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By
Megan Denise Storrar
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Abstract

The objective of this thesis was to study the adsorption and desorption characteristics of natural organic matter (NOM) adsorbed on granular activated carbon (GAC). Five different natural waters (Ottawa River, ON; St. Lawrence River, ON; Vars Ground Water, ON; Buffalo Pound Lake, SK; Ohio River, OH) were studied to see if the characteristic of irreversible adsorption was a universal phenomenon. This was studied by comparing desorption isotherms to adsorption isotherms. Preliminary long-term kinetic studies were used to ensure that the contact time was sufficient for equilibrium. The waters were also fractionated to further study the differences in adsorption and desorption properties of various surface waters. The fractionation techniques used were; ultrafiltration by membrane separation, extraction of humic acids using a methylmethacrylate resin (XAD8) and size exclusion chromatography using a sephadex gel in a glass column.

Using Calgon F- 400 carbon (40 X 50 mesh) and a dosage of 0.03 g/l in batch reactors, the contact time required to equilibrium for adsorption was found to be 30 days. By transferring the carbon from adsorption testing into organic free water, a desorption kinetics experiment was conducted. The time required for desorption equilibrium was found to be 60 days.

Adsorption isotherms were completed with the five waters using Calgon F- 400 carbon (40 X 50 mesh). The Freundlich isotherm, fitted via a non-linear regression routine in Microsoft Excel, fit all waters. The isotherms were all found to have an unfavourable

shape, which suggested that the NOM was made up of fractions that adsorbed differently. The results of an adsorption isotherm conducted with Ottawa River water that had been stored in a refrigerator for 10 months differed from those of an isotherm conducted with the same water shortly after sampling. This suggested that NOM changes over time even when the water samples are refrigerated. The second isotherms also required a much higher dosage of GAC per volume to define the non- adsorbing NOM fraction.

Ottawa River water isotherms were conducted with two different GAC's, Calgon F-400 (coal based) and Westvaco WV-B (wood based). There was little difference between the coal and wood based GACs for the initial isotherms. However, for the second set of isotherms, wood based GAC achieved higher solid phase concentrations than the coal based GAC, with the same amounts of GAC and Ottawa River water.

Desorption isotherms were mostly irreversible, with some partially reversible points. The majority of partially reversible data points were found for Buffalo Pound Lake and Vars ground water. Partial reversible isotherms were only found at lower GAC dosages. those data points with a higher liquid phase equilibrium concentration in the adsorption isotherm.

Ohio River water and St. Lawrence River water, which had the lowest dissolved organic carbon (DOC) values, had large portions of high molecular weight NOM based on ultrafiltration fractionation and confirmed from size exclusion chromatography. The Buffalo Pound Lake and Vars ground water both had about 50% of the NOM greater than 500 Da but less than 1.000 Da. The Ottawa River had an even distribution of all

ultrafiltration fractions.

Extraction of humic acids with XAD8 resulted in a proportional relationship between DOC and the percentage of humic acids in the water. VGW and BPLW both had large humic acid fractions although the ultrafiltration results found a large portion of small molecular weight NOM for both water sources. The equilibrium liquid phase from adsorption isotherms had a large percentage of humic acids, therefore much of the humic acids did not adsorb into the GAC. Equilibrium liquid phase samples from desorption isotherms also had a large fraction of humic acids. Therefore, fulvics were found to be more irreversible than humic acids for all waters except Buffalo Pound Lake. For humic acids the opposite was true, humic acids were found to be more reversible than fulvic acids for all waters with the exception of Buffalo Pound Lake.

Size exclusion chromatography (SEC) resulted in distinct spectra for all of the natural waters and fulvic acid fractionation samples. The natural waters had peaks between 6200 Da and 900 Da. Fulvic acid samples had peaks in the range of 4950 Da (Ohio River), 3750 (St. Lawrence River), and 2930 – 1850 for all the other waters. The results from SEC were comparable to the UF fractionation and therefore both methods are useful fractionation techniques to estimate molecular size distributions of NOM.

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This Thesis is dedicated to the memory of Dr. Robert Guerriere.

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Nomenclature

ε_b= the void space in the reactor

ρ_s = density of the GAC

A_λ = the absorbance at this wavelength (m^{-1})

b = the energy constant (cm^3/g)

C_{eq} = the equilibrium liquid phase in batch reactor during adsorption isotherms, mass of contaminant / volume

C_{eq}'= the liquid phase in equilibrium during desorption isotherms, mass of contaminant / volume

d_p = diameter of the GAC particle

d_{40} = width of squares in the mesh of US sieve size 40

d_{50} = width of squares in the mesh of US sieve size 50

E_λ = energy of light quanta at this wavelength(eV)

K = Freundlich isotherm regressed constant

L = volume of solution added to the batch reactor

M = mass of GAC added to the batch reactor

n = Freundlich isotherm regressed constant

Q_{eq} = the solid phase in equilibrium, mass of contaminant / mass GAC

Q_M = Langmuire isotherm regressed constant, the monolayer adsorption capacity (g/g)

t = time

Subscripts

b = bed

f = fluid

s = solid

p = particle

λ = wavelength

eq = equilibrium

Acronyms

AC - Activated Carbon

BPLW - Buffalo Pound Lake Water, Buffalo Pound Provincial Park, Saskatchewan, Canada

Bz - Benzenoid Band

DOC – Dissolved Organic Carbon

DOM - Dissolved Organic Matter

DPB – Disinfected By-product

ET – Electron Transfer Band

GAC - Granular Activated Carbon

GFC - Gel Filtration Chromatography

GPC - Gel Permeation Chromatography

HS - Humic Substances

HSDM - Homogeneous Surface Diffusion Model

IAST - Ideal Adsorbed Solution Theory

LE - Local-Excitation Band

MSD - Molecular Size Distribution

MWCO - Molecular Weight Cut Off

MWD -Molecular Weight Distribution

NOM - Natural Organic Matter

OFW - Organic Free Water

OHRW - Ohio River Water, Cincinnati, Ohio, U.S.A.

ORW - Ottawa River Water, Ottawa, Ontario, Canada

PAC - Powdered Activated Carbon

PSS - Polystyrene Sulfonates

PVD – Pore Volume Distribution

SEC - Size Exclusion Chromatography

SLRW - St. Lawrence River Water, Cornwall, Ontario Canada

TOC – Total Organic Carbon

UF - Ultrafiltration

UV - Ultra Violet Absorbance

VGW - Vars Groundwater, Vars, Ontario Canada

WTP - Water Treatment Plant

Definitions

Adsorbate - a material that has been or is capable of being adsorbed

Adsorbent - an adsorptive material, such as activated carbon

Adsorption - the selective removal of a component of a fluid mixture (liquid or gas) on a solid interface

Chromaphores - the functional groups that absorb UV light

Daltons - atomic mass unit, unit of mass for expressing masses of atoms or molecules

Desorption - changing from an adsorbed state on a surface to it's original phase

Fulvic Acid - the fraction of NOM that is soluble in water at pH < 2 (hydrophilic fraction)

Humic Acid - the fraction of NOM that is not soluble in water at pH < 2 (hydrophobic fraction)

Humin - the fraction of NOM that is not soluble in water at any pH

Hysterisis – when the relationship between two variables as a parameter increases or decreases is not unique, the value of one variable depends upon whether the other has been increasing or decreasing

Square Residual - square of the value resulting when predicted values are subtracted from experimental data

Sum of the Square Residual – summation of all square residuals in a data set

Chapter 1: Introduction

Activated carbon (AC) is recommended for removal of trace levels of toxic organic contaminants, as well as taste and odour causing molecules, in drinking water. The high surface area of this material makes it an ideal adsorbent of contaminants but also makes it non-selective. It will remove most compounds in the water source including natural organic matter (NOM).

NOM is not harmful on its own but interferes with the treatment of drinking water in several ways. NOM can combine with chlorine or ozone to create potentially toxic compounds called disinfection by-products (DBPs). NOM also chemically attaches to and holds dissolved toxic metals such as methyl mercury. When AC is used in drinking water applications, NOM strongly competes for adsorption sites and significantly reduces the removal of other target contaminants.

Granular activated carbon (GAC) is often used in water treatment plants as independent filters or as a top layer in mixed media filters. Since the purchase of new GAC is a substantial capital cost, once the active sites have been used GAC is often regenerated on site. For example, furnaces are used for GAC regeneration at the Richard Miller Water Treatment Plant in Cincinnati, Ohio, and at the Buffalo Pound Water Treatment Plant in Saskatchewan. Unfortunately thermal reactivation results in GAC losses of 5 – 15% resulting from transport of the GAC to and from the furnace, as well as losses within the furnace. Reactivation from other techniques such as pH driven desorption obtained by washing the GAC with acidic then basic baths, or electrochemical treatments would be

more economical (McEwen, 2004). Electrochemical regeneration is currently in a development stage.

Past research at McMaster University (Narbaitz, 1986) and at the University of Ottawa (McEwen, 2004) found that the adsorption of NOM on GAC in natural waters is only partially reversible. In particular, research on an electro-cell regeneration technique, conducted at the University of Ottawa by McEwen (2004), found that the regeneration of GAC from drinking water treatment was not as successful as the thermal regeneration in industrial applications. One of McEwen's conclusions was that this was due to the NOM being only partially reversible.

The objective of this thesis was to conduct an in depth study of the adsorption and desorption characteristics of NOM on GAC. The purpose of the research was to find out if NOM desorbs from GAC when loaded GAC is placed in a batch reactor with organic free water, and if so what parts of NOM desorb most readily. All experiments were carried out at room temperature and the natural pH values of the waters. The result of this work will aid others in developing economical regeneration techniques for GAC used to treat natural waters, as well as answer many questions about NOM desorption for other research areas. In particular, the knowledge of which fractions of NOM are more adsorbable and less desorbable will aid in studies of competitive adsorption, regeneration techniques and novel GAC manufacturing.

The experimental plans consisted of a laboratory study, modeling of adsorption and desorption equilibrium of NOM from five different waters and fractionation of the NOM. Since the water sources were filtered by sand filters, or 45μm filters, the NOM was

considered *dissolved* organic matter (DOM). Thus, either of these acronyms could be used throughout this thesis. However, to simplify discussion, the acronym NOM was used preferentially.

To test the universality of the results, experiments were conducted with these five different waters:

- Buffalo Pound Lake, Buffalo Pound Provincial Park, Saskatchewan, Canada
- Ottawa River, Ottawa, Ontario, Canada
- Vars Groundwater, Vars, Ontario, Canada
- St. Lawrence River, Cornwall, Ontario, Canada
- Ohio River, Cincinnati, Ohio, U.S.A

This work was completed in four phases to discuss and investigate the following queries.

1. How long does it take for NOM and GAC to come to equilibrium during the *adsorption* process?
2. How long does it take for GAC and organic free water to come to equilibrium during the *desorption* process?
3. Is the irreversible adsorption behavior of NOM universal?
4. What part of NOM does not easily adsorb?
5. What part of NOM easily adsorbs?
6. What part of NOM does not easily desorb? What part of NOM, if any, easily desorbs?
7. Is there a difference between wood and coal GAC and adsorption behavior?

Chapter 2: Literature Review

This literature review has been divided into five sections that were considered most relevant to this thesis topic. These five subjects are descriptions of; adsorption, desorption, GAC, NOM characteristics and the adsorption and desorption of NOM on GAC. These topics are discussed in the following sections.

2.1 Adsorption

Adsorption is defined as the selective removal of a component of a fluid mixture (liquid or gas) on a solid adsorbent (McKay, 2001). Activated carbon (AC) is the most commonly used adsorbent in water treatment processes. Although adsorption has been used for the treatment of contaminants in liquids and gases for decades, there are still many unanswered questions regarding the particulars of adsorption mechanisms. Some applications include the purification of drinking water, removing pollutants from wastewater effluents, removing ash and other impurities from raw materials for food production, and air pollution control.

Two different types of adsorption processes, chemisorption and physical adsorption, have been used to describe adsorption. If physical adsorption occurs, there is no change in chemical composition of the adsorbate and the process is reversible. With chemisorption adsorption, molecular structures of the adsorbate can change and this kind of adsorption is not always reversible (Sontheimer *et al.*, 1988). It is not known which type of

adsorption NOM/GAC processes follow; however the process is thought to fall somewhere between the two. GAC preloaded with NOM can be regenerated but the desorption process must be initiated with heat or pH change and is not spontaneous. The one conclusion many research sources have in common is that the actual attachment rate of the contaminant onto the GAC is so much faster than the diffusion rate that it is considered to be instantaneous in mass transfer models (Sontheimer *et al.*, 1988).

Although the use of activated carbons to adsorb trace contaminants is a very effective treatment, the design of these reactors can be costly. Designs include year-long pilot plant studies to incorporate seasonal variations and thus yield more reliable results. The use of mathematical models to predict GAC column performance can save money and time but they require an input of equilibrium models (Sontheimer *et al.*, 1988; Weber and Thaler, 1983). Some of these equilibrium models are described in the following sections.

2.1.1 Equilibrium of Adsorption Processes

The performance of GAC columns are highly dependent on the adsorption equilibrium behaviour of NOM as well as GAC properties and adsorption kinetics. These columns have transient behaviour. The transient changes in the effluent concentration are referred to as the breakthrough curve. From pilot-plant studies, it is this breakthrough curve which is one of the most critical aspects of adsorption system scale up (Weber and Thaler, 1983). GAC column performance, as illustrated in figure 2.1, usually follows these steps:

1) The column has an initial breakthrough of NOM in the effluent. This is referred to as the nonadsorbable substances (Sontheimer *et al.*, 1988) and is shown in figure 2.1 as

the concentration C1. NOM is generally quantified in terms of dissolved organic carbon (DOC) concentration.

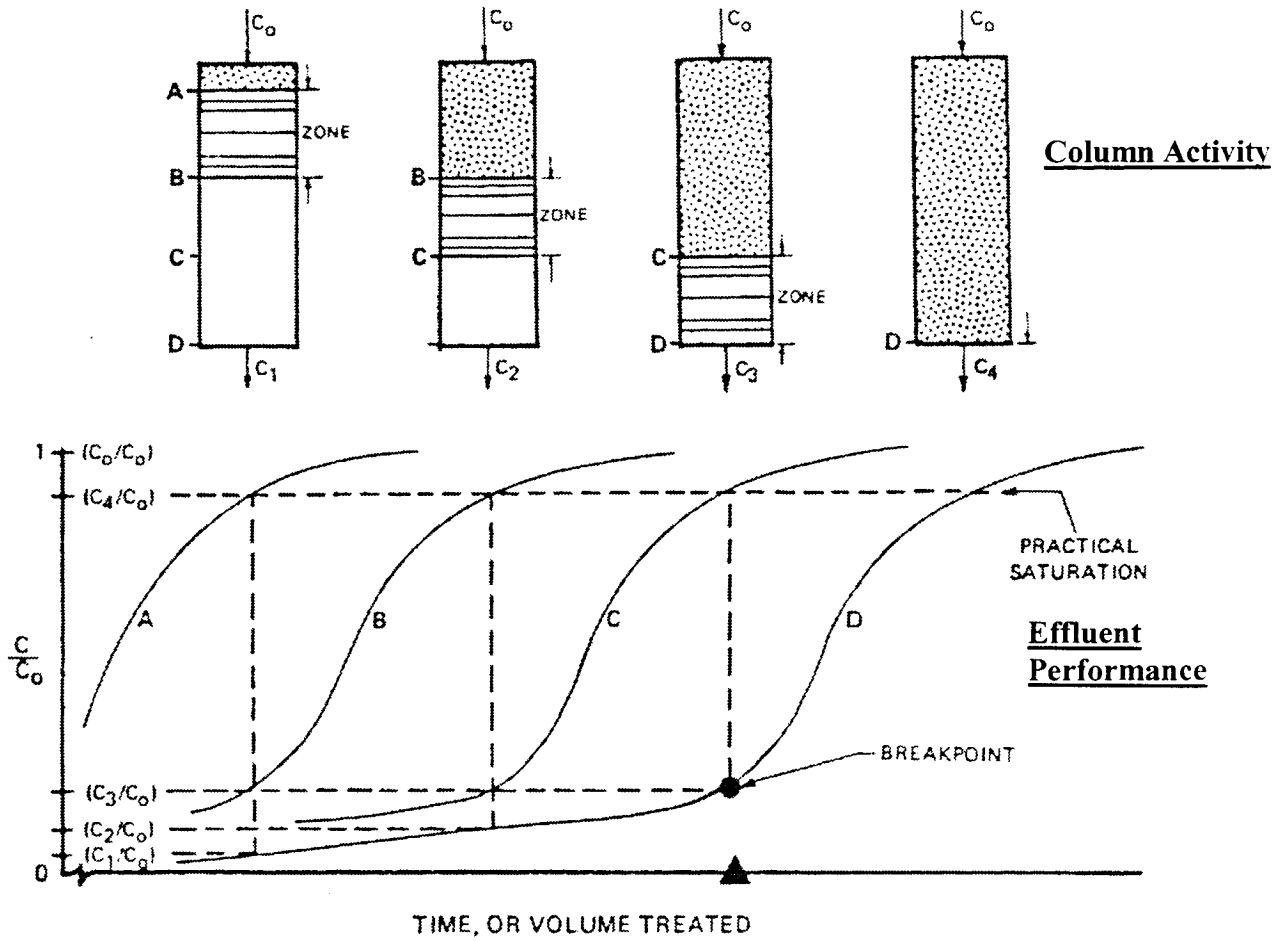

Figure 2.1: Schematic of Mass Transfer Zone (Source, Weber and Thaler, 1983)

2) Over time the effluent DOC concentrations increase to a relatively steady state condition. The effluent is shown in figure 2.1 as the curve labelled 'D', which corresponds to the concentrations at point 'D' of the column in the schematic. The

point labelled 'breakpoint' represents the point when the column is no longer meeting the treatment objective. (which is defined in drinking water treatment by regional quality guidelines)

3) The DOC values in the effluent then increase according to a concentration profile between 50 – 90 % of the initial concentration (Sontheimer *et al.,* 1988). This concentration profile is referred to as the breakthrough curve and is shown as the S-shaped curve D in figure 2.1. The depth of the column that has transient behavior is called the mass transfer zone (Weber and Thaler, 1983; Sontheimer *et al.,* 1988). In figure 2.1, the mass transfer zone has been labelled 'zone'. For some systems the mass transfer zone will grow in depth over time, for others it will remain the same depth and move through the column until the effluent is that of the top of the mass transfer zone. Steady state conditions develop when sufficient time has passed so the adsorption capacity is virtually exhausted and a large bacterial population has developed that removes a fraction of the DOC (Peel, 1980).

4) Other substances, such as the target pollutants, in the water will also start to appear in the effluent. Substances that are poorly adsorbing will be displaced by the competing strongly adsorbable organics and start appearing in the column effluent. In many cases the displacement is so significant that the effluent concentration of the target compound exceeds that in the influent. This is referred to as a chromatographic effect.

To predict the performance of a GAC column, the equilibrium relationships between the GAC and the adsorbate are studied. The resulting phase diagram has the solid phase equilibrium concentration as the ordinate and the equilibrium liquid phase concentration

as the abscissa. It is called an isotherm and derives its name from the fact that the experiment is conducted at a constant temperature. The data for the isotherm graph is generally derived from batch tests, frequently conducted via the bottle-point method. Each data point is the result from contacting the solution of interest with a given mass of GAC for a sufficiently long time to achieve equilibrium. Many bottles containing different masses of AC are used to develop the equilibrium (isotherm) curve. At the end of the contact period the liquid is separated from the AC (i.e., the adsorbent) and the contaminant concentration (i.e., the adsorbate) is measured. The solid phase concentration is immeasurable and is therefore calculated via a mass balance on the system.

A second method used to conduct isotherms is to keep the mass of carbon constant but to vary the concentrations of the solution. Points for the isotherm plot can also be obtained via continuous-flow column experiments.

When the fluid phase is in equilibrium with the GAC the results follow three common trends as shown in figure 2.2. The three trends as illustrated in figure 2.2 are linear, unfavourable and favourable isotherms. The linear isotherm is considered the borderline between unfavourable and favourable isotherms. Favourable and unfavourable isotherms relate to the characteristics of the concentration profile (breakthrough curve) seen in the effluent of GAC columns. Favourable isotherms result in columns that have a constant size mass transfer zone. Systems with unfavourable isotherms have mass transfer zones within GAC filters that increase in depth over time (Sontheimer *et al.*, 1988).

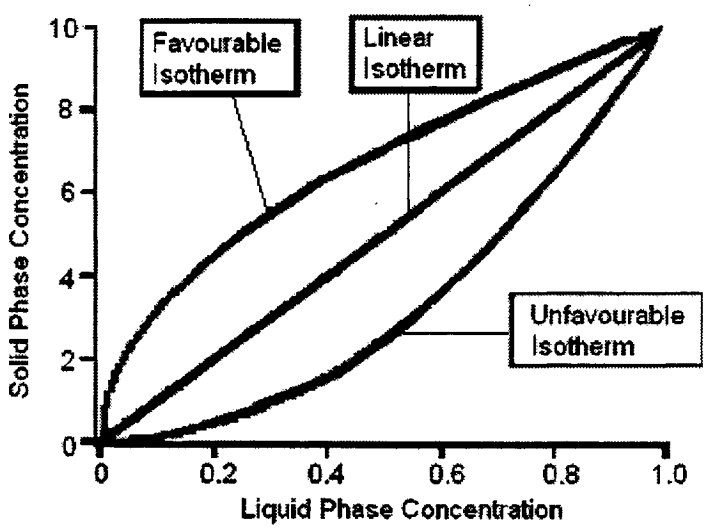

Figure 2.2: Traditional Isotherm Types (Source, modified from Narbaitz, 1986)

There are many different empirical models used to describe isotherms, the two most common isotherm models are the Langmuir and the Freundlich models. All isotherm models are calculated by fitting experimental data to the equilibrium equation and solving for the regressed constants.[1] Figure 2.3 illustrates a more detailed look at isotherm trends in dilute mixtures.

The linear type of isotherm, as shown in figure 2.3, is present in the high carbon dosage area of all isotherms (lower liquid phase concentrations at equilibrium). It is what happens at lower dosages, which determines the shape of the final isotherm. Some will

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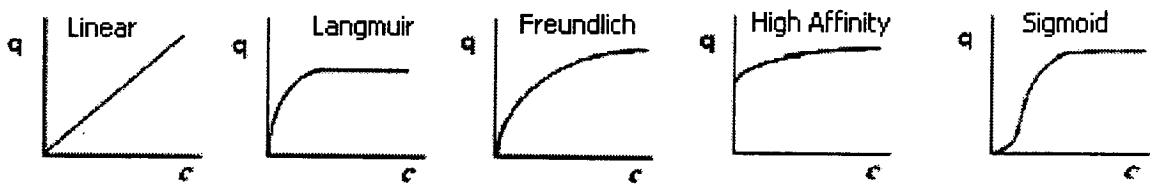
[1] Close attention must be paid to the units of all of these parameters. Once a set of units has been chosen, some parameters may need conversion factors.

stay linear, although this is not common. The Freundlich isotherm suggests that the surface of the carbon is heterogeneous and the sigmoidal and Langmuir isotherms suggest the opposite, that the surface is homogeneous (Moreno - Castilla, 2004).



q = solid phase (mg contaminant/g solid
c = liquid phase (mg contaminant/l of solution)

Figure 2.3: Isotherm Types (Source, Moreno- Castilla, 2004)

The linear type of isotherm, as shown in figure 2.3, is present in the high carbon dosage area of all isotherms (lower liquid phase concentrations at equilibrium). It is what happens at lower dosages, which determines the shape of the final isotherm. Some will stay linear, although this is not common. The Freundlich isotherm suggests that the surface of the carbon is heterogeneous and the sigmoidal and Langmuir isotherms suggest the opposite, that the surface is homogeneous (Moreno - Castilla, 2004).

Initial concentrations of NOM and pH, as shown in figures 2.4 and 2.5, affect isotherm shapes and the adsorbability of the DOC (Sontheimer *et al.,* 1988). Shown in figure 2.4, humic substances were used to simulate NOM at different initial concentrations. Varied

doses of Fuhrberg humic substances[2] were diluted in organic free water and brought to equilibrium with the same GAC. The result was isotherms that shifted and changed shape. Figure 2.5 shows the results from isotherms using Lake Constance water in West Germany at different pH values. The change in pH transformed the isotherm from a favourable shape at ph 3 to an unfavourable isotherm shape at pH values of 7 and higher.

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[2] Furhberg humic substances are separated from groundwater in Furhberg Germany and used in the preparation of *simulated* natural water. This procedure is more predictable because researchers know exactly what is in the water.

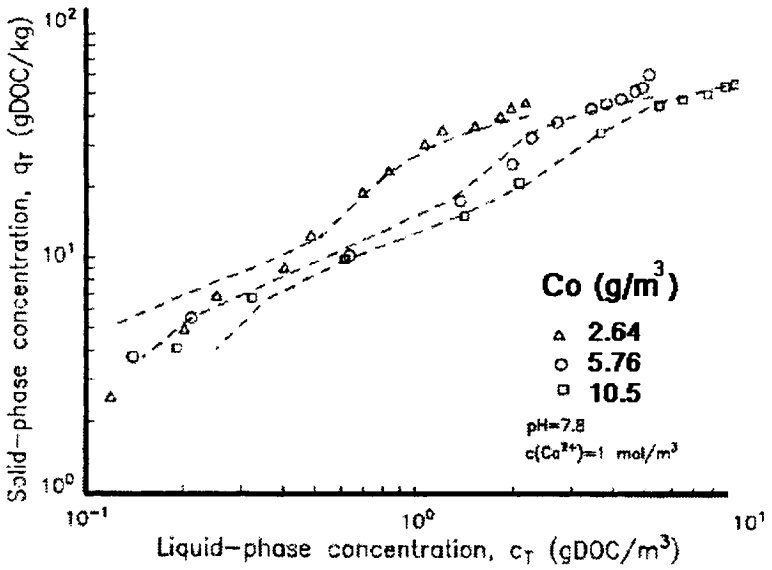

Figure 2.4: Affect of Concentration of Humics on Isotherms (Source, Sontheimer *et al.*, 1988)

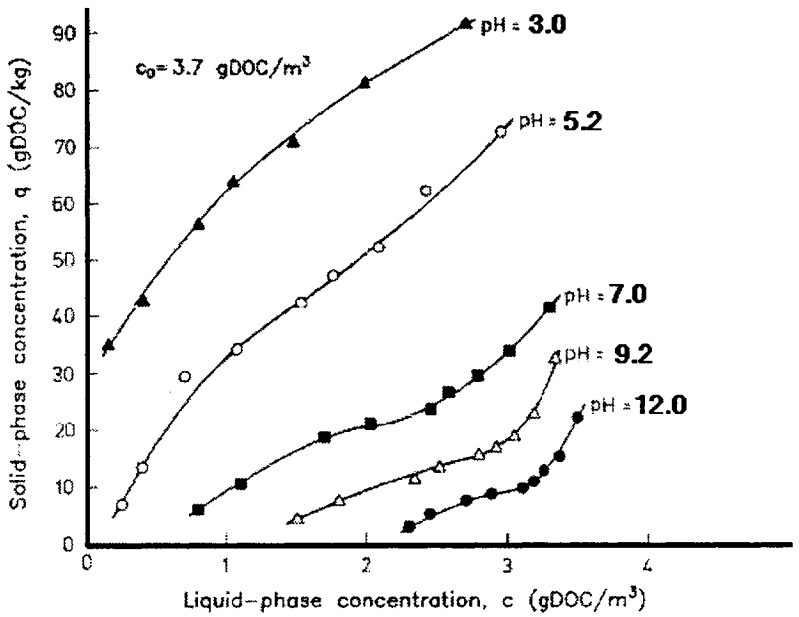

Figure 2.5: Affect of pH of Humic Solutions on Isotherms (Source, Sontheimer *et al.*, 1988)

2.1.2 Non-Competitive, Single Component Isotherm Models

The most common isotherms are non-competitive isotherms and the most frequently used models are the Freundlich and Langmuir isotherms. These are presented in the following sections. The Toth and Radke-Prausnitz isotherms were also chosen as examples of models with more adjustable parameters.

Isotherm results are strongly dependent on experimental practices. The most important factors are carbon preparation, solution properties and equilibration time (Peel, 1980; Randtke and Snoeyink, 1983; Narbaitz, 1986; Summers, 1986; Sontheimer *et al.,* 1988). Many results differ between researchers due to different definitions of equilibration time. One way to ensure reported isotherms are at equilibrium is to conduct kinetic experiments in advance.

2.1.2.1 The Freundlich Isotherm Model

The Freundlich isotherm is chosen for many applications due to its simplicity. The Freundlich equation follows a power law function and is described as:

$$q_{eq} = k\ C_{eq}^{\ n} \tag{2.1}$$

Where : q_{eq} = the solid phase in equilibrium with C_{eq} (mass of contaminant / mass of AC); C_{eq} = the liquid phase at equilibrium (mass of contaminant / volume); k and n are regressed constants.

This model generally only works for small ranges of solution concentrations. However, it

can be used with different k and n values over numerous ranges of solution concentration (Narbaitz, 1986; Sontheimer *et al.*, 1988).

2.1.2.2 The Langmuir Isotherm Model

The Langmuir model is based on an assumption that all adsorption sites on the GAC have the same energy for adsorption and the layer of adsorbed molecules is a monolayer. It was originally developed for modelling the adsorption of gases on solids. Some data sets can be described by both the Freundlich and Langmuir isotherms, however the Langmuir generally does not fit liquid phase adsorption as well as the Freundlich model. Sontheimer, *et al.* (1988) described the main difference between the Freundlich and Langmuir isotherms in terms of adsorbent surface. The Langmuir isotherm represents a homogeneous surface and the Freundlich represents a heterogeneous surface.

The Langmuir mathematical model is shown in equation 2.2.

$$q_{eq} = \frac{Q_M b\, C_{eq}}{1 + bC_{eq}} \qquad (2.2)$$

Where : Q_M = the monolayer adsorption capacity (mass of contaminant /mass of AC), b = the energy constant (cm^3/g).

The Langmuir isotherm has two limitations. As can be derived by looking at equation 2.2, at low concentrations the model reduces to a linear isotherm. As well, at high concentrations the solid phase concentration $q_{eq} = Q_M$ approaches the expression and thus becomes independent of the solution concentration (Sontheimer *et al.*, 1988).

2.1.2.3 The Toth Isotherm Model

Toth based his model on the fact that adsorption equilibrium curves plotted on logarithmic scales usually produce a straight line. This leads to a model with a power law function such as the Freundlich model. Since this model has three adjustable parameters it has a greater degree of flexibility than the previous two models. The Toth isotherm model was developed by integrating a power law function as follows.

From the differential equation :

$$\frac{d\ln C}{d\ln q} - 1 = \alpha C_{eq}^{\ \beta} \tag{2.3}$$

By letting

$$q \to q_{\infty} \quad As \quad C_{eq} \to \infty$$

Toth derived the model :

$$q_{eq} = \frac{q_{\infty} C_{eq}}{\left(1 + bC_{eq}^{\ \beta}\right)^{\beta}} \tag{2.4}$$

Where : q_{∞} , b, and β are regressed constants

2.1.2.4 The Radke-Prausnitz Model

The Radke-Prausnitz model is an empirical isotherm model with three fitting parameters. This nonlinear regression model fits most data sets very well. The model equation is shown as equation 2.5.

$$q_{eq} = \frac{abC_{eq}^{\beta}}{\left(a + bC_{eq}^{(\beta-1)}\right)} \qquad \beta < 1 \tag{2.5}$$

Where: a , b, and β are regressed constants

Both the Toth and Radke- Prausnitz models fit wide ranges of concentrations, while this is a limitation with the Freundlich and Langmuir isotherms. This is because they have more adjustable parameters. The Radke-Prausnitz parameters are only fitting parameters and have no physical interpretation (Sontheimer, *et al.*, 1988).

2.1.3 Competitive Adsorption Isotherm Models

Single component isotherm models work satisfactorily for synthetic organic compounds but do not always fit data that contains more than one component or a complex component such as NOM (Sontheimer *et al.*, 1988; Simpson, 1995; Simpson and Narbaitz, 1997). There are two different ways that competition will occur; these are competition for adsorption sites and pore blockage.

Pelekani and Snoeyink (1999) studied the role of pore sizes in activated carbons on competitive adsorption. They stated that from the point of view of adsorption free energies, compounds will be preferentially adsorbed into pores that are similar to their sizes because there will be an increase in contact points. The attraction of several contact points has a greater force than only one contact point.

Newcombe *et al.* (1997b) found that smaller sized NOM fractions provided the greatest competition for adsorption sites when studying the competitive adsorption between NOM and 2-methylisoborneol (MIB). In general, competition was found to occur for compounds that had a similar size and structure. Similarly, Li *et al.* (2003) found that NOM molecules with MW's from 200 to 700 Daltons were responsible for competitive adsorption with atrazine.

Since competitive adsorption plays such an important role in the study of NOM and GAC adsorption, some of the more popular isotherm models are explained in the following sections.

2.1.3.1 The Ideal Adsorbed Solution Theory Isotherm Model (IAST)

Competitive adsorption modeling is often necessary because water frequently contains more than one contaminant. Also, since NOM is such a heterogeneous mixture, single component isotherms models rarely describe NOM adsorption very well (Narbaitz, 1986; Sontheimer *et al.,* 1988; Simpson, 1995; Simpson and Narbaitz, 1997). The IAST model was developed by Radke and Prausnitz (1972) and is based on the assumption that each adsorbate in solution has equal access to adsorption sites. Competition is assumed to be through direct competition for adsorption sites. The IAST model is applied to NOM adsorption by representing the NOM in natural waters as competing *pseudocomponents*. The IAST model has these five governing equations:

$$q_T = \sum_{i=1}^{NC} q_i \tag{2.6}$$

$$y_i = \frac{q_i}{q_T} \tag{2.7}$$

$$\sum_{i=1}^{NC} y_i = 1 \tag{2.8}$$

$$\frac{\pi_i A}{RT} = \int_0^{c_i{}^0} q_i{}^0 \frac{dc^*{}_i{}^0}{c^*{}_i{}^0} \tag{2.9}$$

$$c^*{}_i = c^*{}_i{}^0 y_i \tag{2.10}$$

Where: c^*_i = the liquid phase in equilibrium with q_i (mg/l), q_i = the solid phase at equilibrium (mg/g); y_i = the adsorbed phase fraction of solute i; q_T = the total solid phase concentration on the activated carbon (mg/g), A = the surface area of the adsorbent (m^2/s), π_I = is the spreading pressure of solute i, R = the universal gas constant, T = temperature in K, c_i^o = intermediate liquid phase concentration equal to the product of yi and c*i; q_i^0 = the single solute solid phase concentration(mg/g) in equilibrium with c_i^o

For batch adsorption equilibrium experiments in which the single solute adsorption equilibria is described by the Freundlich model, equations 2.6 through 2.10 simplify to: (Sontheimer *et al.*, 1988)

$$C_i = \left[\frac{q_i}{\sum_{j=1}^{NC} q_j}\right]\left[n_i \frac{\sum_{j=1}^{NC} \frac{q_j}{n_j}}{k_i}\right]^{1/n_i} \tag{2.11}$$

$$C_{io} - \frac{M}{V} q_i - \left[\frac{q_i}{\sum_{j=1}^{NC} q_j}\right]\left[n_i \frac{\sum_{j=1}^{NC} \frac{q_j}{n_j}}{k_i}\right]^{1/n_i} = 0 \tag{2.12}$$

Where: n_i, and k_i = single solute Freundlich parameters of component i; C_{io} = initial concentration of component i; M = mass of carbon (g); V = volume of solution (l); C_i = equilibrium liquid phase concentration of component i; q_i = equilibrium solid phase concentration of component i (mol/g GAC); q_j = equilibrium solid phase concentration of component j (mol/g GAC)

The IAST-NOM pseudocomponent model (Crittenden *et al.*, 1985) has a large number of unknown parameter values that need to be regressed (i.e., k_i, n_i, MW_i, C_{io}) for every pseudomponent. Due to the large number of parameters being regressed, their values tend to be highly correlated. This makes the regressions difficult, very time consuming and yields parameter values that have large confidence limits. Accordingly, Crittenden *et al.* (1985) suggested to use only three pseudocomponents and assume that the MW of the three components are the same. Crittenden *et al.* (1993) and Sorial *et al.* (1994) also suggested using the same value of n for all the pseudocomponents.

Since the initial assumption that all adsorbates compete for all sites (Radke and Prausnitz, 1972) is not realistic, a number of different models have been developed to exclude competition from a portion of reactive sites. Two of these models are the simplified competitive adsorption model (Digiano *et al.* 1978) and the modified simplified competitive adsorption model (Narbaitz and Benedek, 1994, Simpson and Narbaitz, 1997). These models take into account factors such as size exclusion, pore blockage and other adsorption site particulars. These modifications were required to simultaneously describe the adsorption of the target compound(s) and the DOC of the NOM, since the IAST only describes the adsorption of the target compounds well.

2.1.3.2. The Simplified Competitive Adsorption Model (SCAM)

The SCAM model (DiGiano et al., 1978) differs from the simplified IAST model, described by equations 2.11 and 2.12, in that it assumes the n value of the Freundlich isotherm is the same for all competing adsorbates or pseudocomponents. Average Freundlich component values are calculated as:

$$n' = \frac{1}{NC}\sum_{j=1}^{NC} n_j \tag{2.13}$$

$$k' = \left\{\prod_{j=1}^{NC} k_j\right\}^{1/NC} \tag{2.14}$$

The equilibrium expression then becomes:

$$q_i = k'^{\frac{(n'-1)}{n'}}\left(k_i c_i{}^{n'}\right)^{\frac{1}{n'}}\left\{\sum_{j=1}^{NC}\left(\frac{k_j c_j{}^{n_j}}{k'}\right)^{\frac{1}{n'}}\right\}^{(n'-1)} \tag{2.15}$$

Where: n_j, and k_j = single solute Freundlich parameters of component j; c_i = equilibrium liquid phase concentration of component i(mass/volume); q_j = equilibrium concentration of component j (mol/mass of GAC)

2.2 Desorption

Many authors have studied the hysterisis of adsorption and desorption isotherms. This is referred to as irreversible adsorption. There have been many papers written on irreversible adsorption of single component solutions. (Snoeyink *et al.,* 1969; Weber and Pirbazari, 1983; Vidic *et al.,* 1990, de Jonge *et al.,* 1996; Tamon *et al.,* 1996; Tamon and Okazaki, 1996; Terzyk, 2003; Terzyk 2004a; Terzyk, 2004b). Some of these papers are discussed in chronological order on the following pages. Irreversible adsorption of NOM on GAC is discussed in section 2.5.

Snoeyink *et al.* (1969) studied hysteresis effects using phenol. This study found hysteresis to be significant for long equilibration times but not significant for shorter contact times. Approximately 50% of adsorbed phenol desorbed after a two week equilibration period. A comparison of two carbons (coal and coconut based) resulted in differences in isotherm shapes and the authors concluded these differences were due to differences in surface properties.

A number of neutral compounds, such as Carbon Tetrachloride (Weber, and Pirbazari, 1983) and 1,1,2-TCEA (Narbaitz, 1986), have been found to adsorb reversibly on AC. Karimi-Jashni and Narbaitz (1997), studied the reversible adsorption of phenol and 2-nitrophenol on to two different GAC's (coal and wood based) that were preloaded at a pH of 4.6. Initial desorption rates were faster with the wood based AC, and phenol was found to be reversible with both carbons. The same ACs (F-400 and WV-B) were used by Vidic *et al.* (1990) and WV-B was found again to have more reversible adsorption than F-400.

de Jonge *et al.* (1996), conducted work with powdered activated carbon, PAC, and activated sludge. Reversibility of adsorption was studied by conducting isotherm and desorption isotherm studies. The compounds studied were a phenolic compound called o-cresol and 3-chlorobenzoic acid with two different PAC types. The phenolic compound was found to be less reversible than the benzoic acid. For both compounds desorption showed two different kinetic rates. The first was a rapid phase followed by a slower desorption phase. They also concluded that the initial contact time for adsorption was an important factor in the reversibility of adsorption.

Tamon *et al.* (1996) proposed a two state adsorption model to explain irreversible adsorption. First, compounds are adsorbed in a precursor state then move into the irreversible state after a long contact time. Tamon and Okazaki (1996) studied the hysteresis between adsorption and desorption isotherms which suggests the appearance of irreversible adsorption. These researchers used 11 aromatic compounds and found hysteresis with GAC but not with synthetic adsorbents.

Terzyk (2003) reported work on the desorption properties of phenol on four different GAC's. The carbons had identical porosity characteristics but different surface layer chemical compositions. It was concluded that phenol adsorption is irreversible in both anoxic and oxic conditions. This irreversibility was hypothesized to be due to the creation of strong complex compounds between the phenol and carbonyl functional groups on the carbon surface, as well as the formation of lactones from polymerization reactions.

Terzyk (2004a) studied the desorption characteristics of acetanilide on GAC at three different temperatures (300, 310, and 320 K) and pH values at 7 and 1.5. The adsorption

of acetanilide was reversible at neutral pH and high temperatures, but irreversible at the acidic pH and 300K. He concluded that this irreversible behavior at neutral pH and 300K was due to the formation of hydrogen bonds with surface OH^- groups. These bonds collapse at higher temperatures. The irreversible behavior at acidic pH values was hypothesized to be due to chemisorption because these bonds were not affected by the higher temperature.

Terzyk (2004b) presented hysteresis effects between adsorption and desorption isotherms for phenol, acetanilide, paracetamol and aniline on various GACs at three different temperatures (300, 310, 320 K) and pH values of 7 and 1.5. The compound aniline did not adsorb on any GAC at pH 1.5 due to a repulsion between the aniline cation and positively charged surfaces on the GAC at acidic pH values. The adsorption-desorption isotherms of aniline showed hysterisis on all GACs at the neutral pH and all temperatures. Hysterisis decreased as temperature increased, and on GACs with more carboxylic and hydroxyl surface groups. For all compounds irreversible behavior decreased with a rise in temperature. Terzyk (2004b) concluded that hydrogen bonding was responsible for irreversible bonding as increasing the temperature makes these bonds weaker.

2.2.1 Desorption Isotherm Modeling

The desorption *isotherm* referred to by many authors is in fact many different desorption isotherms. or each data point on a batch adsorption isotherm there is one resultant desorption isotherm. (Narbaitz, 1986). If AC is loaded via a batch adsorption experiment it will contain adsorbate on its surface as well as within micro and macro pores. A batch desorption isotherm consists of placing the loaded GAC within an ultra-pure water for a suffciently long time that equilibrium is reached. The result of each desorption isotherm can be one of the three types as shown in figure 2.6. These are irreversible, no desorption occurs; partial irreversibility, some desorption occurs; or completely reversible when the solid phase concentration (or loading) at the end of the desorption cycle is described by the adsorption isotherm.

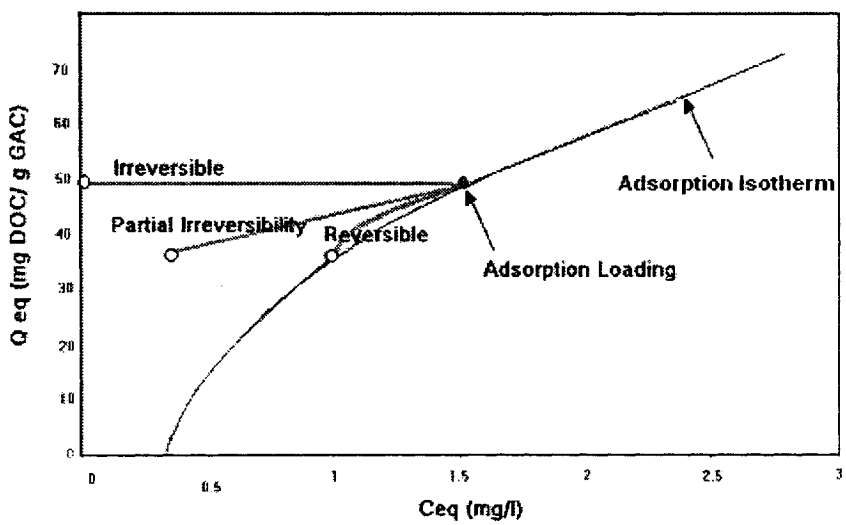

Figure 2.6: Desorption Isotherm Types

2.3 Granular Activated Carbon (GAC)

The first use of GAC was in gas masks in the First World War. Prior to this point in history only large charcoal and powdered forms of carbon were successfully manufactured (Sontheimer *et al.,* 1988). Today activated carbon is found in many novel forms such as fabrics and fibres. For clarity, a diameter cutoff size of 0.05 mm for a powdered activated carbon (PAC) was defined by Sontheimer *et al.* (1988). Particles with diameters less than 0.05 mm are PAC and those with diameters greater than 0.05mm are GAC.

GAC can be manufactured from any material that contains a large fraction of carbon. Some examples of carbonaceous raw materials are coal, wood, and coconut shells. The activation process involves two steps. First the material is heated to extreme temperatures in the absence of oxygen, then blasted with steam to clean impurities out of the resulting void spaces (pores). The surface area produced will be from 300 to 2,500 m^2 per gram of carbon (Sontheimer *et al.,* 1988). This quality makes GAC a very effective adsorbent for trace levels of toxic organic pollutants as well as the removal of colour, taste and odour. It is a very flexible method of water treatment that can be used everyday or only as needed.

The main disadvantages of this treatment method are a high cost and a lack of control over adsorption and desorption results. An example of the latter disadvantage is what is a chromatographic effect. This is the desorption from GAC columns of previously adsorbed contaminants resulting in a contaminant peak in the effluent which exceeds the influent concentration of that particular contaminant. It occurs because more weakly

adsorbed compounds can be displaced by compounds with a higher affinity for the activated carbon. These are called. competitive adsorption effects.

Since GAC is such an important material with many end uses (gas masks, gas purification, sugar decolorizing, among many others) the literature reports are vast. To be concise, this section was divided into four separate discussion topics chosen as those most relevant to this thesis. These are the basic properties of GAC, surface chemistry, anoxic and oxic solution conditions and activation processes.

2.3.1 Properties of GAC

The structure of AC is constructed of many linked crystalline planes made up of carbon atoms (Sontheimer, *et al.*, 1988; Summers, 1986; McKay, 1996). This structure, shown in figure 2.7, is very similar to that of graphite. The crystalline planes lie parallel to each other and are randomly connected through tetragonal carbon bonds. The spaces between crystalline planes make up extremely small pores and introduce a complex pore structure. Pore volume distributions (PVDs) of activated carbons are often used to select carbons for various applications. The adsorbent PVD is also an important property in adsorption processes.

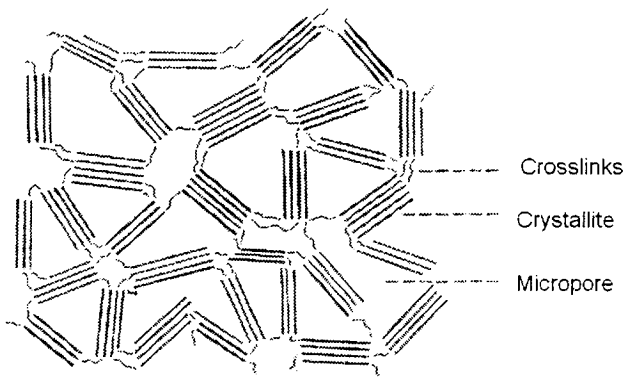

Figure 2.7: Crystalline Structure of GAC (Source, Sontheimer *et al.*, 1988)

The extremely large surface area per weight of activated carbon is due to this intricate network of pore spaces throughout the entire volume of the particle. There are two different types of pores called macropores and micropores. The distinction between the two is found in the diameter of the pore with the micropores defined as those with a diameter of less than 2nm, and macropores with a diameter greater than 50nm. Some literature accounts refer to a mid range called transition pores (Peel, 1980, Pelekani *et al.*, 1999). The large surface area per unit mass is due to the micropore region, with up to 90% of this surface area found in the micropore region (Karanfil *et al.*, 1999; Pelekani *et al.*, 1999; Sontheimer *et al.*, 1988). An alternative definition for macro versus micro pores was provided by Peel (1980). Peel defined a macropore as being many magnitudes larger than the contaminant molecule while a micropore is nearly the same size as the

contaminant.

The electron microscope photos in figure 2.8 illustrate the extreme difference in the diameter of these pores. The macropores are clearly visible at all magnifications, while even at the greatest magnification (1 micron per cm) micropores are difficult to see. This is significant because it is thought to be these complex pore structures that make the modelling of adsorption on GAC very difficult. Simple models do not always describe the experimental data. For example, diffusive movement of the contaminant through the micropores is thought to be extremely slow while being much faster through the macropores (Peel, 1980; Narbaitz and Benedek, 1994, Narbaitz, 1986; McKay, 1996).

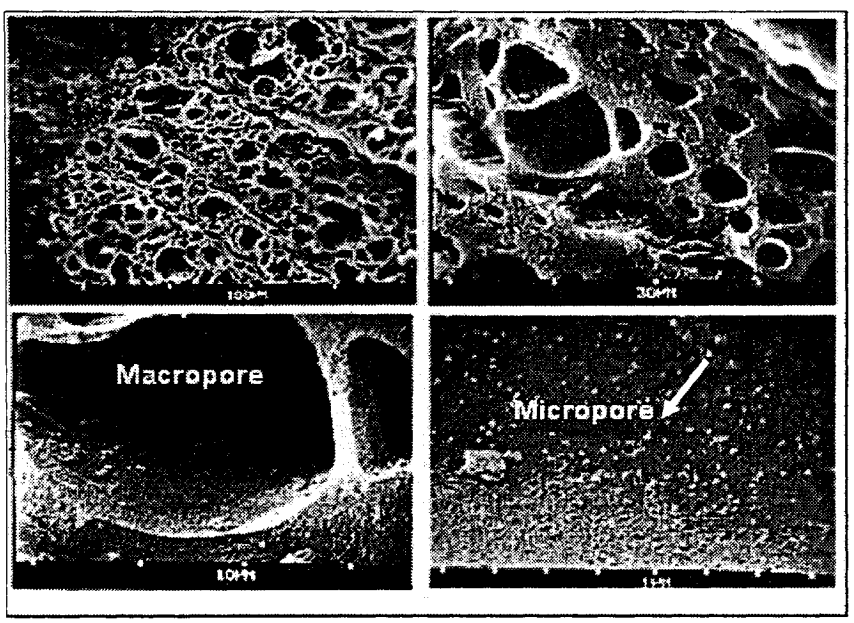

Figure 2.8: Electron Microscope Photos of a GAC Particle (Source, Sontheimer *et. al*, 1988)

2.3.2. Surface Chemistry of Granular Activated Carbon

Both chemical and physical factors are involved in the adsorption of target contaminants by activated carbons. Some important variables in the process are molecular structure of the contaminant, surface chemistry of the activated carbon, solution chemistry, temperature and pH (Sontheimer *et al.,* 1988; Morris and Newcombe, 1993; Newcombe, 1994; Terzyk, 2004b). GAC contains some non carbon elements, usually from 5 – 20% by weight (Sontheimer *et al.,* 1988). These non carbon elements are mainly metal and surface bound oxygen (Terzyk, 2001; Terzyk, 2004b). These surface elements are usually a function of the source material for the GAC as well as the activation process. For example, if the GAC was chemically activated residual amounts of the activating agent will be integrated into the carbon structure (Calgon, 2004; Sontheimer *et al.,* 1988). Surface oxide functional groups such as carboxylic, hydroxyl, carbonyl, lactone, and carboxylic acid are believed to occur at the crosslinks and along the edges of crystalline planes (Sontheimer *et al.,* 1988; Terzyk, 2004b).

GAC surface chemistry can be used to optimize NOM adsorption. For example, at a neutral pH, NOM will have a negative charge, therefore the activated carbon surface should be positive for the optimum adsorption (Dashgheib *et al.,* 2004). Enhanced removal of NOM requires activated carbons with an overall positive charge, specific functional groups that have high affinities for NOM, and more mesopores than micropores (Dashgheib *et al.,* 2004).

Morris and Newcombe (1993) found that the adsorption of NOM onto the GAC surface changed the surface properties of the GAC. In particular, the surface charge on the GAC decreased after NOM adsorption. They hypothesized that the NOM transfers it's negative charge while adsorbing as well as the possibility that functional groups on the AC may have been involved in the adsorption process. Newcome (1994) and Terzyk (2004b) had similar results.

2.3.3 Anoxic and Oxic Solution Conditions

The presence of dissolved oxygen has been found to affect adsorption characteristics. Dissolved oxygen is present in the headspace of isotherm bottles, in the adsorbate solutions themselves, and entrapped in GAC pores. This oxygen increases the numbers of acidic oxide groups on the carbon surface (Vidic *et al.*, 1990; Vidic and Suidan, 1991). Vidic and Suidan (1991) studied the capacity of o-cresol adsorption on GAC under both anoxic and oxic conditions. They found the adsorption efficiency of GAC adsorption decreased under oxic conditions. GC-MS analyses found that a polymerization reaction took place on the surface of the AC.

Introducing an anoxic environment allows the researcher to study other parameters while knowing oxygen competition is not present. Oxygen is eliminated to prevent polymerization reactions that might occur on the surface of the carbon (Vidic and Suidan, 1991; Karanfil *et. al*, 1996). Since water treatment processes are always under oxic conditions, this thesis only considered oxic solution conditions.

2.3.4 Activation Processes

GAC is made from many different materials, all having a high carbon content. Differences in raw materials and activation processes result in different final properties of the GAC product. In addition, activation can be accomplished through thermal or chemical activation, producing yet other differences. Chemical activation results in trace amounts of the solvent on the carbon surface.

Thermal activation can be further categorized into two different production methods, those of re-agglomeration and direct activation. Re-agglomeration results from pulverizing the coal, adding an inert binder, re-agglomerating into briquettes, then crushing the briquettes. The crushed briquettes are activated by heating to 425° C (800° F) in an absence of oxygen, then thermally activating in temperatures up to 1056 ° C (1900° F). Direct activation skips the first two steps in the re-agglomeration process. Re-agglomeration adds a man-made pore structure to the GAC. This results in a more uniformly activated product. Direct activation often results in granules that are more activated along the outer edge than the core (Calgon, 2004). These differences lead to variations in pore radius distributions and surface areas as found by Summers, 1986 and shown in figure 2.9.

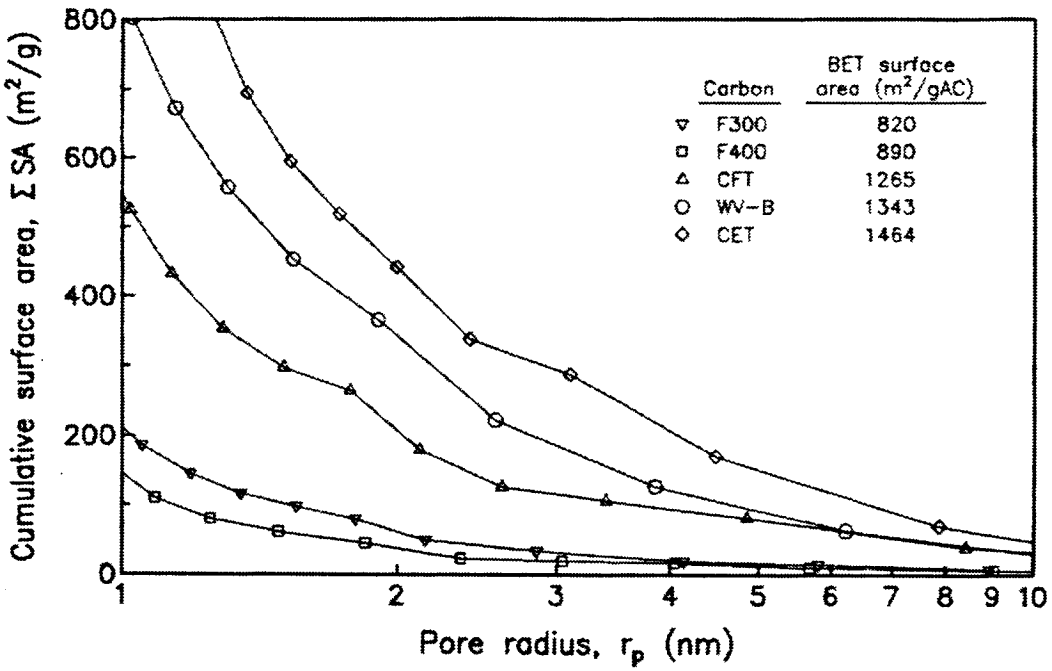

Figure 2.9: Surface Area Versus Pore Radius for Various GACs (Source, Summers, 1986)

2.4 Natural Organic Matter (NOM)

NOM is the residual organic matter resulting from the long-term biodegradation of animal and plant matter. It is found in varying concentrations in all natural waters and in soil. Since it has already been naturally degraded, it is very stable and has a long half-life. NOM is composed of extremely complex and large heterogeneous molecules.

There are different names given to NOM from researchers. After reading many literature sources, the terms dissolved organic matter (DOM), NOM, and humic substances (HS) were all found to refer to similar components of the same class of compounds in natural waters. DOM differs from NOM in that it refers only to natural organic materials that will pass through a 0.45 μm filter (Aiken *et al.*, 1985; Suffet and MacCarthy, 1989).

Humic substances are defined by Suffet and MacCarthy (1989) as materials resulting from the decomposition of plant and animal matter that is not a part of the classes of compounds of proteins, polysaccharides, or polynucleotides. However, past research has found that proteins, polysaccharides and biopolymers are contributors to NOM structures (Aiken *et. al*, 1985; Croué *et. al*, 2000; Piccolo, 2001; Suffet and MacCarthy, 1989). Even if NOM were separated into separate components and these studied separately, the response would not be the same as the original NOM because of intermolecular interactions that exist in these large molecules (Suffet and MacCarthy, 1989).

Chemists have studied NOM since the 1800's, however, research has gained momentum since a 1974 report of carcinogenic by-products formed from the chlorination process and NOM (Rook, 1974). Other concerns caused by NOM are the interference by NOM on

unit operations in water treatment plants, and the tendency of NOM to attach to and hold dissolved toxic metals. NOM has been found to reduce the effectiveness of GAC filters (Li *et al.;* Narbaitz, 1986; Narbaitz and Benedek, 1994; Pelekani and Snoeyink, 1999). Target pollutants in drinking water treatment are often present at concentrations of three to six orders of magnitude lower than NOM, thus the presence of NOM reduces adsorption capacities (Pelekani and Snoeyink, 1999). Within water treatment plants, to a limited extent, NOM can also act as a substrate for biogrowth (Summers *et al.*, 1989; Croué *et al.*, 2000).

