CHARACTERIZATION OF DISSOLVED ORGANIC CARBON IN PRAIRIE SURFACE WATERS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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By

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ABSTRACT

Surface water reservoirs in rural areas of the Canadian prairies often have poor water quality due to contamination by dissolved organic carbon (DOC). DOC can activate growth of microorganisms in water distribution systems and form disinfection by-products (DBPs) in water treatment. The presence of microbiological contaminants and DBPs are potentially harmful to human health. Therefore, rapid and simple methods for DOC characterization are needed to evaluate potential water sources and to assist in understanding how best to remove DOC.

The first objective of this project was to develop a sample preparation and analysis procedure utilizing Fourier Transform Infrared Spectroscopy (FTIR) to characterize the DOC content of water samples. The second objective was to compare FTIR analysis results for fractionated and un-fractionated water samples to more convention DOC characterization methods (such as UV, SUVA and specific THMFP). The third objective was to demonstrate the application of the procedure to source water assessment and water treatment process evaluation by characterizing the DOC content of several typical treated and un-treated prairie water samples at several locations in Saskatchewan.

In the first phase of the study prepared samples of known DOC concentration were separated into six fractions (hydrophobic acid (HPOA), hydrophobic neutral (HPON) and hydrophobic base (HPOB); and hydrophilic acid (HPIA), hydrophilic neutral (HPIN) and hydrophilic base (HPIB)) using resin fractionation techniques. FTIR and conventional UV spectroscopic measurements, DOC concentration, and trihalomethane formation potential (THMFP) measurements were taken on the un-fractionated samples and their fractions.

A water matrix interference problem in the FTIR measurements was overcome by depositing a residue of dry solids from the aqueous solution containing the DOC on a

flat, organic compound free and non-infrared absorptive gold plated slide before analysis. This simple evaporation procedure developed for concentrating water samples successfully deposited a solid residue for FTIR scanning. Scanning of the solid residue of each sample at multiple locations successfully produced a spectrum of average results suitable for interpretation.

Each organic fraction separated from the prepared samples of known DOC was then assessed using FTIR analysis. Comparison of the spectra from the resin adsorption fractions gave an indication of the relationship between functional groups and the hydrophobic/hydrophilic nature of the DOC. The results suggest that the hydrophobic fractions contain more aromatic functional groups. This demonstrates that the FTIR spectra can provide information regarding the hydrophobic/hydrophilic nature of the DOC as an alternative to the resin separation procedure.

The sample preparation and FTIR analysis procedure was then used to characterize the DOC content of source and treated waters at several locations within Saskatchewan. The results of these initial investigations indicate the method can effectively identify the major organic functional groups present in source waters and the changes in the major functional groups that occur as the water is subjected to water treatment unit operations and processes. Further, the presence of several key functional groups is related to an increase in THMFP.

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Table of Contents

List of Figures

List of Tables

List of Abbreviations

AOC – assimilable organic carbon
BDOC – biodegradable dissolved organic carbon
DBP – disinfection by product
RO/DI – reverse osmosis and deionized
DOC – dissolved organic carbon
DOM – dissolved organic matter
FA – fulvic acid
FTIR – fourier transform infrared spectroscopy
HA – humic acid
HAAs – haloacetic acids
HPIA – hydrophilic acid
HPIB – hydrophilic base
HPIN – hydrophilic neutral
HPOA – hydrophobic acid
HPOB – hydrophobic base
HPON – hydrophobic neutral
HS – humic substances
IR – infrared spectroscopy
MF – microfiltration
MS – mass spectrometry
NF – nanofiltration
NHS – non humic substances
NMR – nuclear magnetic resonance
NOM – natural organic matter
RO – reverse osmosis
SUVA – specific UV absorbance
THMs – trihalomethanes
TOX – total organic halides
UF – ultrafiltration
UV – ultraviolet

CHAPTER 1. INTRODUCTION

1.1 Background

According to (Corkal 1997) and (Putz 2002), surface water reservoirs are one of the main sources of drinking water in rural areas of the Canadian prairies. These surface water reservoirs often have poor water quality due to contamination by natural organic matter (NOM). NOM is an extremely complex mixture of organic compounds found in all potable water sources (Croue et al. 2000).

Most efforts to characterize NOM in drinking water sources have focused on dissolved organic compounds, which typically contain more than 90% of the NOM (Croue et al. 2000). The other portion of the NOM is made up of particulate and colloidal organic carbon that can be separated from the water samples by centrifugation, filtration and/or ultra filtration methods prior to characterization (Aiken and Leenheer 1993, Rees et al. 1991).

Operationally, the soluble portion of the NOM that will pass through a 0.45 μm pore size filter is called dissolved organic matter (DOM). DOM is a heterogeneous mixture of aromatic and aliphatic organic compounds containing oxygen, nitrogen, and sulphur functional groups (e.g., carboxyl, phenol, enol, alcohol, carbonyl, amine, and thiol) (Chen et al. 2003). DOM is generally quantified in terms of its dissolved organic carbon (DOC) content (Her et al. 2002; Korshin et al. 1997; Leenheer and Croue 2003; Perminova et al. 2003). In this research project, the terminology DOC is always used instead of DOM.

Because DOC compounds have a wide range of molar masses and chemical structures, they can play a multifunctional role in the natural environment. For example, they can activate growth of microorganisms and promote growth of biofilm in water

distribution systems or treatment units because DOC can serve as a carbon and energy source for microorganisms (Kim and Yu 2005). The presence of microbiological contaminants in water can cause negative health impacts for humans and animals consuming polluted water (Putz 2000).

Another potential effect of DOC is the formation of disinfection by-products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), and total organic halides (TOX) formed in the reactions between DOC in untreated water and chlorine added as a microbial destruction agent during the water treatment process (Chen et al. 2003; Kanokkantapong et al. 2006; Kim and Yu 2005). DBPs are potentially harmful to human health (Barrett et al. 2000) by increasing the risk of cancers (United States Environmental Protection Agency 2003).

Due to the multiple hazards posed by DOC, it is necessary to understand the DOC chemistry. However, due to the complexities of DOC molecules, DOC structures are not well defined (Snoeyink and Jenkins 1980) and it is not realistic to evaluate its properties based on a comprehensive compilation of the individual compounds (Croue et al. 2000). Therefore, methods for DOC characterization are essential for evaluating potential water sources and in understanding how best to remove DOC.

Several DOC characterization methods are available (LeChevallier 1999). One of the first approaches that researchers used to characterize DOC was elemental analysis for carbon, hydrogen, oxygen, nitrogen, sulphur, and the non oxidizable element content 'ash' (Croue et al. 2000). A second approach was to characterize DOC based upon its potential utilization by microorganisms. Biodegradable dissolved organic carbon (BDOC) (Charnock and Kjonno 2000; LeChevallier 1999; Servais et al. 1989) is the portion of the overall DOC content that can be utilized by a mixed population of microorganisms as substrate for cell growth and multiplication. Assimilable organic carbon (AOC) is a portion of the BDOC (Charnock and Kjonno 2000; LeChevallier 1999). AOC can only be utilized by specific microorganisms and generally consists of the lower molecular weight organic molecules (Huck 1990).

Molecular weight and molecular size distribution of compounds has also been used to characterize DOC. The common approaches for determining molecule weight

and size are: gel permeation chromatography, ultrafiltration, electron microscopy, ultra centrifugation, osmometry, viscometry and electrophoresis (Abbt-Braun et al. 2004). A column resin adsorption technique for isolating and fractionating DOC is a very popular method and it often separates DOC in to six fractions based upon pH and hydrophilic/hydrophobic characteristics (Croue et al. 2000). These DOC characterization methods outlined above are time consuming, subject to experimental variability and require complex sample handling procedures. Therefore, for routine water investigations, more rapid and simple methods for DOC characterization are needed.

Spectroscopic methods for characterizing DOC have been investigated by several researchers because of their ease of operation and time efficiency (Chen et al. 2003; Chouparova et al. 2004; Christman et al. 1989; Kanokkantapong et al. 2006; Kim and Yu. 2005; Lin et al. 2001; Parson 1989; Peuravuori et al. 2002; Schulten et al. 2002). Ultraviolet and visible, infrared, mass, Raman, nuclear magnetic resonance and fluorescence are the commonly used spectroscopic methods. The current research project investigates Fourier transform infrared spectroscopy for characterization of DOC.

1.2 Objective and Scope

The objectives of this project are as follows:

1. To develop a simple water sample preparation procedure for the characterization of DOC using Fourier Transform Infrared Spectroscopy (FTIR) analysis
2. To compare FTIR analysis results for fractionated and un-fractionated water samples to more convention DOC characterization methods (such as UV, SUVA and specific THMFP)
3. To investigate the use of the sample preparation procedure and FTIR analysis for source water assessment and water treatment process evaluation by characterizing the DOC in water samples from several locations in Saskatchewan.

The scope of this project includes water sample collection, preparation of standard water samples, water sample fractionation, measurement of DOC concentration, FTIR sample preparation, UV and FTIR spectroscopic measurement, and

analysis of water samples for potential formation of THMs. The project is mainly focused on the development of a qualitative method for characterization of DOC in water samples rather than a quantitative method.

CHAPTER 2. LITERATURE REVIEW

2.1 DOC Origin, Structure, and Composition

Decomposition of soil and plant materials is the main source contributing to the DOC content of surface waters (Thurman 1985). The DOC content of surface water often varies with water source, for example, South Saskatchewan River water has a DOC content of 2 to 4 mg/L, whereas average rural dugout water DOC content has been reported to be approximately 13 mg/L (Corkal 1997).

Aquatic DOC is composed of humic substances (HS) and non humic substances (NHS) (Drewes et al. 2006; Sachse et al. 2005). HS are an extremely complex and diverse group of organic materials whose structure is not well defined. They are a mixture of poorly biodegradable decomposition products of natural organic matter produced by both plants and animals (Snoeyink and Jenkins 1980). HS have larger molecular weights (with over 500 gram/mole) than NHS (Lin et al. 2001; Thurman 1985). Aquatic HS are polar, straw-coloured, organic acids that are derived from soil humus and terrestrial and aquatic plants (Thurman and Malcolm 1981). NHS often serve as substrate of microorganisms while HS are generally less biodegradable (Hesse et al. 1999). Estimates of the proportion of HS in aquatic DOC are in the ranges of 50-70% (Thurman 1985). NHS mainly include identifiable organic compounds, e.g. amino acids, nucleic acids, carbohydrates, hydrocarbons, fatty acids and phenolic compounds (Thomas 1997). HS are the major contributors to DOC in natural water (Thurman 1985).

Aquatic HS are often separated into two acid types: humic acids (HA) and fulvic acids (FA). HA can only be dissolved in base solutions whereas FA can be dissolved in both acid and base solutions. Aquatic FA are of molecular weight 500 to 2000 atomic mass units (gram/mole), whereas aquatic HA are larger and often colloidal in the range of 2000 to 5000 atomic mass units, and sometimes up to 100,000 (Thurman 1985).

Perdue and Ritchie (2003) state that approximately 60% of DOC in typical natural water is HS, and HS is generally distributed in a 3:1 ratio between FA and HA.

HS contain a large number of chemical functional groups (e.g. C=O, O-H, and N-H). Consequently there is no single analysis method to isolate and fractionate HS (Peuravuori et al. 2002). Although the chemical structure of HA and FA in HS is not precisely known, the nature of the major functional groups present is fairly well defined. The major functional groups that contain oxygen in aquatic HS are carboxyl, hydroxyl, carbonyl, and phenolic hydroxyl (Thurman 1985). The general chemical and physical properties of HA and FA are presented in Table 2.1 (Snoeyink and Jenkins 1980). Often, HS are defined operationally based on the procedures of isolation and fractionation. They are described as those organic compounds that have water-repelling molecular structures and are attracted to macroporous[1] resins such as XAD-4 and DAX-8 resins (Leenheer and Huffman 1976).

Table 2.1 General chemical and physical properties of HA and FA (from Snoeyink and Jenkins 1980).

Property	HA	FA
Elemental Composition (% by weight)		
C	50-60	40-50
H	4-6	4-6
O	30-35	44-50
N	2-4	< 1-3
S	1-2	0-2
Solubility in strong acid	Not soluble	Soluble
Molecular weight range	Few 100 – several million	180-10,000
Functional group distribution	Percent of oxygen in indicated functional group	
carboxyl –COOH	14-45	58-65
phenol -Ph	10-38	9-19
Alcohol –R-OH	13-15	11-16
Carbonyl –C=O	4-23	4-11
Methoxyl –O-CH_3	1-5	1-2

2.2 Isolation and Fractionation of DOC

In order to understand the characteristics of DOC, it is often necessary to isolate and fractionate the DOC into separate molecular groups having similar chemical or

[1] Macroporous: A macroporous material is a material containing pores with diameters greater than 50 nm.

physical characteristics. Two commonly used methods to fractionate DOC are adsorption on macroporous resins such as XAD/DAX, and separation by membranes.

2.2.1 Fractionation of DOC by Adsorption on Macroporous Resins

Since the development of macroporous resins, the resin column adsorption fractionation technique which simultaneously isolates and fractionates specific organic solutes from other dissolved constituents has been widely used (Thurman and Malcolm 1981; Peuravuori et al. 2002). Nonionic macroporous adsorption media composed of styrene divinylbenzene (e.g. XAD-2, XAD-4) or acrylic esters (e.g., XAD-7, XAD-8, or DAX-8 material) are commonly used (Abbt-Braun et al. 2004). In current studies of DOC isolation, XAD-8, or DAX-8 are the most commonly used resin. The manufacture of the widely used Amberlite XAD-8 resin ended some years ago and it is not commercially available any more. Therefore, Supelite™ DAX-8 resins which has similar structure have been substituted for XAD-8 resin in many DOC fractionation processes (Chow 2006). This type of resin has a large specific surface area and numerous sites for reversible adsorption of organic molecules. This feature makes them well suited for the isolation and fractionation of aquatic DOC (Perdue and Ritchie 2003). XAD-8 (or DAX-8) is recommended for isolation of hydrophobic organic solutes because it can recover over 96% of HS present (Malcolm and MacCarthy 1992). The resins XAD-2 and XAD-4 are unsatisfactory for recovering high molecular weight hydrophobic organic solutes in natural water (Gustafson et al. 1968; Leenheer and Huffman 1976).

The organic fractions commonly retained by using XAD/DAX resins are operationally defined as hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophilic base (HPIB), hydrophilic acid (HPIA), and hydrophilic neutral (HPIN). Hydrophobic fractions are HS while the hydrophilic fractions are NHS. An overview of the fractionation procedure is shown in Figure 2.1. In the procedure, XAD resin or DAX resin first isolates the HS (HPOB, HPOA and HPON) from the water sample (Imai et al. 2001). The second column containing cation exchange resin is then used to isolate the HPIB fraction from the water sample. The HPIA fraction is retained in the last column containing anion exchange resin. Finally, the remaining sample that passes through the last column is the HPIN fraction.

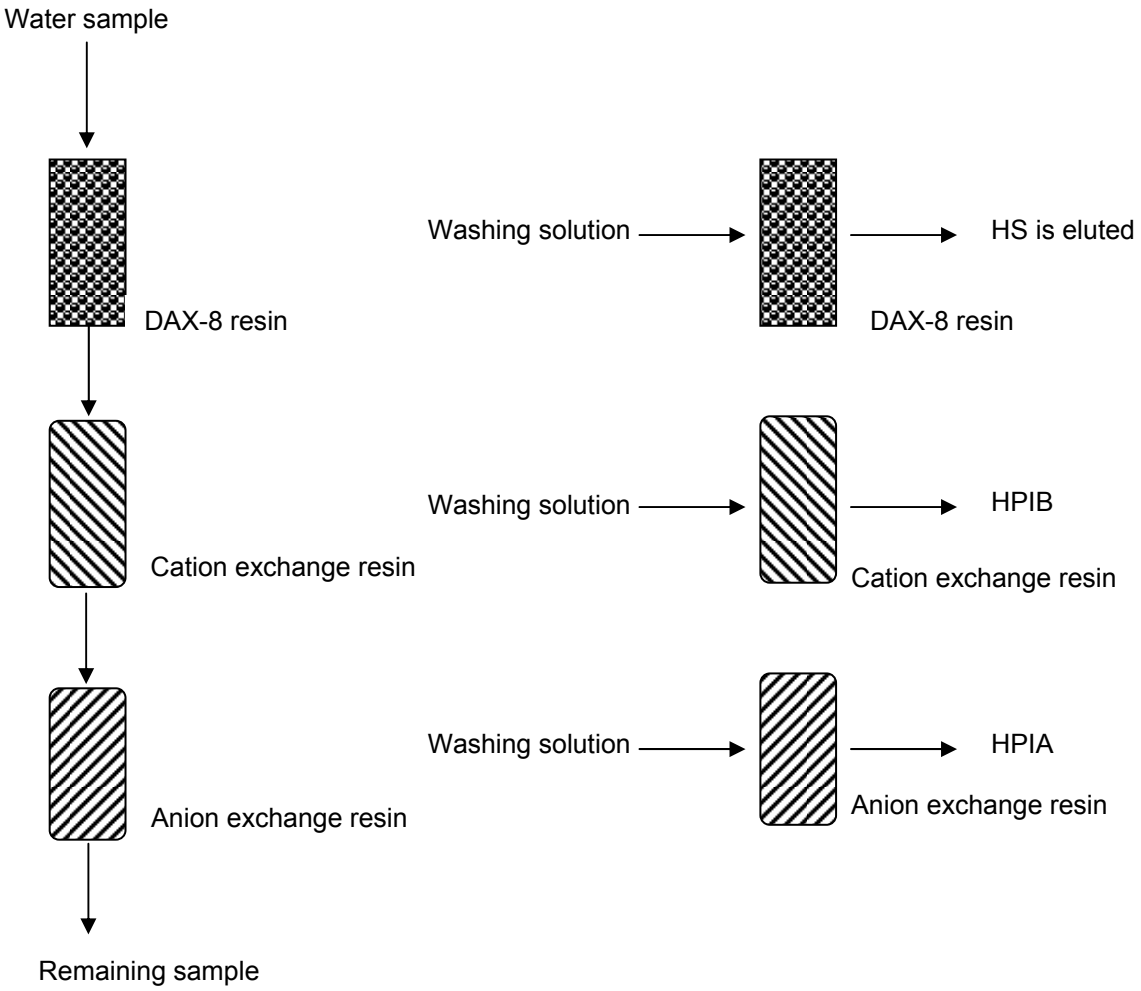


Figure 2.1 Flowchart of the resin fractionation method (adapted from Abbt-Braun et al. 2004).

In the resin column fractionation technique the hydrophobic fractions are defined as those organic solutes adsorbed on macroporous resin surfaces of low and intermediate polarity[2] (Leenheer and Huffman 1976). Supelite™ DAX-8 has moderate polarity and is often used for isolation of hydrophobic fractions. Hydrophobic organic compounds have portions of their molecular structure that repel water but can be attached to hydrocarbon surfaces of the macroporous resin by means of Van der Waals force (Leenheer and Huffman 1976; Aiken et al. 1979). Van der Waals force is used as a synonym for the summation of intermolecular forces which act between stable

[2]Polarity: In chemistry, polarity refers to the electric dipole-dipole intermolecular forces between one molecule or another molecule.

molecules and is weak compared to chemical adsorption (IUPAC 1994). Adsorption[3] rather than absorption[4] is the main binding mechanism of the organic solutes on the surface of DAX-8 resins (Leenheer and Huffman 1976). In the process, solute molecules first transport to the resin surface, then diffuse through the pores of the resin, and finally are adsorbed on the internal surfaces of the resin.

Most dissolved organic compounds show some affinity for XAD-8/DAX-8 resin, therefore their classification as hydrophobic or hydrophilic is not clear-cut (Leenheer 1981). However the terms "hydrophobic and hydrophilic" used in the resin column fractionation are operationally defined by the separation procedures (Leenheer and Huffman 1979). The dissolved organic compounds that adsorb on XAD-8 are termed hydrophobic, whereas those not adsorbed on the XAD-8 resin are termed hydrophilic. Although the hydrophobic DOC is largely water insoluble, hydrophilic portions of very large complex aquatic DOC molecules can cause the hydrophobic portions to be more water soluble.

In the resin column fractionation technique, HPOB, HPOA, and HPON can be selectively eluted from the resin by adjusting the pH of the wash solution. HPOA and HPOB are functionally defined as the hydrophobic organic compounds that are desorbed by aqueous base and acid solutions, respectively (Leenheer and Huffman 1976). HPON is defined as the hydrophobic organic compounds that are not desorbed by either aqueous base or acid solution.

According to Leenheer and Huffman (1976), hydrophilic organic compounds have functional groups distributed over their molecular structure such that the molecule can not act in a hydrophobic manner. Hydrophilic organic compounds are usually separated from water samples by using ion exchange resins. An ion exchange resin is composed of three important elements: an insoluble matrix, fixed ionic sites, and ions of opposite charge attached to the fixed sites (Small 1989). HPIB and HPIA are hydrophilic organic compounds that are adsorbed on cation and anion exchange resins

[3] Adsorption: It is the adhesion of molecules to a surface. The adhesion to the surface is usually weak and reversible.
[4] Absorption: It is a physical or chemical phenomenon or a process in which one substance enters a bulk phase through minute pores or spaces between its molecules.

respectively. HPIN is not adsorbed to either cation or anion exchange resin and therefore remains in solution after the adsorption procedure. HPIB can be efficiently adsorbed on strong acid cation exchange resins and can be desorbed by ammonium hydroxide. However, according to Peuravuori et al. (2002), the reaction of ammonia with ketone, ester, and quinine groups may alter these compounds during the elution process. It is very difficult to elute HPIA from strong base anion exchange resins, however HPIA can be recovered very effectively from weak base anion exchange resins (Peuravuori et al. 2002). The commonly used ion exchange resins are AG-MP-50 cation resin and WA 10 weak anionic resin.

The resin column fractionation procedures can be applied to water samples whose DOC concentrations range between 5 and 25 mg/L, and whose specific conductance is less than 2000 μmhos/cm at 25ºC (Leenheer and Huffman 1979). DOC concentrations greater than 25 mg/L should be diluted with organic ultra pure water to a DOC concentration less than 25 mg/L prior to analysis. Marhaba et al. (2003) proposed a modified DAX-8 resin column fractionation procedure for low DOC concentration ($\leq$ 5 mg/L). The procedure can provide an accurate measure of DOC distribution in each fraction. This technique was developed by using three columns of DAX-8 resin, one column of AG-MP-50 cation resin, and another column of WA 10 weak anionic resin in sequence. The first three columns adsorb HS from which HPOB, HPOA, and HPON can be eluted using methanol, HCl and NaOH respectively. AG-MP-50 cation resin was used to adsorb HPIB from the sample and WA 10 weak anionic resin to adsorb HPIA. The remaining DOC in the sample after passing through the five columns is HPIN. This procedure was used for fractionation of water samples in this project.

The XAD/DAX resin column fractionation technique is widely used in water treatment plant evaluation, oil refinery effluent characterization and other research areas. Marhaba (2000) used XAD resin fractionation analysis results to develop a fluorescence technique for rapid identification of dissolved organic compounds. Fractionation and characterization of dissolved organic matter in a shallow eutrophic lake was conducted by Imai et al. (2001) using the XAD adsorption technique. Kim and Yu (2005) also used this technique to isolate DOC from source and treated waters at a conventional water treatment plant to investigate the water characteristics. Their results showed that

the trihalomethanes (THMs) formation potential was highly influenced by the hydrophobic fraction, and that conventional water treatment could remove the hydrophobic fraction more effectively than the hydrophilic fraction.

Li et al. (2005) employed the XAD-8 resin column fractionation technique and several spectroscopic methods for comprehensive characterization of oil refinery effluent. The XAD-8 resin column fractionation technique was also employed to classify the hydrophobic organic content of a drinking water source (Kanokkantapong et al. 2006). They found that the hydrophobic organic compounds contributed as much as 56% of the total haloacetic acid formation potential. Drewes et al. (2006) investigated the characteristics and fate of organic compounds in reclaimed water used for ground water recharge. In their study, water samples were fractionated into hydrophobic acids, transphilic acids, and hydrophilic carbon using an alternate XAD resin-based protocol. Dai et al. (2006) conducted research on the characterization of FA obtained by sequential extractions with pH buffers, water, and ethanol from paddy soils by eluting FA through XAD-8 resin.

2.2.2 Fractionation of DOC by Membranes

Ultrafiltration (UF), microfiltration (MF), reverse osmosis (RO), and nanofiltration (NF) membranes are commonly used to separate DOC into size fractions. In the membrane separation technique, a large volume of water can be processed in a short period of time and the structural properties of the organic matter will never be altered (Peuravuori et al. 2002). During processing, water samples are placed under pressure and passed through a semipermeable membrane to retain a concentrated solution (retentate solution) (Perdue and Ritchie 2003). The concentrated solution can retain more than 90% of the original DOC, but it always contains a relatively high inorganic carbon concentration which will interfere with further analysis (Abbt-Braun et al. 2004).

Different pore size membranes can be used to further separate the concentrated solution into different DOC molecular size fractions. Porous membranes such as UF and MF use the sieving mechanism to separate molecules into different size ranges (Thanjekwayo 2005). Non-porous membranes (RO and NF) use differences in

molecular solubility and diffusivity in the membrane to separate the solute from the solvent (Lonsdale 1965).

2.2.3 Comparison of Resin and Membranes Fractionation

Resin column fractionation methods separate the organic molecules from a water sample on the basis of hydrophobicity, and XAD-8/DAX-8 resin is specifically designed to isolate the HS from water (Perdue and Ritchie 2003). Membrane methods separate the molecules mainly on the basis of molecular size rather than isolating specific fractions such as HA or FA or specific functional groups (Ma et al. 2001). Because HS organic compounds are the main precursors for the formation of DBP (Kanokkantapong et al. 2006; Kim and Yu 2005), the XAD-8/DAX-8 resin column fractionation method is generally more suitable for DOC characterization analysis.

During the XAD-8/DAX-8 resin column fractionation procedure, loss or transformation of certain organic compounds is unavoidable, but minor losses are of less concern in the context of understanding DOC distribution. The fractionation procedure (as described in Section 2.2.1) doesn't have to recover 100% of the DOC as long as a representative portion can be recovered that is suitable for spectral analysis and reactivity studies (Leenheer et al. 2000). In the membrane technique, in addition to the inorganic carbon interference, membrane fouling is a problem which strongly affects the size cut-off of the membranes (Abbt-Braun et al. 2004). Membranes adsorb the higher molecular size organic compounds (i.e., HS) preferentially. If the organic concentration of the water exceeds a critical value, a gel like layer will form and increases the resistance to water flux (Chang and Benjamin 1996, Chang et al. 1998, Peuravuori et al.2002). Therefore, for the characterization of aquatic DOC, the XAD-8/DAX-8 resin fractionation procedure is preferred.

2.3 DOC Concentration Measurement

The most commonly used approach to quantify DOC is measuring the organic carbon mass in a sample using a total organic carbon analyzer. In Standards Methods 5310 (APHA et al. 2005), high temperature combustion, persulfate-ultraviolet or heated-persulfate oxidation and wet-oxidation methods are described. These methods utilize

high temperature, catalysts, and oxygen, or lower temperature (<100 ^{o}C) with ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide (CO_2). The CO_2 is then measured by a non-dispersive infrared detector and the results are related back to the DOC concentration in the water sample via a calibration to known standard solutions.

2.4 Ultraviolet and Visible Spectroscopy (UV/VIS)

UV/VIS spectroscopic methods provide information about compounds with unsaturated bonds (e.g. aromatics). For these compounds light absorption is mainly caused by the excitation of the outer electrons of the atom or molecule (Pons et al. 2004). The absorption of both VIS and UV light by the water sample is attributed to the aromatic chromophores[5] (light absorbing sub units) present in the DOC, primarily in HS molecules. Because UV light is more readily absorbed by organic compounds UV spectroscopic methods are more popular than VIS. UV absorbance is attractive also because it is simple to carry out, the required instrumentation is relatively inexpensive, and minimal sample preparation is required (Peuravuori et al. 2002). Furthermore, as indicated by the literature, HS are likely to be the predominant organic compounds involved in the formation of DBPs.

UV absorption in the wavelength range from 200 to 400 nm is widely attributed to the aromatic chromophores (light-absorbing sub-units) present in DOC, primarily in humic substances (Peuravuori et al. 2002). An UV spectrum is a plot of light absorbance versus wavelength in the ultraviolet range. However, UV absorption spectra are typically broad and nearly featureless (Wang et al. 1990). Therefore, UV spectra are difficult to interpret because there are relatively few adsorption peaks but many possible chromophores (Peuravuori et al. 2002). In HS, the absorption mostly results from chromophores with C=C and C=O double bonds (Abbt-Braun et al. 2004). As a matter of practicality, the wavelength of 254 nm in UV light spectrum is commonly employed to roughly indicate the level of the aromatic materials in the water sample (Allpike et al. 2005; Chen et al. 2003; Chouparova et al. 2004; Croue et al. 2000; Kanokkantapong et al. 2006).

[5] Chromophore: It is the chemical group in a molecule that gives color to a molecule.

The specific UV absorbance (SUVA) (the ratio between UV absorbance and DOC mass concentration) is often calculated and used as an indicator of the aromatic, hydrophobic characteristics of the aquatic DOC. High SUVA values often indicate high molecularsize, hydrophobic and aromatic components (Jame et al. 2003; Kanokkantapong et al. 2006; Liang and Singer 2003; Thompson et al. 1997). Therefore, SUVA can be used as an indicator of DBP organic precursors (Krasner and Amy 1995). Kim and Yu (2005) also used the ratio of UV absorbance at 253 and 203 nm (UV_{253}/UV_{203}) to indicate the functional distribution of DOC between the phenolic fraction and carboxylic fraction. The higher the UV_{253}/UV_{203} ratio, the larger the phenolic content and an increased potential for formation of DBP (Kim and Yu 2005).

2.5 Infrared (IR) Spectroscopy

2.5.1 Basis of IR Spectroscopy

IR is used to identify the functional groups in organic compounds based on the characteristic frequency of bond vibrations caused by stretching and bending motions. When a compound is subjected to radiation with a frequency that is equal to the bond vibration frequency, the molecule absorbs energy and exhibits an absorption band in the infrared spectrum (Bruice 2004). Each functional group has its own specific absorption bands which are indicated by wavenumber υ (Bruice 2004). Wavenumber is given by

$$\upsilon\ (\text{in cm}^{-1}) = 10^4 / \lambda\ (\text{in } \mu\text{m})$$

where λ is the wavelength in μm.

The wavenumber range of the IR spectrum which is of greatest interest to researchers is approximately 4000-600 cm^{-1} (Sorrell 1988). Absorption that occurs in this region mainly results in the excitation of vibrational, rotational and bending modes of the organic molecules. Figure 2.2 gives a visual representation of these vibrational modes. The most important absorptions in the IR spectrum are the simple stretching vibrations. The stretching vibrations of typical organic molecules tend to fall within distinct regions of the IR spectra as listed below (Young 1996):

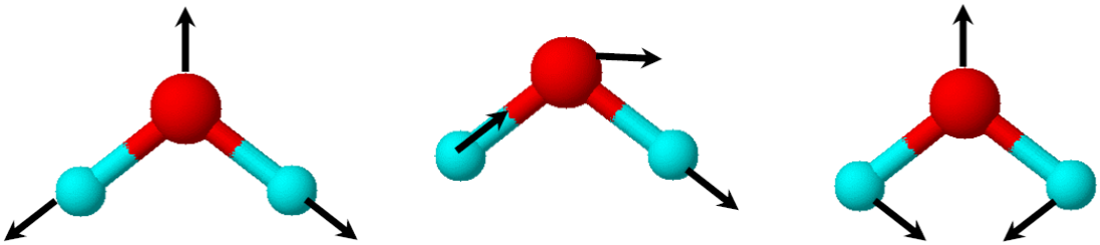
3700-2500 cm^{-1}: X-H stretching (X=C, N, O, S)

2300-2000 cm^{-1}: C≡X stretching (X=C or N)

1900-1500 cm^{-1}: C=X stretching (X=C, N, O)

1300-800 cm^{-1}: C-X stretching (X-C, N, O)

Because most organic molecules have single carbon bonds, the region below 1300 cm^{-1} becomes quite complex and is called the fingerprint region.



Symmetric Stretching **Asymmetric Stretching** **Symmetric Bendind**

Figure 2.2 Typical vibration modes
(from http://www.chem.uic.edu/web1/OCOL-II/WIN/SPEC/IR).

2.5.2 Interpretation of IR Spectra

Comprehensive interpretation of IR spectra of pure organic compounds is complex because many absorption bands are generated. However, it is easier to interpret the IR spectra of the aquatic DOC because only the strongest bands can be identified and associated with the predominant structures (Peuravuori et al. 2002). The frequency assignment approach is the most popular and straightforward method to interpret IR spectra (Sorrell 1988). This method doesn't need other information about the molecular structure of the organic compounds.

If the general molecular formula is known an alternative strategy is to check for functional groups with a heteroatom[6] present. For example, if the compound only contains C, H, and O, there are only a few possible functional groups. First, check the O-H group at 3600-3200 cm^{-1}. Next examine the region between 1800 and 1650 cm^{-1} associated with carbonyl group. If neither of the regions is represented, then the molecule must be ether which can be confirmed by checking for the C-O stretching band at 1300-1000 cm^{-1}. Also the compounds that contain nitrogen, sulphur and halogens can be targeted by checking their related functional groups (Sorrell 1988).

[6] Heteroatom: It refers to any atom that is not carbon or hydrogen in the structure of a compound.

In this project, the composition of the DOC compounds is unknown, so the frequency assignment approach is more suitable to use. The frequency assignment approach is illustrated in Figure 2.3 and described by Sorrell (1988). A summary of this procedure is presented below.

When interpreting an IR spectra, the first step is to look at the carbonyl (C=O) bond stretching frequency in the region near 1700 cm^{-1}. This stretching frequency is always intense and will rarely be confused with any other absorption. If no absorption band is observed in this region, several classes of compounds can be eliminated (see Figure 2.3). If a peak is present near 1700 cm^{-1} the organic compounds can be classified into aldehydes, amides, anhydrides, carboxylic acids, acid chlorides, esters, or ketones. Confirmation of additional absorption frequencies can then be used to distinguish the carbonyl-containing groups from each other. Table 2.2 presents detailed information on the distinguishing spectroscopic features of various carbonyl compounds.

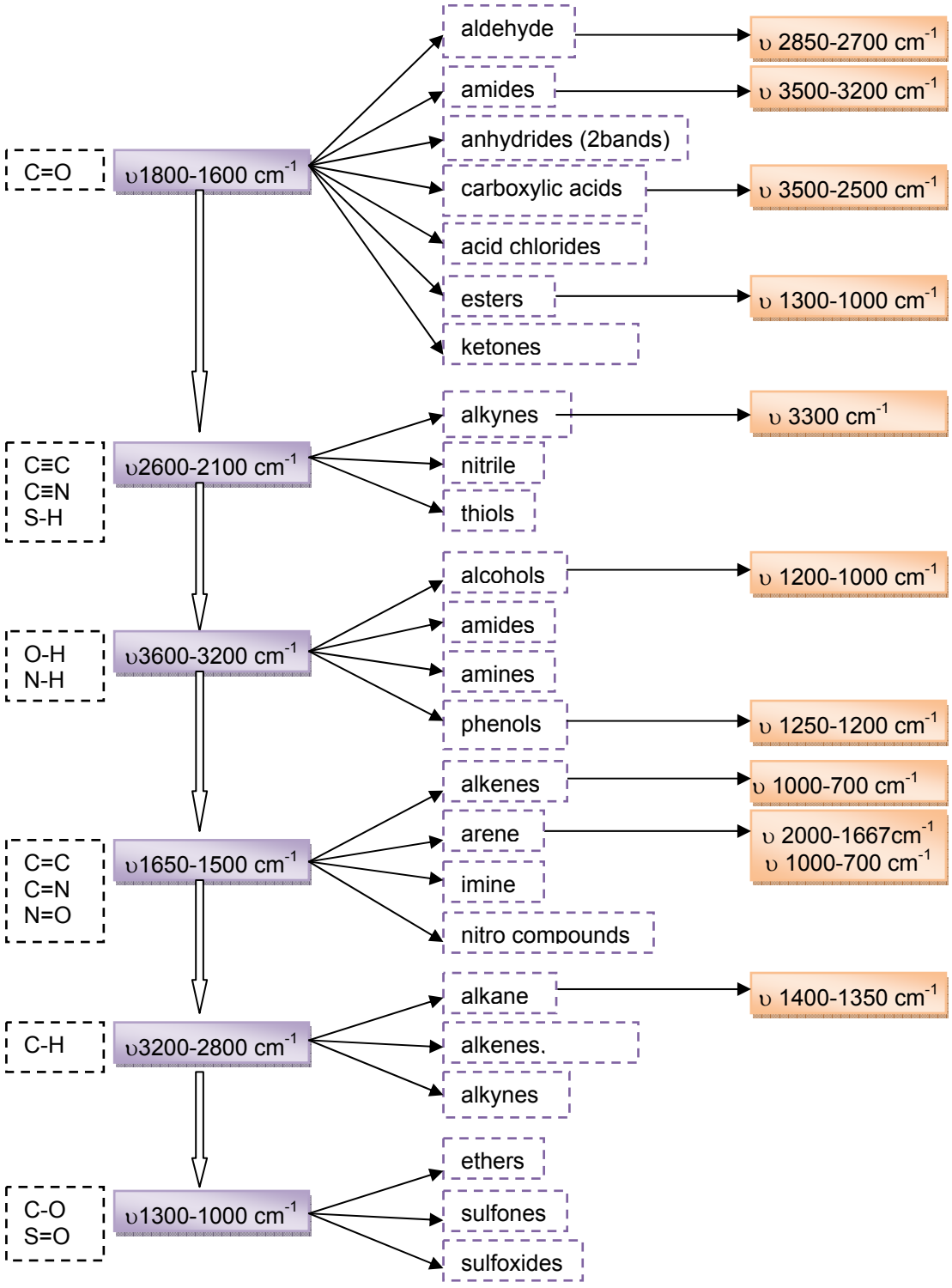


Figure 2.3 Systematic strategy of IR spectra interpretation (from Sorrell 1988).

Table 2.2 Distinguishing spectroscopic features for carbonyl compounds (Sorrell 1988; Smith 1999).

