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## Coagulation and disinfection by-products formation potential of dissolved organic matter fractions

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## ABSTRACT

### COAGULATION AND DISINFECTION BY-PRODUCTS FORMATION POTENTIAL OF DISSOLVED ORGANIC MATTER FRACTIONS

by  
Neeraj S. Pipada

Both the proposed United States Environmental Protection Agency (USEPA) Disinfectants- Disinfection By-Products and Enhanced Surface Water Treatment rules have provisions for minimizing the formation of undesirable precursors of disinfection by-products (DBPs) in drinking water. Natural Organic Matter (NOM) contains many of the precursors to the DBPs formed following disinfection of drinking water. DAX-8 resin procedures were used to isolate and fractionate NOM into six dissolved organic matter (DOM) fractions; Hydrophobic acid (FA), base (FB), neutral (FN), and hydrophilic acid (PA), base (PB) and neutral (PN). Aluminum sulfate (alum) jar coagulation tests were performed to determine the optimum coagulation ranges of each fraction. Different levels of pH, fraction concentrations, and coagulant levels were used in the experiments. Trihalomethane formation potential tests were performed on all the samples to check the removal of DBP precursors. Given the reactivities of the individual fractions to the formation of selected DBPs (i.e. trihalomethanes, haloacetonitriles, haloacetic acids), one can optimize on the removal of specific problematic fractions. Hence, if minimization of DBP formation was solely due to specific removal of precursors, microbial inactivation issues would be resolved due to the fact that CT may be increased without an increase in DBP formation.

**COAGULATION AND DISINFECTION BY-PRODUCTS FORMATION  
POTENTIAL OF DISSOLVED ORGANIC MATTER FRACTIONS**

by  
**Neeraj S. Pipada**

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**APPROVAL PAGE**

**COAGULATION AND DISINFECTION BY-PRODUCTS FORMATION  
POTENTIAL OF DISSOLVED ORGANIC MATTER FRACTIONS**

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**To my beloved family  
and  
my wonderful brothers: Dhiraj and Pankaj**



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# CHAPTER 1

## INTRODUCTION

### 1.1 Objective

The objective of this thesis is to evaluate coagulation as a mean for the removal of individual DOM fractions, which are precursors to DBP formation. The thesis discusses the history and ongoing work in the techniques of DOM fraction characterization, their removal and DBP formation potential. A secondary objective is to demonstrate the use of a modified resin adsorption fractionation technique for source water characterization of DOM, which has the potential to target operationally defined problematic fractions.

Source water characterization techniques for DOM are essential to identify problematic components being discharged from point or non-point sources. With the increase in the number and stringency of the drinking water regulations proposed by the USEPA, it has become essential to develop such characterization techniques. Characterization of DOM gives an insight into the nature of the site-specific organic matrix present in water at a particular location. A modified characterization technique by DAX-8 resin-fractionation was developed and applied to several different sampling locations in two New Jersey water treatment plants (Marhaba *et al.*, 1998a). The method characterizes DOM into the six fractions on the basis of adsorption on anionic/cationic resins. Main advantages of the modified technique are its applicability to DBP formation studies and more consistency in adsorption and mass fraction production. Mass balance

was performed on the fractions at the sampling stations examined to check the accuracy of the method. Results are discussed in the subsequent chapters.

The amenability of various DOM fractions to their removal by coagulation was studied in order to optimize the removal of potential fraction precursors to DBP formation. The fractions were subjected to different set of coagulation conditions and the DBP formation potential was studied under these conditions. The total trihalomethanes (TTHMs) (EPA Method 551.1) for the fraction were checked for the Stage 1 and Stage 2 compliance with the disinfectant/ disinfection by-products (D/DBP) Rule maximum contamination levels (MCLs). This work is the first attempt to study the formation potential of six DOM sub-fractions and their removal based on a broader fractionation procedure, which classifies DOM as hydrophobic/ hydrophilic and then into six sub-fractions. This research would be of interest to the regulatory agencies, water treatment purveyors, wastewater treatment authorities, and consultants.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 General

Natural Organic Matter (NOM) is a term used to describe the complex matrix of organic matter that is present in natural waters. Before the 1970s, research into the nature of NOM in drinking water and into methods of its removal was driven primarily by the desire to remove color from public water supplies (Krasner *et al.*, 1996). Since then, several other problems associated with NOM have been identified including its potential to transport metals and hydrophobic organic chemicals, its potential to contribute to corrosion, its tendency to interfere with the removal of other contaminants and its contribution to the DBP formation (Drikas, 1997). In 1979, regulations for DBPs forced water utilities to improve NOM removal (Jacangelo *et al.*, 1995). The stringency of the proposed drinking water regulations related to DBPs and precursors provides the grounds for the development and use of NOM characterization techniques for source waters.

For engineers, scientists, and researchers in the field of water treatment, the study of NOM has become critically important as it significantly influences many aspects of water treatment, including the behavior of unit processes (i.e. oxidation, coagulation, adsorption), the application of disinfectants and biological stability (AWWARF, 1993; Jacangelo *et al.*, 1995; Drikas, 1997). NOM represents the raw organic material in the influent water of a treatment plant and plays a role in many of the regulatory challenges facing water utilities.



## 2.2 NOM Characterization

There have been numerous attempts to define NOM. Historically, organic matter in natural waters has been arbitrarily divided into dissolved organic carbon (DOC) and particulate organic carbon (POC) based on filtration through a 0.45 micron filter. But no natural cutoff exists between these two fractions, as there is an overlapping colloidal fraction in between. Several filters with different pore size cutoffs such as  $<0.1\mu\text{m}$ ,  $<0.45\mu\text{m}$ ,  $<1.0\mu\text{m}$ , have been used by various researchers to provide an operational definition of NOM as dissolved, colloidal and particulate organic matter, respectively, at these cutoff values (AWWARF, 1993; Leenher, 1981; Day *et al.*, 1991).

Numerous researchers have studied the classification of DOM (Krasner *et al.*, 1996; Peuravuori and Pihlaja, 1997; Owen *et al.*, 1995). However, it has been shown that DOM cannot be simply defined as particular chemical structures but only be broadly characterized into generic groupings. These definitions are complicated by the seasonal and temporal variability to which DOM is subjected.

Essentially, there have been two approaches in elucidating the complex nature of DOM: a nonperturbing approach which includes, but is not limited to, (1) Total Organic Carbon (TOC), (2) Ultra Violet Absorbance (UVA) and (3) fluorescence, and a perturbing approach which includes, but is not limited to, (1) molecular weight (MW) fractionation and (2) resin adsorption fractionation. TOC and UVA correlations can be developed to give a better understanding of the character of the DOM. But, TOC and UVA are aggregate parameters and do not necessarily target specific problematic compounds of concern. Ultrafiltration characterizes DOM according to molecular weight fractions and hence the fractions lack the chemical characterization needed for precursor

identification. More recently, fluorescence techniques and resin fractionation have proven to have a potential in the identification of problematic DOM fractions in source waters (Marhaba and Washington, 1998).

The various resin fractionation techniques attempt to classify DOM into operationally defined fractions which lack a clear chemical definition. The characterization of DOM as hydrophobic/hydrophobic or humic/nonhumic, is not very clear as there is an overlap between these fractions. Therefore, a more rigorous and thorough characterization is necessary for further studies, for example, disinfection by-products formation potential of each fraction. In this study, DOM was isolated from different locations using a modified resin adsorption fractionation method (Marhaba *et al.*, 1998a).

### 2.3 Removal of DOM Fractions

Various water treatment technologies target DOM fraction removal, with coagulation, granular activated carbon (GAC), and ozonation being commonly used in the United States. The ability of ozone to alter DBP precursors, while improving turbidity removal, has generated a great interest in the research of combining ozonation with other water treatment processes such as coagulation, chlorination and GAC. Except for coagulation, the later two technologies are expensive, and significant information on the treatability of waters nationwide using GAC and is not currently available (Hooper *et al.*, 1996). An important aspect of the USEPA Information Collection Rule (ICR), however, is the evaluation of the effectiveness and costs associated with implementing GAC at many large systems throughout the United States.

Coagulation is considered one of the most effective techniques of removing DOM from water. Its effectiveness controls the efficiency of subsequent processes such as sedimentation and filtration. With different fractionation methods employed for the characterization of DOM, different operationally defined fractions such as humic/fulvic acid and hydrophobic/hydrophilic substances may be obtained. The concentration of these fractions in the source waters is site-specific and as the fractions are chemically dissimilar, it is possible that the optimal removal of each fraction occurs at different set of coagulation conditions. Data available on the removal of individual DOM fractions by coagulation is limited and the fractionation methods employed in previous studies are diverse. Nevertheless, some general conclusions can be drawn;

- Coagulation has been shown to remove certain DOM fractions preferentially.
- Humic (hydrophobic) DOM and higher-molecular weight DOM are more effectively removed than their counterpart DOM fractions (Krasner and Amy, 1995).

The treatment challenge is to have coagulation remove sufficient DBP precursors to allow the use of free chlorine as a primary and residual disinfectant while meeting the microbial disinfection requirements and the proposed DBP MCL standards (USEPA, 1994a; Crozes *et al.*, 1995). The USEPA, in the proposed Enhance Surface Water Treatment Rule has identified enhanced coagulation as a best available technology (BAT) for the control of precursors to organic DBPs such as total trihalomethanes (TTHM's) and haloacetic acids-5 (HAA-5) (USEPA, 1994b).