2.4.1 Properties of NOM

2.4.1.1 Chemical Structure

NOM is not a repeated monomer but has molecular weights comparable to polymers. Due to it's multicomponent nature, NOM concentrations are usually measured as the lumped parameters total organic carbon, TOC, or dissolved organic carbon, DOC. DOC is defined as the concentration of carbon in the dissolved organic substance. These measurements are usually made by oxidation of the substance to CO_2.

2.4.1.2 Molecular Weight

Since NOM is a heterogeneous mixture it does not have a single molecular weight. Like polymers, the molecular weight of NOM is a range of values and the recording of this property should be either the weight average molecular weight, or the number average molecular weight. Literature reports have found that molecular weights of NOM can range from several hundred to more than 100,000 Da (Chin *et al.,* 1994; Cai, 1999; Conte

and Piccolo, 1999; Assemi *et al.,* 2004). However the maximum molecular weights in drinking water should be expected to be closer to 10,000 Da due to the removal of the larger fractions in various unit operations (Pelekani *et al.,* 1999; Marhaba and Van, 2000).

The molecular weight distributions (MWDs) of NOM are usually measured using ultrafiltration, (UF) or size exclusion chromatography (SEC). Studies conducted by Pelekani and Newcombe (1999) as well as O'Driscoll (1998) found that the use of size exclusion chromatography was a reliable method for calculating the molecular weight distributions of NOM in river and lake waters. However, both of these methods sort the NOM fractions into molecular *size* not molecular *weight* and this distribution should be referred to as the molecular *size* distribution (MSD). The MSD as determined from UF and SEC is affected by internal influences such as steric effects, the molecular structures, hydrophobicity, and molecular charge. Therefore, it is only an estimate of the true MSD of the NOM in the water source.

2.4.1.3 Sources of NOM

NOM found in freshwaters is generated by the biological breakdown of materials in the ecosystems surrounding the water source (allochthonous) as well as within the water body (autochthonous). As a result of how the NOM is formed it is not isolated from other compounds in nature. It will be mixed either physically or chemically with amino acids, sugars, dissolved metals, aliphatic acids, and aromatic acids (Aiken *et al.,* 1985; Suffet and MacCarthy, 1989).

2.4.2 Characterization and Fractionation of NOM

The techniques used to study NOM depend on the study and the information sought. There are many different methods that have been developed to analyze NOM. Due to the complex multicomponent nature of NOM, the best method for study is to divide the material into fractions with different operational characteristics. The task of dividing NOM into discrete components is nearly impossible. Partitioning the water into more homogeneous fractions is called fractionation and is carried out by all natural water researchers via one or more methods. Some of these methods are described in the following sections. Many studies concentrate the water before the fractionation processes. However, solution concentration can change the structure of the organic compounds that comprise NOM (Clair *et al.,* 1991; Croué *et al.,* 2000; Leenheer, 1984a).

2.4.2.1 Humic and Fulvic Acid Fractionation

Traditional fractionations are based on molecular weight/size and chemical characteristics. The chemical fractionations used most often are humic acids, fulvic acids, and humin. They are defined as (Aiken *et al.,* 1985; Suffet and MacCarthy1989; Leenheer, 1984a):

Humic Acid: the fraction of NOM that *is not* soluble in water at pH < 2

Fulvic Acid: the fraction of NOM that *is* soluble in water at pH < 2

Humin: the fraction of NOM that *is not* soluble in water at any pH

These acids are best secluded from one another using a methylmethacrylate resin called XAD8. This is the method used by the International Humic Substances Society to separate and isolate and produce standard humic samples from the Suwannee river (Suffet and MacCarthy, 1989).

2.4.2.2 Differences Between Humic and Fulvic Acids

Every water source will have different NOM characteristics and even these will change with the annual seasons. However, some properties of humic and fulvic acids have been universally accepted. Some of these are:

- Humic acids have greater molecular weights than fulvic acids (Aiken *et al.*, 1985). For the Suwanee River fractionation, the molecular weights of humic and fulvic acids were found to be 1061 and 800 Da, respectively (Chi and Amy, 2004).
- Chi and Amy, 2004, also found that the higher molecular weight fractions of fulvic acids are aromatic, and more preferentially absorbed; while the lower molecular weight portion of humic acids are more likely to be sorbed.
- Fulvic acids have more oxygen functional groups such as COOH, OH, and C = O (Aiken *et al.*, 1985; Suffet and MacCarthy1989).

2.4.2.3 Ultra Violet Absorbance of NOM

Ultraviolet, UV, absorbance is often used to study NOM in natural waters using the fluorescence in the range of λ_{200nm} to λ_{400nm}. This range is studied because inorganics will absorb substantial amounts of light at wavelengths less than 200 nm (Korshin *et al.,* 1997). Bromides and nitrates are especially problematic (Croué *et al.,* 2000; Croué, 2004). The functional groups that absorb UV light are called chromaphores. The chromaphores in NOM are largely aromatic groups and mostly from the humic acid fraction of the NOM (Korshin *et al.,* 1997). All NOM samples will have many different types of chromophores and they change with the seasons. For this reason the linear relationship found between DOC and UV absorbance is not always reliable.

UV absorbance measurements are very popular because the analysis is fast and the samples do not require preparation. The limitations of UV spectroscopy are that it is pH sensitive and it is not reliable at low DOC concentrations. Absorbance values are also a function of pathlength. Many researchers do not mention the pathlengths used in their analytical equipment so this makes comparisons of data difficult.

NOM has a broad featureless spectrum so the study of UV has mainly been divided into discrete wavelengths for study, the most popular being 254nm, 280nm and 350nm. For example, some water treatment plants use a ratio called SUVA to estimate the amount of coagulant dosage required. [3]

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[3] Using a 10 mm cell pathlength

$$SUVA = \frac{\text{Absorbance at } 254\text{nm } (\text{m}^{-1})}{\text{DOC (mg/l)}} \qquad (2.16)$$

UV absorbance decreases at all wavelengths as chlorination byproducts form. However, traditionally the value of UV absorbance at λ_{254nm} is used to predict the possibility of DBP's from chlorination. The absorbance values at λ_{272nm} are also used to study how much NOM has been converted to DBPs (Li *et al.*, 2000; Li *et al.*, 2002; Korshin and Benjamin, 1997; Korshin *et al.*, 2002). Korshin and Benjamin (1997), stressed the fact that studying only one wavelength of UV absorbance of NOM would leave out important spectra information. He stated:

> *Collection and interpretation of absorbance data at only a single wavelength fails to take advantage of the substantial information that must be embedded in the rest of the UV spectral data.*

To achieve this improved interpretation of absorbance data Korshin and Benjamin (1997), introduced the idea of studying electron bands. The recommended bands are the local-excitation (LE), benzenoid (Bz) and electron-transfer (ET) bands as shown in figure 2.10. These are three types of electronic transitions typical in aromatic compounds attributed to the work of Jaffe and Orchin (1962).

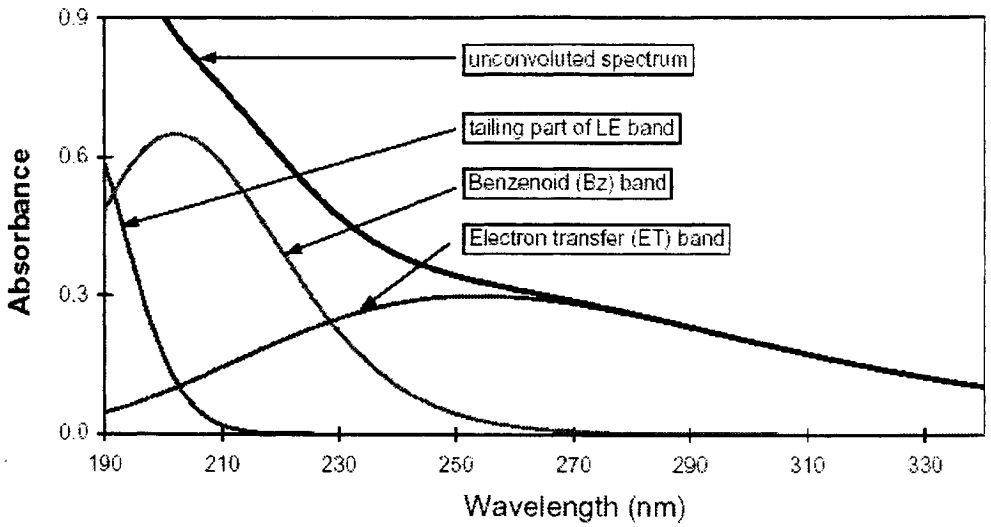

Figure 2.10 : Use of UV Absorbance to Characterize NOM (Source, Croué *et al.*, 2000)

The electron transfer band is defined as: (Korshin and Benjamin, 1997)

$$\Delta ET = \sqrt{\frac{4\ln 2(E\lambda_2 - E_o)^2 - (E\lambda_1 - E_o)^2}{\ln\left(A_{\lambda 2}/A_{\lambda 1}\right)}} \qquad (2.17)$$

Where: E_λ= energy of light quanta at this λ(eV), A_λ is the absorbance at this wavelenght (m^{-1})

For the wavelengths of $\lambda_1 = 350$ and $\lambda_2 = 280$, this equation simplifies to: (Croué *et al.*, 2000, Korshin and Benjamin, 1997)

$$\Delta ET = \frac{2.18}{\sqrt{\frac{A_{280}}{A_{350}}}} \tag{2.18}$$

2.4.2.4 Ultra-Filtration

Although this method for molecular weight distribution of the NOM is simple, it has not been found to be accurate (Newcombe *et al.,* 1997a; Newcombe *et al.,* 2002). The manufactured molecular weights are usually over estimated (Newcombe *et al.,* 1997a; Newcombe *et al.,* 2002). The reasons given for this are because the calibration of the membranes uses chemicals that act very different to NOM at the same molecular weight. Most of the ultrafiltration membranes are calibrated using globular proteins, which tend to be spherical, while NOM can often be in the form of long chains (Newcombe *et al.,* 2002).

NOM can be found in many different sizes and functional groups all reacting with the membrane materials in different ways. It is difficult to determine if fractions retained on the membrane or allowed to pass through are actually within the molecular range given by the manufacturer. This is why size exclusion chromatography is more frequently recommended for molecular weight analysis, or a combination of both methods.

2.4.2.5 Size Exclusion Chromatography

Size exclusion chromatography (SEC) separates molecules by size. The experimental material generally used are porous polymer gels. The process of SEC using gel is called gel permeation chromatography (GPC) or gel filtration chromatography (GFC). In the literature, the terms SEC and GPC were used interchangeably.

The gel matrix consists of spherical beads with pores of a specific size distribution. Separation occurs when molecules of different sizes are excluded from the pores. As small molecules diffuse into the gel pores, their flow through the column is retarded, while large molecules bypass the pores and are eluted in the column's void volume. Consequently, molecules are separated according to size and elute in order of decreasing molecular weight. This process is illustrated in figure 2.11.

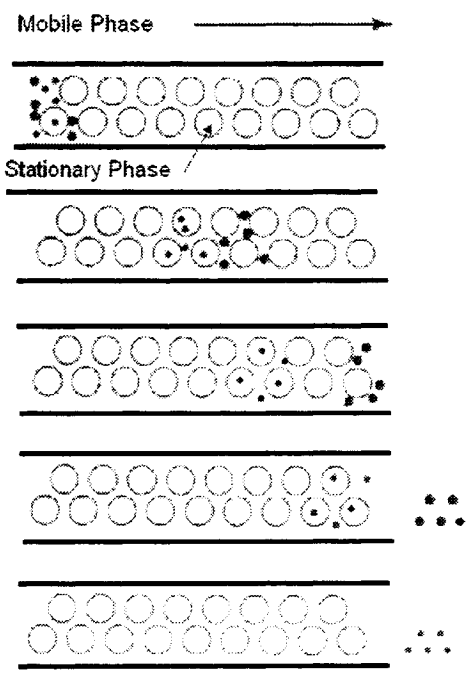

Figure 2.11: Separation During Size Exclusion Chromatography (Source, Mori, 1999)

Typical SEC applications include: molecular weight determination of proteins, nucleic acid separation, removal of unincorporated nucleotides polysaccharide fractionation and desalting. In desalting, the molecule of interest is eluted in the void volume, while smaller molecules are retained in the gel pores. To achieve the desired separation, the gel matrix should have an exclusion limit smaller than the molecule of interest. For desalting applications, the sample volume can be as much as 30–40% of the total bed volume, and short, wide columns are used (Croué *et al.,* 2000).

In fractionation, molecules with a range of molecular weights are separated within the gel matrix. With this method, the molecules of interest should fall within the fractionation range of the gel. Results depend on particle size, pore size, flow rate, column dimensions, and sample volume. For NOM the best results are obtained with low flow rates (2–10 cm/hr), long, narrow columns, small-particle-size gels, and small sample volumes (1–5% of the total bed volume) (Croué *et al.,* 2000). The sample is introduced into the gel column and the rentention time and response peaks are measured. The analyzed peak is determined from the maximum response with an appropriate analytical technique. Many researchers use a refractometer connected to the bottom of the column. Some studies have used UV absorbance analysis (Newcombe *et al.*, 2002; O'Driscoll and Evans, 2000).

2.5 Adsorption and Desorption Characteristics of NOM on GAC

There have been many research projects conducted on adsorption and desorption properties of many different substances with various adsorbents. However, most of these have dealt with either single component adsorbents or with manufactured humic substances. Many have also focused on surface properties and other characterizations of the adsorbent (GAC) rather than the adsorbate (NOM). Selected published work most relevant to the topic of this thesis is described in the following paragraphs.

Newcombe (1994) studied humic substances adsorbed on GAC with the goal of improving regeneration at the Australian Water Quality Centre. An alkali treatment was used to desorb humic substances from GAC surfaces. GAC was regenerated with NaOH to see if this was a good regeneration technique for influents containing NOM. The maximum removal of DOC was 60% of the initial concentration. This treatment improved the efficiency of GAC for two reasons. The first reason was because the surface area of reactive sites increased when the humic material was removed. The second was because the acid treatment introduced a negative charge on the surface of the carbon. This work hypothesized that large molecules are attached in large pores on several sites. The pore diameters are likely similar to that of the adsorbed species. There may be many contact points and a higher adsorption energy. For desorption to take place this energy must be over come. From this study, Newcombe (1994) concluded that desorption will depend on: the size of the molecule, the number of contact points, surface concentration, the concentration of adsorbed species, temperature and pH.

Narbaitz (1986) conducted a study of the competitive effects of NOM with 1,1,2-trichloroethane (TCEA), as well as studies of the desorption of these solutions. This study found that the TCEA adsorption was completely reversible from single component tests. The 1,1,2 TCEA solution was found to be completely reversible as a single component. NOM adsorption was virtually irreversible. From competitive adsorption studies, NOM was found to decrease the adsorption capacity of 1,1,2 TCEA. Multisolute isotherm models could not describe the competitive isotherm. 1,1,2 TCEA only marginally affected the adsorption of NOM.

Summers *et al.* (1989) treated three solutions directly from the Rhine river in Germany, one with NOM and trichloroethylene (TCE), one with NOM and 1,2,4 - trichlorobenzene (TCB) and the third with just NOM. All streams were treated with GAC columns at a velocity of 10 m/h and height of 1.56 m. After a breakthrough of 5% of the contaminants, desorption studies were carried out by running distilled water through the column. They did not report the NOM desorption, only TCE. They compared the desorption of TCE from the top of the column and the bottom of the column. At the bottom of the column, NOM adsorbed on the GAC first. In this portion there was less TCE desorption than at the top of the column where NOM and TCE adsorbed onto the GAC at the same time. Overall, they concluded that the presence of NOM adsorbed onto the GAC , hindered both the adsorption and desorption of TCE.

Summers and Roberts (1988) studied desorption of various humic substances from GAC at different temperatures and pH values. Desorption of 0 – 25% of the adsorbed mass occurred only when the pH was raised above 10.5. They used five activated carbons and

four types of purchased dry humic substances. Overall they conducted 31 desorption experiments with desorption of the humic substances into milli-Q water. The time for allowed for desorption was 21 – 90 days. They compared this absence of desorption to polymers, phenols and substituted phenols adsorbed on solids. A hypothesis was given that the adsorption of NOM on GAC contains elements of polymer adsorption as well as chemisorption onto the heterogeneous surface of the GAC. Desorption at higher pH values was explained by surface electrostatics. Increasing pH changed the surface charge of the GAC from being positively charged to negatively charged. This causes a repulsion between the negatively charged NOM and the negatively charged surface, thus allowing desorption.

Chapter 3: Experimental Methods

Description of the experimental methods followed in this thesis has been divided into four parts. These are descriptions of 1)the experimental plan, 2)experimental methods used for analysis of water characteristics, 3)experimental methods for kinetics studies and equilibrium tests (i.e., isotherms), and 4)experimental methods for NOM fractionation. They are presented in the following sections.

3.1 Experimental Plan

In order to complete the main objective of this thesis, which was to conduct an in depth study of the adsorption and desorption characteristics of NOM on/from GAC, many different laboratory tests were performed. For organizational purposes, this project was completed in four different "phases", or areas of focus. They are as follows.

Phase 1:

Analysis of source waters: The purpose of this first phase of experimental work was to determine the differences between five different natural waters and be able to later draw conclusions about the amount of reversible adsorption behavior of each. For each water source the following were determined at room temperature:

- DOC
- pH
- Conductivity
- Alkalinity, total hardness, calcium hardness
- Colour and turbidity

Analysis conducted during experimental work: Ultraviolet absorbance was determined for each sample during kinetics and equilibrium studies. DOC analysis was conducted for one half of all samples during experimental work. A correlation between UV absorbance and DOC allowed for samples without direct DOC analysis to be estimated from this correlation.

Phase 2:

Kinetics studies: These studies were conducted to establish the time required for equilibrium. This ensured that conclusions regarding adsorption and desorption of NOM were relevant and could be applied to the equilibrium state.

Phase 3:

Isotherm and Desorption Isotherm study: The purpose of this phase was to see if irreversible adsorption of NOM was universal by studying five different water sources. All five waters had adsorption and desorption isotherms determined using Calgon F-400 GAC.

Ottawa River Water NOM adsorption was evaluated with two different carbons, one wood-based and one bituminous coal-based, to see if there was a difference in their irreversible adsorption behavior due to differences in the GAC selection. There was also a second run conducted with both carbons and this water for verification purposes.

Phase 4:

NOM fractionation: Since NOM is a heterogenous mixture, the best method to study NOM was by separating the water according to operational characteristics. This is called fractionation. NOM fractionation was performed using untreated source waters as well as samples from adsorption and desorption isotherms. The following fractionations were performed on all five natural waters.

- Molecular size fractionation using ultrafiltration
- Fulvic acid fractions were extracted using XAD8 resin
- Molecular size fractionation was conducted using size exclusion chromatography

A more detailed description of the four phases is presented in the following sections.

3.2 Experimental Procedures for Water Characteristics

Since some of the procedures used in this study were lengthy, full descriptions have been presented in appendix A. Refer to appendix A1 through A6 for detailed methodologies. For example, to see how glassware cleaning was conducted please refer to appendix A1.

3.2.1 Materials

The adsorbents used were two ACs; Calgon F-400 (bituminous coal) and Westvaco WV-B (wood). The adsorbates were five natural waters as described and listed in section 3.2.2. Organic free water (OFW) used for cleaning glassware as well as in the desorption studies, was filtered using the Millipore Milli-Q ultrapure water system (Millipore

Corporation, Billerica, MA).

UV absorbance at 254nm was conducted using a Beckman Spectrophotometer (model DU-40, Beckman Coulter, Inc., Fullerton, CA). The pH of the water samples was monitored using an Accumet pH meter (model 910, Fisher Scientific, Hampton, NH) calibrated using buffer solutions from Sigma Aldrich (Sigma Aldrich, Milwaukee, WI) which were standardized against N.I.S.T. standard reference materials.

UF membranes were purchased from Millipore (Millipore Corporation, Billerica, MA) and came with a pre-calibrated molecular weight cut off, MWCO values. They are listed in table 3.4.

A methyl methacrylate resin called XAD8 (Fisher Scientific, Hampton, NH) was used to extract humic acids from the NOM of the natural waters. The column was cleaned with 0.1 N NaOH (Certified ACS Grade; Fisher Scientific, Hampton, NH) and the natural waters were acidified with 10% 1M HCl (Certified ACS Grade; Fisher Scientific, Hampton, NH).

For SEC, Sephadex gel G25 (Sigma Aldrich, Milwaukee, WI) was used with the fractionation range of 100 – 5000 MW. The column gel was buffered by adding a 0.1M $NaSO_4$ (Certified ACS Grade; Fisher Scientific, Hampton, NH) solution to the column until the effluent consistently had a pH of 6.

3.2.2 Water Collection

Sampling information on the five water sources is shown in table 3.1 and more in-depth information is included in appendix B. There were five different locations chosen for analysis, and all were directly from water treatment plants, WTPs. The selection and number of waters was chosen to determine whether results were universal to all or most natural waters. Two of these sources were chosen because these WTP's use GAC filters after dual media filtration.

These waters were the Buffalo Pound Lake WTP and the Richard Miller WTP. The Ottawa River was chosen as a source because this WTP has seasonal problems with taste and odour problems and has previously conducted a pilot plant study using GAC columns to evaluate their effectiveness. Vars groundwater was chosen to study the differences, if any, between NOM in surface waters and in groundwater. Vars water is treated via large GAC filters for colour removal. The Cornwall WTP uses St. Lawrence River water and it was chosen for several reasons. First, because this plant has filter adsorbers, i.e., the upper layer of the mixed media filters consists of GAC. Secondly, because the St. Lawrence River water is essentially Great Lakes water, which is the potable water source for millions of Canadians.

The water samples were personally collected on site for all locations except for the sample from the Richard Miller WTP in Cincinnati, Ohio. This sample was sent in a 100 litre drum that had been rinsed twice with the same water. The other water samples were collected in glass 20 litre carboys that had been cleaned with diluted chromic acid, alconox soap, and rinsed with organic free water (described in appendix A1). When the

sample arrived at the lab, it was transferred to cleaned 100 – 200 litre drums and stored in a refrigerator at 8° C until used.

Table 3.1: Water Sources

Body of Water	Location	Sampling Location	Amount Collected/date
Buffalo Pound Lake	Buffalo Pound Provincial Park, Saskatchewan, Canada	WTP* after clarifiers	40 litres/ Aug. 2004
Ottawa River	Ottawa, Ontario, Canada	WTP after clarifiers	200 litres/ May 2004
Vars Groundwater	Vars, Ontario, Canada	Directly from well #2	200 litres/ Nov. 2004
St. Lawrence River,	Cornwall, Ontario, Canada	WTP after clarifiers	200 litres/ Oct. 2004
Ohio River	Cincinnati, Ohio, U.S.A.	WTP, after mixed media filter	100 litres/ Dec. 2004

* WTP = water treatment plant

The water treatment processes that usually precede GAC filters such as coagulation, flocculation and mixed media/sand filters typically remove up to 50% of dissolved humic substances (Newcombe, 1994) and these are mainly concentrated humic acids as well as highly charged fulvic acids. The samples were collected at points in the treatment plants that are just prior to when the water would come in contact with GAC. As shown in table 3.1, only one of the water samples in this study did not undergo some previous treatment (i.e., Vars groundwater). Thus, these water sources represented typical feed water to GAC filters.

3.2.3 Initial Water Characteristics Analysis – Standard Methods

Before other experimental studies took place, initial water characteristics were determined using the standard methods reported in table 3.2.

Table 3.2: Standard Methods Used For Water Characteristic Analysis

Property	Standard Method*
Colour	2120B
Conductivity	2510B
Turbidity	2130B
Calcium Hardness	2340C
Total Hardness	2340B
Alkalinity	2320B

*APHA, 1999.

3.2.4 DOC Determination

DOC Analysis was determined using a low level TOC Analyzer (Dohrman model DC-180; Dohrman Instruments, Santa Clara, CA; or a Tekmar-Dohrman, Phoenix 8000, Cincinnati, OH). These analyzers use the Standard Method 5310C, persulfate-ultraviolet oxidation method, (APHA, 1999) to calculate total organic carbon. Each water sample was filtered through a 0.45 μm filter, thus the results were DOC values.

Calibration was conducted using potassium hydrogen phthalate (KHP) standards. The analyzer was calibrated to a KHP standard of 10 mg carbon /l. Prior to analyzing samples, a daily check of the calibration was performed. Standards of 1 ppm. 2 ppm, 4 ppm, and 10 ppm carbon were run through the analyzer daily and a calibration curve was developed to ensure the analyzer was properly calibrated. During analysis, frequent samples of the 1 ppm standard were tested as a quality control measure.

For each sample, four determinations were made from each vial and the first reading was discarded to minimize the impact of sample carryover from one sample to the next. Therefore, the sample size for this study was kept at three for most samples. The error of this method was determined by the manufacturer to be ± 0.1 mg/l.

3.2.5 UV Spectroscopy

A correlation curve was established for each source water by relating the UV absorbance results at the wavelength of 254_{nm} to the DOC results from the same sample in mg C/l. The purpose of this curve was to reduce the number of DOC analyses, which is more time consuming, as well as to have a quality control check on results. All samples had UV absorbance analyses and one half of the samples were analyzed for DOC.

UV absorbance at 254_{nm} was conducted using a Beckman Spectrophotometer (model DU-40, Beckman Coulter, Inc., Fullerton, CA). The spectrophotometer was calibrated to zero while the cell filled with organic free water (OFW)[4] was in front of the lamp. Readings were taken in triplicate. The work was begun using a 10mm quartz cell. However, the samples had low initial DOC concentrations, ranging from 1.91 mg C/l to 4.01 mg C/l. Correlations therefore used DOC values as low as possible and a longer pathlength was required to accurately develop a DOC vs. UV correlation. A 100 mm pathlength quartz cell was purchased and used for all except the adsorption kinetics study. This was because the adsorption kinetics study was conducted prior to the purchase of the longer pathlength cell. The different cell designs are shown in figure 3.1. This cell required a new holder, which was designed by University of Ottawa technicians.

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[4] Organic Free Water, OFW was prepared with a Milli-Q Water System by Millipore (Bedford, MA), using mixed bed ion exchange resins, synthetic activated carbon, organic scavengers and membranes.

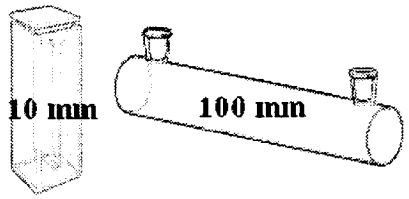

Figure 3.1: UV Spectrophotometer Cells

3.2.5.1 Interferences With UV Spectrophotometry

UV absorbance results when a molecule absorbs light. Vibration and rotation of molecules as well as inter-molecular interactions makes absorption peaks in the UV spectrum broad and featureless. That factor, along with the fact that any sample of NOM comprises molecules with a wide variety of chromophores, eliminates sharp features from the UV spectra of natural waters (Korshin *et al.,* 1997; Croué *et al.,* 2000). UV absorbance is also pH sensitive and not reliable at low concentrations such as those less than 0.1 mg C/l (Croué *et al.,* 2000).

3.2.6 pH Measurements

The pH of the water samples was monitored using an Accumet pH meter (model 910, Fisher Scientific, Hampton, NH). The meter was calibrated using buffer solutions from Sigma Aldrich (Sigma Aldrich, Milwaukee, WI) which were standardized against N.I.S.T. standard reference materials. The electrode was calibrated to a 7.0 pH buffer then checked with the 4 and 10 pH buffers to ensure calibration. The accuracy of this method was ± 0.01 pH at 25 °C. As a quality control measure, the pH values of OFW, and the five source waters were measured periodically to ensure the meter was consistent.

3.3 Adsorption Kinetics and Equilibrium

Equilibrium studies were performed to study the irreversible behavior of NOM adsorption on GAC. Both adsorption and desorption equilibrium isotherms were conducted. However to insure the data was at the equilibrium state, kinetics studies were completed prior to the equilibrium tests. The experimental procedures followed for this work are described in the following sections.

3.3.1 Preparing the GAC for Kinetics and Equilibrium Studies

Many researchers studying GAC take advantage of the faster kinetics of PAC when developing isotherms. The most common way to obtain PAC is by crushing GAC to powdered form and sorting the particles using sieves. This method was used for this research by reducing the carbon sizes to those that fell between US mesh sizes 40 and 50. The GAC used in this Thesis were Filtrasorb F-400 (Calgon Corp., Pittsburg, PA) and Nuchar WVB (Westvaco, Covington, WV). Some of the properties of these carbons are reported in table 3.3.

Table 3.3: Properties Provided by the Manufacturer

Reported Parameter	Calgon – F-400	Westvaco, WV-B
Starting Material	Bituminous Coal	Wood
Activation Method	Agglomerated, Steam	Chemical
Starting US Mesh Size	12 X 40	10 x 25
Iodine No. (mg/g)	1000	900
Surface Area (m^2/g) (Nitrogen BET method)	890*	1400 - 1600
Moisture Content (%)	2	10
Apparent Density (g/L)	440	240 - 305

* Source: Summers R.S., 1986

F-400 was chosen for this work because it is one of the most popular GACs used for water treatment with GAC, and there are many literature references that have used this GAC. WV-B was chosen because it is wood based and would be a good comparison for the coal based carbon. Previous work has also shown that WV-B GAC may adsorb NOM more reversibly than F-400. (Vidic *et al.* 1990; Karimi-Jashni and Narbaitz, 1997)

Prior to use, both GACs were sieved, sorted, ground and cleaned. All studies were completed using the same batches of GACs. The process used was as follows.

1) The GAC, as received from the manufacturer, was sieved and sorted into size fractions ranging from US mesh sizes #30 to #200.

2) The portion between # 40 and #50 US mesh size sieves was set aside. The portions smaller than # 50 were appropriately labeled and placed in laboratory storage. The portion that was retained between the #30 and # 40 US mesh size sieves was ground in a laboratory blender.

3) The GAC from the blender was again sorted through the same sieves as in step number two. GAC that was retained between the #30 and # 40 US mesh size sieves was returned to the blender. Those between # 40 and #50 were collected in clean glassware.

4) When a sufficient amount of GAC had been collected that was between the mesh sizes of #40 and #50, the carbon was placed in a 100ml beaker full of OFW.

5) The OFW in this beaker was heated to boiling. This was performed to have enhanced

leaching of impurities that may result from the GAC manufacturing process.

6) Rigorous boiling was allowed to occur for one hour.

7) The water and carbon was poured over the #50 US mesh size sieve. At this point, fines were separated from the sorted AC. The carbon was rinsed with OFW while still collected on the US sieve #50. This washed out fines that were entrapped between GAC particles.

8) Steps 4 through 7 were repeated three more times.

9) The GAC was then placed on clean aluminum foil and put in a convective oven overnight.(18 hours)

10) The GAC was weighed then returned to the oven,

11) Every hour the GAC was weighed and placed back in the oven until the weight was unchanged.

12) The GAC was placed in a dessicator to dry.

At this point the GAC was ready for use in the kinetics and equilibrium studies. The result of this sorting was GAC with the US sieve size range of 40 X 50 and a mean particle diameter of 3.53×10^{-4} m.[5] The majority of 40x50 mesh GAC used was obtained via grinding and sieving, while some was obtained by just sieving.

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[5] $d_P = \sqrt{(d_{40} * d_{50})} = \sqrt{(0.42 * 0.297)} = 3.53 \times 10^{-4} m$

3.3.2 Kinetics Experiments

In order to ensure isotherms were in fact at the equilbrium state, kinetics studies were conducted for both the adsorption and desorption systems. The procedure used is outlined in the following steps.

Adsorption Kinetics:

1) For adsorption kinetics, 50 500ml bottles were cleaned, weighed and filled with ORW. (glassware cleaning instructions are included in appendix A1)

2) Each bottle was weighed when full.

3) The volume of solution was calculated from the difference between the weight of the bottle full and empty, divided by the density of water.

4) Sieved, sorted and cleaned GAC was carefully added to the bottles, containing ORW, to achieve the exact same dosage in each bottle. The dosage used was 0.03 g GAC/l.

5) The time GAC was added to the bottle was noted. The bottle was sealed with Teflon tape around the rim then secured with a screw on cap lined with Teflon.

6) The bottles were placed in an end – over - end tumbler rotating at 12.5 rpm. (the tumbler was designed and constructed by technicians at the University of Ottawa)

7) The reaction time was varied by removing the bottles from the tumbler at different times and filtering the solution to stop adsorption. For example, on the first day bottles were taken out of the tumbler at the times of 2 min, 5min, 10min, 15min, 30min, 60min, then every hour. For the second day of kinetics, the sample time

was increased to every 2 hours. The third day, samples were analyzed every 6 hours. The samples were analyzed every 12 hours until the end of six days, then every 24 hours. Analysis continued until there was little change between the solution DOC concentrations. This was assumed to be equilibrium.

The solution was filtered by vacuum filtration using a 300ml Millipore glass funnel and glass filter holder (Millipore Corporation, Billerica, MA). The glass parts were cleaned using the same method as all glassware as described in appendix A1. The filters were manufactured using Cellulose Ester with a filter pore size of 0.22 μm and a 47mm membrane diameter (Millipore Corporation, Billerica, MA). This filter and filtration set up was found to have a flowrate of 40 ml/min by timing the filtration of several samples.

Desorption Kinetics:

1) For desorption kinetics, 70 500ml bottles were cleaned, weighed then filled with ORW. (glassware cleaning instructions are included in appendix A1)

2) Each bottle was weighed when full.

3) The volume of solution was calculated from the difference between the weight of the bottle full and empty, divided by the density of water.

4) Sieved, sorted and cleaned GAC was carefully added to the bottles containing ORW to achieve the exact same dosage in each bottle. The dosage was 0.03 g GAC/l.

5) The time GAC was added to the bottle was noted. The bottle was sealed with Teflon tape around the rim then secured with a screw on cap lined with Teflon.

6) These bottles were placed in an end – over - end tumbler rotating at 12.5 rpm and allowed to come to equilibrium. The equilibrium time was determined from the adsorption kinetics study. This equilibration time was determined to be 30 days.

7) After the bottles had been allowed enough time for equilibrium to be achieved, they were removed from the end-over-end tumbler and filtered using the same vacuum filtration method described previously.

8) The retentate (GAC) from the vacuum filtration step was added to prepared bottles filled with OFW. This preparation is described in steps 9 and 10.

9) 70 500ml bottles were cleaned, weighed, then filled with OFW, (glassware cleaning instructions are included in appendix A1), then steps 2 and 3 above were used to calculated the volume of the solution.

10) OFW was added or taken from the bottle using a clean dropper to ensure the volume of the OFW was exactly the same as the volume of solution in a corresponding bottle of ORW that was brought to equilibrium.

11) After the carbon from step 8 was added to these bottles, they were placed in the end – over - end tumbler rotating at 12.5 rpm.

12) Similar to the adsorption kinetics, desorption time was varied by pulling the bottles out of the tumbler at different times. The only difference between the two was that desorption was anticipated to be slower and take longer, therefore more bottles were used and the staggering of contact times was greater.

3.3.3 Bottle Point Isotherms

Isotherms (i.e. equilibrium) tests were conducted via the bottle point method. The name arises in that numerous bottles are used as separate batch reactors and each generates a point in the isotherm curve. The term isotherm is due to the fact that the entire equilibrium experiment takes place at a constant temperature, that of room temperature (approximately 23°C). The volume of the bottle and concentration of the solution were kept constant while the GAC dosage was changed. The dosage of GAC (ratio of the mass of carbon, M, over the volume of water, V, was from 0.005 to 3 mg/l. This decision was based on the work of Narbaitz (1986), Peel (1980) and McEwen (2004).

The same water was contacted with different dosages of GAC in an end - over - end tumbler rotating at 12.5 rpm, until equilibrium was reached. The water was then separated from the GAC using vacuum filtration. The filtrate was analyzed to determine the equilibrium concentration of the NOM, as quantified by the DOC. A mass balance was then used to calculate the equilibrium solid phase concentration on the system. This mass balance is described in equations 3.1 through 3.4.

$$Mass\ \ of\ \ NOM\ \ \ initially\ \ in\ \ the\ \ system = V(C_0) \tag{3.1}$$

$$Mass\ \ of\ \ NOM\ \ \ left\ in\ \ liquid\ \ at\ \ equilibrium = V(C_{eq}) \tag{3.2}$$

Where: V = the volume of the batch reactor (l), C_o = the initial concentration (mg DOC /l), C_{eq} = the equilibrium concentration (mg DOC /l).

The solid concentration in mg of NOM therefore contained the difference between 3.1 and 3.2.

$$Solid\ \ Phase\ \ \ mass\ \ \ of\ \ \ NOM = V\left(C_0 - C_{eq}\right) \tag{3.3}$$

The solid concentration was expressed as solid phase concentration per mass of AC in the system. The final mass balance equation used is shown in equation 3.4.

$$Q_{eq} = \frac{V}{M}\left(C_0 - C_{eq}\right) \tag{3.4}$$

Where: Q_{eq} = the solid phase equilibrium concentration per mass AC (mg DOC/g GAC), M = the mass of AC added to the batch reactor in grams.

In order to determine the equilibration time, kinetic tests were conducted as described in section 3.3.2. The AC was sieved, sorted, and cleaned then dried in a laboratory convective oven before use as explained in section 3.3.1. The sieve portion remaining on mesh size 50 and smaller than size 40 was used throughout the isotherms and kinetics studies. There were two different carbons used with the ORW. These were Calgon F-400 and Westvaco WV-B. The other four waters were studied with Calgon F-400 water.

For more details regarding isotherm procedures please see appendix A2.

3.3.4 Desorption Isotherms

For every data point on the adsorption isotherm, a desorption isotherm test was conducted. Since each data point on a bottle point isotherm is the result of one batch reactor (bottle) the solid phase from each bottle was used to conduct one desorption test using OFW as the solute. Desorption isotherms use the loaded carbon from the adsorption isotherm and desorb the NOM into organic free water, OFW.

When the solution was filtered during the adsorption isotherm, the filtrate was analyzed. However, the retentate was carefully transferred into a bottle containing the same volume, V, of organic free water as the filtrate solution brought to equilibrium in the adsorption isotherm. The concentration of NOM at time zero was assumed to be that of the OFW. The OFW was filtered using the Millipore Milli-Q ultrapure water system (Millipore Corporation, Billerica, MA). This water had measurements of DOC of 0.05mg/l and 0.03 mg/l on the Dohrman DC-180 and Dohrman Pheonix 8000 DOC analyzers, respectively. A mass balance was then used to calculate the equilibrium solid phase concentration of the desorption system. This mass balance is shown in equations 3.5 and 3.6.

At time zero, C_o = 0.03 mg NOM /l, Q_{eq} = known value from adsorption isotherm (mg NOM/g GAC). Thus the NOM leaving the solid phase and entering the liquid phase was:

$$Mass\ \ of\ \ Desorbed\ \ NOM = C_o V - C_{eq}' V \qquad (3.5)$$

Where: C_{eq}' = equilibrium concentration of the water at the completion of the desorption

test (mg DOC/ l), V = the volume of solute in the batch reactor/bottle (l).

The equilibrium concentration in the solid phase was then calculated as:

$$Q_{eq}^{'} = Q_{eq} - \frac{(Desorbed\ \ NOM)}{M} \tag{3.6}$$

Where: Qeq = the solid phase equilibrium from the adsorption isotherm (mg DOC/g GAC), M = the mass of AC added to the system (g GAC) Q_{eq}' = the solid phase equilibrium concentration per mass AC after contact with OFW for a sufficiently long time to reach equilibration (mg DOC/g GAC)

To calculate the percentage of desorbed NOM, the NOM(in mg) introduced to the system was:

$$Mass\ \ of\ \ NOM\ \ introduced = Q_{eq} M \tag{3.7}$$

and the mass of desorbed NOM was provided by equation 3.5. Then, the percentage of desorbed NOM was:

$$Percentage\ \ of\ \ desorbed\ \ NOM = \frac{Q_{eq} M}{C_o V - C_{eq}^{'} V} \tag{3.8}$$

For more detail please refer to appendix A3.

3.4 Procedures for NOM Analysis

Initial analysis was conducted on the NOM in the source waters and the equilibrium concentrations as described in section 3.2. However, since NOM is a heterogeneous mixture, fractionation techniques are an interesting approach to study the changes in NOM during adsorption and desorption on GAC. The NOM from each of the five test waters was fractionated using the techniques of ultrafiltration, size exclusion chromatography and XAD8 resin extraction. These techniques are described in the following sections.

3.4.1 Molecular Weight Distribution Using Ultrafiltration

Ultrafiltration-based molecular weight distributions were conducted using an Amicon Ultrafiltration Stirred Cell (model Micron 8050, Amicon Inc., Beverly, MA) and membranes of molecular weight cut offs (MWCO) of 500, 1000, 3000, 5000, 10 000 and 30 000 Daltons (Millipore, Billerica, MA).

The natural waters were filtered through the membranes in a progressive fashion as shown in figure 3.2. This method is referred to as the Cascade, or 'In Series', method and was used by Summers (1986), Summers and Roberts (1988), Kilduff *et al.* (1996a), Pelekani *et al.* (1999a), and O'Driscoll and Evans (2000). The result was seven water fractions plus the original raw water. UV absorbance and DOC analysis of the filtrate were used to calculate the weight percentage of NOM in each fraction. The retentate, the fractions between membrane sizes, was used for calibrating the size exclusion chromatography columns.

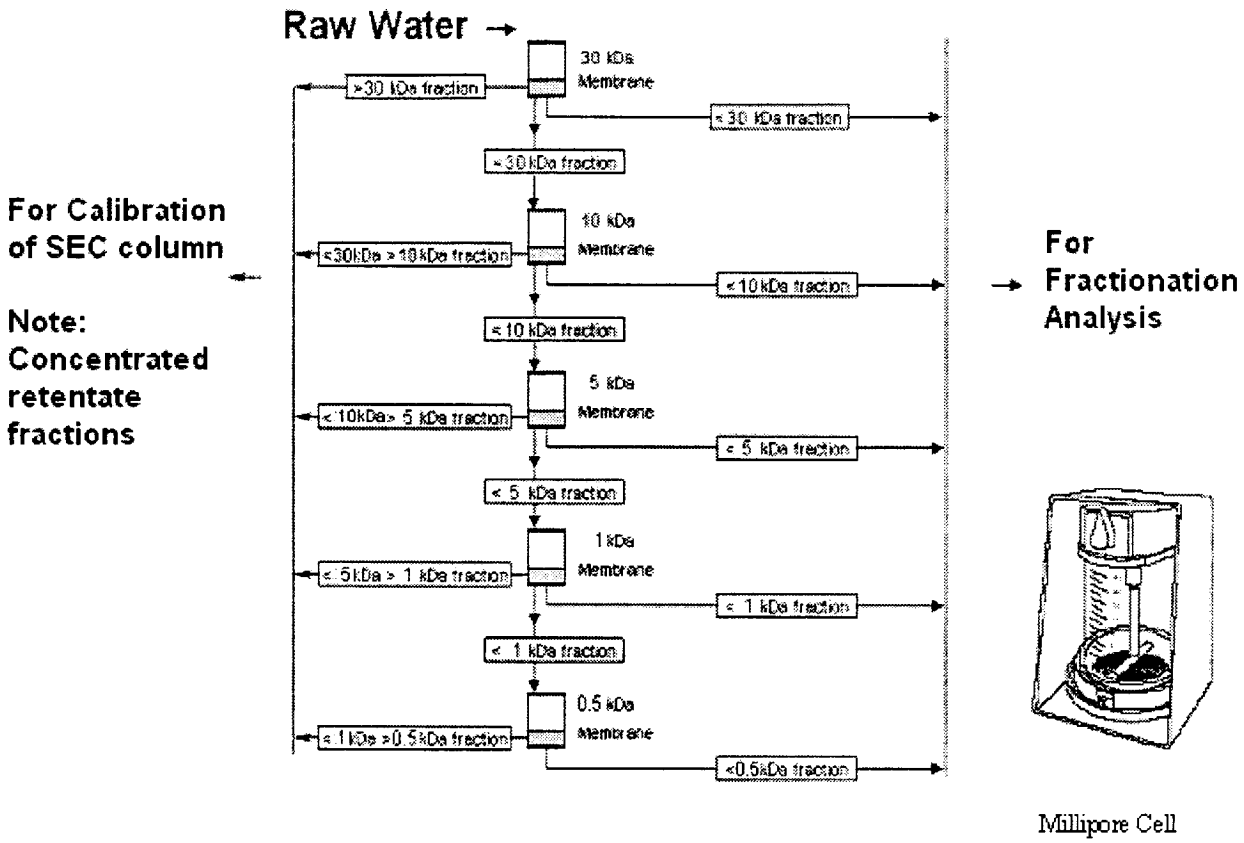

Figure 3.2: Cascading Ultrafiltration Procedure (Source, Modified from O'Driscoll , 1998)

3.4.1.1 Errors Involved with the Use of Ultrafiltration

The UF membranes were purchased from Millipore (Millipore Corporation, Billerica, MA) and came with pre-calibrated molecular weight cut off, MWCO values. There were some steric hindrance effects expected when the particles contacted the surface of this membrane as well as interference from molecular charge, hydrophobicity and chemical structure.

The membranes were manufactured and calibrated using different materials as shown in table 3.4. For the calibration of UF membranes with MWCO of 3000 Da and less, sugars and polysaccharides are used, while proteins are used to calibrate higher MWCO membranes (Pelekani *et al.,* 1999a). The membranes themselves also have a range of different pore sizes as shown in figure 3.3. It is important to note that NOM is thought to be mainly linear in structure at neutral to low pH values, and thus the waters used in this study were expected to have overestimated MSDs by these UF membranes (Aiken *et al.*, 1985; Suffet and MacCarthy, 1989).

Table 3.4: Ultrafiltration Membranes Used in This study

Filter Code	MWCO	Calibrated with	Filter Material
YC05	500	Sugars and polysaccharides	Cellulose Acetate
YM1	1000	Sugars and polysaccharides	Regenerated Cellulose
YM3	3000	Sugars and polysaccharides	Regenerated Cellulose
YM5	5000	Proteins	Regenerated Cellulose
PM10	10,000	Proteins	Polyethersulfone
PM30	30,000	Proteins	Polyethersulfone

Source: Millipore, (Billerica, MA) ; Maximum Operating Pressure = 70 psi

Since proteins are globular in structure, and NOM at neutral pH tends to be more linear in structure, the results from fractionation at MWCO's greater than 3000 will be inaccurate. Pelekani *et al.(*1999) estimated that the true nominal MWCO for the NOM will be less than that from UF because the size to mass ratio of NOM is larger than that of proteins. For more detail please see appendix A4.

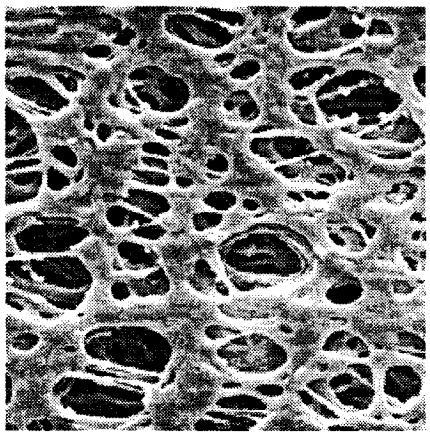

Figure 3.3: Magnified Surface of an UF Membrane (Source, Millipore Corporation).

3.4.2 Molecular Size Distribution Using Size Exclusion Chromatography

Size exclusion chromatography is based on filtration through an unreactive gel and the fact that smaller compounds will diffuse into the pores between the gel particles and display longer retention times than larger sized molecules. The procedure followed in this study was that described by Kilduff *et al.* (1996a), Mori (1999), O'Driscoll and Evans (2000), and Wu (2004). Sephadex gel G25 (Sigma Aldrich, Milwaukee, WI) was used with the fractionation range of 100 – 5000 MW. The sample is introduced into the gel column and the rentention time and response peaks are measured. The analyzed peak is

determined from the maximum response with an appropriate analytical technique. Many researchers use a refractometer connected to the bottom of the column. Some studies have used UV absorbance analysis (Newcombe *et al.*, 2002, O'Driscoll and Evans, 2000). See appendix A5 for more details regarding this procedure.

3.4.2.1 Errors Inherent in the Use of SEC Columns

A key assumption in the use of gels for SEC is that the surface of the gel is non-reactive. Therefore the only reason one molecule takes longer than another to elute is because this molecule is caught in pores within the gel. If there were any *attractions* between the NOM and the gel due to van der waals or electrostatic forces this would affect the retention time of molecules and the calculated molecular size distribution, MSD. Any electrostatic *repulsion* would result in molecular weight distributions that are higher than actual. A second potential error in the adsorption of hydrophobic compounds onto any reactive sites on the gel surface. The sephadex gel used in this study is made of silica. Silica may have silanol groups (SiOH) on the surface which may be reactive with some molecules (Mori, 1999).

Another potential error is that of the choice of calibration compounds. The calibration solutions should behave in the same way as NOM for correct results. In this study both the use of polystyrene sulfonates (PSS) and the UF retentate samples were used as standards, as recommended by Pelekani *et al.* (1999a) and Chin *et al.* (1994). It was assumed that the UF fractions would behave in a similar fashion to the same molecular size portions in unfractionated water.

3.4.3 Extraction of Humic Acid and Fulvic Acid Fractions Using XAD8 Resin

The chemical fractionations used most often are humic acids, fulvic acids, and humin defined as:

Humic Acid: the fraction of NOM that *is not* soluble in water at pH < 2

Fulvic Acid: the fraction of NOM that *is* soluble in water at pH < 2

Humin: the fraction of NOM that *is not* soluble in water at any pH

These acids are best separated from one another using a methyl methacrylate resin called XAD8 (Fisher Scientific, Hampton, NH). This XAD8 procedure was from Thurman and Malcolm (1981). It consisted of acidifying the source waters to a pH less than or equal to 2.0. Then, the water was passed through a column filled with XAD8 resin three times. The insoluble humic acids were extracted from the water and were retained on the XAD8 resin. The fulvics acid molecules, which were still soluble, were present in the effluent. A mass balance allowed for calculation of the fractions of humic and fulvic acids in the water. For more detailed information, please refer to appendix A6.

Chapter 4: Experimental Results - Initial Analysis

Initial analysis was conducted on all source waters to determine parameters such as pH, conductivity, colour and hardness. The results of this preliminary work are provided in table 4.1. One noteworthy result was the high colour unit value of 25, and conductivity of 0.9 milli - ohm for Vars Ground Water (VGW). The high conductivity was expected as groundwaters are highly mineralized, and it is known that this water has a high iron content. The high colour unit may have been from the iron content in the water or from NOM, as some NOM are responsible for colour in natural water. Other results of importance were that Buffalo Pound Lake Water (BPLW) and VGW had the highest DOC values of 3.50 ± 0.038 mg/l and 4.01 ± 0.017 mg/l, respectively. These waters also had the highest pH values, which were 7.29 for BPLW and 7.45 for VGW.

Table 4.1: Water Properties

Water Source	Site of Sampling	Date	Symbol	DOC (mg C/l)	pH	Conductivity (milli-ohms)	Colour
Ottawa River Water	Ottawa WTP, Ontario; after the clarifiers	May, 2004	ORW	3.15 ± 0.02	6.97	0.710	5
Ohio River Water	Cincinnati WTP, Ohio, after Sand Filtration	November, 2004	OHRW	1.92 ± 0.03	6.65	0.800	10
Buffalo Pound Lake Water	Buffalo Pound WTP, Saskatchewan, after clarifiers	August, 2004	BPLW	3.50 ± 0.04	7.29	0.835	5
Vars Ground Water	Vars Wells, Ontario; straight from Well #2	November, 2004	VGW	4.01 ± 0.02	7.45	0.900	25
St. Lawrence River Water	Cornwall WTP, Ontario; after the clarifiers	September, 2004	SLRW	2.62 ± 0.04	6.69	0.705	2.5

Symbol	Turbidity (NTU)	Alkalinity (mg $CaCO_3$/L)	Total Hardness (mg $CaCO_3$/L)	Calcium Hardness (mg $CaCO_3$/L)	UV absorbance at 254nm. (100mm pathlength, m^{-1})	SUVA (m^{-1} L/ mg C)
ORW	0.261 ± 0.002	2.4	25.8	22.1	0.525	0.17
OHRW	0.173 ± 0.001	5.2	118	67.3	0.370	0.19
BPLW	0.414 ± 0.005	5.1	138	63.3	0.375	0.11
VGW	0.616 ± 0.002	15.0	166	82.8	1.266	0.32
SLRW	0.366 ± 0.012	11.6	109	64.4	0.325	0.12

The water characteristics were compared to published values when possible. The water quality of the samples collected was within the levels reported in the literature. These are noted in the following sections. More detailed information on each water is included in appendix B.

For organizational purposes, the DOC and UV absorbance correlations are reported as part of initial analysis. Every sample from this thesis was analyzed for UV absorbance and the DOC vs. UV absorbance relationships were determined using isotherm data.

4.1 Ottawa River Water

The ORW characteristics reported in table 4.1 were in agreement with properties found by Karimi-Jashni, (1997a) and those of other graduate students currently working at the University of Ottawa during 2004. Karimi-Jashni (1997a) found an initial DOC value of 3.6 mg C/l while this study found a DOC value of 3.15 $\pm$ 0.02 mg C/l at the same sampling port of the Britannia WTP.

The DOC vs. UV absorbance relationship for this water is shown in figures 4.1 and 4.2. Figure 4.1 shows the data from all four isotherms conducted with this water, and the relationship was linear. However, as shown in figure 4.2, a different straight line correlation was found for each isotherm. Thus, the UV absorbance of the water changed with different GACs and with time.

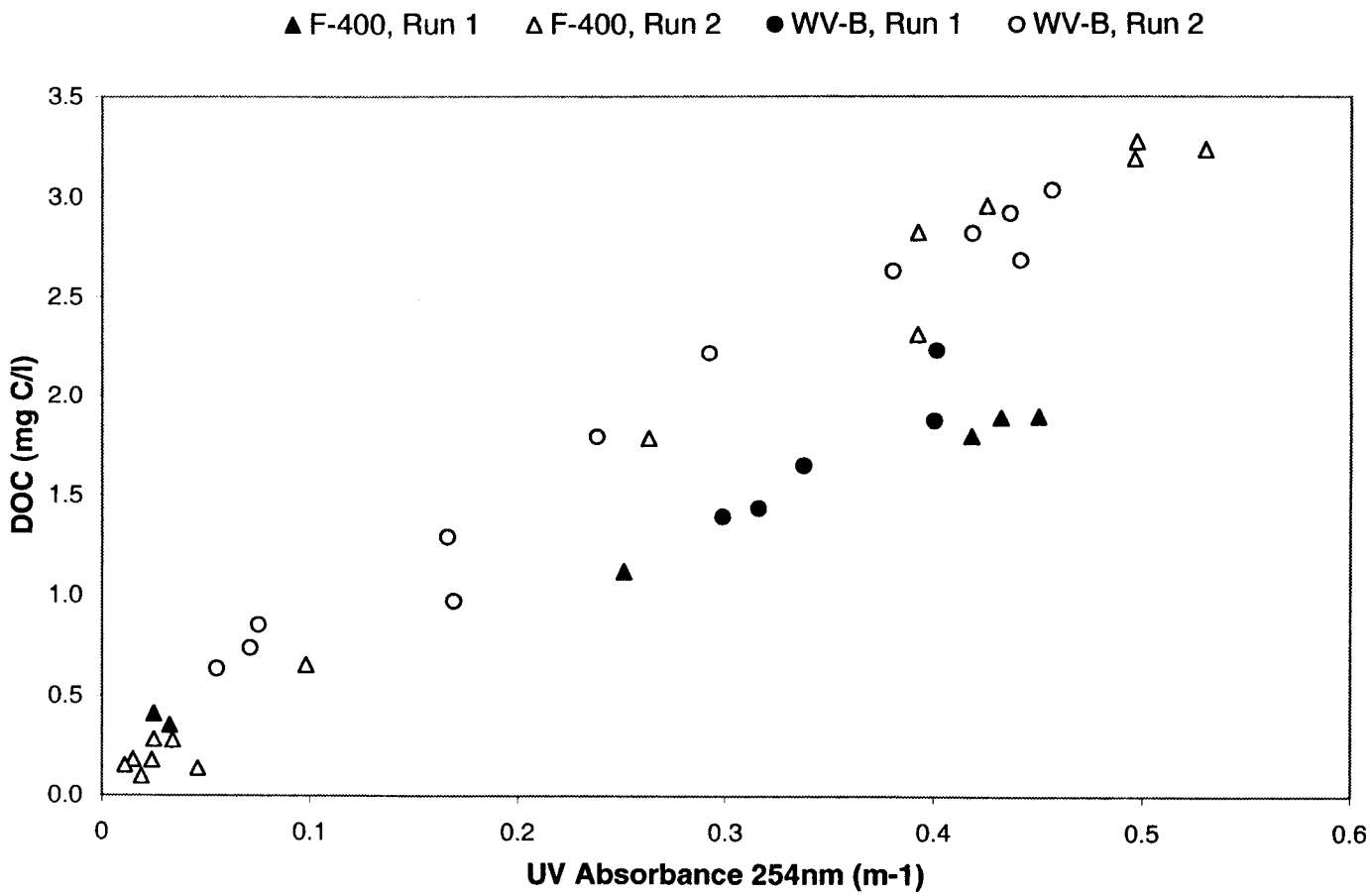

Figure 4.1: DOC and UV Absorbance Relationship for ORW (100 mm Pathlength)
(Note: Run 1 was conducted during September, 2004 and Run 2 during April 2005)

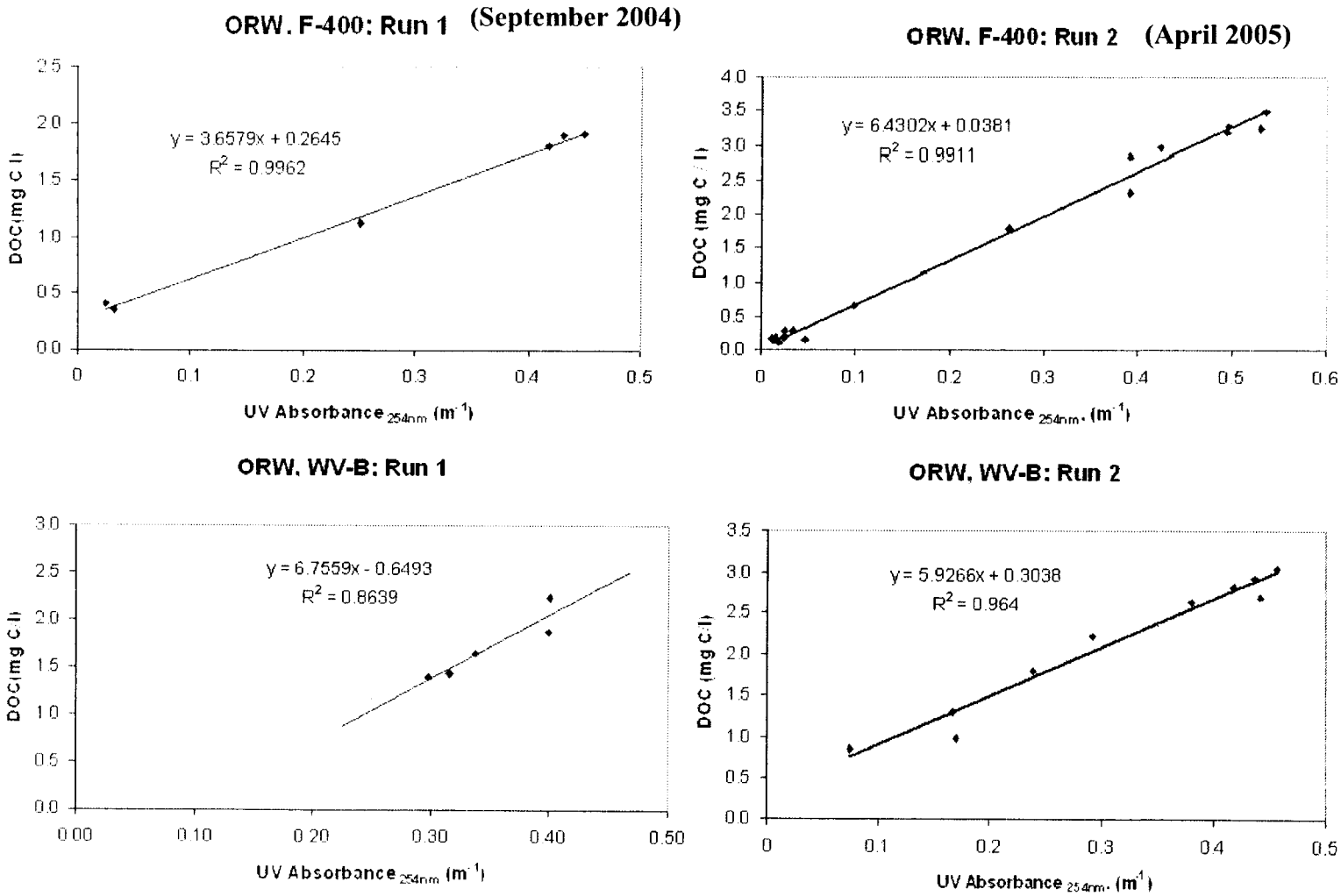

Figure 4.2: Comparison of the DOC Versus UV Relationship with Different GACs

4.2 Ohio River Water

GAC adsorption of NOM in Ohio River water has been previously studied and published in journals (Westerhoff and Miller, 1986; Warta *et al.*, 1995) and previous work has been conducted on this water at the University of Ottawa (McEwen 2004). The properties reported in table 4.1 were in agreement with the water characteristics of OHRW reported in these sources. Both Warta *et al.* (1995) and McEwen (2004) collected OHRW from the same sampling port at the Richard Miller WTP. Their initial DOC values were 2.5 mg C/l and 1.5 mg C/l., respectively. The sample used in this study had a DOC value of 1.92 ± 0.03 mg C/l, a value between these published results. The linear relationship found between DOC and UV absorbance for OHRW is shown in figure 4.3.