C=O compound types	υ (cm^{-1})	Principal spectroscopic features to look for
Acid chloride	Around 1800	Single C=O stretch near upper end of the carbonyl range; presence of chlorine
Aldehyde	Saturated 1730±10 Aromatic 1710-1685	C-H stretch near 2720 (medium intensity)
Anhydride	Around 1820 and around1760	Two bands in the carbonyl region; broad and strong C-O stretch 1300-1000
Amide (1^o, 2^o)	1680-1630	N-H stretch around 3300; two bands in the carbonyl region (C=O stretch and N-H bend)
Amide, 3^o	1680-1630	Single C=O stretch near lower end of the carbonyl range
Carboxylic acid	1730-1680	O-H stretch between 3500 and 2500 (very broad and strong)
Ester	Saturated 1750-1735 Aromatic 1730-1715	Strong, broad band around 1200, sometimes more intense than C=O stretch
Ketone	Saturated 1715±10 Aromatic 1700-1640	No outstanding spectroscopic features

The next spectra region to examine is the one in which triple bonds and S-H stretching vibrations appear (2600-2100 cm^{-1}). Usually this region is almost blank, since relatively few molecules have those functional groups. But in the event there are absorption bands in this region, the functional groups present can be identified by the information presented in Table 2.3. In order to distinguish between alkynes and nitriles, Sorrell (1988) suggested using mass spectroscopy to confirm the absence or presence of nitrogen.

Table 2.3 Ranges of stretching frequencies for groups absorbing in the triple bond region (Sorrell 1988; Smith 1999).

Triple bond Functional Group	υ (cm^{-1})
Alkyne, terminal	2150-2120
Alkyne, internal	2260-2190
Nitrile	Saturated 2260-2240; Aromatic 2240-2220
Thiol	2580-2550

Following the sequence shown in Figure 2.3, the high frequency region in which O-H and N-H stretching vibrations appear (3600-3200 cm^{-1}) is next. For O-H stretching,

the band in carboxylic acid begins around 3500 cm^{-1} and extends to about 2500 cm^{-1}. However, the band in alcohols and phenols is not as broad as that. If the band is ascribed to the O-H group, examining the C-O stretching region between 1250 and 1000 cm^{-1} can differentiate between the different types of alcohols and phenols. Since the DOC spectrum is the combination of various organic compounds, this region can not be used to distinguish O-H stretching from N-H stretching. Further clarification can be achieved by checking the N-H bending region (1640-1560 cm^{-1}) which is unique for the N containing organic compounds. Table 2.4 illustrates the frequency range for O-H and N-H bond stretching by compound type.

Table 2.4 Summary of frequency ranges for OH and NH bond stretching by compound type (Sorrell 1988; Smith 1999).

OH or NH Compound type	OH or NH stretching υ (cm^{-1})[b]	Other diagnostic band υ (cm^{-1})
Alcohol (H-bonded) ("free" OH)	3500-3200 (s, br) 3650-3600 (s, sh)	1210-1000
Phenol (H-bonded) ("free" OH)	3500-3200 (s, br) 3650-3600 (s, sh)	1260-1200
1^o amine	Saturated 3380-3280 (v, 2 bands) Aromatic 3500-3340(v, 2 bands)	N-H bending:1650-1580
2^o amine	Saturated 3320-3200 Aromatic ~3400	N-H bending: ~1500

[b]s=strong, br=broad, sh=sharp, v=variable.

The next step is to examine the double bond stretch region (1650 to 1550 cm^{-1}) of C=C, C=N, and N=O. The latter two are fairly rare among organic compounds but many compounds contain C=C bonds. For the C=C bond stretching, the major issue is to distinguish between alkene and arene (aromatic hydrocarbons). Table 2.5 and 2.6 present the frequency bands of alkenes and benzene rings. When interpreting spectra in the double bond stretch region it is best to combine all the information together and to examine it collectively.

Table 2.5 The C=C stretching, C-H stretching, and C-H bending bands of alkenes (Sorrell 1988; Smith 1999).

Alkene structure	C=C stretching υ (cm^{-1})	C-H stretching υ (cm^{-1})	Out of plane C-H bending υ (cm^{-1})
Vinyl	1660-1630	3090-3075	990±5 or 910±5
Vinylidine	1660-1630	3090-3075	890±5
Cis	1660-1630	3050-3000	690±50
Trans	1660-1665	3050-3000	965±5
Trisubstituted	1660-1665	3050-3000	815±25
Tetrasubstituted	1660-1665	-	-

Table 2.6 Bands for mono- and di-substituted benzene ring (Sorrell 1988; Smith 1999).

Benzene ring substitution pattern	Out of plane C-H bending υ (cm^{-1})
Mono	770-710
Ortho	770-735
Meta	810-750
para	860-790

The next region to check is the C-H stretching. Because almost every organic molecule contains hydrogen, the region of C-H stretching (3300-2700 cm^{-1}) provides little useful information about the compound structure especially for complex DOC samples. Therefore, it is better to use other more unique regions of the spectrum to identify the functional groups present.

The last region to examine in the IR spectrum is 1400-700 cm^{-1}. According to Sorrell (1988), this region may contain C-O, S=O, and C-X stretching bands. For ether C-O stretching frequencies (1300-1000 cm^{-1}), we need to be certain that the C-O frequency band is not from an alcohol or ester. For S=O stretching, sulfoxides have the range 1070-1030 cm^{-1} and sulfites have the range 1240-1180 cm^{-1} (Smith, 1999). Table 2.7 shows the frequency range of C-X bond stretching for halogenated organic molecules.

Table 2.7 The C-X bond stretching frequencies for halogenated organic molecules (Smith, 1999).

Bond	C-X stretching frequency υ (cm^{-1})
C-F	1300-1000
C-Cl	800-600
C-Br	650-550
C-I	570-500

2.5.3. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is the most commonly used IR spectroscopic method because of its sensitivity and relatively short time for analysis (Bruice 2004). A conventional IR method conducts a single scan to produce an infrared spectrum. An FTIR method uses an interferometer and makes several scans. It then uses Fourier transforms to convert the interferogram into an infrared spectrum. Recent research in IR spectroscopy always refers to FTIR. Several researchers (as described below) have used FTIR and fractionation procedures to characterize DOC collected from several stages of a water treatment process.

Kanokkantapong et al. (2006) used FTIR and resin fractionation to identify organic compounds associated with formation of haloacetic acids (HAAs) such as carboxylic acids, amides, amino acids, ketones and aromatics. They reported the HPOB and HPIB fractions were the most active precursors for HAAs.

Kim and Yu (2005) used FTIR to characterize the hydrophobic fraction of DOC in source and treated waters at a conventional water treatment plant. In their study, the aromatics in the hydrophobic fraction decreased while the aliphatics increased after pre-chlorination relative to the raw water. Following coagulation and sedimentation, the aliphatics decreased relative to the aromatics.

FTIR combined with resin fractionation of the organic compounds in water has also been widely applied in other research. For example, it was used to qualitatively describe the influence of HS functional groups on the performance of UF membranes (Lin et al. 2001); to compare the characteristics from three rivers in metropolitan Phoenix, AZ (Chen et al. 2003); to characterize oil refinery effluent-derived HS (Li et al. 2005); and to evaluate soil-aquifer treatment (Drewes et al. 2006).

FTIR spectroscopy with synchrotron light provides increased sensitivity for gaining insights into the nature of all organic compounds. The wavenumber resolution that can be achieved with synchrotron light is 1/14 μm^{-1}(Jones et al. 2006) compared to conventional FTIR with a resolution of 2 to 4 cm^{-1}(Lin et al. 2001; Drewes et al. 2006). Several studies have been done using FTIR and synchrotron light to analyze water extracts from harbour sediments and refinery effluents for petroleum organic compounds (Chouparova et al. 2004; Jones et al. 2006; Song et al. 2001).

2.5.4 DOC Sample Preparation for FTIR Measurement

Aqueous samples contain hydrogen bonds between hydroxyl groups. These bonds have a broad spectral response that masks the response of the dissolved organic components in the water in FTIR measurements. Therefore, in order to overcome this problem, the DOC content of the water must be concentrated into a solid for analysis.

Several researchers have used the pressed-pellet method to remove the hydrogen bonds interference (Chen et al. 2003; Drewes et al. 2006; Kanokkantapong et al. 2006; Kim and Yu 2005; Li et al. 2005). In this method the water samples are freeze-dried or air-dried to remove the water. Pellets were made using dried sample with different amount of optical-grade potassium bromide. Then the mixture was ground using a mortar and pestle and then pressed into a pellet using a screw press. The pellet sample was allowed to sit for at least 15 minutes prior to analysis to allow the KBr to fuse (Drewes et al. 2006). Lin et al. (2001) and Jones et al. (2006) simply placed the aqueous sample onto FTIR reflecting slides to evaporate and dry. The thin film of residue left on the slide was then subjected to FTIR scanning. The reflecting slides should be flat, organic compound free and non-infrared absorptive materials in order to get a good quality spectrum (Lin et al. 2001).

2.5.5 Other Spectroscopic Methods

Many DOC analysis methods are available, such as chemical/physical, chromatographic, and spectroscopic methods. Spectroscopic methods are popular because of their ease of operation and they are less time consuming. In addition to the spectroscopic methods mentioned above, several others are available, e.g. mass

spectrometry (MS), Raman, nuclear magnetic resonance spectroscopy (NMR) and fluorescence. MS is commonly used to determine the organic molecules in combination with other methods such as chemical/physical degradation methods, pyrolysis-GC/MS, hydrolysis-GC/MS, oxidation-GC/MS (Christman et al. 1989; Parson 1989; Schulten et al. 2002). Raman spectroscopy can also qualitatively determine the functional groups of organic compounds (Abbt-Braun et al. 2004). NMR spectroscopy has become the most important spectroscopic method for structural characterization of HS because information about chemical bonding modes of H, C, N, and P can be obtained by various NMR techniques (Abbt-Braun et al. 2004). However, the technique gives similar results to FTIR measurements (Kim and Yu 2005). Fluorescence is also mainly used to qualitatively measure the organic materials but it has also been studied for quantitative characterization of DOC (Bengraïne and Marhaba 2003; Chen et al. 2003). The main disadvantage for these spectroscopic methods is that they are more complicated and the equipment is more expensive.

2.6 Biodegradable Dissolved Organic Carbon (BDOC)

A portion of the DOC present in water can serve as carbon substrate for a mixed population of aerobic microorganisms. This portion is termed as BDOC and it tends to be the medium to small molecular size compounds which can be broken down by microorganisms (LeChevallier 1999). Since the molecular size is small, one could expect that higher the hydrophilic organic content, the higher the BDOC content. However, previous researchers found that no significant correlation was established between these two parameters （Martin-Mousset et al. 1997). BDOC is measured based on the heterotrophic bacteria aerobic reaction. The value of BDOC is the difference between initial DOC concentration and after-incubation DOC concentration at a specific temperature for specific period of time (Hesse et al. 1999; Nguyen et al. 2005). Typical BDOC concentrations are in the range of 0.1 to a few mg/L or around 10 to 30% of the total DOC (Escobar and Randall 1999).

CHAPTER 3. METHODOLOGY FOR DOC CHARACTERIZATION

3.1 Overview

The major objective of this research is to develop a FTIR spectroscopic method to characterize the DOC in water samples. Prepared samples of known DOC concentration (spiked samples) were used to develop the method. FTIR and conventional UV spectroscopic methods, DOC mass content, and THMFP measurements were also taken on the spiked samples. The spiked water samples were then separated into six fractions using the resin fractionation techniques described in Chapter 2, i.e. HPOB, HPOA, HPON, HPIB, HPIA, and HPIN.

Each fraction separated from the spiked water samples was analyzed using the FTIR method and the conventional measurements. The measurement results for each fraction were then compared to each other and with those of the original spiked sample. Therefore the usefulness of the FTIR spectroscopic method for DOC characterization was investigated based upon comparison of FTIR and conventional analysis results for un-fractionated and fractionated water samples. The DOC characterization method was then applied to several typical prairie water samples.

Suwannee River NOM in powdered form (ordered from the International Humic Substances Society (IHSS)) was dissolved in purified water treated by reverse osmosis and deionization (RO/DI) to produce a 'spiked' water sample. Initially 5 mg of powdered Suwannee River NOM was fully dissolved into 1 L RO/DI water. The measured DOC concentration of this mixture was 2.13 mg/L. Therefore, 30 mg of powdered Suwannee River NOM was needed to prepare a DOC sample of about 12 mg/L.

The spiked sample was then separated into six fractions, i.e. HPOB, HPOA, HPON, HPIB, HPIA, and HPIN using the resin fractionation techniques. A flowchart illustrating the general experimental procedure for the spiked sample is shown in Figure 3.1. Fractionation and analyses of spiked samples were conducted over the course of the study period from January 2008 to October 2008. The whole process was repeated four times.

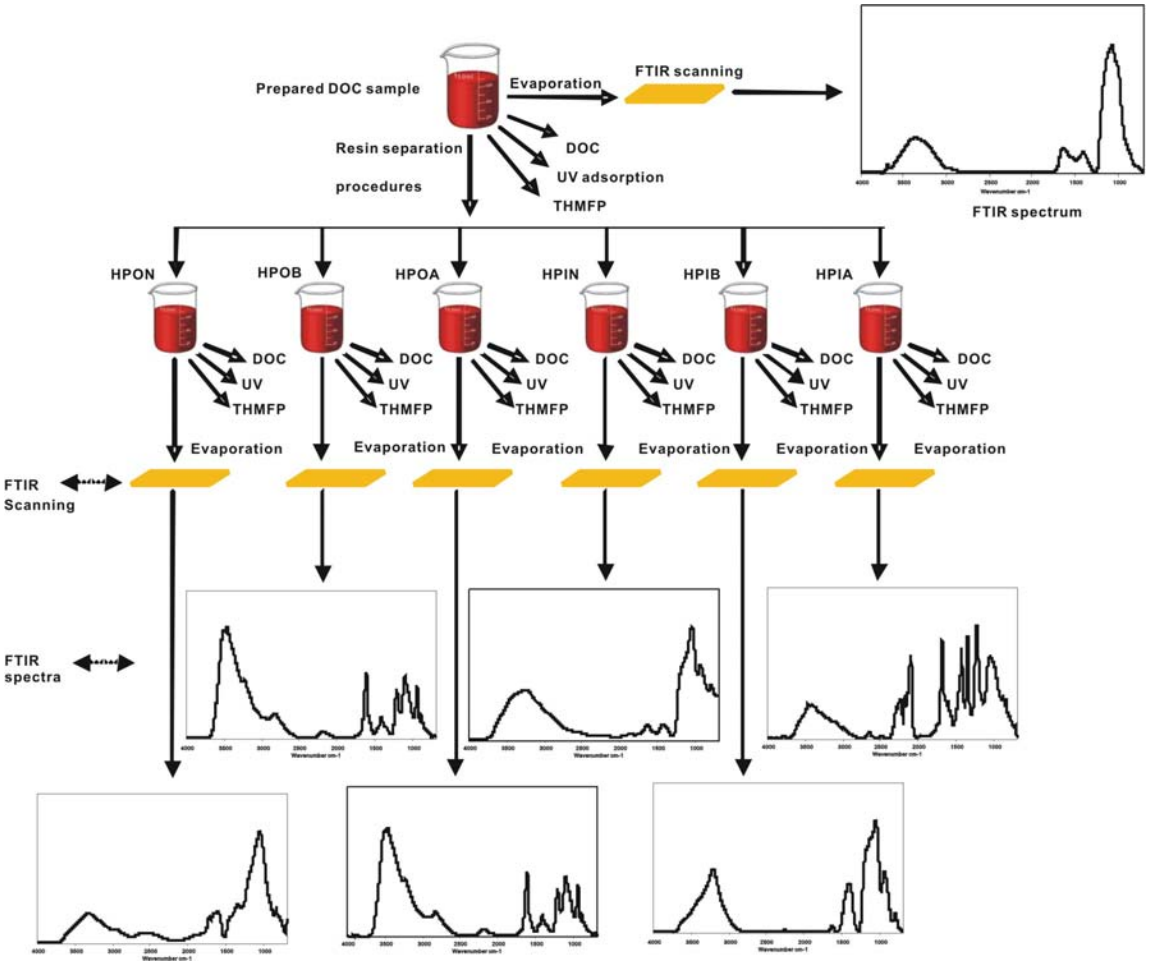


Figure 3.1 General experiment method for spiked sample with specific DOC concentration.

3.2 Materials for Spiked Sample Preparation

Powdered standard NOM (Cat. No. 1R101N) from IHSS was used to prepare spiked water samples of known DOC content. The average elemental composition of the standard NOM provided by the supplier is shown in Table 3.1. The standard NOM is prepared from the Suwannee River which rises in the Okefenokee Swamp in South

Georgia and flows southwest to the Gulf of Mexico. Decomposing vegetation provides most of the DOC. The DOC concentration in the Suwannee River ranges from 25-75 mg/L (http://ihss.gatech.edu).

The exact carbon content of a small quantity of the powdered NOM is not accurately known due to uncertainty in water content and small sample variability. Therefore the spiked sample concentrations were measured. The DOC concentration of the spiked sample was estimated to be 12± 0.6 mg/L. The estimate of "5% error" comes from three parts, the error in preparing the solution due to small sample variability in the NOM powder provided by IHSS, the balance measurement error, and the TOC analyzer analysis measurement error. Within these three types of error, the first one plays the key role in the estimated "5% error".

Table 3.1 Average elemental composition of Suwannee River NOM (http://ihss.gatech.edu).

Sample*	Cat. No.	H_2O	Ash	C	H	O	N	S	P
Suwannee River	1R101N	8.15	7.0	52.47	4.19	42.69	1.10	0.65	0.02

***H_2O** content is the %(w/w) of H_2O in the air-equilibrated sample (a function of relative humidity).
Ash is the %(w/w) of inorganic residue in a dry sample.
C, **H**, **O**, **N**, **S**, and **P** are the elemental composition in %(w/w) of a dry, ash-free sample.

RO/DI water was used for dilution water, glassware rinsing, resin washing and the preparation of blank samples. RO/DI water was prepared in the Environmental Engineering Lab at the College of Engineering, University of Saskatchewan. The RO/DI water purification process is illustrated in Figure 3.2. The softening process removes the multivalent cations contained in the tap water such as calcium and magnesium. Following that a RO membrane removes organic content, and 98% of the total dissolved solids (TDS) and suspended solids. Then a high capacity ion exchange bed removes TDS down to 99.5%. Next an initial high purity ion exchange bed removes TDS down to 99.8% and finally the last high purity ion exchange bed removes TDS down to 99.9%. The highly purified water eluted from the last bed is called RO/DI water which has DOC concentration less than 0.01 ±0.0005 mg/L.

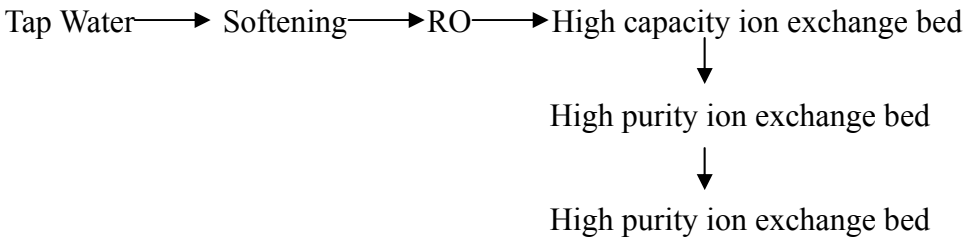


Figure 3.2 Flow chart of RO/DI water purification.

Three types of resins were used for fractionation of the water samples: DAX-8 (Superlite^{TM} DAX-8, SUPELCO, Supelco Park, Bellefonte, PA); AG-MP-50 cationic resin (BIO-RAD, Hercules, CA); and Diaion WA 10 (SUPELCO) weak anionic resin. Reagent grade methanol, acetone, NaOH, and HCl were used to clean and elute the DOC fractions from the resins. The fractionation columns were prepared using 2.45 cm inner diameter glass columns with 1 m (containing DAX-8 resin), 1.5 m (containing AG-MP-50 cationic resin) and 0.5 m (containing Diaion WA 10 resin) length.

3.3 Resin Cleanup Procedures and Regeneration

3.3.1 Superlite^{TM} DAX-8

It is very important to thoroughly clean the resin before the fractionation process because un-cleansed resin will have a significant level of DOC bleeding (Kim and Yu 2005) which will cause an error in the measured DOC content of the adsorbed fraction. The cleaning method used was modified from the sequential Soxhlet extraction method proposed by Thurman and Malcolm (1981) and Leenheer (1981). The modified cleaning and regeneration procedures described below are consistent with those used by Ma et al. (2001) and Kim and Yu (2005).

DAX-8 resin was packed into the glass column and the two ends of the column were stuffed with glass wool. The resin was then rinsed with RO/DI water until the DOC concentration of the effluent from the column decreased to less than 50 mg/L. The remaining organic contaminants were removed by sequentially flushing the resin with methanol for 24 hr. In each flush the first 200 mL of rinse solvent was discarded and the remaining solvent recycled through the resin column. Finally the resin column was rinsed sequentially with RO/DI water until the DOC of the effluent was less than

0.2 mg/L and the conductivity was lower than 2 μmho/cm. The cleaning steps outlined above were repeated to regenerate the DAX-8 resin after each fractionation experiment.

3.3.2 Bio-Rad AG-MP-50 Cation Exchange Resin

The cleaning method used for the cation exchange resin was according to Leenheer (1981). The resin was flushed sequentially with methanol for 24 hours using a peristaltic pump setup. The first 200 mL of methanol effluent was discarded and the remaining methanol was repeatedly recycled through the resin column. The resin was then rinsed with RO/DI water and a 2 N NaOH solution was passed through the column until the breakthrough occurred. Finally four bed volumes of 2 N HCl was passed through the column and the resin rinsed with RO/DI water until the specific conductance of the effluent was less than 5 μmho/cm. This cleaning process was repeated to regenerate and reuse the cation exchange resin after each fractionation experiment.

3.3.3 Diaion WA-10 Weak Basic Anion-exchange Resin

The cleaning method for the anion exchange resin was modified from the method proposed by Leenheer (1981). Fines were first removed from the resin by slurrying it in RO/DI water and then decanting fine suspended particulates. The resin slurry was then slowly poured into the glass column plugged at the bottom with glass wool. The excess water was drained through the bottom of the column, but the liquid level was not allowed to fall below the top of the resin bed. The resin was then flushed sequentially with acetone for 24 hours using a peristaltic pump setup. The first 200 mL of acetone effluent was discarded and the remaining acetone was repeatedly recycled through the resin column.

Next 1 N HCl was passed through the resin until the DOC in the effluent was less than 0.5 mg/L and then 1 N NaOH was pumped through the column until the resin was in the free-base form. In the free-base form the resin has a yellow colour whereas the HCl form has an off white colour. Finally, the resin was rinsed with RO/DI water until the specific conductance of the effluent was less than 10 μmho/cm. This cleaning process was repeated to regenerate and reuse the anion exchange resin after each fractionation experiment.

3.4 Column Breakthrough Tests

Breakthrough tests were conducted to determine the resin quantity required to adsorb the target organic fraction from a specified volume of water sample passing through the column.

3.4.1 DAX-8 Resin

Approximately 25 mL of DAX-8 resin was packed into a 2.45 cm dia. × 50 cm long glass column. Two glass columns were prepared and filled with the same amount of resin. Applying the procedure given in Leenheer (1981), the water quantity that can be treated by 25 mL of resin is theoretically 1200 mL. Allowing for a safety factor of two, then at least 600 mL of water can be fully treated.

In the break through test, 30 mg IHSS Suwannee River NOM powder was dissolved in RO/DI water to produce a total volume of 1000 mL. The prepared DOC concentration was 11.73 mg/L, UV adsorption at 254 nm was 0.539 and pH was 7.07. The sample was passed through the resin packed column at a flow rate of 5 mL/min controlled by a peristaltic pump. Sequential effluent samples of 60 mL were taken and analysed for DOC concentration and UV 254 nm absorbance. The tests were repeated twice.

3.4.2 AG-MP-50 Cation Exchange Resin

According to the documentation supplied by the resin manufacturer (BIO-RAD, Hercules, CA) approximately 5 grams of resin is required to treat 100 mL of sample. Therefore, if about 20 g resin was packed into a glass column then 400 mL of water could be fully treated. A solution of KCl with pH 2 ± 0.1 and conductivity 32 ± 1.6 μmho/cm was prepared to test the adsorption capacity of the resin. The tests were repeated twice. The flow rate was controlled at <5 mL/min.

3.4.3 WA-10 Weakly Basic Anion Exchange Resin

The capacity of WA-10 resin to adsorb a H_2SO_4 solution with pH 2 was determined. The capacity of WA-10 was estimated using the formula presented by Leenheer (1981) and further multiplied by a safety factor of 2. This calculation

indicated that 220 mL of WA-10 resin packed into the glass column can treat 10000 mL water.

3.4.4 Breakthrough Test Results

The column breakthrough test results confirmed the following quantities of resin are required to treat 4000 mL of water sample: 250 mL DAX-8 resin; 200 g of AG-MP 50 resin and 80 mL WA-10 resin. The detailed results of the breakthrough tests are presented in Appendix A.

3.5 DOC Fractionation Procedures

A modified DOC fractionation technique as described by Marhaba et al. (2003) was used in this investigation. The water samples were separated into six fractions: HPOB, HPOA, HPON, HPIB, HPIA, and HPIN as shown in Figure 3.3. The methods for the adsorption and separation of the HPOB, HPOA, and HPON fractions of HS were based on the conventional procedures illustrated in Figure 3.4. Modified procedures were developed by Marhaba et al. (2003) for low DOC content (<5mg/L) waters and could potentially be applied for the rapid detection of precursors for DBPs. As a matter of practice, the modified procedures for extracting HS fractions from the water samples were much easier to operate.

The fractionation procedure is briefly described as follows:

- First, all of the cleaned resin columns were rinsed with RO/DI water until the DOC in the effluent was less than 0.2 mg C/L and the conductivity was lower than 2 μmho/cm (Kanokkantapong et al. 2006).
- The water samples were initially adjusted to approximately pH 7 and then passed through the first of the series of resin columns (Figure 3.3);
- The first DAX 8 resin column adsorbed HPON and later desorbed the fraction by methanol extraction;
- The pH of the water sample was then adjusted to 10 before passing it through the second DAX 8 resin column where HPOB was adsorbed and later eluted using a HCl solution;

- Next the water sample was adjusted to pH 2 and passed through the third DAX 8 resin column. HPOA was adsorbed in the third column and later extracted using a NaOH solution;
- The fourth column containing AG-MP-50 cation exchange resin was used to adsorb the HPIB fraction that was later extracted using HCL;
- HPIA was adsorbed in the last resin column containing WA-10 anion exchange resin and later extracted using NaOH; and
- Finally the remaining water that has passed through all the columns contains HPIN which can not be adsorbed by any of the resins.

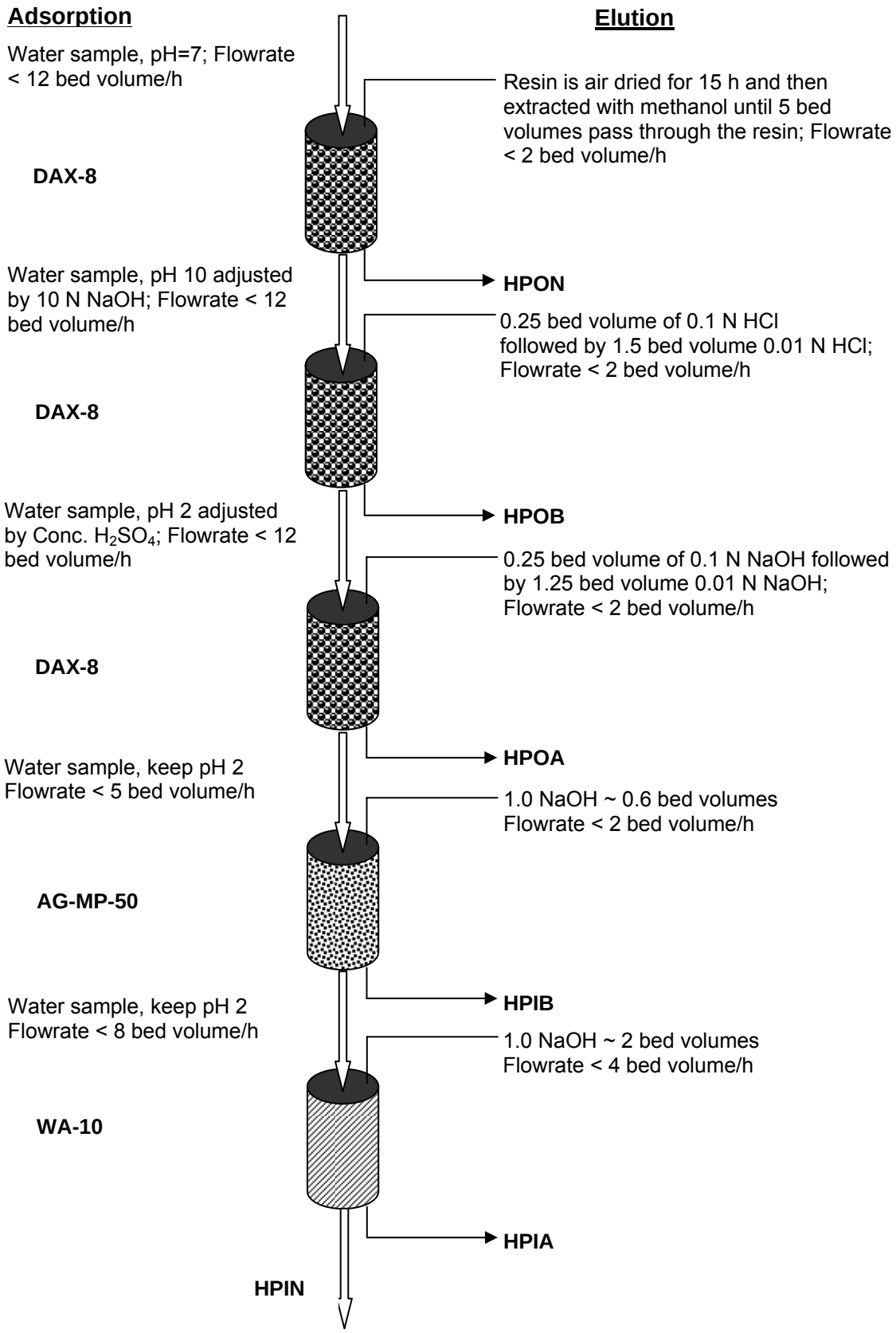


Figure 3.3 Schematic flow chart of the modified resin fractionation procedure.

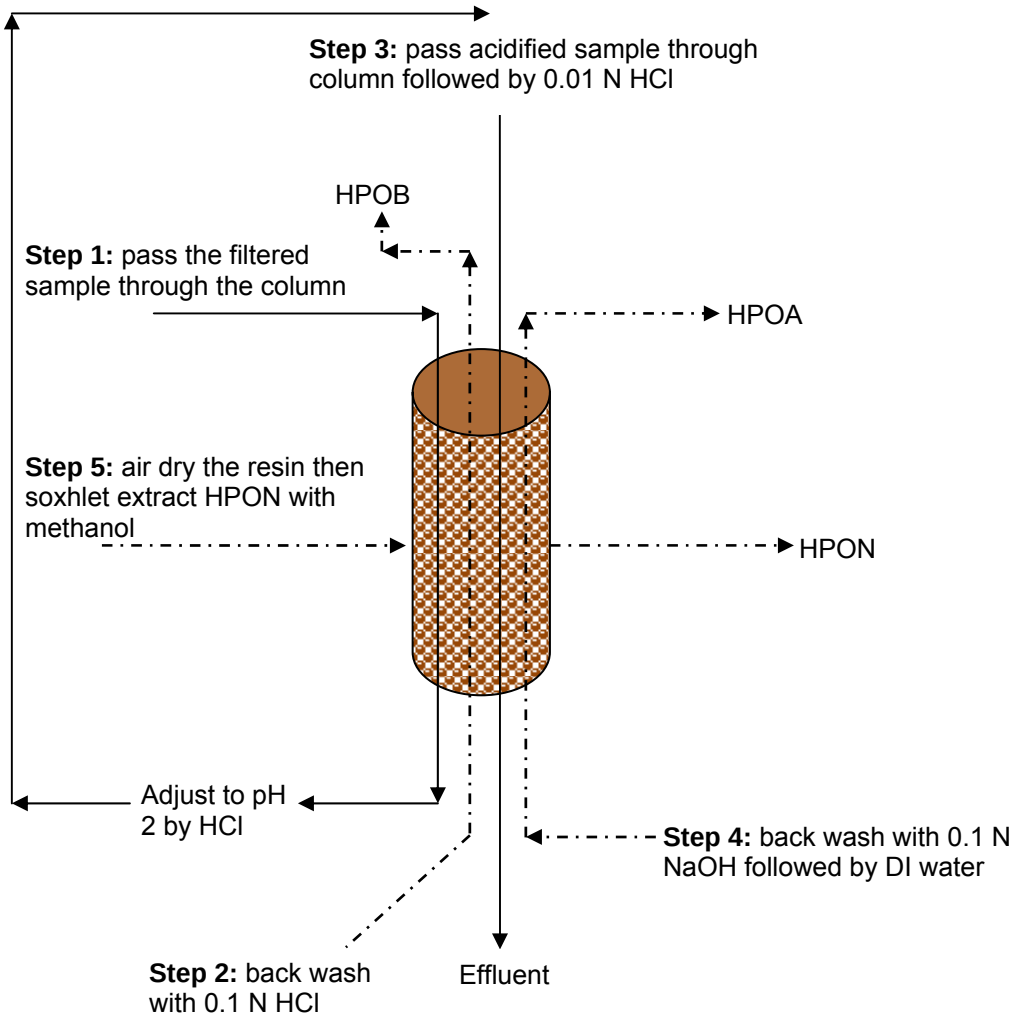


Figure 3.4 Conventional analysis procedures for HS fractionation (Leenheer 1981)

3.6 Determination of Physicochemical Characteristics

3.6.1 DOC Concentration

DOC concentration measurements were conducted with a Tekmar Dohrmann Phoenix 8000 UV-persulfate TOC analyzer (Figure 3.5) following Standard Method 5310C (APHA et al. 2005). The instrument was first calibrated with sodium peroxydisulfate solution (0, 1, 2.5 and 10 mg/L range) before analysis of the water samples. RO/DI water was used for sample dilution and the blank sample. For each sample measurement, at least three replicate analyses were performed and analysis precision was typically within ±5%.

Figure 3.5 Phoenix 8000 UV-persulfate TOC analyzer.

3.6.2 UV Spectroscopy and SUVA

A Hach DR/4000U UV/VIS spectrophotometer (Figure 3.6) was set at wavelengths of 203 nm and 254 nm to measure the UV light adsorption of the water samples. A Hellma 10 mm quartz cell was used for UV measurements and RO/DI water was used for cleaning. All samples were adjusted to pH 7 with H_2SO_4 or NaOH before measurement.

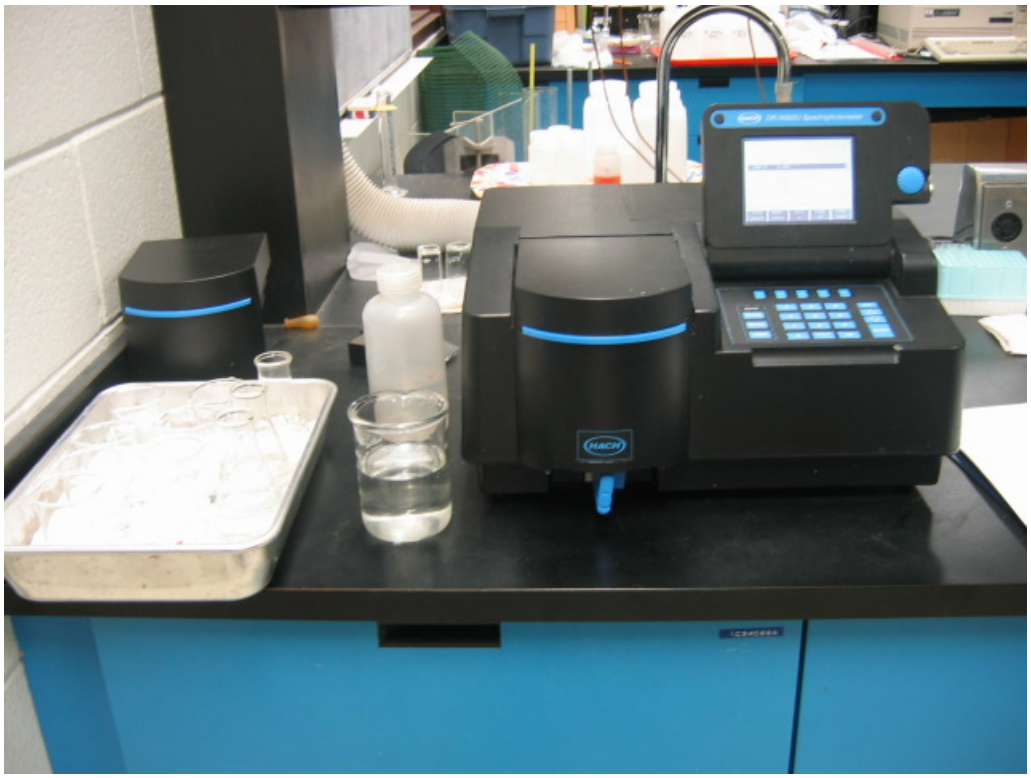


Figure 3.6 Hach DR/4000U UV/VIS spectrophotometer.

SUVA was used as an index of the aromatic organic content of the sample (Kanakkantapong et al. 2006). It was calculated as the ratio of UV absorbance at 254 nm to DOC concentration measured in mg/L using the TOC analyzer and divided by the length of light absorbing layer (1 cm was used during the measurements). The ratio of UV_{254}/UV_{203} was used to indicate the phenolic content of the DOC (Kim and Yu 2005).

3.6.3 Trihalomethane Formation Potential (THMFP)

A 7-day chlorination THMFP test was carried out in accordance with the Standard Method 6232 (APHA 2005). A chlorine dosage of 30 mg/L free chlorine was used for each sample. All samples were adjusted to a pH 8±0.2 using H_2SO_4 or NaOH. The pH adjusted solution was then held at 25 ± 2 ^oC in amber bottles for 7 days. A Varian star 3400CX Gas chromatographer with *hp* 7675A purge trap sampler (Figure 3.7) was used for determining the THMFP.

