

**The Characterization of Dissolved Organic Material  
in Natural Waters and the Phase-Change Behavior of  
Organic Matter During Chemical Coagulation**

by

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Thesis submitted to the Graduate Faculty of the  
Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the

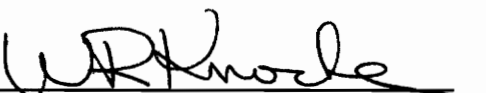
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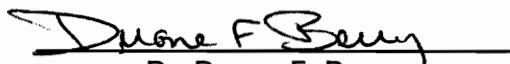
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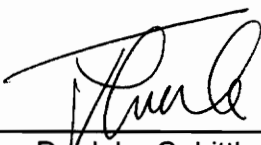
IN

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August, 1997

Key words: alum, coagulation, DOC, fractionation, ultrafiltration

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**THE CHARACTERIZATION OF DISSOLVED ORGANIC MATERIAL  
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ORGANIC MATTER DURING CHEMICAL COAGULATION**

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**(ABSTRACT)**

Research efforts pertaining to natural organic material (NOM) have focused primarily on the dissolved portion of NOM since it is the most prevalent fraction. Numerous procedures have been developed to separate dissolved organic material (DOM) into fractions but methods were not fully refined in the areas of quantitative analysis, DOM recovery, and DOM isolation.

This research chemically and physically characterized DOM using synthetic resin adsorption and ultrafiltration, respectively. A 0.45  $\mu\text{m}$  filter separated the NOM into particulate and nonparticulate fractions prior to characterization. The DOM of two natural waters were fractionated into six separate organic fractions (hydrophobic bases, acids, neutrals and hydrophilic bases, acids, neutrals). Apparent molecular weight distributions were performed on the two natural waters and six organic fractions via ultrafiltration. The effects of pH on coagulation removal efficiency were investigated on four of the organic fractions (acidic and neutral). A procedure was developed to investigate the synergistic/antagonistic effects of the hydrophobic acid fraction and the

hydrophobic neutral fraction on each other during coagulation. Ultrafilters (30K and 100K nominal molecular weight cutoff) were utilized to analyze the phase-change behavior of DOM during coagulation.

Results indicated the coagulation pH affected the removal of the organic acidic fractions but not the neutral fractions. A further study showed poorer removal of the hydrophobic neutral fraction resulting from the greater presence of the hydrophobic acid fraction in a solution composed of the two fractions and vice versa. At less than enhanced doses of both alum and ferric chloride there existed the presence of colloidal metal bound organic material. This colloidal fraction can be effectively removed by the addition of a nonionic polymer, providing a cost effective alternative to the higher coagulant doses often required to achieve enhanced coagulation of surface waters.

## **ACKNOWLEDGMENTS**

The author of this thesis would like to thank the Virginia Water Resources Research Center and the Via Department of Civil Engineering for the partial funding of this research. He thanks Dr. W. R. Knocke, his advisor, for his guidance, support, knowledge, and humor. He also would like to thank his advisory committee members, Dr. Duane F. Berry and Dr. John C. Little. He thanks Julie Petruska for lab tips and directing the author to the location of necessary lab equipment. Marilyn Grender also receives thanks for repairing analytical equipment and performing numerous analytical procedures. He especially thanks Chris Tadanier for providing guidance, suggestions, support, and answers to numerous questions. The author also acknowledges his family whose love and support kept him motivated during the “tough” times. Most importantly, the author gives all glory to Jesus Christ, his Lord and Savior.

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## Chapter I

### INTRODUCTION

Natural organic material (NOM) is of interest to researchers who focus on water treatment issues since NOM influences many aspects of water treatment. The presence of NOM affects the behavior of unit processes such as coagulation and filtration. NOM also aids in the concentration and transport of inorganic and organic pollutants through a water treatment plant. The interaction of NOM and chlorine (a commonly used water disinfectant) often forms carcinogenic disinfection by-products (DBPs) including trihalomethanes, haloacetic acids, and other organohalides. For this reason, the Environmental Protection Agency (EPA) established a maximum contaminant level of 0.10 mg/L for trihalomethanes in 1978. These disinfection by-products are the primary reason much interest and research is focused on the removal of NOM.

