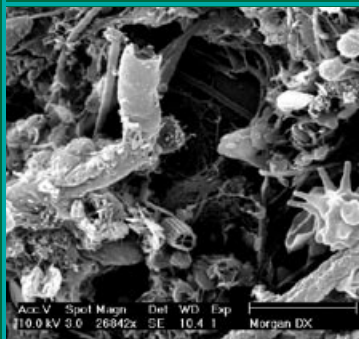
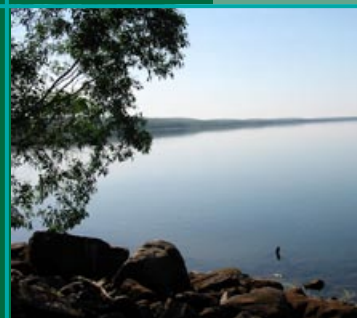




Optimisation of Adsorption Processes



Research Report

16

Optimisation of Adsorption Processes

Gayle Newcombe, Chris Hepplewhite, Mick Bjelopavlic and David Cook

Research Report No 16

OPTIMISATION OF ADSORPTION PROCESSES

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FOREWORD

The work described in this report was undertaken at the **Australian Water Quality Centre** as part of the CRC project 3.2.2 Optimisation of Adsorption Processes. The researchers involved at this node were:

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EXECUTIVE SUMMARY

The adsorption of natural organic material (NOM) and a range of algal metabolites (MIB, geosmin, saxitoxins) onto activated carbon was studied. The main finding was that the major influence on the adsorption of a range of compounds is firstly the pore volume distribution of the carbons. The surface chemistry of the carbons, for example surface charge and surface functional groups also has an important role to play. However, the net effect, or the macroscopic major influence, was always the size of the carbon pores. This is in fact not too surprising as for these contaminants to adsorb, they must have the adsorption sites within the carbon (i.e. the pores) in which to adsorb. Given equivalent pore sizes in different carbons, the surface chemistry influence can be seen.

The importance of pore size is also clear in the kinetics of adsorption of these contaminants. In the application of both powdered and granular activated carbon there is a limited time in which the removal can occur. The most effective activated carbon should have both pores of the appropriate size for the contaminant (i.e. slightly larger than the contaminant molecular size) and larger pores to allow easy access to the adsorption sites. This results in a carbon with a high adsorption capacity, and also a rapid adsorption.

Natural organic material has a dramatic effect on the adsorption of other contaminants. The adsorption of the odour compound MIB in the presence of different types of NOM was studied in detail. It was found that the large decrease in the adsorption of the target compound MIB in the presence of NOM was mainly due to the low molecular weight compounds which competed directly for the adsorption sites for MIB. The very dramatic effect of the NOM was due to the much higher concentration of these compounds compared with the MIB (this can also be expected to apply to other micro contaminants). The effect of NOM was found to vary slightly between carbons, but once again the factor of major importance was found to be the most favourable distribution of pore sizes within the carbon for the contaminant of interest.

On a practical level it was found that:

- Carbons with a large volume of very small pores, and some pores in larger size ranges were the best for the removal of MIB, geosmin, and saxitoxins. These carbons also showed good kinetics, and reduced competitive effects with NOM
- If possible powdered activated carbon should not be applied at the same time as other water treatment chemicals such as alum and chlorine as these may interfere with the adsorption process
- As the lower molecular weight NOM compounds are those that provide the greatest effect in terms of adsorption competition with low molecular weight contaminants such as MIB, geosmin and saxitoxins, there may be no real advantage to the addition of PAC after alum coagulation. Although alum can remove up to 60% of the NOM on a consistent basis, the majority of the NOM removed is in the higher molecular weight range, and the remaining low molecular weight compounds are more likely to interfere with activated carbon adsorption.

Work on this latter aspect is continuing.

TABLE OF CONTENTS

FOREWORD	3
EXECUTIVE SUMMARY.....	4
1. INTRODUCTION	11
2. ISOLATION AND CHARACTERISATION OF NOM USING A RANGE OF METHODS	13
2.1 Introduction.....	13
2.2 Comparison of Characteristics of Fractionated NOM from Two Reservoirs	13
2.2.1 Introduction	13
2.2.2 Methods	14
2.2.3 Results and discussion	14
2.2.4 Conclusions	17
2.3 Characterisation of NOM Ultrafiltration Fractions Isolated Using Three Techniques	17
2.3.1 Introduction	17
2.3.2 Materials and methods	18
2.3.3 Results and discussion	20
2.3.4 Summary and conclusions.....	24
2.4 NOM Character Changes During Biodegradation.....	25
2.4.1 Introduction	25
2.4.2 Materials and methods	26
2.4.3 Results and discussion	28
2.4.4 Summary and conclusions.....	38
2.5 Investigation of the Mechanisms Controlling Molecular Weight Analysis	39
2.5.1 Introduction	39
2.5.2 Materials and methods	43
2.5.4 Results and discussion	43
2.5.5 Summary and conclusions.....	68
2.6 References	69
3. MECHANISMS OF ADSORPTION OF NOM ONTO ACTIVATED CARBON.....	73
3.1 Introduction.....	73
3.2 Adsorption of NOM onto Activated Carbon: Effect of Surface Charge, Ionic Strength and Pore Volume Distribution.....	73
3.2.1 Introduction	73
3.2.2 Materials and methods	75
3.2.3 Results and discussion	77
3.2.4 Summary and conclusions.....	87
3.3 References	88
4. THE INFLUENCE OF WELL-CHARACTERISED NOM ON THE ADSORPTION OF MIB ONTO ACTIVATED CARBON.....	89
4.1 Introduction.....	89
4.2 Simultaneous Adsorption of MIB and NOM onto Activated Carbon: I Characterisation of the System and NOM Adsorption	89
4.2.1 Introduction	89
4.2.2 Materials and methods	90
4.2.3 Results and discussion	92
4.2.4 Summary and conclusions.....	101
4.3 Simultaneous Adsorption of MIB and NOM onto Activated Carbon: II Competitive Effects	102
4.3.1 Introduction	102
4.3.2 Materials and methods	103
4.3.3 Results and discussion	103
4.3.4 Conclusions	113
4.4 PAC Removal of T&O Compounds: Why Does NOM Compete so Effectively?.....	114
4.4.1 Introduction	114
4.4.2 Materials and methods	115

OPTIMISATION OF ADSORPTION PROCESSES

4.4.3 Results and discussion	118
4.4.4 Summary and conclusions.....	126
4.5 References	126
5. OPTIMISATION OF THE APPLICATION OF ACTIVATED CARBON FOR TREATMENT OF A RANGE OF ALGAL METABOLITES.....	130
5.1 Introduction.....	130
5.2 A Guide to Success with Earthy-Musty Taste and Odour Removal Using PAC.....	130
5.2.1 Introduction	130
5.2.2 Materials and methods	131
5.2.3 Results and discussion	131
5.2.4 Conclusions	135
5.3 Tastes and Odours and Algal Toxins, Which PAC is Best?.....	136
5.3.1 Introduction	136
5.3.2 Materials and methods	137
5.3.3 Results and discussion	138
5.3.4 Summary and conclusions.....	141
5.4 Influences on the Removal of Tastes and Odours by PAC.....	141
5.4.1 Introduction	141
5.4.2 Materials and methods	142
5.4.3 Results and discussion	143
5.4.4 Conclusions and recommendations	153
5.5 Removing tastes and odours using activated carbon: Is your cheap PAC costing you too much?	154
5.5.1 Introduction	154
5.5.2 Choosing the right PAC and the correct doses	155
5.5.3 When will we need to change our PAC doses?.....	159
5.5.4 Conclusions	159
5.6 References	161
6. THE INFLUENCE OF NOM CHARACTER ON OTHER WATER TREATMENT PROCESSES ..	163
6.1 Introduction.....	163
6.2 Size IS Important, or The Effect of Molecular Weight Distribution of NOM on Water Treatment Processes	163
6.2.1 Introduction	163
6.2.2 Materials and methods	164
6.2.3 Results and discussion	165
6.2.4 Conclusions	170
6.3 References	171
7. SUMMARY AND CONCLUSIONS.....	172
7.1 Isolation and Characterisation of Natural Organic Material	172
7.2 Mechanisms of Adsorption of NOM onto Activated Carbon.....	173
7.3 The Influence of Well-Characterised NOM on the Adsorption of MIB onto Activated Carbon.....	173
7.4 Optimisation of the Application of Activated Carbon for the Treatment of a Range of Algal Metabolites.....	174
7.5 The Influence of NOM Character on other Water Treatment Processes.....	175
8. APPENDIX A List of publications from project 3.2.2 (AWQC only)	176
9. APPENDIX B Extended abstracts submitted for conference proceedings.....	178
In the (Adsorption) Competition Between NOM and MIB, Who is the Winner and Why?.....	178
How to Win in the Battle Against Tastes and Toxins in Drinking Water Using Activated Carbon ..	180
Predicting PAC Doses for the Removal of Algal Metabolites: How Can NOM Characterisation Techniques Help Us?	182
NOM and MIB, Who Wins in the Competition for Activated Carbon Adsorption Sites?.....	185

LIST OF FIGURES

Figure 2.1 Percent carbon in each functional group(¹³ C NMR).....	16
Figure 2.2 Percent carbon in carboxyl groups.....	16
Figure 2.3 Size exclusion chromatograms for ultrafiltration fractions	17
Figure 2.4 Schematic of the process used to obtain the DAX 8 and XAD 4 isolates.....	18
Figure 2.5 Ultrafiltration of raw water	19
Figure 2.6 Desorption of NOM from DAX 8 or XAD 4 resins	19
Figure 2.7 UF fractionation of NOM	20
Figure 2.8 Percentage of carbon in each functional group for the 500-1,000 fractions	22
Figure 2.9 Percentage of carbon in each functional group for the >30000 fractions	23
Figure 2.10 Percentage of carbon present in each functional group for Hope Valley fractions.....	24
Figure 2.11 HPSE chromatograms of the X4 fractions	29
Figure 2.12 HPSE chromatograms of effluents from MIEX, DAX 8 and XAD 4 resins	30
Figure 2.13 Scanning electron micrographs of Morgan treatment plant filter sand	31
Figure 2.14 DOC concentration vs. time	32
Figure 2.15 Percent BDOC of each NOM fraction at 8 days (%BDOC ₈)	33
Figure 2.16 O alkyl :alkyl ratio vs. BDOC ₈	33
Figure 2.17 HPSE chromatograms of samples taken during the biodegradation of fraction D8F2	34
Figure 2.18 UV response (taken from HPSE chromatograms) at several molecular weights vs. degradation time, X4 and D8 fractions	35
Figure 2.19 Derivative of the UV response vs time curve for X4F5.....	36
Figure 2.20 Specific absorbance, at several wavelengths, of D8F5 as a function of degradation time.....	36
Figure 2.21 HPSEC response at 2 molecular weights vs. specific absorbance for four fractions	37
Figure 2.22 Conceptual model for the degradation of NOM as suggested by Confer and Logan (1997b).....	37
Figure 2.23 Representation of a HPSEC column.....	40
Figure 2.24 Representation of a flow field flow fractionation channel.....	40
Figure 2.25 Representation of ultrafiltration apparatus	41
Figure 2.26 HPSE chromatograms of standards under different solution conditions	44
Figure 2.27 HPSE chromatograms of Suwannee fulvic acid at pH 6.8 and 4.....	45
Figure 2.28 Molecular structures of model compounds	46
Figure 2.29 HPSE chromatograms of mellitic acid.....	47
Figure 2.30 HPSE chromatograms of pyromellitic acid.....	47
Figure 2.31 HPSE chromatograms of tetrahydrofuran, tetracarboxylic acid.....	48
Figure 2.32 HPSE chromatograms of 9,10-anthraquinone-2,6-disulphonic acid.....	48
Figure 2.33 HPSE chromatograms of dibenzoyl-l tartaric acid	49
Figure 2.34 HPSE chromatograms of glycyrrhic acid	49
Figure 2.35 HPSE chromatograms of XAD isolates.....	53
Figure 2.36 HPSE chromatograms of DAX 8 isolates.....	54
Figure 2.37 HPSE chromatograms of MIEX isolates	54
Figure 2.38 FIFF fractograms of DAX 8 fractions.....	55
Figure 2.39 FIFF fractograms of XAD 4 fractions.....	55
Figure 2.40 FIFF fractograms of MIEX fractions	56
Figure 2.41 HPSE chromatograms and FIFF fractograms of F1 fractions.....	57
Figure 2.42 HPSE chromatograms and FIFF fractograms of F2 fractions.....	57
Figure 2.43 HPSE chromatograms and FIFF fractograms of F5 fractions.....	58
Figure 2.44 Average molecular weights determined by HPSEC and FIFF.....	59
Figure 2.45 UF results, MIEX isolate, 30K membrane, 0.01 M and 0.20 M NaCl.....	60
Figure 2.46 UF results, MIEX isolate, 1K membrane, 0.01 M and 0.20 M NaCl.....	61
Figure 2.47 UF results, XAD 4 isolate, 30K membrane, 0.01 M and 0.20 M NaCl.....	61

OPTIMISATION OF ADSORPTION PROCESSES

Figure 2.48 UF results, XAD 4 isolate, 3K membrane, 0.01 M and 0.20 M NaCl	62
Figure 2.49 UF results, XAD 4 isolate, 1K membrane, 0.01 M and 0.20 M NaCl	62
Figure 2.50 UF results, MIEX isolate, 0.20 M NaCl, 30K and 1K membranes	63
Figure 2.51 UF results, MIEX isolate, 0.01 M NaCl, 30K and 1K membranes	63
Figure 2.52 UF results, XAD 4 isolate, 0.20 M NaCl, 30K and 3K membranes	64
Figure 2.53 UF results, XAD 4 isolate, 0.20 M NaCl, 30K and 1K membranes	64
Figure 2.54 UF results, XAD 4 isolate, 0.01 M NaCl, 30K and 3K membranes	65
Figure 2.55 UF results, XAD 4 isolate, 0.01 M NaCl, 30K and 1K membrane	65
Figure 2.56 HPSE chromatograms of solutions during ultrafiltration experiments, MIEX isolate, 0.1. M NaCl	67
Figure 2.57 HPSE chromatograms of solutions during ultrafiltration experiments, XAD 4 isolate, 0.1 M NaCl	67
Figure 3.1 Charge on 500-3,000 MW NOM ultrafiltration fraction versus pH in 0.01M NaCl	77
Figure 3.2 Surface charge of activated carbons	78
Figure 3.3 Surface Density (Γ) versus equilibrium concentration (C_{eq}) for 7 carbons at; (a) pH 7 and (b) pH 4 and 0.01M NaCl.	80
Figure 3.4 DOC concentration per unit pore volume (Γ_{vol}) versus equilibrium concentration (C_{eq}) for 7 carbons at; (a) pH 7 and (b) pH 4 and 0.01M NaCl	83
Figure 3.5 NOM adsorption onto SA30 at; (a) pH 4, (b) pH 7 and (c) pH 9 at two salt concentrations.	84
Figure 3.6 NOM adsorption onto PCO at; (a) pH 4, (b) pH 7 and (c) pH 9 at two salt concentrations	85
Figure 4.1 Pore size distributions of activated carbons	93
Figure 4.2 Surface charge vs. pH of activated carbons	93
Figure 4.3 DRIFT spectra of activated carbons	94
Figure 4.4 High performance size exclusion chromatograms of NOM solutions	95
Figure 4.5 ^{13}C NMR spectra of freeze dried NOM	97
Figure 4.6 DOC removed as a function of carbon dose	98
Figure 4.7 UV response of HPSEC vs. time. Activated carbon dose, 20 mg L ⁻¹	100
Figure 4.8 Relative rates of adsorption of UV absorbing compounds at 5 minutes for three carbons in raw and effluent Myponga water	101
Figure 4.9 Adsorption isotherms of MIB onto six activated carbons in the presence and absence of competing NOM	104
Figure 4.10 Relationship between surface concentration of MIB, taken from the isotherms at a solution concentration of 50 ng L ⁻¹ , and volume of pores of 1.0-1.2 nm width in F1 NOM	105
Figure 4.11 Adsorption of MIB as a function of contact time in F1 NOM.	106
Figure 4.12 Adsorption isotherms for MIB in the presence of six NOM solutions. Points are experimental data, dotted lines are isotherms obtained using the IAST in combination with the EBC model (see text)	107
Figure 4.13 Fraction remaining of MIB as a function of time in six NOM solutions (P1100)	110
Figure 4.14 RAR ₅ of carbons in NOM solutions relative to RAR values in NOM-free water	111
Figure 4.15 Change in fraction of MIB adsorbed between 2 and 120 hours (HP and PCO).	112
Figure 4.16 Representation of the carbon structure illustrating potential competitive effects	112
Figure 4.17 The structure of 2-methylisoborneol	114
Figure 4.18 A diagrammatic representation of the isolation procedures	116
Figure 4.19 ^{13}C -NMR spectra of the Loire River NOM isolates (7/98)	119
Figure 4.20 Relationships between some structural characteristics	121
Figure 4.21 Percentage of MIB as a function of carbon dose in all NOM fractions	122
Figure 4.22 The correlation between the percentage of MIB remaining with a 30 mg/L HP dose and the Carbon to Nitrogen ratios (A), the percentage of aromatic (B) and carboxyl (C) carbon in the competing NOM	122
Figure 4.23 Equilibrium isotherms for the adsorption of MIB by PCO and HP, in the presence of pure water, Loire HPO and TPI (PCO) and Blavet HPO and TPI (HP)	124
Figure 4.24 Equilibrium isotherms for the adsorption of MIB by PCO and HP, in the presence of all of the fractions	124

Figure 5.1 Factors that affect the performance of PAC for MIB and geosmin removal	130
Figure 5.2 Comparison of geosmin removal in the two water samples	133
Figure 5.3 Effect of DOC concentration on MIB adsorption and PAC dose required for the reduction of influent MIB concentration to 10 ng/L	133
Figure 5.4 MIB removal as a function of time, DOC concentration and turbidity	134
Figure 5.5 Effect of pre-chlorination on MIB removal.....	135
Figure 5.6 Equilibrium adsorption of MIB and geosmin for each PAC.....	138
Figure 5.7 Comparison of MIB and geosmin removal with 15 mg/L of each PAC	139
Figure 5.8 Saxitoxin removal from Hope Valley WTP inlet water (DOC = 5.7 mg/L) after treatment with 30 mg/L of PAC and contact time of 180 minutes. Total saxitoxin concentration = 7.8 µg/L, concentration and the relative abundance of individual toxins is shown above.	140
Figure 5.9 Saxitoxin equivalent removal with 30 mg/L of each PAC after 180 minutes. Initial STX eq = 1.1 µg/L.....	141
Figure 5.10 Adsorption isotherms of MIB onto five activated carbons.....	144
Figure 5.11 Fraction of MIB remaining vs. contact time for 5 activated carbons. Starting concentration of MIB, 100 ngL ⁻¹ , carbon dose, 20 mgL ⁻¹	145
Figure 5.12 Percent MIB and geosmin removed at equilibrium, 4 mgL ⁻¹ carbon dose, a), and 60 minutes contact, 9 mgL ⁻¹ carbon dose, b). Starting concentration of both compounds, 100 ngL ⁻¹ ..	146
Figure 5.13 Predicted PAC doses required to reduce geosmin concentration by 50% for two PAC particle sizes	147
Figure 5.14 Experimental data and HSDM predictions for MIB removal	148
Figure 5.15 Fraction MIB remaining at equilibrium as a function of PAC dose for a range of waters	149
Figure 5.16 Relationship between water quality parameters and PAC dose required to reduce MIB concentration by 50% in 60 minutes.....	150
Figure 5.17 MIB removal as a function of time in chlorinated and non-chlorinated River Murray water....	151
Figure 5.18 MIB removal as a function of time in chlorinated and unchlorinated Myponga Reservoir water. Residual chlorine was quenched prior to experiment.....	152
Figure 5.19 Apparent molecular weight distributions of chlorinated and unchlorinated River Murray and Myponga Reservoir water	152
Figure 5.20 The effect of turbidity - a) and DOC concentration - b), on the accuracy of HSDM predictions for the removal of geosmin.....	153
Figure 5.21 Fraction of MIB remaining vs. contact time for four activated carbons. Myponga Reservoir water	156
Figure 5.22 . Cost advantage associated with the smaller particle size (10 days dosing, 50 ML flow)	157
Figure 5.23 Cost estimates for prolonged PAC dosing	158
Figure 6.1 Effect of chlorination on NOM along the Mannum-Adelaide pipeline	165
Figure 6.2 HPSEC chromatograms of Hope Valley UF NOM fractions	166
Figure 6.3 HPSEC chromatograms of chlorinated Hope Valley UF NOM fractions	167
Figure 6.4 HSEC of raw and treated Myponga water	167
Figure 6.5 Normalised SEC plots for treated Myponga and 500-1000 fraction of raw Myponga water.....	168
Figure 6.6 Effect of carbon adsorbent on the adsorption kinetics of 500-3000 fraction.....	169
Figure 6.7 SEC of 500-3000 NOM fraction after Picatif PCO adsorption	170
Figure 6.8 SEC of 500-3000 NOM fraction after Picazine HP adsorption	170

LIST OF TABLES

Table 2.1 Percent of DOC in each fraction.....	15
Table 2.2 Percentage of NOM in each ultrafiltration fraction	21
Table 2.3 Specific UV absorbance (SUVA), specific colour, molar absorptivity (@280 nm), and E_2/E_3 of the >30K and 500 –1K fractions of the various isolates	21
Table 2.4 The percentage of the total carbon found each region of the ^{13}C NMR spectra, MW peak, Mw, and Mn values for the >30000 and 500-1000 fractions	23
Table 2.5 Description of NOM fractions used for the BDOC analysis.....	27
Table 2.6 NOM fraction characteristics determined by UV-visible absorbance, ^{13}C NMR and HPSEC..	28
Table 2.7 N:C elemental ratios determined without ash content and percentage of NOM <1000.....	29
Table 2.8 Retention times and apparent molecular weights of model compounds.....	50
Table 2.9 pK_a values of model compounds.....	52
Table 2.10 Average values of charge per molecule at each pH	52
Table 2.11 Average molecular weights of fractions determined by HPSEC and FIFFF	58
Table 2.12 Percent organic carbon retained on membranes, and the percent of UV absorbing DOC in the range >1K, >3K and >30K measured by HPSEC.....	68
Table 3.1 Materials, activation processes and manufacturers of activated carbons used in this study.....	76
Table 3.2 Surface areas and pore volumes of activated carbons	78
Table 3.3 Charge on NOMads at Γ^{int} at pH 4, 7 and 9.....	86
Table 4.1 Description of NOM solutions obtained from Myponga Reservoir water	91
Table 4.2 Starting material, mode and extent of activation of six activated carbons.	92
Table 4.3 Characteristics of NOM solutions obtained from Myponga Reservoir water.....	96
Table 4.4 Elemental analysis of NOM isolates (in weight percent)*	96
Table 4.5 Relative adsorption rates of MIB from F1 NOM solution onto six activated carbons.....	106
Table 4.6 Initial EBC concentrations ($\mu\text{mol L}^{-1}$). In brackets, equivalent DOC concentrations in mg L^{-1} assuming molecular weight of competing substances =300 g mol^{-1} and mass C=50% mass NOM.....	109
Table 4.7 P1100 carbon doses required to reduce MIB concentration from 20 to 10 ng L^{-1} in one hour.	110
Table 4.8 Physical chemical characteristics of the source waters	115
Table 4.9 Structural information on the powdered activated carbons.....	115
Table 4.10 DOC recovery of the isolation protocol	116
Table 4.11 Structural characteristics of the NOM isolates	118
Table 4.12 Integrated areas of ^{13}C -NMR spectra of the Loire River NOM fractions.....	120
Table 4.13 Surface concentration of MIB calculated from a solution concentration of 50 ng/L for all of the fractions	125
Table 5.1 Predicted minimum PAC dose (mg/L) for the reduction of 30 ng/L of MIB or geosmin to 5 ng/L with a contact time of 50 minutes	132
Table 5.2 NOM character parameters for Hope Valley Reservoir water.....	133
Table 5.3 Character of diluted and undiluted waters.....	134
Table 5.4 Guide as to how PAC dose may change with a change in PAC particle size, water quality and water treatment process	136
Table 5.5 Physical characteristics of PACs.....	137
Table 5.6 Choice of PAC as a function of contact time and taste and odour compound.....	139
Table 5.7 Water quality parameters and PAC doses required to reduce the concentration of MIB by 50% in one hour. 11 water samples.	149
Table 5.8 NOM parameters for chlorinated and unchlorinated Myponga and River Murray water.....	152
Table 5.9 Doses required for the removal of MIB from 20 to 10 ngL^{-1} for four activated carbons, and costs associated with dosing at a 50 ML per day flow for 10 days. Myponga Reservoir water	156
Table 6.1 Physical properties of activated carbons.....	164
Table 6.2 Effect of chlorination on NOM chemical properties.....	166
Table 6.3 Chemical properties of raw and treated Myponga water	168

1. INTRODUCTION

Activated carbon adsorption is one of the few water treatment processes that does not involve the addition of chemicals to the aqueous phase. This aspect, as well as the relatively low technology involved, and high efficiency of the process, make it a very useful tool for water suppliers to deal with a range of water quality issues.

Activated carbon can be used in two forms:

- Granular (GAC), where the adsorbent is used either as a replacement for sand/antracite in conventional filters, or in additional filters, after treatment, as a final polishing step. To date this form of application has not been used widely in Australia as it is relatively expensive; particularly where a separate filter is retrofitted to an existing plant, it has a limited lifetime for the effective removal of the target compound, and there are no regeneration facilities currently in Australia, so the used carbon must be discarded, usually to landfill.
- Powdered (PAC), which can be applied at various positions in the treatment plant. The advantages are that it can be applied where and when required, and therefore the costs can be controlled. The disadvantages are that it is difficult to handle as a fine black powder, and the costs associated with dosing can be excessive if the doses required are high over a prolonged period.

For optimisation of the application of the adsorbent for the treatment of drinking water a number of aspects should be taken into account by the water authority considering its use:

- What compound is targeted for removal? For example, natural organic material (NOM), taste and odour compounds, industrial pollutants, agricultural pollutants, algal toxins.
- Which activated carbon is the most effective for that target compound?
- Would the most appropriate mode of application be GAC or PAC?
- What contact time is available?
- What is the effect of the background water quality?
- How long will the filter last for the required removal of the target compound (GAC)? Or what dose is required for the available contact time (PAC)?

In this project the main emphasis was on the application of PAC, as this is still the most commonly used form of activated carbon both here and overseas. The aim of the work was to aid the water industry in the optimisation of activated carbon application by investigating and understanding the effect of each of the factors outlined above.

The investigation took place in stages, each considered to be crucial in the understanding of the processes involved when activated carbon is used as an adsorbent in drinking water treatment. The stages are outlined below.

Characterisation of NOM

As all water treatment processes are affected by NOM, including activated carbon adsorption, the characterisation of NOM was considered of particular importance. NOM from different water sources was fractionated and characterised, and subsequently the NOM was used in the activated carbon studies. Some of the characterisation methods were also investigated in greater detail in this stage. This work is described in Chapter 2.

Mechanisms of adsorption of NOM onto activated carbon

This work was important in order to optimise the activated carbon removal of NOM, and also to understand the effect of NOM on adsorption of other compounds. This research is covered in Chapter 3.

The influence of well-characterised NOM on the adsorption of MIB onto activated carbon

The effect of NOM on the adsorption of the taste and odour compound 2-methylisoborneol (MIB) was investigated in depth. The compound was chosen as activated carbon is the most effective process for its removal, which is strongly adversely affected by NOM. MIB is a small compound, and can be considered a model for the adsorption of other small compounds. Chapter 4 covers this topic. In

OPTIMISATION OF ADSORPTION PROCESSES

addition, the PhD thesis, "The Isolation, Fractionation and Characterisation of Natural Organic Matter from Water and its Effect on the Adsorption of Taste and Odour Compounds by Activated Carbon" by Chris Hepplewhite expands on some of the results not directly covered in this project report.

Optimisation of the application of activated carbon for treatment of a range of algal metabolites

In this section of the work the study was expanded to geosmin, another taste and odour compound, and the saxitoxin range of algal toxins. These compounds are also of importance to the Australian and international water industry. A study was also conducted on the effect of water quality and other treatment processes on the removal of MIB and geosmin by activated carbon. The results of this work are given in Chapter 5.

The influence of NOM character on other water treatment processes

In chapter 6 a brief overview is given of some other effects of NOM in the treatment process.

Finally a brief summary and conclusion of the work is given in Chapter 7.

The project extended over four years and the work produced many valuable publications. This report has been prepared as a compilation of those publications, therefore an advantage is that most sections of each chapter can be read independently as they contain an introduction, methods section, results and discussion and conclusions.

Overall the objectives of the study have been successfully achieved, and the Australian water industry now has a valuable resource to aid in the optimisation of the application of activated carbon.

2. ISOLATION AND CHARACTERISATION OF NOM USING A RANGE OF METHODS

2.1 INTRODUCTION

NOM is present in all source waters, and is therefore present during drinking water treatment. Concentrations can range from below 1 mg/L in a very good quality water source, to over 50 mgL⁻¹ in some swampy waters; however, at all concentrations it interferes with every step in the treatment process. For example NOM

- exerts a high demand for coagulants
- reduces the effectiveness of activated carbon
- can form potentially dangerous by-products when oxidation treatments are applied
- can be a food source for bacteria, causing bacterial regrowth in the distribution system.

The extent of the impact of NOM depends strongly on the character of the mixture, the importance of which is illustrated by the various CRC for Water Quality and Treatment (CRCWQT) projects which have placed such a strong emphasis on characterisation of NOM. When working with NOM it is important to utilise as many techniques as possible, gaining complementary information which can be used to obtain a better overall picture of the NOM composition.

This chapter describes the isolation and characterisation of a range of NOM fractions most of which were used in subsequent adsorption studies. In section 2.2, the fractions described were isolated from Myponga and Hope Valley reservoir water using anion exchange. The isolates were then fractionated using ultrafiltration and characterised in order to compare the characteristics of the fractions, and the NOM of the different waters. Section 2.3 describes the isolation, ultrafiltration fractionation and characterisation of Hope Valley NOM isolated using four techniques, three different resins and a membrane isolation technique. The work described in section 2.4 was undertaken on nine of the isolates described in section 2.3. In section 2.5 three of the commonly used NOM characterisation techniques are investigated in further detail, also using some of the isolates described in section 2.3.

2.2 COMPARISON OF CHARACTERISTICS OF FRACTIONATED NOM FROM TWO RESERVOIRS

2.2.1 Introduction

Natural organic material (NOM) impacts on all aspects of drinking water treatment, from coagulation and flocculation, activated carbon adsorption, and disinfection, to the maintenance of microbiological quality throughout the distribution system. The physical characteristics of NOM have a major influence on its impact on water treatment (Owen *et al.*, 1995; Collins *et al.*, 1986) and it is therefore of value to obtain information on the character of NOM in raw water sources providing water for treatment.

Studies have generally shown a variation in NOM properties from different water sources. Aiken and Cotsaris (1995) found the type of soil had a large impact on the amount and character of the NOM leaving catchments. Owen *et al.* (1995) found a significant difference in the character of NOM from a range of different sources around the USA.

Characterisation techniques generally fall into 2 categories, those which can be undertaken on the bulk water sample, such as UV absorbance, Dissolved Organic Carbon (DOC), fluorescence, colour, size exclusion chromatography, ultrafiltration, and those that can only be undertaken on samples that have been pre-concentrated, such as ¹³C NMR, pyrolysis GCMS, IR. The latter techniques provide extremely useful information on the functional groups present in NOM.

XAD-8 and XAD-4 resins are very often used for isolation of NOM. They are very useful for concentration of water samples and the isolation of NOM can be maximised when the two resins are used in series (Krasner *et al.*, 1996). NOM can also be characterised according to the ratio of XAD-8-adsorbable, XAD-4-adsorbable and non-adsorbable fractions. A disadvantage of this isolation method is the effect of extremes of pH necessary for adsorption onto, and desorption from, the resins. There is a risk of some change of character of the organics as a result of such extreme procedures. The Australian Water Quality Centre has been investigating the use of an anion exchange resin for the

concentration of NOM. Under certain conditions 80% of the NOM present in the raw water sources tested so far can be isolated using this technique. The removal of the NOM from the resin requires a high ionic strength NaCl solution. Only the most strongly-adsorbed NOM is removed using high pH solution. The concentrated NOM solution is then desalted using ultrafiltration membranes. The desalted solution is further fractionated using ultrafiltration. The result is a series of concentrated NOM fractions which have been obtained under conditions which have minimal impact on the character of the NOM. The aim of the work presented here was to obtain fractions from two very different water sources and to characterise the fractions to determine any similarities or differences. These characterised fractions will then be used in future work to determine the effect of NOM characteristics on water treatment processes.

2.2.2 Methods

Isolation and ultrafiltration

The methods of isolation and ultrafiltration are described in detail elsewhere (Newcombe and Drikas, 1996).

¹³C NMR

A Bruker CXP 100 Instrument, of frequency 22.6 MHz was used to analyse freeze-dried samples of the NOM fractions. Chemical shift ranges used to calculate the carbon functional groups are as follows:

0-50 ppm	alkyl
50-110 ppm	O-alkyl
110-165 ppm	aromatic
165-190 ppm	carboxyl
190-210 ppm	carbonyl (Ricca and Severini, 1993; Wilson, 1987)

Size exclusion chromatography

Size exclusion chromatography (SEC) was performed using a Waters Protein Pak 125 glycol-functionalised silica gel column. The column was calibrated with polystyrene sulphonate standards (1.8K, 4.6K, 8K, 18K).

2.2.3 Results and discussion

The two reservoirs chosen for this study were the Myponga Reservoir, about 40 kms south of Adelaide, South Australia, and Hope Valley Reservoir, approximately 15 kms north-east of Adelaide. The two reservoirs have different catchment areas, with different soil types and vegetation. Both reservoirs serve water treatment plants which, combined, supply water to up to 30% of the population of Adelaide. The concentration and ultrafiltration procedures resulted in two sets of ultrafiltration fractions of nominal molecular weights : <500, 500-3000, 3000-10000, 10000-30000 and >30000.

The percentage of DOC found in each fraction is shown in Table 1. In both cases the majority of the NOM was found in the ultrafiltration fractions less than 3000. This is consistent with other literature values of molecular weight distributions of natural water (Aiken and Cotsaris, 1995; Collins *et al.*, 1986). The major difference between the two samples is the percentage of DOC less than 500. As mentioned above, the two reservoirs have very different catchment areas, including types of vegetation and soil. These differences may have resulted in the Myponga water having a larger amount of DOC broken down by bacteria into these smaller molecular weight compounds. It is also possible that the fraction of DOC not adsorbed in the concentration procedure for Hope Valley Reservoir water was the very low molecular weight compounds. Recent studies have indicated that there is very little difference in the size distribution of NOM in natural water from these two reservoirs.

Figure 2.1 shows the percent carbon in different functional groups as determined by ¹³C NMR. There are several points to notice in this figure.

- There is a decrease in aliphatic, and increase in O-alkyl, carbon with molecular weight for both sources. This trend indicates the higher molecular weight NOM has a higher carbohydrate content than the lower molecular weight compounds, which contain a higher percentage of recalcitrant aliphatic carbon. This trend has been noted previously and attributed to a microbial degradation sequence (Baldock *et al.*, 1992).

- For both sources there is a general trend of decreasing aromaticity with increasing molecular weight. This could also be attributed to the more recalcitrant moieties being more prevalent in the biological degradation products in the lower molecular weight fractions. There is an anomalous low value for aromaticity shown by the 500-3000 fraction of the Hope Valley fractions. This value corresponds well with spectroscopic parameters measured for the fractions.
- The trends and percentages of carbon in carboxyl groups are very similar for the two water sources. Figure 2.2 compares the values directly. The similarity is not unexpected as the NOM was concentrated using the same anion exchange resin.

In summary, the general trends shown by the fractions from the two sources are similar, however the percentages of carbon within each functional group, except the carboxyl, differs slightly between the two sources. Definite conclusions cannot be drawn from this difference as the percent of total NOM isolated from the two sources was also different.

Table 2.1 Percent of DOC in each fraction

Ultrafiltration Fraction	Percent DOC	
	Hope Valley	Myponga
percent of total DOC isolated	50	80
< 500	12%	32%
500-3000	56%	50%
3000-10000	14%	7%
10000-30000	7%	4%
>30000	11%	8%

Figure 2.3 shows the molecular weight distributions of the fractions obtained using size exclusion chromatography (SEC). SEC was the final characterisation technique used on the fractions; unfortunately there was not sufficient Myponga 10000-30000 fraction to obtain the molecular weight distribution data. However, the trends apparent in Figure 3 are similar for the two sources. The molecular weight distributions for the two smallest fractions, <500 and 500-3000, obtained using size exclusion chromatography are approximately those expected from the ultrafiltration molecular weight cut-offs. The Myponga 3000-10000 fraction is also reasonably close to the distribution indicated by the ultrafiltration cut-off values, however the three Hope Valley fractions that are greater than 3000 and the Myponga fraction >30000 have a lower molecular weight distribution than expected. This is probably due to the type of molecules used for the calibration of the higher molecular weight ultrafiltration membranes. The globular proteins that are used cannot be expected to behave as NOM in solution, and therefore the ultrafiltration molecular weight cut-off values cannot be assumed to be the true molecular weights of the ultrafiltered compounds.

OPTIMISATION OF ADSORPTION PROCESSES

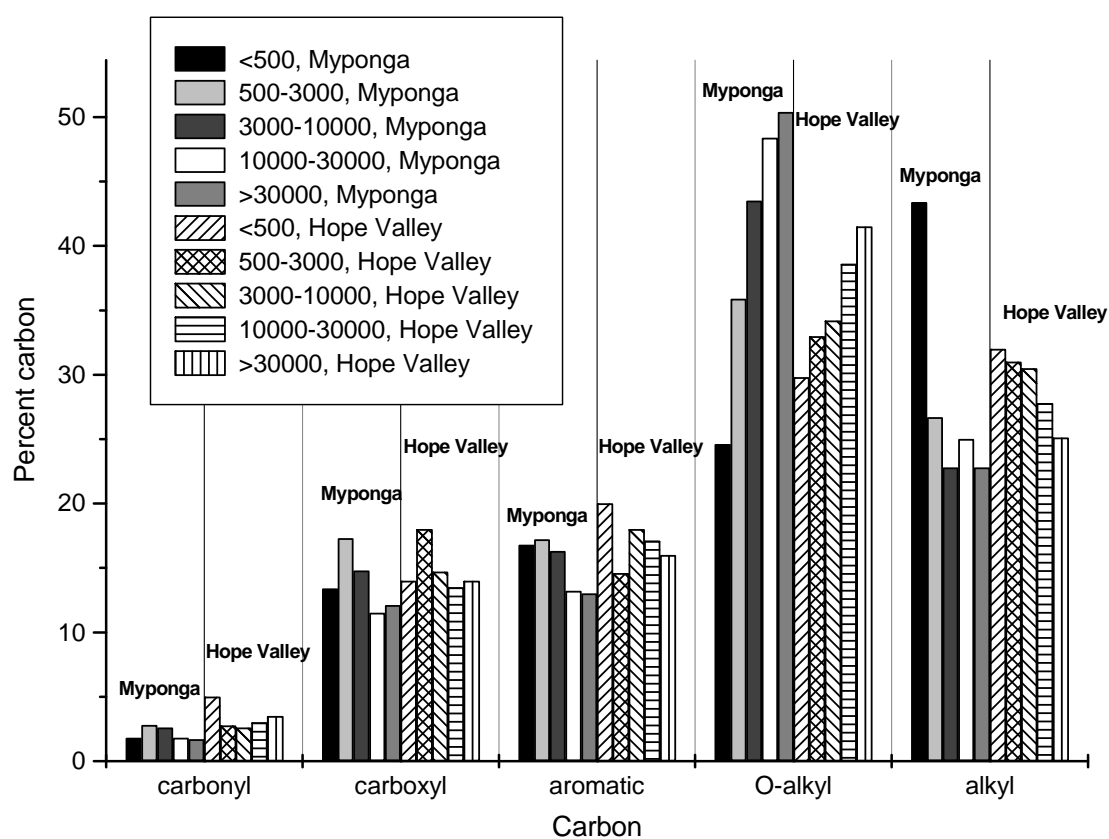


Figure 2.1 Percent carbon in each functional group(¹³ C NMR).

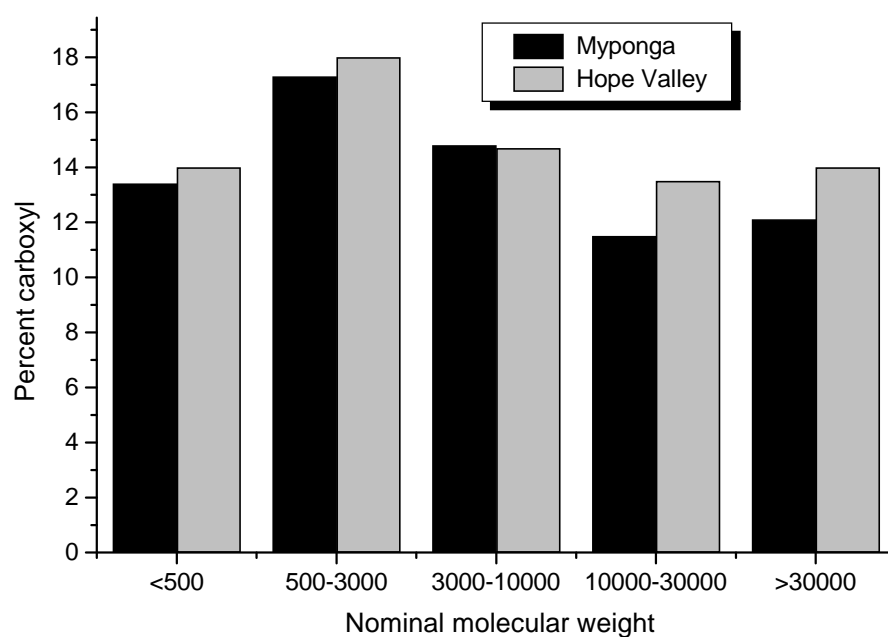


Figure 2.2 Percent carbon in carboxyl groups

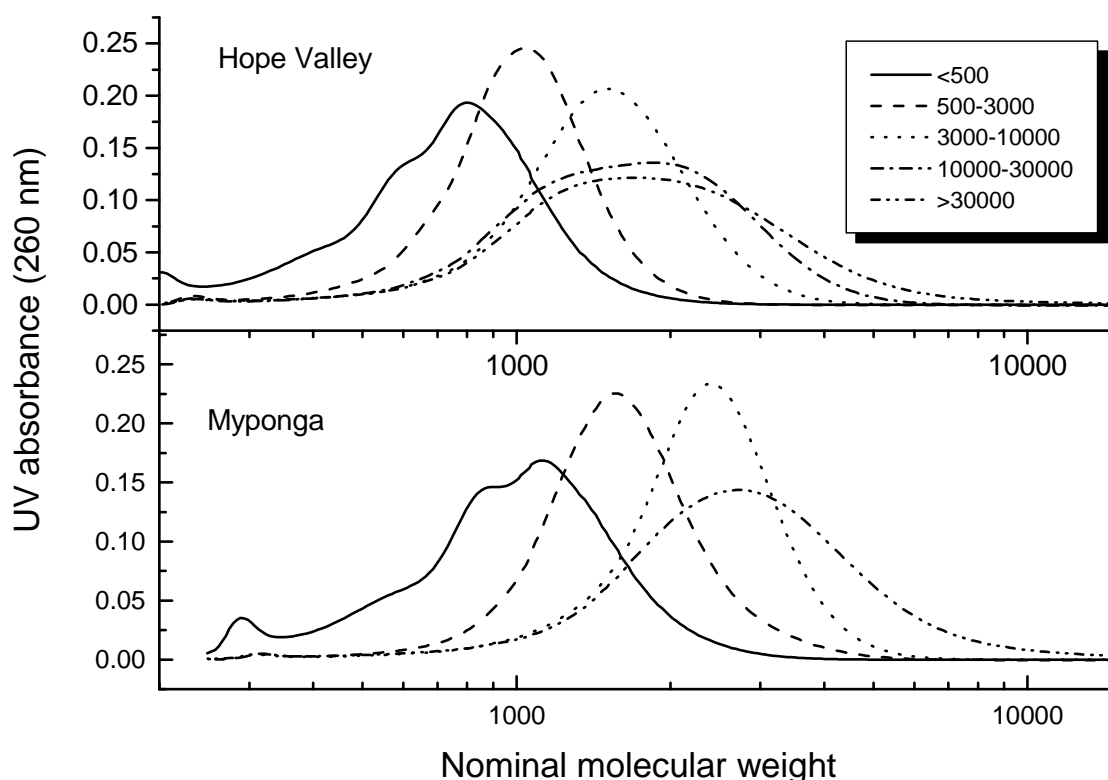


Figure 2.3 Size exclusion chromatograms for ultrafiltration fractions

2.2.4 Conclusions

Ultrafiltration fractions of concentrated NOM from two reservoirs showed similar structural trends. The decrease in O-alkyl carbon with decrease in molecular weight may be indicative of a microbial degradation sequence. The molecular weights of the ultrafiltration fractions were lower than expected, probably due to the calibration standards used for the UF membranes.

2.3 CHARACTERISATION OF NOM ULTRAFILTRATION FRACTIONS ISOLATED USING THREE TECHNIQUES

2.3.1 Introduction

Objectionable tastes and odours in drinking water, from both natural and industrial sources are common problems throughout the world (Persson 1995). Conventional treatments using coagulation, flocculation, sedimentation and/or filtration are usually only partially successful at removing these compounds. Activated carbon has been identified as one of the best technologies to remove these and other contaminants found in very low concentrations in potable water (Chen *et al.* 1996 and Kilduff *et al.* 1996). However, in all applications where activated carbon is used to remove trace amounts of micropollutants, natural organic matter (NOM) adversely affects the adsorption of these compounds by either competing for adsorption sites and/or by coating the surface of ("fouling") the carbon (Newcombe *et al.* 1997b).

Newcombe *et al.* (1997b) and Kilduff *et al.* (1996) both showed that the adsorption of organic compounds by activated carbon is largely controlled by both the molecular weight distribution of the compounds and the relationship of the molecular weight distribution to the pore volume distribution of the activated carbon. Larger molecules can only adsorb in larger pores whereas although smaller molecules can adsorb in both the larger and smaller pores they tend to adsorb most strongly in smaller pores. As most taste and odour compounds are relatively small it is the lower molecular weight

NOM that competes with them for their preferred adsorption sites (Newcombe *et al.* 1997b). However, Newcombe *et al.* (1997a) found that the molecular weight fractions obtained by ultrafiltration displayed different structural characteristics that may have influenced their competitive effect. This study was designed to clarify the effects of the chemical characteristics of UF fractions of isolated NOM on the adsorption of taste and odour compounds by activated carbon. By producing NOM fractions that have different chemical characteristics but similar molecular weight distributions, the effects of molecular size could be reduced and the effects of functional chemistry on activated carbon adsorption processes studied further.

2.3.2 Materials and methods

Isolation of NOM

Raw water (200 litres) was collected from Hope Valley Reservoir, South Australia, every 3 days. All water was filtered through a 0.45 µm cartridge before the NOM was isolated.

Isolation by DAX-XAD resins

The procedure (Figure 2.4) was similar to Malcolm and MacCarthy (1992). The resins: Supelco's DAX 8 and XAD 4, were cleaned using the method developed by Standley and Kaplan (1995). Raw water, (pH adjusted to 2 with conc. HCl) was pumped through glass columns (50 mm i.d.) each containing 750 mL of resin using a Watson and Marlow 505s pump (Chemcon, Melbourne) at a flow rate of empty bed volume (EBV)/25 min.

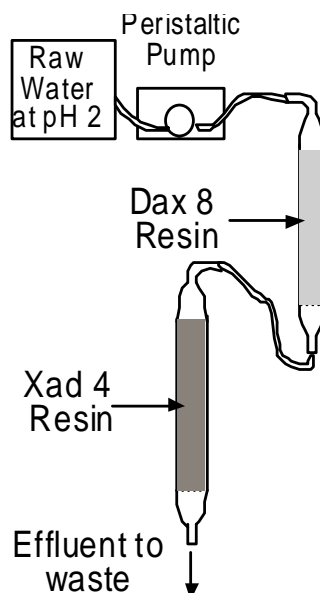


Figure 2.4 Schematic of the process used to obtain the DAX 8 and XAD 4 isolates

Isolation by MIEX®

The MIEX[®] resin (SCO1, Orica Pty Ltd) was cleaned using 2 EBV of 2M NaCl followed by 2 EBV of 0.2M NaOH and rinsed with 10 bed volumes of Milli Q water. The isolation procedure was as described above except that the raw water required no pH adjustment.

Isolation by ultrafiltration

The UF membranes (YC05 150mm dia, nominal molecular weight cut-off = 500D, Amicon) were cleaned by gently stirring in a 0.01M NaCl for 30 minutes, then passing 0.01M NaCl through until the UV absorbance of the effluent was the same as the influent. Figure 2.5 shows a schematic of the process used to obtain the UF isolate. Pre-treatment of the water was by the procedure of Crum *et al.* (1996) and replaced large bivalent cations with H⁺ and remove HCO₃⁻ as CO₂. The permeate from the membrane was passed through 150ml of MIEX[®] to concentrate the <500 fraction.

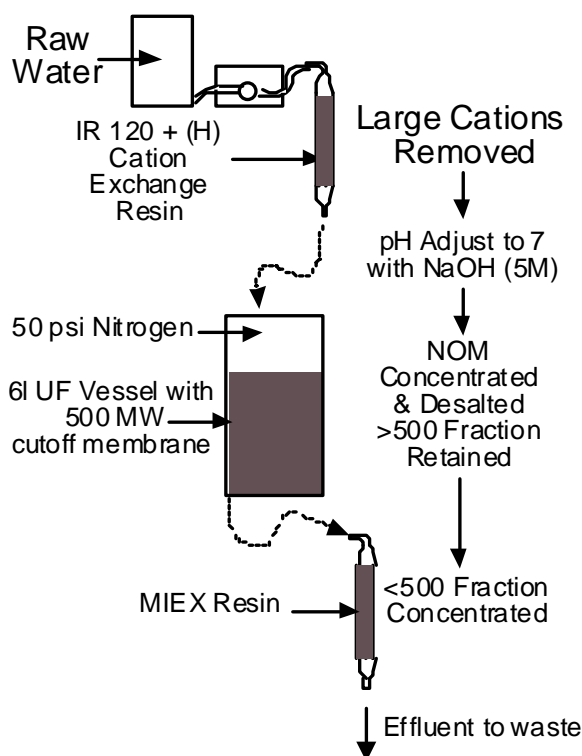


Figure 2.5 Ultrafiltration of raw water

Desorption of NOM

Desorption of NOM from DAX 8 and XAD 4. Figure 2.6 shows the procedure used to desorb the NOM from the DAX 8 and XAD 4 resins. The organic compounds were desorbed with two bed volumes of NaOH at pH 13 at half the flow rate used in the isolation procedure. This was followed by rinsing with Milli Q until the eluent was nearly colourless. The desorbed solution was immediately passed through a column of Amberlite IR-120+ (H^+) to remove the salts added through desorption with NaOH, reduce the pH of the isolate and ensure the protonation of the organic compounds.

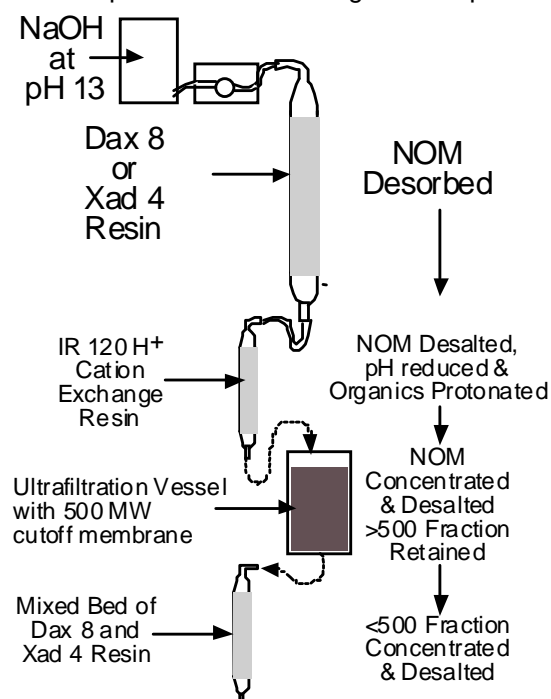


Figure 2.6 Desorption of NOM from DAX 8 or XAD 4 resins

Desorption of NOM from MIEX®. Desorption was with 2 EBV of 2M NaCl followed by Milli Q at a flow rate of 1 EBV/60 minutes. Rinsing continued until the eluent was nearly colourless. This process was used for both the MIEX® isolate and the UF <500 fraction that was concentrated using MIEX®.

Fractionation of isolates

The fractionation of the NOM by UF was based on work by Newcombe *et al.* (1997a) (Figure 2.7). This separated the NOM into fractions with different molecular weight distributions. In addition this process concentrated and de-salted the >500 portions. The NOM was rinsed through each membrane with 0.01M NaCl until the permeate had a UV absorbance at 254 nm <0.1. The <500 MW permeates were concentrated and de-salted using a mixed bed of DAX 8 and XAD 4 resins (700mL, of a 50/50 mix), with a flow rate of 1 EBV/hr with desorption as in the DAX/XAD procedure above.

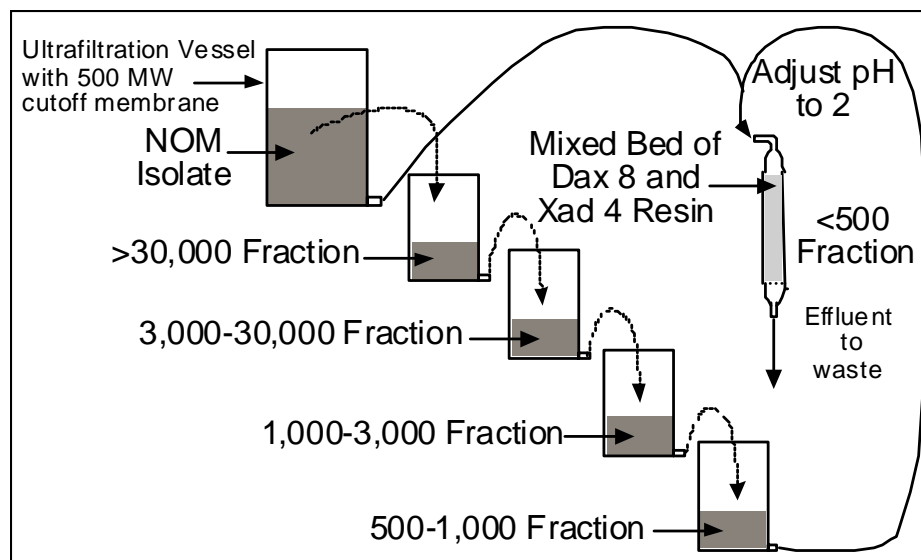


Figure 2.7 UF fractionation of NOM

Characterisation of the NOM

Measurement of UV absorbance and colour was carried out on a GBC UV/VIS 918 Spectrometer. Colour was determined by comparing the absorbance of the sample, at 456 nm and a 50 mm path length, with a platinum/cobalt standard (50 Hazen Units (HU)). The ^{13}C NMR analysis of freeze dried samples was carried out using a Bruker CXP 100 22.6 MHZ instrument. The HPSEC analysis was based on Chin *et al.* (1994). The column (Shodex Protein KW-802.5, molecular weight range 0.1K-50K, Waters Australia) was calibrated using polystyrene sulphonates; 35K, 18K, 8K, 4.6K and acetone. Samples were run using a flow rate of 1 mL/min and an injection volume of 150 μL . The mobile phase was 20 mM NaH_2PO_4 , pH 6.8, with the ionic strength adjusted to 0.1 M using NaCl. Detection was by a UV absorbance at 260 nm (484 UV/Vis detector, Waters Australia Pty Ltd) with data collection by a PC running Millennium software (Waters Australia Pty Ltd).

2.3.3 Results and discussion

The isolation and fractionation process resulted in 20 fractions: >30K, 3-30K, 1-3K, 500-1K and <500 MW for each of the 4 isolates; MIEX, DAX 8, XAD 4 and UF. Throughout this paper the fractions will be identified by the ultrafiltration cut-off values prefixed by the isolation method. However, it should be understood that the cut-off values should not be considered true molecular weight values as the cut-off values of the membranes are obtained using globular proteins that have different structures and densities from NOM.

The percentages of NOM in the various fractions are given in Table 1. The UF isolation method had the highest removal and yield, therefore the NOM isolated by this method is probably the most representative of the NOM in raw water. By comparing the NOM in each of the fractions with the equivalent UF fraction the size of NOM isolated by each method can be inferred. The results indicate:

- In the MIEX[®], DAX 8 and XAD 4 isolates the smaller molecular weight fractions (<3K) comprise the majority of the NOM which is consistent with other investigations of DOC in natural waters (Aiken and Cotsaris 1995). In the UF isolate, the opposite is true, with the >3K fractions comprising 56% of the NOM.
- The >30K fractions from the UF and DAX 8 isolation methods contain similar percentages of NOM. However, the percentage of NOM in the MIEX[®] and XAD 4 >30K fractions is much less than that of the other two. This is probably due to the preferential removal of larger hydrophobic compounds by DAX 8 and UF.
- The opposite trend is seen in the 1-3K fractions. Whereas the UF and DAX 8 1-3K fractions contain similar percentages of NOM, these percentages are much less than those found in the equivalent XAD 4 or MIEX[®] fractions. This is consistent with preferential removal of median to lower molecular weight compounds by the MIEX[®] and XAD 4 resins.

Table 2.2 Percentage of NOM in each ultrafiltration fraction

	MIEX	DAX 8	XAD 4	Ultrafiltration
>30K	15	26	15	28
3-30K	8	8	5	28
1-3K	24	10	20	14
500-1K	38	37	38	16
<500	15	18	22	14

Chemical characterisation of the ultrafiltration fractions

UV absorbance data

The UV absorbance was undertaken on diluted samples of each of the UF fractions and a summary of the results for the >30K and 500-1K fractions are given in Table 2. Both specific colour (colour (HU)/DOC (mg/L)) and SUVA ((UV abs at 254 nm/DOC (mg/L))*100) decrease for all isolates, as the molecular weight distributions decrease. This has been noted in earlier work on MIEX[®] and XAD isolates (Newcombe *et al.* 1997a and Peuravuori and Pihlaja 1998).

Table 2.3 Specific UV absorbance (SUVA), specific colour, molar absorptivity (@280 nm), and E₂/E₃ of the >30K and 500 –1K fractions of the various isolates

	SUVA	Specific Colour	Molar Absorptivity @280	E ₂ /E ₃ (250nm/365nm *100)
MIEX>30K	4.2	7.4	386	9.9
MIEX 500-1K	3.5	2.4	293	6.1
DAX 8>30K	5.6	12.4	523	11.3
DAX 8 500-1K	3.9	4.1	334	7.9
XAD 4>30K	3.3	3.0	286	7.2
XAD4 500-1K	2.3	1.2	181	5.3
UF>30K	3.2	4.6	285	9.0
UF 500-1K	2.2	1.4	178	5.3

¹³C NMR

¹³C NMR spectra were divided into five regions corresponding to carbons contained in alkyl, O-alkyl, aryl, carboxyl or carbonyl groups. The results of the integration of these regions for the >30K and 500-1K fractions given in Table 3 indicate:

- The percent of carbons in the alkyl, aryl, carboxyl and carbonyl regions all increase with decreasing molecular weight distribution, with the exception of the DAX 8 and XAD 4 aryl carbons which stay the same.
- The percent of O-alkyl carbon decreases with decreasing molecular weight as does the ratio of O-alkyl to alkyl carbons.

OPTIMISATION OF ADSORPTION PROCESSES

These trends agree with those reported by Newcombe *et al.* (1997a) and are consistent with the changes to the NOM during bio-degradation i.e. the larger NOM compounds contain high concentrations of carbohydrate moieties (i.e. high O-alkyl to alkyl carbon ratios), which are readily consumed by micro-organisms. This results in the generation of smaller NOM compounds with relatively higher concentrations of aromatic and alkyl carbons, which are not easily degraded.

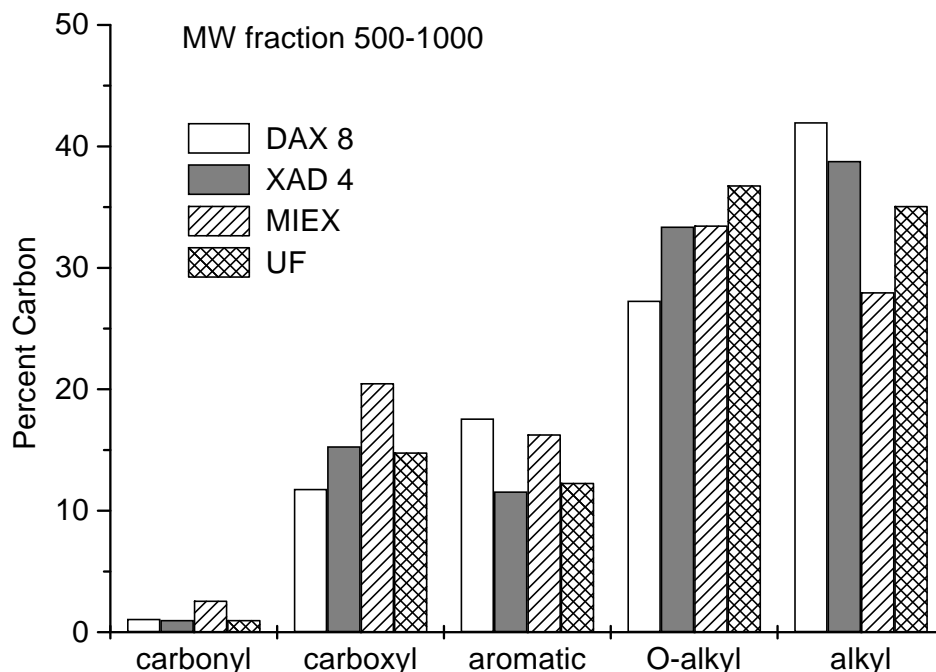


Figure 2.8 Percentage of carbon in each functional group for the 500-1,000 fractions

Chin *et al.* (1994) and Peuravuori and Pihlaja (1998) both found a strong relationship between the percent of aromatic carbon and molar absorptivity at 280 nm and, to a lesser extent, the ratio of absorbance at 250 nm and 365 nm (E_2/E_3) (Tables 2 and 3). In this study both these relationships were poor, $r^2 = 0.36$ and 0.11 respectively. Peuravuori and Pihlaja (1998) also state the percent of aryl carbon in their XAD 8 and UF isolates increased with increasing molecular weight. Although the percent aryl carbon in our DAX 8 isolate remained the same with increasing molecular weight all other isolates showed decreases in this value (Table 3).

Table 2.4 The percentage of the total carbon found each region of the ^{13}C NMR spectra, MW peak, Mw, and Mn values for the >30000 and 500-1000 fractions

Carbon Region	% Alkyl C	%O-Alky C	%Aryl C	%Carboxyl C	%Carbonyl C	O-Alkyl C/ Alkyl C	Mw Peak	Mw	Mn	Mw/Mn
Fraction										
MIEX>30K	24	53	11	11	1	2.26	1652	1244	785	1.6
MIEX 500-1K	28	34	16	20	2	1.19	1148	597	458	1.3
DAX 8>30K	30	40	18	11	1	1.31	1700	1294	603	2.1
DAX 8 500-1K	42	27	18	12	1	0.65	1200	582	360	1.6
XAD 4>30K	30	46	12	11	1	1.53	1573	893	687	1.3
XAD4 500-1K	39	33	12	15	1	0.86	1168	543	411	1.3
UF>30K	22	58	8	12	0	2.64	1448	977	577	1.7
UF 500-1K	35	37	12	15	1	1.05	1111	453	331	1.4

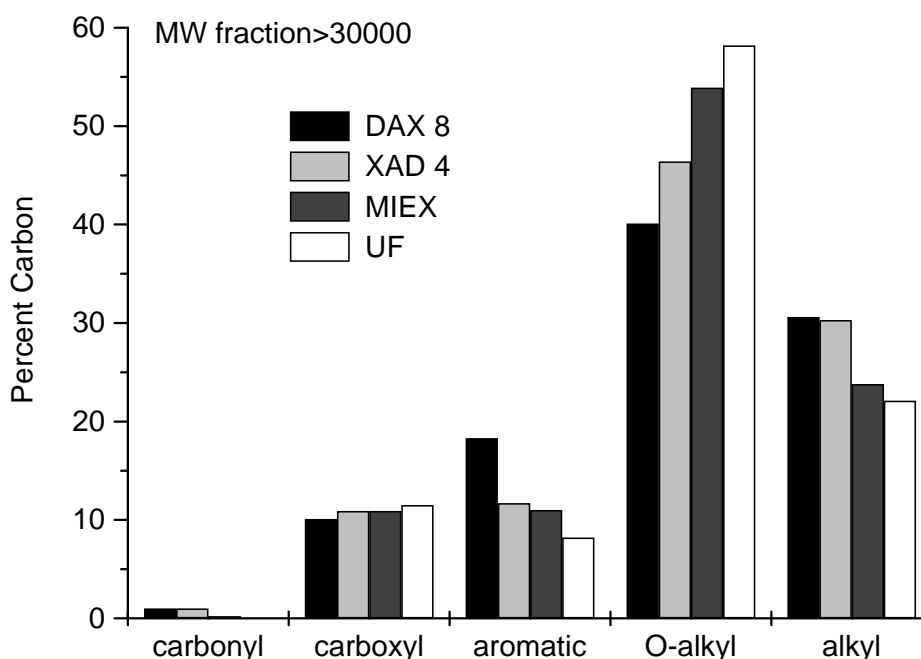


Figure 2.9 Percentage of carbon in each functional group for the >30000 fractions

The variations in functional chemistry of the 500-1000 and >30000 fractions of the isolates, in Figures 2.8 and 2.9 indicate:

- High percentages of aromatic carbons in the DAX 8 isolates. This can be attributed to the affinity of DAX 8 resin for hydrophobic aromatic compounds.
- The highest concentrations of O-alkyl carbons were found in the UF fractions. If the UF isolate is the most representative of the NOM in the raw water, then the other isolation methods appear to be missing some of the carbohydrate containing DOC.
- The percent carbon (%C) in the carboxyl regions of each of the fractions show no clear trends, however, in Figure 2.9 the effects of the isolation techniques can be seen.

OPTIMISATION OF ADSORPTION PROCESSES

- The MIEX[®] isolate has the highest carboxyl %C as might be expected from an anion exchange resin.
- The lowest carboxyl %C was in the DAX 8 isolate, which is consistent with the isolation of hydrophobic compounds with lower concentration of hydrophilic oxygen-containing groups such as carboxylic acid groups.
- The carboxyl %C of the >30000 fractions (Fig. 2.9) are all nearly the same.

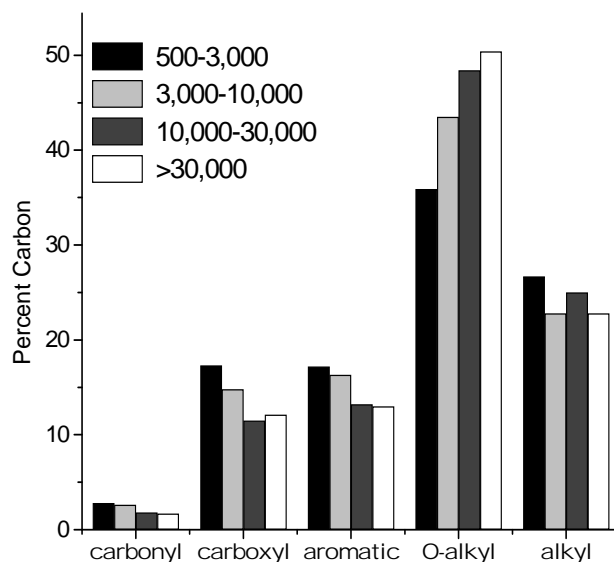


Figure 2.10 Percentage of carbon present in each functional group for Hope Valley fractions

Of particular significance to this study is the comparison of Figure 2.9 with Figure 2.10. The trends within the same molecular size fractions, >30K, from the different isolation techniques (2.9) are very similar to the trends within the different sized fractions of a MIEX[®] isolate (2.10; Newcombe *et al.* 1997c). By comparing the competitive behaviour of fractions that contain NOM with similar molecular weight distributions but different functional chemistry, with that of NOM fractions that have different molecular weight distributions but functional chemistry similar to the above fractions, the effects of size on adsorption by activated carbon can be reduced. This should allow a better understanding of the effects of functional chemistry on the adsorption process.

HPSEC

Table 3 contains a summary of the HPSEC data for the >30000 and 500-1000 fractions. The molecular weight (Mw) and molecular number (Mn) averaged molecular weights along with the peak molecular weight (Mw peak) values for the >30000 fractions are much lower than the membrane cut-off values but are similar to those reported by other workers (Chin *et al.* 1994). This is probably due to either the NOM having a very different structure to the globular proteins used to calibrate these membranes, or charge rejection of NOM by membrane pores (Newcombe *et al.* 1997 a).

2.3.4 Summary and conclusions

The isolation and fractionation of natural organic material from Hope Valley reservoir resulted in the generation of 20 NOM fractions with different chemical and spectroscopic characteristics. The fractions showed a clear trend of high molecular weight, highly coloured compounds with higher carbohydrate carbon content ranging to lower molecular weight compounds with higher carboxyl, alkyl and aryl carbon content. The Mw peak, Mw and Mn values of the fractions from within each isolation method show that ultrafiltration resulted in fractions with different molecular weight distributions. In addition, the Mw peak, Mw and Mn values for the same UF fractions indicate that they have similar molecular weight distributions, regardless of isolation method. The molecular weight distributions of

the fractions were lower than the quoted UF membrane cut-offs, but this is consistent with earlier work.

Characterisation of the NOM isolated and fractionated in this study has confirmed that we succeeded in producing several chemically different fractions with similar molecular weight distributions. The use of these fractions in studies of adsorption by activated carbon should facilitate a better understanding of the effects of chemical structure and charge on the adsorption process.

2.4 NOM CHARACTER CHANGES DURING BIODEGRADATION

2.4.1 Introduction

Biological processes in water treatment are gaining increased significance as water authorities attempt to minimise the addition of chemicals to potable water. Biological removal of dissolved organic carbon (DOC) is of interest due to the influence of organic carbon on the cost of treating water to attain an acceptable quality. Issues associated with the presence of DOC in water include, high coagulant doses, decreased lifetime of granular activated carbon filters and formation of disinfection by-products. The removal of biodegradable DOC in particular would result in a more biologically stable water in the distribution system, minimising the danger of bacterial regrowth (Withers and Drikas, 1998). A greater understanding of biological removal of DOC, for example the types of organic material most easily assimilated and the character of the DOC after treatment, will aid the optimisation of the process.

Although biological processes of DOC removal have been studied for many years, the mechanism of biodegradation of complex organic compounds is still not fully understood. It is well known that micro-organisms can only directly assimilate compounds of molecular weight 1000 Dalton or lower (Confer and Logan 1998a), larger molecules must first be broken down via enzyme hydrolysis. Larson and Harremoës (1994) believed that the enzymes were released by the organisms and the hydrolysis took place in the bulk solution. In contrast, more recent work by Confer and Logan (1998a, 1997a, 1997b, 1998b) indicated that, in the case of biofilms, <3% of the enzyme activity took place in the bulk solution. They studied model compounds such as proteins, glucose, dextrin and dextran, and found that for fixed biofilms, suspended cultures and in wastewater treatment effluent from a trickling filter, the great majority of breakdown of larger molecules took place at the cell wall, and the rate of hydrolysis at the wall was 5 times that in the bulk solution. They proposed a mechanism where the organic compound adsorbs onto the cell wall and hydrolytic fragmentation takes place at the surface. Biodegradable compounds formed during this process can be taken into the cell. Other fragments are released back into solution or into the biofilm to be further transformed by the same, or other, micro-organisms. They measured an increase in small molecular weight compounds in solution, providing strong evidence for this hypothesis.

During the biodegradation of a complex mixture such as natural organic material (NOM) several processes would occur simultaneously. Two possible processes are:

- a) the larger compounds are hydrolysed, some of the products are consumed and some are released into solution and,
- b) smaller molecular weight compounds are directly assimilated.

Both of these pathways would result in a shift in the overall molecular weight distribution of the NOM with biodegradation. The direction of the shift, towards smaller or larger molecular weights, will depend on the relative importance of the processes, and the relative importance will depend on the character of the NOM. A shift in the specific UV absorbance, or UV absorbance per mass of dissolved carbon, of the NOM could also be expected with both a) and b). In general, small molecular weight NOM has a lower UV absorbance than higher molecular weight compounds (Croué *et al.* 2000), therefore a shift in the molecular weight distribution would result in a shift in the UV absorbance spectrum. In addition, UV absorbance caused by conjugation or aromaticity could be expected to be reduced when bonds are severed and consequently conjugation is reduced. Two types of character changes during biodegradation have been reported in the literature; a shift to higher molecular weight, higher specific UV absorbance, higher proportion of humic material (Westerhoff and Pinney 2000, Namour and Muller 1998, Hesse and Frimmel 1999) and the opposite shift, to lower specific UV absorbance and lower molecular weight (Confer and Logan 1998a, Confer and Logan 1997a, Confer and Logan 1997b,

Westerhoff and Pinney 2000, Charnock and Kjonno 2000, Volk *et al.* 1997). The biodegradation of wastewater was the focus of most of these studies.

This change in character also has important implications for water treatment downstream of the biological treatment. For example Westerhoff and Pinney (2000) found a decrease in trihalomethane formation potential (THM-fp), but an increase in specific THM-fp (THM-fp per milligram of DOC) after biodegradation of wastewater effluent. Cipparone *et al.* (1997) studied the combination of ozone and granular activated carbon (functioning as a biofilm substrate as well as an adsorbent) for the removal of DOC. They found that, although the combined treatment produced an enhancement of the biodegradability of the NOM, the reactivity with chlorine was lower due to the character of the NOM. As a consequence, the chlorine residual was maintained much longer in the distribution system, ameliorating the effects of the higher concentration of biodegradable DOC.

The susceptibility of NOM to biological removal will depend on the preferred food source of the particular micro-organisms. Elements of NOM that have been found to be readily biodegradable include: proteins (Namour and Muller 1998, Drewes and Jekel 1998), carbohydrates (Volk *et al.* 1997, Drewes and Jekel 1998, Agbekodo and Legube 1995, Gremm and Kaplan 1998) amino acids (Namour and Muller 1998, Volk *et al.* 1997, Agbekodo and Legube 1995, Prevost *et al.* 1998), carboxylic acids (Drewes and Jekel 1998, Agbekodo and Legube 1995, Carlson and Amy 1997), aldehydes and ketones (Agbekodo and Legube 1995, Carlson and Amy 1997, Siddiqui *et al.* 1997), humic substances (Volk *et al.* 1997), non-humic substances (Gremm and Kaplan 1998) and phenolics (Almendros and Dorado 1999). Presumably, if a larger molecule contained a moiety with these characteristics within its structure, enzyme hydrolysis could render that portion small enough for biodegradation. Newcombe *et al.* (1997) found one high molecular weight ultrafiltration fraction of a NOM isolate (>30000), contained significant carbohydrate character, determined using ¹³C NMR, whereas the low molecular weight fraction had a more aliphatic and aromatic character. It could be expected that the latter would be more recalcitrant to biodegradation, and the authors proposed that the bulk of the low molecular weight compounds represented the non-assimilable products of biodegradation. In contrast, the high molecular weight NOM contained humic-bound carbohydrate elements, which could have been rendered biodegradable by enzyme hydrolysis. Several authors have postulated that the low molecular weight compounds in wastewater are more readily biodegradable than the high molecular weight compounds (Westerhoff and Pinney 2000, Hesse and Frimmel 1999). Westerhoff and Pinney (2000) observed preferential removal of low molecular weight organic compounds in wastewater when their samples were applied to soil columns acting as both adsorbents and biofilters. In contrast, when the effluents from the soil columns were analysed for biodegradable dissolved organic carbon (BDOC) using a method similar to that described by Joret *et al.* (1991), the same method as used in this study, they found preferential removal of the high molecular weight compounds. Almendros and Dorado (1999) studied humic substances degrading in contact with soils and concluded that molecular size had the greatest effect on the early biological degradation stages, whereas the structural components had a greater effect on the advanced transformation stages.