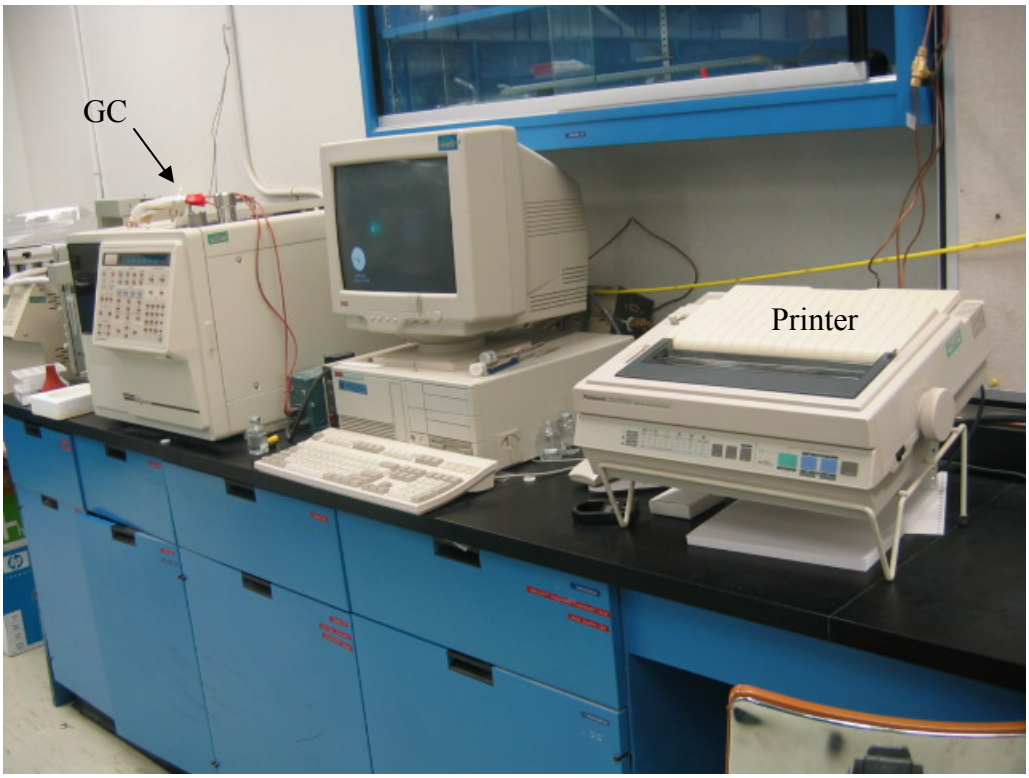


Figure 3.7 Varian star 3400CX Gas chromatographer with *hp* 7675A purge trap sampler.

3.7 FTIR Analysis

FTIR spectroscopic measurements with standard infrared light were conducted at the Canadian Light Source located at the University of Saskatchewan, Saskatoon, SK, Canada. The original intention of this project was to use Synchrotron light with FTIR. Initial trial runs were conducted to assess the need for the sensitivity provided by synchrotron light. A fulvic acid solution with DOC concentration 15 ±0.75mg/L was prepared. Residue from the solution was placed on a 1''×3''×0.04''gold plated slide (EMF, NY) by placing the slide in a beaker containing the solution and evaporating the solution at 30 to 40 °C. After the liquid was dried the thin film of residue left on the slide was subjected to FTIR scanning. This assessment was done in consultation with Dr. L. Quaroni from Canadian Light Source (Quaroni 2007).

Due to the inorganic materials contained in the solution, crystals formed in the residue deposited on the slide surface. However, most inorganic compounds have bond vibrations that do not appear in the middle infrared range (4000-400 cm^{-1}). Inorganic

response is generally in the far infrared region (< 400 cm^{-1}) but is very weak in comparison to organic molecules. Therefore, inorganic compounds in the solution did not affect the characterization of the organic content of samples.

The IR analysis results showed that the high energy, high sensitivity light source (synchrotron beamline) caused significant noise in the spectral response. Therefore, sample measurements were better conducted with lower sensitivity conventional light source. However, since the FTIR equipment was also required for synchrotron beamline work, our analyses had to be scheduled around the beamline operations. Figure 3.8 shows the FTIR equipment at Canadian Light Source.

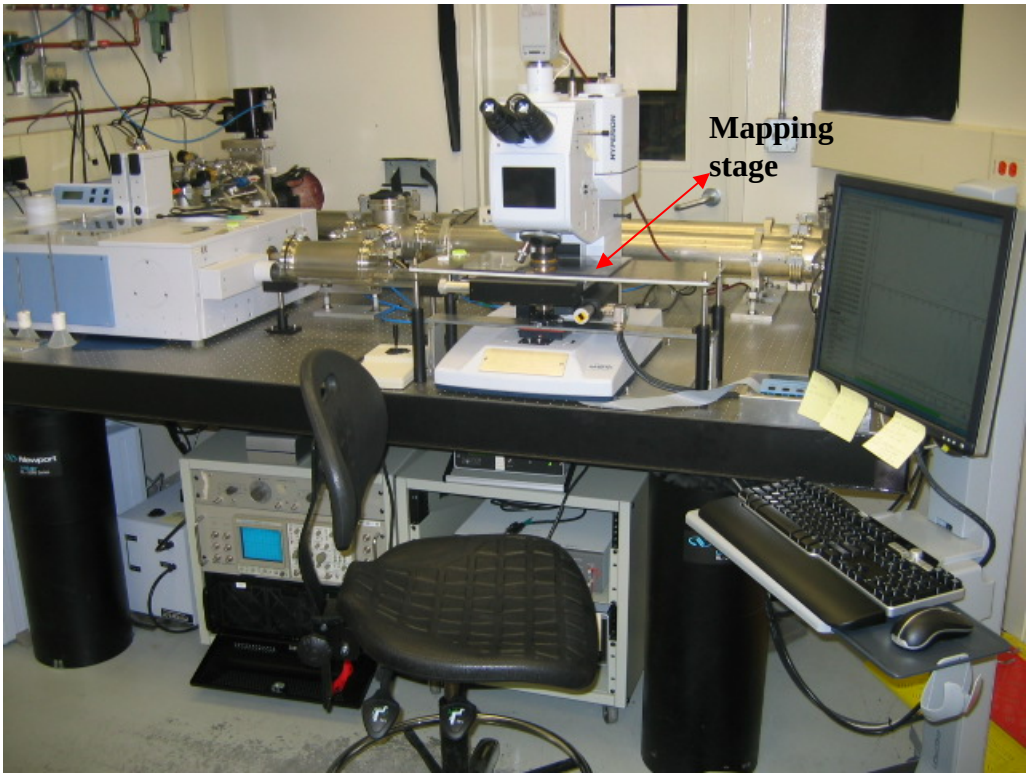


Figure 3.8 FTIR spectrophotometer and microscope in the IR beamline experimental hutch.

As indicated in Chapter 2 aqueous samples containing DOC must be pre-processed before FTIR analysis can be conducted. In this project, a modified version of the method proposed by Jones et al. (2006) was used for depositing a residue of aqueous solution containing DOC on an IR reflective surface. Due to the low DOC concentration of the spiked samples (<15 mg/L) used in the preliminary test it was difficult to produce

high quality FTIR spectra. Therefore, before depositing the sample residue the spiked samples and their fractions were concentrated by 20 times. The procedures are illustrated in Figure 3.9 and described as follows:

- First a 100 mL of the water sample was placed in a graduated cylinder and concentrated by evaporation down to 5 mL at 60°C in an oven;
- The concentrated sample was then transferred to a small glass vial for easier handling. A 50 μL syringe was used to draw a 25 μL volume from the small glass vial;
- Individual drops of 25 μL concentrated sample were then deposited on a 1''×3''×0.04''goldplated slide (EMF, NY); and
- Finally the drops were dried at room temperature leaving a thin film of residue on the slide that was subjected to FTIR scanning.

The gold-plated slide with the organic residue spots was put onto the mapping stage with the -plated side facing the microscope lens as shown in Figures 3.7 and 3.8. The mapping stage was covered with a transparent plate to achieve a closed environment and a vacuum applied to avoid air interference to the infrared spectrum. Since the gold plated slide is not transparent the reflecting measurement mode of the FTIR equipment was used in the scanning.

The scanning operation procedures are described as follows: 1) visible light was used to focus the scanning area (75×75μm); 2) infrared light was used to adjust the signal to achieve the largest amplitude; 3) a blank area was selected to conduct and save background absorption measurements; 4) an organic residue spot was focused on and scanned to produce and save an absorption spectrum in excess of background measurements. After the scanning operation, the infrared spectrum can be displayed. Since the DOC content in the organic residue is not evenly distributed, 5 spots were scanned in each drop of residue. For each water sample, there are 12 drops on a slide and 5 spectra from each drop. The total number of spectra was 60 for each sample. The spectrum for each sample shown in the later chapters is the averaged results of the 60 scans.

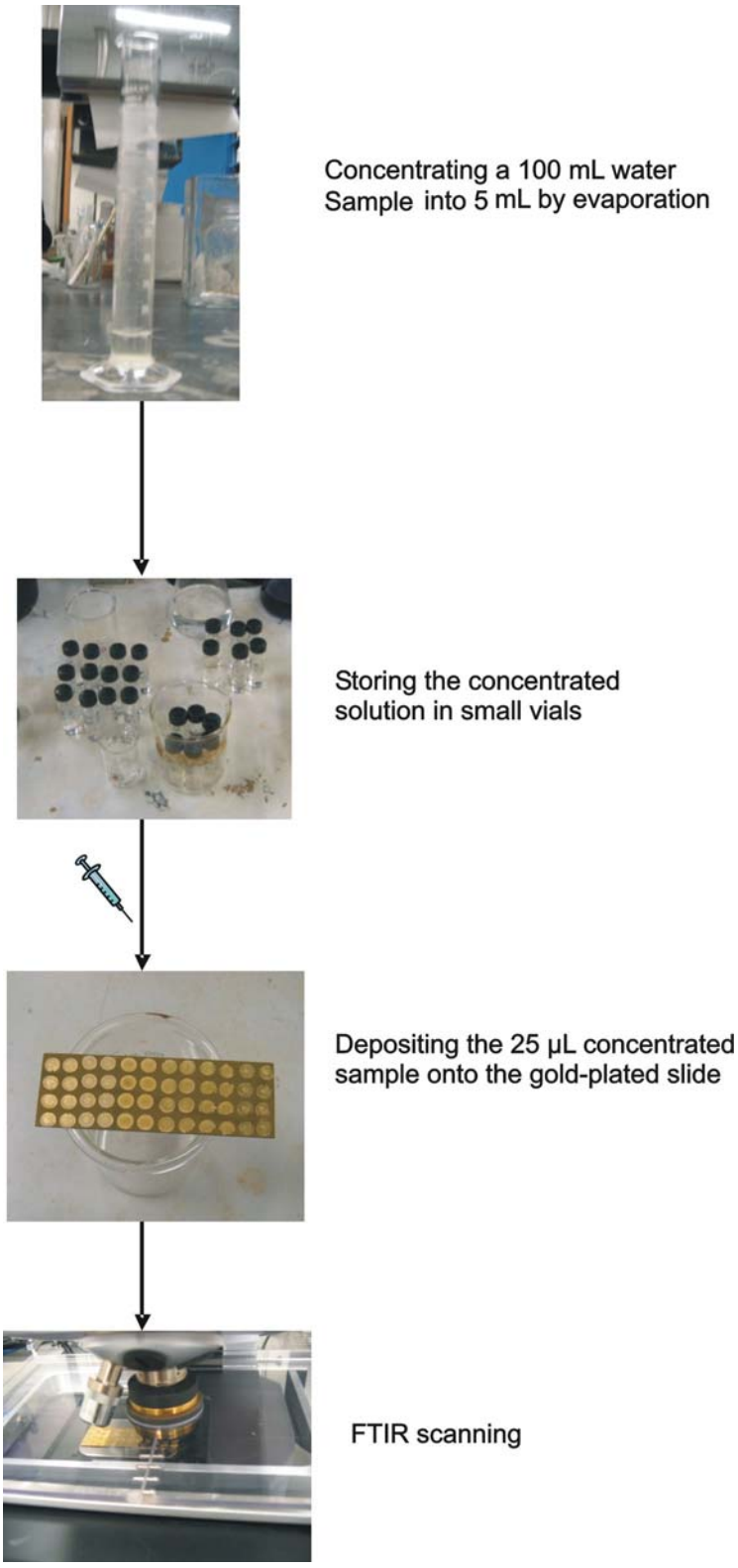


Figure 3.9 Residue Deposition Procedure.

CHAPTER 4. SUWANNEE RIVER DOC SPIKED SAMPLE RESULTS AND DISCUSSION

4.1 DOC Concentration

Table 4.1 summarizes the DOC measurement results for the three spiked samples prepared using Suwannee River NOM. The measured DOC content of each un-fractioned sample was 12.09, 6.05, and 3.14 mg/L. Summation of the average measurements for each fraction of the sample resulted in DOC content of 11.47, 5.79, and 3.02 mg/L which represent mass recoveries of 95%, 96% and 96% respectively. The sequence of the six organic fractions ordered from largest to smallest average DOC content is: HPOA > HPIA > HPON > HPIN > HPIB > HPOB as listed in Table 4.1. However, when considering the associated experimental error several of the fractions are of equivalent magnitude. A detailed listing of all water sample replicate data is presented in Appendix B.

Based upon the full strength sample data presented in Table 4.1 the distribution of DOC among the six organic fractions can be determined as shown in Figure 4.1. The hydrophobic fractions contain 54% of the DOC in the full strength sample. The HPOA fraction accounted for the largest mass percentage with 35% of the DOC. In contrast the HPOB fraction had the smallest mass percentage with only 5% of the DOC. The results also show the distribution of the DOC between acid, neutral and base fractions. The acid fractions (HPOA and HPIA) had the largest percentage mass (55% of DOC), followed by the neutral fractions (HPON and HPIN) with 30% and base fractions (HOPB and HPIB) with only 15%.

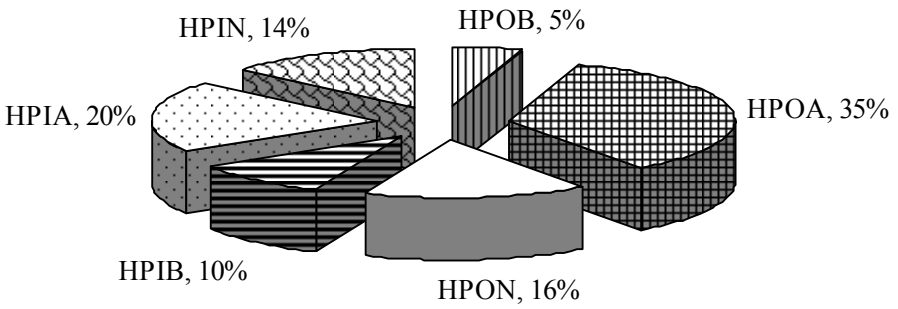


Figure 4.1 Distribution of DOC among organic fractions of Suwannee River DOC.

Table 4.1 DOC concentration of spiked water samples and their organic fractions.

Sample Fraction	Full strength (mg/L)	Half strength (mg/L)	Quarter strength (mg/L)
Un-fractioned	12.09[†]±0.68[§]	6.05±0.10	3.14±0.15
HPOA fraction	4.02±0.26	1.97±0.54	1.01±0.20
HPIA fraction	2.28±0.26	1.23±0.30	0.68±0.06
HPON fraction	1.90±0.46	0.94±0.02	0.49±0.05
HPIN fraction	1.60±0.29	0.76±0.16	0.42±0.07
HPIB fraction	1.15±0.20	0.57±0.14	0.25±0.06
HPOB fraction	0.57±0.13	0.32±0.10	0.17±0.06
Σ of avg. fraction conc.	11.47	5.79	3.02
Avg. % mass recovered	95%	96%	96%

[†] Results shown are the average of four replicate measurements

[§] Uncertainty given by $(t_{\alpha,n-1}SE)/(n)^{½}$, where n is the number of replicates, SE is the standard error, $t_{\alpha,n-1}$ is the student test parameter for 95% confidence (i.e. α=0.05) and n-1 degrees of freedom

4.2 SUVA and UV_{254}/UV_{203} Ratio

The SUVA readings for the full strength (12.09 mg/L DOC) spiked water sample and its fractions are presented in Table 4.2. High SUVA values indicate a large proportion of the organic components have hydrophobic and aromatic characteristics (Jame et al. 2003; Kanokkantapong et al. 2006; Liang and Singer 2003; Thompson et al. 1997). The measured SUVA for the full strength spiked water sample was 4.34 L/mg/m. The SUVA readings for each of the six organic fractions are shown in Table 4.2. A detailed listing of all water sample replicate data is presented in Appendix C.

The sequence of the six fractions from largest to smallest average readings is: HPOB > HPOA > HPON > HPIB > HPIA > HPIN. The HPOB fraction produced the largest average value (3.45 L/mg/m), whereas the HPIN fraction had the smallest

average value (0.64 L/mg/m). This result is similar to that reported by Croue et al. (2000) who found that the HPIN fraction possessed the lowest level of SUVA for Suwannee River DOC. All the hydrophobic fractions exhibited larger SUVA values than the hydrophilic fractions. This indicates the hydrophobic fractions are composed of more aromatic structured components than the hydrophilic fractions.

The ratio of UV absorbance at 254 and 203 nm (UV_{254}/UV_{203}) of the full strength spiked water sample and its fractions was also determined. This parameter was used by Kim and Yu (2005) to characterize NOM from source and treated waters at a conventional water treatment plant. They reported that the UV_{254}/UV_{203} ratio can be used as an indicator of the phenolic content of the dissolved organic matter in the water. The data in Table 4.2 show that the hydrophobic fractions of Suwannee River DOC have larger values of UV_{254}/UV_{203} than the hydrophilic fractions. The six fractions ordered from largest to smallest based upon the average magnitude of the UV_{254}/UV_{203} ratio is as follows: HPOB > HPOA > HPON > HPIB > HPIN > HPIA.

Table 4.2 SUVA and UV_{254}/UV_{203} characteristics of Suwannee River DOC and its fractions.

DOC sample	SUVA (L/mg/m)	UV_{254}/UV_{203}
Un-fractionated	4.34[†]±0.28[§]	0.66[†]±0.08[§]
HPOB fraction	3.45±1.16	0.36±0.01
HPOA fraction	3.17±1.02	0.34±0.13
HPON fraction	2.96±0.24	0.30±0.08
HPIB fraction	2.08±0.43	0.33±0.05
HPIA fraction	1.34±0.18	0.05±0.00
HPIN fraction	0.70±0.80	0.28±0.06

[†] Results shown are the average of four replicate measurements

[§] Uncertainty given by $(t_{\alpha,n-1}SE)/(n)^{½}$, where n is the number of replicates, SE is the standard error, $t_{\alpha,n-1}$ is the student test parameter for 95% confidence (i.e. α=0.05) and n-1 degrees of freedom

4.3 THMFP and Specific THMFP

THMFP is a measure of the potential of the dissolved organic materials to form THM after they have reacted with excess free chlorine. In this work, THMFP is reported as total THMFP and specific THMFP. Total THMFP is the concentration of THM formed after reaction with free chlorine. The total THMFP of the Suwannee River

DOC spiked water sample used in this investigation was 823.29 µg/L (with DOC concentration 12.09 mg/L). Specific THMFP is the ratio between THM formed from a sample and the DOC concentration of that sample. Therefore, the units of Specific THMFP are µg chloroform per mg DOC. The Specific THMFP is an indication of the actual reactivity of the dissolved organic compounds for the formation of THM. A detailed listing of all water sample replicate data is presented in Appendix D.

Table 4.3 compares the DOC content, total THMFP and Specific THMFP for the Suwannee River DOC full strength spiked water sample and its fractions. The sequence of DOC fractions ordered from largest to smallest average Specific THMFP is: HPOA > HPOB > HPON > HPIA > HPIB > HPIN. HPOA was found to be the most abundant of all fractions (33% of total DOC) and also the main organic precursor for THMs (highest total and Specific THMFP). The results also indicate that the main precursors for THM for Suwannee River DOC were the hydrophobic fractions. Further, within the hydrophobic and hydrophilic fractions the acid fraction always has the highest Specific THMFP while the neutral fraction has the lowest.

In the previous section, it was shown that the hydrophobic fractions exhibited the higher levels of SUVA. Figure 4.8 shows that SUVA and Specific THMFP are positively correlated ($R^2 = 0.64$). Therefore, the results from this work indicate that water sources with higher SUVA have higher potential of THM formation which is consistent with previous research by (Leenheer et al. 2001). Kim and Yu (2005) reported that water samples with significant phenolic content indicated by increased UV_{254}/UV_{203} values resulted in higher formation potential of THM. However, Figure 4.9 shows there is little correlation between UV_{254}/UV_{203} ratio and Specific THMFP for the Suwannee River DOC fractions. At best the UV_{254}/UV_{203} ratio appears to be a weak indicator of hydrophobicity rather than THM formation potential.

Table.4.3 THMFP of the Suwannee River DOC and its fractions.

DOC sources	DOC concentration (mg/L)	THMFP (μg/L)	Specific THMFP (μg chloroform/mg C)
Un-fractionated	12.09[†]±0.68[§]	823.3[†]±119.2[§]	68.1[†]±2.8[§]
HPOB	4.02±0.26	41.6±8.9	81.8±15.6
HPOA	2.28±0.26	361.6±82.1	90.6±25.6
HPON	1.90±0.46	126.6±16.1	66.7±8.4
HPIB	1.60±0.29	58.0±3.0	50.4±2.5
HPIA	1.15±0.20	120.8±16.7	53.6±7.4
HPIN	0.57±0.13	58.2±13.4	36.4±8.4

[†] Results shown are the average of four replicate measurements

[§] Uncertainty given by $(t_{\alpha,n-1}SE)/(n)^{1/2}$, where n is the number of replicates, SE is the standard error, $t_{\alpha,n-1}$ is the student test parameter for 95% confidence (i.e. α=0.05) and n-1 degrees of freedom

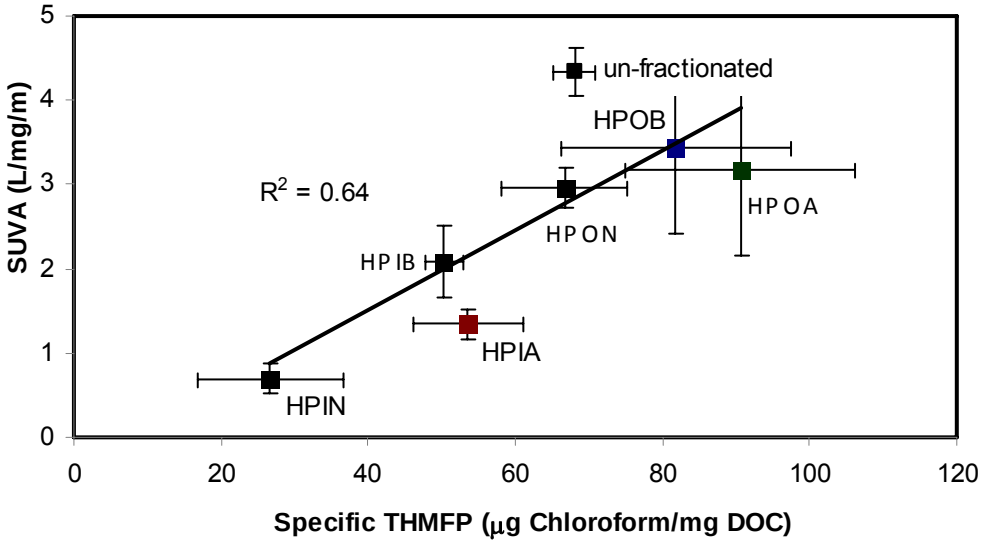


Figure 4.2 Relationship between THMFPs and SUVA for un-fractionated DOC and its fractions.

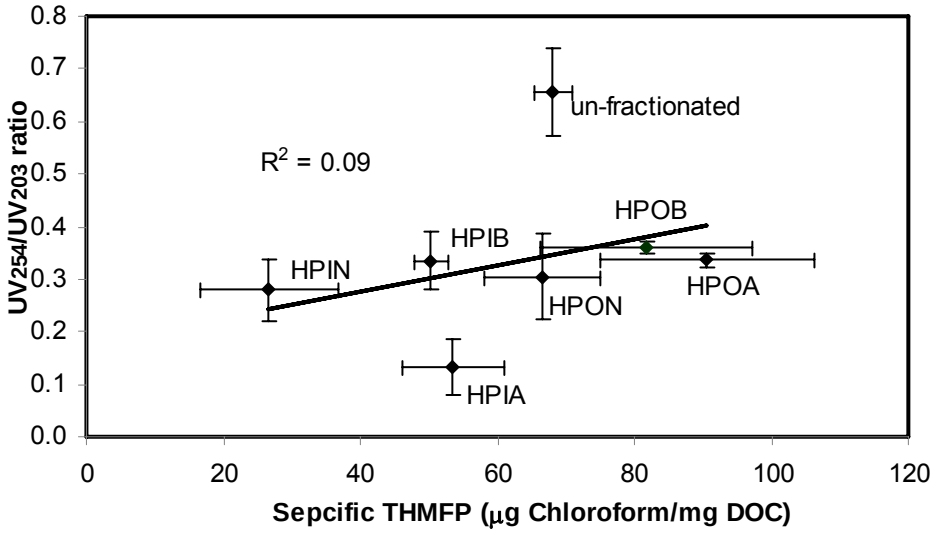


Figure 4.3 Relationship between UV_{254}/UV_{203} ratio and Specific THMFP for Suwannee River DOC spiked water and its DOC fractions.

4.4 FTIR Spectra

The individual FTIR spectra of the un-fractionated and fractionated samples are presented in Appendix E. The interpretation of the spectra from the FTIR analysis run on the Suwannee River DOC samples (as described in Section 2.5.2) is presented below.

4.4.1 HPOB

The spectrum from the FTIR analysis of the HPOB fraction of the Suwannee River DOC sample is shown in Figure 4.4. The following statements demonstrate (using the HPOB spectrum as an example) how to identify the major functional groups through logical interpretation. The peak at 1630 cm^{-1} is assigned to C=O stretching. The main diagnostic absorbance peak occurring at 1614 cm^{-1} belongs to a 1o amine N-H deformation (NH_2 bending) and absorbance peaks in the range 3500-3300 cm^{-1} indicate the presence of an aromatic N-H stretching band. Further peaks at 1350-1020 cm^{-1} were caused by aromatic C-N stretching, and peaks at 2825-2810 cm^{-1} and 950-850 cm^{-1} showed there is likely N-methyl stretching in the compounds. Therefore, the absorption spectrum clearly illustrates that amino acids are the main functional group present in the HPOB. This result is consistent with Leenheer and Huffman (1979) who reported amino acid was the main functional group present in HPOB. Table 4.4 lists bond type

absorption bands (diagnostic bands) presented in the literature and the absorption peaks present in the Suwannee River HPOB spectrum.[7]

The HPOB fraction exhibited larger SUVA values, UV_{254}/UV_{203} ratio and specific THMFP than the other DOC fractions (Tables 4.2 and 4.3). These conventional measurement results combined with the FTIR spectral analysis of the HPOB fraction indicate amino acids have significant potential to form THM relative to other organic fractions. This agrees with the findings of Marhaba and Van (1999) and Butterfield et al. (2002) who stated that amino acids in the HPOB fraction were prone to and could rapidly react with chlorine to produce DBPs. Also Kim and Yu (2005) suggested that high C/N ratio compounds such as amino acids, or amide groups present in hydrophobic compounds with high SUVA values is one of the major characteristics of the HPOB fraction. Therefore, these statements and the experimental results of this study show that the HPOB fraction can be an important precursor for the generation of THMs.

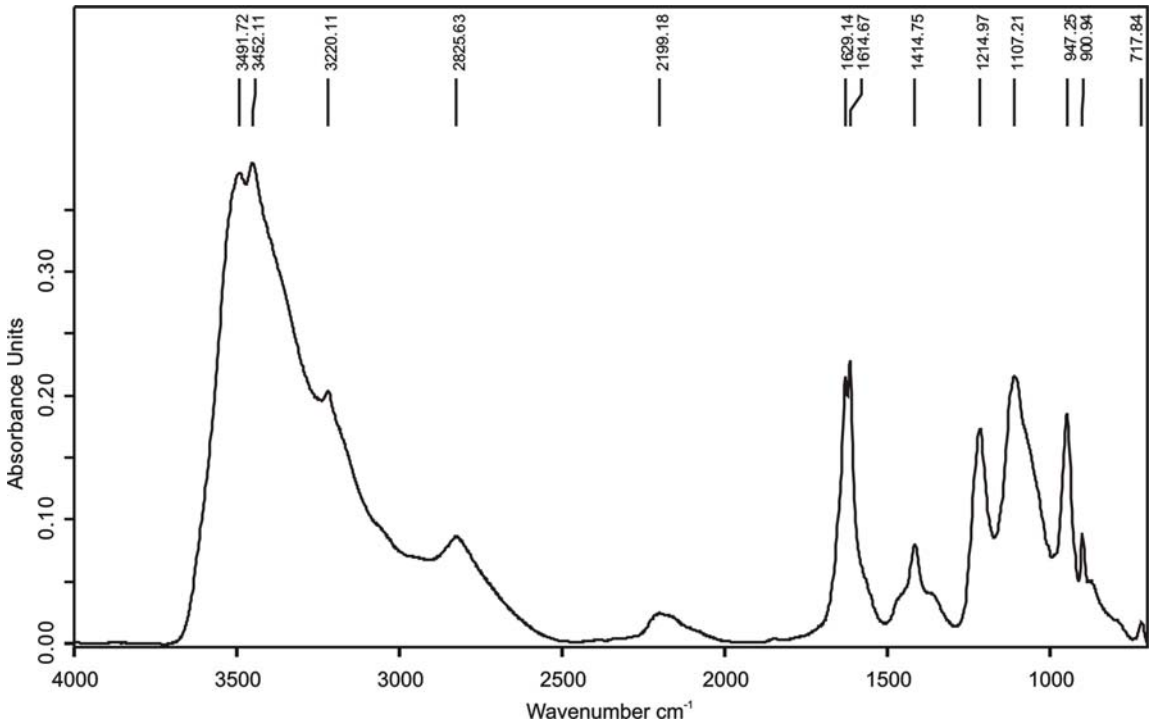


Figure 4.4 FTIR spectrum of the HPOB fraction of a Suwannee River DOC spiked water sample (0.57mg/L DOC).

[7] The logical interpretation results for all other FTIR spectra examined in this thesis will be presented in summary tabular format only similar to Table 4.4.

Table 4.4 HPOB functional groups.

Dominant functional groups	Diagnostic Band (cm^{-1})	Absorption Peak (cm^{-1})
Amino acid	C=O stretching: 1800-1600	1630
	Aromatic N-H stretching: 3500-3420 (2 bands)	3491 and 3452
	N-H bending: 1650-1580	1614
	Aromatic C-N stretching: 1350-1200	1214
	Saturated C-N stretching: 1180-1030	1107
	N-methyl stretching: 2825-2810 and 950-850	2825, 947 and 900

The magnitude of the absorbance values on the *y*-axis of an FTIR spectrum can provide approximate information regarding the relative solution strength. For example, the absorbance units on the *y*-axis of the full strength solution sample is approximately two times that of the half strength solution and four times of that of quarter strength as illustrated in Figure 4.5.

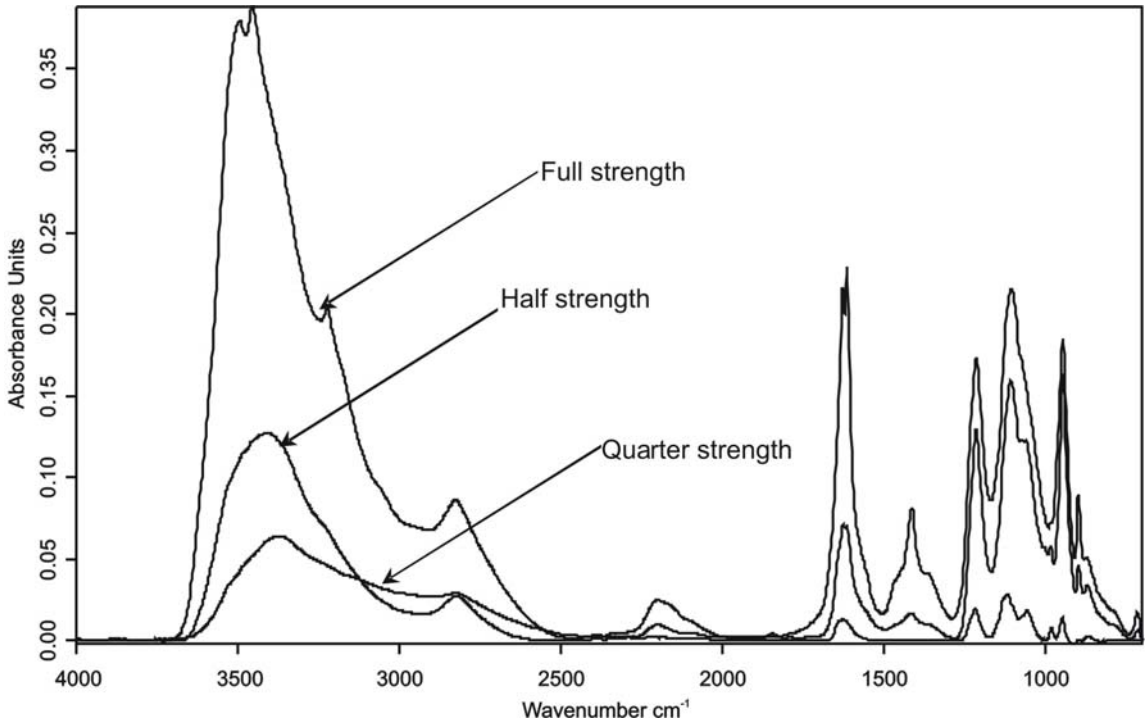


Figure 4.5 FTIR spectrum of the HPOB fraction of three different dilutions of Suwannee River DOC spiked water samples.

4.4.2 HPOA

The FTIR spectrum of the HPOA fraction of the Suwannee River DOC spiked water sample is shown in Figure 4.6. Table 4.5 lists the diagnostic bands and the absorption peaks present in the spectrum. The absorbance peaks indicate that carboxylic

acids are a major functional group in the HPOA fraction. The SUVA values, UV_{254}/UV_{203} ratio, and Specific THMFP results (Tables 4.2 and 4.3) and the FTIR analysis results indicate the HPOA fraction contains significant concentrations of aromatic carboxylic acids, and these functional groups play an important role in forming THM.

Leenheer and Huffman (1979) reported that phenol was one of the functional groups in the HPOA fraction. The absorbance peak at 1354.49 cm^{-1} in Figure 4.7 fits within the O-H in-plane bending frequency range (1350±50 cm^{-1}) characteristic of phenol compounds. However, the C-O stretching peak in the range of 1260-1200 cm^{-1} required for phenol is absent in Figure 4.6. Kanokkantapong et al. (2006) also found that phenols were not observed in HPOA.

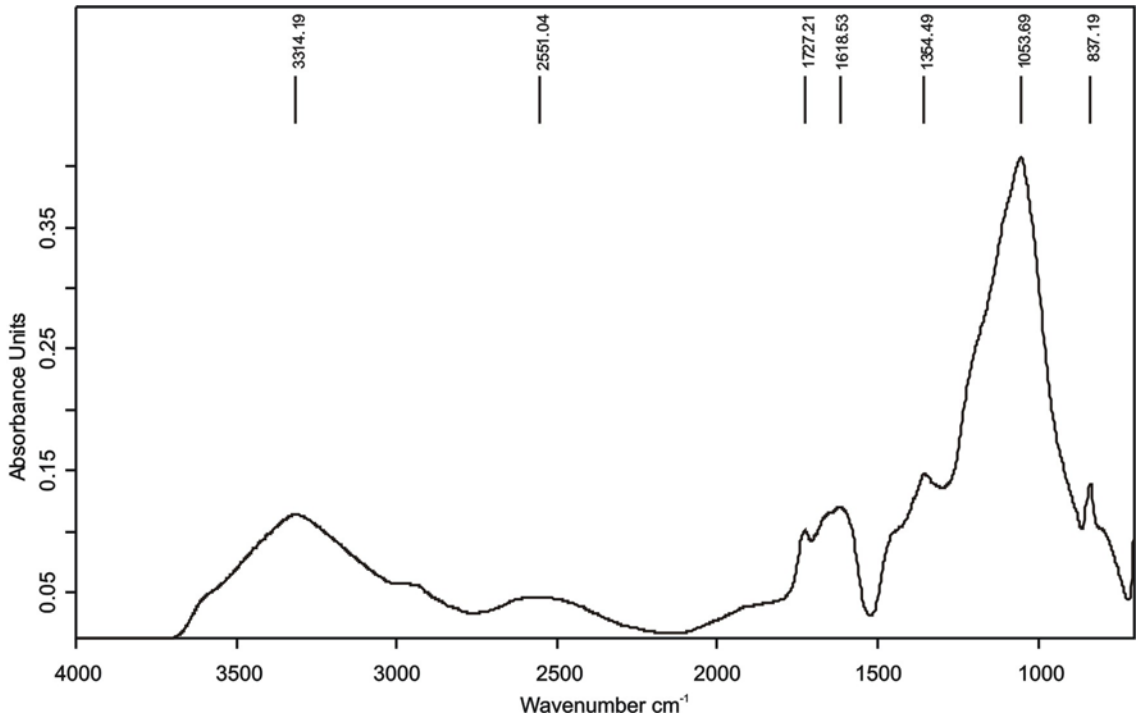


Figure 4.6 FTIR spectrum of HPOA fraction of a Suwannee River DOC spiked water sample (4.02 mg/L DOC).

Table 4.5 HPOA functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Absorption Peak (cm^{-1})
carboxylic acid	Aromatic C=O stretching: 1730-1680	1727
	ionized carboxyl:1650-1540	1618
	O-H stretching: 3500-2500	3314
	C-O stretching: 1300-1000	1053

Figure 4.7 presents the absorbance spectra of the HPOA fractions extracted from full strength, half strength, and quarter strength DOC spiked samples. As discussed above the overall absorption response is approximately in proportion to the DOC concentration.

