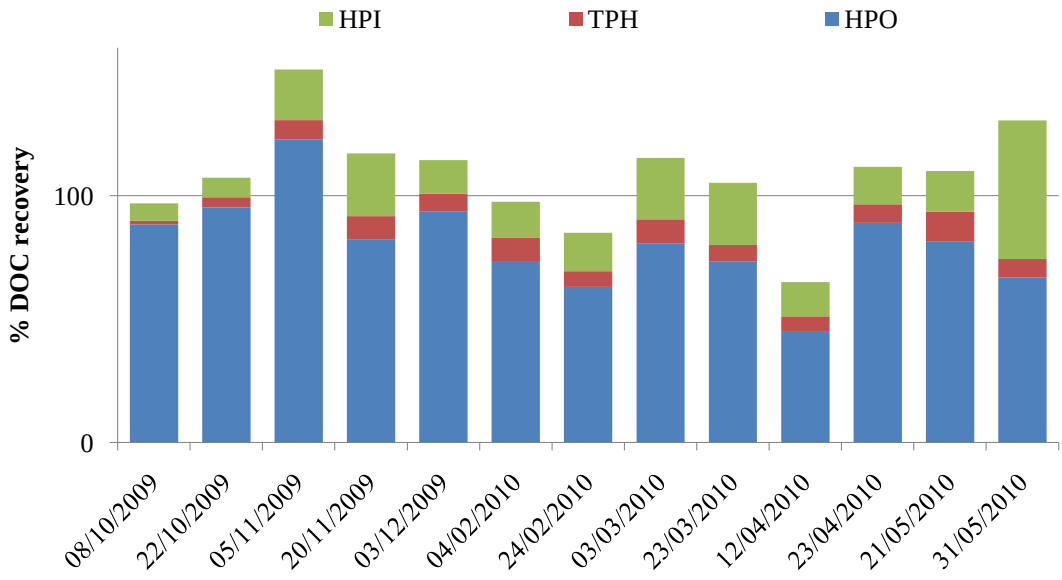


Figure 41: The NOM recovered using a column fractionation with back elution technique as a % of the raw water concentration. Samples were taken from Butterley reservoir between 08/10/09 – 31/05/10. Resin was changed after 03/12/09 and 23/03/10. Column fractionations were not repeated.

However, the large variations between Butterley samples, in terms of total recovery, mean the measured concentration of each fraction cannot be used to compare seasonal NOM variation. Instead, seasonal variation was identified by assuming 100% recovery, and comparing each of the fractions as a % of raw water DOC (mgC/L) (Figure 42). This makes seasonal trends in NOM type more detectable, but assumes that the deviation from 100% recovery was the same for all fractions and water sample, and is a source of error. As the HPI fraction, does not require back elution as was calculated from the column effluent, it is unlikely this fraction had the same error as the HPO and TPH fractions. However, these errors could not be quantified and results must therefore be used cautiously.

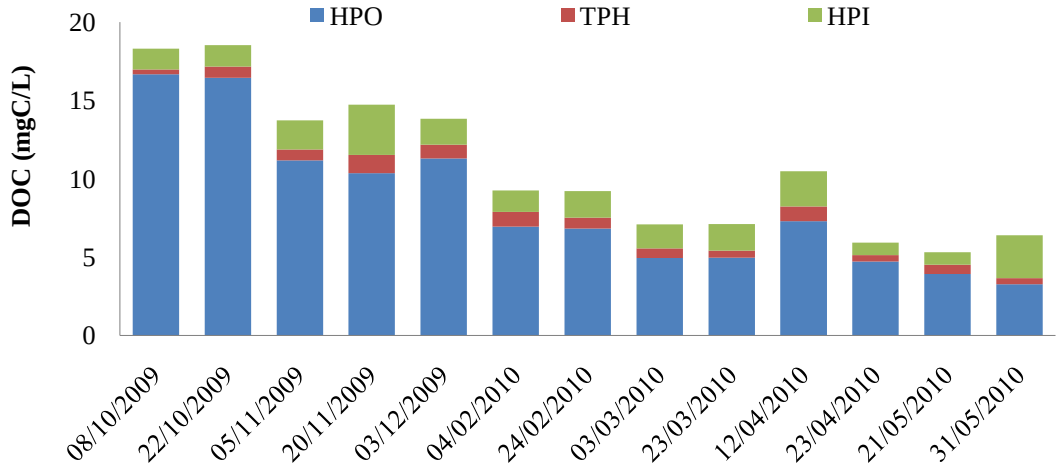


Figure 42: The seasonal variation of NOM in Butterley reservoir, in mgC/L of raw water. The fractions were created using column fractionation with back elution.

Butterley reservoir receives water from a peat moorland catchment and as a result, the NOM type of all samples is dominated by the HPO fraction. The raw water DOC at Butterley reached a maximum DOC concentration of 18.5mgC/L on 22/10/09. DOC concentrations then decreased uniformly over the sample period (other than a slight peak of 10.5mgC/L on 12/04/10) to a minimum of 5.3mgC/L on the 21/05/10. This change in raw water concentration was predominantly caused by the change in the HPO concentrations of the water, which followed the same seasonal trend (peaking at 16.7mgC/L on 08/10/09 and dropping to a minimum of 3.3mgC/L during 31/05/10). As a result the NOM water type varies over the time period, from 91% HPO on the 08/10/09, to only 51% HPO on the 31/05/10. The concentration of both TPH and HPI NOM showed no real seasonal trend. TPH NOM ranged from 0.31mgC/L on 08/10/09 to a maximum of 1.2mgC/L during 20/11/09, whilst HPI NOM ranged from 3.2mgC/L on 20/11/09 to a minimum of 0.8mgC/L on 21/05/10.

6.1.ii. Rapid batch fractionation

Each natural water sample was also analysed for the HPO fraction using the rapid batch fractionation procedure with mass analysis, with DOC and UV_{254} used to identify NOM fractions. The TPH fraction could not be analysed using this batch mixing technique as samples were taken from the mixture at different time increments throughout the procedure and so the method did not allow for the determination of a TPH fraction. Three replica rapid batch fractionations were completed for the Butterley sample taken on 03/12/09 (Figure 43) to provide an assessment of the repeatability of this rapid test for natural waters. The remaining twelve natural water

samples were analysed once using the rapid fraction fractionation procedure (full results reported in Appendix II).

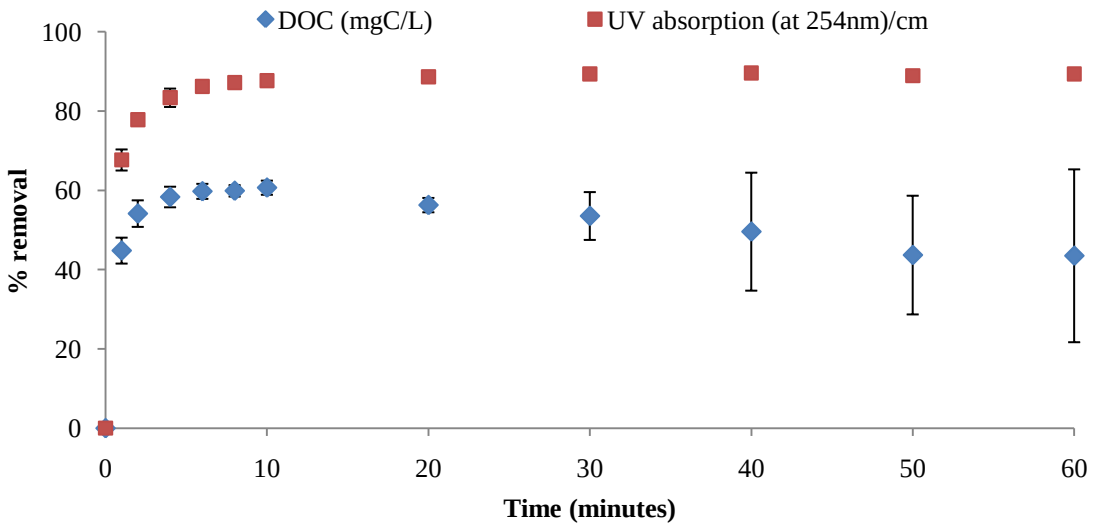


Figure 43: The % removal of DOC (mgC/L) and UV_{254} absorption (cm^{-1}) for a 160mL water sample taken from Butterley reservoir on 03/12/09, and mixed with 40mL XAD-7HP resin.

Rapid batch fractionation shows good repeatability for removal of the HPO fraction to XAD-7HP over the first 20 minutes of mixing with the Butterley 03/12/09 sample. For this water sample, a maximum HPO removal of 60-61% occurred after 6-10 minutes of mixing with XAD-7HP. All other seasonal Butterley water samples also reached maximum removal between 6-10 minutes, but the % of DOC removed as the HPO fraction varied between water samples. The highest % HPO fraction was seen for the 20/11/09 sample (72%) with the lowest % HPO fraction observed in late spring, for the 31/05/10 sample (23%). This showed that the batch fractionation procedure was able to identify differences in the HPO fraction from different water samples.

The small standard deviations in % reduction of UV_{254}, observed for all sample from 03/12/09, confirms a strong repeatability over the 60 minutes sample period for UV_{254} absorption. The equilbria % reduction of UV_{254} (87-89%) was maintained in all of the samples after 8 minutes of mixing with XAD-7HP, and a similar equilbria UV_{254} was maintained for all other Butterley water samples (varying from 85-93%) over the same time period. Therefore, removal of DOC showed a greater seasonal variation than the % reduction in UV_{254}. UV_{254} is a measure of aromatic NOM and the results therefore suggest this NOM is consistently removed using rapid batch fractionation, verifying its ability to removing HPO NOM. The results also show that aromatic

NOM constituted a lower proportion of total DOC in Butterley samples from spring 2010 than from samples in autumn 2009. By analysing both DOC and UV_{254} during rapid fractionation, the tool has successfully highlighted seasonal variations in the NOM type at Butterley reservoir.

After 10 minutes of mixing with XAD-7HP, the % DOC removal for the 03/12/09 sample began to decrease and reached a minimum removal of 44% after 60 minutes. This reduction in DOC removal was not significant (at p=0.05) due to the high standard deviation of % DOC removal after 20 minutes of contact between the resin and solution. However, eight of the twelve other natural waters samples also showed a drop in % DOC removal of over 10% between 10 minutes and 60 minutes of mixing. In contrast none of the natural water samples showed a decrease in UV_{254} of above 1% during the same time period. Therefore, the aromatic NOM (with a high UV_{254}) removed by the resin stayed sorbed to the resin over the full 60 minutes. Similar reduction in DOC removal with no corresponding reduction in % UV_{254} absorbance were observed when model compounds were fractionated using the rapid batch mixing procedure (see section 5.2.ii.). The source of this excess solution DOC is explored in detail in section 7.2.

6.1.iii. Single sample rapid fractionation.

A final examination of the Butterley water samples was completed using the single sample fractionation method, with natural waters mixed for 6 minutes with each macroporous resin. Three replicas of each fractionation (onto XAD-7HP followed by XAD-4) were analysed for both DOC adsorption and UV_{254} absorption using mass analysis, with each fraction presented as % of the raw waters DOC and UV_{254} (Figures 44 & 45). As was seen with the other fractionation tools, the single sample rapid fractionation tool identified the Butterley sample from autumn 2009 to have a higher raw water DOC (mgC/L) concentration, and higher % HPO fraction than samples from spring 2010. The average raw water DOC concentration from 08/10/09-20/11/09 was 11.5mgC/L, with an average HPO fraction of 73%. In contrast the average raw water DOC concentration from 04/02/10-31/05/10 was 6.8mgC/L, with an average HPO fraction of 56%.

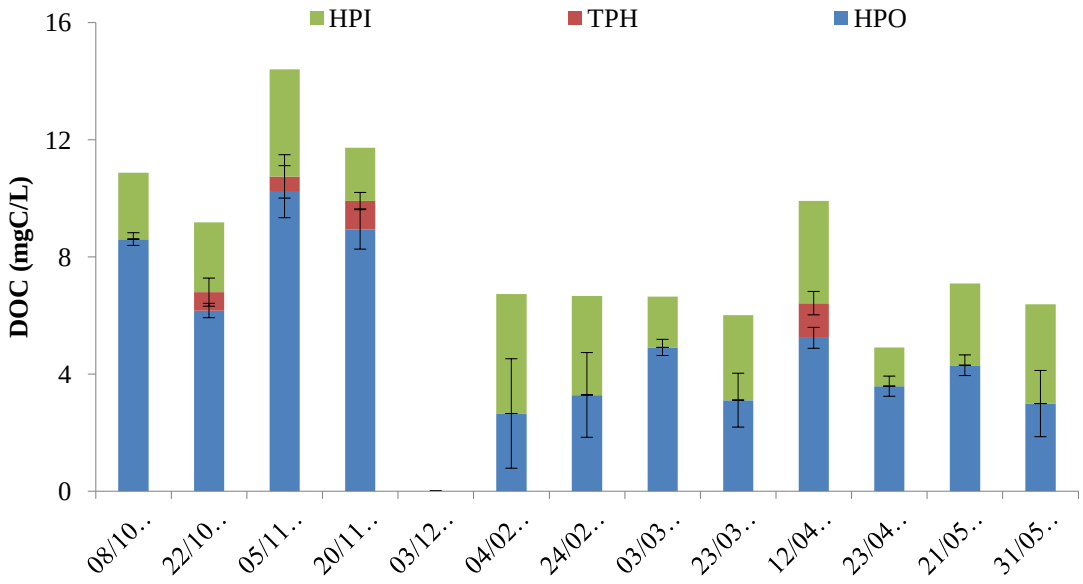


Figure 44: The HPO, TPH and HPI fractions of Butterley water sampled from 08/10/09-31/05/10 using a single sample fractionation procedure with DOC (mgC/L) of each fraction analysed by mass analysis.[18]

The standard deviations for DOC removal (shown as the error bars in Figure 44) onto XAD-7HP show wide variability. Whilst some samples showed good repeatability in fractionations (08/10/04 and 03/03/10) the high standard deviations of the HPO fraction for Butterley 04/02/10 mean it was not significantly greater than zero (at p=0.05). Therefore some of the fractions produced during single sample rapid fractionation had considerable variation between replica experiments, which reduces the value of the fractions produced.

The single sample fractionation tool could not be used to reliably produce the TPH fraction (analysed by mixing the effluent from the XAD-7HP with XAD-4 for 6 minutes). For nine of the thirteen water samples, mixing with the XAD-4 resulted in a negative DOC removal. This indicated contamination from an external DOC source (which is identified in section 7.2.) and so the TPH fraction could not be calculated for these samples. In the four samples in which further DOC removal was achieved by mixing with XAD-4 (to produce the TPH fraction), this extra removal was not significantly different from the level of removal achieved using only XAD-7HP. Therefore, a significant TPH fraction was not obtained for any Butterley Reservoir sample using the single sample rapid fractionation tool. As the single sample rapid

[18] The fractionations for 03/12/09 were not included due to an error in the raw water concentration analysis.

fractionation uses a mass analysis approach the HPI fraction was calculated as either the effluent from the XAD-4 (when a positive TPH fraction was obtained) or as RAW DOC – HPO DOC (when a negative TPH fraction was obtained).

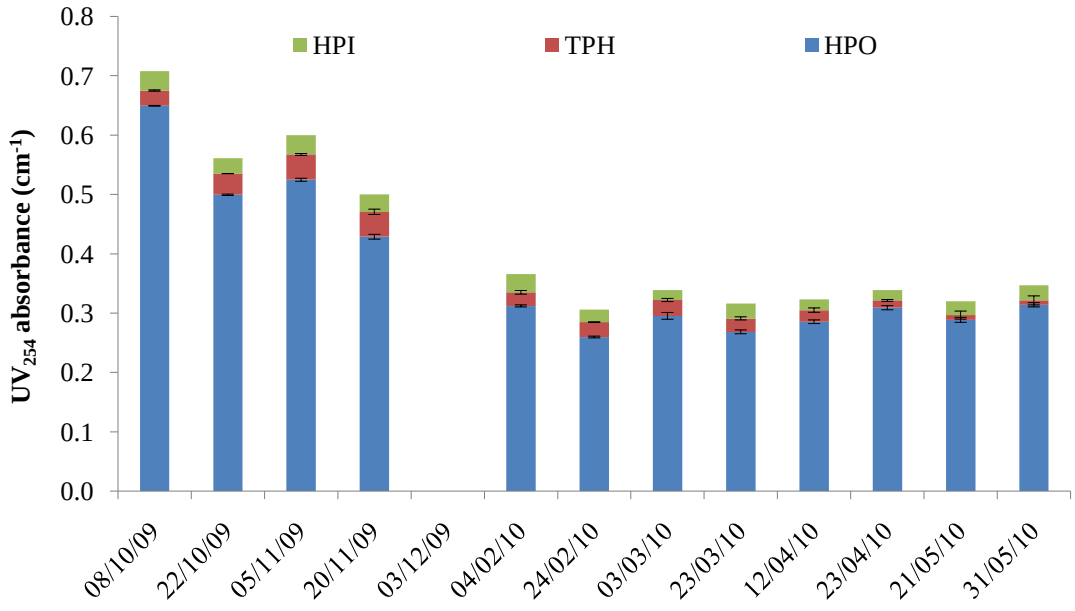


Figure 45: The HPO, TPH and HPI fractions of Butterley water sampled from 08/10/09-31/05/10 analysed using a single sample fractionation procedure for UV_{254} absorbance. Results for raw water 08/10/09, 21/05/10 and 31/05/10 were analysed three weeks after the single sample fractionations were completed.

As seen for the DOC analysis, the results for the raw waters UV_{254} showed a higher total UV_{254} absorbance during autumn 2009, than in spring 2010. UV_{254} absorption shows strong repeatability between replica fractionation, with small standard deviations for all samples. This suggests that similar removal of aromatic NOM occurred in all replicas. Unlike DOC, UV_{254} gave positive values for all TPH fractions. This suggests that the DOC contributing to the reduced removal over time did not have a noticeable UV_{254} absorbance.

Whilst UV_{254} of raw water showed strong seasonal variation, unlike measurements of DOC, there was no seasonal variation in the % of UV_{254} contained in the HPO fraction (an average of 88% for 08/10/09-20/11/09 and 04/02/10-31/05/10). This is explained by considering the relationship between UV_{254} and aromatic (or HPO DOC). As seen in section 3.3.ii, raw water UV_{254} and raw DOC showed good correlation (r^2=0.58) (not shown) for the Butterley water samples. However, a stronger correlation (r^2=0.71) is seen between UV_{254} and the concentration of DOC adsorbed to XAD-7HP as the HPO fraction (Figure 46). Therefore, UV_{254} can be used

to estimate the concentration of the HPO fraction, when raw water DOC concentration is known. However, UV_{254} does not measure the TPH or HPI fraction. Therefore, seasonally changes in the HPO fraction concentration (mgC/L) can be estimated by measuring raw water UV_{254} absorbance, but seasonal changes in raw water NOM type (i.e. the % HPO, TPH and HPI) cannot be estimated using UV_{254}. Therefore, the analysis of XAD fractionations must be done using DOC.

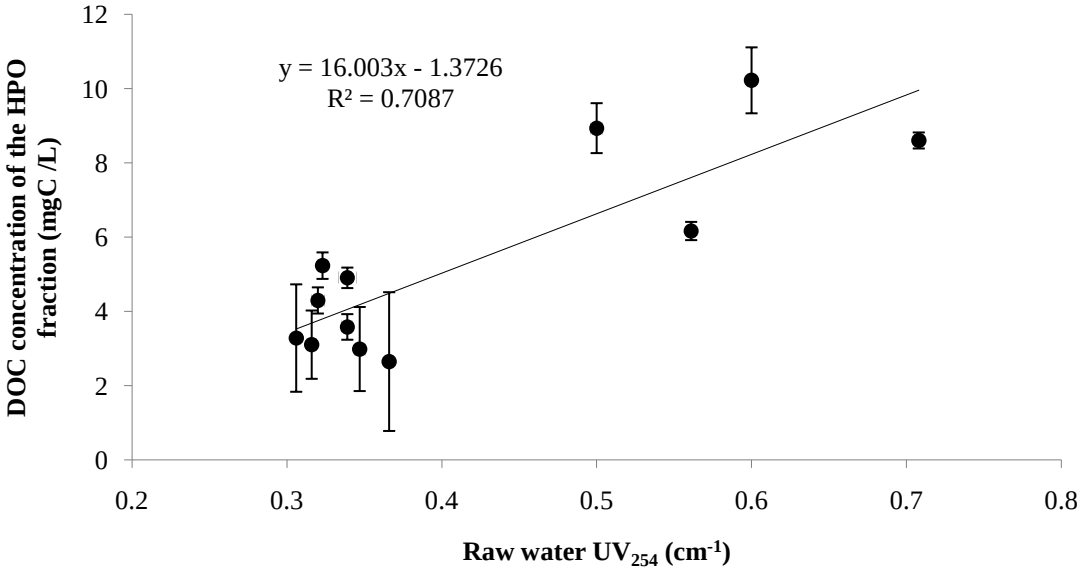


Figure 46: The correlation between UV_{254} of raw water and DOC of the HPO fraction for Butterley water samples between 08/10/09-31/05/10. The regression line is significant at p=0.01.

6.2. A comparison of column fractionation with back elution, rapid batch fractionation and single sample rapid fractionation

The fractionation results obtained for each natural water sample were compared to assess if the different fractionation procedures could provide similar results.

6.2.i. Raw water concentrations

The analysis of raw water DOC concentration prior to each of the fractionation procedures (Figure 47) showed some variation between samples. Due to the time required to develop the new fractionation techniques, water from the beginning of the sampling period were not analysed, using rapid batch or single sample fractionation, for up to seven months after collection. The extended storage of these samples could account for the big differences between raw water NOM concentrations seen for both 08/10/09 and 22/10/09 samples.