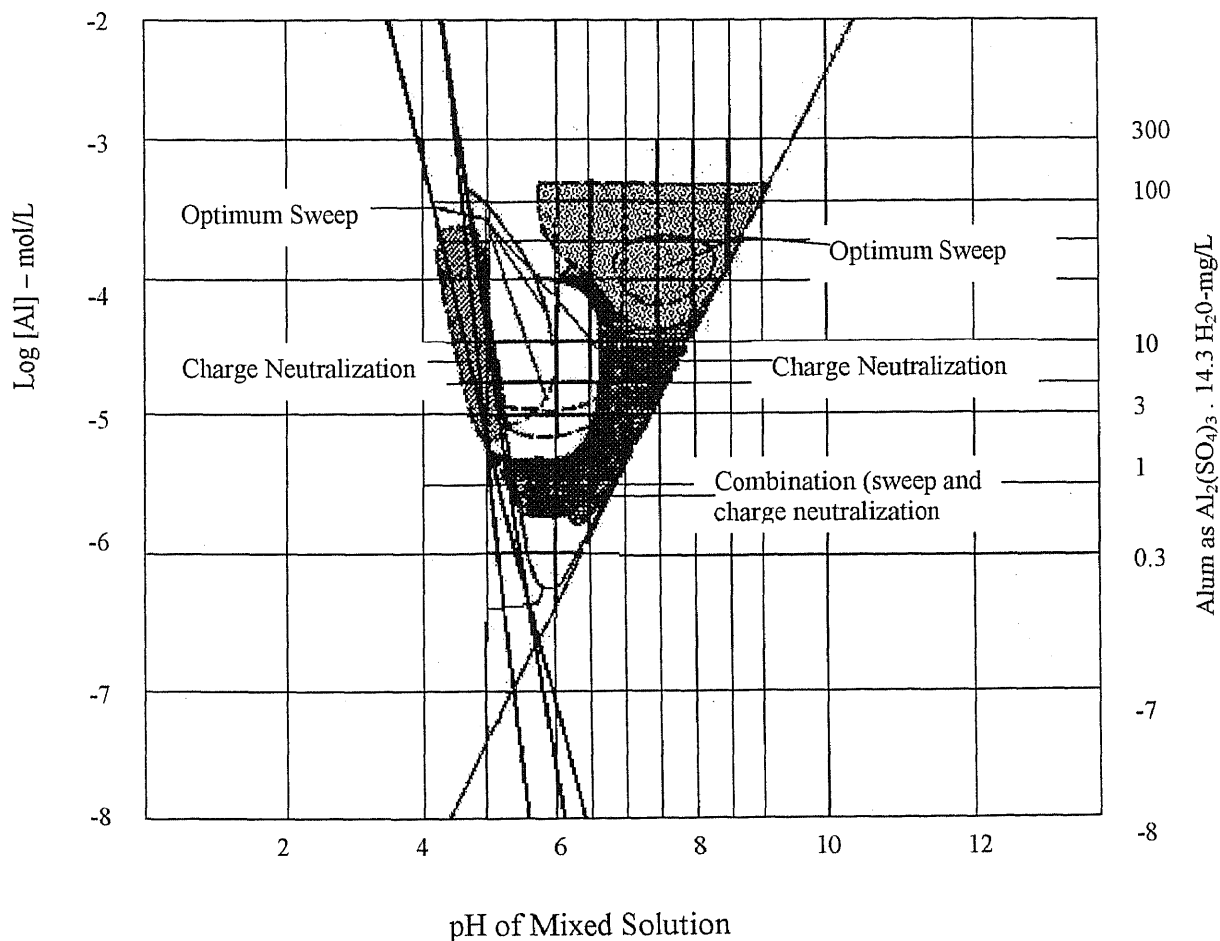
## 2.4 Mechanisms of Coagulation

Metallic salts of aluminum and Fe (III) are typically used as coagulants, the most common being aluminum sulfate (i.e. alum). Alum is widely used as a coagulant in the United States for the treatment of surface water supplies (Hubel and Edzwald, 1987). Polyaluminum chloride is widely used in Japan. Polyelectrolytes have also been developed as coagulants (Dennett *et al.*, 1995). Though there have been reports of iron salts outperforming alum, at lower coagulant dosages the differences were not substantial. The most favorable pH conditions for coagulation of DOM are around pH 5 to 6 for Al(III) salts and around pH 4 to 5 for Fe(III) salts (Dennett *et al.*, 1995). At lower pH values, the level of organic protonation increases, thus reducing the coagulant demand. Also, the coagulating species are more positively charged at lower pH. As a consequence, adsorption becomes more favorable and the required coagulant dosage decreases. Also, the alkalinity consumed during the formation of the metal hydroxides is two times higher for ferric chloride than alum. As a result, for a similar coagulant dosage, the coagulation pH will be lower with ferric chloride than with alum.

Different mechanisms of destabilizing contaminants using chemical coagulants have been identified. These mechanisms include double layer compression, adsorption-charge neutralization, sweep coagulation, precipitation, coprecipitation and interparticle bridging. They are discussed in detail elsewhere (Dempsey, 1984, Dennett *et al.*, 1995, O'Melia, 1972). Each mechanism is favored by a particular set of operational conditions, however, in practice, it is likely that more than one mechanism will be responsible for removal of DOM.

Removal of humic substances and fulvic acids by coagulation has been studied by

various researchers. This fractionation, though different from the fractionation method employed in this study, provide an indication of the predominant DOM removal mechanisms. Humic substances are similar to hydrophobic substances and fulvic acids are similar to hydrophilic acids. Dempsey (1984), Edwards and Amirtharajah (1985), and Amy *et al.* (1989), have identified two mechanisms by which dissolved humic substances are removed from solution during coagulation. These mechanisms are (1) precipitation by cationic species (charge neutralization) and (2) adsorption on organic or inorganic solids



**Figure 1.** Design and Operation Diagram for Alum Coagulation  
Source [Amirtharajah and Mills, 1982]

(sweep coagulation). The mechanism that occurs is dependent on pH conditions. For  $\text{pH} < 5$ , removal is thought to occur by charge neutralization and for  $\text{pH} > 7$ , removal is thought to occur by direct adsorption onto a solid hydroxide precipitate (Krasner and Amy, 1995). Figure 1 is a design and operation diagram for alum coagulation that shows the areas in which various coagulation mechanisms predominate.

Adsorption-Charge Neutralization- Charge neutralization involves the interaction of a chemical coagulant and a charged contaminant. It has been reported that under conditions of charge neutralization, stoichiometry exists between the coagulant and the contaminant (Dempsey, 1984).

Sweep Coagulation- The removal of contaminants through the formation of a solid precipitate is referred to as sweep coagulation. Voluminous hydroxide precipitates form because the water is supersaturated to several orders of magnitude above the solubility of the metal salts (AWWA Coagulation Committee, 1989). Slow mixing is an important step when the mechanism is sweep coagulation.

These mechanisms mainly apply to the removal of colloidal NOM, typically higher MW hydrophobic acids. These acids generally have low charge densities and therefore require low coagulant doses to induce destabilization. However, the more soluble fraction of NOM (hydrophilic acids) has higher anionic charge densities that facilitate their dissolution. The sweep coagulation mechanism, which operates most effectively on colloidal NOM, is unlikely to remove these soluble hydrophilic acids. Charge neutralization may remove hydrophilic acids, but high doses of coagulant will be required to neutralize the high anionic charge. The high coagulant dose required by soluble hydrophilic acid is likely to correspond to overdosing of hydrophobic acid

colloids resulting in restabilization of the colloids (Gregor *et al.*, 1997). The nature of hydrophilic acid is also an important parameter for its removal. For example, low molecular weight and size hydrophilic acids are relatively more hydrophilic and not amenable to removal by coagulation. Hydrophilic acids with a higher carboxylic acidity (and thus higher charge density) are more difficult to coagulate chemically by charge neutralization than hydrophobic acids with a lower charge density (Amy *et al.*, 1992).

Enhanced coagulation- Enhanced coagulation is defined in the proposed D/DBP Rule (USEPA, 1994a) as the addition of excess coagulant for improved removal of DBP precursors by conventional filtration treatment. It has been extensively used by water treatment plants for DOM fraction removal. The implementation of enhanced coagulation process, however, raises several issues. It is also possible that, optimum turbidity removal may not be achieved under enhanced coagulation conditions, and it will increase the overall cost for coagulation and for final pH adjustment for corrosion control. However, coagulation pH adjustment with sulfuric acid reduced the cost of enhanced coagulation by reducing the required primary coagulant dose (Crozes *et al.*, 1995). A secondary advantage of lowering the coagulation pH is the diminution of sludge production. Enhanced coagulation is a valuable means of controlling DBP formation without requiring significant capital investment such as GAC or ozonation. Though higher alum dosage increases the coagulation cost, the over all cost is considerably reduced. The following table compares different parameters for conventional and enhanced coagulation:

**Table 1.** Comparison of Conventional and Enhanced Coagulation  
Source [Hooper *et al.*, 1996]

Parameter	Conventional Coagulation	Enhanced Coagulation
Alum dosage (mg/l)	11	71
TOC (mg/l)	2.2	1.7
TOC removal- percent	9	31
TOC removal required for enhanced coagulation-percent	20	20
pH	7.8	6.5
UV <sub>254</sub> - l/cm	0.047	0.028
Specific absorbance-L/ mg-cm	0.021	0.016
Specific absorbance after GAC - L/ mg-cm	0.013	0.009
TTHMs (µg/ L)	72	46
HAA5 (µg/ L)	28	17

Enhanced coagulation shows better removal of DOM as well as the formation of DBPs is considerably lower by enhanced coagulation as compared to conventional coagulation.

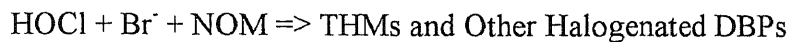
## 2.5 Disinfection By-Products

Disinfection of water can be achieved by using various techniques such as the addition of chlorine, ozone, chlorine dioxide, potassium permanganate and chloramines. Chlorine has by far been the disinfectant of choice for nearly 100 years and is used by majority of water treatment systems for the protection against waterborne diseases. But the discovery that chlorination of the most natural waters produces chlorinated byproducts with potential chronic health risks (Kavanaugh, 1978) has caused a major reassessment of water treatment practices in the United States.