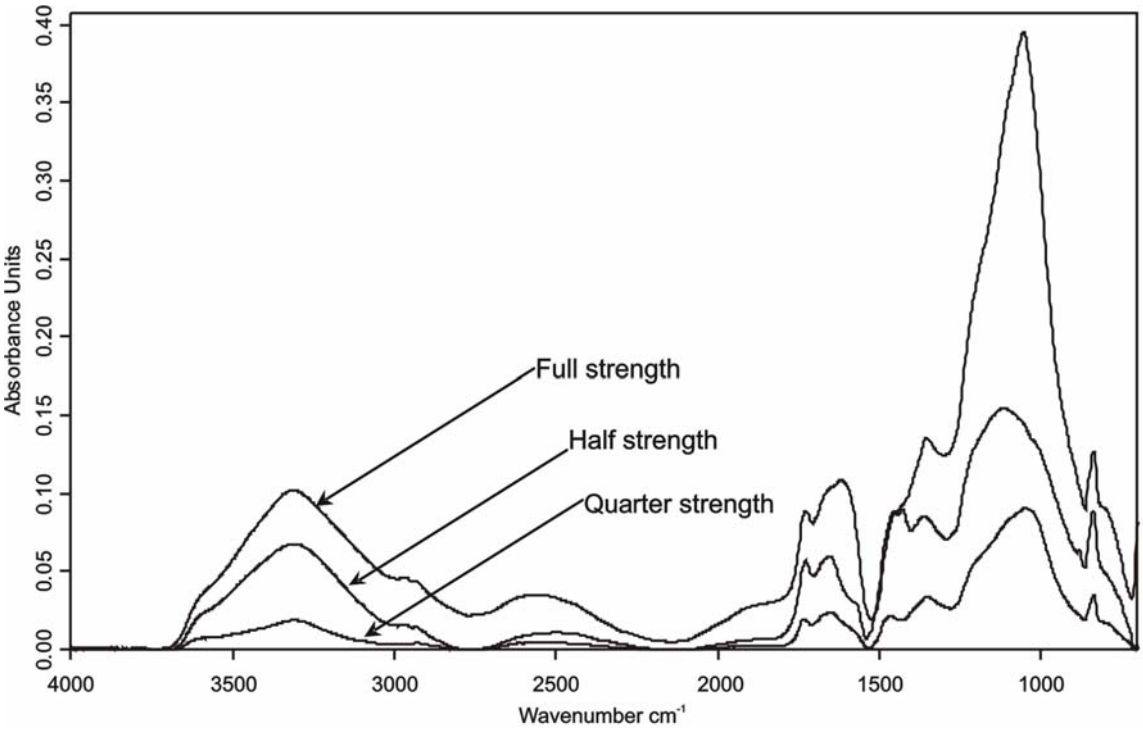


Figure 4.7 FTIR spectrum of the HPOA fraction of three different dilutions of Suwannee River DOC spiked water samples.

4.4.3 HPON

The FTIR spectrum of the HPON fraction of the Suwannee River DOC is shown in Figure 4.8. Table 4.6 identifies the dominant functional groups present based upon interpretation of the spectrum. Alcohol is identified as one of the dominant functional groups. Leenheer and Huffman (1979) stated that HPON consisted of alcohol in aliphatic structure which is not active in the generation of THM. Aromatic ketone and amides are the other dominant functional groups present in the Suwannee River HPON. They were also reported as functional groups in HPON by Leenheer and Huffman (1979). Previous research by Kanokkantapong et al. (2006) found that the combined peak from ketone and amides disappeared after it reacted with chlorine. This suggests they may be precursors for THM formation.

Leenheer and Huffman (1979) reported aldehyde was an additional functional group present in HPON. However, there was no clear evidence of aldehyde stretching bands in the range from 2850-2750 cm^{-1} in the Suwannee River DOC spiked water sample. Kanokkantapong et al. (2006) also found no evidence of aldehyde but speculated this could be due to the overlap of its absorbance peak and the O-H peak.

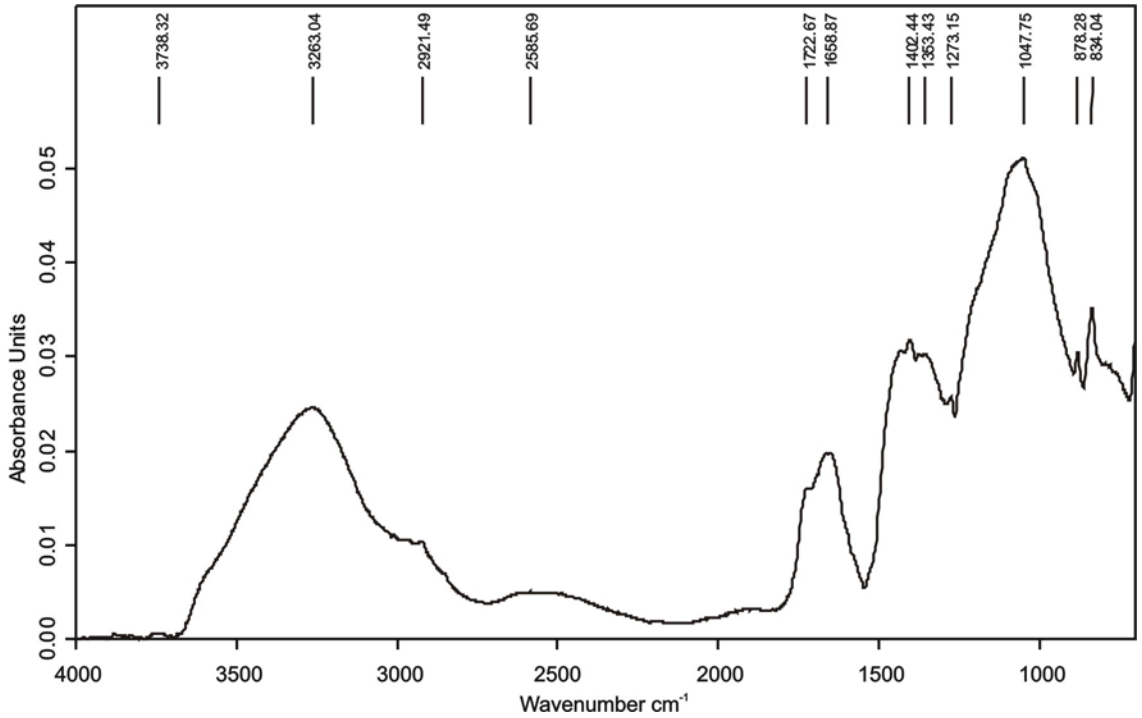


Figure 4.8 FTIR spectrum of HPON fraction of a Suwannee River DOC spiked water sample (1.90 mg/L DOC).

Table 4.6 HPON functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Absorption Peak (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3263
	C-O stretching: 1200-1000	1047
	O-H bending: 1410-1260	1363 and 1273
Ketone	Aromatic C=O stretching: 1700-1640	1658
Amide	C=O stretching: 1680-1630	1658
	N-H stretching: 3370-3170	3263
	C-N stretching: 1430-1390	1402

The FTIR absorbance spectra for the full, half and quarter strength solutions of the HPON fraction of Suwannee River DOC spiked water are presented in Figure 4.9.

Consistent with the plots presented for the HPOB and HPOA fractions the absorbance units are approximately proportion to the relative DOC concentration.

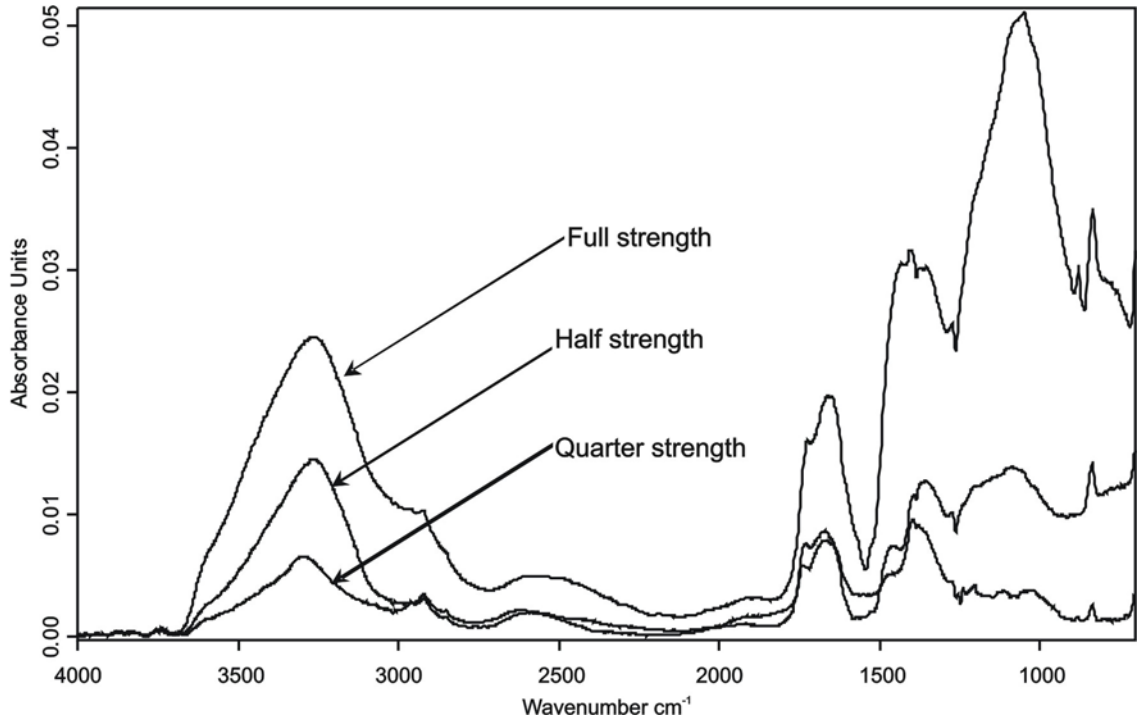


Figure 4.9 FTIR spectrum of the HPON fraction of three different dilutions of Suwannee River DOC spiked water samples.

4.4.4 HPIB

The FTIR spectrum of HPIB fraction of the Suwannee River DOC sample is shown in Figure 4.10. Table 4.7 lists the diagnostic bands and the absorption peaks present in the spectrum. Aliphatic amine is identified as the main functional group present in the HPIB fraction based on the absorption peaks present within the diagnostic bands. This result is consistent with Leenheer and Huffman (1979) who also stated that aliphatic amine was the main functional group in the HPIB fraction. Leenheer and Huffman (1979) reported that HPIB is also comprised of pyridines, pureness, and pyrimidines. However, there were no peaks found for these compounds in the spectrum for the HPIB fraction of Suwannee River DOC. The relatively low values of SUVA and Specific THMFP of the HPIB fraction (Table 4.2 and 4.3) compared with the HPOB fraction indicates that HPIB compounds are less effective precursors for THM than HPOB compounds.

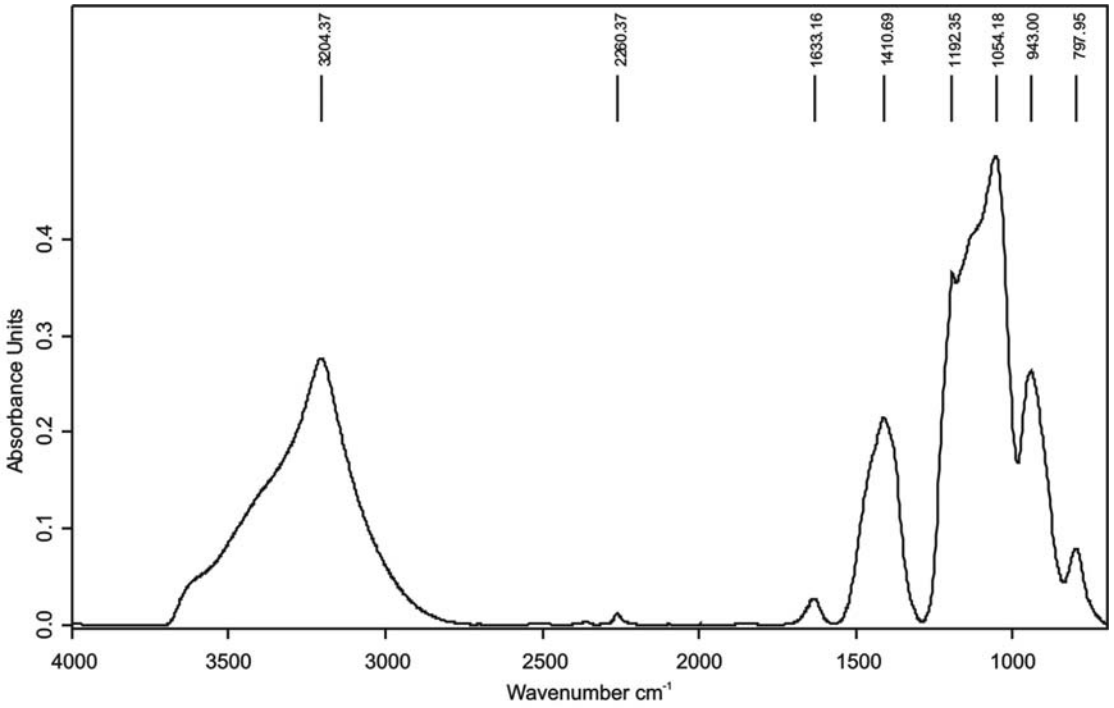


Figure 4.10 FTIR spectrum of the HPIB fraction of a Suwannee River DOC spiked water sample (1.15 mg/L DOC).

Table 4.7 HPIB functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Absorption Peak (cm^{-1})
Aliphatic amine	Saturated N-H stretching: 3320-3200	3204
	N-H bending: 1650-1580	1633
	Saturated C-N stretching: 1180-1030	1054

The FTIR absorbance spectra for the full, half and quarter strength solutions of the HPIB fraction of Suwannee River DOC spiked water are presented in Figure 4.11. Unlike the trend observed for the hydrophobic fractions, absorbance units on the *y*-axis for HPIB have not decreased in proportion to the strength of the solution.

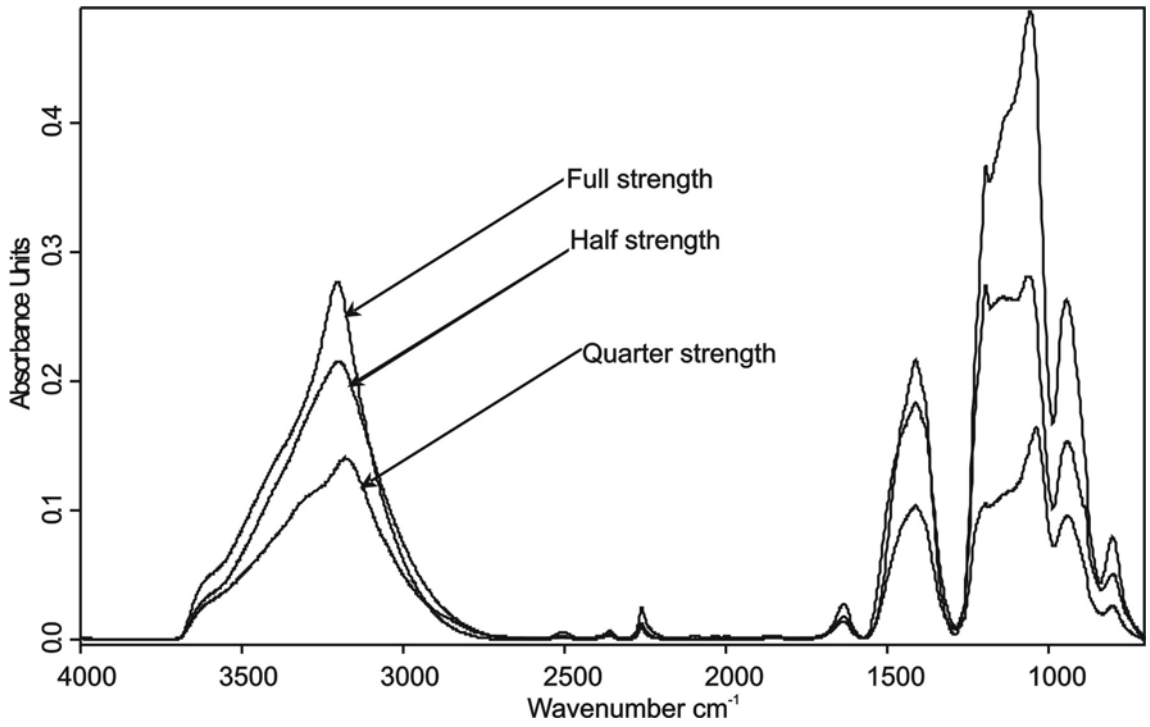


Figure 4.11 FTIR spectrum of the HPIB fraction of three different dilutions of Suwannee River DOC spiked water samples.

4.4.5 HPIA

The FTIR spectrum from the HPIA fraction of the Suwannee River DOC sample is shown in Figure 4.12. Table 4.8 lists the diagnostic bands and the absorption peaks present in the spectrum. Carboxylic acid is identified as the main functional group present in the HPIA fraction. In comparison to the HPOA fraction the HPIA contains more aliphatic than aromatic carbon as indicated by the peak in the C=O stretching band and lower SUVA (Table 4.2). The extremely low UV_{254}/UV_{203} ratio also illustrates the aliphatic property of the HPIA fraction. The low specific THMFP values (Table 4.3) indicated that the structure of this fraction is more hydrophilic and less active in generating THM than HPOA.

Peaks in the range 2600-2100 cm^{-1} are an indication of C≡N stretching which means nitrile is contained in the HPIA fraction. However, the quantities are small as shown by the limited absorbance response. Curiously this wavelength range was almost blank in the un-fractionated Suwannee River DOC sample (see Section 4.4.7). It is suspected the response in this range may not come from compounds in the DOC sample,

but rather from compounds leached from the resin materials as a result of the high pH washing solution (3N NaOH) used during elution.

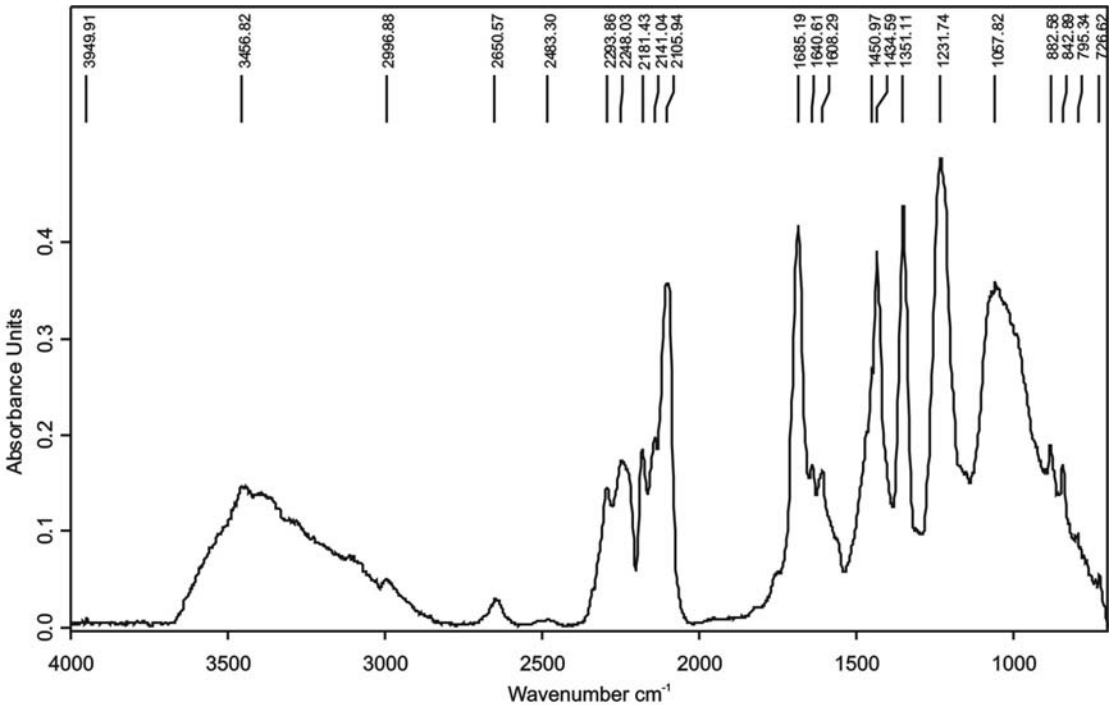


Figure 4.12 FTIR spectrum of the HPIA fraction of a Suwannee River DOC spiked water sample (2.28 mg/L DOC).

Table 4.8 HPIN functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Absorption Peak (cm^{-1})
carboxylic acid	Saturated C=O stretching: 1710-1680	1685
	O-H stretching: 3500-2500	3456
	C-O stretching: 1300-1000	1231 and 1057
	O-H in-plane bending: 1440-1395	1434
Nitrile	C≡N stretching: 2600-2100	2293, 2248, 2181,2141,and 2105

The FTIR absorbance spectra for the full, half and quarter strength solutions of the HPIA fraction of Suwannee River DOC are presented in Figure 4.13. Similar to the HPIB fraction the absorption response is not proportional to relative concentration.

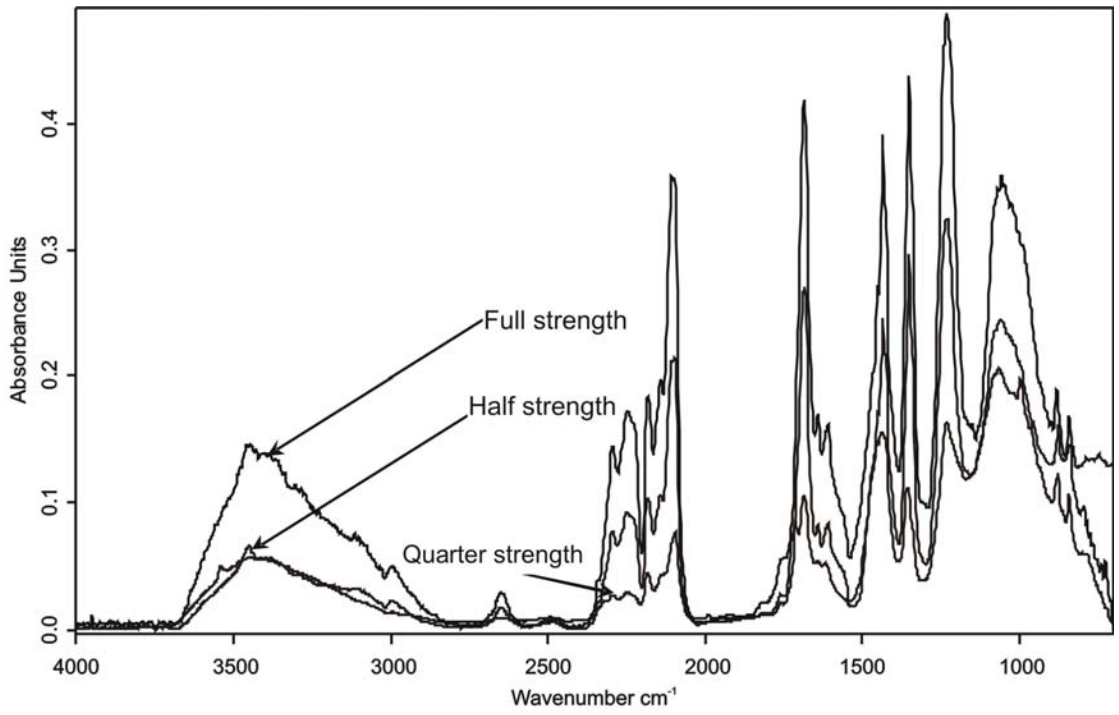


Figure 4.13 FTIR spectrum of the HPIA fraction of three different concentrations of Suwannee River DOC spiked water samples.

4.4.6 HPIN

The FTIR spectrum of the HPIN fraction of the Suwannee River DOC sample is shown at Figure 4.14. Table 4.9 lists the diagnostic bands and the absorption peaks present in the spectrum. Alcohol and amide are identified as the main functional groups present in the HPIN. Alcohol in the HPON fraction did not show clear activity in the formation of THM as stated above.

The absence of the C=O stretching band near 1715±10 cm^{-1} in Figure 4.14 indicates that aliphatic ketone is not contained in this fraction. However, the peak at 1634 cm^{-1} is within the range of the C=O stretching band for aromatic ketone and amides. Since this fraction is hydrophilic the peaks may be caused by the stretching band from amides. Kanokkantapong et al. (2006) suggested that ketone in the HPIN fraction is a precursor for forming HAA. However, for the Suwannee River DOC the lowest Specific THMFP occurred for the HPIN fraction. This suggests that Suwannee River HPIN excludes ketone and therefore is not active in the formation of THM.

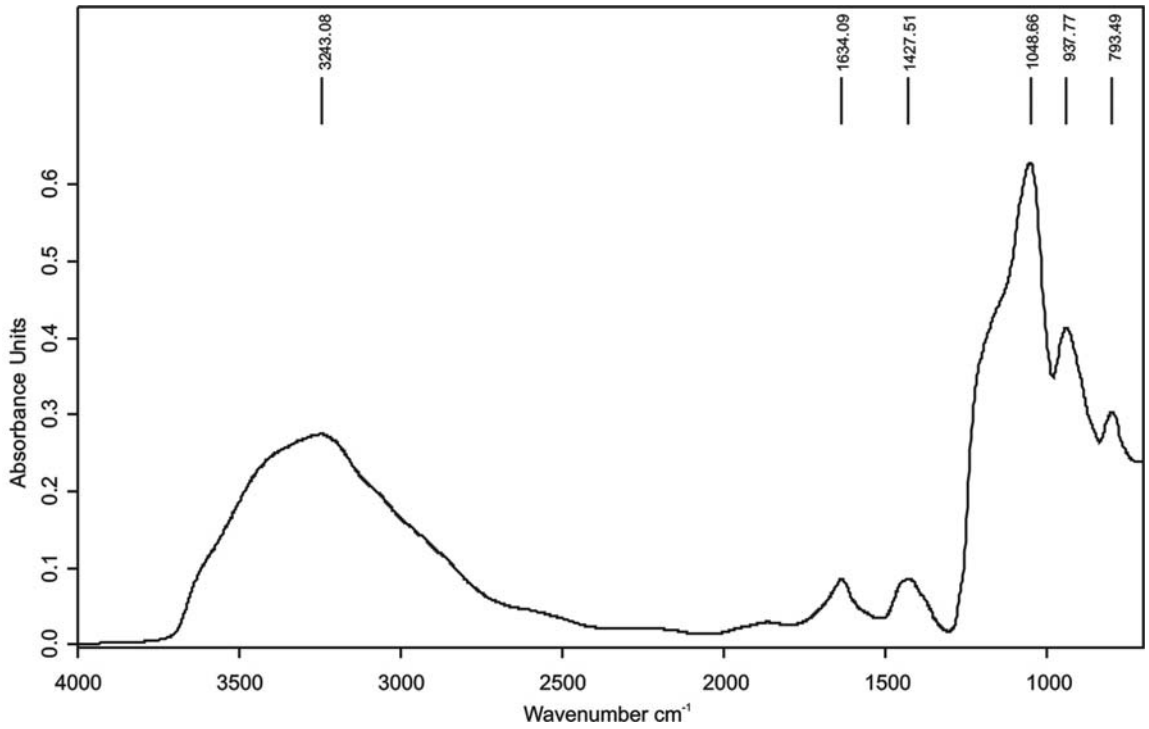


Figure 4.14 FTIR spectrum of the HPIN fraction of the Suwannee River DOC spiked water sample (1.60 mg/L DOC).

Table 4.9 HPIN functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3243
	C-O stretching: 1200-1000	1048
Amide	C=O stretching: 1680-1630	1634
	N-H stretching: 3370-3170	3243
	C-N stretching: 1430-1390	1427

The FTIR absorbance spectra for the full, half and quarter strength solutions of the HPIN fraction of Suwannee River DOC spiked water are presented in Figure 4.15. Consistent with the HPIB and HPIA fractions the absorption response is not proportional to relative concentration.

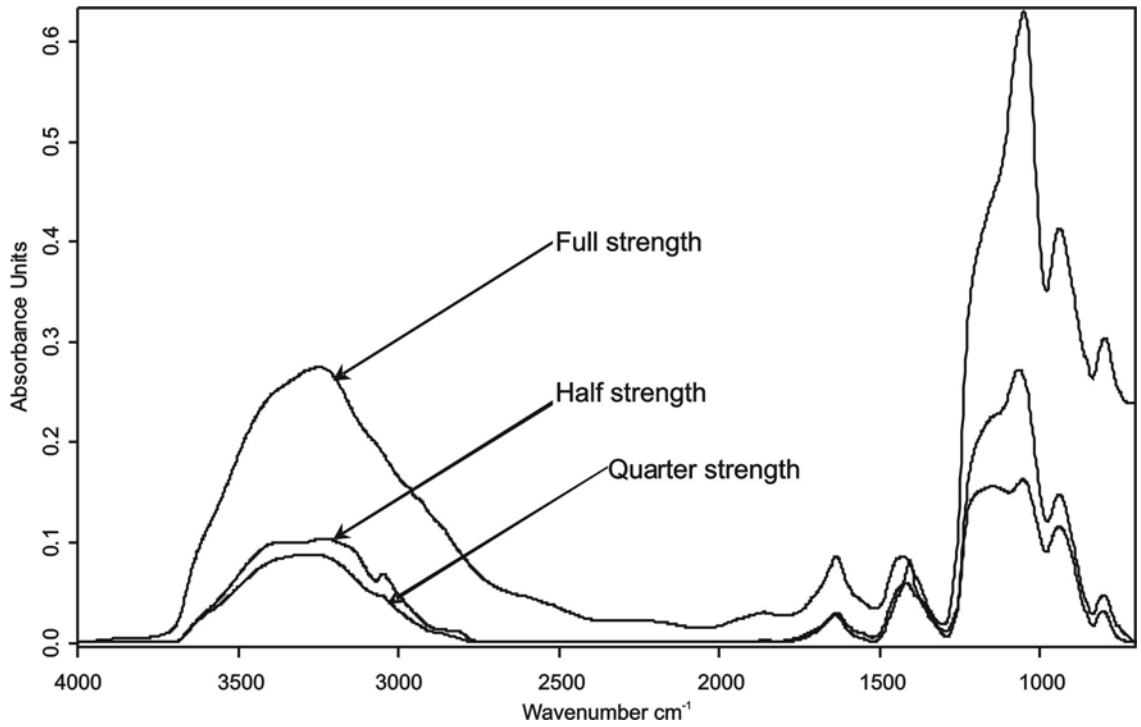


Figure 4.15 FTIR spectrum of the HPIN fraction of three different concentrations of Suwannee River DOC spiked water samples.

4.4.7 Analysis of Un-fractionated and Fractionated Suwannee River DOC.

The FTIR spectra of the un-fractionated Suwannee River DOC sample and its fractions are shown in Figure 4.16. The un-fractionated sample has the largest absorbance which indicates it has the highest DOC concentration. The spectra also indicate that the un-fractionated sample and the fractions are largely free of FTIR detectable inorganic constituents such as carbonates, nitrates, phosphates, silica and sulfates. The diagnostic bands of inorganic functional groups are listed in Table 4.10. However, some ionic nitrate (NO_3^{-1}) was present in the HPIA fraction as indicated by the peak at 1351 cm^{-1}. The ionic nitrate may also be present in the un-fractionated sample but its absorbance peak is masked by response from organic components with stronger absorbance peaks. Some other inorganic compounds may be present in the HPIA with peaks in the range of 2300-2100 cm^{-1}. However, these peaks were not evident in the un-fractionated sample spectrum so they are most likely caused by compounds leached from the resin materials as discussed in Section 4.4.5.

The spectra shown in Figure 4.16 indicate several functional groups containing N are part of the base fraction HPOB and the neutral fractions HPON and HPIN. Acidic

fractions were dominated by carboxylic acid. Alcohol, and amides were mostly present in the neutral fractions and ketone was only contained in HPON. The aliphatic hydrocarbon peak at around 1400 cm^{-1} in the hydrophilic fractions was more significant than in the hydrophobic fractions.

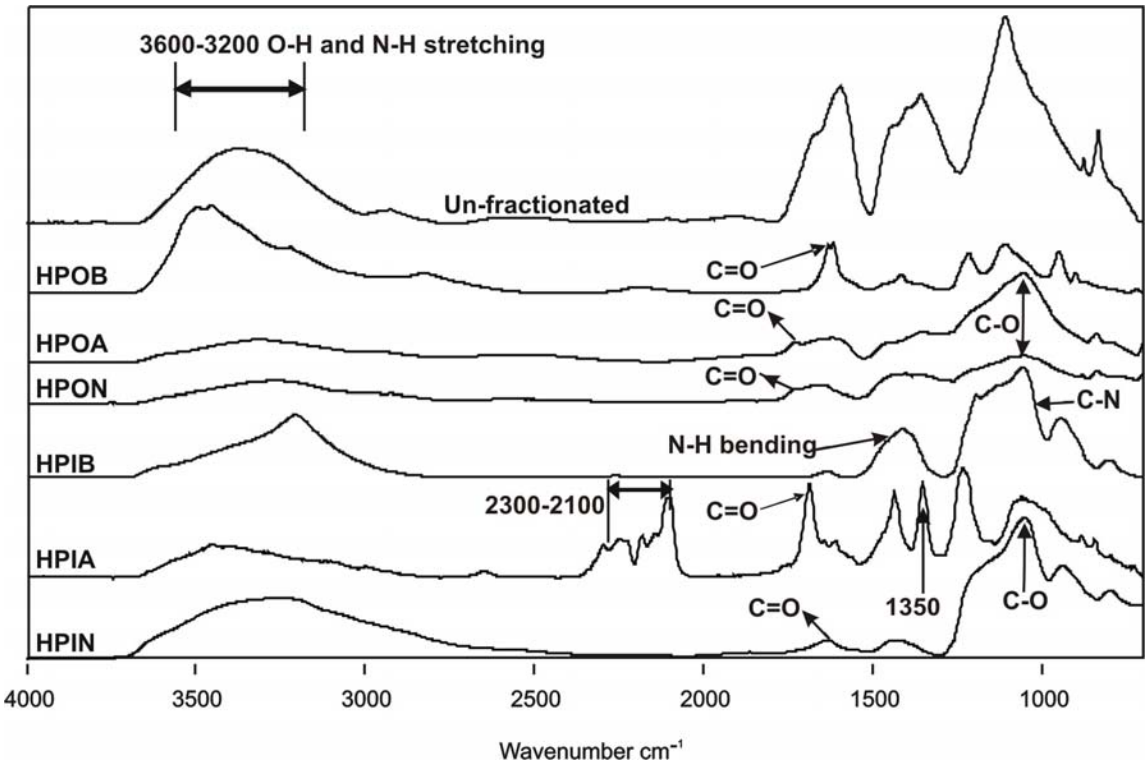


Figure 4.16 FTIR spectra of un-fractionated Suwannee River DOC and fractions. (All the spectra have the same base line and the same unit scale in the y-axis)

Table 4.10 Inorganic functional groups (Smith 1999).

Inorganic functional groups	Diagnostic bands (cm^{-1})
Carbonates	C-O stretching: 1510-1410 C-O out of plane bending: 880-860 C-O in plane bending: 740
Nitrates	N-O stretching: 1400-1340 N-O out of plane bending: 840-810 N-O in plane bending: 720
Phosphates	PO_4^{-3} stretching: 1100-1000 PO_4^{-3} bending: 600-500
Silica	Si-O stretching: 940 Si-O-Si symmetric stretching: 805 Si-O-Si bending: 450
Sulfates	S-O stretching: 1140-1080 S-O bending: 680-610

4.5 Important Functional Groups

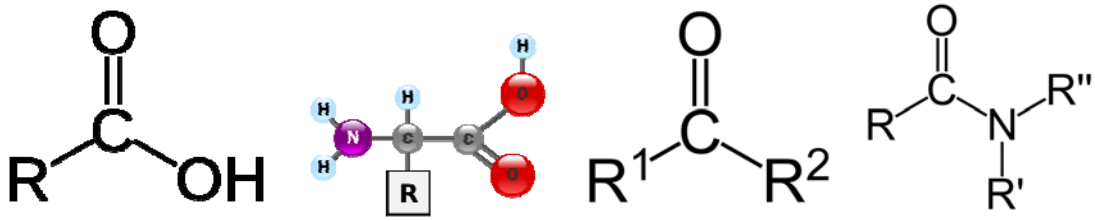
Table 4.10 summarizes the important function groups present in each fraction that are precursors for the formation of THM. The important functional groups are amino acid, amine, carboxylic acid, alcohol, ketone, and amides. The fractions containing carboxylic acids (whether hydrophobic or hydrophilic) always produced higher Specific THMFP values. Aromatic carboxylic acids in HPOA are more active THM precursors than the aliphatic carboxylic acids contained in HPIA. The carboxyl functional groups in amino acid are likely the reason HPOB has higher potential to create THM than HPIB. The absence of ketone in HPIN decreases its ability to form THM in comparison to HPON. Based upon the result shown in Table 4.11, the order of THMFP within either the hydrophobic or hydrophilic fractions can be ranked as follows: carboxylic acids > amino acid or amine > amides/ketone.

Table 4.11 Possible functional groups for HPIN

samples	Dominant functional groups	diagnostic bands	Specific THMFP (μg chloroform/mg C)
Un-fractionated			68.1±5.6
HPOB	Amino acid	C=O stretching: 1800-1600 Aromatic N-H stretching: 3500-3420 N-H bending: 1650-1580 Aromatic C-N stretching: 1350-1200 Saturated C-N stretching:1180-1030	81.8±31.2
HPOA	Aromatic carboxylic acid	Aromatic C=O stretching: 1730-1680 ionized carboxyl:1650-1540 O-H stretching: 3500-2500 C-O stretching: 1300-1000	90.6±51.3
HPON	Alcohol, ketone, amide	O-H stretching: 3600-3200 C-O stretching: 1200-1000 O-H bending: 1410-1260 C=O stretching: 1680-1630 N-H stretching: 3370-3170 C-N stretching: 1430-1390	66.7±16.9
HPIB	Aliphatic amine	Saturated N-H stretching: 3320-3200 N-H bending: 1650-1580 Saturated C-N stretching: 1180-1030	50.4±5.1
HPIA	Aliphatic carboxylic acid	Saturated C=O stretching: 1710-1680 O-H stretching: 3500-2500 C-O stretching: 1300-1000 O-H in-plane bending: 1440-1395	53.6±14.9
HPIN	Aliphatic alcohol, amide	O-H stretching: 3600-3200 C-O stretching: 1200-1000 C=O stretching: 1680-1630 N-H stretching: 3370-3170 C-N stretching: 1430-1390	36.4±16.8

As discussed above the organic compounds which are most active in THM formation are amino acid, carboxylic acid, ketone, and amides. These compounds have either the C=O and/or N-H bonding structure as illustrated in Figure 4.17. Alcohol does not contain C=O or nitrogen in its molecular structure. Furthermore the literature cited in Sections 4.4.3 and 4.4.6 indicated alcohol was not active in the formation of Specific THMFP. Therefore, alcohol is not an important compound for formation of THM.

The main stretching bands of C=O and/or N-H bonding in the FTIR spectra are in the area of 1800-1650 cm^{-1} and 3620-3600 cm^{-1}. The N-H stretching band is hard to distinguish from the O-H stretching band. Therefore, the N-H bending band (1650-1580 cm^{-1} or 1650-1500 cm^{-1} depending upon literature cited) is used as an alternative diagnostic band for the element N. Because carboxylic acid is the most important organic compound for the generation of THM, then the carboxyl C=O stretching band at 1710-1680 cm^{-1} should be checked as the first step in the interpretation of FTIR spectra. Therefore, when analyzing FTIR spectra of any DOC sample the key absorption bands of interest are the C=O stretching and N-H bending band. The organic compounds related to these two bands' are the most likely to cause higher THM.