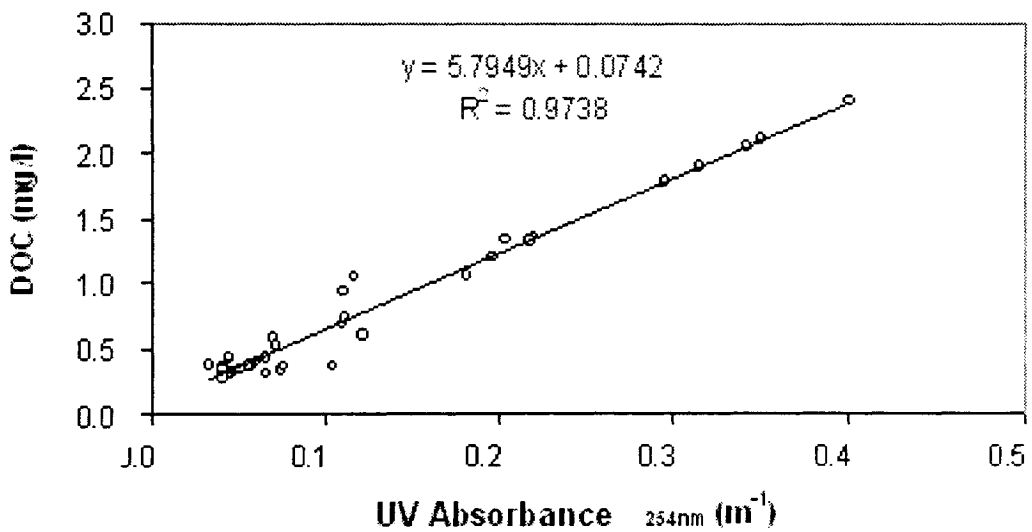

Figure 4.3: DOC and UV Absorbance Relationship for OHRW

4.3 Buffalo Pound Lake Water

The properties of BPLW have also been previously published (Srinivasan, P.T., and Virarghavan, T., 2002; McEwen, 2004; Buffalo Pound Water Administration Board, 2004). The Buffalo Pound WTP reported an average DOC value prior to the GAC filter (same sampling port as this study and McEwen, 2004) during August, 2004 of 3.5 mg C/l.(Buffalo Pound Water Administration Board, 2004) McEwen (2004) found a DOC value of 3.2 mg C/l, while the water sample used in this study had a DOC value of 3.50 ± 0.04 mg C/l. All of the other water characteristics were in agreement with the water quality reported by the Buffalo Pound Water Administration Board (2004). The DOC vs. UV correlation results are shown in figure 4.4.

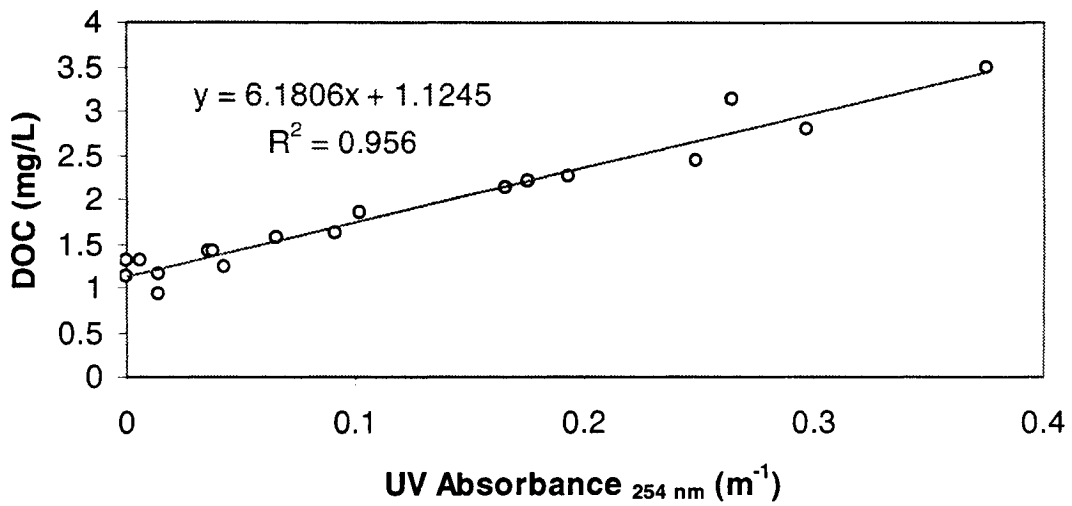

Figure 4.4: DOC and UV Absorbance Relationship for BPLW

4.4. Vars Ground Water

There has not been published data on the characteristics of VGW, besides annual reports supplied by the City of Ottawa. (City of Ottawa Drinking Water Services, Ottawa, Ontario, 2003) DOC values were not reported, however the average turbidity of treated water was reported as 0.52 NTU, while this study found the turbidity from the well to be 0.616 NTU. The average iron content in treated VGW was reported as 0.20 mg/l.

The DOC vs. UV absorbance relationship for VGW is shown in figure 4.5 below.

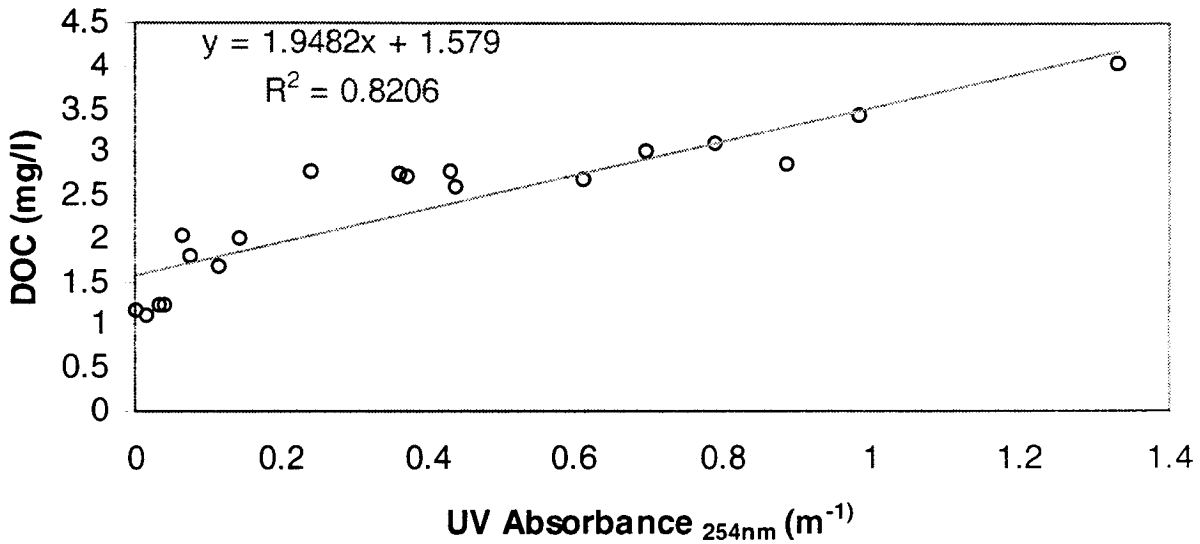

Figure 4.5: DOC and UV Absorbance Relationship for VGW

4.5 St. Lawrence River Water

Water characteristics from the SLRW at the Cornwall WTP are published in Ontario Drinking Water Surveillance Program (2002). For September 2000 through 2002, the DOC value of treated SLRW was 2.0 mg C/l. The DOC value was found in this study to be 2.62 ± 0.04 mg C/l with the sample drawn after the clarifiers in the WTP. Other water characteristics were also found to be in agreement with this report. The DOC vs. UV absorbance relationship for SLRW is shown in figure 4.6. As with the other water sources, this relationship was found to be linear.

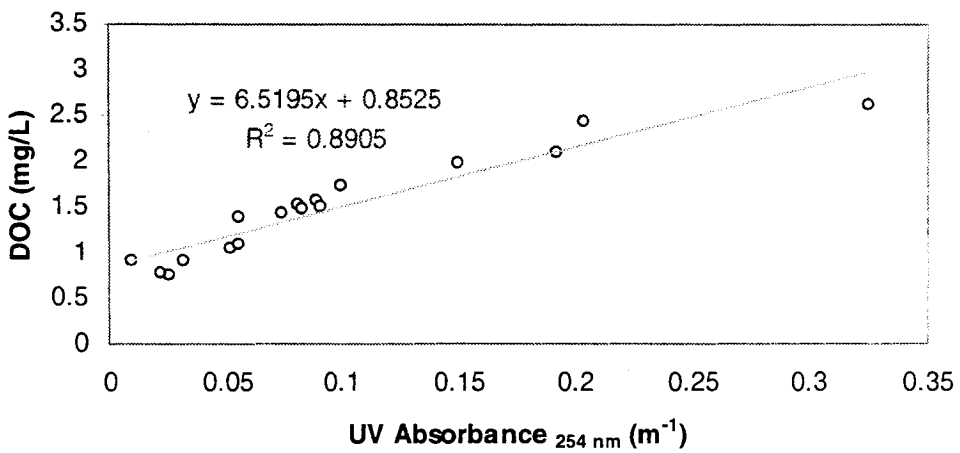

Figure 4.6: DOC and UV Absorbance Relationship for SLRW

The remaining experimental results are reported in the following three chapters. First the results from initial kinetics studies are shown and discussed in chapter 5. Adsorption and desorption isotherms are included in chapter 6, then NOM analysis work is reported in chapter 7. This work includes fractionation by ultrafiltration, extraction of humic acid on XAD8 resin, and size exclusion chromatography.

Chapter 5: Experimental Results - Kinetics

Kinetic tests were performed for both adsorption and desorption to determine equilibrium time necessary for the adsorption and desorption equilibrium tests (i.e. isotherms). It should be noted that in essence the kinetic experiments were conducted via the bottle-point technique, thus many 500 mL glass bottles containing the same water and the same carbon dose are used as batch reactors with different contact periods. The results of these bottles are then jointly analyzed as a single kinetics test. The variability in data during adsorption and desorption kinetics may be in large part due to this fact. Some of the error may be due to the scale of the work and the highly adsorptive characteristics of GAC. It was difficult to weigh exactly the small target amount of GAC necessary to maintain the carbon dosage constant for all bottles which was 0.03 g/l, or 0.015g per 500ml bottle. The weighing was further complicated by the fact that the GAC absorbs moisture from the air and this has a measurable impact on the balance reading while conducting the weighing.

The results from these adsorption and desorption kinetic tests are described in the following sections.

5.1 Adsorption Kinetics

To justify all results from this study, a kinetics analysis was performed on both adsorption and desorption kinetics. The water source used for this work was ORW and the AC was Calgon F-400. This data is recorded in appendix C.

For this initial study, the DOC was determined for one half of the samples, while the UV absorbance was measured for all samples. This was done to take advantage of the fact that UV measurements take much less time to complete. The UV absorbance was conducted using a quartz cell with a 10 mm pathlength. The calibration of DOC (mg/l) vs. UV_{254nm} (m^{-1}) relationship was established from the *isotherm* data, not the kinetics data. The kinetics results were set aside until after an equilibration time was concluded from DOC analysis, then the isotherm was completed (and with it the correlation relationship between DOC and UV), and finally the kinetics were analyzed. The DOC vs. UV relationship had a straight line relationship as shown in figure 5.1, and using Microsoft Excel it was determined by least squares regression to be:

$$DOC = 9.32(\text{Absorbance at } 254nm) - 1.75 \qquad (5.1)$$

The regression correlation coefficient, R^2, was 0.95. As shown in figure 5.2, UV absorbance was also studied at the wavelengths of 280 nm and 350 nm. Measurements at the latter two wavelengths were conducted to further characterize NOM adsorption as suggested by Korshin et al. (1997). There was a significant amount of scatter in the data. The UV absorbance at wavelengths of 254nm and 280nm changed rapidly in the

beginning of the kinetics experiment then settled to an equilibrium level. However the absorbance values at the wavelength of 350nm showed little change over time.

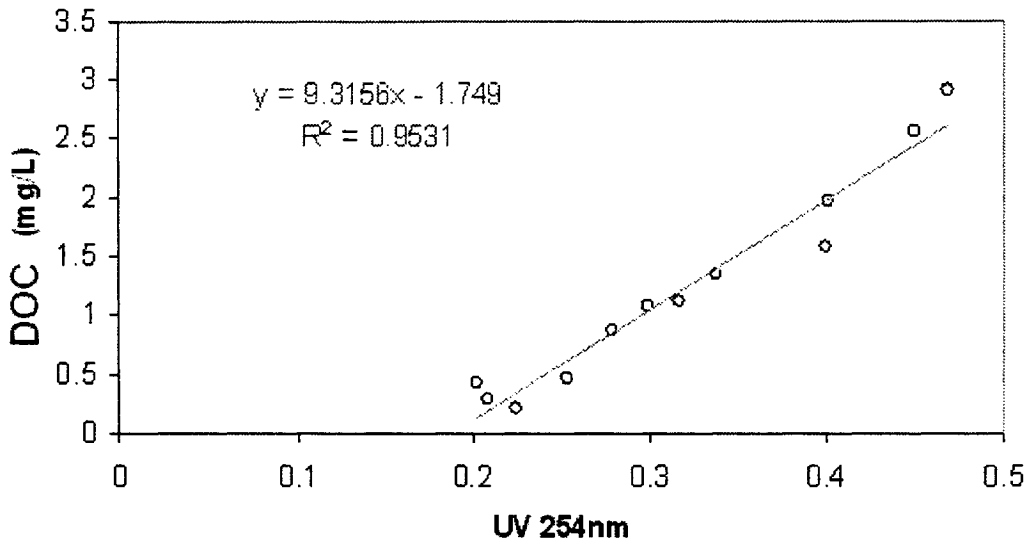

Figure 5.1: Relationship Between DOC and UV Absorbance, ORW, F-400 AC, 10mm Pathlength

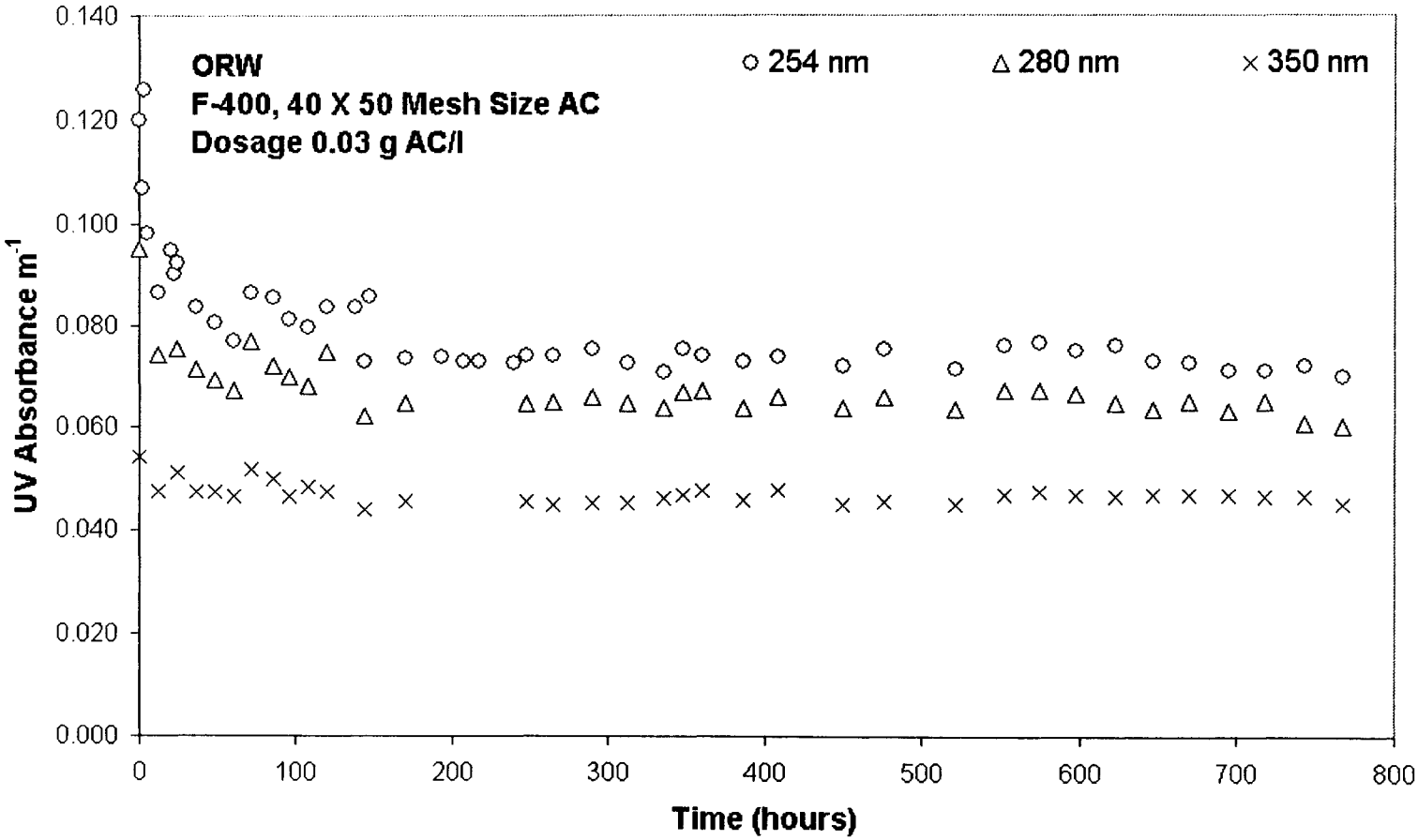

Figure 5.2: UV Absorbance Spectra of Kinetics Analysis , 10 mm Pathlength

The electron transfer band, as defined in equation 2.17, was calculated for the adsorption kinetics run using the absorbance data at 280 and 350 nm. As illustrated in figure 5.3, the electron transfer band value decreased over time. According to *Croué et al.*(2000), Korshin *et al.*((1997), and Korshin *et al.*(2002) this means that the portion of aromatics in the water decreased over time. Since the analyzed water represented the compounds that did not adsorb, this meant that the aromatics were adsorbing at a faster rate than other NOM functional groups, such as carboxylics, were adsorbing.

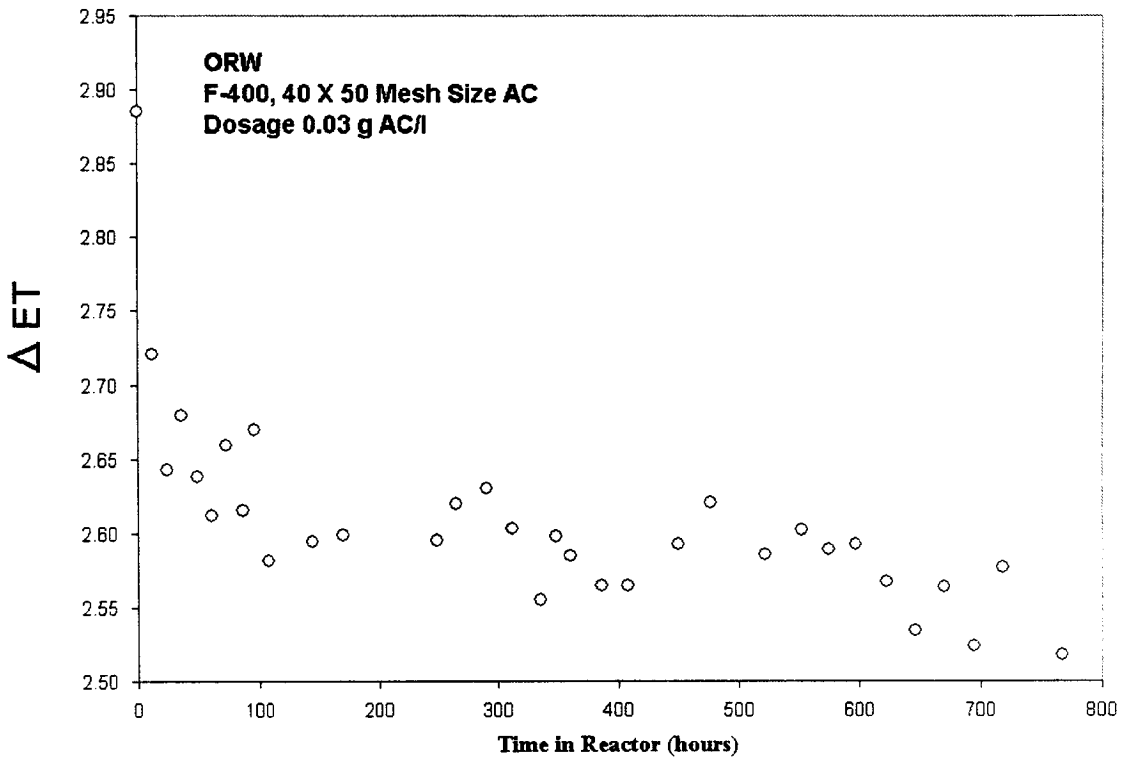

Figure 5.3: ORW Adsorption Kinetics Using F-400 -The Electron Transfer Band

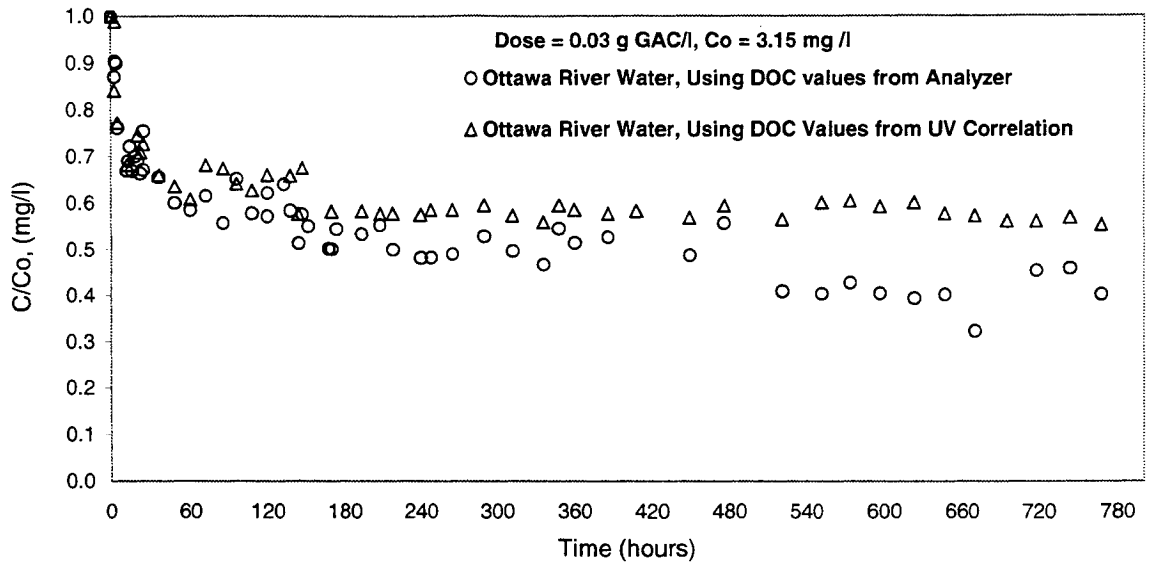

Figure 5.4: Adsorption Kinetics Concentration Decay Curve from Batch Ezperiments

The adsorption kinetics experiment continued until there was little change in the liquid DOC concentration of the batch reactor. As shown in figure 5.4, the experiment continued for 800 hours. When DOC was calculated from equation 5.1, equilibrium was reached after 250 hours. When looking at experimental DOC values, equilibrium was achieved after 600 hours (25days). The equilibrium time of 30 days was chosen to ensure all experiments came to a full equilibrium condition. After 30 days ORW had an equilibrium value of 1.274 ± 0.073 mg C / l (57% Co), at a carbon dose of 0.03 g/l. This finding was in agreement with those of Narbaitz (1986). This comparison is shown in table 5.1 below.

Table 5.1: Comparison of Adsorption Equilibrium Times

Study	GAC/Mesh Size	M/V (g/l)	NOM Source	Equilibration Time
Current	F-400, 40 X 50	0.03	Ottawa River	30 days
Narbaitz(1986)	F-400, 40 X 50	0.04691	Fauquier River	> 15 days

5.2 Desorption Kinetics

Based on the experimental data, equilibrium occurred after 1600 hours, as is demonstrated in figure 5.5. Although there was quite of bit of variability, equilibrium appears to have been reached after about 1600 hours. From 1600 hours to 1920 hours the DOC concentration was 0.136 ± 0.022mg C/ l (average and standard deviation using the remaining points) After 1920 hours organic free water, OFW, had a DOC value of 0.131 ± 0.007mg/l (8.3% of the DOC known to be adsorbed on the AC). Based on these results it was decided to use a 60 day contact period for the desorption kinetics. The fact that there was an immediate presence of DOC measured in the water during the desorption kinetics suggests that there was some DOC adsorption directly on the outer surface of the carbon, which did not desorb during the vacuum filtration step.

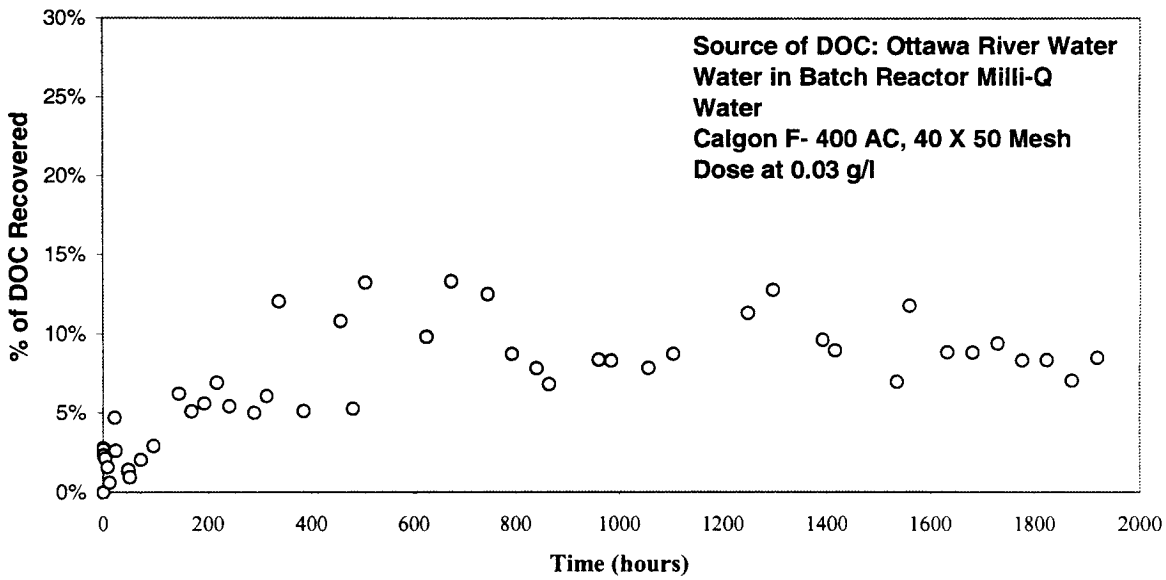

Figure 5.5: Desorption Kinetics Growth Curve from Batch Experiments

The UV absorbance data showed no change in absorbance at any wavelength. This is because the DOC values were too low for a DOC vs. UV correlation, at the pathlength of 10mm.

The variation observed in this experiment resulted from the fact that the data incorporated experimental errors from the sorption (or loading) step as well as those associated with the desorption step. This demonstrates the need of using many data points while conducting this type of experiment. The manufacturer's manual for the low temperature DOC analyzer (Dohrman model DC-180; Dohrman Instruments, Santa Clara, CA) reported that the reproducability of DOC measurements at low level concentrations was ±0.01 mg C/l. For the desorption kinetics study the standard deviation ranged from 0.002 mg C/l to 0.066 mg C/l for the DOC values of 0.136 mg C/l and 0.259 mg C/l, respectively. This standard deviation range was 1.5% to 25% of the measured DOC values.

Please refer to appendix D for more detail on this data.

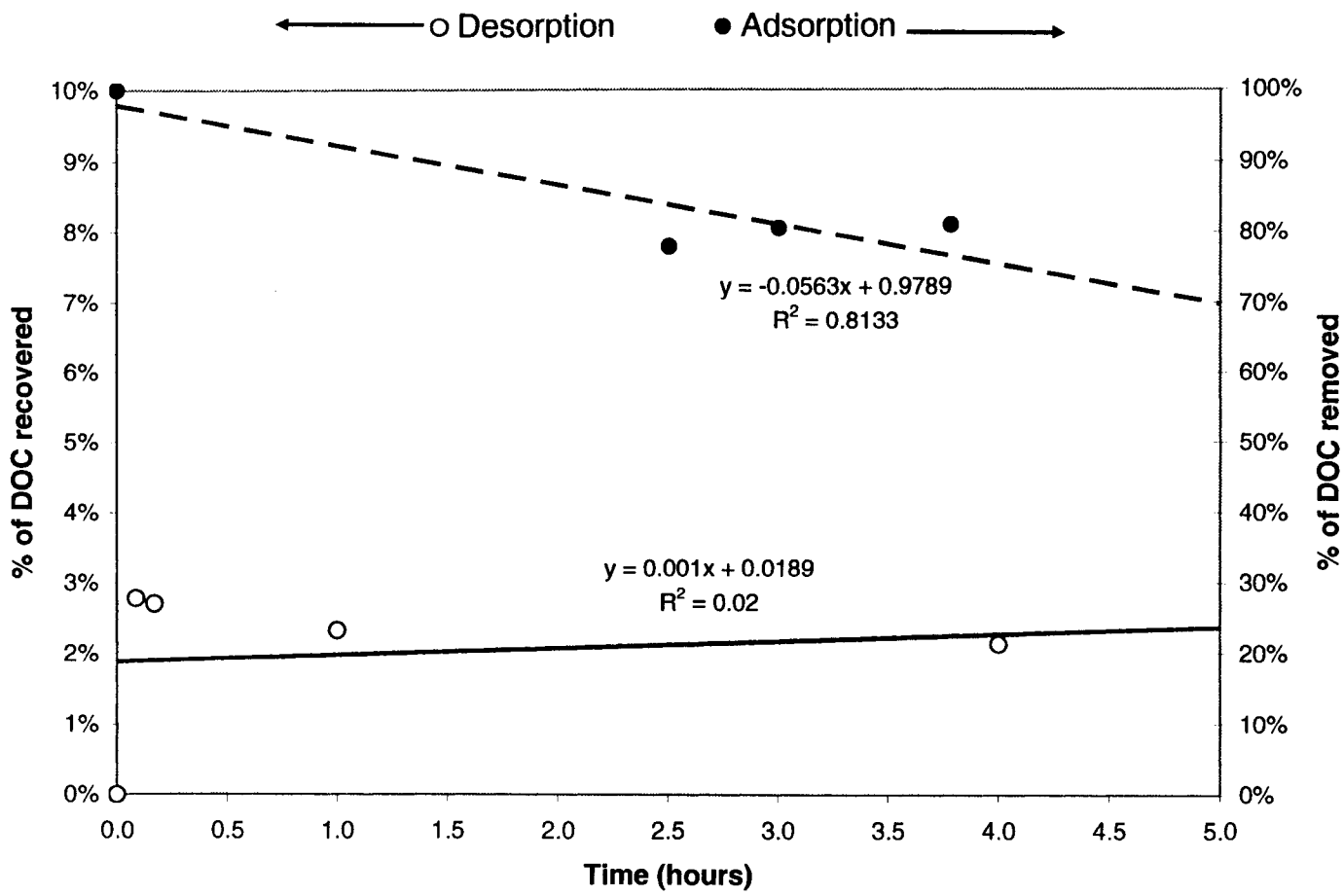

Figure 5.6: Comparison of Early Adsorption and Desorption Kinetics

Early kinetics data points for the adsorption and desorption experiments were compared as shown in figure 5.6. The adsorption kinetics had a linear relationship with time and were rapid, however the desorption kinetics did not have a linear relationship and were quite slow. It is not known if this lack of a linear relationship was due to the very slow kinetics of the desorption or errors that are inherent in the set up process for desorption kinetics. For each desorption data point; one bottle was brought to 30 days equilibrium with ORW at the GAC dose of 0.03g/l. Then this water was filtered and the filtrate added to OFW. It is possible that there were measurement errors while preparing the GAC dose. These errors set up the desorption kinetics for inconsistencies even before the filtrate was added to the OFW. Other errors may have been introduced during the transfer from vacuum filtration to the desorption bottles.

Chapter 6: Experimental Results - Isotherms

6.1 Adsorption Isotherms

Bottle point isotherms were conducted following the procedure outlined in appendix A2. Incremental GAC dosages, M/V, were measured out into clean 500 ml and 1000 ml bottles. A 30 day equilibration period was used, during which time the bottles were agitated in an end – over - end tumbler, rotating at 12.5 rpm. To ensure the data was following logical trends, a plot of the solid phase equilibrium versus M/V was conducted. Shown in figure 6.1, the liquid phase equilibrium decreased with increased and increasing GAC dose. Initially the decrease was very sharp then became more gradual and eventually reached a constant value. This constant value is the concentration of the non – adsorbable fraction of the NOM in the waters.

Section 6.1.1 shows a comparison of two GACs with ORW. These GACs were F-400 and Westvaco WV-B. The wood based carbon, WV-B was chosen because it has been shown that the adsorption of phenolics on this brand of GAC under oxic conditions did not result in irreversible adsorption and thus possibly more reversible NOM adsorption could be expected (Karimi-Jashni and Narbaitz, R., 1997b; Vidic *et al.* 1990).

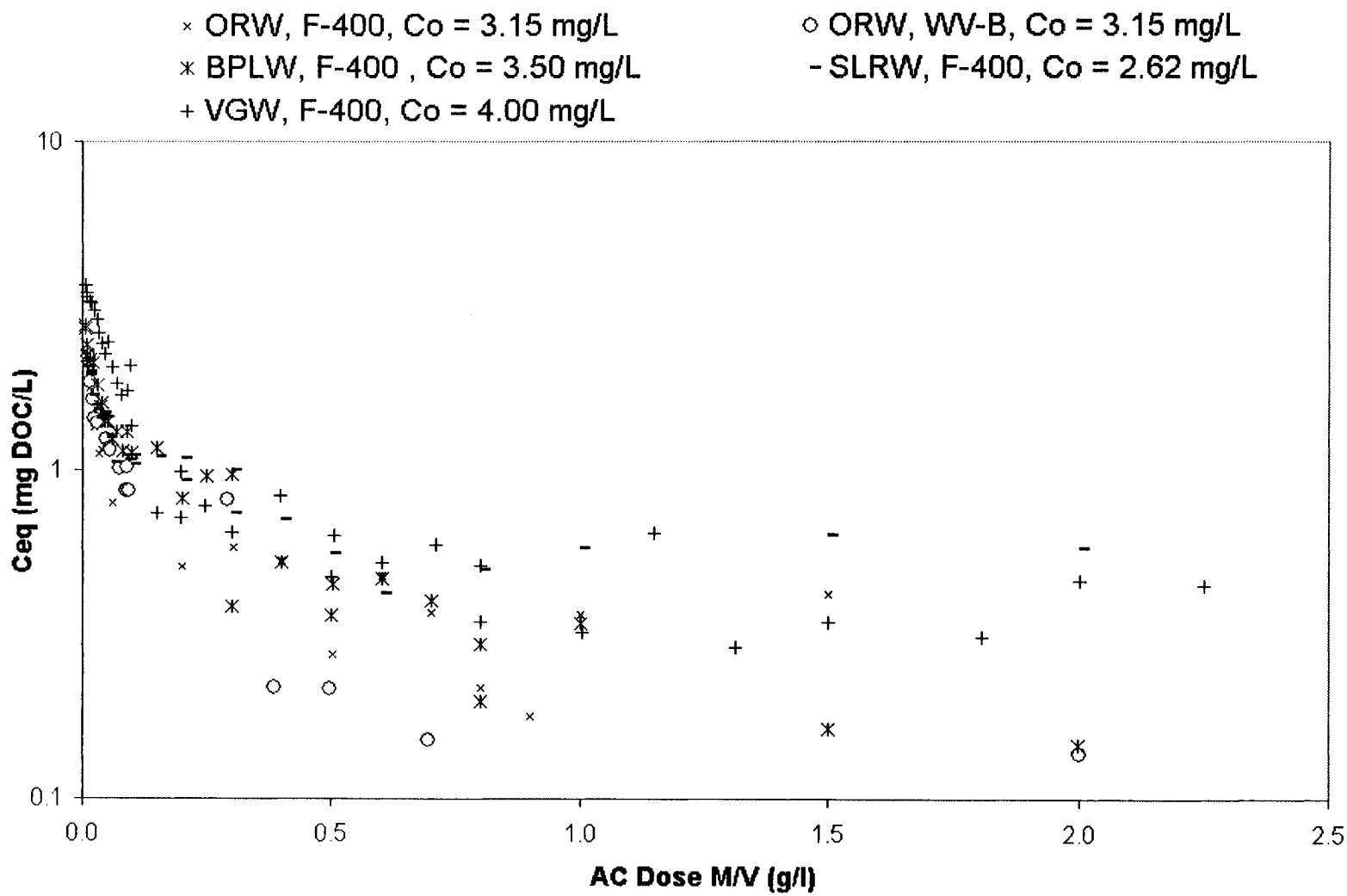

Figure 6.1: Trend of Liquid Phase Equilibrium Versus Carbon Dosage for All Waters

Adsorption isotherm data for two of the natural waters, SLRW and OHRW, with F-400 GAC is shown in figure 6.2. These waters were selected as an illustration of how the non-adsorbing fraction is evident after completing the mass balance required for the isotherm graph. The logarithmic scale allowed for better observation of the non-absorbing fraction of NOM, which can be seen in figure 6.2 where the equilibrium value of the liquid phase varies very little even though the solid phase increases. On a linear scale isotherm graph, these points show as a 'cluster' near the abscissa.

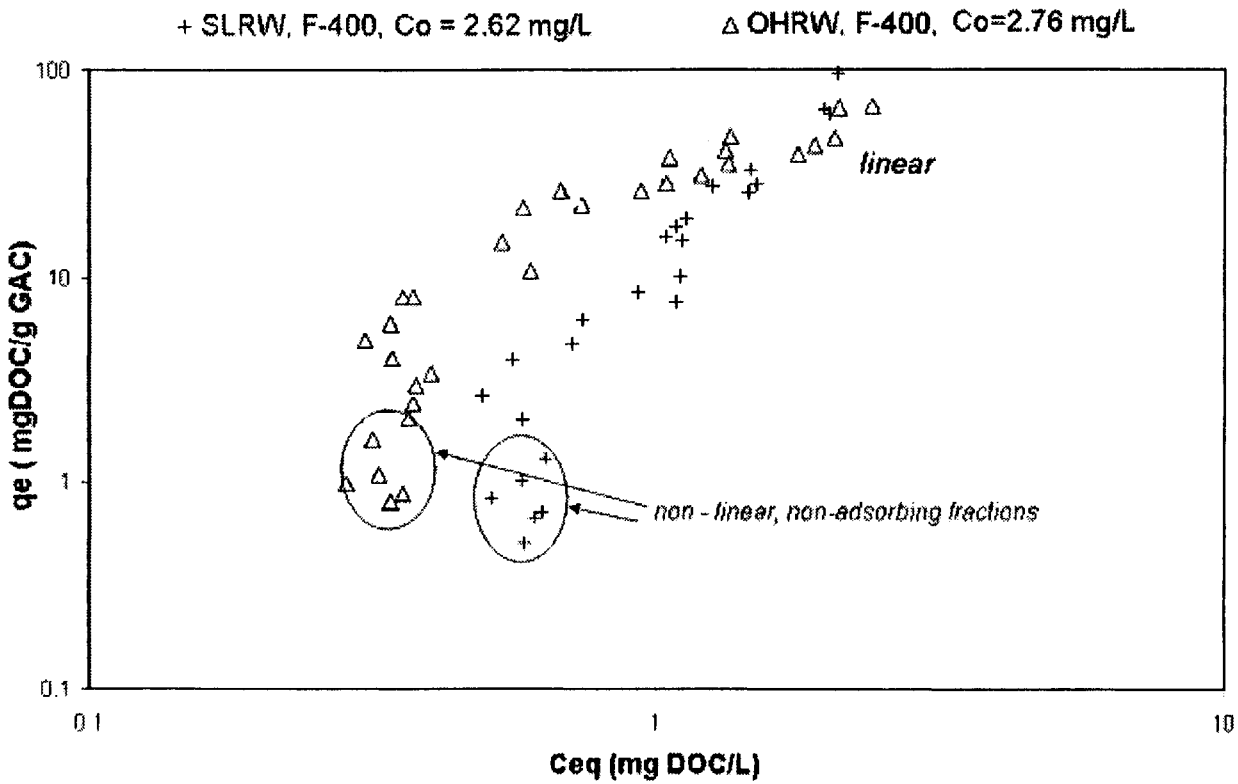

Figure 6.2: Isotherms of Two Natural Waters with F-400 Carbon

Working with all GAC dosages introduced errors such as moisture and oxygen entrapment on the GAC during weighing. However, it is important to note the limitations with measuring and conducting mass balances at low carbon dosages. The mass of GAC can become very low and the value provided by laboratory balances may not be accurate. To improve accuracy, 1000 ml bottles were used for the four smallest GAC masses. These represent the highest equilibrium concentrations. They should be considered as low precision data points. The mass balance at these low GAC doses introduces an uncertainty in the value of $Q_{eq} = (C_o - C_{eq})V/M$ as C_{eq} approaches the value of C_o.

A nonlinear regression routine was conducted to calculate the Freundlich parameters k and n, for each isotherm. The sum of the square residuals was minimized using the Microsoft Excel program's 'solver'. For clarification, a description of this method is included in appendix F.

6.1.1 Ottawa River Water

Four adsorption isotherms were conducted with Ottawa River water, ORW. Two were with Calgon F-400, a coal based GAC and two were with the wood based GAC Westvaco WV-B. All of the GAC was cleaned according to the process outlined in appendix F. These results are shown in figure 6.3. The hollow symbols shown in figure 6.3, represent the early isotherms with ORW (water collected in May 2004 and isotherms conducted in September 2004), and the solid symbols represent the later isotherms (water collected in May 2004 and isotherms conducted in April 2005). The second set of isotherms were conducted because some of the loadings in the first set of isotherms were

somewhat lower than those generated by Karimi - Jashni (1997a) for Filtrasorb F-300 and ORW. For the first sets of isotherms, there was very little difference in the best fit isotherms of the bituminous coal and wood based GACs although the data showed some scatter. However, for the second set of isotherms, wood based GAC achieved higher solid phase concentrations than the coal based GAC, with the same amounts of GAC and ORW.

As shown in figure 6.3, the isotherms conducted ten months after the initial experimental work are very different. The isotherm with F-400 GAC changed from being unfavourable to favourable, as evident in the change from a concave shape to a convex shape. The isotherm with WV-B had a similar shape but was less adsorptive. It was concluded that this was due to the transient nature of NOM (Aiken *et al.*, 1985; Croué *et al.*, 2000; Suffet and MacCarthy, 1989).

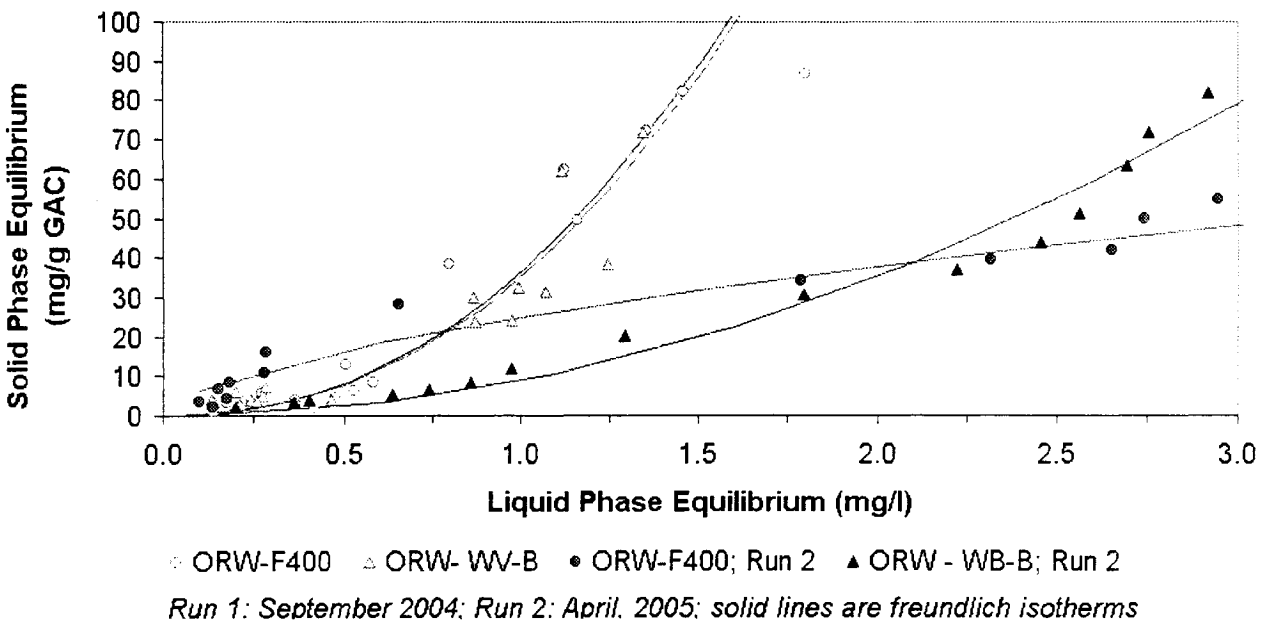

Figure 6.3: Ottawa River Bottle Point Isotherms

Although the water was stored in a refrigerated, air tight drum, the macromolecules have agglomerated over time. Even though the DOC value of the water was the same, the NOM molecules had changed. Thus it is recommended that water samples should only be collected immediately prior to the start of adsorption experiments.

The Freundlich parameters and results from the nonlinear regression are reported in table 6.1. The non adsorbing fraction of NOM ranged from 0.200 mg/L to 0.027 mg/L. The second isotherms required more than twice the amounts of carbon to obtain the non-adsorbing value of NOM(i.e. point where isotherm crossed abscissa of isotherm graph). The dosages, M/V, at which Ceq did not change with increased dosage are reported in table 6.1.

Table 6.1: Ottawa River Water Adsorption Isotherms

Carbon	Run	Non Adsorbing NOM (mg/L)	M/V* (g/L)	Freundlich Regressed Constants		Sum of Square Residuals**
				K	n	
F-400	1	0.15	0.2	34.95	2.22	3723.26
F-400	2	0.10	1.0	24.86	0.6	622.86
WV-B	1	0.03	0.6	36.60	2.19	2152.31
WV-B	2	0.20	1.5	8.78	2.00	302.01

* = the dosage(M/V) at which lowest Ceq occurred, then remained at this value with all higher dosages
** = calculated from Excel nonlinear regression routine described in appendix F

One interesting result was that the AC dosage, M/V, required to reach a point where C_{eq} no longer changed with further dosages increased for both ACs. However, the C_{eq} value at this point decreased for the F-400 isotherm and increased for the WV-B isotherm. If the NOM agglomerated during the ten months of refrigerated storage, it would likely

have resulted in an increase in the non-adsorbable fraction of NOM, due to larger molecular sizes and steric hindrance.

6.1.2 All Other Source Waters (OHRW, SLRW, BLPW, VGW)

Shown in figures 6.4 through 6.7, the other four water sources were studied in a similar fashion as ORW. The Freundlich parameters and non adsorbable properties are reported in table 6.2. The 'non adsorbing' fraction of NOM was defined as the value of C_{eq} at which increasing GAC dosage did not reduce C_{eq}. This is shown in figures 6.4 through 6.7 as a clutter of data points on the abscissa.

Table 6.2: Adsorption Isotherms for Four Source Waters

Water	Non Adsorbing NOM	At Dosage*	Freundlich Regressed Constants		Sum of Square
	(mg/L)	(g/L)	k	n	Residuals
OHRW	0.31	0.5	28.3	1.3	935
SLRW	0.51	2.5	11.7	2.61	1015
BPLW	0.13	0.9	18.6	1.9	3122
VGW	0.22	3.0	11.0	1.4	864

* = the dosage (M/V) at which Ceq did not reduce with increasing dose
All isotherms were conducted with F-400 GAC at mesh size range from 40-50. Note that some isotherms have more data points so the sum of square residuals are not comparable as reported. Regression was conducted on data from DOC analyzer only. n values greater than 1 are unfavourable isotherms.

The Freundlich isotherm fit all data reasonably well except for the adsorption isotherm for the Ohio River. This isotherm had more shape variation than the others. It is linear for higher solid phase adsorption capacities, then is unfavourable for lower values. For this reason, this water source was chosen for an example of isotherm modeling using a pseudocomponent method, regressing the data over different C_{eq} regions.

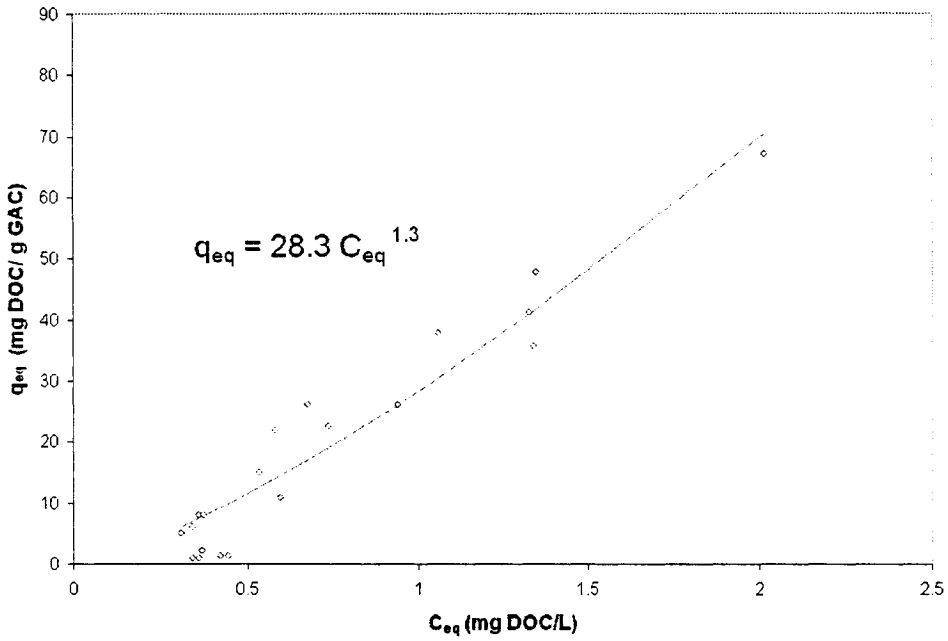

Figure 6.4: Ohio River Isotherm, F-400 GAC, 40 X 50 Mesh Size

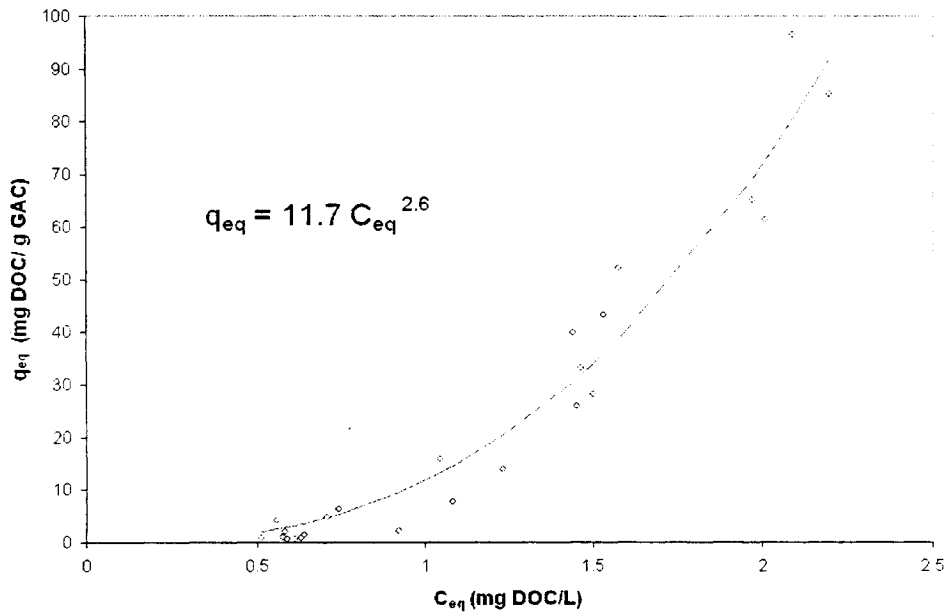

Figure 6.5: St. Lawrence River Isotherm, F-400 GAC, 40 X 50 Mesh Size

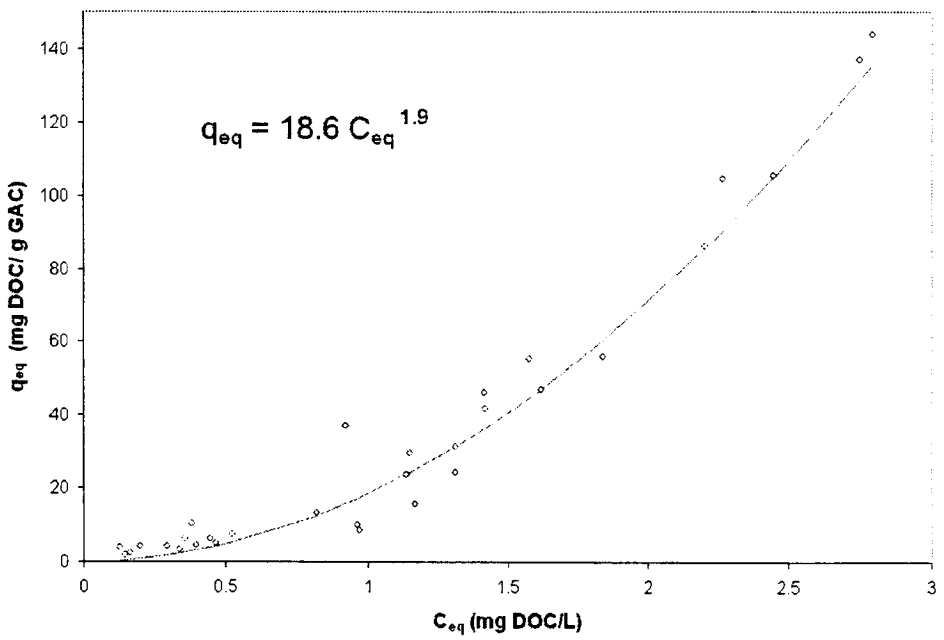

Figure 6.6: Buffalo Pound Lake Isotherm, F-400 GAC, 40 X 50 Mesh Size

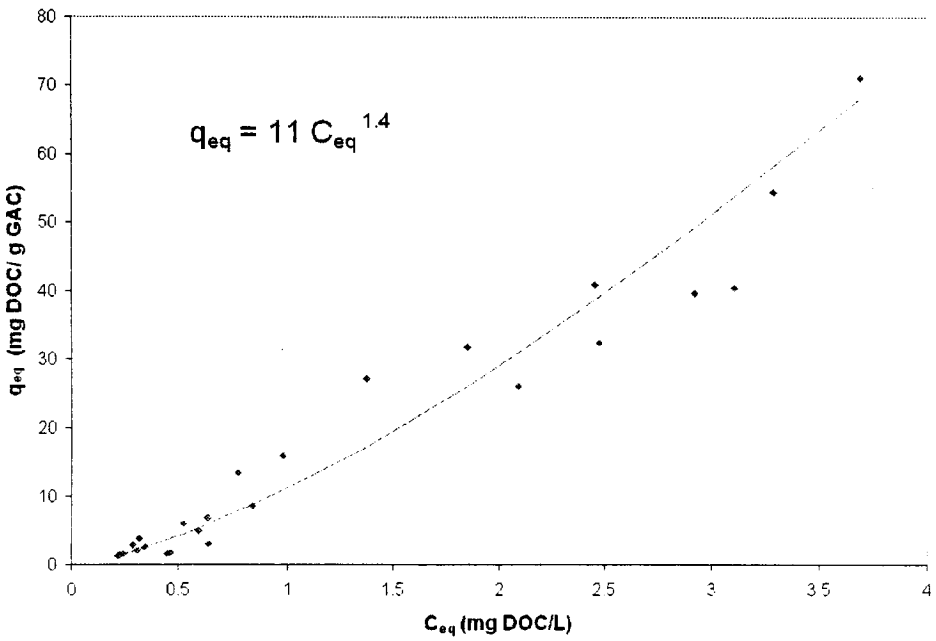

Figure 6.7: Vars Ground Water Isotherm, F-400 GAC, 40 X 50 Mesh Size

6.1.3 Freundlich Parameters from Pseudocomponents

The Ohio River water, OHRW, adsorption isotherm was divided into three subsections as shown in figure 6.8 and reported in table 6.3. The number of pseudocomponents and Freundlich regression constants for each pseudocomponent was determined using the same nonlinear regression technique as the other isotherms. The sum of the square residual, defined as:

$$SSR = \left(q_{eq} - q_{predicted}\right)^2 \tag{6.1}$$

was minimized using the solver routine in Excel, as described in appendix F. As shown in table 6.4, this resulted in a lower sum of the square residual value for the same number of data points.