Chlorinated DBPs form when free chlorine (HOCl) is added to water. Chlorine



acts as an oxidant and reacts with the NOM present. The generalized equation describing the formation of the halogenated DBPs is:



The major halogenated DBPs that are commonly identified from chlorine treatment are THMs, HAAs, HANs, cyanogen halides and halopicrins (Krasner *et al.*, 1989). Some of the major types of these DBPs are listed in Table 2.

**Table 2.** Chlorinated DBPs  
Source [Marhaba and Washington, 1998]

Chemical Class	Chemical Compound
Trihalomethanes (THMs)	Chloroform Bromodichloromethane Dibromochloromethane Bromoform
Haloacetic Acid (HAAs)	Monochloroacetic Acid (MCAA) Dichloroacetic Acid (DCAA) Trichloroacetic Acid (TCAA) Monobromoacetic Acid (MBAA) Dibromoacetic Acid (DBAA)
Haloacetonitrile (HANs)	Dichloroacetonitrile Trichloroacetonitrile Dibromoacetonitrile Bromochloroacetonitrile
Cyanogen Halides	Cyanogen Chloride Cyanogen Bromide

In the absence of bromide ion ( $\text{Br}^-$ ), only the chlorinated by-products are formed.

In the presence of bromide ion, free chlorine (HOCl) rapidly oxidizes bromide ion to hypobromous acid (HOBr), which then reacts, along with the remaining HOCl, with NOM to produce the mixed chloro-bromo DBPs (Marhaba and Washington, 1998).

In 1974, Rook reported the discovery of THMs, though at that time, the health implications of THMs were not known. In 1976, the National Cancer Institute released a report that showed that high dosages of chloroform, the most prevalent THM in drinking water, could cause cancer in laboratory rats. Since then, many studies have generated data on NOM and THM formation precursor removal.

The USEPA has set a MCL of 100  $\mu\text{g/L}$  for TTHMs and has proposed a new MCL of 80  $\mu\text{g/L}$  in Stage 1 of the D/DBP Rule (USEPA, 1994). In addition to these standards, a MCL for HAA5 of 60  $\mu\text{g/L}$  is proposed (USEPA, 1994). More stringent requirements of 60  $\mu\text{g/L}$  for TTHMs and 40  $\mu\text{g/L}$  for HAA5 are proposed in Stage 2 of the D/DBP Rule. TTHMs is defined as the sum of four individual THMs: chloroform, bromoform, dibromochloromethane and bromodichloromethane. One approach that water utilities have focused on, is chlorination modification to meet TTHM standards. This include reducing chlorine dosage, switching to another peroxidant or converting free chlorine to combined chlorine after a short period of contact time.

Another approach has been the removal of precursors to THM formation before they are brought in contact with chlorine with methods such as enhanced coagulation. The later approach has been widely used by various water utilities and forms the basis for the present study. But exact pathways for the formation of THMs are not fully understood (AWWRF, 1995). Though humic material is still considered to be the source of most precursors for THMs in natural waters, Reckhow and Singer (1985) pointed out the

importance of aliphatic compounds (which may be non-humic substances) as precursors to THMs. Because aliphatic compounds react in a predictable way with chlorine, Reckhow and Singer were able to establish a reaction pathway. A similar reaction pathway for aromatics could not be established because of difficulties in predicting the extremely reactive nature of the aromatics with respect to chlorine. This ongoing research attempts to distinctly identify and target NOM precursors to THM formation.

## CHAPTER 3

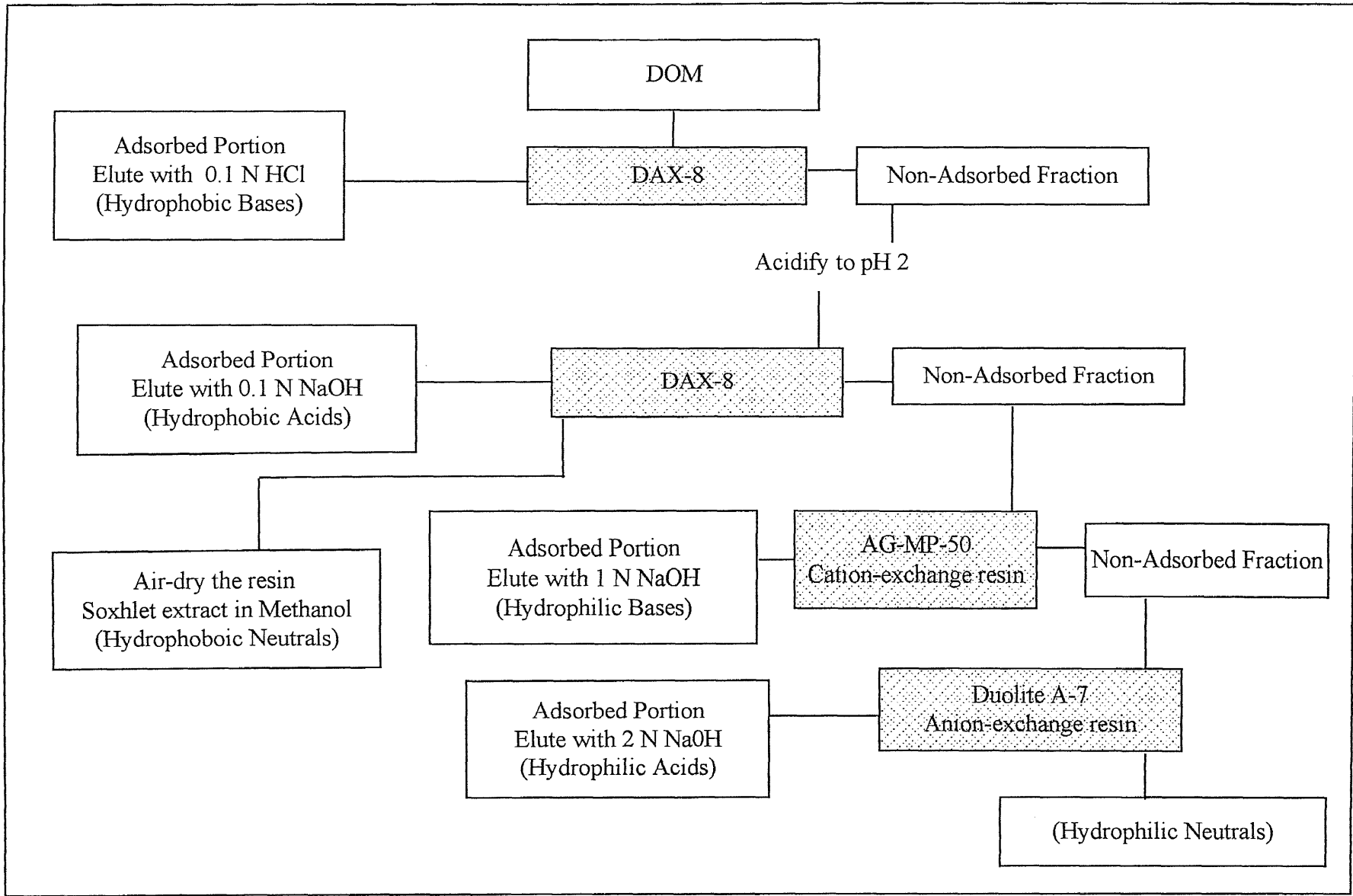
### EXPERIMENTAL TECHNIQUES AND METHODOLOGY

#### 3.1 Introduction

To meet the research objectives discussed in Chapter 1, fractions were obtained by resin fractionation and diluted to concentrations typically found in natural waters. Initial alkalinity, pH, TOC, UVA of the fractions were measured. Preliminary jar tests were conducted to select the range of pH and alum dosage for the particular water sub-fraction. TOC was used to measure reduction in DOM. Jar test analysis, TOC, UV-254, and TTHM formation potential tests were then conducted for all the fractions.

#### 3.2 Resin Adsorption Fractionation

The resin fractionation technique used to fractionate NOM in the present study is a modification to the fractionation procedure described by Leenheer (1981), (Marhaba *et al.*, 1998a). Samples were collected at different locations within the Canal Road (CR) and Raritan/Millstone (R/M) water treatment plants of the Elizabeth Water Company in Westfield, New Jersey. The volume of samples collected was 9-liters each. Vacuum filtration was used to filter all samples through a 0.45 $\mu$ m cellulose filter to collect dissolved fraction of the total organic carbon. Amberlite resin DAX-8, (Supelco, Bellefonte, PA), AG-MP-50 Cation-Exchange Resin (BioRad, Hercules, CA) and Duolite A7 Anion-Exchange Resin (Supelco, Bellefonte, PA) were all purified by soxhlet extraction method. Filtered samples were pumped through the DAX-8 column. The



**Figure 2.** Modified Resin Adsorption Method for DOM Fractionation  
(Source: Marhaba et al, 1998a)

hydrophobic base was then eluted by a passing 0.1N HCl, followed by 1.5 bed volumes of 0.01N HCl. The sample effluent from the DAX-8 column was then acidified to pH 2 with HCl and recycled through the DAX-8 column. The adsorbent, hydrophobic acid was then eluted with 0.1N NaOH. The DAX-8 resin was then dried prior to being soxhlet-extracted with anhydrous methanol. The methanol solution at the end of the process contained the hydrophobic neutral fraction. The effluent was pumped through the AG-MP-50 resin column from which the adsorbent, hydrophilic base was eluted with 1N NaOH. The effluent was then pumped through a third column containing Duolite A7 resin. The effluent was collected as the hydrophilic neutral fraction and the adsorbent was eluted by 2N NaOH as hydrophilic acid fraction and inorganic salts. The rate of flow through all the columns was regulated by air or vacuum pressure as necessary.