NOM consists of particulate organic carbon (POC) and dissolved organic carbon (DOC) of which DOC is the most prevalent and difficult to remove. DOC has been traditionally removed through the physical/chemical process of coagulation using a common chemical coagulant such as aluminum sulfate (alum) or ferric chloride. Unfortunately, conventional coagulation has failed in many cases to remove sufficient DOC in order to comply with existing DBPs regulations. Also, the mechanisms of coagulation and the chemistry of DOC are not completely understood. A better understanding of the chemistry, molecular size, and nature of DOC is necessary to develop new processes and technologies to better remove DOC. Numerous physical and chemical separation methods have been developed to characterize DOC; however,

very few studies have both investigated the nature of DOC and the response to coagulation of the separated organic fractions to changes in solution pH

During coagulation, metal hydroxide monomers and polymers interact with NOM to destabilize and remove the organic material. Most NOM proceeds from a dissolved state to a solid/particulate state and then is removed through solid/liquid separative processes. As mentioned previously, a better understanding of coagulation mechanisms (specifically the phase-change behavior of organic material) is needed.

The specific objectives of this research were:

1. To characterize the dissolved organic material in two natural waters with respect to certain chemical and physical parameters;
2. To investigate the effect of pH on the ability of chemical coagulants to remove various organic fractions from solution;
3. To investigate the synergistic or antagonistic effect of the concentration of one organic fraction in relation to another during coagulation;
4. To evaluate the phase-change behavior of organic material in terms of DOC removed by various chemical coagulants.

The overall goal of this research effort was to generate added knowledge that would allow water treatment engineers and utility operators to more efficiently and economically remove DOC through chemical coagulation.

## **Chapter II**

### **LITERATURE REVIEW**

This chapter addresses the following topics:

1. Natural Organic Material
2. Disinfection By-Products
3. Isolation and Characterization of Natural Organic Material
4. Removal of Natural Organic Material by Coagulation

#### **Natural Organic Material**

##### **Terminology and Definitions**

Natural organic material (NOM) describes the complete spectrum of organic material in natural waters and is the result of the biological degradation of plant and animal remains, plant and animal residues, and byproducts of microorganisms (Schnitzer, 1978). The genesis of NOM can be either aquatic or terrestrial. Aquatic organic material (AOM) originates in the hydrosphere (e.g. decay of aquatic plant life) and is termed autochthonous. Soil organic material (SOM) originates in the lithosphere (e.g. decay of fallen leaves) and is termed allochthonous. SOM can enter the aquatic realm through a variety of pathways such as runoff and seepage. The contribution of AOM and SOM to the NOM of a water body depends on climate, geography and topography.

Classification of NOM into further subdivisions is necessary in order to gain a better understanding of NOM as a whole. Although a general consensus exists on the

definition of NOM, definitions regarding subgroups of NOM are varied. Thurman (1985) further divided natural organic matter into particulate organic matter (POM), colloidal organic matter (COM), and dissolved organic matter (DOM). These are operational definitions as POM, COM, and DOM are typically separated via filtration. POM is the organic material retained on a 0.45  $\mu\text{m}$  silver or glass-fiber filter while COM is the organic material between 0.45  $\mu\text{m}$  to 1 nm. Thurman chose a 0.45  $\mu\text{m}$  filter since it will also filter out all fungi and most bacteria. The presence of fungi and bacteria in DOM will result in degradation of the DOM. Organic material less than 1 nm is termed DOM.

Through an extensive survey of waters, Thurman (1985) found that COM constitutes less than 10% of the organic matter in most natural waters although it is an important fraction in marsh and swamp waters. Due to the difficulty of filtering large amounts of water through a 1 nm filter, Thurman's definition of COM will not be used in the current study. Instead, for research reporting purposes, NOM was defined to consist of POM (organic material greater than 0.45  $\mu\text{m}$ ) and DOM (organic material less than 0.45  $\mu\text{m}$ ). Unfortunately, organic material is difficult to measure and quantify. However, organic carbon is relatively easy to measure.