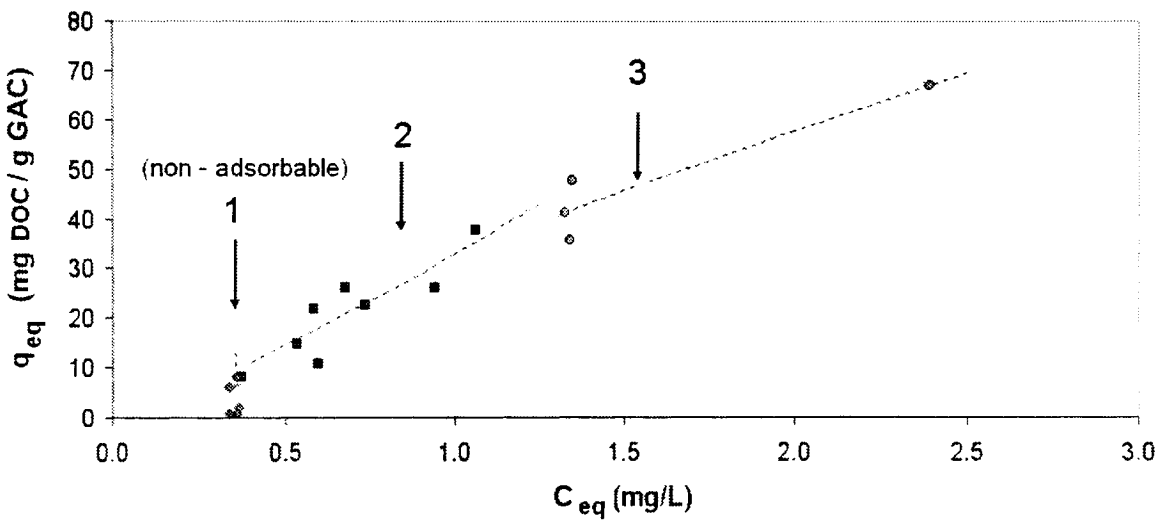

Figure 6.8: Ohio River Adsorption Isotherm Divided into Pseudocomponents

Table 6.3: Ohio River Water Isotherm with Pseudocomponents

Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)	Freundlich Parameters k	n
2.40	0.16	0.14	67.05	32.5	0.83
1.35	0.05	0.04	47.70		
1.34	0.16	0.14	35.61		
1.33	0.10	0.09	41.10		
1.06	0.18	0.16	37.74	32.8	1.19
0.94	0.15	0.13	26.04		
0.74	0.25	0.22	22.55		
0.68	0.01	0.006	26.15		
0.60	0.07	0.06	10.86		
0.58	0.08	0.07	21.81		
0.54	0.003	0.003	14.84		
0.37	0.006	0.005	7.97	10.8	0.86
0.37	0.008	0.007	2.08		
0.36	0.005	0.004	8.01		
0.36	0.005	0.004	0.87		
0.34	0.02	0.02	0.81		

Table 6.4: Comparison of Pseudocomponent Approach and Single Component Isotherm

Pseudocomponent Regressed Isotherm Parameters				**Original Regressed Isotherm Parameters**	
				Freundlich Parameters	**k = 28 and n = 1.08**
Freundlich Parameters		**Predicted**	**Square**	**Predicted**	**Square**
k	**N**	**qeq**	**Residual**	**qeq**	**Residual**
32.5	0.83	67.08	0.00	67.08	0.00
		41.70	36.00	41.70	36.00
		41.50	34.61	41.50	34.61
		41.21	0.01	41.21	0.01
32.8	1.19	35.26	6.12	34.21	12.45
		30.53	20.13	30.95	24.08
		22.85	0.09	25.31	7.60
		20.62	30.57	23.56	6.68
		17.82	48.46	21.29	108.88
		17.29	20.44	20.85	0.92
		15.61	0.59	19.42	20.97
10.8	0.86	4.63	11.18	14.38	41.12
		4.56	6.18	14.19	146.77
		4.47	12.58	13.90	34.69
		4.47	12.91	13.90	169.78
		4.27	11.99	13.32	156.57
Sum of the Square Residuals			**252**		**801**

6.1.4 Comparisons of Adsorption Isotherms to Other Data

The adsorption isotherms of three of the five waters were compared to other experimental data. These were ORW, OHRW, and BPLW. Overall, data was different between studies. NOM adsorption isotherms are not predictable since NOM changes with seasons and location. The two data sets that had the best agreement was the work with the ORW of 2004 compared to work conducted by Karimi-Jashni (1997a). Although Karimi-Jashni (1997a) used the Calgon AC F-300 while the current study used F-400, these GAC differ only in particle size. Particle size has not been found to affect equilibrium loadings, only equilibration time (Sontheimer *et al.*, 1988). The smaller particle sizes of powdered activated carbons (PACs) results in a faster equilibration time. Once again, the lower capacities of the second isotherm conducted with ORW is consistent with the hypothesis that the NOM in the ORW was transformed into larger, less adsorbing, molecules while being stored in a fridge for ten months.

The OHRW isotherm shown in figure 6.10, conducted by McEwen (2004) used regenerated carbon instead of fresh carbon. Although the AC was thermally regenerated the adsorptive capacities were not as great as the capacity with the sorted and cleaned, fresh F-400 GAC used in this study.

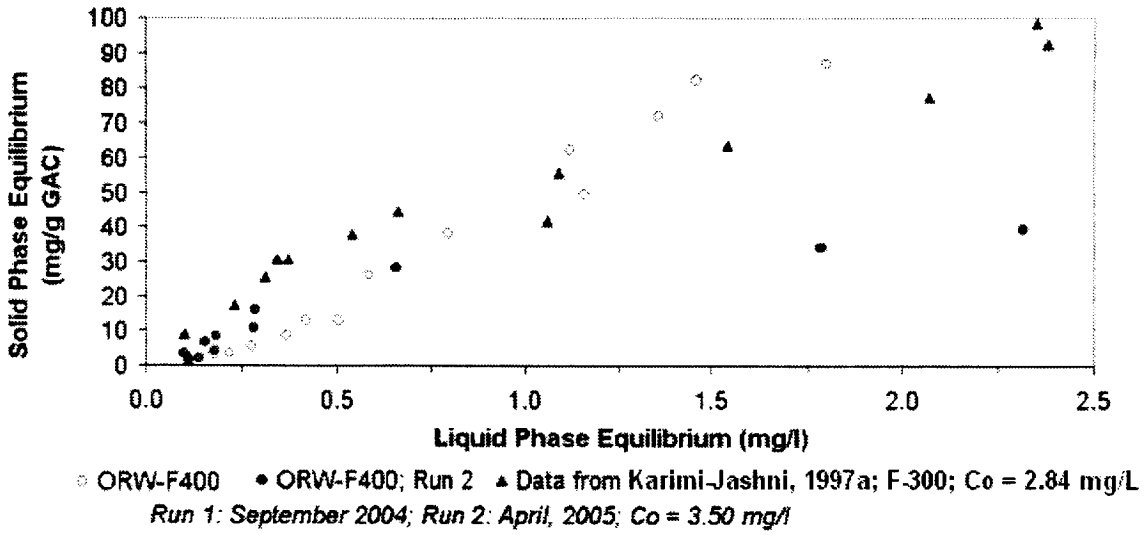

Figure 6.9: Comparison of ORW Isotherm to Other Data

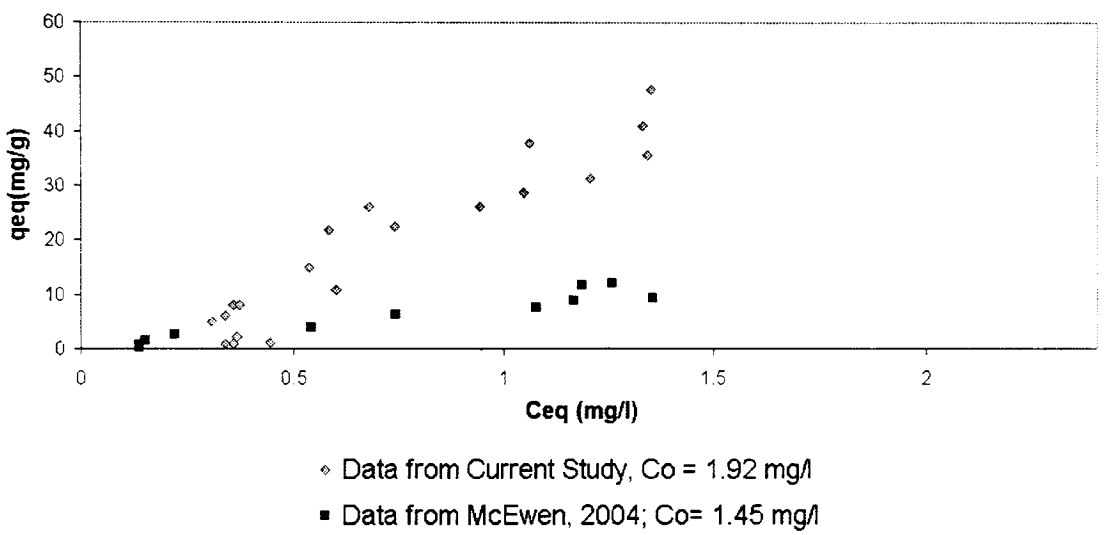

Figure 6.10: Comparison of OHRW Isotherm to Other Data

The comparison shown in figure 6.11 is a good example of the performance of different GAC types with the same water. The work conducted by McEwen in 2004 used the GAC Jacobi that had also been regenerated. The data from this present study used fresh F-400 AC and had a more adsorptive isotherm. Different GAC types have been found to result in significantly different isotherms (Roberts and Summers, 1982; Karimi-Jashni and Narbaitz, 1997; Vidic *et al.* 1990).

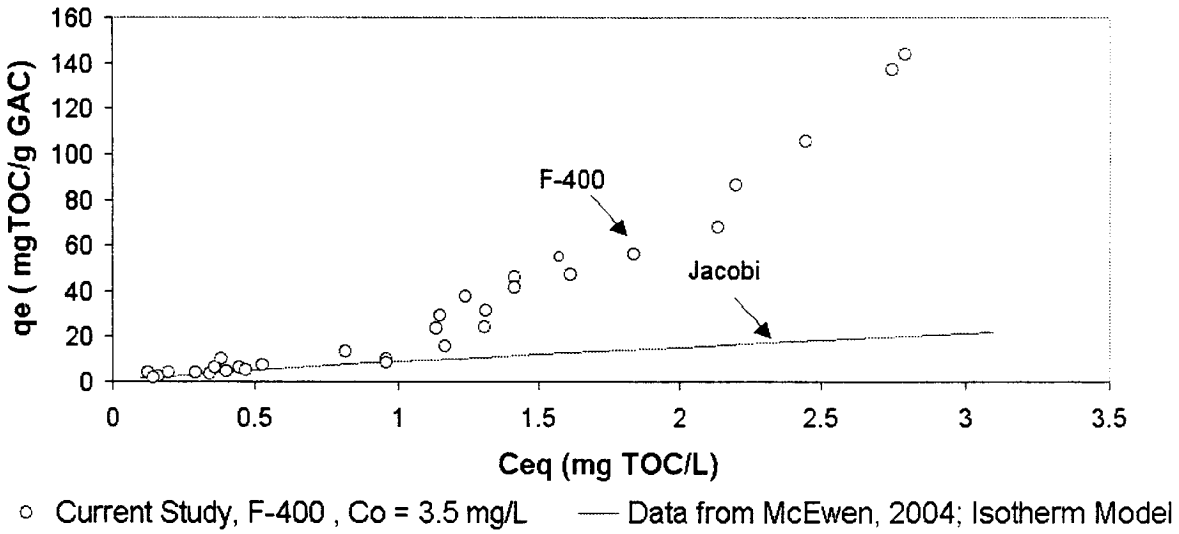

Figure 6.11: Comparison of BPLW Isotherm to Other Data

6.2 Desorption Isotherms

Desorption isotherms were conducted according to the procedure described in appendix A.3. Six desorption isotherms were conducted, each evaluating via the bottle point technique the NOM desorption from the GAC loaded during the adsorption isotherm tests. It is important to note that since the desorption loading included two experimental steps, some of the limited desorption seen in these tests could be the result of experimental error.

As illustrated in figure 6.12, ORW displayed irreversible adsorption behaviour on F-400. The adsorption of the ORW NOM on WV-B was fully irreversible as shown in figure 6.13, except at lower GAC dosages (higher Q_{eq} values). OHRW, desorption isotherms are shown in figure 6.14. Most of the isotherms are irreversible, except a few at lower AC dosages. SLRW, data as shown in figure 6.15 the NOM adsorption on F-400 is also irreversible, there is only one exception and the apparent partial reversibility may be the result of experimental error, given that all the other bottle tests showed irreversible adsorption.

In figures 6.16, and 6.17, the F-400 desorption isotherms for the NOM in BPLW and VGW, show that most NOM adsorption is irreversible but showed more partially reversible behaviour than the other waters. VGW had the most desorption isotherms with partial reversible behavior. Thus, these desorption isotherms demonstrated that the adsorption NOM in these five different waters was completely irreversible or had very limited reversibility.

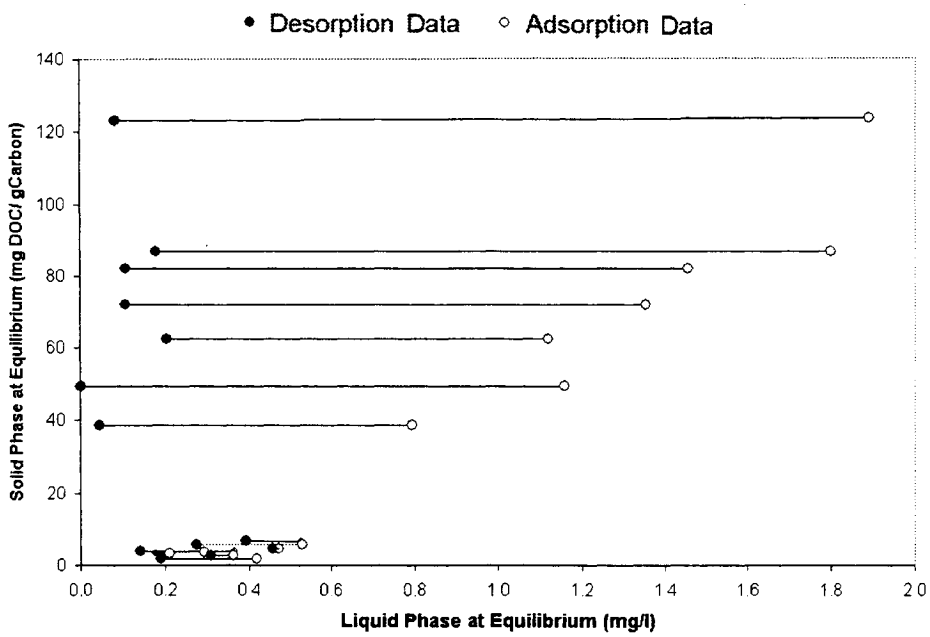

Figure 6.12: Desorption Isotherms for ORW with F-400 AC, 40 X 50 Mesh Size

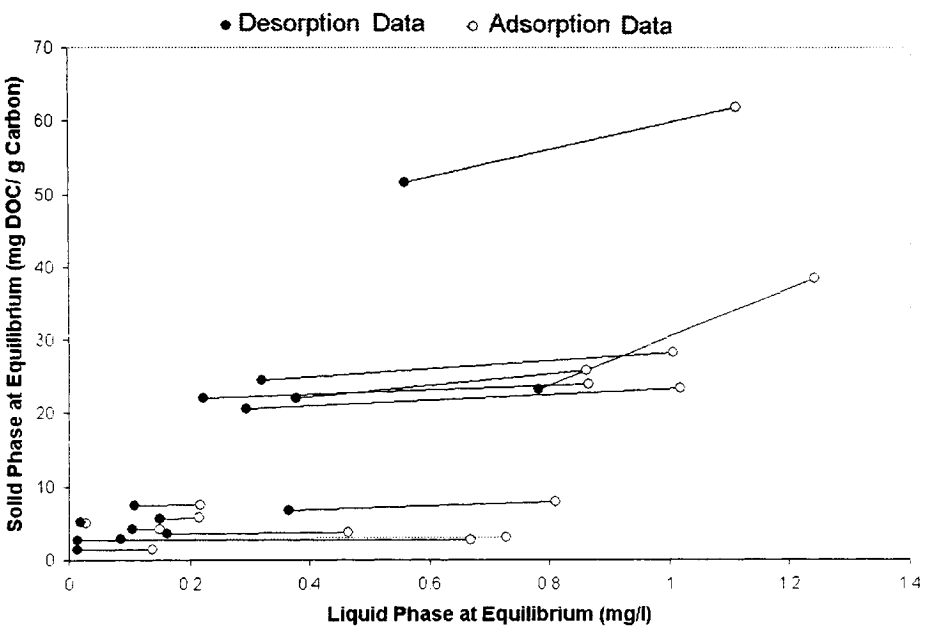

Figure 6.13: Desorption Isotherms for ORW with WV-B AC, 40 X 50 Mesh Size

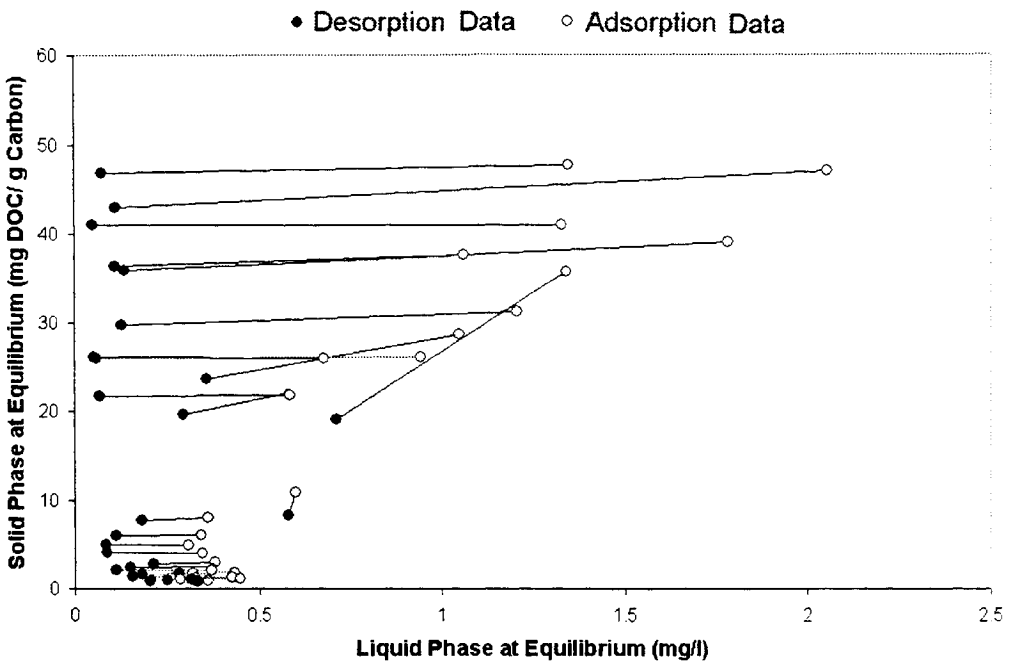

Figure 6.14: Desorption Isotherms for OHRW with F-400 AC, 40 X 50 Mesh Size

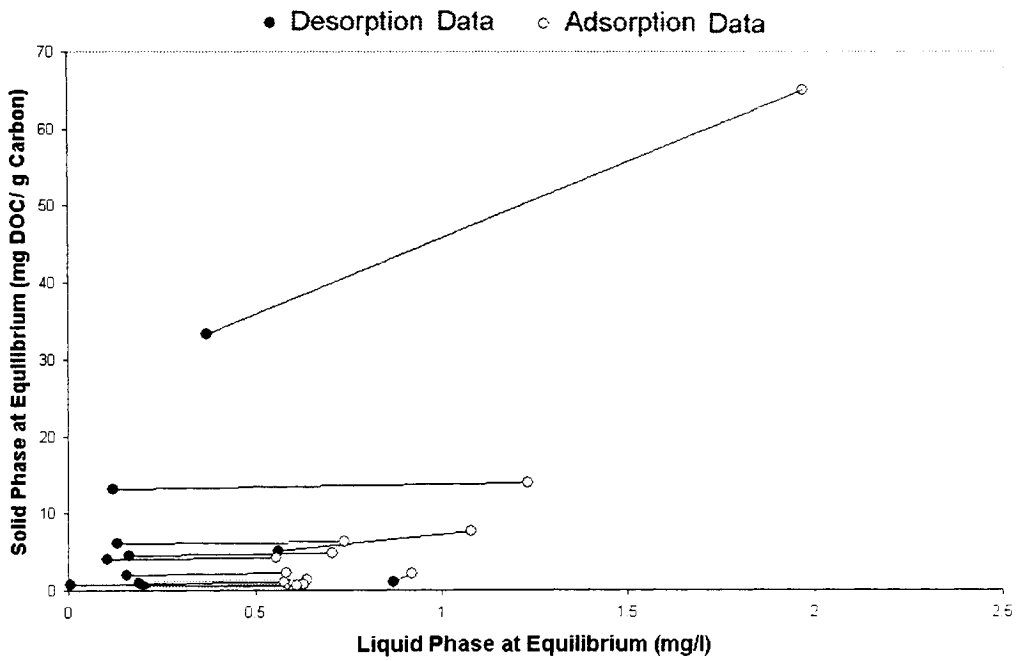

Figure 6.15: Desorption Isotherms for SLRW with F-400 AC, 40 X 50 Mesh Size

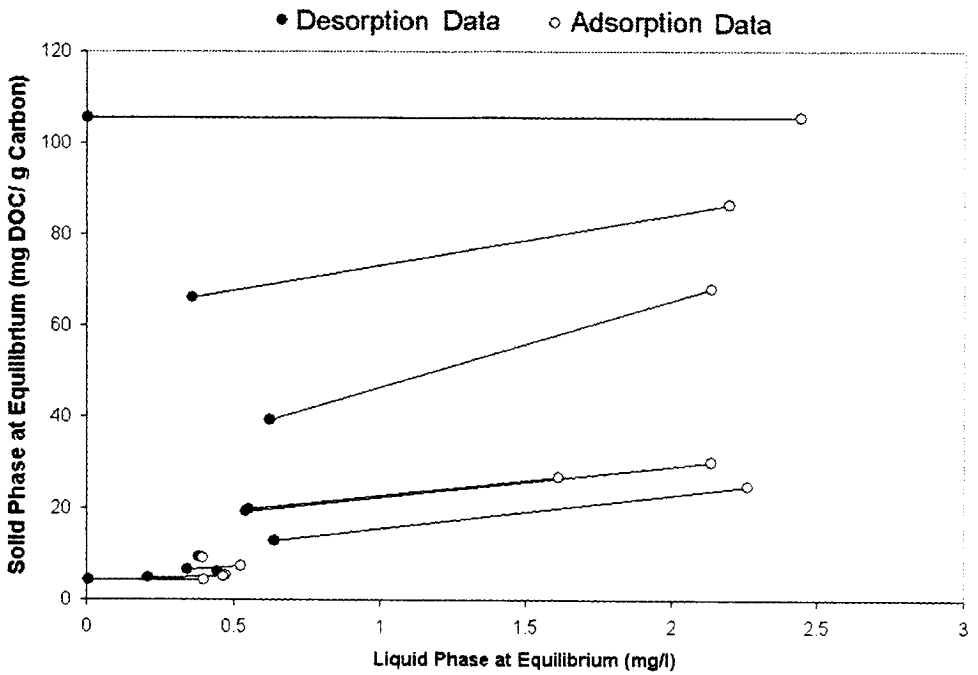

Figure 6.16: Desorption Isotherms for BPLW with F-400 AC, 40 X 50 Mesh Size

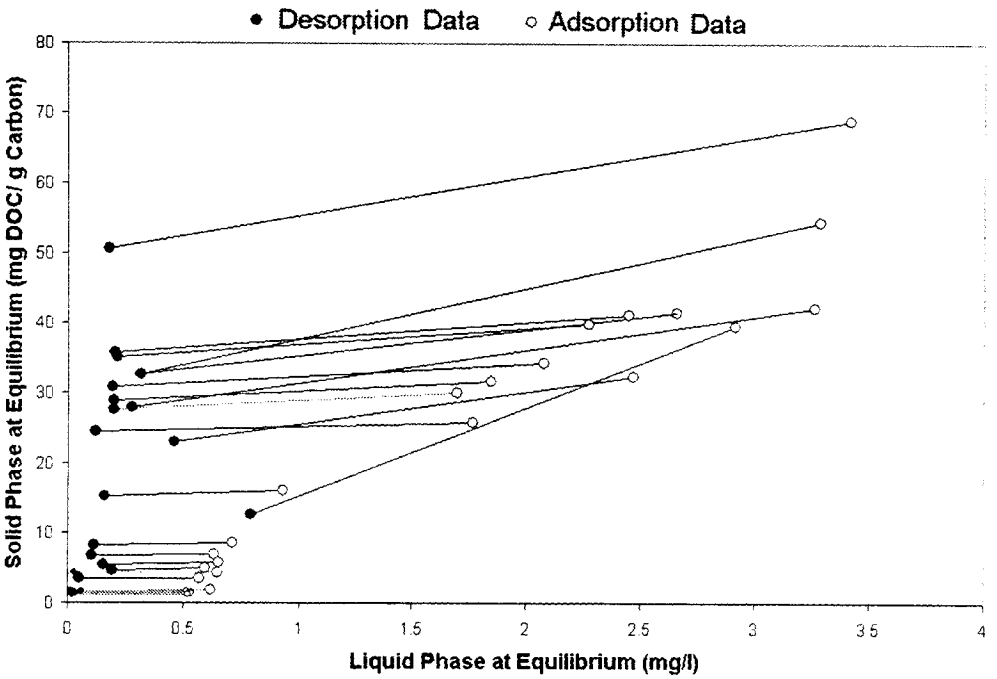

Figure 6.17: Desorption Isotherms for VGW with F-400 AC, 40 X 50 Mesh Size

The desorption isotherm data was rearranged to study the percentage of NOM desorbed. This differed from the traditional hysterisis studies conducted in the literature (Summers, 1989; Summers and Roberts, 1988; Tamon and Okazaki, 1996; Tamon *et al.*, 1996). The maximum desorption percentages for each test are shown in table 6.5. The maximum percentage was for VGW, followed by SLRW, BPLW and OHRW. This data was plotted in figures 6.18 and 6.19 with the mass of AC per volume of solution on the abscissa so results could be directly compared.

Another way of looking at the data is comparing how many points from the desorption isotherm study are above a certain percentage of NOM desorbed. The value of 20% was chosen because most waters showed little desorption above this point. Desorption below this point may be due to experimental errors, as can be seen from the 95% confidence values plotted in figures 6.18 and 6.19.

Table 6.5: Desorption and Maximum Desorption of NOM from Various Water Sources

Water	GAC	Initial DOC (mg C/l)	Dose of max. desorption M/V	Mass of NOM at this dose at time zero (mg) {QeqM}	Mass of NOM that Desorbed (mg) {Ceq'V}	% of adsorbed NOM that desorbed*	Average % Desorbed	No. points with >20% NOM Desorbed	No. of desorption isotherms
ORW	F-400	3.15 ± 0.02	0.302	0.297	0.086	28.97	8.5	1	14
ORW	WV-B	3.15 ± 0.02	0.048	0.215	0.085	39.74	10.4	2	15
SLRW	F-400	1.92 ± 0.03	0.799	0.191	0.092	48.41	12.2	2	13
OHRW	F-400	3.50 ± 0.04	0.04	0.664	0.309	46.5	8.1	2	24
BPLW	F-400	4.01 ± 0.02	0.05	0.58	0.276	47.53	20.8	7	11
VGW	F-400	2.62 ± 0.04	0.029	0.556	0.355	63.85	12.2	5	23

*Maximum desorption values were chosen

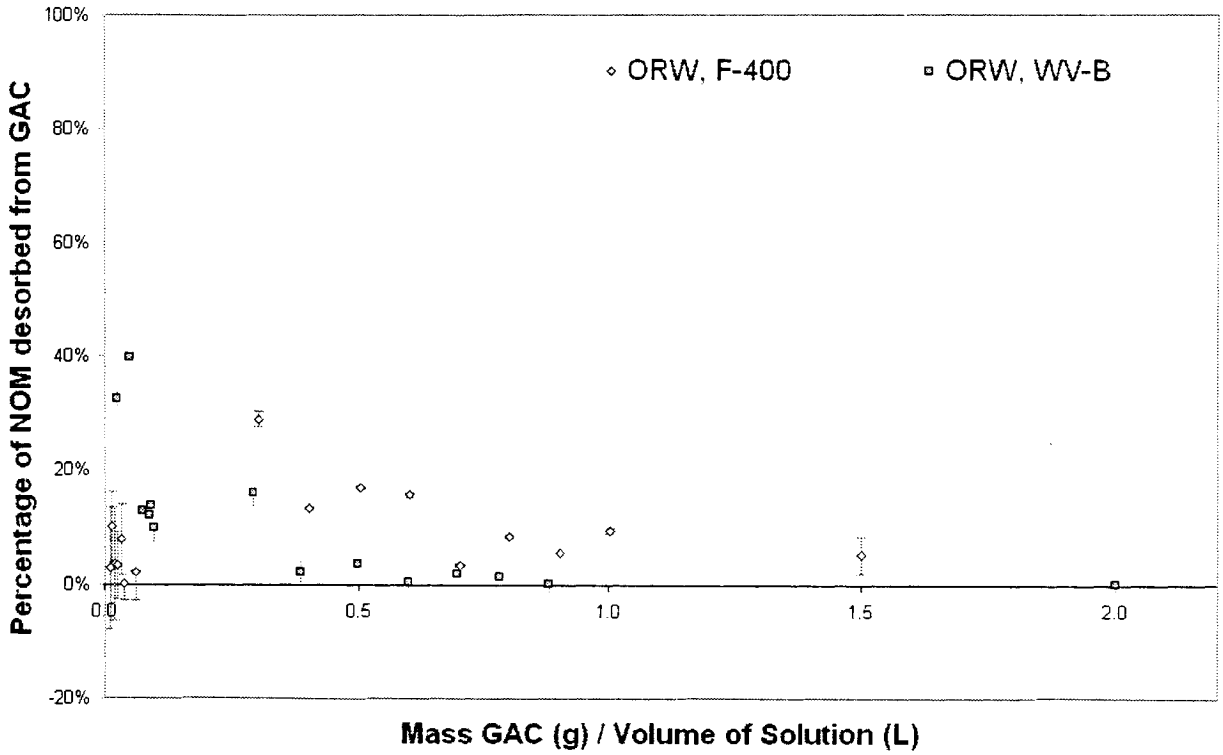

Figure 6.18: Percentage of Initial NOM Desorbed from ORW Tests

Shown in figure 6.19, there were few data points that had percentages of desorbed NOM greater than 20%. BPLW had the greatest number of points in this range, with 7. VGW was next with 5 points. One trend found in all five waters was that most of the points with a significant percentage(>20%) of NOM desorbed from the GAC were those with smaller M/V ratios.

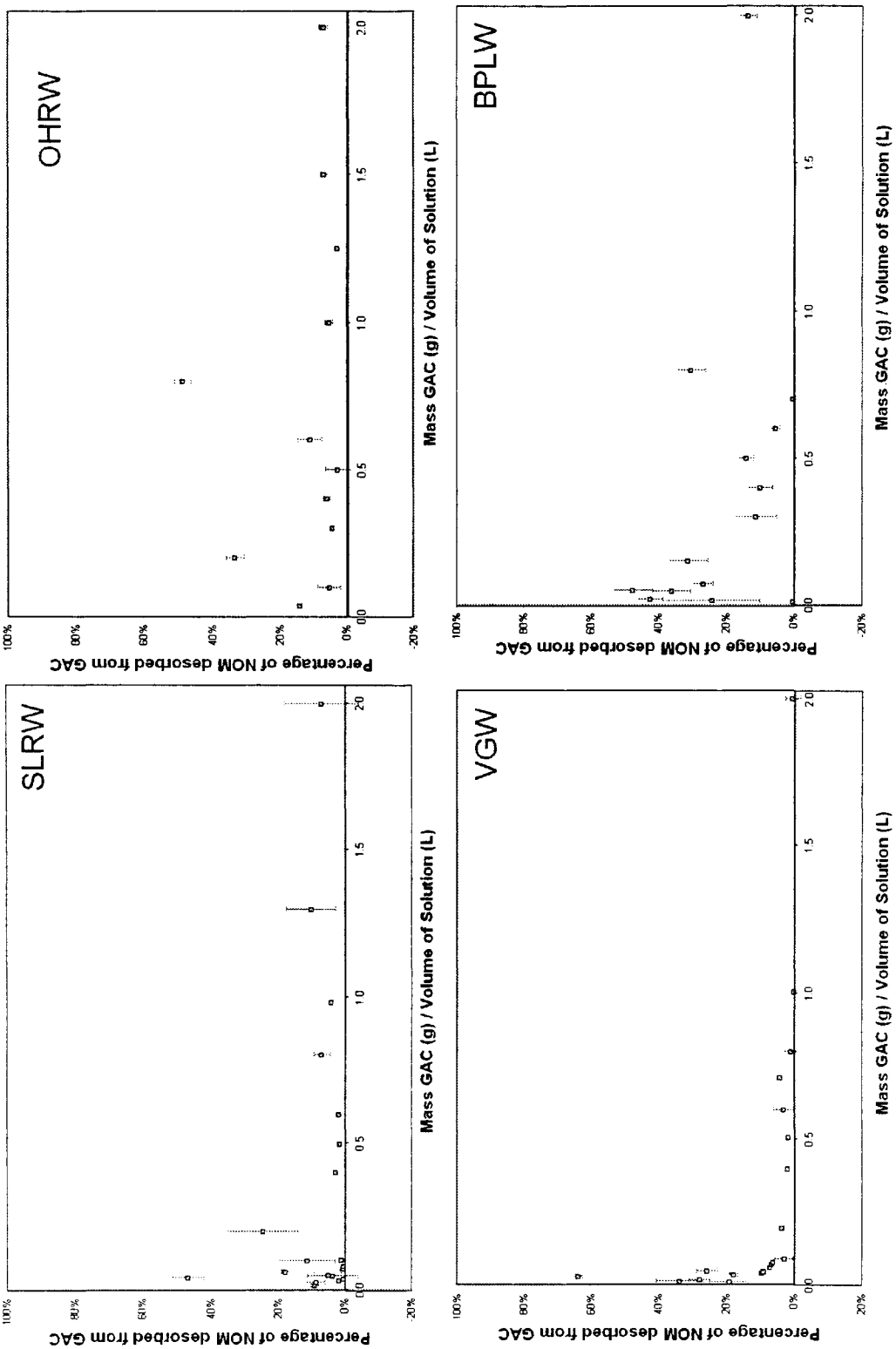

Figure 6.19: Percentage of Initial NOM Desorbed from Four Natural Waters

Chapter 7: Experimental Results - NOM analysis

NOM in the five natural waters was fractionated by ultrafiltration, size exclusion chromatography, and by extraction of humic acids on XAD8 resin. The first two methods separated the NOM according to molecular size. This is important knowledge since the transport of toxins with dissolved organics (Cai, 1999) as well as interference during potable water treatment (Collins *et al.*, 1986) have been found to be strongly related to the molecular size. XAD8 chromatography determines the hydropholic/hydrophobic fractions of the NOM. This is relevant information because the hydrophobic fraction (humic acids) has been reported as a strong disinfection by-product precursor (Kitis *et al.*, 2002).

Operational differences in the NOM from the five waters were also used to develop a hypothesis for why some waters showed more irreversible adsorption behavior than others did. The results of these studies are reported in the following sections.

7.1 Ultrafiltration

Ultrafiltration fractionation was carried out according to the procedure outlined in appendix A.4. Results from all five water sources are shown in figures 7.1 and 7.2 and all percentages are weight percent. One unexpected result was the large percentage of high MW (i.e. >30k) NOM found in OHRW and SLRW, of 16% and 13% respectively. ORW had only 8% of NOM in this range. BPLW and VGW had 0.43% and 1% respectively. ORW had a relatively even distribution of all UF fractions and other than the largest fraction was very similar to SLRW.

Another interesting result was the large fraction of NOM in the range of >500 to <1000 Da found in the waters BPLW and VGW of 47% and 52% respectively. The only thing these sources have in common is that they are both located near wetlands, which are sources of 'young allochthonous' NOM molecules (Aiken *et al.*, 1985; Suffet and MacCarthy, 1989).

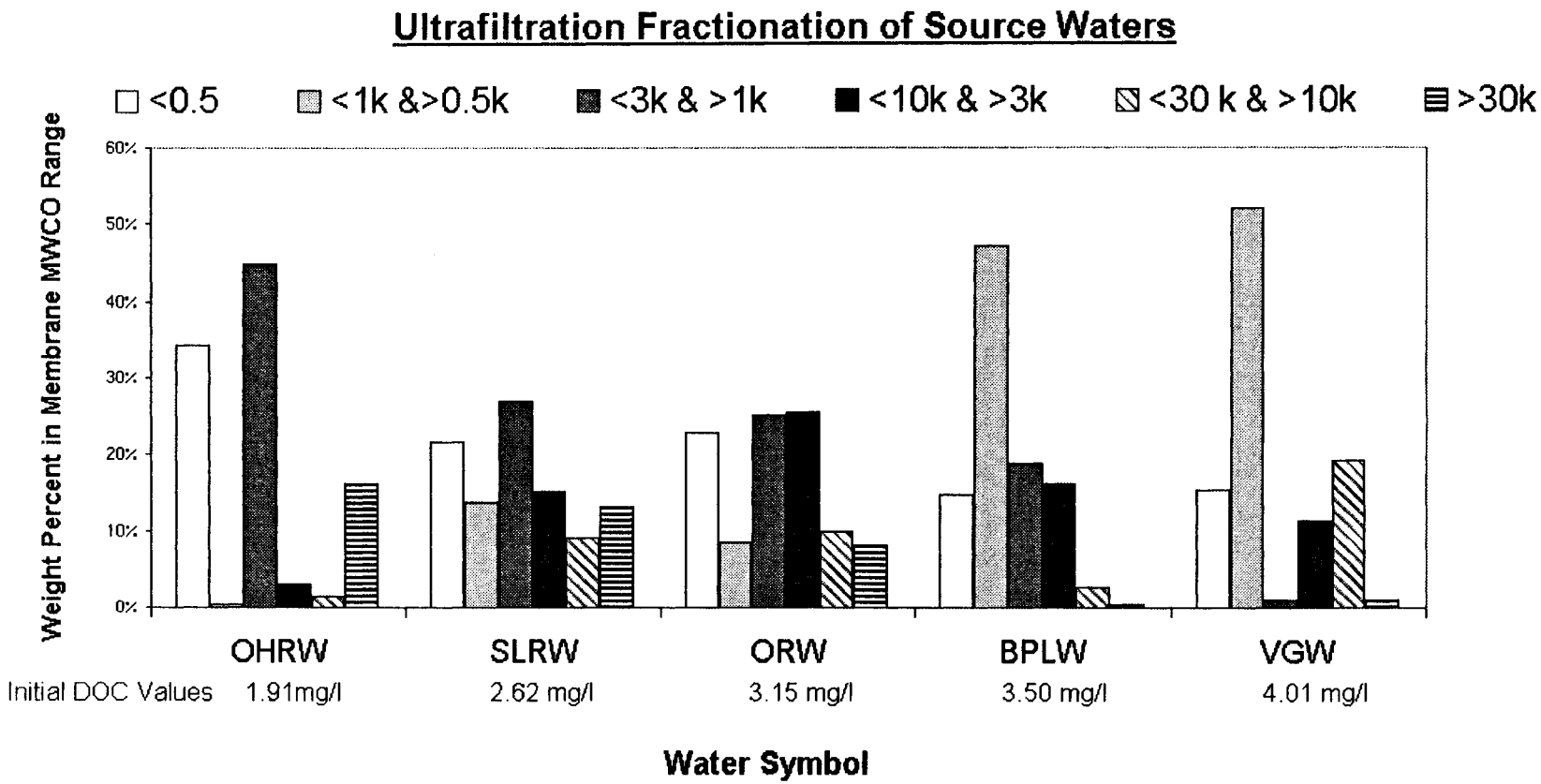

Figure 7.1: Ultra Filtration Fractionation of Five Natural Waters

Newcombe *et al.* (1997a) found through ^{13}C NMR analysis that larger fractions from UF had highly branched carbohydrate structures while the smaller fractions had lower carbohydrate structures. This breakdown of the carbohydrate structure may be a sign of microbiological breakdown in the water (Aiken *et al.*, 1985; Newcombe *et al.* , 1997a).

If VGW and BPLW both have less highly branched NOM entities, it is possible that these NOM molecules were not attached to as many sites in the GAC during adsorption, and therefore were more reversible. During the desorption step, these NOM molecules were able to detach from the GAC reactive sites. While the other waters (ORW, OHRW and SLRW) had larger NOM fractions with more highly branched carbohydrate structures, which were less likely to be reversible.

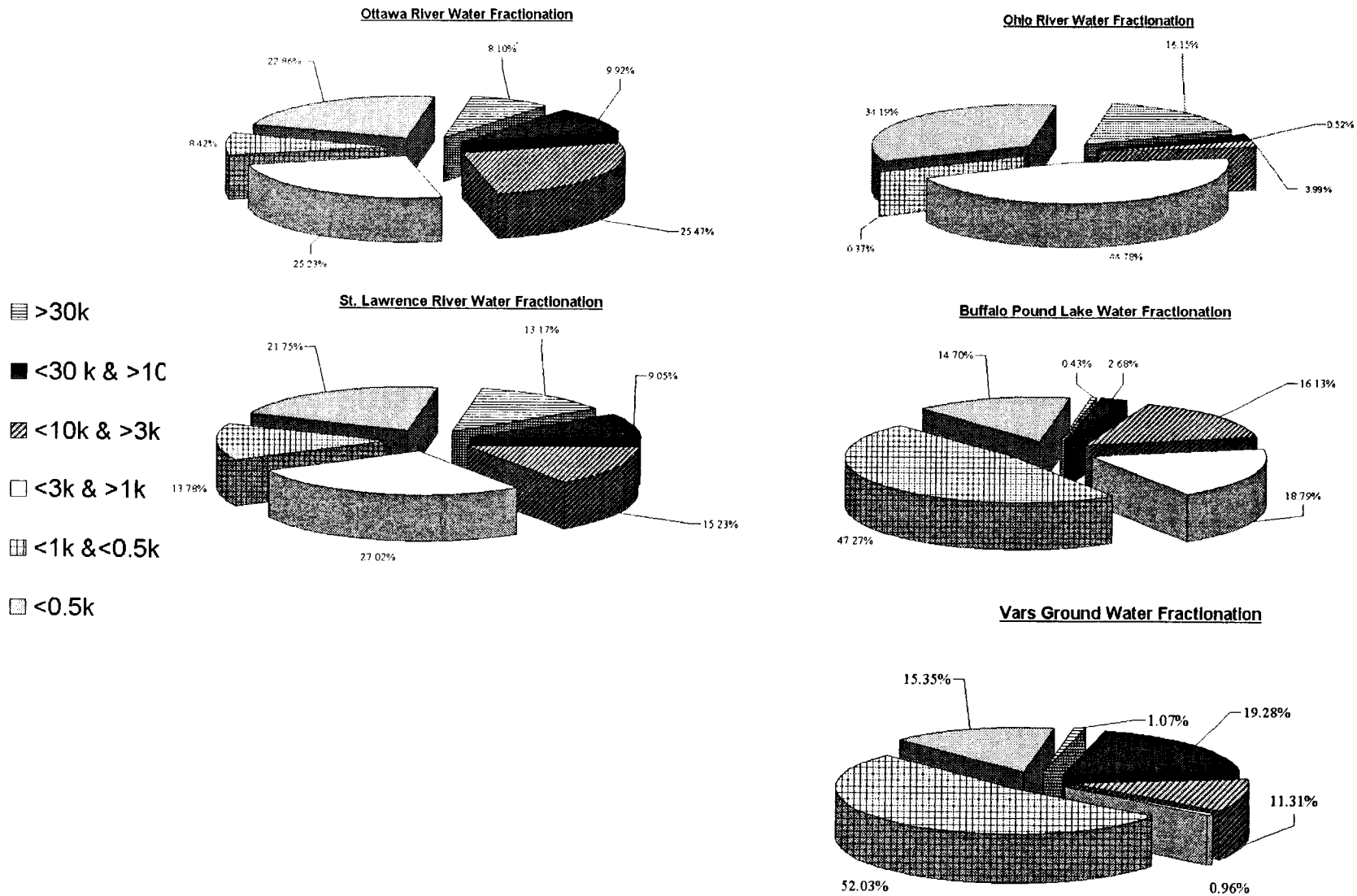

Figure 7.2: Pie Chart Illustrations of UF Fractionation

The filtrate from UF fractionation was analyzed using UV absorbance. A spectrum was conducted at 254nm, 260nm, 280nm, 300nm, 320nm and 350nm. The data from all waters are included in appendix B. As is shown in figure 7.3, the UV absorbance spectra is not always directly related to TOC values. The unfractionated sample had a greater absorbance value than the fractionated samples, except for the <30k portion. This may be due to interferences from macromolecules in the unfiltered water (*Croué et al., 2000*, Korshin *et al.*,1997). The results for OHRW have been included in figure 7.3 as an example. This example was typical of all five waters, as can be seen from comparing results reported in appendix B. The UF fractions were analyzed for UV absorbance at the wavelength of 254nm by Collins *et al.* (1986) and the results were similar. Decreasing molecular sized NOM had decreasing UV absorbance values.

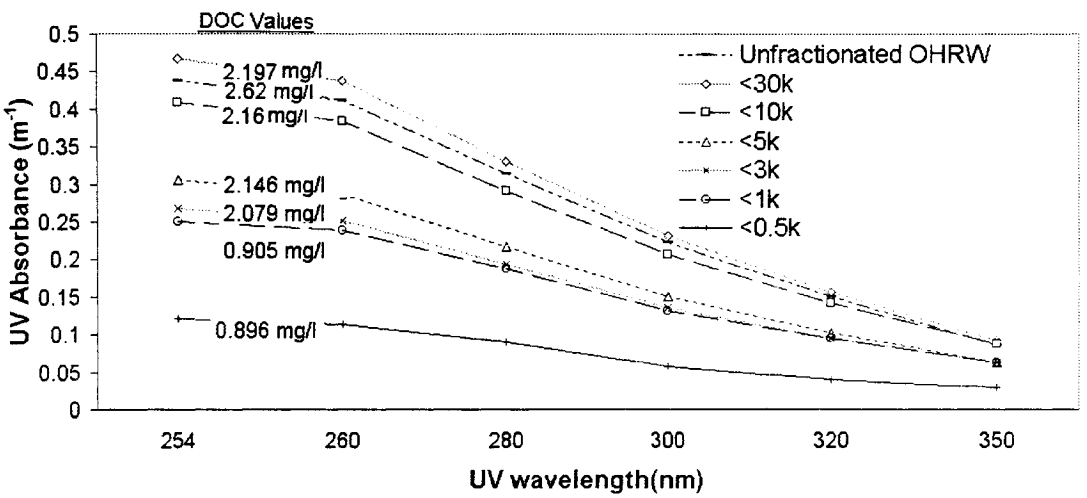

Figure 7.3: UV Absorbance Spectra for OHRW, UF Filtrate Samples

Retentate samples were not studied using UV absorbance since they were concentrated as a result of the UF procedure. The UV absorbance was possible (would have been greater than other samples) but would not have provided any practical comparisons.

7.2 Humic Acid Extraction on XAD8

Humic acids were extracted from water samples using the resin XAD8. The effluent from the XAD8 column was collected and assumed to be the hydrophilic/fulvic acid portion of the NOM. This was based on the work of Thurman and Malcolm (1981), as well as Collins *et al.,* (1986). The portion adsorbed on the XAD8 resin is operationally referred to as aquatic humic substances, and it accounts for 85% to 100% of the visible colour found in natural waters. (Collins *et al.,* 1986). The hydrophilic fraction contains what is defined as non-humic substances, which include simple carbohydrates, uronic acids, and hydroxy acids.

The procedure used is recorded in appendix A4. All data is reported in table 7.1. From the DOC data, fractions of humic and fulvic acid were calculated for the raw water sources, adsorption equilibrium water, and desorption equilibrium water. These calculations are illustrated in figures 7.4, 7.5, and 7.6. From a mass balance, the fractions of humic and fulvic acids that adsorb, do not adsorb, desorb and do not desorb were calculated. These are shown in figures 7.7 and 7.8.

Illustrated in figure 7.4, BPLW and VGW again had similarities. They both contained a large percentage of humics. This was unexpected since humics are usually larger in MW than fulvics, and both of these waters were found to have a large portion of smaller MW NOM molecules during the UF fractionation. However, VGW was found from UF to have 20% of DOC due to a molecular size fraction between 10,000 and 30,000 Da, and BPLW 16% between 3,000 and 10,000 Da. Perhaps these portions are those being found to be humics as well as some smaller MW humics. Both of these waters also had high colour values. Therefore, it is likely that they would have high humic acid portions since humics are largely responsible for colour in natural waters (Collins *et al.,* 1986). However, some of the colour in VGW is known to be from a high iron content in this water (City of Ottawa Drinking Water Services, 2003).

Table 7.1: Results of Humic Acid Extraction on XAD8 Resin

ORW F-400	DOC(mg/l)	SLRW	DOC(mg/l)	BPLW	DOC(mg/l)
Raw	3.152	Raw	1.856	Raw	3.497
Raw Fulvics	0.789	Raw Fulvics	0.781	Raw Fulvics	0.239
Adsorption	1.174	Adsorption	1.519	Adsorption	1.139
Adsorption Fulvics	0.153	Adsorption Fulvics	0.477	Adsorption Fulvics	0.148
Desorption	0.616	Desorption	0.276	Desorption	0.991
Desorption Fulvics	0.006	Desorption Fulvics	0.049	Desorption Fulvics	0.090

ORW WV-B	DOC(mg/l)	OHRW	DOC(mg/l)	VGW	DOC(mg/l)
Raw	3.152	Raw	2.082	Raw	4.010
Raw Fulvics	0.789	Raw Fulvics	1.309	Raw Fulvics	0.347
Adsorption	1.068	Adsorption	0.832	Adsorption	1.310
Adsorption Fulvics	0.170	Adsorption Fulvics	0.040	Adsorption Fulvics	0.110
Desorption	0.681	Desorption	0.281	Desorption	0.795
Desorption Fulvics	0.021	Desorption Fulvics	0.039	Desorption Fulvics	0.034

Adsorption and Desorption Dosages were at 0.03 g GAC/ L

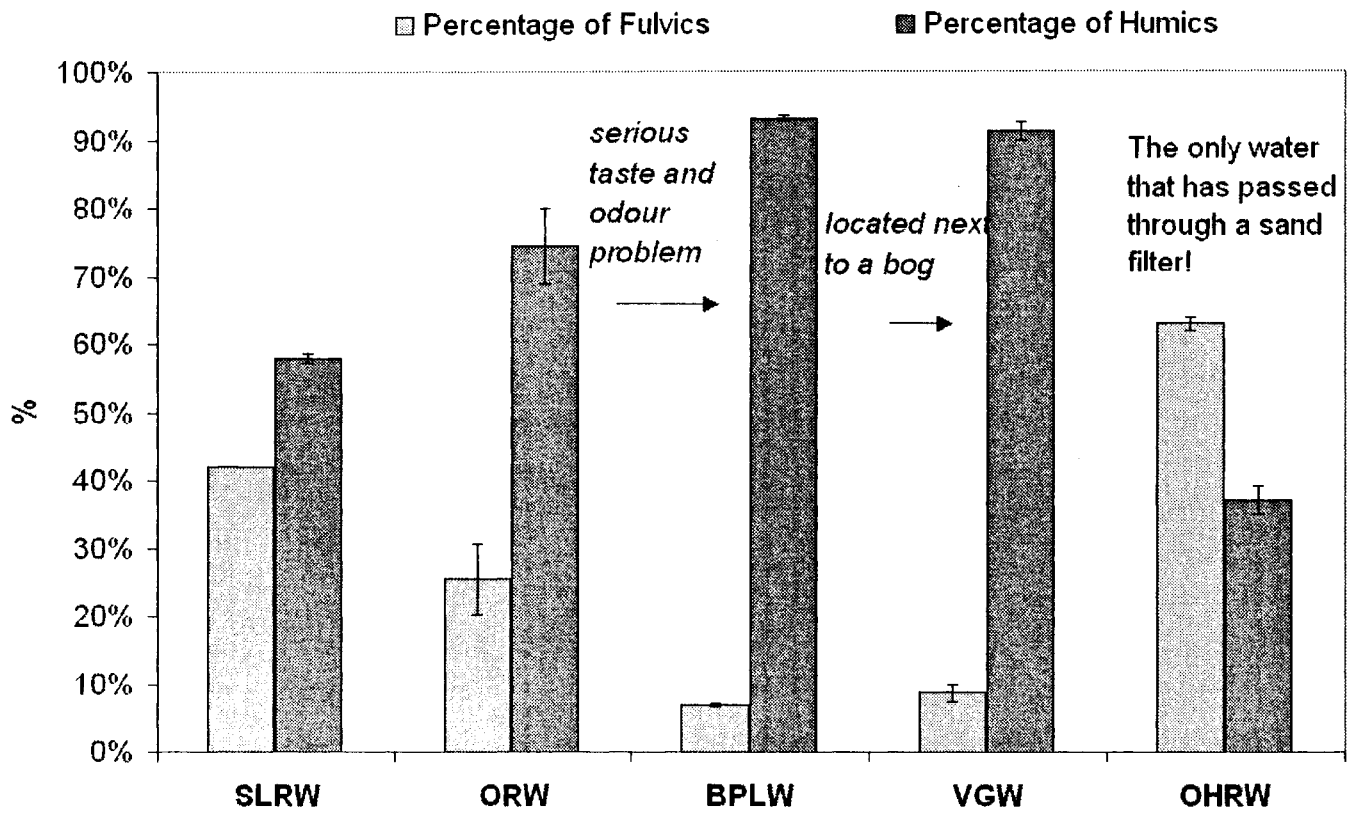

Figure 7.4: Humic Acid Extraction for All Source Waters Without GAC Treatment

The relationship between the DOC value of each natural water and the fraction of humic acid found from XAD8 extraction is shown in figure 7.5. There was a linear relationship found between the two.