For the work reported in this paper, the biodegradability of nine well-characterised NOM fractions was monitored using the biodegradable dissolved organic carbon (BDOC) method described by Joret *et al.* (1991). NOM was isolated from Hope Valley Reservoir South Australia, using anion exchange, XAD4 and DAX8 resins. These isolates were fractionated using ultrafiltration into fractions with nominal molecular weights < 500, 500-1000 and >30000. The assimilation of the NOM was monitored by DOC concentrations and the character of the NOM was investigated using high performance size exclusion chromatography (HPSEC) and UV absorbance. The aims of the work were:

- to determine the characteristics of the NOM contributing to the biodegradability and,
- by studying the changes in NOM character during biodegradation, to verify the conceptual model for the mechanism of biodegradation proposed by Confer and Logan (1998b).

2.4.2 Materials and methods

Materials

All solutions were prepared using deionised water from a Millipore MilliQ system (Millipore Pty Ltd, France) and filtered through 0.45 µm membranes (Supplier, Crown Scientific Australia). All glassware

was cleaned by immersion in 2M KOH for 1 hour, followed by rinsing in deionised water and drying at 105°C. Industrial dry air (Air Liquide, Adelaide) was used for the aeration of the BDOC samples.

The ultrafiltration membranes were Amicom Ym30, Ym01 and Yc05 (Supplier, Adela Scientific, Adelaide). These were the 30000, 1000 and 500 Dalton molecular weight cut-off membranes respectively. The Ym series of membranes are regenerated cellulose whereas the Yc05 is made from cellulose acetate. The UF vessels were constructed by the technical workshop of the University of Adelaide, Waite campus.

All chemicals were Analar grade (BDH, Sydney Australia). Solutions were made using deionised water from a Millipore Milli Q system (Millipore Pty Ltd, France).

Methods

NOM isolation and fractionation

Fractionated NOM isolates of Hope Valley Reservoir water were used in this study. Three resins were used for NOM isolation: DAX 8 (Supplier, Supelco Australia, Sydney), XAD 4 (Supplier, Supelco Australia, Sydney), and MIEX[®] DOC resin (SCO1, Orica Pty. Ltd, Melbourne). DAX 8 and XAD 4 resins were cleaned using the method developed by Standley and Kaplan (1995). The resins were then loaded into separate glass columns of 50 mm internal diameter and were used in series. Hope Valley Reservoir water, adjusted to pH 2 with HCl, was pumped through the columns, this was followed by elution of the sorbed NOM with 0.1 M NaOH. The NaOH solution containing concentrated NOM was immediately passed through a cation exchange resin for the neutralisation of the solution and removal of Na⁺ ions. The procedure was based on the work of Croué *et al.* (2000) and is described in detail in Hepplewhite (2000). This process yielded two isolates, D8, from the DAX 8 resin, and X4, from the XAD 4 resin. The MIEX[®] DOC anion exchange resin was packed in a glass column and cleaned using 2 empty bed volumes (EBV) of 2 M NaCl followed by 2 EBV of 0.2M NaOH and rinsed with deionised water. Hope Valley Reservoir water was then pumped through the resin at an empty bed contact time of 15 minutes. The NOM was eluted from the resin using 2M NaCl. Details of the desalting procedure for the MIEX isolate are given in Hepplewhite (2000) and Newcombe *et al.* (1997). This procedure produced the MX isolate. The three isolates were then fractionated using ultrafiltration membranes used in series. The ultrafiltration fractions used for this study were the <500, 500 to 1000, and >30000 fractions. These molecular weights are based on the membrane nominal molecular weight cut-off values, which have been shown to overestimate the actual molecular weight distributions of NOM (Newcombe *et al.* 1997b). Hereafter the fractions will be referred to as F1, F2 and F5 respectively.

A detailed description of all isolation and fractionation procedures is given in Hepplewhite (2000).

Table 2.5 gives the names and the descriptions of the fractions used throughout this paper.

Table 2.5 Description of NOM fractions used for the BDOC analysis

NOM fraction	Isolation technique	Membrane fraction
MXF1	anion exchange resin	<500
MXF2	anion exchange resin	500-1000
MXF5	anion exchange resin	>30000
D8F1	DAX8 resin	<500
D8F2	DAX8 resin	500-1000
D8F5	DAX8 resin	>30000
X4F1	XAD4 resin	<500
X4F2	XAD4 resin	500-1000
X4F5	XAD4 resin	>30000

Biodegradable organic carbon analysis

The method was based on that of Joret *et al.* (1991) Filter sand was collected from the Morgan Water Filtration Plant in South Australia. The Morgan plant was chosen as there was no chlorination prior to filtration, as chlorine would have restricted the development of the biofilm. The biologically active sand

(BAS), was then rinsed using a back washing method. A large flat Buchner funnel was two thirds filled with sand and deionised water was pumped up through the BAS bed. With gentle stirring of the fluidised bed, this method was sufficient to remove the coagulated NOM but not the biofilms attached to the sand. Flow was stopped periodically and any anthracite, used as an inert filter capping material, which had been brought to the surface of the sand was removed.

Two litres of the MX, D8 and X4 F1, F2 and F5 fractions were prepared at a DOC concentration of 10 mgL^{-1} and an ionic strength of 0.01 M NaCl . 300 gram of drained sand was added to each sample flask and 800 mL of the NOM sample was added slowly to prevent disturbing the sand. Aeration (4 L/hour) through a cindered glass sparger provided oxygen for biodegradation. Samples were taken at regular intervals for DOC, UV absorbance and molecular weight distribution analysis. Each BDOC analysis was undertaken in duplicate and results were within $\pm 0.5 \text{ mgL}^{-1} \text{ DOC}$.

Dissolved organic carbon - concentration and character analysis

After $0.45 \mu\text{m}$ filtration of each sample, the DOC and UV absorbance were measured. Measurement of UV absorbance was carried out on a GBC UV/VIS 918 Spectrometer zeroed using deionised water from a Millipore MilliQ system (Millipore, France). DOCs were measured using a Seivers 820 Total Organic Carbon Analyser. The high performance size exclusion chromatography (HPSEC) analysis was based on the method used by Chin *et al.* (1994). The column (Shodex Protein KW-802.5, molecular weight range $0.1\text{K}-50\text{K}$, Waters Australia) was calibrated using polystyrene sulphonates of molecular weight 35K, 18K, 8K, 4.6K and acetone. These compounds are considered to best represent the structure and conformation of NOM in solution. Ultraviolet absorbance at 260 nm was used for detection. ^{13}C NMR and elemental analysis techniques are described in Hepplewhite (2000).

2.4.3 Results and discussion

NOM characterisation

The isolation/fractionation procedure resulted in 9 fractions with quite different properties. Tables 2 and 3 give some indication of the significant differences in character between the fractions. Specific UV absorbance at 254 nm (SUVA) is considered to relate to the degree of aromaticity of the NOM (Croué *et al.* 2000), although such a relationship between SUVA and aromaticity, measured by ^{13}C NMR, is not indicated with these fractions ($R=0.58$, $P=0.1$). Neither is there a relationship between SUVA and molecular weight (average or peak molecular weight). Specific colour gives a good indication of the degree of conjugation of the NOM, and generally increases with molecular weight ($R=0.85$, $P=0.004$). Newcombe *et al.* (1997a) studied ultrafiltration fractions of MIEX resin and found two significant trends, increasing percent aromatic carbon and a decreasing ratio of O-alkyl to alkyl carbon (measured by ^{13}C NMR) with decreasing molecular weight. The authors postulated that the higher molecular weight fractions contained more carbohydrate-type moieties and should therefore be more biodegradable. The F5 fractions of the three isolates studied here all have higher O-alkyl to alkyl ratios than the lower molecular weight fractions, and all spectra display an anomeric carbon peak, indicative of polysaccharides (Hejzlar *et al.* 1994).

Table 2.6 NOM fraction characteristics determined by UV-visible absorbance, ^{13}C NMR and HPSEC

NOM fraction	Specific UV absorbance (254 nm)	Specific colour (HU)	Aromaticity	O-alkyl:alkyl	Molecular weight (peak)
MXF1	4.1	4.4	20	1	1209
MXF2	3.6	2.9	16	1.1	1148
MXF5	4.2	7.7	11	2.3*	1752
D8F1	4.1	4.5	22	0.7	1130
D8F2	4.3	4.6	16	0.6	1207
D8F5	5.1	11.4	19	1.3*	1808
X4F1	2.6	1.1	13	1.0*	973
X4F2	2.7	1.5	11	0.8*	942
X4F5	3.5	3.3	12	1.5*	1572

* presence of anomeric peak in spectrum, indicative of polysaccharides (Hejzlar *et al.* 1994)

Table 2.7 N:C elemental ratios determined without ash content and percentage of NOM <1000

NOM fraction	N:C	% NOM <1000
MXF1	0.02	23
MXF2	0.05	31
MXF5	0.06	5
D8F1	0.01	34
D8F2	0.02	31
D8F5	0.04	8
X4F1	0.03	45
X4F2	0.04	41
X4F5	0.12	8

Proteins, amino acids and other N containing NOM have been shown to be easily biodegradable (Namour and Muller 1998, Volk *et al.* 1997, Agbekodo and Legube 1995, Prevost *et al.* 1998). Results in Table 3 show none of the fractions are enriched in nitrogen, although the X4 fractions generally have higher overall nitrogen content.

Figure 2.11 shows the molecular weight distributions of the three X4 fractions. The fractions of the other isolates show similar trends. As mentioned in the previous section, the molecular weights do not correspond to the ultrafiltration membrane cut-off values. However, X4F5 has a significantly higher concentration of UV absorbing compounds in the high molecular weight region than the other two fractions. F1 and F2 have a similar distribution, with the main difference seen in the ratio of compounds represented by the peaks and shoulders in the molecular weight region 200-1000. If size were the main factor influencing biodegradability, it could be expected that the fractions with the greatest percentage of compounds <1000 would display the greatest biodegradability. The percentage of each fraction with molecular weight <1000 is also given in Table 3. These values were calculated by dividing the total area under the chromatograms by the area up to 1000 apparent molecular weight. For all isolates F1 and F2 have significantly more NOM <1000.

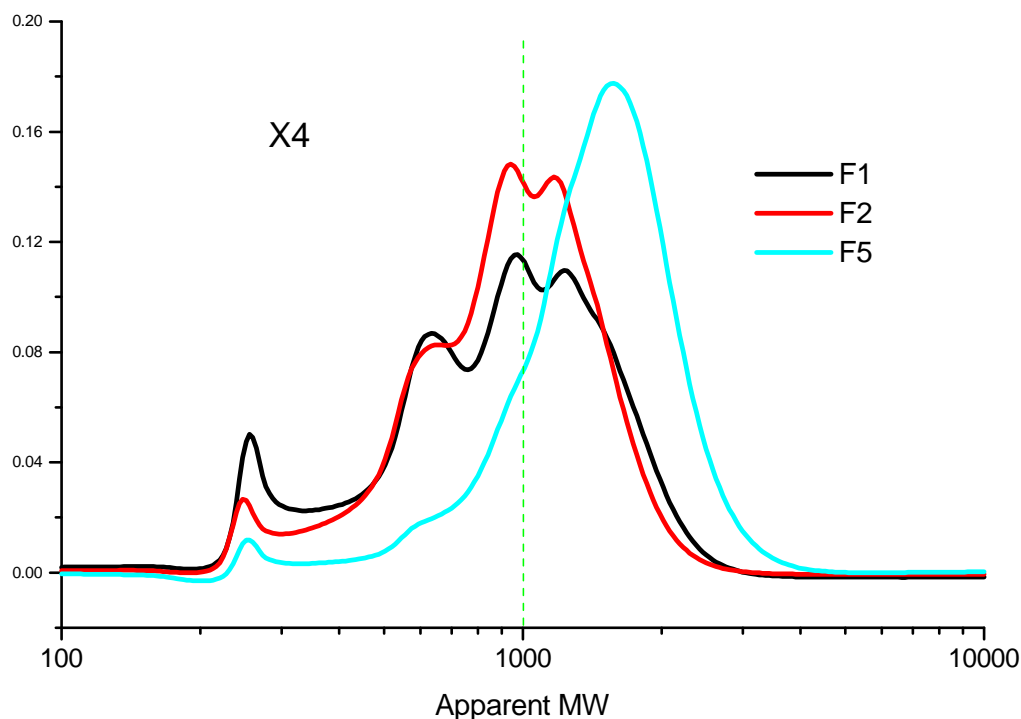


Figure 2.11 HPSE chromatograms of the X4 fractions

Discussion of the character of the isolates would not be complete without information on the compounds that were not isolated by the resins. Figure 2.12 shows the molecular weight distributions of the NOM contained in the effluent of each column. The MIEX resin preferentially isolates the larger molecular weight compounds and is not very effective for the very low molecular weight compounds. DAX 8 and XAD 4 are more effective for the isolation of the very low molecular weight compounds (up to 500 Dalton) than the MIEX; however, they do not isolate some compounds around molecular weight 1000. Compounds that are not isolated by a combination of these DAX 8 and XAD 4 resins are described as hydrophilic NOM and have been studied in detail by Croué *et al.* (2000). They found that the hydrophilic fractions of a Suwannee River isolate displayed higher carboxylic acid and carbohydrate character, with higher proportions of O, N and H.

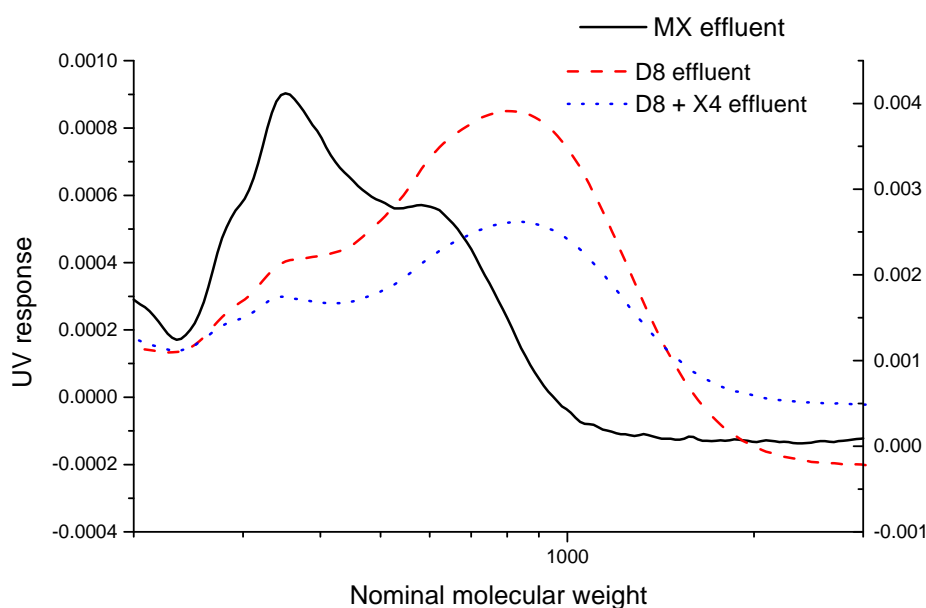


Figure 2.12 HPSE chromatograms of effluents from MIEX, DAX 8 and XAD 4 resins

Filter sand

Scanning electron micrographs of the filter sand from Morgan water filtration plant revealed a good diversity of micro-organisms. Diversity within the microbial community is important for the synergistic effects necessary for effective biodegradation of NOM (Confer and Logan 1997a, 1997b). Micro-organisms appear to be present in semi-isolated patches rather than a continuous smooth biofilm. However, the drying process for SEM analysis was harsh and could have resulted in the destruction, or damage to the extracellular polysaccharide material expected to make up a major part of the biofilm.

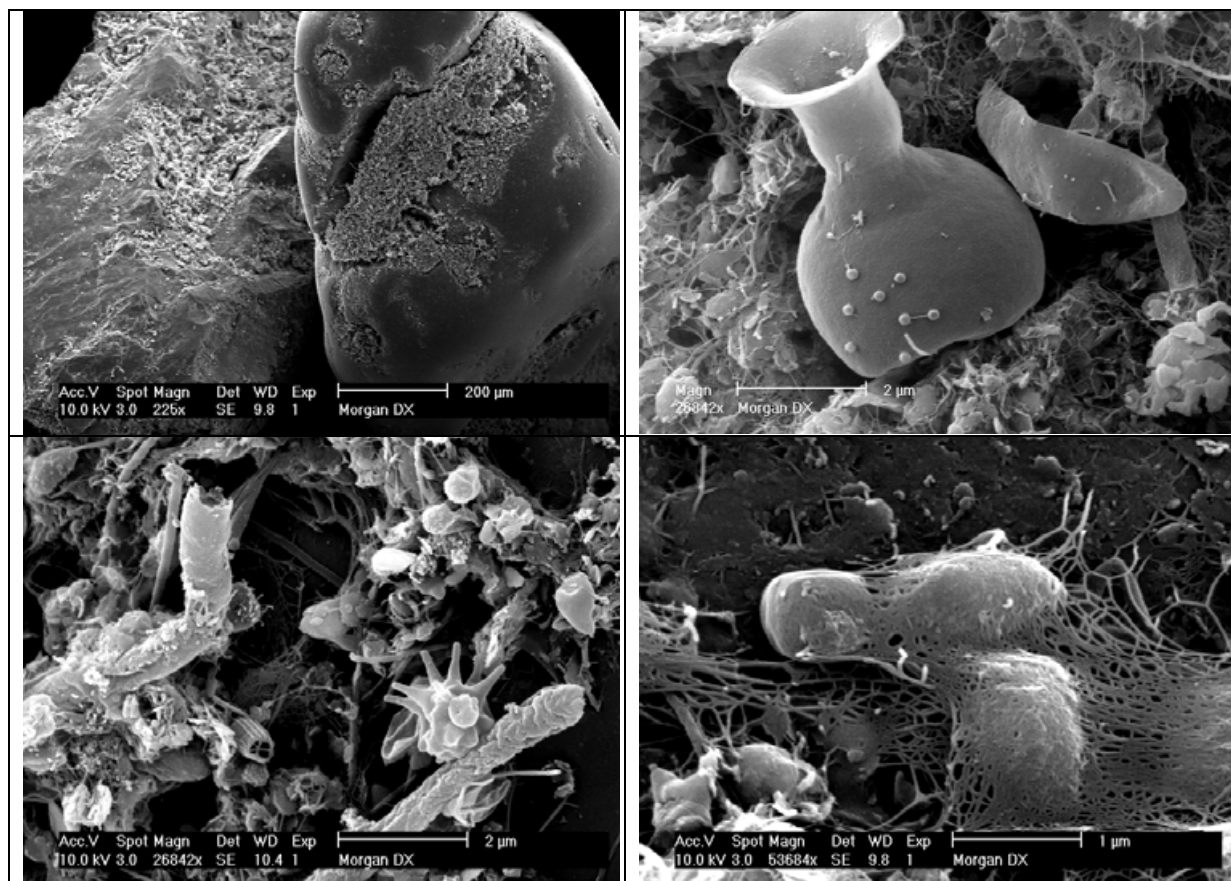


Figure 2.13 Scanning electron micrographs of Morgan treatment plant filter sand

Biodegradable organic carbon analysis

Assimilation of dissolved organic carbon

Figure 2.14 shows the DOC concentration as a function of time, results are the average of duplicate samples. All fractions show a strong decrease from the first sample, and considerable variation in rate of DOC assimilation with time. Only the MXF1 and F2 samples (and duplicates) showed a significant release of DOC during the trial. The cause of this release may be the death of some of the organisms on depletion of the easily assimilable food source. A similar effect was described by Siddiqui *et al.* (1997) in their study of biodegradation of ozonated NOM on a plug-flow bioreactor. They found that DOC reached a minimum after 48-75 hrs then increased before decreasing to prior levels within 24 hrs. This was attributed to the initial high growth of biomass with the presence of easily biodegradable material, then a decrease, then again an increase with further acclimatisation of the micro-organisms with time. The MX fractions also reverted to showing a net assimilation of DOC after several days. The other fractions continued to show a decrease in DOC for the duration of the trials, with X4F5 showing a significant reduction in the rate of assimilation after 15 days, with only a small decrease in DOC over the following 13 days. Large differences between fractions F1/F2 and F5 of each isolate would have been expected if the concentration of compounds <1000 was the major influence on the biodegradability. Such large differences are not apparent in Figure 2.14. BDOCs are compared at 8 days (BDOC₈), prior to the release of DOC shown by the MX samples, in Figure 2.15.

OPTIMISATION OF ADSORPTION PROCESSES

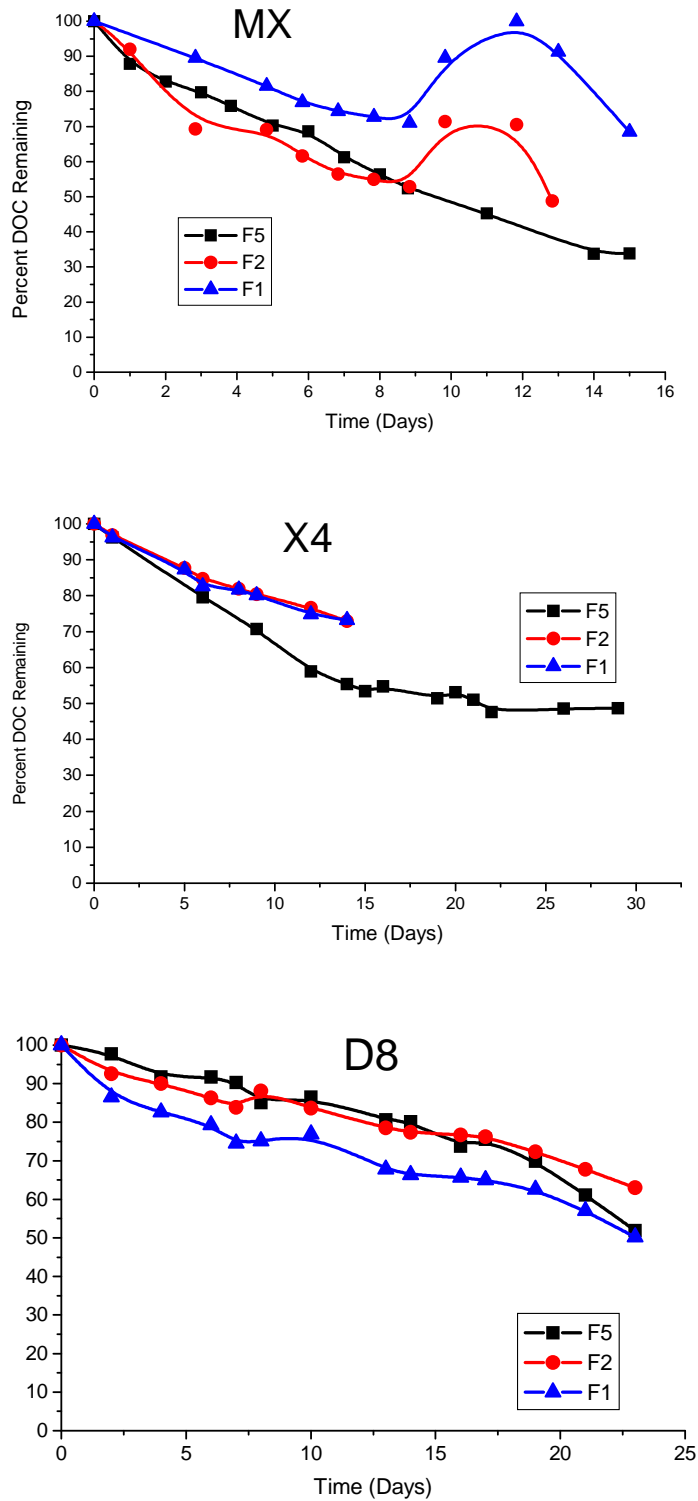


Figure 2.14 DOC concentration vs. time

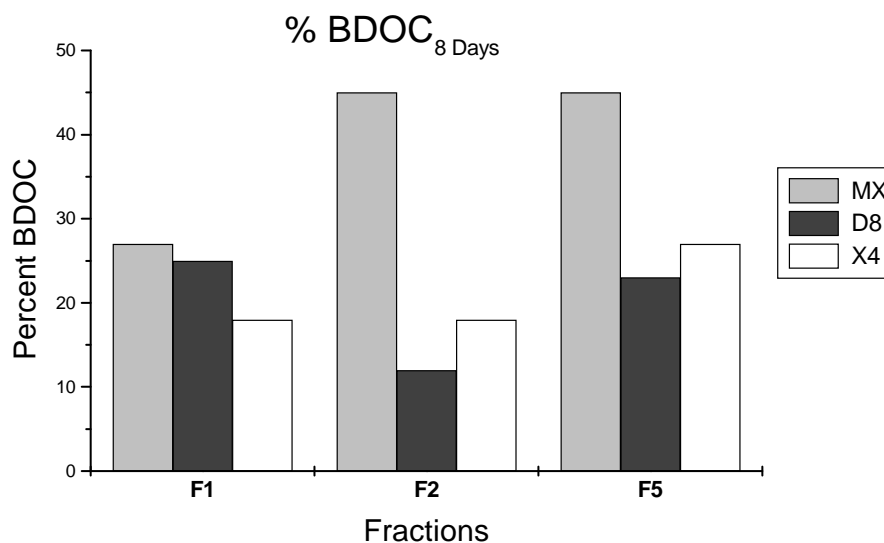


Figure 2.15 Percent BDOC of each NOM fraction at 8 days (%BDOC₈)

The two MX fractions, F2 and F5 have significantly higher BDOC₈ than any other sample. This cannot readily be related to any of the characterisation data. However, if the data are plotted as O alkyl:alkyl ratio vs. BDOC₈ in the absence of the MXF2 fraction a weak trend can be seen (Figure 2.16). As all samples are still in the biodegradation process at 8 days, and the rates of assimilation continued to change, it is not possible to extrapolate such a relationship to longer, or shorter degradation times.

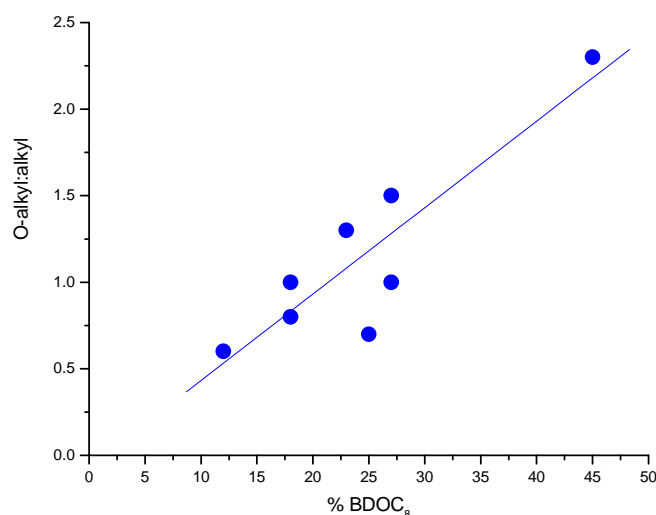


Figure 2.16 O alkyl :alkyl ratio vs. BDOC₈

Namour and Muller (1998) found that the most readily biodegradable compounds were those not isolated by the DAX 8 resin. It is possible that the compounds not adsorbed onto the XAD 4 and DAX 8 resins due to particular characteristics – as discussed in the previous section, are highly biodegradable. This may explain why the MXF2 and MXF5 were significantly more biodegradable over the first 8 days than the D8 or X4 isolates. MXF1 would not contain any of these compounds as the lowest molecular weight MX fraction was concentrated and desalted using a mixed bed of DAX 8 and XAD 4 resins (described in Hepplewhite (2000)).

Changes in molecular weight and specific absorbance during biodegradation

All fractions showed a trend towards lower molecular weights and lower specific absorbance during biodegradation. For simplicity only the data relating to the D8 and X4 isolates will be discussed in this section. All discussion of molecular weight distribution relates only to the UV absorbing compounds detected at 260 nm; the analysis of molecular weight distributions by UV absorbance is known to underestimate the concentration of compounds in the low molecular weight region. There are compounds present in the NOM that cannot be detected by UV absorbance, and these may also be biodegradable. However, trends shown and discussed in this section are assumed to be valid for the majority of NOM in these fractions.

Figure 2.17 shows the transformation in the character of the NOM of the D8F2 fraction during biodegradation. There is a substantial decrease in the UV response at all molecular weights, as well as a shift in the peak molecular weight from 1221 initially to 821 after 23 days. The variation of molecular weight with biodegradation was investigated in more detail by plotting the UV response for several molecular weights, as a function of degradation time. The results for the X4 and D8 fractions are shown in Figure 2.18.

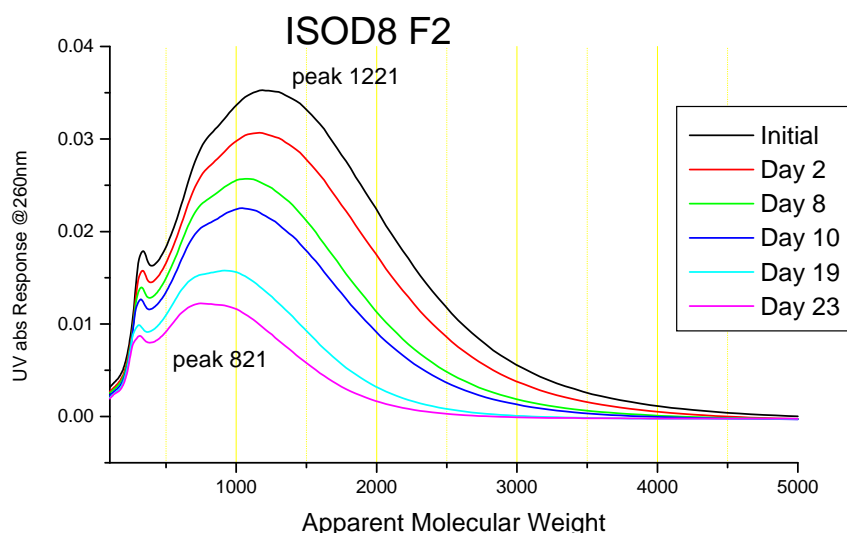


Figure 2.17 HPSE chromatograms of samples taken during the biodegradation of fraction D8F2

The X4 fractions show similar general trends. The lowest molecular weight studied, 600 Dalton, displayed the lowest extent and rate (indicated by the slope of the curve) of UV removal. The higher molecular weight compounds (>1200) showed greater extent and rate of removal than compounds <1200. This effect is significant in X4F5. Derivatives of the curves showed a reduction in the rate of removal around 10 days, then an increase (Figure 2.19). In particular, in X4F5, the high molecular weight compounds (>1600) continue to decrease significantly while the concentration of lower molecular weight compounds decreases to a lesser extent. During this period the DOC of the sample decreased only slightly (Figure 2.13). Trends are similar for the D8 fractions, with a preferential reduction of the high molecular weight compounds apparent in all fractions. In D8F1 and D8F2 the UV response at molecular weight 3000 had decreased to zero by 8 and 14 days respectively. It is likely that several mechanisms are operating simultaneously causing these effects, these will be discussed in detail in the following section.

The variation in specific UV absorbance with degradation of D8F5 is shown in Figure 2.20. A decrease in specific absorbance is seen at all wavelengths. While the absolute reduction in specific absorbance is highest for 254 nm, 400 nm showed the highest percentage decrease over the degradation period (71% for 400 nm and 57% for 254 nm). As the molecular weight of the fraction decreased over the degradation period it is perhaps not surprising that the specific absorbance was found to also decrease. Again, no relationship was found between specific absorbance and the average molecular

weights of the samples (M_w , M_n or M_{peak}) however, a very strong relationship was found between the specific absorbance at 254 nm and the UV response at molecular weight 1600 for all fractions, with the linear regression decreasing with decreasing molecular weight. The results for four fractions are shown in Figure 2.21. The decreasing specific absorbance (254 nm) with time is simply a reflection of the decrease in the concentration of the higher molecular weight compounds, but cannot be related to the average molecular weight.

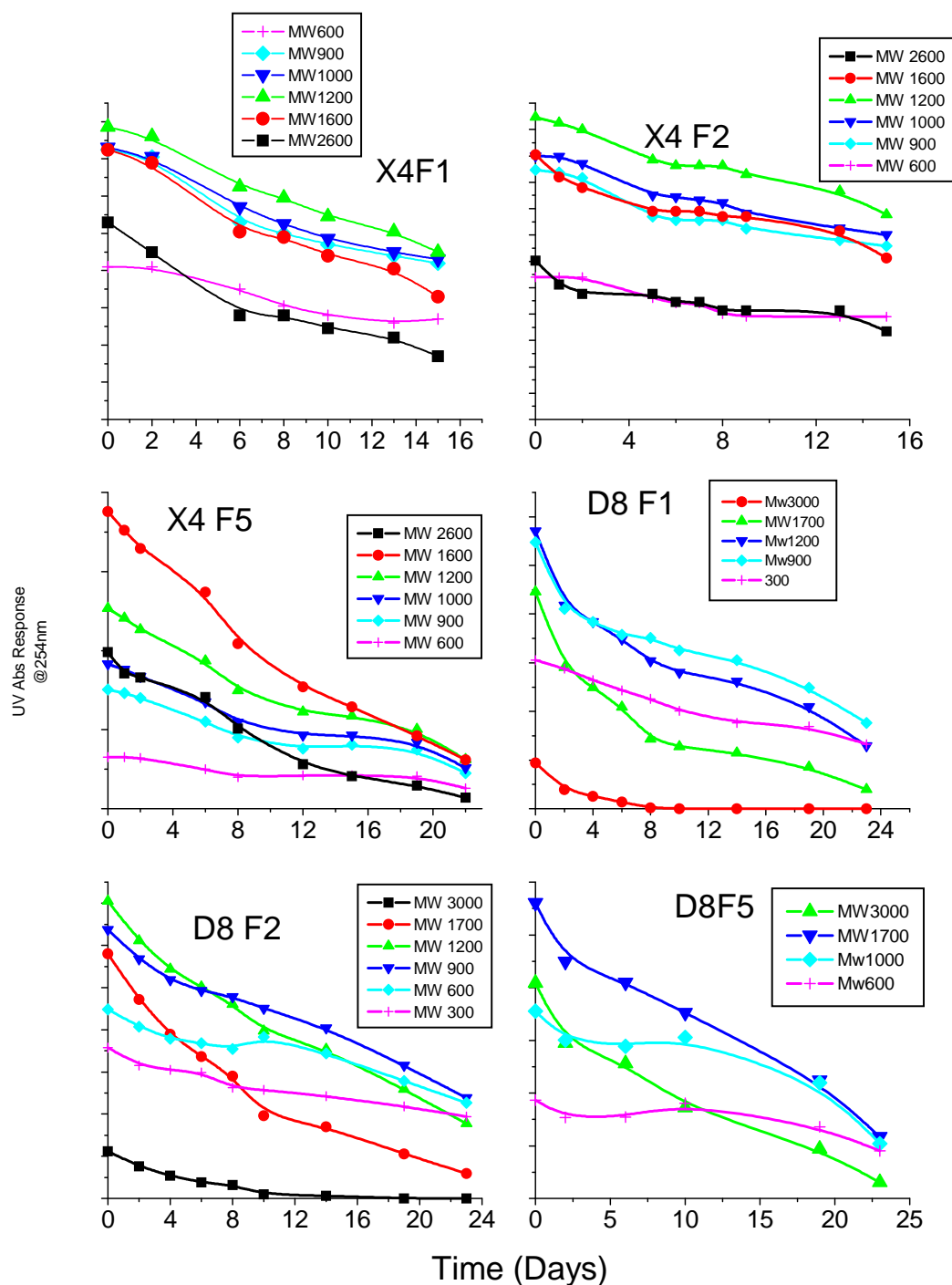


Figure 2.18 UV response (taken from HPSE chromatograms) at several molecular weights vs. degradation time, X4 and D8 fractions

OPTIMISATION OF ADSORPTION PROCESSES

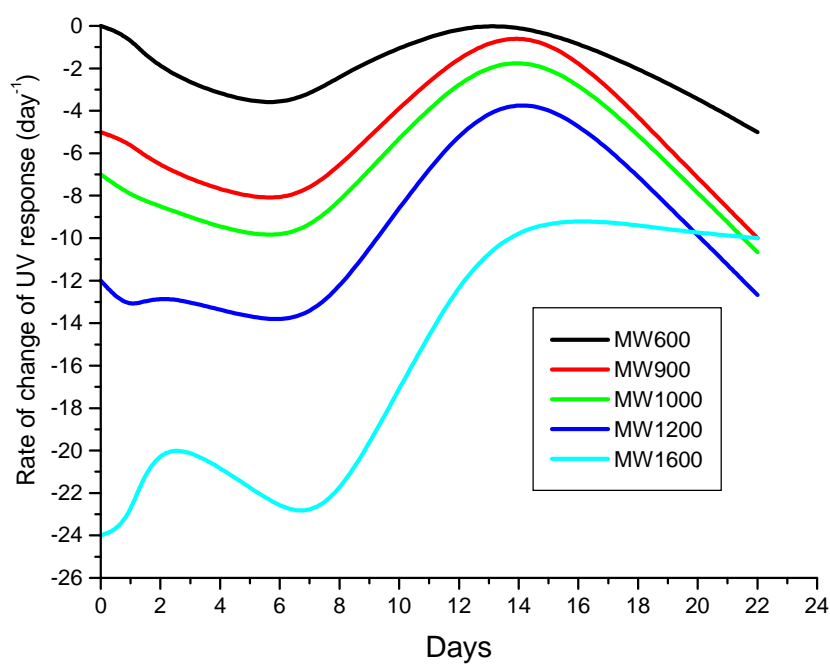


Figure 2.19 Derivative of the UV response vs time curve for X4F5

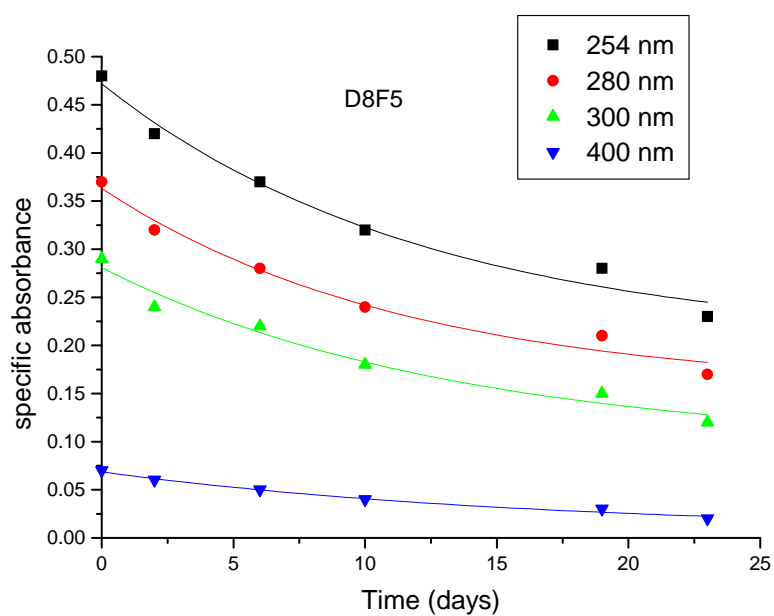


Figure 2.20 Specific absorbance, at several wavelengths, of D8F5 as a function of degradation time

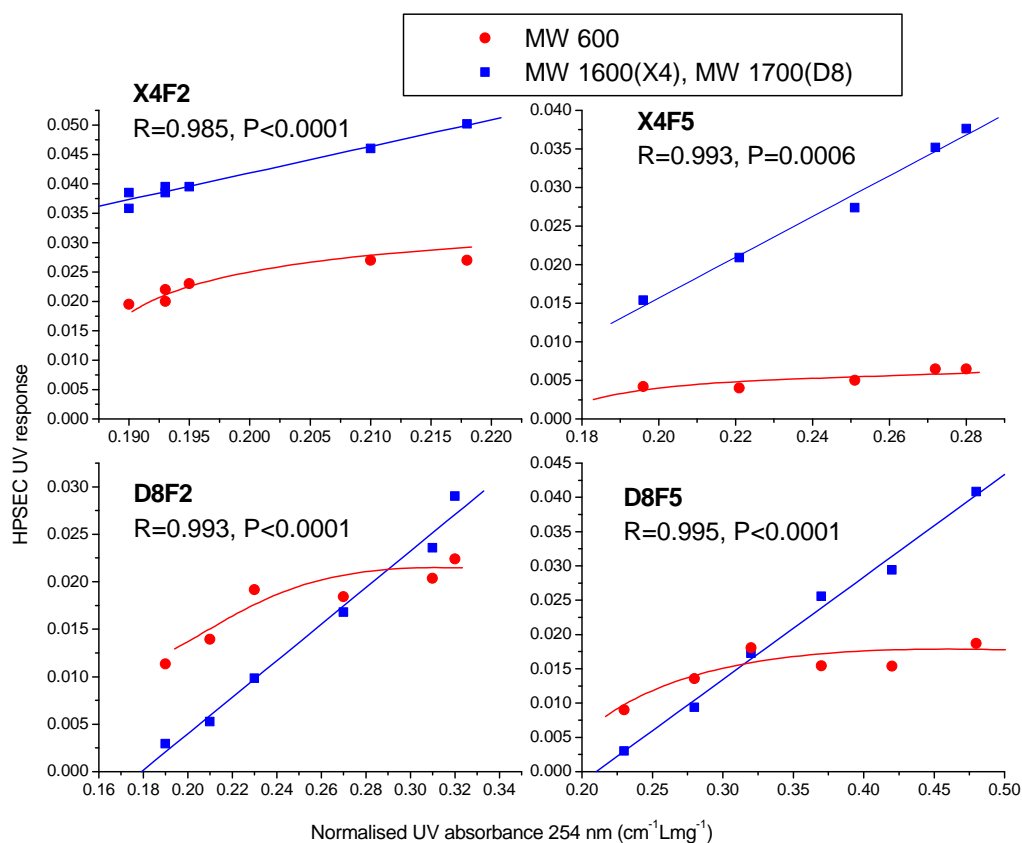


Figure 2.21 HPSEC response at 2 molecular weights vs. specific absorbance for four fractions

Discussion of conceptual model of Confer and Logan

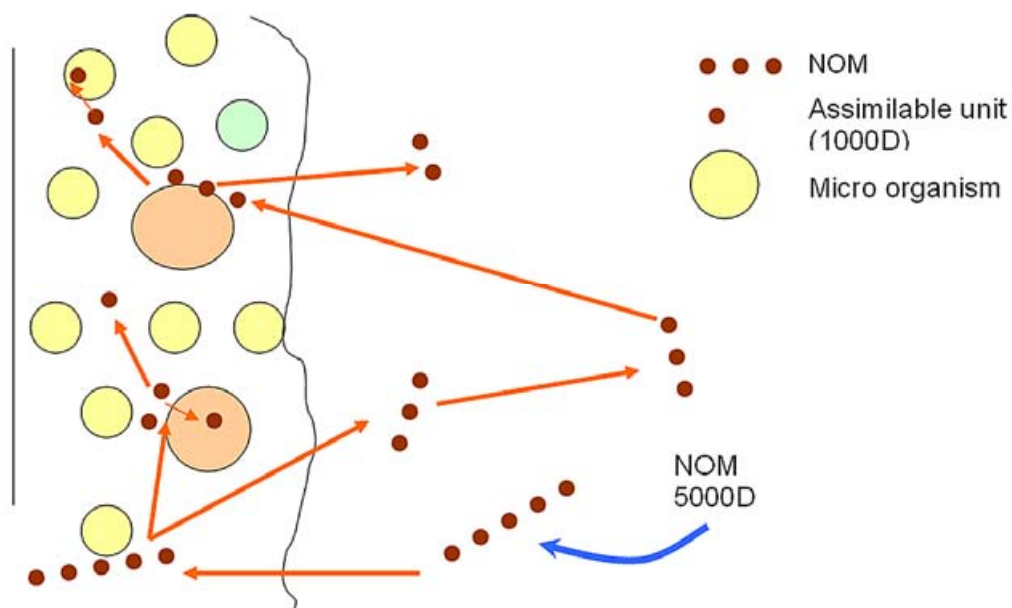


Figure 2.22 Conceptual model for the degradation of NOM as suggested by Confer and Logan (1997b)

OPTIMISATION OF ADSORPTION PROCESSES

As mentioned in the introduction, large organic molecules are not able to cross bacterial cell membranes, they must first be broken into smaller fragments. Confer and Logan suggested a conceptual model for the breakdown of large organic macromolecules (1998a, 1997a, 1997b) - a large molecule, 5000 or greater for example, must go through several fragmentations before compounds of the correct size are produced. As it is unlikely that one type of enzyme will produce a variety of cleavages, different sized fragments are likely to be released back into the solution before further cleavage by other enzymes attached to the same, or different, bacteria can occur. Figure 2.22 illustrates the type of processes that could take place during the assimilation and transformation of NOM. The proposed steps during assimilation are provided in point form below:

- A 5000 Dalton NOM molecule is fragmented at a cell wall; a 3000 (3 ka) compound is released back into solution and a 2000 (2 ka) compound remains in the biofilm
- 3 ka remains in the bulk solution for a period (up to several days)
- 2 ka is further hydrolysed at another cell into 1 ka and 1 kb, both 1000
- 1 ka is immediately taken into the cell
- 1 kb is released back into the biofilm
- 3 ka returns to the biofilm and is fragmented into 2 kb (2000) and 1 kc (1000)
- 2 kb is released back to solution
- 1 kc returns to the biofilm to be assimilated by another micro-organism.

If the compounds going through the biological transformation are of uniform molecular weight these processes would result in an accumulation of low molecular weight compounds in solution, as seen by Confer and Logan (1997a) in their study of model compounds. In the diverse system such as natural or isolated NOM from potable water sources, or wastewater NOM, a range of molecular weight compounds would be simultaneously entering the biofilm, some to be degraded to smaller molecular weight and some to be assimilated.

This model can be used to interpret the effects described in the previous sections during biodegradation of the NOM isolates. When the solution containing NOM first comes in contact with the filter sand, compounds of all molecular weights approach by diffusion and enter the biofilm. Some smaller molecular weight compounds remain and are assimilated. Other small compounds are recalcitrant and re-enter the bulk solution or are irreversibly absorbed within the biofilm. This would lead to a net decrease in DOC and increase in average molecular weight as the smallest compounds are assimilated. Simultaneously, the larger compounds are fragmented at the cell surfaces. Some fragments are small enough, and of the suitable structure, to be assimilated, while other fragments are released back into solution. This would result in a net decrease in DOC and decrease in molecular weight as the larger compounds are transformed into smaller ones. Overall this would result in a decrease in the concentration of high molecular weight compounds, while the concentration of low molecular weight compounds would decrease, due to assimilation, and increase, due to the release of fragments back into the bulk solution. The net effect in the low molecular weight region would depend on the relative rates and extents of the different processes, and these could change with time as the different micro-organisms become acclimatised to the changing substrate. For example, in the case of wastewater, where there has been minimal prior biodegradation, the low molecular weight compounds may be readily biodegradable, and the resulting solution would present an increase in average molecular weight and SUVA. NOM that had already undergone substantial biodegradation, as in most surface and groundwaters, would show some effect in the low molecular weight region, but the main effect would be in the biodegradable higher molecular weight region. While an oversimplification, this model provides a useful explanation for the character changes observed during the biodegradation of these NOM isolates.

2.4.4 Summary and conclusions

NOM was isolated from Hope Valley Reservoir South Australia, using anion exchange, XAD 4 and DAX 8 resins. These isolates were further fractionated using ultrafiltration into fractions with nominal molecular weights <500, 500-1000 and >30000. The nine fractions displayed a range of characteristics. Biodegradable dissolved organic carbon (BDOC) content did not follow any strong trend with the NOM characteristics expected to influence biodegradability such as carbohydrate content, nitrogen content, specific UV absorbance or molecular weight distribution. The significantly higher biodegradability of two of the anion exchange isolates may have been due to the hydrophilic compounds of molecular weight around 1000 preferentially isolated by that resin. Although the two

lowest molecular weight fractions of all isolates contained a high percentage of compounds in the range of molecular weights expected to be susceptible to biodegradation (<1000), these fractions did not show enhanced biodegradability. It is possible that these low molecular weight compounds themselves may have been the more recalcitrant products of prior biodegradation. The transformation of the NOM characteristics with biodegradation was followed using UV absorbance and high performance size exclusion chromatography. In all fractions the higher molecular weight compounds showed a decrease in concentration with biodegradation that was equal to or greater than the decrease in lower molecular weight compounds. This was attributed to a combination of the enzyme-induced hydrolytic fragmentation of NOM >1000 and the simultaneous assimilation of degradable compounds <1000. The significant decrease in specific absorbance at 254 nm with biodegradation for all fractions was caused by the decrease in the higher molecular weight NOM.

The changes in character observed during this study were a result of the character of the NOM, which in turn was a result of the prior degradation history. Organic material with little prior biodegradation (for example wastewater effluent) would show a preferential assimilation of the readily degradable low molecular weight compounds, leading to the opposite shift in character, i.e. to higher average and peak molecular weight and higher specific UV absorbance.

2.5 INVESTIGATION OF THE MECHANISMS CONTROLLING MOLECULAR WEIGHT ANALYSIS

2.5.1 Introduction

Molecular weight, or size distribution is one of the most important properties of NOM affecting treatment processes. Ultrafiltration (UF) and high performance size exclusion chromatography (HPSEC) are techniques commonly used for the determination of molecular weight of dissolved NOM; flow field flow fractionation (FIFFF) is a valuable method that is less commonly used. There are weaknesses associated with each of the techniques, and the best procedure for the molecular weight determination of NOM samples is to compare several methods. The techniques and their strengths and weaknesses are described below.

High performance size exclusion chromatography

High performance size exclusion chromatography (HPSEC) separates a mixture of compounds such as NOM on the basis of size. A HPSEC column contains porous material with a range of pore sizes corresponding to the range of compounds to be separated. The sample is injected into a mobile phase which carries it into the column at a certain flow rate. Only the smallest compounds are able to diffuse into all of the pores in the solid phase, the larger molecules will diffuse into some pores and be excluded from others. Theoretically, assuming no interaction between the solute and the solid phase, the largest compounds will elute first, as these will diffuse into fewer pores; the smallest compounds will diffuse into all of the pores and be consequently slower to elute. A UV detector is situated at the outlet of the column and the variation of intensity of the response with the elution volume is converted to concentration of UV absorbing NOM vs molecular weight, after suitable calibration. Figure 2.23 shows the basis of the technique.

Strengths: Ease of operation, relatively inexpensive

Weaknesses: Possibility of both attractive (dispersive or electrostatic interactions) and repulsive (electrostatic) interactions with the solid phase, sensitive to solution conditions

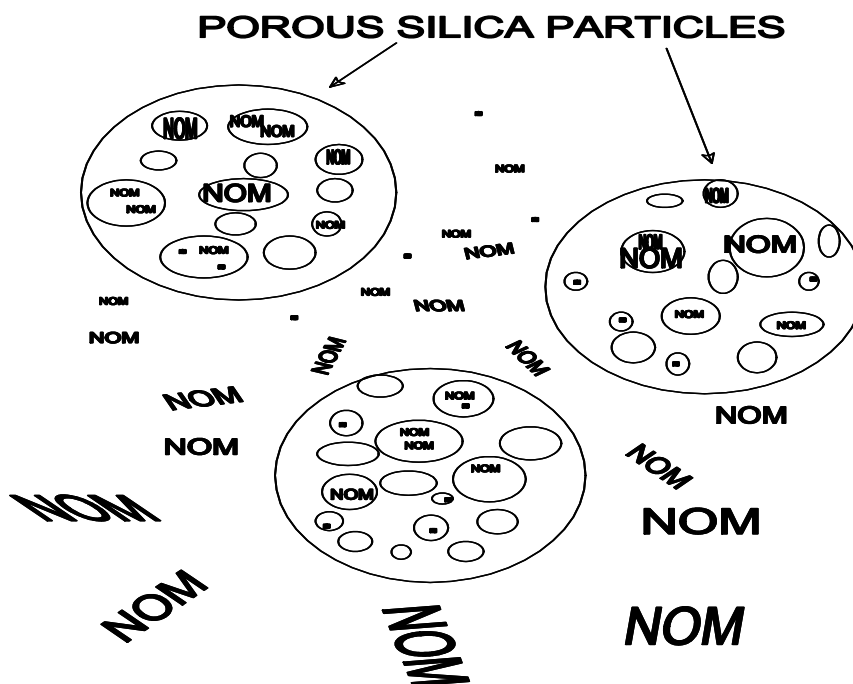


Figure 2.23 Representation of a HPSEC column

Flow field-flow fractionation

The technique of flow field flow fractionation (FIFFF) separates molecules of different molecular weight according to their diffusion coefficient. The solution is injected into a channel with porous upper and lower walls. There is a flow of mobile phase buffer solution along the channel and a cross flow in a perpendicular direction. The interaction of the channel flow profile with the dissolved compounds results in the compounds with a high diffusion coefficient (smaller molecular weight) travelling faster down the channel and eluting first. The eluant is analysed using UV detection, as with HPSEC. A diffusion co-efficient is calculated for the output, and a molecular weight can be calculated after calibration with suitable standard materials. A representation of the FIFFF channel is shown in Figure 2.24.

channel flow inlet

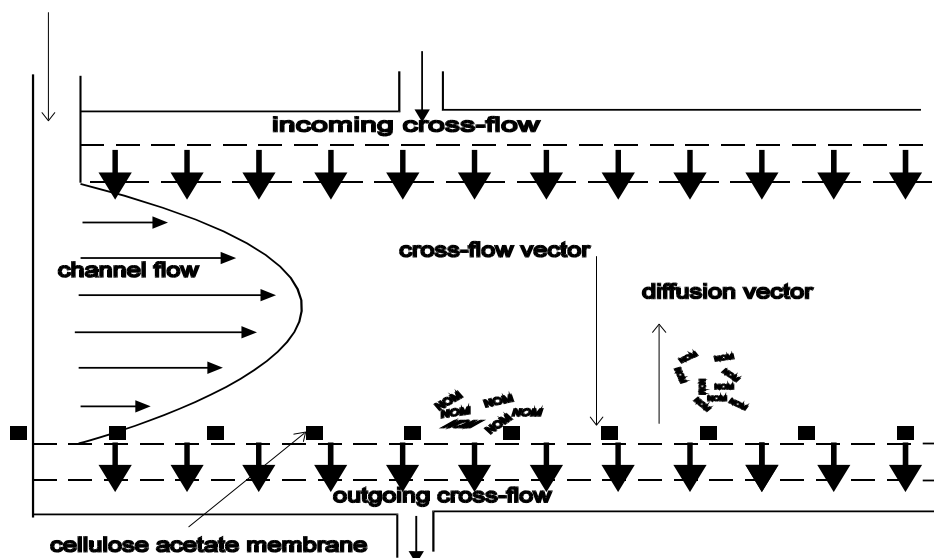


Figure 2.24 Representation of a flow field flow fractionation channel.

Strengths: Minimal possibility of solid phase interactions, gives a direct measurement of diffusion coefficient from which the hydrodynamic diameter can be determined, without the need of calibration

Weaknesses: Possibility of loss of analyte through the porous membrane, requires experienced operator

Ultrafiltration

Ultrafiltration is a pressure filtration technique using membranes of different nominal molecular weight cut-off values. The sample is generally stirred in a pressurised cell and the compounds of molecular weight smaller than the nominal membrane cut-off will permeate through the membrane. Any number of different membranes can be used, and a mass balance of DOC will give a molecular weight distribution. A representation of the usual ultrafiltration apparatus is given in Figure 2.25.

Strengths: Easy and quick to obtain results, no real training required

Weaknesses: Results depend strongly on calibration of membranes and solution conditions. Membranes have a wide distribution of pore sizes, so molecular weight cut-offs are not distinct.

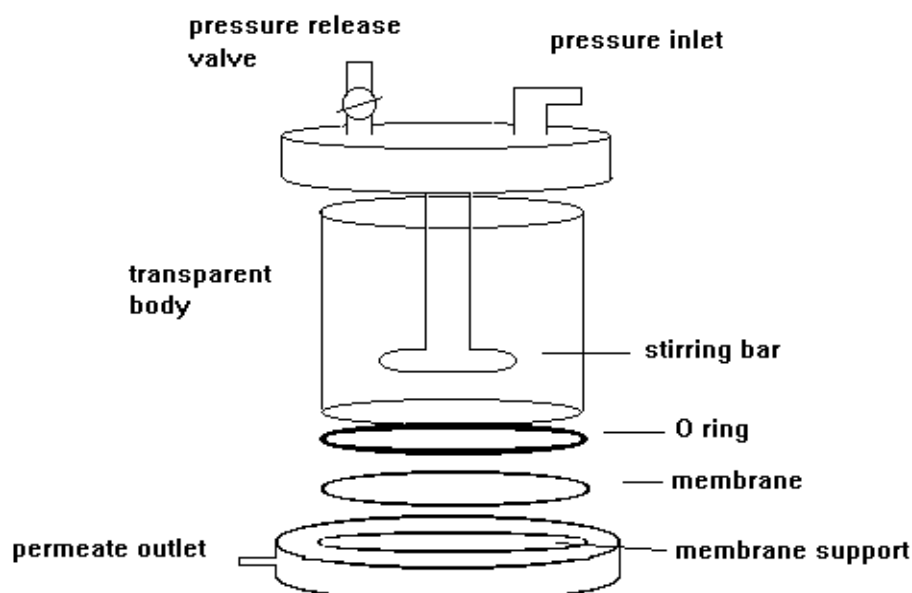


Figure 2.25 Representation of ultrafiltration apparatus

As both UF and HPSEC are size exclusion methods of fractionation the measured molecular weight depends strongly on factors such as conformation and structure (Buffle *et al.*, 1992). Consequently the compounds used to calibrate these techniques should be chosen to represent the “average” molecular structure of NOM, an extremely difficult task. According to Amicon literature (Laboratory Separation, Membrane filtration chromatography, Amicon publication number 716) compounds such as sucrose and raffinose are used to calibrate the lowest molecular weight ultrafiltration membranes, polysaccharides, antibiotic molecules and enzymes to characterise the mid-range molecular weight membranes, and globular proteins for the high molecular weight membranes. As dissolved NOM is known to have generally a high negative charge in solution, it is unlikely NOM will behave like globular proteins in solution (El-Rehaili and Weber, 1987; Reid *et al.*, 1990). They could be expected to have an extended configuration to allow more distance between the charged carboxyl groups at natural pH, whereas the globular proteins have a coiled configuration, displaying a smaller size per unit molecular weight. Therefore the molecular weight cut-off values determined using proteins as calibration standards would not be expected to relate to NOM retention on membranes. This effect was reported by Newcombe *et al.* (1997) and Assemi *et al.* (1998) who fractionated NOM isolates using UF and measured the molecular weight distributions using HPSEC and FIFFF. They found that the average molecular weight of the smaller fractions were approximately as expected, however the fractions

obtained using the 10000 and 30000 Dalton membranes (those calibrated using globular proteins) had a much lower molecular weight than that designated by the manufacturer. This work supported previous research by Aster *et al.* 1996, who found poor correlation between gel permeation chromatography and UF for larger molecular weight compounds, and Chin and Gschwend (1991) who studied the optimisation of the use of HPSEC. Chin and Gschwend (1991) calibrated their column with both globular proteins and polystyrene sulphonate (PSS) standards. They obtained two very different calibration curves; for example a globular protein of molecular weight 10000 Dalton eluted at a volume which corresponded to a molecular weight of 2000 using the PSS calibration curve; conversely, a PSS standard of molecular weight 4000 appeared to have a molecular weight of 16400 using the globular protein calibration curve. Aiken (1984) understood that the usual methods for calibration of ultrafiltration membranes were inappropriate for NOM fractionation; a fulvic acid with molecular weight of 1500, estimated by small angle X-ray scattering, was 76% retained on one type of membrane with a nominal molecular weight cut-off value of 10000. Beckett *et al.* (1987) correlated values of molecular weights of humic substances from the literature with results of FIFFF (calibrated using PSS standards) and concluded that PSS standards were more acceptable for the calibration of techniques for molecular weight analysis of NOM than globular proteins. In summary, most of the evidence indicates that polystyrene sulphonate molecules do not have the same configuration in solution as globular proteins, and that the former are more appropriate as standards for NOM analysis. As a result, the nominal molecular weight cut-off values given to UF membranes by manufacturers should not be taken as relevant to NOM fractionation/molecular weight determination.

Solution conditions which influence the size of large molecules, the extent of aggregation or solid-solute interactions, such as pH, ionic strength and concentration, will also influence the measured molecular weight of NOM samples (Kuchler and Miekeley, 1994; Ceccanti *et al.*, 1989). Solution conditions will have a pronounced effect on the way the compounds permeate a membrane (UF), enter into a pore of particular diameter (HPSEC), or diffuse in a buffer solution (FIFFF). Some compounds are known to physically interact with the surface of some HPSEC column porous material. Miles and Brezonik (1983) studied the molecular weight distributions of a range of humic materials using HPSEC and concluded that the presence of aromatic groups in the NOM resulted in adsorption and retarded elution, and therefore a lower measured molecular weight.

Charge can also play a part in molecular weight determination, for example, if the UF membrane is charged, some solutes of the same charge may not permeate easily. In addition, any adsorption of a charged solute onto the membrane will have the same effect as a charged membrane (Wershaw and Aiken, 1985; Buffle, *et al.*, 1992). An example of a repulsive electrostatic effect for UF was seen by Kuchler and Miekeley (1994), who found that an ultrafiltration membrane of nominal molecular weight 1000 retained a more highly charged fulvic acid in preference to a humic acid, although the humic acid had a higher molecular weight. UF membranes come in a range of molecular weight cut-off values, and the materials from which they are made vary depending on the manufacturer and the molecular weight cut-off. The interactions therefore will vary from membrane to membrane. Similarly, if there is some residual negative charge on the HPSEC solid phase there will be repulsion between the solid and solute (Miles and Brezonik, 1983; Becher *et al.*, 1985) and there may be a repulsive interaction between the membrane used in the FIFFF apparatus and the NOM (Hanson *et al.*, 1989). The shift in the measured molecular weight will be different for each of the techniques: retention of solutes due to charge will result in a higher measured UF molecular weight distribution, as will charge repulsion causing early elution in HPSEC, whereas any repulsive interaction between the membrane and the NOM in FIFFF will result in a lower molecular weight distribution. Conversely, a positively-charged compound will be attracted to a negatively-charged surface, for HPSEC and FIFFF this would result in a lower and higher molecular weight distribution respectively.

Minimisation of both electrostatic and non-electrostatic interactions in HPSEC has been the focus of a number of studies (Hongve, *et al.* 1996; Ceccanti *et al.*, 1989). Results from a comprehensive study by Chin *et al.* (1994) have been adopted by many workers as the optimum conditions for minimising electrostatic interactions by increasing ionic strength of the eluent, while ensuring there is no aggregation or adsorption of the NOM onto the solid surface. Recent work by Perminova *et al.* (1998) explored the artefacts associated with the use of HPSEC by examining a wide range of model compounds and humic substances. They concluded that both the hydrophobicity and the charge density of the analytes should be taken into account when interpreting data using the technique.

A number of studies have compared various molecular weight determination techniques. Beckett *et al.* (1987) compared results of their FIFFF molecular weight determinations on standard humic substances with published values obtained using VPO and small angle X-ray scattering. The agreement was excellent. Aiken (1984) compared UF of standard fulvic acid with results from small angle X-ray scattering and found poor agreement which he attributed to possible interactions with the UF membrane surface and calibration difficulties. Chin *et al.* (1994) found molecular weight distributions obtained using HPSEC compared favourably with previously published results of VPO and FIFFF determinations. Most of these comparative studies compare their results with those of other authors using standard fulvic and humic compounds. However, Peuravuori *et al.* (1998) used two techniques, VPO and HPSEC, on over twenty NOM isolate samples. They found poor agreement between the two techniques. Their HPSEC data were consistently higher than the VPO, as well as being higher than most recent work reported for NOM isolates. VPO data is influenced by impurities such as salts, perhaps explaining the lower than expected molar masses observed. In addition, the polydispersities of their HPSEC measurements (number average molecular weight divided by the weight average molecular weight) were much higher than seen previously in the literature. This inevitably leads to some doubt as to the confidence to be placed in those results.

The aim of the work presented in this section was to elucidate some of the interactions taking place during molecular weight determination, and to compare the advantages and disadvantages of each technique.

2.5.2 Materials and methods

Model compounds

Mellitic acid Pyromellitic acid Tetra hydrofuran tetracarboxylic acid 9,10-Anthroquinone-2,6-disulphonic acid Dibenzoil-I tartaric acid Glycyrrhic acid were obtained at reagent grade purity

NOM fractions

Prepared as described in section 2.3

HPSEC

The HPSEC was undertaken as described elsewhere (Pelekani *et al.* 1999) where there was no variation in pH and ionic strength. Where other solution conditions were required, both the sample and the mobile phase were prepared in those solution conditions of ionic strength and pH.

FIFFF

FIFFF was undertaken as described in Pelekani *et al.* 1999

UF

NOM samples (400 mL) were placed in the ultrafiltration vessel and filtered under pressure until 250 mL remained in the vessel as the retentate. This resulted in the first sample (permeate). The volume in the vessel was made up to 400 mL with Milli-Q water prepared to the appropriate ionic strength using NaCl, and filtered again until 250 mL remained. The permeate was sampled as rinse 1. This was repeated either once or twice more, depending on the DOC remaining in the permeate i.e., if there was negligible DOC in rinse 2 rinse 3 was not required.

2.5.4 Results and discussion

High performance size exclusion chromatography of model compounds under different solution conditions

In this work the aim was to determine the effect of varying pH and ionic strength on the apparent molecular weights of a range of low molecular weight compounds, in order to clarify the role of surface interactions in the measurement of MW using HPSEC. The first step in this investigation was to determine the effect of a change of solution conditions on the chromatograms of PSS standards used for calibration of the HPSEC column.

Figure 2.26 shows the HPSEC chromatograms of the range of PSS standards under the conditions usually used to measure the samples (pH 6.8, 0.1 M NaCl), and at elevated pH and ionic strength (pH 9 and 0.2 M NaCl). The chromatograms of the PSS standards, a mixture of the standards (PSSMIX) and an IHSS fulvic acid standard (Suwannee) showed no significant effect of the change in solution

conditions. Similar results were seen for pH 6.8 with no salt, and 0.2 M NaCl. As sulphonic acids are considered to be strong acids these compounds may be fully charged at both pH, resulting in no change in retention times with an increase in pH. The increase in added salt to 0.2 M NaCl resulted in no change in the retention times of the compounds. The buffer solution itself (0.02 M NaH_2PO_4) contributes an ionic strength of 0.1 M to the solution, an increase of 0.1 or 0.2 M did not change the electrostatic effects, if any were present. A further increase in ionic strength may have resulted in some shielding of any repulsive effects

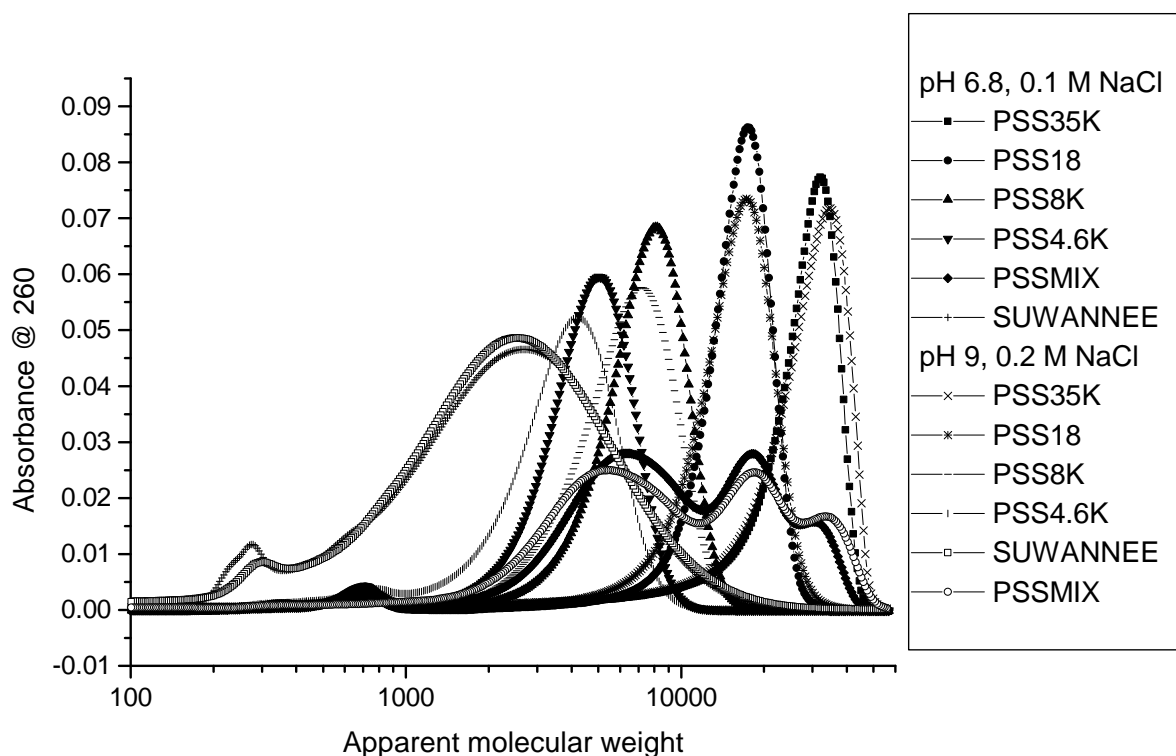


Figure 2.26 HPSE chromatograms of standards under different solution conditions

However, at lower pH, pH 4, there was a very strong effect of the solution conditions. None of the PSS standards eluted at this pH, indicating a very strong compound-surface interaction.

An effort was made to discover the pK_a s of the PSS standards. However, there appears to be a dearth of information in the literature. One paper used PSS standards at pH 2 for surfactant binding experiments and assumed that the polymers were still fully ionised (Neivandt *et al.* 1997). No evidence was given for this assumption. As mentioned previously, organic sulphonic acids are considered to be strongly acidic in the monomer form. However it is well established that polyelectrolytes show quite different charge behaviour, and the pK_a varies with the charge on the molecule. That is, it becomes more difficult to remove a hydrogen ion from the polyion as the charge on the ion increases (Nyman 1984). Nyman (1984) studied the pH titration behaviour of a range of lignins extracted from wood pulp, including lignosulphonate compounds, aromatic polymers with repeating sulphonic acids groups. She found that apparent pK_a values ranged from 4.5-5.8 as the fraction of ionised groups varied from 0.3 to 0.9. At lower degrees of ionisation the compounds precipitated. These results indicate that at pH 4 at least some of the sulphonic acids groups on the PSS standards are protonated, reducing the solubility of the compounds drastically, producing extremely hydrophobic compounds capable of interacting strongly with the column surface due to strong hydrophobic/dispersion interactions. This may also be an indication that at higher pH there was some electrostatic repulsion occurring between the surface and the PSS compounds that was not shielded by the increase in ionic strength.

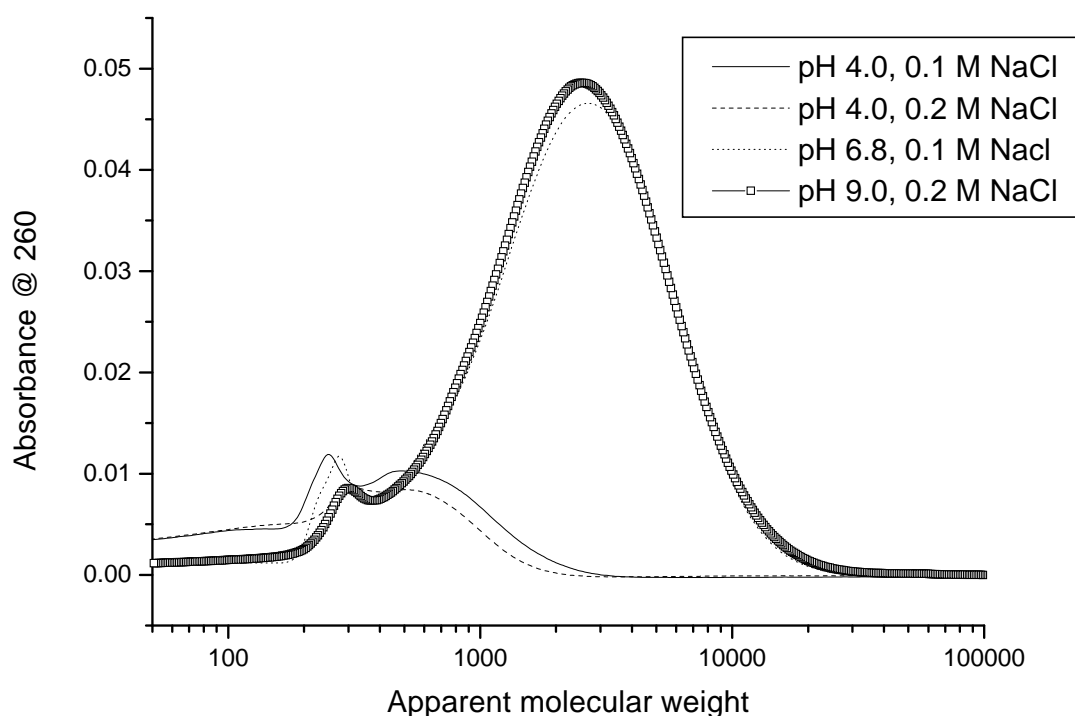
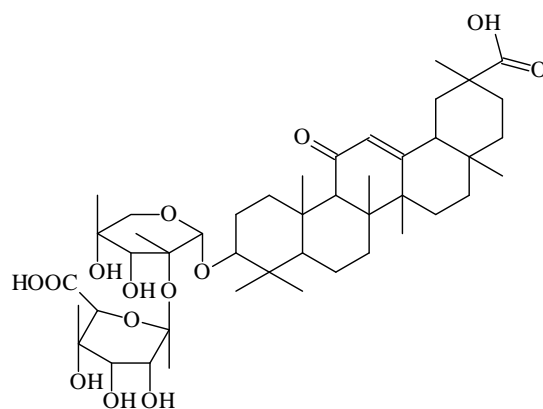


Figure 2.27 HPSEC chromatograms of Suwannee fulvic acid at pH 6.8 and 4

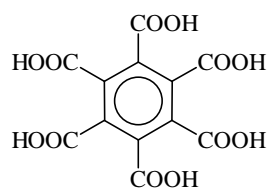
Figure 2.27 shows the effect of solution conditions on the elution of the Suwannee fulvic acid. As with the PSS standards, increasing pH from 6.8 to 9, and ionic strength to 0.2 M NaCl had no effect on the retention time of the Suwannee fulvic acid, indicating that electrostatic interaction with the surface is not an issue under these conditions. The lower apparent MW seen at pH 4 indicates a significantly longer retention time than at the higher pH, again indicating interaction with the HPSEC column surface. In this case some of the sample eluted, as the fulvic acid would not be expected to be fully protonated at pH 4 (Newcombe *et al.* 1997), and the fulvic acid is comprised of a wide range of compounds with a range of acidities.