The terms total organic carbon (TOC), particulate organic carbon (POC), and dissolved organic carbon (DOC) pertain to a measurement technique to quantify the amount of organic material in a water. TOC, POC, and DOC are determined by oxidizing organic material (either thermally or chemically) to carbon dioxide and measuring the resulting amount of carbon dioxide via infrared spectrometry. Typically, the terms NOM/TOC, POM/POC, and DOM/DOC are used interchangeably. Technically, however, the terms are different with NOM, POM, and DOM pertaining to



the entire molecule thereby including elements such as hydrogen and oxygen while TOC, POC, and DOC refer to the amount of measurable organic carbon. A general approximation is that NOM, POM, and DOM are two times the amount of TOC, POC, and DOC (Thurman, 1985). From this point forward, both terms will be used interchangeably. The amount of POC in natural waters can range from less than 10% of the TOC for lakes and small streams to 50% of the TOC for large rivers (Thurman, 1985).

DOC is of particular interest to researchers since it is dissolved and is the most reactive fraction chemically. Thurman (1985) found rivers and lakes to have a DOC range from 2 to 10 mg/L while swamps and bogs have a DOC range from 10 to 60 mg/L. These ranges are general as Bellamy (1992) found the DOC of the Dismal Swamp to be over 100 mg/L.

Many methodologies have been developed to further fractionate DOC resulting in numerous operational definitions. The first method developed to fractionate DOC in natural waters resulted from a method to fractionate soil organic material (Schnitzer, 1972). This classical method of fractionation relies on the solubility of SOM in aqueous solutions at varying pHs. Organic material soluble at pH 12 is termed humic material while the organic material insoluble at pH 12 is termed humin. Humic material consists of two more fractions, again based of solubility. Humic material soluble at pH 2 is termed fulvic acid while humic material insoluble at pH 2 is termed humic acid. While these definitions are concrete, acquiring large amounts of these fractions for study through this method is time consuming, costly, inefficient, and labor intensive. In the past 20 years, many fractionation procedures have been developed to better isolate and

concentrate dissolved organic material for study. A separate section of this chapter discusses other methodologies for fractionating and concentrating DOC. An important point to remember is that the nature of the organic material in any DOC fraction highly depends on the fractionation procedure.

### **Disinfection By-Products**

NOM is of most interest to researchers in water treatment since NOM influences many aspects of water treatment. First, the presence of NOM affects the behavior of unit processes such as coagulation and filtration. For example, high NOM levels can increase the frequency of backwash cycles in filter beds. Second, NOM can aid in the concentration and transport of inorganic and organic pollutants through a treatment plant. Pathogens can effectively “hide” behind or within NOM and pass through disinfection. Third, NOM reacting with chlorine (a common disinfectant) has been shown to be a precursor to carcinogenic disinfection by-products (DBPs). These disinfection by-products are the primary reason so much interest and research is focused on NOM, particularly DOC.

In the mid-1970s, researchers discovered the presence of organohalides in finished drinking water (Bellar et al., 1974). These organohalides included compounds such as chloroform, bromodichloromethane, and dibromochloromethane. Along with bromoform, these compounds were named trihalomethanes (THMs). In 1976, the National Cancer Institute stated that under laboratory conditions, chloroform causes cancer in rats and mice (Cotruvo and Wu, 1978). For this reason, the EPA established a maximum contaminant level of 0.10 mg/L for THMs. Later research confirmed the presence of other organohalides such as haloacetic acids. Although the levels of

organohalides in treated drinking water are not acutely toxic to humans, the effects of chronic exposure are unknown.