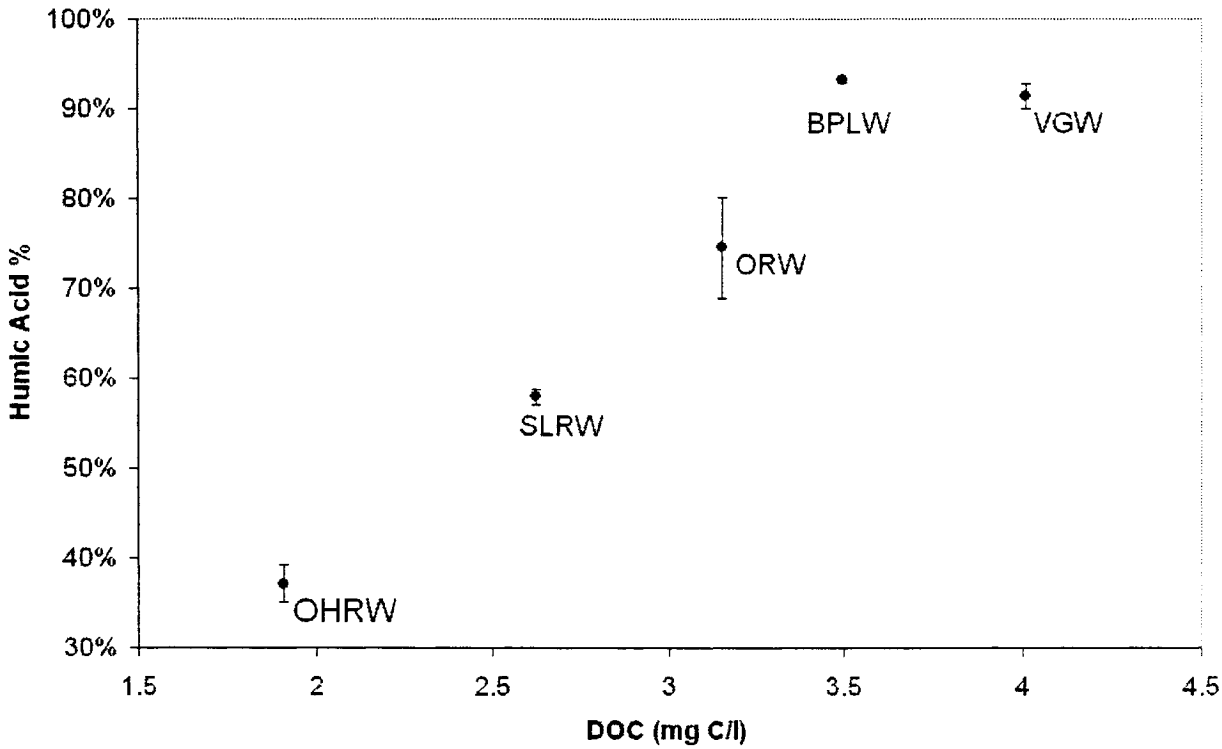

Figure 7.5: Relationship Between Fraction of Humic Acid and DOC Value of Natural Waters

Figures 7.6 and 7.7 show the portions of humics and fulvics left in the solution following adsorption and desorption (i.e. these were the portions that *did not* adsorb, and that *did* desorb). In general, the humic fraction was found to be proportional to DOC for this study.

These fractionated samples represent:

1. what was left in the adsorption water, the portion that did not adsorb
2. what was found in the desorption water, the portion that desorbed

As shown in figure 7.6, the majority of NOM present in the adsorption liquid phase was humics, except in the case of SLRW. Since this represents the portion of NOM that did not adsorb, the conclusion was made that in most cases fulvics adsorb more easily than humics.

From the data plotted in figure 7.7, it is shown that humics made up the majority of NOM present in the desorption liquid phase. Since this represents the NOM that did desorb, the conclusion was drawn that humics desorb more easily than fulvics.

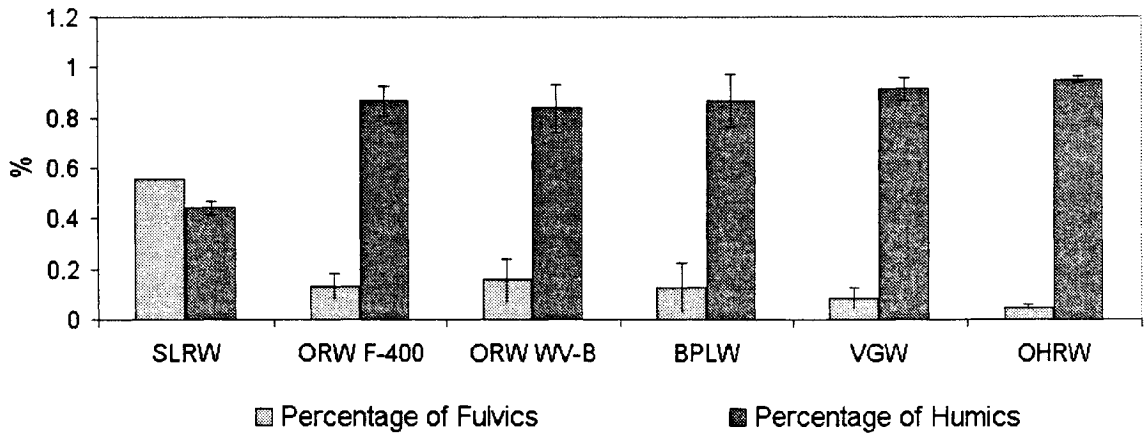

Figure 7.6: Humic Acid Extraction for Adsorption Liquid Phase Samples

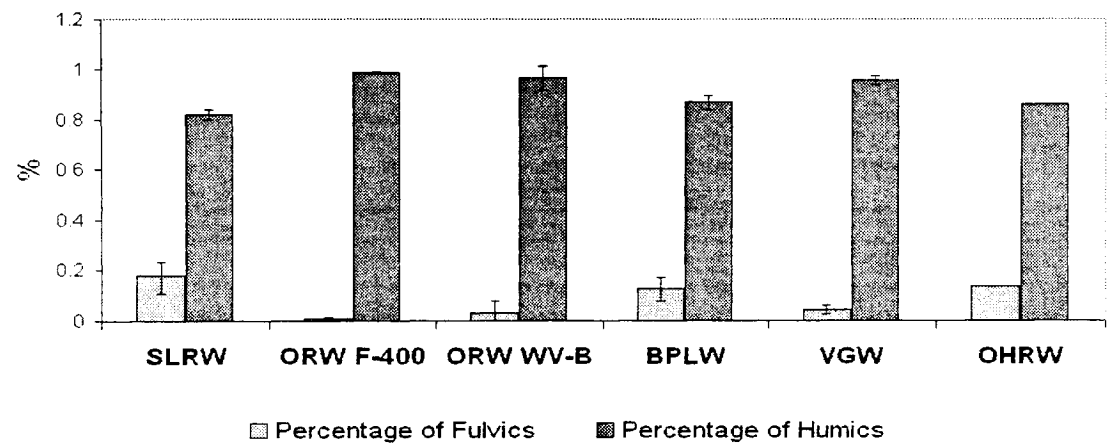

Figure 7.7: Humic Acid Extraction for Desorption Liquid Phase Samples

The mass balances shown in figures 7.8 and 7.9 illustrate the information gained from the data in table 7.1. From the mass balances reported in figures 7.8 and 7.9, there are some general trends that were concluded. [6] In general, fulvic acids adsorbed easier than humic acids. Except for the case of BPLW, the fulvic portions of NOM were more irreversible than the humic portions. The humic portions were more reversible than the fulvics, again with BPLW as an exception.

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[6] Mass Balance Calculations were performed as:

$$\frac{\text{DOC of water - DOC of adsorption water}}{\text{DOC of water}} = Portion \quad adsorbed$$

$$\frac{Portion \quad Adsorbed - DOC \quad of \quad desorption \quad water}{Portion \quad Adsorbed} = Portion \quad remaining \quad in \quad GAC$$

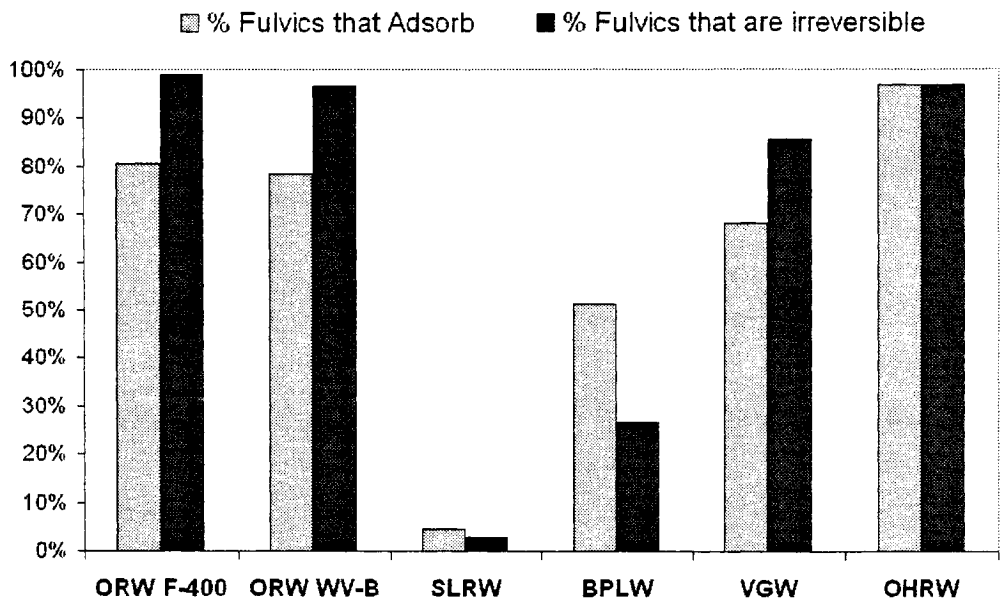

Figure 7.8: Fulvic Acid Behaviours

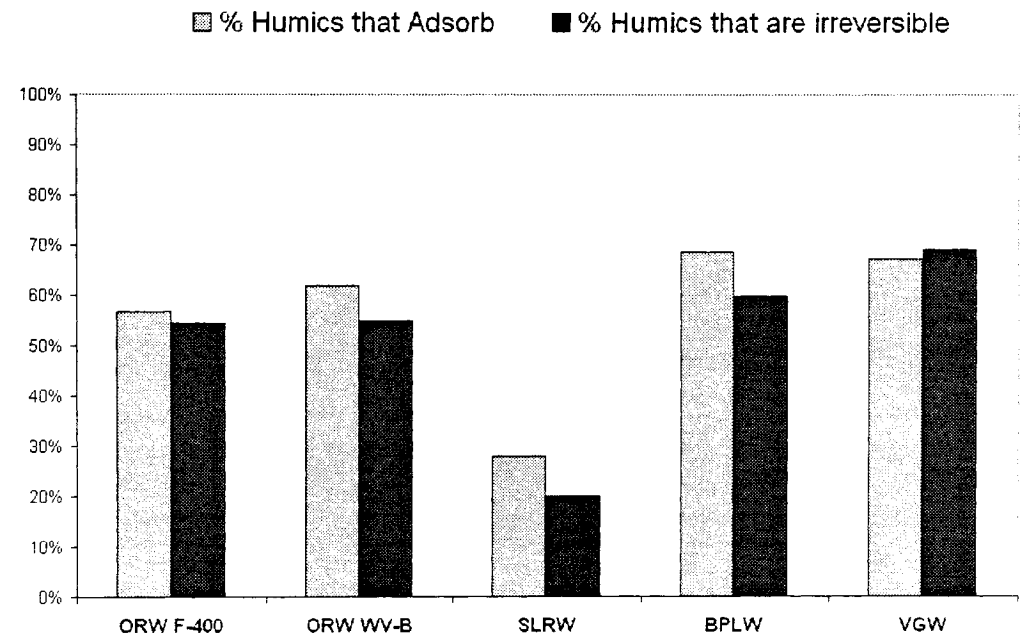

Figure 7.9: Humic Acid Behaviours*

** data from OHRW not available*

7.3 Size Exclusion Chromatography

Equilibrium calibration curves were calculated using various standards before the waters were run through the sephadex column. The method used for size exclusion chromatography fractionation is described in appendix A5. Unfortunately the solvent used for the purchased polystyrene standards caused uniform cracking and air entrapment in the sephadex gel throughout the column. The data is shown in figure 7.12. The sephadex gel was then replaced and the column was recalibrated using only the retentate samples saved from the cascade method of ultrafiltration. These spectra results and the calibration curve are shown in figure 7.11. The resulting calibration with the UF fractions was:

$$\text{Log MW} = -0.0134 \text{ (retention volume in ml)} + 3.896$$

Shown in figures 7.13 and 7.14, each water was found to have distinctive peaks with retention time. The fulvic acid samples were also analyzed with the SEC column. However, the humic acid portion could not be analyzed because it was eluted and collected from the XAD8 resin column. This procedure was beyond the scope of this thesis.

The corresponding molecular weight for each peak was calculated using the calibration relationship given above. These results are summarized in table 7.2.

Table 7.2: SEC Results

Water Source	Molecular Size of Peaks for Unfractionated Sample (Da)	Molecular Size of Peaks for Fulvic Acid Sample (Da)
ORW	5700, 2400, 1700	2930
OHRW	4700(small peak) 2400, 1200, 900	4950; 1850
SLRW	4700, 1700; 1200	3750; 2000
BPLW	3000; 1200	2930; 2000
VGW	2300; 1200	2430; 1900

Note: the manufacturer provided a molecular range for the sephadex gel which was 100 – 5000 Da. Therefore, values above 5000 Da are extrapolated data.

These results were in agreement with the molecular size information gained from ultrafiltration fractionation. Again, the BPLW and VGW had similar molecular size fractions. Both waters had peaks at 1200. Overall, the VGW sample had the smallest molecular size fractions and ORW the largest.

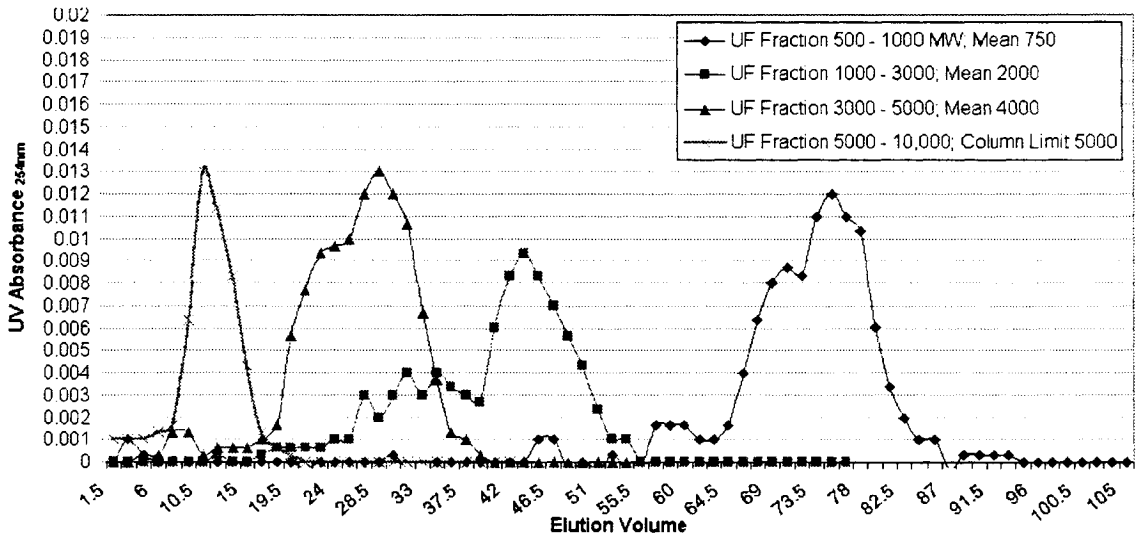

Figure 7.10: Spectra of Standards Passed through Sephadex G25 Column

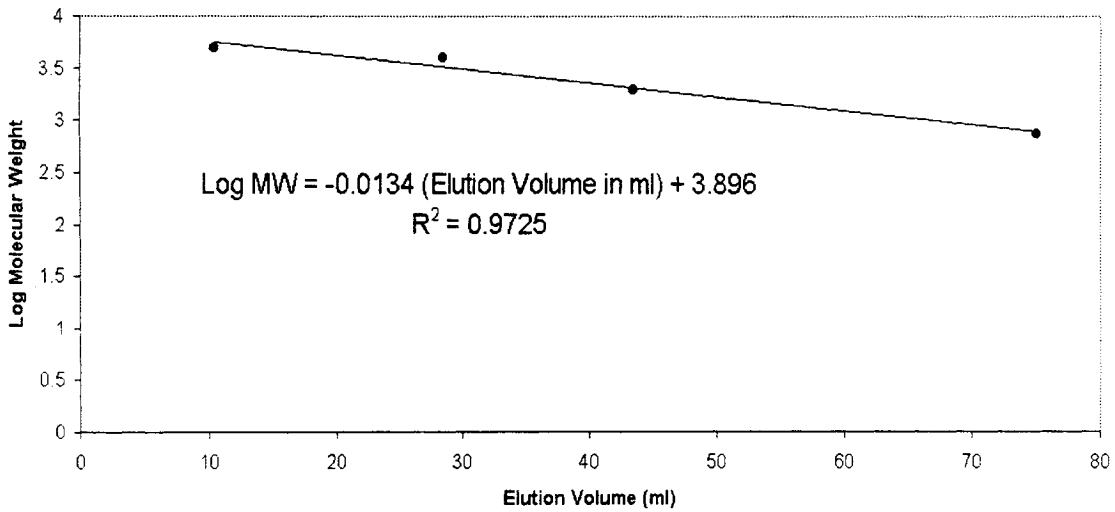

Figure 7.11: Calibration of Sephadex G25 Column With UF Fractions

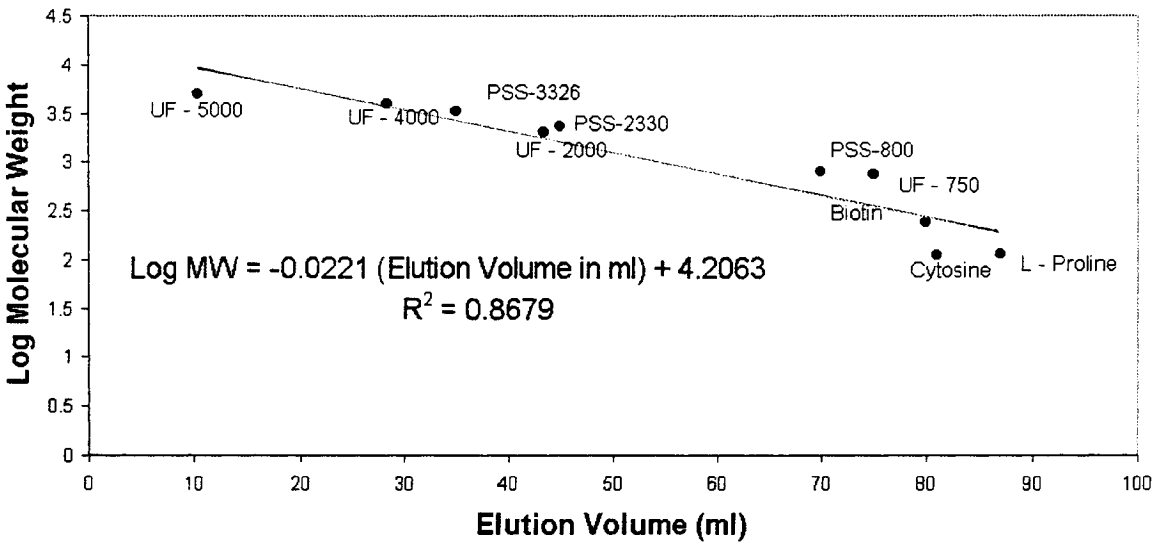

Figure 7.12: Calibration of Sephadex G25 with All Standards

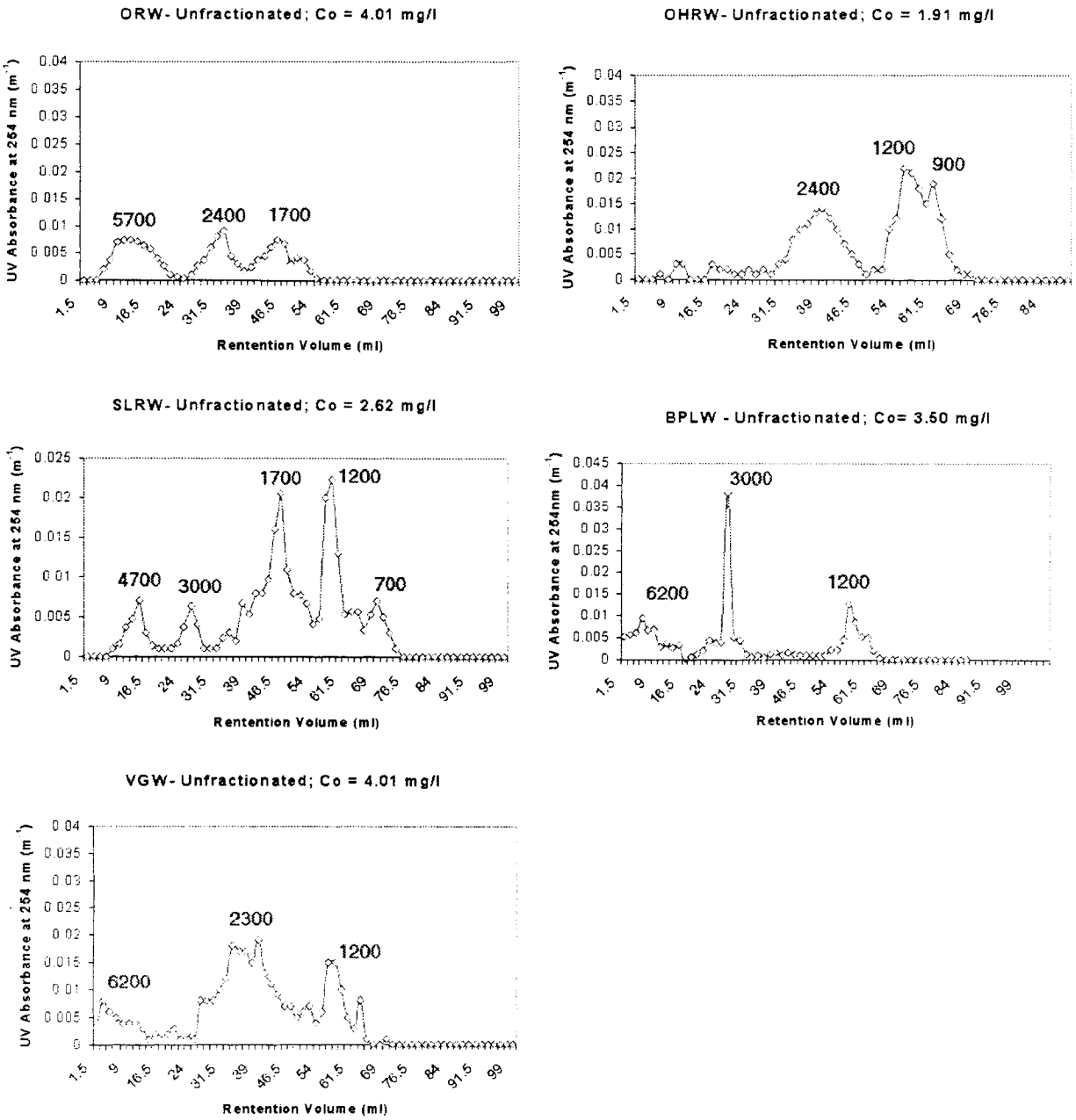

Figure 7.13: Size Exclusion Chromatography Results for All Source Waters

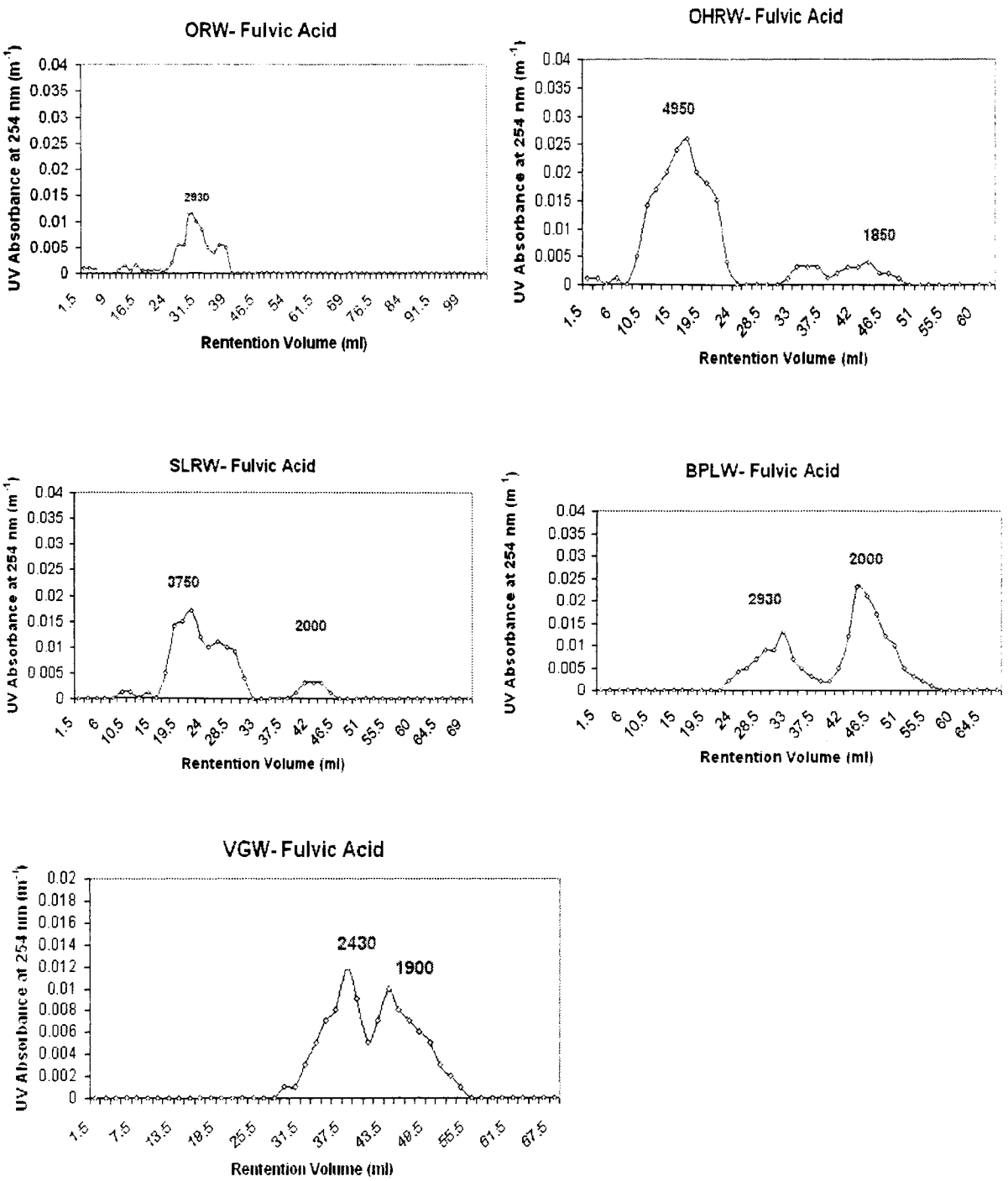

Figure 7.14: Size Exclusion Chromatography Results for Fulvic Acid Fractions

The SEC data can also be 'overlapped' , as shown in figure 7.15, to see the differences between unfractionated samples and the fulvic acid samples. The humic acids were never collected from the XAD8 column so this data does not exist on its own. We could assume that the area between the data points represents humic acids. If this is true, for many waters there is a portion of smaller humics as well as large humics. This concept is illustrated in figures 7.16 and 7.17. The fractionation process of XAD8 extraction followed by SEC is expected to contain accumulating errors. (see section 3.4.2.1) Therefore this simplification was not used in this thesis. The differences in UV absorbance intensity may be due as much to losses in the fractionation process as it is the discrepancy between fulvic and humic acid molecular sizes.

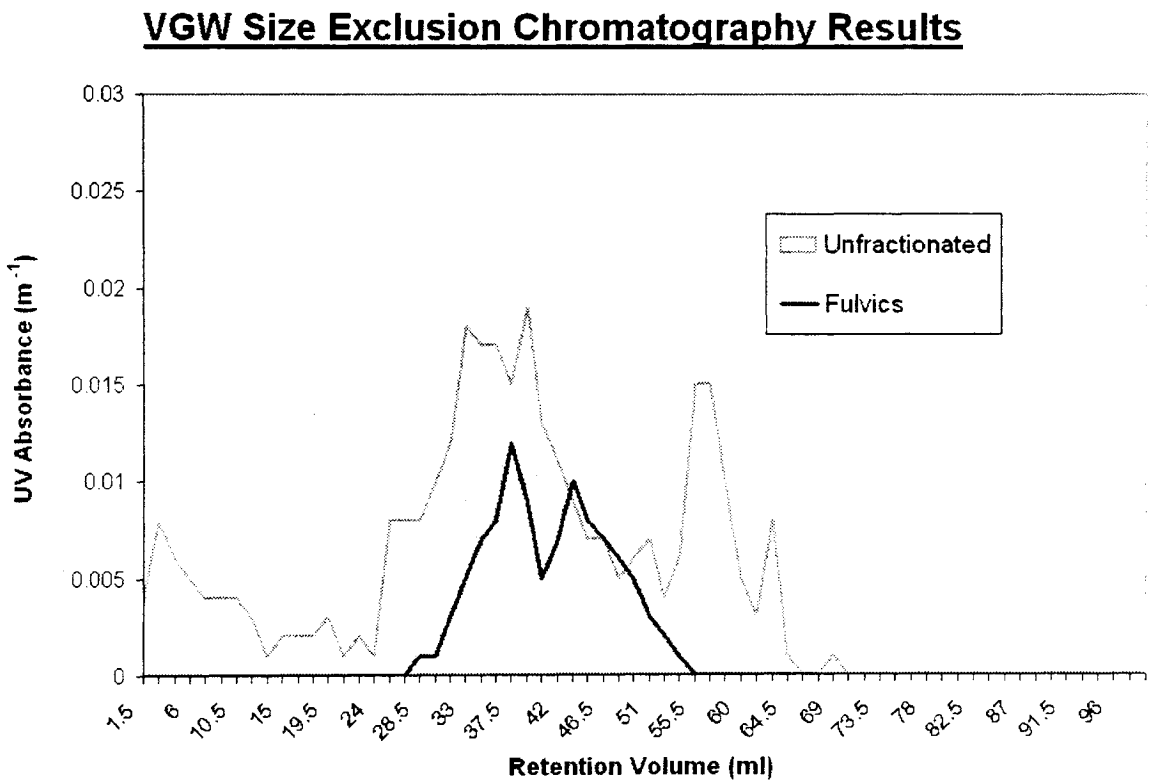

Figure 7.15: Overlap of SEC Data for VGW

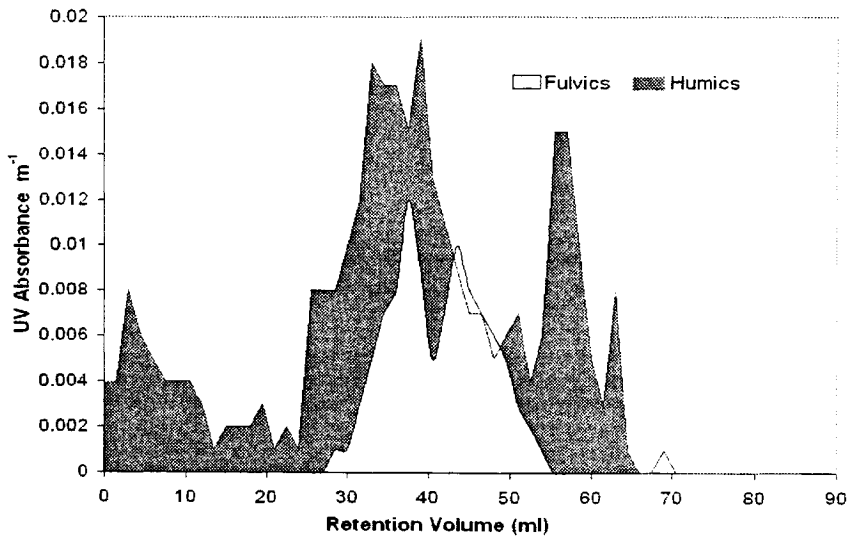

Figure 7.16: Estimation of Fulvic and Humic Portions in VGW

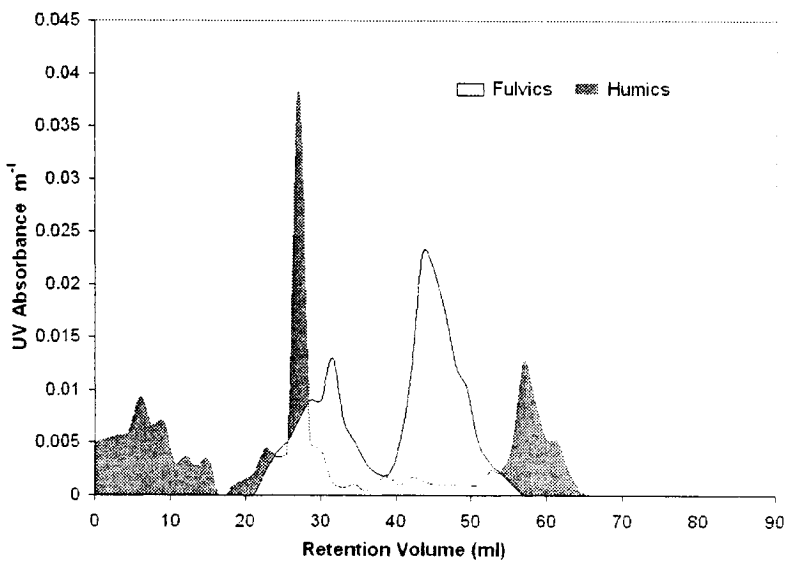

Figure 7.17: Estimation of Fulvic and Humic Portions in BPLW

Chapter 8: Summary, Conclusions and Recommendations

The objective of this thesis was to conduct an in depth study of the adsorption and desorption characteristics of NOM on GAC. The purpose of the research was to find out if NOM desorbs from GAC when loaded GAC is placed in a batch reactor with organic free water, and if so what parts of NOM desorb most readily. The irreversible adsorption behaviours of five natural waters were studied through equilibrium studies and various fractionation techniques. In the following sections, this data is summarized, conclusions are stated and some recommendations are provided.

8.1 Summary

Some of the key results have been summarized in table 8.1. Both BPLW and VGW had high DOC values, higher pH values, and the largest fraction of humic acids. SEC and UF fractionation both found these waters to have smaller molecular sized NOM.

The DOC values of the five natural waters ranged from 1.92 ± 0.025 mg/L to 4.01 ± 0.017 mg/L. The highest DOC values were for BPLW and VGW which were 3.50 ± 0.038 mg/L and 4.01 ± 0.017 mg/L, respectively. BPLW and VGW also had the highest pH values of 7.29 and 7.45. VGW had a high colour unit of 25 CU, and a high conductivity of 0.9 milli - ohm.

Table 8.1: Summary of Key Results

Water	GAC Type	Initial DOC (mg C/l)	pH	%Fulvics	%Humics	SEC Molecular Size at Peaks (Da)	Largest portions UF	No. points with >20% NOM Desorbed
ORW	F-400	3.15 ± 0.015	6.97	25.4%	74.6%	5700, 2400, 1700	25.5.%,<10k & >3k; 25.2%, <3k & >1k	1
ORW	WV-B	3.15 ± 0.015	6.97	25.4%	74.6%	5700, 2400, 1700	25.5.%,<10k & >3k; 25.2%, <3k & >1k	2
OHRW	F-400	1.92 ± 0.025	6.65	62.9%	37.1%	4700(small peak);2400, 1200, 900	44.8%, <3k & >1k	2
BPLW	F-400	3.50 ± 0.038	7.29	6.8%	93.2%	3000; 1200	47.3%, <1k &>0.5k	7
VGW	F-400	4.01 ± 0.017	7.45	8.7%	91.3%	2300; 1200	52.0%, <1k &>0.5k	5
SLRW	F-400	2.62 ± 0.039	6.69	42.1%	57.9%	4700, 1700; 1200	27.0%,<3k & >1k ; 21.7%, <0.5k	1

Adsorption kinetics (conducted with ORW) required 30 days to reach equilibrium, and desorption kinetics required 60 days. Early adsorption kinetics were fast and linear, while early desorption kinetics were slow and non linear. During the adsorption kinetics study the electron transfer band for the organics remaining in the liquid phase decreased. This suggested that the aromatics were adsorbing at a faster rate than the other compounds in ORW NOM.

Desorption isotherms for the NOM in BPLW and VGW, showed that most NOM adsorption is irreversible but showed more partially reversible behaviour than the other waters. VGW had the greatest number of desorption isotherms demonstrating some partial reversible behavior. Thus, these desorption isotherms confirmed that the adsorption NOM in these five different waters was completely irreversible or had very limited reversibility.

8.2 Conclusions

A study was conducted of the NOM adsorption and desorption characteristics of five waters. These waters originated from different locations and received different degrees of pretreatment. The conclusions of the study were:

1. The Freundlich isotherm, with a non linear regression routine in Microsoft Excel, fit all waters well.

2. Isotherms conducted with ORW eight months later than initial isotherms had very different outcomes. There was little difference between the performance of wood and coal based carbon for the initial isotherm. Eight months after the initial isotherm, the ORW NOM was not as adsorbable. It is hypothesized that the water changed over time although it had been refrigerated in an air tight drum. If it is true that the humic fraction was less adsorbable, the water may have agglomerated in humic acid fractions, and larger MW NOM molecules. The second isotherms also required a much higher dosage to define the non- adsorbing fraction.

3. Desorption isotherms showed that adsorption of NOM in ORW, OHRW an SLRW was irreversible and slightly reversible results found for BPLW and VGW.

4. Ultrafiltration fractionation had some unusual results. For example, OHRW and SLRW, which had the lowest initial DOC values, were found during ultrafiltration to have large portions of high molecular size NOM. BPLW and VGW both had about 50% of NOM in the range of > 500 Da but < 1000 Da. ORW had an even distribution of all UF fractions. Therefore, not all of the UF filtrate samples had a

direct relationship between DOC and UV absorbance

5. Extraction of humic acids with XAD8 found a proportional relationship between DOC and the percentage of humics in the water. VGW and BPLW both had large humic fractions although the UF results found a large portion of small MW NOM for both water sources.

6. From XAD8 extraction, the majority of NOM present in the adsorption liquid phase was found to be humics, except in the case of SLRW. Since this represents the portion of NOM that did not adsorb, the conclusion was made that in most cases fulvics adsorb more easily than humics. Desorption waters also had a large fraction of humic acids. Since this represents the NOM that did desorb, the conclusion was drawn that humics desorb more easily than fulvics

7. Size exclusion chromatography resulted in distinct spectra for all of the waters and fulvic acid fractionation samples. The natural waters had peaks between 6200 Da and 900 Da. The provided range of the sephadex gel was 100 to 5000 Da, therefore the greatest peak should be corrected from 6200 Da to 5000 Da. Fulvic acid samples had peaks in the range of 4950 Da (OHRW), 3750 (SLRW), and 2930 – 1850 for all the others waters.

8. The irreversible adsorption behavior of NOM was found to be universal. The humic acid portion of NOM was less adsorbable than the fulvic acids and was more likely to desorb. The fulvic acid fractions were largely irreversible. One explanation for conclusion 6 is that the humic acids that did adsorb had low energy bonds with the

GAC, or adsorbed last, and therefore these are the NOM molecules that desorbed. Fulvics were found to be more irreversible than humic acids for all waters except BPLW. For humic acids the opposite was true, they were found to be reversible for all waters except BPLW.

8.3 Recommendations

To test the hypothesis that waters change over time during storage, fractionation of a water source could be conducted every two months for a year using the same water sample stored in a fridge.. A comparison of UF, XAD8 extraction and SEC would tell the researcher a lot about the nature of NOM.

There is also a need to study the impact of NOM variability on the adsorption characteristics of GAC over different seasons. A similar study could be conducted using the natural water source over time. Every two months a sample from the ORW could be fractionated and compared both with the other ORW samples and those from the refrigerated test.

Some isotherms should be repeated such as the comparison of wood and coal, as well as fresh GAC and regenerated GAC.

Fractionation during kinetics studies would tell the researcher which functional groups of NOM adsorb and desorb first, and is recommended as an independent research topic for the study of NOM adsorption and desorption characterisitics.

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Appendix A: Experimental Procedures

Appendix A1: Cleaning of Glassware

Since the work in this thesis involved water samples of relatively low DOC (1.62 mg/l – 3.5 mg/l) and very low DOC (0.05 mg/l) values in the desorption water, the cleaning of glassware was an extremely important process. The process chosen was based on both the work conducted by Narbaitz (1985) and the recommended procedure in the operation manual for the Dohrman DC-180 (Dohrman, Santa Clara, CA.). DOC analyzer.

The glassware cleaning process was conducted in the following steps:

1. First, the washing and rinse water was prepared using the Millipore Milli-Q ultrapure water system (Millipore Corporation, Billerica, MA). , which consists of. distilled water feed, cartridges that remove ioinic and organic contaminants to trace levels, and a pharmaceutical-grade, absolute 0.22 μm Millipak membrane. This was considered to be organic free, with an electroconductivity of 18 megaohm-cm. This water had measurements of DOC of 0.05mg/l and 0.03 mg/l on the Dohrman DC-180 (Santa Clara, CA). and Tekmar/ Dohrman Pheonix 8000 (Cincinnati, OH) TOC analyzers, respectively. This water will be referred to as organic free water, OFW.

2. The soap used for washing the glassware was prepared using OFW and Alconox soap (Sigma Aldrich, Milwaukee, WI). The soap was made by heating 1 litre of OFW to boiling and adding 30 grams of this powdered detergent.

The glassware was then:

3. Rinsed with distilled water.
4. Filled with the HOT Alconox soap mixture, and the sides scrubbed with a small brush.
5. Allowed to soak for two hours
6. Rinsed five times with the OFW
7. Dried in a convective laboratory (Model 26, Thermo Electron Corporation. Waltham, MA) oven overnight at 110°C
8. Allowed to cool to room temperature
9. Filled with chromic acid and allowed to soak for two hours
10. Rinsed ten times with OFW
11. Dried in a convective laboratory oven (Model 26, Thermo Electron Corporation. Waltham, MA) overnight at 110°C

Appendix A2: Bottle Point Isotherm Loading

Because the desorption isotherm results depend on the accuracy of measurements made in the adsorption isotherm, the addition of the GAC was conducted with great care. The bottle point isotherm derives it's name from the fact that the experiment is conducted at a constant temperature and each data point is the result of one bottle of water loaded with GAC.

The AC dose (mass of carbon, M over the volume of water, V), ranged from 0.005 to 3 mg/l. This decision was based on the work of Narbaitz (1985), Peel (1980), and McEwen (2004).

There were two blank samples placed in the tumbler at the start of each isotherms. These samples did not have any AC dose added. The purpose of these samples was to see if the water underwent any biodegradation, or adsorption to the surface of the bottle or cap during the 30 day equilibration time. These samples are referred to as 'Control" in the data.

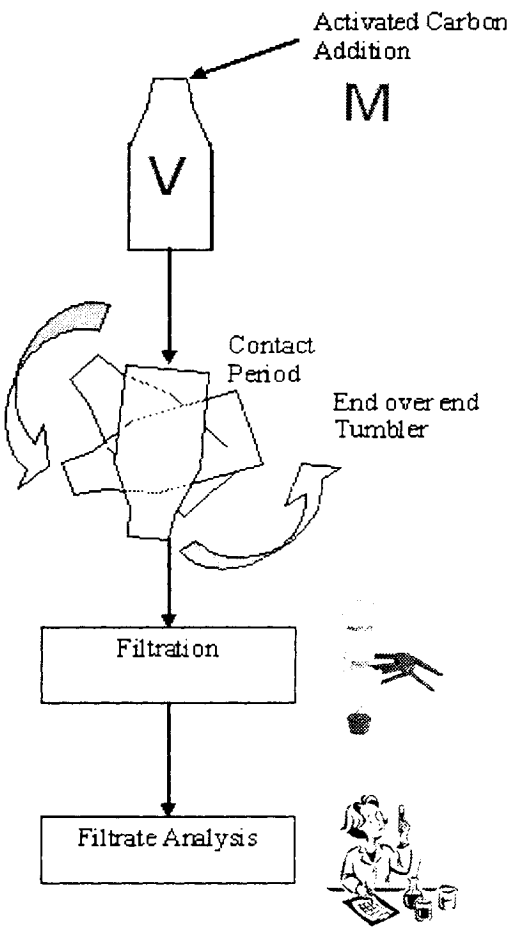

Figure A2.1: Steps Taken for Isotherms

The subsequent steps were followed for each adsorption isotherm (see figure A2.1):

1. Clean glassware according to the procedure in Appendix A1, also clean caps with OFW

2. Label then weight empty bottle without cap

3. Rinse bottle twice with the water to be used in the isotherm, for example rinse twice with Ottawa River Water for the Ottawa River Water Isotherm.

4. Fill the bottle with the water to be analyzed but allow some room, about 5ml, at the top of each bottle to allow for air bubbles. These air bubbles later allow better mixing to occur in an end over end tumbler.

5. Weigh the bottle again, without the cap.

6. The difference in weight between step 5 and step 2 was used to calculate the volume of water. Since the laboratory scale (PC4400, Mettler-Toledo Inc., Columbus, OH) used for these weights was accurate to 0.0l g, the volume measurement was accurate to 0.01ml.

7. The volume was multiplied by the AC dose, M/V and the required carbon was weighed on an analytic balance(Sartorius, Goettingen, Germany) with an accuracy of 0.1mg, or 10^{-4} g. Before the carbon was used, it was sieved and cleaned. The US sieve size range used throughout this work was 40 X 50 with a mean particle diameter of 3.53×10^{-4} m.

8. This carbon was then carefully transferred into the bottle using a clean soft bristle

paint brush.

9. The rim of the bottle was lined with Teflon tape to make sure the attachment of the cap and the bottle was airtight. The interior of the bottle cap had a Teflon disk liner, so that the adsorbate was only in contact with glass or Teflon.

10. The bottle cap was also secured onto the bottle using electrical tape around the exterior.

11. The bottle was then placed in the end over end tumbler shown in figure A2.2 and allowed a contact time of 30 days.

12. After 30 days the water was filtered with vacuum filtrations using a glass Millipore filter holder and 47 mm diameter Cellulose Ester membrane filters with a nominal pore size of 22 μm (Millipore Corporation, Billerica, MA).

13. The AC retained on the filter was cleaned with 10ml of OFW then reused in the desorption isotherms.

14. The filtrate samples were analyzed for DOC and UV absorbance.

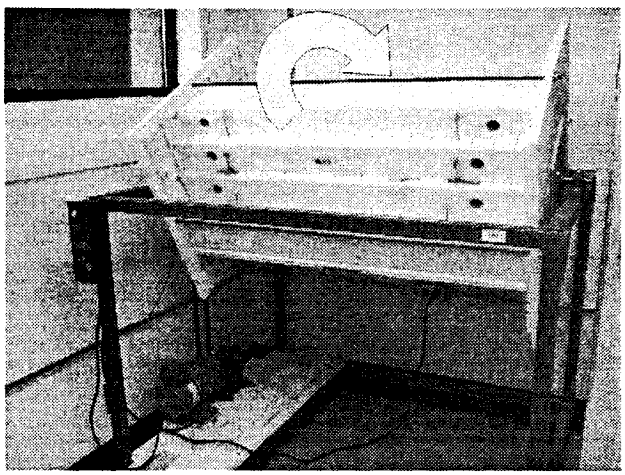

Figure A2.2: Laboratory Tumbler

Appendix A3: Desorption Isotherm Loading

The following steps were required for the analysis of desorption isotherms.

1. The glassware was cleaned as described in appendix A1.

2. The volumes from step 6 in appendix A2 were required for this method. Once these volumes were located and noted, clean bottles were filled with these same volumes of OFW.

3. The carbon from step 12 of appendix A2 was rinsed with 10ml of OFW then added to the prepared bottles.

4. The bottles were sealed with Teflon tape, the cap was screwed on, further secured with electrical tape, then rotated in the end-over-end tumbler for 60 days.

5. After 60 days the water was filtered via vacuum filtration using a glass Millipore filter holder and 47 mm diameter 22 um pore size Cellulose Ester membrane filters. (Millipore Corporation, Billerica, MA)

6. The filtrate was analyzed for DOC concentration and UV absorbance. However, the UV absorbance relationships were not accurate at these low concentrations so this data was not useful.

Appendix A4: Ultrafiltration

There are two methods commonly used for ultrafiltration. These are the parallel method and the cascade method. Parallel ultrafiltration uses raw water for each membrane size, then the weight percentage of the different fractions are calculated from a mass balance. Cascade ultrafiltration uses the rententate from the previous membrane size in the next membrane being studied. A good analogy for the cascade method of ultrafiltration is that it is similar to using a sieve shaker for particle size analysis. The only difference is we would pull out samples before the sand enters the next sieve. This method is shown in the schematic of figure A4.2.

The ultrafiltration cell used in this study is shown in figure A4.1. It is an Amicon Micron 8050 ultrafiltration cell with a cell capacity of 50ml. The pressure used was 35psi for all membranes and the gas used for pressurization was air.

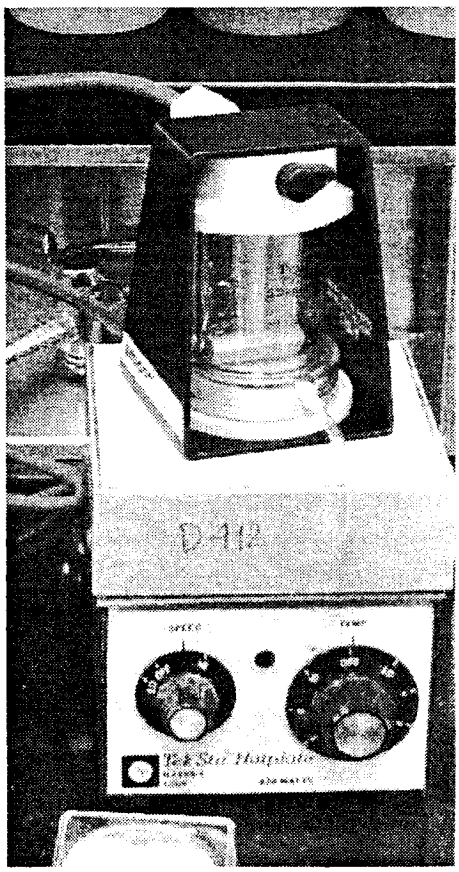

Figure A4.1: The Ultrafiltration Cell

Procedure

Preparation of Membranes: The membrane sizes listed in table A4.1 were chosen for the fractionation based on the molecular size fractionation results of other researchers. (Newcombe, 1997, O'Driscoll 1998, O'Driscoll and Evans, 2000, Pelekani, 1999) The membranes are coated with glycerin by the manufacturer to prevent them from drying during storage. The glycerin gives the membranes a shiny appearance so the user also knows which side to place upwards in the cell. To remove this coating the membranes were soaked with the shiny side down in OFW. After the membranes were cleaned, the following steps were taken:

1. After the membranes were cleaned, the cell was also cleaned with OFW. The cell was filled with 50ml of OFW and pressurized with air, and the magnetic stirrer turned on. 75% of the water was allowed to run through the membrane and clean the system. The remaining OFW was discarded.
2. The cell was then filled (overfilled slightly) with 55ml of the water being fractionated.
3. The cell was pressurized to 35psi using air and stirred with a magnetic stirrer. The first 5ml of sample was discarded. 40ml of the permeate was collected and the pressure turned off.
4. The remaining 10ml left in the cell was collected as the fraction of water with NOM of a molecular size larger than the membrane size.
5. Samples of the retentate and the permeate were set aside for later analysis.

6. Extra samples of the permeate were required for use in the membranes of smaller pore sizes to complete the cascade analysis shown in figure A4.2.

7. The fractions of NOM retained on each membrane were calculated by weight percent through a mass balance.

Since the permeate was concentrated they served as ideal calibration solutions for the size exclusion chromatography analysis.

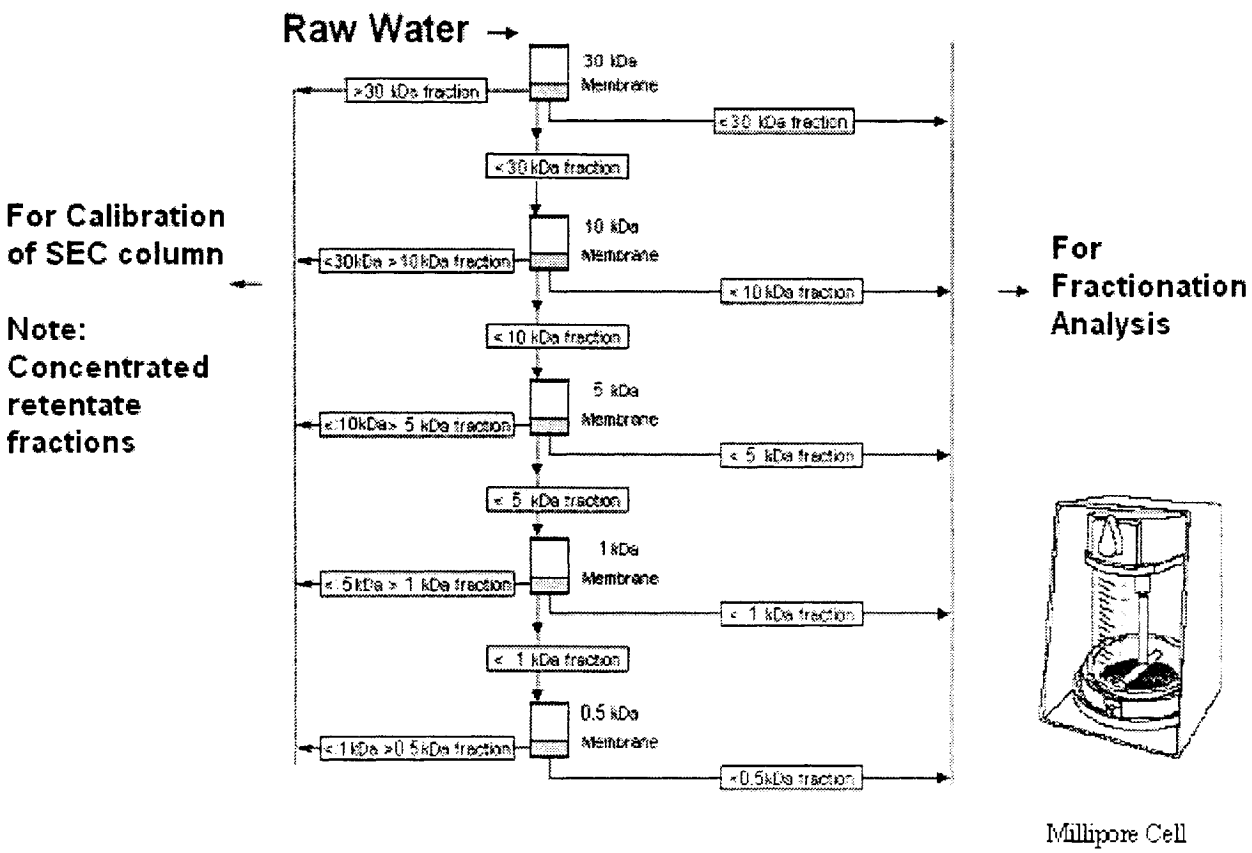

Figure A4.2: Schematic of Cascade Method of Ultrafiltration Fractionation

Table A4.1: Millipore Membranes Used for Study

Filter Code	MWCL	Calibrated with	Filter Material
YC05	500	Sugars and polysaccharides	Cellulose Acetate
YM1	1000	Sugars and polysaccharides	Regenerated Cellulose
YM3	3000	Sugars and polysaccharides	Regenerated Cellulose
YM5	5000	proteins	Regenerated Cellulose
PM10	10,000	proteins	Polyethersulfone
PM30	30,000	proteins	Polyethersulfone

Appendix A5: Gel Permeation Chromatography

Procedure:

1. The columns were ordered from Ace Glass in Ottawa and were designed with the same dimensions used by O'Driscoll (1998). (i.e., length of 40cm and an inner diameter of 1.5 cm). The apparatus is shown in figure A5.1.

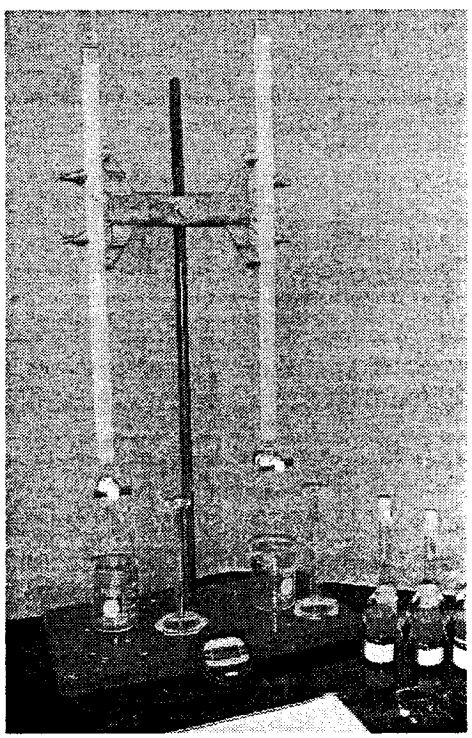

Figure A5.1: Experimental Apparatus for SEC

2. The columns were cleaned with OFW.

3. The gel particles were dissolved in OFW according to manufacturers recommendations. The particles swelled immediately. (1 gram swells to 5 ml). The Sephadex G25 column had a height of 43.6 cm and the Sephadex G75 column had a height of 36.1 cm.

4. Empty column space was allowed above the gel to be filled by OFW. The gels must never be allowed to dry so during storage they are always filled with OFW as a solvent and overfilled to the top of the column to ensure no drying through evaporation. The top of the columns were sealed with parafilm.

Calibration

5. Natural water standards were made by saving the retentate from cascade ultrafiltration.

6. The column gel was buffered by adding a 0.1M $NaSO_4$ (Certified ACS Grade; Fisher Scientific, Hampton, NH) solution to the column until the effluent consistently had a pH of 6. The OFW resting on top of the column was allowed to elute through the column and the top of the column was allowed to be free of OFW only for several seconds

7. 1 ml of the standard was introduced into the column

8. After the 1ml had penetrated the gel column, the space at the top of the column was again filled with OFW

9. Immediately, 1.5ml samples were collected and analyzed. The combination of these samples is called 'time sliced output' and the goal is to find a peak in the elution concentration. An illustration of these time slices is shown in figure A5.2. The analyzed peak is determined from the maximum response with an appropriate analytical technique. Many researchers use a refractometer connected to the bottom of the column. Some studies have used UV absorbance analysis (Newcombe *et al.*, 2002, O'Driscoll and Evans, 2000). UV absorbance was used for this study.