Figure 2.28 shows the structures of the other model compounds chosen for this study. Pelekani *et al.* (1999) also investigated the interactions of these compounds on the HPSEC column under solution conditions usually utilised during the HPSEC analysis. In this study the work was extended to investigate the effect of variation of pH and ionic strength. Figures 2.29-2.34 and Table 2.8 show the results of these experiments.

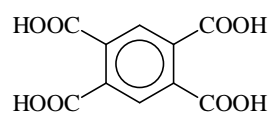
OPTIMISATION OF ADSORPTION PROCESSES



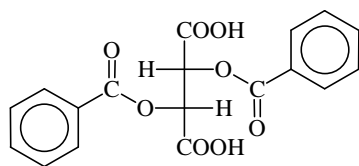
Glycyrrhizic Acid



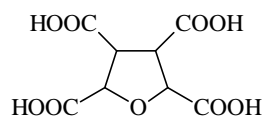
Mellitic Acid



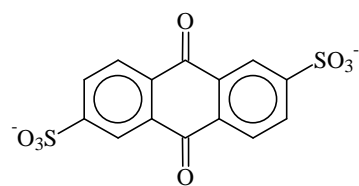
Pyromellitic Acid



(-) - O-O'-Dibenzoyl-L-Tartaric Acid



Tetrahydrofuran Tetracarboxylic Acid



9,10-Antraquinone-2,6-Disulfonic Acid

Figure 2.28 Molecular structures of model compounds

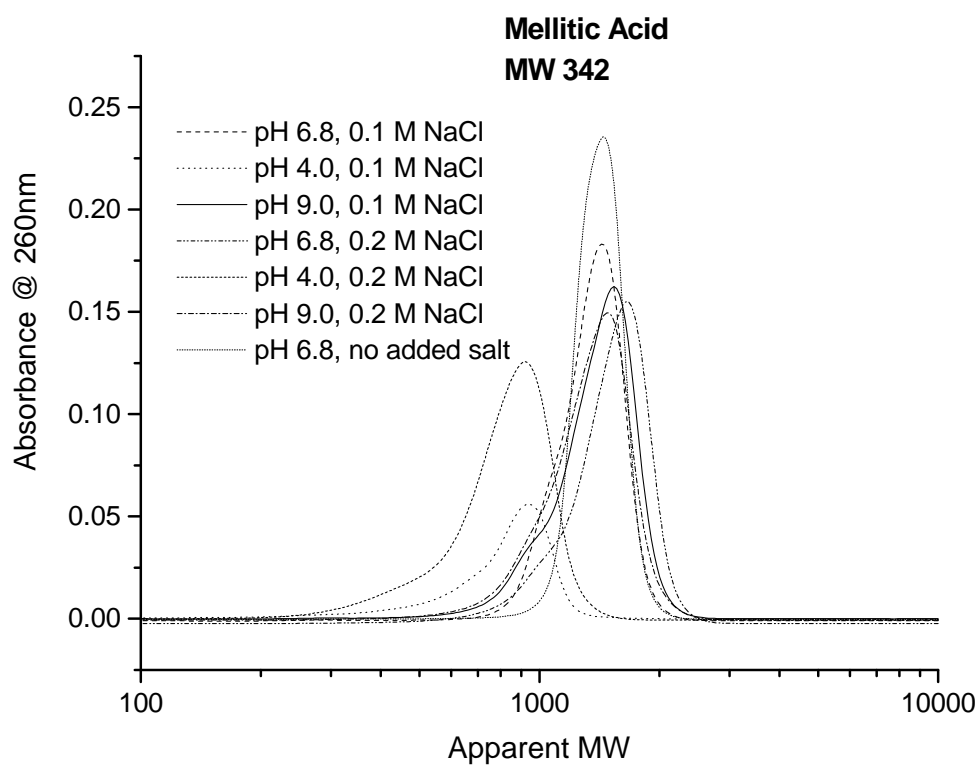


Figure 2.29 HPSE chromatograms of mellitic acid

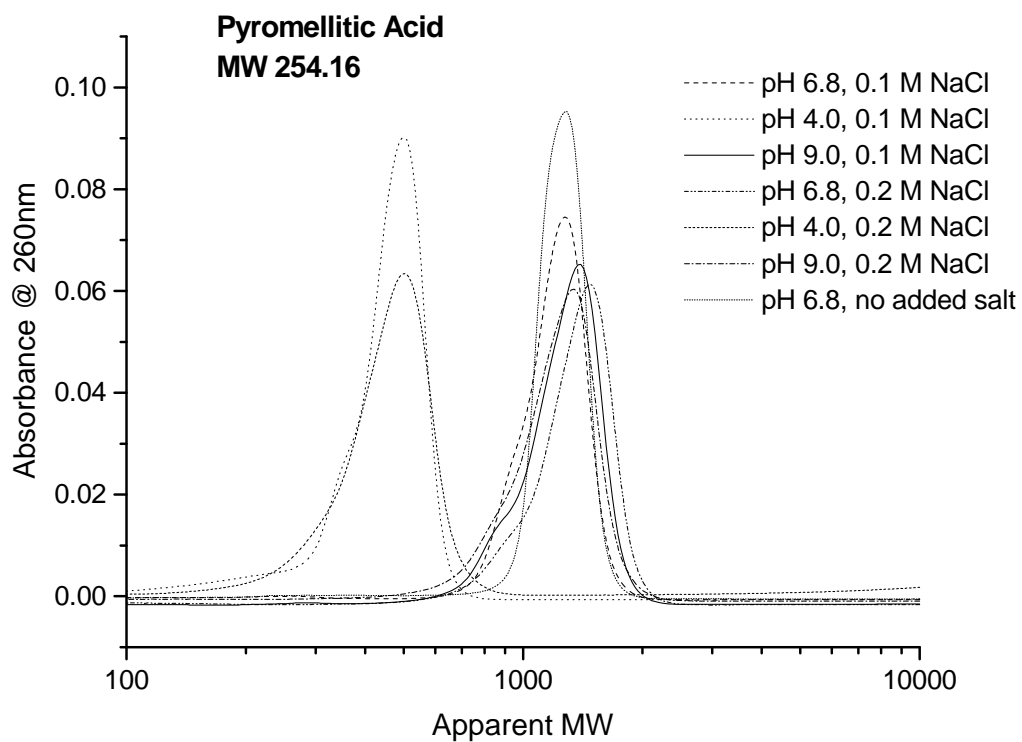


Figure 2.30 HPSE chromatograms of pyromellitic acid

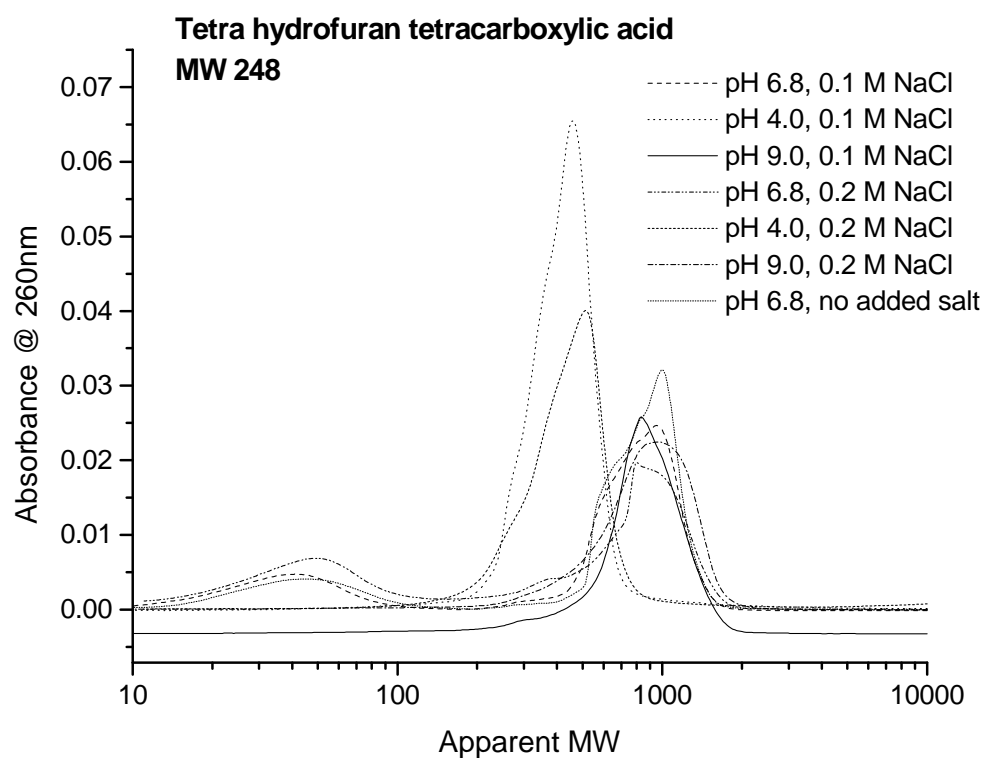


Figure 2.31 HPSE chromatograms of tetrahydrofuran, tetracarboxylic acid

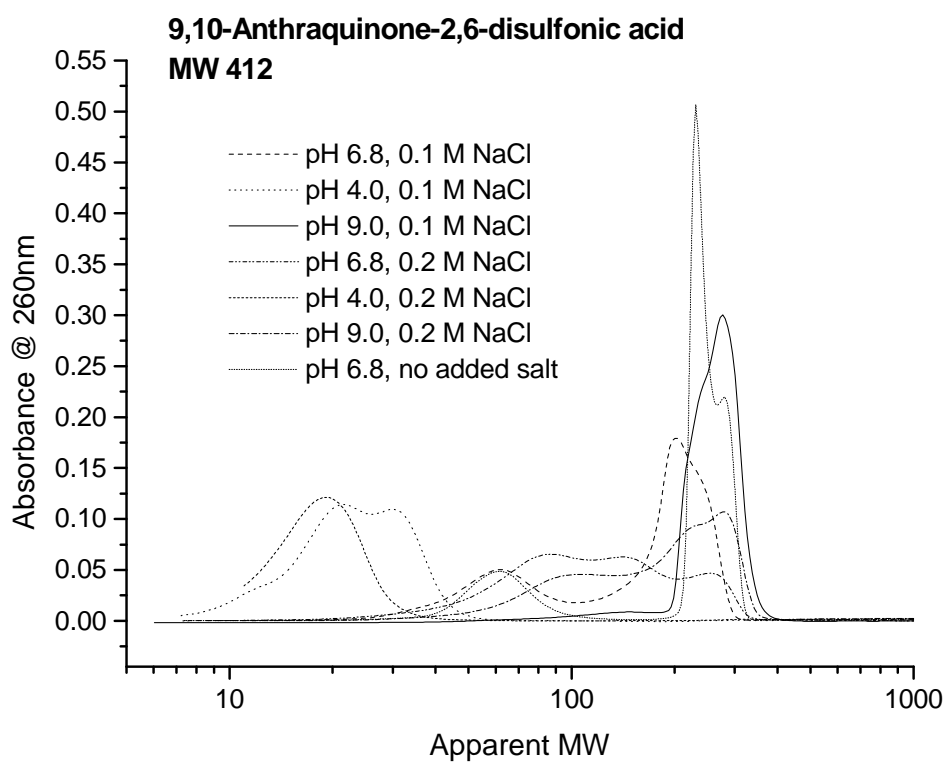


Figure 2.32 HPSE chromatograms of 9,10-anthraquinone-2,6-disulphonic acid

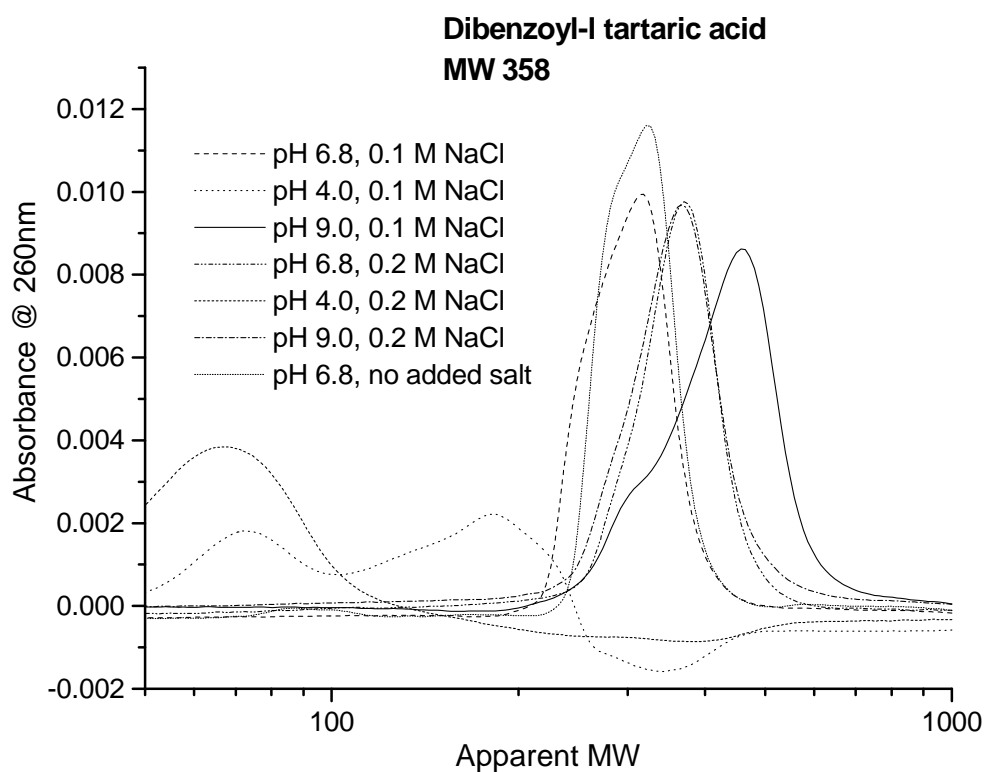


Figure 2.33 HPSE chromatograms of dibenzoyl-I tartaric acid

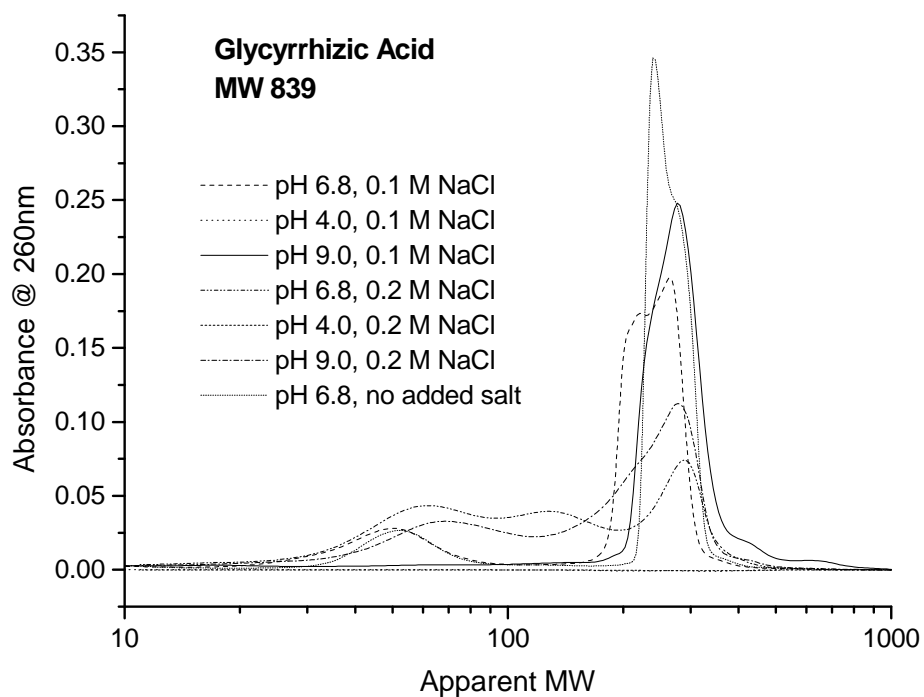


Figure 2.34 HPSE chromatograms of glycyrrhizic acid

OPTIMISATION OF ADSORPTION PROCESSES

Table 2.8 Retention times and apparent molecular weights of model compounds

Mellitic acid Molecular weight 342 Theoretical retention time 11.1 minutes	Retention time (min)	Measured molecular weight (gram mol ⁻¹)
pH 9, 0.1 M	9.4	1510
pH 9, 0.2 M	9.8	1290
pH 6.8, no salt	9.6	1433
pH 6.8, 0.1 M	9.6	1433
pH 6.8, 0.2 M	9.6	1433
pH 4, 0.1 M	10.1	932
pH 4, 0.2 M	10.2	922
Pyromellitic acid Molecular weight 254 Theoretical retention time 11.3 minutes	Retention time (min)	Measured molecular weight (gram mol ⁻¹)
pH 9, 0.1 M	9.5	1375(1372)
pH 9, 0.2 M	9.9	1333(1341)
pH 6.8, no salt	9.8	1289(1273)
pH 6.8, 0.1 M	9.8	1270(1273)
pH 6.8, 0.2 M	9.7	1442(1446)
pH 4, 0.1 M	10.7	499(499)
pH 4, 0.2 M	10.9	498(505)
Tetra hydrofuran tetracarboxylic acid Molecular weight 248 Theoretical retention time 11.4 minutes	Retention time (min)	Measured molecular weight (gram mol ⁻¹)
pH 9, 0.1 M	10.1	910
pH 9, 0.2 M	10.2	910
pH 6.8, no salt	10.0	910
pH 6.8, 0.1 M	10.1	910
pH 6.8, 0.2 M	10.3	910
pH 4, 0.1 M	10.8	454
pH 4, 0.2 M	10.9	508

Table 2.8 contd

9,10-Anthroquinone-2,6-disulphonic acid Molecular weight 412 Theoretical retention time 10.9 minutes	Retention time (min)	Measured molecular weight (gram mol ⁻¹)
pH 9, 0.1 M	11.2	277
pH 9, 0.2 M	11.4,12.4	281,99
pH 6.8, no salt	11.5,12.9	230,60
pH 6.8, 0.1 M	11.6,12.9	210,60
pH 6.8, 0.2 M	11.6,12.5,12.8	86,138,254
pH 4, 0.1 M	13.5,13.9	21,30
pH 4, 0.2 M	14.4	18
Dibenzoyl-l tartaric acid Molecular weight 358 Theoretical retention time 11.1 minutes	Retention time (min)	Measured molecular weight (gram mol ⁻¹)
pH 9, 0.1 M	10.6	462
pH 9, 0.2 M	11.6	371
pH 6.8, no salt	11.6	321
pH 6.8, 0.1 M	11.2	319
pH 6.8, 0.2 M	11.2	371
pH 4, 0.1 M	11.7,12.6	182
pH 4, 0.2 M	13	62
Glycyrrhic acid Molecular weight 840 Theoretical retention time 10.2 minutes	Retention time (min)	Measured molecular weight (gram mol ⁻¹)
pH 9, 0.1 M	11.1	276
pH 9, 0.2 M	11.4,12.9	276,71
pH 6.8, no salt	11.5,13	240,50
pH 6.8, 0.1 M	11.4,13	264,50
pH 6.8, 0.2 M	11.5,12.4,13.2	281,127,60
pH 4, 0.1 M	No response	-
pH 4, 0.2 M	No response	-

Of the six compounds we were only able to discover pK_a values for three, mellitic acid (MA), pyromellitic acid (PMA) tetra hydrofuran tetracarboxylic acid (THTA). The values are given in Table 2.9 In Table 2.10, average values of charge per molecule at each pH are given; these values were calculated using the pK_a values and the Henderson Hasselbach equation (Nyman, 1984).

OPTIMISATION OF ADSORPTION PROCESSES

Table 2.9 pK_a values of model compounds

Compound	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{a5}	pK_{a6}
MA	0.8	2.3	3.5	5.2	6.5	7.7
PMA	1.9	2.7	4.3	5.5	-	-
THTA	1.4	2.1	3.7	7.7	-	-

Table 2.10 Average values of charge per molecule at each pH

pH	MA	PMA	THAT
4.0	3.2	2.3	2.7
6.8	4.7	3.9	3.1
9.0	6	4	4

At pH 6.8 and 9, at all salt concentrations, the three compounds display an apparent MW significantly higher than their actual values (Figures 2.29-2.32). This is a reflection of the retention times which are much lower than the theoretical retention times (Table 2.8). The results indicate a strong electrostatic repulsion between the surface of the column and the negatively charged compounds, preventing the compounds from diffusing into all the pores normally available to smaller molecules. This effect was not reduced by the increase of ionic strength of the solution. The slightly longer retention time displayed by THTA could be due to a combination of the lower charge (at pH 6.8) and the smaller size of the molecule. Reducing the pH to 4 had a significant effect on the three compounds. The retention times increased with the decrease in pH, therefore the apparent molecular weights were closer to the actual values for the three compounds under these conditions. The greatest reduction in the apparent molecular weight was shown by PMA, which may be a consequence of the greater reduction in average charge from pH 6.8 to 4 (a 41% reduction compared with 32% and 13% for MA and THTA respectively). Once again an increase in ionic strength had no effect on the retention times. It should be noted here that the MWs are calculated from the pH 6.8 calibration curves as the PSS standards did not elute at this pH. From Table 2.9 it can be seen that, even at pH 4 the molecules have a fairly high charge to mass ratio.

The other three compounds display quite different behaviour. 9,10-Anthroquinone-2,6-disulphonic acid (AQA) in general showed retention times higher than the theoretical value, and displayed multiple chromatographic peaks under most solution conditions. The former observation could be attributed to the lower charge density and higher hydrophobicity of this compound. The latter observation is accompanied by an effect of increasing ionic strength at the three pH. This is either an indication of changing electrostatic shielding with increasing ionic strength, or changing speciation of the compound with the variation in solution conditions. The retention times at pH 4 and the third peak at pH 6.8 in 0.2 M NaCl indicate an interaction with the column surface, either due to decreased charge on the compound, or decreased solubility of the compound in increasing salt solution concentration.

Dibenzoyl-L tartaric acid (DTA) displayed elution behaviour consistent with its molecular weight except at pH 4. Once again this compound, if fully charged, has a lower charge density than MA, PMA or THTA. The additional COO^- groups may render the molecule less hydrophobic than AQA, and in fact the compound could be behaving in a manner similar to the charged PSS standards. At pH 4 the acidic groups are possibly protonated, resulting in a more hydrophobic molecule, and a longer retention time.

Glycyrrhizic acid (GA) is a relatively large molecule with only one acid group that could be expected to be charged at the higher pH. The compound displays a significantly higher retention time than expected at all solution conditions, indicating a strong interaction with the surface and this interaction increases with decreasing pH and increasing ionic strength. This compound did not elute at all at pH 4.

Comparison of molecular weight analysis of NOM fractions using HPSEC and FIFFF

Nine characterised NOM fractions, isolated from Hope Valley Reservoir using three different techniques (see previous sections and Hepplewhite, 2000), were analysed for their molecular weight distributions using FIFFF and HPSEC. The aim was to determine the relative merits of each technique using a range of samples with known physical properties.

Table 2.5 identifies the samples and summarises the isolation/fraction procedure. Figures 2.35-2.43 show the HPSEC chromatograms and the FIFFF fractograms for the nine NOM fractions. Table 2.11 summarises the average MW data obtained from the two techniques.

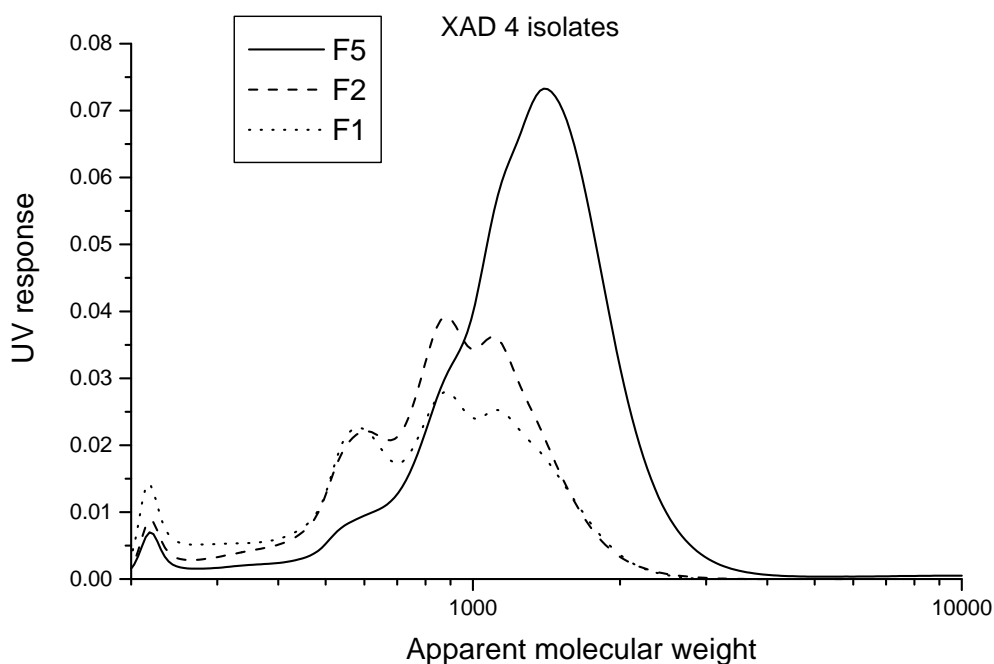


Figure 2.35 HPSEC chromatograms of XAD isolates

OPTIMISATION OF ADSORPTION PROCESSES

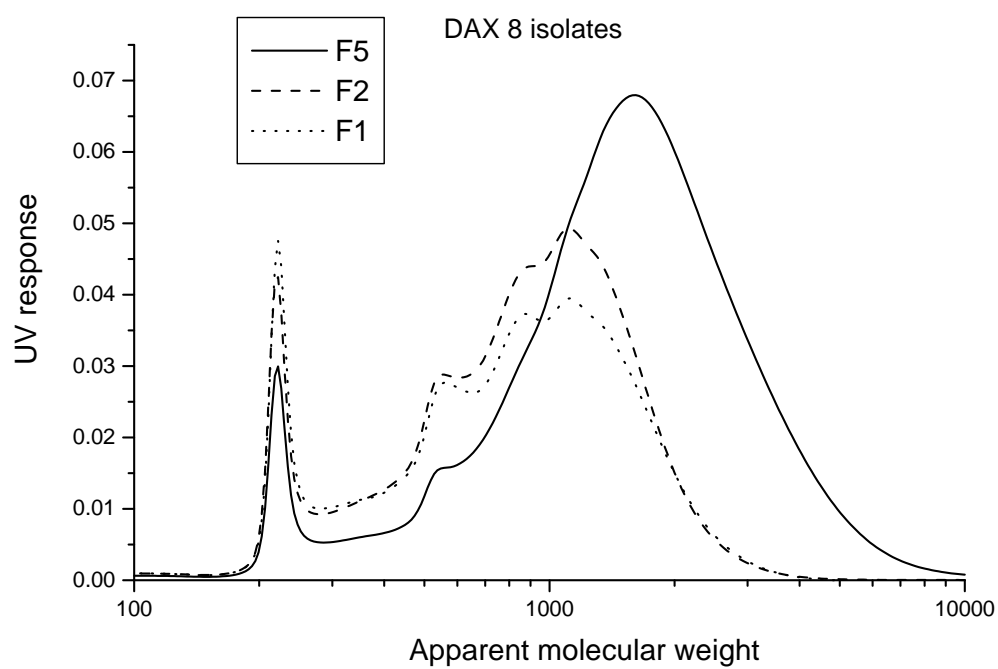


Figure 2.36 HPSE chromatograms of DAX 8 isolates

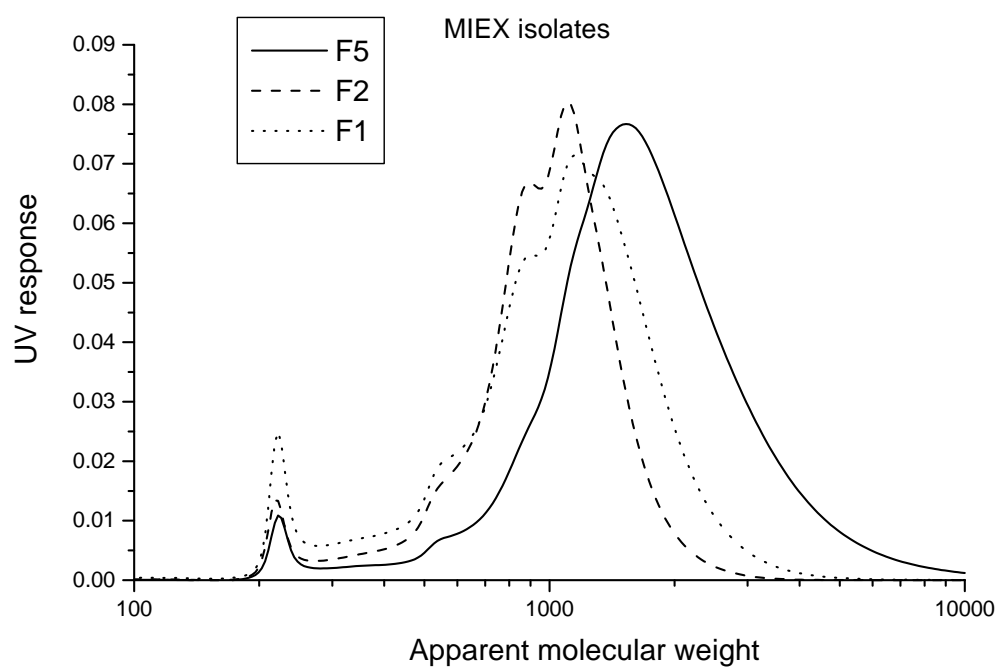


Figure 2.37 HPSE chromatograms of MIEX isolates

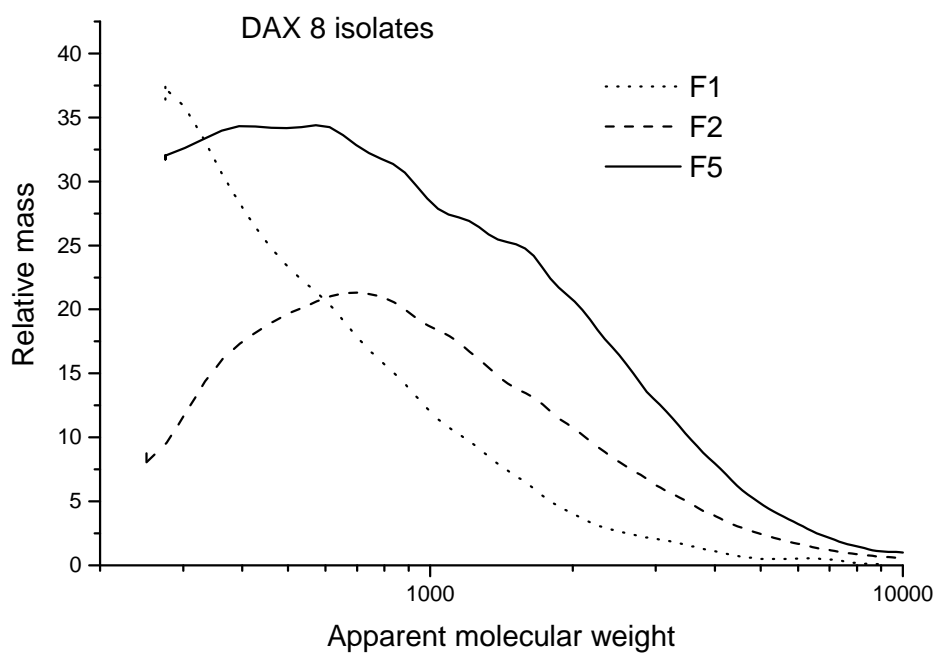


Figure 2.38 FIFF fractograms of DAX 8 fractions

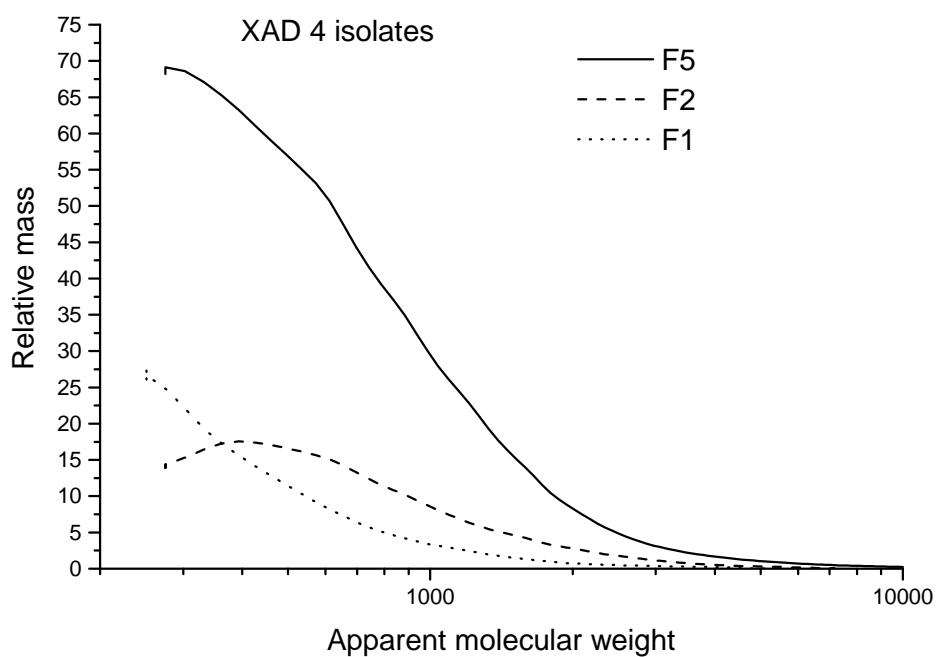


Figure 2.39 FIFF fractograms of XAD 4 fractions

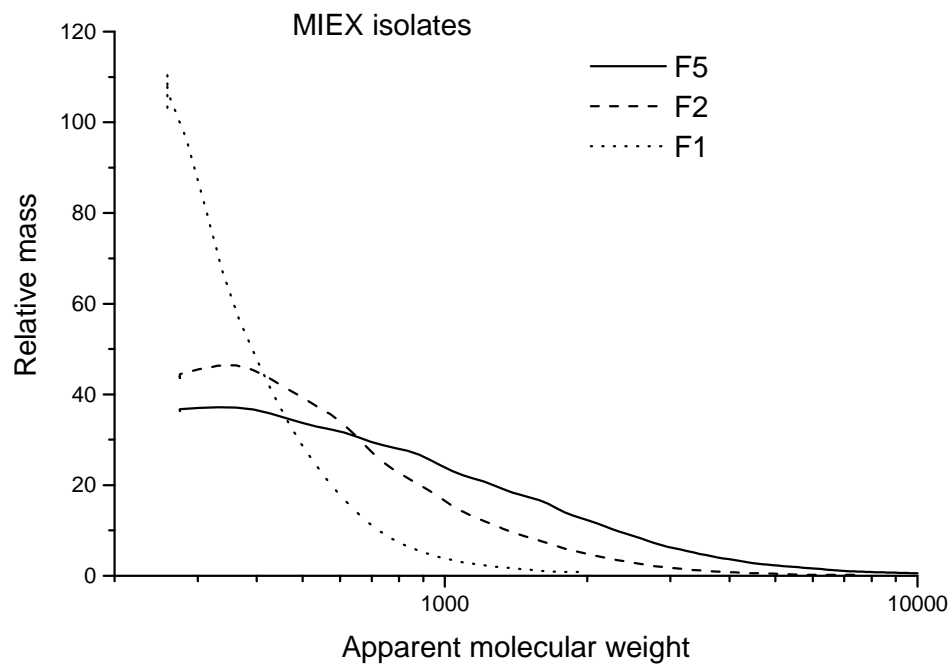


Figure 2.40 FIFF fractograms of MIEX fractions

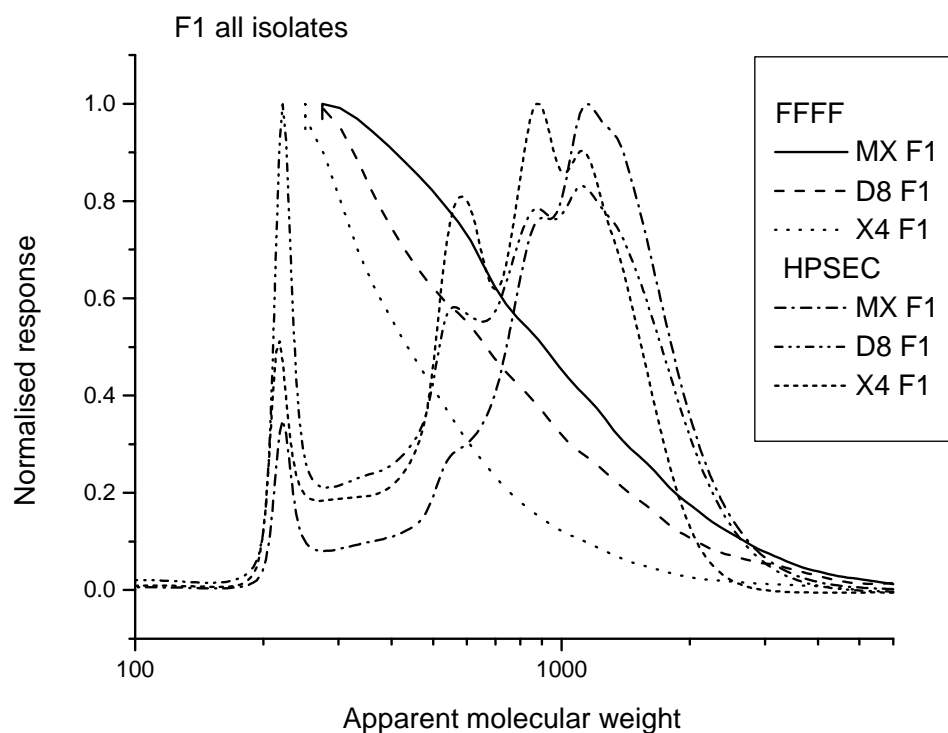


Figure 2.41 HPSE chromatograms and FIFF fractograms of F1 fractions

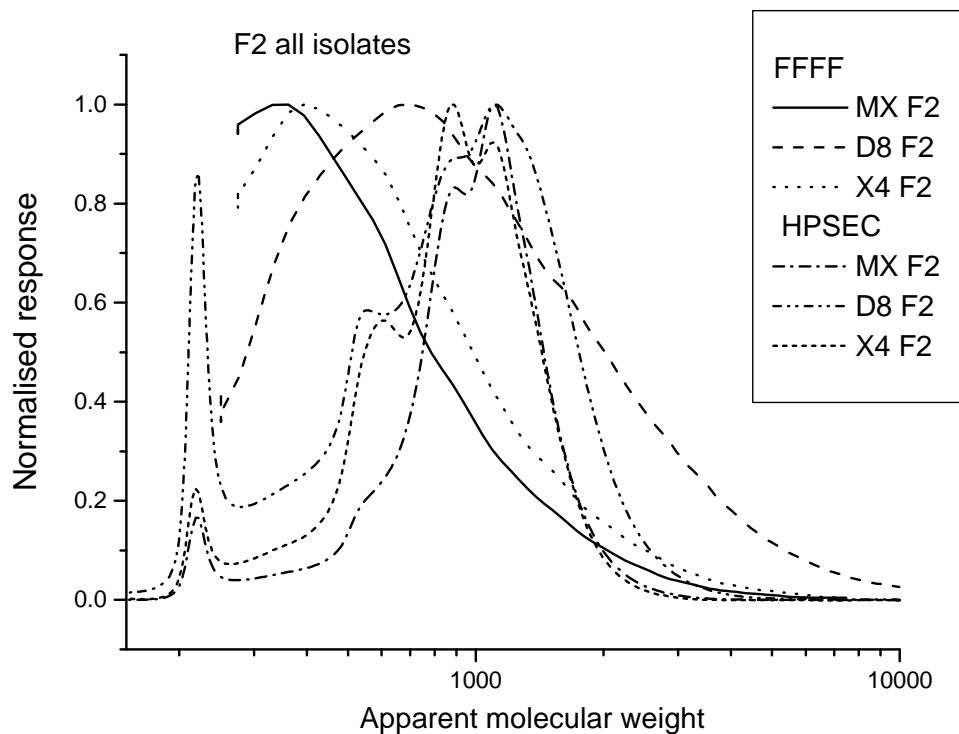


Figure 2.42 HPSE chromatograms and FIFF fractograms of F2 fractions

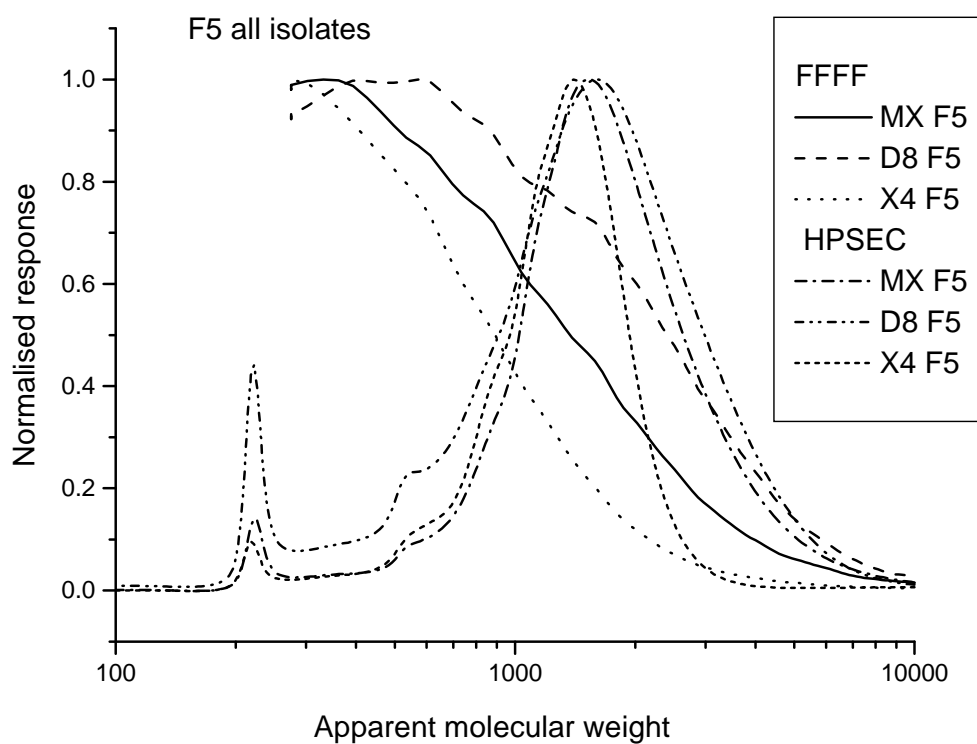


Figure 2.43 HPSEC chromatograms and FIFFF fractograms of F5 fractions

Table 2.11 Average molecular weights of fractions determined by HPSEC and FIFFF

fraction	HPSEC			FIFFF		
	M_n	M_w	M_p	M_n	M_w	M_p
MX F1	458	597	1209	759±71	1566±192	275
MX F2	463	697	1148	721±4	1202±10	346±15
MX F5	785	1244	1752	1095±93	2401±250	356±70
D8 F1	330	553	1130	802±11	1611±100	259±9
D8 F2	360	582	1207	1276±41	3126±25	659±42
D8 F5	603	1294	1808	1305±45	3009±310	440±63
X4 F1	375	544	973	542±63	804±167	265±10
X4 F2	411	543	942	835±39	1411±76	427±34
X4 F5	687	893	1572	752±34	1432±186	275

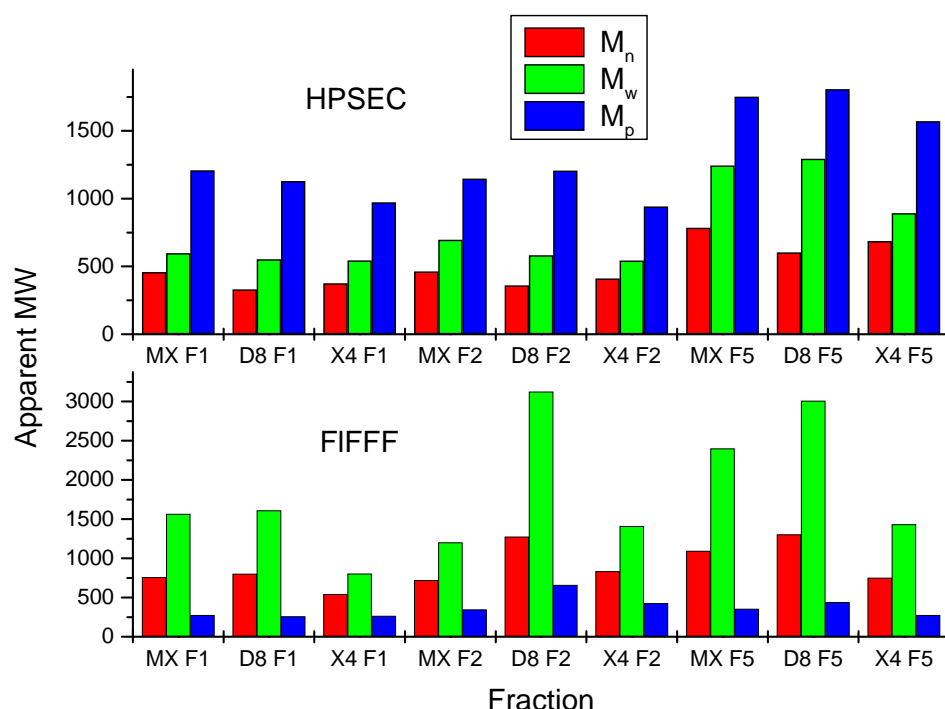


Figure 2.44 Average molecular weights determined by HPSEC and FIFFF

Figure 2.44 summarises the data in Table 2.11.

The main points of difference between the two techniques are:

- HPSEC chromatograms show more detail, with peaks and shoulders clearly resolved
- FIFFF displays wider distributions, the HPSEC peak at 200 MW is undetectable in FIFFF
- HPSEC major peaks are consistently at higher MW than the FIFFF
- HPSEC average MWs are significantly lower than those determined using FIFFF.

The main cause of the differences is the chromatographic peak distribution shown by the HPSEC analysis, compared with the broad distributions, with no significant maximum and minimum values, given by the FIFFF. It is possible that the relatively narrow peaks and shoulders shown by HPSEC are due to interactions of the same types of molecules with the surface of the column; conversely it is possible to argue that the diffusion of the compounds in the channel of the FIFFF would result in a greater mixing of the compounds, and broader distributions. Either way, it is clear that the HPSEC technique offers more information in terms of concentrations of compounds of various MWs. In fact, the low MW peak, around 200, which is not detectable with the FIFFF technique, can be directly attributed to the compounds that are of particular interest for the study of adsorption competition on activated carbon (see following Chapters). This is of significance for the D8 isolates, which all have large peaks in this region as well as a relatively high concentration of high molecular weight (HMW) NOM. In addition, both ozone and chlorine are shown to increase the UV absorbance in the low MW region of the HPSEC chromatogram (Chapter 6 and Ho *et al.* 2002) an effect that would not be identified if FIFFF were the only technique to be used for analysis.

The effect of solution conditions on ultrafiltration

As mentioned in previous sections, ultrafiltration through membranes for the purpose of preparing NOM fractions has some serious drawbacks, including the formation of a gel layer on the surface of the membrane, effectively reducing the pore size of the membrane and preventing smaller molecules from permeating. Another possible effect that was suggested was the electrostatic repulsion between the negatively charged NOM and the membrane surface. The aim of the work described in this section was to investigate the effect of DOC concentration on the ultrafiltration of some of the NOM fractions

OPTIMISATION OF ADSORPTION PROCESSES

described earlier, and to attempt to minimise any electrostatic effects by increasing the ionic strength of the filtration solution. The study focussed on the >30K fractions of the MX and X4 isolates, and ultrafiltration of the isolates through 30K and 1K membranes in the presence of NaCl at an ionic strength of 0.01 and 0.20 M. The X4 fraction was also tested through a 3K membrane. Figures 2.45-2.55 show the UV absorbance, colour, DOC, in milligram (i.e. mass of organic carbon present), SUVA, specific colour, and average MW of the initial solution, the first permeate through the membrane, and either 1 or 2 rinses through the membrane using Milli-Q water at the appropriate ionic strength. The parameters of the final retentate are also shown

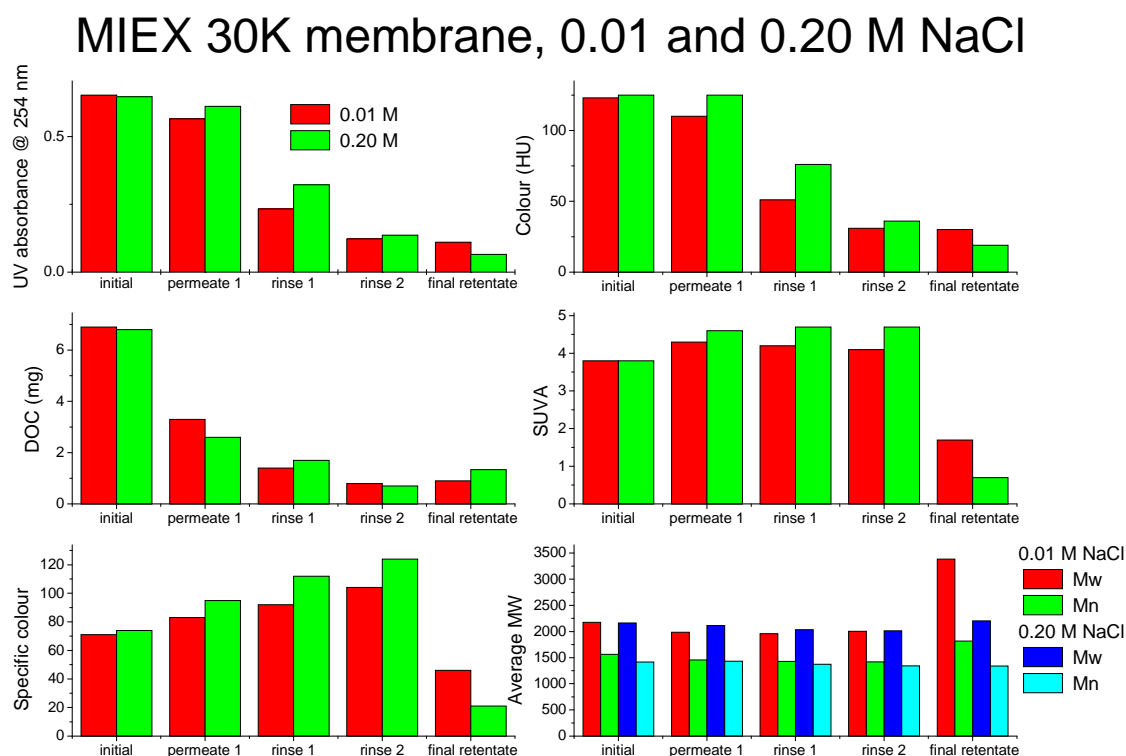


Figure 2.45 UF results, MIEX isolate, 30K membrane, 0.01 M and 0.20 M NaCl

MIEX 1K membrane, 0.01 and 0.20 M NaCl

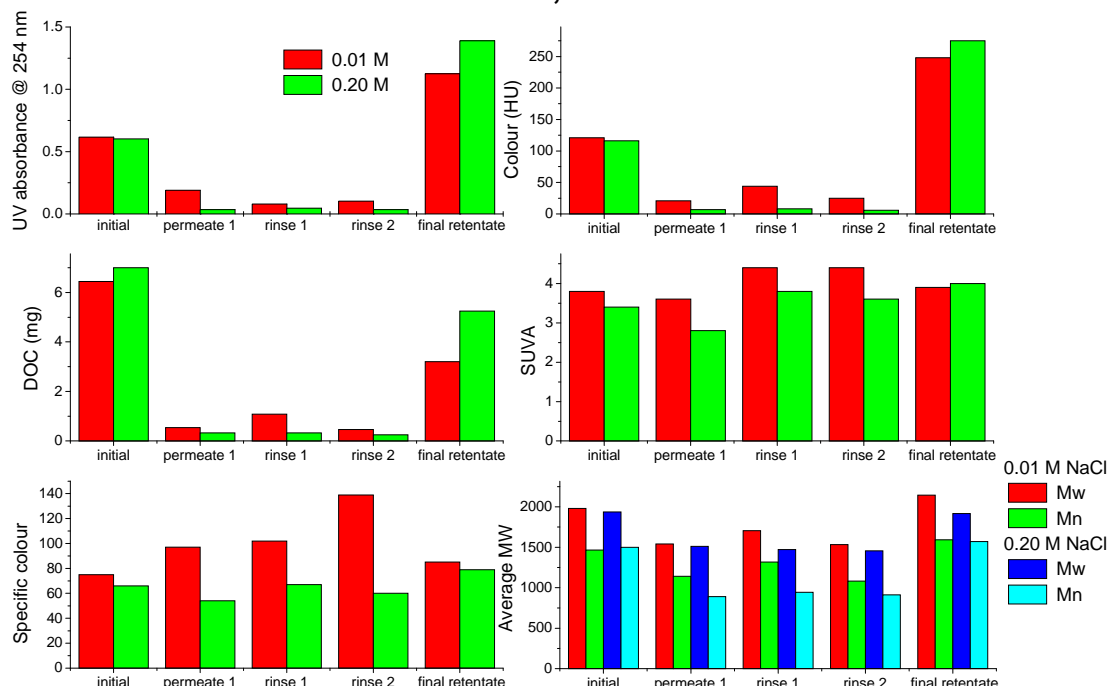


Figure 2.46 UF results, MIEX isolate, 1K membrane, 0.01 M and 0.20 M NaCl

XAD 4 30K membrane, 0.01 and 0.20 M NaCl

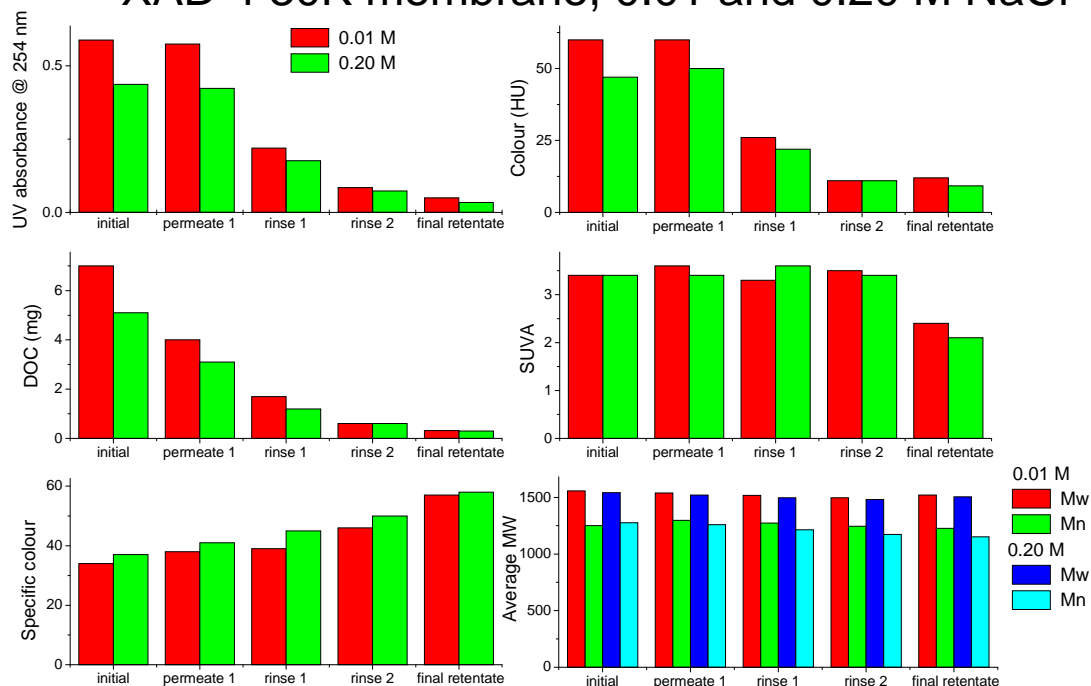


Figure 2.47 UF results, XAD 4 isolate, 30K membrane, 0.01 M and 0.20 M NaCl

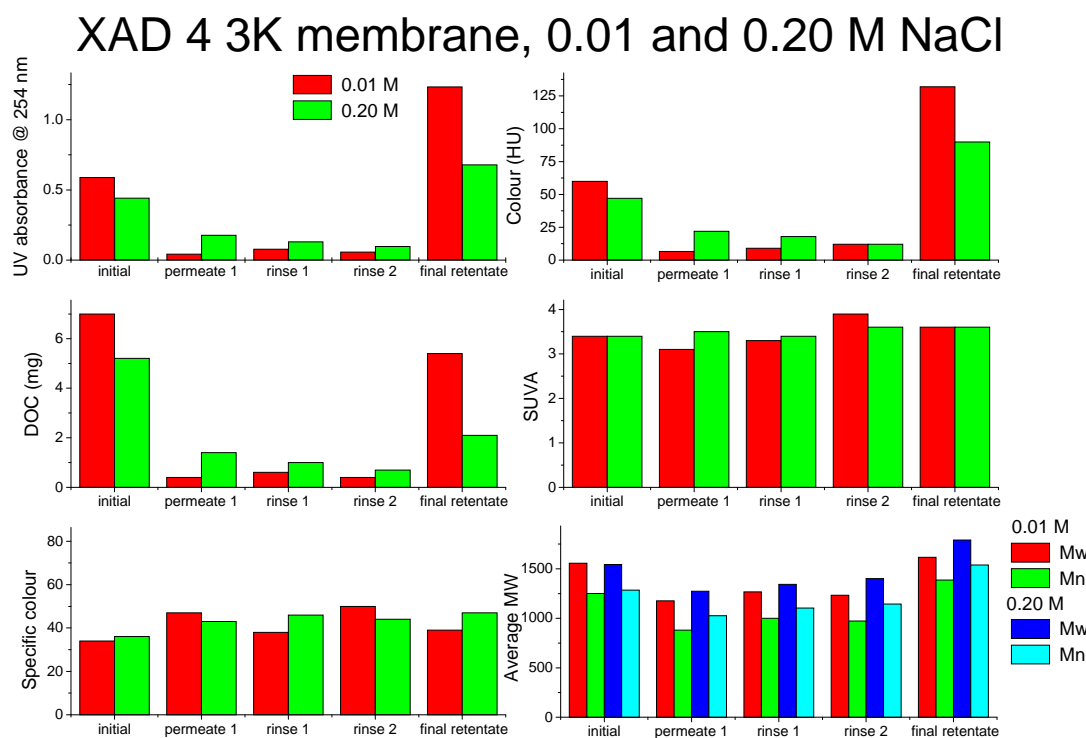


Figure 2.48 UF results, XAD 4 isolate, 3K membrane, 0.01 M and 0.20 M NaCl

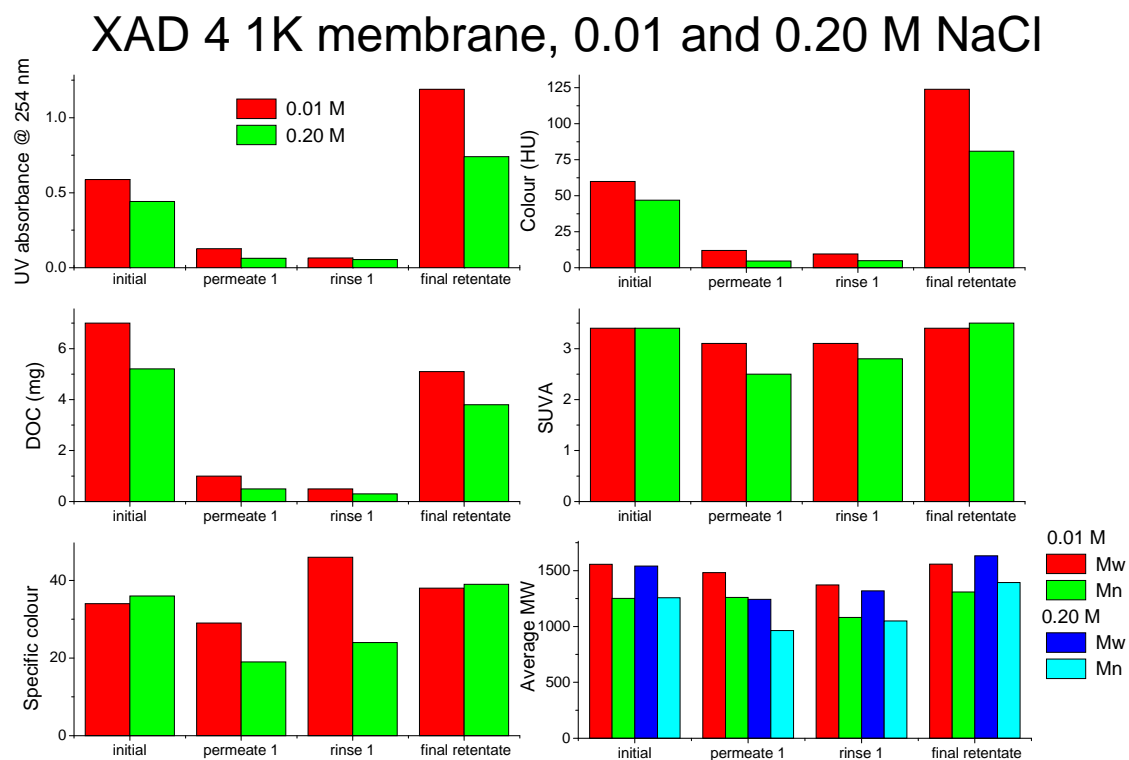


Figure 2.49 UF results, XAD 4 isolate, 1K membrane, 0.01 M and 0.20 M NaCl

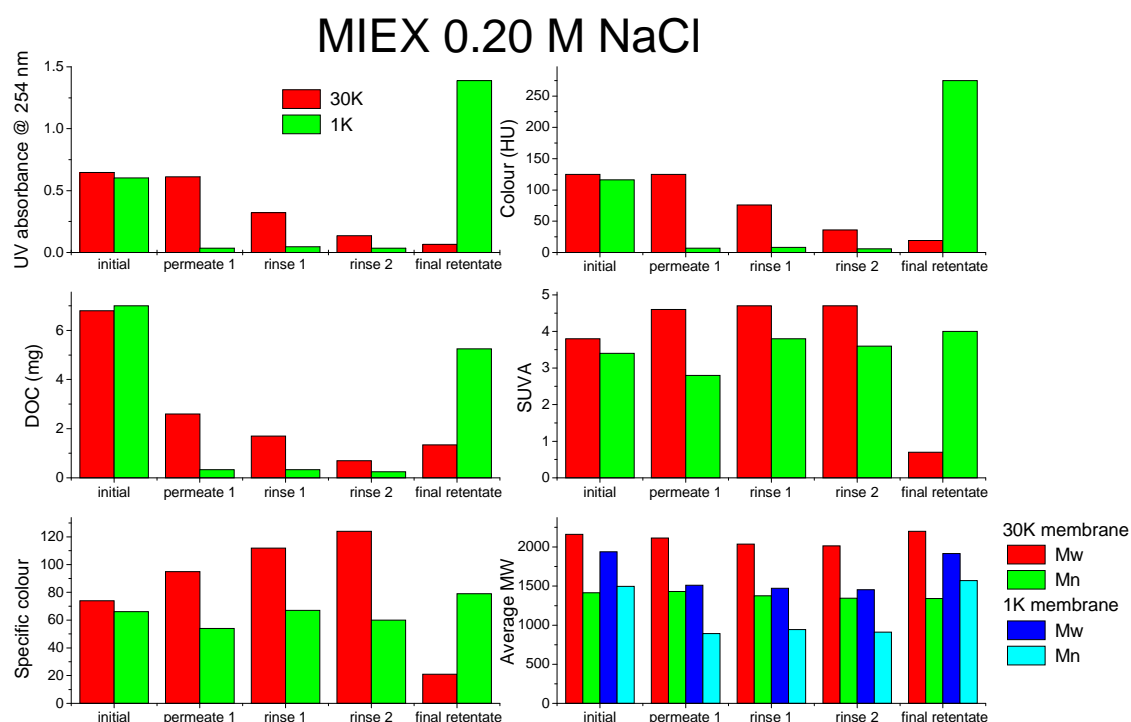


Figure 2.50 UF results, MIEX isolate, 0.20 M NaCl, 30K and 1K membranes

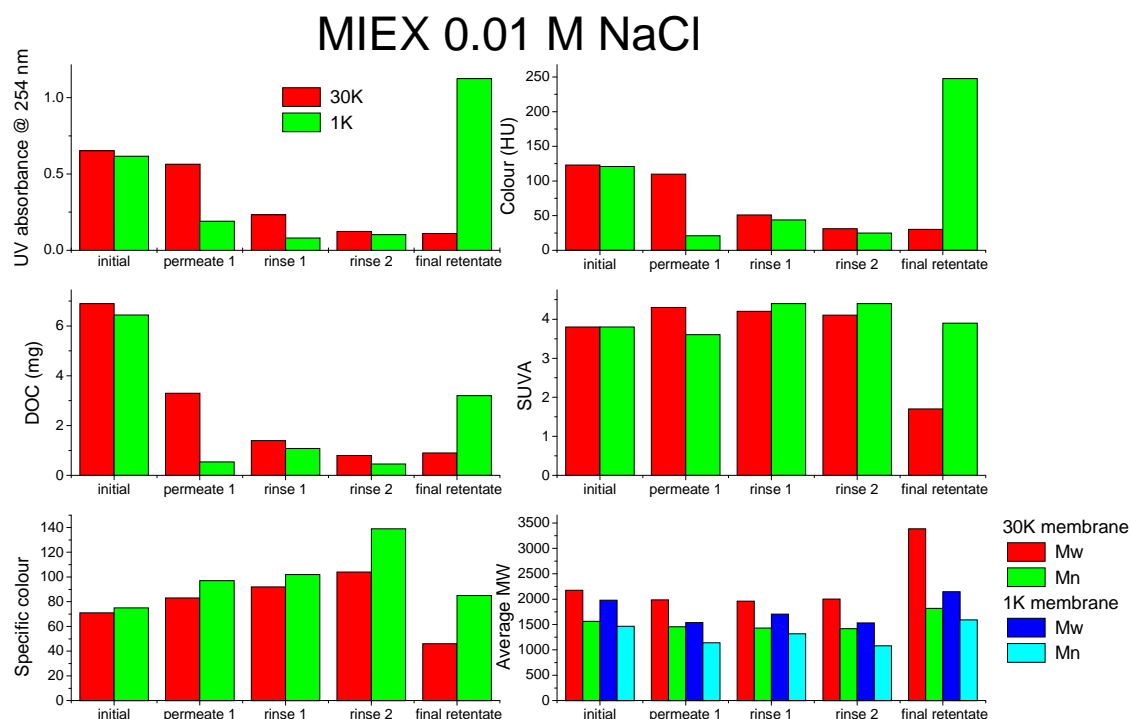


Figure 2.51 UF results, MIEX isolate, 0.01 M NaCl, 30K and 1K membranes

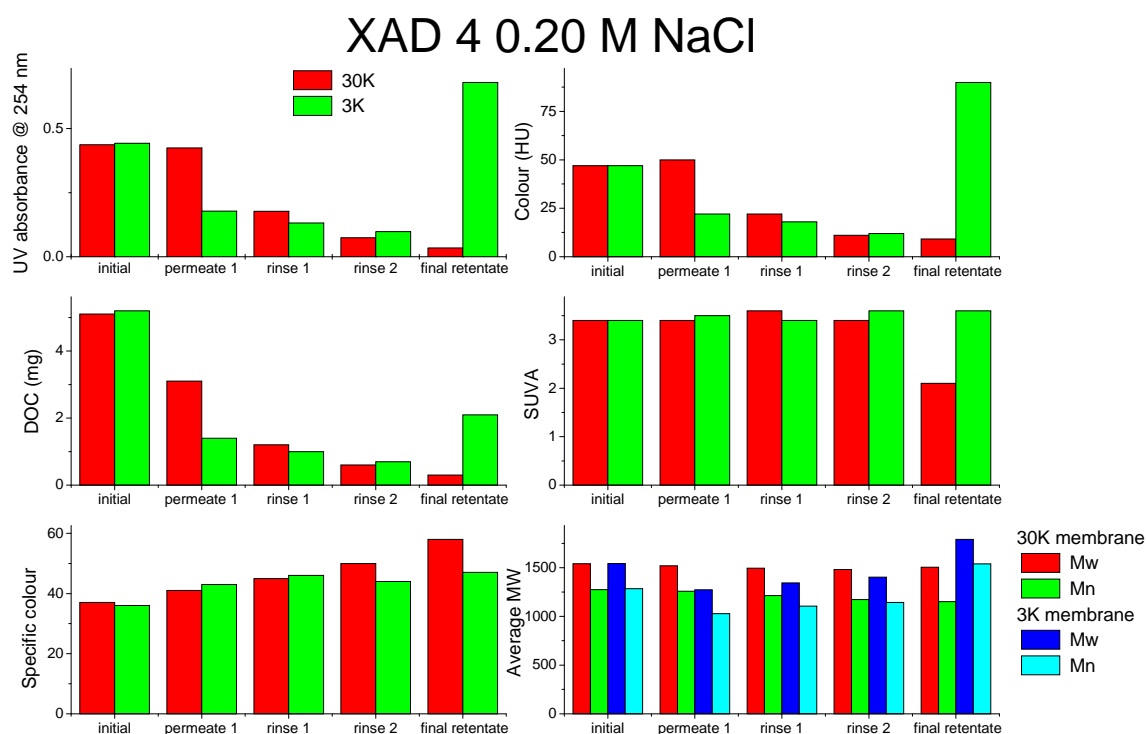


Figure 2.52 UF results, XAD 4 isolate, 0.20 M NaCl, 30K and 3K membranes

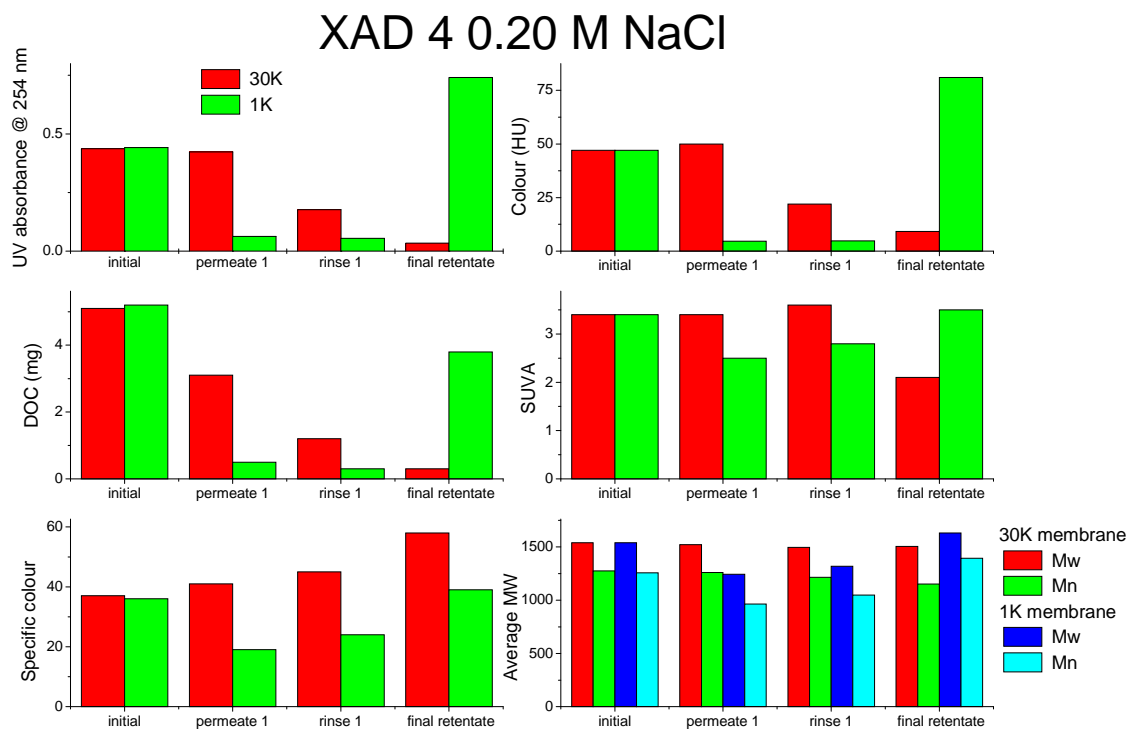


Figure 2.53 UF results, XAD 4 isolate, 0.20 M NaCl, 30K and 1K membranes

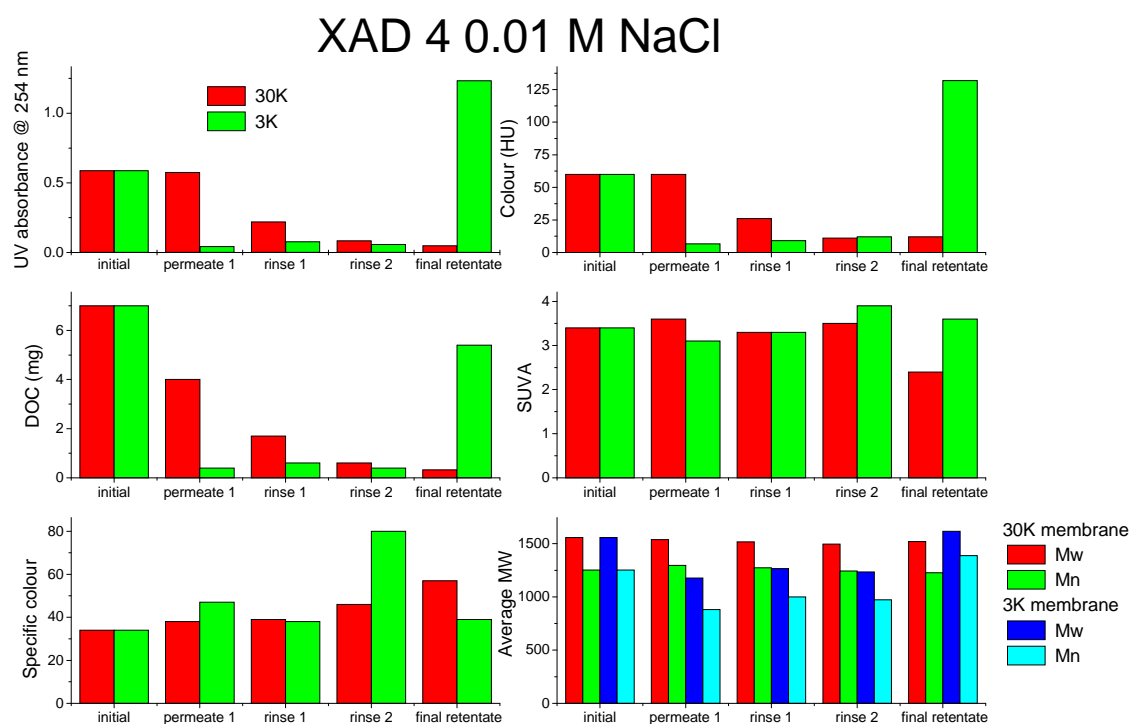


Figure 2.54 UF results, XAD 4 isolate, 0.01 M NaCl, 30K and 3K membranes

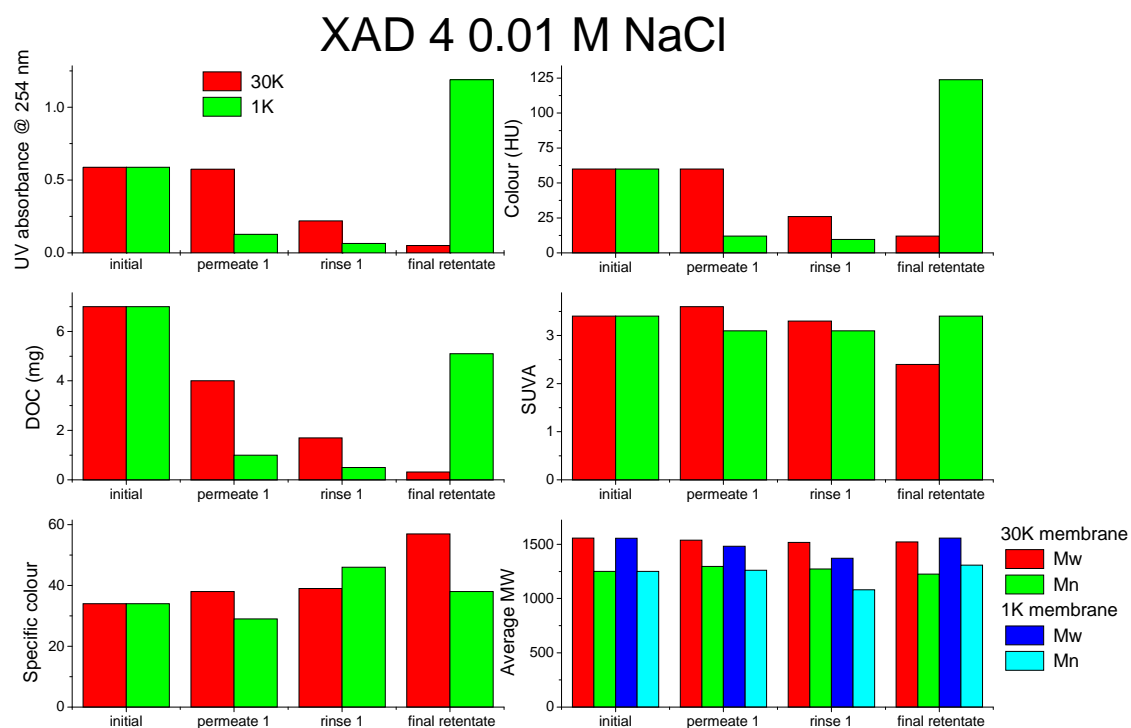


Figure 2.55 UF results, XAD 4 isolate, 0.01 M NaCl, 30K and 1K membrane

Effect of increased ionic strength (Figures 2.45-2.49)

If electrostatic repulsion played a major role in the rejection of NOM by the membrane it could be expected that there would be higher DOC, UV, colour and average MW found in the permeate samples at higher ionic strength, where such interactions would be shielded to a certain extent. As a result one might expect a lower DOC in the retentate of that sample. There is some evidence of this for the X4 3 and 1K membranes although it does not appear to be significant, and there is no such trend for the MX sample. There was no consistent, clear trend to indicate that the electrostatic interactions were playing a major role in this ultrafiltration system.