Other variations in raw water concentration assessment could be caused by differences in the measurement of organic carbon between the different fractionation procedures. For example, in the column fractionation a TC-IC method was used (as NPOC required all samples to be acidified, but in the back elution procedure, the desorbed fractions are in alkali solution). NPOC analysis was used for the rapid and single sample procedure. Some loss of volatile NOM is likely during the NPOC analysis, which could account for the lower raw water concentration using this procedure. Finally, as each analysis of TOC relies on a machine calibration, sight variations in this calibration can lead to differences in reported concentrations.

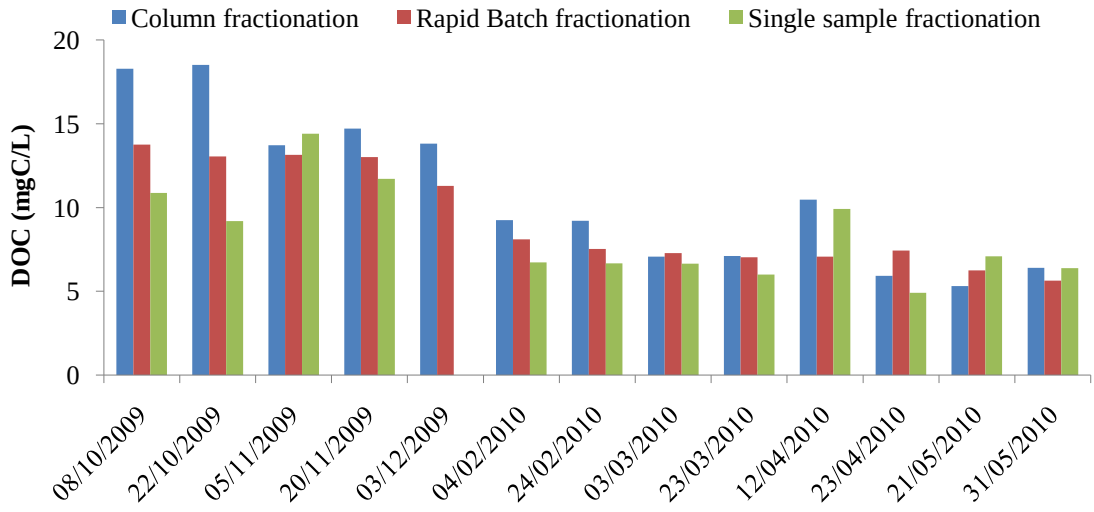


Figure 47: The raw water concentration of Butterley reservoir samples as measured for each fractionation.

Due to the variations in raw water concentration analysis (over 3mgC/L in three cases), the fractions produced using each NOM classification tool were compared by displaying results as a % of total raw water concentration (Figure 48). This allowed deviations in results, caused by the inconsistent analysis of raw water concentration, to be limited, and highlighted the differences in the fractions produced. Error bars refer to one standard deviation of the single sample rapid fractionation results but could not be created for the other fractionation procedures, as these experiments were not replicated.

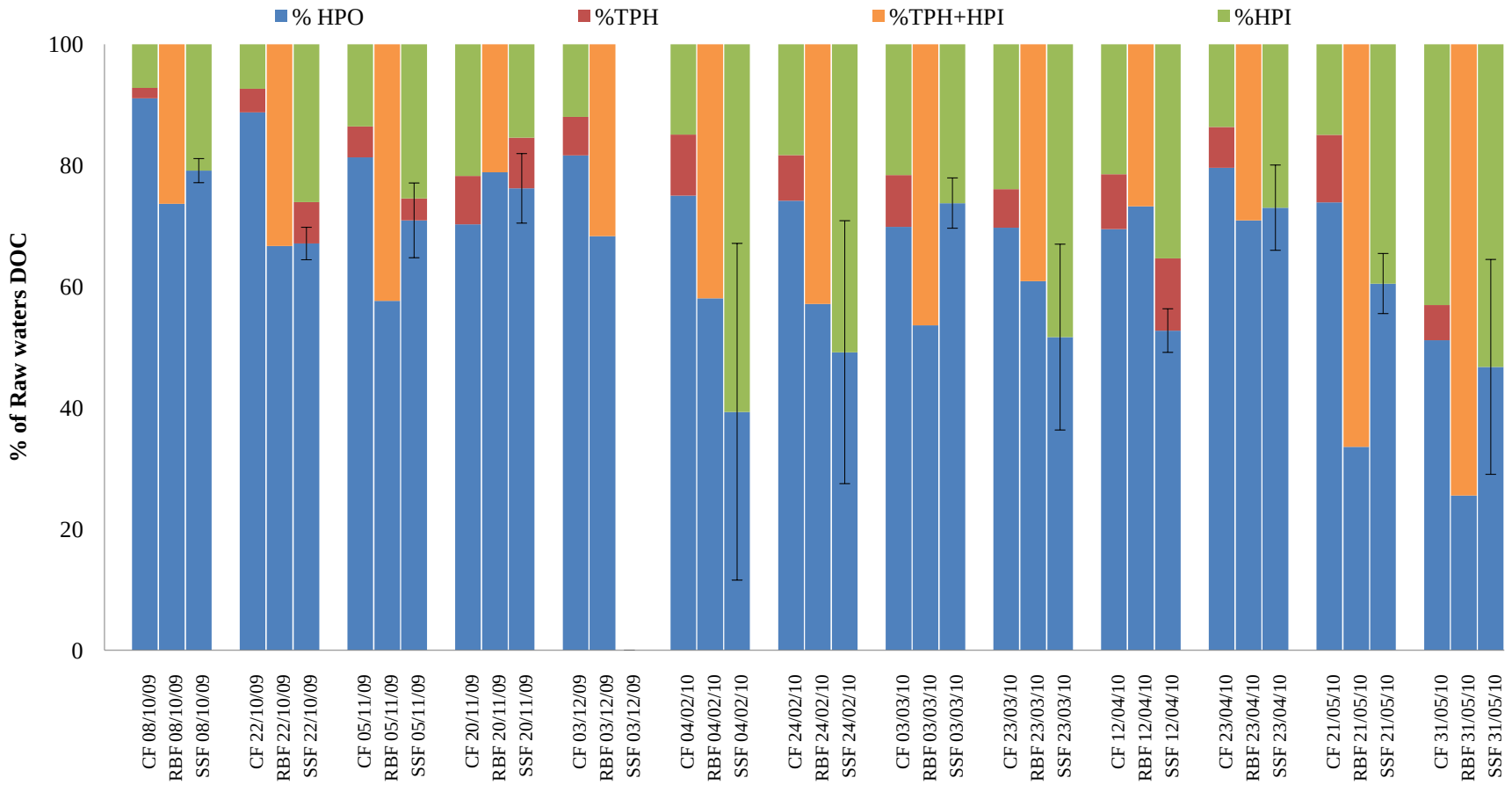


Figure 48: A comparison of the fractions created for Butterley reservoir samples by the traditional column fractionation with back elution (CF), rapid batch mixing (RBF), and the single sample rapid fractionation (SSF) procedure. Fractions are shown as % of raw water DOC (mgC/L). The results for the rapid batch fractionation are taken as the highest DOC removal observed between 4-8 minutes of mixing. As the TPH fraction could not be calculated in this method development stage, the DOC not adsorbed to the XAD-7HP has been referred to as a mixture of TPH and HPI DOC.

6.2.ii. NOM fractions (as a % of raw water)

For all but two samples (20/11/09 and 12/04/09), a lower % HPO fraction was adsorbed during rapid batch fractionation than in column fractionation. For three samples, the DOC absorbed as the HPO fraction using the rapid batch fractionation procedure was over 20% lower than for the column fractionation (05/11/09 (24%), 21/05/10 (40%) and 31/05/10 (26%)). The single sample rapid fractionation tool also adsorbed a significantly lower % HPO fraction than the column fractionation for four samples (08/10/09, 22/10/09, 12/04/09 and 21/05/09). Whilst the % HPO fraction for single sample fractionation was also lower than column fractionations for 04/02/10 (36%), 24/02/10 (25%) and 23/03/10 (18%) these were not significantly different due to the high standard deviation in the single sample fractionation results.

In order to identify if the three fractionation methods gave statistically different mean adsorption to XAD-7HP for the same Butterley raw water samples, F-tests followed by t-tests for matched pairs were performed to compare the means of: the column and rapid fractionations, the column and single sample fractionations, and the rapid and single sample fractionations:

This gave $F_{samples}$ = 2.36, 2.06 and 1.14 (3.s.f) for Column vs Rapid, Column vs Single sample and Rapid vs Single sample respectively. As $F_{critical}$ (3.28 for p=0.05) is greater than all F_{sample} values, the variance between column fractionation, rapid fractionation and single sample fractionation were not significantly different. This allowed matched t-tests to be performed on the data:

For column vs. rapid fractionation, $\mathbf{t_{sample} = 4.38}$

For column vs. single sample fractionation, $\mathbf{t_{sample} = 3.35}$

For rapid vs. single sample fractionation, $\mathbf{t_{sample} = 0.87}$

From a $t_{critical}$ distribution table, the means of the data sets are statistically different (p=0.05) if t_{sample} exceeds 2.179. The statistics therefore confirmed that both rapid and single fractionation have significantly lower means for the % DOC adsorbed to XAD-7HP than column fractionation with back elution for the thirteen Butterley samples. The rapid tools underestimates the HPO fraction of NOM that would be separated using the traditional column fractionation procedure. There was no significant difference in fractions produced from the rapid batch and single sample rapid

fractionation tools. The errors associated with the identification of the TPH fraction in single sample rapid fractionation mean no meaningful comparison with column fractionation can be made for this fraction.

Quantifying filter errors

For the column fractionation of Butterley waters, samples were initially filtered using a filter size of 0.7µm[19] and this filter size was also used for raw waters prior to rapid fractionations. The single sample rapid fractionation had been designed to use a 0.45µm filter to separate the sample from the resin at reaction termination based on the use of this filter size in traditional column fractionations. Larger NOM molecules such as those between 0.7-0.45µm are generally of HPO nature, and the majority of these species could therefore be expected to sorb to the XAD-7HP resin. However, for some fractionations a slight discoloration of the filter was observed during resin/solution separation, indicating some NOM removal occurred due to the filter. This would lead to an overestimation of the NOM material removed as the % HPO fraction in the single sample rapid fractionation. In order to quantify the maximum additional removal, which may have resulted from the 0.45µm filter, raw water samples were filtered at both 0.7µm and 0.45µm and analysed for DOC (mgC/L) and UV_{254} absorption (Figures 49 & 50).

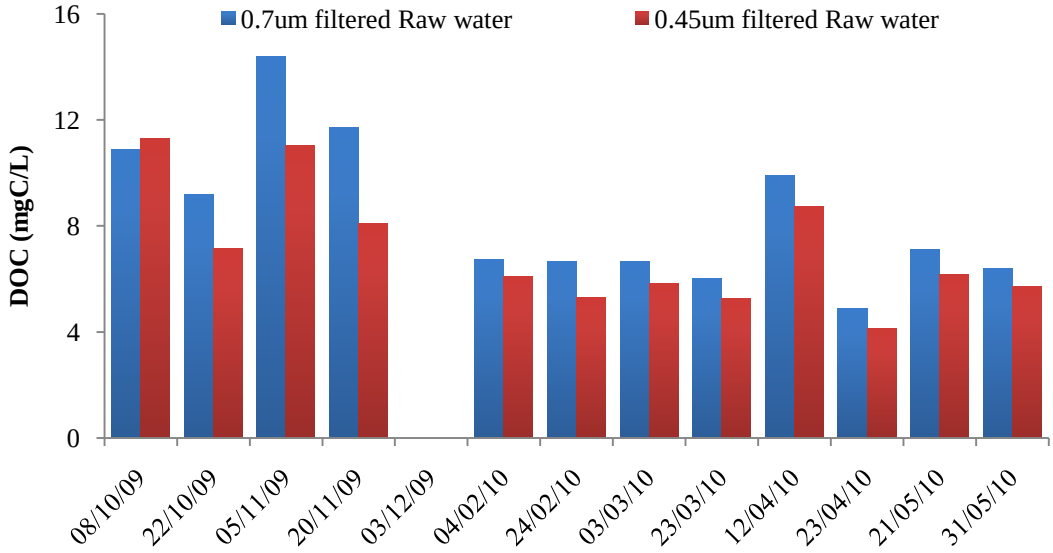


Figure 49: The DOC (mgC/L) of Butterley water sample filtered at 0.7 and 0.45µm.

[19] This was to maintain consistency between the Butterley column fractionations and fractionation of other waters within the Longwood WTW catchment, which were completed by Dr E. Goslan.

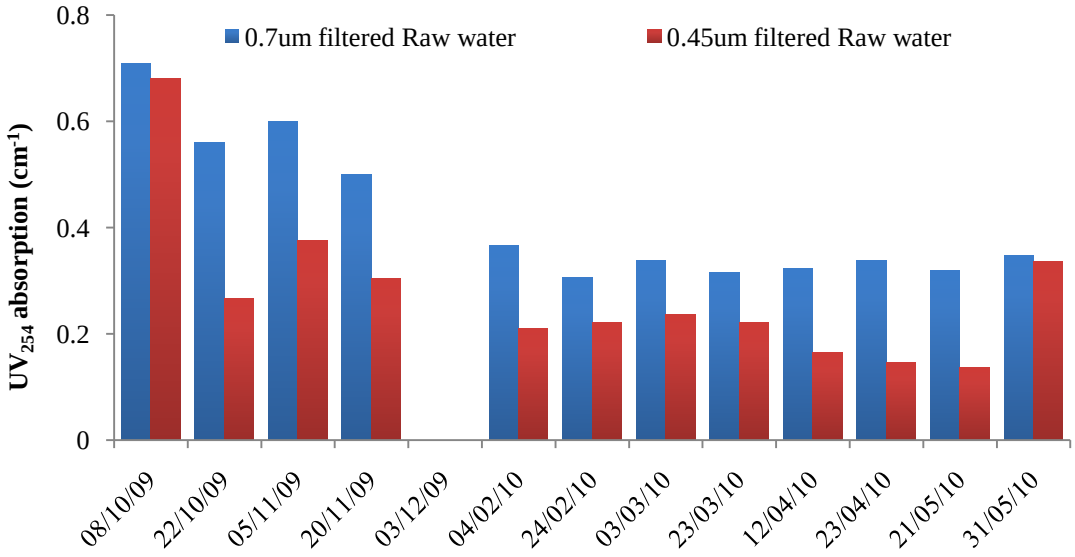


Figure 50: The UV_{254} absorption (cm^{-1}) of Butterley water sample filtered at 0.7 and 0.45μm.

Samples filtered using a 0.45μm filter had an average DOC of 85% (standard deviation of 8.4%) (mgC/L) of the DOC of samples filtered with a 0.7μm filter and 64% of the UV_{254} absorbance (standard deviation of 17.4%). In order to investigate if the differences in DOC concentration and UV_{254} were significant a F-test (to assess the variance) and matched paired samples t-test (to compare the means) were performed according to the methods described by Fowler and Cohen, (1995):

Where $F_{samples} = \sigma^2$ (sample set 1)/ σ^2 (sample set 2) **Eq.8**
And σ^2 (sample set 1) >σ^2 (sample set 2)

$t = \sum d / \sqrt{[(n\sum d^2 - (\sum d)^2)/(n-1)]}$ **Eq.9**
Where d = the difference between each matched pair.

As F_{sample} (1.44) < $F_{critical}$ (3.28), the variance in DOC (mgC/L) between samples filtered at 0.7 and 0.45μm was not significant (p=0.05). Similarly (F_{sample} (1.03) < $F_{critical}$ (3.28) for the variance in UV_{254}. As there was no significant different in the variance, t-tests for matched pairs could be performed.

As t_{sample} (4.26) > $t_{critcal}$ (2.179), the mean DOC concentrations (mgC/L) were statistically different (p=0.05). A similar calculation (t_{sample} (6.53) > $t_{critcal}$ (2.179)) also confirmed a statistical difference between UV_{254} for samples filtered at 0.7 and 0.45μm. This difference could therefore have caused an overestimation in DOC and UV_{254} removal for the rapid batch and single sample rapid fractionations when compared with the column fractionations.

6.2.iii. The relationship between the % HPO fraction calculated using column, rapid batch and single sample rapid fractionation

Both rapid batch and single sample rapid fractionation tended to give a lower estimation of % HPO fraction for the Butterley water samples when compared to column fractionation. If a similar difference between the fractionation methods exists for each sample then results from rapid fractionations could be used as an alternative to the column fractionation procedure. The concentrations of NOM removed as the HPO fraction are compared for the three fractionation methods (Figures 51-53). Only samples in which raw water concentration measured prior to each fractionation varied by less than 3mgC/L were used in these comparisons. Errors are measured as one standard deviation for the three replica single sample fractionations and in terms of the % DOC recovery achieved using column fractionation with back elution (which varied from 151-65%). Error bars could not be calculated for the rapid batch fractionations, which were not replicated.

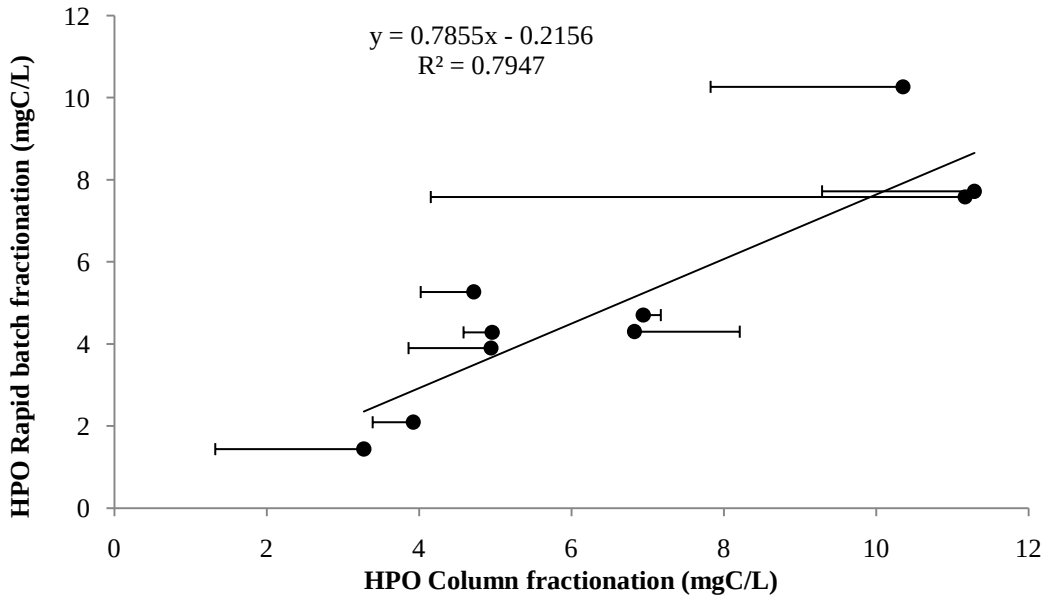


Figure 51: The relationship between the concentration of HPO fraction measured using the column fractionation and rapid batch fractionation procedures (regression line significant at p=0.01).

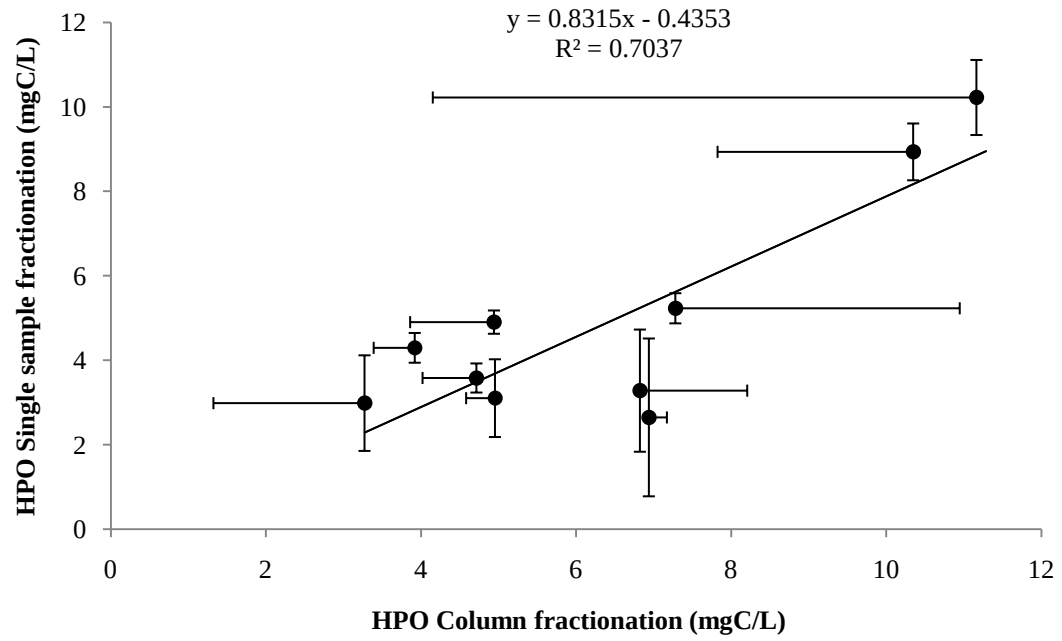


Figure 52: The relationship between the concentration HPO fraction measured using the column fractionation and single sample fractionation procedures (regression line significant at p=0.01).