Carboxylic acids Amino acids Ketone Amides

Figure 4.17 Molecular structure of important functional groups (http://en.wikipedia.org).

CHAPTER 5. DOC CHARACTERIZATION OF TYPICAL PRAIRIE WATER SAMPLES

In the previous chapters the development of the method for sample preparation and FTIR analysis to characterize the DOC content of a water sample was described. In this chapter the method was applied to characterize water samples collected from various locations within Saskatchewan. These include Buffalo Pound Lake, Yellow Quill Water Treatment Plant, South Saskatchewan River at Saskatoon and water from a dugout water supply system near Craik.

5.1 Buffalo Pound Water Treatment Plant

5.1.1 Study Site

The Buffalo Pound Water Treatment Plant is shown in Figure 5.1. It is jointly owned and operated by the cities of Moose Jaw and Regina, Saskatchewan and has been in operation since 1955. It is located near Moose Jaw on Buffalo Pound Lake about 226 km south from Saskatoon. The plant supplies treated drinking water to Regina and Moose Jaw and the surrounding region. The water is taken from Buffalo Pound Lake, a shallow reservoir in the Qu'Appelle Valley. The average residence time of water in the lake varies from six to thirty months (Wandzura 2006). The main source of the water is local snow-melt and runoff supplemented with controlled flow from Lake Diefenbaker. Lake Diefenbaker water originates from the mountains of Alberta collected by various tributaries draining to the South Saskatchewan River. Buffalo Pound Lake is rich in nutrients from runoff from agricultural fields and commonly subject to algae growth (diatoms in the winter and blue-green types in the summer) (Wandzura 2006).

Figure 5.1 Buffalo Pound Water Treatment Plant.

5.1.2 Water Treatment System

The treatment system was designed to remove bacteria, algae, clay particles, and dissolved organic materials in order to make the treated water clear, colourless, odour-free, aesthetically pleasing and safe to drink (Wandzura 2006). The treatment process consists of six main stages: chlorination, cascade de-gasification, coagulation flocculation, clarification, filtration and carbon adsorption. Water softening is not conducted. Near the end of the treatment process granular activated carbon (GAC) is used to remove dissolved organic matter. GAC contains many microscopic pores for adsorbing dissolved organic compounds which cause taste and odour. The GAC adsorption treatment process at the Buffalo Pound Lake Water Treatment Plant is only used during periods of poor taste and odour in the source water (Wandzura 2006). This period is normally from May until November.

5.1.3 Sample Collection

Samples of source water, after coagulation\flocculation\settling (CFS), and after GAC adsorption were collected in 4 L amber glass bottles at the Buffalo Pound Lake Water Treatment Plant on September 30, 2008. The samples were filtered through a pre-rinsed 0.45µm filter to remove particles and suspended organic matter and then stored in a dark room at 4 ºC to minimize microbial growth and transformation of organic compounds.

5.1.4 Analysis Methods

DOC concentration measurements were conducted with a Phoenix 8000 UV-persulfate TOC analyzer (TEKMAR DOHRMANN). At least three measurements were performed for each sample. The analysis precision was typically within ±5%. UV absorbance was measured with a HACH DR/4000U UV/VIS spectrophotometer at wavelengths of 203 and 254 nm using a 1 centimetre quartz cell. All samples were adjusted to pH 7 with H_2SO_4 and/or NaOH before measurement. A 7-day chlorination THMFP test was carried out in accordance with Standard Method 5710B (APHA et al. 2005). Residue samples were prepared on reflective slides as described in Section 3.6.4 to be scanned in the CLS Mid-infrared lab.

5.1.5 Results and Discussion

5.1.5.1 Characteristics and Removal of Buffalo Pound Lake DOC during treatment

The DOC, SUVA, ratio of UV_{254}/UV_{203}, and Specific THMFP in source and treated waters at the Buffalo Pound Water Treatment Plant are shown in Figure 5.2. A detailed listing of all water sample data is presented in Appendix F. DOC decreased from 7.05 mg/L in the source water to 3.44 mg/L and then 3.13 mg/L through the coagulation\flocculation\settling (CFS) and AC adsorption processes respectively. The AC adsorption treatment process only removed 9% of the DOC remaining after CFS treatment.

The SUVA value after CFS treatment was larger than for source water. This indicates the DOC in the water after CFS treatment has a larger proportion of hydrophobic compounds than the raw water. In other words, CFS treatment is more effective in removing the hydrophilic DOC fractions than the hydrophobic (aromatic) DOC content.

After AC treatment, the SUVA number decreased due to adsorption of the hydrophobic fractions. Previous researchers found that smaller DOC (generally hydrophilic) molecules are preferentially adsorbed on AC because a large percentage of the surface area of the AC is associated with micro-pores that cannot be accessed by larger DOC (generally hydrophobic) molecules (Summers and Roberts 1988). However,

the water samples were collected in the latter portion of 2008 when the AC beds are normally approaching their adsorption capacity. Under these conditions the AC internal adsorption sites are likely occupied and the small molecules would not have had a competitive advantage over the larger molecules. Van der Waals forces strongly influence the adsorption of non-polar DOC molecules. Hence, the hydrophobic fractions which contain a higher proportion of non-polar molecules have enhanced adsorption on the AC.

In Figure 5.2, the UV_{254}/UV_{203} ratio decreased from 0.33 before AC treatment to 0.11 after treatment. Kim and Yu (2005) reported that the UV_{254}/UV_{203} ratio depends on the phenolic content of the water. Therefore the AC treatment appears to remove a portion of the phenolic fraction.

The Specific THMFP of source, after CFS and after AC treated waters were 45.7, 58.5, 37.6 µg chloroform/mg C, respectively. This indicates the CFS treated water has a higher potential for generating THM and correspondingly a larger hydrophobic fraction with larger SUVA values. The Specific THMFP was decreased after AC treatment. It appears the AC adsorption reduced the potential of the DOC for generating THM by removal of hydrophobic compounds as discussed above.

SUVA is positively correlated (R^2=0.99) with specific THMFP as shown in Figure 5.3. As stated in previous research (Kanokkantapong et al. 2006), the THMFP is mainly caused by aromatic organic components. These results illustrate that the treatment process after AC at Buffalo Pound Lake Water Treatment Plant removes a significant portion of the aromatic fraction of the DOC. Further, the altered SUVA and THMFP readings after the treatment process indicate the DOC characteristics were changed.

The UV_{254}/UV_{203} ratio and specific THMFP is plotted in Figure 5.4. No relationship is evident which contradicts the statement in the literature that the UV_{254}/UV_{203} ratio can be a good indicator of the tendency of the water to form THM (Kim and Yu, 2005).

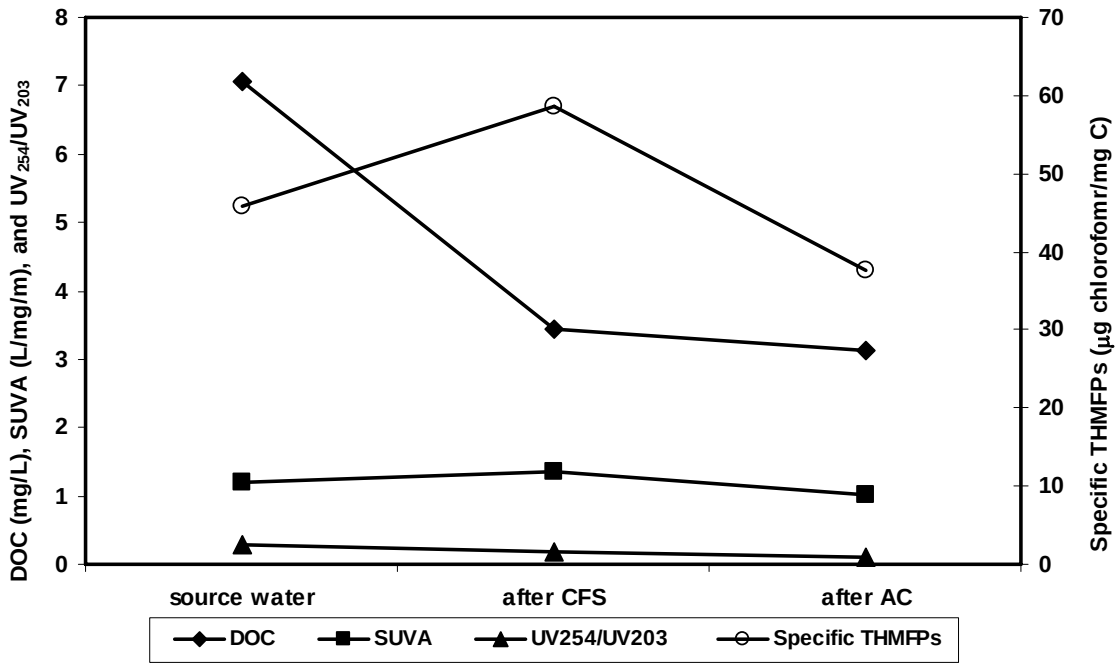


Figure 5.2 Variation in source and treated water quality at the Buffalo Pound Water Treatment Plant.

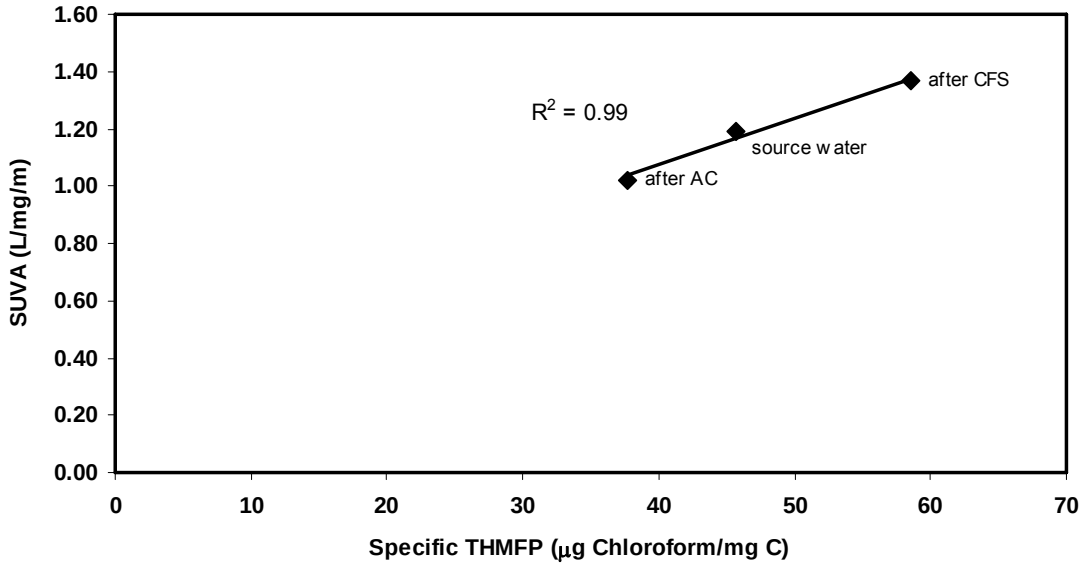


Figure 5.3 Relationship between SUVA and specific THMFP of treated water at the Buffalo Pound Water Treatment Plant.

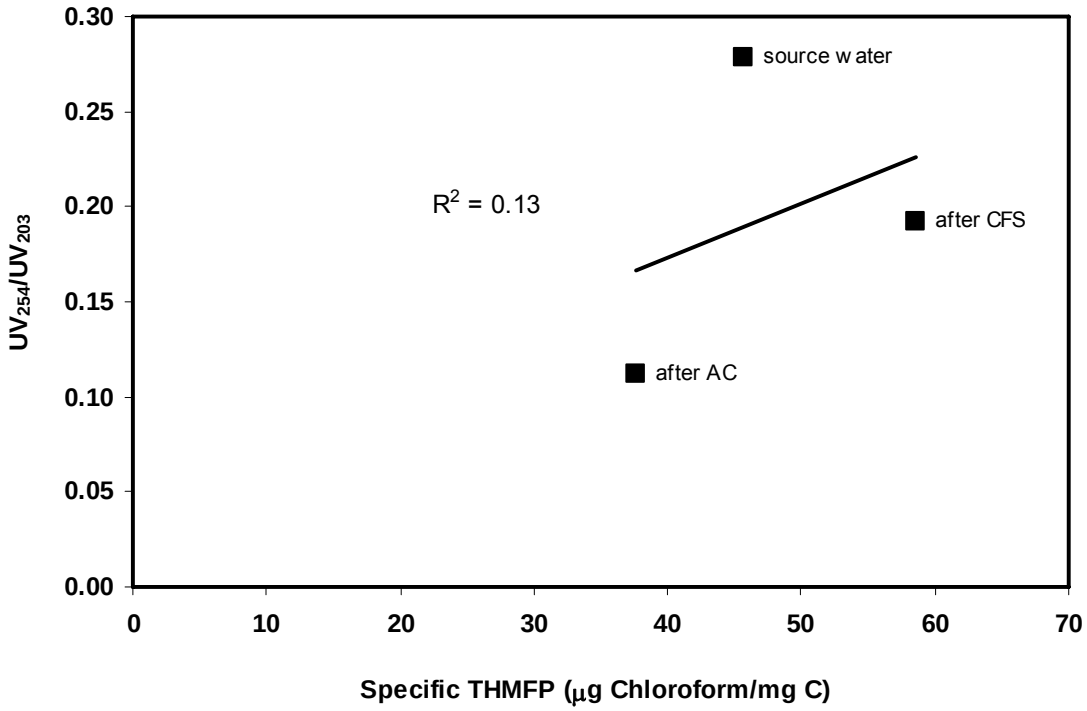


Figure 5.4 Relationship between UV_{254}/UV_{203} ratio and specific THMFP of treated water at the Buffalo Pound Water Treatment Plant.

5.1.5.2 FTIR Spectra of Buffalo Pound Water Treatment Plant Samples' DOC

The FTIR spectrum[8] of Buffalo Pound Water Treatment Plant source water is shown at Figure 5.5. Table 5.1 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that aromatic ketone, amide and alcohol are the major functional groups in the source water DOC. Also, the peak at 1540 cm^{-1} is assigned to NO_2 asymmetric stretching of aromatic nitro functional group (Smith 1999). However, because the peak at 1540 cm^{-1} is not significant compared with other bands the sample may only include a few nitro functional groups. There is no possibility of phenol being present due to the absence of C-O stretching in the range of 1260-1200 cm^{-1}. The peak at 1413 cm^{-1} is assigned to aliphatic C-H deformation (e.g. cyclohexane (a cyclic compound) or hexane (an acyclic compound)) (Lin et al. 2001).

[8] The replicate FTIR spectra of all the source and treated water samples are presented in Appendix E.

Table 5.1 Buffalo Pound Water Treatment Plant source water functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3377
	C-O stretching: 1210-1000	1103
Ketone	Aromatic C=O stretching: 1700-1640	1661
Amide	C=O stretching: 1680-1630	1661
	N-H stretching: 3370-3170	3377
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1413

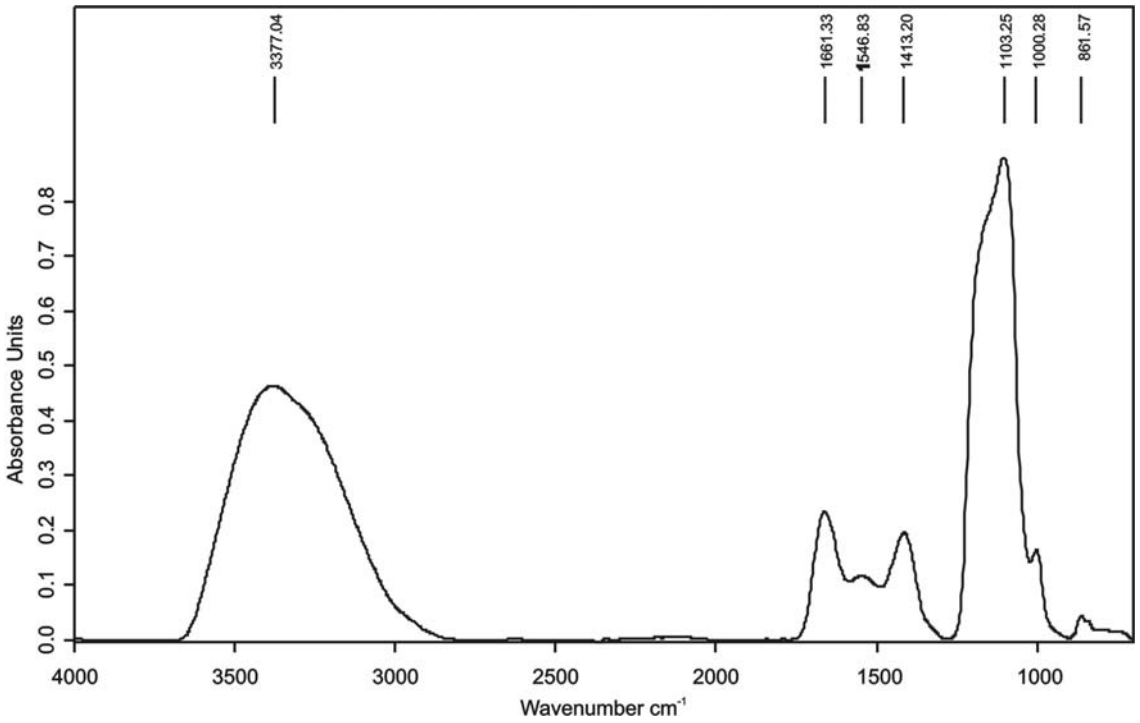


Figure 5.5 FTIR spectrum of source water at the Buffalo Pound Water Treatment Plant.

The FTIR spectrum of water after CFS treatment at the Buffalo Pound Water Treatment Plant is shown in Figure 5.6. Table 5.2 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that aromatic ketone, amide and alcohol are the major functional groups in the water after CFS treatment. Since the absorbance intensities were decreased in Figure 5.6 compared with those in Figure 5.5 the DOC concentration have been decreased.

The main difference between the source water sample and CFS treated water is the intensity of the absorbance peaks for the major functional groups have decreased. There is especially a significant decrease for aliphatic compounds. Therefore the CFS

treatment has more effectively removed the aliphatic organic compounds. Further, the nitro functional groups stretching band disappeared after CFS treatment.

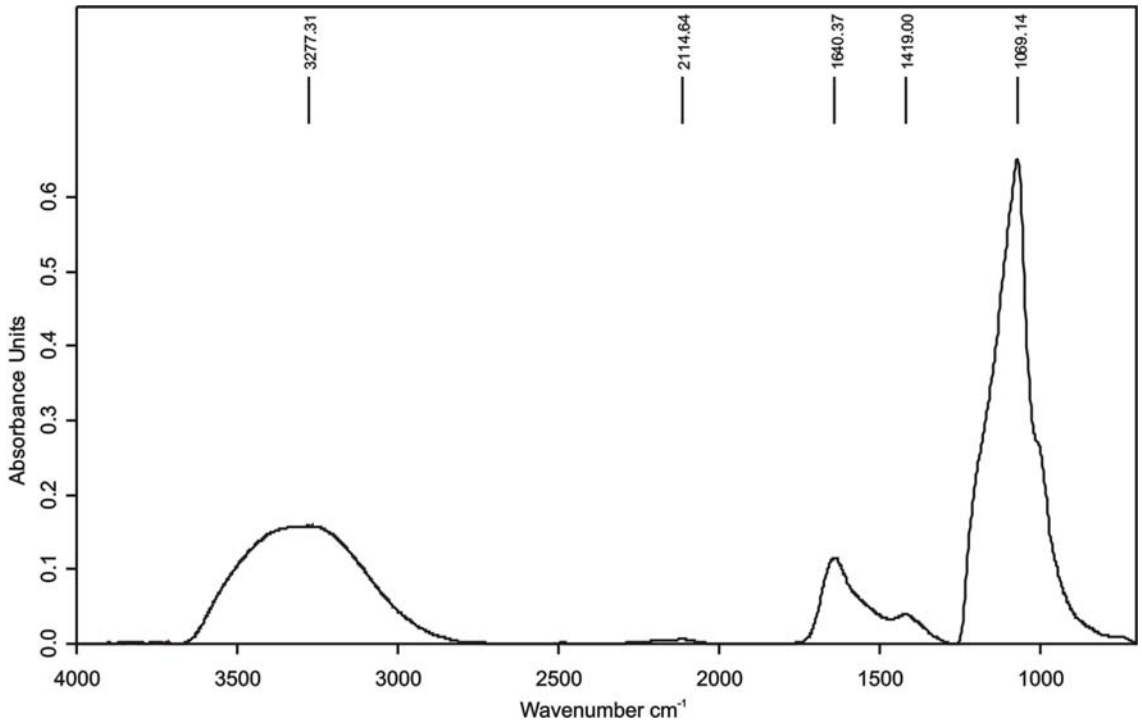


Figure 5.6 FTIR spectrum of CFS treated water at the Buffalo Pound Water Treatment Plant.

Table 5.2. Buffalo Pound Water Treatment plant CFS treated water functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3277
	C-O stretching: 1210-1000	1069
Aromatic Ketone	Aromatic C=O stretching: 1700-1640	1640
Amide	C=O stretching: 1680-1630	1640
	N-H stretching: 3370-3170	3277
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1419

The FTIR spectrum of water after AC treatment at the Buffalo Pound Lake Water Treatment Plant is shown at Figure 5.7. Table 5.3 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol and amide are the major functional groups in the AC treated water. Ketone is not present because there is no response in the C=O stretching band at 1700-1640 $cm^{-1.}$

The peak absorbance values of this sample are only slightly lower than those of the CFS treated sample. This indicates that the AC treatment further reduced DOC concentration but not as significantly as the CFS treatment.

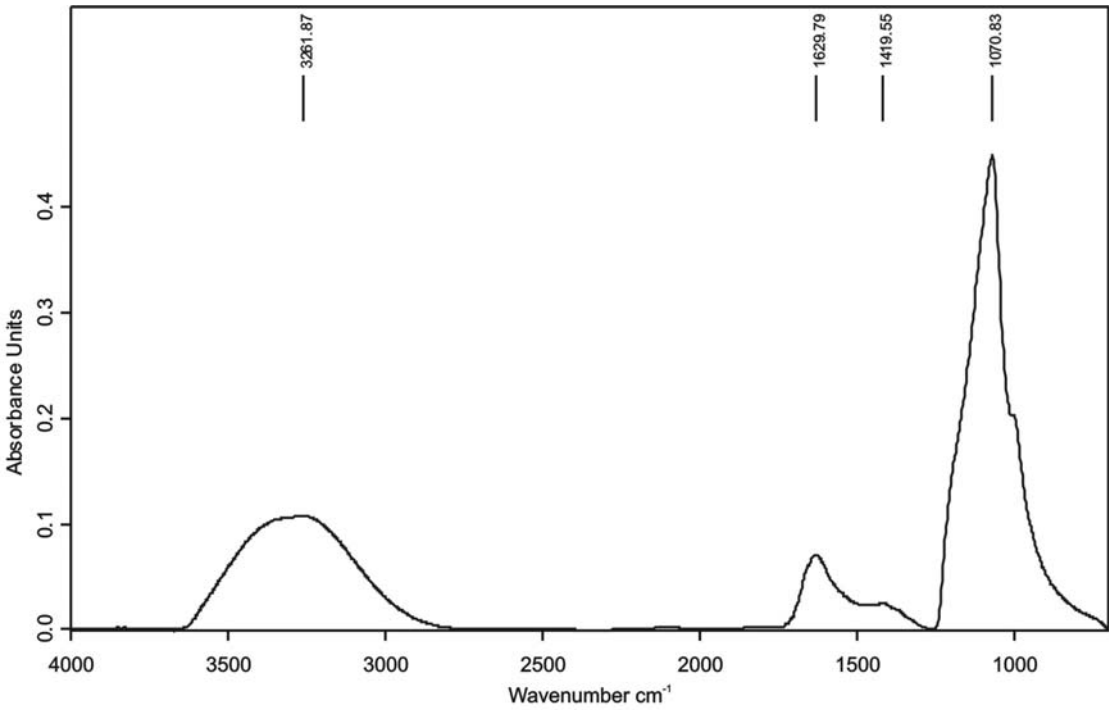


Figure 5.7 FTIR spectrum of AC adsorbed water at the Buffalo Pound Water Treatment Plant.

Table 5.3 AC treated water DOC functional groups at the Buffalo Pound Water Treatment plant.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3261
	C-O stretching: 1210-1000	1070
Amide	C=O stretching: 1680-1630	1630
	N-H stretching: 3370-3170	3261
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1419

The spectra of all three samples collected at Buffalo Pound Water Treatment Plant are shown in Figure 5.8. The largest absorbance response is produced by the source water sample which suggests the source water has the highest DOC concentration. The decreases in DOC concentration caused by CFS and AC adsorption treatment are indicated by the decrease in peak response measured in absorbance units on the y-axis.

Comparison of the response pattern of the three spectra indicates the peak around 1420 cm^{-1} caused by aliphatic C-H deformation decreased significantly after CFS and was further reduced after AC adsorption. Therefore, CFS followed by AC adsorption seems to be quite effective at the removal of aliphatic organic compounds. The nitro functional group indicated by the absorption peak at 1540 cm^{-1} in the raw water spectrum was also removed by CFS treatment and ketone was removed after AC adsorption.

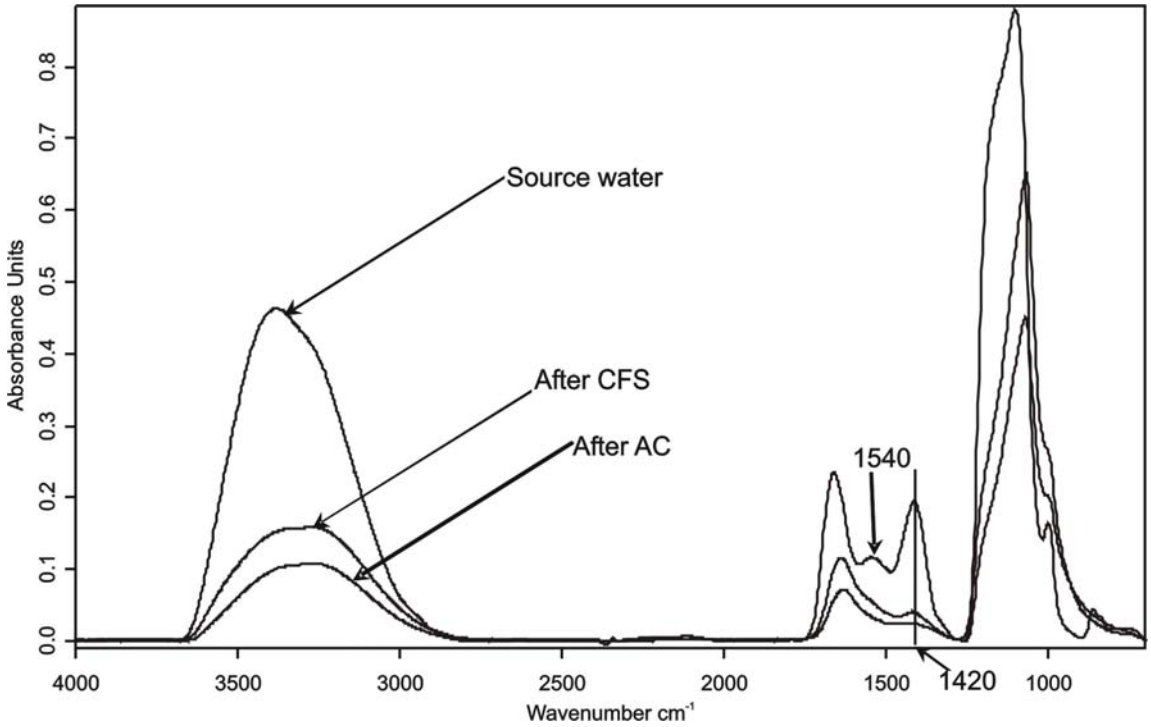


Figure 5.8 FTIR spectra of Buffalo Pound Lake Water Treatment Plant water samples.

5.2 Yellow Quill Water Treatment Plant

5.2.1 Study Site

Yellow Quill is an aboriginal community of around 1,000 people. In the past its drinking water source was a polluted creek that only flowed between 5 and 14 days each spring (Neapetung 2006) (Figure 5.9). Due to the extremely poor water quality the water source was switched to a well. The water was being successfully treated[9] through

[9] Unfortunately the plant was destroyed by fire on January 31, 2010.

a process developed by H. Peterson of the Safe Drinking Water Foundation as shown in Figure 5.10 (Peterson 2008).

Figure 5.9 Previous source water for the Yellow Quill Water Treatment Plant (Neapetung 2006).

5.2.2 Water Treatment System

The Yellow Quill water treatment system is an integrated biological filter and reverse osmosis membrane treatment system as shown in Figure 5.10. The attached growth media in the biological filter looks like coffee grounds (Figure 5.11) and provides adsorption sites for bacteria. In the biological filter system bacteria remove iron and oxidize ammonium. The goal is to remove all compounds that are either a nutrient or an energy source for bacteria so that no further bacterial growth can occur in the reverse osmosis (RO) filtration. Figure 5.12 shows the biological treatment system in the plant. After biological filtration the RO treatment (Figure 5.13) removes most of the remaining organic compounds without plugging or fouling of the membrane.

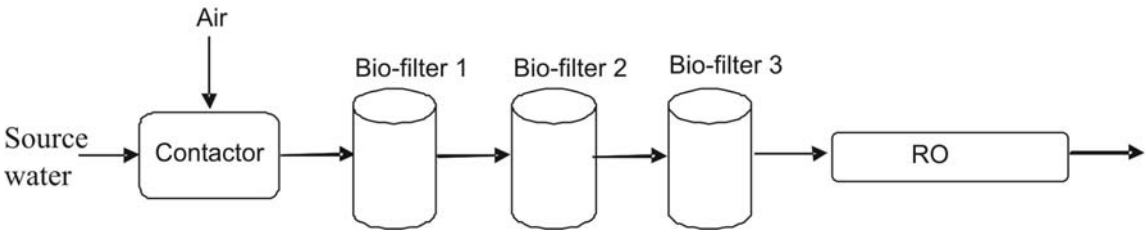


Figure 5.10 Flow chart of the Yellow Quill Water Treatment System.

Figure 5.11 Bio-filter media in Yellow Quill treatment system (Neapetung, 2006).

Figure 5.12 Biological filter system in the Yellow Quill Water Treatment Plant.

Figure 5.13 Reverse Osmosis system in the Yellow Quill Water Treatment Plant.

5.2.3 Sample Collection

Samples of source water, biologically treated water and RO treated water were taken in 4 L amber glass bottles (Figure 5.14) from the Yellow Quill Water Treatment Plant on October 15, 2008. The source water and biologically treated water samples were filtered through pre-rinsed 0.45µm filters to remove particulates and suspended organic matter. The samples were stored in a dark room at 4 ºC before analysis to minimize microbial growth and transformation of organic compounds.

Figure 5.14 Sampling bottle used at the Yellow Quill Water Treatment Plant.

5.2.4 Analysis Methods

The analysis methods used were the same as those described in Section 5.1.4.

5.2.5 Results and Discussion

5.2.5.1 Characteristics and Removal of Yellow Quill DOC during treatment

The DOC, SUVA, ratio of UV_{254}/UV_{203}, and specific THMFP in source and treated waters at Yellow Quill Water Treatment Plant are shown in Figure 5.15. A detailed listing of all water samples data is presented in Appendix F. DOC concentrations of source water and bio-filtered water are 9.86 mg/L and 10.08 mg/L, respectively. Iron rather than organic carbon compounds is utilized as an energy source by bacteria during bio-filter treatment. Under these conditions the DOC would not be expected to decrease significantly (Peterson 2008). That is why the bio-filtered water DOC concentration is not decreased. The subsequent RO membrane treatment decreased the DOC concentration to 1.08 mg/L.

The SUVA values and specific THMFP followed similar trends as the change in DOC concentration. The UV_{254}/UV_{203} ratio gradually decreased during treatment. The SUVA value is positively correlated with Specific THMFP (R^2=0.91) as shown in Figure 5.16. However the UV_{254}/UV_{203} ratio has no linear relationship with Specific THMFP (Figure 5.17).

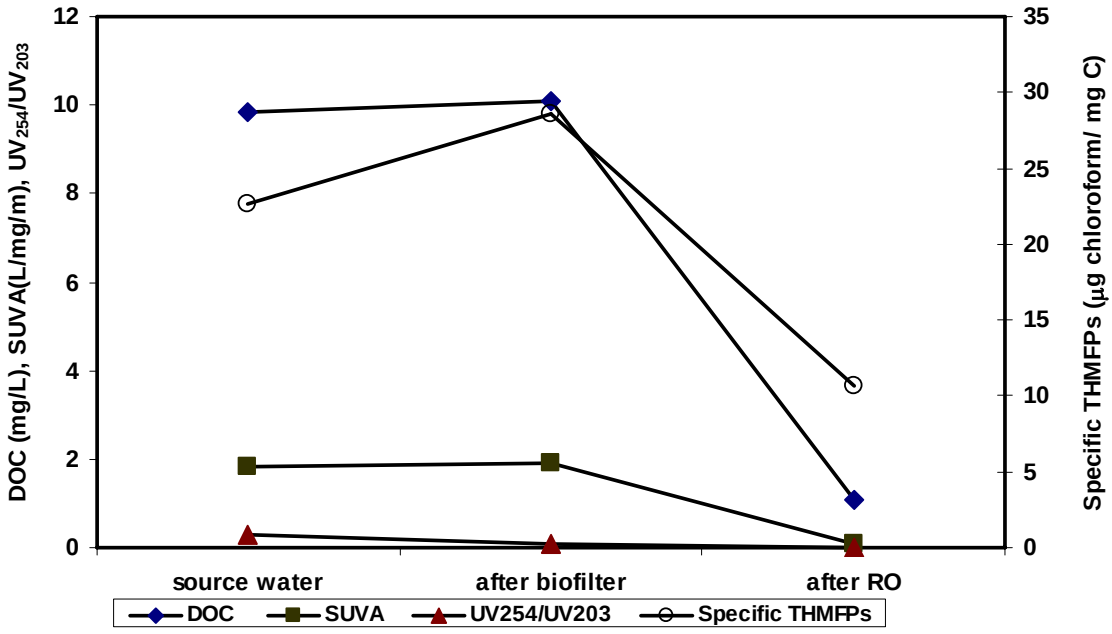


Figure 5.15 Variation in source and treated water quality at the Yellow Quill Water Treatment Plant.

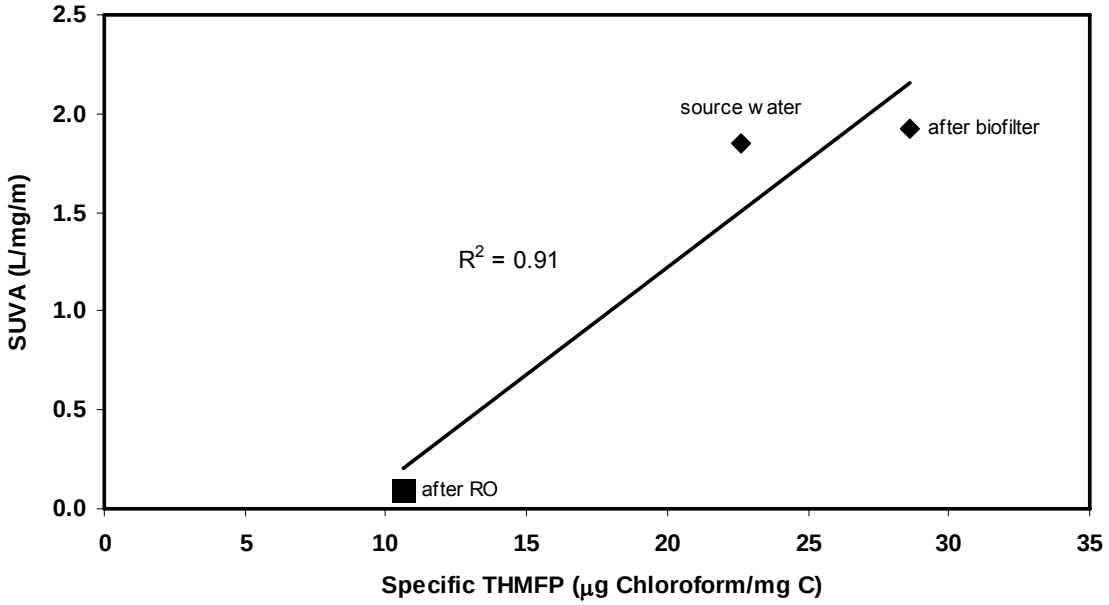


Figure 5.16 Relationship between SUVA and Specific THMFP of treated water at the Yellow Quill Water Treatment Plant.

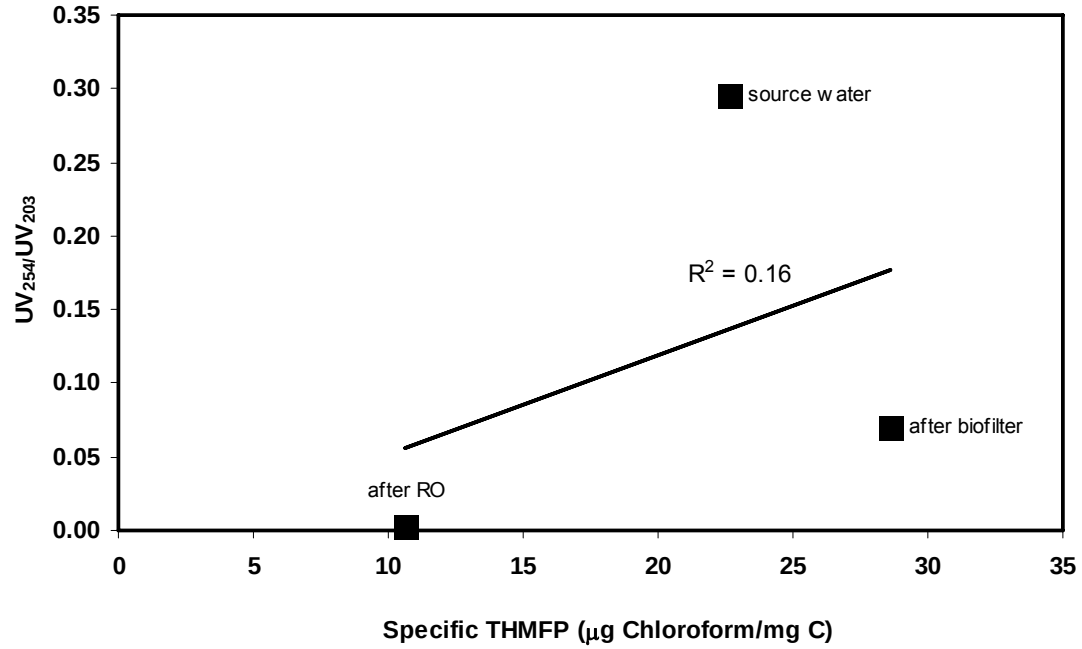


Figure 5.17 Relationship between UV_{254}/UV_{203} ratio and Specific THMFP of treated water at the Yellow Quill Water Treatment Plant.