Effect of concentration of NOM and membrane pore size (Figures 2.50-2.55)

The concentration of the NOM during preparation of these sample was several hundred mgL^{-1} DOC. In the experiments reported here the concentrations were 12-18 mgL^{-1} . The figures show that the formation of a gel layer, probably due to the higher concentration of NOM in the preparative fractions, played a major role in the final molecular weight distribution of fractionated samples. The fractions prepared using a 30K membrane are not retained on that membrane when a lower concentration is applied under the same experimental conditions (other than concentration of NOM). Table 2.12 shows that only 5-19% of the organic carbon is retained on the 30K membranes under these conditions, and up to 50% of the NOM permeates the 1K membranes. The HPSE chromatograms of the two fractions were analysed to determine the percentage of UV absorbing compounds <1K, the results are also given in Table 2.12.

Molecular weight distributions

As can be seen in the figures below (2.56, 2.57), there was little effect of salt on the average molecular weights. The only discrepancy is the MX retentate of the 30K filtration which appears to have an unexpectedly high M_w due to significant tailing in the HPSE chromatogram. This is probably an experimental artefact as it is inconsistent with the other data. In general, the average MWs did not show much variation with the filtration and rinsing through the membranes. However, the chromatograms themselves, when normalised to the peak maxima, showed the expected trends (Figures 2.56 and 2.57). The chromatograms of the experiment using the 30K membranes showed little difference between the permeate and the retentate, once normalised, as the two solutions were the same in character and only differed in concentration. Another reason for the similarity in the distribution could be due to the non-UV absorbance of some of the NOM retained on the membranes. That is, the higher molecular weight compounds, retained on the 30K membrane, could have been predominantly carbohydrate-type compounds, with negligible UV absorbance. In contrast, major differences were seen using the 1K membrane, as only a portion of the NOM present could pass through that membrane.

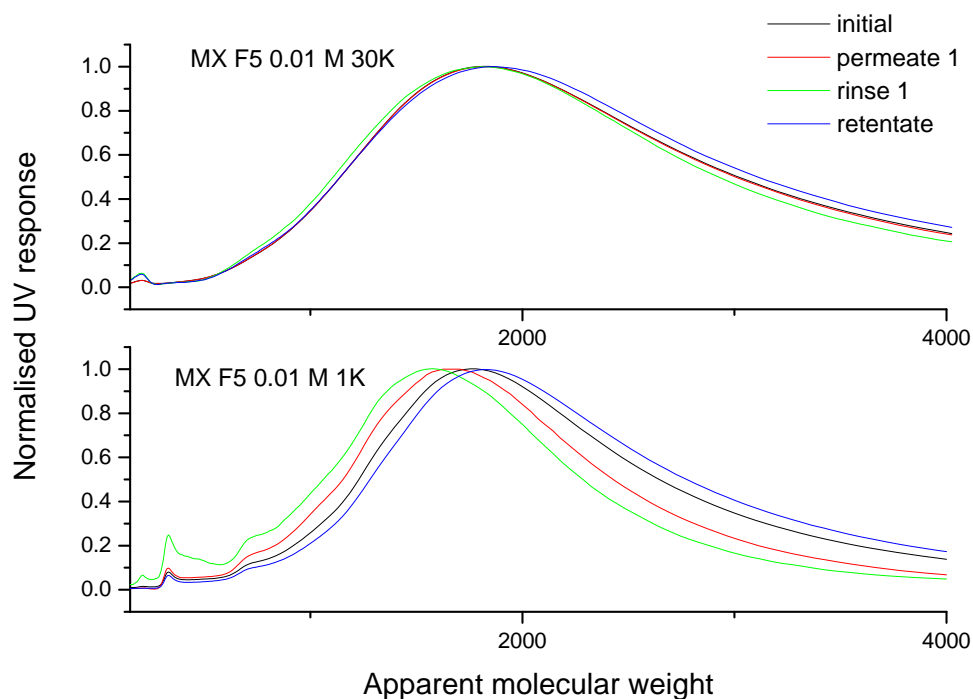


Figure 2.56 HPSE chromatograms of solutions during ultrafiltration experiments, MIEEX isolate, 0.1. M NaCl

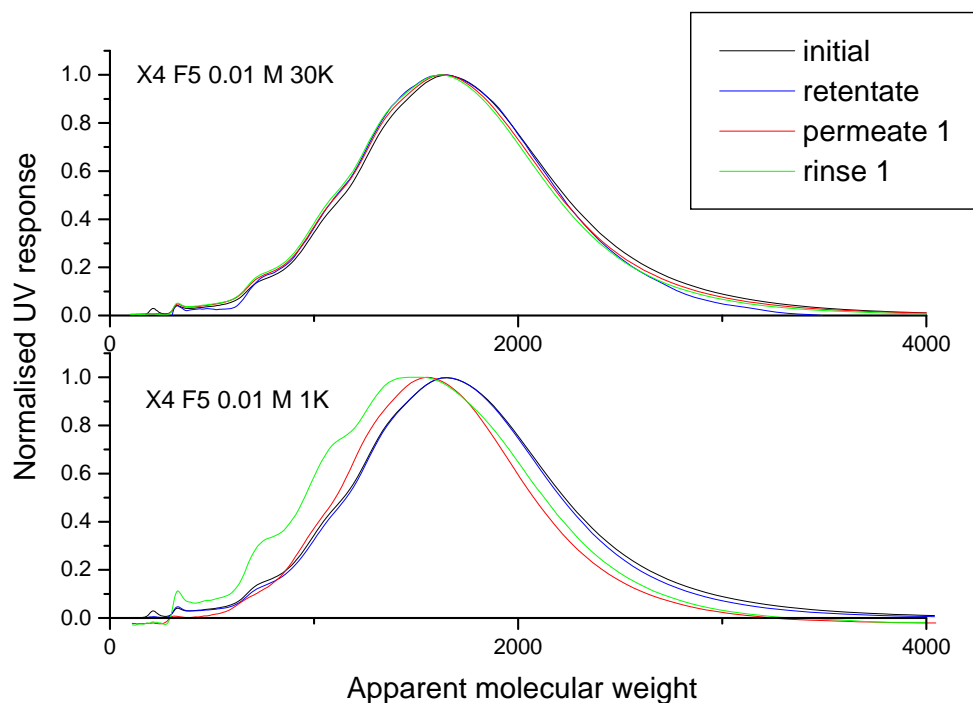


Figure 2.57 HPSE chromatograms of solutions during ultrafiltration experiments, XAD 4 isolate, 0.1 M NaCl

OPTIMISATION OF ADSORPTION PROCESSES

Table 2.12 shows the percentage of the NOM fractions in the MW ranges >1K, >3K and >30K, determined by integration of the FIFFF and HPSEC distributions compared with the percentage of the DOC retained on the 1K, 3K and 30K membranes during these filtration experiments. There is clearly a major discrepancy between these results. There are two possible causes of the discrepancy,

- The membrane cut-off values are not accurately determined for the NOM or
- Some of the NOM <1K and >3K has a very low absorbance and is not detectable using UV detection.

Table 2.12 Percent organic carbon retained on membranes, and the percent of UV absorbing DOC in the range >1K, >3K and >30K measured by HPSEC.

	Percent UV abs DOC > MW HPSEC, FIFFF			Percent DOC > MW (membrane)		
	>1K	>3K	>30K	>1K	>3K	>30K
MXF5 0.01 M	95, 63	-	0, 0	51	-	13
MXF5 0.20 M	95	-	0	75	-	19
X4F5 0.01 M	92, 44	3, 11	0, 0	76	80	5
X4F5 0.20 M	92	3	0	81	40	6

2.5.5 Summary and conclusions

High performance size exclusion chromatography, while a very useful technique, has some limitations due to strong interactions that can take place between organic compounds and the surface of the column packing material. This was shown by the retention times of a series of model compounds. Those with a very high charge to size ratio eluted earlier than would be expected by their molecular weight, while hydrophobic compounds eluted later, providing inaccurate molecular weights when compared with the elution times of the PSS standards. This may be the cause of the resolved peaks and well-defined shoulders evident in most of the HPSEC chromatograms of NOM fractions and natural waters. There is very little resolution seen in results of the flow field flow fractionation, which may be an artefact of the technique, where separation of molecular sizes is based on the different diffusion coefficients. The comparison of the two analytical techniques suggests that, although NOM compounds in general have a wide, fairly regular, or smooth, size distribution, the chemical structure, the cause of possible interactions with the HPSEC column packing, may not be found in such an even distribution. That is, while the NOM compounds are found in a range of sizes, some chemical characteristics are common to all NOM eluting where the peaks and shoulders are detected.

The preparation of the largest molecular weight fractions of the Hope Valley isolates (>30K UF fractions) was strongly influenced by the concentration of the initial NOM solution used for the fractionations. It is probable that a gel layer formed quite quickly on the membrane during the membrane filtration, forming an effective additional filter of lower molecular weight cut-off. As a result, when solutions of two of the >30K fractions - at much lower initial concentrations - were ultrafiltered through the 30K membrane, much of the NOM passed through into the permeate. Filtration of these NOM samples through membranes of lower molecular weight indicated that most of the NOM was in the size range able to permeate the 30K membrane, and be retained on the 1K membrane.

The percentage of dissolved organic carbon retained on the membranes was then compared with the percentages of NOM greater than the membrane cut-off molecular weight, measured using HPSEC and FIFFF. The results obtained by HPSEC and FIFFF were quite different from the membrane results for the 3K and 1K molecular weights. This indicated that, either the membrane cut-off values could not be applied to the NOM fractions, as suggested earlier, or a proportion of the DOC retained on the membranes was non-UV absorbing, thus it was not detected using the other techniques.

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3. MECHANISMS OF ADSORPTION OF NOM ONTO ACTIVATED CARBON

3.1 INTRODUCTION

In this stage of the work the mechanisms of adsorption of NOM onto a range of well-characterised activated carbons were studied under different solution conditions of pH and ionic strength. The NOM fractions were those described in section 2.2 and Newcombe *et al.* (1997).

3.2 ADSORPTION OF NOM ONTO ACTIVATED CARBON: EFFECT OF SURFACE CHARGE, IONIC STRENGTH AND PORE VOLUME DISTRIBUTION

3.2.1 Introduction

Dissolved natural organic matter (NOM) is present in all drinking water sources and is a complex mixture of compounds formed from the breakdown of plant and animal material in the environment. Although strongly dependent on the nature of the local environment (Aiken and Cotsaris 1995), NOM consists of small, low molecular weight species such as carboxylic and amino acids and proteins, through to larger, high molecular weight (from <500 to >30000 Daltons in Australian waters) humic and fulvic acids (Belin 1993, Choudry 1984). These humic and fulvic species can have both aliphatic and aromatic character (Choudry 1984). The negative charge present on most NOM molecules (attributed to carboxylic acid and phenolic functionalities (Perdue and Lytle 1983, Perdue *et al.* 1980) means that the larger compounds behave as polyelectrolytes in aqueous solution (Ephraim *et al.* 1986, de Wit *et al.* 1990).

The presence of NOM has been shown to impact upon all drinking water treatment processes, from alum coagulation (the removal of particulate matter using aluminium sulphate) through to chlorine disinfection (Brauch and Sontheimer 1989). It also has a deleterious effect on activated carbon adsorption as NOM is usually present in much higher concentrations (mg levels) than problematic species such as pesticides, algal toxins (μg levels) and taste and odour compounds (ng levels) and competes directly for adsorption sites. This can have the effect of changing the surface properties of a carbon filter, resulting in reduced adsorption capacity and useful life of the activated carbon (Najm *et al.* 1991). This process is known as "carbon fouling", and is of particular concern in water treatment plants.

The total free energy of adsorption (ΔG_{ads}) of NOM onto activated carbon can be conveniently expressed as the sum of an electrostatic (ΔG_{elec}) and specific (ΔG_{spec}) component;

$$\Delta G_{\text{ads}} = \Delta G_{\text{elec}} + \Delta G_{\text{spec}} \quad (1)$$

contributions to which may favour or oppose adsorption (Hough and Rendall 1993). Clearly, for adsorption to occur, ΔG_{ads} must be negative.

Contributions to ΔG_{elec} may comprise both coulombic and dipole interactions and include;

- (i) Surface-NOM electrostatic interactions which may favour (in the case of a positively charged carbon) or oppose (in the case of a negatively charged carbon) adsorption. Where the surface charge of an activated carbon can be varied from positive to negative (traversal of the isoelectric point) by varying solution pH, attractive or repulsive interactions will depend on pH.
- (ii) Lateral electrostatic repulsion between adsorbed NOM molecules (NOM_{ads}) which opposes adsorption.
- (iii) Repulsive interactions between NOM_{ads} and NOM in solution (NOM_{soln}) which also opposes adsorption.

The relative contributions of (i), (ii) and (iii) to ΔG_{elec} will be a function of the surface concentration (Γ). Surface-adsorbate interactions as described in (i) generally occur at low surface concentrations (Muller *et al.* 1985). As the charge from adsorbed NOM builds up on the carbon surface, factors (ii) and (iii) will become the dominant contributions to ΔG_{elec} (Muller *et al.* 1985, van de Steeg *et al.* 1992). Hence at low surface concentrations, the afore mentioned factors may favour or oppose

adsorption, depending upon surface charge, while at high surface concentrations, these contributions will oppose adsorption.

ΔG_{spec} represents all other interactions which are specific to the system. Factors which contribute to ΔG_{spec} include;

- (i) The pore size distribution of the carbon and the relationship between pore size and adsorbate size (Summers and Roberts 1988, Donati *et al.* 1994).
- (ii) Hydrophobic interactions between the graphitic carbon surface and hydrophobic portions of the NOM (Cini *et al.* 1980, Faust and Aly 1983).
- (iii) π -interactions between aromatic portions of the NOM and the carbon surface (Mattson *et al.* 1969, Coughlin *et al.* 1968).
- (iv) Hydrogen bonding between functional groups on the NOM and those on the carbon surface (Adamson, 1967).

For the adsorption of NOM onto activated carbon from aqueous solution, ΔG_{spec} can be expected to be negative, meaning that ΔG_{elec} may be attractive or repulsive, as long as $\Delta G_{\text{spec}} + \Delta G_{\text{elec}} < 0$.

By varying the solution conditions, the competing effects of various interactions in polyelectrolyte adsorption can be studied in detail. Electrostatic interactions can be minimised by decreasing the pH to a value where the negative charge on the NOM is negligible. Newcombe *et al.* (1994) adsorbed NOM onto 10 activated carbons at pH 3 and found a linear relationship between mesopore volume (width 2-50 nm) and adsorption capacity, clearly demonstrating that the main factor influencing adsorption under the chosen conditions was the volume of pores in the appropriate size range. The factors influencing adsorption were the same, per volume of mesopores, for each carbon and were most likely due to hydrophobic attraction. At pH 7, where the negative charge of the NOM was large, electrostatic interactions became significant, resulting in much decreased adsorption and no direct relationship between mesopore volume and adsorption of NOM was found.

Electrostatic interactions can be reduced by increasing the ionic strength of the solution. Added salt "screens", and thus reduces, both attractive and repulsive electrostatic interactions (Cohen Stuart *et al.* 1991). Therefore, where electrostatic interactions between the polyelectrolyte and the surface are attractive and Γ is sufficiently low, an increase in ionic strength will decrease adsorption. Conversely, if the surface and adsorbate carry the same charge and non-electrostatic forces govern adsorption, or for high Γ where lateral electrostatic interactions predominate, increased ionic strength will increase adsorption.

In their numerical calculations modelling the adsorption of polyelectrolytes onto oppositely charged surfaces, van de Steeg *et al.* (1992) identified two regions of adsorption, the "screening reduced" and "screening enhanced" adsorption regimes. Defining Γ_0 as mass adsorbed under conditions of negligible screening and Γ_∞ as mass adsorbed where electrostatic interactions are minimised, $\Gamma_0 > \Gamma_\infty$ was taken to represent the screening reduced regime. Electrostatic attraction dominates in this region and can be screened and thus reduced with added salt, the amount adsorbed eventually falling to zero if electrostatic attraction is the sole adsorption mechanism. $\Gamma_0 < \Gamma_\infty$ represents the screening enhanced regime and is a region where non-electrostatic attractive forces dominate adsorption. The effect of increased salt screens repulsion between charged segments of the polyelectrolyte, thereby resulting in increased adsorption.

Most of the literature dealing with the adsorption of NOM onto activated carbon describes the adsorption enhanced regime, where increased ionic strength increases adsorption (La France and Mazet 1989, Randtke and Jepsen 1982, Weber *et al.* 1983). Summers and Roberts (1988) detected an adsorption reduced regime (although not describing it as such) when they studied the adsorption of fractionated humic acid onto a positively charged activated carbon. Most recently, Newcombe and Drikas (1997) studied the adsorption of a well characterised NOM sample onto two activated carbons (F400 and HP) with very different surface properties at low and high ionic strengths over a range of pH values. They found that at high surface concentrations, NOM adsorbed onto both carbons in the screening enhanced regime at all pH, the added salt effectively screening electrostatic repulsions between adsorbed NOM molecules. At low surface concentrations, however, where direct surface-NOM electrostatic interactions were predominant, one carbon (F400) displayed a change from screening reduced to screening enhanced adsorption regimes. The isotherms undertaken at high and

low ionic strength displayed a “crossover” or intersection point, which Newcombe and Drikas (1997) interpreted as the point where the negative charge from the adsorbed NOM balanced the positive charge on the activated carbon surface. This interpretation was in agreement with the “charge compensation” theory of Norde and Lyklema (1978) for the adsorption of a polyion onto a positively charged surface.

The aim of this study was to expand the work reported by Newcombe and Drikas (1997) by examining the adsorption of NOM onto seven activated carbons, each with different properties, in order to elucidate the adsorption mechanisms. A detailed knowledge of NOM adsorption onto activated carbon can then be used to understand and help ameliorate current water treatment problems.

3.2.2 Materials and methods

Water was obtained from a Milli-Q water purification system (conductivity $<1 \times 10^{-6} \text{ Scm}^{-1}$). All chemicals were analytical reagent grade. High purity, oxygen-free nitrogen was used for titration experiments. Glassware was cleaned with concentrated potassium hydroxide solution followed by copious rinsing with Milli-Q water.

Concentration and fractionation of natural organic material

Dissolved natural organic material was concentrated from raw water from the Myponga Reservoir in South Australia. Reservoir water was pre-filtered through a $0.45 \mu\text{m}$ cartridge filter then pumped through an anion exchange resin column; the concentration of dissolved organic carbon (DOC) post column was monitored until removal decreased to $<80\%$. The loss of NOM during this procedure was therefore less than 20%, and presumably consists of nonionic, non-humic material. The adsorbed organics were then eluted using 2M NaCl solution. This procedure was repeated 6 times and the samples of concentrated NOM in 2M NaCl were combined. This solution was desalted by ultrafiltration through a Amicon YC 05 membrane with a nominal molecular weight cut-off of 500 Daltons. Ultrafiltration continued until the permeate conductivity was $<100 \mu\text{Scm}^{-1}$. The retentate contained desalted NOM of >500 nominal molecular weight. The desalted retentate was then fractionated using a second ultrafiltration membrane (Amicon YM) with a nominal molecular weight cut-off of 3,000 Daltons. It should be noted that the membranes are calibrated using a globular protein solute which is 90% rejected by the membrane. The molecular weight of the NOM compounds retained on, or permeating through the membrane will depend on the shape, charge and polarity of the compound. The molecular weight cut-offs should not, therefore, be accepted as true molecular weight of the NOM fraction.

Measurement of concentration of NOM

The concentration of NOM in solution was measured directly in terms of dissolved organic carbon (DOC) content using a Skalar total organic Carbon (TOC) analyser. A calibration curve of measured DOC versus UV absorbance at 254 nm displayed a linear relationship between the two parameters in the concentration range studied. As a result, UV absorbance was used as a surrogate parameter and converted to DOC using the calibration plot.

Titration of NOM

Titration of NOM was performed using an Orion 960 automatic titrator. A known concentration of NOM was equilibrated for 10 minutes at a constant temperature of $25 \pm 0.5^\circ\text{C}$ in 0.01M NaCl. The equilibration and the experiment were performed under nitrogen in order to purge the solution of dissolved CO_2 and to prevent the further dissolution of CO_2 and consequent lowering of the pH. A known amount of base was added and the solution was then titrated to pH 3.00 using 0.01M HCl. A blank titration was also performed under the same conditions.

As the NOM was already in solution, the initial degree of ionisation was unknown. As this is a difficult value to determine, an approximation must usually be made (Nederlof *et al.* 1993). From previous work by Newcombe *et al.* (1994), it was assumed the NOM would be fully protonated (degree of ionisation, $\alpha=0$) at pH 3. This was taken as the starting point of the titration for both the blank and the NOM solution. While there may be some degree of ionisation of NOM at pH 3, it was found by Newcombe *et al.* (1994) that the electrostatic effects of the NOM at pH 3 were negligible, therefore the error associated with the assumption that $\alpha=0$ at pH 3 was considered acceptable. The difference between the blank curve and the NOM titration curve was attributed to the “titratable” acidic groups on the NOM.

Activated carbons

The seven activated carbons used in this study were; P1100, CA10, SA30, F400, PCO, HP, and Hydrodarco. Their respective starting materials, method of activation and manufacturers are summarised in Table 3.1. Two of the activated carbons, F400 and HP, were used in the earlier study by Newcombe and Drikas (1997). All carbons are commercially available. Prior to experiments, all carbons were treated by extensive washing in Milli-Q water using a Soxhlet extraction apparatus. They were then dried for 48 hrs at 110°C, cooled and stored in a desiccator.

Table 3.1 Materials, activation processes and manufacturers of activated carbons used in this study

Carbon	Starting Material	Activation Method	Manufacturer
SA30	Wood*	steam	Carbochem
CA10	Wood*	chemical	Carbochem
HP	wood	chemical	PICA
PCO	coconut	steam	PICA
P1100	coconut	steam	PICA
F400	coal	steam	Calgon
Hydrodarco	lignite	steam	Norit

*same wood

Surface area analysis

Nitrogen adsorption isotherms were measured at a temperature of 77K using a Coulter Omnisorp 100 in static mode. Samples were outgassed at 383K for 16 hrs to a residual pressure of less than 10^{-5} Torr prior to each analysis. A BET plot was constructed and the apparent BET surface area was extracted from the linear region (relative pressure = 0.01-0.10). Allocation of pore size distribution involved subdividing adsorbed amount in the relative pressure ranges 0-0.01, 0.01-0.40, and 0.40-0.95, corresponding broadly to adsorption in primary micropores, secondary micropores and mesopores respectively. Amount adsorbed was converted to liquid volume by assuming a molar volume of liquid nitrogen of $35 \text{ cm}^3 \text{ mol}^{-1}$.

Surface charge determination

Surface charge titrations were carried out using the same apparatus and conditions as the NOM titrations. 0.10 g of carbon was placed into 400 cm^3 of electrolyte solution and allowed to equilibrate for 30 minutes after the addition of 0.75 cm^3 of 0.10 M NaOH. The carbon was then titrated with 0.10M HCl to pH 3, with 6 minutes equilibration time between additions. Two electrolyte concentrations were used for each carbon; 0.01M and 0.3M NaCl. A blank titration was also performed at two electrolyte concentrations under the same conditions. Relative surface charge was determined from the difference between the surface titration curves and the blank curves using the equation:

$$|\sigma| = n/m \quad (2)$$

where $|\sigma|$ = the magnitude of relative surface charge (mmol g^{-1}),
 n = difference between the blank and activated carbon curves (mmol), and
 m = the mass of activated carbon (g).

When relative surface charge was plotted against pH for the two electrolyte concentrations, the pH at which the two curves crossed was taken as the pH at which the absolute charge on the surface was zero (pHpzc), this being the only point where the surface charge is independent of the electrolyte concentration. The curves were then shifted relative to the y-axis until the pHpzc was situated at zero surface charge, with the resultant plot giving absolute surface charge versus pH.

NOM adsorption isotherms

0.03 g of carbon and 30 cm³ of NOM solution was shaken in a glass vessel for three days. The suspension was filtered and the final concentration of DOC was determined by UV absorbance at 254 nm. The surface concentration was then determined by the difference between the initial and final DOC concentration.

3.2.3 Results and discussion**Character of NOM.**

The NOM used in this study was fractionated using ultrafiltration into a 500-3,000 nominal molecular weight (MW) fraction. Since this is a size exclusion method, the molecular weight values should therefore not be considered to be absolute values. However, the peak hydrodynamic diameter of the fraction was found to be 1.1 nm using flow field-flow fractionation, which correlated to an average molecular weight of 1,371 Daltons, well within the ultrafiltration range. A detailed discussion on the characteristics of the NOM fraction can be found in the earlier works of Newcombe and Drikas (1997) and Newcombe *et al.* (1997), who used the same NOM fraction for their studies.

Figure 3.1 shows the charge behaviour of the NOM fraction between pH 3 and 9, which is generally considered to be the carboxyl region (Collins *et al.* 1986). Assuming the NOM was uncharged at pH 3, the negative charge increased steeply until a plateau was reached between pH 7-9, which Newcombe *et al.* (1997) attributed to full ionisation of the NOM carboxyl groups. In the context of the present work, only the magnitude of the negative charge between pH 4 and pH 9 is important, the reader is referred to Newcombe *et al.* (1997) for a more comprehensive discussion.

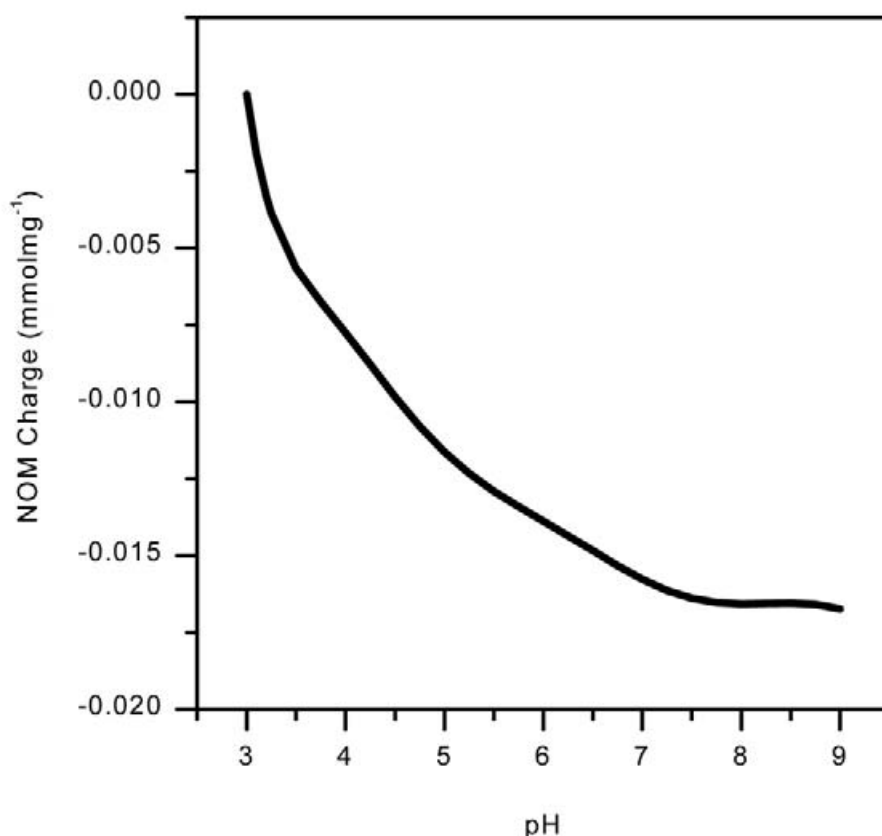


Figure 3.1 Charge on 500-3,000 MW NOM ultrafiltration fraction versus pH in 0.01M NaCl

Activated carbons

Seven activated carbons with different surface properties were studied; SA30, CA10, HP, PCO, P1100, F400 and Hydrodarco. Net surface charge was determined by potentiometric titration, the results are shown in Figure 3.2. Table 3.2 shows the surface areas and pore volume distributions of the seven carbons.

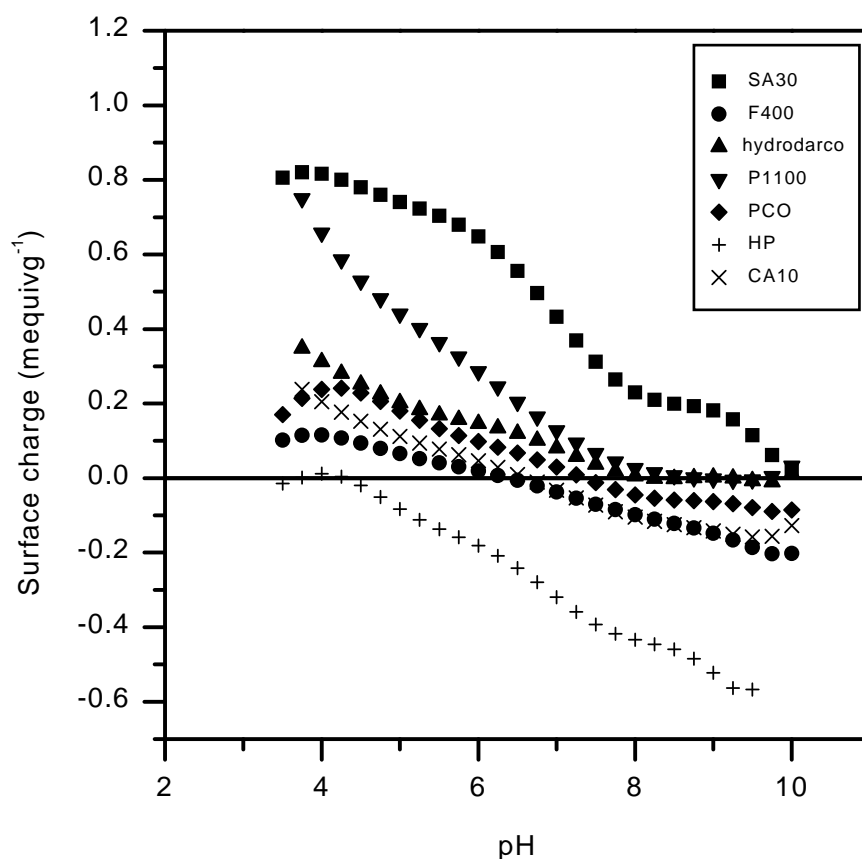


Figure 3.2 Surface charge of activated carbons

Table 3.2 Surface areas and pore volumes of activated carbons

Carbon	Surface area (m^2g^{-1})	PORE VOLUME (cm^3g^{-1})		
		primary micropores $w < 0.8\text{ nm}$	secondary micropores $0.8 < w < 2\text{ nm}$	mesopores $2 < w < 50\text{ nm}$
SA30	1077	0.35	0.13	0.09
CA10	1491	0.39	0.47	0.41
HP	2183	0.57	0.54	0.51
PCO	987	0.31	0.13	0.03
P1100	1241	0.38	0.18	0.05
F400	1047	0.34	0.12	0.09
Hydrodarco	717	0.23	0.12	0.29

The net surface charges of carbons SA30, P1100 and Hydrodarco are mainly positive, while HP is mainly negative. For carbons F400 and CA10, the surface charge varies from positive at $\text{pH} < 6.5$ to negative at higher pH values, while for PCO, the change from positive to negative surface charge occurs at $\text{pH} > 7.2$. Examination of Table 3.2 shows that, except for Hydrodarco, all seven carbons have a high surface area and primary micropore volume. Carbons CA10 and HP have a high

secondary micropore volume, while the other carbons have a moderate secondary micropore volume. In terms of mesopores, carbons CA10, HP and Hydrodarco have a high volume, indicative of an "open" pore structure, while the other carbons only have a small volume and thus a much more "closed" pore structure. The activated carbons used in this study therefore represent a wide range of surface properties.

Adsorption of NOM

Adsorption at pH 7 and pH 4. Figures 3.3(a) and 3.3(b) show the isotherms for the adsorption of NOM onto all seven activated carbons at low salt concentration (0.01M) and pH 7 and pH 4 respectively. The adsorption results at pH 9 have been omitted as the trends are identical to those at pH 7. Due to the average size of the NOM molecules used in this study (determined by flow field-flow fractionation), they would be expected to adsorb in secondary micropores and mesopores only, i.e. there will be little adsorption in primary micropores. Indeed, this was shown by Newcombe and Drikas (1997) for the adsorption of a 500-3,000 MW NOM fraction onto activated carbons at pH 3.

Figure 3.1 shows the titration curve of the NOM fraction used in this study. The curve shows that at pH 4 the NOM is negatively charged ($-0.008 \text{ mmolmg}^{-1}$), and at pH 7 and 9 the magnitude of the negative charge (-0.016 and $-0.017 \text{ mmolmg}^{-1}$ respectively) is twice that at pH 4. It would therefore be expected that for a positively charged activated carbon, at low surface concentrations, there should be an attractive electrostatic interaction, while for negatively charged carbon surfaces, the NOM-surface interaction should be repulsive.

Figure 3.3(a) shows that at pH 7, NOM adsorption increases approximately with available pore (secondary micropore volume plus mesopore volume) in the order;

PCO<P1100<F400<Hydrodarco<SA30<CA10<HP.

When the pH is decreased to 4 (Figure 3.3(b)), NOM adsorption increases and adsorption is in the order;

PCO<P1100<SA30<F400<Hydrodarco<CA10 \approx HP.

OPTIMISATION OF ADSORPTION PROCESSES

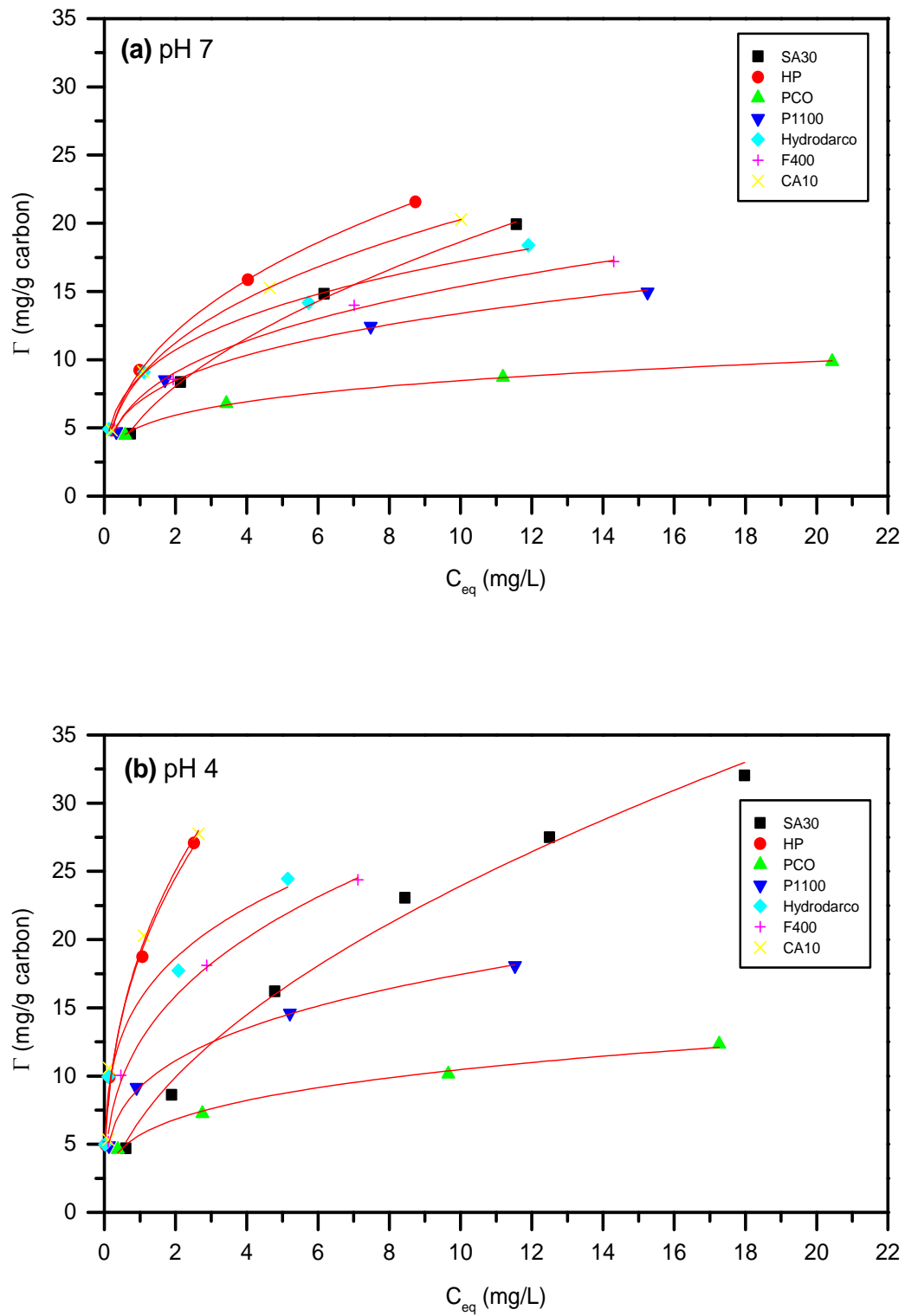


Figure 3.3 Surface Density (Γ) versus equilibrium concentration (C_{eq}) for 7 carbons at; (a) pH 7 and (b) pH 4 and 0.01M NaCl.

These orders have been determined by fitting a Freundlich isotherm to the curves and estimating the surface concentration at a solution concentration of 10 mg/L. The order changes, depending on the solution concentration chosen, due to the different slopes of the plots. For example, the rating of SA30 at a solution concentration of 1 mg/L of DOC at pH 7 is below that of P1100, whereas at a solution concentration of 30 mg/L SA30 is estimated, using the Freundlich isotherm, to have higher adsorption of NOM than either hydrodarco or F400. Freundlich isotherm parameters will not be reported in this discussion, due to the strong effect of the solution concentration, and the comparison of the behaviour of the carbons will be qualitative, based on the observed adsorption in the concentration ranges shown.

The orders mentioned above are reasonably consistent with NOM adsorption increasing with available pore volume. PCO has the lowest pore volume in the 0.8-50 nm range, SA30, P1100 and F400 are very similar, hydrodarco has a moderate pore volume, and CA10 and HP possess the highest volumes. Available pore volume is an important factor in the adsorption of the NOM, although other factors have an impact due to high electrostatic interactions (repulsive) between the negative charge of the NOM (see Figure 3.1) and the negative surface charge of most of the carbons (see Figure 3.2). Both lateral ($\text{NOM}_{\text{ads}}\text{-NOM}_{\text{ads}}$) and surface-NOM interactions are important. At pH 7 there is an anomaly in the order, with the relative positions of hydrodarco and SA30 being reversed from what would be expected from pore volume considerations only. This could be influenced by the surface charge of the carbons; SA30 has a large positive charge at this pH relative to hydrodarco. At pH 4, the negative charge of the NOM decreases, thereby effectively decreasing repulsive lateral interactions. The surface charges of the activated carbons also become positive, except for HP which has a negligible surface charge, and the adsorption of NOM subsequently increases. This effect has been seen previously by many authors (Newcombe *et al.* 1994, 1997, McCleary and Snoeyink 1980). As was the case for pH 7, available pore volume is not the only factor influencing adsorption. For example, F400 shows a higher adsorption than SA30 and P1100 although they have very similar pore volume (Table 3.2). This cannot be explained by surface charge effects as SA30 and P1100 have significantly higher positive surface charge than F400, but lower adsorption. These results are consistent with previous work by Newcombe *et al.* (1994, 1997) which clearly showed that the adsorption of NOM, at surface concentrations reaching capacity values, could be directly related to available pore volume only at pH of 3, or lower, where the electrostatic effects are minimised. At pH above this value, the adsorption is influenced by a range of factors, including surface and NOM charge.

Figures 3.4(a) and 3.4(b) emphasise this effect. Here the adsorption isotherms illustrated in Figure 3.3 have been replotted in terms of the mass of DOC adsorbed per cm³ of available pore volume (Γ_{vol}), calculated by dividing the adsorption density (Γ) by the sum of the secondary micropores and mesopores (i.e. the “available” pore volume for this fraction) (Newcombe *et al.* 1997).

At pH 7, the volume of pores occupied increases in the order;
HP<CA10<Hydrodarco<PCO<P1100<F400<SA30.

At pH 4, the volume occupied per cm³ is higher than at pH 7, and increases in the order;
HP<CA10<PCO<Hydrodarco<P1100<SA30<F400.

The chemically activated wood based carbons (HP and CA10) show the lowest adsorption of NOM per unit volume at pH 7 and pH 4. Again, this cannot be explained by surface charge effects as CA10 has a similar surface charge to some of the other activated carbons, namely F400, PCO and Hydrodarco, while HP is mainly negatively charged. Indeed, the surface charge profile of CA10 is much different from other chemically activated wood-based carbons such as HP and those studied previously by Newcombe *et al.* (1994). This suggests that CA10 may have fewer oxygen-containing surface groups and thus a much different surface chemistry from other chemically activated wood-based carbons. Chemical (or specific) factors must therefore be involved in the adsorption mechanisms, probably attributable to the surface chemistry and associated functional groups of both activated carbons.

Figure 3.4b) indicates that (as mentioned previously) F400 displays significantly higher adsorption than SA30 over a wide NOM concentration range, although SA30 has a much higher positive surface charge than F400 at this pH. Fourier transform infrared spectra of the carbons display no significant differences in surface functional groups (unpublished data). This is clearly an extremely complicated system where the adsorption of NOM cannot be explained by available pore volume and surface

charge effects alone. Figure 3.3 shows that, despite the high positive surface charge, SA30 has a lower adsorption affinity at low solution concentrations at both pH than all the other carbons (except for PCO) as indicated by the shape of the isotherms. This is another indication of the importance of surface properties of the carbons that are not easily detected by the techniques used in this study to date.

Effect of ionic strength. Figures 3.5(a-c) and 3.6(a-c) show the adsorption isotherms of the NOM fraction onto carbons SA30 and PCO respectively, at two salt concentrations and pH of 4, 7 and 9. The initial portions of the isotherms show higher adsorption densities at low salt concentration, after which the curves intersect and show higher adsorption densities at high salt concentration. The intersection point of the isotherms, Γ_{int} , marks the transition from the screening reduced to the screening enhanced adsorption mode. Carbons CA10, P1100, F400 and Hydrodarco exhibit similar adsorption behaviour. Carbon HP however, displays no Γ_{int} , the adsorption being entirely screening enhanced. Not all adsorption isotherms could be included in this paper, however the relevant information obtained from the isotherms is summarised in Table 3.3. Also given in Table 3.3 is the carbon surface charge and the charge of the adsorbed NOM at Γ_{int} (calculated using the charge per milligram of the dissolved NOM at each pH multiplied by the surface concentration).

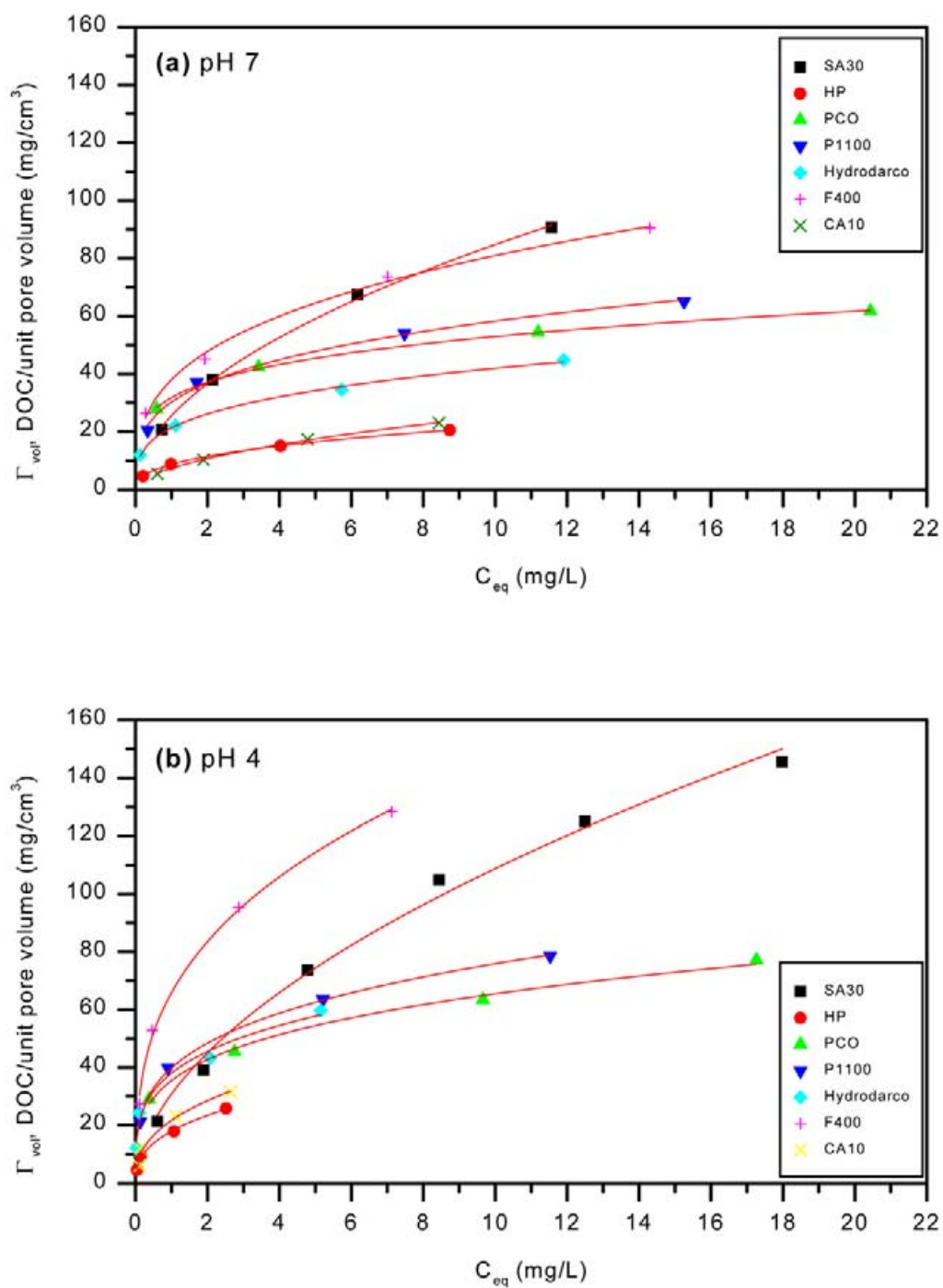


Figure 3.4 DOC concentration per unit pore volume (Γ_{vol}) versus equilibrium concentration (C_{eq}) for 7 carbons at; (a) pH 7 and (b) pH 4 and 0.01M NaCl.

OPTIMISATION OF ADSORPTION PROCESSES

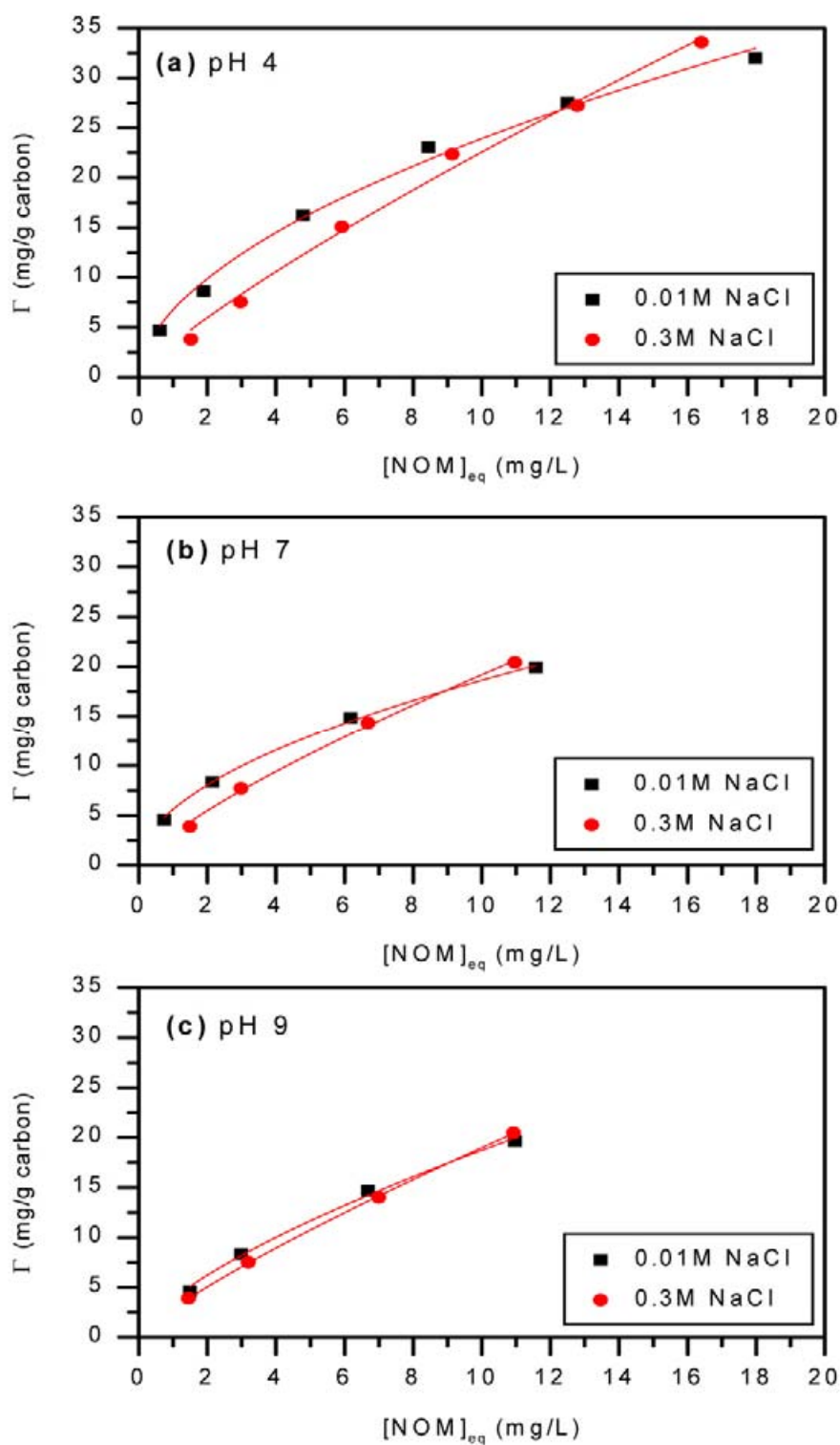


Figure 3.5 NOM adsorption onto SA30 at; (a) pH 4, (b) pH 7 and (c) pH 9 at two salt concentrations.

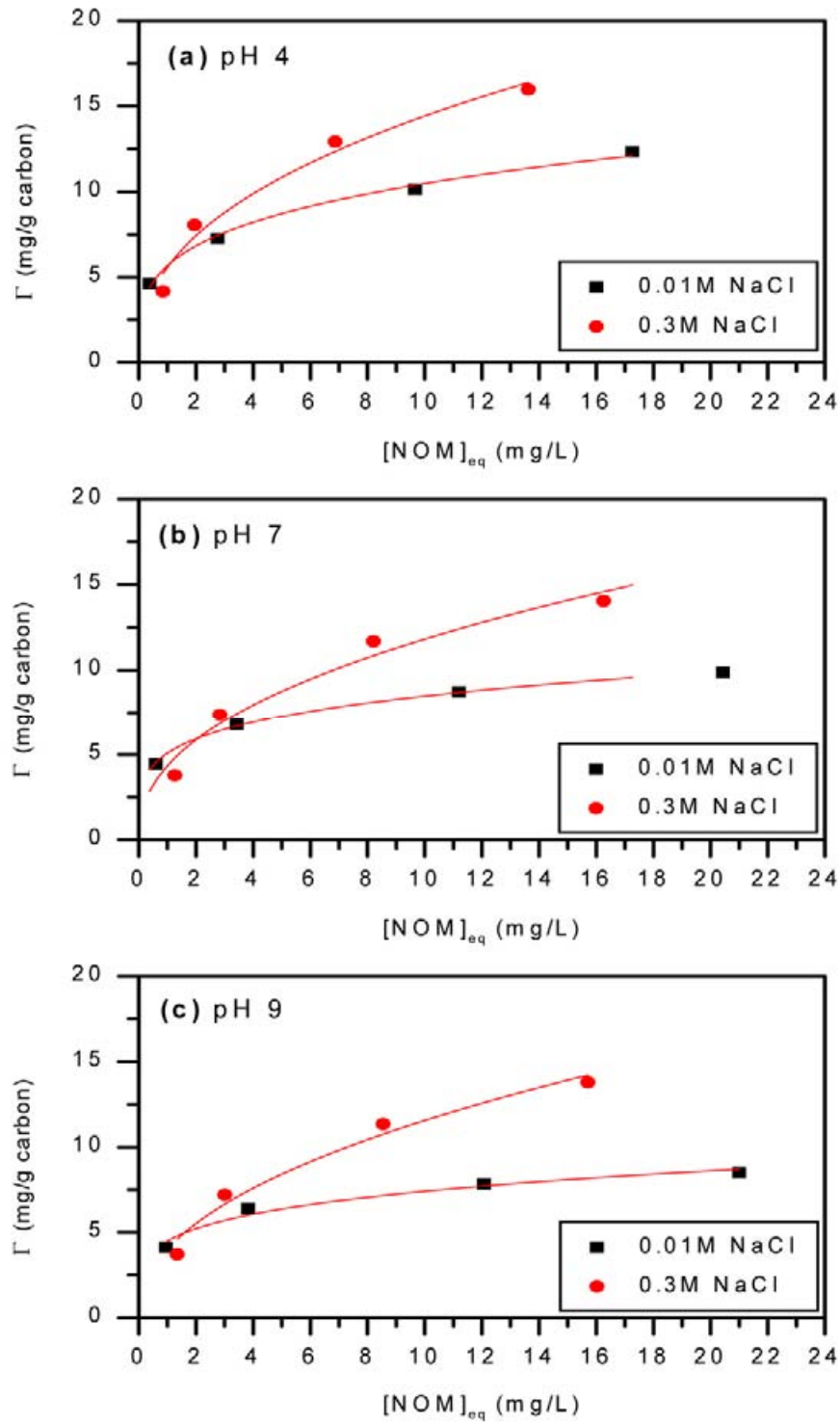


Figure 3.6 NOM adsorption onto PCO at; (a) pH 4, (b) pH 7 and (c) pH 9 at two salt concentrations

OPTIMISATION OF ADSORPTION PROCESSES

Table 3.3 Charge on NOMads at Γ_{int} at pH 4, 7 and 9

carbon	pH	Γ_{int} (mg. g ⁻¹)	Γ_{vol} (pH 4) (mg. cm ⁻³)	carbon surface charge (mmol. g ⁻¹)	NOMads charge at Γ_{int} (mmol. g ⁻¹ carbon)
SA30	4	27	123	+0.82	-0.22
	7	18		+0.43	-0.29
	9	17		+0.18	-0.29
CA10	4	29	33	+0.20	-0.24
	7	14		-0.05	-0.22
	9	12		-0.15	-0.20
HP	4	no cross-over point observed		0	
	7			-0.30	
	9			-0.52	
PCO	4	6	38	+0.22	-0.05
	7	6		+0.03	-0.10
	9	5		-0.08	-0.08
P1100	4	14	61	+0.65	-0.11
	7	10		+0.12	-0.16
	9	8		0	-0.13
F400	4	14	67	+0.10	-0.11
	7	9		-0.05	-0.14
	9	6		-0.16	-0.10
Hydrodarco	4	21	51	+0.31	-0.17
	7	12		+0.10	-0.19
	9	11		0	-0.18

Newcombe and Drikas (1997), in a study that formed the basis of this work, found that F400 displayed a crossover point (Γ_{int}) while HP did not. The results presented in Table 3.3 for F400 and HP are thus consistent with that preliminary work. In the present study, for F400, the NOM_{ads} charge balances the surface charge at Γ_{int} at pH 4 ($\Gamma_{int,4}$), indicating charge compensation of the positively charged surface by the negatively charged NOM, consistent with the polyion adsorption theory of Norde and Lyklema (1978). At this point it should be noted that the surface charge curve of F400 (and indeed the values of Γ_{int}) in this study is somewhat different from that obtained by Newcombe and Drikas (1997). This can be attributed to a number of factors such as sample age, sample cleaning efficiencies, and different carbon batch. The slightly different surface charge properties of the current sample should then be expected to show somewhat different adsorption behaviour, and this was reflected in the values of Γ_{int} which are 40-50% lower than those obtained by Newcombe and Drikas (1997). However, examination of Table 3.3 shows that the results give the same trends as described by Newcombe and Drikas (1997), i.e. at pH 4 for carbon F400, the charge of NOM_{ads} balances the carbon surface charge at Γ_{int} .

HP, the most negatively charged carbon examined, did not display an intersection of the isotherms, again consistent with the results of Newcombe and Drikas (1997), who stated that if there were an electrostatic attraction, Γ_{int} could not be determined (and hence no crossover point observed) as the surface concentrations involved were below the detection limits of the DOC measurements. They therefore concluded that the adsorption of NOM onto HP must be governed mainly by non-electrostatic chemical forces, i.e. the adsorption is controlled by ΔG_{spec} .

CA10 is the only other activated carbon examined which displayed charge compensation at pH 4 as described by Newcombe and Drikas (1997). For the other carbons (SA30, PCO, P1100 and Hydrodarco) at $\Gamma_{int,4}$, the surface charge is significantly greater than the charge of the adsorbed NOM. This indicates that electrostatic repulsive forces begin to dominate adsorption before the positive surface charge is fully compensated, possibly due to lateral interactions increasing as the surface concentration increases (Figure 3.4(b)).

Table 3.3 also shows the surface concentration per unit adsorption volume (Γ_{vol}) at $\Gamma_{int,4}$. SA30 has a very high Γ_{vol} at $\Gamma_{int,4}$, relative to all other carbons studied, thereby indicating that the adsorbed NOM molecules may be in closer proximity to each other than on the other carbons. The high positive charge of the SA30 surface may influence the lateral interactions, although this interpretation is

inconsistent with other results. For example, F400 and P1100 have similar available pore volume and similar values of $\Gamma_{\text{int},4}$, but P1100 has a much higher positive surface charge at pH 4 than F400. Therefore in this case, the surface charge does not appear to influence the lateral interactions and thus allow a higher value of $\Gamma_{\text{int},4}$. These results indicate that the appearance of charge compensation at pH 4 for F400 and CA10 may be fortuitous, and that the surface concentration at which $\Gamma_{\text{int},4}$ occurs, i.e. where the adsorption changes from the adsorption reduced to the adsorption enhanced regimes, is probably dependent on many factors such as surface charge, pore structure, surface chemistry, position and concentration of charged and uncharged oxygen-containing functional groups, surface impurities, etc., and is thus difficult to predict for most activated carbons. It is also possible that for those activated carbons where charge compensation did not occur (SA30, PCO, P1100 and Hydrodarco), the excess positive charge may be located in regions inaccessible to the NOM, i.e. the primary micropore region. However the location of the positive charge within activated carbons is difficult to determine experimentally, therefore these results are not readily interpreted.

Newcombe and Drikas (1997) also found for F400 as pH was increased, Γ_{int} decreased, although the charge of the NOM_{ads} at Γ_{int} remained relatively constant. They attributed this to the number of positive sites on the carbon surface remaining constant from pH 4-9, while the net charge was determined by increasing ionisation of negative surface groups. Table 3.3 shows that this effect was also present for the carbons studied in the present work, namely, as the pH increases, the net charge on the activated carbons becomes more negative (or less positive) (Fig. 3.2), the amount of adsorbed NOM decreases (Figure 3.3), the negative NOM charge increases (Figure 3.1), while the total charge of the adsorbed NOM at Γ_{int} remains relatively constant.

3.2.4 Summary and conclusions

The effect of ionic strength, pH, pore volume distribution and surface charge on the adsorption of natural organic material by seven activated carbons was studied. The present work confirmed the existence of crossover points in the adsorption isotherms undertaken at two ionic strengths which were indicative of a change in adsorption mechanism from the screening reduced to the screening enhanced modes. The “charge compensation” mechanism for NOM adsorption at low surface concentrations proposed by Newcombe and Drikas (1997) did not hold for four of the seven activated carbons studied. Rather, the adsorption appears to be attributable to a number of factors such as available pore volume, pore structure, electrostatic attractive and repulsive forces, specific (chemical) interactions between the NOM and the surface functionalities of the activated carbons, and access to the positive adsorption sites, making a detailed interpretation of the results extremely difficult. However, the finding that the charge on the adsorbed NOM at the cross-over point of the isotherms was independent of the pH for all carbons was consistent with the findings of Newcombe and Drikas (1997), and indicated that the amount of negative charge on the NOM participating in electrostatic adsorption interaction depended only on the number of available positive surface sites on the carbon, and not on the net charge of the surface.

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4. THE INFLUENCE OF WELL-CHARACTERISED NOM ON THE ADSORPTION OF MIB ONTO ACTIVATED CARBON

4.1 INTRODUCTION

Sections 4.2 and 4.3 describe the characterisation of NOM fractions and a range of activated carbons, and the competitive adsorption effects between the NOM and the odour compound MIB. The NOM fractions were isolated from Myponga Reservoir water and haven't been previously described in this report. Section 4.4 describes the competitive behaviour of NOM fractions isolated from two French rivers by Professor Jean -Philippe Croué and his team at the University of Poitiers, France.

4.2 SIMULTANEOUS ADSORPTION OF MIB AND NOM ONTO ACTIVATED CARBON: I CHARACTERISATION OF THE SYSTEM AND NOM ADSORPTION

4.2.1 Introduction

2-methylisoborneol (MIB) is a musty odour compound produced as a secondary metabolite by some cyanobacteria and actinomycetes. It causes significant problems for drinking water suppliers as it is perceived by most consumers as an unpleasant odour and taste in water at very low concentrations (around 10 ng L⁻¹). The compound, an aliphatic tertiary alcohol, is not easily oxidised by chlorine or ozone; consequently activated carbon is currently considered the best technology for the treatment of affected water.

A moderately hydrophobic compound of low molecular weight (168 g mol⁻¹), MIB is readily adsorbed by microporous activated carbon in the absence of competing compounds (Newcombe *et al.* 1997). However, in natural waters where the concentration of natural organic material (NOM) can be more than 100,000 times that of the target compound MIB (for example, 10 mg L⁻¹ compared with 100 ng L⁻¹), the effect of the competition for adsorption sites is dramatic (Newcombe *et al.* 1997, Chudyk *et al.* 1979, Chen *et al.* 1997). As a result, a large proportion of the adsorption volume within the activated carbon is not utilised for MIB removal. An increased knowledge of the mechanisms of competition, and the types of NOM contributing the majority of the competitive effect, could result in the production of activated carbons which minimise such effects, and consequent substantial cost savings to the water supplier.

Before the competitive effect can be fully understood, a comprehensive, controlled study, using a well characterised system is required. Newcombe *et al.* (1997) compared the equilibrium adsorption of MIB in NOM-free water with adsorption in five molecular weight NOM fractions and a natural water. Only two carbons were studied, at one carbon dose. The results indicated that the competitive effect was probably due to the presence of low molecular weight compounds, and the authors suggested that the bulk of the effect was due to direct competition for adsorption sites between MIB and very low molecular weight NOM compounds. Sugiura *et al.* (1997) studied the competitive effects between MIB and a commercially available humic acid. In addition, they studied several organic compounds which they suggested were model compounds for low molecular weight NOM. All compounds reduced the adsorption of MIB, and for the three activated carbons studied the humic acid solution showed the most competition. However, as there was no attempt to characterise the activated carbon or the humic acid, the authors were unable to infer competitive mechanisms. The concentrations of MIB used were considerably higher than those found in practice.

Competitive mechanisms between NOM and industrial and agricultural micropollutants have been studied by several authors. Kilduff and Weber (1998) found the greatest effect on adsorption of trichloroethylene (TCE) was achieved by pre-loading the activated carbon with low molecular weight humic acids. They suggested the NOM occupied the high energy adsorption sites, thus decreasing site heterogeneity, and the decrease in adsorption of TCE was due to the decrease in suitable adsorption sites rather than a pore blockage mechanism. Pelekani (1999) and Pelekani and Snoeyink (2000, 2001) undertook a comprehensive investigation of competitive effects between model compounds and the pesticide atrazine on well characterised carbon fibres. The authors found that competitive mechanism depended on both the size of the competing compound and the pore volume distribution of the adsorbent. Investigations on one natural water using two activated carbon fibres supported the interpretation of these effects (Pelekani and Snoeyink 1999).

In the present study, the competitive effects of NOM on the adsorption of MIB were investigated at equilibrium and shorter contact times. The six carbons studied were commercially available, and have been considered for use in the mitigation of odour episodes in water treatment plants within Australia. The conditions under which they were studied can be related directly to practical applications in terms of carbon dose and contact time. The simultaneous adsorption of MIB and dissolved organic carbon (DOC) in raw Myponga water, diluted raw water and NOM isolated using anion exchange was investigated, and the effect on MIB adsorption was related to information from the extensive characterisation of the activated carbons and the NOM. The objectives were to determine:

- the NOM responsible for the greatest competitive effect,
- the most likely competitive mechanisms in this system and
- the characteristics of the activated carbon that could be expected to minimise that effect,
- in the context of the conceptual model of competition proposed by Pelekani (1999).

In Part I the extensive characterisation of the system and the identification of the important adsorption processes for the competitive compounds in the various NOM solutions are described. In the next section (4.3) MIB adsorption data are presented and the observed competitive effects are interpreted based on the information reported in this section.

4.2.2 Materials and methods

All solutions were prepared using deionised water from a Milli Q system (Millipore Pty Ltd, France). All glassware was cleaned by immersion in 2M KOH for 1 hour, followed by rinsing in deionised water and drying at 105°C. All chemicals were Analar grade (BDH, Sydney Australia).

The ultrafiltration membranes used were Amicom Ym30, Ym01 and Yc05 (Supplier, Adela Scientific, Adelaide). These correspond to molecular weight cut-off values of 30,000, 1,000 and 500 g mol⁻¹ respectively. The Ym series of membranes are regenerated cellulose whereas the Yc05 is made from cellulose acetate. The ultrafiltration vessels were constructed by the technical workshop of the University of Adelaide, Waite campus.

The powdered activated carbons (PAC) were Soxhlet extracted with Milli Q water for three days, sieved to < 45µm, then dried at 120 ° C and cooled and stored in a vacuum desiccator.

Activated carbon characterisation

Pore volume distributions

Nitrogen adsorption/desorption experiments were carried out volumetrically at 77K using an Autosorb apparatus (Quantachrome Corp.). All samples were degassed overnight at 200°C to relative pressures of between 10⁻⁵ and 10⁻⁶. The micropore size distribution was based on Density Functional Theory (DFT) (El-Merraoui *et al.* 2000) using the software supplied by Quantachrome Corporation.

Surface charge

Surface charge determinations were undertaken using an Orion Autotitrator, as described elsewhere (Bjelopavlic *et al.* 1998).

Diffuse Reflectance Fourier Transform Spectroscopy (DRIFT).

DRIFT spectroscopy was performed using a Nicolet 750 Magna spectrometer. Powdered carbon samples were mixed with granulated KBr to reach a concentration by weight of approximately 1%. Granulated KBr was used as the background.

Preparation of NOM solutions

Myponga raw and diluted

Eighty litres of Myponga reservoir water was filtered through 0.45 µm membrane (supplier, Crown Scientific Australia) and stored at 4°C until required. A 50% dilution was prepared using 0.01 M NaCl, determined to be the same ionic strength as the raw Myponga water.

Anion exchange isolates

MIEX[®] DOC anion exchange resin was packed in a glass column and cleaned using 2 bed volumes (BV) of 2 M NaCl followed by 2 BV of 0.2 M NaOH and rinsed with deionised water. Sixty litres of the filtered Myponga Reservoir water was then pumped through the resin at an empty bed contact time of 15 minutes. The NOM was eluted from the resin using 2 M NaCl. Details of the desalting procedure for the MIEX[®] isolate are given in Newcombe *et al.* (1997). The isolate was then fractionated using ultrafiltration membranes in a pressurised cell, operated in dead end mode. Details are also given in Newcombe *et al.* (1997). The ultrafiltration fractions used for this study were the <500, 500 to 1000, and >30000 fractions. These molecular weights are based on the membrane nominal molecular weight cut-off values, which have been shown to overestimate the actual molecular weight distributions of NOM (Pelekani *et al.* 1999). These fractions were chosen as together they represent the majority of the NOM in the Myponga water, and they also represent the extremes in terms of chemical character and molecular weight. Hereafter the fractions will be referred to as F1, F2 and F5, respectively. The final 20 litres of the effluent from the anion exchange column were collected. At this stage the removal of DOC by the resin had reached a steady state of approximately 66%. Therefore the effluent NOM solution contained those molecules not isolated by the anion exchange resin at the end of the isolation. During the initial stages of the isolation procedure >85% of the NOM, measured as dissolved organic carbon, was removed by the resin. As the anion exchange resin had negligible impact on the ionic content of the Myponga water, other than removing negatively charged NOM, the inorganic matrix of the effluent NOM was effectively identical to that of the raw water. A detailed description of all isolation and fractionation procedures is given by Hepplewhite (2000). The name of isolate, isolation technique and percentage of whole water NOM are given in Table 4.1.

Table 4.1 Description of NOM solutions obtained from Myponga Reservoir water

NOM solution	Isolation technique	Percentage of whole water NOM	Fraction
F1	anion exchange resin	15	<500 (ultrafiltration)
F2	anion exchange resin	45	500-1000 (ultrafiltration)
F5	anion exchange resin	15	>30000 (ultrafiltration)
Effluent	NOM remaining after ion exchange	32	Whole isolate
Raw	none	100	Whole water
50% dilution of raw	none	100	Whole water, diluted

NOM characterisation

DOC was measured using a Sievers 820 Total Organic Carbon Analyser. UV absorbance (at 254 nm) and colour (at 456 nm) measurements were carried out on a GBC UV/VIS 918 Spectrophotometer. Specific UV absorbance (SUVA) and specific colour were calculated as follows:

$$\text{SUVA} = \text{UV absorbance @ 254 nm (cm}^{-1}\text{)} / \text{DOC (mg L}^{-1}\text{)} \times 100$$

$$\text{Specific Colour} = \text{Colour (HU)} / \text{DOC (mg L}^{-1}\text{)}$$

¹³C nuclear magnetic resonance spectroscopy (NMR)

A Bruker CXP 100 Instrument of frequency 22.6 MHz was used to analyse freeze-dried samples of the NOM fractions. Chemical shift ranges used to calculate the carbon functional groups are described by Wilson (1987).

High performance size exclusion chromatography

The high performance size exclusion chromatography (HPSEC) analysis was based on the method of Chin *et al.* (1994). The HPSEC analysis is based on the fact that small compounds will diffuse into the pores of the column packing material and display longer retention times than larger molecules. Retention times are converted to apparent molecular weights using suitable molecular weight standards. The column (Shodex Protein KW-802.5, molecular weight range 0.1K-50K, Waters Australia) was calibrated using polystyrene sulphonates of molecular weight 35K, 18K, 8K and 4.6K,

[®] MIEX is a registered trademark of Orica Australia Pty Ltd

and acetone. These compounds are considered to best represent the structure and conformation of NOM in solution (Chin *et al.* 1994). Ultraviolet absorbance at 260 nm was used for the detection of NOM. For a detailed discussion of the use of HPSEC for the determination of molecular weight distribution of NOM refer to Pelekani *et al.* (1999).

Equilibrium adsorption experiments

NOM solution was added to clean dry Pyrex bottles to a level allowing minimum headspace. MIB was added followed by the appropriate dose of PAC. The bottle was sealed and agitated for 3-5 days. DOC concentrations were obtained prior to the experiment, and at the conclusion. The experiments were undertaken at the natural pH of the solutions, 7-8.

Kinetics experiments.

MIB stock was added to 2.2 L of NOM solution stirring in a 2 L volumetric flask. The narrow neck of the flask minimised the surface area and thus minimised volatilisation of the MIB. The flask was stoppered with a rubber bung through which a teflon tube had been placed. This tube extended down into the solution and allowed samples to be taken via syringe. The solution was mixed using a magnetic stirrer. After 15 minutes of mixing a sample was taken to determine the initial DOC concentration. PAC (pre-wetted overnight) was added, with samples taken at predetermined intervals over four hours. Samples were filtered through 0.45 µm disposable filters to remove the PAC and the molecular weight distributions were determined.

4.2.3 Results and discussion

Activated carbon characterisation

Table 4.2 provides information on the starting materials and method and extent of activation of the six carbons investigated.

Table 4.2 Starting material, mode and extent of activation of six activated carbons.

Carbon	Manufacturer	Starting material	Activation method
F400	Chemviron	Coal	Steam
CA10	Carbochem	Wood*	Chemical
SA30	Carbochem	Wood*	Steam
P1100	PICA	Coconut [†]	Steam, high level of activation
PCO	PICA	Coconut [†]	Steam, low level of activation
HP	PICA	Wood	Chemical

*[†] same material

Figure 4.1 gives the pore size distributions of the carbons, calculated using density functional theory. The carbons display a wide range of pore size distributions, as expected for a diverse range of starting materials and activation processes. The figure also illustrates the change in the order of the carbons, in terms of pore volumes, with increase in pore size. For example, at a pore width of 1.1 nm, the ranking of the carbons is SA30>P1100=F400>PCO>CA10>HP, whereas the trend in pores of 1.6 nm width is CA10>HP>SA30>P1100>F400>PCO. The variation of net charge on the surface of the carbons with pH is shown in Figure 4.2. Three of the carbons display both positive and negative charge, depending on the pH, with points of zero charge in the pH range 7-8, whereas the other three are markedly different. HP, a chemically activated wood carbon, shows little evidence of positive surface charge. SA30 and P1100 show little evidence of negative surface charge. For the coconut carbon, P1100, this is possibly an indication that the higher level of activation resulted in fewer acidic groups compared with PCO, the lower activation level coconut carbon (Sontheimer *et al.* 1988). It should be noted that, since the titration method of surface charge determination measures net surface charge only, it is not possible from these results to determine the actual concentration of positive and negative sites.