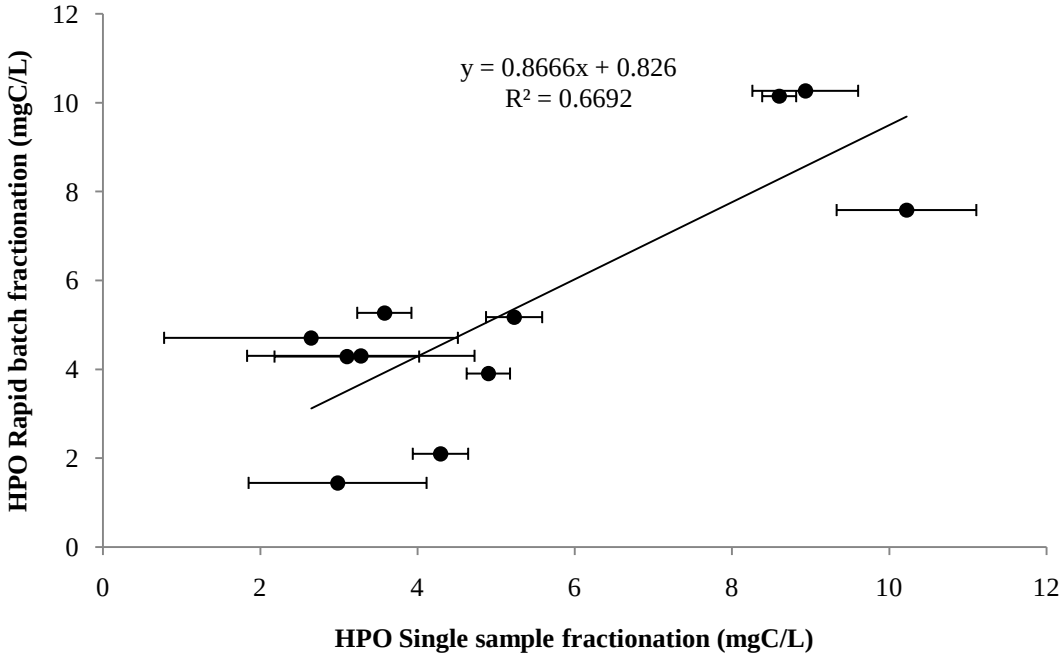


Figure 53: The relationship between the concentration of HPO fraction measured using the single sample and rapid batch fractionation procedures (regression line significant at p=0.01).

There was a good relationship between the concentration of HPO fraction analysed using the column fractionation and both the rapid batch fractionation (r^2= 0.79) and single sample fractionation (r^2=0.70) for Butterley water samples. There was also a good relationship between rapid batch and single sample rapid fractionation (r^2=0.67).

All regression lines were significant at p=0.01, using methods from Fowler and Cohen (1995). This indicates that the rapid fractionation has the potential to improve NOM catchment monitoring and can be used as an alternative to traditional column fractionations. Both column and rapid fractionations show some large error margins in their estimation of the HPO concentration of NOM samples. If the standard deviation of replica singles sample fractionations could be reduced it would improve the tools usefulness in catchment monitoring. The rapid fractionation tools were hindered in their analysis of the HPO and TPH fractions by a contaminant DOC and it is possible that this uncontrolled error caused some of the variation in replica fractionation results. Further analysis of the cause and solutions to this problem was therefore required (see section 7.2).

6.3. Investigating the treatment of NOM at the WTW using column and single sample fractionation

The next stage in the development of the rapid test was to apply it to a range of different source waters and waters treated by a WTWs. Raw and treated water, taken from the Longwood WTW catchment on 23/04/2010, was characterised for NOM type using both column fractionation with back elution and single sample rapid fractionation. Sample of raw water were also taken from Oswestry WTW (on 12/05/2010) and analysed using column, rapid batch (see Appendix III) and single sample rapid fractionation. This was to trial the rapid tool on a catchment with a different source water type, as Oswestry water has less colour and a lower DOC content than waters from the Longwood catchment.

6.3.i. Column fractionation with back elution

As seen in the analysis of the Butterley reservoir waters, the % of DOC recovered using column fractionation with back elution deviates widely from 100%. For the six waters analysed in this catchment study, % DOC recovery ranged from 72% (for Eastergate intakes) to 182% (for filtered water from Longwood WTW). As with the seasonal data from Butterley, the recovery of each fraction has therefore been converted to a % of the raw water concentration (Figure 54).

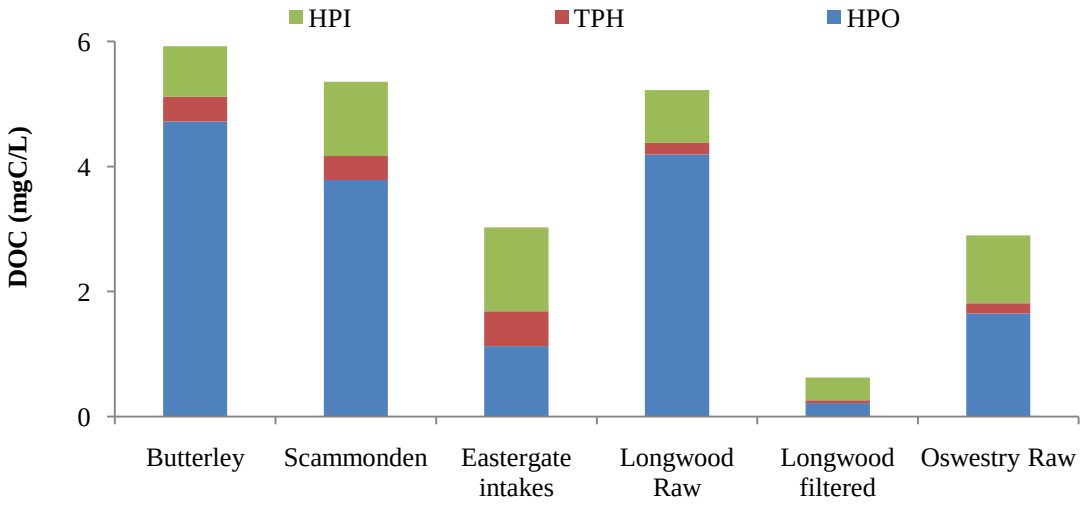


Figure 54: The concentration of raw waters in the Longwood WTW catchment on 23/04/2010 and at Oswestry WTW on the 12/05/2010.

Based on characterisation by column fractionations, of the three raw waters that combine to produce the influent to Longwood WTW, both Butterley and

Scammonden reservoirs have similar waters in terms of NOM concentration and type. They were predominantly HPO in nature with 80% and 71% of the raw DOC contained in the HPO fraction, for Butterley and Scammonden respectively. In contrast the Eastergate intakes water was of lower DOC concentration and a more intermediate NOM hydrophobicity with the HPI and TPH fractions accounting for 37% and 19% of the DOC concentration respectively. After treatment, the DOC concentration was reduced to 0.6mgC/L and was dominated by the HPI fraction (59%). Oswestry WTW had a lower raw water concentration than that of the Longwood WTW catchment, with an intermediate NOM hydrophobicity (57% HPO), similar to Eastergate intakes.

6.3.iii. Single sample rapid fractionation

Three replica single sample fractionations were performed for each of the water samples (Figures 55 & 56). Of the three raw waters in the Longwood catchment, Butterley had the highest % HPO fraction and Eastergate the highest % TPH fraction. Scammonden was of an intermediate hydrophobicity and had the highest raw water DOC concentration (8.9mgC/L). These waters combined to produce a water of intermediate hydrophobicity. The DOC concentration of the Longwood treated sample was unexpectedly high at 5.8mgC/L, and was likely to have been overestimated as this was only 1.4mgC/L below the concentration of the combined Longwood raw sample.

The main difference in the NOM type of Longwood raw and Longwood filtered water was a reduction in the HPO content of the filtered water, and an increase in the TPH content. Longwood filtered water was the only natural water analysed using single sample rapid fractionation in which the sorption to XAD-7HP followed by XAD-4 (producing the TPH fraction) was significantly higher ($p=0.05$) than the sorption to XAD-7HP (producing the HPO fraction). As was seen in the analysis of the TPH fraction for the seasonal Butterley samples, negative TPH fraction results were obtained for Longwood Raw and Oswestry WTWs. At Oswestry WTW the raw water type was of a more HPI nature than that at the Longwood WTW catchment. For all waters investigated the order of % HPO fraction was (from highest to lowest): Butterley>Scammonden>Longwood Raw>Eastergate>Longwood filtered>Oswestry Raw.

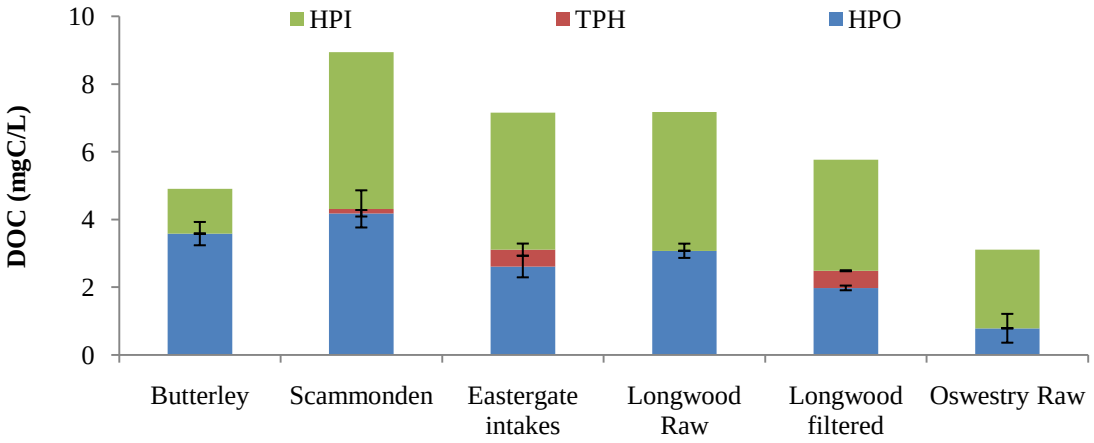


Figure 55: The DOC (mgC/L) of different fractions for waters from Longwood WTW (23/04/10) and Oswestry WTW (12/05/10) catchments using single sample rapid fractionation

The UV_{254} measurements (Figure 56) confirm that the UV_{254} absorbing NOM is predominantly found in the HPO fraction. If total UV_{254} is compared for the waters from the Longwood WTW catchment, this follows the same trend as % HPO fraction:Butterley>Scammonden>Longwood Raw>Eastergate>Longwood filtered. Water from Oswestry WTW had a higher UV_{254} absorbance than the % HPO fraction would predict. When the concentration of the HPO fraction and UV_{254} for these waters were plotted alongside the result from the seasonal Butterley samples (see section 6.1.iii, Figure 46) the correlation between HPO fraction (mgC/L) and UV_{254} was increased to r^2=0.75 (Figure 57).

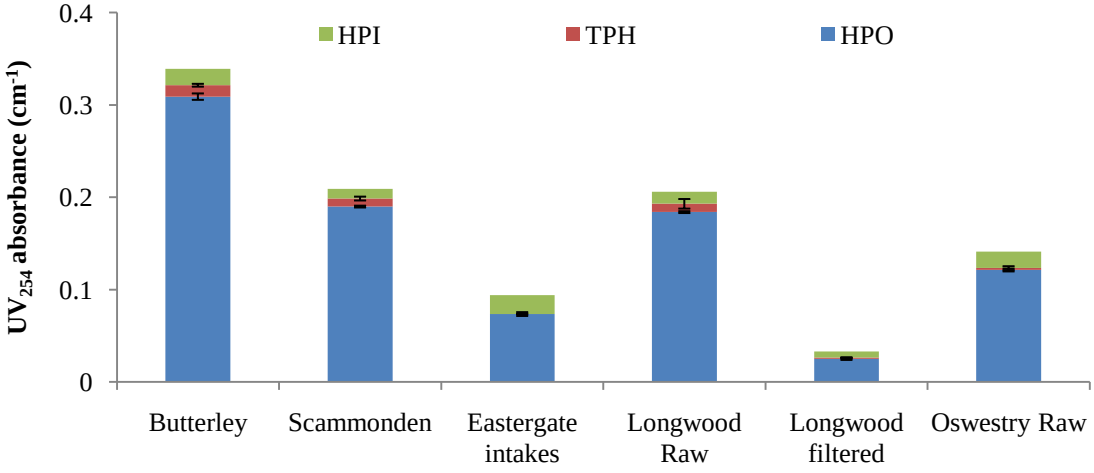


Figure 56: The UV_{254} absorbance (cm^{-1}) of different fractions for waters from Longwood WTW (23/04/10) and Oswestry WTW (12/05/10) catchments.

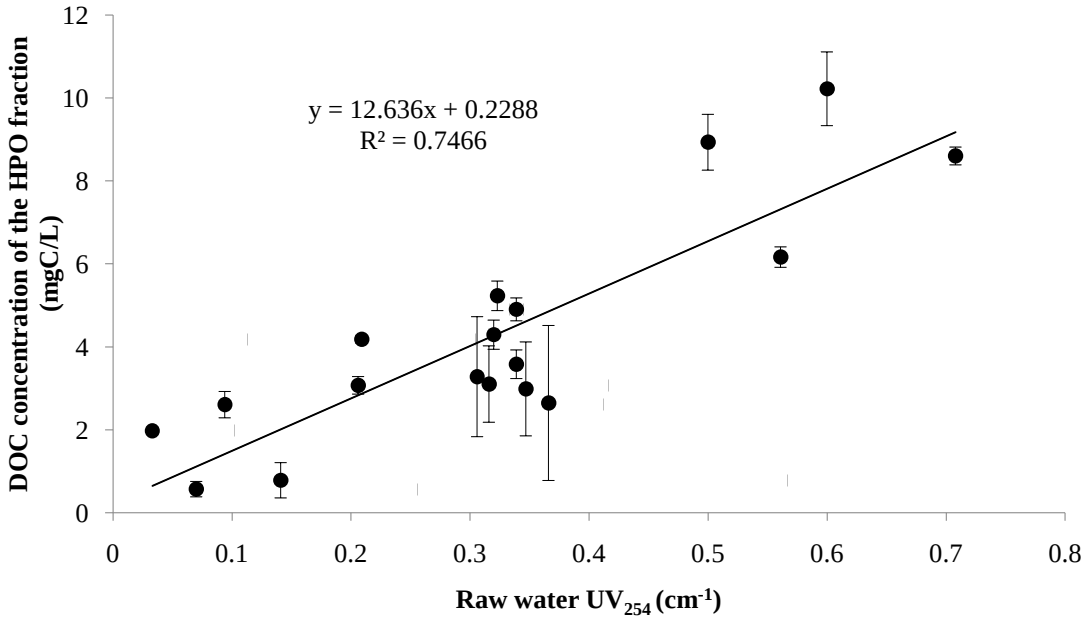


Figure 57:The correlation between UV_{254} of raw water and DOC of the HPO fraction for Butterley water samples between 08/10/09-31/05/10, Longwood catchment (23/04/2010) and Oswestry WTW (12/05/2010). The regression line is significant at p=0.01.

6.3.iv. A comparison of the fractionation techniques in the analysis of Longwood WTW and Oswestry WTW raw and treated waters

As with the seasonal Butterley samples, there were very large variations in the raw water concentrations analysed. The raw DOC (mgC/L) concentration for Longwood treated water appears to have been overestimated for the single sample rapid fractionation (5.8mgC/L) as it was much higher than the result for the sample water sample when analysed prior to the column fractionation (0.6mgC/L). This lower DOC concentration is more likely based on the low UV_{254} of the water, as measured prior to the single sample fractionation. The DOC concentrations of the Butterley, Scammondon and Longwood raw waters also show wide variations when analysed before each fractionation. For this reason, in comparing the NOM fractions produced for each method, results have been presented as % of raw water (Figure 58).

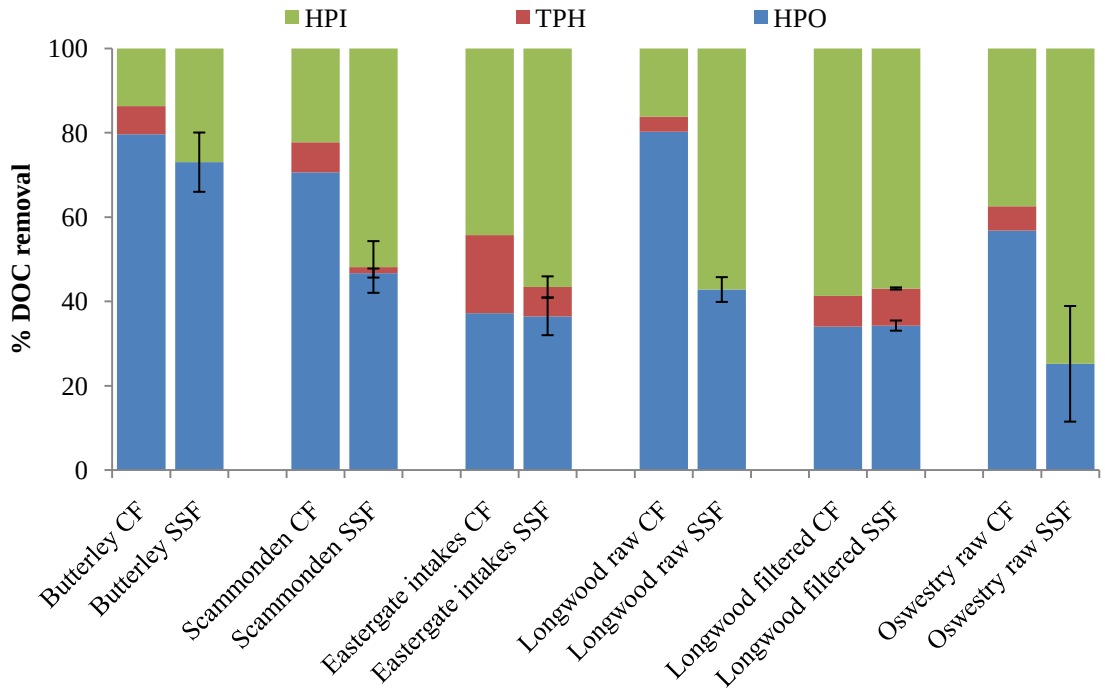


Figure 58: A comparison of the NOM fractions created using both column fractionation (CF) with back elution and single sample fractionation (SSF).

The two fractionation methods gave similar HPO results for the samples from Butterley, Eastergate and the Longwood filtered sample (Figure 58). However, there was a significant difference in the fractionation tools estimations of the HPO fraction of Scammonden and Longwood Raw waters ($p=0.05$), with a lower HPO fraction predicted by the rapid tool. For a moorland catchment such as Longwood WTW, waters are expected to have a high % HPO fraction and it is therefore suggested that the single sample rapid fractionation tool has underestimated the HPO fraction for these samples.

Both fractionation techniques resulted in an increased HPI content for the filtered Longwood WTW compared to the raw water NOM type. As HPO NOM is more easily treated at the WTW than HPI NOM (see section 3.3.i), a higher HPI content was therefore expected in treated natural waters. Both techniques also agree on a strongly hydrophobic water type for the Butterley reservoir sample and a more intermediate hydrophobicity for the Eastergate intakes.

For Oswestry raw water, DOC concentrations analysis gave similar results before all fractionation procedures ranging from 2.9, 3.3 and 3.1mgC/L for the column, rapid batch and single sample rapid fractionation. After 6 minutes both the rapid batch

fractionation and the single sample rapid fractionation predicted similar HPO contents for the Oswestry Raw water, at 24% and 25% respectively. However, both estimates were lower than the HPO fraction predicted by the column fractionation with back elution (57%). As raw water concentrations were similar, it was likely that the variation in the fractions produced was a result of the different fractionation methods.

6.4. A summary of the natural water fractionation results

The results obtained in the analysis of seasonal and spatial variations in NOM type and concentration and NOM treatability, using the different fractionation procedures can be summarised by the following:

- All fractionation procedures showed similar seasonal trends in Butterley reservoir samples. Peak DOC concentrations occurred in autumn 2009, and dropped to a minimum during late spring 2010.
- All fractionation procedures identified a similar seasonal trend, of a reduction in the HPO fraction between 08/10/09 and 31/05/10. This suggests the rapid fractionation tool was successful in identifying natural water seasonal variability.
- UV_{254} showed strong correlation with the HPO fraction (mgC/L) isolated for Butterley reservoir samples (r^2=0.71), and can be used to confirm the removal of aromatic NOM is maintained throughout rapid batch and single sample rapid fractionation. However, UV_{254} could not be used to assess seasonal trends in NOM type, for Butterley reservoir.
- The DOC recovered during column fractionation with back elution deviates from 100%, which reduces the reliability of the fractionation results.
- The DOC of the TPH fraction could not be reliably estimated using the single sample rapid fractionation method with only one natural water (the Longwood filtered sample) producing a significant TPH fraction (p=0.05). The negative DOC removal, analysed using mass analysis suggests the solution had been contaminated by another DOC source (investigated in section 7.2).
- A comparison between fractionation techniques suggests both rapid batch fractionation and single sample rapid fractionation underestimate the % HPO fraction compared to column fractionation with back elution. Further investigation of this tool, which may include the comparison of fractionations

with jar testing, are required to identify if the fractions created can be directly related to the level of NOM treatment possible using coagulation at WTWs.

- For the Butterley reservoir samples, the % HPO fraction obtained using column fractionation with back elution shows a good correlation with the concentration of the HPO fraction obtained using rapid batch (r^2=0.79) and single sample rapid fractionation (r^2=0.70).

7. Results III: Analysis of the adsorption of DOC onto three macroporous resins

Stepwise reductions in the amount of resin used for model compound DOC adsorption were carried out so that sorption sites, rather than DOC available for sorption, became the limiting factor for DOC removal. This was carried out to enable a range of DOC equilibrium to be plotted as adsorption isotherms for each macroporous resin. Previous investigations (see section 5.1.ii.) had shown that 15mL resin/L model compound could remove all available DOC, and as a result the resin concentrations used in this section were all below this concentration. Adsorption isotherms provide information on the adsorption processes governing DOC removal. The contaminant DOC observed in sections 5 & 6, was hypothesized to be caused by leaching from the resin and this was investigated by comparing DOC (mgC/L) and UV_{254} (cm^{-1}) against a control model compound solution, which had no contact with macroporous adsorption resin.

7.1. The adsorption of tannic acid to varying concentrations of three macroporous resins.

The adsorption of the HPO model compound, tannic acid, onto the three macroporous resins was tested for % DOC removal and % reduction in UV_{254} over a range of resin concentrations (Figures 59-64). Error bars show one standard deviation from the mean. Both the rate of adsorption, and the total amount of adsorption (at equilibria) increased uniformly with increasing resin concentration. However, after prolonged mixing (with all resins) the DOC concentration of the solutions began to increase, which suggested either that maximum DOC adsorption was not maintained or DOC contamination of the solution.