5.2.5.2 FTIR Spectra of Yellow Quill Water Treatment Plant Samples' DOC

The FTIR spectrum of Yellow Quill Water Treatment Plant source water is shown in Figure 5.18. Table 5.4 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol, amide, and phenol

are the major functional groups in the source water. The peak at 2143 cm^{-1}, which was completely absent in the spectrum for Buffalo Pound Lake water, could be an indication that C≡C in alkyne or C≡N at nitrile is present. The peak at 1425 cm^{-1} is assigned to aliphatic C-H deformation.

Table 5.4 Source water DOC functional groups at the Yellow Quill Water Treatment plant.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3509
	C-O stretching: 1210-1000	1091 and 1000
Amide	C=O stretching: 1680-1630	1669
	N-H stretching: 3370-3170	3200
Phenol	O-H stretching: 3600-3200	3509
	C-O stretching: 1260-1200	1225
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1425

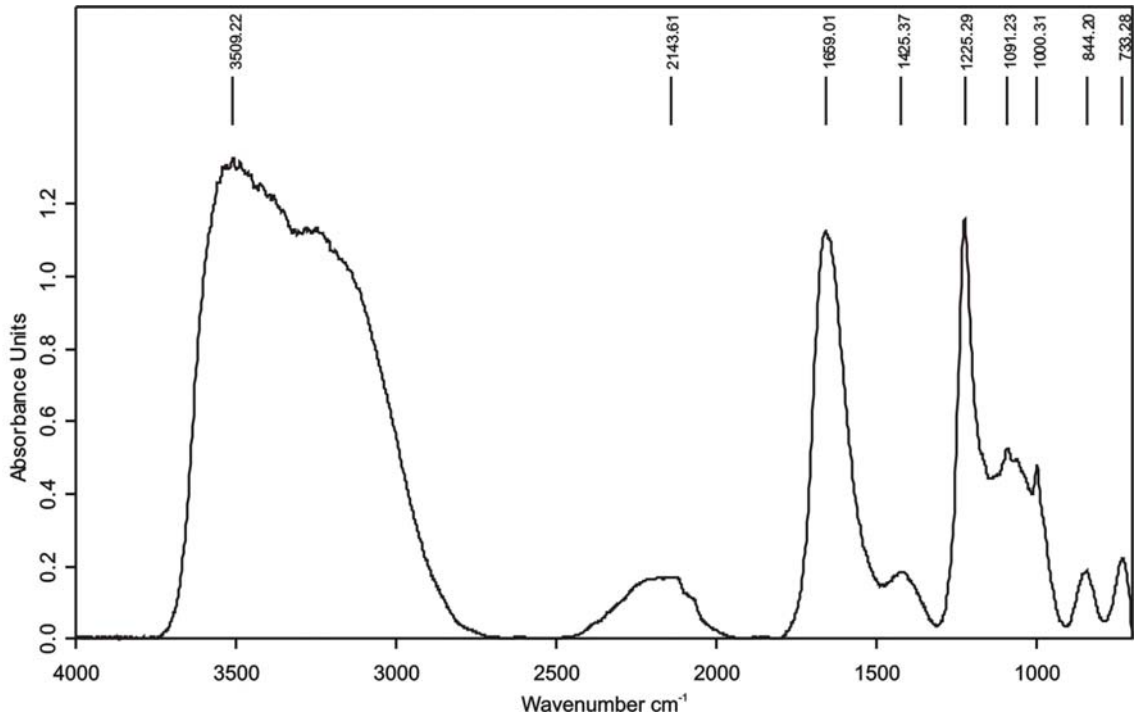


Figure 5.18 FTIR spectrum of source water at the Yellow Quill Water Treatment Plant.

The FTIR spectrum of bio-filter treated water from the Yellow Quill Water Treatment Plant is shown at Figure 5.19. Table 5.5 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol,

amide, and phenol are the major functional groups present which is similar to the source water.

Changes in the source water and bio-filtered water FTIR spectrum indicate the bio-filter is altering the organic compound distribution in the DOC but not reducing the total DOC concentration. This conclusion is based upon the following observations:

- the peak at 1090 cm^{-1} for C-O stretching in alcohol was increased and the peak at 1658 cm^{-1} for C=O stretching in amide has decreased;
- the response in the 3600-3200 cm^{-1} band is a combination of the O-H stretching band in alcohol and the N-H stretching in amide; and
- the intensity of the response in the 3600-3200 cm^{-1} band remains the same.

Further, the band at 1470-1420 cm^{-1} is stronger than that in Figure 5.18 which indicates the aliphatic structures were increased after bio-filter treatment. In addition, the peak at 2122 cm^{-1} for C≡C from alkyne or C≡N from nitrile was decreased.

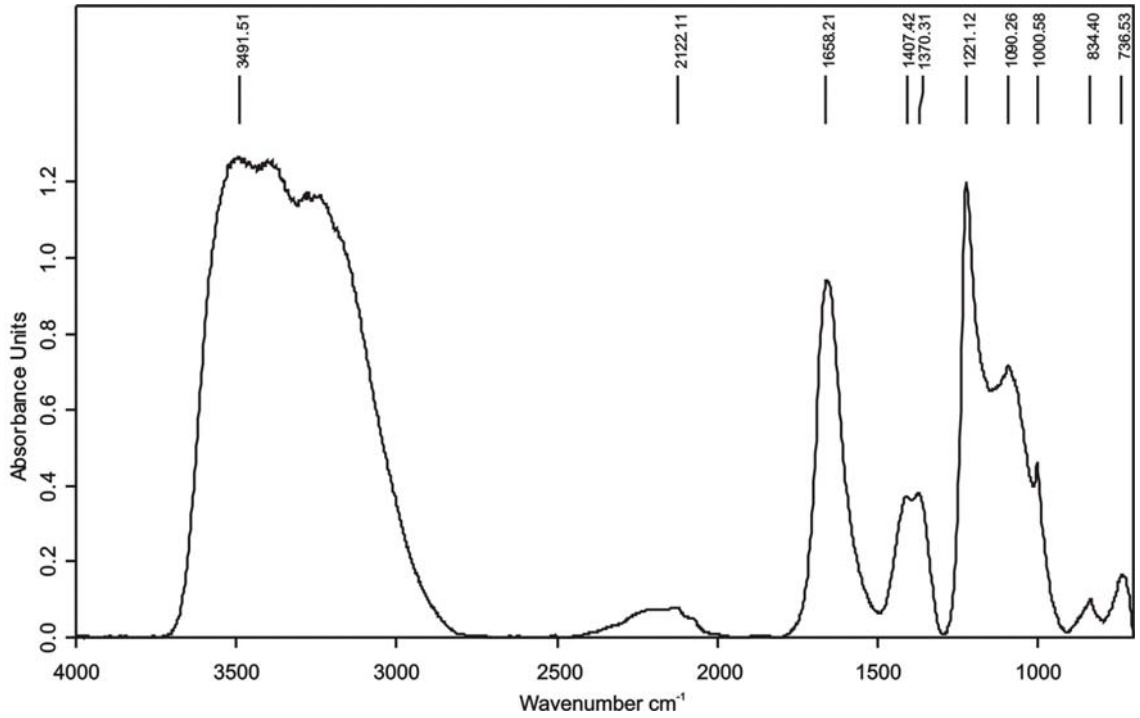


Figure 5.19 FTIR spectrum of bio-filter treated water at the Yellow Quill Water Treatment Plant.

Table 5.5 Bio-filtered water DOC functional groups at the Yellow Quill Water Treatment plant.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3491
	C-O stretching: 1210-1000	1090 and 1000
Amide	C=O stretching: 1680-1630	1658
	N-H stretching: 3370-3170	3200
Phenol	O-H stretching: 3600-3200	3491
	C-O stretching: 1260-1200	1221
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1407 and 1370

The FTIR spectrum of RO filtered water at the Yellow Quill Water Treatment Plant is shown in Figure 5.20. Table 5.6 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol is the major functional group. Note the change in vertical scale between Figure 5.19 and 5.20 because all absorbance responses have been greatly reduced in comparison to the bio-filtered water.

After RO treatment amide is almost gone as indicated by the very weak C=O stretching band with peak 1665 cm^{-1} (Figure 5.20). A large portion of the DOC after RO treatment is alcohol as indicated by the response in the C-O and O-H stretching bands. There is no peak in the 1260-1200 cm^{-1} C-O stretching band for phenol (Figure 5.20). Therefore phenol has been removed by RO treatment. In addition the C-H deformation band at 1361 cm^{-1} suggests that aliphatic organic structures are still present in a relatively large proportion.

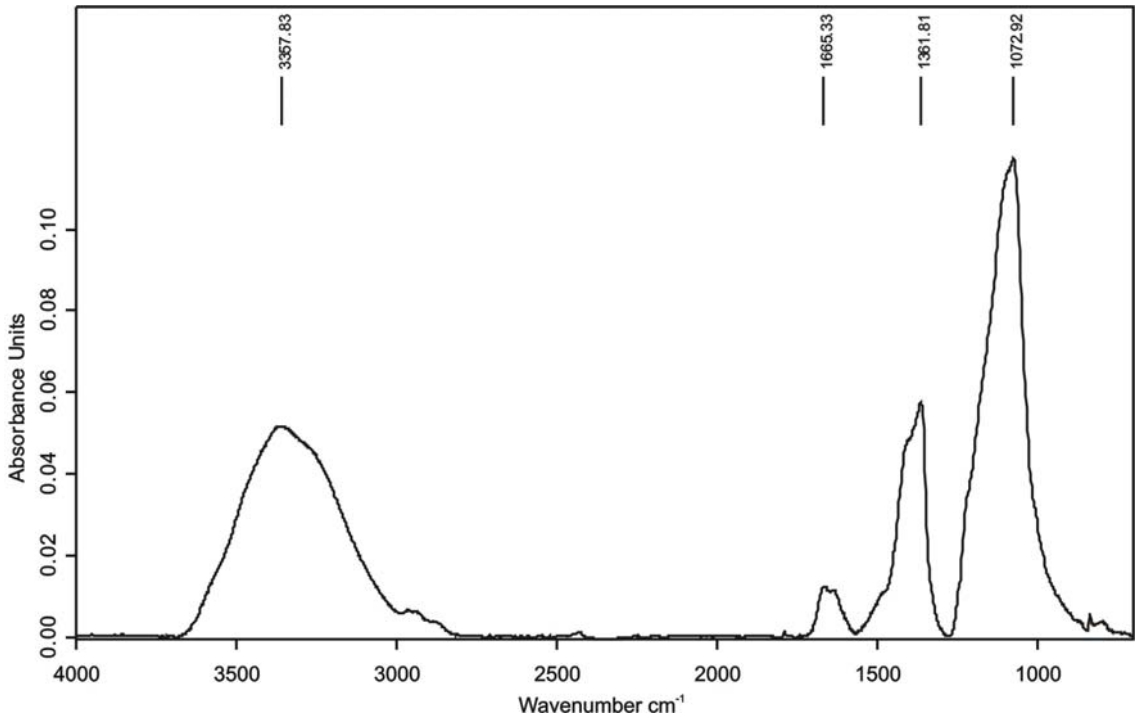


Figure 5.20 FTIR spectrum of RO treated water at the Yellow Quill Water Treatment Plant.

Table 5.6 RO treated water DOC functional groups at the Yellow Quill Water Treatment Plant.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3357
	C-O stretching: 1210-1000	1072
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1381

A comparison of all the FTIR spectra from the Yellow Quill Water Treatment Plant is shown in Figure 5.21. The spectra of the source water and bio-filtered water are very similar in response bands and peaks. The C-O stretching peak from alcohol was increased and the C≡C peak from alkyne or C≡N from nitrile was decreased after the bio-filter. The aliphatic C-H deformation peak at 1470-1420 cm^{-1} is much stronger in the bio-filter treated water than the source water. The band at 1658 cm^{-1} for C=O amide stretching is decreased. Therefore, the bio-filter altered the water's characteristics without decreasing the DOC concentration.

The spectrum of the RO membrane treated water shows that only the C-O stretching in alcohol and aliphatic C-H deformation bands clearly stand out and other

bands have almost disappeared. Further, the low absorbance units on the y-axis indicate only a tiny amount of organic compounds remained after RO treatment. This is consistent with the dramatic drop in measured DOC concentration from above 10 mg/L to 1.07 mg/L shown in Figure 5.15.

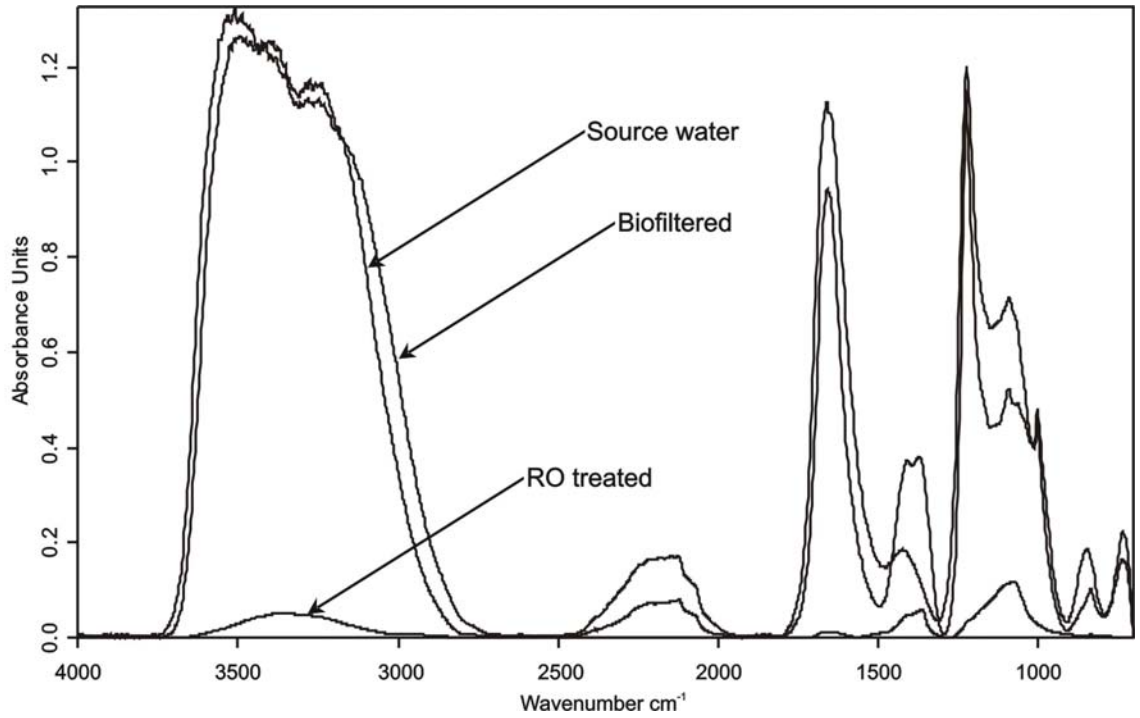


Figure 5.21 FTIR spectra of Yellow Quill treatment plant water sample.

5.3 Saskatoon Water Treatment Plant

5.3.1 Study Site

The Saskatoon Water Treatment Plant is shown in Figure 5.22. The facility is regulated by rigid provincial and national standards outlined in the Permit to Operate issued by Saskatchewan Environment (Keller 2006). The South Saskatchewan River is the source water for the treatment plant which has a production capacity of 268 million litres per day (Keller 2006).

Figure 5.22 Aerial view of Saskatoon Water Treatment Plant (Keller 2006).

5.3.2 Water Treatment System

The Saskatoon water treatment system consists of screening, sand separation, coagulation, flocculation, settling, lime softening, chlorination and filtering as shown in Figure 5.23.

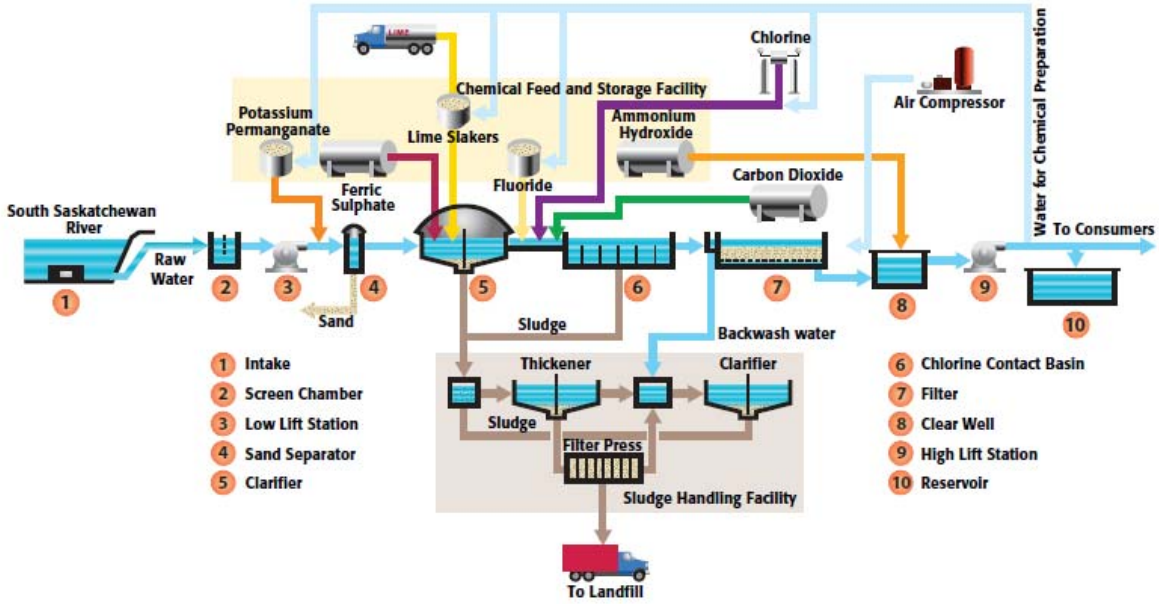


Figure 5.23 Water treatment process at the Saskatoon Water Treatment Plant (Keller 2006).

5.3.3 Sample Collection

Source water and treated water samples were taken in 4 L amber glass bottles from the Saskatoon Water Treatment Plant on October 21, 2008. All samples were filtrated through a pre-rinsed 0.45µm filter to remove particle and suspended organic matter. The samples were stored in a dark room at 4 ºC to minimize microbial growth and transformation of organic compounds.

5.3.4 Analysis Methods

The analysis methods used were the same as those described in Section 5.1.4.

5.3.5 Results and Discussion

5.3.5.1 Characteristics and Removal of South Saskatchewan River DOC during Treatment

The DOC, SUVA, ratio of UV_{254}/UV_{203}, and Specific THMFP in source and treated water at the Saskatoon Water Treatment Plant is shown in Figure 5.24. A detailed listing of all water samples data is presented in Appendix F. DOC concentration decreased from 5.05 to 4.45 mg/L which represents around 12% removal by the treatment plant.

SUVA values also decreased marginally which indicates that aromatic organic compounds were removed by the treatment system. The UV_{254}/UV_{203} ratio decreased from 0.20 to 0.13. As reported in Kim and Yu (2005) the ratio primarily depends on the phenolic content of the organics, hence the treatment system is removing a portion of the phenolic fraction. The Specific THMFP decreased from 50.32 to 28.02 µg chloroform/mg C which indicates the potential for generating THM is lowered.

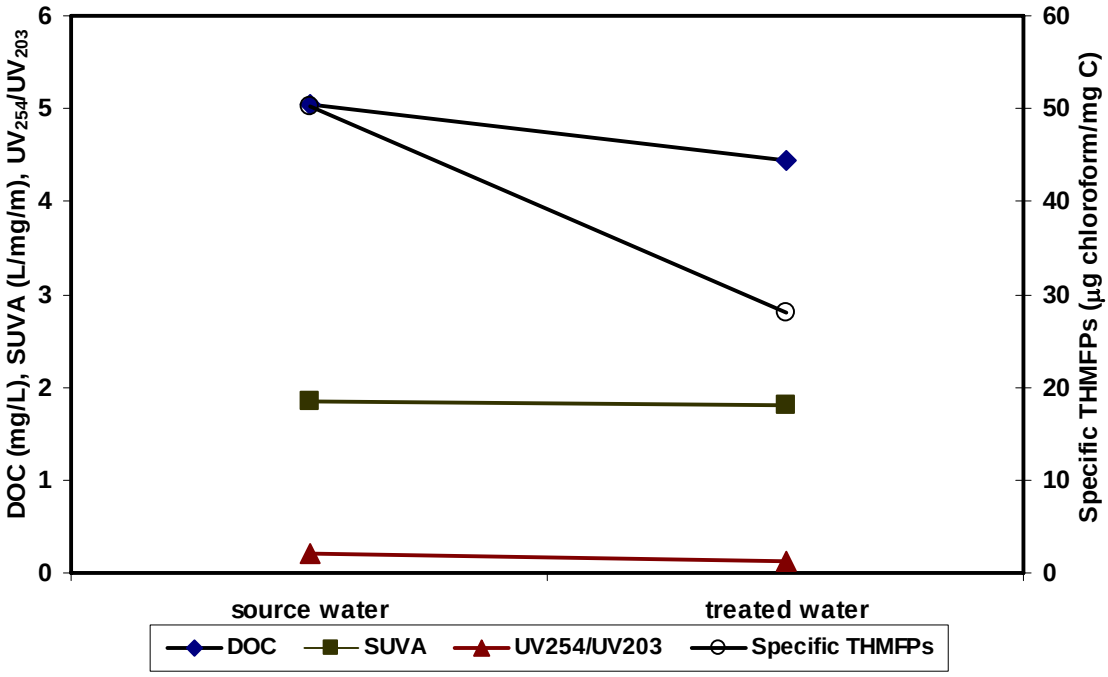


Figure 5.24 Variation in Source and treated water quality at the Saskatoon Water Treatment Plant.

5.3.5.2 FTIR Spectra of Saskatoon Water Treatment Plant Samples' DOC

The FTIR spectrum of the Saskatoon Water Treatment Plant source water is shown in Figure 5.25. Table 5.7 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol and amine are the major functional groups in the source water. The peak at 1406 cm^{-1} is caused by aliphatic or CH_3 groups.

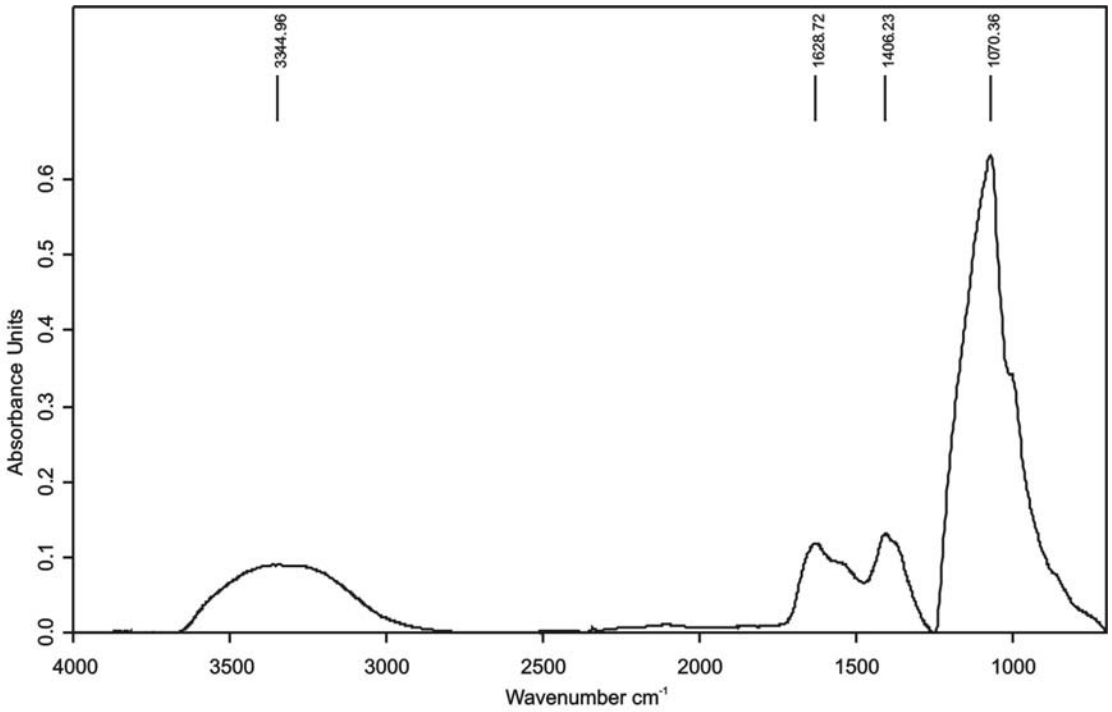


Figure 5.25 FTIR spectrum of source water at Saskatoon Water Treatment Plant.

Table 5.7 South Saskatchewan River Water DOC functional groups.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3345
	C-O stretching: 1210-1000	1070
Amine	N-H stretching: 3600-3200	3345
	N-H bending: 1640-1560	1629
Aliphatic or CH_3 groups	C-H deformation: 1470-1400	1406

The FTIR spectrum of treated water from the Saskatoon Water Treatment Plant is shown at Figure 5.26. Table 5.8 lists the diagnostic bands and the absorbance peaks present in the spectrum. Alcohol and amine are identified as the main functional groups in the treated water sample. The peak at 1406 cm^{-1} is caused by aliphatic or CH_3 groups. The unchanged functional groups suggest that the DOC characteristics are not changed by the water treatment process.

Table 5.8 Treated water DOC functional groups at the Saskatoon Water Treatment.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3316
	C-O stretching: 1210-1000	1075
Amine	N-H stretching: 3600-3200	3316
	N-H bending: 1640-1560	1631
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1410

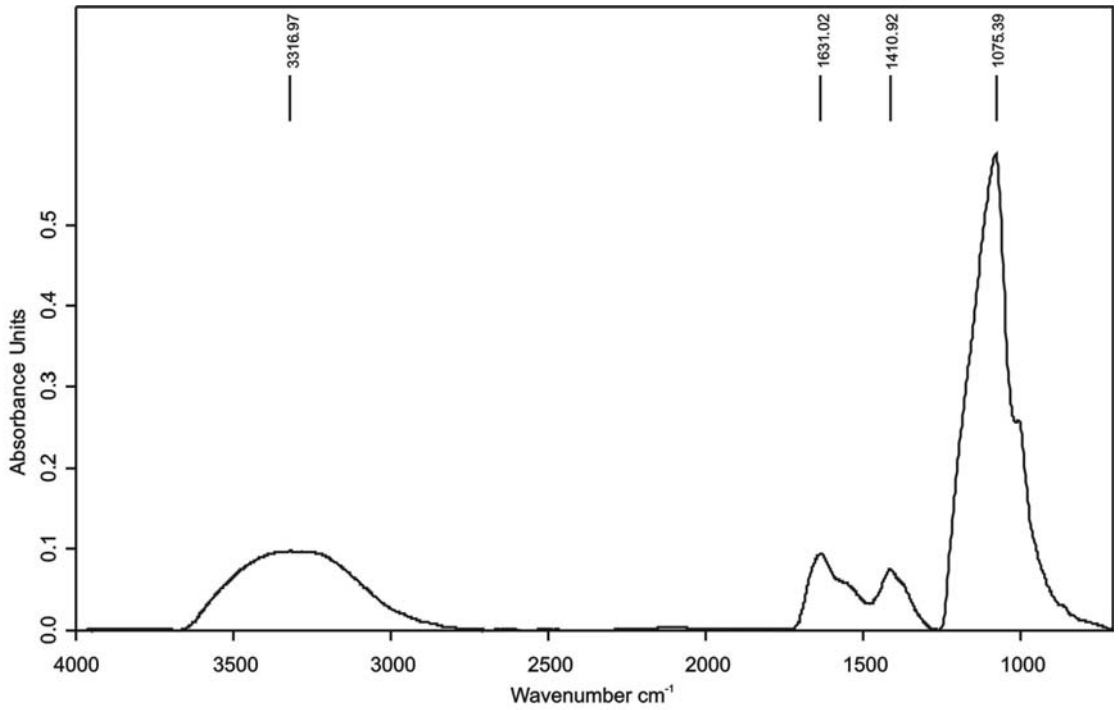


Figure 5.26 FTIR spectrum of treated water at the Saskatoon Water Treatment Plant.

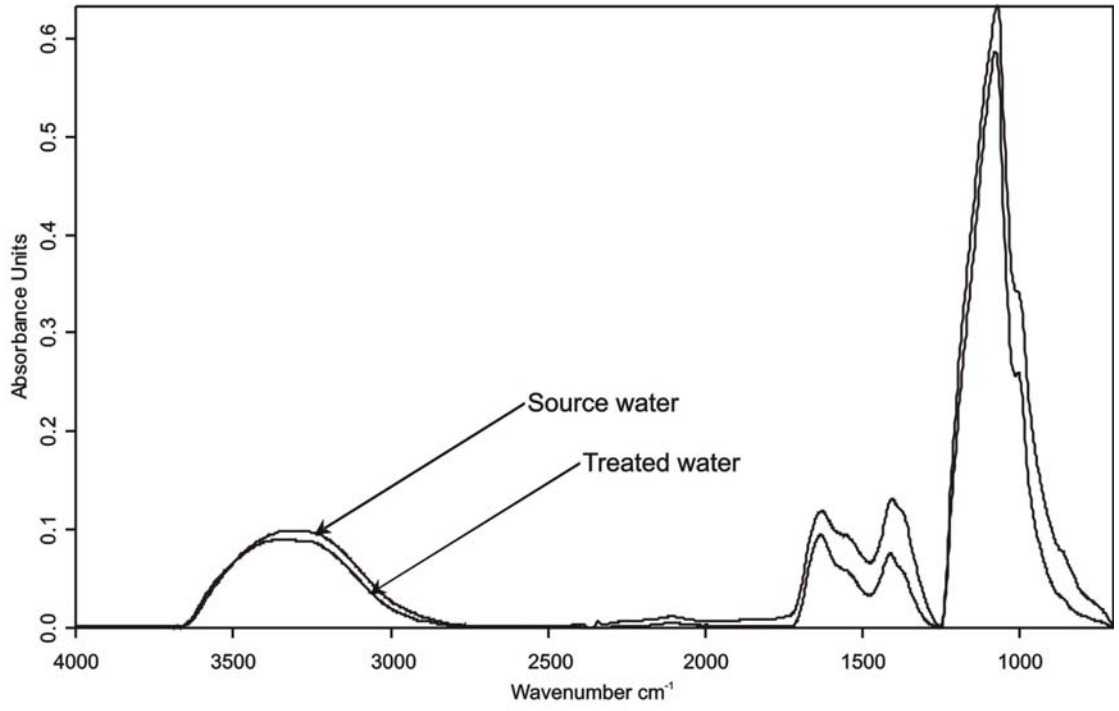


Figure 5.27 FTIR spectra of Saskatoon Water Treatment Plant water samples.

FTIR spectra of the source and treated water are shown in Figure 5.27. Similar functional groups exist in each sample with little alteration in the components. This

indicates the treatment process removes DOC without significantly altering the functional group characteristics.

5.4 Prairie Dugout Water Treatment System

5.4.1 Study Site

The source and treated waters from the Ehman farm near Craik, Saskatchewan were examined. The Ehman farm is located about one mile west of Highway 11 on the first East-West grid road south of Craik. The drinking water is drawn from a dugout system outside the farm house. The source of water for the dugout is runoff from spring snowmelt or summer rain storms. According to Peterson et al. (1997) the water demand at the Ehman farm is around 230 L/day.

5.4.2 Water Treatment System

A flow chart of the water treatment system is shown in Figure 5.28. A unique feature of the Ehman treatment system is an in-bank sand filter between the dugout and the wet well. The in-bank sand filter functions as a biofilter to remove DOC in the water before it is delivered to the in-house treatment system (Peterson et al. 1997). In this portion of the treatment system air is pumped into the biological activated carbon filter (BAC) to keep the aerobic microorganisms active. Backwash of the slow sand bio-filter is conducted every 4 to 6 months according to Mrs. Ehman. However, backwash of the BAC is only conducted once a year. The RO filter is not replaced until it is fouled with retained materials.

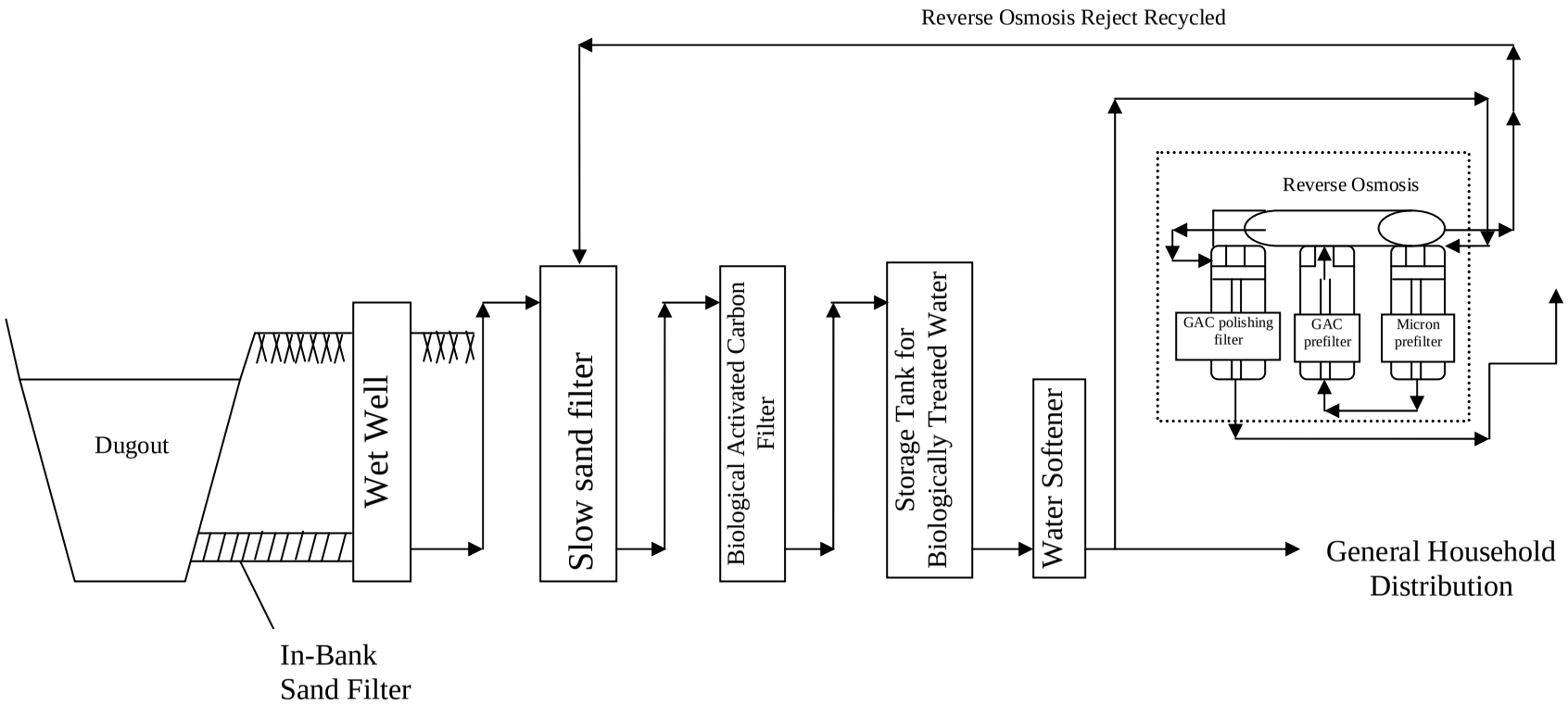


Figure 5.28 Flow chart of the Ehman water treatment system.

5.4.3 Sample Collection

Samples of water from the dugout, wet well, and after slow sand filtration, BAC treatment, and RO filtration were taken in 4 L amber glass bottles from the Ehman dugout water treatment system on November 11, 2008. Figure 5.29 to 5.32 illustrate the sampling points at different stages of the treatment process. All samples except RO treated water were filtered through a pre-rinsed 0.45 μm filter to remove particulates and suspended organic matter. All samples were stored in the dark at 4 ºC to minimize microbial activity and alteration of the organic content.

Figure 5.29 Sampling at dugout.

Figure 5.30 Slow sand filtration and biological activated carbon treatment vessels.

Figure 5.31 RO filtration system.

Figure 5.32 Sampling of RO filtered water.

5.4.4 Analysis Methods

DOC concentration measurement, UV absorbance, THMFP tests and FTIR measurement were the same as those described Section 5.1.4.

5.4.5 Results and Discussion

5.4.5.1 Characteristics and Removal of Dugout Water DOC during Treatment

The DOC, SUVA, ratio of UV_{254}/UV_{203}, and Specific THMFP in source and treated waters in the Ehman water treatment system are shown in Figure 5.33. A

detailed listing of all water samples data is presented in Appendix F. The DOC concentration of the water decreased by 99.9% as it passed through the system (from 25.43 initially to 0.03 mg/L after RO filtration). The most significant drop in DOC concentration occurred in the in-bank sand filter (from 25.43 mg/L to 8.36 mg/L). The BAC filter actually caused a slight increase of DOC concentration. Sloughing of biomass from the BAC media could be the reason for the increase in DOC concentration.

SUVA values and UV_{254}/UV_{203} ratio gradually decreased through the system. Specific THMFP followed the same trend as the DOC concentration. The Specific THMFP of the dugout water and the various stages of treated water were 76.6, 60.5, 47.7, 48.1, and 5.3 µg chloroform/mg C, respectively. This indicates dugout water has the highest potential for generating THM and the RO treated water is very clean with a very low value for Specific THMFP. The Specific THMP values of slow sand filtered and BAC treated water are 47.71 and 48.11 µg chloroform/mg C, respectively. The sloughing of biomass from the BAC media might be the reason for the small increase which is consistent with the small increase in DOC concentration.