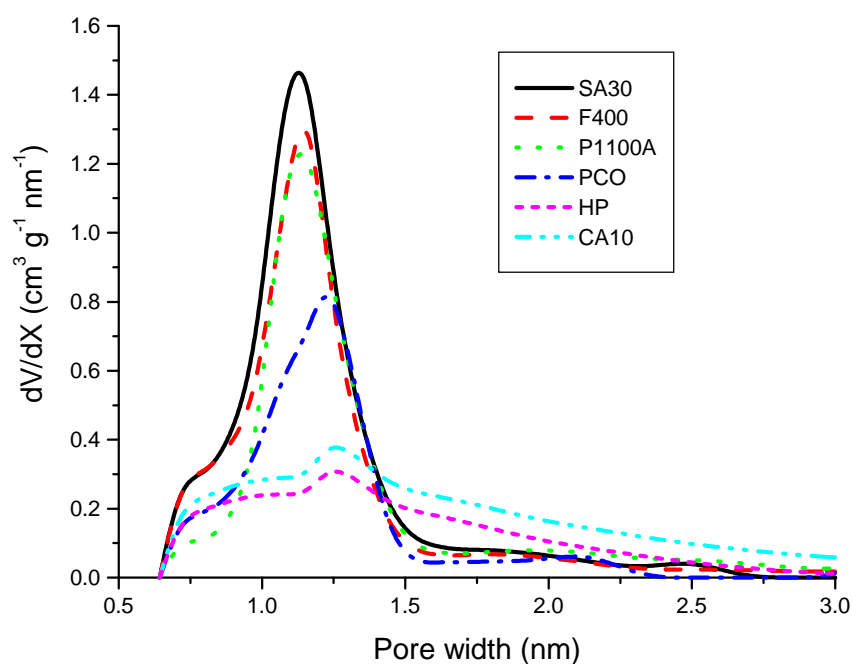


Figure 4.1 Pore size distributions of activated carbons

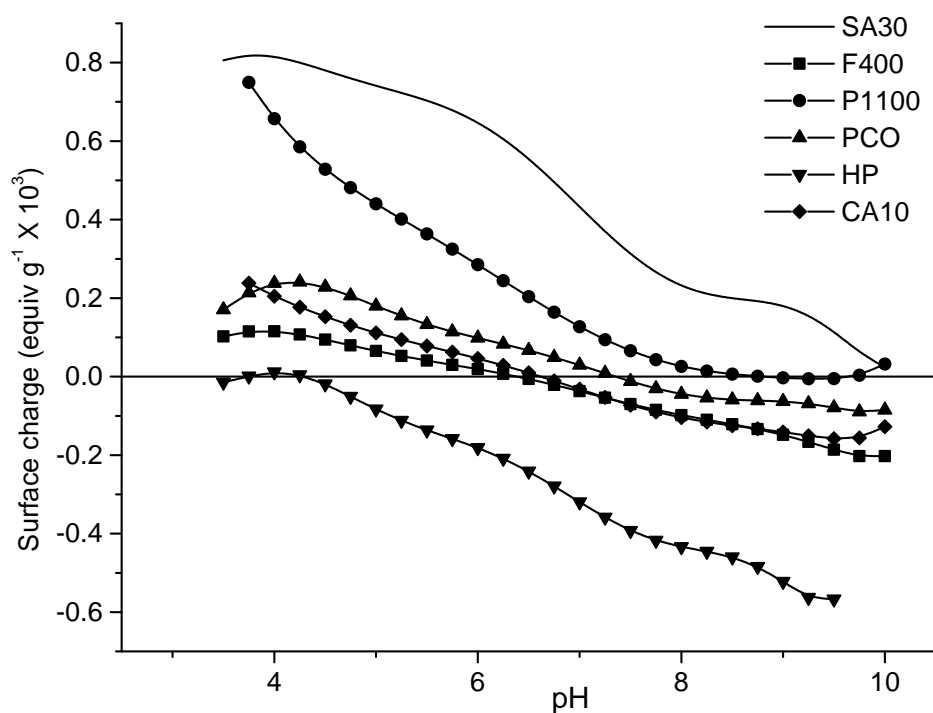


Figure 4.2 Surface charge vs. pH of activated carbons

Figure 4.3 shows the diffuse reflectance Fourier transform (DRIFT) spectra of the six carbons. This technique is simple to utilise as it does not require a KBr disc, the sample is simply mixed with KBr crystals; however, it cannot be used to gain quantitative data.

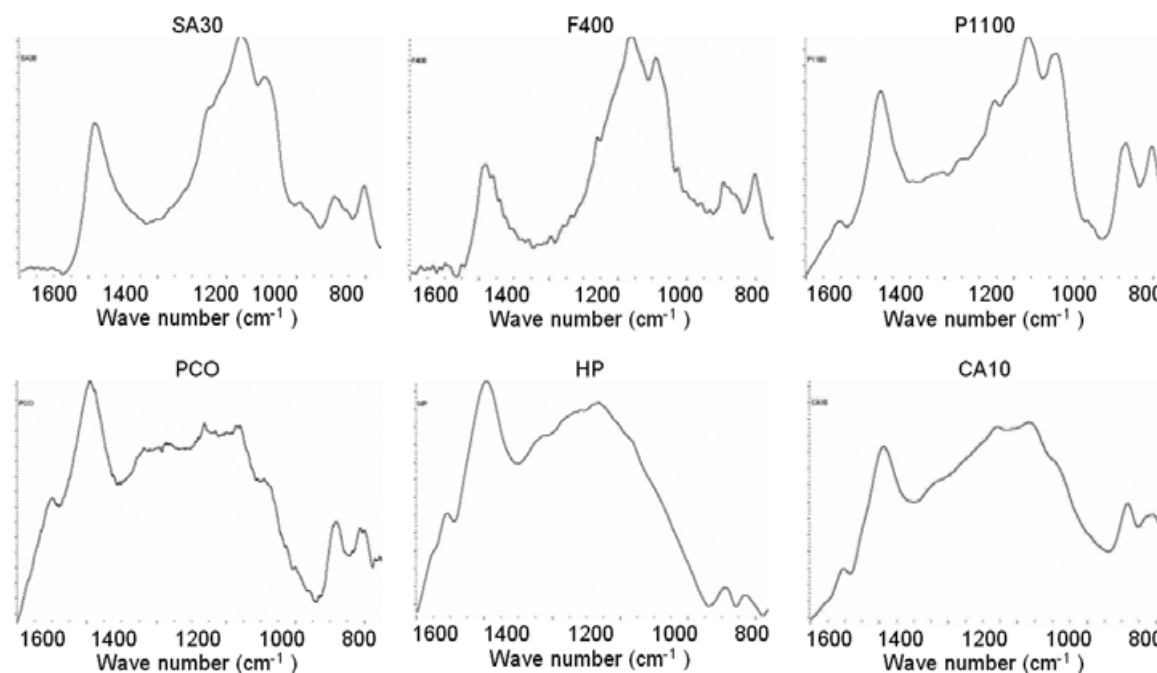


Figure 4.3 DRIFT spectra of activated carbons

From the spectra, two main types of carbon surface are apparent. PCO, HP and CA10 show similar spectra, as do SA30, F400 and P1100. PCO, HP and CA10 also display a peak at 3060 cm^{-1} (not shown), considered to be indicative of carboxyl groups (Bansal *et al.* 1988) that is not discernible in the other spectra. Two major differences in the shapes of the spectra apparent in Fig. 3 are

- in the region $1250\text{--}1400\text{ cm}^{-1}$, PCO, HP and CA10 display strong absorbance. There is some evidence of absorbance in that region for P1100, and little for F400 and SA30
- the relative peak height at 1580 cm^{-1} is higher for PCO, HP and CA10.

IR absorbance at 1350 and 1580 cm^{-1} is strongly influenced by the presence of oxygen groups, in particular phenolic OH and C=O groups (Bansal *et al.* 1988). The differences between the carbons can be investigated qualitatively by examining the ratio of absorbance at 1350 and 1580 cm^{-1} , with the absorbance at 1150 cm^{-1} , a region where all carbons have a high absorbance. The ratios of the absorbances indicate that the relative abundances of the groups represented by the absorbances at 1350 and 1580 cm^{-1} are approximately in the order: chemically activated wood > low activation coconut > high activation coconut > steam activated wood > steam activated coal.

NOM characterisation

Figure 4.4 shows the high performance size exclusion chromatograms (HPSECs) of the raw water and 4 NOM isolates used in this study. A different y-axis scale was used for the effluent distribution as the UV absorbance of that NOM solution was very low. Tables 4.3 and 4.4 show some of the physical characteristics and elemental composition of the NOM. The results indicate that the anion exchange resin preferentially removed the higher molecular weight, highly coloured compounds from the raw Myponga water, with the smaller compounds with low specific UV absorbance (SUVA) and colour remaining in the effluent. The molecular weight distributions reflect the difficulties associated with the use of UV detection for the HPSEC technique. For example, if the chromatograms were a true reflection of the concentration of compounds in each isolate the integral of the effluent curve should represent approximately 33% of the area under the raw curve. In fact, the effluent curve, when plotted to the same scale, represents only 3% of the raw Myponga chromatogram.

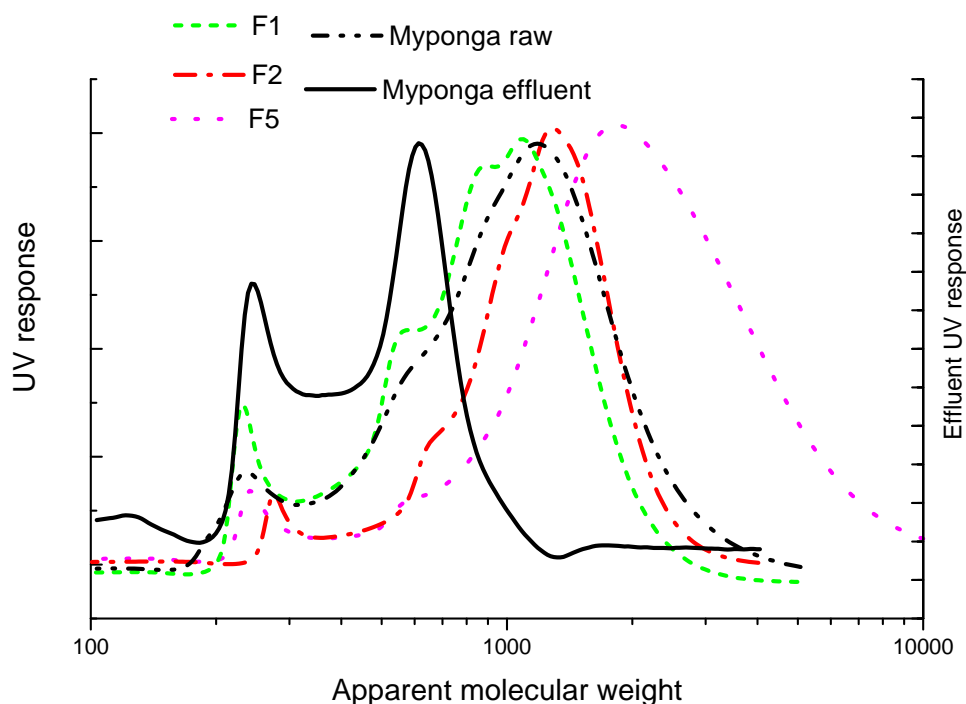


Figure 4.4 High performance size exclusion chromatograms of NOM solutions

The HPSEC of the effluent is very similar to the UV HPSEC of the hydrophilic neutral fraction of Moorool River water presented by Bolto *et al.* (1999). The authors also undertook HPSEC on the same sample using DOC analysis for detection. Although the majority of the NOM was of very low molecular weight, a small shoulder was apparent, not observed in the UV chromatogram, indicating relatively high molecular weight non-UV absorbing compounds. The authors attributed this shoulder to compounds such as long-chain, uncharged, non-conjugated sugars and/or proteinaceous compounds.

Clearly the molecular weights of the anion exchange fractions measured by HPSEC do not correspond to the molecular weight cut-off values of the ultrafiltration membranes. This has been noted and described previously (Newcombe *et al.* 1997, Pelekani *et al.* 1999) and the most likely cause of the discrepancy is the different compounds used to calibrate the methods. While polystyrene sulphonates are considered to represent the configuration of NOM in solution, the globular proteins used to calibrate the ultrafiltration membranes display different solution behaviour from NOM. Proteins tend to spherical, compact conformations in solution, whereas highly charged compounds such as NOM are generally found in the expanded form. As a result, a protein molecule of several tens of thousands of g mol^{-1} can permeate an ultrafiltration membrane that a lower molecular weight, extended molecule cannot. In addition, preparative ultrafiltration of concentrated NOM solutions leads fairly rapidly to a gel layer deposited on the membrane. This layer functions as a lower molecular weight, highly charged barrier to the permeation of the smaller charged molecules. Consequently, most of the NOM retained on the 30000 membrane have a much lower molecular weight when measured using HPSEC.

OPTIMISATION OF ADSORPTION PROCESSES

Table 4.3 Characteristics of NOM solutions obtained from Myponga Reservoir water

NOM solution	DOC (mgL ⁻¹)	Specific colour ^a	SUVA ^b	Average molecular weight (M _n , M _w ^c)
F1	10.0	4.4	3.7	670, 949
F2	10.0	2.9	3.9	965, 1232
F5	10.0	7.7	4.6	1511, 2647
Raw	12.5	5.0	3.5	676, 1113
Raw diluted	6.3	5.0	3.5	676, 1113
Effluent	4.0	0.7	1.5	300, 362

a Units of specific colour, HU L mg⁻¹

b Units of SUVA, L mg⁻¹ m⁻¹

c M_n, number average molecular weight, M_w, weight average molecular weight (Chin *et al.* 1994)

Figure 4.5 illustrates the very different structures of the NOM, as determined by ¹³C NMR. F1 displays a relatively high alkyl, aromatic and carboxyl content, while F5 has a low alkyl and aromatic content and high O-alkyl content. These results support previous work by Newcombe *et al.* (1997), who found two significant trends with increasing molecular weight of MIEX[®] anion exchange fractions – decreasing percent aromatic carbon and a increasing ratio of O-alkyl to alkyl carbon (measured by ¹³C NMR). The aromatic carbon content of the NOM, as indicated by the aromatic peaks in Figure 4.5, shows the same trend as the C:H ratio (Table 4.4), also often related to the aromatic content (Croué *et al.* 1999). F5 has the highest nitrogen content, and the shoulder at around 55 ppm on the NMR spectrum may be indicative of amino sugars, as suggested by Croué *et al.* (1999) for their colloidal NOM fraction. These results also show that the compounds not readily removed by the resin, represented by the effluent NOM, have relatively low aromatic and carboxyl content and are relatively highly aliphatic, in agreement with UV absorbance results. There is evidence of O-alkyl carbon, possibly indicative of high molecular weight carbohydrate-type compounds, as mentioned above. However, the elemental analysis, in particular the C:O ratio (Table 4.4), suggests a lower oxygen content in this fraction than the other NOM, indicating that aliphatic compounds may predominate. The effluent NMR spectrum is similar to that presented by Croué *et al.* (1999) for the hydrophobic neutral fraction obtained during isolation of NOM from the South Platte River, France. This fraction was found by the authors to have the highest total dissolved carbohydrates and amino acids of all the NOM isolated from this water. However, the effluent sample does not appear to be enriched in nitrogen compared with the other fractions, which may indicate the absence of high levels of amino acids.

Table 4.4 Elemental analysis of NOM isolates (in weight percent)*

NOM	Carbon	Oxygen	Hydrogen	Nitrogen	C:H ratio	C:O ratio
F1	39.8	57.1	2.1	0.2	19.0	0.70
F2	40.6	54.3	4.6	1.9	8.8	0.75
F5	40.9	54.7	4.5	2.3	9.1	0.75
Effluent	54.0	36.9	7.4	2.0	7.3	1.46

* no results obtained for raw, results corrected for the ash content contributed by NaCl

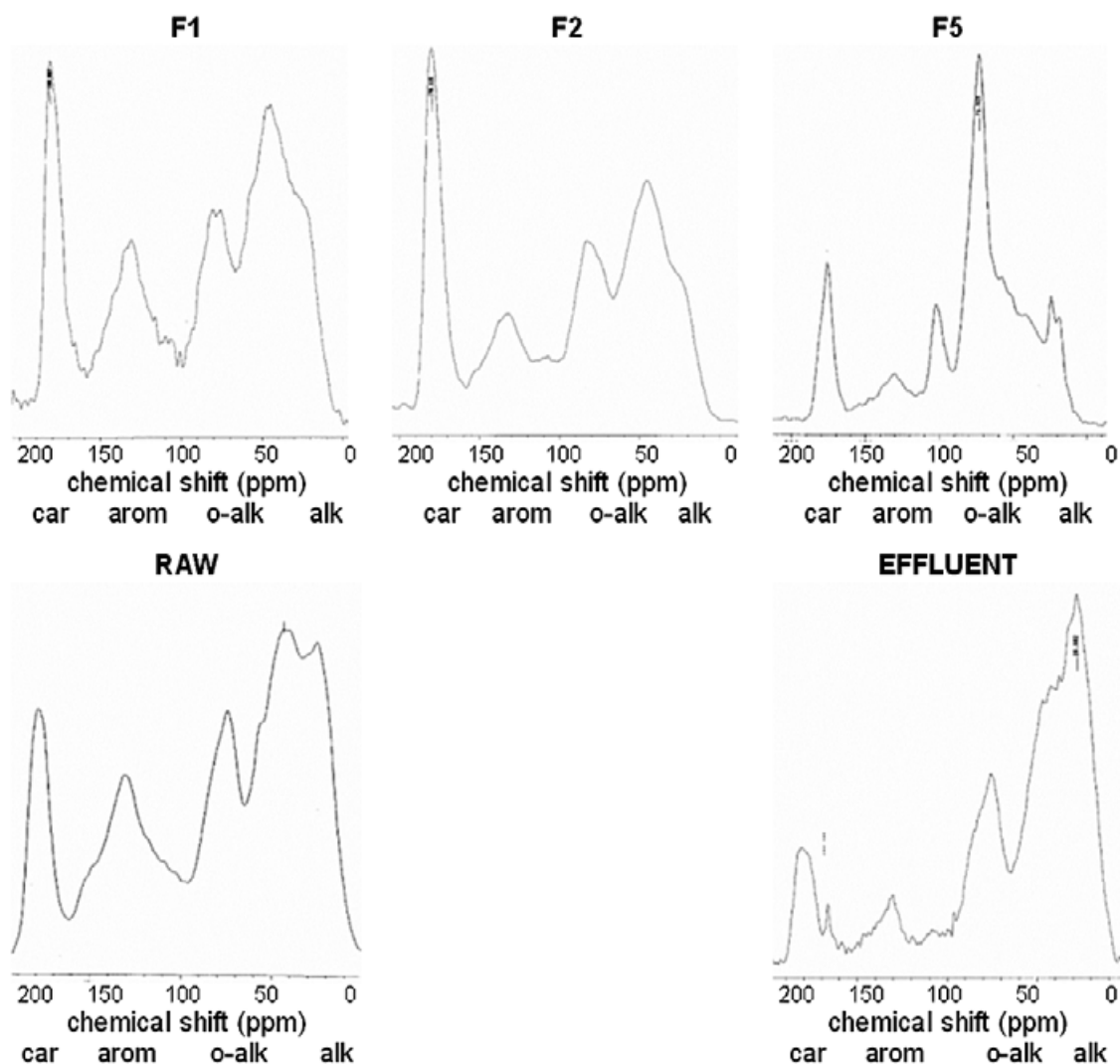


Figure 4.5 ^{13}C NMR spectra of freeze dried NOM

NOM adsorption

DOC removal

Many studies on the adsorption of NOM have been reported in the literature. Some studies have shown that the surface chemistry, in particular surface charge, of the activated carbon has a strong influence on the adsorption (Bjelopavlic *et al.* 1998, Newcombe *et al.* 1997, Summers and Roberts 1988). The pore size distribution is also significant, as is the character and the molecular weight distribution of the NOM (Summers and Roberts 1988, Lee *et al.* 1988, Kilduff *et al.* 1996). In addition, the type of NOM adsorbing has been found to be dependent on the carbon dose, with the more adsorbable compounds within the complex mixture adsorbing preferentially, particularly at low carbon doses (Kilduff *et al.* 1996). The overall consensus is that the adsorption behaviour of NOM onto activated carbon is system dependent. Therefore, with such a wide range of carbons and NOM, it was considered necessary to study the adsorption of NOM simultaneously with the adsorption of MIB, in an effort to clarify the competitive mechanisms occurring.

Simultaneous MIB/NOM adsorption experiments were undertaken at a range of carbon doses on all carbons in solutions F1, F2 and F5. Four carbons were also tested in raw, a 50% dilution of the raw and effluent. DOC analysis was undertaken for all experiments except those with HP, F400 and PCO in F5. This omission was due to instrument failure. Carbon doses were representative of practical application in a drinking water treatment plant. Under these circumstances the removal of DOC is

OPTIMISATION OF ADSORPTION PROCESSES

generally very low, of the order of 10-30% for a 20 mg L^{-1} activated carbon dose, depending on the type of carbon and the DOC concentration and character.

Figure 4.6 shows the dissolved organic carbon removed (in mg L^{-1}) as a function of carbon dose for the NOM solutions. Adsorption isotherms were not used as the mode of display for the data, as the experimental conditions, chosen to simulate practical application, resulted in a very narrow range of solution and surface concentration for the isotherms. Figure 4.6 shows that the adsorption of effluent NOM is similar for three of the four carbons, with PCO adsorbing slightly less. Similar behaviour is seen for the adsorption of F1, although in this case PCO adsorbs significantly less than the other carbons. For the adsorption of F2 the carbons show significant differences, with $\text{HP} \sim \text{CA10} > \text{F400} \sim \text{SA30} > \text{P1100} > \text{PCO}$, and for the adsorption of raw NOM, $\text{HP} > \text{SA30} > \text{P1100} > \text{PCO}$.

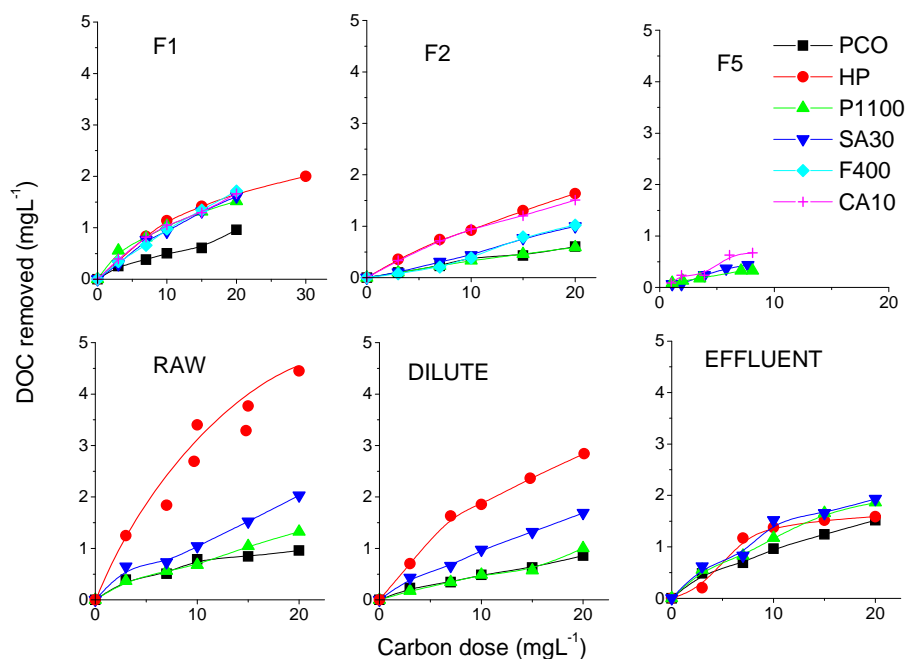


Figure 4.6 DOC removed as a function of carbon dose.

Although it is widely acknowledged that surface chemistry will have an effect on the adsorption of a range of organic compounds, the major influence here appears to be the pore volume distribution of the activated carbons. Pore volume has been found to be a major influence on the adsorption of NOM by several authors (Summers and Roberts 1988, Lee *et al.* 1988, Kilduff *et al.* 1996). For the small, aliphatic compounds present in the effluent, the differences between the carbons are not major, indicating that the majority of the adsorbing compounds may have a diameter of around 1.3 nm, where the pore volumes of the carbons are similar, as indicated in Fig. 1. In this case the very different surface chemistries of the carbons do not have a significant effect. As the average molecular weight of the compounds, and in particular the concentration of larger NOM compounds, increases in the NOM fractions, so does the size of the pores required for adsorption, and differences between the carbons become apparent. Higher adsorption of raw, dilute, F1 and F2 NOM is seen in HP and CA10 due to the higher volume of larger pores in the chemically activated wood-based carbons. This is despite the fact that HP has a high negative charge, expected to reduce adsorption if electrostatic effects were predominant; a similar, but opposite, argument can be made for SA30, a highly positive carbon. In this system the characteristics of the NOM do not appear to play a major role in controlling the adsorption either. For example, F1 and F2 are not chemically very different, as indicated by their SUVA values and ^{13}C NMR spectra, whereas their adsorption behaviour is significantly different. The lower molecular weight NOM anion exchange isolates have a higher carboxyl content (Fig. 5) and generally have a higher negative charge in solution (Newcombe *et al.* 1997), yet they adsorb to a greater extent than the F5 fraction. These effects can only be attributed to the difference in the molecular size of the isolates and the difference in accessible pore volumes of the activated carbons.

For the three carbons where results are available for F5, the DOC adsorption is the least in that fraction. Carbon doses were lower in that fraction as MIB adsorption was high (Section 4.3). For the other fractions, F2 displays the lowest adsorption of the NOM solutions, probably due to the lower concentration of low molecular weight components in this fraction. For three of the four carbons tested with all NOM solutions, the effluent NOM adsorbs approximately the same extent as the raw NOM. For the fourth carbon, the mesoporous chemically-activated wood carbon HP, the raw water, and diluted raw NOM is adsorbed to a significantly greater extent. As the effluent represents approximately 33% of the raw NOM this indicates that the low molecular weight, low charge and low UV absorbing compounds are the most adsorbable on three of the four carbons. This is perhaps not surprising as the three carbons are microporous, while the fourth, HP is a highly mesoporous carbon with the ability to adsorb compounds with a range of molecular weights. However, this also indicates that none of the other NOM adsorbs, whereas both F1 and F2 adsorb to a reasonable extent, and these NOM fractions represent the majority of the remaining NOM i.e. raw NOM without effluent NOM. The results suggest that the fractions adsorb to a greater extent when fractionated than when present in the raw water. There are several possible reasons for this behaviour, including:

- competition for adsorption sites between the effluent NOM and the remaining NOM. Several authors have suggested such competitive mechanisms between components within NOM (Sontheimer *et al.* 1988, Matsui *et al.* 1998).
- adsorption of some larger NOM compounds at the entrance to pores restricting access for the smaller, effluent NOM. Thus the adsorption of effluent NOM is hindered in the whole water.

In the latter case such pore restriction could be expected to be less pronounced in carbon with a large volume of mesopores such as HP (Pelekani 1999).

Change in molecular weight distribution

Dissolved organic carbon is a bulk measurement of a complex mixture. A relatively simple method, using HPSEC, was utilised for tracking the changes in concentration of compounds with specific molecular weights. As mentioned above, the major drawback of this technique is the specificity of the detection system for UV absorbing compounds, and the interpretation of the data must be undertaken with this in mind.

The decrease in UV absorbance at a range of molecular weights, due to adsorption, was determined from the HPSECs at each carbon dose. As expected, the low molecular weight compounds were more susceptible to adsorption than the higher molecular weight compounds due to size exclusion effects. For the raw NOM solution, HP showed the highest removal of UV absorbing compounds at a range of molecular weights, including the low molecular weight peak at around 200 g mol^{-1} (see Fig. 4). As HP has the lowest volume of small micropores, this is consistent with the suggestion that the higher molecular weight compounds restrict access to the adsorption sites for smaller NOM compounds on the three microporous carbons, while access is not restricted in the mesoporous carbon.

HPSECs were also obtained as a function of contact time and, as with the equilibrium data, the decrease of UV response at several molecular weights was determined. Figure 4.7 shows the data for two carbons in raw water and effluent. The analysis of kinetic data and comparison of adsorption kinetics onto such a range of carbons is not a trivial exercise. A very simple method of comparison was chosen, namely the ratio of the UV response removed at a short contact time (in this case 5 minutes) to the amount removed at 240 minutes. In this way a comparison can be made of the amount adsorbed over short contact times by different carbons, without the equilibrium adsorption value exerting too strong an influence. The value is designated the relative adsorption rate at 5 minutes (RAR_5). For example, for HP, molecular weight 1600 in raw water (Figure 4.7), the difference between the UV absorbance at $T=0$ and at $T=5 \text{ min}$, (ΔUV_5) was divided by the difference between the initial UV and the UV response at 240 min (ΔUV_{240}), and $\text{RAR}_5 = \Delta\text{UV}_5 / \Delta\text{UV}_{240}$. Figure 4.8 shows the RAR_5 of several molecular weights, for three of the carbons in raw and effluent NOM solution. For both NOM solutions HP displayed the highest RAR_5 for the low molecular weight HPSEC peak (200 g mol^{-1} , peak 1). This is probably a result of the high volume of transport pores present in this wood-based activated carbon, allowing easier and quicker access to adsorption sites for small compounds. This is discussed further in Section 4.3. When the RAR_5 values were compared with respect to molecular weight, an unexpected trend became apparent. For the three microporous carbons the RAR_5 values increased with increasing molecular weight for all NOM solutions tested. This result was surprising, as larger compounds would have lower diffusion coefficients and are therefore expected to diffuse more slowly

OPTIMISATION OF ADSORPTION PROCESSES

through the carbon structure. This may be the cause of the decrease in RAR_5 with molecular weight shown by HP. For the microporous carbons, these results indicate that, although the higher molecular weight compounds adsorb to a lesser extent, the change in concentration of these compounds is higher at shorter contact times. This could be a reflection of the location of the adsorption sites for the larger NOM molecules. If these compounds adsorb closer to the external surface of the particle, i.e. they have less distance to diffuse, then the bulk solution concentration could be expected to change more rapidly. This effect was suggested by Pelekani (1999) to explain the adsorption competition, attributed to pore blockage, seen between atrazine and large dye molecules. Suitable adsorption sites for HP are possibly found throughout the carbon, and are similarly placed for all molecular weights.

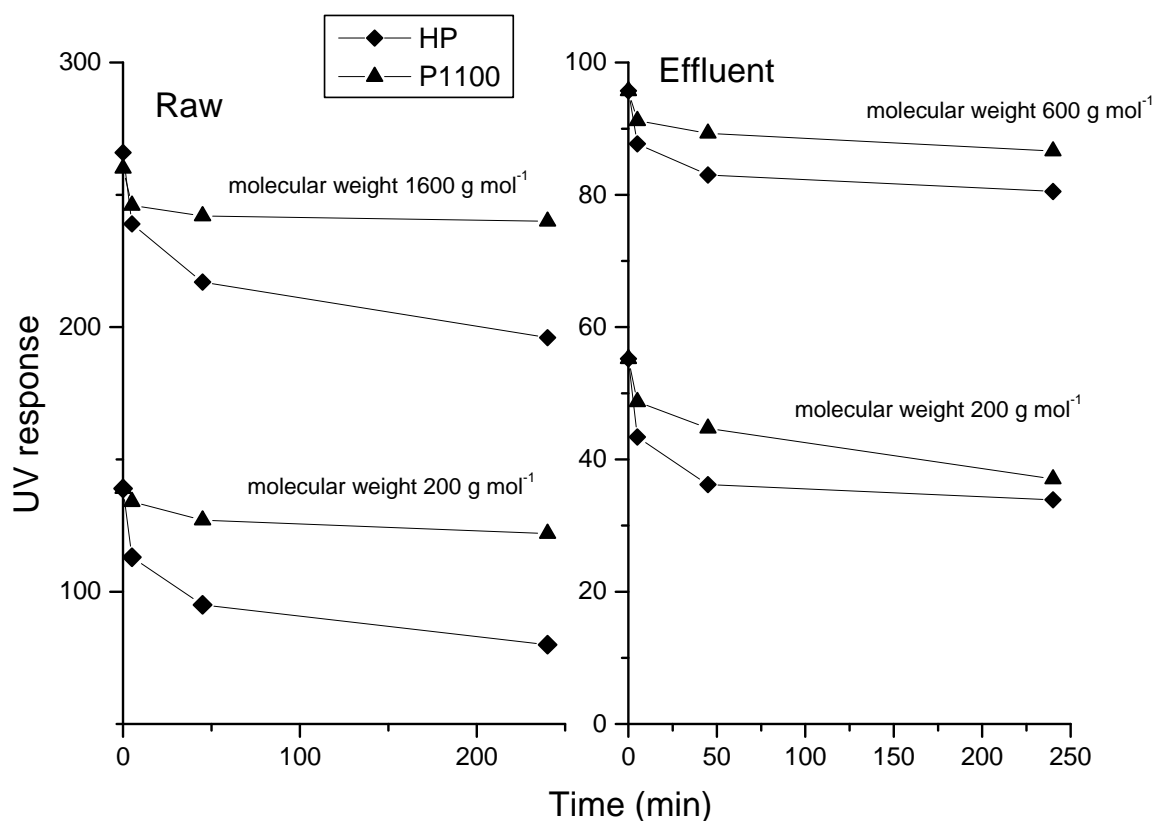


Figure 4.7 UV response of HPSEC vs. time. Activated carbon dose, 20 mg L⁻¹.

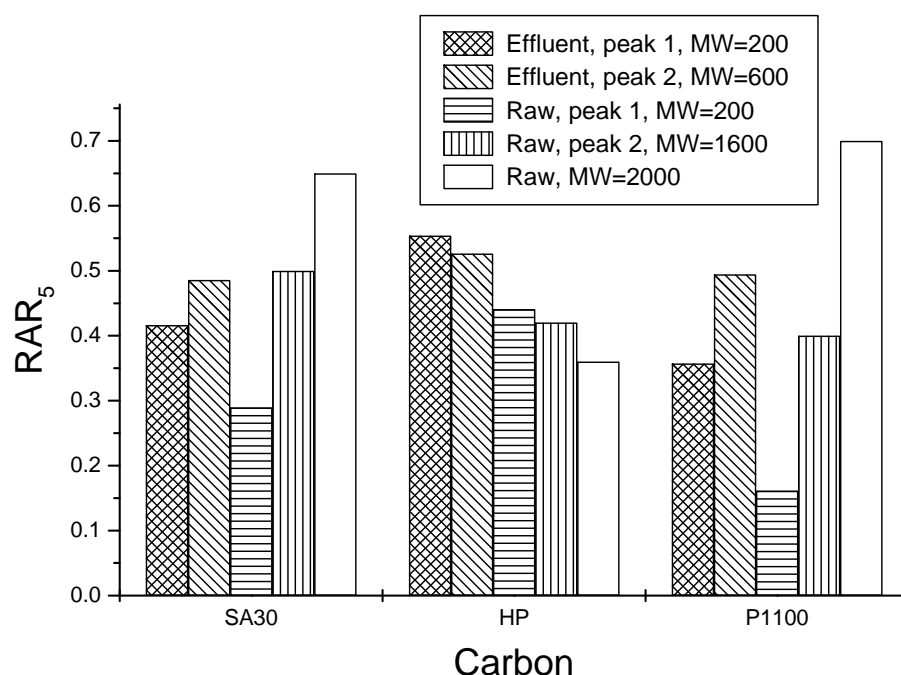


Figure 4.8 Relative rates of adsorption of UV absorbing compounds at 5 minutes for three carbons in raw and effluent Myponga water.

4.2.4 Summary and conclusions

The activated carbons chosen for this study displayed a wide range of both textural and chemical surface properties. Both are known to affect adsorption of micropollutants, and adsorption competition provided by NOM. The characteristics of the NOM isolates ranged from low molecular weight, low charge, low colour, to relatively highly charged NOM of high molecular weight, and high colour. The raw water from which these NOM solutions were isolated was also studied.

A series of equilibrium and kinetics experiments were undertaken to investigate the competitive effects between these NOM solutions and MIB. The results of those experiments are reported in Section 4.3. Dissolved organic carbon concentrations were measured after equilibrium competitive adsorption experiments, and high performance size exclusion chromatography was used to investigate the changes in molecular weight distribution as a function of carbon dose and contact time.

The main findings of this work were the following:

- Adsorption of the NOM isolates was controlled predominantly by the relationship between the molecular weight distribution of the NOM, and the pore size distribution of the carbon. The low molecular weight compounds were adsorbed to a greater extent than the larger compounds, due to size exclusion effects.
- There is evidence that the larger NOM molecules restrict the adsorption of smaller compounds to some degree in microporous carbons
- For the very low molecular weight compounds, represented by the peak at around 200 apparent molecular weight in the HPSECs, the mesoporous carbon showed rates of adsorption greater than the microporous carbons, attributed to a broader pore size distribution. The higher volume of transport pores in the mesoporous carbon allowed more rapid diffusion to adsorption sites.
- The mesoporous carbon displayed a slight decrease in the relative rates of adsorption with an increase in molecular weight, attributed to the decrease in diffusion coefficient with increase in NOM size. In contrast, the microporous carbons showed an increase in the relative rate of adsorption with increase in molecular weight. It is proposed that the mesoporous carbon's pore size distribution allowed adsorption of a range of molecular weights throughout its internal structure. In the microporous carbons, as the molecular weight of the adsorbing compound increased, the access to adsorption sites was reduced to those available in relatively large pores

closer to the external surface. Although the extent of adsorption was thus reduced, the distance of diffusion was also reduced, resulting in a higher relative adsorption rate.

4.3 SIMULTANEOUS ADSORPTION OF MIB AND NOM ONTO ACTIVATED CARBON: II COMPETITIVE EFFECTS

4.3.1 Introduction

The adsorption of 2-methylisoborneol (MIB) has been shown to be very dependent on the type of activated carbon adsorbent used (Lalezary *et al.* 1985, Chudyk *et al.* 1979). Several authors have found that wood-based, chemically activated carbons display inferior adsorption for this compound compared with coconut or coal-based carbons (Newcombe *et al.* 1997, Chen *et al.* 1997) and evidence has been produced that the surface chemistry of the carbon plays an important role (Considine *et al.* 2001). However, Pelekani (1999) and Newcombe (2002) have reported that rigorous pore size distribution analysis of several chemically-activated wood carbons, using density functional theory, revealed a relatively low volume of micropores in the appropriate size range, suggesting that pore size could also play an important role.

The effect of adsorption of natural organic matter (NOM) on the efficiency of activated carbon for drinking water treatment is significant, and results in high costs to water authorities treating affected water due to the high carbon doses required. The presence of NOM reduces the equilibrium capacity of activated carbon for MIB, and also influences the kinetics of adsorption, a very important aspect, particularly for the application of powdered activated carbon (PAC) (Hepplewhite, 2000). Hepplewhite (2000) found that the kinetics of adsorption of MIB onto a microporous carbon were influenced by low molecular weight NOM, whereas the rate of MIB removal by a mesoporous carbon was adversely affected by larger NOM molecules, although these molecules did not appear to affect the equilibrium capacity. Cook *et al.* (2001) also found quite contrary effects of NOM character on equilibrium capacities and rates of adsorption. The authors compared the adsorption of both MIB and geosmin (another earthy odour compound) onto a microporous carbon in four reservoir waters, and found that the water with the highest DOC concentration also showed the lowest level of competition at equilibrium (i.e. the highest adsorption), but the lowest adsorption of the odour compounds at contact times of 5-60 minutes. The character of the NOM - highly coloured, with high UV absorbance- was considered to exert a strong, and conflicting, influence on the competitive effect at equilibrium, and at shorter contact times. The rate of adsorption, and the effect of adsorption competition on kinetics, is of greatest importance to the water supplier, as it controls the activated carbon dose required for reduction of odour compounds to an acceptable level, and therefore the costs associated with treating the water.

Pore blockage and direct site competition are generally considered the most likely mechanisms affecting activated carbon adsorption in the presence of NOM. It has been suggested that pore blockage by large NOM molecules is unlikely to be a major mechanism for competition with small target compounds as the diffusion coefficients would be sufficiently different to ensure superior kinetics of the smaller compound (Newcombe *et al.* 1997, Kilduff *et al.* 1998). Thus MIB, for example, could be expected to reach an adsorption site before pore blockage by larger compounds could occur. Newcombe *et al.* (1997) and Kilduff *et al.* (1998) suggested direct competition for adsorption sites was the most likely mechanism of competition between NOM and low molecular weight target compounds. In support of this suggestion, Newcombe *et al.* (1997) showed that low molecular weight NOM compounds exerted a higher competitive effect on MIB adsorption than the larger compounds, and Kilduff *et al.* (1998) presented similar evidence for trichloroethylene (TCE). More recently, Pelekani (1999), Kilduff and Wigton (1999) and Ebie *et al.* (2001) suggested that pore blockage could also be a major contributing factor to the competitive adsorption effect between NOM and smaller target molecules. Ebie *et al.* (2001) showed that ideal adsorbed solution theory (IAST), which applies only to direct site competition, could only predict their data if a pore blockage mechanism is also taken into account. Pelekani and Snoeyink (1999, 2000, 2001) developed a conceptual model for competitive effects using atrazine as the target compound and a series of dyes, as well as natural organic material from one ground water source, as the competing compounds. The adsorbents in the study were a series of activated carbon fibres with well defined and narrow pore size distributions. Using the data from a suite of preload and simultaneous adsorption experiments, the authors concluded that the competitive mechanism depends strongly on the pore size distribution of the carbon, as well as the relative sizes of the target and competing compounds. In particular, they suggested that the smaller

NOM compounds could also participate in pore blockage, or pore restriction without pore blockage. They found that a wider pore size distribution in the adsorbent resulted in less pore blockage and consequently less evidence of competition.

Clearly, direct competition can only occur when the competing compounds are able to access the same sites. This situation will arise when the compounds are the same size and compete for the same pores, or when the target compound adsorbs in a larger pore (with lower adsorption energy) and the larger competing compound (with a higher adsorption energy), is able to displace it. Both Pelekani and Snoeyink (1999) and Ebie *et al.* (2001) suggested that the former direct competition mechanism is not likely with NOM, as the compounds in NOM are larger than the target compounds under investigation. In contrast, Newcombe *et al.* (1997) suggested that only a very low concentration of low molecular weight NOM is required to have an impact on MIB adsorption by the direct competition mechanism, as the target compound is present at nanogram per litre levels. In addition, Hepplewhite (2000) recently showed that competitive effects observed at equilibrium between MIB and a range of NOM isolates could be directly related to the concentration of NOM with molecular weight below 600 g mol⁻¹.

In Section 4.2 characterisation of six activated carbons and six NOM solutions was described. The adsorption of the NOM onto the activated carbons was studied and interpreted in terms of the characterisation data. In Part II the adsorption competition between MIB and the six NOM solutions is described and related to the characteristics of the carbons, and to the NOM solutions. The aim of the work presented in this paper is to gain greater insight into the competitive effects caused by the presence of NOM, both at equilibrium, and at contact times more relevant for the application of powdered activated carbon (PAC). The practical outcome will be minimisation of these adverse effects for the water supplier, and therefore minimisation of the cost of activated carbon, while ensuring an adequate water quality for the consumer.

4.3.2 Materials and methods

Water was obtained from a Milli-Q water purification system (conductivity $<1 \times 10^{-6}$ S cm⁻¹). ¹⁴C-labelled 2-methylisoborneol (¹⁴C-MIB), dissolved in ethanol, was obtained from American Radiolabeled Chemicals. The solution was found to be >99% pure by GC/MS analysis. Stock solutions were made up using Milli-Q water, and the resulting ethanol concentration in the adsorption solutions was below the detection of the DOC analyser.

Analysis of MIB concentration

A sample (2.5 mL) from the reaction vessel was pressure filtered through a 0.45 µm Millipore membrane filter and mixed with 17.5 mL of scintillation cocktail (Canberra Packard) in a 20 mL polyethylene scintillation vial. The activity of the sample was determined as disintegrations per minute using a Beckman LS3801 liquid scintillation counter, and this value was converted to ng L⁻¹ of MIB using the activity of the ¹⁴C-MIB (55 mCi mmol⁻¹).

Equilibrium adsorption

The NOM solutions (raw, dilute, effluent, F1, F2 and F5, described in Section 4.2) were added to clean dry Pyrex bottles to a level allowing minimum headspace. Stock MIB was added to obtain a starting concentration of 100 ng L⁻¹, the required dose of PAC was then added. Doses ranged from 2 to 30 mg L⁻¹. The bottle was sealed and agitated on a rotary mixer for 3-6 days.

Rate experiments

Rate experiments were undertaken as described in Section 4.2. Samples were taken at predetermined intervals over the following four hours, filtered through 0.45 µm disposable filters to remove the PAC, and analysed for MIB concentration.

4.3.3 Results and discussion

Adsorption of MIB

Equilibrium adsorption

Figure 4.9 shows the adsorption isotherms of MIB onto six activated carbons in NOM-free water and in NOM fraction F1.

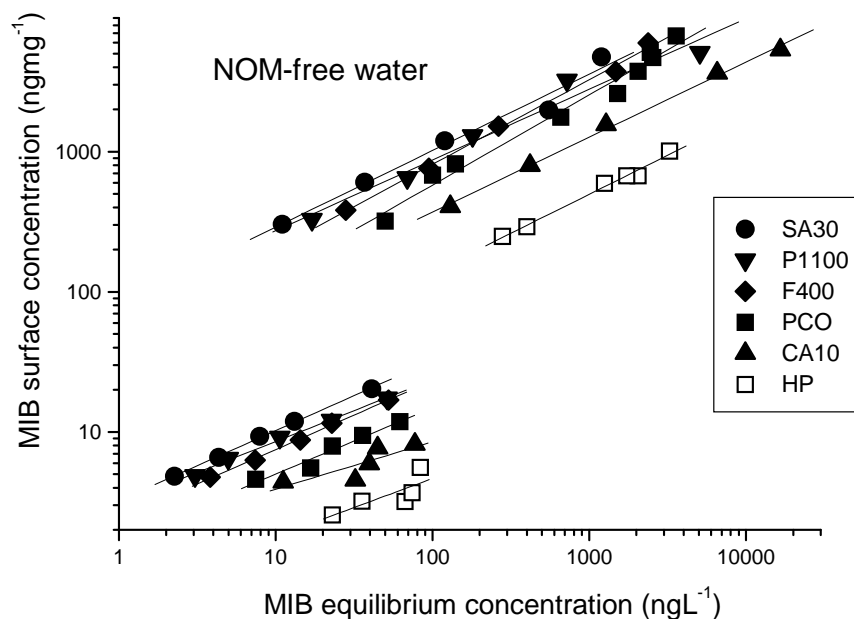


Figure 4.9 Adsorption isotherms of MIB onto six activated carbons in the presence and absence of competing NOM

The characterisation of the NOM and the activated carbons is reported in Section 4.2. The adsorption capacities shown by the carbons are very different and can be related to the pore size distributions (Figure 4.10). The y axis in Fig. 4.10 represents the surface concentration of MIB at a solution concentration of 50 ng L^{-1} in NOM fraction F1. This relationship is essentially linear and the adsorption can be related directly to the volume of pores with widths of approximately 1.0-1.2 nm. The relationship is also linear in the absence of NOM ($R^2 = 0.96$, $P = 0.0007$). Although surface chemistry has been shown to play a role in MIB adsorption (Considine *et al.* 2001), where the surface oxygen level was varied while maintaining a constant pore volume distribution, in this system the over-riding influence is the pore size distribution. It should be noted that surface chemistry may well be influencing the adsorption to a certain extent; however, the net effect is due to the pore distributions, while other effects are negligible in comparison. Also demonstrated in Fig. 1 is the significant effect of the presence of NOM on MIB adsorption. The presence of the F1 NOM fraction reduces MIB adsorption by as much as 99%.

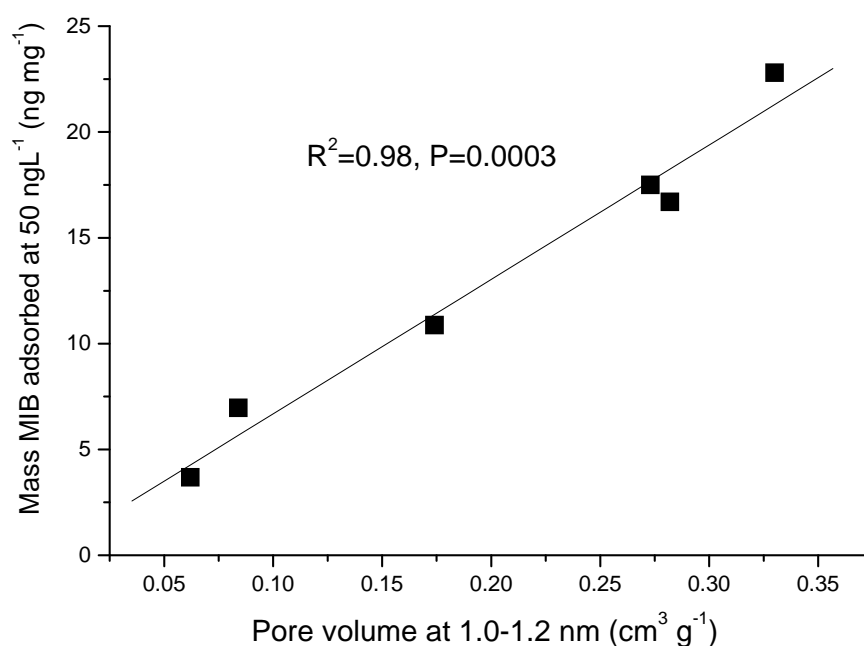


Figure 4.10 Relationship between surface concentration of MIB, taken from the isotherms at a solution concentration of 50 ng L⁻¹, and volume of pores of 1.0-1.2 nm width in F1 NOM

Kinetics of adsorption.

Figure 4.11 shows the adsorption of MIB from F1 NOM solution onto five of the six carbons at contact times more applicable to those found in a water treatment plant. The results for the sixth carbon, F400, were very similar to that of SA30, and these data were omitted for clarity. At equilibrium, the trend in adsorption capacity of these carbons is: SA30>P1100~F400>PCO>CA10>HP (see Figure 4.9). After 4 hours, a similar trend is already apparent in Figure 4.11. However, at shorter contact times the carbons behave quite differently. Two of the high capacity carbons, F400 and SA30, performed well over the contact period. The most striking feature is the unfavourable kinetics of the coconut carbons (P1100 and PCO), which have a relatively high equilibrium capacity, compared with the very favourable kinetics of the chemically activated wood-based carbons (HP and CA10), with low equilibrium capacity. These results indicate that the choice of the most efficient activated carbon for the removal of MIB in a water treatment plant will depend strongly on the contact time available for adsorption. These effects are readily explained by the different pore structures of the carbons. As described in Section 4.2, coconut carbons have a very narrow pore size distribution, possessing negligible macro and mesopore volume, while the wood-based carbons have a high volume of larger pores, or transport pores, favouring rapid diffusion to adsorption sites.

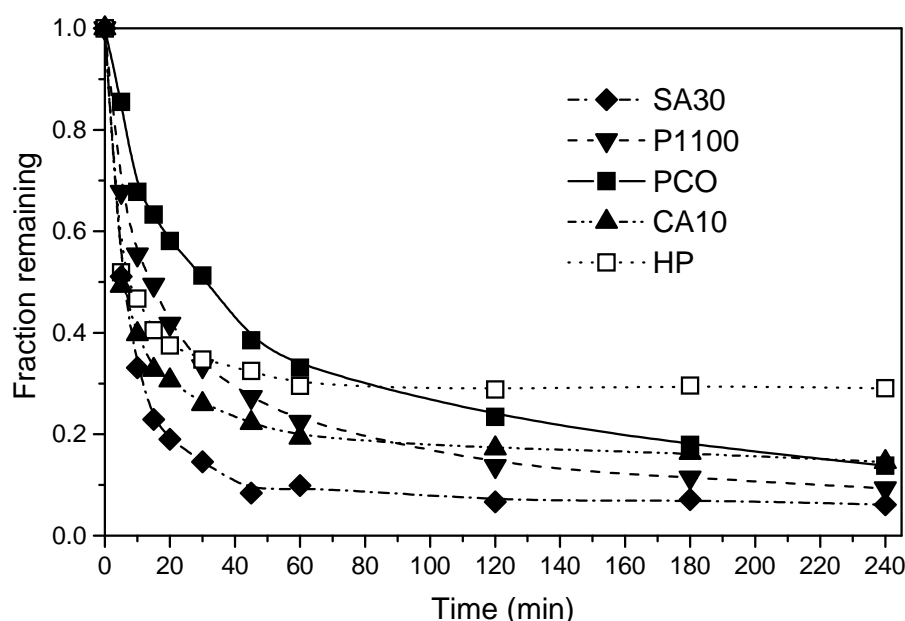


Figure 4.11 Adsorption of MIB as a function of contact time in F1 NOM.

Comparing the kinetics of adsorption of a range of carbons is not a trivial exercise. Diffusion coefficients can be obtained using the appropriate adsorption model. For example, the Homogenous Surface Diffusion Model (HSDM) is known to apply to MIB adsorption on some activated carbons (Gilligly *et al.* 1998, Graham *et al.* 2000, Huang *et al.* 1996) and it can be used to extract a diffusion coefficient for MIB. However, in this study it was found that the HSDM could not be used to predict the very fast initial adsorption seen in the two chemically-activated wood carbons. This may be due to the very different external structure of these chemically-activated wood carbons, as seen in scanning electron micrographs (Newcombe 2002). The rate of adsorption (i.e. the slope of the concentration vs time curve) can be strongly affected by the equilibrium adsorption capacity, and does not provide information regarding the diffusion of the compound to the adsorption site. For example, Cook *et al.* (2001) determined the diffusion coefficients of MIB and geosmin onto P1100 in four reservoir waters and found that the values for geosmin were an order of magnitude lower than those found for MIB. However, when the kinetics curves are analysed as first order reactions, the rate constants for geosmin are significantly higher than those found for MIB (unpublished data). In this work a more straightforward method was used to compare the kinetics of the carbons, the 5 minute relative adsorption rates (RAR_5). These values are calculated by the equation:

$$RAR_5 = \text{amount adsorbed at 5 minutes} / \text{amount adsorbed at 240 minutes}$$

Table 4.5 Relative adsorption rates of MIB from F1 NOM solution onto six activated carbons.

	SA30	F400	P1100	PCO	CA10	HP
RAR_5	0.52	0.52	0.36	0.17	0.58	0.68

The RAR_5 values are given in Table 4.5. They illustrate the behaviour shown in Fig. 3, and are similar to the 5 minute RAR values of the very low molecular weight peaks (VLMW, around 200 g mol^{-1}) of the NOM solutions discussed in Section 4.2. In particular, the VLMW peak of the effluent NOM showed similar adsorption behaviour to the MIB, displaying the same cross-over point for the HP and P1100 carbons shown in Figure 4.11. This result, together with the NMR spectra obtained for the effluent sample, indicates that some compounds present in the effluent NOM may be similar in structure and size to MIB, and thus display similar adsorption behaviour.

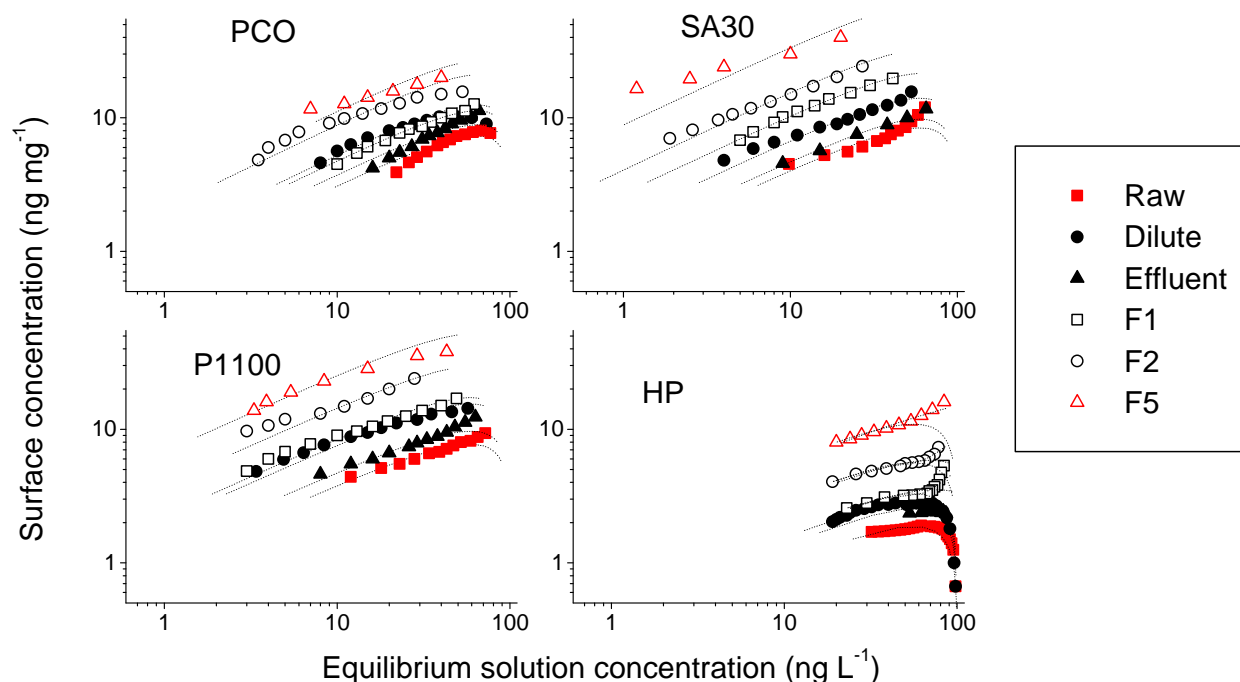
Competitive effects*Competitive effects observed at equilibrium*

Figure 4.12 Adsorption isotherms for MIB in the presence of six NOM solutions. Points are experimental data, dotted lines are isotherms obtained using the IAST in combination with the EBC model (see text).

Figure 4.12 shows the effect of the different types of NOM on the equilibrium adsorption of MIB onto four of the activated carbons. The competitive effect for the carbons HP, P1100, PCO and SA30 was in the order raw>effluent>dilute raw>F1>F2>F5, and for the other two carbons (F400, CA10), F1>F2>F5. In fact, the effect of the NOM solutions relative to the raw water, which contains all of the competing substances, was similar for the four carbons. Comparing the amount of MIB adsorbed at a solution concentration of 50 ngL⁻¹ with raw water NOM (i.e., relative competitive effect = surface concentration at 50 ngL⁻¹ in raw water/ surface concentration at 50 ngL⁻¹ in other NOM solutions), the relative competitive effects are:

Effluent	0.76 ± 0.06
Dilute raw	0.60 ± 0.08
F1	0.46 ± 0.09
F2	0.37 ± 0.04
F5	0.22 ± 0.02

The fact that the trend is the same for all carbons is strong evidence that the predominant competitive mechanism occurring at equilibrium is likely to be the same for all carbons. In addition, the results show that the major effect on MIB adsorption is the molecular weight distribution of the competing compounds. In particular, the low molecular weight (LMW) compounds (<600 g mol⁻¹) present in both the raw water and the effluent, those not removed by the anion exchange resin after considerable loading, are the major contributors to the competition. It could be argued that there may also be high molecular weight (HMW) compounds, greater than 1000 g mol⁻¹, for example, present in the effluent, and the raw water, that are not visible through the UV detection of the HPSEC, as shown by Bolto *et al.* (1999) and that these may contribute to the competition. However, the results for fractions F1, F2 and F5, show a clear increase in competitive effect as the concentration of larger compounds is

reduced, supporting the contention that the smaller NOM compounds, similar to those found in the effluent, have the greatest impact on MIB adsorption. As described in Section 4.2, these compounds also have a structure most similar to MIB, low molecular weight, low UV absorbance and colour, high degree of aliphatic nature, and relatively low carboxyl and oxygen content (Tables 4.3 and 4.4 and Figure 4.5, in Section 4.2).

Although the competitive effect increases with decreasing molecular weight, F5, the fraction with the highest average molecular weight, also has a significant competitive effect, reducing the MIB capacity to between 6 and 13% of the single solute adsorption at 50 ng L⁻¹ MIB. While this may appear to be a contradiction, HPSEC shows evidence of low molecular weight compounds being present in this fraction as well. These compounds, while present in the lowest concentration in F5, would still have a significantly higher concentration than the target compound (100 ng L⁻¹). As a result, there is significant competition, even in the fraction with the highest average molecular weight, due to the (relatively) high concentration of LMW compounds.

The adsorption of DOC on most of the carbons was in the order: raw \approx effluent > dilute > F1 > F2 > F5. This is also the order of the competitive effect for the fractions and is most likely a reflection of the greater adsorbability of the LMW compounds, which also contribute most to the competitive effect, rather than a result of the higher mass of NOM adsorbed, as measured by dissolved organic carbon concentration.

Several competitive adsorption models were used in an attempt to describe these effects, a Langmuir model (Jain and Snoeyink, 1973), the simplified competitive adsorption model (SCAM) (Di Giano *et al.* 1978) and ideal adsorbed solution theory (IAST) (Radke and Prausnitz 1972). None was successful. The disadvantage of these models rests in the requirement for an adsorption isotherm of the competing compound, i.e., knowledge of which NOM component accounts for the majority of the competitive effect, and how that component adsorbs. Using a bulk parameter such as DOC adsorption is unlikely to be appropriate as the crucial components of the NOM would not necessarily display the same adsorption behaviour as the bulk of the NOM. Ebie *et al.* (2001) also found the IAST model incapable of predicting the isotherms of several agricultural chemicals in the presence of competitive NOM. They concluded that the model was inappropriate as it did not take into account pore blockage as a potential competitive mechanism. However, the authors used the isotherm for the bulk DOC as the isotherm of the competitive compound, a process unlikely to result in a good model fit for the reasons mentioned above. The authors argued that their NOM, the product of alum coagulation of a surface water, was less diverse than the original NOM. While this is correct, the NOM still displayed a wide range of molecular weights (approximately 1000-5000 g mol⁻¹), while the target compounds had molecular weights of between 207 and 290 g mol⁻¹. The molecular weight distributions themselves appear doubtful, as the range is much higher than generally accepted for dissolved aquatic NOM, especially after alum coagulation.

The equivalent background compound (EBC) model can be used to obtain the adsorption isotherm of competing compounds when the adsorption of the target compound is known in the presence and absence of the NOM (Najm *et al.* 1991, Knappe *et al.* 1998). The EBC is not considered to be the entire NOM present in natural waters, as only an unknown portion of the NOM will compete. The model uses IAST to obtain the EBC adsorption parameters (Freundlich K, 1/n and initial EBC concentration) by the minimisation of the error between the experimental adsorption isotherm in the presence of NOM and the adsorption isotherm obtained from the IAST model. The EBC isotherm determined through this procedure can then be used to predict the adsorption isotherms of the target compound in the same NOM solution at a range of initial concentrations. Initial EBC concentrations (C₀), in $\mu\text{mol L}^{-1}$, and estimates of the DOC concentrations of the EBC, in mg L⁻¹, for the six NOM solutions are summarised in Table 4.6. The EBC parameters for each activated carbon/NOM system were obtained by varying K and C₀ and by holding the 1/n value constant at 0.42. For a given data set, feasible solutions were obtained for Freundlich exponent values in the range of about 0.3 to 0.5, and the chosen Freundlich exponent of 0.42 represents an average value of this range. This 1/n value is similar to Freundlich exponents reported in prior studies that employed the EBC or other fictive component methods (e.g., Graham *et al.* 2000, Knappe *et al.* 1998). Apart from the isotherm curvature at very low carbon doses, K values of about 1,000 ($\mu\text{mol/g})(\text{L}/\mu\text{mol})^{1/n}$ and greater had no effect on the IAST model output. Observing a K-value of about 1,000 ($\mu\text{mol/g})(\text{L}/\mu\text{mol})^{1/n}$ or greater suggests the presence of a highly adsorbable NOM fraction. Nonetheless, a K-value of this magnitude appears to be reasonable, especially when considering that K values in the order of 10,000 ($\mu\text{mol/g})(\text{L}/\mu\text{mol})^{1/n}$

have been reported for strongly adsorbing micropollutants such as heptachlor (Snoeyink and Summers 1999). Consequently C_0 was the principal parameter affecting the MIB isotherm fits in the presence of NOM. IAST model outputs obtained with the initial EBC concentrations reported in Table 4.6 as well as with K values greater than 1000 ($\mu\text{mol/g})(\text{L}/\mu\text{mol})^{1/n}$ and a $1/n$ value of 0.42 were in excellent agreement with the experimental MIB isotherm data collected in the NOM solutions (Fig. 4).

Table 4.6 Initial EBC concentrations ($\mu\text{mol L}^{-1}$). In brackets, equivalent DOC concentrations in mg L^{-1} assuming molecular weight of competing substances = 300 g mol^{-1} and mass C=50% mass NOM.

	P1100	PCO	SA30	HP
Raw	8.4(1.3)	6.1(0.92)	5.0(0.75)	1.1(0.17)
Effluent	4.8(0.72)	3.5(0.52)	3.4(0.51)	0.55(0.08)
Diluted	1.6(0.24)	1.4(0.21)	1.4(0.21)	0.41(0.06)
F1	1.2(0.18)	1.8(0.27)	0.48(0.07)	0.32(0.05)
F2	0.32(0.05)	0.31(0.05)	0.18(0.03)	0.095(0.01)
F5	0.084(0.01)	0.164(0.02)	0.026(<0.01)	0.022(<0.01)

As expected the values of C_0 were found to be in the order: raw>effluent>diluted>F1>F2>F5. All DOC concentrations appear reasonable and are of the order of 10000 times the starting concentration of MIB for the least competitive fraction, F5. Even when taken as only an estimate of the concentration of competitive DOC, the figures for the anion exchange isolates in particular show clearly why bulk DOC isotherms cannot be used to predict the competitive effects.

Among the evaluated adsorbents, the competitive effect of NOM on the MIB adsorption capacity at an equilibrium liquid-phase MIB concentration of 50 ng/L (i.e., the percent loss of single-solute MIB adsorption capacity attributable to the presence of competing NOM) was in the order: P1100 \approx PCO>SA30>HP. This trend is also reflected in the initial EBC concentrations (Table 4.6), which were larger for adsorbents with narrower pore size distributions (P1100, PCO, SA30) than for the adsorbent with the wider pore size distribution (HP). The results of the current study are in agreement with the suggestions of Pelekani (1999) and Ebie *et al.* (2001), who both found a lower competitive effect on carbons with a wider range of pore sizes. The adsorption of DOC (in the order HP>CA10>F400>P1100>PCO) did not give an indication of the competitive effects with MIB. Ebie *et al.* (2001) also reported that the greatest competitive effects were not displayed by the carbon with the highest DOC adsorption, and Pelekani (1999) found significant effects on the adsorption of atrazine in the presence of very low surface concentrations of the competing compound, particularly where the suggested mechanism was pore blockage at the particle surface.

When compared with the large differences in adsorption of the target compound between the carbons (see Figure 4.9), the difference in the competitive effects shown by the carbons are negligible. Therefore the trends in the effectiveness of the carbons are the same in the presence or absence of NOM.

Previously evidence of the greater effect of smaller NOM compounds was considered to support the theory of direct site competition; however, in the light of the studies of Pelekani and Snoeyink (1998, 1999, 2000), other mechanisms should also be considered for these low molecular weight compounds. These will be discussed in the following sections.

Competitive effects observed at short contact times

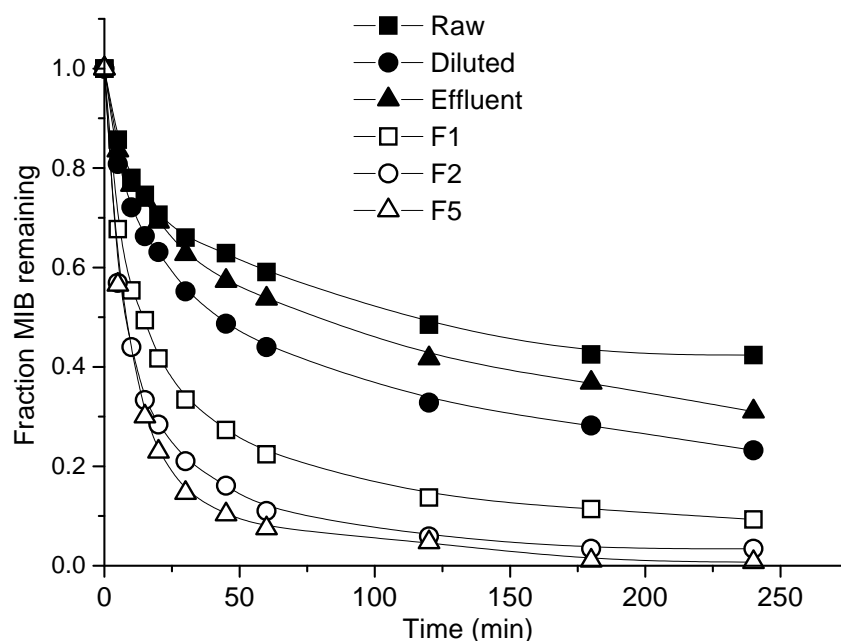


Figure 4.13 Fraction remaining of MIB as a function of time in six NOM solutions (P1100).

Figure 4.13 shows that the effect of the different NOM solutions at shorter contact times is in the same order as the equilibrium results. This was the case for all carbons. A comparison of the fraction remaining at 60 minutes (a common contact time available during coagulation and flocculation of PAC) shows very large differences in the quality of water produced at the same contact time and carbon dose in the presence of different types and concentrations of NOM. The kinetic data obtained with P1100 (Fig. 5) were well described by the HSDM (Cook *et al.* 2001), which was used to predict the carbon doses required to reduce 20 ng L^{-1} MIB to 10 ng L^{-1} over a 60 minute contact period. This would be a common scenario in treatment plants with a problematic odour episode. Table 4.7 illustrates in a practical manner the very large effect of the concentration and character of the NOM, and therefore the importance, financially, of a greater understanding of the competitive process.

Table 4.7 P1100 carbon doses required to reduce MIB concentration from 20 to 10 ng L^{-1} in one hour.

NOM solution	Raw	Dilute	Effluent	F1	F2	F5
DOC concentration (mg L^{-1})	12	6	4	10	10	10
Carbon dose (mg L^{-1})	31	20	22	11	9	3

Figure 4.14 shows the RAR_5 of the four carbons relative to the RAR_5 in NOM-free water. The equation used was:

$$\text{Fraction of pure } \text{RAR}_5 = \text{RAR}_5 \text{ in NOM solution} / \text{RAR}_5 \text{ in NOM-free water}$$

From the figure the following can be seen:

- The highest reduction in RAR_5 due to the presence of NOM is of the order of 40%, therefore the effect of NOM on the kinetics of adsorption can be considered much less than the effect on equilibrium adsorption
- PCO is the carbon most affected
- The RAR_5 of HP is only affected by the HMW fraction (F5)

For the other carbons there is a similar effect for raw, dilute and effluent, with a lower effect for the anion exchange isolates such that $F5 < F2 < F1$.

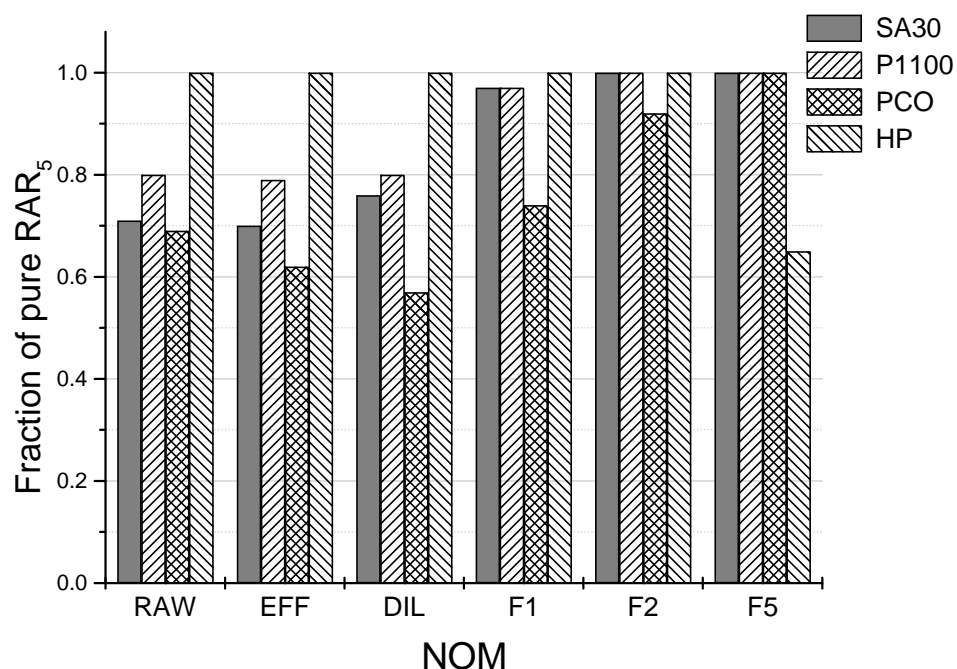


Figure 4.14 RAR_5 of carbons in NOM solutions relative to RAR values in NOM-free water

From these results it appears that the HMW NOM affects the adsorption kinetics of the carbon with a large volume of mesopores, whereas the LMW compounds affect the microporous carbons. This is in agreement with the work of Hepplewhite (2000), who found the RAR_5 of MIB in solutions containing a range of isolates decreased with an increase in the average molecular weight of the NOM on a mesoporous carbon, whereas on a microporous carbon the RAR_5 decreased with decreasing average molecular weight. Possible mechanisms are discussed in the next section.

An interesting effect noted for CA10 and HP was the desorption of MIB over time in the presence of NOM. This effect had been reported previously for MIB on wood-based carbons (Newcombe *et al.* 1994, Hepplewhite 2000), and for atrazine on a mesoporous carbon fibre (Pelekani and Snoeyink 2000). Figure 4.15 shows the changes in the fraction of MIB removed between times 2 hours and 120 hours for HP and PCO carbons. The results for PCO reflect the large impact of competitive NOM on MIB adsorption kinetics, in agreement with the high impact shown by the RAR_5 of PCO. On HP the MIB is displaced over longer contact times by NOM with higher adsorption energies.