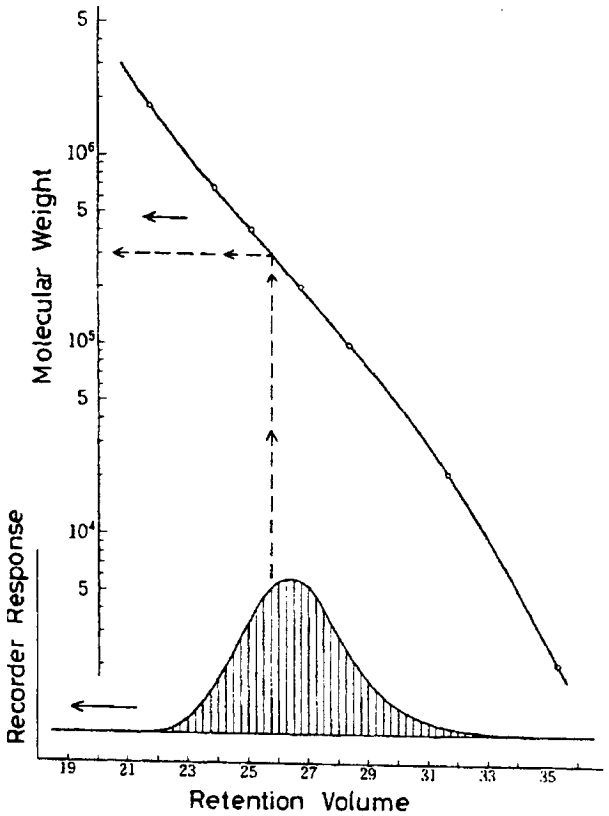

Figure A5.2: 'Time Slice' Peak Analysis (Source, Mori, 1999)

10. Analysis was continued until the cumulative volume was 80ml. This was chosen because the lowest molecular weight had a peak at 75ml. Some water samples may also have more than one peak. Waiting for a consistent zero reading was required to ensure the sample was finished eluting. The cumulative volume of the samples is referred to as the retention volume (see abscissa of figure A5.2).

11. The samples were analyzed during the run for UV absorbance at 224 and 254 nm

for the polystyrene sulfonate(PSS) and natural waters, respectively.

12. The UV absorbance was plotted vs. retention volume to obtain peaks for each molecular weight. The molecular weight calibration curve was then produced using this data, similar to the example shown in figure A5.3.

13. Polystyrenes do not react in exactly the same manner as NOM but are used by many researchers as the best representation of NOM (Newcombe, 2002, O'Driscoll, 2000). The PSS solvent used was acetone as recommended by the manufacturer of sephadex gels. Unfortunately the use of this solvent caused cracking in the column. Therefore, steps 5 through 12 were repeated using the fractions obtained in the Ultrafiltration method described in appendix A4. These standards were used to calculate the molecular weight of the natural waters.

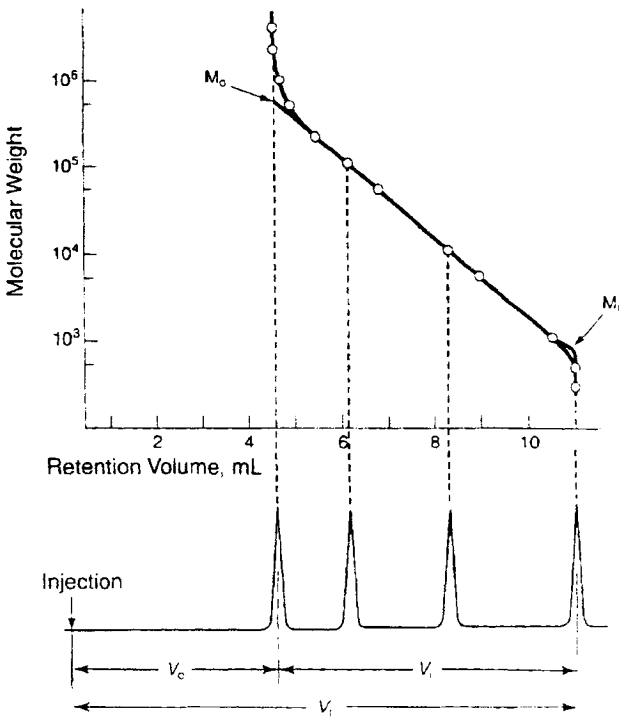

Figure A5.3: Calibration of the SEC Column (Source, Mori, 1999)

Sample Analysis

14. 2ml of the sample was introduced into the column

15. After the 2ml had entered the gel column the empty space at the top of the column was filled with OFW

16. Immediately, 1.5ml samples were collected and the UV absorbance measured at 254nm.

17. Samples were collected until the cumulative retention volume was 80ml. It was determined in the early analysis with this column that the column would return to UV absorbance values of zero before 80ml. The response range was between 5ml and 75ml. To be consistent, all runs were continued until 80ml retention volume had been collected.

18. The UV absorbance was plotted vs. retention volume to study the unique molecular weight distributions for each sample

19. The peaks were compared to the calibration curve of molecular weight of the standards vs. retention time to obtain a molecular weight distribution curve

Making the Standards

Polystyrene Standards

Polystyrene standards were purchased from Sigma Aldrich (Sigma Aldrich, Milwaukee, WI) as listed in table A5.1. These were diluted according to the recommendations of Mori (1999). Molecular weight averages will differ for the same molecular weight at different concentrations. They recommend for an 8mm diameter column of length 25 cm, to use a dilution of 0.1%(mass/volume) for high molecular weight samples. The highest concentration recommended was 0.2%(mass/volume) High MW standards require lower concentrations, and low MW standards require higher concentrations. For this study a concentration of 0.1% (mass/volume) was chosen.

The specific gravity of the polystyrene standards was 1.047g/ml. In a 50 ml flask full of acetone, 0.05 g of dry polystyrene standard was diluted. Pelekani (1999a) used a dilution of 1g of polystyrene standard per litre of solvent. The detection of the standard eluted was determined by UV analysis at a wavelength of 224nm, after the methods of Pelekani (1999a). The dilution concentration of the standards has been found to affect results as shown in figure A5.4. The effects from different solvents are shown in figure A5.5. As mentioned in step 13, the acetone reacted with the sephadex gel creating a cracking effect. The results are shown in this thesis but the calibration of the natural water standard was used for the MWD of the source waters.

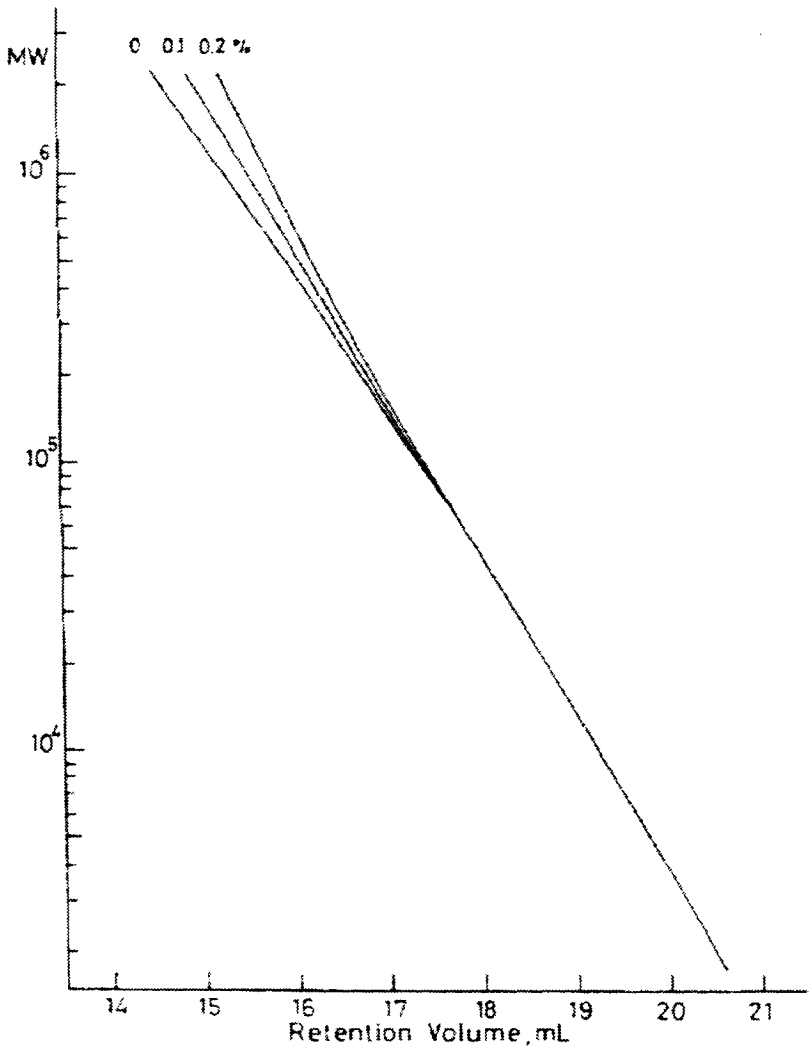

Figure A5.4: Affect of Standard Concentration on Calibration (Source, Mori, 1999)

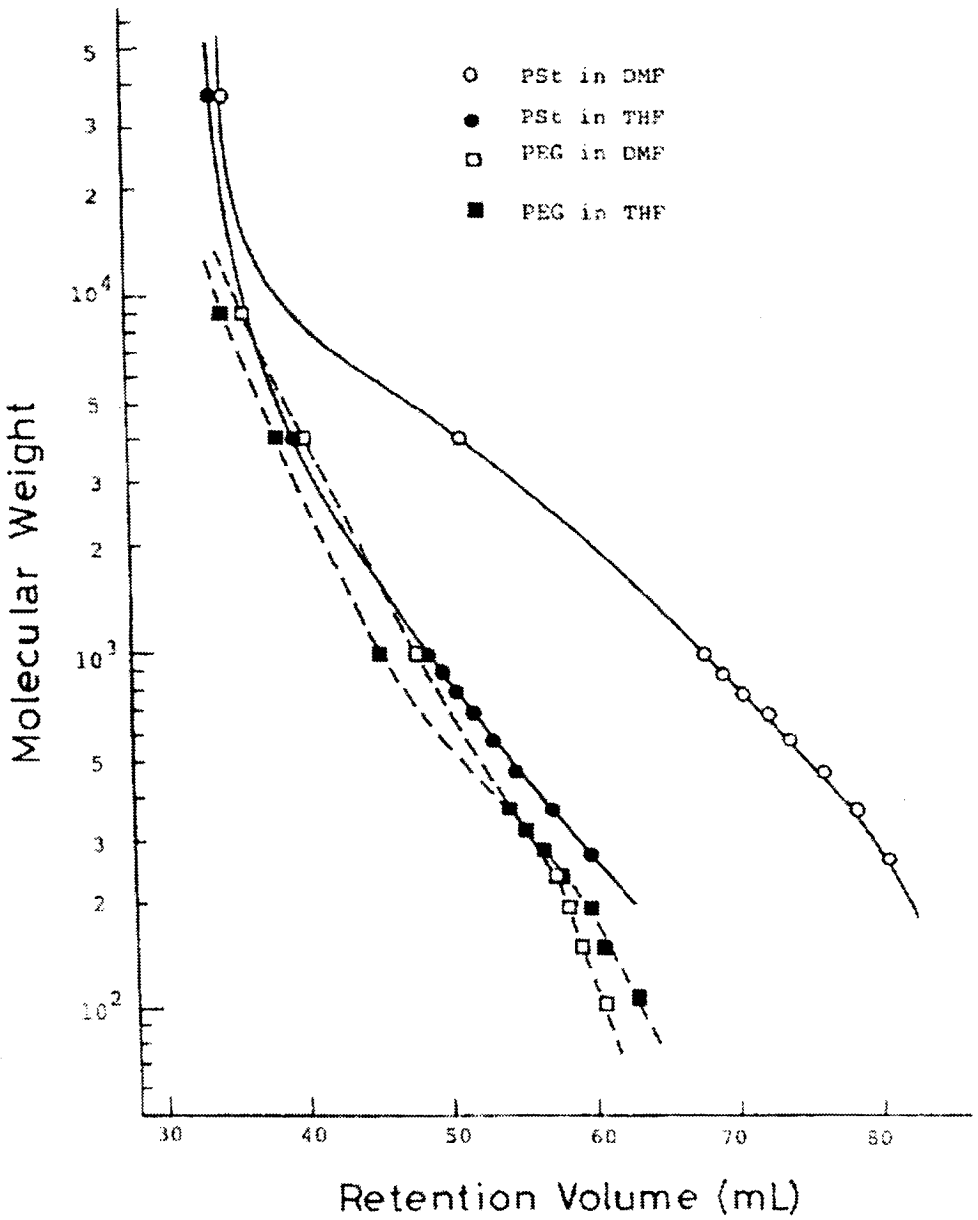

Figure A5.5: Affect of Solvent on Calibration (Source, Mori, 1999)

Protein Standards

Various proteins were also used to calibrate the columns. These are shown in table A5.2.

Table A5.1: Polystyrene Standards Used for Calibration of SEC

Synthetic Polymer	Molecular Weight (Daltons)	For Column:	Dilution Concentration	Solvent
Polystyrene	800	SG-25	0.1%(w/v)	Methanol
Polystyrene	2330	SG-25	0.1%(w/v)	Methanol
Polystyrene	3326	SG-25	0.1%(w/v)	Methanol
Polystyrene*	13,700	SG-75*	0.1%(w/v)	Methanol
Polyvinyl*	10,000	SG-75*	0.1%(w/v)	Methanol

* Not required for the source waters in this thesis, recommended for other research

Table A5.2: Protein Standards Used for Calibration of SEC

Protein Source	For Column:	Molecular Weight (Daltons)	Dilution Concentration	Solvent
L-Proline	SG-25	115.1	0.1%(w/v)	Water
Biotin – Vitamin H	SG-25	244.3	0.02%(w/v)	Water
Cytosine	SG-25	111.1	0.05%(w/v)	Water

Appendix A6: XAD8 Resin Fractionation

This XAD8 procedure is adapted from Thurman and Malcolm (1981). The apparatus used in this study is shown in figure A6.1.

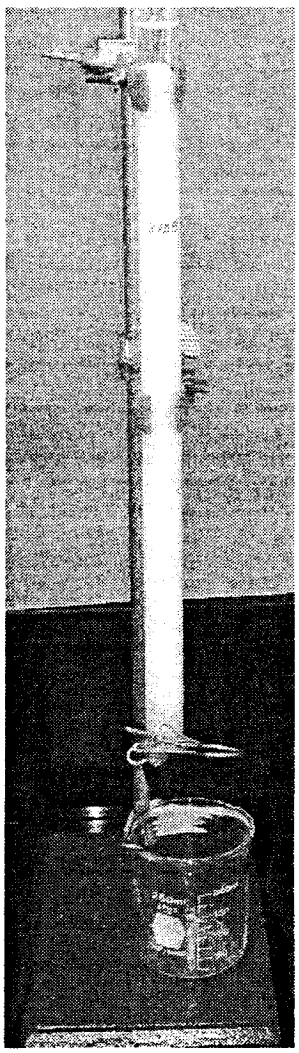

Figure A6.1: XAD8 Experimental Apparatus

Preparing the Column:

1. Clean the resin according to the manufacturers recommendations
2. Rinse column with 0.1 N NaOH (Certified ACS Grade; Fisher Scientific, Hampton, NH) for ~1-3 hours.
3. Rinse column with five column volumes of hot OFW between each sample. Remove the column from the stand, secure a stopper at both ends and shake the column vigorously.
4. Rinse column once with OFW and 10% 1M HCl (Certified ACS Grade; Fisher Scientific, Hampton, NH) acid
5. Analyze the OFW and the effluent from the column using the DOC analyzer. The DOC of both should be the same. If the effluent has a higher DOC than the influent OFW, repeat steps 3 and 4. Do this until the influent and effluent have the same DOC.

Sample Preparation:

6. Obtain a 200 ml sample and vacuum filter with a 0.45 μm membrane filter to remove any precipitates, these would be humins.

7. Adjust the pH of the sample water to 2.0 with HCl. 200ml samples required 2.5ml of 10% 1M HCl (Certified ACS Grade; Fisher Scientific, Hampton, NH)

8. Pass the sample of water through the column of XAD8 resin (methyl methacrylate, Fisher Scientific, Hampton, NH)

9. Allow the first 100ml to go to waste. This portion is used only for washing the column, and eluting any remaining OFW in the column.

10. The fulvic acid portions will be in the effluent.

11. Pass the remaining 100 ml of sample through the column 2 more times

12. Conduct DOC and UV analysis of the effluent (fulvic acid portion).

13. A simplified schematic of this procedure is shown in figure A6.2 below. Rinsing with NaOH is only necessary when a solution of high concentration has been passed through the column, or when collection of humics is the goal. The rule of thumb used in this study was to clean the column when the XAD8 resin started to appear orange, or when using a sample known to have a DOC value much lower than the previous sample. Otherwise it is best to keep the column acidic, keeping humic acids precipitated and adsorbed on the surface of the resin.

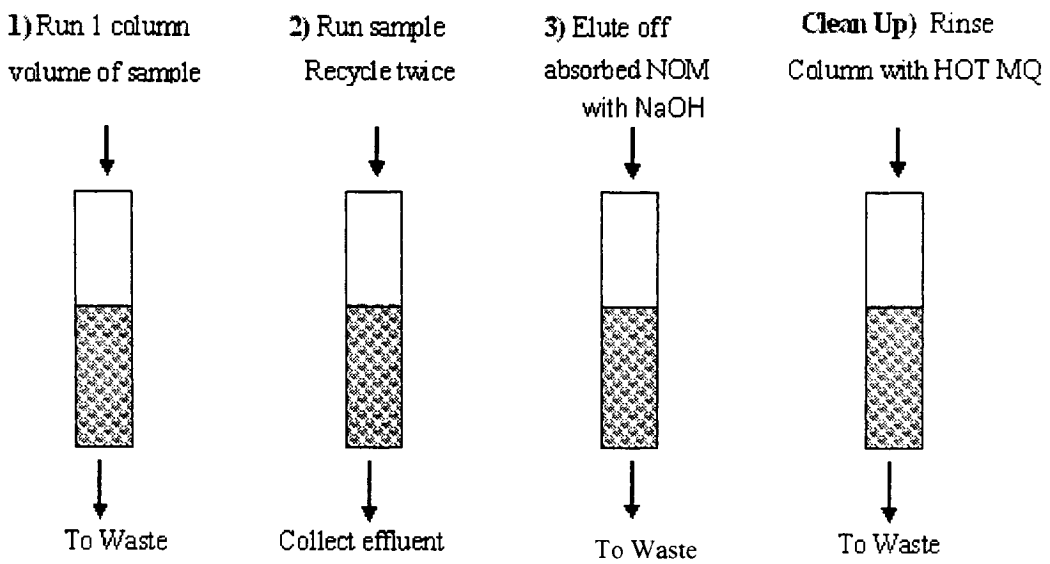

Figure A6.2: Schematic of Cyclic Procedure

Appendix B: Detailed Look at the Water Sources

Approximate geographical positions of the five water sources are shown in figure B.1 below.

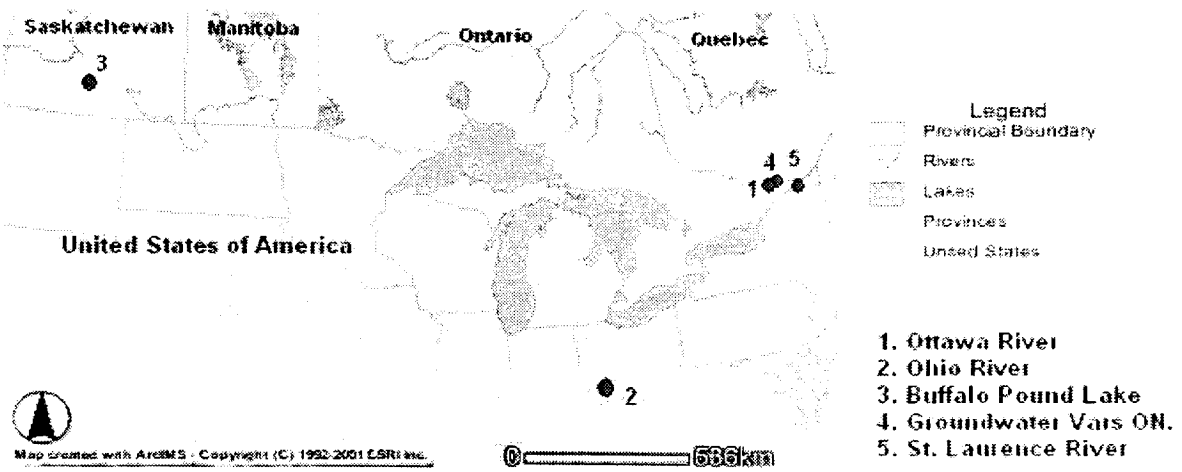

Figure B.1: Geographical Location of Water Sources

Appendix B1: Ottawa River Water - ORW

B.1.1 Location

The Ottawa River is the source of drinking water for the city of Ottawa, Ontario, which has approximately 750,000 inhabitants. The city has two treatment plants that produce drinking water from Ottawa River water, they are the Lemiux Island Plant and the Britannia Water Treatment Plant. A 200 liter water sample was collected May 2004 from the Brittania water treatment plant, from the process stream between the clarifiers and mixed media filters.

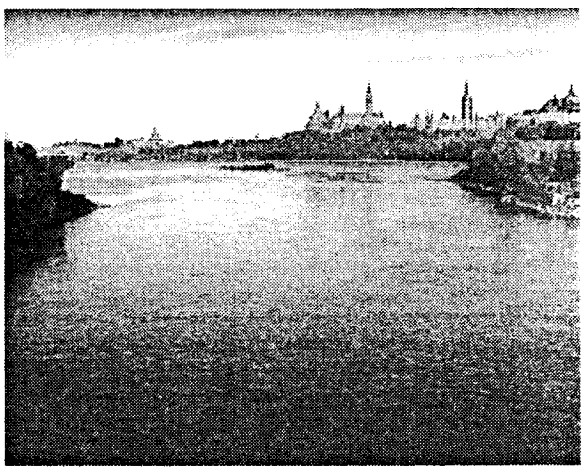

Figure B.2: Photo of the Ottawa River

Table B1.1: ORW Properties

Water Source		Ottawa River Water
Site of Sampling		Ottawa WTP, Ontario
Symbol		ORW
	(Units)	
DOC	**mg/l**	3.15 ± 0.015
pH		6.97
Conductivity	**milliohms**	0.710
Colour		5
Turbidity	**NTU**	0.261 ± 0.002
Alkalinity	**mg $CaCO_3$/L**	2.4
Total Hardness	**mg $CaCO_3$/L**	25.76
Calcium Hardness	**mg $CaCO_3$/L**	22.08
UV abs . 254 nm	**m^{-1}**	0.525

B.1.2 UV and DOC correlation

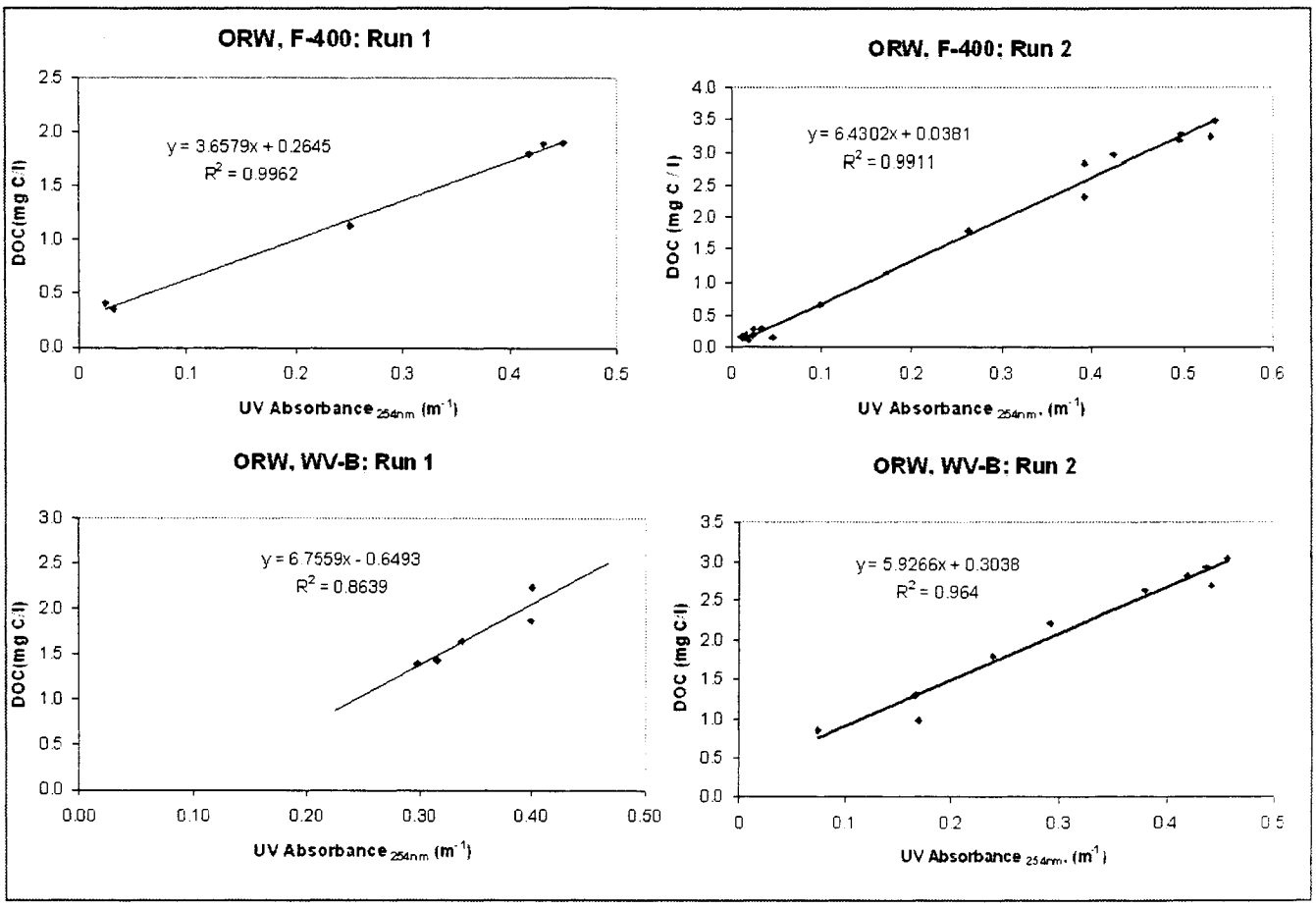

Figure B.3: DOC and UV Correlations at 254nm for Ottawa River Water, 100mm Pathlength

B.1.3. Isotherms

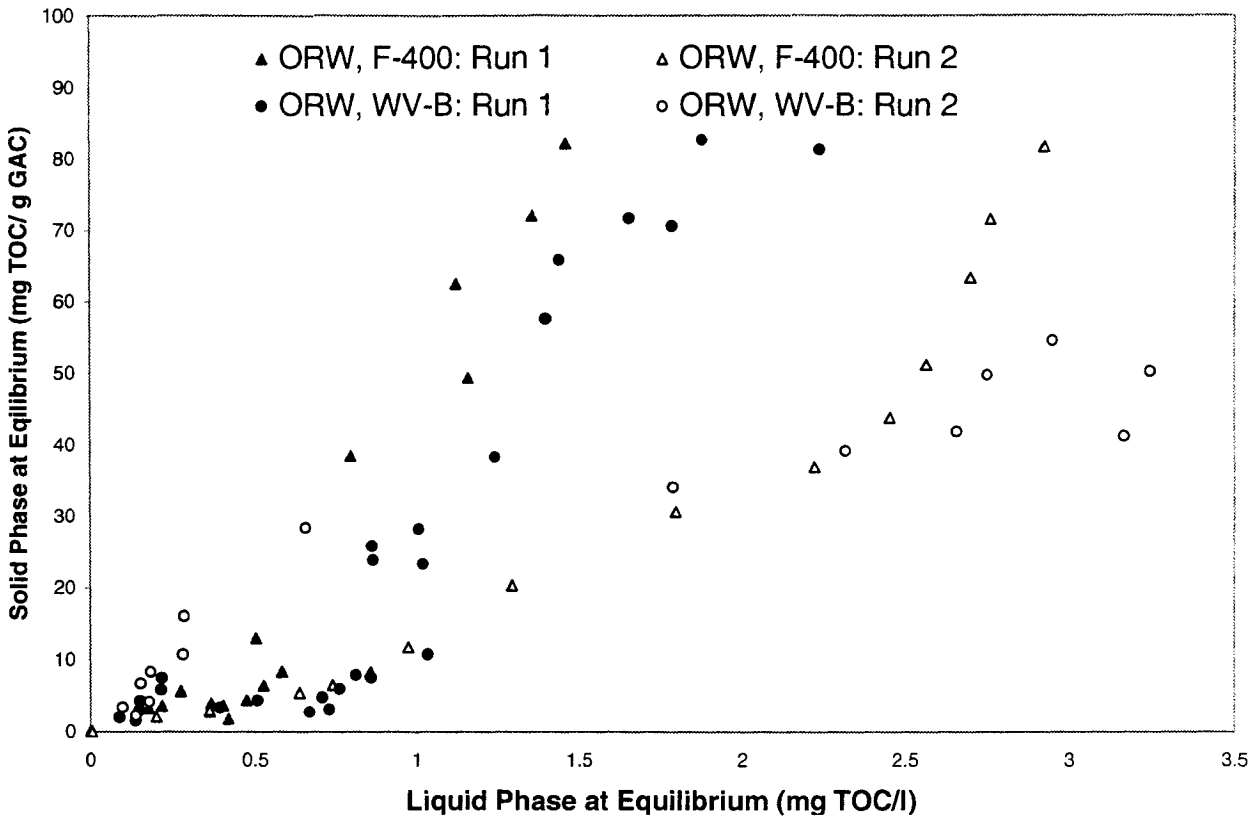

Figure B.4: Ottawa River Water Isotherms, 40X50 Mesh Size

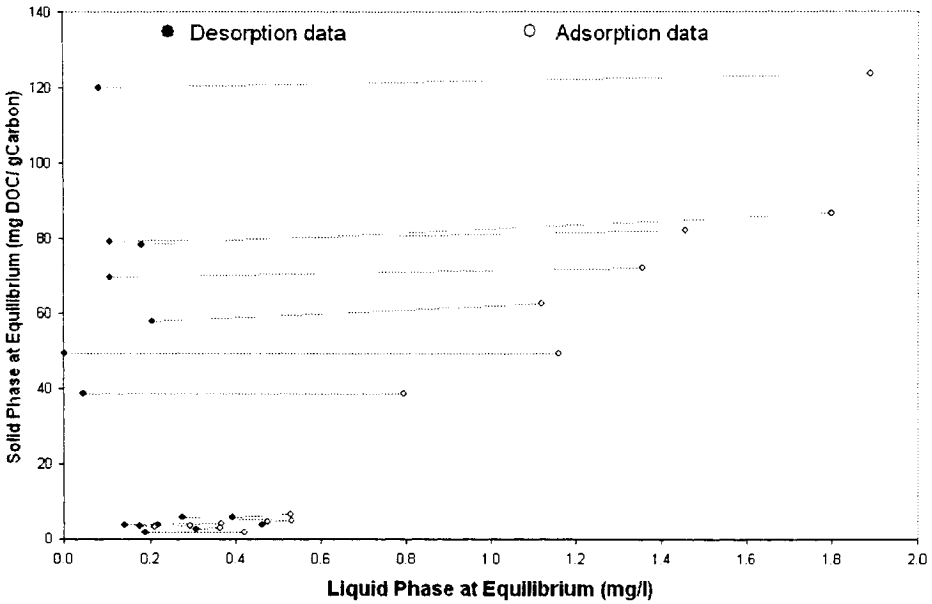

Figure B.5: Desorption Isotherms, ORW and F-400 GAC, 40X50 Mesh Size

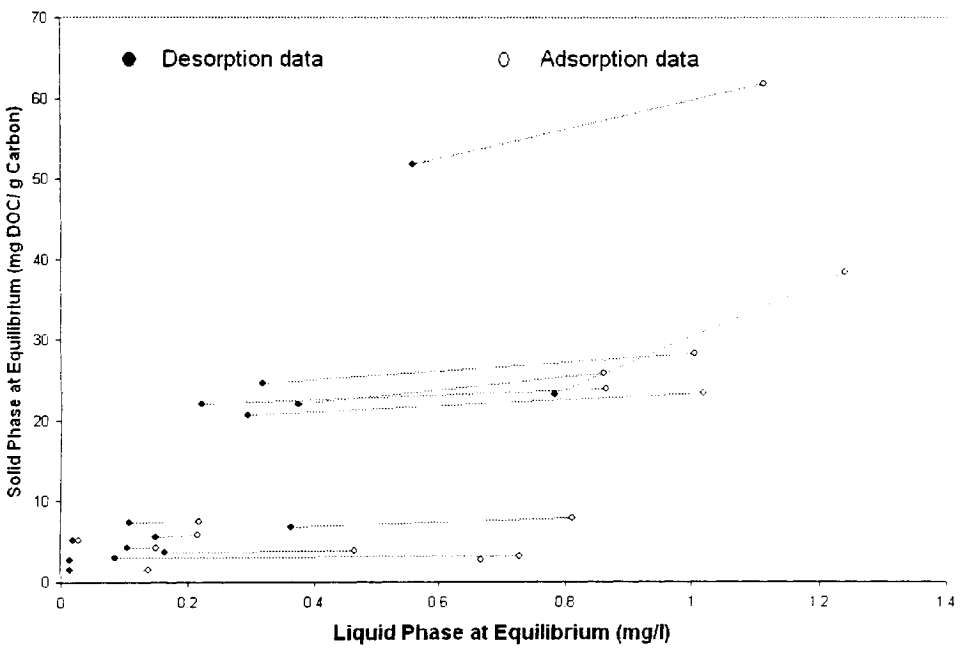

Figure B.6: Desorption Isotherms, ORW and WV-B GAC, 40X50 Mesh Size

B.1.4 Fractionation – Ultrafiltration

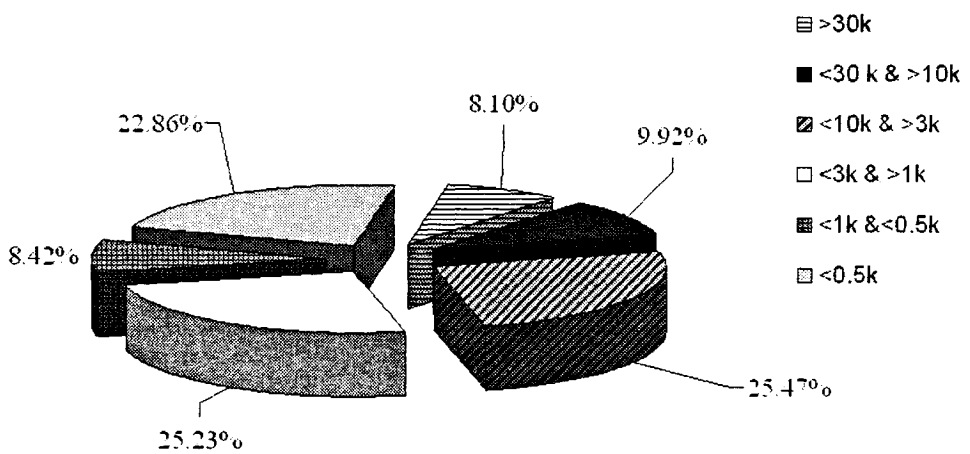

Figure B.7 : Ottawa River UF Fractionation

Table B1.2: ORW UF Results

Fraction	Weight Percent In fraction	DOC mg/l	Standard Deviation	95% Confidence
>30k	8.10%			±
<30k	91.90%	2.895	0.010	0.011
<30 k & >10k	9.92%			
<10k	81.99%	2.583	0.032	0.036
<10k & >3k	25.47%			
<3k	56.51%	1.780	0.012	0.014
<3k & >1k	25.23%			
<1k	31.29%	0.986	0.008	0.008
<1k &<0.5k	8.42%			
<0.5k	22.86%	0.720	0.008	0.009

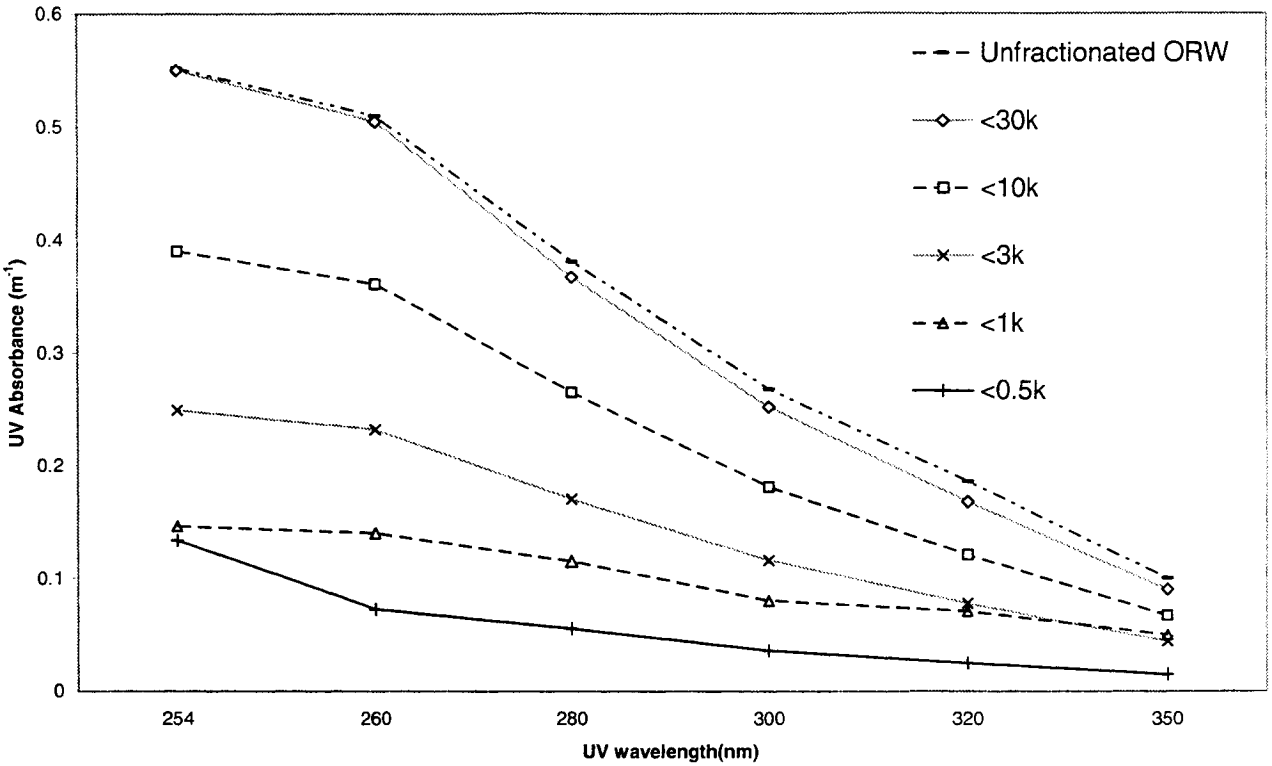

Figure B.8: ORW, UV Absorbance for Different UF fractionations

B.1.5 Fractionation – Humic Acid Extraction

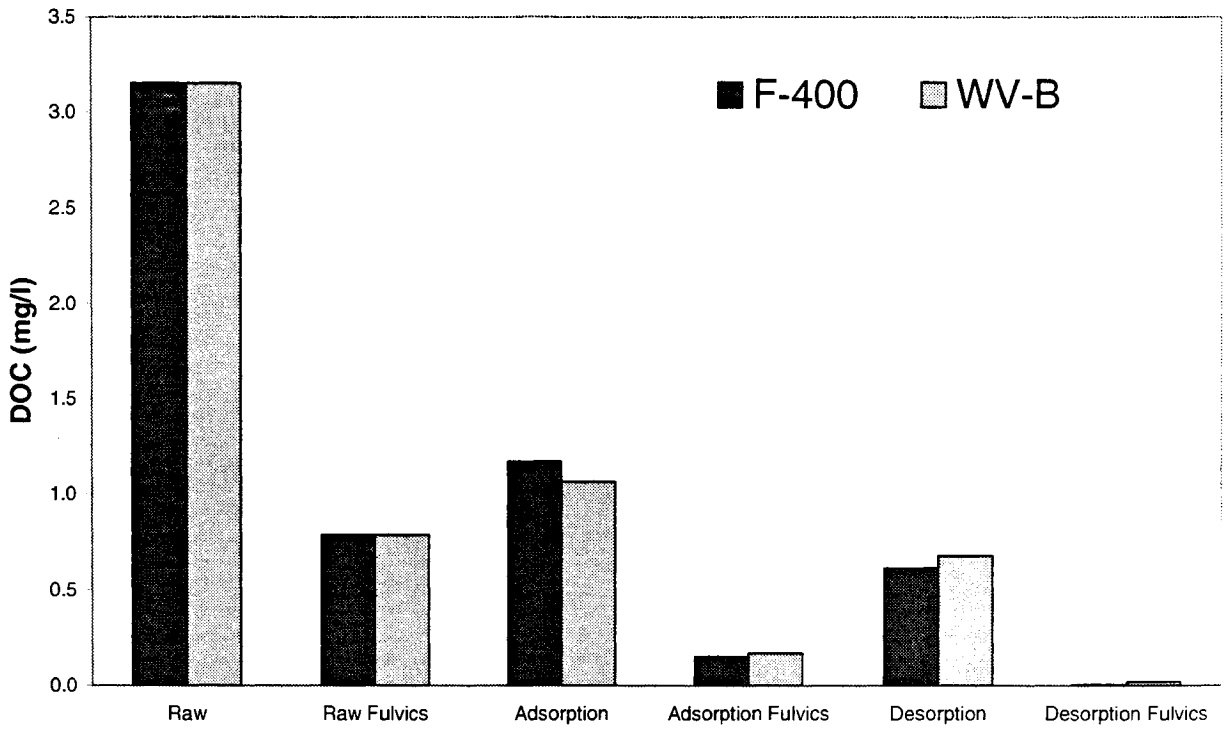

Figure B.9: XAD8, DOC Results from ORW Humic Acid Extraction

B.1.6 Fractionation – Size Exclusion Chromatography

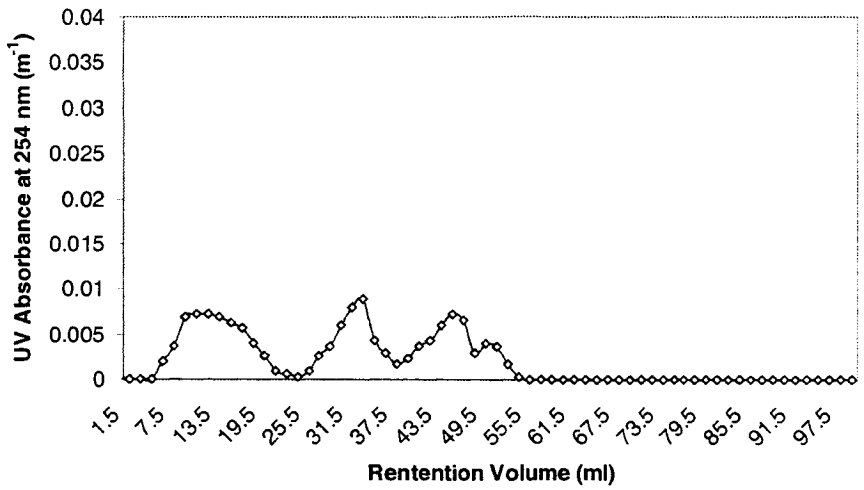

Figure B.10: SEC Results from Unfractionated ORW

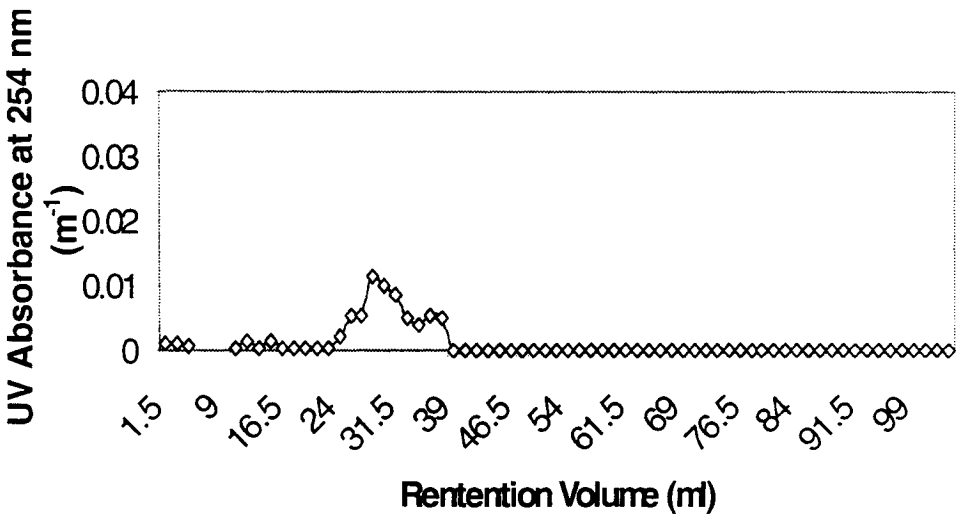

Figure B.11: SEC Results from ORW Fulvic Acid

Appendix B2: Ohio River Water - OHRW

B.2.1 Location

The Ohio River is 981 miles long and eventually empties into the Mississippi River. The Ohio River is a source of drinking water for more than three million people including the cities of Pittsburgh, Pennsylvania, Cincinnati, Ohio, and Cairo Illinois. A 100 litre sample was shipped from the Richard Miller Water Treatment Plant in October, 2004. The sample was collected after a mixed media filter and right before a GAC filter.

Figure B.12: The Ohio River, Cincinnati, Ohio

Table B2.1: OHRW Properties

Water Source		Ohio River Water
Site of Sampling		Cincinnati WTP, Ohio
Symbol		OHRW
	(Units)	
DOC	**mg/l**	1.91 ± 0.025
PH		6.65
Conductivity	**milliohms**	0.800
Colour		10
Turbidity	**NTU**	0.173 ± 0.001
Alkalinity	**mg $CaCO_3$/L**	5.2
Total Hardness	**mg $CaCO_3$/L**	117.76
Calcium Hardness	**mg $CaCO_3$/L**	67.344
UV abs . 254 nm	**m^{-1}**	0.37

B.2.2. UV and DOC correlation

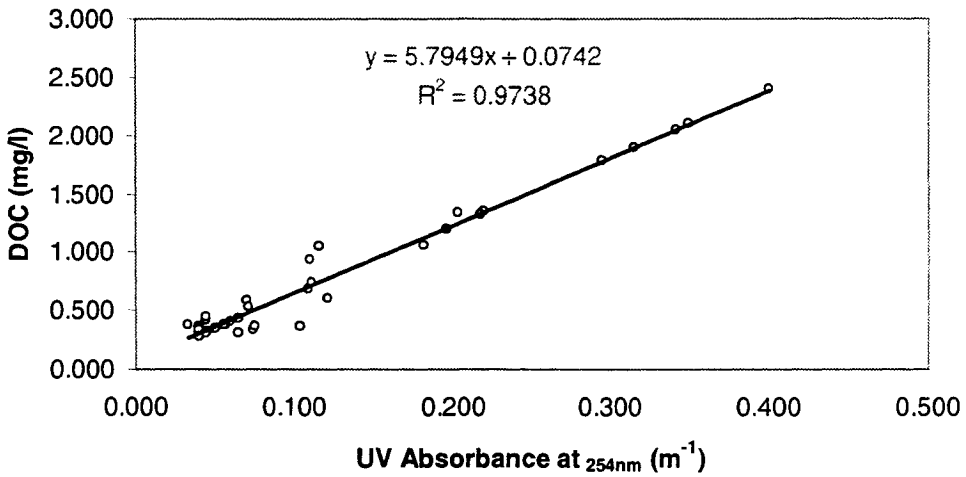

Figure B.13 : DOC and UV Correlation for Ohio River Water with F-400 GAC

B.2.3. Isotherms

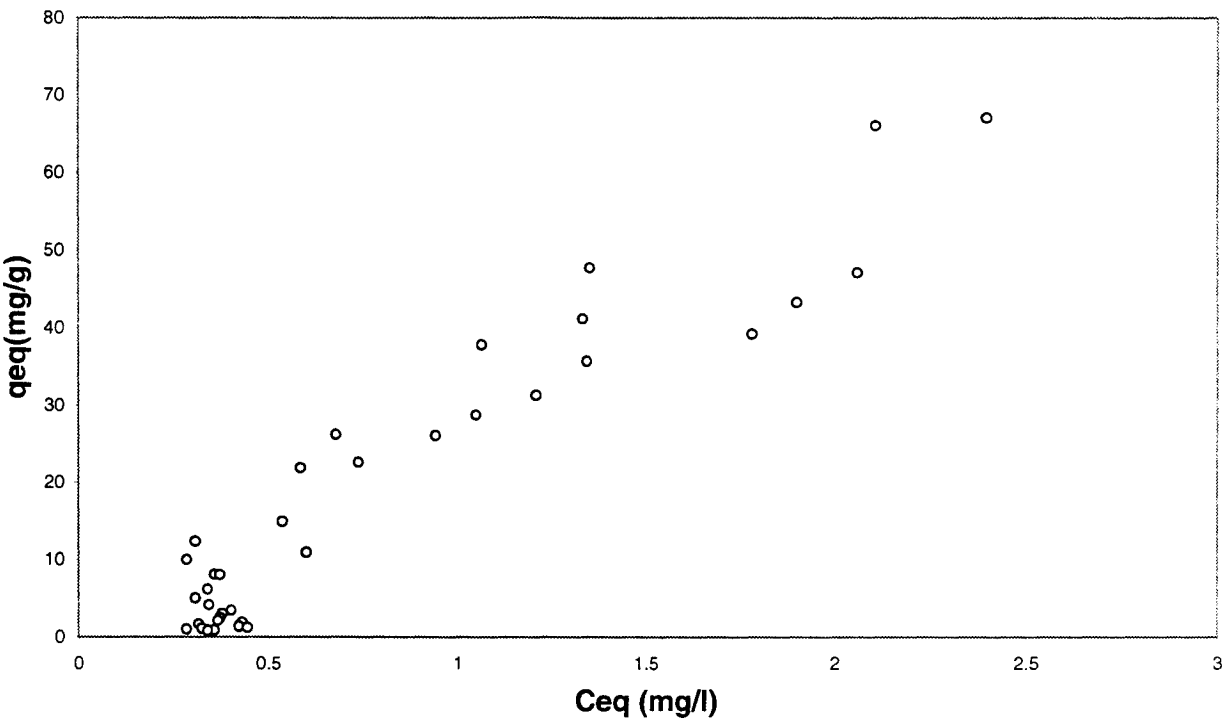

Figure B.14: OHRW Isotherm with F-400 GAC, 40X50 Mesh Size

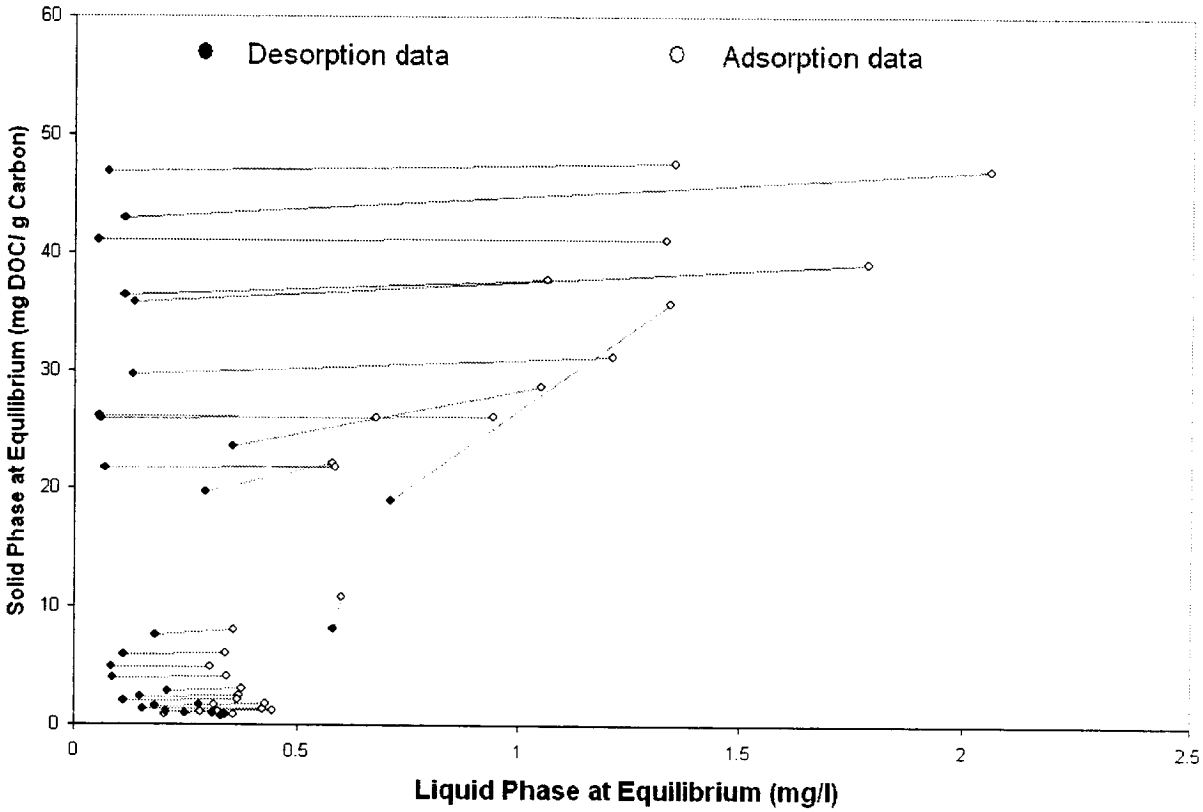

Figure B.15: OHRW Desorption Isotherms, F-400 GAC, 40 X 50 Mesh Size

B.2.4. Fractionation – Ultrafiltration

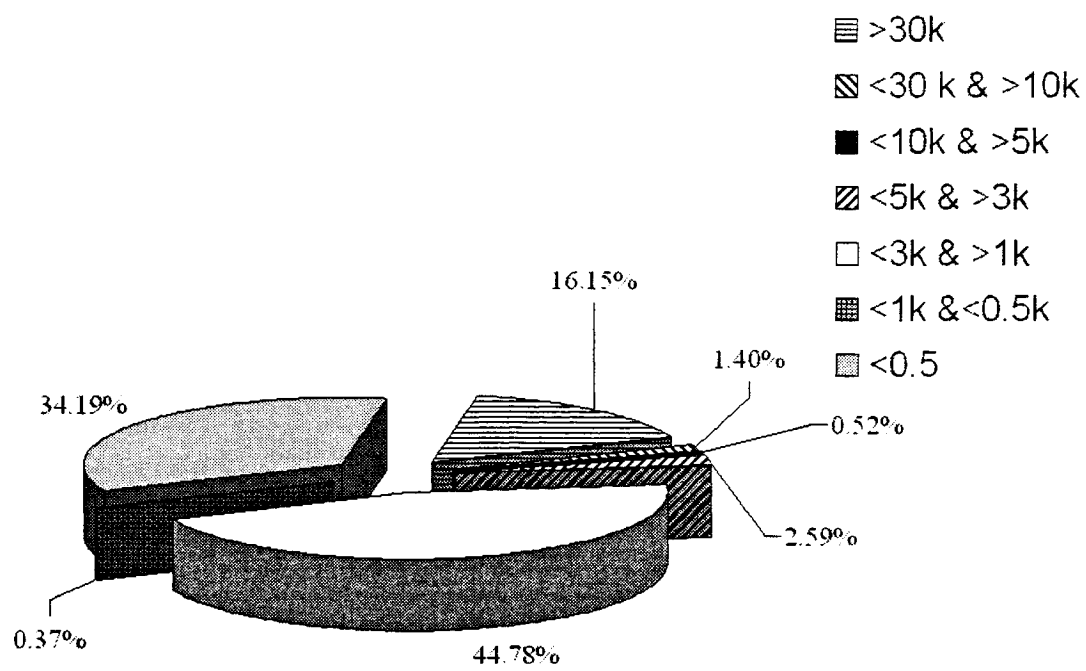

Figure B.16: OHRW UF Fractionation

Table B2.2: OHRW UF Results

Fraction	Weight Percent In fraction	DOC mg/l	Standard Deviation	95% Confidence ±
>30k	16.15%	2.3884	0.014	0.016
<30k	83.85%	2.1968	0.016	0.018
<30 k & >10k	1.40%	3.7095	0.025	0.028
<10k	82.44%	2.16	0.006	0.008
<10k & >5k	0.52%	5.5152667	0.022	0.025
<5k	81.92%	2.1463333	0.019	0.021
<5k & >3k	2.59%	3.4847333	0.032	0.036
<3k	79.33%	2.0785	0.030	0.022
<3k & >1k	44.78%	3.07065	0.008	0.010
<1k	34.55%	0.9053333	0.003	0.003
<1k &>0.5k	0.37%	6.367	0.011	0.015
<0.5 k	34.19%	0.8957	0.025	0.028

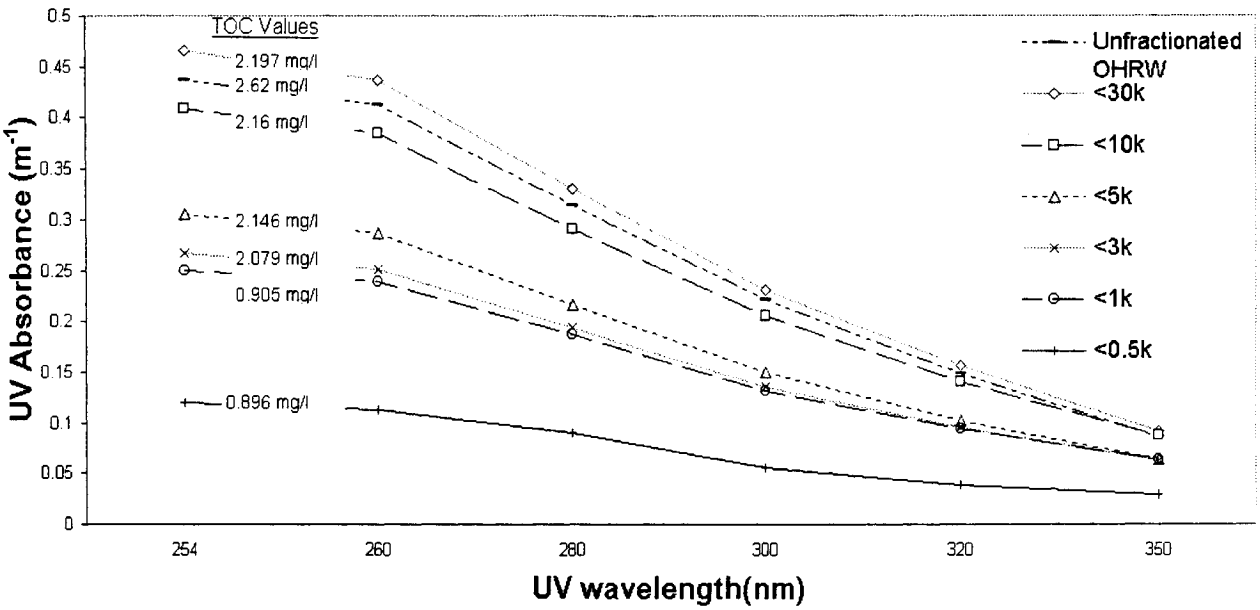

Figure B.17: OHRW UV Absorbance with Different UF Fractionations

B.2.5. Fractionation – Size Exclusion Chromatography

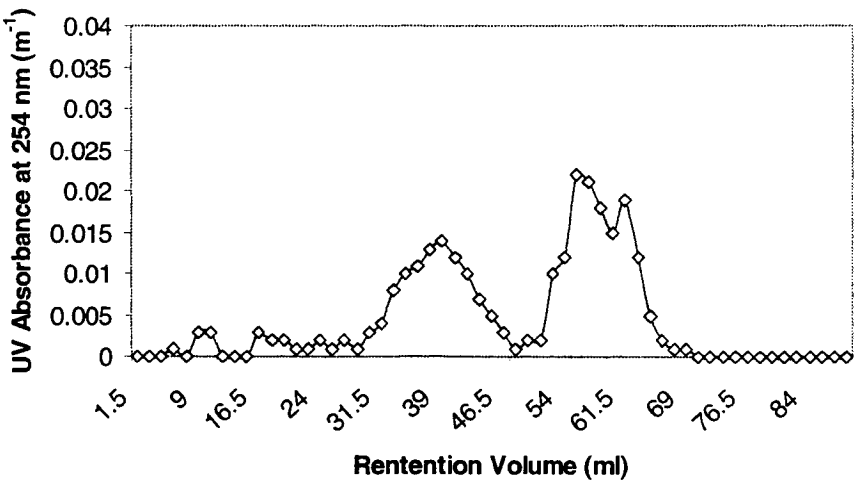

Figure B.18: SEC Results from Unfractionated OHRW

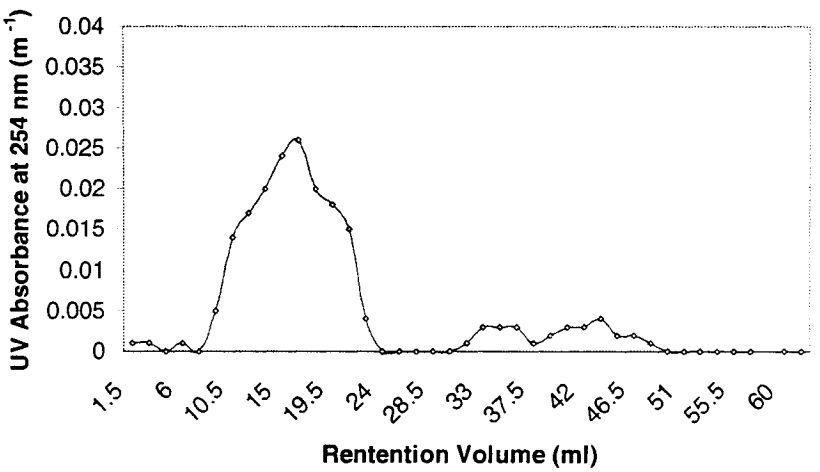

Figure B.19: SEC Results from OHRW Fulvic Acid

Appendix B3: Buffalo Pound Lake Water – BPLW

B.3.1. Location

Construction of a dam in 1955 created Buffalo Pound Lake from the South Saskatchewan and Qu'Appelle Rivers. Buffalo Pound Lake is 35km long and 2 km in width. It is situated 90 kilometers west of Regina and 25 kilometers northeast of Moose Jaw and is the drinking water source for both cities. It serves approximately 250,000 people. A 40 litre water sample was collected at the Buffalo Pound Water Treatment plant after the clarifiers in August, 2004.