Some modifications to the Leenheer's (1981) procedure were proposed and conducted. NaOH of appropriate normality was used for elution instead of  $\text{NH}_4\text{OH}$ , to address the concern of possible formation of chloramine in subsequent trihalomethane formation potential study (Korshin *et al.*, 1997). All elutions in this procedure were done in a forward direction or gravity flow (not backflush). This was to facilitate the recovery procedure. Forward elution was conducted by Day (1991) and is the preferred recovery method. As a result of the above fractionation technique, 6 fractions of the dissolved organic matter (DOM) were isolated based on chemical characteristics.

### 3.3 Jar Test Coagulation

Coagulation was simulated by using a jar-test apparatus (Phipps and Bird, Richmond, VA). Regular-grade alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ] was added as a coagulant followed by

rapid mixing at 100 rpm for 1 minute, flocculation at 30 rpm for 30 minutes and quiescent settling for 1 hour. The supernatant sample from each beaker was pipetted to exclude the settled particles and flocs. Coagulation was carried out at controlled pH (6 to 8, using NaOH or H<sub>2</sub>SO<sub>4</sub>) over a range of alum dosages (up to 60 mg/L). The temperature during coagulation ranged from 22° C to 25° C. Alkalinity of the samples was determined by *Standard Methods* 2320-B (1995) by using 0.02 N H<sub>2</sub>SO<sub>4</sub> as a titrant. The samples were continuously mixed on a magnetic stirrer during titration. Alkalinity ranged from 60 to 100 mg/L as CaCO<sub>3</sub> before coagulation and 30 to 70 mg/L at optimum coagulation for the fractions investigated.

#### 3.4 Total Organic Carbon (TOC) Analysis

TOC was used as a measure of fraction concentration in the water. TOC of all the samples was measured by a total organic carbon analyzer (O.I. Corp., College Station, TX) using the method of sodium persulfate oxidation (*Standard Methods* 5310-D, 1995). All the samples were filtered through a 0.45µm cellulose filter prior to analysis to remove suspended particles. The analyzer was regularly calibrated with 1000-ppm potassium hydrogen phthalate (KHP) standard as recommended by the manufacturer. Each sample was prepared and diluted differently depending on whether the solvent was 0.1N HCl, 1N NaOH or 2N NaOH. The analyzer was programmed accordingly with the proper amount of acid, oxidant and reaction time as recommended by the manufacturer. At least 3 blanks were analyzed prior to the analysis of each sample to establish and verify the appropriate background for quality assurance and control.

### 3.6 UV-254 Analysis

Ultraviolet Absorbance (UVA) was measured at a single wavelength of 254 nm, using a DMS UV/visible spectrophotometer (Varian, Victoria, Australia) using 1-cm path length. UV light source was used for this purpose (monochromator between 310 and 190 nm). The instrument was regularly calibrated to zero absorbance by placing two blank solvents. The UVA of all the samples was measured with reference to the standard reference blank solvent. The instrument was also calibrated using standard dichromate solution as recommended by the manufacturer (Varian Operating Manual, 1987).

### 3.7 Disinfection By-Products Formation Potential

The chlorine dosing solution was prepared using commercial  $\text{Ca}(\text{OCl})_2$  (calcium hypochlorite) solution. The samples were buffered to a pH between 6-7 and chlorinated by a concentration of 100-ppm  $\text{Cl}_2$  using calcium hypochlorite. These chlorinated samples were incubated for 7 days at 25 °C. After the incubation period, the samples were dechlorinated with ammonium chloride and analyzed for THMs, and HANs using liquid-liquid extraction gas chromatography (GC), as described in EPA Method 551.1.

The DBP formation potentials (DBFPF) were obtained when high chlorine doses were applied for 1 week, thus enabling precursors to react. This test measures the precursor concentration.

The GC analysis of the extracts was performed using a Varian 3400 Gas Chromatograph (Walnut Creek, CA) equipped with two electron capture detectors (ECDs) and an autosampler to ensure that the injection procedure is identical for all samples. The primary column was a DB-1 Column and the confirmation column was a



DB-1301 Column from J&W Scientific (Folsom, CA). Data was collected using a computer equipped with PC Minichrom™ software (Cheshire, England). The Minichrom software was used to store the calibration and analytical parameters required for this method.

### **3.8 Quality Assurance and Quality Control**

To ensure the validity of the results of this investigation and to identify the source of any errors, several quality assurance and quality control (QA/QC) measures were utilized. In addition to the QA/QC measures for jar test coagulation, the TOC analysis, UV analysis, fluorescence spectroscopy and THM/HAN analysis all require additional QA/QC protocols.

All glassware used for this study were of the highest quality. The samples were stored in amber bottles (Fisher Scientific, Pittsburgh, PA), and were stored at a temperature of 4°C when not in use. For all analysis, reagent blanks were tested to ensure there were no impurities or interferences that would alter the results in some unexpected way. Duplicates were run for approximately 10 percent of all samples to ensure that the analysis is repeatable and to determine if any errors were undetected in the experiment. All solutions were prepared from reagent grade chemicals. The calibration of the instruments used for analysis, including pH meters, conductivity meters etc., were checked on a regular basis by running samples of known concentrations to determine if recalibration was required.

Prior to performing the resin adsorption fractionation, all the resins were cleaned and purified by soxhlet extraction for 24 hours. The flow rates through each resin are

different and were kept constant by controlling the air or vacuum pressure as required. Glass columns with Teflon end caps and the connecting tubings were of Teflon. The resins was regenerated or fresh resins were regularly prepared and clean as required (Leenher, 1981), to avoid the high bleed of TOC initially. The THM/HAN analysis required two additional QA/QC measures. Decafluorobiphenyl was added to each sample prior to the liquid-liquid extraction for use as a surrogate standard. In addition to this standard, 4-Bromofluorobenzene (4-BFB) was added to each sample after the extraction for use as an internal standard. The surrogate standard was used to determine the accuracy of the extraction procedure by comparing its known concentrations with the concentration determined by the GC. The internal standard was added in identical amounts to the extract for each sample.

## **CHAPTER 4**

### **RESULTS AND DISCUSSIONS**

#### **4.1 Scope of Experiments**

The results of the experiments discussed in Chapter 3 are presented here in the following six sections. Section 4.2 contains the results of the application of the resin adsorption method for the fractionation of NOM. Section 4.3 tabulates TOC and specific absorption of DOM fractions before and after coagulation. The removal of these fractions by coagulation is compared in Section 4.4. The THM formation potential of the six fractions and the reduction in THM formation potential at various coagulation conditions is shown in Section 4.5. Correlations between TOC, UVA and THM formation potential have been established in Section 4.6.

#### **4.2 DAX-8 Resin Adsorption Fractionation**

An important aspect of the resin adsorption fractionation method is the recovery of the fractions through various resin columns and to check for losses, if any. In order to achieve this, mass balances were performed at all the four locations of the treatment plant. The results tabulated in Table 3 show that a recovery of 110-115% for the DOM fractions was achieved.

**Table 3.** Mass Balance of DOM Fractions

Location	MASS (mg)						
	DOC	FB	FA	FN	PB	PA	PN
Intake	34.02	2.03	4.13	6.21	1.32	16.44	7.07
Sedimentation Basin	26.64	1.60	3.08	5.83	1.92	15.00	2.70
Filter	21.01	1.12	1.84	4.50	1.29	12.60	1.35
Distribution Water	19.80	1.06	1.68	4.38	1.38	10.00	1.80

The tolerance of 10-15% confirms the effectiveness of the modified resin fractionation procedure. Similar tolerance was reported by Day (1991), although it was on the deficit side of the recovery, which was due to loss of the hydrophilic acid fraction from the strong anionic nature of the AG-MP-1 resin. Surplus recovery in this study was probably due to the attribution of inorganics that were introduced in the process such as HCl and NaOH for acidity adjustment as well as elution. The percentage component of each fraction of the total DOM at each stage is tabulated in Table 4. These values were found to be well within the range of typical values found in similar studies (Aiken *et al.*, 1993, Day *et al.*, 1991, Korshin *et al.*, 1997).

**Table 4.** Percentage DOM Fractions

Plant Location	Percentage (%) of the total DOM recovered				
	Intake	Sedimentation Basin	Filter	Distribution Water	Typical Values
FB	5.46	5.31	4.93	5.22	0-22
FA	11.11	10.22	8.11	8.27	19-68
FN	16.69	19.35	19.82	21.58	0-25
PB	3.55	6.38	5.68	6.80	1.5-10
PA	44.19	49.78	55.50	49.26	8-50
PN	19.00	8.96	5.95	8.87	1-35

### 4.3 Alum Coagulation

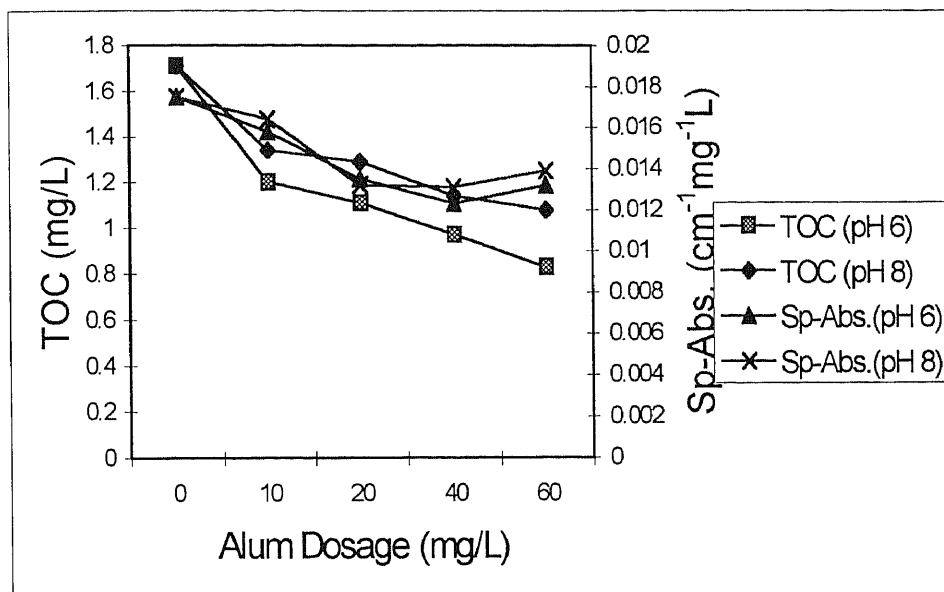
The above method of resin fractionation gives a rigorous classification of DOM into six operationally defined fractions: FA, FB, FN, PA, PB, and PN. The fractions were diluted to the various concentrations typically found in the source water. The initial pH and alkalinity of the fractions were different as the fractions were eluted differently in 0.1N HCl, 1N NaOH or 2N NaOH as described in the resin adsorption fractionation method. After pH adjustment, the coagulated samples were analyzed for TOC and UV-254.