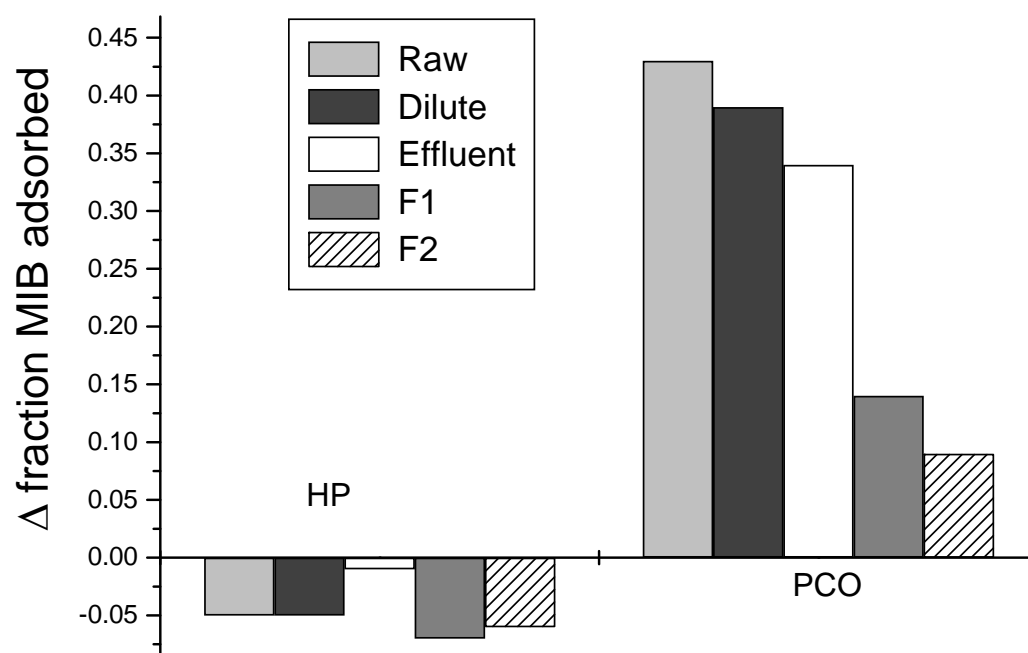


Figure 4.15 Change in fraction of MIB adsorbed between 2 and 120 hours (HP and PCO).

Representation and discussion of the competitive effects.

Figure 4.16 is a representation of the internal structures of a microporous carbon (left) and a mesoporous carbon (right). The figures were extracted from transmission electron micrographs and, although they should not be regarded as exact representations of the porous structure, have been constructed to illustrate several points regarding NOM adsorption, MIB adsorption, and their competitive effects.

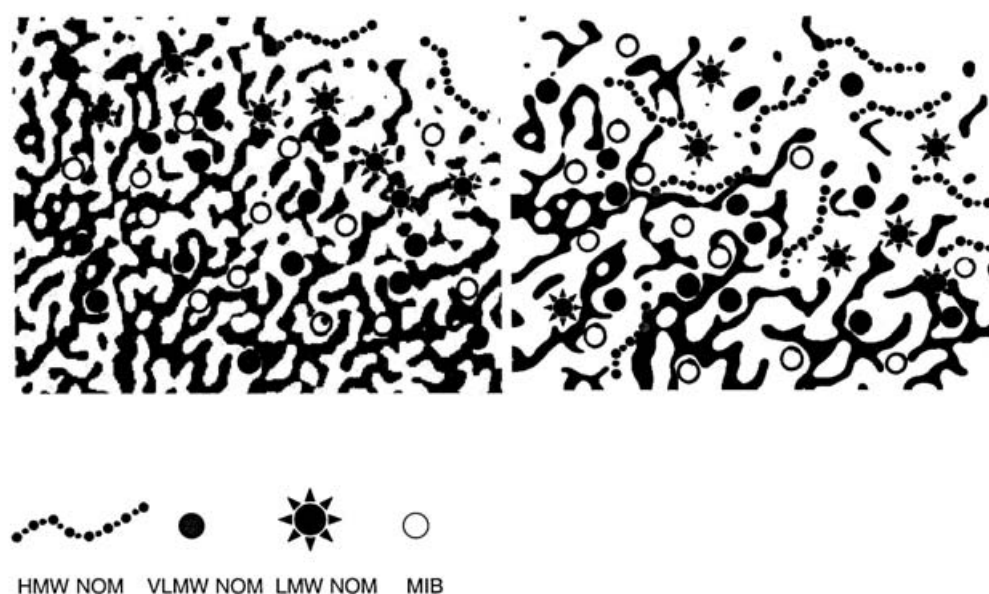


Figure 4.16 Representation of the carbon structure illustrating potential competitive effects

In the microporous carbon only VLMW NOM compounds are adsorbed throughout the carbon structure. As a result, the overall DOC adsorption on this carbon is low. However, these compounds are similar in size to MIB and can compete strongly and directly for the adsorption sites (where the NOM is of the same size), and/or can block pores leading to high energy adsorption sites for MIB (where the NOM is slightly larger). As suggested by Kilduff *et al.* (1998), these two mechanisms become indistinguishable as the competing and target compounds become closer in size. The blockage caused by these VLMW NOM could also be expected to reduce the rate of adsorption by restricting direct access to adsorption sites, necessitating a more tortuous diffusion path for the MIB. The NOM compounds represented in Figure 4.16 as LMW are larger than MIB, and therefore are able to access fewer adsorption sites. They are unable to diffuse throughout the structure, and are adsorbed closer to the external surface. It is possible that these compounds totally block access to some adsorption sites, and thus reduce equilibrium adsorption. They may also narrow the existing transport pores, resulting in a reduced rate of adsorption for MIB. The HMW NOM adsorbs only at or near the external carbon surface, and does not affect the adsorption of MIB significantly. However, these compounds may block narrow pore entrances sufficiently to affect the adsorption of the larger LMW NOM molecules.

These factors result in a) higher relative adsorption rates for HMW and LMW NOM, due to the shorter distances diffused and b) lower rate of adsorption and equilibrium capacity of MIB with an increase in VLMW and LMW NOM concentration.

In contrast, a range of NOM compounds can access the entire structure of a more mesoporous carbon. Therefore the relative adsorption rates of the NOM decreases slightly with increasing molecular weight as the diffusion coefficients decrease. The equilibrium adsorption capacity of MIB is lower in this carbon as there are fewer pores of the appropriate size, and the main competitive mechanism could be expected to be direct site competition, with some pore blockage by the VLMW and LMW possible. This pore blockage mechanism is expected to be less in the mesoporous carbon, resulting in a lower overall competitive effect than in the microporous carbons. The kinetics of adsorption of VLMW NOM and MIB are favourable in this mesoporous carbon as the adsorption sites are much more accessible. However, HMW NOM is able to adsorb on pore walls and restrict that access to a certain extent, resulting in a lower relative adsorption rate for MIB. Adsorption of MIB on pore walls, or in larger pores, where the adsorption energy is low, can result in desorption caused by displacement by NOM.

Such a combination of effects is to be expected in these diverse systems, and the mechanisms described are consistent with those suggested by Pelekani and Snoeyink (1998, 1999, 2000).

4.3.4 Conclusions

The majority of the competition between NOM and MIB in the systems studied can be attributed to compounds of similar size and chemical characteristics to the target compound. As a result, the production of an activated carbon with the aim of minimising the competitive effect becomes problematic. On a practical level, a powdered activated carbon with an extremely narrow pore size distribution, allowing only access to MIB, and minimal access to VLMW NOM, is difficult, and therefore, expensive, to manufacture, and could be expected to display very poor kinetic properties. An ideal carbon for the adsorption of MIB would have a bimodal pore distribution, allowing rapid access to adsorption sites, while minimising pore blockage and restriction by VLMW and LMW NOM. This conclusion was also reached by Pelekani (1999) in his study focusing mainly on the adsorption of atrazine and model competing compounds on activated carbon fibres. Such an adsorbent could also be expected to show good adsorption of the microcystin group of algal toxins, an important aspect of the treatment of water affected by algal blooms.

The study described in this paper takes the conceptual competitive adsorption model of Pelekani (1999) several steps further in its application to another adsorbate, a range of commercially available activated carbons that are used in practice, and a range of natural and isolated organic material. The confirmation that the same mechanisms are applicable in a less ideal system provides support to the notion that the model can aid drinking water suppliers in their selection of activated carbons.

4.4 PAC REMOVAL OF T&O COMPOUNDS: WHY DOES NOM COMPETE SO EFFECTIVELY?

4.4.1 Introduction

Taste and odours (T&O) in water have long been recognised as a significant problem for water authorities (Cotsaris *et al.* 1995, McGuire 1995). Organic compounds present at only nanograms per litre can cause T&O problems in water and can be difficult to remove (3, 4, 5). As governments and consumers demand larger quantities of safe, palatable drinking water with better aesthetic quality, the cost of supplying that water increases.

2-methyl isoborneol (MIB) (Figure 4.17) is a T&O compound commonly associated with blue-green algae blooms (Cotsaris *et al.* 1995). As with many T&O compounds, the major problems associated with MIB are due to its chemical structure and low detection threshold. MIB has no net charge, which makes it difficult to remove using conventional coagulation, flocculation and filtration. As most people can detect MIB's odour at the low nanogram L⁻¹ level, almost complete removal of MIB is necessary to avoid consumer complaints.

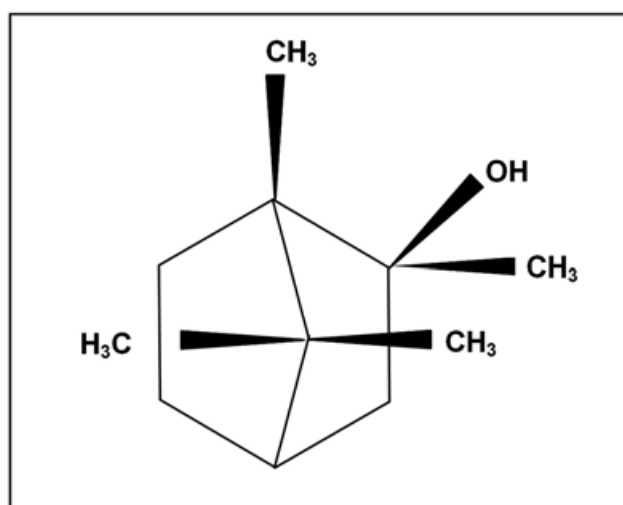


Figure 4.17 The structure of 2-methylisoborneol

Powdered activated carbon (PAC) can be used to remove T&O compounds, such as MIB, and be applied to water in conventional water treatment plants with only minor infrastructure changes. As the occurrence of T&O events is generally seasonal and episodes may only last days, the ability to dose PAC only as you need it and in the amounts you need can represent a significant cost saving over more permanent treatment options.

The one disadvantage to the PAC procedure is that the carbon is often dosed into water prior to treatment, where it contains its maximum concentration of NOM. Compounds within the NOM have been shown to compete with micropollutants, such as MIB and atrazine, for adsorption sites on activated carbon, thus reducing the effectiveness of the procedure (Zimmer *et al.* 1989, Najm *et al.* 1991, Newcombe *et al.* 1997b).

Both the size and chemical character of NOM affect the competition between NOM and MIB for adsorption sites on activated carbon. The aim of this study was to investigate the effects of the chemical characteristics of NOM on its competition with MIB for adsorption sites on activated carbon. The surface chemistries and pore volume distributions of activated carbons can have an effect on the adsorption of NOM. These variations in the adsorption of NOM could influence the mechanism of competition provided by the NOM for adsorption sites. The two PACs used in this study were chosen as they have different surface chemistries and pore volume distributions and Bjelopavlic *et al.* (1999) proposed different mechanisms of adsorption of NOM onto these two carbons, which may lead to different competitive effects. Studying the competition between MIB and NOM for adsorption sites on the two carbons should reveal any variations in competition mechanism.

4.4.2 Materials and methods

All chemicals were Analar grade (BDH, Sydney Australia) and all solvents of HPLC grade. Solutions were made using deionised water from a Millipore Milli Q system (Millipore Pty Ltd, France).

Source waters

Fractions of NOM were isolated from three French surface waters, two high humic-content waters, the Blavet River and the Gartempe River, and a low humic-content water the Loire River. The Loire was sampled in the summer of 1997, and the winter of 1998. Some physical chemical characteristics of the source waters are given in Table 4.8.

Table 4.8 Physical chemical characteristics of the source waters

River	Period of sampling	DOC (mg C/ L)	SUVA ($\text{m}^{-1} \cdot \text{L} / \text{mg C}$)	Conductivity ($\mu\text{S} / \text{cm}$)
Loire	11/97	2.9	3.1	263
Loire	7/98	3.3	3.3	259
Blavet	7/96	6.6	4.8	145
Gartempe	2/97	6.5	4.4	85

Activated carbons

The activated carbons chosen were PICA PCO (Suppliers, Carbon Products Australia, Melbourne) a steam activated coconut shell based carbon and PICA Picazine HP (Suppliers, Carbon Products Australia, Melbourne) a wood based chemically activated carbon. Both carbons are commercially available. Prior to experimentation the carbons were thoroughly washed using Milli Q deionised water in a soxhlet apparatus. The structural information for the carbons is shown in Table 4.9.

Table 4.9 Structural information on the powdered activated carbons

Carbon	Starting Material	Activation	Surface Area (m^2/g)	Pore Volume ($\text{cm}^3/\text{g}^{-1}$)		
				Primary Micropores Width<0.8nm	Secondary Micropores 0.8<w<2nm	Mesopores 2<w<50nm
PCO	Coconut shell	Steam	987	0.31	0.13	0.03
HP	Wood	Chemical	2183	0.57	0.54	0.51

The values in Table 4.9 show that the two PACs are distinctly different. The HP has a high surface area and relatively high proportions of mesopores and micropores, which is indicative of an “open” pore structure. The PCO has a much lower surface area and almost no mesopores but a high proportion of primary micropores. This indicates the pore structure of the PCO is more “closed” than the HP. Newcombe and Drikas (1997) showed that the adsorption of MIB correlated with the micropore volume of several powdered activated carbons. However Newcombe (1999) showed that chemically activated wood based carbons, such as HP, did not follow this relationship, and in general showed a much lower MIB adsorption.

NOM isolation procedure

Fractions of NOM were isolated according to the procedure described by Croué *et al.* (2000). Figure 4.18 shows a schematic of the basic isolation procedures used.

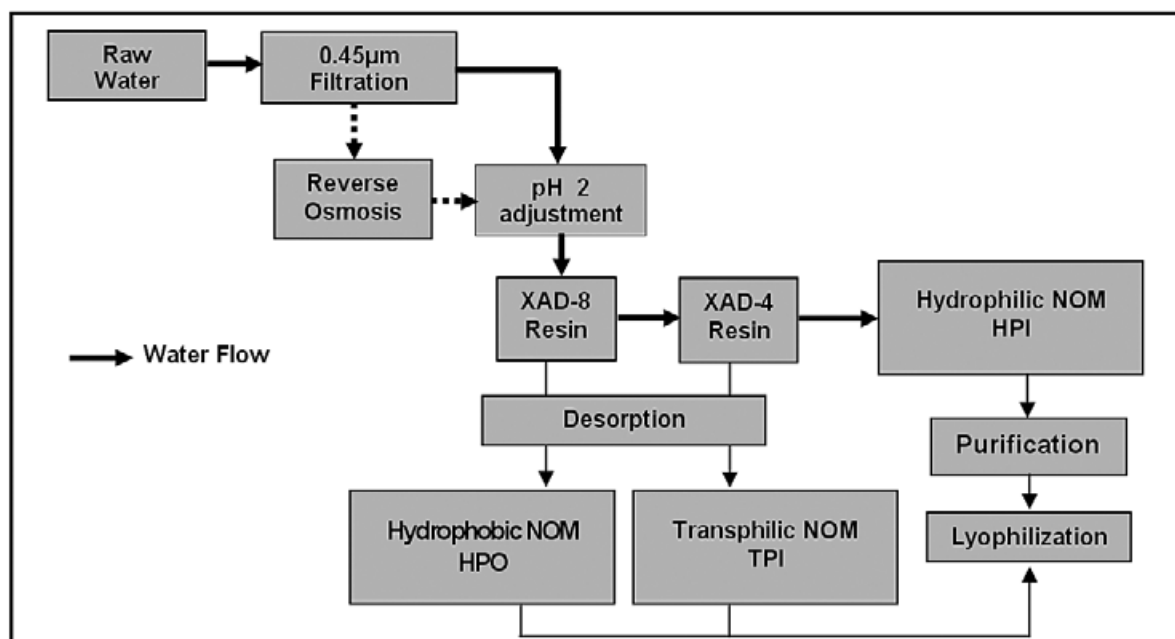


Figure 4.18 A diagrammatic representation of the isolation procedures

Raw waters filtered onto 0.45 µm membrane and acidified at pH 2 with HCl were pumped through XAD-8 and XAD-4 resins, used in series. Because of its low DOC concentration the Loire River was preconcentrated using reverse osmosis (Filmtec TW30 40/40 RO membrane) after softening on a Na⁺-exchange resin. Compounds adsorbed onto both resins were desorbed with 0.1 N sodium hydroxide (Blavet River) or a mixture of acetonitrile and water (75%/25%) (Gartempe River and Loire River). Before lyophilisation, sodium hydroxide eluates were pumped through an H⁺-cation exchange resin while the acetonitrile of the acetonitrile/water eluates was removed by rotary evaporation. The isolate from the XAD-8 resin is called the hydrophobic, or HPO fraction, and that from the XAD-4 resin, the transphilic, or TPI fraction. The hydrophilic acid NOM fraction (HPIA) was purified according to procedure described by Aiken and Leenheer (1993). This purification step was operated on the Loire River only.

Isolation recoveries shown in Table 4.10 and expressed in term of DOC were determined based on the carbon content of the isolates (i.e. elemental analysis). One can notice that the major part of the loss of materials observed for the HPO isolated from the Loire River winter sample was due to co-precipitation of NOM with clay (shown by FT-IR analysis conducted on the precipitate) after acidification at pH 1, used for the separation of the colloidal material before XAD resin filtration.

Table 4.10 DOC recovery of the isolation protocol

Sample	HPO	TPI	HPIA	Total
	Relative proportion (% DOC)			
Loire River (winter)	38	15	7	60
Loire River (summer)	66	17	4	87
Blavet River	56	17	Not performed	73
Gartempe River	53	16	Not performed	69

Powder activated carbon adsorption

The equilibrium experiments were performed on the isolates using both the PCO and HP carbons. The one exception was the Loire River HPIA fractions as they contained insufficient material to conduct all of these experiments. For each carbon, 2 L samples of each NOM solution were prepared at 10 mg L⁻¹ DOC using 0.01M NaCl, the approximate ionic strength of the natural waters. The solutions of each fraction were then divided into six 310 mL Pyrex bottles. 40 µL of a concentrated C¹⁴ radiolabelled MIB (American Radiolabeled Products) solution was added to each bottle, to give a solution concentration of approximately 100 ng L⁻¹ MIB. The appropriate PAC dose was then added and the bottle closed. The sealed bottles were placed on a tilting roller for a period no less than 4 days and no more than 6 days. A Milli Q 100 ng L⁻¹ MIB blank containing no carbon was also run in conjunction with each experiment.

When the bottles were removed from the rollers, 100 mL of the solution was filtered through a 0.45 µm membrane. 2.5 mL of the filtered solution was added to 17.5 mL of scintillation cocktail (Starcint, Packard Australia) and the resulting beta counts recorded using a LS2800 model scintillation counter (Beckman). The count was then converted to MIB concentration using the following equation :

$$\text{MIB concentration} = (\text{Actual Count} - \text{Background Count}) \times 0.55792$$

DOC and UV absorbance analyses were performed on the remaining filtered sample.

NOM characterization

All solutions of NOM were filtered through 0.45 µm membrane (Millipore, Crown Scientific) before analysis. Measurements of UV absorbance were carried out in a 1 cm quartz cell using a "Safas" spectrophotometer "Double energy system 190 DES". Specific UV absorbance (SUVA) is defined as the UV absorbance of a given sample determined at 254 nm and divided by the DOC concentration of the solution. It is expressed in units of m⁻¹ L mg⁻¹ OC. Analyses were carried out using spectrometers zeroed using Milli Q water.

The DOC was measured using a Dohrmann DC 80 Carbon Analyzer or a Seivers 820 Total Organic Carbon Analyzer.

Potentiometric titration of carboxyl content was performed on 200 mg/L NOM isolate prepared in 0.1 M KCl using 0.02 M NaOH in the presence of a continuous nitrogen flow above the solution to avoid CO₂ dissolution. The end point of titration for carboxyl was approximately pH 8 for all samples (determined by a double differential plot).

High performance size exclusion chromatography (HPSEC) analyses were conducted based on the method of Chin et al. (16). The HPLC system included a WATERS 717 plus autosampler, a WATERS 600 pump and a WATERS 996 Diode Array detector. Solutions of NOM fractions (50 mg C/L) were prepared with the mobile phase and injected on a ProteinPak 125 column (ID : 7.8 mm ; length : 30 cm) using a 20 µL loop. The molecular weight calibration was determined using polystyrene sulfonates (8, 5.4 and 1.8 KD), terephthalic acid and acetone (linear regression R² = 0.998).

Elemental analyses were carried out by the laboratory of the Centre National de la Recherche Scientifique (CNRS) in France. Microanalyses developed at the CNRS laboratory allow the determination of the C, H, O, N, S contents (in %) with an absolute precision of 0.3 % and a standard deviation of 0.2 %.

Solid-state cross-polarisation magic angle spinning (CPMAS) ¹³C-NMR spectra were obtained from the United States Geological Survey laboratory at Arvada, Colorado USA using a 200 megahertz (MHz) Chemagnetics CMX spectrometer with a 7.5 mm diameter probe. The spinning rate was 5000 Hz. The acquisition parameters for the freeze-dried samples included a contact time of 1 ms, pulse delay of 1 s, and a pulse width of 4.5 µs for the 90° pulse.

4.4.3 Results and discussion

Characterisation of the fractions of NOM

Table 4.11 gives some important structural characteristics of the isolated NOM fractions.

Table 4.11 Structural characteristics of the NOM isolates

		Elemental analysis				Titration		Molecular weight		
River		C	H	N	O	Ash	COOH	Mw	Mn	SUVA
		%	%	%	%	%	meq/g C	Dalton	Dalton	m ¹ .L/mg C
Loire (Winter)	HPO	49.7	5.0	2.1	33.5	5.4	9.6	1060	690	2.9
	TPI	45.7	5.0	4.2	39.8	1.9	9.4	820	550	2.0
	HPIA	26.0	3.5	4.3	36.1	19.1	16.5	820	590	1.8
Loire (Summer)	HPO	49.7	5.0	2.6	35.0	3.5	9.0	950	630	3.1
	TPI	44.2	5.0	4.9	40.0	2.5	9.5	780	530	1.9
	HPIA	20.2	2.5	2.7	29.7	9.6	14.3	770	480	1.2
Blavet	HPO	46.5	4.6	2.1	38.4	2.8	10.2	1490	940	5.2
	TPI	41.7	4.2	2.5	44.9	3.5	14.5	1280	880	3.2
Gartempe	HPO	46.9	4.7	1.9	38.0	7.1	7.6	1560	850	4.0
	TPI	43.2	4.7	2.6	44.4	2.0	10.1	1160	850	2.9

The elemental analysis indicates that the HPO and TPI fractions are almost pure NOM with a very low ash content. The proportion of residues in the HPIA fractions is significantly higher, results which confirm the difficulty of separating the organics from the mineral matrix in the XAD-4 filtrate. As observed with other sources waters, the C/O, C/N, and C/H ratios of the fractions decrease with the increase of the hydrophilic character of the NOM. The more hydrophilic NOM fractions (i.e. TPI and HPIA fractions) are enriched in nitrogenous moieties and oxygenated functional groups compared with the HPO fraction. No significant difference could be observed in the elemental analysis between the corresponding Loire winter and Loire summer isolates except a slightly higher nitrogen content in the summer isolates as expected due the presence of a more abundant biomass.

The HPSEC analysis showed that for a given water source the HPO fraction incorporates the largest proportion of high molecular weight structures (i.e. higher Mw and Mn) among the three isolated fractions, and also incorporates the largest proportion of UV absorbing moieties as indicated by the higher SUVA. These results are consistent with the work by Aiken *et al.* (1992) which showed that the HPO fractions contained higher molecular weight (MW) NOM than the TPI fraction. The difference between the TPI and HPI fractions appeared to be relatively minor, nevertheless, the UV absorbing moieties seem to be more abundant in the TPI fraction (i.e. higher SUVA). The Mw and Mn values for each of the fractions can be seen in Table 4.11. Note that while the Mw tends to be influenced by the high molecular weight content of the fraction, it is the lower molecular weight material that influences the Mn. Therefore it is possible for a fraction to have both a higher Mw and lower Mn than other fraction(s) from the same source, as is the case with the Gartempe HPO. This would indicate that while these fractions contain higher MW NOM they also contain lower MW compounds than their TPI counterparts. As the higher MW NOM generally has higher SUVAs than the lower MW material, it could be possible for a small concentration of high SUVA, high MW NOM to exert a much greater influence on the average molecular weight than the low SUVA, low MW NOM.

The integrated areas under various portions of the C^{13} NMR spectra curves can be assigned to specific features of the average functional group content of a sample. Table 4.12 contains the assignments used in this study along with the values obtained for all of the fractions and Figure 4.19 shows the spectra obtained for the Loire summer NOM isolates as an example. Although there are some differences between the HPO and TPI fractions, the overall values are within similar ranges to those found by other workers (Newcombe *et al.* 1997b, Croué *et al.* 1994, Croué 1999). The results confirmed that the HPO fraction of NOM is enriched in aromatic carbon compared with the TPI fraction.

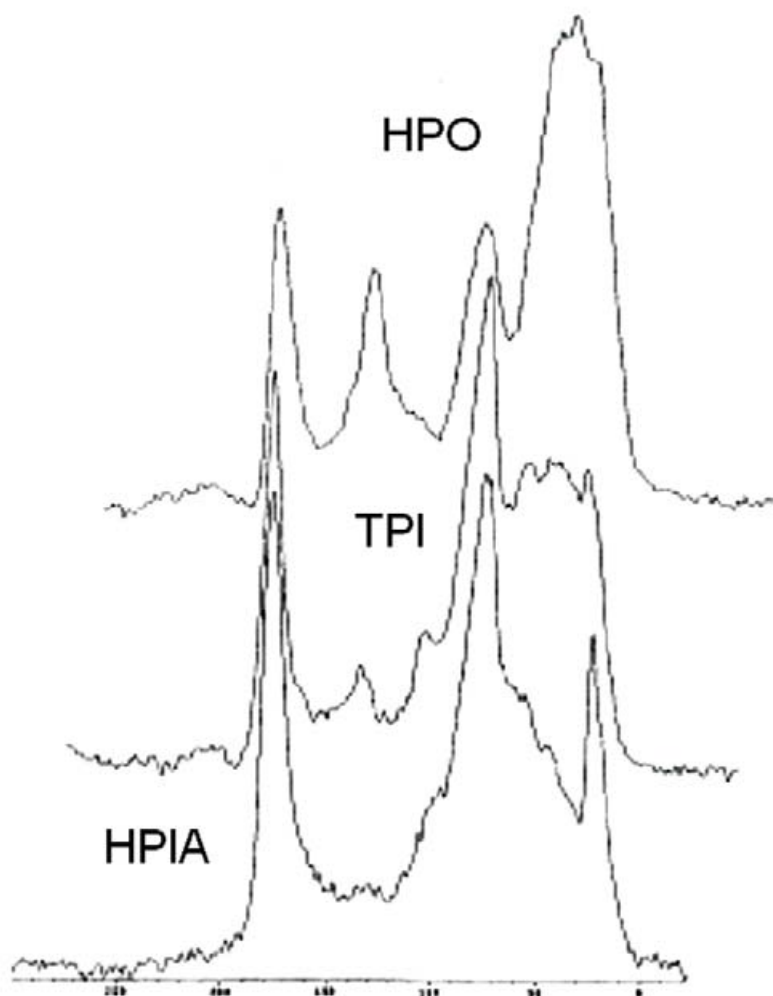


Figure 4.19 ^{13}C -NMR spectra of the Loire River NOM isolates (7/98)

The spectrum of the HPIA (Figure 4.19) fraction shows nearly no signal above the background in the 110 – 160 ppm chemical shift region (i.e. aromatic carbon domain).

OPTIMISATION OF ADSORPTION PROCESSES

Table 4.12 Integrated areas of ^{13}C -NMR spectra of the Loire River NOM fractions

		Shift (ppm)					
River	Fraction	0-60 C-C/C-H	60-90 C-O	90-110 O-C-O	110-160 Aromatic C	160-190 COOH	190-220 C=O
Relative Area (%)							
Loire (winter)	HPO	45	16	5	18	14	2
	TPI	36	26	6	11	18	2
	HPIA	30	32	8	8	20	1
Loire (summer)	HPO	49	18	5	15	11	2
	TPI	39	30	6	8	16	1
	HPIA	29	34	8	6	22	1
Blavet	HPO	41	19	5	20	13	2
	TPI	35	25	7	12	19	2
Gartempe	HPO	37	18	6	22	14	3
	TPI	38	25	7	13	17	1

As already indicated by potentiometric titration, the HPAI fraction of NOM is enriched in COOH functional groups compared with the TPI and the HPO fractions.

In accordance with the trend observed for the C/O ratio, the TPI and HPIA fractions are also enriched in C-O bond (i.e. aliphatic alcohols, ethers and esters) and anomeric carbon (i.e. sugars, 90 – 110 ppm chemical shift) compared with the HPO fractions. Consequently the HPO fraction does contain a larger proportion of aliphatic C-C and C-H, an indicator of its stronger hydrophobic character. The presence of a well defined peak at 22 ppm in the ^{13}C -NMR spectra of the HPIA fraction (Figure 4.19), also noticeable for the TPI fraction, may correspond to the methyl of the N-acetyl group that is specific of aminosugars. Again, Loire winter and Loire summer NOM isolates appeared to be quite similar with regard to the results obtained by ^{13}C -NMR spectroscopy. However, one can notice that the winter NOM seems to be slightly more aromatic in nature. Variability in the aromatic carbon content is the major difference that can be observed between similar fractions of different origin.

Using the XAD-8/XAD-4 isolation approach, and as already mentioned by Croué *et al.* (2000) and shown in Figure 4.20, there is a strong relationship between SUVA and aromaticity of the isolated fractions (i.e. samples with high SUVA had high aromaticity). Figure 4.20 also indicates that there is a good relationship between SUVA and average molecular weights Mw or Mn (not shown). A trend can be proposed between SUVA and the carboxyl content, the higher the SUVA the lower the carboxyl. As a general trend, NOM fractions isolated from high-humic content source water (i.e. Blavet and Gartempe Rivers) are enriched in aromatic moieties, depleted in carboxyl and of higher average molecular weight (i.e. more hydrophobic in nature) compared with low-humic content source water (i.e. Loire River).

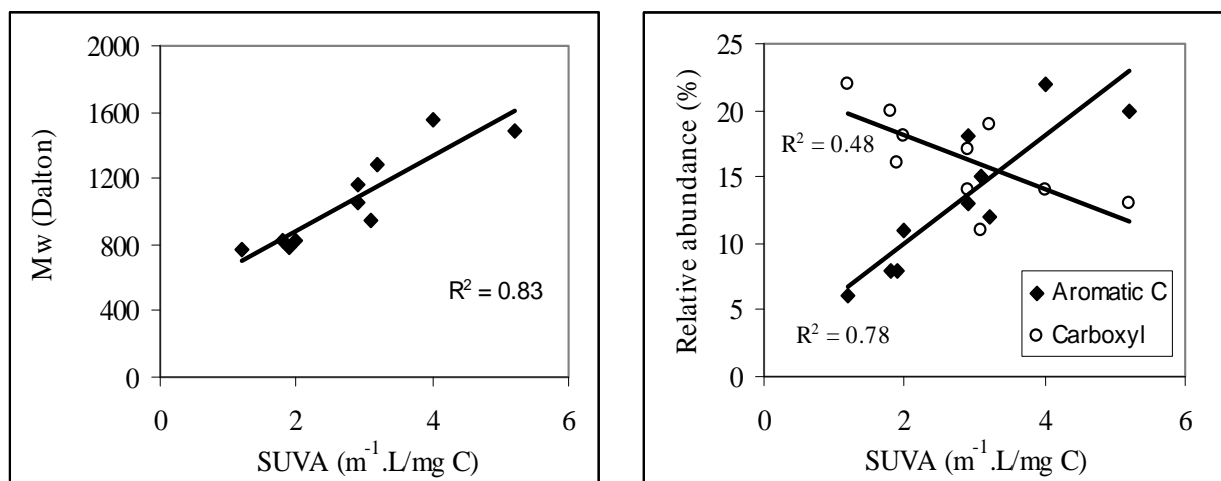


Figure 4.20 Relationships between some structural characteristics

Competitive adsorption: equilibrium experiments

Figure 4.21 shows the equilibrium adsorption of MIB by PCO and HP, in the presence of all of the fractions. For both carbons all of the fractions show some level of competition. The HPO fractions always showed the greatest competitive effect, thus in Figure 4.21 the percentage of MIB remaining in solution was highest in the presence of HPO. This effect was most evident with the HP carbon. Note that just as their average chemical characters were very similar, so was the competition provided by the Loire Summer and Winter fractions. Also note that the PCO removed more MIB than the HP even in the presence of the same fraction which is consistent with work by Newcombe (1999).

The aim of this study was to determine the influence of NOM character on the adsorption of MIB by activated carbon. The HPO fractions consistently showed higher competition than the other isolates but could this trend be linked to the characteristics discussed above? The most noticeable differences in the structural characteristics of the HPO fractions were their high SUVA's, high percentages of alkyl and aromatic carbons, higher M_w values, and the low percentage of O-alkyl carbons. Figure 4.22 shows the correlations between the percentage of MIB remaining with a HP dose of 30 mg/L and the carbon to nitrogen ratios (A) and percentages of carboxyl (B) and aromatic carbons (C) in the competing NOM. Note that the competition shows similar trends to these parameters.

OPTIMISATION OF ADSORPTION PROCESSES

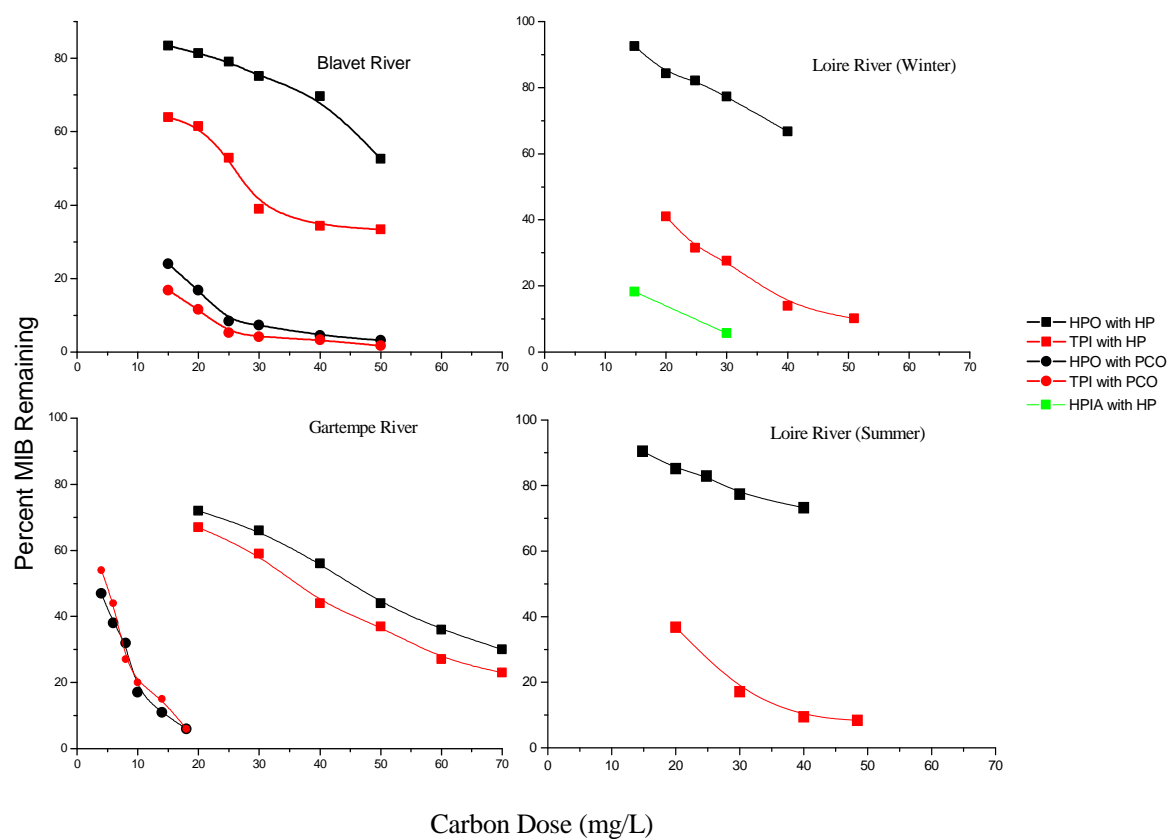


Figure 4.21 Percentage of MIB as a function of carbon dose in all NOM fractions

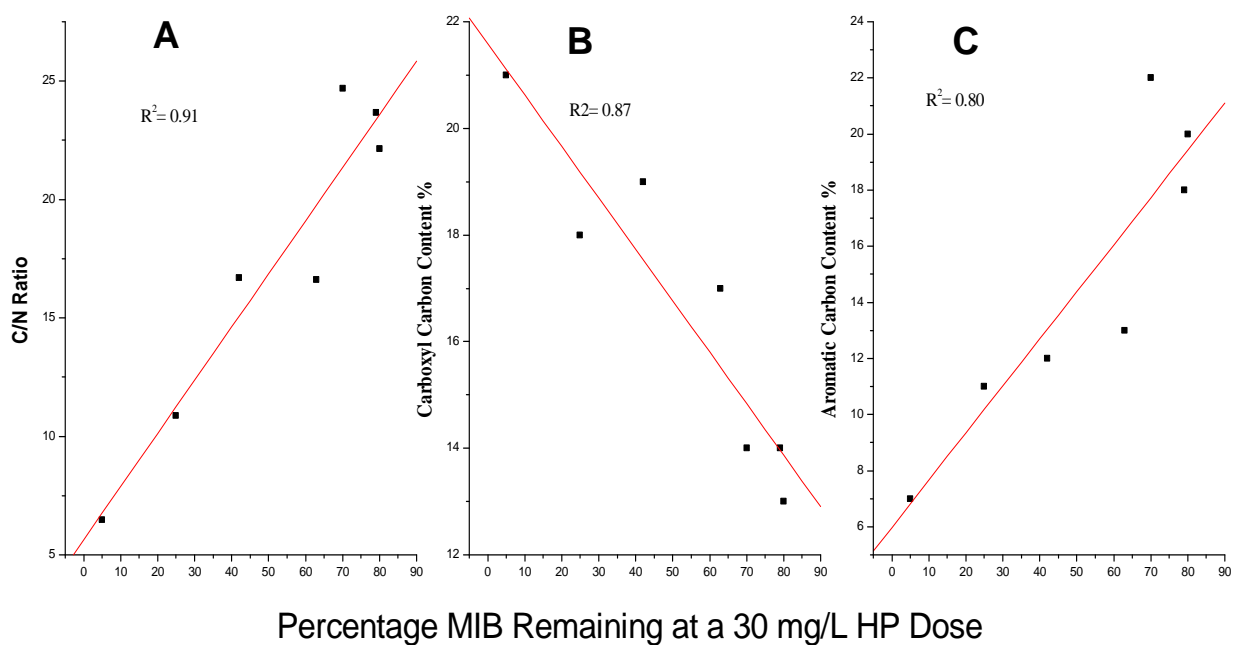


Figure 4.22 The correlation between the percentage of MIB remaining with a 30 mg/L HP dose and the Carbon to Nitrogen ratios (A), the percentage of aromatic (B) and carboxyl (C) carbon in the competing NOM

Although these trends were consistent with the order of competition for the fractions from each water, i.e. the level of competition decreases as the SUVA, C/N ratio and percentage of aromatic and alkyl carbons decrease and O-alkyl and carboxyl carbons increase, these characteristics do not account for the similarity of the competition provided by the chemically quite different Gartempe HPO and TPI fractions. If these characteristics had more important effects the Gartempe HPO and TPI fractions should show more significantly different competitive effects. Also of interest is that it is the fractions with the higher Mw values that are competing the most. This contradicts work by Hepplewhite (2000), that showed the lower molecular weight UF fractions of NOM isolates, with Mw's and Mn's of 540-600 and 330-450 respectively, competed the most.

Figure 4.21 clearly shows that HP has a lower capacity for MIB than the PCO, which is consistent with Pendleton *et al.* (1997) who showed that the low adsorption of MIB was possibly associated to the surface chemistry of the PAC. They linked the low adsorption of MIB by the chemically activated wood based carbons to the hydrophilicity of the carbon surface which in turn was related to the high oxygen content of the wood-based, chemically-activated carbons. They proposed that it is difficult for MIB to displace water adsorbed on hydrophilic adsorption sites. The percentage of oxygen present in the HP used for this study was lower than that of the PCO (Bjelopavlic *et al.* 1999). This would indicate that given with the similarities in the primary and secondary micropore volumes, the HP should adsorb more MIB than the PCO, which clearly was not the case. This suggests that oxygen is probably not the only influence on the hydrophilicity of PAC surfaces, or that hydrophilicity does not control the adsorption of MIB.

Newcombe and Drikas (1997) suggested that low MIB adsorption on HP was related to the difference in surface chemistry and or the presence of residual phosphoric acid in its pores. The activated carbon manufacturer Norit has shown that the chemically-activated wood-based carbons have a completely different surface structure and therefore it is probably not useful to compare them with steam-activated carbons, as suggested recently by Newcombe (1999).

It is difficult to determine the relative effects of competition by the fractions on the two carbons. It is necessary to compare the adsorption of MIB in the presence of the NOM fractions with that in the absence of NOM. Adsorption isotherms were constructed for all fractions and for pure water. Figure 4.23 shows the equilibrium isotherms for pure water, Loire HPO and HPIA for HP and Blavet HPO and TPI for PCO. The competitive effect of the fractions is clearly visible as the reduction of the surface concentration of MIB with a given solution concentration (Γ) compared with the adsorption seen in pure water.

OPTIMISATION OF ADSORPTION PROCESSES

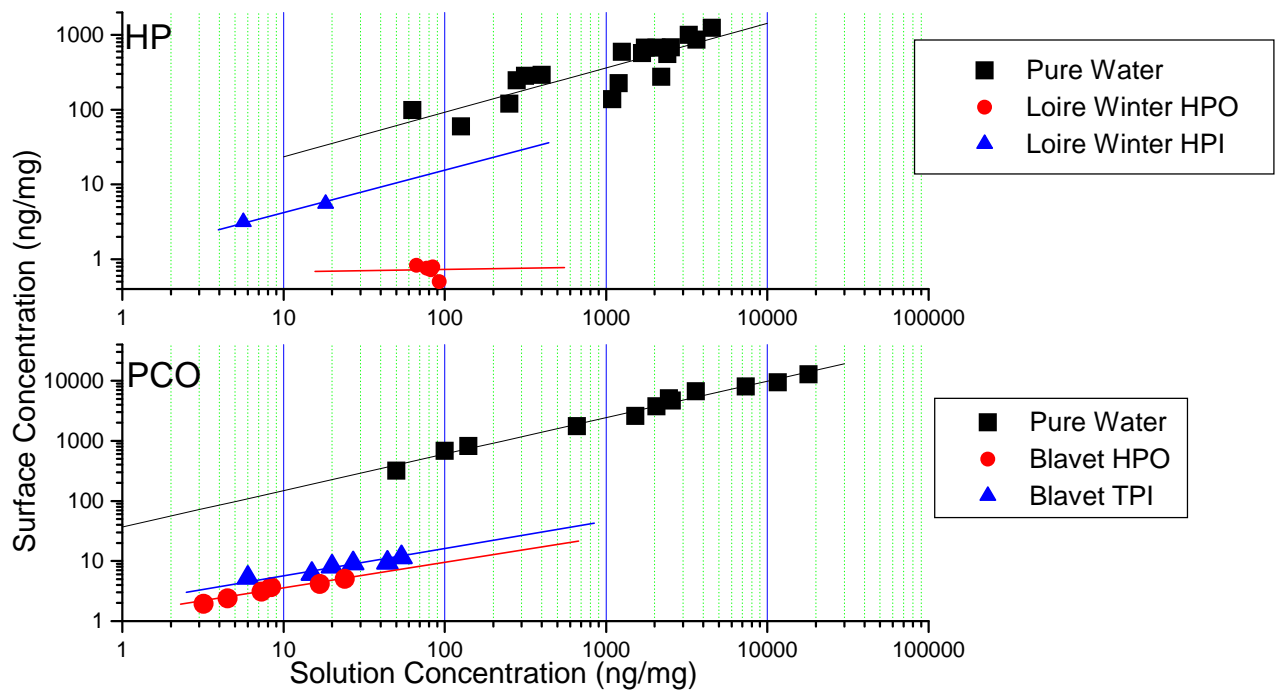


Figure 4.23 Equilibrium isotherms for the adsorption of MIB by PCO and HP, in the presence of pure water, Loire HPO and TPI (PCO) and Blavet HPO and TPI (HP)

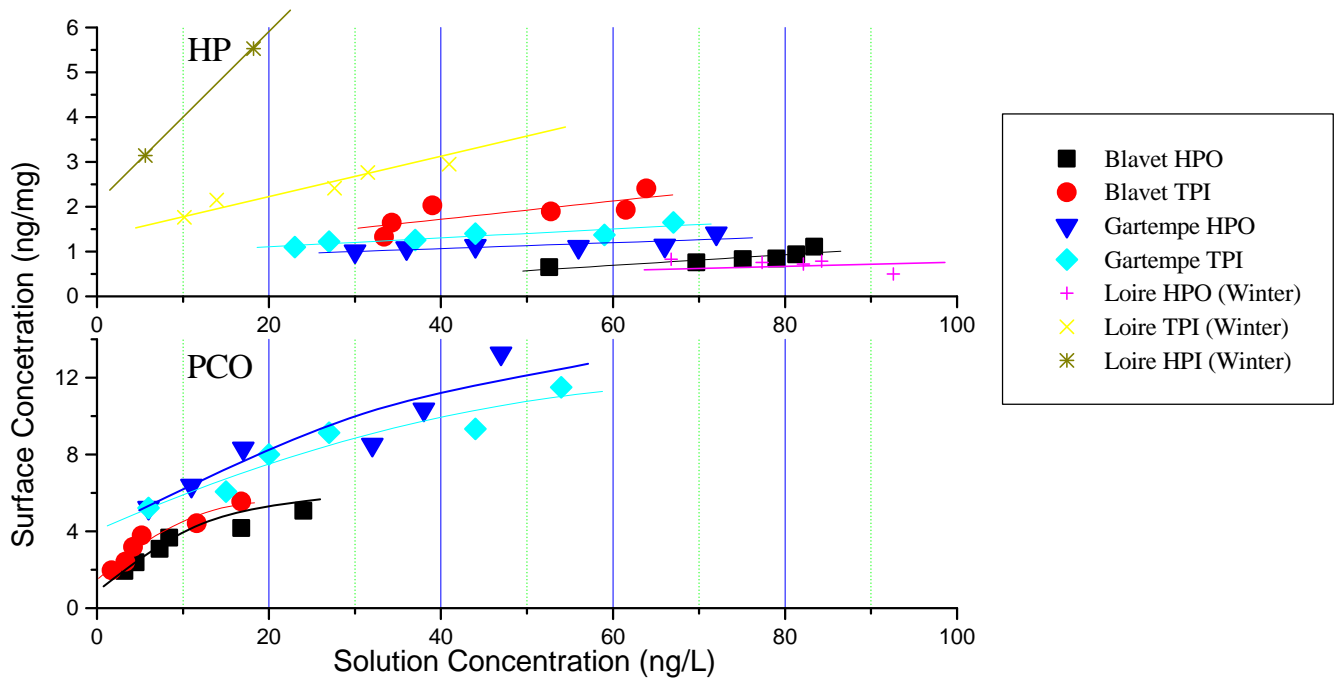


Figure 4.24 Equilibrium isotherms for the adsorption of MIB by PCO and HP, in the presence of all of the fractions

Figure 4.23 shows that there is a large difference between the adsorption of MIB by activated carbon in pure water and in the presence of NOM. The difference between the adsorption in the presence of the different NOM fractions is relatively small and would not be clear if all the fractions had been plotted in Figure 4.23. Figure 4.24 shows the equilibrium adsorption isotherms for all of the fractions.

The competitive effects of the various fractions can be directly compared using the surface concentrations at a given solution concentration. A solution concentration of 50 ng/L was chosen as this represented a concentration that could be expected in a water treatment plant. Table 4.13 contains the surface concentration calculated from a solution concentration of 50 ng/L using the constructed isotherms for both carbons.

Table 4.13 Surface concentration of MIB calculated from a solution concentration of 50 ng/L for all of the fractions

Fraction	Carbon	
	Γ PCO (ng/mg)	Γ HP (ng/mg)
Blavet HPO	6	0.5
Blavet TPI	7	1.9
Gartempe HPO	12	1.2
Gartempe TPI	10	1.4
Loire HPO (Winter)	na	0.3
Loire TPI (Winter)	na	3.4
Loire HPIA (Winter)	na	11
Pure Water	444	61.6

A low surface concentration of MIB indicates a high competitive effect for that NOM fraction. Therefore the order of competitive effect for HP is: Loire HPO \approx Blavet HPO > Gartempe HPO \approx Gartempe TPI > Blavet TPI > Loire TPI >> Loire HPIA. Although, there was correlation between order of competition provided by the fractions and the C to N ratio from the elemental analysis (Table 4.12), the R^2 value (0.8) was not as high as with the correlation in Figure 4.22.

For the PCO the order is only slightly different: Blavet HPO > Blavet TPI = Gartempe TPI > Gartempe HPO. The variation in the order of competitive effect from the PCO indicates that the mechanism of competition of the NOM on the HP is different to that on the PCO. This may be due to the differences in the carbon structures discussed earlier.

Of interest is the total effect of the highest and lowest competitive fractions with each carbon. For PCO the surface concentration of MIB at a solution concentration of 50 ng/L, in the presence of Blavet HPO is reduced to 1 or 2% of the surface concentration in the absence of competition. On HP the surface concentration is reduced to less than 1% of that of the pure water isotherm. For the Loire HPIA and Gartempe HPO, the least competitive fractions, the reduction of surface concentration is 97% for PCO and 82% for HP. Note the difference in the reduction of MIB surface concentration between the most and least competitive fractions is 1-3% for PCO and 1-17% for HP. This indicates that although the NOM fractions have a similar effect on the adsorption of MIB by PCO and HP, the differences in the NOM fractions might be slightly more important for the adsorption by HP than with PCO in relative terms.

Although there are some differences in the competitive behaviour of the fractions, even the least competitive fraction, Loire HPIA, was able to reduce the adsorption of MIB by up to 82% of that in pure water. Both carbons showed significant decreases in their capacity for MIB, while the adsorption of DOC by PCO was very low. The initial concentration of MIB, 100ng/L, was chosen as it represents a concentration that could reasonably be expected in a water treatment facility. However the DOC concentration this corresponds to is very low. One hundred nanograms per L of MIB would equal 77.4 ng/L DOC. If there were to be one thousand times the concentration of MIB of strongly competitive NOM molecules this would still only be 77000 ng or 70 μ g or less than 1% of the total DOC in the NOM solutions.

When considered in this way it is surprising that MIB adsorbs at all. There must be sites available to MIB on both carbons that are i) inaccessible to any NOM compounds and/or ii) bind MIB with a high adsorption energy which cannot be overcome by the adsorption of any of the NOM compounds present. This is consistent with work by Narbaitz and Benedek (1994) who used predictive models to describe the competitive adsorption of 1,1,2 trichloroethane (TCEA) in the presence of NOM. They chose a model, which incorporated the possibility of adsorption sites on which there would be no competition, i.e. only NOM or only TCEA molecules adsorb on certain sites. Their results suggested that 70% of TCEA and 16% of NOM molecules were competing for the same adsorption sites.

While overall chemistry of the NOM does show some correlation to its competitive behaviour, another factor appears to have a greater influence on MIB's access to adsorption sites on PAC. Note again that the order of competition appears to contradict Newcombe *et al.* (1997b), with the hydrophobic fractions being the most competitive, even though these fractions were shown to have higher average molecular weights than the transphilic or hydrophilic fractions. However, the results are consistent with Hepplewhite (2000), where the competition provided by fractions of XAD 8, XAD 4 and anion exchange isolates was compared and the order of competition was the same as in this study. Hepplewhite (2000) also showed that it was the low MW, low SUVA, higher carboxyl fraction, found in the XAD 8 isolate, that was competing the most. To gain further insight into the influence that the high and low molecular weight NOM compounds have on the adsorption of MIB by PAC, the use of ultrafiltration fractionation combined with high performance size exclusion chromatography to better examine the NOM before and after adsorption is planned and should provide a useful tool to examine the competition between NOM and MIB for the adsorption on PAC.

4.4.4 Summary and conclusions

Natural organic matter was isolated from three different surface waters in two different seasons. Despite the differences in the source waters, the isolation and fractionation techniques along with removal and recoveries of the NOM, the average chemical characteristics for the equivalent fractions, as determined by C¹³ NMR, UV absorbance and HPSEC were not vastly different.

The NOM fractions were used in powdered activated carbon adsorption experiments to compete with the T&O compound MIB. In general the hydrophobic NOM was the most competitive, and several correlations between the competition and the average chemical characteristics as determined by C13 NMR and elemental analysis, were seen. However, the correlations between the surface concentrations of MIB, calculated from the equilibrium isotherms, and the chemical data were not as significant.

Of interest was that although the hydrophobic fraction is generally considered to have a higher average molecular weight, it had a strong competitive effect and this would appear to contradict earlier work in which lower molecular UF fractions had been shown to compete the most. Further study into the competitive effects of the molecular weights of the NOM fractions on the PAC adsorption of MIB will be carried out and should provide a more definitive answer to the question: The battle between NOM and MIB for PAC: winners and losers and why?

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5. OPTIMISATION OF THE APPLICATION OF ACTIVATED CARBON FOR TREATMENT OF A RANGE OF ALGAL METABOLITES

5.1 INTRODUCTION

The adsorption of NOM and MIB was studied in detail, on a fairly fundamental level, to determine the mechanisms of adsorption, and of adsorption competition, and the results were reported in previous sections. In this chapter the adsorption of other algal metabolites (geosmin and the saxitoxin class of cyanotoxins) are also explored, on a more applied level, with the application of the knowledge obtained from the earlier work. The effects of water quality and water treatment processes on the adsorption of MIB and geosmin are discussed along with the objective of aiding the water supplier to understand the factors affecting the application of PAC for the removal of algal metabolites.

5.2 A GUIDE TO SUCCESS WITH EARTHY-MUSTY TASTE AND ODOUR REMOVAL USING PAC

5.2.1 Introduction

The presence of blue-green algae blooms in water supplies poses problems to water authorities because blooms often result in musty-earthly taste and odour episodes in distribution systems. Two algal metabolites associated with these problems are 2-methylisoborneol (MIB) and geosmin. These are of concern because they can be detected by consumers at low nanogram per litre (ng/L) levels and are not removed by conventional water treatment (coagulation / flocculation / sedimentation / filtration). The addition of powdered activated carbon (PAC) to the water treatment process can effectively remove MIB and geosmin. PAC is often ineffective because many factors that affect adsorption are either not known or are not considered. To successfully use PAC the appropriate PAC is required, and the effect of changes in water quality and water treatment processes on adsorption should be considered. These effects are summarised in Figure 5.1. Determining the PAC dose is difficult because the efficiency of adsorption of MIB and geosmin can vary from one PAC to another (Newcombe and Drikas 1995, 1996; Gillogly *et al.*, 1998a;), is affected by natural organic matter (NOM) present in all raw waters (Newcombe *et al.* 1997) and depends on contact time. The aim of this study was to provide information to water authorities on how the factors shown in Figure 5.1 affect taste and odour removal. This information will allow water treatment personnel to make more informed choices regarding the type of PAC and the dose to apply for the best outcome for both consumers and water suppliers.

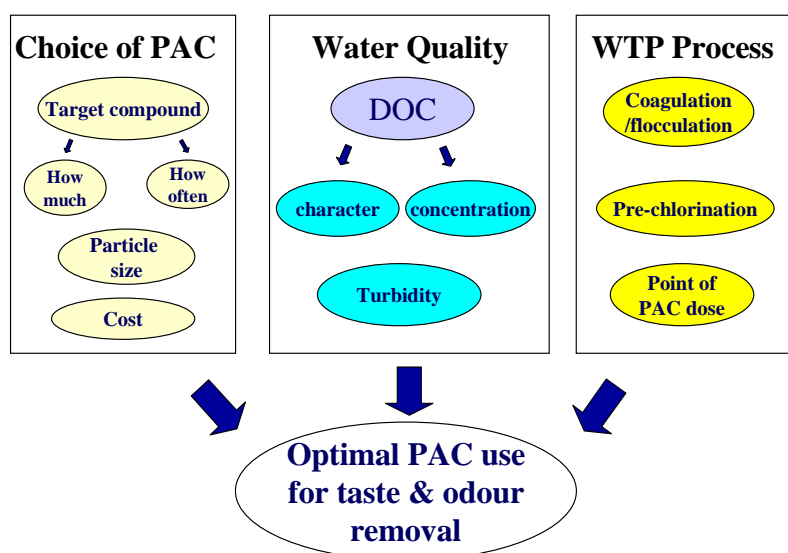


Figure 5.1 Factors that affect the performance of PAC for MIB and geosmin removal

5.2.2 Materials and methods

Water samples

Water samples obtained were split into two samples, one filtered through a 0.2 µm cartridge filter for equilibrium and kinetics experiments while the other unfiltered portion was kept for jar tests. All waters were stored at 4°C until used.

Powdered activated carbon

Picatif 1100 PAC was supplied from PICA and is a coconut-based, steam-activated carbon. The PAC was dried at 105°C for 24 hours then cooled and stored in a desiccator.

Experimental procedures

Equilibrium isotherms

Raw water was added to clean, dry pyrex bottles to a level where the headspace was minimal. MIB or geosmin was added, the solution shaken and then allowed to stand. After several minutes PAC was then added and the bottle was sealed and agitated for 3 days.

Kinetics

MIB and geosmin were added to constantly stirred raw water. After 15 minutes of mixing subsamples were taken to determine the initial concentration. PAC was added and further subsamples were taken at predetermined intervals over the following 4 hours. Subsamples were then pressure filtered through 0.45 µm disposable filters to remove the PAC.

Jar tests

The jar test conditions were set up to simulate conditions at the four water treatment plants (WTPs). PAC and alum were dosed during the rapid mix stage with mixing at maximum velocity (160 rpm) for 1 minute. The flocculation speed, flocculation and sedimentation time were determined by the operating conditions at the WTPs.

Turbidity spiking

Natural turbidity was obtained by filtering the test water and River Murray water (a high turbidity water) through a 0.45 µm cartridge filter. The captured particles were removed from the filter by backwashing with the test water. A volume of concentrated turbidity solution was added to the test water to give the desired turbidity.

Predicting MIB and geosmin removal using the HSDM

The Homogenous Surface Diffusion Model (HSDM) was used to predict the kinetics of MIB and geosmin adsorption. This was carried out as described by Cook *et al.* (1999). Traegner and Suidan (1989) and Najm *et al.* (1991) give a full explanation of the HSDM.

Analytical methods

Geosmin was analysed using Solid Phase Microextraction - Gas Chromatography/Mass Spectrometry (SPME-GC/MS).

¹⁴C-labelled MIB was analysed using a liquid scintillation counter as outlined by Gillogly *et al.* (1998a).

5.2.3 Results and discussion

PAC

There are numerous PACs available. Among the many differences between each one, particle size, starting material (commonly, wood, coal or coconut shell), and activation method (steam or chemical) will have the greatest impact on the effectiveness of the PAC to remove undesirable compounds. Cook *et al.*, (2000) found that for short contact times (<60 minutes) chemically-activated, wood-based PACs performed the best, while for longer contact times, a steam-activated, wood-based PAC was the most effective. In this study the effect of particle size was studied.

Particle size

The particle size of activated carbon is an important factor in adsorption kinetics because it influences the distance between the external surface of the particle and adsorption site. The time taken to reach the adsorption site will be lower for a shorter distance travelled (Najm *et al.*, 1990). Batch kinetic tests

OPTIMISATION OF ADSORPTION PROCESSES

carried out by Najm *et al.*, (1990) showed that the rate of 2,4,6 - trichlorophenol (TCP) removal increased as the particle size of the PAC decreased. Improved kinetics of MIB and geosmin removal is important in the water treatment plant (WTP) as contact times are often less than 1 hour. Better kinetics result in a reduction of the minimum PAC dose required hence a saving on PAC costs. The effect of activated carbon particle size on the adsorption kinetics was investigated using Picactif P-1100 carbon with median particle diameters of 10 μm and 22.9 μm . The raw waters used to test this PAC were taken from the inlets to four Adelaide metropolitan WTPs listed in Table 5.1. The advantage of the smaller particle size PAC is shown in Table 5.1 where a reduction in minimum PAC dose of 7.5 mg/L or greater is predicted. A disadvantage is that as the particle size decreases the PAC can be more difficult to handle. The water treatment plant design may also determine the minimum PAC particle size as small particles may break through the sand filters and result in grey water in the distribution system.

Table 5.1 Predicted minimum PAC dose (mg/L) for the reduction of 30 ng/L of MIB or geosmin to 5 ng/L with a contact time of 50 minutes

Raw Water	Median PAC particle diameter				Difference in predicted minimum PAC dose (mg/L)	
	22.9 µm		10 µm			
	geosmin	MIB	geosmin	MIB	geosmin	MIB
Anstey Hill	30	52.5	no result	40	no result	12.5
Happy Valley	27.5	50	20	40	7.5	10
Hope Valley	27.5	50	20	37.5	7.5	12.5
Myponga	40	>50	20	40	20	>10

Water quality

Background natural organic matter (NOM)

NOM competes for adsorption sites with the target compound, reducing the amount adsorbed (Najm *et al.*, 1991). A change in the concentration and character of the background NOM will most likely result in a change in adsorption behaviour. The analysis of inlet water to the WTP over time will indicate if the concentration and character of the NOM is changing. Useful techniques for the characterisation of NOM include - dissolved organic carbon (DOC), UV absorbance at 254 nm, colour, SUVA (ratio of UV absorbance at 254 nm to DOC) and specific colour (colour to DOC ratio). An example of a change in NOM in Hope Valley WTP inlet water is shown in Table 5.2. The concentration of DOC has almost doubled indicating there is more organic material in the water, while SUVA and colour to DOC ratio have decreased indicating that the character of the NOM is less aromatic and conjugated in nature. The influence of a change in NOM character on adsorption was investigated by measuring the removal of MIB and geosmin (Figures 5.2 and 5.3) in the two samples described above.

Figures 5.2 and 5.3 show that the kinetics of geosmin removal were unaffected by the change in NOM while MIB adsorption was reduced. By plotting the minimum PAC dose required for a range of MIB concentrations (Figure 5.3a) the reduction in MIB adsorption can be described in terms of increase in PAC dose. In the example given the amount of PAC needed to reduce an influent concentration of 30 ng/L to 10 ng/L in 50 minutes has increased from 24 to 30 mg/L.

Table 5.2 NOM character parameters for Hope Valley Reservoir water

Sample date	UV Absorbance (254 nm)	DOC (mgL ⁻¹)	SUVA (Lm ⁻¹ mg ⁻¹)	Colour (HU)	Colour/DOC (HUmg ⁻¹ L)
21/04/99	0.150	8.3	1.8	12	1.4
23/07/98	0.106	4.1	2.6	11	2.7

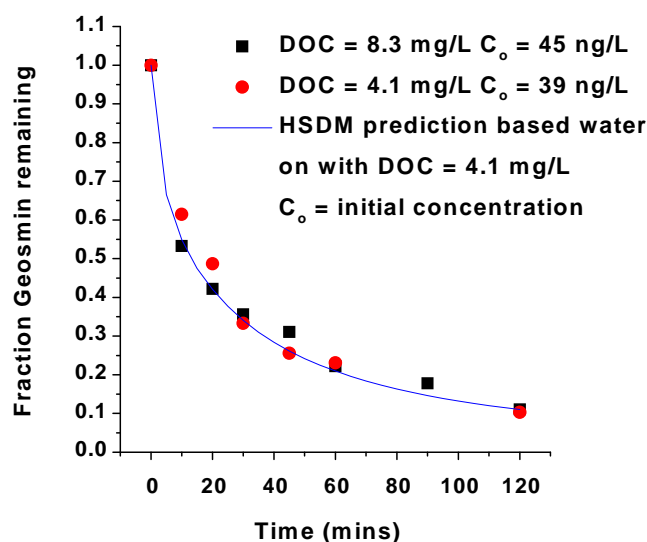


Figure 5.2 Comparison of geosmin removal in the two water samples

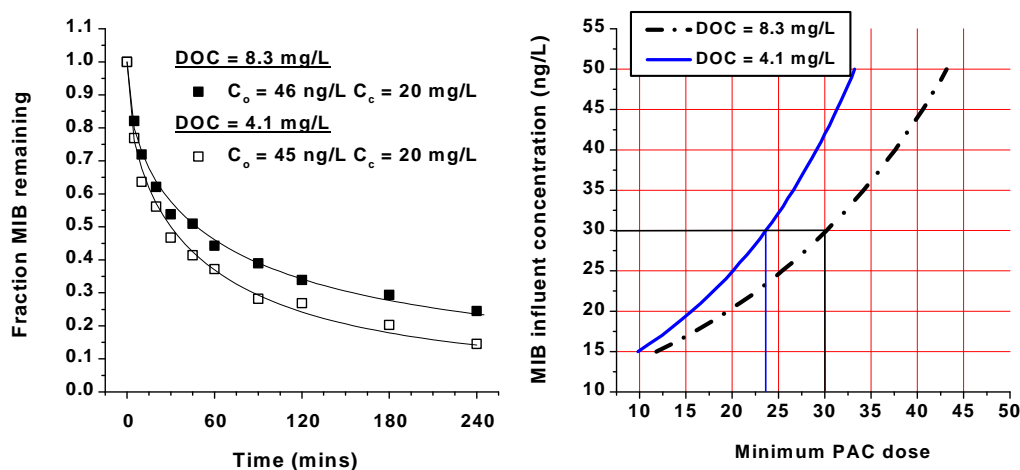


Figure 5.3 Effect of DOC concentration on MIB adsorption and PAC dose required for the reduction of influent MIB concentration to 10 ng/L

Water treatment processes

Coagulation and flocculation with alum

When alum is used as a primary coagulant and dosed with PAC at the rapid mix stage of the water treatment process, the PAC can become incorporated in the floc, reducing its effectiveness. The adsorbate must diffuse through the part of the floc surrounding the PAC particle and then into the PAC

particle itself to be adsorbed (Snoeyink 1990). Snoeyink (1990) describes a study by Gauntlett and Packham (1973) that showed the rate of removal of chlorophenol by PAC was most rapid in the absence of alum, and that PAC added after alum gave a better rate of removal than when added just before alum. However, Najm *et al.*, (1991) reported that the presence of coagulants had little effect on the capacity and rate of TCP removal by PAC in two waters with an initial turbidity of 8 NTU. Cook *et al.*, (1999) found that MIB and geosmin adsorption was lower during coagulation and flocculation when the turbidity was above 26 NTU than in the absence of alum.

The effects of DOC concentration and turbidity on adsorption were investigated by measuring MIB adsorption during alum coagulation in waters with different DOC concentrations and turbidities. Happy Valley reservoir water, raw and diluted 1:1 with Milli-Q® water, was spiked with natural turbidity to achieve a range of turbidities between 10 and 90 NTU. Table 5.3 shows the NOM characteristics of the undiluted and diluted waters. Figure 5.4 shows that in the undiluted water (high DOC) a change in turbidity had no effect on MIB removal as the amount of MIB could accurately be predicted with the HSDM. In the diluted water, as the turbidity increased from 17.7 to 54.3 NTU the amount of MIB removed decreased. As the turbidity increased the accuracy of HSDM predictions decreased. A decrease in adsorption was not found for a turbidity of 85 NTU in this water because the alum dose used (50 mg/L) was too low. A higher dose should have been used to effectively remove turbidity. The alum dose was determined from jar tests with this water but with a turbidity of 14.4 NTU. At the highest turbidity with the alum dose used, there would be insufficient floc to effectively bind up the PAC, hence MIB removal was as predicted by the HSDM. These results indicate that the greatest effect of coagulation on taste and odour adsorption will be encountered in waters with both a high turbidity (> 26 NTU) and a DOC less than 4.6 mg/L.

Table 5.3 Character of diluted and undiluted waters

Sample	UV	DOC	SUVA	Colour	Colour/
	Absorbance	(mgL ⁻¹)	(Lm ⁻¹ mg ⁻¹)	(HU)	DOC
	(254 nm)				(HUmg ⁻¹ L)
not diluted	0.266	8.6	3.1	37	4.3
diluted	0.136	4.5	3	19	4.2

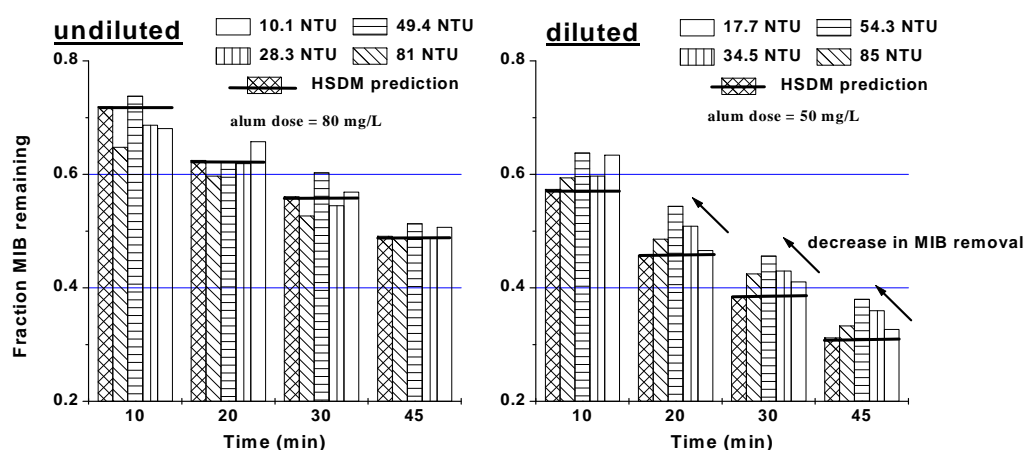


Figure 5.4 MIB removal as a function of time, DOC concentration and turbidity

Chlorination

The character of NOM plays an important role in adsorption. Any treatment that can change its nature has the potential to affect MIB and geosmin removal. The equilibrium capacity (amount adsorbed after 3 days) for MIB was lower in Anstey Hill WTP influent water (receiving chlorinated River Murray water (DOC = 4.2 mg/L)) than in Myponga WTP influent water (DOC = 10.0 mg/L). Batch kinetic tests were completed to determine if chlorination of the source water was affecting MIB adsorption. In these tests River Murray water was chlorinated with 8 mg/L of chlorine and allowed to react for 5 days. A combined chlorine residual of 0.6 mg/L was present prior to the experiment. Previous experiments indicate that this amount of chlorine will not effect MIB adsorption for the dose of PAC used. The kinetic curves (Figure 5.5) indicate that the presence of chlorination by-products reduce the rate of MIB adsorption. Similar experiments with Myponga WTP influent (Figure 5.5), Hope Valley WTP influent, and Lake Michigan water (Gilligly *et al.*, 1998b) showed no difference in MIB removal due to chlorination by-products. The reduction in Anstey Hill WTP influent water and not in the other waters may be due to the difference in the character of the NOM present in each of the waters. The character of the NOM in Anstey Hill WTP influent water was such that the reaction with chlorine forms compounds that compete more strongly for adsorption sites than the original NOM. In contrast, the NOM in the other waters forms chlorination by-products that do not compete any more strongly for adsorption sites than the original NOM. The presence of chlorine (a residual at point of dosing) was found to reduce MIB and geosmin adsorption onto PAC by Lalezary-Craig *et al.*, (1988); and Gilligly *et al.* (1998b). Gilligly *et al.*, (1998b) showed that the extent of the effect of chlorine depends on the amount of chlorine reacted per unit mass of PAC.

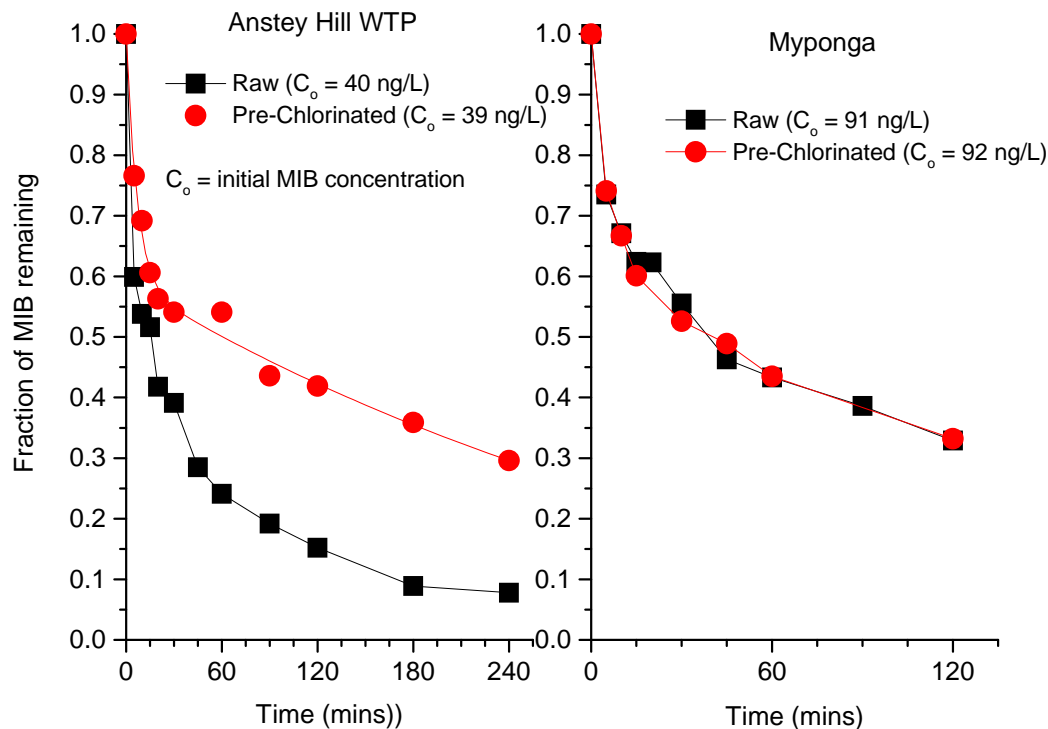


Figure 5.5 Effect of pre-chlorination on MIB removal

5.2.4 Conclusions

A summary of the effect the above factors have on PAC dose is shown in Table 5.4. At this stage of our research broad recommendations are suggested as there is not enough data to be able to specify for example, a PAC dose increase for a particular increase in DOC. Future work will involve determining whether this type of prediction can be made for specific water quality.

Table 5.4 Guide as to how PAC dose may change with a change in PAC particle size, water quality and water treatment process

Parameter	Effect on PAC dose to remove MIB and geosmin
Particle size	A decrease in particle size will decrease required PAC dose for both MIB and geosmin.
DOC	A DOC increase will generally lead to an increase in required PAC dose for MIB and geosmin.
Coagulation and flocculation with alum	a) When PAC is applied at least 30 minutes prior to alum - no effect. b) When PAC is applied with alum an increased dose will be required at turbidities >26 NTU when the DOC ≤8 mg/L. At higher DOC, and lower turbidity, coagulant should not have an effect on PAC dose.
Chlorination	If chlorine is present an increased dose may be required depending on PAC dose and chlorine residual. If no residual, most likely no effect on dose.

5.3 TASTES AND ODOURS AND ALGAL TOXINS, WHICH PAC IS BEST?

5.3.1 Introduction

Cyanobacterial blooms in waters used as a source to produce potable water are of concern as they can produce some compounds that are aesthetically unpleasant and others that can be toxic if consumed. Musty-earthly taste and odours can be caused by cyanobacterial metabolites such as 2-methylisoborneol (MIB) and geosmin at low ng/L levels.