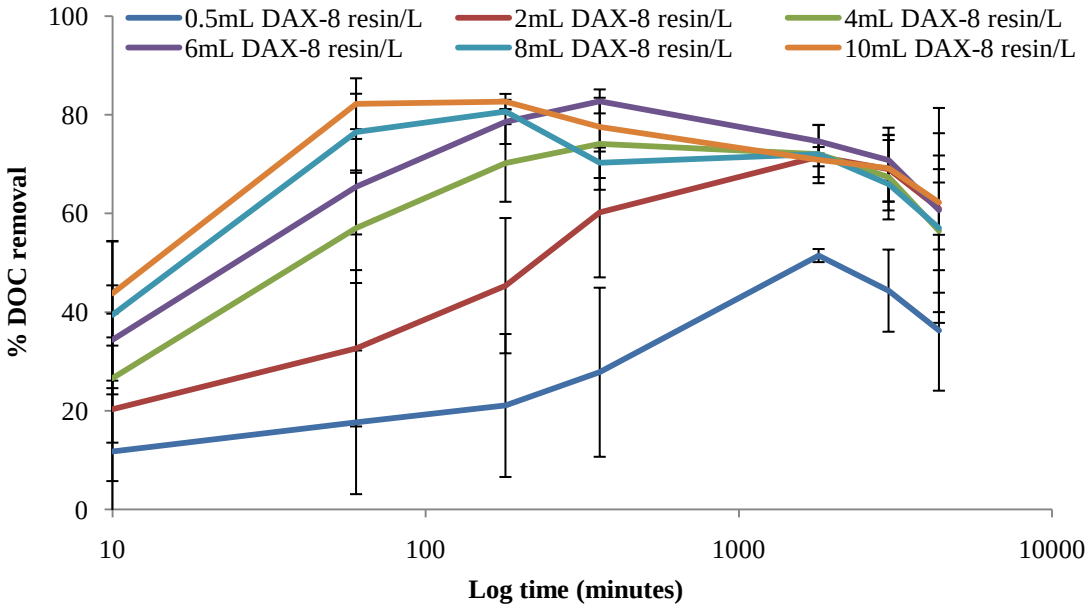


Figure 59: The % DOC removal for 20mgC/L tannic acid solution using 1L solution and 0.5-10mL DAX-8 resin.

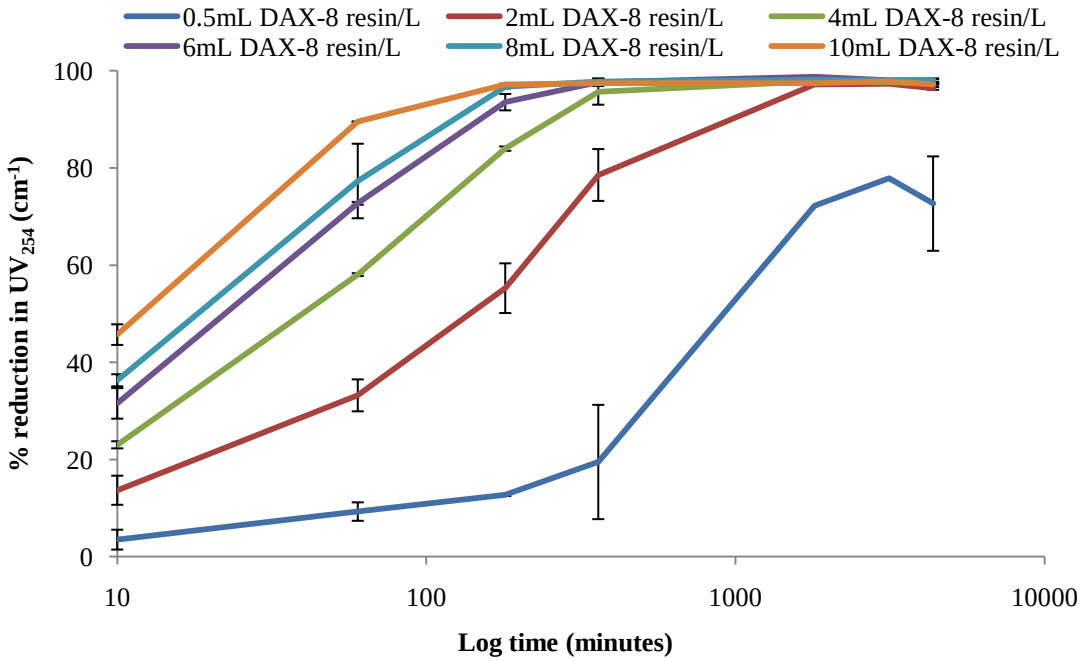


Figure 60: The % reduction in UV_{254} for 20mgC/L tannic acid solution using 1L solution and 0.5-10mL DAX-8 resin.[20]

[20] UV_{254} data failed to be collected for one replica test and as a result the data presented in Figure 59 is an average of only two replica experiments so no significance test could be completed for these data.

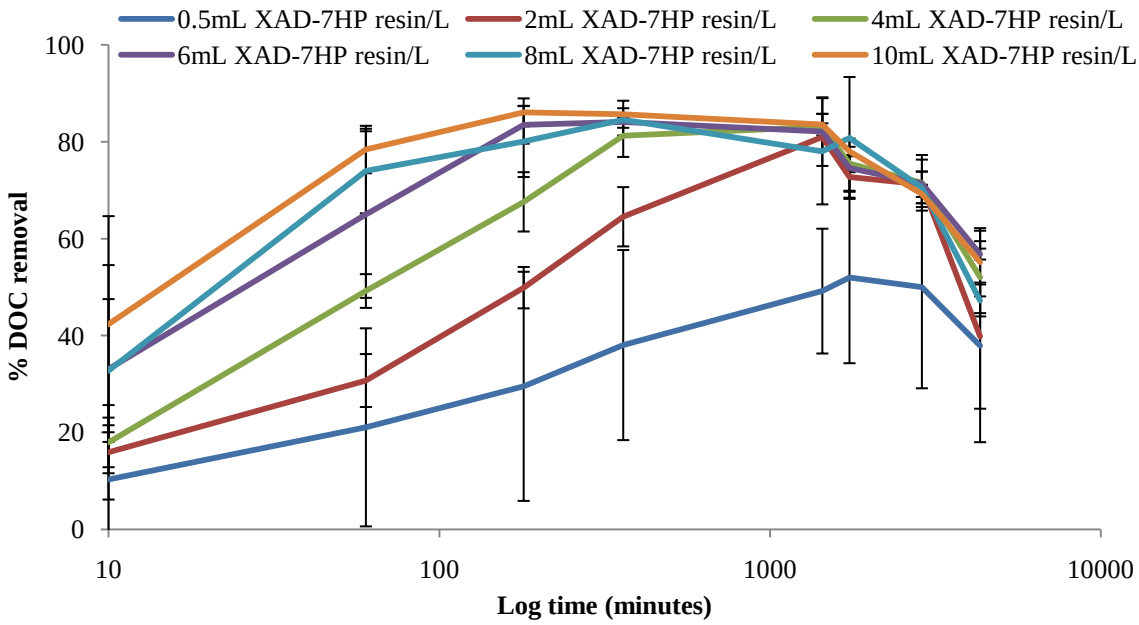


Figure 61: The % DOC removal for 20mgC/L tannic acid solution using 1L solution and 0.5-10mL XAD-7HP resin.

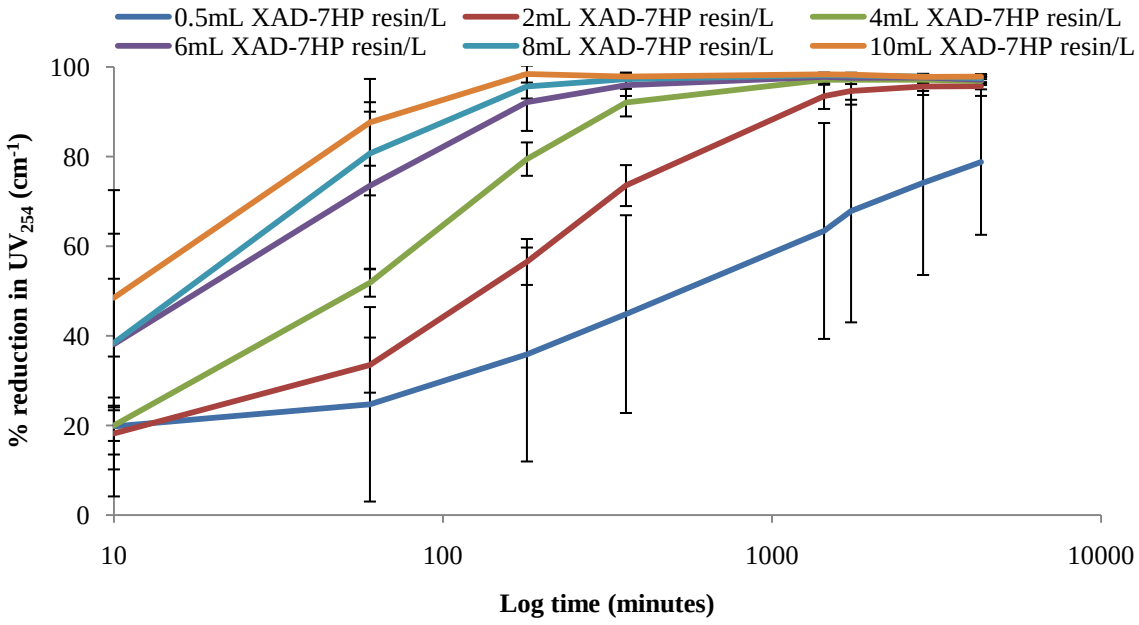


Figure 62: The % reduction in UV_{254} for 20mgC/L tannic acid solution using 1L solution and 0.5-10mL XAD-7HP resin.

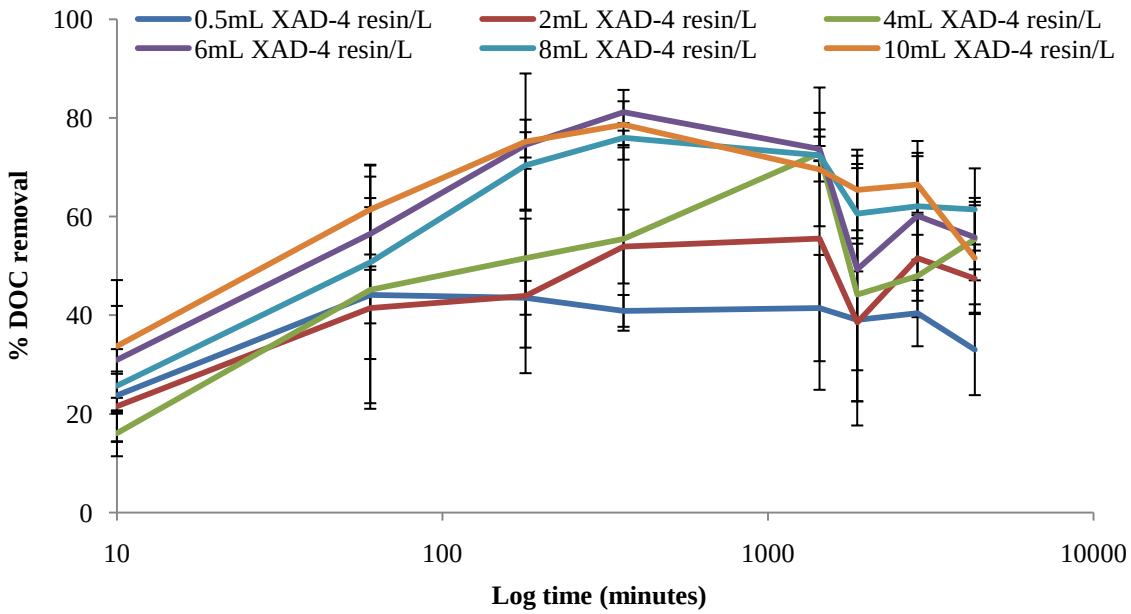


Figure 63: The % DOC removal for 20mgC/L tannic acid solution using 1L solution and 0.5-10mL XAD-4 resin

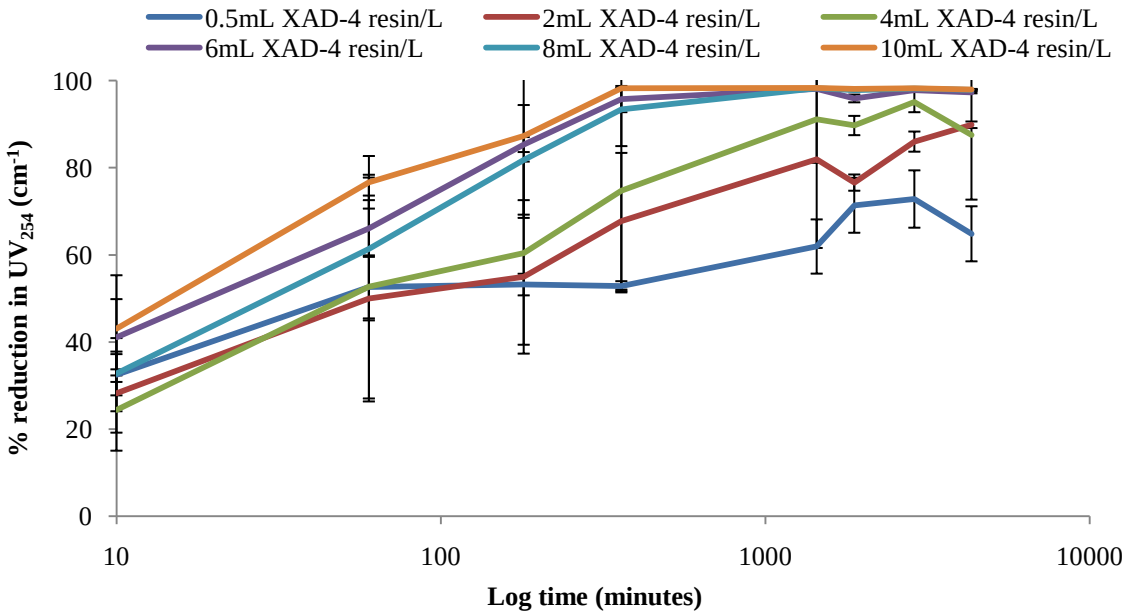


Figure 64: The % reduction in UV_{254} for 20mgC/L tannic acid solution using 1L solution and 0.5-10mL XAD-4 resin.

7.1.i. Standard deviations between replica experiments

Wide variability in the DOC removal achieved for replica experiments was shown by the high standard deviations seen using each resin concentration and type. Standard deviations tended to be highest during the initial removal period and for the lower resin/solution concentrations. The reasons for this were linked to the sampling procedure used. Due to a centrifugal effect, equal resin distribution was not possible

throughout the reaction vessels in this batch mixing procedure. During sampling, it is therefore likely that the amount of resin remaining in the reaction vessel did not remain exactly in the same proportion, which would explain the variability seen in replica experiments. Small changes in the resin/solution concentration would have the greatest effect on the vessels with the lowest resin concentrations.

7.1.ii. Amount of DOC adsorption and UV_{254} absorption

For all three resins, both % DOC removal and % reduction in UV_{254} increased with resin concentration. Maximum DOC removal for DAX-8, XAD-7HP and XAD-4 (82%, 86% and 79% respectively) and reduction in UV_{254} (98% for all resin), occurred using the highest resin/solution concentration (10mL/L). There was no significant difference in the maximum DOC and UV_{254} removal achieved for the three resins ($p=0.05$). The removal achieved for the three resins was also similar to that achieved using 250mL/L (81%, 85%, 79% respectively) ($p=0.05$) (see section 5.1.iii). This suggested that, at 10mL/L, all the DOC available for sorption had been removed from the solution.

There was no significant difference in the maximum % DOC removal observed for resin concentrations between 6-10mL/L ($p=0.05$) for any resins. However for all the lower resin concentrations, maximum % DOC and UV_{254} removal increased uniformly: 0.5mL<2mL<4mL<6mL with the difference in maximum % DOC between 0.5mL and 2mL significant for DAX-8 ($p=0.05$), and the difference between 0.5mL and 6mL significant for XAD-4 ($p=0.05$). There was also a significant difference in maximum % UV_{254} removal for 2mL and 6mL of XAD-4 ($p=0.05$).

7.1.iii. Rate of removal

As an adsorption reaction proceeds, the tendency of sorbed matter to desorb increases. This leads to a reduction in removal rates over time, until an equilibrium is reached in which sorption and desorption occur simultaneously (Faust and Aly, 1998). This occurred for the removal of DOC and UV_{254} onto all concentrations of all resins. For example, the rate of removal onto 10mL of each resin in the first 10 minutes was 0.83, 0.82, and 0.64mgC/min for DAX-8, XAD-7HP and XAD-4 respectively. However, in the following 50 minutes the rate of removal reduced to 0.15, 0.14 and 0.11mgC/min. Both DAX-8 and XAD-7HP show similar rates of removal, whilst XAD-4 tends to remove DOC and UV_{254} at a slower rate.

For both DAX-8 and XAD-7HP resins, the time to reach maximum % DOC and UV_{254} removal increased from 3 hours (using 10mL/L) to 30 hours (using 0.5mL/L) as resin concentration was decreased. The increase in removal between 3 and 30 hours for the 0.5mL/L concentration was not significant (at p=0.05) due to the high standard deviations. However, there was a significant increase in DOC and UV_{254} removal between 3 hours and 24 hours for 2mL/L of XAD-7HP (p=0.05), which confirms that the 2mL/L resin concentrations had not reached maximum removal after 3 hours. The relationship between resin concentration and the time to reach maximum DOC and UV_{254} removal was less clear for XAD-4. The 0.5mL/L resin concentration, reached maximum DOC removal (of 44%) after 1 hour, ahead of all other concentrations. However, for the other five resin concentration, the time to reach maximum % DOC and UV_{254} removal did decrease as resin concentration increased.

7.1.iv. Lack of DOC removal equilbria

For all resins, once reached, the maximum % UV_{254} removal was maintained. This was not the case for the maximum % DOC removal, with the concentration of DOC in the solution increasing after prolonged resin contact for all resin types and concentrations. The increase in solution DOC after maximum removal was not significant for DAX-8 or XAD-4 (due to the large standard deviations and small number of sample replicas) but was significant for 6mL/L and 8mL/L of XAD-7HP after 72 hours of mixing (p=0.05). A similar reduction in DOC removal over time was observed during the use of rapid batch fractionation in the removal of model compounds and natural waters (see sections 5.2.ii, 6.1.ii & 6.3.ii).

7.2. Assessing the lack of a DOC removal equilibrium

DOC adsorption isotherms are created based on equilibrium resin/solution DOC concentrations. As maximum % DOC removal was not maintained in the previous section, further analysis was required before the data could be used in the creation of adsorption isotherms. As tannic acid is a single compound, both DOC and UV_{254} should be removed equally, and the relationship between the two variables should be constant both before and during absorption. Analysis of this relationship was carried out to determine the reason behind the lack of DOC removal equilibria for all macroporous resins.

7.2.i. The relationship between DOC and UV_{254}

In section 5.2.ii a greater reduction in % UV_{254} than % DOC was reported for both tannic acid and 1,3 acetonedicarboxlyic acid. This was also seen in section 7.1 with approximately 80% DOC removal and 100% UV_{254} removal occurred for resin concentrations of 10mL/L, with approximately 50% DOC removal and 70% UV_{254} removal for resin concentrations of 0.5mL/L.

Whilst both % removal of DOC and UV_{254} increased during the first 3 hours for all resin concentrations, after 72 hours DOC removal decreased, but UV_{254} removal did not. This suggested an alteration in the relationship between DOC and UV_{254} after 72 hours, which was investigated by comparing DOC and UV_{254} levels after 60 minutes and after 72 hours of contact between the tannic acid solution and each resin. Both data sets were compared against the relationship between DOC and UV_{254} for control tannic acid solutions (0-40mgC/L), which had not been in contact with any resin (Figures 65-67). Acidified ultra pure water was also mixed with 10mL/L resin concentrations and sampled over 72 hours to show if any DOC was released from the resin.

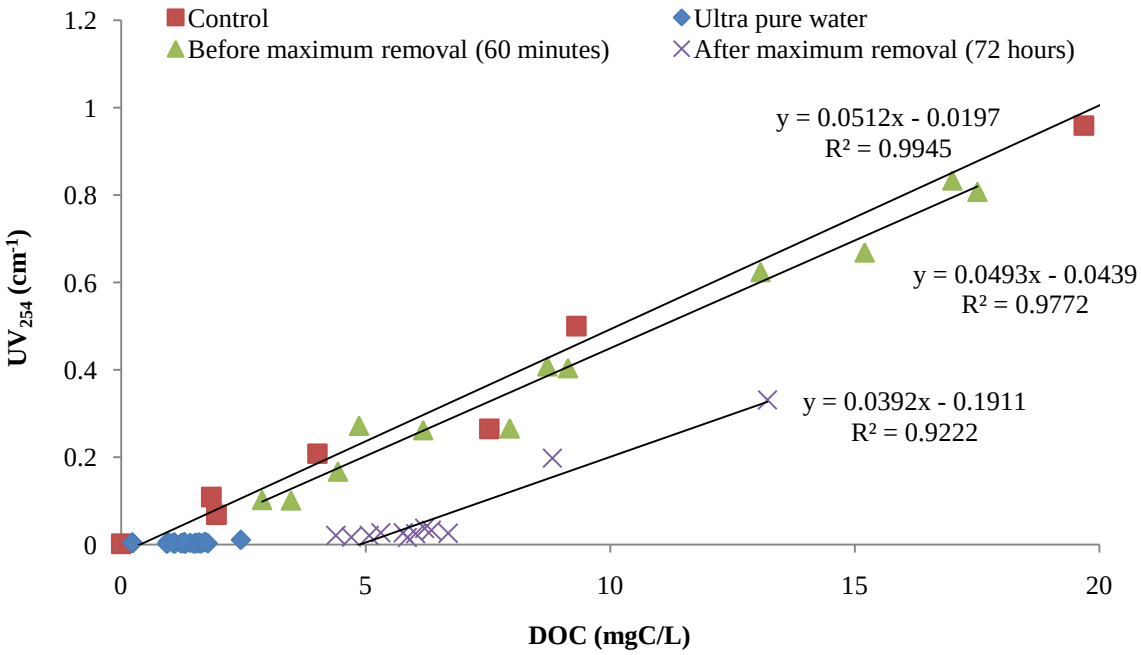


Figure 65: Comparing the relationship between DOC (mgC/L) and $UV_{254}cm^{-1}$ for 20mgC/L tannic acid solutions which were in contact with DAX-8 resin for 60 minutes and 72 hours.