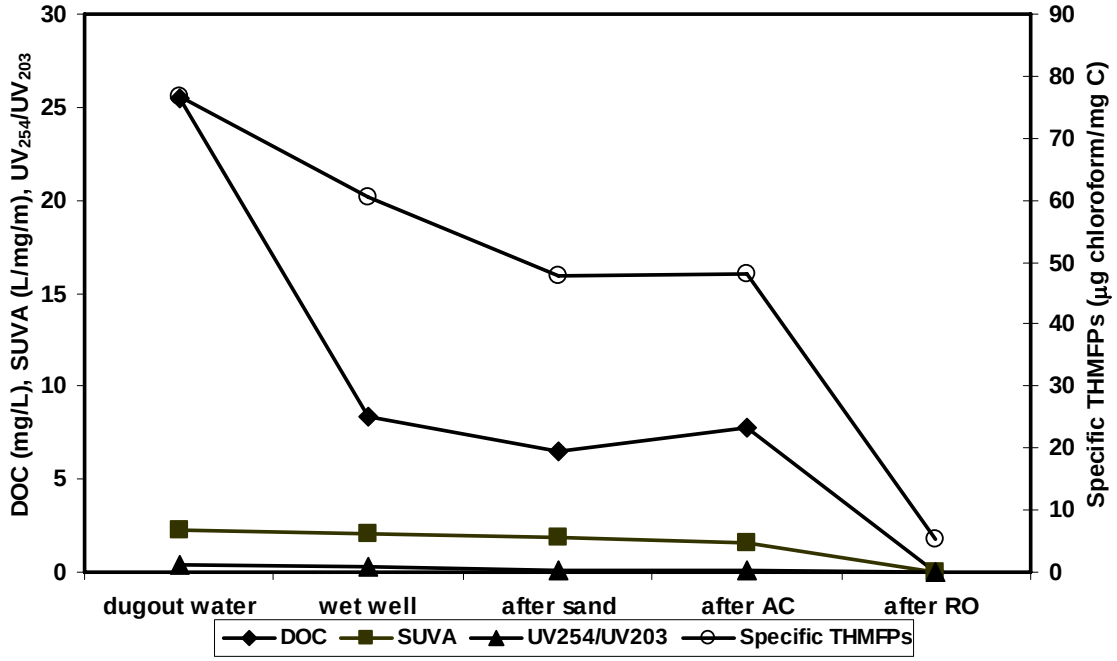


Figure 5.33 Variation in source and treated water quality at the Ehman water treatment system.

SUVA and the UV_{254}/UV_{203} ratio are both positively correlated with specific THMFP (R^2=0.95, 0.72 respectively) as illustrated in Figure 5.34 and 5.35. The results show that the aromatic organic content and phenolic content were effectively removed by the treatment system.

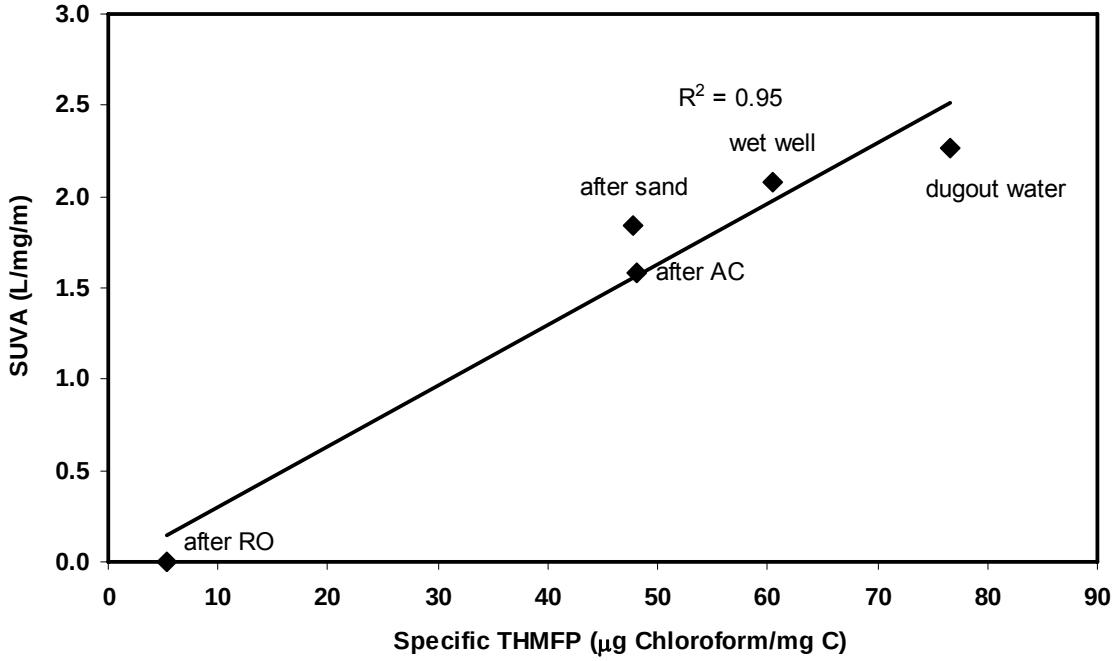


Figure 5.34 Relationship between SUVA and specific THMFP of water at the Ehman treatment system.

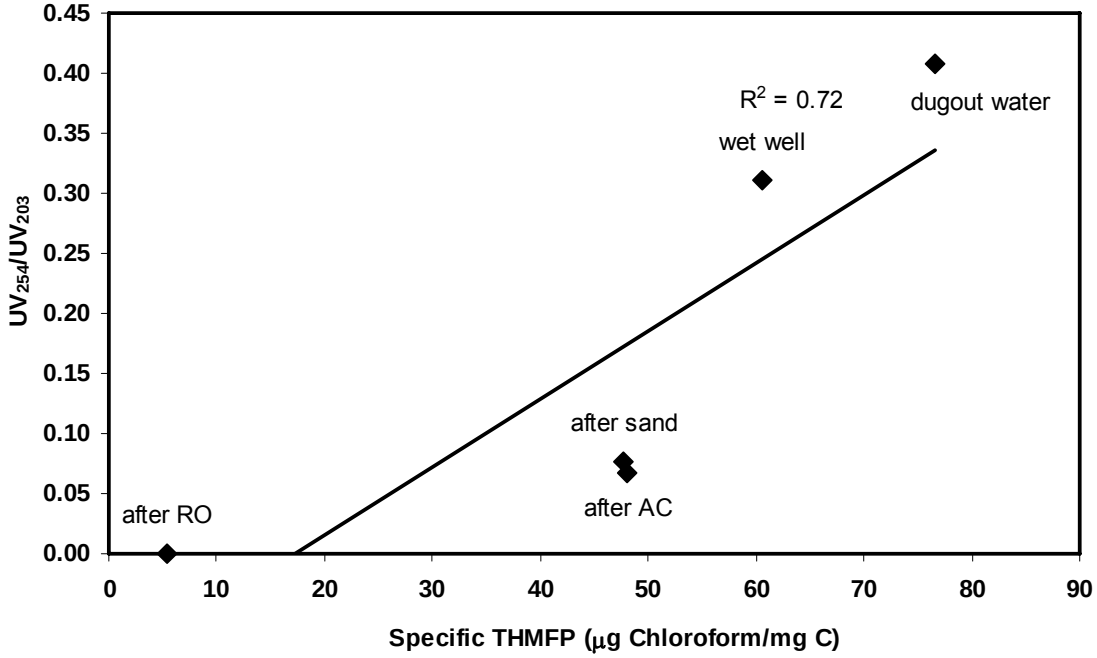


Figure 5.35 Relationship between UV_{254}/UV_{203} ratio and specific THMFP of water at the Ehman water treatment system.

5.4.5.2 FTIR Spectra of Ehman Dugout Water Treatment System DOC

The FTIR spectrum of water from the Ehman water treatment system is shown in Figure 5.36. Table 5.9 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol and amine are the major functional groups in the dugout water. Alcohol is not active in THM formation as described previously so amine is the only organic compound present which causes THM. The peak at 1414 cm^{-1} is mainly caused by aliphatic or CH_3 groups.

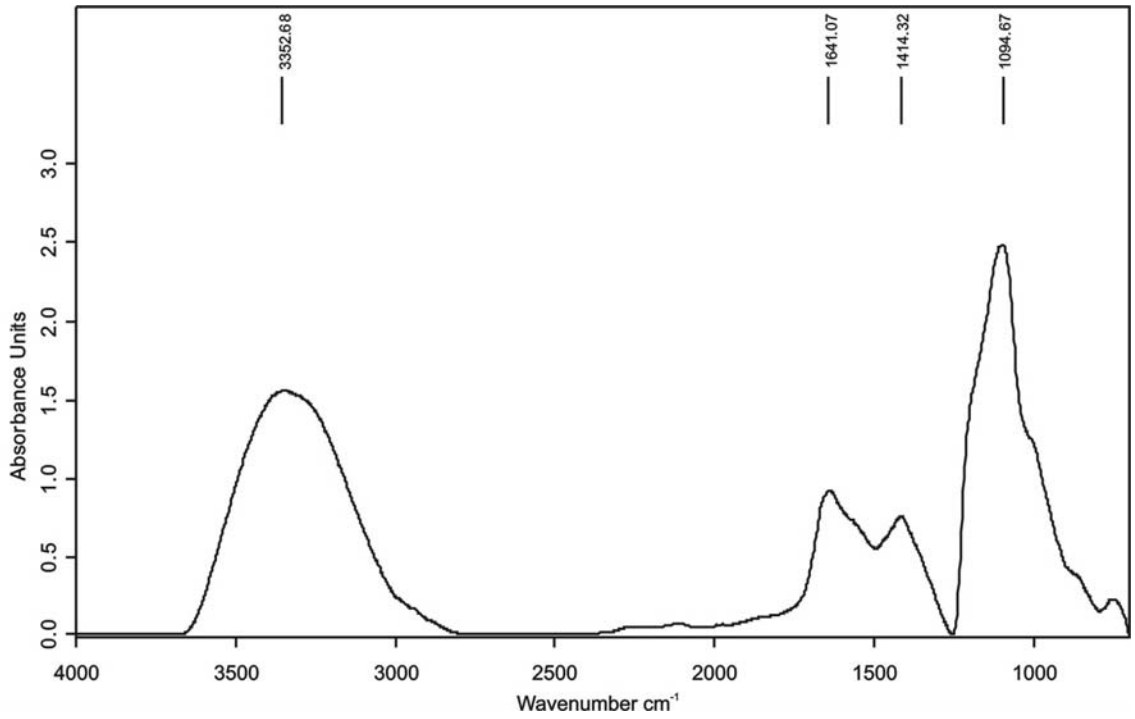


Figure 5.36 FTIR spectrum of dugout water at the Ehman water treatment system.

Table 5.9 Dugout water DOC functional groups at the Ehman water treatment system.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3352
	C-O stretching: 1210-1000	1094
Amine	N-H stretching: 3600-3200	3352
	N-H bending: 1640-1560	1641
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1414

The FTIR spectrum of wet well water at the Ehman water treatment system is shown in Figure 5.37. Table 5.10 lists the diagnostic bands and the absorbance peaks

present in the spectrum. The absorbance peaks indicate that both alcohol and amine continue to be present as major functional groups. In addition, phenol has appeared as a new functional group. There is also other evidence of change in the organic compound characteristics of the water. A peak has occurred in the range of 2600-2100 cm^{-1} which is caused by unsaturated bonds of C≡C or C≡N stretching in alkyne and nitrile.

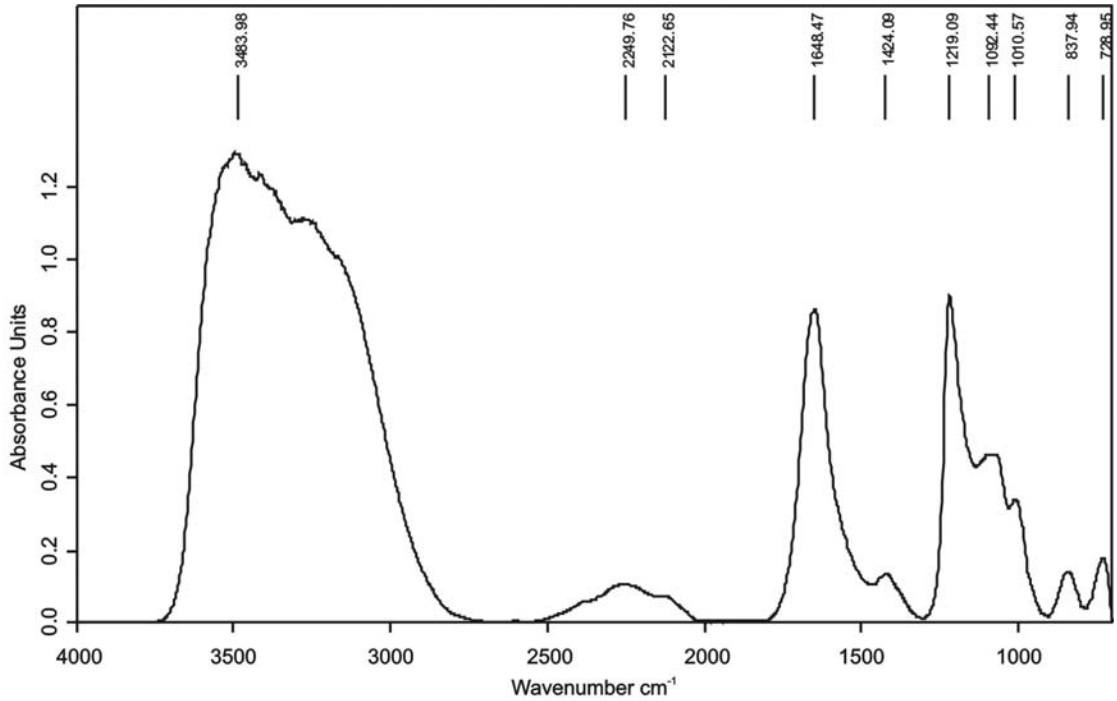


Figure 5.37 FTIR spectrum of wet well water at the Ehman water treatment system.

Table 5.10 Wet well water DOC functional groups at the Ehman water treatment system.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3483
	C-O stretching: 1210-1000	1092 and 1010
Amine	N-H stretching: 3600-3200	3483
	N-H bending: 1640-1560	1648
Phenol	O-H stretching: 3600-3200	3384
	C-O stretching: 1260-1200	1219
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1424

The FTIR spectrum of the slow sand filtered water at the Ehman water treatment system is shown in Figure 5.38. Table 5.11 lists the diagnostic bands and the

absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol, amide and phenol are the major functional groups in the slow sand filtered water. Also, aliphatic or CH_3 groups and unsaturated bonds of C≡C or C≡N continue to be present in the water. During slow sand treatment filtration amine was removed and amide appeared.

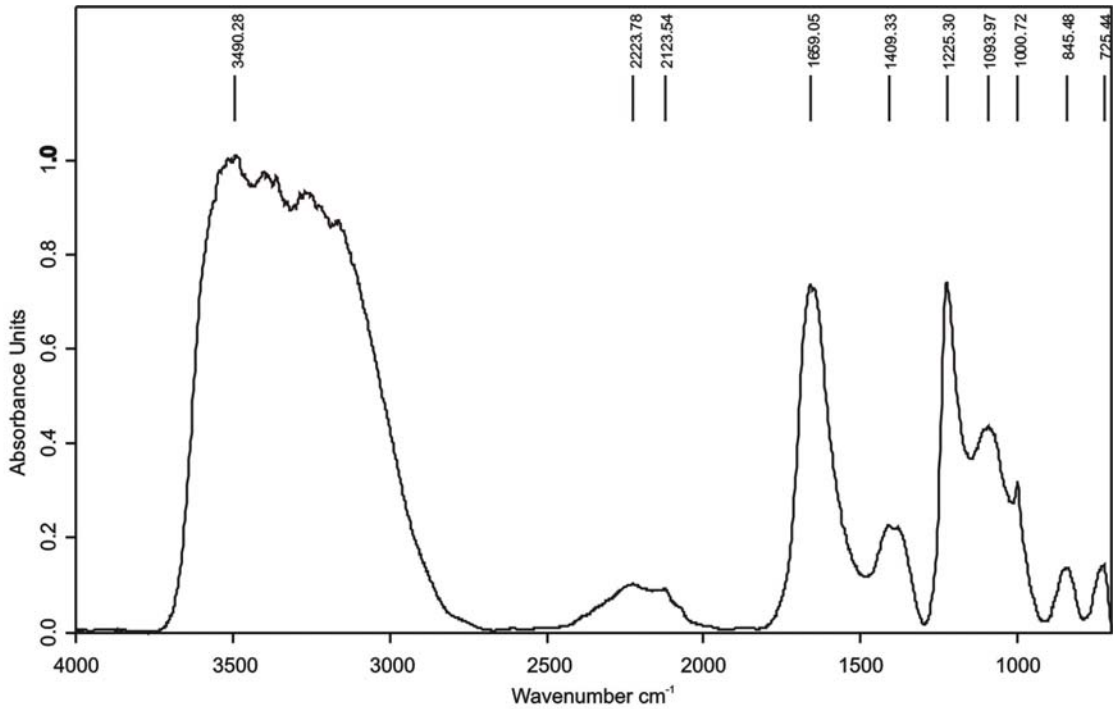


Figure 5.38 FTIR spectrum of slow sand filter treated water at the Ehman water treatment system.

Table 5.11 Slow sand filtered water DOC functional groups at the Ehman water treatment system.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3490
	C-O stretching: 1210-1000	1093 and 1000
Phenol	O-H stretching: 3600-3200	3490
	C-O stretching: 1260-1200	1225
Amide	C=O stretching: 1680-1650	1669
	N-H stretching: 3370-3170	3200
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1409

The FTIR spectrum of BAC treated water at the Ehman surface water treatment system is shown in Figure 5.39. Table 5.12 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol,

amide and phenol are the major functional groups in the BAC treated water. The diagnostic band composition of the BAC treated water sample is similar to the spectrum of the slow sand treated water sample. Hence the BAC treatment did not change the DOC characteristics of the water. However, the absorbance values are higher than those in the wet well water's spectrum. This indicates that the BAC filter was ineffective for removal of organic content. The cause of this unexpected result may be because the AC adsorption capacity was exhausted and biomass sloughing was occurring from the media.

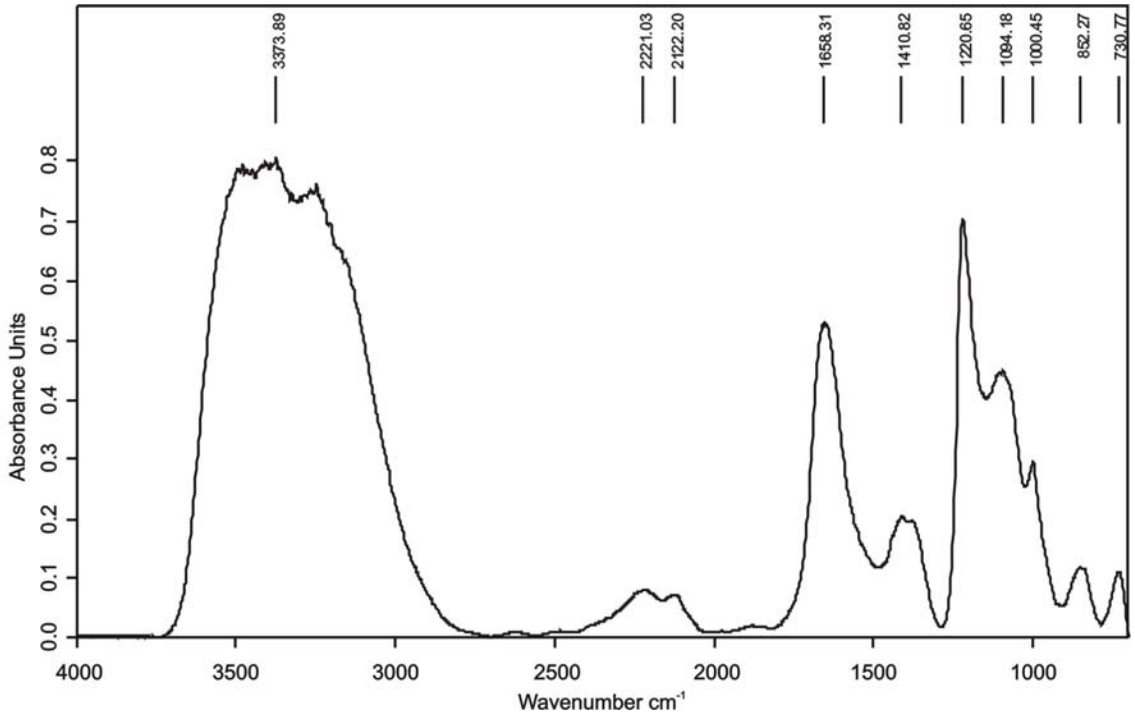


Figure 5.39 FTIR spectrum of BAC treated water at the Ehman water treatment system.

Table 5.12 BAC treated water DOC functional groups at the Ehman water treatment system.

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3373
	C-O stretching: 1210-1000	1094 and 1000
Phenol	O-H stretching: 3600-3200	3373
	C-O stretching: 1260-1200	1220
Amide	C=O stretching: 1680-1650	1658
	N-H stretching: 3370-3170	3373
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1410

The FTIR spectrum of the RO treated water from the Ehman surface water treatment system is shown in Figure 5.40 (note the absorbance units on the y axis are approximately one tenth of those shown in the previous spectra). Table 5.13 lists the diagnostic bands and the absorbance peaks present in the spectrum. The absorbance peaks indicate that alcohol, amine, alkyne/nitrile and are the major functional groups in the RO treated water. After RO treatment amide was removed. Phenol has also been removed but amine has appeared again.

Alkane is indicated by peaks of 2916 cm^{-1} for C-H stretching and 1350 cm^{-1} for C-H deformation. The diagnostic bands for alkane are typically masked by the response of other organic compounds. However, because of the low concentrations after RO treatment the alkane absorbance is revealed.

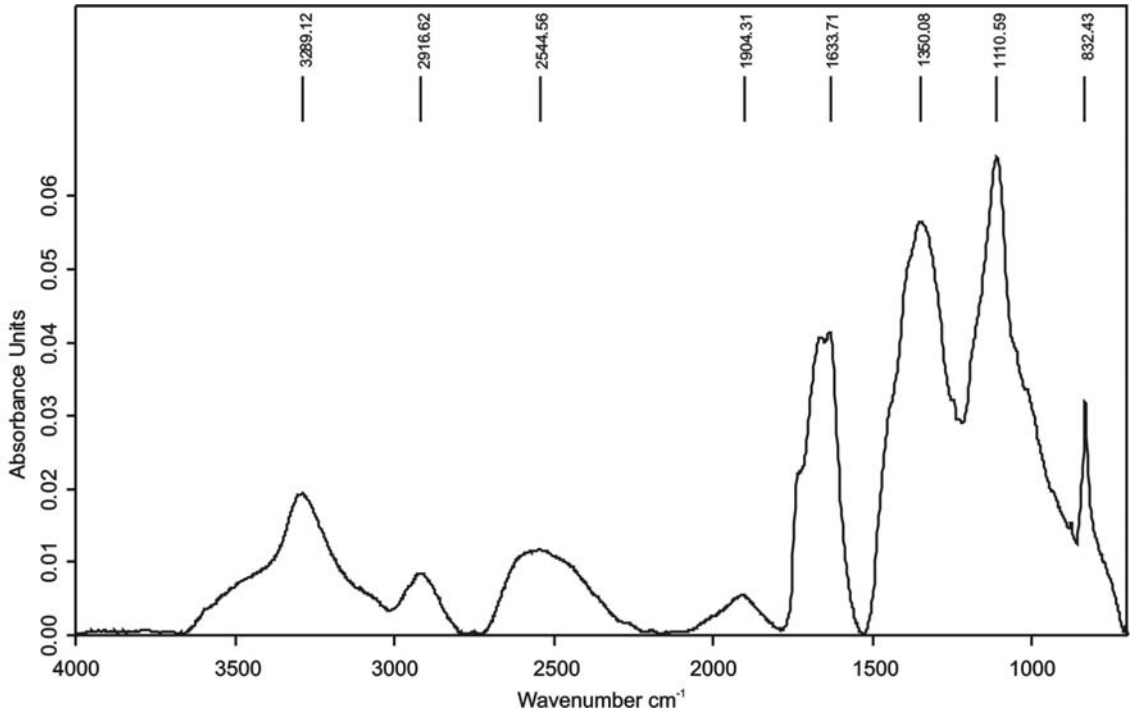


Figure 5.40 FTIR spectrum of RO filtered water at Ehman water treatment system.

Table 5.13 RO treated water DOC functional groups at the Ehman water treatment

Dominant functional groups	Diagnostic bands (cm^{-1})	Peak in the spectrum (cm^{-1})
Alcohol	O-H stretching: 3600-3200	3289
	C-O stretching: 1210-1000	1110
Amine	N-H stretching: 3600-3200	3289
	N-H bending: 1640-1560	1633
alkyne/nitrile	C≡C or C≡N stretching: 2600-2100	2544
Aliphatic or CH_3 groups	C-H deformation: 1470-1365	1350

The spectra of all the Ehman treatment system water samples are presented in Figure 5.41. Removal of DOC during the treatment process is indicated by the decrease of absorbance values on the y-axis. The treatment system gradually removes aliphatic groups and CH_3 groups as indicated by the weakening peaks in the range of 1470-1365 cm^{-1}.

In comparing the DOC characteristics of Ehman treatment system waters at various stages of treatment, the dugout water is the simplest because it only contains amine and alcohol. Phenol with a featured peak at 1219 cm^{-1} was created during the in-bank filtration. The slow sand caused amides to occur with a band at 1659 cm^{-1}. The spectrum pattern after BAC treatment did not change indicating the characteristics of DOC were not altered by this treatment step. The RO filtered water spectrum showed almost no absorbance response compared with previous samples as a result of the low DOC concentration of 0.03 mg/L.

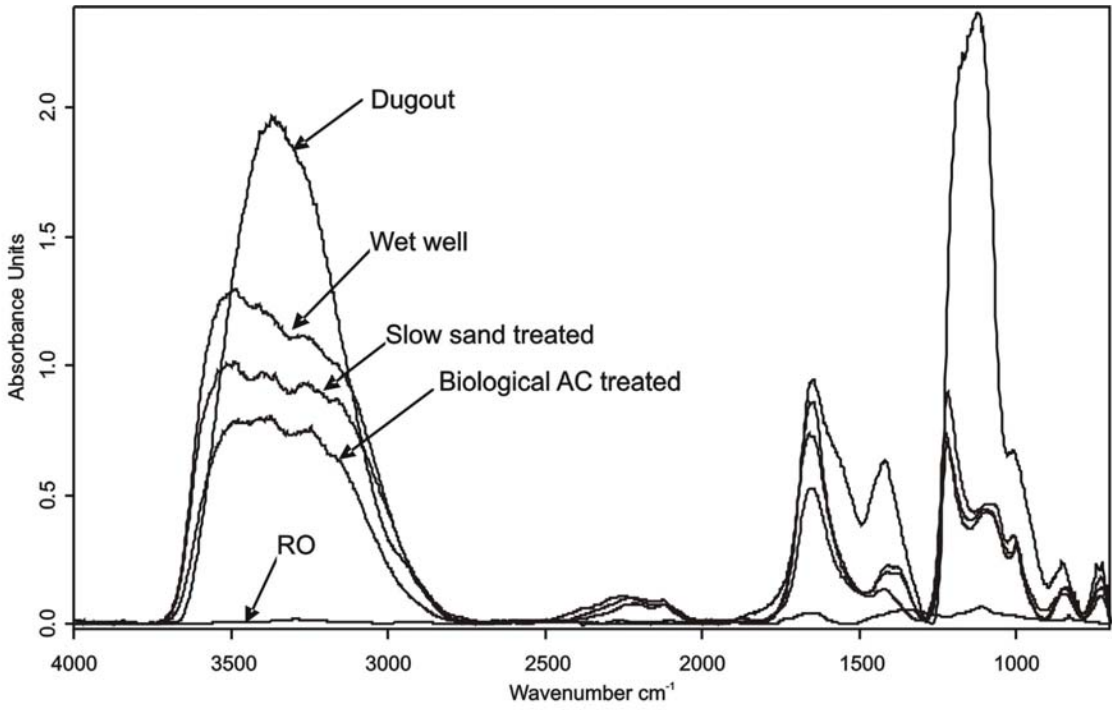


Figure 5.41 FTIR spectra of water samples from the Ehman water treatment system.

5.4.5.3 Biodegradable Dissolved Organic Carbon (BDOC)

A unique feature of the Ehman system is the in-bank sand filter between the dugout and the wet well. The in-bank sand filter provides media for microorganisms to live on. The DOC concentration of the water in the wet well was significantly lower than that of the dugout. This indicates the in-bank sand filter provides biological treatment. Therefore, the DOC removed by the in-bank sand filter can be considered readily biodegradable and represents the BDOC proportion of the DOC.

An indication of the BDOC characteristics can be obtained by comparing the DOC concentration, SUVA, Specific THMFP, and FTIR test results of the water samples from the Ehman treatment system before and after the in-bank filter. The data in Table 5.14 show the DOC concentration was significantly changed from 25.43 to 8.36 mg/L by the biological treatment. The FTIR spectra of Figure 5.36 and 5.37 indicate that the aliphatic organic compounds (diagnostic band 1470-1365 cm^{-1}) were removed. BDOC is generally composed of aliphatic organic compounds which are usually the medium to small molecular weight compounds (Trulleyova and Rulik 2004). Alcohol in the dugout water was also removed by the biological treatment as indicated by the significant decrease in the diagnostic band at 3600-3200 cm^{-1} and 1210-1000 cm^{-1}. The decreases in SUVA and Specific THMFP values indicate hydrophobic compounds were partially removed. Therefore, as a result of the in-bank biological treatment aliphatic organic compounds and alcohol have been preferentially consumed by microorganisms. In addition, some hydrophobic organic compounds were biodegraded.

Table 5.14 Characteristics of Ehman dugout water and wet well water.

Source		DOC (mg/L)	SUVA (L/mg/m)	UV_{254}/UV_{203}	Specific THMFP (µg chloroform/mg C)
Ehman	dugout	25.43	2.27	0.41	76.60
	wet well	8.36	2.08	0.31	60.52

5.5 Discussion of Test Results from All Locations

The average conventional test results for all source and treated waters analysed are shown in Table 5.15. A detailed listing of all water sample replicate data is presented in Appendix E.

In comparing all the source waters the Ehman farm dugout water had by far the largest DOC concentration and Specific THMFP. This result is typical of the poor water quality in prairie dugouts that collect local surface runoff from agricultural fields rich in organic matter and nutrients that promote algal growth.

The South Saskatchewan River water had the lowest DOC concentration of all source waters analysed. This result is not unexpected because the South Saskatchewan River downstream of Diefenbaker Lake is a high quality surface water source. However, the South Saskatchewan River water had the second highest potential for formation of THMs with a Specific THMP comparable in magnitude to Buffalo Pound Lake which chronically suffers from organic carbon input and nutrient enrichment. This observation is an indication that the composition of the DOC in source water is as significant a factor as DOC concentration when assessing potential to form THM.

The AC adsorption treatment at Buffalo Pound Water Treatment Plant only marginally decreased DOC concentration. The limited success in removal of DOC at this location might be because the AC had been used for several months without regeneration and therefore many of the adsorption sites in the AC were occupied. The Yellow Quill Water Treatment Plant bio-filter and the Ehman water treatment system BAC filter demonstrate that biological treatment without adequate maintenance can potentially cause a higher DOC concentration. Biomass sloughing from the media is likely the cause of increased DOC after the bio-filters. This degradation of water quality could be prevented if backwash or replacement of AC media is regularly conducted.

DOC was effectively removed by RO membrane filtration in the final treatment step at Yellow Quill Water Treatment Plant and Ehman water treatment system.

Table 5.15 Conventional test method results for source and treated waters.

Source		DOC (mg/L)	SUVA (L/mg/m)	Specific THMFP (μg chloroform/mg C)
Buffalo Pound	source	7.05	1.19	45.74
	after CFS	3.44	1.37	58.53
	after AC	3.13	1.02	37.68
Yellow Quill	source	9.86	1.85	22.61
	Biof-ilter	10.08	1.92	28.61
	RO	1.08	0.09	10.63
Saskatoon	source	5.05	1.84	50.32
	treated	4.45	1.80	28.02
Ehman	source	25.43	2.27	76.60
	wet well	8.36	2.08	60.52
	slow sand	6.53	1.84	47.71
	BAC	7.73	1.58	48.12
	RO	0.03	0.00	5.32

The FTIR absorbance spectra of the source water samples from Buffalo Pound Lake, Yellow Quill First Nation, South Saskatchewan River at Saskatoon and Ehman farm near Craik are shown in Figure 5.42.

Interpretation of the absorbance peaks for the Buffalo Pound source water indicates amide, aromatic ketone, and alcohol are likely the main DOC functional groups present. In comparing the Buffalo Pound Lake water spectrum to the Suwannee River DOC spectra in Figure 4.16 the absorption response is similar to the HPIN fraction and there are also several common peaks with the HPON and HPOA fractions. Hence a large proportion of Buffalo Pound DOC is composed of HPIN aliphatic compounds. The HPIN aliphatic compounds are removed by CFS (Table 5.15) leaving the more potent THM forming aromatic compounds typical of HPON and HPOA after treatment which cause the THMFP of the water to rise.

The FTIR spectrum for South Saskatchewan River water is very similar to the HPIB fraction of Suwannee River DOC. The likely functional groups present are aromatic alcohol and amine. It appears DOC is not very effectively removed by the treatment process (Table 5.15) but its potential to form THM is modified (Table 5.15), perhaps by the elevated pH of the lime softening process.

Interpretation of the FTIR spectrum for the Yellow Quill source water indicates the main functional groups present are aliphatic amide, alcohol, phenol and alkyne. Further, the Yellow Quill FTIR spectrum has similar absorption response to the HPIN and HPIA fractions of Suwannee River DOC and therefore is likely a combination of these two fractions. The Yellow Quill source water had relatively high DOC content (9.86 mg/L) yet less than half the THMFP of the other source water samples. The lower potential for THM formation of the HPIN and HPIA fractions (Table 4.10) correlates well with this observation.

The FTIR spectrum for the Ehman source water indicates the two main functional groups present in the DOC are amine and alcohol. In addition, the spectrum for the Ehman source water (although less complex) has similar absorption response to the un-fractionated Suwannee River spectrum indicating the DOC in the Ehman source water is likely a mixture of hydrophobic and hydrophilic compounds. The hydrophobic content of the Ehman source water is likely a large contributor to its high potential to form THM as reported in Table 5.15.

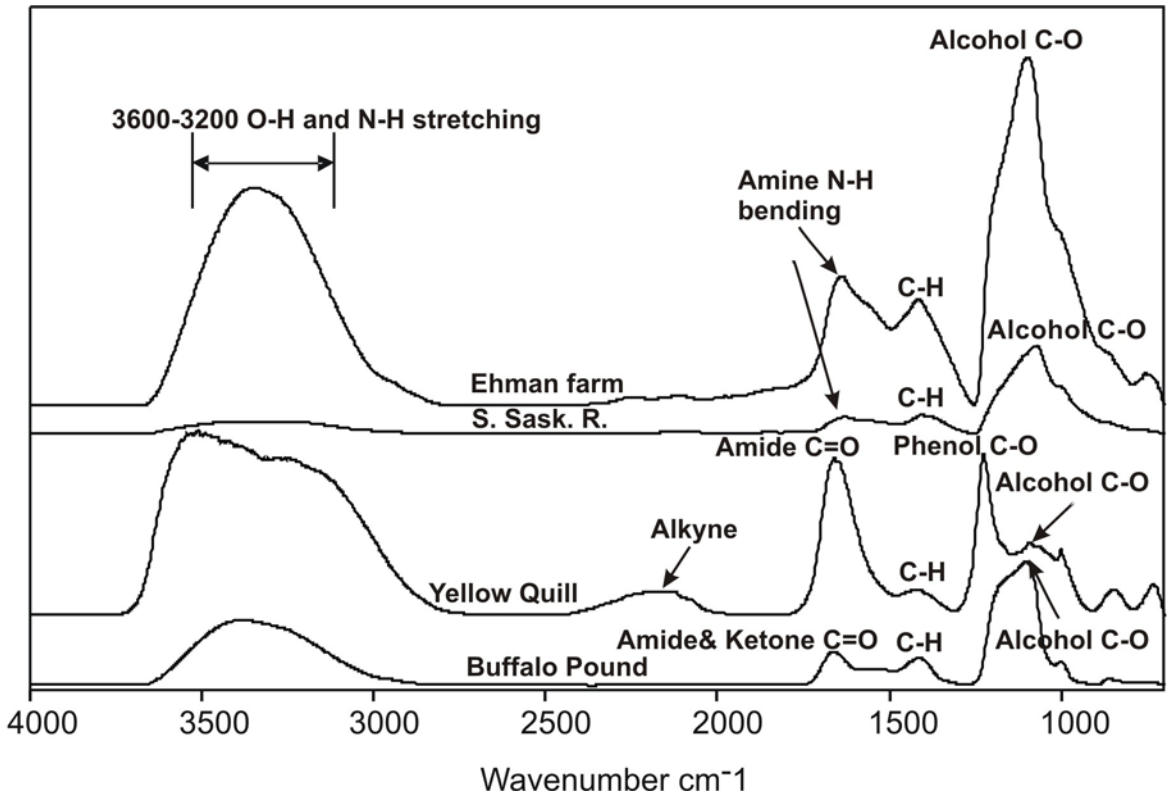


Figure 5.42 FTIR spectra of source water samples.

CHAPTER 6. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The objectives of this study were: to develop a sample preparation and analysis procedure utilizing FTIR to characterize the DOC content of water; to compare the FTIR characterization results with more conventional DOC related analytical methods using resin fractionation techniques; and to demonstrate the applicability of the developed procedure to source water DOC characterization and water treatment process evaluation.

6.1 Summary and Conclusions

6.1.1 Procedure Development

Hydrogen bonds between hydroxyl groups in aqueous samples have a broad spectral response that masks the response of the DOC components during FTIR measurements. Therefore, in order to overcome this water matrix problem the concentrated samples were dropped on a 1''×3''×0.04'' flat, organic compound free and non-infrared absorptive gold plated slide (EMF, NY). The water drops were dried at room temperature to deposit a thin film of solid residue on the slide which was then subjected to FTIR scanning measurements. This simple evaporation procedure developed for concentrating water samples successfully deposited a solid residue for FTIR scanning. Since the DOC content in the organic residue is not evenly distributed, multiple locations were scanned for each sample's residue. The spectrum for each sample is the averaged results of 60 scanned locations. This replicate scanning successfully produced spectra suitable for interpretation.

The conventional resin column adsorption fractionation procedure was applied to separate Suwannee River DOC into six organic fractions (hydrophobic acid, neutral and base; hydrophilic acid, neutral and base). Breakthrough tests were conducted to determine the resin quantity required to adsorb the DOC content from 4 L of a

prepared Suwannee River DOC water sample. As a result of these tests it was shown that the theoretical equations to estimate resin adsorption capacity published in the literature can be directly used to estimate the resin quantity required.