Two types of algal toxins of concern are the hepatotoxic microcystins and the neurotoxic saxitoxins. In Australia the main source of microcystins in drinking water sources is the cyanobacterium *Microcystis aeruginosa*. The microcystins have been found to cause liver damage and promote tumours in mice. More than 60 different hepatotoxic microcystins have been characterised (Sivonen and Jones (1999)). Studies have concentrated on the most toxic hepatotoxin, microcystin-LR. A provisional guideline value of 1 µg/L of microcystin-LR has been adopted by the World Health Organisation.

Saxitoxins (or paralytic shellfish poisons) are commonly produced by *Anabaena circinalis* in Australian waters (Humpage *et al.*, 1994; Negri *et al.*, 1997). This group of compounds is well known for causing illness and sometimes death in people eating contaminated marine shellfish. No illness similar to paralytic shellfish poisoning has been reported in humans from the consumption of drinking water containing saxitoxins (Fitzgerald *et al.* 1999). Saxitoxins can be divided into three groups of variants according to their chemical structure, which in turn affects their toxicity. Due to the different toxicities and concentrations of saxitoxins the extent of PAC adsorption should be examined in terms of total toxicity removal. This can be accomplished by converting toxin concentration to saxitoxin equivalent (STX-eq) concentration.

Powdered activated carbon (PAC) is often considered as a treatment option for removing tastes and odours and cyanotoxins as it can be very effective and easy to apply. Newcombe and Drikas (1995) tested ten PACs for the adsorption of MIB and geosmin. They rated the PACs in order of effectiveness for the removal of the two compounds. They found that at equilibrium, the ranking of the carbons was the same for the two compounds; i.e., the best carbon for MIB removal was also the best for geosmin removal. The authors made the assumption that the kinetics of adsorption of the two compounds would also be similar, and they tested the ten PACs at shorter contact times for the adsorption of MIB only. They found that the ratings changed at shorter contact times, and the three PACs with a high volume of mesopores (transport pores) rated higher at a shorter contact time of 1.25 hours than they did with a contact time of three days. The authors assumed that the same rating would apply for geosmin adsorption. However, recent work by Bailey *et al.* (1999) indicated that the kinetics of adsorption of geosmin may be quite different from that of MIB, and that the most effective carbon for MIB removal under water treatment plant conditions is not necessarily also the best for geosmin removal.

PAC adsorption studies of microcystin-LR by Donati *et al.* (1994) and Schumann *et al.* (1997) showed that the amount of microcystin-LR adsorbed at equilibrium onto PAC could be directly related to the volume of mesopores (1 nm<w<50 nm). The mesoporous wood-based PACs displayed superior microcystin-LR adsorption efficiency at equilibrium and at short contact times expected in a water treatment plant.

Little research has focused on saxitoxin adsorption with PAC. Bailey *et al.* (1999) report greater than 90% removal of saxitoxin with four wood and coal based PACs. However, this was for the removal of one saxitoxin analogue (STX). To assess the capability of PAC to remove saxitoxins, the removal of the various analogues at concentrations expected in a natural bloom needs to be examined.

So far, there is no “universal” PAC capable of removing all of these problem compounds to the desired levels. Some activated carbons may be more suitable for the removal of tastes and odours, whereas others are superior for toxin removal. This is partly due to the difference in the structure, functionality and molecular weight of the compounds in question. MIB and geosmin are relatively small molecular weight compounds of 168 and 182 respectively, compared with the saxitoxins and the microcystins that have molecular weights between 300-500 and 909-1115 respectively. The aim of this work was to determine the best activated carbon for the adsorption of MIB, geosmin, and the saxitoxins, and to compare these results with previous work on microcystin-LR.

5.3.2 Materials and methods

Powdered activated carbon

Six commercially-available activated carbons were used in this study. Before use each PAC was dried at 105°C for at least 24 hours and allowed to cool in an airtight desiccator. Table 5.5 shows the characteristics of the PACs.

Carbon characteristics

Pore size distribution was determined as outlined in Donati *et al.* (1993).

Table 5.5 Physical characteristics of PACs

CARBON	Pore Volume (cm ³ .g ⁻¹)				Starting Material	Activation Method
	Surface Area m ² .g ⁻¹	primary micropores w<0.8nm	secondary micropores 0.8<w<2nm	mesopores 2<w<50nm		
HP	2183	0.57	0.54	0.51	wood	chemical
CA-10	1491	0.39	0.47	0.41	wood	chemical
SA-30	1077	0.35	0.13	0.09	wood	steam
*F-400	1047	0.34	0.12	0.09	coal	steam
P-1100	1241	0.38	0.18	0.05	coconut	steam
PCO	987	0.31	0.13	0.03	coconut	steam

* GAC ground to a PAC

w refers to pore width

Analysis

Geosmin was analysed using solid phase microextraction-gas chromatography/mass spectrometry (SPME - GC/MS).

¹⁴C-labelled MIB was analysed using a liquid scintillation counter.

Saxitoxins were quantified as outlined by Rositano *et al.* (1998)

Equilibrium adsorption

Raw water was added to clean, dry Pyrex bottles to a level just below the top to obtain minimum headspace. The required amount of MIB or geosmin was added and the solution shaken and then allowed to stand. After several minutes PAC was added and the bottle sealed and agitated for 3 days.

Kinetics

Dry carbon was weighed out 24 hours prior to use and pre-wetted with 3-5 mL of deionised water. MIB, geosmin or saxitoxins were added to a constantly stirred raw water sample. After 15 minutes of mixing, a sample was taken to determine the initial concentration. PAC was added and samples were taken at predetermined intervals. Samples were pressure filtered through 0.45 µm disposable filters to remove the PAC.

5.3.3 Results and discussion

MIB and geosmin

Six PACs were tested for equilibrium removal of MIB. Four of those carbons were also tested for adsorption of geosmin (Figure 5.6). The conditions for these experiments were PAC dose = 4 mg/L, natural water, Myponga Reservoir water, DOC = 10.7 mg/L. As expected, the equilibrium adsorption of the two compounds showed similar trends.

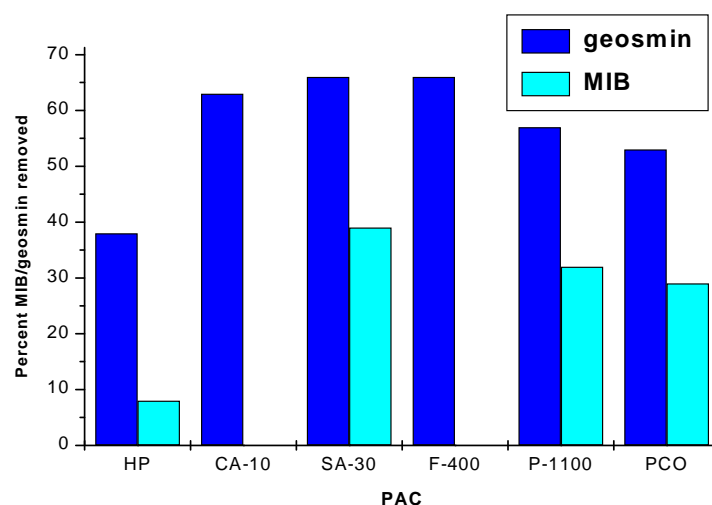


Figure 5.6 Equilibrium adsorption of MIB and geosmin for each PAC

Figure 5.7 shows the percentage removal of the two compounds at contact times that could reasonably be applied in most water treatment plants. The figure shows that the kinetics of adsorption for the two compounds is indeed different. For example at a contact time of 60 minutes HP is not effective for MIB while it is the best for geosmin removal. CA-10 was also effective for geosmin removal. The mesopore volume of HP is 0.51 cm³/g and 0.41 cm³/g for CA-10. The higher volume of transport pores allows quicker access to adsorption sites, hence better adsorption at shorter contact times. These results indicate that mesopore volume may be an important factor concerning the successful removal of geosmin. Further experimentation with other mesoporous PACs is required for validation of this proposition. These results along with those reported by Donati *et al.* (1994) for microcystin-LR adsorption indicate that the same PAC could be applied to remove both geosmin and microcystin-LR. However, this PAC would not be considered the best one for the removal of MIB.

Table 5.6 shows how the choice of PAC can change when contact time and the compound that is causing taste and odour problems are considered. For example, at a contact time of 60 minutes, HP would be the PAC of choice for the removal of geosmin, while for contact times above 60 minutes CA-10 would be chosen. Similarly for MIB removal the best PAC changes from CA-10 to SA-30 for contact times below and above 60 minutes. When choosing the appropriate PAC, selection should be based on the most likely operating conditions at the water treatment plant (contact time) and the taste and odour compound(s) of importance.

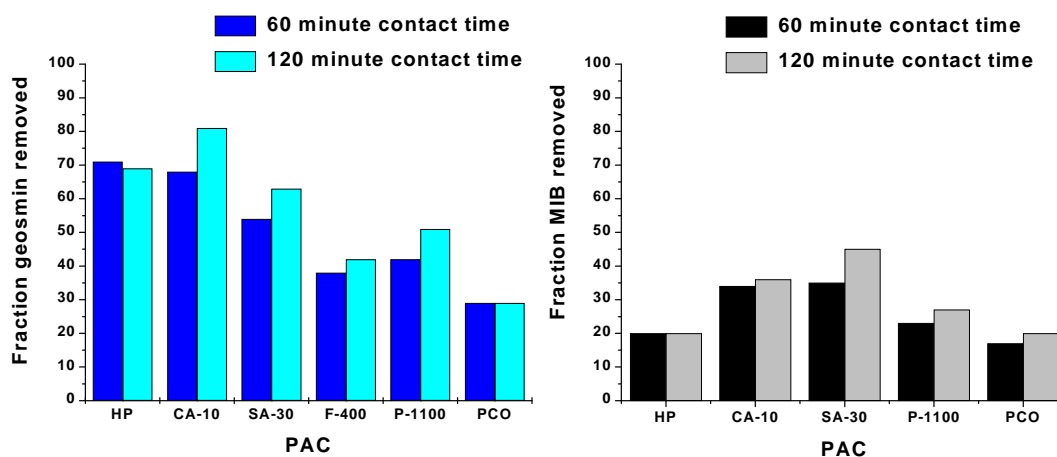


Figure 5.7 Comparison of MIB and geosmin removal with 15 mg/L of each PAC

Table 5.6 Choice of PAC as a function of contact time and taste and odour compound

Contact time (min)	Compound(s) causing taste and odour problem		
	geosmin	MIB	MIB and geosmin
60	HP	CA-10/SA-30	CA-10
120	CA-10	SA-30	SA-30

Saxitoxins

The results reported here are for saxitoxins that would most likely be found in a bloom of toxic *Anabaena circinalis*. The saxitoxin profile (Figure 5.8) was very similar to those reported by Negri *et al.* (1997) and Velzeboer *et al.* (1998).

Figure 5.8 shows some interesting trends for saxitoxin adsorption. These trends can be summarised:-

- (i) Doses higher than 30 mg/L PAC and/or longer contact times are required to completely remove all saxitoxins.
- (ii) Removal efficiency varies among the PACs tested.
- (iii) The different saxitoxin analogues show various removal efficiencies. The general trend of saxitoxin removal appears to be GTX4 > STX > GTX2 \cong GTX 3 > C1 \cong C2.

OPTIMISATION OF ADSORPTION PROCESSES

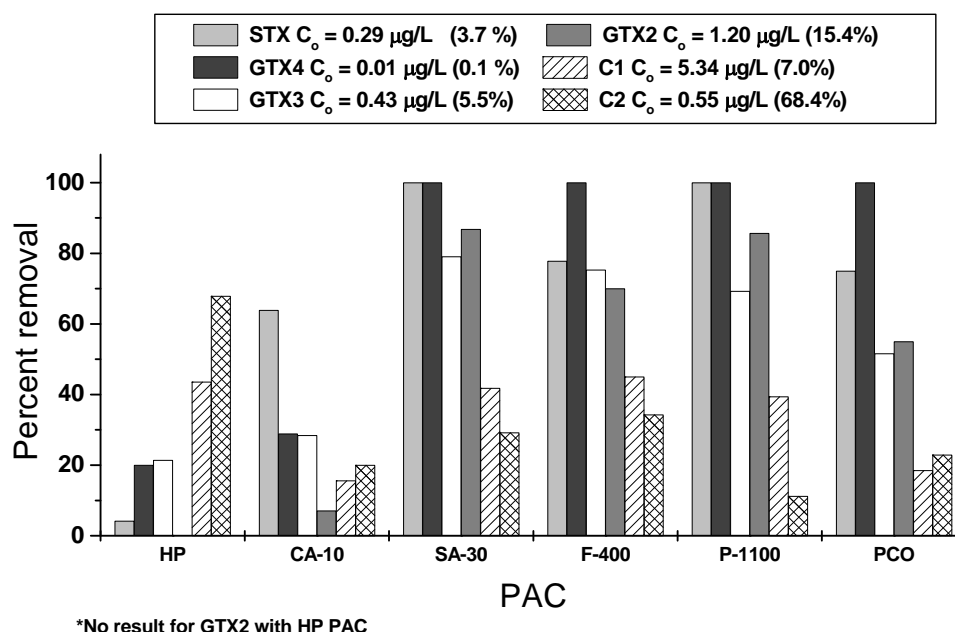


Figure 5.8 Saxitoxin removal from Hope Valley WTP inlet water (DOC = 5.7 mg/L) after treatment with 30 mg/L of PAC and contact time of 180 minutes. Total saxitoxin concentration = 7.8 $\mu\text{g/L}$, concentration and the relative abundance of individual toxins is shown above.

Figure 5.9 shows that SA-30, P-1100, and F-400 were the most effective PACs for reducing toxicity in terms of STX-eq. Treatment with SA-30, P-1100, and F-400 reduced the toxin concentration expressed as STX-eq to 0.17, 0.22 and 0.31 $\mu\text{g/L}$ respectively. These values are significantly lower than the proposed 3 μg STX-eq/L health alert level (Fitzgerald *et al.* 1999). At a contact time of 60 minutes SA-30, P-1100, and F-400 PACs removed 66, 65, and 73% of toxin as STX-eq respectively. These results show that a significant amount of saxitoxin, or, more importantly, saxitoxin equivalents, can be removed at a contact time relevant to a water treatment plant with a reasonable dose of PAC.

The selection of a PAC for saxitoxin adsorption should be based on the removal of the saxitoxin analogues that are most likely to be present and the desired reduction in terms of STX-eq. As toxin profiles Australia-wide have not been found to vary significantly, the best method to assess a PAC would be to spike test waters with extracted toxins from bloom material. Examining the adsorption of one saxitoxin analogue such as STX (the most toxic) may be risky as it is a minor constituent of all the toxins present and successful removal of this compound may not mean a PAC will successfully remove the dominant C-toxins and gonyautoxins. The saxitoxin removal here could not be related to the pore size distribution of the PACs shown in Table 5.5.

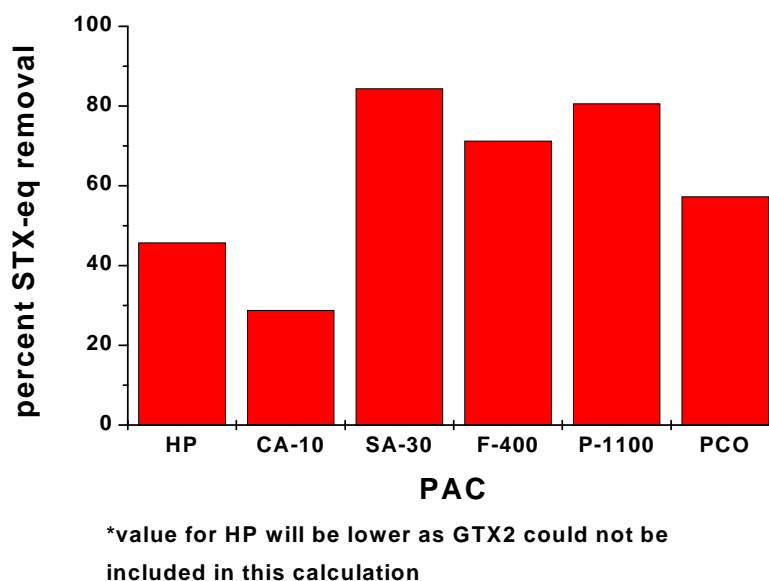


Figure 5.9 Saxitoxin equivalent removal with 30 mg/L of each PAC after 180 minutes. Initial STX eq = 1.1 µg/L

5.3.4 Summary and conclusions

For MIB and geosmin removal the best activated carbon depended on the contact time. For geosmin adsorption the wood-based PACs HP and CA-10 with a higher volume of transport pores allowing quicker access to adsorption sites, performed very well at short contact times. These types of activated carbons were found by Donati *et al.* (1993) to be the most effective for microcystin LR removal. At longer contact times, several other carbons were superior. At very long contact times, the ranking of the activated carbons for geosmin and MIB removal was similar; i.e., the best carbon for MIB was also the best for geosmin. However, at shorter contact times of less than two hours, the ranking was found to be different for the two compounds. None of the PACs completely removed all of the saxitoxins, although some performed better than others. The most toxic, STX and GTX 2, 3 and 4 analogues were more easily removed than the less toxic C-toxins (C1 and C2). Higher PAC doses or longer contact time would be required to completely remove all the saxitoxins. Based on reported levels of saxitoxins found in natural blooms PAC may be a viable option for the treatment of contaminated waters at moderate doses (eg 30 mg/L) provided there is sufficient contact time. The carbons displaying the best removal for these toxins were also the most effective for MIB removal.

In summary, none of the PACs was the best at removing all the compounds tested. At contact times of 2 hours or less, it was found that one activated carbon could be applied to remove both geosmin and microcystin-LR while that activated carbon would not be considered the optimum for the removal of MIB and saxitoxins.

5.4 INFLUENCES ON THE REMOVAL OF TASTES AND ODOURS BY PAC

5.4.1 Introduction

2-methylisoborneol (MIB) and geosmin are earthy/musty odour compounds produced as secondary metabolites by some cyanobacteria and actinomycetes. They can cause significant problems for drinking water suppliers as they are perceived by most consumers as an unpleasant odour and taste in water at very low concentrations (around 10 ngL⁻¹). As the compounds have an aliphatic structure not readily oxidised by the weaker oxidants such as chlorine and potassium permanganate (Lalezary *et al.* 1986), ozone as an oxidative treatment option has received the most attention in the literature. As with most micro-contaminants, the destruction of MIB and geosmin by ozone is strongly dependent

on water quality parameters such as NOM concentration and character, alkalinity, pH and temperature (Morioka *et al.* 1993, Ho *et al.* 2002). In general, studies indicate 100% destruction by ozone cannot be expected under conditions commonly utilised in water treatment. Ozone can be used in combination with granular activated carbon (GAC); however some studies have shown that the lifetime of GAC for MIB and geosmin would be relatively short when adsorption is the predominant mechanism of removal (Gilligly *et al.* 1999, Ridal *et al.* 2001). Powdered activated carbon (PAC) can be very effective, and is often the only mode of application of activated carbon available to water authorities for the removal of taste and odour compounds.

The advantages are that PAC:

- Can be applied only when required
- Is relatively inexpensive
- Can be retro-fitted to existing plants

The major disadvantage of PAC application is that prolonged use may lead to significant costs, and this is exacerbated by the lack of knowledge regarding correct doses for the production of water of the desired quality. Dosing at levels greater than necessary can result in very high costs to the water supplier and, conversely, under-dosing leads to consumer complaints and is clearly an inefficient use of the adsorbent. Recently Cook *et al.* (2001) reported the application of the homogenous surface diffusion adsorption model (HSDM) for predicting activated carbon doses required at four water treatment plants supplying the city of Adelaide, Australia. The HSDM has been successfully applied for the prediction of the kinetics of adsorption of a range of compounds onto activated carbon (Knappe, 1998; Graham *et al.* 2000). It has also been found to be an appropriate kinetics model for the adsorption of MIB and geosmin (Gilligly *et al.*, 1998a; Huang *et al.*, 1996). The model predicts the diffusion of a molecule from the external surface of the adsorbent particle, along pore surfaces, to the adsorption site. The other three mass transfer steps taking place during adsorption, transfer from bulk liquid to surface film surrounding the particle, transfer through this surface film, and the adsorption step, are not considered rate limiting in this model. The PAC particles are considered to be spherical and of homogenous structure, and Fick's first law of diffusion is applied for the calculation of the adsorbent surface concentration as a function of the radial position within the particle. The change in bulk liquid phase concentration with time is then calculated using a mathematical model appropriate for the configuration of the system, for example, batch, plug flow or completely-stirred tank reactors (Knappe, 1996). A derivation of the model and description of its use can be found in Traegner and Suidan (1989). For the application to the prediction of activated carbon doses, equilibrium and kinetic experimental results were obtained in each water and a "search" computer program, utilising the HSDM, was used to determine the diffusion co-efficient which best fitted the data. Other input data for this program included the PAC particle diameter and density. The diffusion coefficient was then used to predict the removal of the compounds at a range of carbon doses, contact times and initial concentrations. These predictions are specific to activated carbon and water type.

Following from the study of Cook *et al.* (2001), this work highlights the factors influencing the removal of geosmin and MIB using PAC, and in particular, reports the circumstances where increased dosing may be required to achieve the desired result.

5.4.2 Materials and methods

Materials

¹⁴C-labelled 2-methylisoborneol (¹⁴C-MIB) was obtained from American Radiolabeled Chemicals. The solution was found to be >99% pure by GC/MS analysis. Geosmin (99.9%) was supplied by Wako Pure Chemical Industries Ltd. All other chemical used were analytical grade.

Analysis

Geosmin was analysed using solid phase microextraction - gas chromatography/mass spectrometry (SPME - GC/MS). Detection limit for geosmin using this method was 2 ngL⁻¹.

Radiolabelled MIB was analysed using a scintillation count method first reported by Gilligly *et al.* (1998a) and described in detail in Cook *et al.* (2001). This method was found to be reproducible to ± 2 ngL⁻¹.

NOM analysis and characterisation

Samples were filtered through a 0.45 µm membrane. Dissolved organic carbon (DOC) was measured using a Seivers 820 Total Organic Carbon Analyser. UV absorbance at 254 nm was obtained using a GBC UV/Vis 918 spectrophotometer. The specific UV absorbance (SUVA) was calculated using the equation: $SUVA = 100 * (abs_{254} / DOC)$. The molecular weight distributions were determined using high performance size exclusion chromatography analysis based on the method used by Chin *et al.* (1994). The column (Shodex Protein KW-802.5, molecular weight range 0.1K-50K, Waters Australia) was calibrated using polystyrene sulphonates of molecular weight 35K, 18K, 8K, 4.6K and acetone. These compounds are considered to best represent the structure and conformation of NOM in solution. Ultraviolet absorbance at 260 nm was used for detection.

Experimental methods*Equilibrium isotherms*

Reservoir water was added to clean, dry pyrex bottles to a level allowing minimum headspace. MIB or geosmin was added followed by PAC. The bottle was sealed and agitated for 3-5 days. MIB and geosmin concentrations were varied between 20 and 300 ngL⁻¹, activated carbon doses were varied between 2.5 and 25 mgL⁻¹.

Kinetics

MIB or geosmin was added to a constantly stirred raw water sample. After 15 minutes of mixing a sample was taken to determine the initial concentration. PAC (pre-wetted overnight) was added, with samples taken at predetermined intervals over the following four hours. Samples were pressure filtered through 0.45 µm disposable filters to remove the PAC.

Jar tests

The jar test conditions replicated the conditions at the particular water treatment plant at the time the water samples were taken. Details are given in Cook *et al.* (2001)

Chlorination

A stock chlorine solution was prepared by dissolving chlorine gas into Milli-Q water. Water samples were chlorinated by adding an amount of chlorine water sufficient to achieve the desired dose. Reaction conditions (chlorine dose and reaction time) were set either to simulate chlorination in the distribution system relevant to the water sample, or to significantly change the nature of the NOM in the water. Chlorine concentration was determined by titration with DPD/FAS (APHA 1998).

5.4.3 Results and discussion**What PAC is best?**

The most important factor influencing the removal of MIB and geosmin is the type of activated carbon used. The adsorption of MIB and geosmin has been shown to vary between activated carbons with chemically-activated wood-based carbons usually showing inferior adsorption at equilibrium (Newcombe *et al.* 1997; Chen *et al.* 1997). Pendleton *et al.* (1997), in their study of MIB adsorption onto five activated carbons suggested this was due to the high oxygen content of wood-based carbons, producing a more hydrophilic surface and resulting in a lower adsorption energy for MIB. More recently, Newcombe (2001) showed that, for a wide range of activated carbons the equilibrium adsorption of both MIB and geosmin can be related to the volume of micropores between 1.0 and 1.2 nm width. Adsorption isotherms of MIB onto four activated carbons are shown in Figure 5.10. Raw materials and activation conditions of the carbons are given in the figure. Starting concentration of MIB was 100 ngL⁻¹, and the experiments were undertaken in Myponga Reservoir water, DOC= 6 mgL⁻¹.

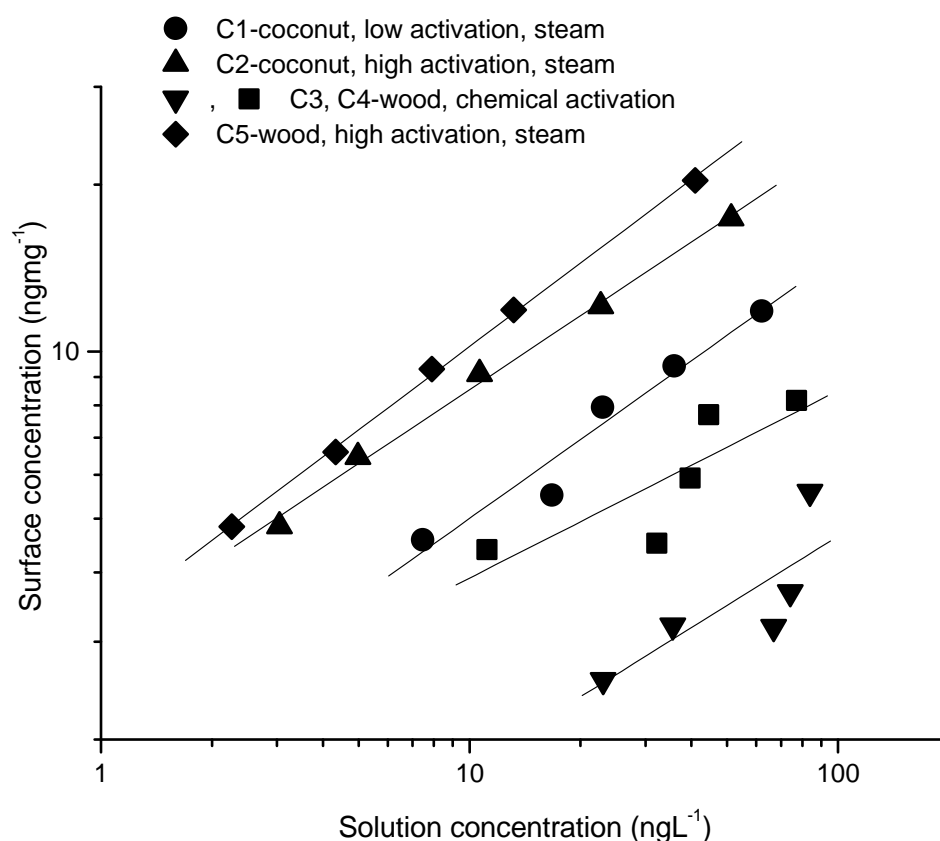


Figure 5.10 Adsorption isotherms of MIB onto five activated carbons

In terms of the application of PAC for the removal of MIB and geosmin, the more important factor is the removal at contact times of two hours or less. The kinetics of adsorption of these compounds is dependent on both the equilibrium capacity of the carbon, and the volume of larger, transport pores, which allow rapid access to adsorption sites. Figure 5.11 shows the fraction of MIB remaining vs. time, for five activated carbons. Starting concentration of MIB was 100 ngL^{-1} , carbon dose was 20 mgL^{-1} , water was Myponga Reservoir water, as above. The variation of the fraction remaining with time will depend on the carbon dose, but is independent of the initial MIB concentration at both equilibrium, and shorter contact times. This has been shown to be applicable to micro-contaminants in the presence of NOM by a number of authors for pesticides (Knappe *et al.* 1998) and MIB and geosmin (Graham *et al.* 2000, Cook *et al.* 2001).

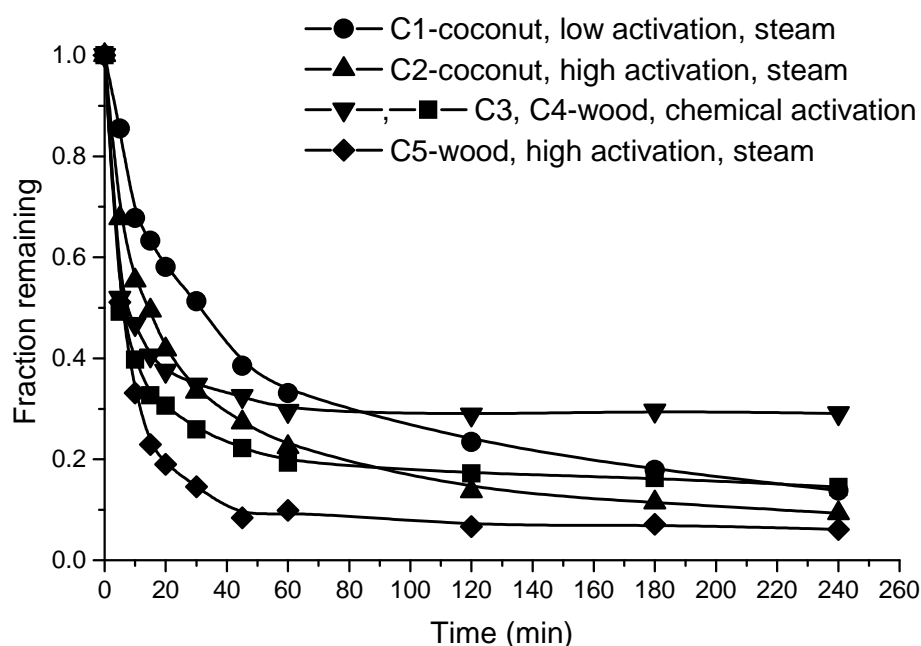


Figure 5.11 Fraction of MIB remaining vs. contact time for 5 activated carbons. Starting concentration of MIB, 100 ngL^{-1} , carbon dose, 20 mgL^{-1}

At 4 hours contact time, the trend in adsorption capacity of these carbons is: $C5 > C2 > C1 > C4 > C3$, the same as seen at equilibrium (Figure 5.10). At shorter contact times an interesting feature of the results is the unfavourable kinetics of the coconut carbons, which have relatively high equilibrium capacity, compared with the very favourable kinetics of the chemically-activated wood-based carbons, with low equilibrium capacity. These results indicate that the most efficient activated carbon for the removal of MIB in a water treatment plant will depend strongly on the contact time available for adsorption, with wood-based carbons favoured at very short contact times. These effects are readily explained by the different pore structures of the carbons. Generally, coconut carbons have a very narrow pore size distribution, possessing negligible macro and mesopore volume (i.e. pores $>2 \text{ nm}$ width), while the wood carbons have a high volume of larger pores, or transport pores, favouring rapid diffusion to adsorption sites. Carbon C5 has a high volume of pores in the range of $1.0\text{-}1.2 \text{ nm}$, as well as some pores in the larger range (Newcombe *et al.* 2001).

Figure 5.12 a) shows the percent of MIB and geosmin removed at equilibrium for four of the five carbons. The carbon dose was 4 mgL^{-1} . Geosmin adsorbs to a greater extent than MIB, as has been noted previously (Lalezary-Craig *et al.* 1988). Geosmin has a slightly lower solubility than MIB, and is flatter in structure, both of which can be expected to have an influence on the adsorption. Apart from the difference in the overall adsorption, the trend for the activated carbons is the same for the two compounds.

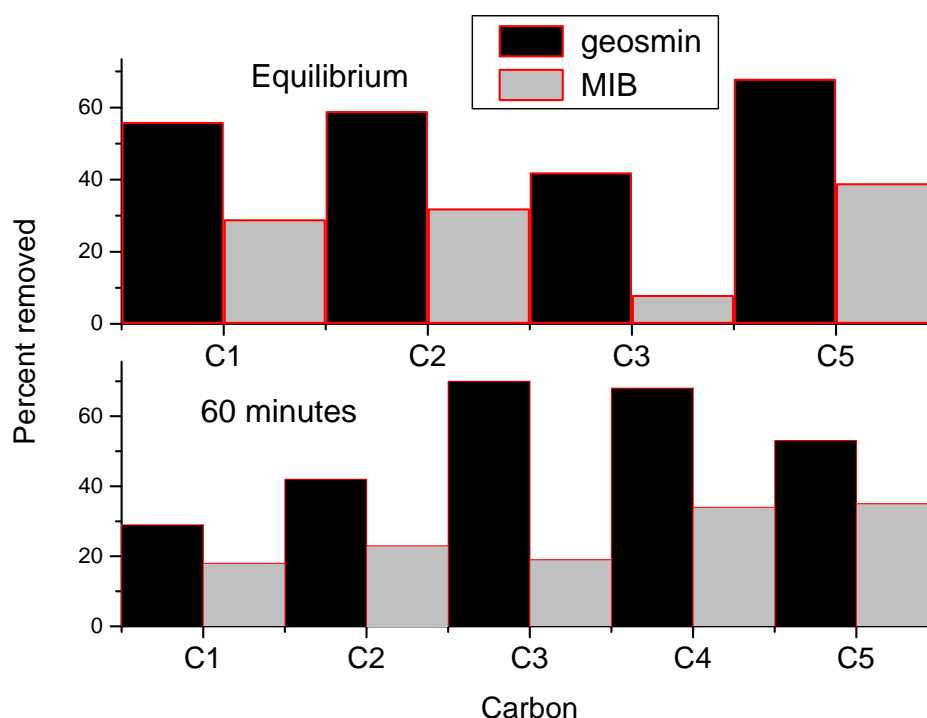


Figure 5.12 Percent MIB and geosmin removed at equilibrium, 4 mgL⁻¹ carbon dose, a), and 60 minutes contact, 9 mgL⁻¹ carbon dose, b). Starting concentration of both compounds, 100 ngL⁻¹

In contrast, at 60 minutes the trends are different for the two compounds (Figure 5.12b). For geosmin, the two wood-based chemically-activated carbons, C3 and C4, are far superior to the other carbons at 60 minutes contact time, whereas for MIB the differences are smaller. This indicates that the advantage to the kinetics of adsorption provided by the transport pores of the chemically-activated wood carbons was more pronounced for geosmin. This supports the finding by Cook *et al.* (2001) that the kinetics of adsorption of geosmin were slower than MIB on a coconut carbon, with diffusion coefficients for MIB in four reservoir waters an order of magnitude higher than those for geosmin. This result also suggests that chemically activated wood carbons containing a large volume of transport pores may be the carbons of choice for geosmin, whereas for MIB the best carbon will be dependent on the contact time available.

It should be noted that desorption of MIB from chemically-activated wood carbons has been reported (Newcombe & Drikas 1994; Hepplewhite 2000; Newcombe *et al.* 2001) and may affect treated water quality, depending on the residence time of sludge in sedimentation basins. Desorption of geosmin has not been investigated.

PAC particle size also plays an important role in the kinetics of adsorption of MIB and geosmin. A smaller particle size results in shorter distances for the compound to travel before reaching adsorption sites, and a higher external surface area for the adsorbate to access the internal pore structure of the carbon, and consequently improved kinetics would be expected. For example Figure 5.13 illustrates the difference in the doses required for the reduction of geosmin concentration to 10 ngL⁻¹ in 60 minutes for a range of influent concentrations. The doses were calculated using the HSDM as described in the introduction.

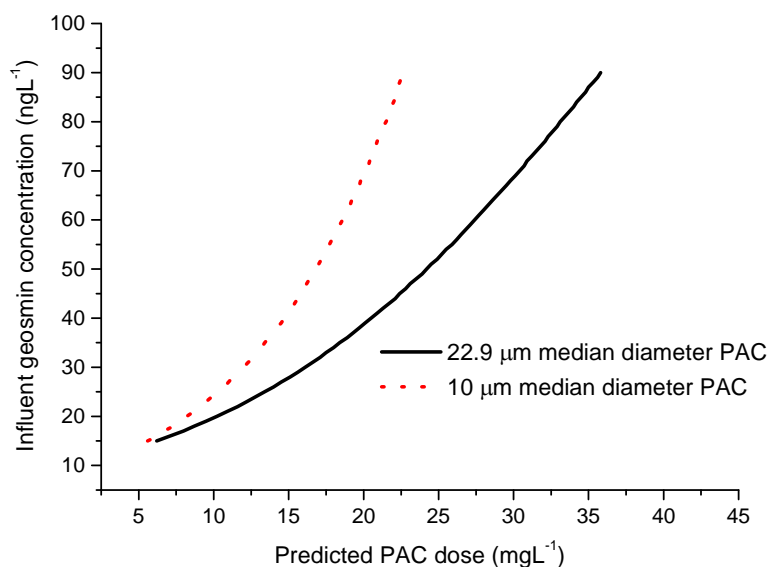


Figure 5.13 Predicted PAC doses required to reduce geosmin concentration by 50% for two PAC particle sizes

Clearly there is a particle size limit below which ease of handling of the PAC becomes an issue. A very small particle size may also result in removal difficulties using conventional methods, and possible breakthrough into the distribution system. The 10 µm median particle size has proven to be optimum for the water treatment plants supplying Adelaide, using both conventional and dissolved air flotation technology.

PAC dose predictions

Once the most appropriate activated carbon has been chosen for the water treatment plant conditions, the determination of appropriate dosing criteria is the most important aspect of PAC application. The application of the correct dose for achieving the desired water quality is the aim of the water treatment operator.

The homogenous surface diffusion computer model (HSDM) has been applied to PAC adsorption in inlet waters to four water treatment plants around Adelaide, and has been shown, under most circumstances, to predict the level of removal of geosmin and MIB obtained in laboratory jar tests (Cook *et al.* 2001). The conditions under which the model is less successful are described in the following sections. Figure 5.14 shows experimental data for the removal of MIB at three activated carbon doses (activated carbon C2) in Hope Valley Reservoir water (DOC=5 mgL⁻¹). Curve (a) data was used to determine the parameters required for the application of the model, along with equilibrium adsorption data (not shown). Those parameters were applied to predict the removals at two other carbon doses (Curves b and c). The figures show that the predictions were excellent. Similar experiments were undertaken in inlet water from the other three plants, and from this information, PAC dosing tables were constructed for the water treatment plants. These tables are now used for the determination of PAC application rates. Investigation of historical data showed that the predictions can be directly related to the actual removals of geosmin, with an R^2 value of 0.74, indicating that the application of the dose tables should result in correct PAC dosing regimes (Cook *et al.* 2000).

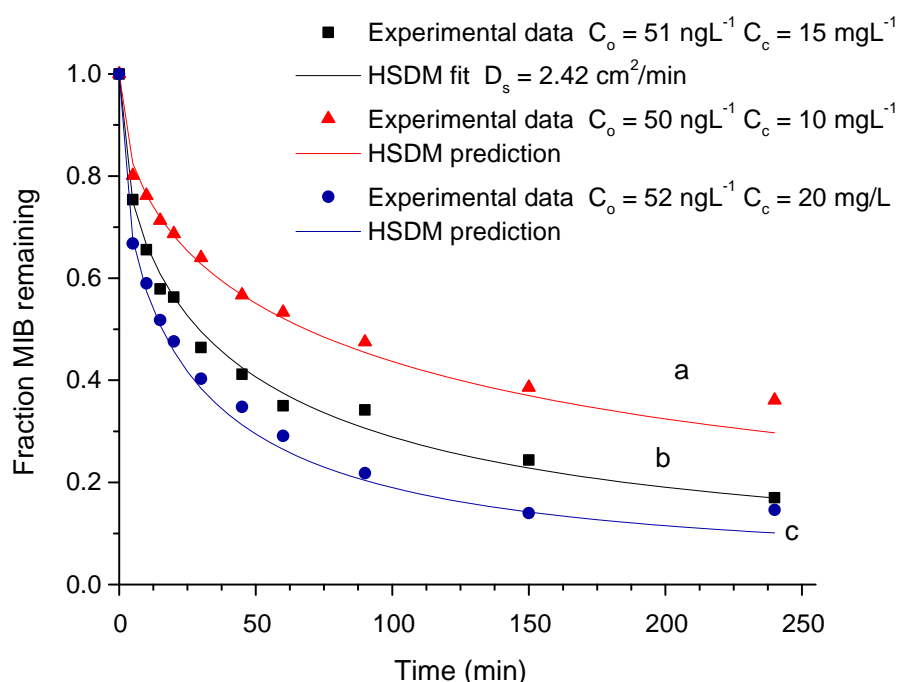


Figure 5.14 Experimental data and HSDM predictions for MIB removal

Factors influencing PAC doses for MIB and geosmin removal

Water quality effects

Once the appropriate PAC doses have been determined for a particular water source, the question to be answered is "How will changes in raw water quality affect PAC doses?"

Alkalinity, pH, ionic strength. Alkalinity, ionic strength and pH do not appear to affect the adsorption of MIB and geosmin over the ranges generally encountered in drinking water treatment. Extreme pH adjustment results in a decrease in adsorption at pH 4 and below. Although Graham *et al.* (2000) suggested this effect was due to enhanced competition with natural organic material (NOM) at lower pH, the effect was also seen in the absence of competing substances (Newcombe, unpublished data). The cause of this reduced adsorption is not known, however it will not be encountered under normal plant operating conditions.

Dissolved organic carbon concentration and character. Dissolved organic carbon (DOC) concentration and character have both been reported to strongly affect the adsorption of MIB (Newcombe *et al.* 1997; Cook *et al.* 2001; Newcombe *et al.* 2001). Figure 5.15 shows how seasonal changes in water quality can affect the equilibrium adsorption of MIB. Five water samples were taken from Happy Valley Reservoir at various times during the period 1998-1999. One sample, W4, was also diluted by a factor of two (W4 diluted). Three samples were taken from Hope Valley during this period, and one each from Myponga Reservoir and the inlet to Anstey Hill water treatment plant (prechlorinated River Murray water). Adsorption of geosmin at equilibrium is not affected significantly by water quality changes (Cook *et al.* 2001). As MIB adsorption is not influenced by changes in alkalinity or pH, differences in the equilibrium adsorption shown in Figure 5.15 are attributable to variations in NOM character and concentration

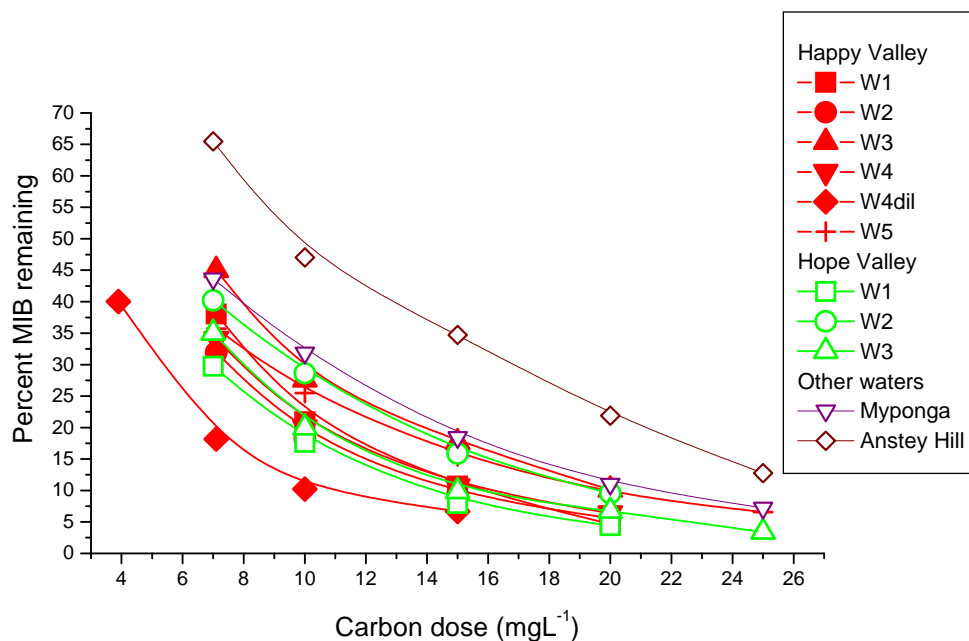


Figure 5.15 Fraction MIB remaining at equilibrium as a function of PAC dose for a range of waters

Table 5.7 shows the DOC concentration, UV absorbance at 254 nm, SUVA and the PAC dose required to reduce the MIB concentration by 50% in one hour in each water.

Table 5.7 Water quality parameters and PAC doses required to reduce the concentration of MIB by 50% in one hour (11 water samples)

	Happy Valley						Hope Valley			Myp	Anst
	W1	W2	W3	W4	W4 dil	W5	W1	W2	W3		
DOC	4.6	6.1	8	8.6	4.5	4.6	8.3	4.1	6.1	10.0	4.2
UV ₂₅₄	0.143	0.198	0.238	0.266	0.136	0.143	0.150	0.106	0.179	0.438	0.087
SUVA	3.1	3.2	3.0	3.1	3.0	3.1	1.8	2.6	2.9	4.4	2.1
PAC dose (mgL ⁻¹)	15.2	17.7	21.3	18.5	11.5	20	19.5	15.6	17.5	20	20

UV absorbance, SUVA and DOC concentration were plotted against the PAC doses given in Table 5.7 in an effort to determine a relationship which could be used in practice. Figure 5.16 shows that there is no significant relationship between carbon dose and these parameters.

OPTIMISATION OF ADSORPTION PROCESSES

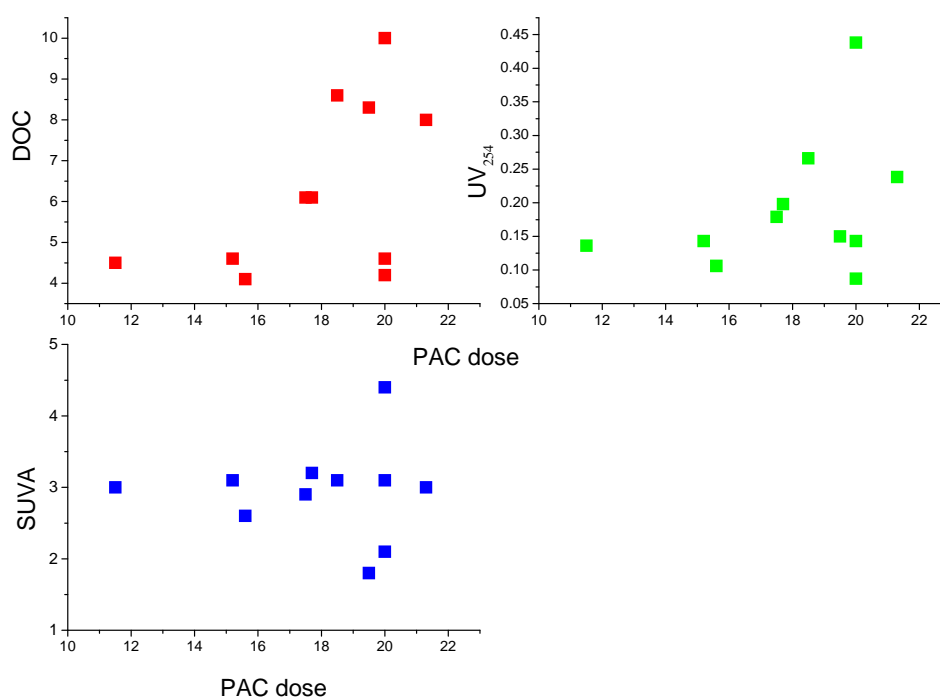


Figure 5.16 Relationship between water quality parameters and PAC dose required to reduce MIB concentration by 50% in 60 minutes.

The lack of any significant relationship is a result of the nature of the competitive effect. The majority of the effect is due to direct competition for adsorption sites between MIB and small, uncharged NOM compounds with low UV absorbance (Hepplewhite 2000; Newcombe *et al.* 2001). The concentration of competitive NOM in Myponga water was estimated using the equivalent background compound model (EBC). This can be used to obtain the adsorption isotherm of competing compounds when the adsorption of the target compound is known in the presence and absence of the NOM (Najm *et al.* 1991; Knappe *et al.* 1998). The EBC is not considered to be the entire NOM present in natural waters, as only an unknown portion of the NOM will compete. The model uses ideal adsorbed solution theory (IAST) to obtain the EBC adsorption parameters (Freundlich K, $1/n$ and initial EBC concentration) by the minimisation of the error between the experimental adsorption isotherm in the presence of NOM and the adsorption isotherm predicted by the IAST model. More detail on this procedure is given in Najm *et al.* (1991) and Newcombe *et al.* (2001). In the latter study the concentration of the EBC, or the competing NOM, was found to be less than 10%, of the total NOM. Therefore bulk characterisation and concentration parameters would not be considered specific enough to give an indication of the extent of competition to be expected in a particular water. A technique sophisticated enough to discriminate the compounds responsible for the reduction in adsorption capacity, such as molecular weight distribution using DOC detection, are out of the reach of water treatment operators. To date, the best predictor of an increased PAC requirement is an increase in the DOC, although this cannot be considered an accurate predictor (Figure 5.16).

Water treatment processes

Chlorination

Several studies have shown that the inlet water to one Adelaide water treatment plant, Anstey Hill, contains organic compounds more capable of effectively competing with MIB for adsorption sites than NOM in other waters (see Figure 5.15). The adsorption of MIB was consistently lower in this water than others of higher DOC (Cook *et al.* 2001; Newcombe *et al.* 1996). The inlet water to Anstey Hill was generally pre-chlorinated, as the water treatment plant is at the terminal of a 60 km pipeline from the River Murray, and several off-takes along the pipe supply households with potable water. Figure 5.17a) shows the removal of MIB with time in four water samples - i) raw River Murray water, ii) Anstey Hill inlet water in the absence of chlorination, iii) water sampled at Mannum, 2 km downstream from the chlorination point in the pipeline, and iv) inlet Anstey Hill water where pre-chlorination was applied at the river off-take. No free chlorine was present during these experiments, as the presence of chlorine has also been shown to reduce the adsorption of MIB and geosmin (Gillogly *et al.* 1998b; Lalezary-Craig *et al.* 1988). Clearly the pre-chlorination of the water has a significant effect on the adsorption of MIB, and the effect occurs early in the pipeline, presumably immediately at chlorination. A simulation of the chlorination of the river water was undertaken in the laboratory, with the same significant decrease in MIB adsorption (Figure 5.17b). The effect can be interpreted as the increase in adsorption competition provided by the chlorination by-products, generally smaller molecules, more likely to provide direct competition with the target compound. This effect has been seen, to a less significant extent, with the laboratory chlorination of a range of NOM isolates from Hope Valley Reservoir (Caire 1998). However the same effect was not seen in a Lake Michigan water in the US (Gillogly *et al.* 1998b) or Myponga Reservoir water (Figure 5.18). DOC, SUVA and UV absorbances of the waters used in Figures 5.17 and 5.18 are given in Table 5.8. Figure 5.19 shows the effect of chlorination on the molecular weight distributions of River Murray and Myponga Reservoir water. It is clear that the chlorination process has a significant effect on the character of the NOM. In the case of the extreme conditions in the Myponga water (30 mgL^{-1} applied chlorine), a large increase in smaller molecular weight NOM is seen. This increase in smaller NOM on chlorination has been reported previously for NOM fractions (Pelekani *et al.* 1998). Once again, none of the characterisation techniques used can aid in the interpretation of the competitive effects with MIB. The main difference apparent between the two waters is that the river NOM appears to be more susceptible to attack by the chlorine as at 5 mgL^{-1} chlorine dose the SUVA was reduced to 1.5, whereas, even at a 30 mgL^{-1} chlorine dose, the SUVA was only reduced to 2.7 in Myponga water. Furthermore, a doubling of the chlorine dose from 15 to 30 mgL^{-1} resulted in no further degradation of the SUVA in Myponga water, indicating that the possible reactions had already gone to completion at the lower dose. This aspect of pre-chlorination requires further investigation, although it appears to date that the effects of chlorination of the River Murray NOM may be specific to this source.

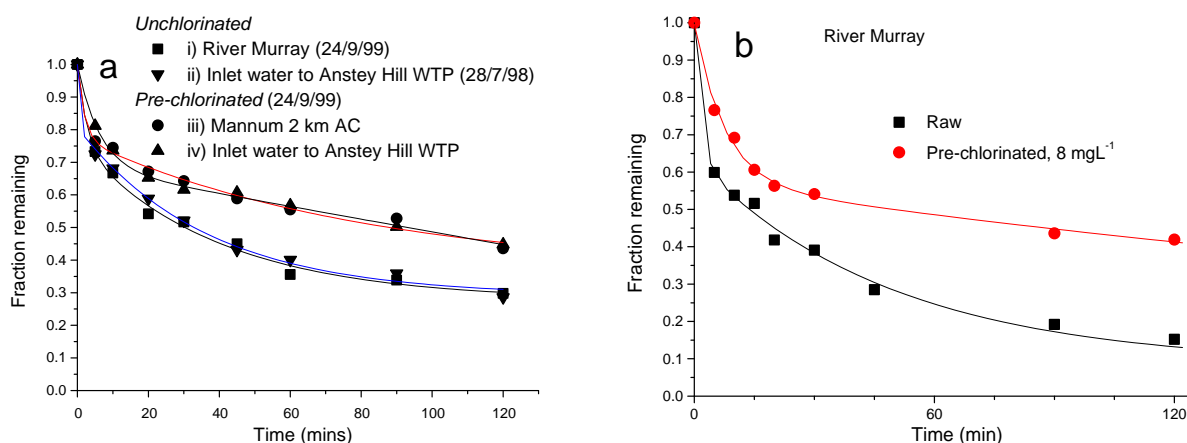


Figure 5.17 MIB removal as a function of time in chlorinated and non-chlorinated River Murray water

OPTIMISATION OF ADSORPTION PROCESSES

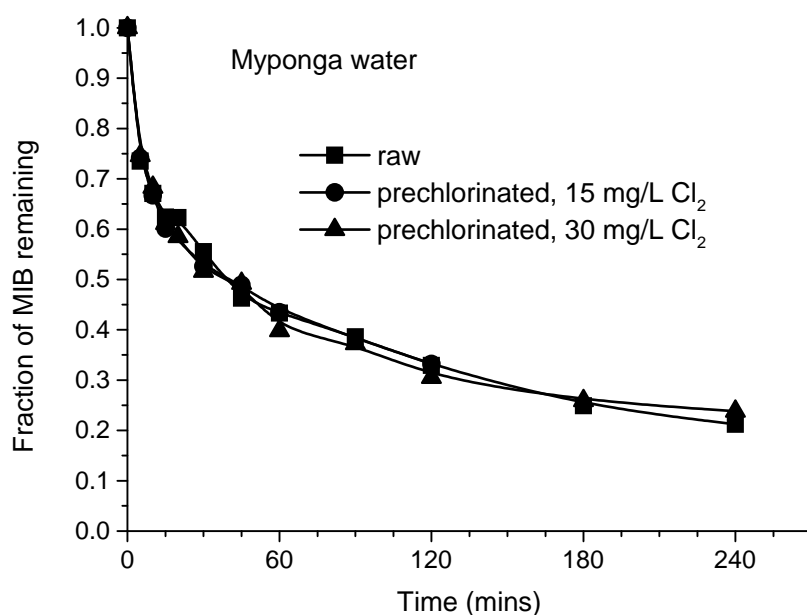


Figure 5.18 MIB removal as a function of time in chlorinated and unchlorinated Myponga Reservoir water. Residual chlorine was quenched prior to experiment

Table 5.8 NOM parameters for chlorinated and unchlorinated Myponga and River Murray water

	River Murray, supply				River Murray, laboratory		Myponga Reservoir, laboratory		
	RM1	RM2	RM3	RM4	RM5	RM6	M1	M2	M3
Chlorinated? (dose, mgL ⁻¹)	×	×	✓ (5)	✓ (5)	×	✓ (8)	×	✓ (15)	✓ (30)
DOC	7.3	5.3	7.3	7.8	ND	ND	9.9	10	9.9
UV ₂₅₄	0.167	0.196	0.114	0.110	0.114	0.083	0.397	0.258	0.270
SUVA	2.3	3.7	1.5	1.4	ND	ND	4.0	2.6	2.7

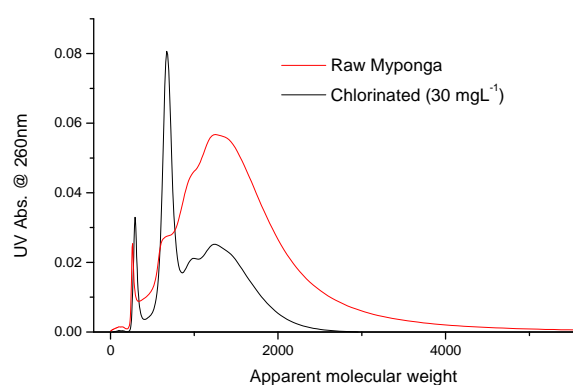
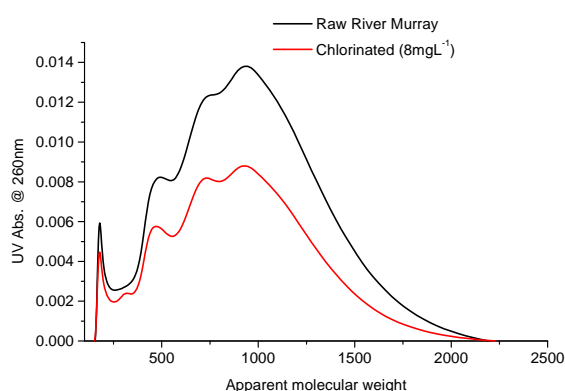


Figure 5.19 Apparent molecular weight distributions of chlorinated and unchlorinated River Murray and Myponga Reservoir water

Coagulation/flocculation

It has been reported that the application of PAC at the point of addition of alum or other coagulants reduces the adsorption efficiency (Najm *et al.* 1991). In their study of a range of waters, Cook *et al.* (2001) found that the efficiency of the activated carbon was only reduced under conditions of high turbidity, and therefore high alum doses. The adsorption of MIB and geosmin are not affected by the presence of high turbidity levels (unpublished data). However, in a jar test where the PAC was added during alum flocculation, the turbidity of the water had a significant effect on the removal of geosmin (Figure 5.20a). The same effect was noted for MIB. The HSDM model was used to predict the removal in the absence of coagulation, and the predicted removals are also shown in Figure 5.20a. In three other waters with turbidities below 26 NTU, no such effect was noted, and the HSDM predicted the removal accurately. This reduction of removal efficiency is attributed to the binding of the PAC in the floc. The effective contact between the water and the PAC will depend on the size and density of the resultant floc; for example, more efficient contact could be expected from a small floc with loosely bound particles, than a large dense floc. Figure 5.20b shows that DOC concentration also has an effect on the removal efficiency when PAC is added during coagulation. In this case Happy Valley Reservoir water was diluted to obtain a lower DOC, then additional turbidity was added, obtained from a 0.2 μm filtration of river water, to obtain the same high turbidity. Therefore, the water represented the same turbidity and NOM character as the original reservoir water, but lower DOC concentration. The results suggest that a decrease in the DOC while the turbidity and alum dose remain constant, may produce a floc that results in a lower effective contact between the PAC and the MIB/geosmin.

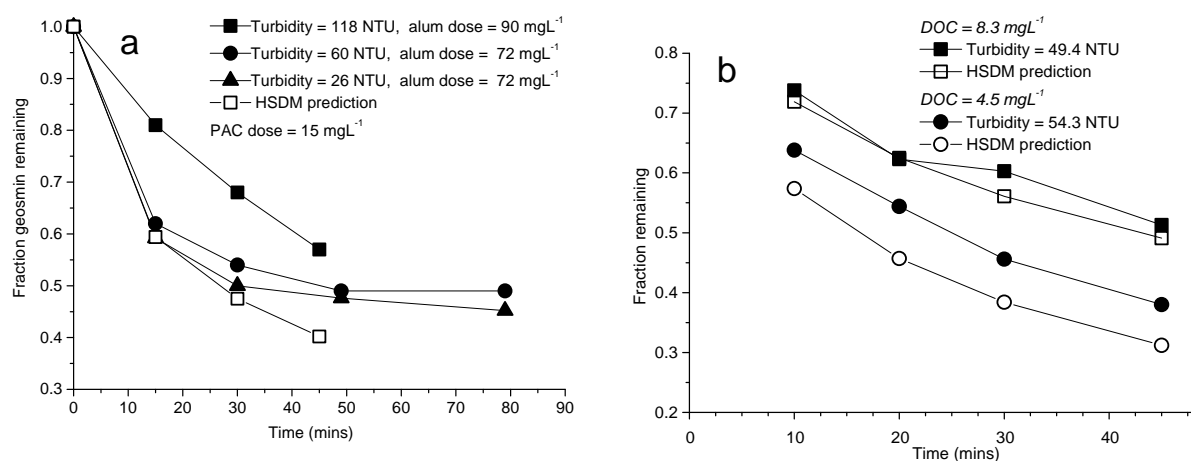


Figure 5.20 The effect of turbidity - a) and DOC concentration - b), on the accuracy of HSDM predictions for the removal of geosmin

5.4.4 Conclusions and recommendations

The first consideration for water suppliers using activated carbon to deal with taste and odour episodes caused by MIB and/or geosmin is choosing the most effective adsorbent. In general, good quality microporous carbons, such as coconut or coal based, will be superior, although at shorter available contact times the chemically-activated wood carbons may provide better adsorption kinetics.

In water treatment plants where taste and odour episodes are common, the homogenous surface diffusion model (HSDM) can be used to estimate powdered activated carbon dose requirements under a range of conditions including inlet concentration and plant flow rates (controlling PAC contact time). This information allows water suppliers to make informed decisions regarding treatment options, and in most cases a good quality PAC may be sufficient for the mitigation of the problem. In cases of prolonged episodes, and high inlet levels, an estimate of the carbon doses required, and knowledge of the common time frame over which the taste and odour compounds will be present, will allow a cost-benefit analysis of PAC application vs. more advanced treatment processes. This is information that most water authorities currently do not have.

When PAC is the desired option, the HSDM predictions can be routinely used for estimates of the required doses when the operators have knowledge of approximate inlet concentrations and available contact times. Such information will soon be utilised at four water treatment plants in Adelaide, Australia, in the form of a "user-friendly" computer program. However, the PAC dose predictions must be used in combination with knowledge of the effect that water quality changes and water treatment chemicals have on the removal.

In general, an increase in DOC, often reflected in an increase of UV absorbance, a parameter more routinely analysed, will result in an increased carbon dose requirement for MIB removal. Geosmin is less sensitive to changes in DOC quantity and quality, and no adjustment in the dose may be required. For example, in Adelaide the major compound of concern is geosmin, and PAC dose predictions have been validated under conditions of a 100% increase in DOC concentration. Pre-chlorination is not recommended in situations where PAC is used for taste and odour mitigation. Evidence is clear that a chlorine residual can reduce the adsorption of MIB and geosmin, and in at least one case, the effect on NOM can lead to increased adsorption competition, and reduced MIB adsorption. Again, geosmin is not affected by the variation in NOM character brought about by chlorination. The application of PAC simultaneously with alum or other coagulants, a common practice, can result in a decrease in the removal of both MIB and geosmin, and therefore an increased dose requirement. The magnitude of the effect will depend on the size and structure of the floc formed containing the PAC particles, which in turn is dependent on alum dose, turbidity, DOC concentration, and colour, if this is one of the criteria for alum dosing. In general terms, a higher alum dose, driven by an increase in turbidity, will probably lead to a higher PAC dose requirement than predicted by the HSDM.

In summary, there is significant scope for the more cost-effective utilisation of powdered activated carbon for the mitigation of taste and odours, as well as a wider range of other micro-contaminants, using tools such as the homogenous surface diffusion model, in conjunction with knowledge of the effects of water quality and water treatment processes.

5.5 REMOVING TASTES AND ODOURS USING ACTIVATED CARBON: IS YOUR CHEAP PAC COSTING YOU TOO MUCH?

5.5.1 Introduction

2-methylisoborneol (MIB) and geosmin are earthy/musty odour compounds produced as secondary metabolites by some cyanobacteria and actinomycetes. They can cause significant problems for drinking water suppliers as they are perceived by most consumers as an unpleasant odour and taste in water at very low concentrations (around 10 ng L⁻¹). The compounds, aliphatic, tertiary alcohols, are not easily oxidised by chlorine or ozone (Lalezary *et al.* 1986), consequently activated carbon is currently considered the best technology for the treatment of affected water.



Blue-green algal blooms (or cyanobacterial blooms) are becoming more prevalent in our water sources as water quality is decreasing due to higher nutrient input.

Powdered activated carbon (PAC) is often the only mode of application of activated carbon available to water authorities for the removal of taste and odour compounds.

The advantages are that PAC:

- Can be applied only when required
- Is relatively inexpensive
- Can be retro-fitted to existing plants

The major disadvantage of PAC application is that prolonged use may lead to significant costs, and this is exacerbated by the lack of knowledge regarding correct doses for the production of water of appropriate quality. Dosing at levels greater than necessary can result in very high costs to the water supplier and, conversely, under-dosing leads to consumer complaints and is an inefficient use of the adsorbent. Recently Cook *et al.* (2001) reported the application of the homogenous surface diffusion adsorption model (HSDM) for predicting activated carbon doses required at four water treatment plants supplying the city of Adelaide. The work aimed to provide tools to help the water supplier minimise the amount of PAC used while still ensuring satisfactory water quality. In this article, those tools are used to undertake cost-benefit analyses related to the application of PAC under practical water treatment conditions, and other factors influencing PAC doses, and therefore costs, are identified.

5.5.2 Choosing the right PAC and the correct doses

The most important factor in the application of PAC for the removal of MIB and geosmin is the removal of the compounds at contact times of two hours or less. Figure 1 shows the fraction of MIB remaining against time, for four activated carbons (designated C1, C2, C3, and C4) in Myponga Reservoir water. Starting concentration of MIB was 100 ngL^{-1} , carbon dose was 20 mgL^{-1} .

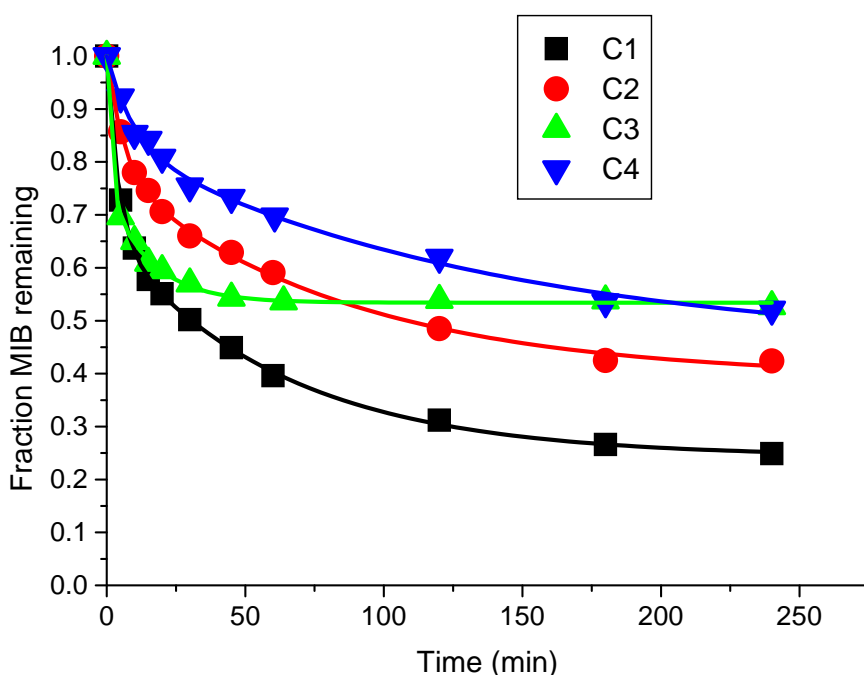


Figure 5.21 Fraction of MIB remaining vs. contact time for four activated carbons. Myponga Reservoir water

Figure 5.21 shows that the most efficient activated carbon for the removal of MIB in a water treatment plant will depend strongly on the contact time available for adsorption. The choice of an activated carbon clearly depends on cost, in addition to performance. In Table 5.9, the costs associated with using the four carbons shown in Figure 5.21 are given. The calculations were based on carbon dose predictions (obtained using the HSDM model, see Cook *et al.* 2001 for details) for a 50% removal of MIB (eg from 20 to 10 ngL⁻¹) at a 50 ML per day flow, over a period of 10 days.

Table 5.9 Doses required for the removal of MIB from 20 to 10 ngL⁻¹ for four activated carbons, and costs associated with dosing at a 50 ML per day flow for 10 days. Myponga Reservoir water

	C1	C2	C3	C4
PAC dose (mgL ⁻¹)	16	31	26	38
PAC required for 10 days dosing (tonne)	8.0	15.5	13.0	19.0
Cost for 10 days dosing (AUS\$)	28000	24800	41600	28500

Although C3 is relatively effective at short contact times, it would probably not be used for taste and odour removal due to the high costs involved. As a low activation coconut-based product, C4 is less expensive per tonne than the high activation carbon, C2; however, there is no cost benefit associated with its use, as the doses required are higher. Although the cost of dosing with C1 is higher than that for C2, the advantage of handling and storing smaller amounts of C1 may be more important for some water suppliers. The use of similar dose predictions can allow authorities to weigh up the advantages and disadvantages and make informed decisions regarding PAC application.

PAC particle size also plays an important role in the adsorption of MIB and geosmin. Figure 5.22 shows the cost benefit associated with a particle size of 10 µm compared with 23 µm, as a function of geosmin inlet concentration (dosing in a 50 ML per day plant over 10 days).

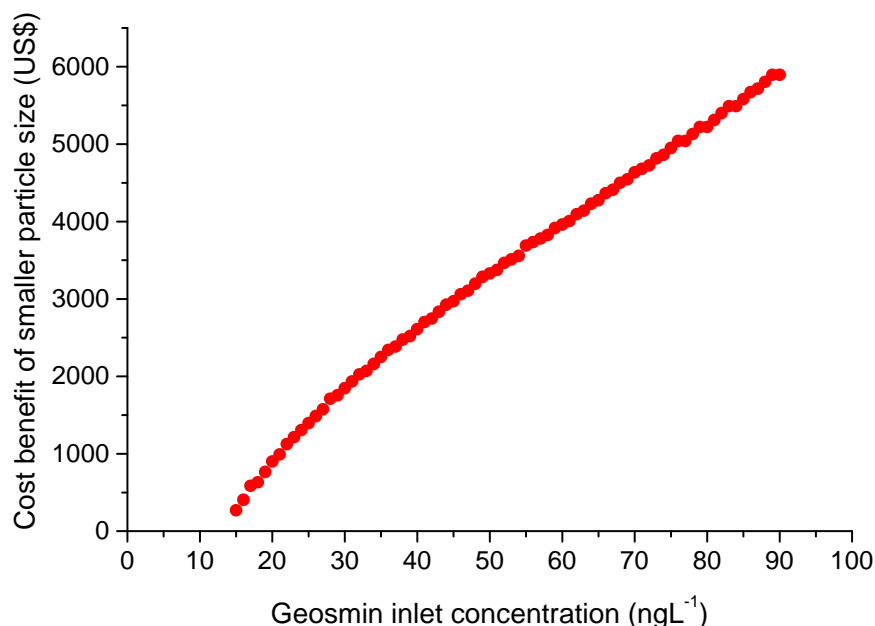


Figure 5.22 . Cost advantage associated with the smaller particle size (10 days dosing, 50 ML flow)

Clearly there is a particle size limit below which ease of handling of the PAC becomes an issue. A very small particle size may also result in removal difficulties using conventional methods, and possible breakthrough into the distribution system. The 10 μm median particle size has proven to be optimum for the water treatment plants supplying Adelaide, using both conventional and dissolved air flotation technology.

PAC dose predictions can also be used to determine when PAC application would no longer be cost effective, and other, more advanced techniques should be considered. Figure 5.23 shows cost estimates for dosing a high activation coconut carbon (C2) for MIB or geosmin for a prolonged period at one Adelaide water treatment plant. The difficulty of removing MIB compared with geosmin is reflected in the cost of PAC dosing.

OPTIMISATION OF ADSORPTION PROCESSES

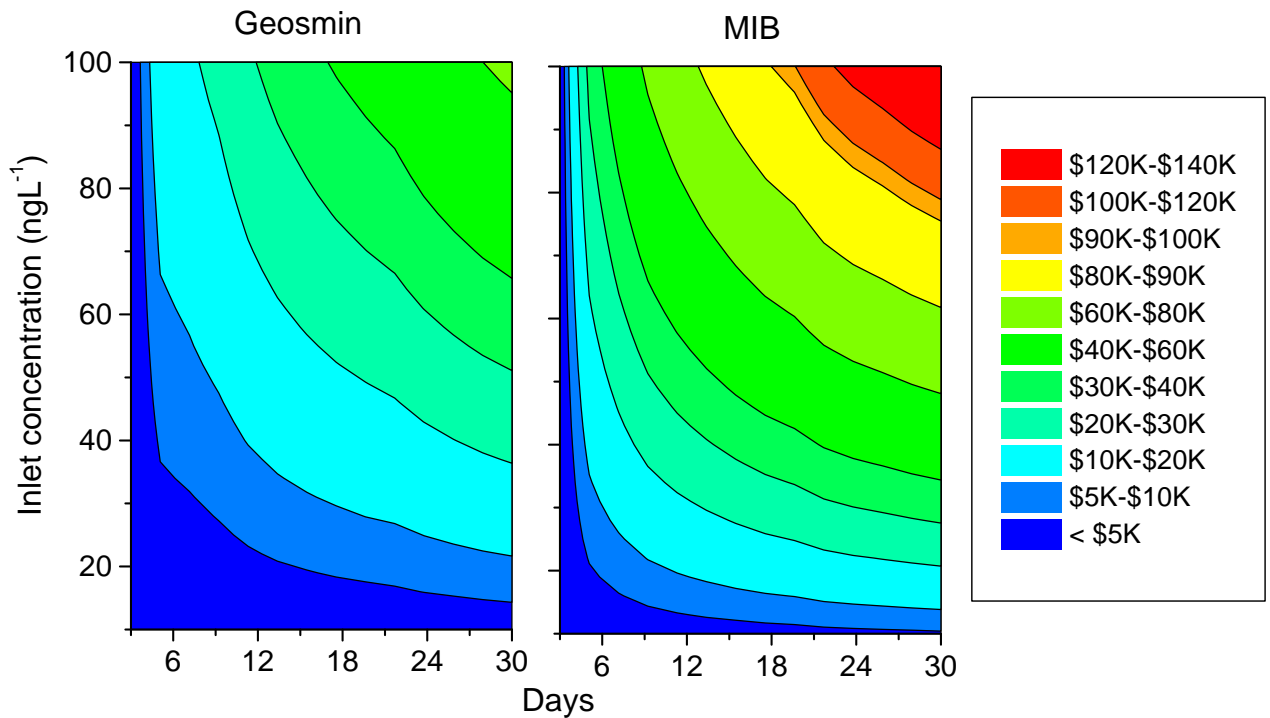


Figure 5.23 Cost estimates for prolonged PAC dosing

If high concentrations of MIB were expected for several months each year, the water authority could make an informed decision regarding other treatment options based on this type of analysis.

Recommendations at a glance:

Step 1. Choose the right PAC, then determine appropriate doses for your water treatment plant

PAC testing

- | | |
|---|---|
| i) Test a range of PACs, under conditions related to the individual treatment plant | 4 |
| ii) Use computer aids to determine the doses you need | 4 |

Cost benefit analysis

- | | |
|--|---|
| i) Weigh up the advantages of lower dose against higher cost | 4 |
| ii) Decide whether an alternative treatment (such as GAC) would be more cost effective over prolonged T & O episodes | 4 |

5.5.3 When will we need to change our PAC doses?

Once the appropriate PAC doses have been determined for a particular water source, the question to be answered is "How will changes in raw water quality and treatment processes affect PAC doses?".