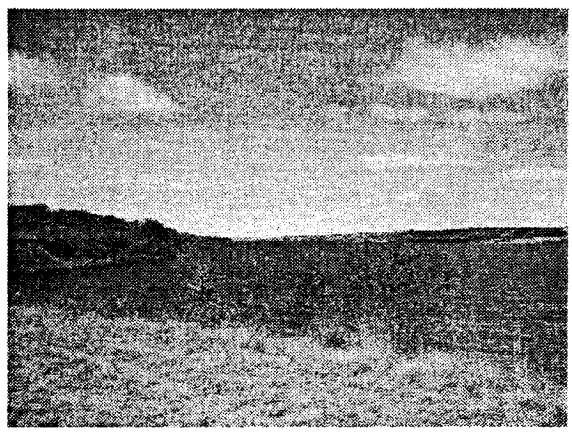

Figure B.20: Photo of Buffalo Pound Lake

Table B3.1: BPLW Properties

Water Source		Buffalo Pound Lake Water
Site of Sampling		Buffalo Pound WTP, Saskatchewan
Symbol		BPLW
	(Units)	
DOC	**mg/l**	3.50 ± 0.038
pH		7.29
Conductivity	**milliohms**	0.835
Colour		5
Turbidity	**NTU**	0.414 ± 0.005
Alkalinity	**mg $CaCO_3$/L**	5.1
Total Hardness	**mg $CaCO_3$/L**	138
Calcium Hardness	**mg $CaCO_3$/L**	63.296
UV abs . 254 nm	**m^{-1}**	0.375

B.3.2. UV and DOC correlation

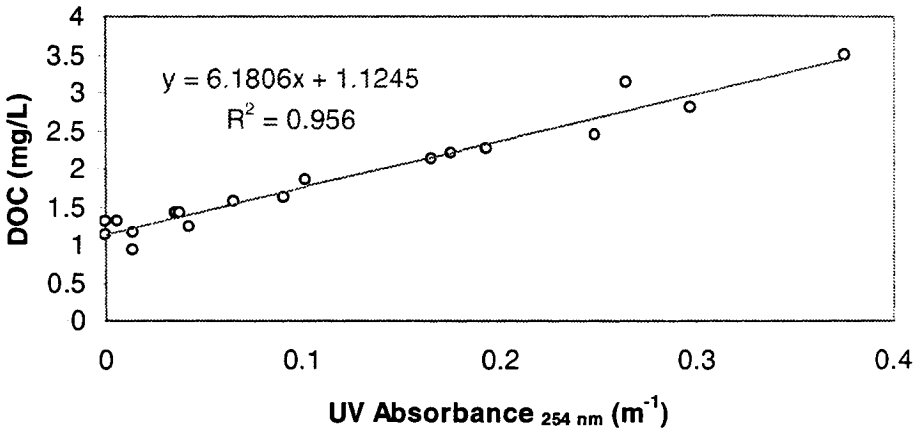

Figure B.21: DOC and UV Correlation for Buffalo Pound Lake Water

B.3.3. Isotherms

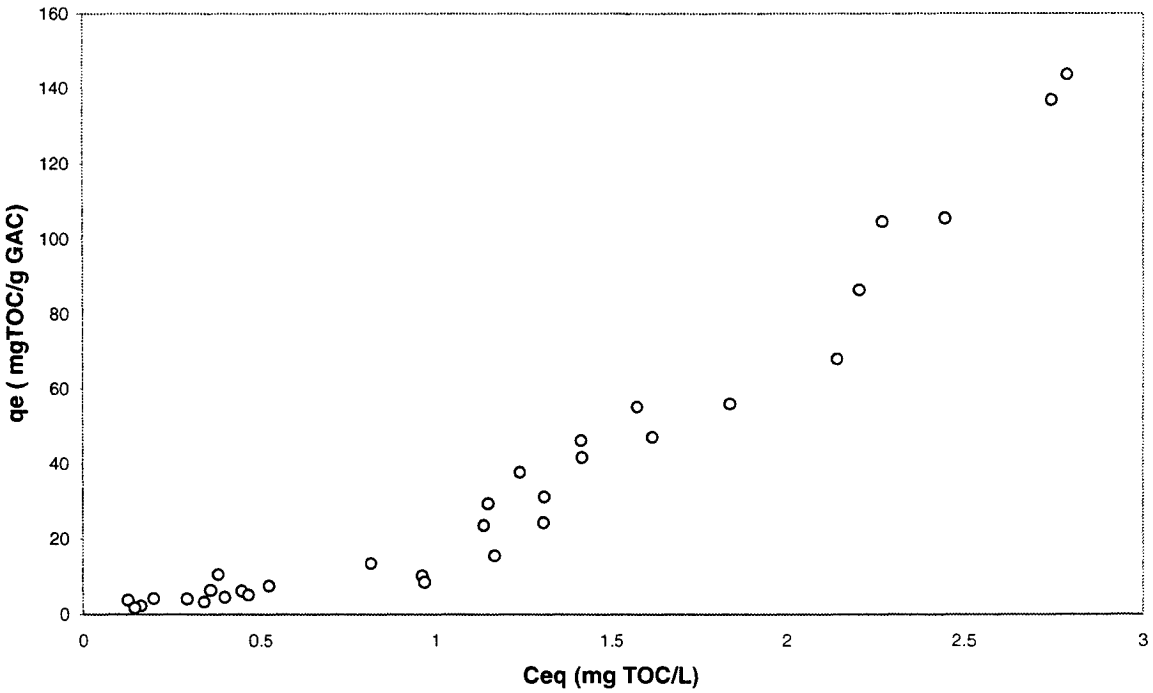

Figure B.22: BPLW Isotherm, with F-400 GAC, 40X50 Mesh Size

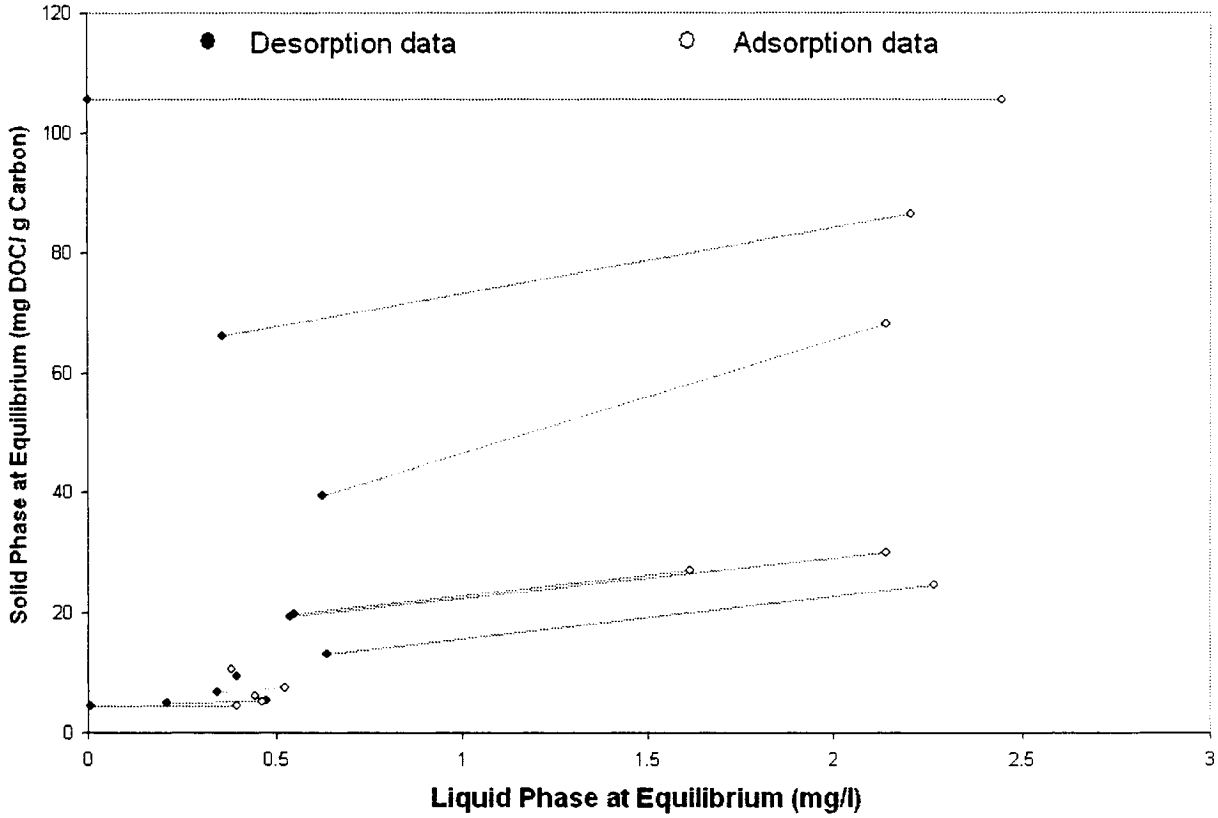

Figure B.23: BPLW Desorption Isotherms, with F-400 GAC, 40X50 mesh size

B.3.4. Fractionation - Ultrafiltration

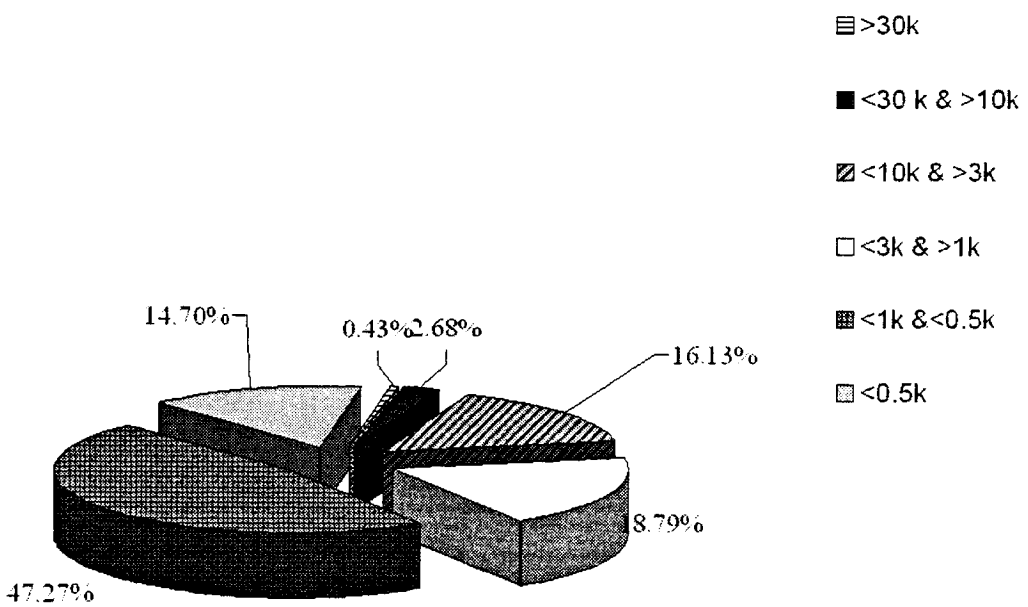

Figure B.24: BPLW Ultrafiltration Fractionation

Table B3.2: BPLW UF Results

Fraction	Weight Percent In fraction	DOC mg/l	Standard Deviation	95% Confidence
>30k	0.43%			±
<30k	99.57%	3.485	0.018	0.021
<30 k & >10k	2.68%			
<10k	96.90%	3.391	0.073	0.082
<10k & >3k	16.13%			
<3k	80.76%	2.827	0.035	0.039
<3k & >1k	18.79%			
<1k	61.97%	2.169	0.019	0.022
<1k &<0.5k	47.27%			
<0.5k	14.70%	0.515	0.066	0.074

B.3.5. Fractionation – Size Exclusion Chromatography

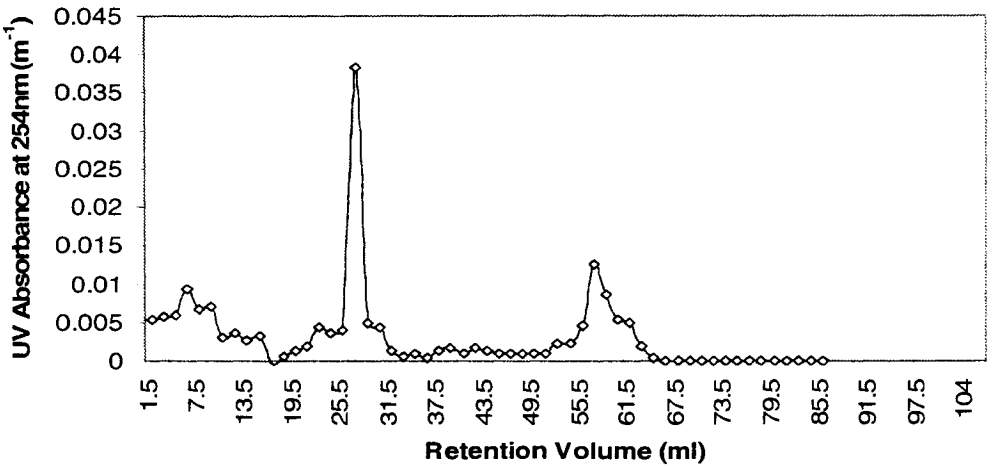

Figure B.25: SEC Results from Unfractionated BPLW

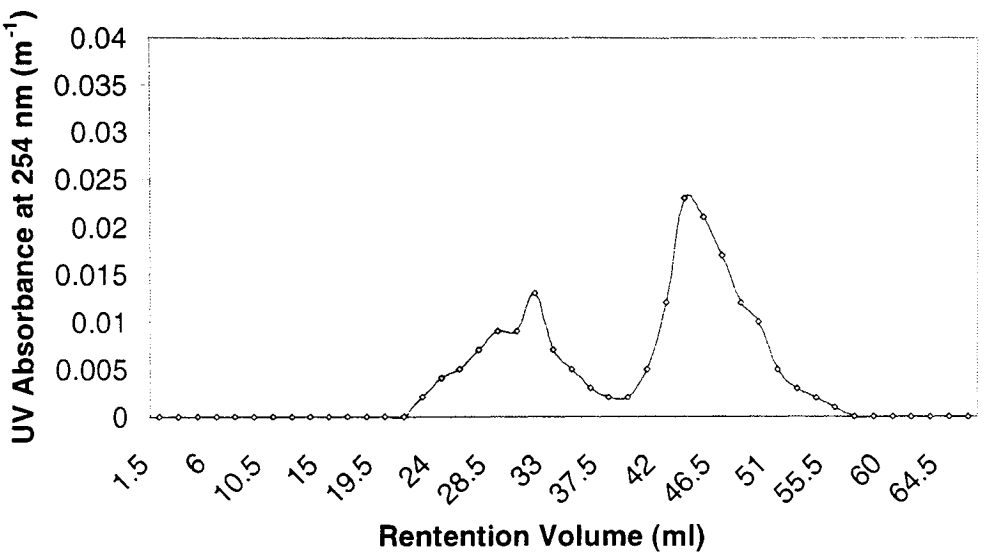

Figure B.26: SEC Results from the Fulvic Acid Portion of BPLW

Appendix B4: Vars Ground Water – VRW

B.4.1. Location

The township of Vars is located 35 km from Ottawa, Ontario. Approximately 1000 people in Vars depend on groundwater from two municipal wells for drinking water. The two wells, that are 15 m apart, are located next to a natural wetland which causes the water to be high in NOM, colour, iron and manganese. A 200 litre sample was collected directly from Well 2 without any treatment in November, 2004.

Figure B.27: Photo of the Wetlands Beside the Vars Groundwater Wells

Table B4.1: VGW Properties

Water Source		Vars Ground Water
Site of Sampling		Vars Well #2, Vars , Ontario
Symbol		VGW
	(Units)	
DOC	**mg/l**	4.01 ± 0.017
pH		7.45
Conductivity	**milliohms**	0.900
Colour		25
Turbidity	**NTU**	0.616 ± 0.002
Alkalinity	**mg $CaCO_3$/L**	15.0
Total Hardness	**mg $CaCO_3$/L**	165.6
Calcium Hardness	**mg $CaCO_3$/L**	82.8
UV abs . 254 nm	**m^{-1}**	1.266

B.4.2. UV and DOC correlation

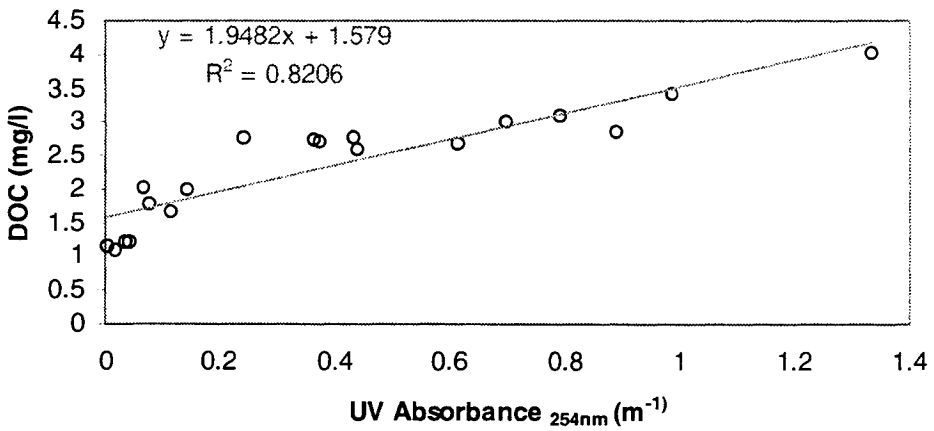

Figure B.28: DOC and UV Correlation for Vars Ground Water

B.4.3. Isotherms

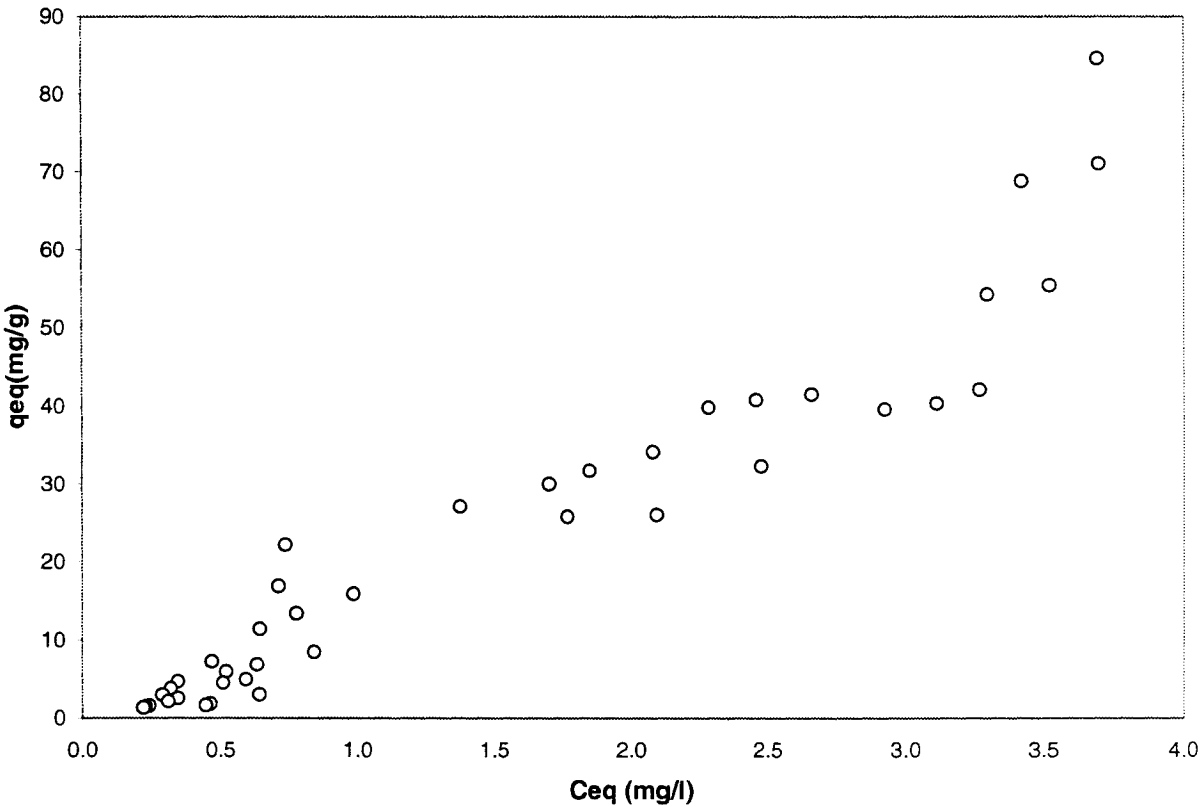

Figure B.29: VGW Isotherm with F-400 GAC, 40X50 Mesh Size

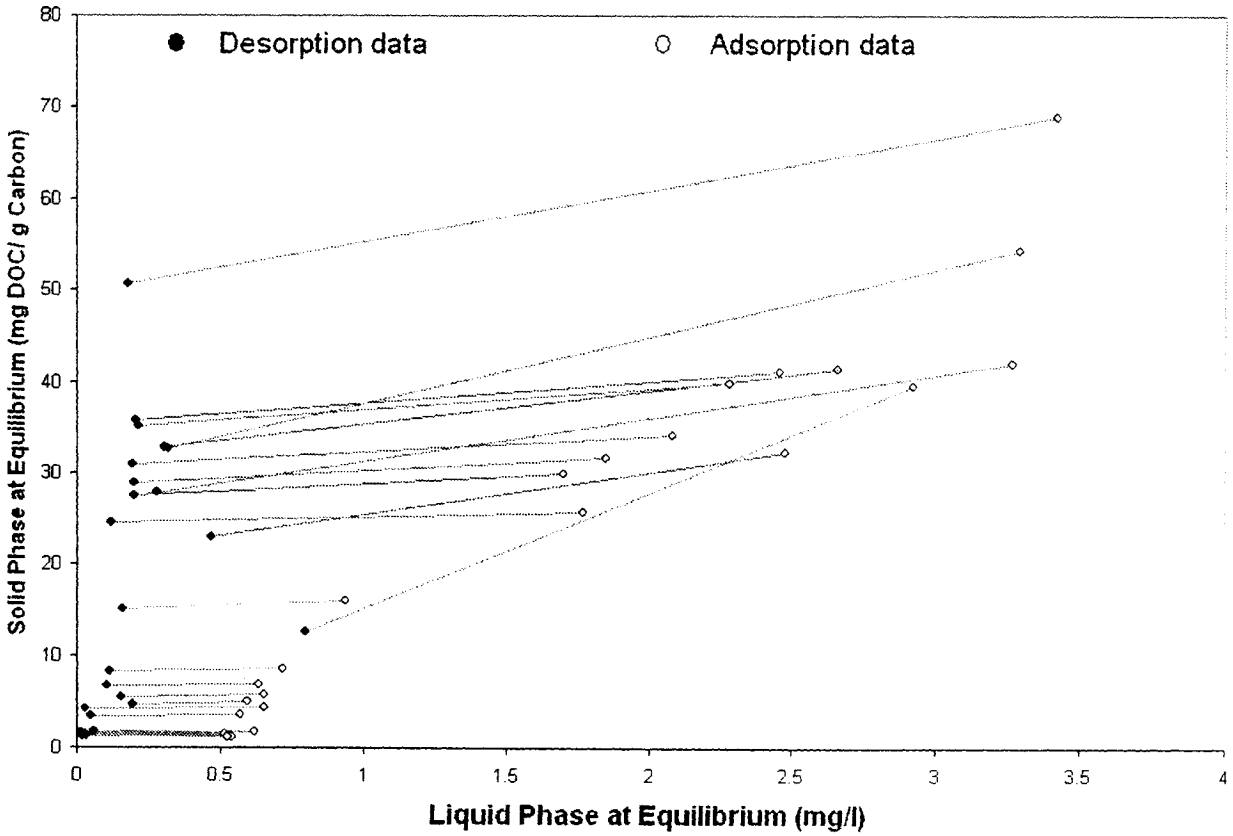

Figure B.30: VGW Desorption Isotherms with F-400 GAC, 40x50 Mesh Size

B.4.4. Fractionation - Ultrafiltration

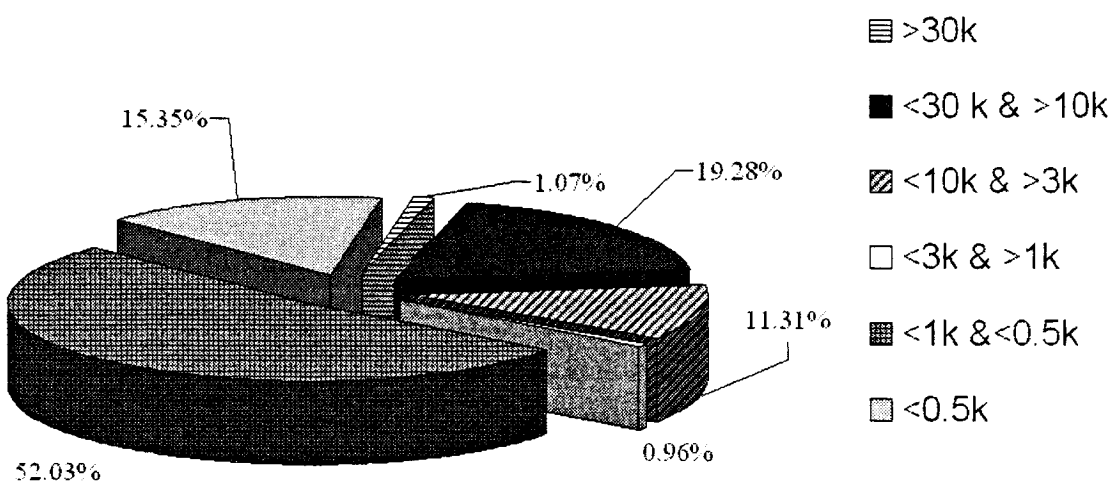

Figure B.31: VGW UF Fractionation

Table B4.2: VGW UF Results

Fraction	Weight Percent In fraction	DOC mg/l	Standard Deviation	95% Confidence
>30k	1.07%			±
<30k	98.93%	3.967	0.120	0.135
<30 k & >10k	19.28%			
<10k	79.65%	3.194	0.027	0.030
<10k & >3k	11.31%			
<3k	68.34%	2.741	0.045	0.051
<3k & >1k	0.96%			
<1k	67.39%	2.702	0.014	0.016
<1k &<0.5k	52.03%			
<0.5k	15.35%	0.616	0.017	0.020

B.4.5. Fractionation – Size Exclusion Chromatography

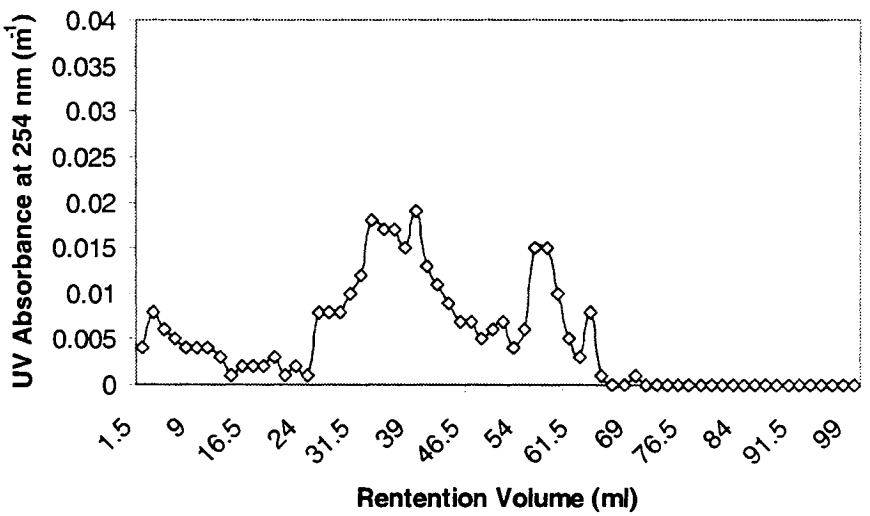

Figure B.32: SEC Results from Unfractionated VGW

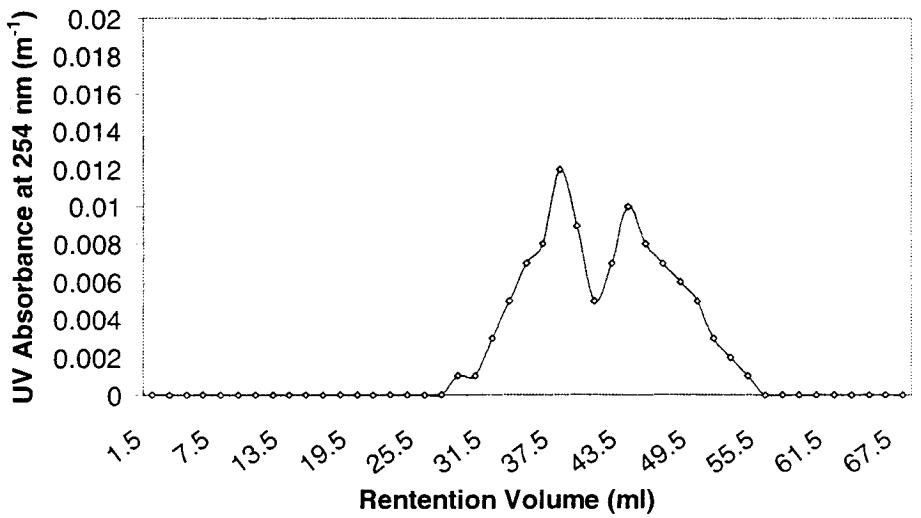

Figure B.33: SEC Results from VGW Fulvic Acid

Appendix B5: St. Lawrence River Water – SLRW

B.5.1. Location

A 200 litre water sample was taken from the Cornwall (Ontario) Water Treatment Plant that withdraws water from the St. Lawrence River. This river is 1287 km long and can be divided in 3 segments: the freshwater river from Lake Ontario to just outside the city of Quebec, the St. Lawrence estuary Quebec City to Anticosti Island, and the Gulf of St. Lawrence which empties into the Atlantic Ocean. Every year approximately 50 tons of cargo passes through this seaway The water sample was taken on site, from the process stream just after the clarifier in October 2004.

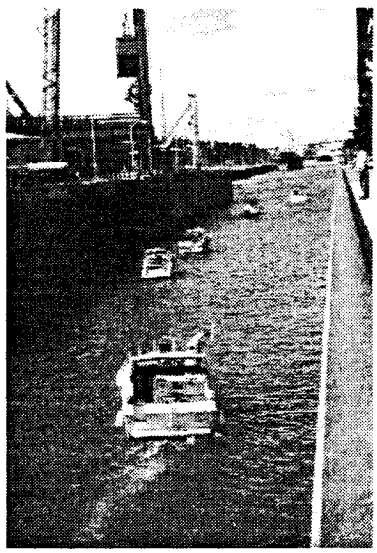

Figure B.34: The St. Lawrence River Sea Way - the St. Lambert Lock

Table B5.1: SLRW Properties

Water Source		St. Lawrence River Water
Site of Sampling		Cornwall WTP, Ontario
Symbol		SLRW
	(Units)	
DOC	**mg/l**	2.62 ± 0.039
pH		6.69
Conductivity	**milliohms**	0.705
Colour		2.5
Turbidity	**NTU**	0.366 ± 0.012
Alkalinity	**mg $CaCO_3$/L**	11.6
Total Hardness	**mg $CaCO_3$/L**	108.56
Calcium Hardness	**mg $CaCO_3$/L**	64.4
UV abs . 254 nm	**m^{-1}**	0.325

B.5.2. UV and DOC Correlation

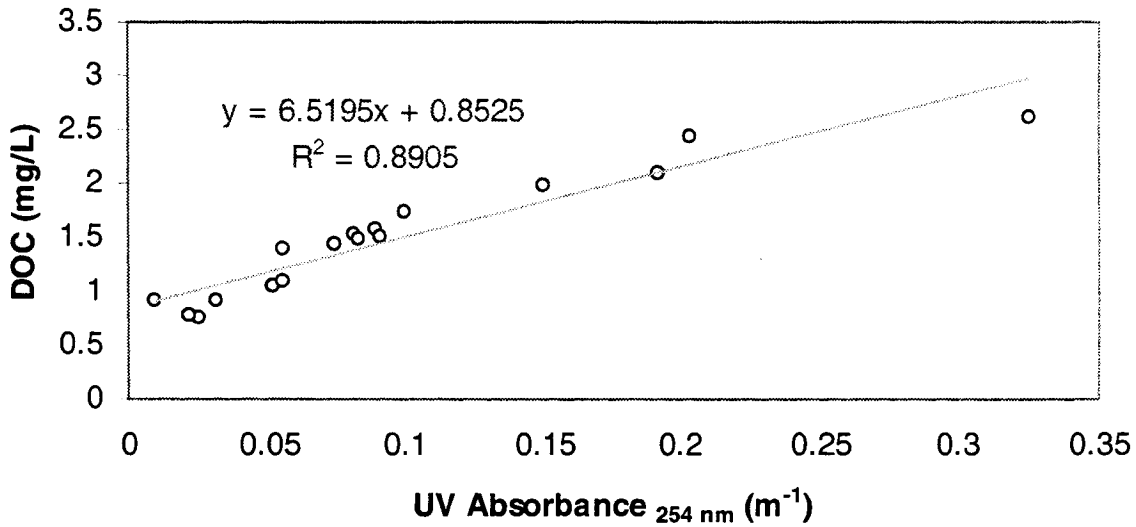

Figure B.35: DOC and UV Correlation for the St.. Lawrence River

B.5.3. Isotherms

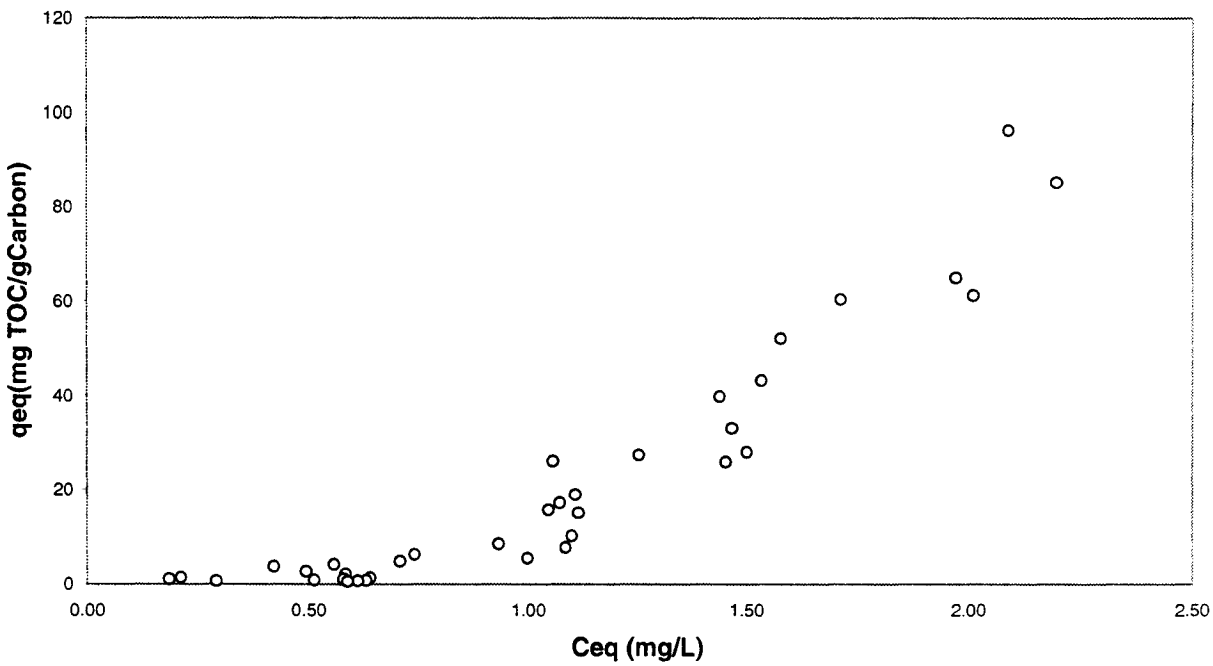

Figure B.36 SLRW Isotherm with F-400 GAC, 40X50 Mesh Size

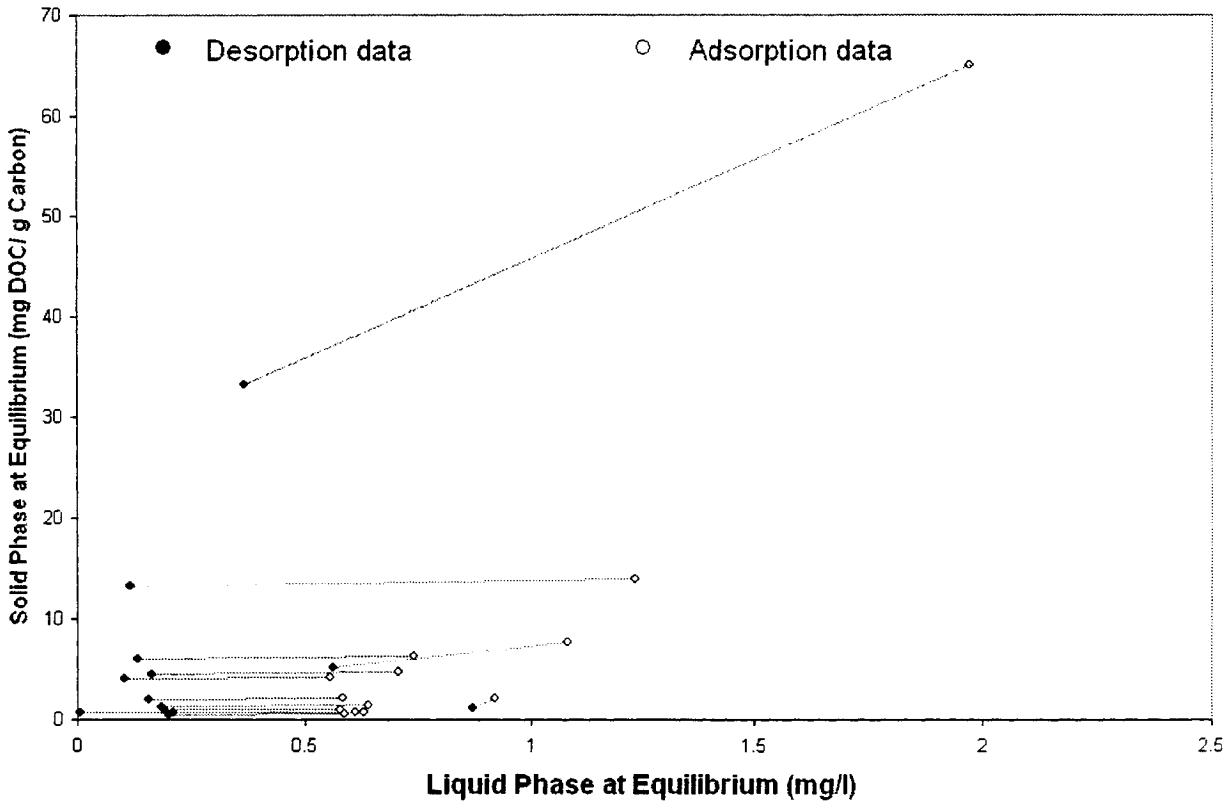

Figure B.37: SLRW Desorption Isotherms with F-400 GAC, 40X50 Mesh Size

B.5.4. Fractionation - Ultrafiltration

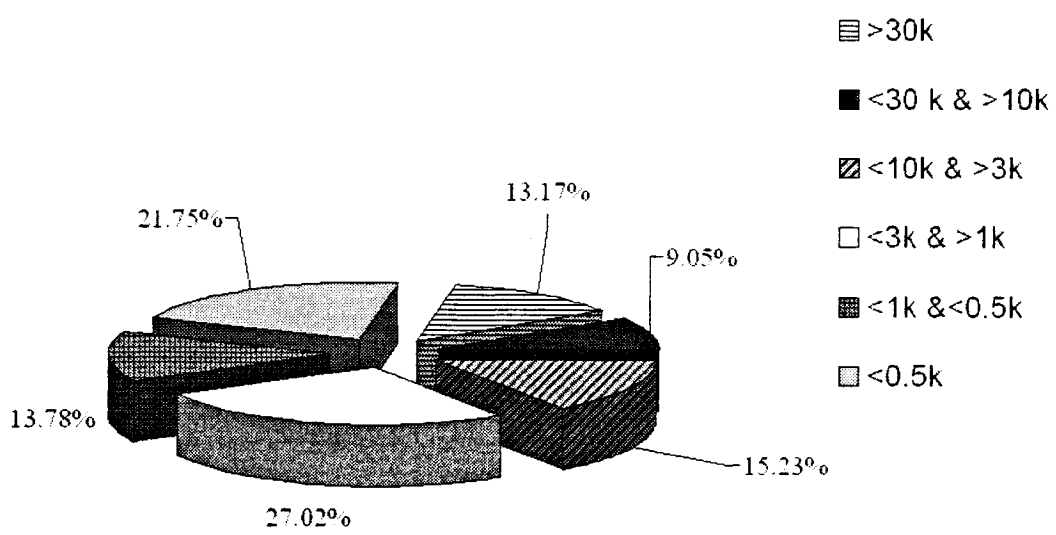

Figure B.38: Ultrafiltraion results with SLRW

Table B5.2: SLRW UF Results

Fraction	Weight Percent In fraction	DOC mg/l	Standard Deviation	95% Confidence ±
>30k	13.17%			
<30k	86.83%	2.275	0.025	0.028
<30 k & >10k	9.05%			
<10k	77.78%	2.038	0.027	0.052
<10k & >3k	15.23%			
<3k	62.55%	1.639	0.008	0.016
<3k & >1k	27.02%			
<1k	35.53%	0.931	0.009	0.010
<1k &<0.5k	13.78%			
<0.5k	21.75%	0.570	0.096	0.109

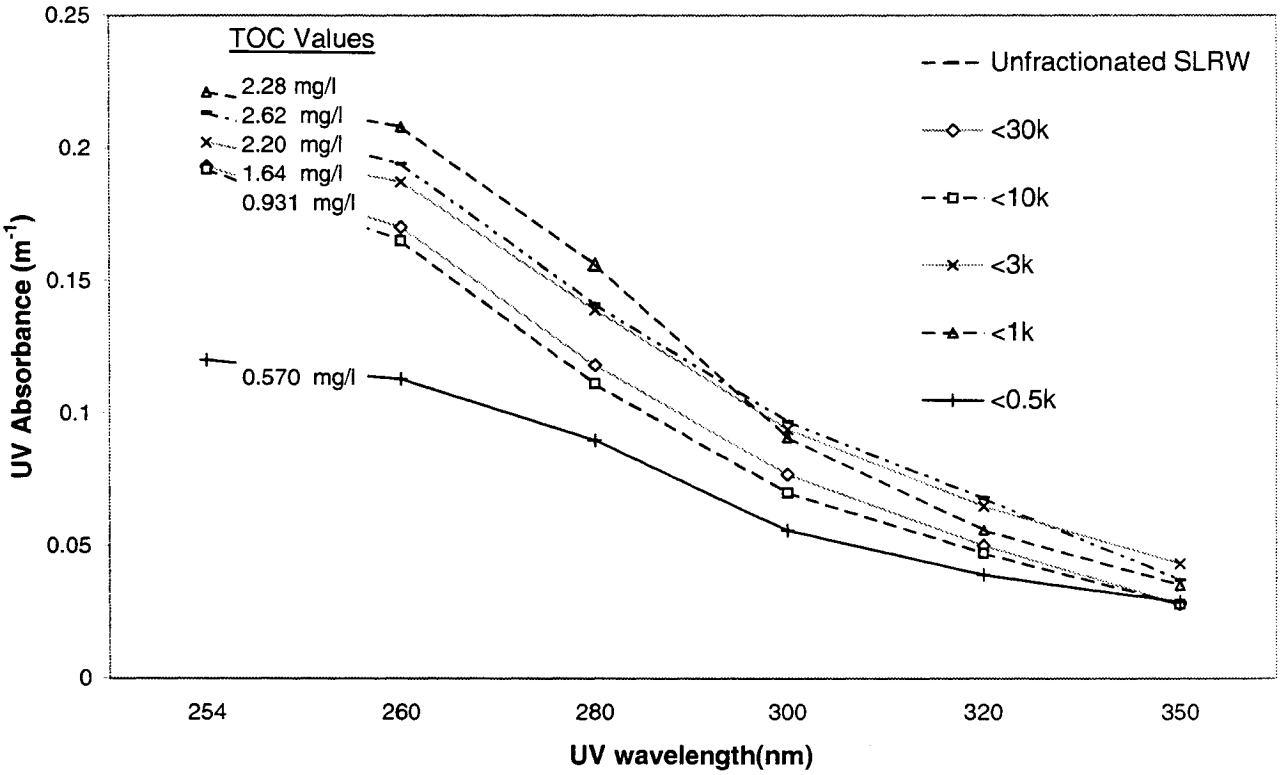

Figure B.39: UV Absorbance for Different UF Fractionation of SLRW

B.5.5. Fractionation – Size Exclusion Chromatography

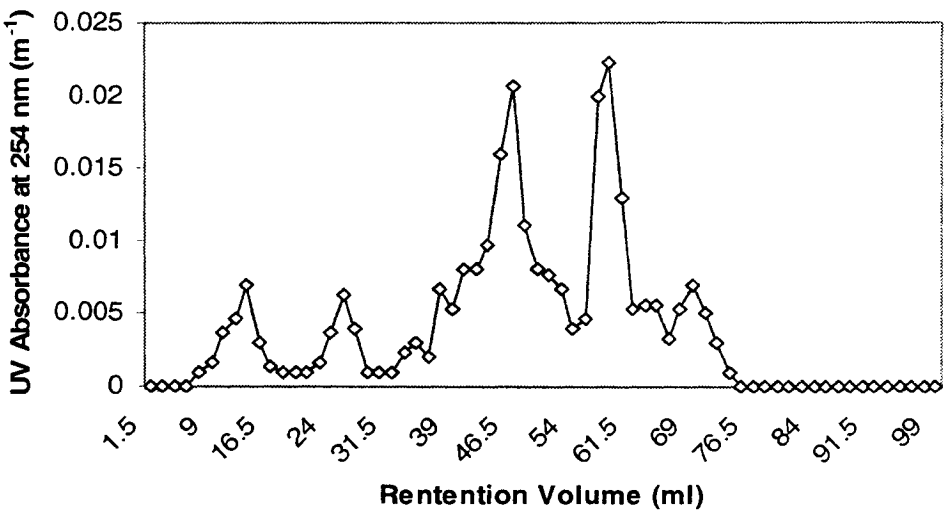

Figure B.40: SEC Results for Unfractionated SLRW

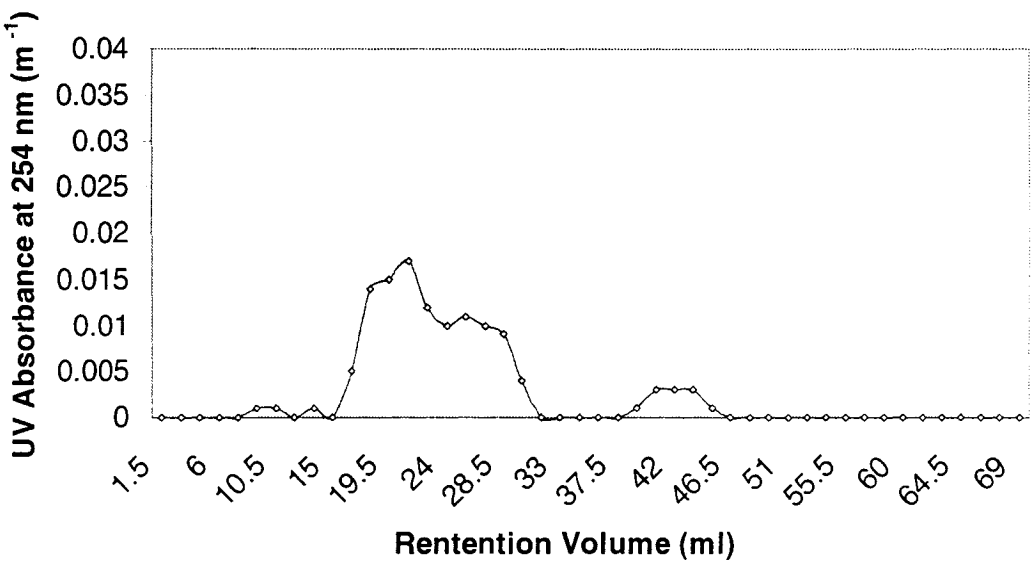

Figure B.41: SEC Results for the Fulvic Acid Portion of SLRW

Appendix C: Isotherms

Table C1: Ottawa River Water, ORW, F-400, Adsorption Isotherm

Run 1: September, 2004 *na = not available, or not applicable due to concentration range*

		From TOC and UV Correlation	From TOC Analyzer			
M/V (g/L)	UV254 m-1	Ceq (mg TOC/L)	Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)
0.005	0.505	2.112	na	na	na	211.731
0.008	0.450	1.911	1.896	0.231	0.205	153.681
0.010	0.432	1.845	1.891	0.193	0.171	123.532
0.015	0.418	1.794	1.798	0.115	0.102	86.866
0.020	0.384	1.667	1.457	0.051	0.045	82.160
0.024	0.298	1.355	na	na	na	72.055
0.032	0.251	1.183	1.120	0.146	0.129	62.540
0.039	0.245	1.159	na	na	na	49.393
0.060	0.145	0.795	na	na	na	38.502
0.100	na	na	0.273	0.014	0.012	28.267
0.200	na	na	0.504	0.032	0.029	12.980
0.250	na	na	0.153	0.078	0.069	11.790
0.302	na	na	0.583	0.004	0.004	8.328
0.401	na	na	0.527	0.010	0.009	6.415
0.502	na	na	0.273	0.009	0.008	5.632
0.600	na	na	0.474	0.034	0.030	4.374
0.701	na	na	0.365	0.033	0.029	3.902
0.800	na	na	0.217	0.133	0.117	3.605
0.900	na	na	0.177	0.011	0.009	3.249
1.000	0.033	0.383	0.362	0.026	0.023	2.737
1.501	0.025	0.356	0.419	0.030	0.026	1.787
CONTROL	0.525	3.534	3.534	0.023	0.017	

Run 2: April, 2005

M/V (g/L)	UV254 m-1	From TOC and UV Correlation Ceq (mg TOC/L)	From TOC Analyzer Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)
0.005	0.53	3.446	3.240	0.053	0.047	50.013
0.008	0.496	3.227	3.194	0.015	0.014	32.815
0.01	0.497	3.234	3.279	0.011	0.013	25.609
0.015	0.425	2.771	2.959	0.032	0.029	47.938
0.02	0.392	2.559	2.826	0.030	0.026	46.563
0.03	0.392	2.559	2.315	0.023	0.020	31.042
0.05	0.263	1.729	1.787	0.023	0.020	35.215
0.1	0.098	0.668	0.656	0.006	0.006	28.217
0.2	0.025	0.199	0.283	0.015	0.013	16.456
0.3	0.034	0.257	0.279	0.010	0.008	10.778
0.4	0.015	0.135	0.182	0.007	0.006	8.389
0.5	0.011	0.109	0.153	0.007	0.006	6.762
0.8	0.024	0.192	0.178	0.007	0.006	4.122
1	0.019	0.160	0.098	0.007	0.006	3.330
1.5	0.046	0.334	0.138	0.011	0.009	2.104
CONTROL	0.535	3.478	3.492	0.014	0.012	

Table C2: Ottawa River Water, ORW, WV-B, Adsorption Isotherm
Run 1: September, 2004

		From TOC and UV Correlation	From TOC Analyzer			
M/V (g/L)	UV254 m-1	Ceq (mg TOC/L)	Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)
0.005	0.469	2.690	3.110	0.062	0.055	85.270
0.008	0.450	2.494	2.781	0.051	0.045	81.273
0.011	0.401	1.993	2.235	0.079	0.069	108.805
0.015	0.400	1.983	1.877	0.077	0.068	78.944
0.020	0.338	1.338	1.652	0.102	0.090	89.773
0.025	0.316	1.116	1.438	0.066	0.059	80.640
0.030	0.299	0.935	1.396	0.031	0.027	74.879
0.040	0.254	0.476	0.461	0.036	0.032	66.635
0.048	0.458	2.880	1.241	0.012	0.010	38.326
0.060	0.225	0.177	0.222	0.056	0.049	49.572
0.074	0.431	2.581	1.006	0.017	0.015	28.220
0.087	0.313	1.276	0.861	0.010	0.009	25.842
0.089	0.370	1.907	1.018	0.064	0.056	23.370
0.094	0.202	na	0.865	0.009	0.008	23.895
0.291	0.108	na	0.810	0.008	0.007	7.867
0.386	na	na	0.217	0.047	0.041	7.475
0.495	na	na	0.215	0.030	0.026	5.824
0.600	na	na	0.028	0.002	0.002	5.123
0.696	na	na	0.150	0.012	0.010	4.242
0.771	na	na	0.729	0.022	0.019	3.077
0.886	na	na	0.668	0.969	0.856	2.746
2.000	0.174	na	0.137	0.005	0.004	1.481
7.018	0.402	na	0.028	0.008	0.007	0.120
7.963	0.220	na	0.027	0.011	0.010	0.389
CONTROL	0.525	3.534	3.534	0.023	0.017	

na = not available, or not applicable due to concentration range

Run 2: April, 2005

M/V (g/L)	UV254 m-1	From TOC and UV Correlation Ceq (mg TOC/L)	From TOC Analyzer Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)
0.005	0.456	3.006	3.037	0.023	0.060	58.433
0.008	0.436	2.888	2.923	0.017	0.044	55.150
0.01	0.418	2.781	2.822	0.006	0.014	54.788
0.015	0.441	2.917	2.686	0.012	0.031	27.438
0.02	0.38	2.556	2.633	0.013	0.033	38.655
0.03	0.292	2.034	2.220	0.011	0.029	43.154
0.05	0.238	1.714	1.796	0.017	0.045	32.293
0.1	0.166	1.288	1.293	0.088	0.026	20.414
0.2	0.169	1.305	0.973	0.038	0.097	10.118
0.3	0.075	0.748	0.856	0.003	0.009	8.602
0.4	0.071	0.725	0.739	0.036	0.092	6.511
0.5	0.055	0.630	0.637	0.010	0.016	5.398
0.8	na	na	0.402	0.016	0.026	3.659
1.0	na	na	0.361	0.011	0.006	2.968
1.5	na	na	0.200	0.024	0.010	2.086
CONTROL	0.535	3.475	3.329	0.053	0.047	