The ratio of UVA to TOC, referred to as specific absorbance ( $\text{cm}^{-1}\text{mg}^{-1}\text{L}$ ) provides a relative index of humic content (AWWARF, 1993). Specific absorbance can suggest the nature of the DOM and its consequent THM formation potential (Krasner *et al.*, 1996). Higher specific absorbance values tend to indicate higher humic content and aromatic compounds. TOC and specific absorbance results of all jar tests are provided in Figures 3-8.

#### Hydrophilic Acid

The hydrophilic acid fraction was found to be the most predominant fraction in the source water (about 50% by weight) (Marhaba *et al.*, 1998b). The initial specific absorbance of the fraction was the lowest of all fractions. As shown in Figure 3 the gradual decrease in TOC and UVA of the sample with increasing coagulant dosage suggests a good reduction of the fraction by coagulation. This is in contrast with some other studies which have found that hydrophilic substances are not well removed by coagulation (Amy *et al.*, 1992, Croue *et al.*, 1995). Optimum removal of this fraction occurred at pH 6 and maximum coagulant

dosage examined (60 mg/L). The PA fraction also showed a reduction of specific absorbance after coagulation, which indicates removal of aromatic compounds. The higher initial concentration of the PA fraction may have resulted in the better removal of the fraction.



**Figure 3.** Coagulation of Hydrophilic Acid Fraction

### Hydrophilic Base

The optimum removal of aromatic compounds present in the hydrophilic base fraction occurred at the 10 mg/L coagulant level (for optimum removal pH 6) as indicated by specific absorbance data shown in Figure 4. Although removal of the fraction increases as coagulant level increases, specific absorbance is not reduced, indicating comparable removal of aromatic and non-aromatic compounds.

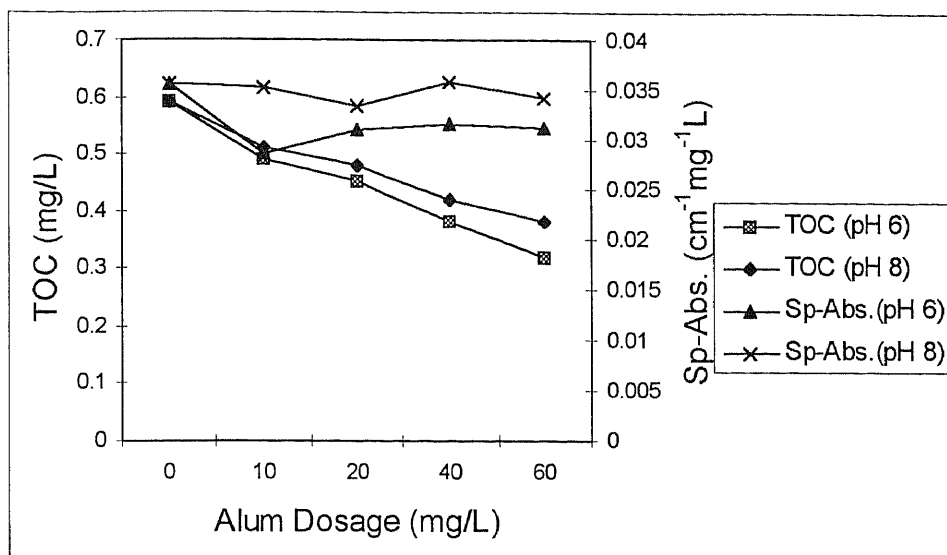
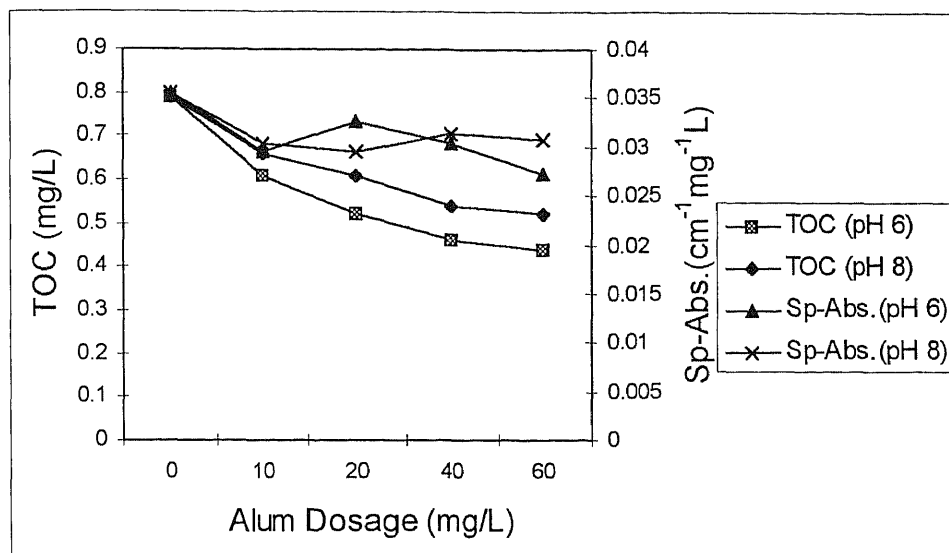


Figure 4. Coagulation of Hydrophilic Base Fraction

### Hydrophilic Neutral

The removal of the hydrophilic neutral fraction is less as compared to other fractions (44% at optimum coagulant conditions). This suggests that the PN fraction is the less reactive and it is composed of low molecular weight compounds, which are not amenable to coagulation. The PN fraction, whose content is made up of polysaccharides, is not reactive with chlorine either (Bruchet *et al.*, 1987), and hence, the formation of DBPs from this fraction is not considered to be of concern. This fraction does not show a noticeable reduction in specific absorbance after the initial reduction at coagulant dosage of 10 mg/L. (See Figure 5.)



**Figure 5.** Coagulation of Hydrophilic Neutral Fraction

### Hydrophobic Acid

The hydrophobic acid fraction, which has similar characteristics as that of humic substances, is well removed by coagulation. It should be noted that the optimum reduction occurred at approximately 40 mg/L of alum dosage for both pHs 6 and 8. The charge reversal at higher dosage resulted in the increase in both the TOC and specific absorbance of the sample as shown in Figure 6.