Each organic fraction separated from the Suwannee River DOC was then assessed using FTIR analysis. Comparison of the spectra from the resin adsorption fractions gave an indication of the relationship between functional groups and the hydrophobic/hydrophilic nature of the DOC. The results suggest the hydrophobic fractions contain more aromatic functional groups. This demonstrates that the FTIR spectra can provide information regarding the hydrophobic/hydrophilic nature of the DOC as an alternative to the resin separation procedure.

6.1.2 Characteristics of Suwannee River DOC

The resin column adsorption fractionation technique as described by Marhaba et al. (2003) was used to separate a prepared Suwannee River DOC sample with 12 mg/L DOC concentration into HPOB, HPOA, HPON, HPIB, HPIA, and HPIN fractions. Measurements of DOC concentration, SUVA values, UV254/UV203 ratio, and Specific THMFP were conducted on the un-fractionated water sample and each separated fraction. The tests results showed that the HPOA fraction was the most abundant in DOC content (35% by mass). The sequence of the six fractions in order from largest to smallest average percent mass was: HPOA > HPIA > HPON > HPIN > HPIB > HPOB.

The SUVA sequence of the six fractions from largest to smallest average readings was: HPOB > HPOA > HPON > HPIB > HPIA > HPIN. The HPOB fraction produced the largest value of SUVA (3.45 L/mg/m), whereas the HPIN fraction had the smallest (0.64 L/mg/m). This result supports previous research findings that large SUVA values indicate increased hydrophobic and aromatic content. The six fractions ordered from largest to smallest based upon the average magnitude of the UV_{254}/UV_{203} ratio was as follows: HPOB > HPOA > HPON > HPIB > HPIN > HPIA. Based on the UV_{254}/UV_{203} ratio values, HPOB had the largest phenolic content.

The average values of Specific THMFP of the DOC fractions ordered from largest to smallest are: HPOA > HPOB > HPON > HPIA > HPIB > HPIN. HPOA was the main organic precursor for THM formation (highest Specific THMFP). HPIN

proved to be the most inactive fraction in generating THM as indicated by the lowest Specific THMFP values. The hydrophobic fractions (HPOB, HPOA, and HPON) were shown to be the main organic materials for the formation of THM which is also consistent with the results reported in the literature that hydrophobic fractions are the main precursors for the generation of THM.

Based on the analysis of the FTIR spectra, amino acid was identified as the main functional group in HPOB. HPOA was dominated by aromatic carboxylic acid and HPON contained alcohol, ketone and amide. HPIB's main functional compound was aliphatic amine. HPIA's main functional groups were aliphatic carboxylic acids while HPIN only contained aliphatic alcohol and amide. The major functional groups associated with THM formation are likely aromatic carboxylic acids, amino acid, amine, amide and ketone. Alcohol did not contribute significantly to THM formation during chlorination.

The FTIR spectra can give an indication of the potential to form THM and the effectiveness of treatment methods for removing specific portions of the DOC. Considering the results summarized above it can be concluded that compounds containing C=O stretching and N-H bending should be removed prior to chlorination to reduce the potential creation of high levels of THM. The main diagnostic bands in the FTIR spectrum for C=O stretching and N-H bending are in the areas of 1800-1650 cm^{-1} and 1650-1580/1650-1500 cm^{-1} respectively.

6.1.3 Characteristics of Prairie Water Samples

The DOC characteristics of source and treated waters from several locations in Saskatchewan were observed and discussed.

Aromatic ketone, amide and alcohol are the major functional groups in the source water DOC from Buffalo Pound Water Treatment. Aromatic nitro functional group was also contained in the water. The Buffalo Pound source water is similar to the Suwannee River HPIN fraction and also has several common peaks with the HPON and HPOA fractions. CFS decreased DOC concentration and removed the nitro functional groups. The AC adsorption step in the Buffalo Pound water treatment process is

effective in decreasing the hydrophobic fraction of the DOC and Specific THM. Aromatic ketone was removed during the AC adsorption processes.

At the Yellow Quill Water Treatment Plant the amide, alcohol, and phenol are the main functional groups in the source water. It has similar spectroscopic features to the HPIN and HPIA fractions of Suwannee River DOC and therefore is likely a combination of these two fractions. The bio-filter in the Yellow Quill treatment process altered the organic compound distribution in the DOC but did not reduce the total DOC concentration. RO filtration removed most of the DOC content after the bio-filter.

The DOC concentration of the source water at Saskatoon Water Treatment Plant was lower than the other source waters. The FTIR spectrum is very similar to the HPIB fraction of Suwannee River DOC. The likely functional groups present are aromatic alcohol and amine. It appears that the DOC of the source water is not very effectively removed by the treatment process but its potential to form THM is lowered perhaps by the elevated pH of the lime softening process.

The Ehman source water DOC concentration was much larger than the other three source waters investigated. The FTIR spectrum indicated the two main functional groups present in the DOC are amine and alcohol. In addition, the spectrum for the Ehman source water had similar spectroscopic features to the un-fractionated Suwannee River spectrum indicating the DOC in the Ehman source water is likely a mixture of hydrophobic and hydrophilic compounds. The hydrophobic content of the Ehman source water is likely a large contributor to its high potential to form THM.

The in-bank bio-filter removed a significant portion of the DOC concentration in the source water. The DOC removed in the bio-filter represents the major BDOC content of the source water. Phenol, alkyne and nitrile appeared as new functional groups after the in-bank bio-filter. During slow sand filtration amine was removed and amide appeared. After RO treatment only a tiny amount of organic content was left in the water (0.03 mg/L DOC).

6.2 Recommendations

6.2.1 Measurements and Sampling Recommendations

In this project, the DOC content in the residue deposited on reflective slides for FTIR analysis was not evenly distributed. Alternative procedures for concentrating and depositing organic residues from water samples for FTIR measurements are described in the literature. In those studies the water samples are freeze dried in powder and packed into a small pressed pellet mixed with potassium bromide (Chen et al. 2003; Drewes et al. 2006; Kanokkantapong et al. 2006; Kim and Yu 2005; Li et al. 2005). Experimentation should be conducted to compare the freeze drying procedure with the evaporation and concentrating procedure described in this work.

The water samples taken in this study were for the purpose of testing the usefulness of the sample preparation and FTIR analysis method for characterization of source and treated waters. In order to conduct a more rigorous characterization of source or treated waters replicate samples should be taken. Replicate sampling and analysis could better document errors associated with the method.

6.2.2 Recommendations for Future Work

The source and treated water samples in this project were all taken in the fall of the year. Therefore the DOC characteristics that were indentified for each are only representative of the characteristics during the autumn. Because the DOC characteristics of source waters are likely to change seasonally these variations should be investigated in a future study. The resin fractionation procedures could also be conducted on the source waters to further characterize the DOC content.

In this project BDOC content and its relationship to DOC characteristics and functional groups was only estimated based upon onsite biological treatment. A future study should specifically investigate DOC characteristics of the BDOC portion of the organic content of source waters using FTIR analysis.

Further investigation of FTIR scanning and analysis is required to develop better interpretation procedures to more conclusively identify functional groups and to possibly develop quantitative measures of the DOC characteristics.

Further study of the characteristics of DOC content in different types of source waters and through sequential water treatment steps should be investigated. Similar to the approach used in this research FTIR analysis should be used to identify the functional groups present and resin adsorption techniques should be employed to characterize the organic carbon content.

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Appendix A. Resin Column Breakthrough Test Results

A.1 DAX-8 Resin

Figures A.1 and A.2 are replicate breakthrough curves for the DAX-8 resin. The DOC concentration and UV absorbance curves have similar trends indicating breakthrough at about 750 mL. During the first stage of the flow, RO/DI water contained in the pore volume was washed out as indicated by the increase in DOC concentration and SUVA values. After the wash out period the parameter values remain stable for a period of time. During the stable stage a volume of flow (about 400 mL in total) passes through the column with a steady DOC concentration which is less than the feed concentration. This region demonstrates the ability of the column to consistently remove a target portion of the DOC from the water sample. During stable stage of the flow, the resin only adsorbs one portion of the total DOC because only the HPON fraction was adsorbed by the resin.

The results of the replicate #1 and replicate #2 tests are very similar. The small differences in the break through curves are likely due to experiment error. Based upon the calculations presented in Chapter 3 the estimated volume of water that could be safely treated by 25 mL of DAX-8 resin was 600 mL. The actual volume that could be treated based upon the breakthrough tests was approximately 750 mL minus the pore volume of the column (15 mL) originally filled with RO/DI water. Therefore, the actual treated volume was about 735 mL. To make certain the amount of DAX-8 resin used in the fractionation of a 4000 mL water sample with 12 mg/L DOC was sufficient the quantity required was based upon the stable stage of the breakthrough test only. Since 25 mL DAX-8 resin could safely treat 400 mL water sample in the breakthrough tests, then 250 mL resin should be used for fractionation of a 4000 mL water sample.

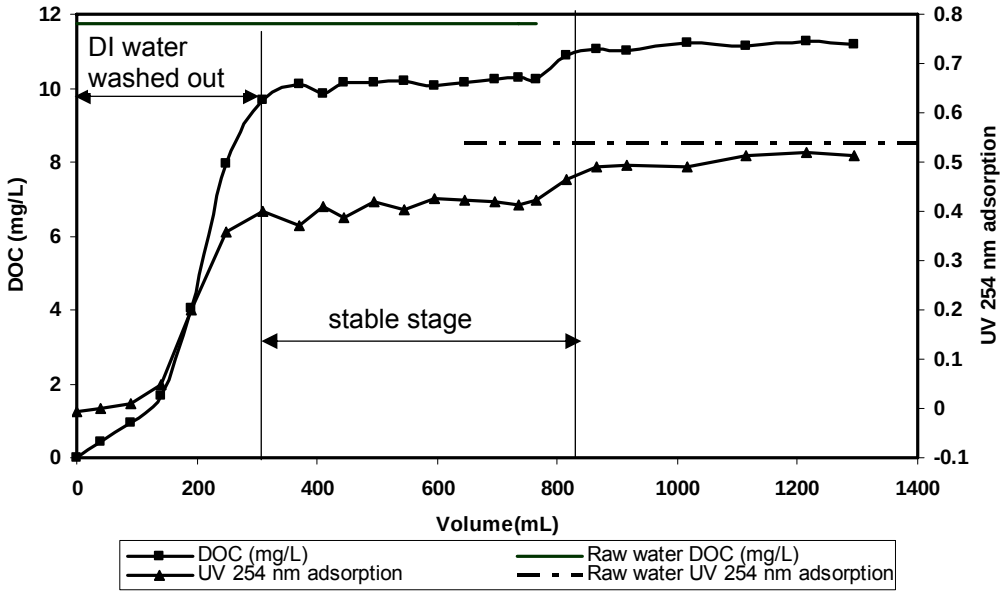

Figure A.1 Breakthrough curve of DAX-8 column (replicate #1).

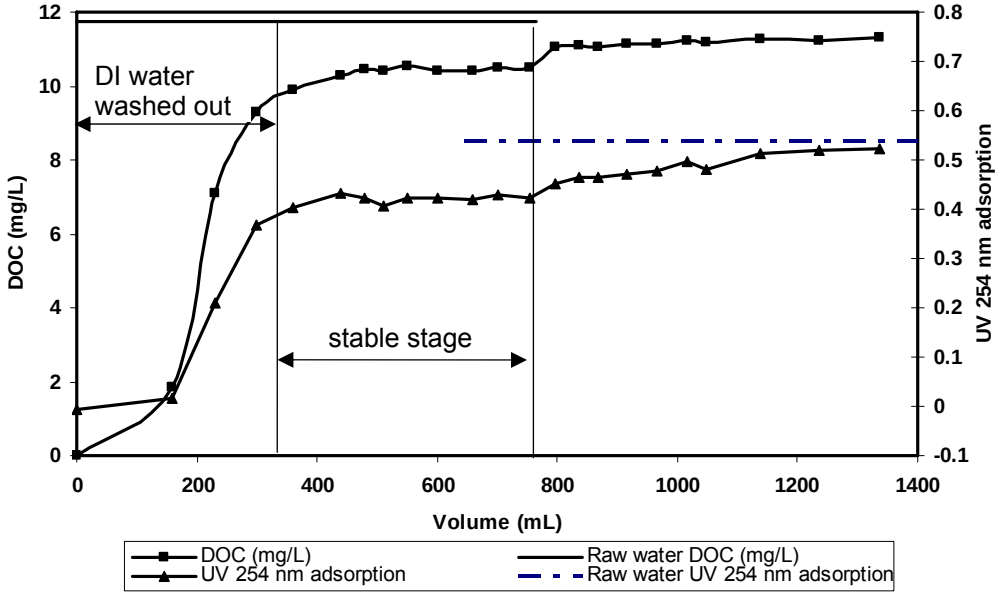

Figure A.2 Breakthrough curve of DAX-8 column (replicate #2).

A.2 AG-MP-50 Cation Exchange Resin

Figure A.3 and A.4 show the breakthrough curves for the AG-MP-50 cation exchange resin. At around 600 mL of water passed, the pH and conductivity breakthrough occurred. At the beginning of the test HCl contained in the resin pore volume was gradually washed out causing a rise in pH and conductivity. After the HCl was displaced and the water sample then occupied the whole resin column, the pH and conductivity remained steady. Using the same approach to determine the resin capacity as outlined in the Section A.1 the curves indicate around 200 mL of initial flow should be subtracted from the 600 mL to breakthrough. Therefore, 400 mL is the breakthrough volume. In other words, 400 mL of water sample can be fully treated by 20 g of AG-MP-50 resin. In the fractionation process, 4000 mL water can be treated by 200 g of resin.

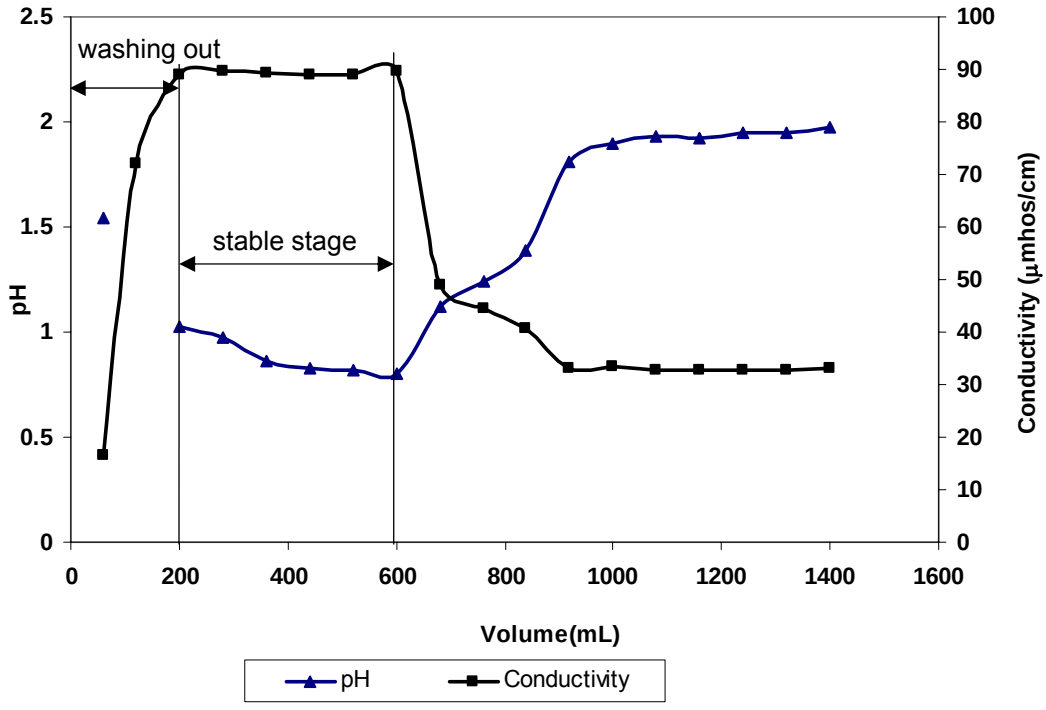

Figure A.3 Breakthrough curve of AG-MP 50 column (replicate #1).

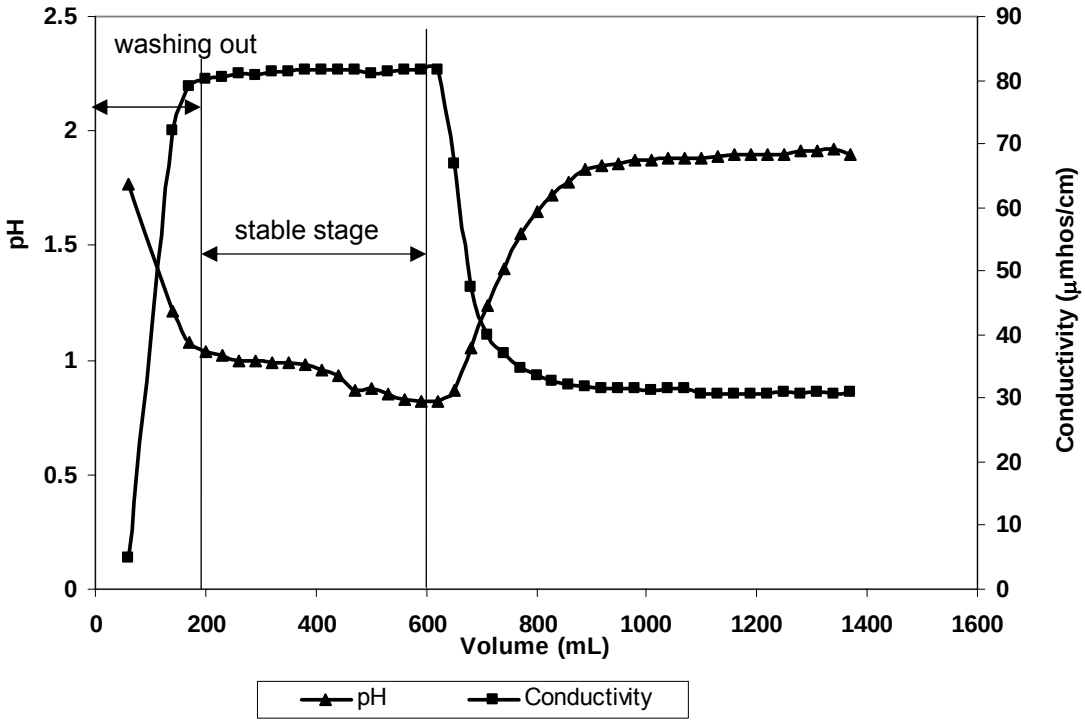

Figure A.4 Breakthrough curve of AG-MP 50 column (replicate #2).

A.3 WA-10 Weakly Basic Anion Exchange Resin

Figure A.5 and A.6 show the breakthrough curves for the adsorption of H_2SO_4 solution (pH 2, conductivity 3330 μmhos/cm, flow rate 10 mL/min) on the WA-10 resin. It can be seen that the breakthrough of pH and conductivity occurred after 11000 mL of H_2SO_4 has passed through the column. This is very close to the estimate provided by the Leenheer (1981) formula. Therefore, in order to treat a 4000 mL water sample, 80 mL WA-10 resin is appropriate.

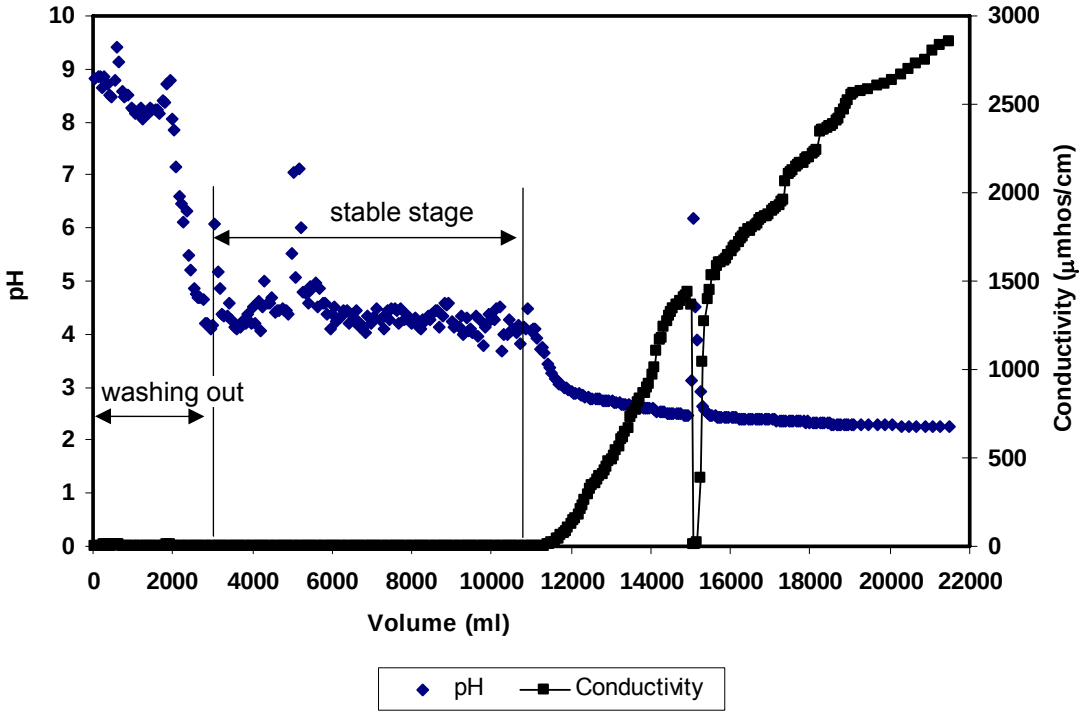

Figure A.5 Breakthrough curve of WA 10 column (replicate #1).

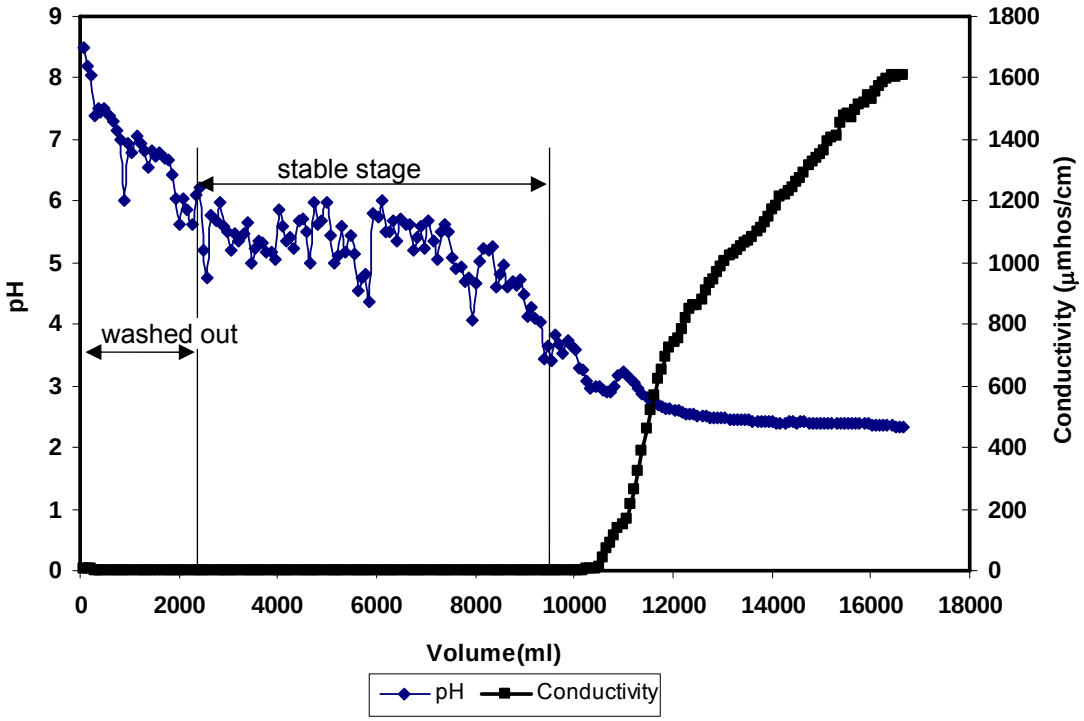

Figure A.6 Breakthrough curve of WA 10 column (replicate #2).

Appendix B. Test Results of DOC Concentration for Suwannee River DOC and Fractions

***Relative error = uncertainty/average value**

Table B-1 DOC concentration of un-fractionaed water samples.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	12.18	6.09	3.13
rep#2	11.48	5.96	3.02
rep#3	12.22	6.09	3.25
rep#4	12.47	6.03	3.15
Ave.	12.09±1.36	6.05±0.20	3.14±0.31
Relative error	0.11	0.03	0.10

Table B-2 DOC concentration of HPOB.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	0.63	0.38	0.18
rep#2	0.54	0.32	0.12
rep#3	0.47	0.23	0.18
rep#4	0.65	0.36	0.21
Ave.	0.57±0.26	0.32±0.21	0.17±0.13
Relative error	0.46	0.66	0.73

Table B-3 DOC concentration of HPOA.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	4.08	2.02	1.12
rep#2	3.74	1.47	0.82
rep#3	4.08	2.18	1.06
rep#4	4.06	2.20	1.06
Ave.	3.99±0.13	1.97±1.08	1.01±0.41
Relative error	0.13	0.55	0.41

Table B-4 DOC concentration of HPON.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	2.07	0.94	0.47
rep#2	2.00	0.93	0.51
rep#3	1.46	0.94	0.46
rep#4	2.06	0.96	0.52
Ave.	1.90±0.93	0.94±0.04	0.49±0.10
Relative error	0.49	0.04	0.20

Table B-5 DOC concentration of HPIB.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	1.15	0.51	0.22
rep#2	1.19	0.60	0.30
rep#3	1.28	0.69	0.26
rep#4	0.98	0.49	0.21
Ave.	1.15±0.40	0.57±0.29	0.25±0.12
Relative error	0.34	0.50	0.48

Table B-6 DOC concentration of HPIA.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	2.33	1.36	0.72
rep#2	2.05	0.95	0.63
rep#3	2.22	1.28	0.65
rep#4	2.43	1.33	0.69
Ave.	2.26±0.53	1.23±0.60	0.68±0.13
Relative error	0.23	0.49	0.19

Table B-7 DOC concentration of HPIN.

Replicates	DOC concentration (mg/L)		
	Full strength	Half strength	Quarter strength
rep#1	1.68	0.86	0.37
rep#2	1.54	0.80	0.40
rep#3	1.38	0.74	0.42
rep#4	1.80	0.63	0.48
Ave.	1.60±0.58	0.76±0.32	0.42±0.14
Relative error	0.36	0.42	0.33

Appendix C. Test Results of UV, SUVA and UV_{254}/UV_{203} for Suwannee River DOC and Fractions

Table C-1 UV_{203} and UV_{254} of un-fractionated water samples.

Replicates	Full strength		Half strength		Quarter strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.980	0.520	0.451	0.251	0.216	0.133
rep#2	0.737	0.499	0.365	0.260	0.180	0.133
rep#3	0.836	0.587	0.396	0.259	0.192	0.126
rep#4	0.852	0.555	0.398	0.262	0.183	0.144
Ave.	0.851±0.317	0.540±0.123	0.4025±0.114	0.258±0.015	0.193±0.052	0.134±0.024
Relative error	0.37	0.23	0.28	0.06	0.27	0.18

Table C-2 UV_{203} and UV_{254} of HPOB.

Replicates	Full strength		Half strength		Quarter strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.027	0.020	0.033	0.008	0.021	0.011
rep#2	0.052	0.018	0.031	0.007	0.021	0.005
rep#3	0.050	0.017	0.029	0.009	0.020	0.006
rep#4	0.040	0.015	0.026	0.008	0.017	0.004
Ave.	0.042±0.019	0.018±0.003	0.030±0.005	0.010±0.001	0.020±0.003	0.007±0.005
Relative error	0.44	0.19	0.16	0.13	0.16	0.78

Table C-3 UV_{203} and UV_{254} of HPOA.

Replicates	Full strength		Half strength		Quarter strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.360	0.102	0.150	0.048	0.100	0.032
rep#2	0.350	0.082	0.180	0.056	0.107	0.037
rep#3	0.360	0.102	0.190	0.055	0.111	0.030
rep#4	0.365	0.183	0.171	0.057	0.118	0.031
Ave.	0.359±0.020	0.142±0.148	0.173±0.054	0.054±0.013	0.109±0.024	0.033±0.010
Relative error	0.06	1.04	0.31	0.24	0.22	0.30

Table C-4 UV_{203} and UV_{254} of HPON.

Replicates	Full strength		Half strength		Quarter strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.178	0.059	0.092	0.033	0.057	0.020
rep#2	0.17	0.057	0.088	0.029	0.053	0.013
rep#3	0.17	0.059	0.080	0.018	0.051	0.013
rep#4	0.174	0.057	0.089	0.028	0.054	0.012
Ave.	0.173±0.012	0.058±0.004	0.087±0.016	0.027±0.020	0.054±0.008	0.015±0.012
Relative error	0.07	0.06	0.19	0.75	0.15	0.81

Table C-5 UV_{203} and UV_{254} of HPIB.

Replicates	Full strength		Half strength		Quarter strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.076	0.02	0.035	0.013	0.015	0.005
rep#2	0.072	0.024	0.034	0.011	0.017	0.006
rep#3	0.067	0.02	0.041	0.013	0.015	0.005
rep#4	0.065	0.023	0.036	0.012	0.015	0.006
Ave.	0.070±0.016	0.02175±0.007	0.037±0.010	0.012±0.003	0.016±0.003	0.006±0.002
Relative error	0.23	0.30	0.27	0.25	0.21	0.33

Table C-6 UV_{203} and UV_{254} of HPIA.

Replicates	Full strength		Half strength		Quarter strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.591	0.026	0.327	0.019	0.171	0.010
rep#2	0.514	0.028	0.318	0.016	0.173	0.009
rep#3	0.529	0.030	0.340	0.016	0.189	0.008
rep#4	0.560	0.030	0.297	0.018	0.172	0.010
Ave.	0.549±0.109	0.029±0.006	0.321±0.058	0.017±0.005	0.176±0.027	0.009±0.003
Relative error	0.20	0.21	0.18	0.28	0.15	0.33

Table C-7 UV_{203} and UV_{254} of HPIN.

Replicates	Full strength		Half strength		Quater strength	
	UV_{203}	UV_{254}	UV_{203}	UV_{254}	UV_{203}	UV_{254}
rep#1	0.023	0.006	0.017	0.005	0.017	0.003
rep#2	0.017	0.005	0.017	0.005	0.017	0.004
rep#3	0.021	0.007	0.018	0.006	0.016	0.005
rep#4	0.023	0.006	0.018	0.005	0.017	0.005
Ave.	0.021±0.009	0.006±0.003	0.018±0.002	0.005±0.002	0.017±0.002	0.004±0.003
Relative error	0.43	0.43	0.10	0.30	0.09	0.72

Table C-8 SUVA of un-fractionated water samples and fractions.

	SUVA (L/mg/m)						
DOC strength	Un-fractionated water	HPOB	HPOA	HPON	HPIB	HPIA	HPIN
Full strength	4.47	3.06	3.56	3.06	1.89	1.26	0.38
Half strength	4.27	3.11	2.74	2.86	2.14	1.40	0.69
Quarter strength	4.27	3.78	3.20	2.95	2.22	1.37	1.02
Ave.	4.34±0.19	3.45±1.49	3.17±1.30	2.96±0.31	2.08±0.54	1.34±0.11	0.70±0.53
Relative error	0.04	0.43	0.42	0.10	0.26	0.09	0.76

Table C-9 UV_{254}/UV_{203} of un-fractionated water samples and fractions.

DOC strength	Un-fractionated water	HPOB	HPOA	HPON	HPIB	HPIA	HPIN
Full strength	0.63	0.41	0.40	0.34	0.31	0.05	0.29
Half strength	0.64	0.34	0.31	0.31	0.34	0.05	0.30
Quarter strength	0.70	0.33	0.30	0.27	0.35	0.05	0.25
Ave.	0.66±0.05	0.36±0.02	0.34±0.09	0.30±0.05	0.33±0.04	0.05±0.00	0.28±0.04
Relative error	0.08	0.04	0.26	0.18	0.11	0.03	0.14

Appendix D. Test Results of Total THMFP and Specific THMFP for Suwannee River DOC and Fractions

Table D-1 Total and specific THMFPs of un-fractionated water samples.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1	0	0	0	798.22	751.86	738.62	762.90	762.90	63.10
rep#2	0	0	0	727.64	796.57		762.11	762.11	63.04
rep#3	0	0	0	998.06	705.96		852.01	852.01	70.47
rep#4	0	0	0	1124.12	708.14		916.13	916.13	75.78
Ave.								823.29±238.36	68.10±19.72
Relative error								0.29	0.29

Table D-2 Total and specific THMFPs of HPOB.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1	0	0	0		54.69	51.80	53.24	53.24	93.13
rep#2	0	0	0		37.93	42.48	40.20	40.20	70.32
rep#3	0	0	0		51.63	46.14	48.89	48.89	85.50
rep#4	0	0	0		61.50	27.74	44.62	44.62	78.04
Ave.								41.64±17.82	81.75±31.18
Relative error								0.43	0.38

Table D-3 Total and specific THMFPs of HPOA.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1	9.59	62.21	35.90	451.46	321.23		386.35	350.44	87.79
rep#2	13.86	62.21	38.04	327.48			327.48	289.44	72.51
rep#3	10.17	62.21	36.19	400.07	393.39		396.73	360.54	90.32
rep#4	14.08	62.21	38.15	524.16		443.99	484.08	445.93	111.71
Ave.								361.59±204.93	90.58±16.13
Relative error								0.57	0.57

Table D-4 Total and specific THMFPs of HPON.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1	0	0	0		139.76	133.78	136.77	136.77	72.06
rep#2	0	0	0	140.20	127.32		133.76	133.76	70.47
rep#3	0	0	0	108.46	97.10	148.35	117.97	117.97	62.15
rep#4	0	0	0	103.19		132.50	117.85	117.85	62.09
Ave.								126.59±32.13	66.69±16.93
Relative error								0.25	0.25

Table D-5 Total and specific THMFPs of HPIB.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1	2.07	62.21	16.07	84.42	65.80	68.21	72.81	56.74	49.24
rep#2	1.62	62.21	15.96	70.36	75.21		72.79	56.83	49.32
rep#3	19.02	62.21	20.31	82.56	82.58	69.16	78.10	57.79	50.16
rep#4	4.62	62.21	16.71	67.66	69.10	95.49	77.42	60.71	52.69
Ave.								58.02±5.91	50.35±5.13
Relative error								0.10	0.10

Table D-6 Total and specific THMFPs of HPIA.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1		62.21	62.21	176.67	172.30	160.33	169.77	107.56	47.69
rep#2		62.21	62.21	183.05	186.27	168.85	179.39	117.18	51.95
rep#3		62.21	62.21		192.64		192.64	130.43	57.83
rep#4		62.21	62.21		190.23		190.23	128.02	56.76
Ave.								120.79±33.54	53.55±14.87
Relative error								0.28	0.28

Table D-7 Total and specific THMFPs of HPIN.

	Blank (μg/L)	Blank (μg/L)	Blank Ave. (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample THMFP (μg/L)	Sample Ave. (μg/L)	Sample correction (μg/L)	Specific THMFP (μg chloroform/mg DOC)
rep#1		62.21	62.21	114.08	113.20		113.64	51.43	32.15
rep#2		62.21	62.21	111.16	115.03		113.10	50.88	31.81
rep#3		62.21	62.21	81.69	105.90		93.79	31.58	19.74
rep#4		62.21	62.21	92.24	121.89	83.05	99.06	36.85	23.04
Ave.								42.69±31.87	26.68±19.93
Relative error								0.75	0.75

Appendix E. FTIR Replicate Spectra

The attached data CD contains replicate FTIR scanning spectra for all the water samples. The foldername listing for the data is shown below.

Suwannee River DOC

- Un-fractionated water sample
- HPOB
- HPOA
- HPON
- HPIB
- HPIA
- HPIN

Typical prairie water samples

- Buffalo Pound Water Treatment Plant
- Yellow Quill Water Treatment Plant
- Saskatoon Water Treatment Plant
- Ehman Dugout Water Treatment System

Appendix F. Test Results of Source Waters and Treated waters

Table E-1 DOC concentration of source waters.

Source		DOC (mg/L)
Buffalo Pound	Source	7.05
	After CFS	3.44
	After AC	3.13
Yellow Quill	Source	9.86
	After biofilter	10.08
	After RO	1.08
Saskatoon	Source	5.05
	Treated	4.45
Ehman farm	Source	25.43
	Wet well	8.36
	After slow sand	6.53
	After BAC	7.73
	After RO	0.03

Table E-2 UV absorption of source water.

Source		UV_{203}	UV_{254}	SUVA (L/mg/m)	UV_{254}/UV_{203}
Buffalo Pound	Source	0.302	0.084	1.19	0.28
	After CFS	0.245	0.047	1.37	0.19
	After AC	0.287	0.032	1.02	0.11
Yellow Quill	Source	0.616	0.182	1.85	0.30
	After bio-filter	2.754	0.194	1.92	0.07
	After RO	0.35	0.001	0.09	0.00
Saskatoon	Source	0.471	0.093	1.84	0.20
	Treated	0.618	0.08	1.80	0.13
Ehman farm	Source	1.41	0.576	2.27	0.41
	Wet well	0.559	0.174	2.08	0.31
	After slow sand	1.583	0.12	1.84	0.08
	After BAC	1.837	0.122	1.58	0.07
	After RO	0.225	0	0.00	0.00

Table E-3 THMFP measurements of source water.

Source		Blank (µg/L)	Blank (µg/L)	Blank Ave. (µg/L)	Sample THMFP (µg/L)	Sample THMFP (µg/L)	Sample THMFP (µg/L)	Sample Ave. (µg/L)	Sample correction (µg/L)	Specific THMFP (µg chloroform/mg DOC)
Buffalo Pound	Source	17.39	4.12	10.75	316.51	346.63	336.59	333.24	17.39	45.74
	After CFS	92.10	90.54	91.32	311.61	273.08	293.66	292.79	92.10	58.53
	After AC	117.18	113.16	115.17	233.67	234.88	230.65	233.07	117.18	37.68
Yellow Quill	Source				222.83			222.83	222.83	22.61
	After bio-filter				288.50			288.50	288.50	28.61
	After RO				11.12	11.74		11.43	11.43	10.63
Saskatoon	Source	172.00		172.00	426.35			426.35	254.36	50.32
	Treated	206.65		206.65	331.27			331.27	124.62	28.02
Ehman farm	Source	0.00		0.00	1986.84	1908.74		1947.79	1947.79	76.60
	Wet well	8.62	1.48	5.05	296.07	726.30		511.18	506.13	60.52
	After slow sand	62.81	57.09	59.95	399.37	343.66		371.52	311.57	47.71
	After BAC	76.41	0.00	38.20	466.49	380.20	383.64	410.11	371.91	48.12
	After RO		81.99	81.99	81.18	83.14		82.16	0.17	5.32