Table C3: Ohio River Water, OHRW, Adsorption Isotherm

M/V (g/L)	UV254 m-1	From TOC and UV Correlation Ceq (mg TOC/L)	From TOC Analyzer Ceq (mg TOC/L)	From TOC Analyzer ± 95% Confidence	From TOC Analyzer Standard Deviation	qeq (mg TOC/g GAC)
0.005	0.400	2.398	na	na	na	74.055
0.006	0.400	2.398	2.015	0.163	0.144	67.045
0.010	0.350	2.104	na	na	na	66.013
0.015	0.342	2.057	na	na	na	47.103
0.020	0.315	1.899	na	na	na	43.251
0.025	0.295	1.782	na	na	na	39.119
0.030	0.220	1.341	1.349	0.045	0.040	47.701
0.035	0.218	1.327	1.330	0.104	0.092	41.096
0.040	0.204	1.244	1.341	0.160	0.142	35.613
0.045	0.182	1.118	1.062	0.180	0.159	37.737
0.050	0.196	1.200	na	na	na	31.230
0.060	0.116	0.731	na	na	na	28.697
0.070	0.110	0.693	0.941	0.148	0.131	26.041
0.080	0.109	0.687	0.677	0.007	0.006	26.147
0.090	0.111	0.701	0.738	0.246	0.218	22.551
0.10	0.090	0.578	na	na	na	22.124
0.100	0.070	0.461	0.584	0.076	0.067	21.809
0.150	0.071	0.467	0.536	0.003	0.003	14.841
0.20	0.121	0.760	0.599	0.070	0.062	10.857
0.200	0.044	0.308	na	na	na	12.279
0.250	0.040	0.285	na	na	na	9.919
0.300	0.033	0.244	0.373	0.006	0.005	7.971
0.30	0.104	0.657	0.358	0.005	0.004	8.013
0.40	0.074	0.486	0.340	0.024	0.021	6.057
0.50	0.065	0.428	0.307	0.004	0.003	4.944
0.60	0.050	0.343	na	na	na	4.046
0.69	0.060	0.402	na	na	na	3.400

0.80	0.056	0.379	na	na	na	2.972
0.98	0.055	0.373	na	na	na	2.433
1.15	0.075	0.490	0.367	0.008	0.007	2.077
1.30	0.065	0.431	na	na	na	1.797
1.50	0.046	0.317	na	na	na	1.635
1.80	0.045	0.311	0.423	0.002	0.001	1.299
2.00	0.044	0.308	0.445	0.007	0.006	1.160
2.25	0.040	0.285	na	na	na	1.100
2.50	0.040	0.285	na	na	na	0.992
2.76	0.040	0.285	0.358	0.005	0.004	0.873
3.00	0.040	0.285	0.340	0.024	0.021	0.809
CONTROL			2.051	.015	.009	

na = not available, or not applicable due to concentration range

Table C4: Buffalo Pound Lake Water, BPLW, Adsorption Isotherm

		From TOC and UV Correlation	From TOC Analyzer			
M/V (g/L)	UV254 m-1	Ceq (mg TOC/L)	Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)
0.005	0.303	2.817	2.790	0.012	0.011	143.678
0.006	0.265	2.565	2.745	0.016	0.014	137.000
0.010	0.249	2.459	2.268	0.063	0.055	104.712
0.010	0.241	2.406	2.445	0.029	0.026	105.583
0.015	0.207	2.181	2.203	0.005	0.004	86.479
0.020	0.203	2.151	Na	na	Na	68.012
0.025	0.226	2.307	2.266	0.017	0.015	49.144
0.030	0.163	1.889	1.837	0.033	0.029	56.055
0.035	0.104	1.498	1.573	0.021	0.018	55.249
0.040	0.119	1.594	1.615	0.023	0.020	47.176
0.045	0.106	1.511	1.414	0.028	0.024	46.256
0.050	0.074	1.299	1.417	0.027	0.024	41.768
0.060	0.062	1.219	Na	na	Na	37.759
0.070	0.049	1.133	0.921	0.017	0.015	36.849
0.070	0.061	1.212	1.311	0.039	0.034	31.272
0.080	0.061	1.212	1.150	0.015	0.013	29.442
0.090	0.059	1.199	1.309	0.007	0.006	24.384
0.100	0.021	0.947	1.138	0.014	0.012	23.629
0.150	0.053	1.159	1.168	0.005	0.004	15.533
0.200	0.015	0.907	0.816	0.007	0.006	13.420
0.250	0.023	0.960	0.962	0.025	0.022	10.153
0.300	0.046	1.113	0.969	0.018	0.016	8.438
0.300	0.011	na	0.381	0.008	0.007	10.385

0.400	0.005	na	0.524	0.012	0.011	7.444
0.500	0.039	na	0.359	0.013	0.011	6.282
0.500	0.005	na	0.446	0.072	0.064	6.104
0.600	0.011	na	0.465	0.032	0.028	5.055
0.701	0.005	na	0.398	0.027	0.024	4.426
0.799	0.011	na	0.293	0.002	0.002	4.011
0.800	0.041	na	0.198	0.010	0.009	4.127
0.899	0.020	na	0.127	0.016	0.014	3.753
1.000	0.023	na	0.341	0.020	0.018	3.158
1.500	0.005	na	0.163	0.009	0.008	2.225
1.999	0.005	na	0.145	0.029	0.025	1.678
6.000	0.003	0.828	na	na	Na	0.445
7.000	0.019	0.934	na	na	Na	0.367
9.002	0.029	0.997	na	Na	Na	0.278
CONTROL			3.49	0.011	0.008	

na = not available, or not applicable due to concentration range

Table C5: Vars Ground Water, VGW, Adsorption Isotherm

		From TOC and UV Correlation	From TOC Analyzer			
M/V (g/L)	UV254 m-1	Ceq (mg TOC/L)	Ceq (mg TOC/L)	± 95% Confidence	Standard Deviation	qeq (mg TOC/g GAC)
0.005	1.067	3.721	3.688	0.060	0.053	84.637
0.006	1.047	3.660	3.694	0.077	0.068	71.141
0.010	0.968	3.418	na	na	Na	68.906
0.010	1.001	3.519	na	na	Na	55.573
0.015	0.957	3.385	3.292	0.091	0.081	54.383
0.019	0.918	3.266	na	na	Na	42.139
0.024	0.900	3.211	3.110	0.051	0.045	40.363
0.029	0.774	2.826	2.920	0.118	0.104	39.573
0.034	0.719	2.658	na	na	Na	41.500
0.040	0.665	2.493	2.454	0.141	0.124	40.859
0.045	0.595	2.279	na	na	Na	39.852
0.050	0.636	2.404	2.473	0.040	0.035	32.323
0.059	0.529	2.078	na	na	Na	34.207
0.071	0.462	1.873	1.847	0.092	0.081	31.740
0.080	0.405	1.699	na	na	Na	30.034
0.090	0.427	1.766	na	na	Na	25.861
0.096	0.366	1.580	2.09197	0.04060	0.04592	26.079
0.100	0.239	1.192	1.374	0.042	0.037	27.137
0.151	0.090	0.737	0.98480	0.03050	0.03457	15.926
0.198	0.155	0.935	na	na	Na	15.926
0.200	0.082	0.713	na	na	Na	16.913
0.247	0.076	0.694	0.777	0.017	0.015	13.417
0.301	0.060	0.644	na	na	Na	11.447
0.398	0.083	0.716	0.84130	0.00658	0.00744	8.477

0.499	0.056	0.633	0.469	0.044	0.038	7.253
0.504		0.462	0.634	0.001	0.001	6.848
0.601	0.063	0.655	0.52170	0.00198	0.00224	5.930
0.710	0.043	0.593	0.593	0.027	0.024	4.920
0.800	0.030	0.554	0.344	0.006	0.006	4.679
1.005	0.035	0.569	0.31830	0.00955	0.01080	3.750
1.149	0.051	0.618	0.642	0.009	0.008	2.998
1.313	0.038	0.578	0.28820	0.02480	0.02809	2.893
1.500	0.046	0.603	0.345	0.018	0.016	2.495
1.805	0.051	0.618	0.30950	0.03640	0.04121	2.093
2.003	0.052	0.621	0.46260	0.00233	0.00264	1.810
2.252	0.054	0.627	0.446	0.014	0.016	1.617
2.500	0.024	0.535	0.24070	0.00433	0.00490	1.538
2.748	0.025	0.538	0.22660	0.11500	0.12994	1.405
3.002	0.020	0.523	0.21873	0.00029	0.00033	1.289
CONTROL			3.95	0.013	0.008	

na = not available, or not applicable due to concentration range

Table C6: St. Lawrence River Water, SLRW, Adsorption Isotherm

M/V	UV254	From TOC and UV Correlation Ceq	From TOC Analyzer Ceq	± 95%	Standard	qeq
(g/L)	m-1	(mg TOC/L)	(mg TOC/L)	Confidence	Deviation	(mg TOC/g GAC)
0.005	0.180	2.071	2.198	0.024	0.021	85.262
0.006	0.177	2.049	2.089	0.018	0.016	96.356
0.010	0.191	2.151	2.010	0.009	0.008	61.361
0.010	0.159	1.917	1.970	0.036	0.032	65.021
0.015	0.131	1.713	na	na	na	60.458
0.020	0.123	1.655	1.577	0.013	0.011	52.137
0.025	0.110	1.560	1.533	0.023	0.021	43.292
0.030	0.095	1.450	1.438	0.073	0.065	39.832
0.035	0.096	1.458	1.466	0.006	0.005	33.065
0.040	0.100	1.487	1.500	0.010	0.009	28.027
0.045	0.097	1.465	1.452	0.043	0.038	25.891
0.050	0.068	1.253	na	na	Na	27.406
0.060	0.041	1.056	na	na	Na	26.144
0.070	0.155	1.888	na	na	Na	10.456
0.080	0.048	1.107	na	na	Na	18.953
0.090	0.043	1.071	na	na	Na	17.242
0.100	0.036	1.020	1.046	0.011	0.010	15.745
0.1	0.049	1.115	1.233	0.006	0.006	13.869
0.150	0.047	1.100	na	na	Na	10.126
0.2	0.045	1.085	1.082	0.018	0.016	7.689
0.200	0.024	0.932	na	na	Na	8.438
0.3	0.032	0.991	0.741	0.008	0.007	6.263
0.300	0.033	0.998	na	na	Na	5.407
0.4	0.036	1.020	0.707	0.073	0.065	4.782

0.5	0.041	1.056	0.557	0.119	0.105	4.126
0.6	0.055	1.158	na	na	Na	2.436
0.8	0.040	1.049	0.920	0.002	0.002	2.125
1	0.035	1.012	0.583	0.016	0.014	2.037
1.25	0.031	0.983	na	na	Na	1.309
1.5	0.034	1.005	0.639	0.094	0.083	1.321
1.75	0.037	1.027	na	na	Na	0.910
2	0.029	0.969	0.578	0.130	0.115	1.021
2.25	0.030	0.976	na	na	Na	0.731
2.5	0.030	0.976	0.512	0.042	0.037	0.843
2.75		0.757	0.630	0.009	0.008	0.724
3		0.757	0.611	0.008	0.007	0.670
3.5	0.064	1.224	na	na	Na	0.399
4		0.757	0.588	0.008	0.007	0.508
CONTROL			2.105	0.009	0.007	

na = not available, or not applicable due to concentration range

Table C7: Desorption Isotherm Data, ORW

ORW
F-400
40 X 50 Mesh

M/V (g GAC/L)	V (L)	M (g)	Qeq (mg TOC/g GAC)	Ceq' (mg TOC/L)	95% Conf.	Standard Deviation	Initial NOM (mg)	Desorbed NOM (mg)	% Desorbed	95% Conf.
0.302	0.118	0.036	8.328	0.778	0.035	0.031	0.297	0.086	28.92%	1.38%
0.502	0.119	0.060	5.632	0.531	0.007	0.006	0.336	0.057	17.01%	0.24%
0.600	0.117	0.070	4.374	0.460	0.011	0.010	0.307	0.048	15.63%	0.43%
0.401	0.121	0.048	6.415	0.392	0.008	0.007	0.311	0.041	13.31%	0.32%
0.015	0.453	0.007	86.866	0.180	0.082	0.072	0.590	0.059	10.01%	6.27%
1.000	0.473	0.473	2.737	0.308	0.012	0.010	1.294	0.122	9.41%	0.43%
0.800	0.121	0.097	3.605	0.293	0.006	0.005	0.349	0.029	8.44%	0.21%
0.032	0.484	0.015	62.540	0.205	0.121	0.107	0.957	0.075	7.84%	6.10%
0.900	0.120	0.108	3.249	0.210	0.002	0.002	0.350	0.019	5.46%	0.06%
1.501	0.482	0.723	1.787	0.189	0.089	0.079	1.291	0.067	5.20%	3.33%
0.020	0.465	0.009	82.160	0.109	0.165	0.145	0.763	0.027	3.60%	10.02%
0.024	0.470	0.011	72.055	0.108	0.100	0.088	0.821	0.027	3.33%	5.72%
0.701	0.119	0.083	3.902	0.139	0.008	0.007	0.325	0.011	3.26%	0.29%
0.010	0.469	0.005	123.532	0.084	0.129	0.114	0.566	0.016	2.81%	10.71%
0.060	0.465	0.028	38.502	0.046	0.058	0.052	1.071	0.022	2.01%	4.70%
0.039	0.471	0.019	49.393	0.002	0.003	0.003	0.914	0.001	0.09%	2.75%

ORW
WV-B
40 X 50 Mesh

M/V (g GAC/L)	V (L)	M (g)	Qeq (mg TOC/g GAC)	Ceq' (mg TOC/L)	95% Conf.	Standard Deviation	Initial NOM (mg)	Desorbed NOM (mg)	% Desorbed	95% Conf.
0.048	0.116	0.006	38.326	0.783	0.012	0.010	0.215	0.085	39.74%	0.63%
0.025	0.473	0.012	61.905	0.559	0.026	0.023	0.739	0.241	32.57%	1.67%
0.291	0.121	0.035	7.867	0.365	0.008	0.007	0.277	0.044	15.92%	2.51%
0.091	0.118	0.011	25.842	0.377	0.020	0.018	0.279	0.039	13.85%	0.85%
0.075	0.107	0.008	28.220	0.319	0.017	0.015	0.226	0.029	12.75%	0.81%
0.086	0.120	0.010	23.370	0.294	0.009	0.008	0.241	0.029	12.11%	0.44%
0.095	0.116	0.011	23.895	0.222	0.008	0.007	0.263	0.026	9.79%	2.56%
0.495	0.116	0.057	5.824	0.150	0.030	0.026	0.334	0.012	3.45%	1.03%
0.386	0.120	0.046	7.475	0.108	0.070	0.061	0.347	0.007	2.00%	2.41%
0.696	0.117	0.081	4.242	0.104	0.012	0.010	0.345	0.006	1.84%	0.40%
0.781	0.119	0.093	3.077	0.085	0.007	0.006	0.286	0.004	1.47%	0.29%
0.597	0.113	0.067	5.123	0.019	0.002	0.002	0.345	0.001	0.30%	1.37%
0.878	0.115	0.101	2.746	0.014	0.006	0.005	0.278	0.001	0.18%	1.90%
2.000	0.114	0.228	1.481	0.014	0.005	0.004	0.338	0.000	0.12%	1.51%

Table C8: Desorption Isotherm Data, OHRW

OHRW F-400 40 X 50 Mesh										
M/V (g GAC/L)	V (L)	M (g)	Qeq (mg TOC/g GAC)	Ceq' (mg TOC/L)	95% Conf.	Standard Deviation	Initial NOM (mg)	Desorbed NOM (mg)	% Desorbed	95% Conf.
0.040	0.46691	0.018654605	35.61253429	0.7122	0.032476491	0.0287	0.664	0.309	46.54%	2.28%
0.199	0.095	0.019	10.857	0.581	0.057	0.050	0.206	0.051	24.52%	2.62%
0.060	0.469	0.028	28.697	0.357	0.012	0.011	0.805	0.144	17.86%	0.71%
2.997	0.106	0.316	0.809	0.332	0.027	0.024	0.256	0.030	11.63%	1.12%
0.099	0.102	0.010	22.124	0.294	0.078	0.069	0.224	0.025	11.15%	3.58%
2.254	0.116	0.261	1.100	0.314	0.023	0.020	0.287	0.030	10.64%	0.92%
1.298	0.120	0.156	1.797	0.281	0.027	0.024	0.281	0.028	9.89%	1.18%
0.015	0.510	0.008	47.103	0.113	0.006	0.006	0.361	0.032	8.90%	0.90%
0.025	0.483	0.012	39.119	0.133	0.009	0.008	0.475	0.040	8.45%	0.93%
2.498	0.118	0.295	0.992	0.249	0.099	0.087	0.293	0.024	8.03%	3.99%
1.999	0.121	0.243	1.160	0.208	0.028	0.025	0.281	0.019	6.82%	1.22%
0.803	0.111	0.089	2.972	0.211	0.083	0.073	0.266	0.018	6.74%	3.48%
2.757	0.115	0.318	0.873	0.204	0.031	0.027	0.278	0.018	6.38%	1.27%
0.300	0.097	0.029	8.013	0.182	0.007	0.007	0.234	0.013	5.50%	0.31%
1.497	0.115	0.172	1.635	0.182	0.092	0.082	0.282	0.015	5.40%	3.78%
0.050	0.458	0.023	31.230	0.129	0.008	0.007	0.713	0.036	5.07%	0.53%
1.802	0.115	0.207	1.299	0.156	0.063	0.056	0.269	0.012	4.51%	2.71%
0.983	0.103	0.101	2.433	0.148	0.092	0.082	0.246	0.010	4.11%	3.86%
0.045	0.472	0.021	37.737	0.110	0.006	0.005	0.803	0.028	3.54%	0.36%
1.154	0.111	0.128	2.077	0.113	0.013	0.012	0.267	0.007	2.62%	0.55%
0.400	0.112	0.045	6.057	0.113	0.006	0.006	0.270	0.007	2.58%	0.27%
0.030	0.454	0.013	47.701	0.074	0.013	0.011	0.642	0.011	1.72%	0.90%
0.598	0.114	0.068	4.046	0.088	0.004	0.004	0.275	0.004	1.57%	0.17%
0.497	0.100	0.050	4.944	0.085	0.010	0.009	0.246	0.003	1.40%	0.39%
0.100	0.468	0.047	21.809	0.068	0.008	0.007	1.020	0.008	0.81%	0.37%
0.070	0.463	0.032	26.041	0.059	0.013	0.011	0.845	0.004	0.50%	0.69%
0.080	0.482	0.038	26.147	0.054	0.075	0.066	1.005	0.002	0.21%	3.58%
0.035	0.512	0.018	41.096	0.051	0.011	0.010	0.734	0.001	0.08%	0.77%

Table C9: Desorption Isotherm Data, SLRW

SLRW
F-400
40 X 50 Mesh

M/V (g GAC/L)	V (L)	M (g)	Qeq (mg TOC/g GAC)	Ceq' (mg TOC/L)	95% Conf.	Standard Deviation	Initial NOM (mg)	Desorbed NOM (mg)	% Desorbed	95% Conf.
0.799	0.112	0.090	2.125	0.872	0.078	0.075	0.191	0.092	48.41%	4.59%
0.201	0.107	0.022	7.689	0.563	0.161	0.142	0.166	0.055	33.29%	10.43%
0.035	0.120	0.004	65.021	0.368	0.023	0.021	0.273	0.038	13.96%	1.03%
0.600	0.121	0.073	2.436	0.209	0.121	0.107	0.177	0.019	10.85%	8.28%
2.000	0.114	0.228	1.021	0.190	0.150	0.132	0.232	0.016	6.87%	7.34%
1.501	0.116	0.173	1.321	0.184	0.023	0.021	0.229	0.015	6.76%	1.17%
0.400	0.113	0.045	4.782	0.162	0.051	0.045	0.215	0.013	5.88%	2.65%
0.999	0.120	0.120	2.037	0.157	0.227	0.201	0.244	0.013	5.25%	11.16%
0.098	0.114	0.011	13.869	0.119	0.035	0.031	0.155	0.008	5.03%	2.59%
0.301	0.116	0.035	6.263	0.132	0.078	0.069	0.218	0.009	4.33%	4.13%
0.501	0.113	0.057	4.126	0.104	0.011	0.010	0.233	0.006	2.62%	0.53%
1.250	0.114	0.143	1.309	0.093	0.124	0.109	0.187	0.005	2.60%	7.55%

Table C10: Desorption Isotherm Data, OHRW

OHRW										
F-400										
40 X 50 Mesh										
M/V	V	M	Qeq	Ceq'	0.950	Standard	Initial	Desorbed	% Desorbed	**95%**
(g GAC/L)	(L)	(g)	(mg TOC/g GAC)	(mg TOC/L)	Conf.	Deviation	NOM (mg)	NOM (mg)		**Conf.**
0.040	0.467	0.019	35.613	0.712	0.032	0.029	0.664	0.309	46.5%	2.3%
0.199	0.095	0.019	10.857	0.581	0.057	0.050	0.206	0.051	24.5%	2.6%
0.060	0.469	0.028	28.697	0.357	0.012	0.011	0.805	0.144	17.9%	0.7%
0.099	0.102	0.010	22.124	0.294	0.078	0.069	0.224	0.025	11.2%	3.6%
1.298	0.120	0.156	1.797	0.281	0.027	0.024	0.281	0.028	9.9%	1.2%
0.015	0.510	0.008	47.103	0.113	0.006	0.006	0.361	0.032	8.9%	0.9%
0.025	0.483	0.012	39.119	0.133	0.009	0.008	0.475	0.040	8.4%	0.9%
1.999	0.121	0.243	1.160	0.208	0.028	0.025	0.281	0.019	6.8%	1.2%
0.803	0.111	0.089	2.972	0.211	0.083	0.073	0.266	0.018	6.7%	3.5%
0.050	0.458	0.023	31.230	0.129	0.008	0.007	0.713	0.036	5.1%	0.5%
0.983	0.103	0.101	2.433	0.148	0.092	0.082	0.246	0.010	4.1%	3.9%
0.045	0.472	0.021	37.737	0.110	0.006	0.005	0.803	0.028	3.5%	0.4%
0.400	0.112	0.045	6.057	0.113	0.006	0.006	0.270	0.007	2.6%	0.3%
0.030	0.454	0.013	47.701	0.074	0.013	0.011	0.642	0.011	1.7%	0.9%
0.598	0.114	0.068	4.046	0.088	0.004	0.004	0.275	0.004	1.6%	0.2%
0.497	0.100	0.050	4.944	0.085	0.010	0.009	0.246	0.003	1.4%	0.4%
0.100	0.468	0.047	21.809	0.068	0.008	0.007	1.020	0.008	0.8%	0.4%
0.070	0.463	0.032	26.041	0.059	0.013	0.011	0.845	0.004	0.5%	0.7%
0.080	0.482	0.038	26.147	0.054	0.075	0.066	1.005	0.002	0.2%	3.6%
0.035	0.512	0.018	41.096	0.051	0.011	0.010	0.734	0.001	0.1%	0.8%

Table C11: Desorption Isotherm Data, BPLW

BPLW
F-400
40 X 50 Mesh

M/V (g GAC/L)	V (L)	M (g)	Qeq (mg TOC/g GAC)	Ceq' (mg TOC/L)	95% Conf.	Standard Deviation	Initial NOM (mg)	Desorbed NOM (mg)	% Desorbed	95% Conf.
0.050	0.470	0.023	24.751	0.637	0.074	0.066	0.580	0.276	47.53%	6.01%
0.020	0.469	0.009	68.012	0.624	0.052	0.046	0.638	0.269	42.19%	3.82%
0.045	0.466	0.021	30.163	0.539	0.077	0.068	0.633	0.228	35.94%	5.67%
0.150	0.528	0.079	17.183	0.850	0.150	0.133	1.361	0.422	31.02%	5.83%
0.799	0.102	0.082	4.011	1.017	0.134	0.119	0.327	0.099	30.15%	4.19%
0.070	0.523	0.037	26.926	0.552	0.054	0.048	0.986	0.263	26.63%	2.85%
0.015	0.464	0.007	86.479	0.359	0.181	0.160	0.602	0.144	23.84%	13.94%
0.500	0.119	0.059	6.104	0.474	0.066	0.058	0.362	0.050	13.88%	2.15%
1.999	0.114	0.229	1.678	0.499	0.085	0.075	0.384	0.051	13.40%	2.53%
0.300	0.104	0.031	10.385	0.396	0.192	0.170	0.323	0.036	11.08%	6.15%
0.400	0.104	0.042	7.444	0.344	0.107	0.095	0.310	0.031	9.87%	3.61%
0.600	0.115	0.069	5.055	0.210	0.041	0.036	0.350	0.018	5.26%	1.34%
0.701	0.114	0.080	4.426	0.009	0.026	0.023	0.352	0.001	0.30%	0.83%
0.010	0.480	0.005	105.583	0.002	0.001	0.001	0.507	0.001	0.19%	0.05%

Table C12: Desorption Isotherm Data, VGW

VGW
F-400
40 X 50 Mesh

M/V (g GAC/L)	V (L)	M (g)	Qeq (mg TOC/g GAC)	Ceq' (mg TOC/L)	95% Conf.	Standard Deviation	Initial NOM (mg)	Desorbed NOM (mg)	% Desorbed	95% Conf.
0.029	0.477	0.014	39.573	0.795	0.012	0.011	0.556	0.355	63.85%	1.07%
0.015	0.467	0.007	54.383	0.317	0.057	0.050	0.371	0.125	33.59%	7.12%
0.019	0.484	0.009	42.139	0.279	0.024	0.022	0.398	0.111	27.83%	2.96%
0.050	0.508	0.025	32.323	0.463	0.050	0.045	0.820	0.210	25.62%	3.12%
0.010	0.523	0.005	68.906	0.177	0.037	0.033	0.350	0.066	19.00%	5.58%
0.034	0.469	0.016	41.500	0.303	0.017	0.015	0.670	0.119	17.69%	1.19%
0.040	0.471	0.019	40.859	0.203	0.002	0.002	0.769	0.072	9.35%	0.11%
0.045	0.472	0.021	39.852	0.212	0.014	0.012	0.854	0.077	8.97%	0.75%
0.059	0.462	0.027	34.207	0.193	0.002	0.002	0.928	0.066	7.13%	0.08%
0.071	0.506	0.036	31.740	0.197	0.015	0.014	1.133	0.074	6.55%	0.68%
0.080	0.524	0.042	30.034	0.199	0.004	0.004	1.251	0.078	6.22%	0.17%
0.710	0.115	0.081	4.920	0.192	0.016	0.014	0.401	0.016	4.06%	0.46%
0.198	0.116	0.023	15.926	0.160	0.024	0.022	0.365	0.013	3.49%	0.77%
0.601	0.109	0.065	5.709	0.154	0.101	0.089	0.373	0.011	3.04%	2.95%
0.090	0.525	0.047	25.861	0.117	0.061	0.054	1.218	0.035	2.90%	2.65%
0.398	0.114	0.045	8.477	0.116	0.016	0.014	0.384	0.008	1.96%	0.47%
0.504	0.112	0.056	6.848	0.103	0.001	0.001	0.387	0.006	1.53%	0.03%
0.800	0.108	0.086	4.295	0.030	0.006	0.005	0.370	0.003	0.87%	1.64%
2.003	0.114	0.228	1.731	0.062	0.080	0.071	0.394	0.001	0.34%	2.31%
1.005	0.116	0.116	3.500	0.052	0.011	0.010	0.407	0.000	0.05%	0.32%

Appendix D: Kinetics Data

Table D1: Adsorption Kinetics

Time (hours)	DOC (mg/L)	± 95% Confidence	Standard Deviation (mg/l)	C/Co
0	3.150	0.017	0.015	1.000
2.5	2.743	0.051	0.045	0.871
3	2.845	0.052	0.046	0.903
3.78	2.835	0.004	0.003	0.900
5	2.397	0.055	0.049	0.761
12	2.109	0.035	0.031	0.670
13	2.175	0.041	0.037	0.690
14	2.273	0.031	0.028	0.722
16	2.107	0.028	0.025	0.669
18	2.204	0.036	0.032	0.700
20	2.179	0.042	0.037	0.692
22	2.090	0.024	0.021	0.664
24	2.115	0.014	0.013	0.671
24	2.375	0.056	0.049	0.754
36	2.065	0.053	0.047	0.656
48	1.889	0.060	0.053	0.600
60	1.842	0.004	0.004	0.585
72	1.939	0.060	0.053	0.615
85.5	1.756	0.036	0.031	0.557
96	2.054	0.074	0.065	0.652
108	1.820	0.037	0.033	0.578
120	1.801	0.002	0.002	0.572
120	1.958	0.024	0.021	0.622
133	2.015	0.016	0.015	0.640
138	1.838	0.035	0.031	0.584
144	1.618	0.031	0.028	0.514
147.25	1.813	0.031	0.027	0.576
152	1.734	0.024	0.021	0.550
167.5	1.579	0.045	0.040	0.501
170	1.577	0.020	0.017	0.501
174	1.715	0.021	0.019	0.545

193.33	1.679	0.026	0.023	0.533
208	1.739	0.029	0.026	0.552
218	1.573	0.027	0.024	0.500
240	1.515	0.023	0.021	0.481
248	1.517	0.025	0.022	0.482
265	1.540	0.055	0.049	0.489
290	1.662	0.047	0.042	0.528
312	1.562	0.055	0.049	0.496
336	1.470	0.040	0.035	0.467
348	1.717	0.022	0.020	0.545
360	1.618	0.046	0.041	0.514
386	1.658	0.031	0.027	0.526
449	1.535	0.033	0.029	0.487
476	1.753	0.009	0.008	0.557
521	1.289	0.012	0.010	0.409
552	1.270	0.014	0.012	0.403
574	1.345	0.037	0.033	0.427
597	1.274	0.020	0.018	0.404
623	1.240	0.132	0.116	0.394
646.5	1.265	0.140	0.124	0.402
670	1.016	0.036	0.032	0.323
718.25	1.429	0.061	0.054	0.454
744	1.445	0.037	0.033	0.459
768	1.267	0.022	0.019	0.402

Table D2: Desorption Kinetics

Time Hours	DOC Recovered	DOC (mg/l)	95% Confidence	Standard Deviation (mg/l)
0	0.0%	0.011	0.006	0.005
0	0.0%	0.000	0.000	0.007
0.083	2.8%	0.050	0.028	0.024
0.167	2.7%	0.048	0.067	0.059
1	2.3%	0.033	0.004	0.004
4	2.1%	0.040	0.044	0.032
8	1.6%	0.033	0.012	0.010
12	0.6%	0.019	0.009	0.008
22	4.7%	0.077	0.025	0.022
24	2.6%	0.047	0.005	0.004
48	1.3%	0.040	0.005	0.004
48	1.4%	0.030	0.012	0.010
51	1.0%	0.024	0.013	0.011
72	2.0%	0.039	0.005	0.005
96	2.9%	0.051	0.028	0.025
144	6.2%	0.098	0.011	0.010
168	5.1%	0.086	0.006	0.006
192	5.6%	0.090	0.005	0.004
216	6.9%	0.109	0.018	0.016
240	5.4%	0.087	0.010	0.009
288	5.0%	0.081	0.014	0.013
312	6.1%	0.096	0.015	0.013
336	12.0%	0.181	0.043	0.038
384	5.1%	0.083	0.048	0.043

456	10.8%	0.164	0.049	0.043
480	5.3%	0.085	0.041	0.036
504	13.2%	0.198	0.015	0.014
528	17.5%	0.259	0.075	0.066
624	9.8%	0.150	0.022	0.019
672	13.3%	0.199	0.058	0.051
744	12.5%	0.188	0.022	0.019
792	8.8%	0.134	0.004	0.003
840	7.8%	0.121	0.014	0.012
864	6.8%	0.107	0.014	0.013
960	8.4%	0.129	0.006	0.005
984	8.3%	0.128	0.033	0.029
1056	7.9%	0.122	0.005	0.005
1104	8.8%	0.134	0.007	0.006
1248	11.3%	0.171	0.006	0.005
1296	12.8%	0.192	0.011	0.010
1392	9.6%	0.147	0.018	0.016
1416	9.0%	0.138	0.011	0.010
1536	7.0%	0.109	0.008	0.007
1560	11.8%	0.178	0.054	0.047
1632	8.9%	0.136	0.004	0.004
1680	8.8%	0.136	0.002	0.002
1728	9.4%	0.144	0.004	0.003
1776	8.3%	0.129	0.006	0.006
1824	8.4%	0.129	0.017	0.015
1872	7.1%	0.110	0.011	0.009
1920	8.5%	0.131	0.007	0.006

Table D3: UV Absorbance Analysis for Adsorption Kinetics Study

Time (hours)	DOC (mg/l)	UV Absorbance At 254nm (m^{-1})	UV Correlated DOC (mg/l)	C/Co
0	3.150	0.120	3.150	1.000
2.5	2.743	0.107	2.650	0.841
3	2.845	0.126	3.117	0.989
3.78	2.835	0.098	2.430	0.771
5	2.397	0.087	2.147	0.682
12	2.109	0.095	2.348	0.745
13	2.175	0.090	2.233	0.709
14	2.273	0.092	2.290	0.727
16	2.107	0.084	2.078	0.660
18	2.204	0.081	2.000	0.635
20	2.179	0.077	1.914	0.608
22	2.090	0.087	2.147	0.682
24	2.115	0.086	2.123	0.674
24	2.375	0.081	2.020	0.641
36	2.065	0.080	1.975	0.627
48	1.889	0.084	2.080	0.660
60	1.842	0.084	2.074	0.658
72	1.939	0.073	1.816	0.576
85.5	1.756	0.086	2.127	0.675
96	2.054	0.074	1.832	0.582
108	1.820	0.074	1.834	0.582
120	1.801	0.073	1.816	0.576
120	1.958	0.073	1.816	0.576
133	2.015	0.073	1.808	0.574
138	1.838	0.074	1.840	0.584
144	1.618	0.074	1.840	0.584

147.25	1.813	0.075	1.873	0.595
152	1.734	0.073	1.804	0.573
167.5	1.579	0.071	1.761	0.559
170	1.577	0.075	1.873	0.595
174	1.715	0.074	1.840	0.584
193.33	1.679	0.073	1.816	0.576
208	1.739	0.074	1.834	0.582
218	1.573	0.072	1.791	0.569
240	1.515	0.075	1.871	0.594
248	1.517	0.072	1.779	0.565
265	1.540	0.076	1.889	0.600
290	1.662	0.077	1.902	0.604
312	1.562	0.075	1.865	0.592
336	1.470	0.076	1.889	0.600
348	1.717	0.073	1.816	0.576
360	1.618	0.073	1.804	0.573
386	1.658	0.071	1.767	0.561
449	1.535	0.071	1.767	0.561
476	1.753	0.072	1.791	0.569
521	1.289	0.07	1.742	0.553
552	1.270	0.075	1.865	0.592
574	1.345	0.078	1.939	0.615
597	1.274	0.075	1.865	0.592
623	1.240	0.07	1.742	0.553
646.5	1.265	0.07	1.742	0.553
670	1.016	0.07	1.742	0.553
718.25	1.429	0.072	1.791	0.569
744	1.445	0.075	1.865	0.592
768	1.267	0.073	1.816	0.576

Appendix E: NOM Fractionation Data

E.1. XAD 8 Resin: DOC Analysis of Influents and Effluents

Table E1: Results from XAD8 with Source Waters
Influent #1 = Five Water Sources

Effluent #1 = Fulvic Concentration in Waters

Water Source	DOC mg /L	± 95% Confidence	Standard Deviation (mg DOC/l)
OHRW	2.082	0.016	0.018
SLRW	1.856	0.016	0.018
ORW F-400	3.100	0.026	0.029
ORW WV-B	3.100	0.026	0.029
BPLW	3.497	0.019	0.017
VGW	4.010	0.025	0.022

Fulvics Source	mg DOC/L	± 95% Confidence	Standard Deviation (mg DOC/l)
OHRW	1.309	0.033	0.029
SLRW	0.781	0.008	0.006
ORW F-400	0.789	0.167	0.189
ORW WV-B	0.789	0.167	0.189
BPLW	0.239	0.009	0.010
VGW	0.347	0.053	0.060

Table E2: Results from XAD8 with Adsorption Waters
Influent #2 = Adsorption Waters at GAC dosage of 0.03 g/l

Effluent #2 = Fulvic Concentration in adsorption Waters at GAC dosage of 0.03 g/l

Adsorption Water Samples	mg DOC/L	± 95% Confidence	Standard Deviation (mg DOC/l)
OHRW	0.832	0.006	0.007
SLRW	1.519	0.035	0.031
ORW F-400	1.174	0.029	0.025
ORW WV-B	1.068	0.031	0.027
BPLW	1.139	0.019	0.017
VGW	1.310	0.025	0.022

Fulvics	mg DOC/L	± 95% Confidence	Standard Deviation (mg DOC/l)
OHRW	0.040	0.011	0.010
SLRW	0.745	0.021	0.024
ORW F-400	0.153	0.066	0.075
ORW WV-B	0.170	0.096	0.108
BPLW	0.148	0.116	0.132
VGW	0.110	0.057	0.065

Table E3: Results from XAD8 with Desorption Waters
Influent #3 = Desorption Waters at GAC dosage of 0.03 g/l

Effluent #3 = Fulvic Concentration in Desorption Waters at GAC dosage of 0.03 g/l

Desorption Water Samples	Mg DOC/L	± 95% Confidence	Standard Deviation (mg DOC/l)
OHRW	**0.281**	**0.027**	**0.024**
SLRW	0.276	0.032	0.029
ORW F-400	0.616	0.035	0.031
ORW WV-B	0.681	0.038	0.034
BPLW	0.991	0.066	0.059
VGW	0.795	0.011	0.010

Fulvics	Mg DOC/L	± 95% Confidence	Standard Deviation (mg DOC/l)
OHRW	0.039	0.005	0.004
SLRW	0.035	0.011	0.010
ORW F-400	0.006	0.003	0.002
ORW WV-B	0.021	0.033	0.029
BPLW	0.090	0.036	0.032
VGW	0.034	0.014	0.013

E.2. Ultrafiltration Fractionation Results

Table E4: UF Results

	weight %				
	OHRW	**SLRW**	**ORW**	**BPLW**	**VGW**
>30k	0.162	0.132	0.081	0.004	0.0107
<30 k & >10k	0.014	0.091	0.099	0.027	0.1928
<10k & >3k	0.031	0.152	0.255	0.161	0.1131
<3k & >1k	0.448	0.270	0.252	0.188	0.0096
<1k &<0.5k	0.004	0.138	0.084	0.473	0.5203
<0.5	0.342	0.217	0.229	0.147	0.1535

E.3. Size Exclusion Chromatography (SEC) Results

Various calibrations are shown in the following figures. The SEC results for each water source are shown in appendix B.

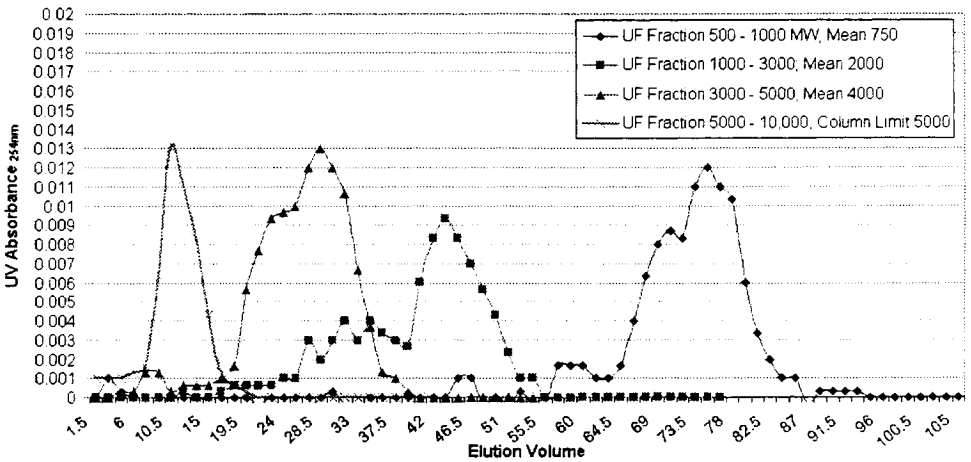

Figure E.1: Spectra of Natural Water Standards Passed Through Sephadex G 25 Column

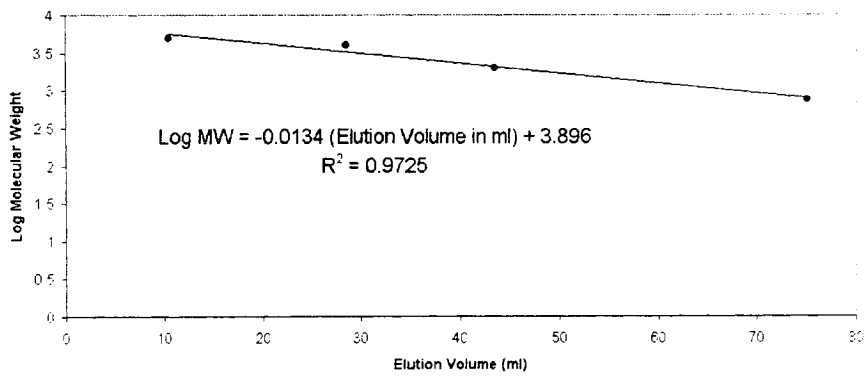

Figure E.2: Calibration of Sephadex G25 Column Using Ultrafiltration Retentate Samples

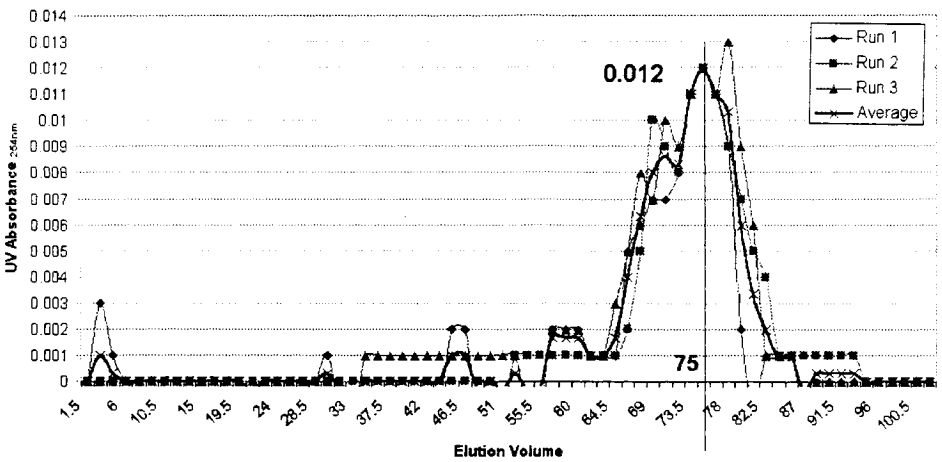

Figure E.3: SEC Results for 750 Mean MW, UF Fraction >500 and <1000, ORW

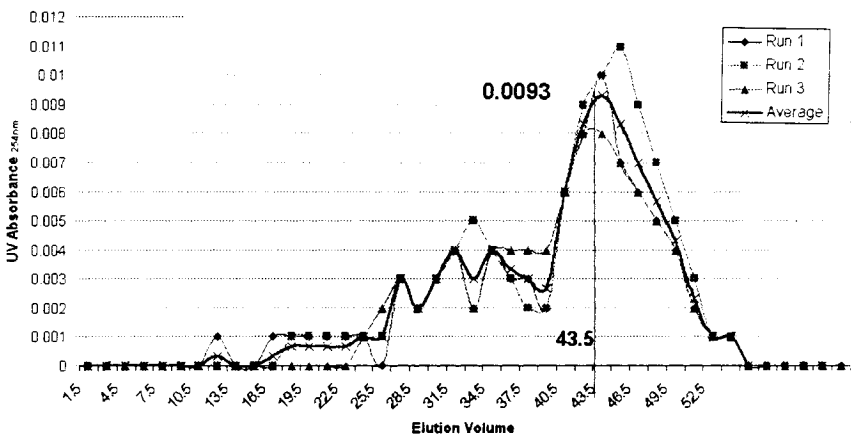

Figure E.4: SEC Results for 2000 Mean MW, UF Fractions >1000 and <3000, ORW

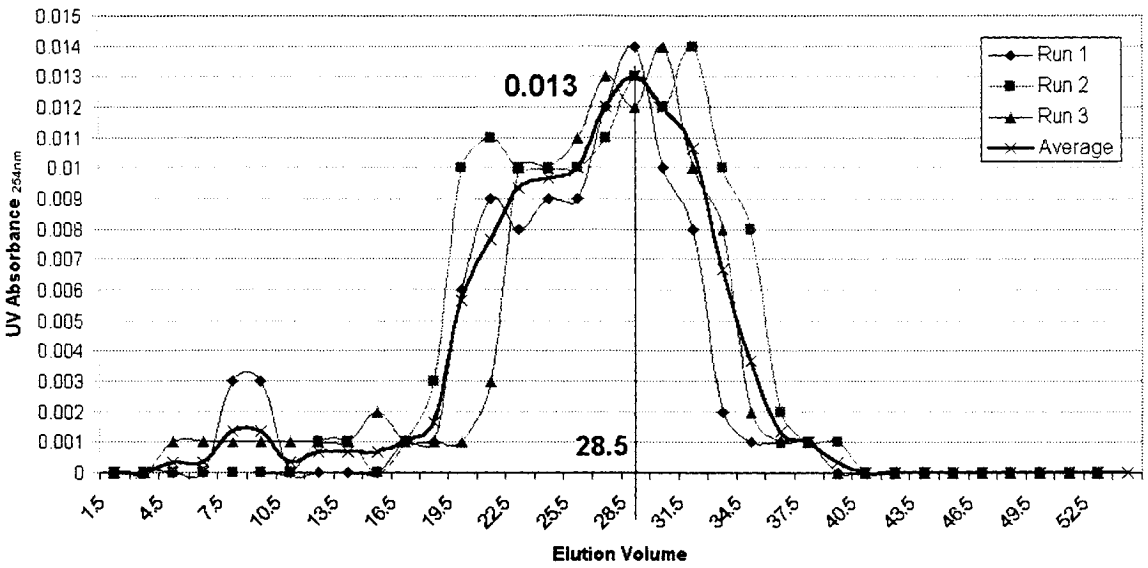

Figure E.5: SEC Results for 4000 Mean MW, UF Fractions >3000 and <5000, ORW

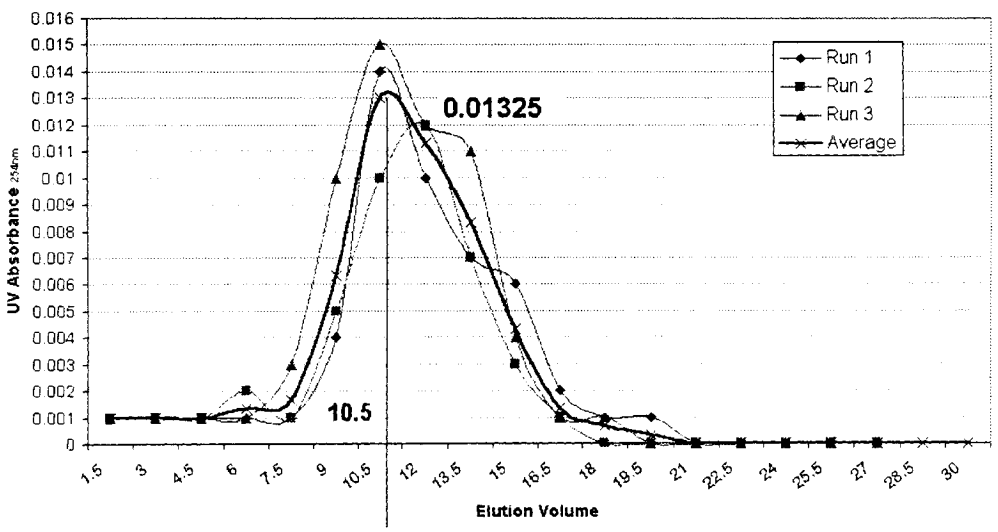

Figure E.6: SEC Results for Column Limit of 5000 MW,UF Fractions > 5000 and <10,000, ORW

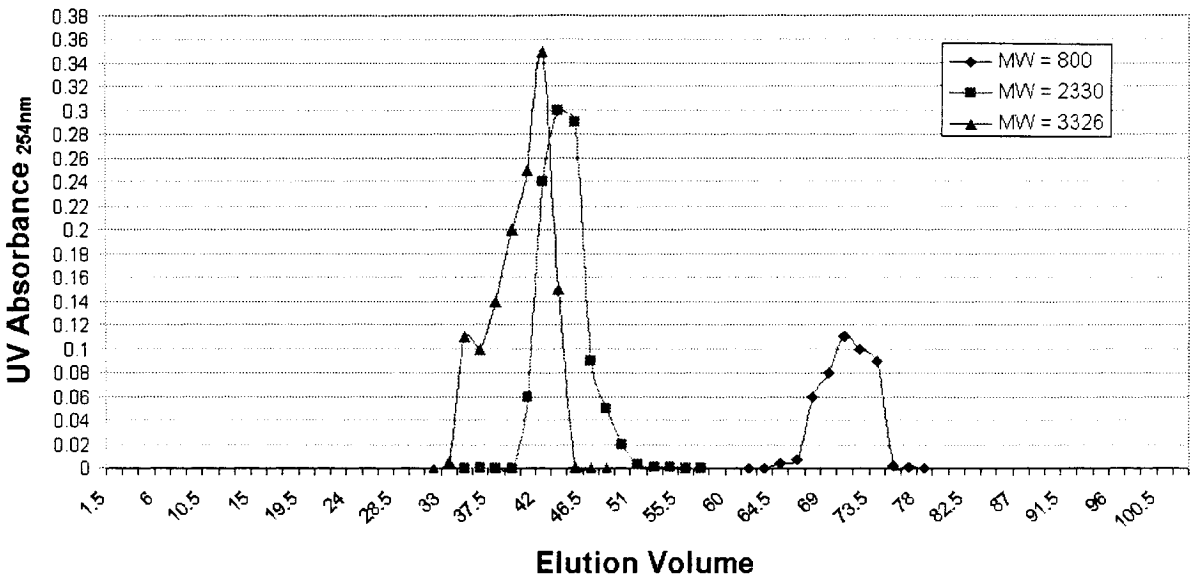

Figure E.7: SEC Results with Polystyrene Sulfonates

Appendix F: Nonlinear Regression

A non linear regression routine was used to solve for the Freundlich constants k and n that provided the smallest sum of the square residual value(the shaded cells shown in figure F.1). A table was set up in Microsoft Excel as shown in figure F.1 below.

	A	B	C	D	E
1					
2					
3			k	0.5292	
4			n	5.6761	
5	TOC Analyzer				
6	Ceq	qeq	predicted	residuals	ss
7	(mg TOC/L)	(mg TOC/g GAC)			
8	1.1881	6.3271	1.4075	4.9196	24.2024
9	0.9359	5.3955	0.3634	5.0321	25.3224
10	0.8197	4.5437	0.1712	4.3725	19.1184
11	0.5060	4.3207	0.0111	4.3096	18.5725
12	0.4124	3.8344	0.0035	3.8309	14.6759
13	0.3511	3.4373	0.0014	3.4359	11.8056
14	0.3458	3.0617	0.0013	3.0605	9.3664
15	1.7531	13.4689	12.8092	0.6598	0.4353
16	1.6343	7.3286	8.6004	-1.2718	1.6175
17	1.6079	5.9685	7.8409	-1.8724	3.5060
18	1.5023	4.5649	5.3319	-0.7669	0.5882
19	1.0217	4.6184	0.5979	4.0205	16.1647
20	0.3643	5.4715	0.0017	5.4698	29.9184
21	0.3220	4.6300	0.0009	4.6291	21.4288
22	0.2943	4.0082	0.0005	4.0077	16.0613
23	0.2969	3.5038	0.0005	3.5033	12.2731
24	0.3458	3.0603	0.0013	3.0590	9.3573
25	2.1624	38.6889	42.1468	-3.4580	11.9576
26	2.5922	108.7877	117.9462	-9.1585	83.8781
27	0.2992	2.7997	0.0006	2.7991	7.8352
28	0.3187	1.8535	0.0008	1.8527	3.4325
29	2.2960	82.1560	59.2345	22.9215	525.3948
30	2.2934	53.8061	58.8502	-5.0442	25.4435
31	2.3015	39.9322	60.0446	-20.1124	404.5095
32	2.0785	42.1703	33.6659	8.5044	72.3255
33	2.1533	33.0626	41.1490	-8.0864	65.3902
34	2.0672	28.8242	32.6434	-3.8193	14.5868
35	1.8389	22.7349	16.7970	5.9379	35.2585
36	2.6051	127.4534	121.3106	6.1428	37.7344
37	2.4560	94.9670	86.8176	8.1495	66.4136
38					
39				sum	1588.5744

Figure F.1: Excel Table Used to Solve Freundlich Isotherm

The constants were solved via the following steps:

1) Enter the experimental data for C_{eq} in column A

2) Input the mass balance calculated data for Q_{eq} in column B

3) Column C was calculated from the isotherm equation by entering the function as shown in figure F.2. This function linked the regressed constants to the liquid phase equilibrium data.

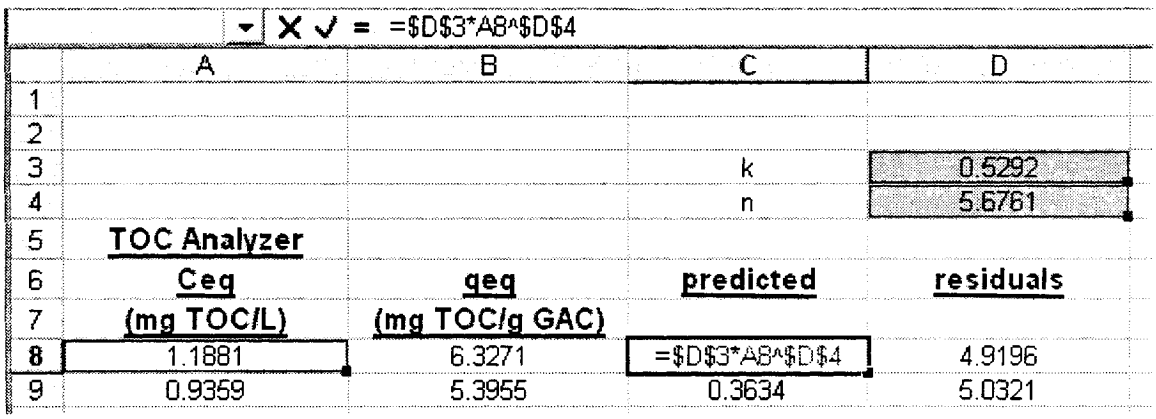

Figure F.2: Function Used for Solid Phase Prediction

4) Column D, 'residuals' was calculated via the function as shown in figure F.3, where residuals = Q_{eq} (as measured experimentally – predicted Q_{eq}

=(B8-C8)

A	B	C	D
		k	0.5292
		n	5.6761
TOC Analyzer			
Ceq (mg TOC/L)	**qeq (mg TOC/g GAC)**	**predicted**	**residuals**
1.1881	6.3271	1.4075	=(B8-C8)
0.9359	5.3955	0.3634	5.0321
0.8197	4.5437	0.1712	4.3725
0.5060	4.3207	0.0111	4.3096

Figure F.3: Function Used to Calculate the Residuals.

5) The sum of the square residual was calculated in column E, which was the squared value of column D.

6) Column D was summed, shown as cell E39 in figure F.1.

7) The Microsoft Addin "solver" was used to minimize the cell containing the sum of the square residuals by altering the cells containing the Freundlich constants. This is shown in figure F.4.

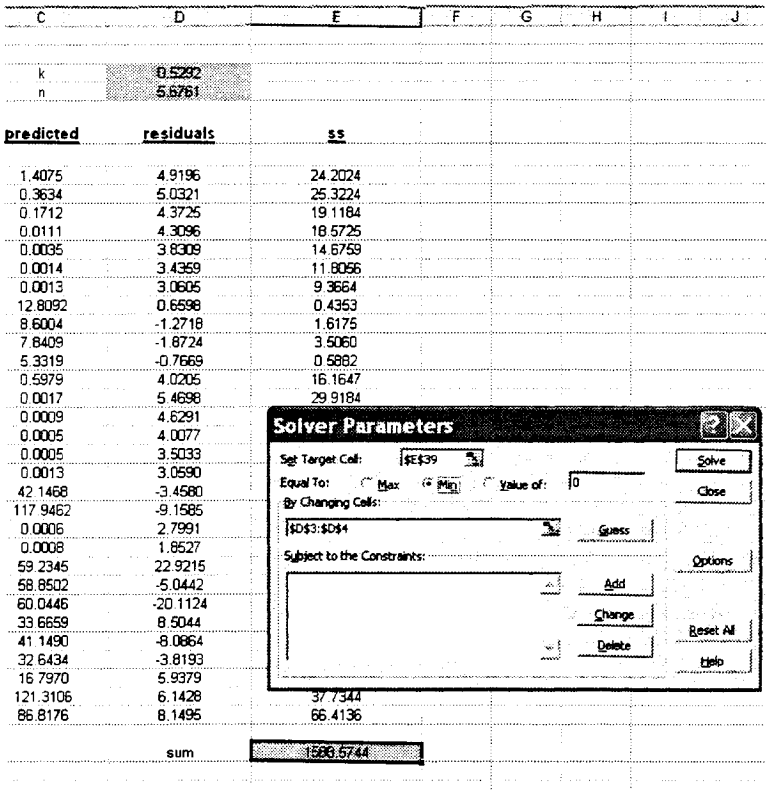

Figure F.4: Solver Routine Used to Calculate Regressed Freundlich Constants