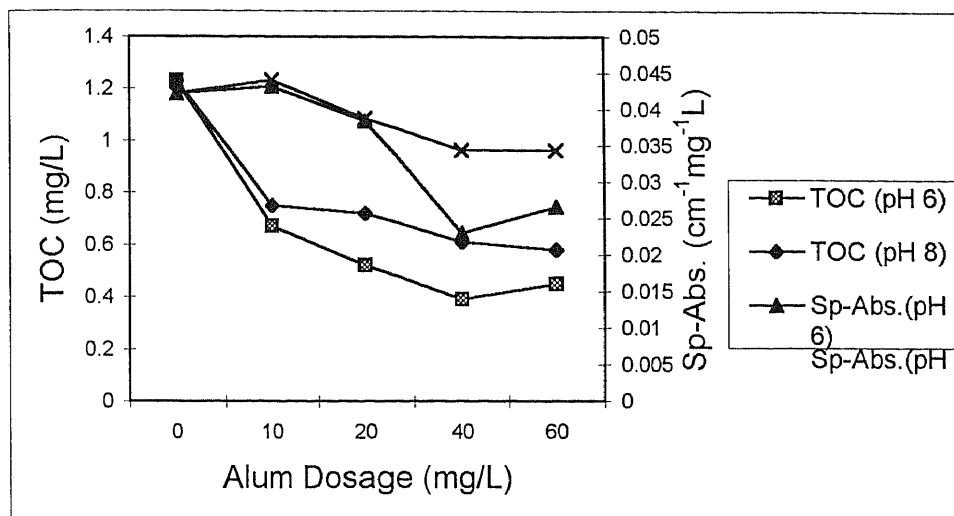


Figure 6. Coagulation of Hydrophobic Acid Fraction

### Hydrophobic Base

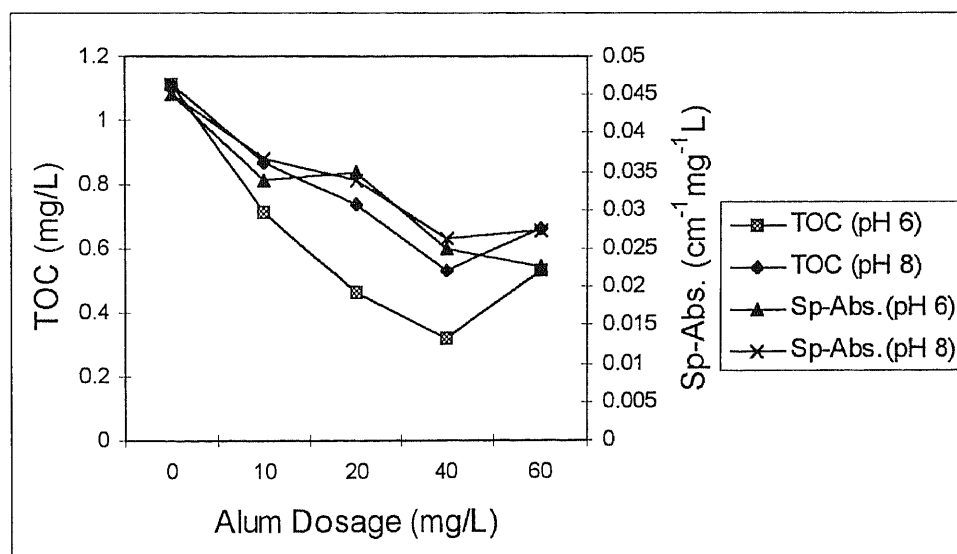
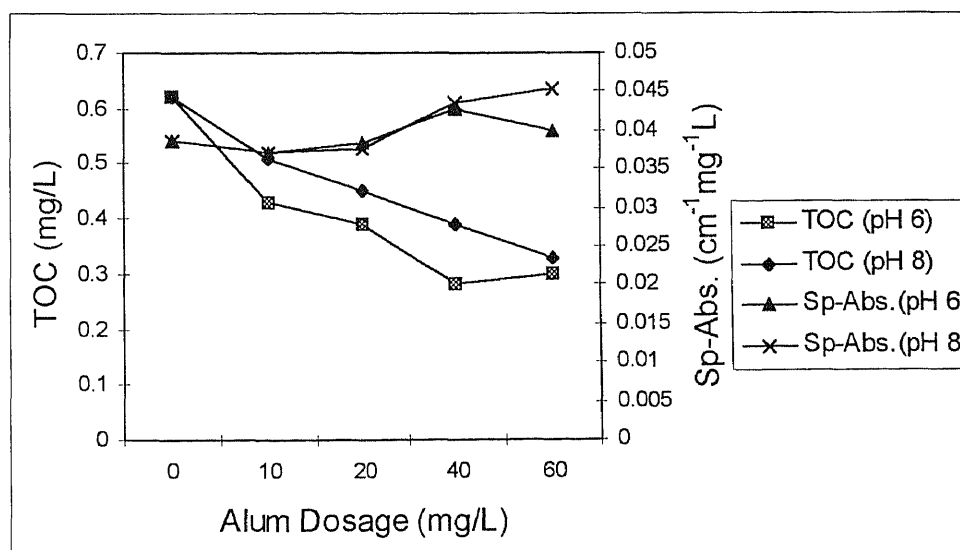


Figure 7. Coagulation of Hydrophobic Base Fraction

The hydrophobic base fraction is by far the best removed by coagulation of all the six fractions. The reduction is significant in both TOC and UVA. Figure 7 shows that the specific absorbance curve shows more reduction of UVA than TOC for this fraction. Similar to the FA fraction, this fraction exhibited charge reversal at higher alum dosages.

### Hydrophobic Neutral

The hydrophobic neutral fraction had the lowest initial TOC of all the hydrophobic fractions. This fraction contains considerable ash and is poor in carbon (Krasner and Amy, 1995). Even though there was a reduction in both TOC and UVA for the FN fraction, the specific absorbance increased (See Figure 8.), as the reduction in TOC is slightly greater than the reduction in UVA. This was the only fraction where the reduction in UVA is less than the reduction in TOC at higher coagulant dosages. This may be due to the charge reversal of mainly aromatic compounds under these conditions.



**Figure 8.** Coagulation of Hydrophobic Neutral Fraction

#### 4.4 Comparing Removal of DOM Fractions

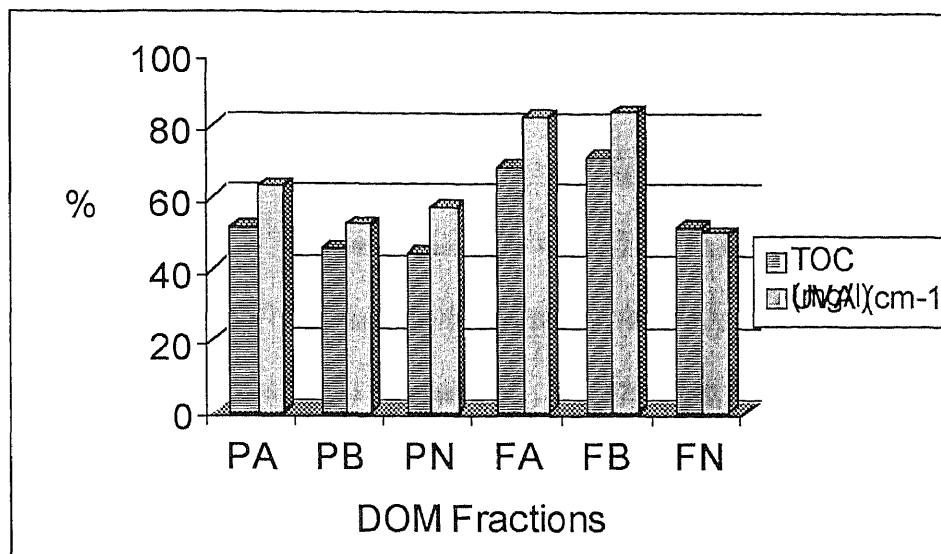
TOC and UVA reduction at optimum alum dosage for the six fractions is tabulated in Table 5. The specific absorbance percentage removal show that coagulation was more effective in removing UVA than TOC. This is in agreement with similar work done by other researchers (Tryby *et al.*, 1993; Croue *et al.*, 1995; Krasner and Amy, 1995). For all the DOM fractions, coagulation was more effective at pH 6 than pH 8 in reducing both TOC and UVA. However, the optimal occurred at different alum dosages. The reduction for the PA, PB, PN and FN fractions was maximum at 60 mg/L of alum dosage (highest dosage used), while for the FA and FB fractions the maximum reduction occurred at 40 mg/L. The effects of higher coagulant dosage were readily apparent, providing more hydrous metal for sweep coagulation. Lower pH reduces the charge density of fractions making them more absorbable. But, with very high coagulant dosage charge reversal and destabilization may occur leading to higher values of DOM surrogates.

Other researchers have reported preferential removal of humic substances over non-humic substances by coagulation (Hubel and Edzwald, 1997; Kavanaugh, 1978). In contrast, good removal of the PA fraction was found which, though operationally defined, is similar to nonhumics. The concentration of PA fraction after the resin adsorption fractionation was also found to substantially more than other fractions in the source water.

**Table 5.** Optimal Removal of DOM Fractions

	Optimum Coagulant Dosage		Pre Coagulation			Post Coagulation			Percentage Removal	
	pH	Alum Dosage (mg/L)	TOC (ppm)	UVA (cm <sup>-1</sup> )	Sp.Abs. (mg <sup>-1</sup> cm <sup>-1</sup> L)	TOC (ppm)	UVA (cm <sup>-1</sup> )	Sp.Abs. (mg <sup>-1</sup> cm <sup>-1</sup> L)	TOC	UVA
PA	6.0	60	1.71	0.030	0.0175	0.83	0.011	0.0132	51.4	63.33
PB	6.0	60	0.59	0.021	0.0356	0.32	0.010	0.0313	45.76	52.38
PN	6.0	60	0.79	0.028	0.0345	0.44	0.012	0.0273	44.30	57.14
FA	6.0	40	1.23	0.052	0.0422	0.39	0.009	0.023	68.29	82.69
FB	6.0	40	1.11	0.050	0.045	0.32	0.008	0.025	71.17	84.0
FN	6.0	60	0.62	0.024	0.0387	0.30	0.012	0.04	51.6	50.0

The percentage removals of the DOM fractions in terms of reduction in TOC and UVA at optimum coagulant dosages vary as shown in Figure 9. The hydrophobic acid and hydrophobic base fractions are more amenable to coagulation and show the highest reduction in both TOC and UVA. It is interesting to note that both the FA and FB fractions have higher values of UVA than other fractions indicating removal of UV absorbing aromatic compounds. The PB and PN fractions on the other hand, are comparatively less amenable to coagulation and show less reduction in TOC and UVA.



**Figure 9.**Percentage Removal of DOM Fractions.

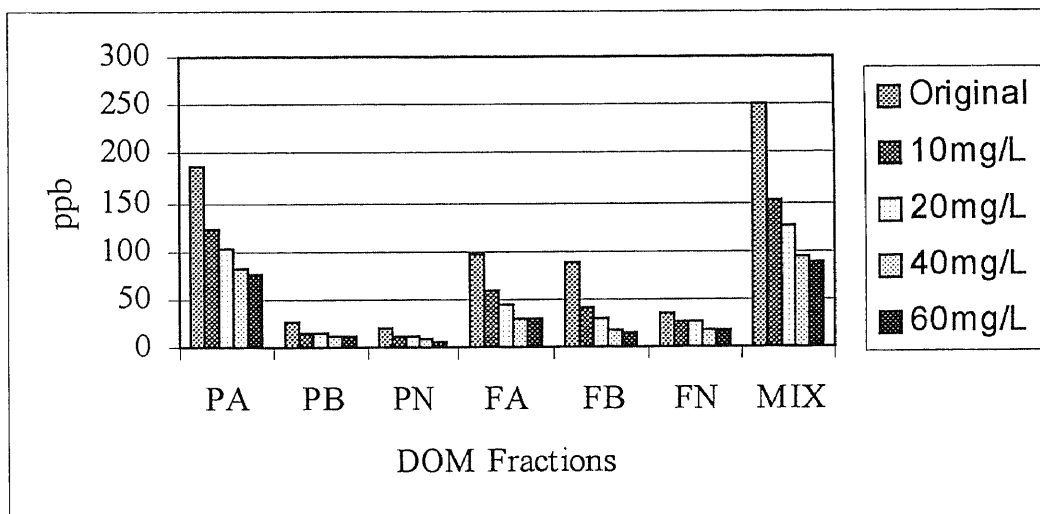
#### 4.5 DBP Formation Potential

The removal of DOM fractions is analyzed by using TOC and UVA as surrogate indicator methods. There is a need to correlate the removal of precursors to DBPs using these surrogate methods. Based on the used fraction concentration which are typical of source waters (see Table 5), the THM formation potential (TTHMFP) of the fractions before and after coagulation are shown in Figures 10-12. HANs formation potential was also measured and the results are listed in Appendix 1. The USEPA has not yet proposed MCLs for HANs. The results indicated that with increase in alum dosage there was a reduction in THM formation potential irrespective of the initial pH of the sample. But similar to DOM surrogates such as TOC and UVA the reduction was greater at lower pH values.