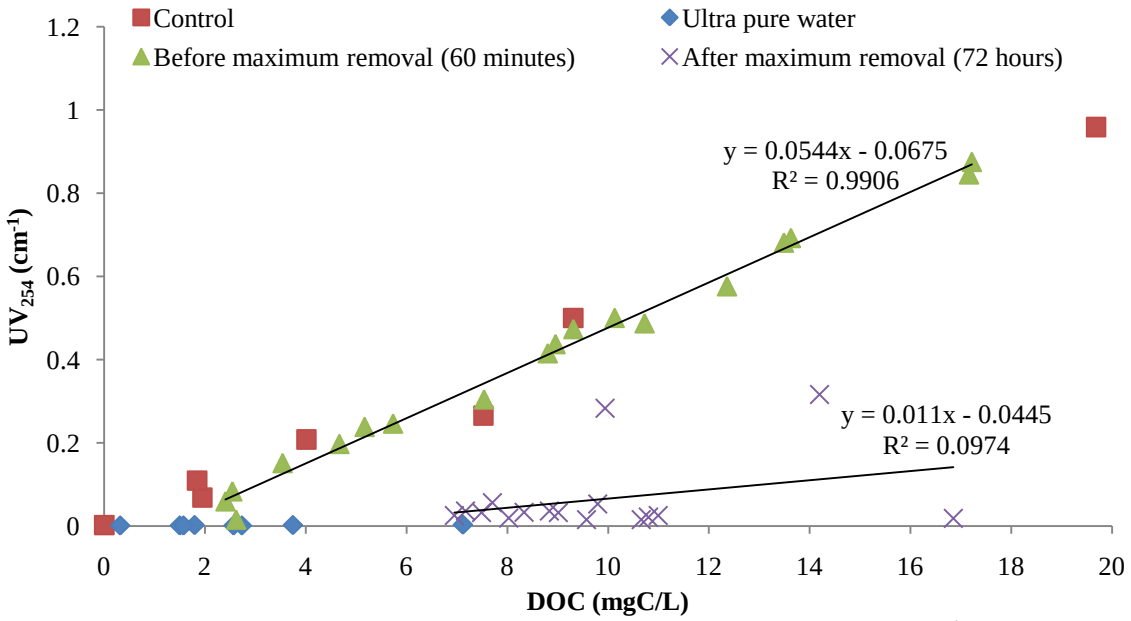


Figure 66: Comparing the relationship between DOC (mgC/L) and $UV_{254}cm^{-1}$ for 20mgC/L tannic acid solutions which were in contact with XAD-7HP resin for 60 minutes and 72 hours.

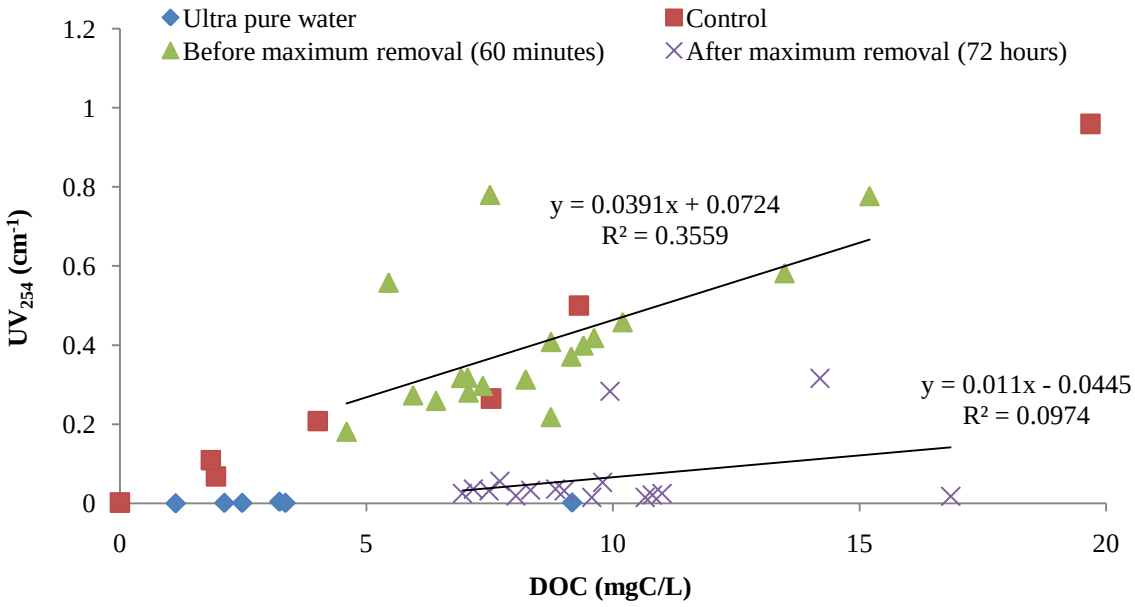


Figure 67: Comparing the relationship between DOC (mgC/L) and UV_{254} (cm^{-1}) for 20mgC/L tannic acid solutions which were in contact with XAD-4 resin for 60 minutes and 72 hours.

After 60 minutes

There was a very strong correlation between DOC and UV_{254} for the control tannic acid solution (r^2=0.99)(shown on Figure 65 but used for all Figures 65-67) and after 60 minutes contact with both 0.5-10mL/L DAX-8 (r^2=0.98) and XAD-7HP (r^2=0.99) resins. These all show a similar relationship between the two variables, which suggest tannic acid was the only carbon compound of any appreciable concentration in

solution after 60 minutes of resin contact which was contributing to UV_{254} and DOC concentrations. After 60 minutes contact between the tannic acid solution and 0.5-10mL/L XAD-4 there was a weak correlation between DOC and UV_{254}. This correlation improved to r^2=0.88 if the two outliers (5.4,0.558 and 7.5,0.78) were omitted and this also gives a more similar relationship between the two variables (y=0.0513x - 0.0762) when compared to the control.

When acidified ultra pure water was mixed with 10mL/L resin concentrations for 60 minutes, DOC concentrations of 1.8mgC/L (with XAD-7HP) and 1.1mgC/L (XAD-4) occurred with corresponding UV_{254} of 0.002cm^{-1} and 0.000cm^{-1}.[21] These results showed that low levels of DOC from a source other than the model compound were present in solution.

After 72 hours

After 72 hours contact with DAX-8 resin, the correlation between DOC and UV_{254} was still strong but the relationship between these variables had deviated from the control (Figure 65). After 72 hours contact with XAD-7HP resin, there was no real correlation between DOC and UV_{254} and the relationship between the variables had also deviated from the control (Figure 66). There was also no real correlation between DOC and UV_{254} after 72 hours of mixing with XAD-4. Acidified ultra pure water samples showed low UV_{254} of 0.006, 0.003, 0.002cm^{-l}, consistent with UV levels after 60 minutes of mixing, but increased DOC concentrations of 1.72mgC/L, 7.12mgC/L and 9.2mgC/L for DAX-8, XAD-7HP and XAD-4 respectively after 72 hours of batch mixing. These results showed that a DOC source other than tannic acid was now present in the solution.

7.2.ii. The significance of the altered relationship

In order to test if the relationships between DOC and UV_{254} after 60 minutes and 72 hours of contact were statistically different from the control tannic acid solution, the 95% confidence interval and confidence limits were calculated for the control tannic acid solutions, using the equations for standard error:

For 95% confidence interval: $S.E = + \sqrt{(S_r^2 \times [(1/n) + ((x' - x)^2/SS_x)]}$ **Eq. 10**

[21] A sample was not taken after 60 minutes of mixing with DAX-8, but after 360 minutes a DOC of 1.3mgC/L and UV_{254} of 0.004cm^{-1} was recorded.

For 95% confidence limit:	$S.E = + \sqrt{(S_r^2 \times [1 + (1/n) + ((x' - x)^2/SS_x)]}$	**Eq. 11**
Where:	$S_r^2 = (1/(n-2)) \times [SS_y - ((SP_{x,y})^2/SS_x)]$	**Eq. 12**
	$SP_{x,y} = \sum xy - (\sum x \sum y)/n$	**Eq. 13**
	$SS_y = \sum y^2 - (\sum y)^2/n$	**Eq. 14**
	$SS_x = \sum x^2 - (\sum x)^2/n$	**Eq. 15**

Fowler and Cohen (1995)

These were plotted for the DOC range 0-20mgC/L alongside the results from batch mixing tests with each resin (Figure 68). After 60 minutes of mixing with both DAX-8 and XAD-7HP the relationship between DOC and UV_{254} was not significantly different from the control relationship between DOC and UV_{254}. However, after 72 hours of mixing with DAX-8 or XAD-7HP none of the samples were within the 95% confidence limit. Therefore after 72 hour there was a significantly different relationship between DOC and UV_{254} to that obtained with a control tannic acid model compound solution (p=0.05). For batch mixing with XAD-4, all but three of the samples taken after 60 minutes had a similar relationship between DOC and UV_{254} to the control tannic acid solution. The three samples outside the 95% confidence limit were therefore assumed to be outliers and were not used in further adsorption isotherm calculations. After 72 hours of mixing with XAD-4, all but two samples had significantly different relationships between DOC and UV_{254} to that obtained with a control tannic acid model compound solution (p=0.05).

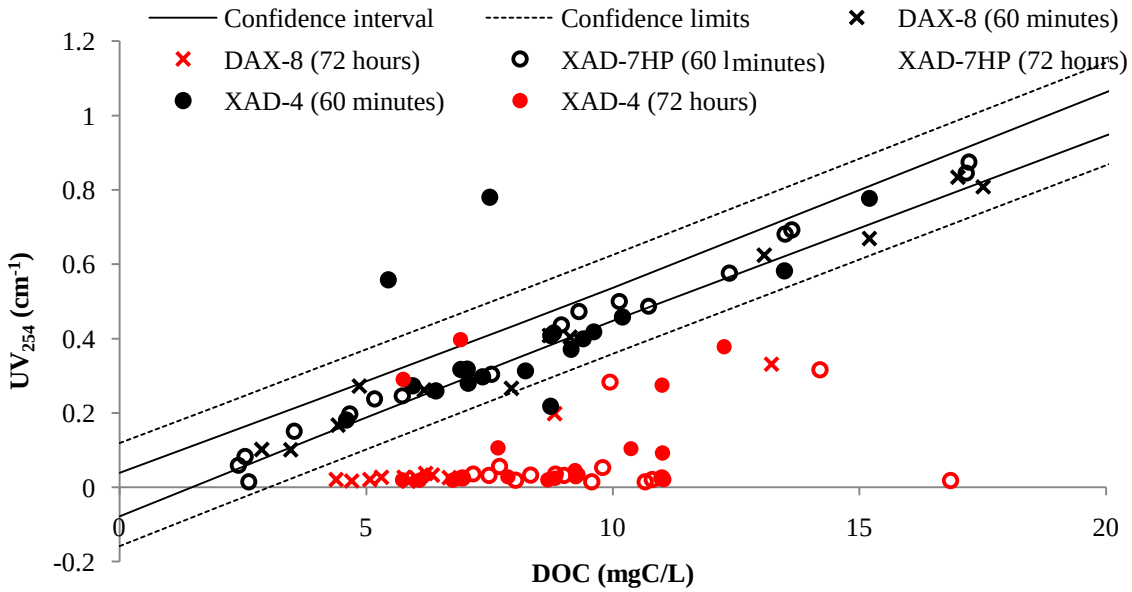


Figure 68: Assessing the significance of the deviation from the relationship between DOC (mgC/L) and UV_{254} (cm^{-1}) of the control, for samples after 60 minutes and 72 hours of mixing with macroporous resins.

Those samples that show a significantly different relationship between DOC and UV_{254} to the control tannic acid solution, must therefore contain some carbon based molecules that have a different structure and UV_{254} absorbance to that of tannic acid to account for this different relationship between DOC and UV_{254}. This difference would also account for the different % removal of DOC and UV_{254} which was identified in all experiments with both tannic acid and 1,3 acetonedicarboxylic acid. Possible sources of DOC with low UV_{254} include leaching from the resin, sample contamination, or desorption and chemical alteration of the tannic acid.

The case for leaching of organics from the resin was confirmed by acidified ultra pure water tests. High levels of DOC were also seen when acidified water was batch mixed with the resin, with DOC concentration increasing over time, until the experiments were halted at 72 hours. As no model compound was present to account for this increase in DOC concentration, it is therefore suggested that the increased DOC content seen in adsorption trials was not caused by desorption or chemical alteration of the tannic acid. As a result, leaching from the resin was identified as the cause of the reduced DOC removal from the solution, seen not only for tannic acid solutions but natural water (sections 6.1.ii & 6.3.ii) and other model compounds (section 5.2.ii.). Therefore the maximum % DOC removal levels can be treated as DOC equilibrium sorption levels for tannic acid. Following this conclusion, samples with maximum % DOC removal were used to create adsorption isotherms instead of those samples in which a reduction in % DOC removal had occurred.

DOC leaching from macroporous resins has a particularly important impact on the NOM fractions produced using these resins when a mass analysis technique is used. Resin leaching would increase the DOC of the fractionation effluent, thereby underestimating the DOC adsorbed to the resin. If resin leaching were dependent on resin surface area, a higher leaching effect would be observed for high resin concentrations, such as those used in the rapid fractionation tool. DOC leaching from the resin would explain the low % HPO fractions and lack of significant TPH fractions seen for natural water rapid fractionations.

7.3. Adsorption Isotherms for the sorption of tannic acid onto macroporous resins

The time at which each of the six resin concentrations achieved maximum DOC removal (see Appendix IV) was substituted for an equilibrium DOC sorption after confirming that the increasing solution DOC concentration was not caused by the tannic acid. This point of equlibria is distinctive to the experimental conditions, and equilibrium points at varying resin/solution concentrations can therefore be used to provide information on, and quantify, the affinity of tannic acid for each resin. The two most commonly used models for the adsorption of DOC from aqueous solution are the Langmuir (assumes monolayer adsorption) and Freundlich (allows for exponential distributions of sites and energies) equations (see section 3.4.iii.). Both models were used to plot the maximum DOC adsorption levels for each resin (Figures 69-74). Significance of each regression line has been established using the F test in ANOVA according to Fowler and Cohen (1995).

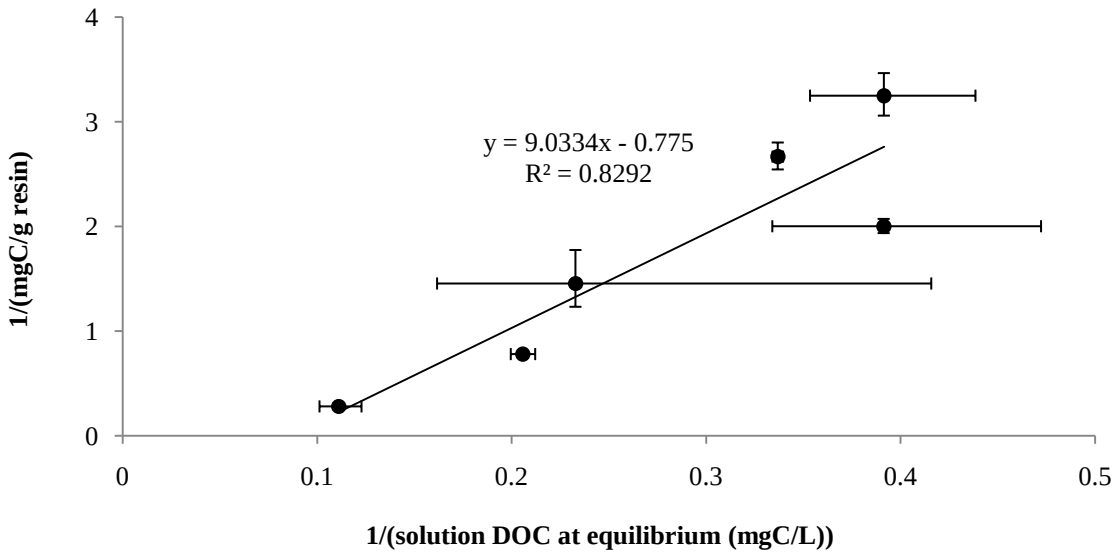


Figure 69: Langmuir isotherm for the sorption of 20mgC/L tannic acid solutions onto 0.5-10mL/L DAX-8 resin (regression line significant at p=0.05).

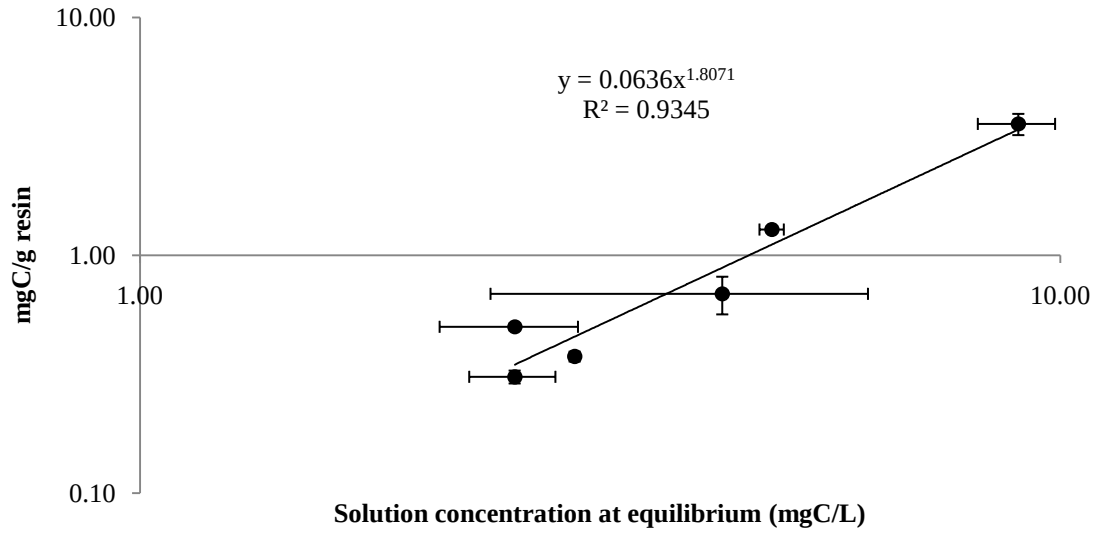


Figure 70: Freundlich isotherm for the sorption of 20mgC/L tannic acid solutions onto 0.5-10mL/L DAX-8 resin (regression line significant at p=0.01).

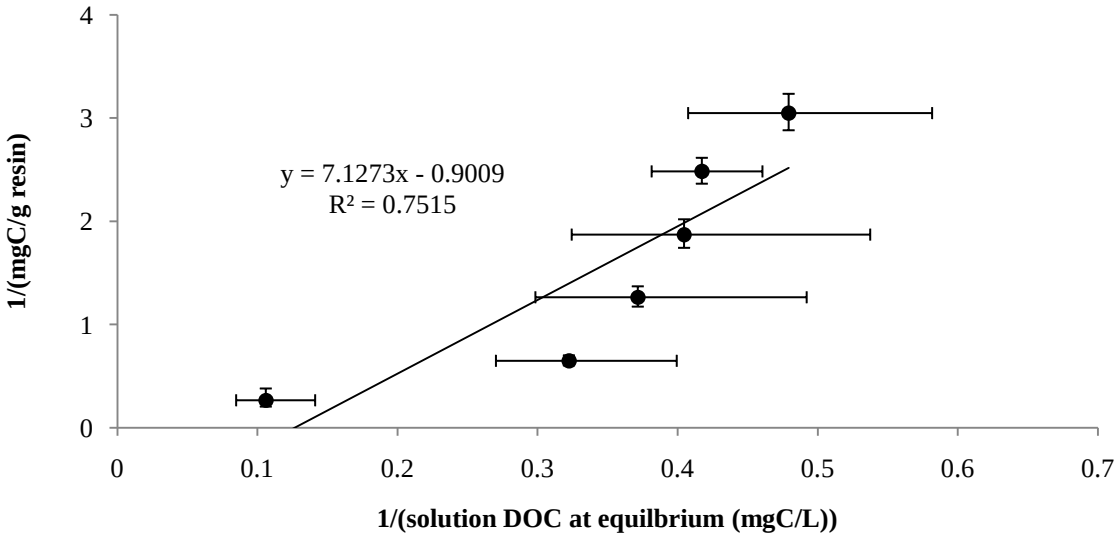


Figure 71: Langmuir isotherm for the sorption of 20mgC/L tannic acid solutions onto 0.5-10mL/L XAD-7HP resin (regression line significant at p=0.05).