Alkalinity, hardness and pH do not appear to affect the adsorption of MIB and geosmin over the ranges generally encountered in drinking water treatment, therefore changes to these water quality parameters will not affect the PAC doses required for taste and odour removal. In contrast, dissolved organic carbon (DOC) concentration and character both strongly affect the adsorption of MIB (Newcombe *et al.* 1997; Cook *et al.* 2001). Geosmin removal, and therefore PAC doses, are not strongly affected by DOC. To date, no clear relationship has been identified between DOC concentration and PAC doses. As a general rule, an increase in DOC concentration (or UV absorbance) will result in an increased PAC dose requirement for MIB removal. Research into this aspect is continuing, with the aim of producing a "DOC factor", which can be used to modify PAC dose predictions.

Some water treatment processes affect the removal of taste and odour compounds using PAC. The presence of a chlorine residual has been shown to reduce the adsorption of both MIB and geosmin (Gilligly *et al.* 1998; Lalezary-Craig *et al.* 1988; Newcombe unpublished data). Pre-chlorination where there is no residual present at the point of PAC application has been shown to have an effect on River Murray water. However, so far no other water has demonstrated a decreased taste and odour removal in chlorinated water in the absence of a residual. It has been reported that the application of PAC at the point of addition of alum or other coagulants reduces the adsorption efficiency (Najm *et al.* 1991). The adsorption of MIB and geosmin are not affected by high turbidity levels alone. However, in a jar test where the PAC was added during alum flocculation, the turbidity of the water had a significant effect on the alum dose and also the removal of geosmin and MIB (Cook *et al.* 2001). This reduction of removal efficiency is attributed to the binding of the PAC in the floc. The effective contact between the water and the PAC will depend on the size and density of the resultant floc; for example, more efficient contact could be expected from a small floc with loosely bound particles, than a large dense floc. The size and structure of the floc will be dependent on turbidity, DOC, and alum dose.

Recommendations at a glance

Step 2. Know how PAC doses may change with the situation. (↑-increase, NE-no effect)

	PAC dose geosmin	PAC dose MIB
DOC/UV absorbance ↑	NE	↑
Turbidity ↑		
i) PAC applied to 30 min prior to coagulation	NE	NE
ii) PAC applied simultaneously with increased coagulant dose	↑	↑
Pre-chlorination		
i) chlorine residual present	↑	↑
ii) no chlorine residual present	NE	NE

5.5.4 Conclusions

The first consideration for water suppliers using activated carbon to control taste and odour episodes caused by MIB and/or geosmin is choosing the most effective adsorbent. In general, good quality microporous carbons, such as coconut or coal based, will be superior, although at shorter available contact times the chemically-activated wood carbons may provide better adsorption kinetics, particularly for geosmin.

In water treatment plants where taste and odour episodes are common, the homogenous surface diffusion model (HSDM) can be used to estimate powdered activated carbon dose requirements under a range of conditions including inlet concentration and plant flow rates (controlling PAC contact time). This information allows water suppliers to make informed decisions regarding treatment options, and in most cases a good quality PAC may be sufficient for the mitigation of the problem. It may also aid in

the often difficult decision, "**How much more will the cheaper activated carbon cost in the long run?**". In cases of prolonged episodes, and high inlet levels, an estimate of the carbon doses required, and knowledge of the common time frame over which the taste and odour compounds will be present, will allow a cost-benefit analysis of PAC application vs. more advanced treatment processes. This is information that most water authorities currently do not have.

When PAC is the desired option, the HSDM predictions can be routinely used for estimates of the required doses when the operators have knowledge of approximate inlet concentrations and available contact times. However, the PAC dose predictions must be used in combination with knowledge of the effect that water quality changes and water treatment chemicals have on the removal.

In general, an increase in DOC, often reflected in an increase of UV absorbance, a parameter more routinely analysed, will result in an increased carbon dose requirement for MIB removal. Geosmin is less sensitive to changes in DOC quantity and quality, and no adjustment in the dose may be required. For example, in Adelaide the major compound of concern is geosmin, and PAC dose predictions have been validated under conditions of a 100% increase in DOC concentration. Pre-chlorination is not recommended in situations where PAC is used for taste and odour mitigation. Evidence is clear that a chlorine residual can reduce the adsorption of MIB and geosmin, and in at least one case, the effect on the natural organic material can lead to increased adsorption competition, and reduced MIB adsorption. Again, geosmin is not affected by the variation in NOM character brought about by chlorination. The application of PAC simultaneously with alum or other coagulants, a common practice, can result in a decrease in the removal of both MIB and geosmin, and therefore an increased dose requirement. The magnitude of the effect will depend on the size and structure of the floc formed containing the PAC particles, which in turn is dependent on alum dose, turbidity, DOC concentration, and colour, if this is one of the criteria for alum dosing. In general terms, a higher alum dose, driven by an increase in turbidity, will probably lead to a higher PAC dose requirement than predicted by the HSDM.

In summary, there is significant scope for the more cost-effective utilisation of powdered activated carbon for the mitigation of taste and odours, as well as a wider range of other micro-contaminants, using tools such as the homogenous surface diffusion model, in conjunction with knowledge of the effects of water quality and water treatment processes.

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6. THE INFLUENCE OF NOM CHARACTER ON OTHER WATER TREATMENT PROCESSES

6.1 INTRODUCTION

NOM affects all water treatment processes, and the character of the NOM influences the effect. During the project a PhD student studying under Prof. Vern Snoeyink, Con Pelekani, spent some time at the AWQC and undertook some studies on the molecular weight distribution of NOM on several other treatments processes. The results are reported below, and the chapter is based on a paper published in *Water* (G Newcombe G, Pelekani C, Hepplewhite CJ and Nguyen K (1998). 'Size is Important' *Water*, 25(6), 16-20).

6.2 SIZE IS IMPORTANT, OR THE EFFECT OF MOLECULAR WEIGHT DISTRIBUTION OF NOM ON WATER TREATMENT PROCESSES

6.2.1 Introduction

Natural organic matter (NOM) present in drinking water sources has been shown to impact all aspects of water quality and treatment processes, including disinfection, coagulation and flocculation, activated carbon adsorption, and bacterial regrowth in the distribution system. Morran *et al.* (1996) provided some examples of the adverse effects NOM has on these processes, including:

- Reacting with coagulants causing slower, less effective flocculation, resulting in increased coagulant demand and coagulant residuals.
- Increasing the disinfectant demand and forming chlorinated disinfection by-products.
- Acting as an organic food source for micro-organisms, resulting in bacterial regrowth in the distribution system.
- Reducing the capacity of activated carbon for target micropollutants (taste and odour compounds, algal toxins) by competing for active sites and blocking pores.
- Reducing the effectiveness of membrane microfiltration by irreversible fouling.

The size of NOM is an important factor in the effect of NOM on water treatment. Chadik and Amy (1986) studied the impact of coagulation and adsorption on the molecular weight distributions of several natural waters in the United States. As a general trend, alum coagulation was found to remove higher molecular weight material, while activated carbon adsorption was observed to remove a broader molecular weight spectrum of material. This is in agreement with the results of other studies (El-Rehaili and Weber Jr., 1987).

The molecular size or weight distribution of NOM can be determined using ultrafiltration (Amy *et al.*, 1992) or aqueous gel permeation chromatography (GPC). However, it is important to note that these procedures are calibrated with compounds (e.g. proteins) which have very different structures from NOM. As a result these methods can only provide a relative size distribution. It is therefore advantageous to obtain supporting data from alternative size evaluation techniques such as Field Flow Fractionation, Vapour Pressure Osmometry (VPO), and Small Angle X-ray Scattering (SAXS).

High performance size exclusion chromatography (HPSEC) is one form of GPC that has been widely used for the analysis of proteins and polymers. HPSEC is a molecular separation based on hydrodynamic size. It is based on the ability of molecules to access pore volume within a porous gel. Small molecules can access a greater fraction of the total pore volume, thus they elute later than larger molecules. The technique was initially developed for purification of biological compounds in the pharmaceutical industry, but has been used for characterising aquatic organic matter since the 1970s (Amy *et al.*, 1992; Amy *et al.*, 1987; Thurman *et al.*, 1982; Gloor *et al.*, 1981; Miles and Brezonik, 1983). Recent work by Chin *et al.* (1994) showed that HPSEC can yield reliable molecular weight distributions of NOM without the complication of significant solute-gel interactions that have plagued the use of this technique for accurate and quantitative size analysis of NOM in the past. HPSEC molecular weight distributions were obtained for a variety of natural waters of different origin, using specific environmental and operating conditions, and calibration compounds. Molecular weight distribution parameters comparable to those obtained using independent measurement techniques such as VPO and SAXS were obtained.

The aim of this research was to use HPSEC to elucidate the effect of different water treatment processes on the molecular weight distribution of NOM from different Australian water sources, and to evaluate whether the technique provides useful information which can be used in the optimisation of water treatment plant operations.

6.2.2 Materials and methods

Natural waters and NOM fractions

Three natural water sources were used in this study: Myponga reservoir, River Murray, and Hope Valley reservoir. Myponga is located 60 kilometres south of Adelaide, and Hope Valley is located 15 kilometres northeast of Adelaide. Raw and treated water were collected from the laboratory of the water treatment plants at Hope Valley and Myponga, River Murray water was collected from Mannum, located 80 kilometres northeast of Adelaide. All samples were filtered through a 0.45 µm cartridge filter and stored in the fridge to minimise biological growth.

NOM fractions prepared from the concentration and ultrafiltration of Hope Valley reservoir water were also used for the adsorption kinetics and simulated chlorination experiments. The NOM was concentrated using a strong anion exchange resin. The isolation and ultrafiltration (UF) procedure is summarised elsewhere (Newcombe and Drikas, 1996).

High performance size exclusion chromatography (HPSEC)

HPSEC was performed according to the method of Chin *et al.* (1994), using a Waters Protein-Pak 125 glycol-functionalised silica gel column (Waters Corp., Milford, MA, USA). However, for the adsorption kinetics and simulated chlorination experiments a Shodex KW802.5 silica gel column (Waters Corp., Milford, MA, USA) was used.

Ultraviolet (UV) absorbance and colour

UV-254 absorbance was measured spectrophotometrically with a 1cm cell. Colour was measured at 456 nm with a 5 cm cell. A platinum-cobalt colour standard of 50 Hazen Units (HU) was used to convert from absorbance to HU.

Dissolved organic carbon (DOC)

DOC was determined by the UV/persulphate oxidation method using a TOC analyser (Skalar).

Activated carbons

Two powdered activated carbons (PAC) with different physicochemical properties were used for the adsorption experiments. Table 6.1 summarises their physical characteristics. The pore volume is divided qualitatively into three regions, based on pore width (d):

- $d < 8 \text{ \AA}$
- $8 < d < 20 \text{ \AA}$
- $20 < d < 500 \text{ \AA}$

These regions correspond broadly to primary micropores, secondary micropores, and mesopores, respectively. These two activated carbons are under consideration for use in suburban and country water treatment plants in South Australia for removal of taste and odour compounds and algal toxins.

Table 6.1 Physical properties of activated carbons

Carbon	Base Material	Activation Method	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)		
				($d < 8 \text{ \AA}$)	($8 < d < 20 \text{ \AA}$)	($20 < d < 500 \text{ \AA}$)
Picazine	Wood	Chemical	2183	0.57	0.54	0.51
Picactif	Coconut	Thermal	987	0.31	0.13	0.03

Adsorption kinetics

Adsorption kinetics experiments were performed with Hope Valley NOM fractions. 1.0 g of activated carbon was added, with constant stirring, to a 5 L volumetric flask containing a solution of 15 mg DOC/L. 20 mL samples were collected at various times and were immediately filtered through a 0.45 µm filter.

Simulated chlorination

Five Hope Valley ultrafiltration NOM fractions diluted to 10 mg DOC/L were chlorinated with a dose of 20 mg/L as chlorine (Cl_2). The reaction mixtures were allowed to stand for 8 days in sealed bottles in the dark at ambient temperature. The chlorinated fractions were quenched with 1 mL of 0.01 M sodium sulphite to neutralise 1 mg/L of chlorine residual. Samples were filtered through a 0.45 µm filter.

6.2.3 Results and discussion

Chlorination

The Mannum-Adelaide pipeline runs for more than 80 kilometres from Mannum, on the River Murray, to the Adelaide Hills. There are several chlorination stations along the pipeline. The objective was to evaluate the impact of chlorination on the NOM molecular weight distribution along the pipeline. At the time the survey was conducted only one chlorination station was in operation. This was the first chlorination point at Mannum. Samples of raw water and chlorinated water at different locations along the pipeline were collected. The chlorine dose applied was approximately 4.5 mg/L as Cl_2 . Figure 6.1 illustrates the SEC results for the chlorination survey.

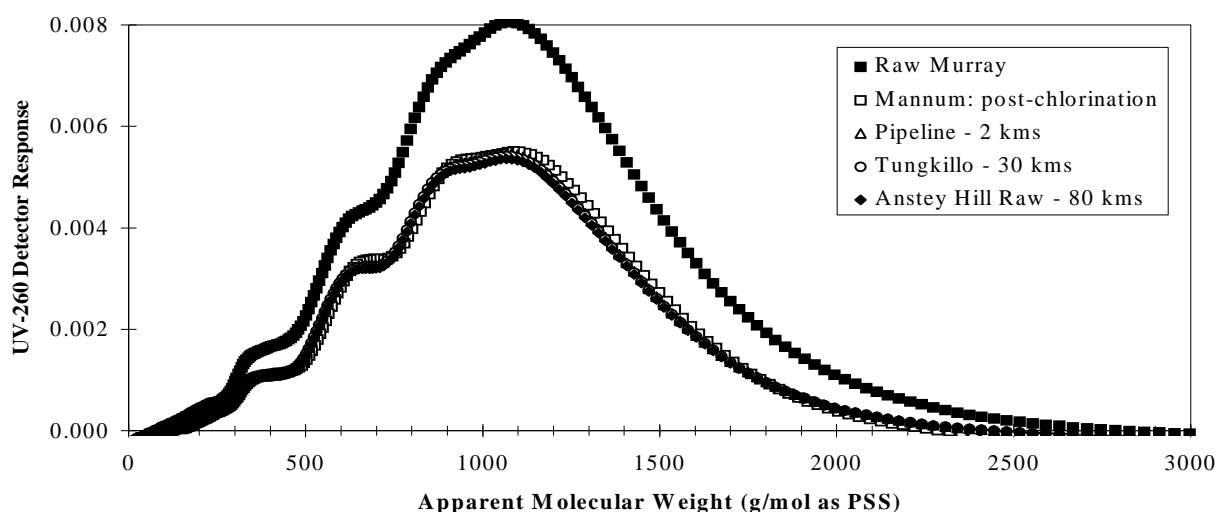


Figure 6.1 Effect of chlorination on NOM along the Mannum-Adelaide pipeline

There was a distinct decrease in UV-260 detector response after chlorination, as well as a shift towards lower molecular weight compounds. These observations indicate that chlorine breaks down larger molecular weight organic compounds into smaller compounds, and also attacks double bonds and aromatic rings. Table 6.2 summarises the changes in absorbable UV and colour after chlorination. Specific UV-254 absorbance (SUVA: defined as 100 times the absorbance through a 1cm cell divided by the DOC concentration), and specific colour decreased by 37 percent and 70 percent, respectively. With increased contact time along the pipeline, there were small decreases in both colour and UV-254. A significant increase in DOC (0.5 mg/L) was observed after the initial chlorination. The following DOC sources were identified as contributing to the increase:

- The release of organic compounds (e.g. extracellular material) from the biofilm present on the distribution pipe wall at the point of chlorination.
- The release of organic compounds adsorbed onto particulate matter after chlorination.

OPTIMISATION OF ADSORPTION PROCESSES

The consistent decrease in DOC after chlorination is most likely due to uptake of organic compounds by micro-organisms present in the pipe wall biofilm.

Simulated chlorination

In addition to the effect of chlorination on the molecular weight distribution of NOM in the distribution system, its effect on NOM fractions with different molecular weight distributions was evaluated. Figure 6.2 illustrates the SEC chromatograms for the five Hope Valley UF fractions before chlorination. Figure 6.3 shows the subsequent impact of chlorination.

Table 6.2 Effect of chlorination on NOM chemical properties

Sample	UV-254	Colour (HU)	DOC (mgL ⁻¹)	SUVA (Lm ⁻¹ mg ⁻¹)	Specific Colour (L.HU.mg ⁻¹)
Raw Murray	0.122	13	4.1	3.0	3.2
Mannum (post Cl ₂)	0.088	4	4.6	1.9	1.0
Pipeline (2 kms)	0.085	4	4.4	1.9	0.8
Tungkillo (30 kms)	0.086	4	4.2	2.0	0.9
Anstey Hill (80 kms)	0.087	4	4.2	2.1	0.9

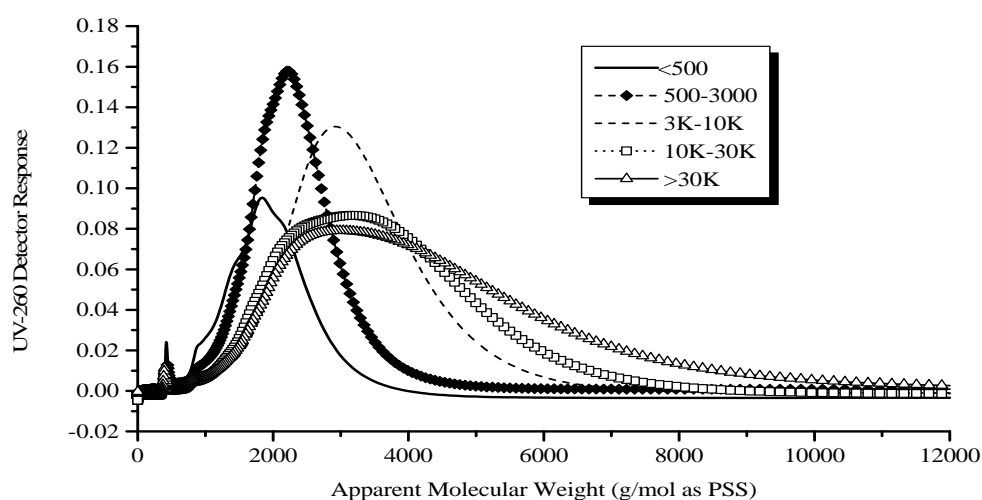


Figure 6.2 HPSEC chromatograms of Hope Valley UF NOM fractions

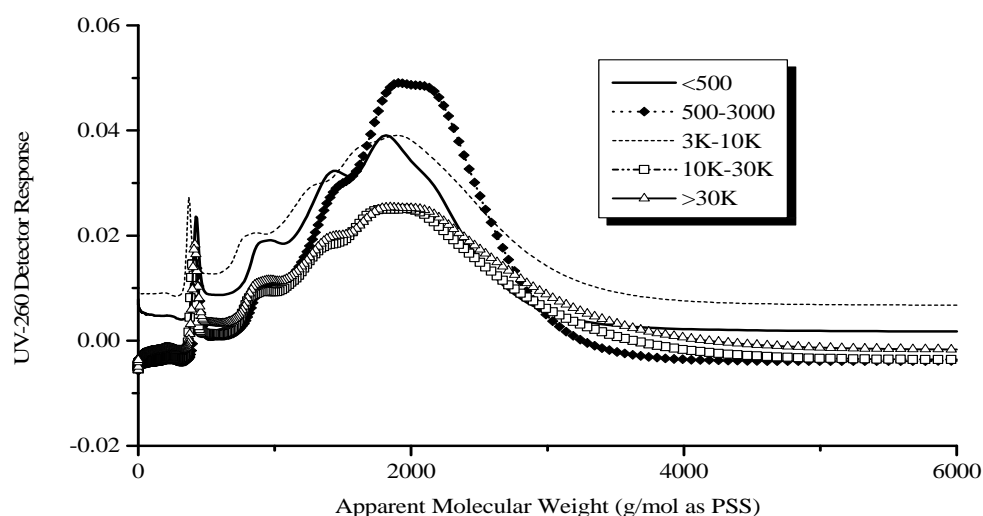


Figure 6.3 HPSEC chromatograms of chlorinated Hope Valley UF NOM fractions

Chlorination had a dramatic impact on both the chemical properties and molecular weight distribution of all fractions. There was a pronounced shift towards lower molecular weights as well as a marked decrease in UV absorbing NOM. This clearly indicated that chlorination results in the breakdown of high molecular weight material to smaller compounds, and also attacks double bonds and aromatics. Furthermore, the molecular weight distributions of all the fractions after chlorination were very similar, peaking at approximately 2000. These results clearly support the results obtained in the distribution system, but show the extreme case given the laboratory treatment conditions (20 mg/L Cl_2 dose for 8 days). These conditions are highly unlikely to be used in conventional treatment practice.

Coagulation

Myponga water was used to evaluate the effect of coagulation on NOM molecular weight characteristics. The water treatment plant utilises the following treatment train: coagulation, flocculation, dissolved air flotation, sand filtration, and chlorination prior to storage and distribution. The plant uses alum as the coagulant, and at the time of sampling the alum dose was 75 mg/L. Aluminium residuals in the treated water were less than 25 $\mu\text{g/L}$. Treated water samples were collected directly after sand filtration. Raw water samples were not chlorinated. Figure 6.4 illustrates the HPSEC results obtained for the raw and treated waters.

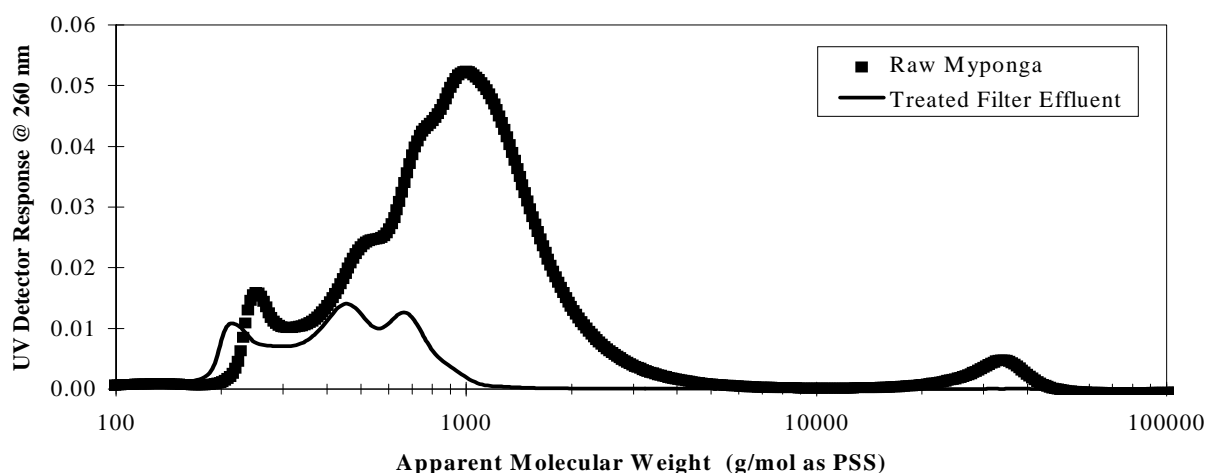


Figure 6.4 HSEC of raw and treated Myponga water

Figure 6.4 shows a very significant removal of the high molecular weight NOM (>1000). This is consistent with other studies which have shown that coagulation preferentially removes the high molecular weight material. The changes in UV-254 and DOC are summarised in Table 6.3. The treatment train effectively removed DOC (63 percent) and UV-254 (77 percent). SUVA decreased by 38 percent. Most of this is likely due to removal of highly coloured large molecular weight material by coagulation, rather than the destruction of aromaticity and double bonds present in NOM.

Table 6.3 Chemical properties of raw and treated Myponga water

Sample	DOC (mgL ⁻¹)	UV-254	SUVA (Lm ⁻¹ mg ⁻¹)
Raw	11.5	0.43	3.7
Treated	4.3	0.098	2.3

Comparison of serial fractionation HPSEC data (samples not pre-concentrated) with the treated Myponga HPSEC showed that the 500-1000 fraction yielded very good agreement (Figure 6.5). The result indicates that it may be possible to model the molecular weight distribution of a treated water (from conventional treatment processes) with a particular UF size fraction. This could be used to optimise treatment strategies for removal of these low molecular weight compounds. One observation is that the peaks of the two chromatograms appear to be slightly skewed. This is a result of the small differences in the semi-logarithmic molecular weight calibration curves.

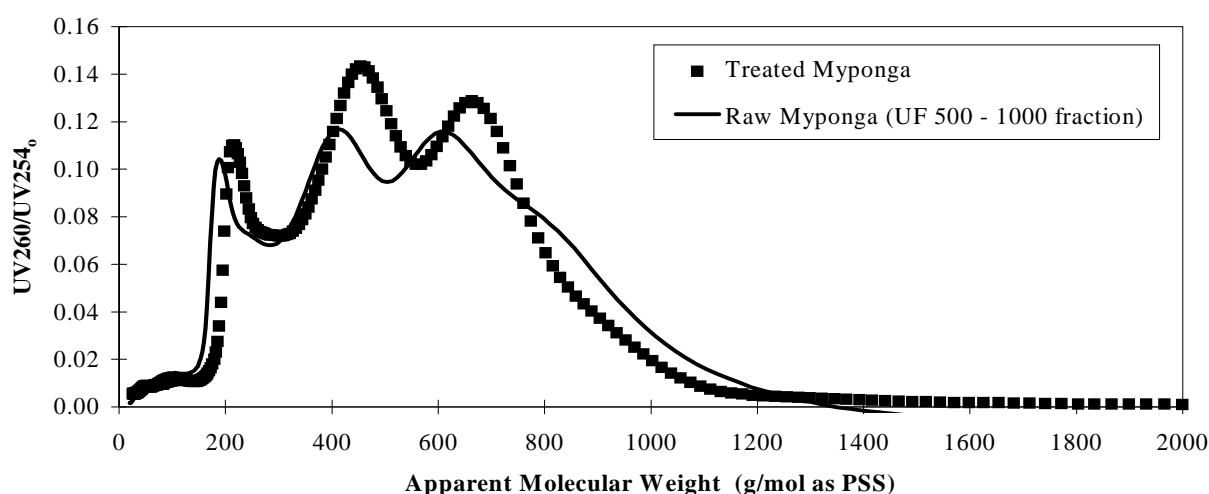


Figure 6.5 Normalised SEC plots for treated Myponga and 500-1000 fraction of raw Myponga water

Adsorption kinetics

Activated carbon is widely used in water treatment for the removal of taste and odour compounds, algal toxins, synthetic organic contaminants, and NOM. For contaminant removal, activated carbon is usually applied in powdered form at the head of the plant to maximise contact time prior to removal at the filters. Granular activated carbon filters are more commonly employed for NOM removal.

Figure 6.6 illustrates the effect of different carbon adsorbents on the rate of adsorption of the UF 500-3000 NOM fraction, for a PAC dose of 200 mg/L.

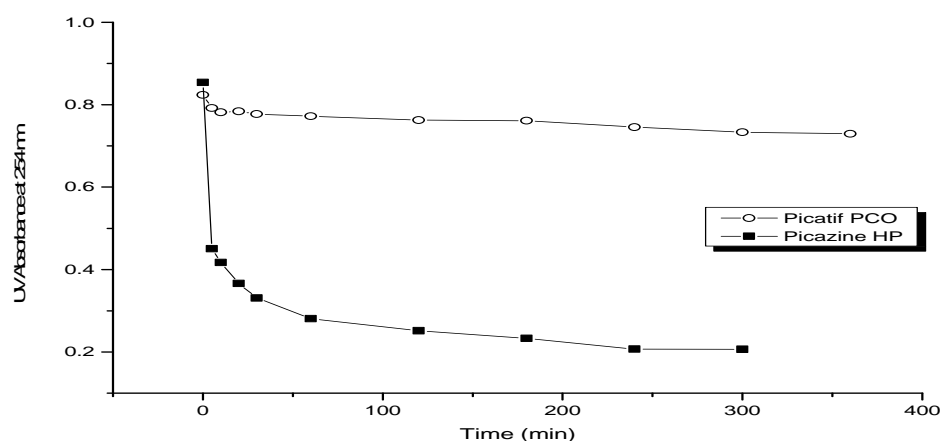


Figure 6.6 Effect of carbon adsorbent on the adsorption kinetics of 500-3000 fraction

Picazine HP showed rapid adsorption, which is a consequence of the large volume of mesopores (Table 6.1) which permit fast transport of NOM molecules to adsorption sites. Picatif PCO however, has negligible mesopore volume, only significant quantities of the smaller primary and secondary micropores. The smaller pores result in a reduction in the rate of diffusion because of molecular steric hindrance. Hence, the pore volume distribution of an activated carbon has a significant impact on the rate of adsorption of NOM. This has implications in water treatment operations where the contact time is often limited. It should be noted however, that the choice of activated carbon for a particular water treatment application should not be made solely on adsorption kinetics, but also on equilibrium studies and the physical properties of the adsorbent and how they will impact treatment performance.

Figures 6.7 and 6.8 show the transient change in molecular weight distribution of the NOM. Picatif PCO showed poor removal over the entire range of molecular weights. This is in contrast to Picazine HP which showed significant removal over all molecular sizes.

OPTIMISATION OF ADSORPTION PROCESSES

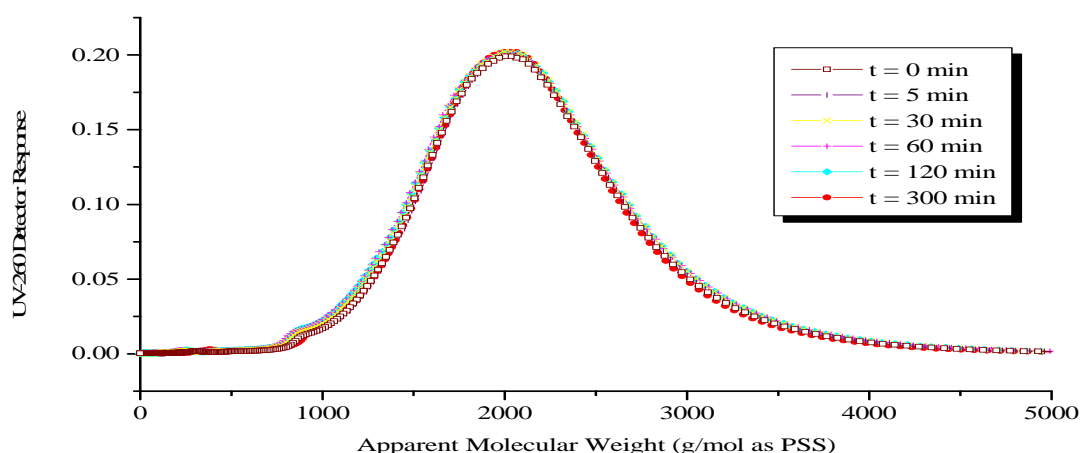


Figure 6.7 SEC of 500-3000 NOM fraction after Picatif PCO adsorption

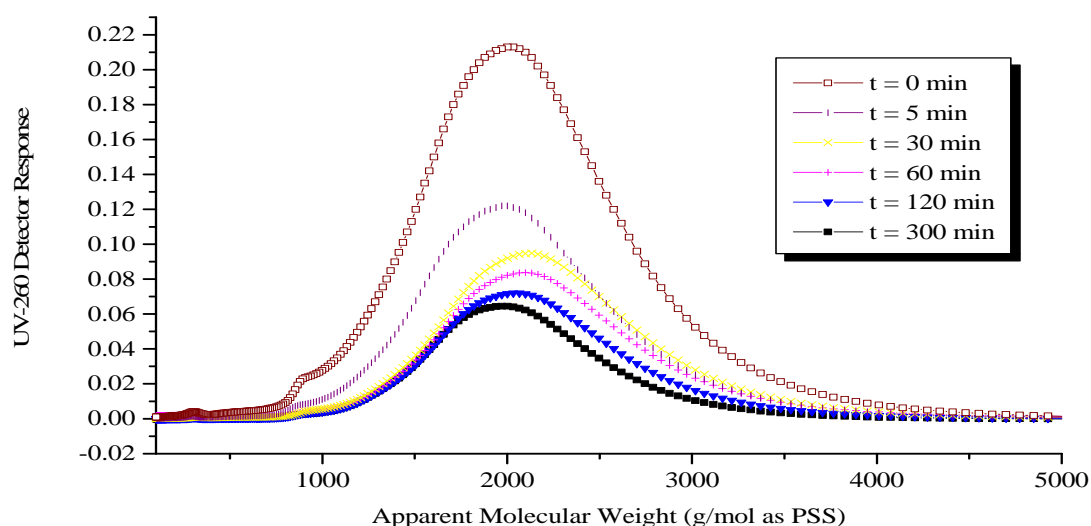


Figure 6.8 SEC of 500-3000 NOM fraction after Picazine HP adsorption

6.2.4 Conclusions

HPSEC is a relatively quick and simple method for obtaining useful molecular weight distributions of natural organic matter. The method was shown to be a powerful tool in determining the impact of selected water treatment processes on the composition of NOM. In the distribution system (source to treatment facility), disinfection using chlorine resulted in the breakdown of large NOM compounds to smaller products with a significant reduction in UV absorbing NOM and colour. Simulated chlorination experiments with isolated NOM fractions supported these observations, and showed that under extreme conditions the products formed by disinfection have similar molecular weight distributions regardless of the initial characteristics of the NOM. Alum coagulation was shown to clearly target the higher molecular weight compounds. Activated carbon adsorption showed that NOM removal takes place over the range of molecular weights, although this effect is dependent to a great extent on the pore volume distribution of the adsorbent.

HPSEC supplies valuable information that can be used in optimisation of various water treatment processes. For example, the low molecular weight fractions of NOM are responsible for the majority of chlorinated disinfection by-products of public health significance (e.g. trihalomethanes and haloacetic acids). Laboratory scale testing of different treatment processes will allow for development and optimisation of methods which target these low molecular weight compounds.

The focus of current research has shifted to validating the HPSEC technique utilised in this study with different column gel materials, as well as more sophisticated independent molecular weight determination techniques, primarily flow field-flow fractionation, in order to obtain estimates of the hydrodynamic size of NOM. This is important from the viewpoint of competition between micropollutants and NOM for adsorption sites on activated carbon where the size of the adsorbates relative to the carbon pore size distribution influences the molecular competition mechanism.

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7. SUMMARY AND CONCLUSIONS

7.1 ISOLATION AND CHARACTERISATION OF NATURAL ORGANIC MATERIAL

Isolation of natural organic material (NOM) from the water matrix is carried out for two main purposes:

- Ease of characterisation
- To undertake experiments on NOM of specific character (i.e., "hydrophobic", or low molecular weight isolates)

Resin adsorption, particularly on ion exchange resins, or DAX 8/XAD 4 combinations is commonly used for this purpose. Ultrafiltration can also be used to fractionate isolated NOM into higher molecular weight ranges. Isolates obtained using DAX 8 are commonly referred to as "hydrophobic" NOM isolates, using XAD 4 the isolates are often termed "transphilic" and using anion exchange the isolates are often called "charged" isolates. This terminology can be very misleading for several reasons:

- There is significant overlap in terms of the character of the isolates obtained using these processes
- The DAX and XAD resin isolates can only be referred to as hydrophobic or transphilic in the state in which they are isolated, i.e. at pH 2. At this pH a significant proportion of the carboxyl groups are protonated and the NOM can be considered to exhibit these characteristics. At neutral pH, however, "hydrophobic" NOM exhibits hydrophilic qualities as the molecules are often highly charged
- As mentioned above, NOM isolated at pH 2 on DAX and XAD resins are in fact mostly charged at neutral pH, therefore differentiation between these isolates and NOM isolated using anion exchange is invalid.

In this study, NOM isolated using these procedures was found to exhibit minimal differences in terms of chemical characteristics. However, ultrafiltration of these isolates produced a range of molecular weight fractions with quite different physical characteristics. The same trends were seen in two waters, five isolations, using three isolation techniques. The major trends with increasing molecular weight were:

- Increasing colour
- Increasing UV absorbance
- Increasing O-alkyl content (indicative of carbohydrates)
- Decreasing aromatic character

Molecular weight, or size distribution is one of the most important properties of NOM affecting treatment processes. Ultrafiltration (UF) and high performance size exclusion chromatography (HPSEC) are techniques commonly used for the determination of molecular weight of dissolved NOM; flow field flow fractionation (FIFFF) is a valuable method that is less commonly used. There are weaknesses associated with each of the techniques, and the best procedure for the molecular weight determination of NOM samples is to compare several methods.

High performance size exclusion chromatography, while a very useful technique, has some limitations due to strong interactions that can take place between organic compounds and the surface of the column packing material. This was shown by the retention times of a series of model compounds. Those with a very high charge to size ratio eluted earlier than would be expected by their molecular weight, while hydrophobic compounds eluted later, providing inaccurate molecular weights when compared with the elution times of the PSS standards. This may be the cause of the resolved peaks and well-defined shoulders evident in most of the HPSEC chromatograms of NOM fractions and natural waters. There is very little resolution seen in results of the flow field flow fractionation, which may be an artefact of the technique, where separation of molecular sizes is based on the different diffusion coefficients. The comparison of the two analytical techniques suggests that, although NOM compounds in general have a wide, fairly regular, or smooth, size distribution, the chemical structure, the cause of possible interactions with the HPSEC column packing, may not be found in such an even distribution. That is, while the NOM compounds are found in a range of sizes, some chemical characteristics are common to NOM eluting where the peaks and shoulders are detected.

The preparation of the largest molecular weight fractions of the NOM isolates (>30K UF fractions) was strongly influenced by the concentration of the initial NOM solution used for the fractionations. It is probable that a gel layer formed quite quickly on the membrane during the membrane filtration, forming an effective additional filter of lower molecular weight cut-off. As a result, when solutions of two of the >30K fractions - at much lower initial concentrations - were ultrafiltered through the 30K membrane, much of the NOM passed through into the permeate. Filtration of these NOM samples through membranes of lower molecular weight indicated that most of the NOM was in the size range able to permeate the 30K membrane, and be retained on the 1K membrane.

The percentage of dissolved organic carbon retained on the membranes was then compared with the percentages of NOM greater than the membrane cut-off molecular weight, measured using HPSEC and FIFFF. The results obtained by HPSEC and FIFFF were quite different from the membrane results for the 3K and 1K molecular weights. This indicated that, either the membrane cut-off values could not be applied to the NOM fractions, or a proportion of the DOC retained on the membranes was non-UV absorbing, thus it was not detected using the other techniques.

7.2 MECHANISMS OF ADSORPTION OF NOM ONTO ACTIVATED CARBON

The effect of ionic strength, pH, pore volume distribution and surface charge on the adsorption of natural organic material by seven activated carbons was studied. The work confirmed the existence of crossover points in the adsorption isotherms undertaken at two ionic strengths which were indicative of a change in adsorption mechanism from the screening reduced to the screening enhanced modes. The “charge compensation” mechanism for NOM adsorption at low surface concentrations proposed by Newcombe and Drikas (1997) did not hold for four of the seven activated carbons studied. Rather, the adsorption appears to be attributable to a number of factors such as available pore volume, pore structure, electrostatic attractive and repulsive forces, specific (chemical) interactions between the NOM and the surface functionalities of the activated carbons, and access to the positive adsorption sites, making a detailed interpretation of the results extremely difficult. However, the finding that the charge on the adsorbed NOM at the cross-over point of the isotherms was independent of the pH for all carbons was consistent with the findings of Newcombe and Drikas (1997), and indicated that the amount of negative charge on the NOM participating in electrostatic adsorption interaction depended only on the number of available positive surface sites on the carbon, and not on the net charge of the surface.

7.3 THE INFLUENCE OF WELL-CHARACTERISED NOM ON THE ADSORPTION OF MIB ONTO ACTIVATED CARBON

The activated carbons chosen for this study displayed a wide range of both textural and chemical surface properties. Both are known to affect adsorption of micropollutants, and adsorption competition provided by NOM. The characteristics of the NOM isolates ranged from low molecular weight, low charge, low colour, to relatively highly charged NOM of high molecular weight, and high colour. The raw water from which these NOM solutions were isolated was also studied.

A series of equilibrium and kinetics experiments were undertaken to investigate the competitive effects between these NOM solutions and MIB. Dissolved organic carbon concentrations were measured after equilibrium competitive adsorption experiments, and high performance size exclusion chromatography was used to investigate the changes in molecular weight distribution as a function of carbon dose and contact time.

The main findings of this work were the following:

- Adsorption of the NOM isolates was controlled predominantly by the relationship between the molecular weight distribution of the NOM, and the pore size distribution of the carbon. The low molecular weight compounds were adsorbed to a greater extent than the larger compounds, due to size exclusion effects.
- There is evidence that the larger NOM molecules restrict the adsorption of smaller compounds to some degree in microporous carbons
- For the very low molecular weight compounds, represented by the peak at around 200 apparent molecular weight in the HPSECs, the mesoporous carbon showed rates of adsorption greater than

the microporous carbons, attributed to a broader pore size distribution. The higher volume of transport pores in the mesoporous carbon allowed more rapid diffusion to adsorption sites.

- The mesoporous carbon displayed a slight decrease in the relative rates of adsorption with an increase in molecular weight, attributed to the decrease in diffusion coefficient with increase in NOM size. In contrast, the microporous carbons showed an increase in the relative rate of adsorption with increase in molecular weight. It is proposed that the mesoporous carbon's pore size distribution allowed adsorption of a range of molecular weights throughout its internal structure. In the microporous carbons, as the molecular weight of the adsorbing compound increased, the access to adsorption sites was reduced to those available in relatively large pores closer to the external surface. Although the extent of adsorption was thus reduced, the distance of diffusion was also reduced, resulting in a higher relative adsorption rate.

The majority of the competition between NOM and MIB in the systems studied can be attributed to compounds of similar size and chemical characteristics to the target compound. As a result, the production of an activated carbon with the aim of minimising the competitive effect becomes problematic. On a practical level, a powdered activated carbon with an extremely narrow pore size distribution, allowing only access to MIB, and minimal access to very low molecular weight (VLMW) NOM, is difficult, and therefore, expensive, to manufacture, and could be expected to display very poor kinetic properties. An ideal carbon for the adsorption of MIB would have a bimodal pore distribution, allowing rapid access to adsorption sites, while minimising pore blockage and restriction by VLMW and low molecular weight NOM. This conclusion was also reached by Pelekani (1999) in his study focusing mainly on the adsorption of atrazine and model competing compounds on activated carbon fibres. Such an adsorbent could also be expected to show good adsorption of the microcystin group of algal toxins, an important aspect of the treatment of water affected by algal blooms.

7.4 OPTIMISATION OF THE APPLICATION OF ACTIVATED CARBON FOR THE TREATMENT OF A RANGE OF ALGAL METABOLITES

The first consideration for water suppliers using activated carbon to deal with taste and odour episodes caused by MIB and/or geosmin is choosing the most effective adsorbent. In general, good quality microporous carbons, such as coconut or coal based, will be superior, although at shorter available contact times the chemically-activated wood carbons may provide better adsorption kinetics.

In water treatment plants where taste and odour episodes are common, the homogenous surface diffusion model (HSDM) can be used to estimate powdered activated carbon dose requirements under a range of conditions including inlet concentration and plant flow rates (controlling PAC contact time). This information allows water suppliers to make informed decisions regarding treatment options, and in most cases a good quality PAC may be sufficient for the mitigation of the problem. In cases of prolonged episodes, and high inlet levels, an estimate of the carbon doses required, and knowledge of the common time frame over which the taste and odour compounds will be present, will allow a cost-benefit analysis of PAC application vs. more advanced treatment processes. This is information that most water authorities currently do not have.

When PAC is the desired option, the HSDM predictions can be routinely used for estimates of the required doses when the operators have knowledge of approximate inlet concentrations and available contact times. Such information will soon be utilised at four water treatment plants in Adelaide, in the form of a "user-friendly" computer program. However, the PAC dose predictions must be used in combination with knowledge of the effect that water quality changes and water treatment chemicals have on the removal.

In general, an increase in DOC, often reflected in an increase of UV absorbance, a parameter more routinely analysed, will result in an increased carbon dose requirement for MIB removal. Geosmin is less sensitive to changes in DOC quantity and quality, and no adjustment in the dose may be required. For example, in Adelaide the major compound of concern is geosmin, and PAC dose predictions have been validated under conditions of a 100% increase in DOC concentration. Pre-chlorination is not recommended in situations where PAC is used for taste and odour mitigation. Evidence is clear that a chlorine residual can reduce the adsorption of MIB and geosmin, and in at least one case, the effect on NOM can lead to increased adsorption competition, and reduced MIB adsorption. Again, geosmin is not affected by the variation in NOM character brought about by chlorination. The application of PAC simultaneously with alum or other coagulants, a common practice, can result in a decrease in the

removal of both MIB and geosmin, and therefore an increased dose requirement. The magnitude of the effect will depend on the size and structure of the floc formed containing the PAC particles, which in turn is dependent on alum dose, turbidity, DOC concentration, and colour, if this is one of the criteria for alum dosing. In general terms, a higher alum dose, driven by an increase in turbidity, will probably lead to a higher PAC dose requirement than predicted by the HSDM.

There is significant scope for the more cost-effective utilisation of powdered activated carbon for the mitigation of taste and odours, as well as a wider range of other micro-contaminants, using tools such as the homogenous surface diffusion model, in conjunction with knowledge of the effects of water quality and water treatment processes.

7.5 THE INFLUENCE OF NOM CHARACTER ON OTHER WATER TREATMENT PROCESSES

In the distribution system, disinfection using chlorine resulted in the breakdown of large NOM compounds to smaller products with a significant reduction in UV absorbing NOM and colour. Simulated chlorination experiments with isolated NOM fractions supported these observations, and showed that under extreme conditions the products formed by disinfection have similar molecular weight distributions regardless of the initial characteristics of the NOM. Alum coagulation was shown to clearly target the higher molecular weight compounds. Activated carbon adsorption showed that NOM removal takes place over the range of molecular weights, although this effect is dependent to a great extent on the pore volume distribution of the adsorbent.

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9. APPENDIX B EXTENDED ABSTRACTS SUBMITTED FOR CONFERENCE PROCEEDINGS

IN THE (ADSORPTION) COMPETITION BETWEEN NOM AND MIB, WHO IS THE WINNER AND WHY?

Extended abstract, Proceedings of the 1st World Conference on Carbon, EUROCARBON 2000, July 2000, Berlin, Germany

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Keywords: activated carbon, adsorption, natural organic material, tastes and odours, water treatment

INTRODUCTION

Removing taste and odour compounds from drinking water is a challenge. In particular, 2 methylisoborneol, MIB, can be detected by consumers at levels as low as 10 ngL^{-1} as a musty odour; therefore the treatment method for this compound must be very effective. The major inhibition to the removal of MIB using activated carbon is the presence of dissolved natural organic material (NOM), which is found in drinking water sources at levels generally between 2 and 15 mgL^{-1} . Even at the low end of the range, NOM concentrations are at least several tens of thousands times that of the problem compound.

NOM is composed of a very complex mixture of organic compounds ranging in Australian waters from a few hundred to ten thousand grammol^{-1} . The important mechanisms proposed for the effect of NOM on micropollutant adsorption are:

- pore blockage and
- direct competition for adsorption sites¹.

It is generally considered that the larger molecular weight compounds could block pores, and the smaller molecular weight NOM may directly compete for adsorption sites with a low molecular weight compound such as MIB (168 grammol^{-1}). The relative importance of each of these mechanisms will depend on the type of NOM and the surface characteristics of the activated carbon. This work identifies and characterises the compounds in the NOM providing the most competition with MIB, and describes the effect on kinetics and equilibrium of adsorption of MIB onto two very different activated carbons.

THE ACTIVATED CARBONS

Table 1. Starting materials, activation methods and physical characteristics of the two activated carbons

	Material and activation	Primary micropore volume (cmg^{-1})	Secondary micropore volume (cmg^{-1})	Mesopore volume (cmg^{-1})	Surface charge, pH 7.5 (meqg^{-1})
Carbon 1	Steam-activated coconut	0.31	0.13	0.03	-0.30
Carbon 2	Chemically-activated wood	0.57	0.54	0.51	+0.03

THE NATURAL ORGANIC MATERIAL

High performance size exclusion chromatograms in Figure 1a show the apparent molecular weight distributions of two NOM isolates and a natural raw reservoir water used for the competitive adsorption studies. These results, along with solid state ^{13}C NMR and ultraviolet absorbance spectra (not shown), indicate large differences in the character of the NOM isolates.

COMPETITIVE ADSORPTION

Figure 1b illustrates the effect of the different NOM character on the equilibrium adsorption of MIB onto carbon 2. NOM isolate 1 produces the greatest competition for adsorption sites, evidenced by the lowest surface concentration of the three adsorption isotherms. As this isolate does not contain any of the larger NOM molecules present in the other solutions, the results indicate that the major influence on adsorption is the lower molecular weight compounds. This supports previous results obtained in this laboratory for a wide range of isolates. The results for the carbon 1 also suggest the major influence on competition at equilibrium is the concentration of low molecular weight compounds particularly those of similar size and character to MIB itself. However, the higher molecular weight compounds influence the kinetics of adsorption onto the carbon with the greater volume of larger pores, carbon 2. For this carbon, the equilibrium value of the adsorption is higher in the presence of the high molecular weight compounds, but it takes longer to reach that value than in the presence of low molecular weight NOM. This is interpreted as pore restriction, where the high molecular weight compounds hinder the kinetics of adsorption while exerting no influence on the equilibrium adsorption. Carbon 1, with negligible mesopore volume is not affected, as the larger molecules cannot enter the very narrow pore structure.

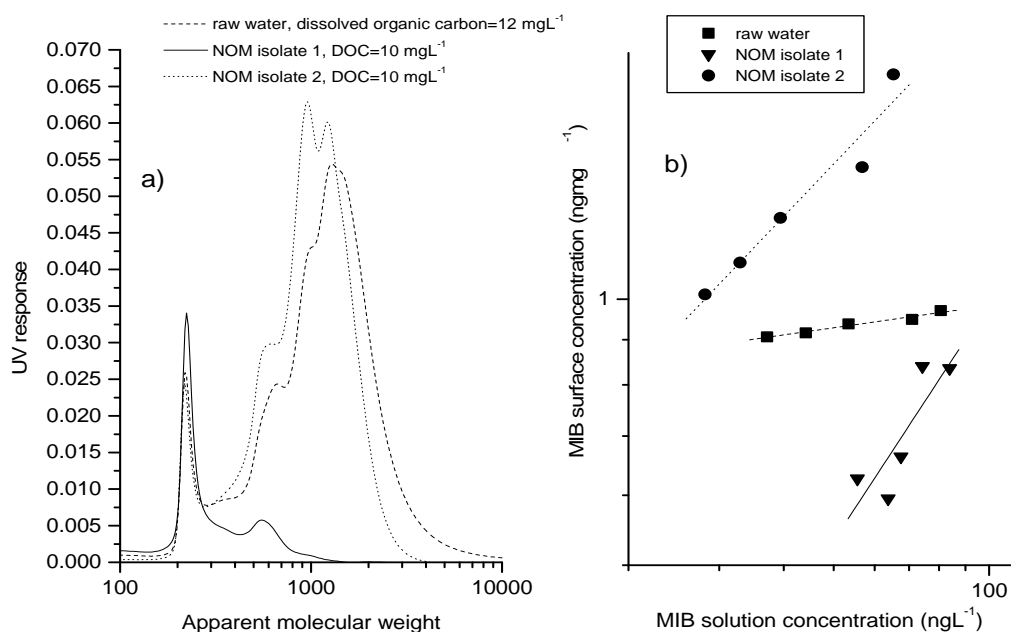


Figure 1 a) High performance size exclusion chromatograms and b) MIB adsorption onto carbon 2 in the presence of two NOM isolates and one raw water

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HOW TO WIN IN THE BATTLE AGAINST TASTES AND TOXINS IN DRINKING WATER USING ACTIVATED CARBON

Extended abstract, Proceedings of the 1st World Conference on Carbon, EUROCARBON 2000, July 2000, Berlin, Germany

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Keywords: activated carbon, adsorption, cyanotoxins, tastes and odours, water treatment

INTRODUCTION

Tastes and odours and toxic compounds in source water are a constant concern for Australian drinking water authorities. These problem compounds come in a range of shapes, sizes and structural characteristics and are produced by a variety of organisms - for example, cyanobacteria, benthic algae and bacteria. The major factors that influence the effectiveness of powdered activated carbon (PAC) for the treatment of these compounds are:

- Structure of the compound
- Pore volume distribution of the PAC
- Surface chemistry of the PAC
- Contact time in the water treatment plant
- Other dissolved organic compounds competing for adsorption sites.

In this study a range of commercially-available activated carbons, with a wide range of surface properties, were tested for the removal of musty-earthy odour compounds geosmin and 2-methylisoborneol (MIB) and the saxitoxin group of neurotoxic algal toxins. The results of previous studies on the hepatotoxin microcystin-LR¹ were also reviewed, and recommendations for the choice of activated carbon for the removal of a range of naturally-occurring micropollutants were proposed.

RESULTS

Figure 1a) shows the percent removal of MIB achieved by four activated carbons at equilibrium. The experiments were undertaken in Myponga Reservoir water, a surface drinking water source in South Australia. There is a wide range of percent removals, with the chemically-activated wood-based carbon, HP, showing significantly lower adsorption than the other three adsorbents. In contrast, the kinetics of adsorption on HP are very rapid, and at short contact times it is superior to two of the other carbons (Figure 1b)). The low equilibrium percent MIB removal for HP is most likely due to the more hydrophilic surface, which is not amenable to the adsorption of MIB². Conversely, the large volume of mesopores (width 2-50 nm) and macropores (width >50 nm) in HP³ promotes the diffusion of small compounds such as MIB (molecular weight 168 g mol⁻¹), and results in very efficient transport to adsorption sites. Geosmin adsorbs in a similar manner to MIB, and displays the same effect of transport pores. Results of previous studies on microcystin-LR (molecular weight 994) indicated that the adsorption of the toxin was strongly influenced by the pore volume of the activated carbon and that the larger transport pores were necessary for efficient adsorption at both long and short contact times¹. Therefore the activated carbon recommended for the removal of MIB and geosmin will depend strongly on contact time. At very short contact times a good carbon for the removal of MIB and geosmin would contain a high volume of large pores. The same carbon would also be effective for the removal of microcystin LR. The recommendation at longer contact times may change according to activated carbon contact time available at the water treatment plant for the odour compounds, whereas for microcystin LR it would remain the same.

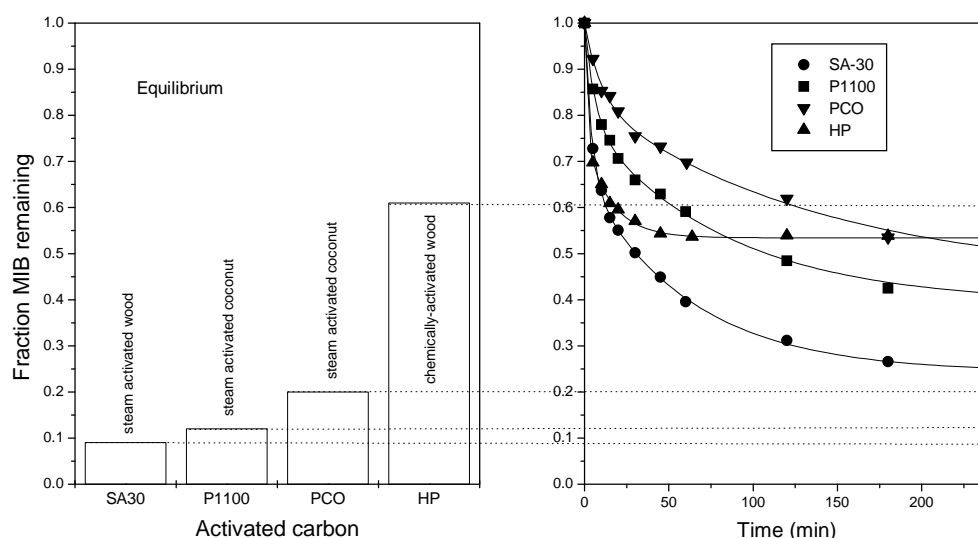


Figure 1. a) Fraction remaining of MIB at equilibrium, and b) fraction MIB remaining vs time for four activated carbons

The saxitoxins are a group of carbamate alkaloids ranging in molecular weight from 176 to 369. They can have a net charge of +2, +1 or 0. The structures can be found in Humpage *et al.*⁴. Preliminary results, obtained at 1 hr contact time, have shown that even at short contact times the most effective activated carbon would be a microporous (pore width <2 nm), hydrophobic carbon such as SA30, P1100 or PCO.

It is possible that a water treatment plant experiencing a range of problems caused by cyanobacteria will require a blend of suitable activated carbons, and these will depend on the particular conditions existing in the treatment train and the compounds to be removed.

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PREDICTING PAC DOSES FOR THE REMOVAL OF ALGAL METABOLITES: HOW CAN NOM CHARACTERISATION TECHNIQUES HELP US?

Extended abstract, CRC WQT/AwwaRF Workshop Relating NOM Characteristics to Improve Water Treatment Process Selection and Performance, 10-12 October 2001, Berlin, Germany

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INTRODUCTION

Removing taste and odour compounds from drinking water is a challenge. In particular, 2-methylisoborneol (MIB), and geosmin, secondary metabolites of some algae and bacteria, can be detected by consumers at levels as low as 10 ngL^{-1} as a musty odour. Therefore the treatment method for these compounds must be very effective. The major inhibition to the removal of MIB and geosmin using activated carbon is the presence of dissolved natural organic material (NOM), which is found in drinking water sources at levels generally between 2 and 15 mgL^{-1} . Even at the low end of the range, NOM concentrations are at least several tens of thousands times that of the target compounds. NOM is composed of a very complex mixture of organic compounds ranging in Australian waters from a few hundred to ten thousand g mol^{-1} . The important mechanisms proposed for the effect of NOM on microcontaminant adsorption are:

- pore blockage and
- direct competition for adsorption sites¹.

It is generally considered that the larger molecular weight compounds could block pores, and the smaller molecular weight NOM may directly compete for adsorption sites with a low molecular weight compound such as MIB (168 g mol^{-1}). The relative importance of each of these mechanisms will depend on the type of NOM and the surface characteristics of the activated carbon. The aim of this work was to identify and characterise the compounds in the NOM providing the most competition with MIB, and to develop tools for the drinking water supplier to enable the prediction of required powdered activated carbon doses under a range of water quality conditions. Geosmin, with similar structure and adsorption properties, can be expected to behave similarly.

RESULTS AND DISCUSSION

Table 1. Description of NOM solutions obtained from Myponga Reservoir water.

NOM solution	Isolation technique	Percentage of whole water NOM	Fraction
F1	anion exchange resin	15	<500 g mol ⁻¹ (ultrafiltration)
F2	anion exchange resin	45	500-1000 (ultrafiltration)
F5	anion exchange resin	15	>30000 (ultrafiltration)
Effluent	NOM remaining after ion exchange	32	Whole isolate
Whole water	none	100	Whole water
diluted	none	100	50% dilution whole water

Figure 1 shows the adsorption isotherms of MIB in the presence of the six NOM solutions. The activated carbon used was a high activity coconut-based carbon. Table 2 shows the DOC concentrations of each solution, and concentrations of the competing part of the NOM, -or equivalent background compound (EBC). The EBC values were calculated using Ideal Adsorbed Solution Theory (IAST) in combination with the EBC model (1). Table 3 shows the specific UV absorbance (SUVA) of the NOM solutions and the PAC doses required to reduce MIB concentration from 20 to 10 ng L⁻¹ in one hour. Using the isolation techniques of anion exchange, we were able to identify the most competitive fraction of the whole water NOM, that is the fraction that did not adsorb onto the resin, or the effluent. The resin removed approximately 70% of the DOC, and only 20% of the competitive compounds. The inference from this data is that the most competitive compounds are those with low molecular weight, low charge, low SUVA. However, bulk characterisation techniques, such as DOC, UV and SUVA are not suitable for the accurate prediction of the competitive effects of NOM, as the competitive fraction is at most 10% of the whole NOM (Table 2). Figure 2 illustrates this point, with the hydrophobic, high SUVA DAX 8 fraction offering more competition than the XAD 4 fraction, with lower SUVA. However, further fractionation of the DAX 8 fraction leads to the conclusion that, although the isolate has a higher concentration of high molecular weight, high SUVA compounds, it also has a higher concentration of smaller, low molecular weight compounds, those providing the most competition (2). More sophisticated techniques such as high performance size exclusion chromatography, can give some insight, although the data is restricted in value as it is reliant on the UV absorbance of the NOM, and the most competitive fraction of the whole water NOM is of low UV absorbance (Figure 3). HPSEC with DOC detection would be of value, however this technique is not readily available to the scientific community, so it is certainly not an option for water treatment operators. A range of whole reservoir waters has also been studied and at present DOC concentration appears to be the most useful, although not very accurate, predictor of competitive effects in a practical situation.

	DOC	EBC
Whole water	12	1.3
Effluent	4	0.72
Diluted	6	0.24
F1	10	0.18
F2	10	0.05
F5	10	0.01

Table 2. Initial DOC and EBC concentrations. in mg L^{-1} assuming molecular weight of competing substances = 300 g mol^{-1} and mass C=50% mass NOM.

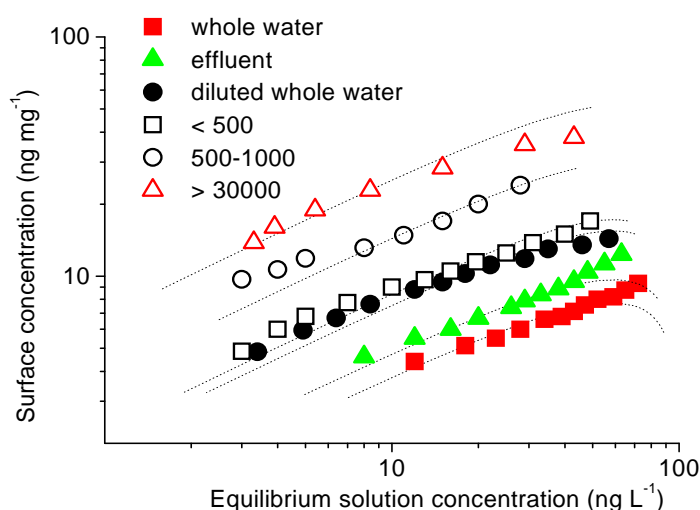


Figure 1. Adsorption isotherms of MIB in 6 NOM solutions.

 Table 3. DOC and SUVA of NOM solutions, and carbon doses required to reduce MIB concentration from 20 to 10 ng L^{-1} in one hour.

NOM solution	Raw	Dilute	Effluent	F1	F2	F5
DOC concentration (mg L^{-1})	12	6	4	10	10	10
SUVA	3.5	3.5	1.5	3.7	3.9	4.6
Carbon dose (mg L^{-1})	31	20	22	11	9	3

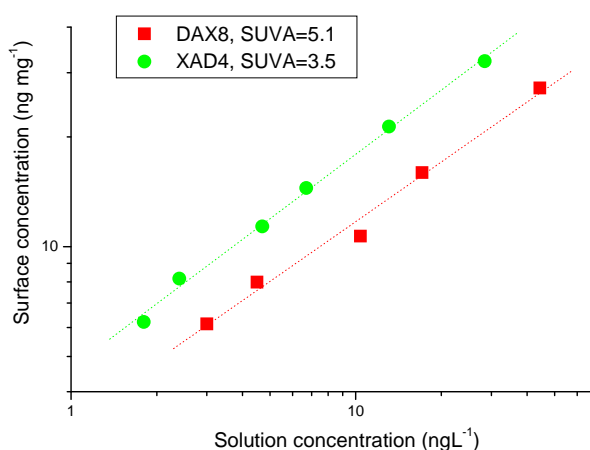


Figure 2. MIB adsorption isotherms in two NOM solutions

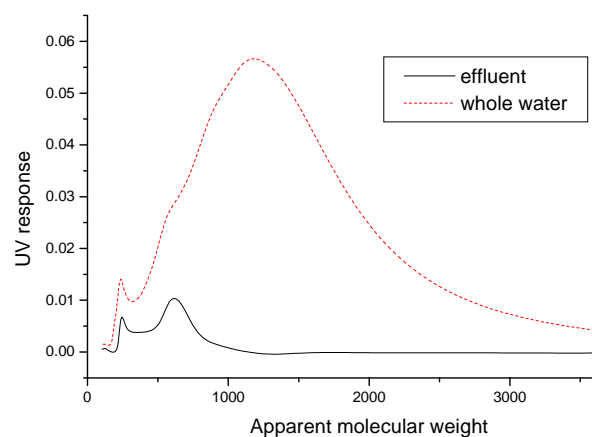


Figure 3. HPSEC of two NOM solutions providing high competition for MIB.

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NOM AND MIB, WHO WINS IN THE COMPETITION FOR ACTIVATED CARBON ADSORPTION SITES?

Extended abstract, Proceedings of The Sixth iwa Symposium on Off-Flavours in the Aquatic Environment, Barcelona, October 2002

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Keywords: activated carbon, adsorption, natural organic material, tastes and odours, water treatment

INTRODUCTION

Removing taste and odour compounds from drinking water is a challenge. In particular, 2-methylisoborneol (MIB) can be detected by consumers at levels as low as 10 ngL^{-1} as a musty odour; therefore the treatment method for this compound must be very effective. The major inhibition to the removal of MIB using activated carbon is reduced adsorption due to the presence of dissolved natural organic material (NOM), which is found in drinking water sources at levels generally between 2 and 15 mgL^{-1} . Even at the low end of the range, NOM concentrations are at least several tens of thousands times that of the problem compound.

NOM is composed of a very complex mixture of organic compounds ranging in Australian waters from a few hundred to ten thousand gram mol^{-1} . The important mechanisms proposed for the effect of NOM on micropollutant adsorption are:

- pore blockage and
- direct competition for adsorption sites.

It is generally considered that the larger molecular weight compounds could block pores, and the smaller molecular weight NOM may directly compete for adsorption sites with a low molecular weight compound such as MIB ($168 \text{ gram mol}^{-1}$). The relative importance of each of these mechanisms will depend on the type of NOM and the surface characteristics of the activated carbon. This work identifies and characterises the compounds in the NOM providing the most competition with MIB, and describes the effect on kinetics and equilibrium of adsorption of MIB onto two very different activated carbons.

THE ACTIVATED CARBONS

Table 1. Starting materials, activation methods and surface charge of the two activated carbons.

	Raw material and activation	Surface charge, pH 7.5 (meqg ⁻¹)
Carbon 1	Steam activated coconut	-0.30
Carbon 2	Chemically-activated wood	+0.03

Table 1 gives the starting materials, activation methods and surface charge of the two activated carbons. Figure 1 shows the pore volume distributions of the carbons and Figure 2 shows the infrared spectra. The two adsorbents are clearly very different in terms of their physical and chemical surface characteristics.

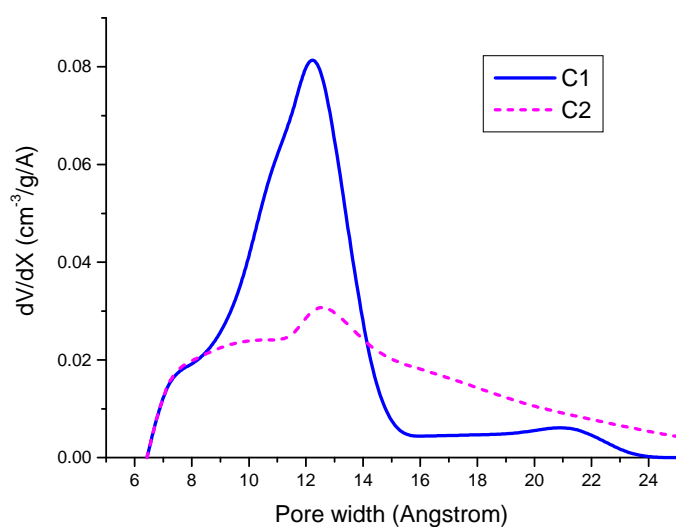


Figure 1. Pore volume distributions of the carbons

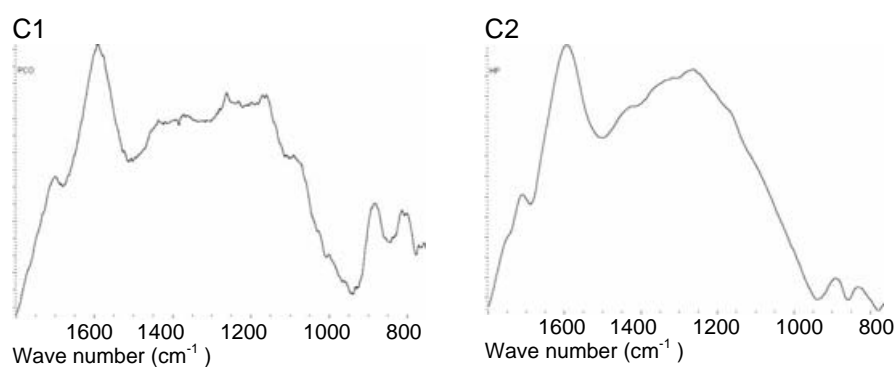


Fig. 2. Infrared spectra of activated carbons.

THE NATURAL ORGANIC MATERIAL

A total of 13 NOM fractions and raw waters were investigated in this study. The NOM isolates were obtained using three resin adsorption techniques - anion exchange, DAX 8 resin and XAD 4 resin - and the isolates were then fractionated according to molecular size using ultrafiltration. High performance size exclusion chromatograms in Figure 3 show the apparent molecular weight distributions of two of the NOM fractions. Molecular weight distributions, solid state ^{13}C NMR and ultraviolet absorbance spectra (not shown), for all fractions indicate large differences in the character of the NOM used for adsorption studies.

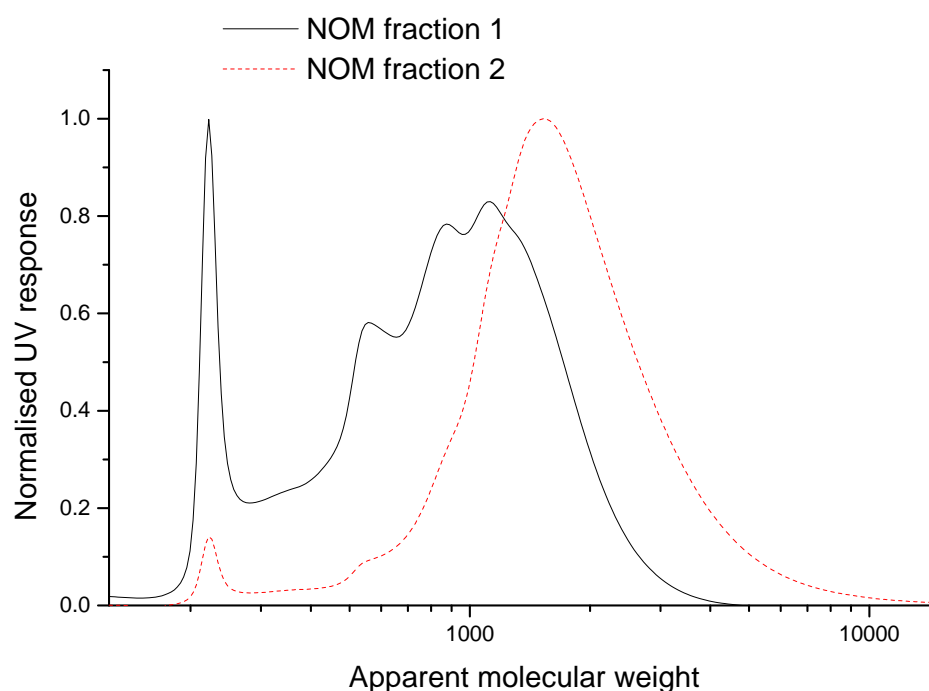


Figure 3. Molecular weight distributions of two NOM fractions. Fraction 1-DAX 8 resin, <500 molecular weight ultrafiltration fraction, Fraction 2-Anion exchange resin, >30000 molecular weight fraction

COMPETITIVE ADSORPTION

Figure 4 illustrates the effect of the different NOM character on the equilibrium adsorption of MIB onto carbon 2. NOM Fraction 1 produces the greatest competition for adsorption sites, evidenced by the lowest surface concentration of the adsorption isotherms. As this isolate contains mainly low molecular weight compounds the results indicate that these exert the major influence on adsorption of MIB. The results for the other fractions support this. The results for carbon 1 also suggest the major influence on competition at equilibrium is the concentration of low molecular weight compounds, particularly those of similar size and character to MIB itself. However, the higher molecular weight compounds influence the kinetics of adsorption onto the carbon with the greater volume of larger pores, carbon 2. For this carbon, the equilibrium value of the adsorption is higher in the presence of the high molecular weight compounds, but it takes longer to reach that value than in the presence of low molecular weight NOM. This is interpreted as pore restriction, where the high molecular weight compounds hinder the kinetics of adsorption while exerting no influence on the equilibrium adsorption. Carbon 1, with negligible mesopore volume is not affected, as the larger molecules cannot enter the very narrow pore structure.

OPTIMISATION OF ADSORPTION PROCESSES

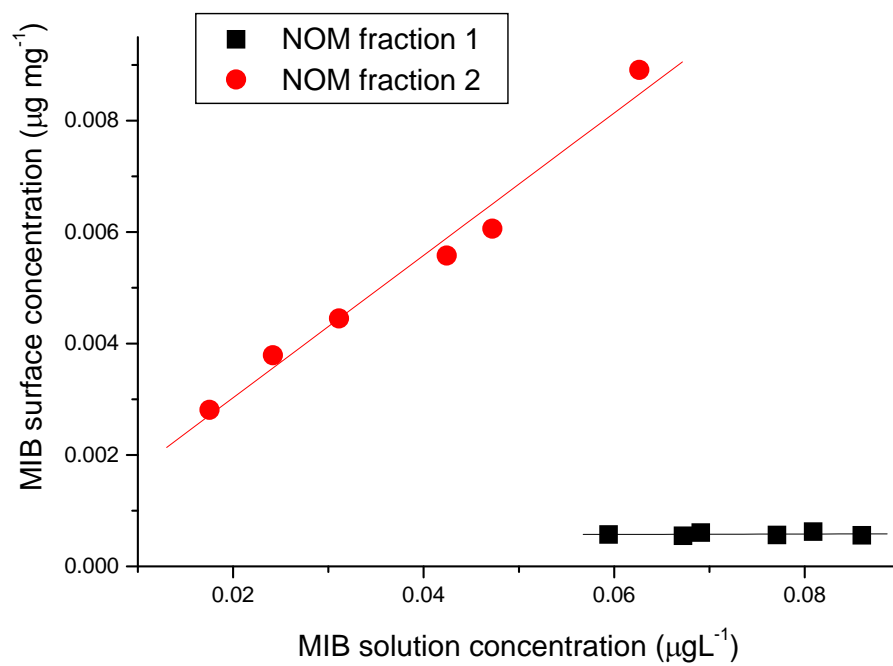


Figure 4. Adsorption isotherms of MIB onto carbon 2 in the presence of NOM fractions 1 and 2



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CRC for Water Quality
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The Cooperative Research Centre (CRC) for Water Quality and Treatment operated for 13 years as Australia's national drinking water research centre. It was established and supported under the Australian Government's Cooperative Research Centres Program.

The CRC for Water Quality and Treatment officially ended in October 2008, and has been succeeded by Water Quality Research Australia Limited (WQRA), a company funded by the Australian water industry. WQRA will undertake collaborative research of national application on drinking water quality, recycled water and relevant areas of wastewater management.

The research in this document was conducted during the term of the CRC for Water Quality and Treatment and the final report completed under the auspices of WQRA.

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