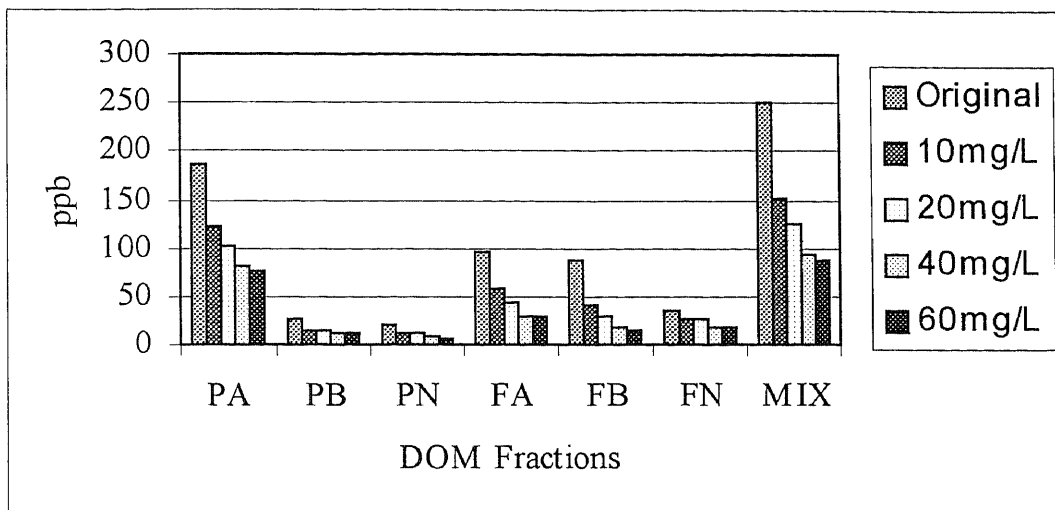
The TTHMFP showed a significant reduction (average, about 40%) at alum dosage of 10mg/L for all the fractions. However, with increase in alum dosage, the incremental decrease in TTHMFP was not as significant, as indicated by the asymptotic nature of the graphs in Figures 10-12. The PA fraction had the highest TTHM formation potential of all the fractions. The PA and PB fractions, which have the least TTHMFP, are also less amenable to coagulation. The mixture of the fractions in proportions typically found in natural water was also analyzed to study the formation of DBPs.

The six DOM fractions showed the THM formation potential in the following order:

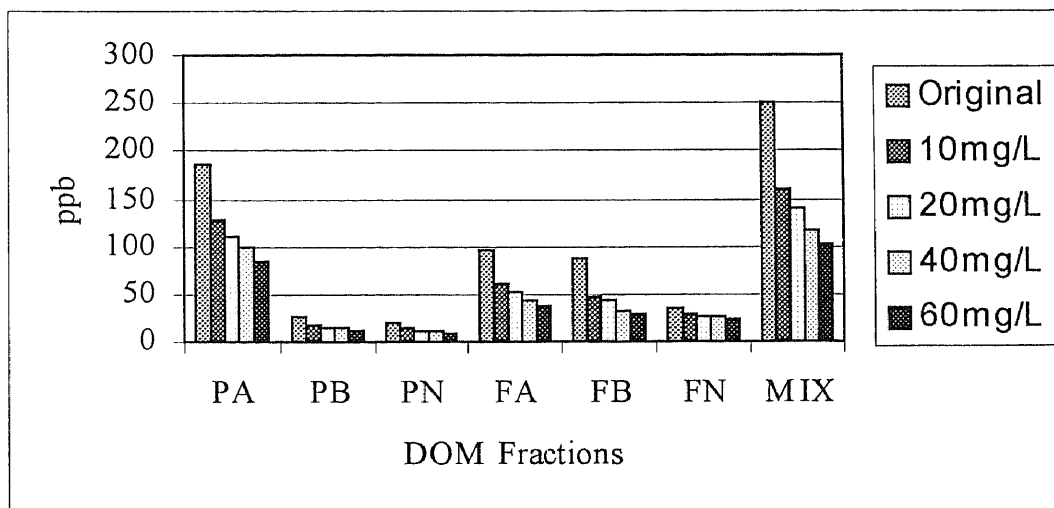
PA > FA > FB > FN > PB > PN.



**Figure 10.** THM Formation Potential of DOM Fractions at pH 6



**Figure 11.** THM Formation Potential of DOM Fractions at pH 7



**Figure 12.** TTHM Formation Potential at pH 8

## CHAPTER 5

### SUMMARY AND CONCLUSIONS

#### 5.1 Overview

The results obtained from this study gives an insight into the nature of NOM and the characteristics of DOM fractions. These results can be utilized for further studies to target problematic compounds like precursors to DBP formation and also for modification of water treatment plant processes. However, it should be noted that the results obtained are subject to seasonal and climatic variations.

#### 5.2 Effectiveness of Resin Adsorption Fractionation Method

Though the resin adsorption fractionation method adopted in this study is time consuming, it gives a rigorous classification of DOM into operationally defined factors.

- At all the four sampling locations the loss of samples due to the used resins was minimal. The recovery of samples was 110-115% obtained at the four sampling stages.
- The hydrophilic acid fraction is most predominant (about 50%) and the good recovery of this fraction coupled with the recovery of other fractions, justifies the modifications proposed in the resin fractionation method used.



### 5.3 Regions of Removal of DOM Fractions

The broader characterization of DOM by resin-fractionation to obtain six fractions has made it possible to evaluate the removal of the suspected problematic fractions (e.g. PA, FN, FA) by jar-test alum coagulation. The following statements are based on the source water fractions under the experimental conditions examined in this study.

- The optimum reduction of all the six fractions occurred at the lower pH 6 value but the coagulant dosages required for optimum reduction were different for each fraction.
- The FA and FB fractions had greater than 70% TOC removals at optimum coagulation (pH 6, alum dosage = 40 mg/L). However, the removal of the PA and FN fractions, which contribute significantly towards THMs and HAAs formation, were equally important, with greater than 50% TOC removals at optimal conditions (pH 6, alum dosage = 60 mg/L). The PB and PN fractions had noticeable removals (45% removals at the same optimal conditions) in contrast to what others have reported on the low removals of hydrophilic substances.
- Except for the FN fraction, the UVA was preferentially removed by coagulation. For FN, the specific absorbance indicated the presence of humic content thought to be associated with high DBP formation potential.
- The reduction in specific absorbance with increase in coagulant dosage indicated more reduction in the UVA than in TOC. Thus, TOC is a more conservative surrogate for measuring DOM removal.
- It was apparent that coagulation was quite versatile in removing various DOM fractions. However, the difference between equivalent weights or charge densities

between these fractions resulted in different optimum coagulant requirements.

- As DOM is site-specific and the concentration of fractions vary with different natural waters, specific problematic DOM fractions may be targeted for their selective removal by coagulation.

#### **5.4 DBP Formation Potential**

- TTHMs were the predominant DBPs and HANs produced were significantly lower for all the fractions as well as the mixture.
- The PA fraction had the highest TTHMFP (185 ppb). The PA and PB fractions had the lowest TTHMFP (20-25 ppb).
- Though the PA and PB fractions have low TTHMFP, source waters containing predominantly hydrophilic substances may not meet TTHMs MCLs by alum coagulation alone, as they are not well removed by alum coagulation.
- The typical mixture used in this study had an initial TTHMFP of 250 ppb. With enhanced coagulation (alum dosage = 60 mg/L) and at lower pH values (pH 6), the given samples meet the Stage 1 MCL of the D/DBP Rule for TTHMs. The TTHMFP is reduced to 87 ppb under these conditions. However, even enhanced coagulation may not be able to meet the Stage 2 MCLs of 60 ppb for THMs. It should also be noted that the results obtained in this study are not average values for TTHMs, as required by the D/DBP Rule.
- Other treatment methods (i.e. using polymers, other coagulants, GAC, ozonation etc.) may be combined with alum coagulation to provide optimal removals of DBP precursors.

## CHAPTER 6

### RECOMMENDATIONS FOR FUTURE RESEARCH

#### 6.1 General

The work presented in this thesis is a part of a larger ongoing project of investigating the nature and removal of NOM fractions. This preliminary work should be considered as a basis for future research. The observations and conclusions reached in the analysis of data need to be confirmed through additional tests. Most of the work reported herein included relatively low-TOC source waters. The applicability of the results and conclusions to higher-TOC sources remains to be demonstrated.

#### 6.2 Applicability to Different Mixtures

The most significant research needed is an investigation into disinfection by-products formation potential of different mixtures and their removal by enhanced coagulation. Though typical concentrations of the six fractions found in source waters were used in the present study, the source water TOC varies from a low of 2 mg/L to as high as 150 mg/L for some source waters (Day *et al.*, 1991). An analysis of a blend of different source waters can provide an insight into the removal of site-specific NOM.