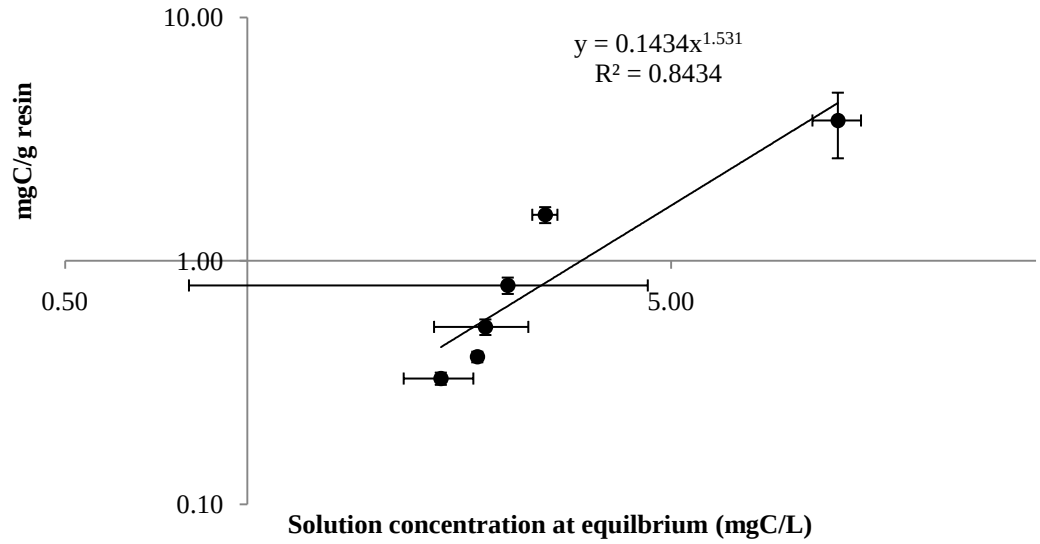


Figure 72: Freundlich isotherm for the sorption of 20mgC/L tannic acid solutions onto 0.5-10mL/L XAD-7HP resin (regression line significant at p=0.01).

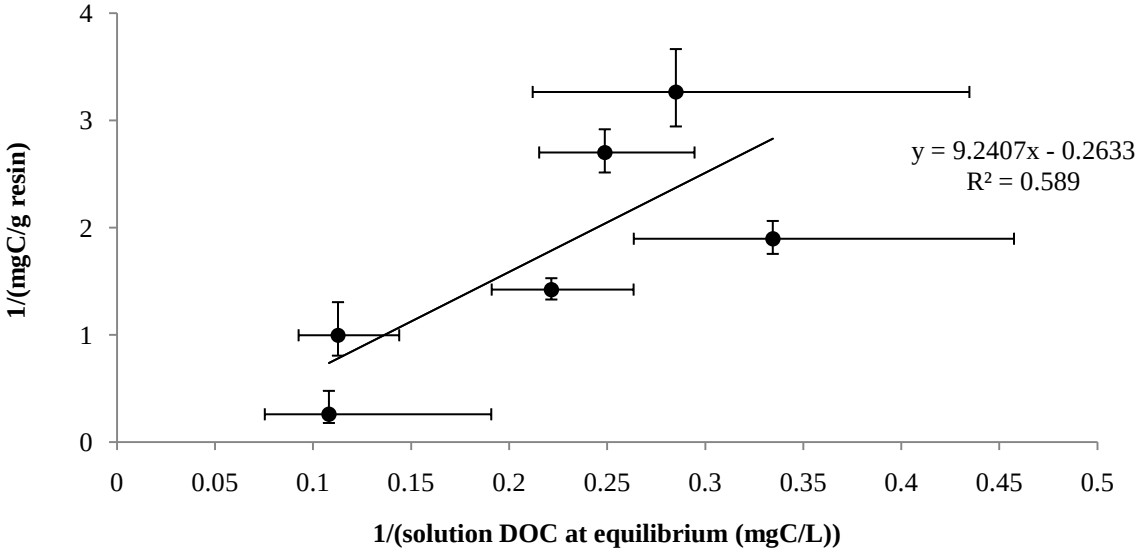


Figure 73: Langmuir isotherm for the sorption of 20mgC/L tannic acid solutions onto 0.5-10mL/L XAD-4 resin (regression line is not significant at p=0.05).

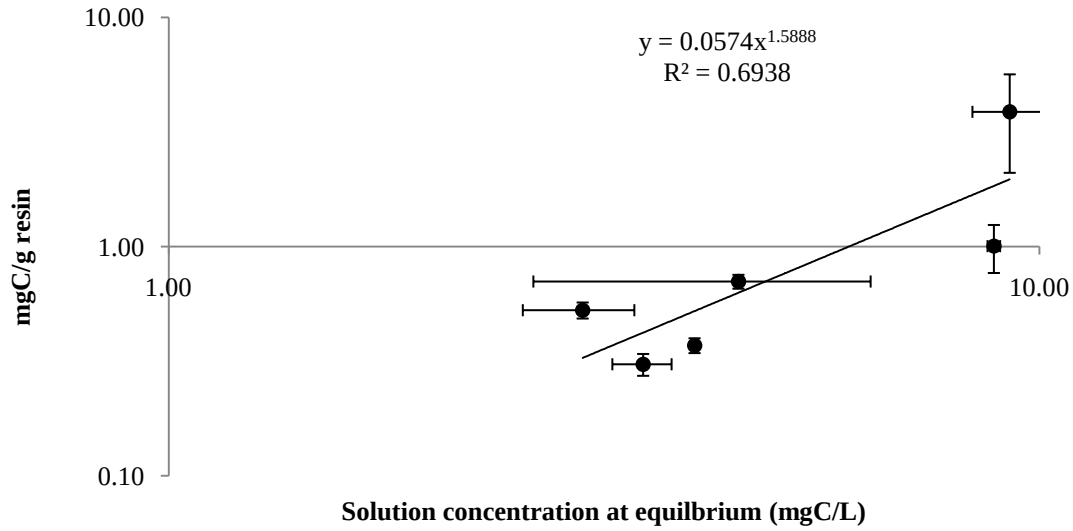


Figure 74: Freundlich isotherm for the sorption of 20mgC/L tannic acid solutions onto 0.5-10mL/L XAD-4 resin (regression line is not significant at p=0.05).

The equations of each isotherm provide adsorption parameters for the Langmuir (X_m and b) and Freundlich (1/n and k) models (see section 3.4.iii), which are given in Table 9. For all macroporous resin adsorption, isotherms modelled using the Freundlich equation had a higher r^2 value for the data than those modelled using the Langmuir equation, suggesting the adsorption followed a Freundlich model. The negative results obtained for all values of X_m, was further indication of a lack of conformity to this model, (Fungaro and Grosche, 2006) and as a result, no further analysis of the Langmuir isotherms was performed.

Table 9: Parameters for the Langmuir and Freundlich isotherms for the adsorption of tannic acid solution to the three macroporous resins investigated in this study. Both X_m and k have been converted from mgC g^{-1} (Figures 68-73) to mg g^{-1}.

	Langmuir isotherm			Freundlich Isotherm		
Sorbant	X_m(mg g^{-1})	b	r^2	1/n	k(mg g^{-1})	r^2
DAX-8	-12.032	-0.044	0.829	1.807	0.593	0.935
XAD-7HP	-10.350	-0.054	0.752	1.531	1.337	0.843
XAD-4	-35.389	-0.015	0.589	1.589	0.535	0.694

1/n is known as the adsorption intensity parameter and refers to the gradient of the isotherm. In the literature, favourable adsorption was indicated by an n value between 1 and 10 (Raji et al., 1997). In this study, all resins had n<1 (DAX-8>XAD-4>XAD-7HP). A few studies have previously reported n<1 (Babu and Ramakrishna, 2003), and these low n values indicate a particularly high adsorptive capacity at high equilibrium concentrations, that reduces rapidly at lower equilibrium concentrations

(Faust and Aly, 1998). In contrast, the adsorption of tannic acid to activated carbon produced a 1/n of 0.275. This suggests that the adsorption capacity for activated carbon is less affected by DOC concentration than the three macroporous resins.

The k value refers to the adsorption capacities for each sorbent and this was of the order: XAD-7HP>DAX-8>XAD-4, for the three resins. The difference between the adsorption capacity for XAD-7HP and DAX-8 was relatively large (k = 1.337 and 0.593 mg g^{-1} respectively). This suggests the two resins have a different affinity for HPO NOM. As a result, any fraction comparisons between studies using XAD-7HP and studies using DAX-8 to fractionation NOM must be done with caution as the NOM contained within the HPO fraction is likely to be different. As XAD-4 is commonly used to adsorb TPH compound, a lower adsorption capacity for the HPO tannic acid was expected. Ucer et al. (2005) reported the adsorption capacity (k) of activated carbon for tannic acid to be 1.552mg g^{-1}. This was higher than all three macroporous resins, and was likely to be due to the larger surface area of the activated carbon (commonly between 750-1700m^2g^{-1} (Lei et al., 2002)) compared to the macroporous resins (160m^2g^{-1}, 380m^2g^{-1}, 725m^2g^{-1} for DAX-8, XAD-7HP and XAD-4 respectively). Both DAX-8, and XAD-7HP have similar structures as are acrylic based resins. If adsorption capacity, per surface area is considered, the affinity of these resins for tannic acid is more similar (3.7 x 10^{-3} and 3.5 x 10^{-3} mg $g^{-1}m^{-2}$ respectively),

7.4. The adsorption of 1,3 acetonedicarboxylic acid and d-xylose to varying concentrations of DAX-8 resin.

As with tannic acid, varying concentration of DAX-8 resin were analysed for % DOC removal of solutions 1,3 acetonedicarboxylic acid (Figure 75) and d-xylose (Figure 76) in an attempt to produce adsorption isotherms. Whilst some adsorption of 1,3 acetonedicarboxylic acid to the 6-10mL/L resin concentrations was observed in the first 60 minutes of mixing, this was not significant, and between 180 minutes and 360 minutes all resin concentrations showed a negative % DOC removal. This was followed by an increasing DOC removal for all resin concentrations between 30 and 72 hours. At no point during the 72 hour contact period did a maximum, or equilibrium, DOC removal occur, and as a result no adsorption isotherm was possible.

For this reason no further analysis of the sorption of 1,3 acetonedicarboxlyic acid to any macroporous resins was completed.

Analysis of the sorption of d-xylose to varying concentrations of DAX-8 resin[22] (Figure 76) confirmed it to be strongly HPI, with no adsorption above 1% occurring for any resin concentration. For samples taken after 180 minutes of mixing, all resin concentrations showed a negative % DOC removal. Due to a lack of sorption of DOC to the DAX-8 resin, no sorption isotherms could be calculated and further analysis with other macroporous resins was not completed.

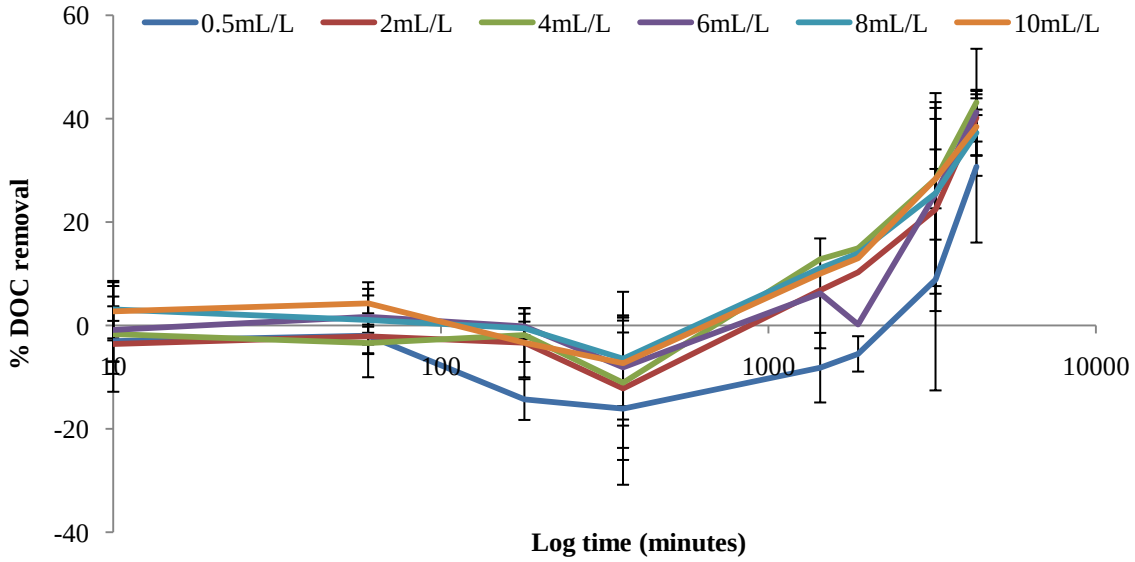


Figure 75: The % DOC removal for 20mgC/L 1,3 acetonedicarboxylic acid solution using 1L solution and 0.5-10mL DAX-8 resin. Two replica experiments were completed.

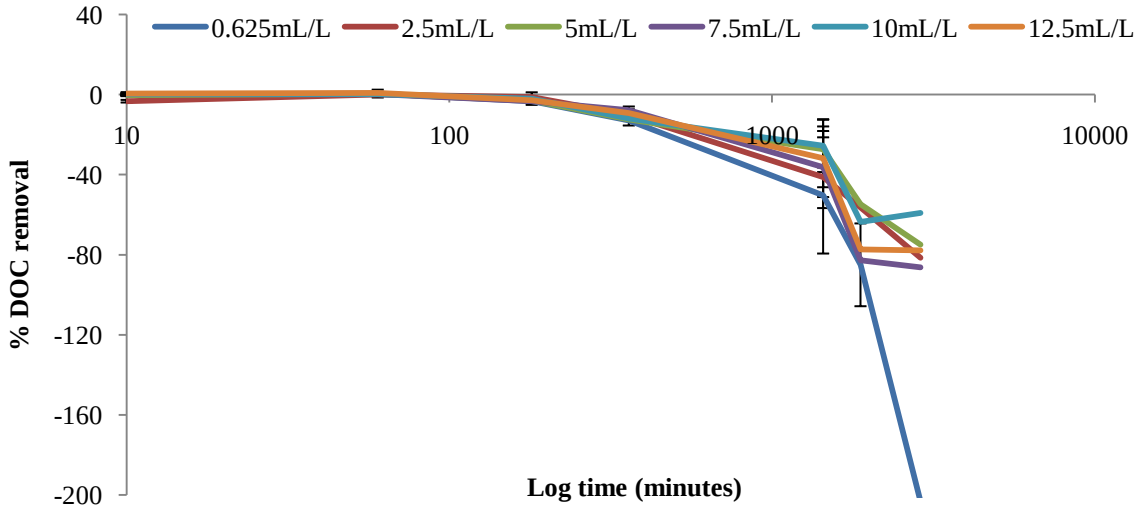


Figure 76: The % DOC removal for 20mgC/L d-xylose solution using 1L solution and 0.625-12.5mL DAX-8 resin. Two replica experiments were completed.

[22] For d-xylose, resins concentrations of 0.625-12.5mL/L were used instead of the 0.5-10mL/L concentrations used in previous adsorption analysis of model compounds.

7.5. A summary of the analysis of adsorption of DOC onto macroporous resins

The production of adsorption isotherms for the three macroporous resins can be summarised by the following:

- For DAX-8 and XAD-7HP the time to reach maximum DOC removal and UV_{254} absorption was dependent upon resin concentration. This could not be confirmed for XAD-4.
- The removal rates of DOC onto each resin were in the order DAX-8>XAD-7HP>XAD-4 in the first 60 minutes of mixing.
- For batch mixtures of resin and 20mgC/L tannic acid solutions over 72 hours, no equilibrium DOC sorption occurred onto any macroporous resin, but equilibrium UV_{254} absorption did occur.
- The confidence intervals and confidence limit for control tannic acid solutions confirmed that, after a reduction in DOC adsorption had been observed, the relationship between the DOC (mgC/L) and UV_{254} absorption was statistically different to the relationship for tannic acid.
- Adsorption isotherms were produced for tannic acid using the maximum % DOC removal values and confirmed a Freundlich model was more appropriate to model sorption to all three macroporous resins than the Langmuir model. Strong correlation with the Freundlich model occurred for DAX-8 (r^2=0.9345) and XAD-7HP (r^2=0.8434) and good correlation for XAD-4 (r^2=0.6938).
- The adsorption capacities of each resin for a 20mgC/L tannic acid solution were in the order XAD-7HP>DAX-8>XAD-4.
- No adsorption isotherms could be created for either 1,3 acetonedicarboxylic acid or d-xylose due to a lack of a maximum % DOC removal.

8. Discussion

The key objectives behind this research were to develop a rapid tool for fractionating NOM by hydrophobicity and to compare this tool against the traditional method. In both methods XAD macroporous resins were used as the DOC adsorbent. The objectives were met by investigating the adsorption of model compound solutions and natural waters for both procedures. The key findings can be summarised as:

- *Resin concentration controls the rate of DOC removal:* Increasing the resin concentration from 15mL/L to 250mL/L increased the rate of DOC removal onto all resins. This enabled DOC removal equilibria to be obtained after 6 minutes, for all resins, thereby achieving rapid fractionation.
- *An increased resin concentration removed a greater proportion of model compound DOC as the HPO fraction:* This was particularly important for the model compound of intermediate hydrophobicity, 1,3 acetonedicarboxylic acid, whose adsorption increased by at least 24% onto all resins when resin concentration was increased from 15mL/L to 250mL/L. The amount of DOC removed as the TPH fraction also increased.
- *The rapid fractionation tool removed a lower proportion of natural water DOC as the HPO fraction:* Whilst the removal of over 85% UV_{254} adsorption confirmed high levels of aromatics were removed from the solution, the average % HPO fraction achieved using rapid fractionation was significantly lower than that achieved using corresponding column fractionations of natural waters. The rapid tool did not produce a reliable TPH fraction.

A brief description of the developed tool and it's differences to traditional fractionation is given before the explanation for each of these key finding is discussed in detail. Finally the future of rapid fractionation is addressed.

8.1. Developing rapid fractionation with increased resin concentration and a different resin/solution contact procedure

During a column fractionation, the DOC concentration and type of the column's effluent solution changes temporally as the number of free adsorption sites in the resin decreases as more of the solution passes through and adsorbs to the resin (Malcolm and MacCarthy, 1992). Therefore, as solution DOC removal varies over time,

fractions cannot be determined by mass analysis until the entire sample has passed through the column (Gadmar et al., 2005). Also, fractions of comparable DOC types can only be produced for different fractionations if the amount of resin and influent DOC concentration (and type) are controlled. For investigating solutions of unknown DOC concentrations, such as natural waters, this is not possible and instead researchers often maintain a common resin/solution concentration of 15mL/L (Goslan et al., 2002; Sharp et al., 2005). The time to achieve this fractionation is dependent on the flow rate through the column. However, the recommended flow rate is below 20 bed volumes per hour (10-15 bed volumes per hour (Malcolm, 1989)) as flows in excess of this reduce the columns adsorption capacity (Thurman and Malcolm, 1978). For these reasons, and to enhance the portability of the fractionation procedure, a batch mixing contact method was trialled as an alternative contact method. The differences in the contact between the resin and solution can, however, impact the removal of NOM.

8.1.i. A comparison of plug flow and batch mixing

Unlike during plug flow, in batch mixing the entire solution receives equal DOC removal and there is constant contact between the resin and solution. Despite these variations the batch mixing method produced similar fractions for model compounds to the column fractionation, for all resins, as the competing molecules for adsorption are all of the same type. However, the difference between a batch mixed and plug flow system (Figure 77) may cause a variation in the treatment of solutions with mixtures of NOM compounds, such as in natural waters.

In column fractionation, competition between species for adsorption sites causes dynamic adsorption to occur, with less hydrophobic molecules displaced by very hydrophobic molecules at the top of the column (Roque-Malherbe, 2007). This leads to the mass transfer of less hydrophobic NOM, which moves down the resin column as adsorption sites fill. A column of stratified hydrophobicty develops (Figure 75) with the most HPO molecules removed preferentially from the solution. Molecules of intermediate hydrophobicity are removed from the solution lower down the column, where there is less competition for adsorption sites.

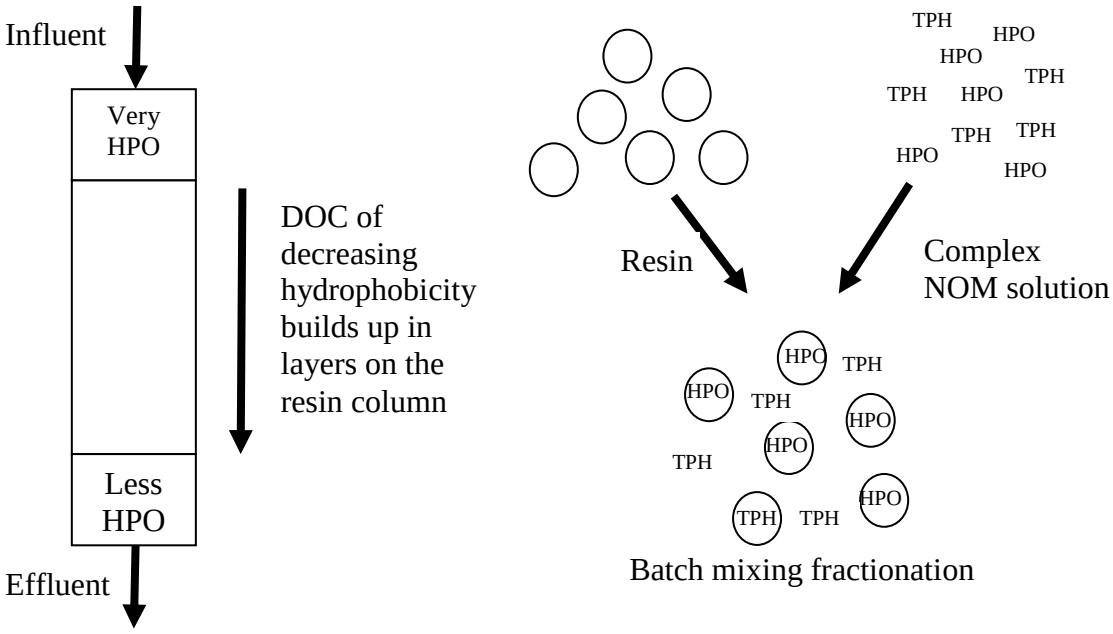


Figure 77: A comparison of the sorption of DOC mixtures using a plug flow column and rapid batch mixing.

In contrast, during batch mixing, all resin sorption sites are directly available for adsorption of any DOC. This leads to competition between molecules of different hydrophobicities for the same adsorption sites (Figure 75). As a result, the adsorption capacity of the resin for a TPH molecule is lower in natural waters than for the same TPH molecule as a model compound solution. This was identified by Matsui et al. (2003) who showed that in the removal of synthetic organics from natural waters onto activated carbon, the synthetic organics and NOM competed directly for the same adsorption sites.

8.1.ii. An increased surface area for adsorption

In batch mixed systems, the time to reach adsorption equilbria is controlled by adsorbent surface area (Faust and Aly, 1998). For all resins, increasing the resin concentration from 15mL/L to 250mL/L increased the adsorption rate (4 fold, 8 fold and 30 fold for DAX-8, XAD-7HP and XAD-4 respectively). A similar phenomenon was seen when MIEX dose was increased by Singer (2002), causing an increased rate of removal and increased total removal of UV_{254}. At 250mL/L, adsorption equlibria were achieved in under 6 minutes for all model compounds onto each resin, and this resin concentration was therefore used in all subsequent test termed rapid

fractionation. However, an increased resin surface area also caused an increased sorption of the model compound of intermediate hydrophobicity, to all resins.

8.1.iii. Choice of adsorbent

The adsorption capacities, of the three macroporous resins commonly used in XAD fractionation were compared for the HPO model compound, tannic acid, to identify which resin was the most appropriate adsorbent of HPO NOM. All three resins showed a best fit with the Freundlich model of adsorption (r^2= 0.94, 0.84 and 0.69 for DAX-8, XAD-7HP and XAD-4 respectively) suggesting each resin was able to exceed monolayer adsorption. This was in agreement with the literature where a Freundlich model of adsorption was also identified for the removal of tannic acid onto XAD-7 (Wang et al., 2010). The ability of XAD resins to exceed monolayer adsorption was identified by Gusler (1993) for the adsorption of phenol onto both XAD-8 and XAD-12.

The Freundlich models created in this study identified the adsorption capacities for tannic acid of the order XAD-7HP>DAX-8>XAD-4. As a result XAD-7HP was identified to have the highest affinity for HPO compounds. This agreed with the result from the rapid fractionation of model compounds onto each resin, as after 6 minutes XAD-7HP identified a higher HPO fraction for tannic acid than the other two resins. XAD-7HP was the most successful resin at adsorbing the HPO fraction and it is therefore chosen as the HPO adsorbent for rapid fractionation. In method development stages XAD-4 showed a higher preference for the model compound of intermediate polarity than XAD-7HP or DAX-8.

8.2. An increased HPO fraction

The use of XAD resins in column fractionation is primarily as an organics characterisation tool (Leenheer and Huffman, 1976). Each organic compound has a different affinity for adsorption to a resin column, given by the column capacity factor k′. Log k′ (using XAD-8) was shown by Thurman et al. (1978) to be inversely related to the (Log) solubility of compounds (r^2=0.9), with a lower k′ indicating increased hydrophilicity. For example butanol (k′=25) is more hydrophilic than tolulene (k′=1406) (Thurman et al., 1978).

The XAD column fractionation procedure can be altered to isolate solutions of different k' (Kitis et al, 2002). In previous research, Croué et al., (1999) decreased the k´ of a column of XAD-4 to 5 to split the traditional HPI fraction, and produce an ultra HPI fraction. An increase of k´ from 50 to 100 showed by Labanowski and Feuillad (2010) to increase the humic like matter (generally found in the HPO fraction) contained within the HPI fraction. The k′ is inversely proportional to the resin void volume (Leenheer, 1981), which means that by increasing the amount of resin, organics of a lower k′ will adsorb to the resin. Therefore, by increasing the resin concentration to 250mL/L, the relative hydrophobicity of each model compound solution has also been increased. This was the reason why a greater HPO fraction was produced for the model compound of intermediate hydrophobicity.

The 15mL/L resin concentration used in traditional column fractionations of natural waters gives k′ = 50 (Leenheer, 1981), which means molecules with k′=50 will be 50% retained to the resin (Labanowski and Feuillad, 2010). At this k′ value over 95% of humic substances are retained to a XAD-8 column (Malcolm 1989). However, variations in the type and concentration of organics within natural water alter the material contained within the HPO fraction (Chow et al., 2005). For example, the proportion of the HPI fraction was increased by increasing the solution concentration from 0-40mgC/L (Gadmar et al., 2005), whilst the same material contained in the HPI fraction for a humic rich water, was found in the HPO fraction for a water of low hydrophobicity (Chow et al., 2005). When studies of natural waters report a k′=50, (Imai et al., 2001; Wei et al., 2008) this is in reference to a hypothetical solution, not the natural water being fractionated. Therefore, the fractions produced for different natural water samples are unlikely to include the same range of NOM molecules

In rapid fractionation, the increased competition for adsorption sites caused by the batch mixing resin was likely to result in a reduced removal of TPH species for non model compound solutions. Estimates of k′ using column fractionation formula are therefore likely to overestimate the DOC removal that actually occurs during rapid fractionation. However, for the three model compounds, a resin concentration of 15mL/L was shown to produce similar fractions for both column fractionations and parallel batch mixed fractionations. This suggests that k′ for the rapid batch

fractionation can be used as an indication of its fractionation of model compounds. Using the equation:

$V_{0.5r}=2V_0(1 + k'_{0.5r})$ **Eq. 16**
$V_{0.5r}$ = the effluent volume of 50% retention and 50% retention
V_0= Void volume **Leenheer (1981)**

k' = 2 (for rapid fractionation)

This was lower than the k′=50 in column fractionation and suggests an increased HPO removal using the rapid fractionation tool. Whilst in this research the rapid fractionation tool was compared with traditional fractionation, the key goal was to design a tool capable of identifying the fractions of NOM that will be removed using coagulation. The k′=50 used in column fractionations is related to the classification of humic material, not the identification of removal of organic compounds in a WTWs. Sharp et al. (2006b) identified a strong relationship (r^2=0.91) between residual NOM and the effluent from a column of XAD-7HP followed by XAD-4 using column fractionation at k′=50. This identifies that k′=50 for XAD-4 is suitable for predicting treatment potential, but that a lower value of k′ than 50 would be required for XAD-7HP if it was used in isolation to predict treatment potential. Therefore the rapid tool, using XAD-7HP has the potential to increase the HPO fraction from the traditional fractionation, making the effluent more similar to residual NOM at the WTWs.

8.3. The rapid fractionation of natural waters

The increased resin concentration and lower k´ used in rapid fractionation increased the amount of DOC able to adsorb to the resin during model compound investigation. However, when this investigation was extended to the fractionation of natural waters, the reverse was seen, with a lower % HPO fraction recovered using the rapid fractionation tool than in column fractionation. There were three main method alterations between these investigations. Firstly, the change from a model compound solution to a complex NOM solution is likely to have resulted in the competitive adsorption for the natural waters previously described in section 8.1.i. Secondly, whilst Soxhlet cleaned resin was used in all model compound investigations the resin was reused without Soxhlet cleaning during investigations of natural waters. Finally, a mass analysis technique was used to assess the HPO and TPH fractions of all rapid fractionations and the column fractionations with model compound. However, in

column fractionations of natural waters, these fractions were analysed using a back elution process. In the following sections, these variations in procedures are used to explain the lower % HPO fraction recorded for natural waters analysed using rapid fractionation.

8.3.i. DOC leaching from the resin

Even with thorough Soxhlet cleaning of XAD resins, followed by rinsing with ultra pure water, it was difficult to achieve (and analyse for due to the TOC5000A limit of dectection) a resin run off below the 0.5mgC/L used in model compound investigation during this research. As a result there was the potential for DOC to be leached from the resin during experiments. In investigations with tannic acid, the relationship between DOC and UV_{254} (for a control solution without resin contact) was utilised to prove leaching from the resin occurred with increased resin contact time. After 72 hours of batch mixing, tannic acid with 0.5-10mL/L of all three macroporous resin the relationship between DOC and UV_{254} was significantly different ($p=0.05$) from the control. Up to 9mgC/L DOC was also recorded for acidified ultra pure water after 72 hours of mixing with 10mL/L resin. In rapid fractionation with model compounds, the same % removal would be expected for both DOC and UV_{254}, but the % UV_{254} removal from the solution was approximately 20% higher than DOC removal. Resin leaching was the likely cause of this lower DOC removal.

Analysis of how different experimental procedures in published work approach resin cleaning highlights some key differences in procedures. For example, Goslan et al. (2002) required resin run off to be <2mgC/L for the fractionations of natural waters, and this level of cleaning was used in natural water investigations for this study. As a result there was more DOC potentially available for leaching from the resin in the natural water fractionations, than in model compound investigations. Evidence of leaching during natural water fractionations was observed for the rapid batch mixing fractionations. A reduction in DOC removal after 10 minutes of mixing occurred for nine Butterley water samples. This caused the DOC in the solution to rise to beyond the raw water's initial DOC concentration in one sample. In contrast, UV_{254} removal, which is a measure of aromatic NOM, maintained an 85%+ reduction in all samples. This indicated aromatic DOC had been adsorbed and retained by the resin, and

suggests the increasing solution DOC concentration after 10 minutes of mixing to be the result of DOC leaching from the resin.

Leaching during natural water fractionation was not quantified. However, the 6 minutes contact time in single sample rapid fractionation was similar to the resin contact time for both column fractionations and initial resin cleaning, which produced <2mgC/L run off before use. As resin leaching was related to contact time in the investigations with model compounds, a maximum leaching of 2mgC/L was estimated for single sample rapid fractionations. DOC leaching from the resin is therefore identified as the major limitation to the rapid fractionation procedure used throughout this investigation. In future identification of DOC removal using mass analysis, only very clean resin (to a run off of below 0.5mgC/L) should be used in fractionation procedures.

8.3.ii. Back elution vs mass analysis

During fractionations with mass analysis, the difference between the column influent and effluent DOC concentration was used to estimate the sorbed fraction. Therefore any leaching would cause an underestimation of the HPO and TPH model compounds, and over estimate the HPI fraction. In column fractionation with back elution, the HPO and TPH fractions are concentrated onto the resin and then desorbed by increasing the pH. The concentrated nature of the sorbed DOC means resin leaching has a lower impact on the desorbed DOC concentration than in mass analysis. However, any leaching from the resin would increase the DOC concentration of the desorbed fraction resulting in an overestimation of the HPO, TPH and HPI fractions. This overestimation was identified in section 6.1.i. by comparing the recovered DOC with the raw water DOC. As the HPO neutral fraction cannot be removed from resin using the back elution procedure (Leenheer, 1981), DOC recoveries of below 100% were expected. However, DOC recoveries of over 100% are common in studies found in the literature. Bond (2009) accepted fractionation with recoveries between 85-115% and Kitis et al. (2002) reports recoveries of up to 109%. In this research the average DOC recovery for Butterley samples was 108%. It is hypothesised that resin leaching therefore caused this overestimated DOC. Leaching would have a greater effect on fractions of lower DOC concentrations (generally the TPH fraction).

Resin leaching can therefore lead to a higher % HPO and TPH fraction for back elutions than for mass analysis. Soh et al. (2008) investigated the difference between the fractions created using these methods. However, whilst a slightly higher total DOC recovery was obtained for the back elution procedure, there was no significant variation in the HPO and TPH DOC recovery.

As Bond (2009) used column fractionation with back elution on the same model compounds that were fractionated using mass analysis during this research, these results can also be compared to evaluate this hypothesis. There was strong comparability in the adsorption results for the HPO compound, tannic acid, using both procedures. However, Bond (2009) reported a higher TPH fraction of 1,3 acetonedicarboxylic acid (26% higher) and d-xylose (6%) compared to the mass analysis technique. This provides some evidence that leaching causes a difference in the fraction created using these two procedures. However, the model compound concentrations used by Bond, (2009) were 50% of those used in this study, which was likely to have contributed to this fraction variation.

As resin leaching could be as high as 2mgC/L, with an average DOC concentration of 10mgC/L for the Butterley water samples, the HPO and TPH fractions could have been underestimated by an average of 20% for rapid fractionation, and overestimated for the column fractionation. Therefore, the differences seen between the HPO fractions created using these two methods were not significant, due to resin leaching. If resin leaching could be quantified, and a significant difference was still seen between column and rapid fractionation, this would be likely to be the result of competitive adsorption in the rapid batch fractionation, showing a true difference between the procedures.

8.4. Recommendations for rapid fractionation

The value of rapid fractionation can be enhanced by consideration of the adsorbent used, resin quantity, leaching potential and it's fitness for purpose:

- *Choice of adsorbent:* XAD-7HP was chosen as the HPO adsorbent due to its higher adsorption capacity of tannic acid. The effluent of XAD-7HP was then fractionation using XAD-4 to produce the TPH fraction.

- *Resin Concentration:* A concentration of 250mL/L successfully fractionates NOM in 6 minutes and is therefore recommended for rapid fractionation.
- *Leaching minimisation:* Resin leaching is seen as the major limitation to rapid fractionation, and only Soxhlet cleaned resin should be used for fractionations. Based on the TOC5000A's limit of detection, Soxhlet cleaned resin should be rinsed with ultra pure water until a run off of <0.5mgC/L is achieved. Prior to rapid fractionation, a sample of acidified ultra pure water should be mixed with the resin and analysed for TOC. This blank sample could be deducted from the effluent in the mass analysis of the HPO and TPH fractions, to determine their true values.
- *Jar testing:* A real comparison of the fractions created using rapid fractionation and the NOM removal potential of coagulation WTWs is still required and this gap could be filled by the jar testing of natural waters in parallel to their fractionation. This may reveal further adaption of the rapid fractionation tool, such as a altered resin concentration, to enhance it's usefulness.

Conclusions

This study has identified the value of NOM fractionation using XAD adsorption resins based on its successful application to NOM characterisation, catchment monitoring and adsorption investigations over the last four decades. However, part of the success is due to the procedures versatility, which allows it to be modified to suit the research purpose. This research identified the need for a rapid fractionation procedure to enable WTWs optimisation based on raw water NOM characteristics. The performance of high concentrations of batch mixed XAD resins was investigated using model compounds and natural waters. The fractions, which were produced in 6 minutes, were compared against those produced by traditional column fractionation. The fractionation tool developed is practical for onsite measurements being portable, easy to use, inexpensive and rapid. This resulted in the following conclusions regarding the use of XAD resins in rapid fractionation:

- Resin concentration was identified in initial method development investigations to control the rate of DOC removal. This was confirmed by the production of adsorption isotherms and following analysis of the kinetics of adsorption. As resin concentration increased, the rate of DOC removal increased due to a higher resin surface area reducing the competition for adsorption sites. An increased resin concentration (from 15mL/L to 250mL/L) was used to considerably reduce the time to reach NOM removal equilibrium to 6 minutes thereby achieving a rapid fractionation batch mixing procedure.
- Both rapid and column fractionation produced similar fractions for HPO and HPI model compounds which meant that an increased resin concentration had not altered the % of NOM removed at equilibrium, just the time to reach this equilibrium. However, a higher proportion of the TPH model compound was found in the HPO fraction for rapid fractionations with all resins. As a species of intermediate hydrophobicity, its level of adsorption was more sensitive to alterations in the competition for adsorption sites and therefore increased with the surface area available for adsorption in rapid fractionation.
- A lower proportion of NOM was removed from natural water solutions as the HPO fraction in rapid fractionations compared to column fractionations. The

reason for this is a combination of: competitive adsorption in batch mixed procedures such as rapid fractionation; DOC leaching from the resin.

- Analysis of the relationship between UV_{254} and DOC for resins mixed with model compounds and acidified ultra pure water confirmed DOC leaching occurred for all resins.
- Resin leaching causes the HPO and TPH fractions to be under estimated using mass analysis.
- Adsorption of the HPO model compound to XAD resins follows a Freundlich model, with the adsorption capacities of the resins in the order XAD-7HP>DAX-8>XAD-4. XAD-7HP was therefore identified as the preferable HPO adsorbent for rapid fractionations.
- The main contribution to errors in rapid fractionation was suggested to be DOC leaching from the resin. The main action required to quantify or remove this error is to complete blank fractionations with ultrapure water prior to each fractionation, and subtract this leached DOC from the tools effluent DOC concentration.
- As raw materials for rapid fractionation are inexpensive, the key economical consideration for rapid fractionation is in the preparation of the resin. An eight day period (not requiring permanent monitoring) is required to Soxhlet clean 1L resin (which provides resin for 25 rapid fractionations). If it were possible to reuse resin without full Soxhlet cleaning (as was completed for natural waters in this study), whilst maintaining a minimal impact from resin leaching, costs for rapid fractionation (estimated at £50-£100/fractionation) would be reduced.

Further work

Before the rapid fractionation tool can be used out in the catchment, as a substitute to traditional column fractionation further investigations of its adsorption behaviour are required. These can be summarised as:

- A comparison of the fractions produced using column fractionation with back elution and the single sample rapid fractionation with mass analysis when resin is Soxhlet cleaned and rinsed to a maximum of 0.5mgC/L. The use of a blank rapid fractionation prior to the sample fractionation should correct for any other resin leaching.
- Compare the adsorption of a greater variety of model compounds for column and rapid fractionation to determine if the increased adsorption of TPH material when using rapid fractionation is uniform.
- Analyse the fractions created for model compound mixture for both column and rapid fractionations, as an intermediate step between model compound and natural water analysis.
- Assess the impact of varying the solution DOC concentration, and pH, on the rapid fractionation tool.
- Trial a greater variety of resin concentration to provide a fractionation that both maximised its ability to predict WTWs treatability and maintain the speed of fractionation.
- Reproduce Freundlich isotherms for changing solution concentration. Using higher solution concentrations should reduce the error caused by resin leaching, and the time to reach equilibrium.
- During this report, the use of a NPOC techniques for NOM analysis was used. An alternative analytical technique (TC-IC) should be trialled to see if DOC leached from the resin is included as the IC component of this analysis. If so, the effect of leaching could be removed without the need for blank fractionations.
- Jar testing is required to assess the ability of rapid fractionation to predict the limits of NOM removal for coagulation techniques.

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Appendix I: TOC limits of detections

Limit of detections and errors associated with the TOC5000A, when using 10 repetitions of each standard solution to create calibrations lines. For this standard solution the NPOC analytical method has a lower limit of detection and was therefore used in the study of model compound solutions.

Table 1: Assessing the error and limit of detection for the TOC5000A.

	TOC (0-10)	NPOC (0-10)	TOC (0-1) (exp)	TOC (0-1) linear	NPOC (0-1)
Intercept	1562.9	1044.7	1333.7	990.42	1377.3
R2	0.9998	0.9997	0.9595	0.8746	0.9995
Limit of Detection (mg/l)	0.4703	0.15	0.289	0.244571	0.0678
Maximum %CV	4.324	9.826*	14.18		4.789
Greatest % Bias**	1.158	-1.458	29.894		2.372

*An outlier (at the 95% level) has been included in this data
** Could not be produced for blanks

Appendix II: Rapid batch fractionation of Butterley Reservoir

The rapid batch fractionation results for each Butterley Reservoir sample (except 03/12/09 which is included in section 6.1.ii.) are presented here:

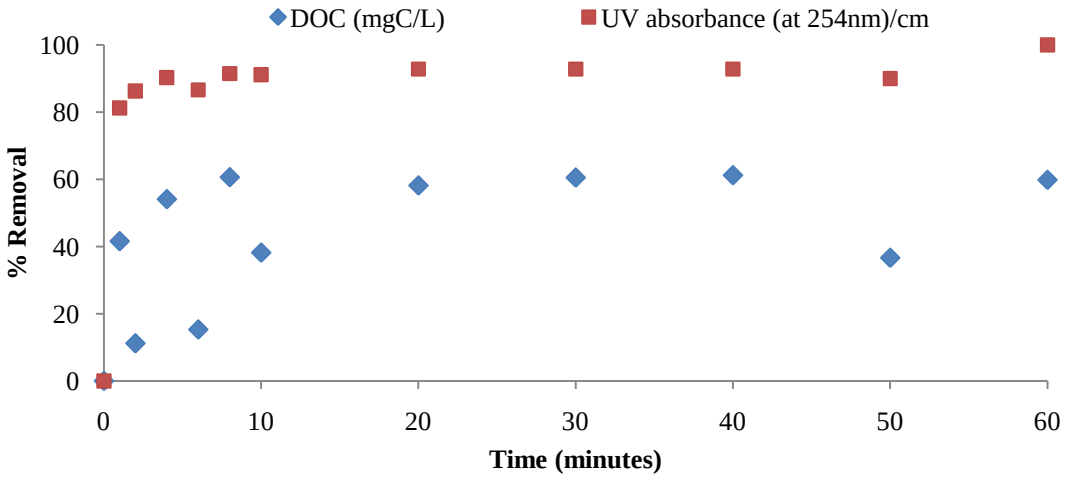

Figure 1: % DOC and UV_{254} removal for 160mL Butterley (08/10/09) mixed with 40mL XAD-7HP resin.

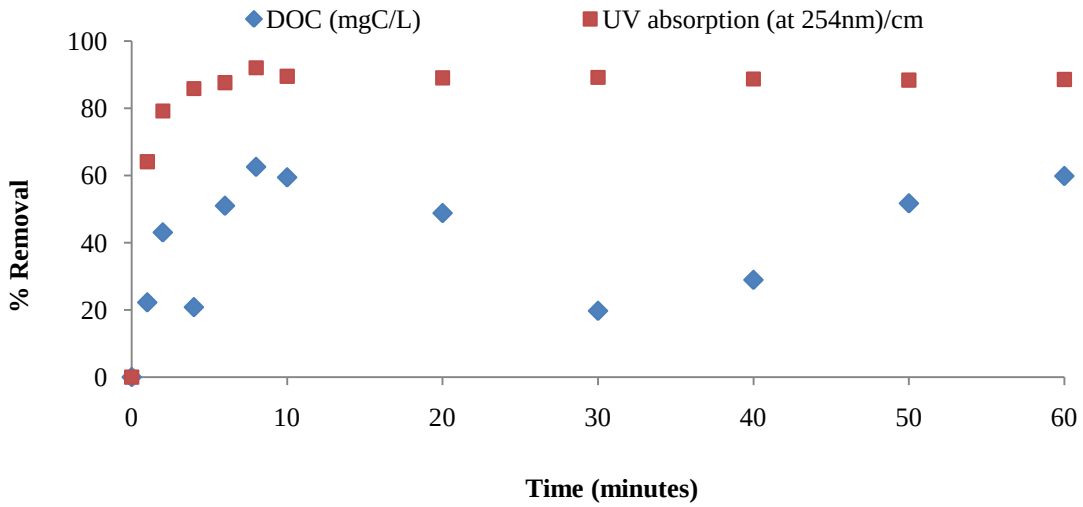

Figure 2: % DOC and UV_{254} removal for 160mL Butterley (22/10/09) mixed with 40mL XAD-7HP resin.