The PA fraction was found to be predominant in the source waters investigated and this fraction also contributed significantly to DBPFM. There is a need to investigate the DBPFP of the PA fraction from different source waters with lower PA content. Similar investigation is needed for concentrations of various DOM fractions

## 6.2 Coagulation Modifications and Other Treatment Options

The results obtained show that source waters with fraction concentrations similar to those investigated in this study may not meet the stringent requirements of Stage 2 of the D/DBP Rule. The use of a range of pH and coagulant dosage in this study has shown that precursors to DBPFP are better removed at lower pH and higher alum dosage. This observation would lead to believe that a substantial reduction of THM formation could be achieved by maintaining a low pH during chlorination and then raising the pH once free residual chlorine is no longer present. However, research by Trussell and Umphers (1978) showed that THM formation could also occur in the absence of chlorine residual once the pH raised. Also, increased alum dosages translate directly into higher sludge production, hence, existing sludge removal and sludge dewatering systems may be undersized. The chemical storage and feed facilities may not be adequate for enhanced coagulation.

With these limitations of alum as a coagulant, other coagulants such as ferric chloride and various polymers need to be investigated for the removal of the six DOM fractions. In addition, the issue of the efficiency of membranes and ozone for removal of lower molecular weight fractions such as PB and PN fractions, which are not amenable to coagulation by alum needs to be addressed. These methods can be combined with enhanced coagulation by alum in order to meet proposed regulations for DBPs.

## APPENDIX A

### RESULTS OF DOM FRACTIONS

**Table A1.** Hydrophilic Acid Fraction

Sample No.	Designation	pH	Alum Dosage mg/L	TOC mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb	HANs ppb
1	PAOrig		0	1.71	0.030	0.0175	185.69	23.45
2	PA610	6	10	1.20	0.019	0.0158	121.44	16.67
3	PA620	6	20	1.11	0.015	0.0135	101.32	14.32
4	PA640	6	40	0.97	0.012	0.0124	82.74	12.27
5	PA660	6	60	0.83	0.011	0.0132	74.89	10.91
6	PA710	7	10	1.28	0.019	0.0148	124.21	15.43
7	PA720	7	20	1.20	0.015	0.0125	99.33	14.28
8	PA740	7	40	1.05	0.012	0.0114	84.19	12.82
9	PA760	7	60	0.96	0.010	0.0104	80.34	11.56
10	PA810	8	10	1.34	0.022	0.0164	126.81	16.79
11	PA820	8	20	1.29	0.017	0.0132	110.43	15.21
12	PA840	8	40	1.14	0.015	0.0131	99.56	13.45
13	PA860	8	60	1.08	0.015	0.0139	85.28	12.01

**Table A2.** Hydrophilic Base Fraction

Sample No.	Designation	pH	Alum Dosage mg/L	TOC Mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb	HANs ppb
1	PBOri		0	0.59	0.021	0.0356	25.91	3.41
2	PB610	6	10	0.49	0.014	0.0286	15.66	2.54
3	PB620	6	20	0.45	0.014	0.0311	13.43	2.23
4	PB640	6	40	0.38	0.012	0.0316	12.48	2.01
5	PB660	6	60	0.32	0.010	0.0313	10.54	1.46
6	PB710	7	10	0.51	0.019	0.0373	15.47	2.65
7	PB720	7	20	0.47	0.016	0.0340	13.86	2.43
8	PB740	7	40	0.40	0.013	0.0325	12.21	2.22
9	PB760	7	60	0.38	0.013	0.0342	11.85	2.05
10	PB810	8	10	0.51	0.018	0.0353	17.58	2.77
11	PB820	8	20	0.48	0.016	0.0333	15.69	2.37
12	PB840	8	40	0.42	0.015	0.0357	13.35	2.29
13	PB860	8	60	0.38	0.013	0.0342	11.59	2.11

**Table A3.** Hydrophilic Neutral Fraction

Sample No.	Designation	pH	Alum Dosage mg/L	TOC Mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb	HANs ppb
1	PNOrig		0	0.79	0.028	0.0354	20.21	3.52
2	PN610	6	10	0.61	0.018	0.0295	12.84	2.62
3	PN620	6	20	0.52	0.017	0.0326	10.67	2.26
4	PN640	6	40	0.46	0.014	0.0304	8.11	2.34
5	PN660	6	60	0.44	0.012	0.0273	5.78	2.28
6	PN710	7	10	0.63	0.020	0.0317	13.97	2.79
7	PN720	7	20	0.53	0.017	0.0321	11.74	2.53
8	PN740	7	40	0.49	0.017	0.0347	11.24	2.41
9	PN760	7	60	0.47	0.015	0.0319	10.12	2.35
10	PN810	8	10	0.66	0.020	0.0303	14.73	2.81
11	PN820	8	20	0.61	0.018	0.0295	11.91	2.64
12	PN840	8	40	0.54	0.017	0.0314	10.23	2.52
13	PN860	8	60	0.52	0.016	0.0307	9.13	2.53

**Table A4.** Hydrophobic Acid Fraction

Sample No.	Designation	pH	Alum Dosage mg/L	TOC mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb	HANs ppb
1	FAOrig		0	1.23	0.052	0.0422	95.46	36.43
2	FA610	6	10	0.67	0.029	0.0432	57.28	21.21
3	FA620	6	20	0.52	0.020	0.0384	42.46	15.32
4	FA640	6	40	0.39	0.009	0.0230	28.44	13.72
5	FA660	6	60	0.45	0.012	0.0266	28.12	14.34
6	FA710	7	10	0.70	0.030	0.0429	59.71	23.10
7	FA720	7	20	0.59	0.023	0.0390	48.23	19.29
8	FA740	7	40	0.49	0.017	0.0347	40.09	16.44
9	FA760	7	60	0.49	0.016	0.0327	38.87	17.21
10	FA810	8	10	0.75	0.033	0.0440	60.22	23.89
11	FA820	8	20	0.72	0.028	0.0388	51.66	19.97
12	FA840	8	40	0.61	0.021	0.0344	44.59	15.21
13	FA860	8	60	0.58	0.020	0.0344	38.81	

**Table A5. Hydrophobic Base Fraction**

Sample No.	Designation	pH	Alum Dosage mg/L	TOC mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb	HANs ppb
1	FBOri		0	1.11	0.050	0.0450	86.19	14.39
2	FB610	6	10	0.71	0.024	0.0338	40.46	6.21
3	FB620	6	20	0.46	0.016	0.0348	29.23	3.23
4	FB640	6	40	0.32	0.008	0.0250	18.54	4.07
5	FB660	6	60	0.53	0.012	0.0226	15.37	4.91
6	FB710	7	10	0.77	0.025	0.0325	45.77	9.37
7	FB720	7	20	0.57	0.018	0.0316	38.51	5.23
8	FB740	7	40	0.40	0.012	0.0300	25.23	5.11
9	FB760	7	60	0.47	0.013	0.0277	21.43	6.12
10	FB810	8	10	0.87	0.032	0.0368	46.51	8.43
11	FB820	8	20	0.74	0.025	0.0338	44.23	4.23
12	FB840	8	40	0.53	0.014	0.0264	31.09	4.85
13	FB860	8	60	0.66	0.018	0.0273	29.60	4.66

**Table A6. Hydrophobic Neutral Fraction**

Sample No.	Designation	pH	Alum Dosage mg/L	TOC mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb	HANs ppb
1	FNOri		0	0.62	0.024	0.0387	34.58	2.54
2	FN610	6	10	0.43	0.016	0.0372	27.33	1.69
3	FN620	6	20	0.39	0.015	0.0384	25.67	1.34
4	FN640	6	40	0.28	0.012	0.0428	18.44	1.23
5	FN660	6	60	0.30	0.012	0.0400	17.10	1.56
6	FN710	7	10	0.46	0.019	0.0413	28.41	1.87
7	FN720	7	20	0.40	0.017	0.0425	25.97	1.58
8	FN740	7	40	0.38	0.017	0.0447	25.21	1.34
9	FN760	7	60	0.33	0.016	0.0485	21.68	1.11
10	FN810	8	10	0.51	0.019	0.0372	28.83	1.75
11	FN820	8	20	0.45	0.017	0.0377	26.51	1.29
12	FN840	8	40	0.39	0.017	0.0435	25.91	1.34
13	FN860	8	60	0.33	0.015	0.0454	22.12	1.33

**Table A7. Mixture**

Sample No.	Designation	pH	Alum Dosage mg/L	TOC mg/L	UVA cm <sup>-1</sup>	Sp.Abs. L/cm.mg	TTHMs ppb
1	PAOrig		0	4.56	0.151	0.0331	249.45
2	PA610	6	10	2.98	0.088	0.0295	151.11
3	PA620	6	20	2.59	0.077	0.0297	123.97
4	PA640	6	40	2.12	0.057	0.0269	92.34
5	PA660	6	60	2.11	0.052	0.0246	87.12
6	PA710	7	10	3.24	0.100	0.0308	158.53
7	PA720	7	20	2.79	0.085	0.0305	139.29
8	PA740	7	40	2.31	0.071	0.0307	107.22
9	PA760	7	60	2.28	0.062	0.0272	94.67
10	PA810	8	10	3.42	0.108	0.0316	161.02
11	PA820	8	20	2.92	0.093	0.0318	139.20
12	PA840	8	40	2.67	0.082	0.0307	115.77
13	PA860	8	60	2.49	0.073	0.0293	102.51



## APPENDIX B

### ABBREVIATIONS

BAT	Best Available Technology
DBPs	Disinfection Byproducts
DOM	Dissolved Organic Matter
FA	Hydrophobic Acid
FB	Hydrophobic Base
FN	Hydrophobic Neutral
HAAs	Haloacetic Acids
ICR	Information Collection Rule
MCL	Maximum Contamination Level
MW	Molecular Weight
NOM	Natural Organic Matter
PA	Hydrophilic Acid
PB	Hydrophilic Base
PN	Hydrophilic Neutral
TOC	Total Organic Carbon
THMFP	Trihalomethanes Formation Potential
TTHMs	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UVA	Ultraviolet Absorbance

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