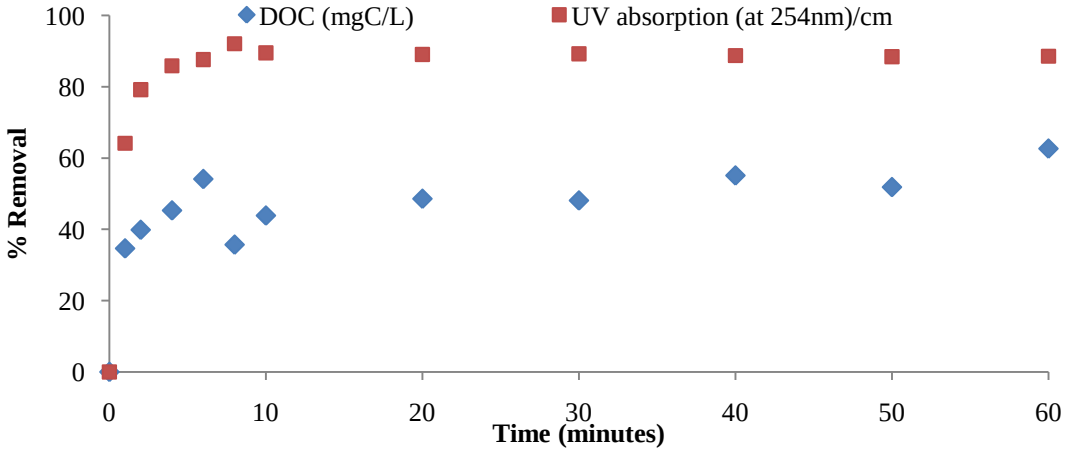

Figure 3: % DOC and UV_{254} removal for 160mL Butterley (05/11/09) mixed with 40mL XAD-7HP resin.

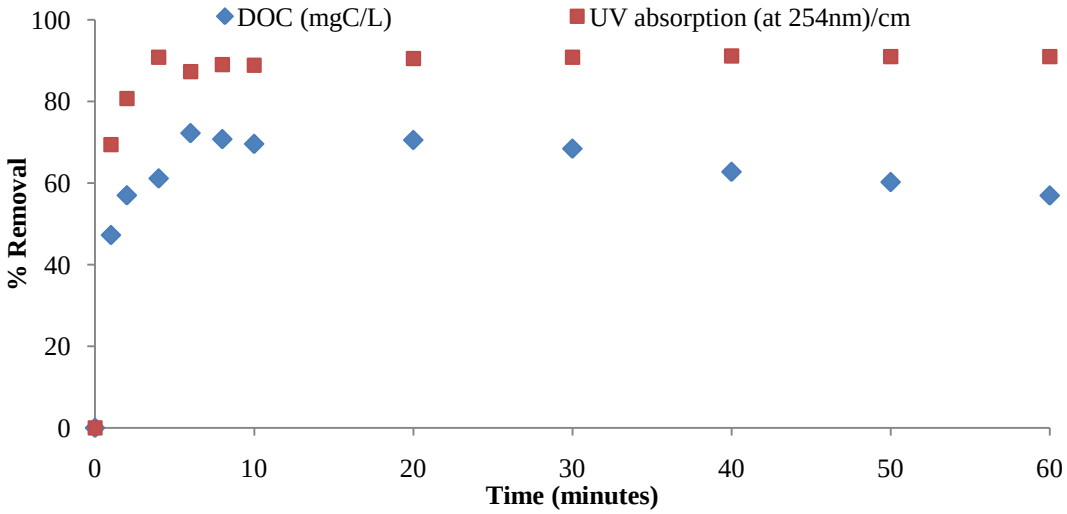

Figure 4: % DOC and UV_{254} removal for 160mL Butterley (20/11/09) mixed with 40mL XAD-7HP resin.

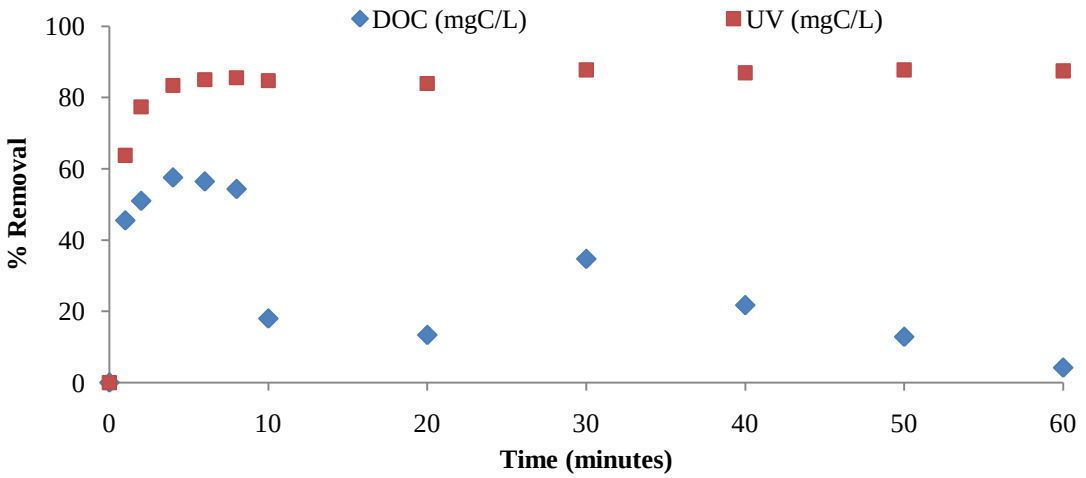

Figure 5: % DOC and UV_{254} removal for 160mL Butterley (04/02/10) mixed with 40mL XAD-7HP resin.

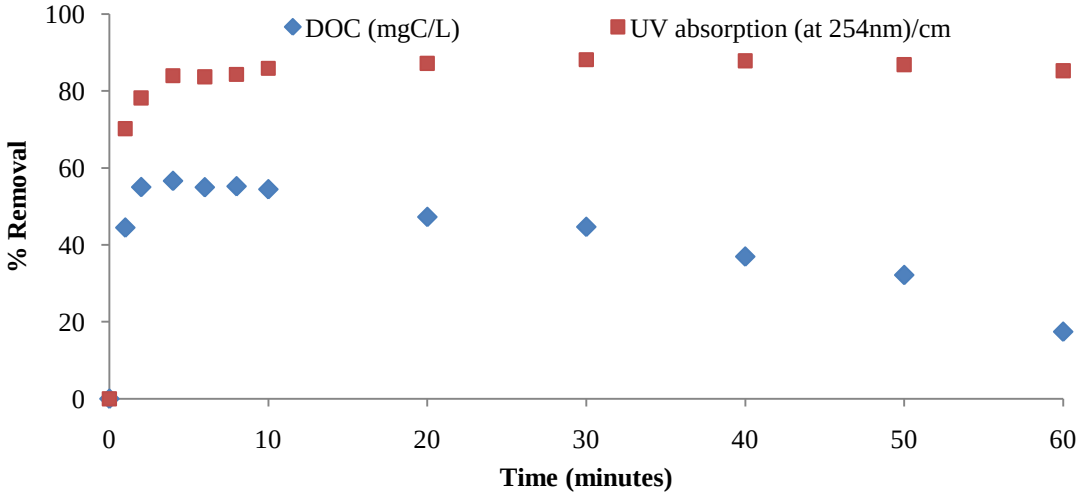

Figure 6: % DOC and UV_{254} removal for 160mL Butterley (24/02/10) mixed with 40mL XAD-7HP resin.

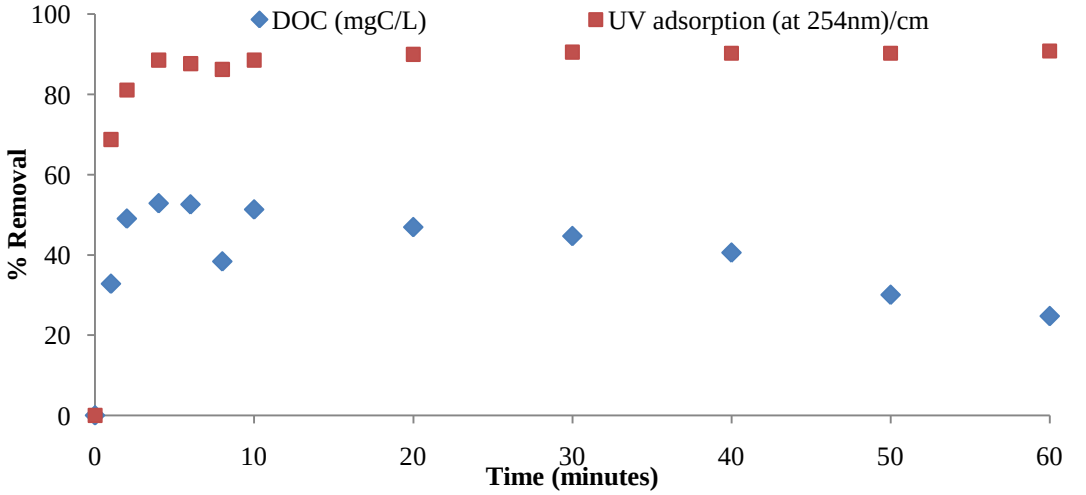

Figure 7: % DOC and UV_{254} removal for 160mL Butterley (03/03/10) mixed with 40mL XAD-7HP resin.

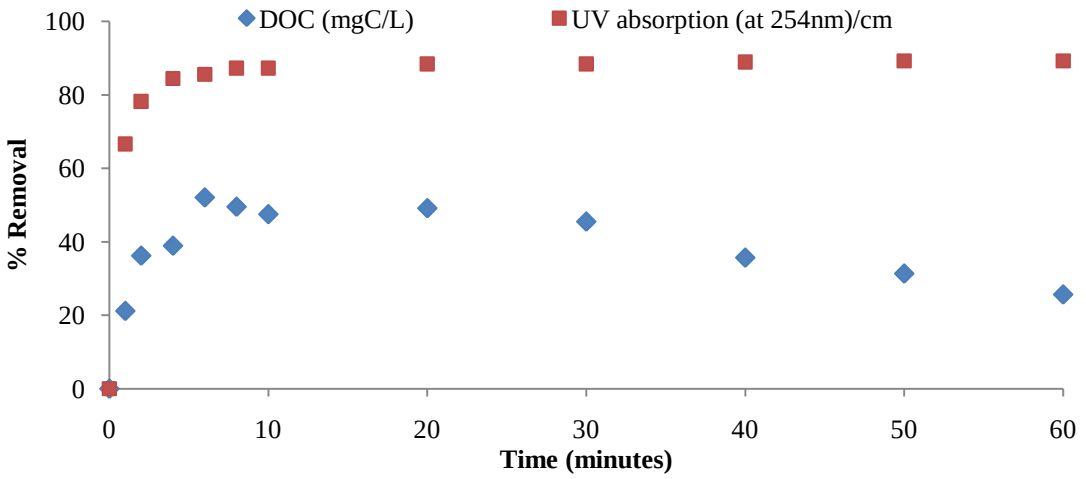

Figure 8: % DOC and UV_{254} removal for 160mL Butterley (23/03/10) mixed with 40mL XAD-7HP resin.

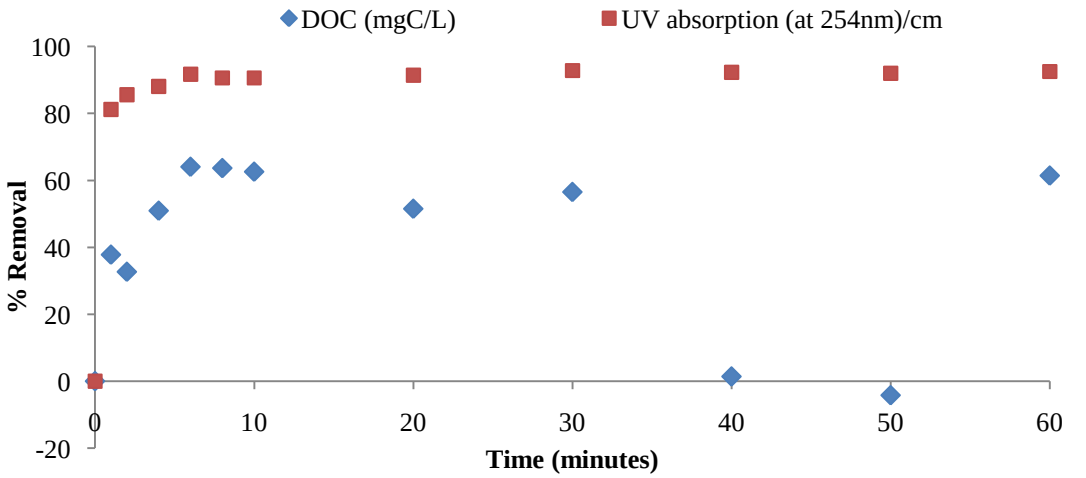

Figure 9: % DOC and UV_{254} removal for 160mL Butterley (12/04/10) mixed with 40mL XAD-7HP resin.

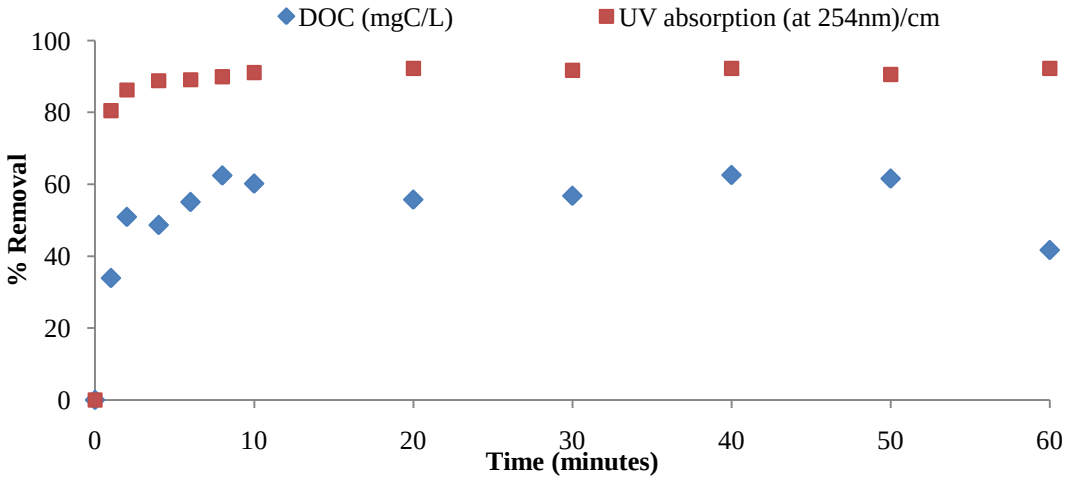

Figure 10: % DOC and UV_{254} removal for 160mL Butterley (23/04/10) mixed with 40mL XAD-7HP resin.

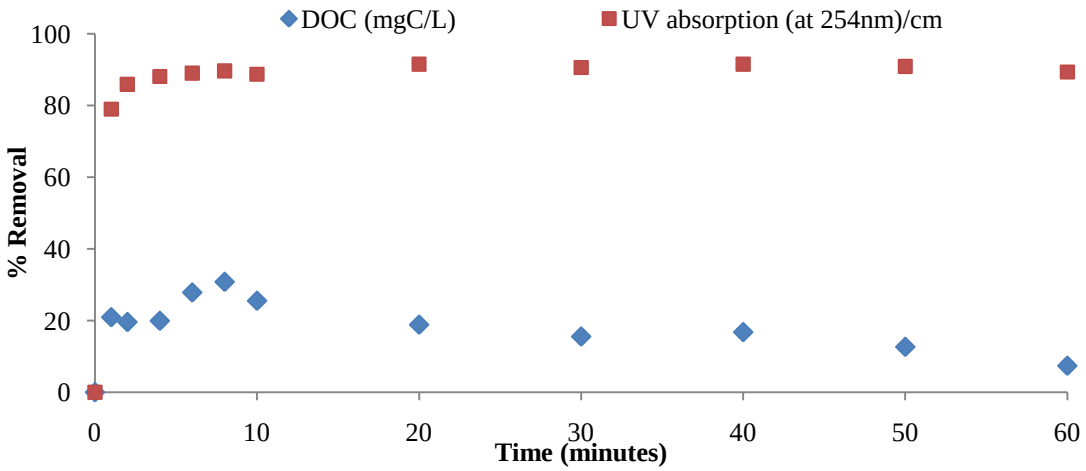

Figure 11: % DOC and UV_{254} removal for 160mL Butterley (21/05/10) mixed with 40mL XAD-7HP resin.

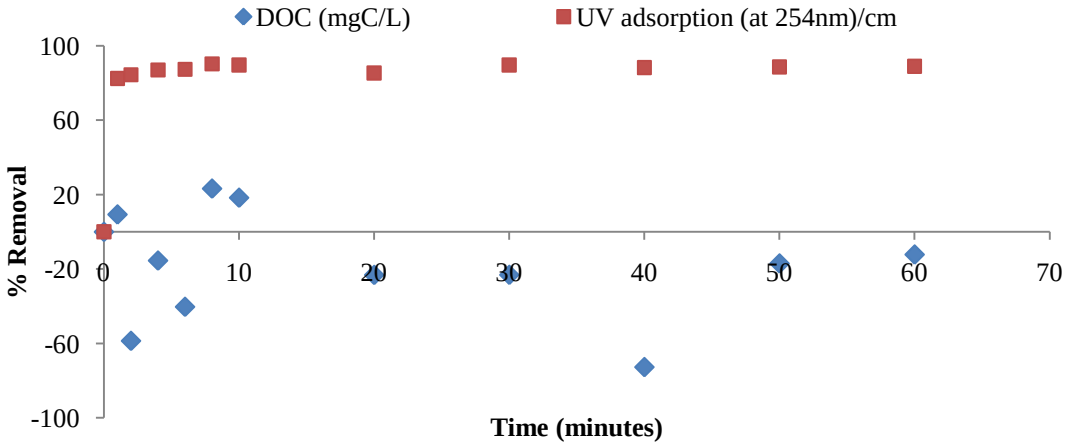

Figure 12: % DOC and UV_{254} removal for 160mL Butterley (31/05/10) mixed with 40mL XAD-7HP resin.

Appendix III: Rapid batch fractionation of Raw Oswestry water.

Oswestry WTW raw water was also analysed using the rapid batch fractionation procedure (Figure 54). A reduction in UV_{254} of 85-90% was observed for all samples taken after 4 minutes, which suggested a high removal of aromatic NOM was maintained throughout the 60 minute mixing time. 24% DOC removal occurred after 6 minutes of mixing but this DOC removal was not maintained. For all samples taken after 20 minutes of mixing, there was a higher DOC solution concentration than was observed in the initial raw water. These results were similar to those seen for Butterley Reservoir sample (31/05/2010), which also gave a negative DOC removal

after 20 minutes and was further evidence of solution DOC contamination after prolonged mixing with macroporous resin (discussed further in section 7.2.).

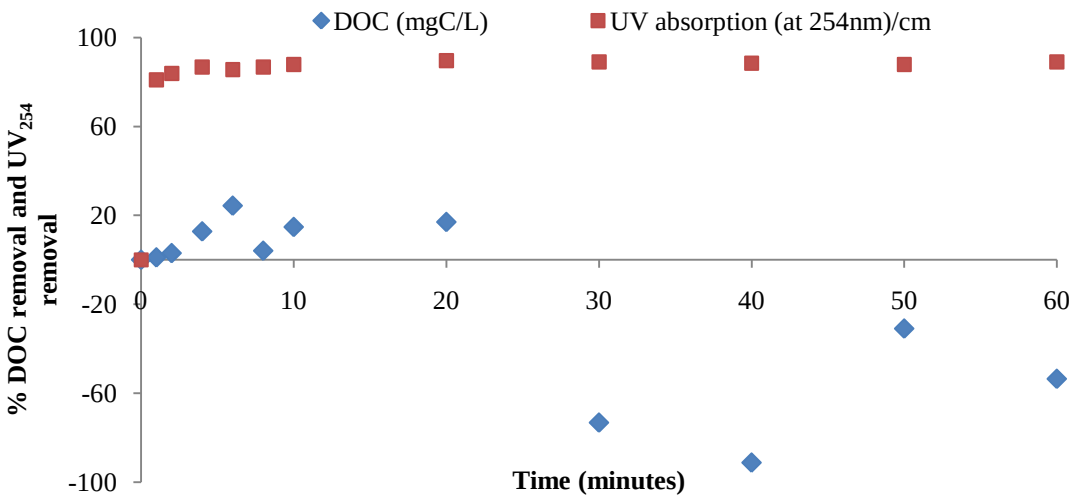

Figure 1: The % DOC removal and UV_{254} reduction of Oswestry raw water (12/05/10) using the rapid batch fractionation procedure.

Appendix IV: The time each resin reached DOC maximum

In the construction of adsorption isotherms for each resin, maximum DOC removal was used. Table 1 gives time each sample was taken and the weight of resin.

Table 1: The resin weight and mixing time used in the creation of adsorption isotherms.

	0.5mL/L	2mL/L	4mL/L	6mL/L	8mL/L	10mL/L
			DAX-8			
Wet resin weight (g)/L solution	0.53	2.12	4.24	6.36	8.48	10.61
Time of maximum concentration	1800	1800	360	360	180	180
			XAD-7HP			
Wet resin weight (g)/L solution	0.53	2.10	4.21	6.31	8.41	10.51
Time of maximum concentration	1440	1440	1440	360	360	180
			XAD-4			
Wet resin weight (g)/L solution	0.51	2.03	4.07	6.10	8.13	10.17
Time of maximum concentration	2880	2880	1440	360	360	360