The origin of organohalides continued to puzzle researchers as little or no evidence of organohalides were discovered in untreated water. Researchers therefore concluded that the formation of the organohalides occurred somewhere in the water treatment process. The most notable presence of organohalides was that of chloroform and other THMs. Since chloroform contains chlorine, it was presumed that the chlorination of water supplies led to the formation of organohalides. Further research proved the presumption correct (Rook, 1974).

Two surveys conducted in the mid-1970s (the National Organics Reconnaissance Survey for Halogenated Organics (Symons et al., 1975) and the National Organics Monitoring Survey (Cotruvo and Wu, 1978)) verified Rook's findings and also pointed to the widespread occurrence of THMs in treated drinking water. Later, researchers discovered the presence of mutagenic activity in chlorinated drinking water. For example, Kringstad et al. (1983) identified mutagens 1,3 dichloroacetone and 2-chloropropenal when chlorinating humic acids in a laboratory. Coleman et al. (1984) also identified other halogenated organic compounds with known mutagenic activity by chlorinating humic acids. The formation of DBPs occurs according to the following equation:



Although the general equation concerning the formation of DBPs is known, the direct pathways of DBPs formation are for the most part unknown. Also, the presence of THMs represents only 20% of the total organohalides found in chlorinated drinking

water (Reckhow and Singer, 1984). An additional problem is that other than chloroform most organohalide compounds exist in extremely trace amounts. Further research is required to identify specific organohalide compounds.

Controlling the formation of DBPs presents three possibilities. As illustrated on the previous page, DBPs are formed when chlorine reacts with organic material. In order to meet regulations, formed DBPs may be removed. Activated carbon, especially granular activated carbon (GAC) beds, have been shown to be successful in removing DBPs. Unfortunately, GAC beds have high capital and maintenance costs. A better option, both logically and financially, is to prevent the formation of DBPs altogether. Much research has been performed in the area of alternative disinfectants such as ozone, chlorine dioxide, chloramines, and ultraviolet light. Like chlorine, each alternative disinfectant has advantages and disadvantages ranging from cost to residual disinfecting strength. The practice of chlorination for disinfection, however, is as widespread in the United States as the prevalence of THMs. A study in 1987 revealed approximately 85% of surface water treatment plants practiced chlorination while 80% of groundwater treatment plants practiced chlorination (McGuire and Meadow, 1988).

The final option to reducing DBPs concerns the precursor material or NOM. Historically, coagulation was practiced to remove turbidity from water typically caused by clays and minerals. Enhanced coagulation refers to coagulation schemes aimed at removing DOC in addition to turbidity. By removing additional NOM, the formation of DBPs can be reduced while still maintaining chlorine levels. Due to the ubiquity of chlorination practices, current research is directed at removal of precursor NOM.

## **Isolation and Characterization of Natural Organic Material**

### **Development of Isolation Procedure Strategy**

Natural organic material is best described as an aggregation of numerous varied compounds with a vast array of physical sizes and chemical properties. In order to better understand the interaction of NOM with other organic compounds and coagulants, methods have been developed to separate NOM based on both chemical characteristics and physical size. The individual NOM fractions can then be studied independently and a better understanding of NOM as a whole will result.

The separation of POM from DOM is easily solved through filtration. POM represents a small fraction of NOM and is readily removed by coagulation and filtration. Isolating and concentrating DOC presents an interesting analytical challenge. The challenge with fractionating DOM or DOC is DOC exists in small concentrations. A typical value of DOC in surface waters suitable for drinking water treatment is less than 10 mg/L. Due to the low DOC level, separation, concentration, and identification of DOC is time consuming, difficult, and expensive.

Any fractionation procedure must not only give accurate results but it must also be practical and economical. Also, the fractionation procedure must account for all organic material. That is, if large amounts of the DOC are lost in the fractionation procedure, any further studies on the DOC will be invalid due to loss of organic material. The fractionation procedure must also have little contamination potential. If contamination of the DOC results due to the isolation procedure, the DOC fractions are worthless. Finally, the more fractions a DOC isolation procedure separates DOC into the better. The behavior of DOC can be better understood with additional fractions.

The identification of specific organic solute compounds and the complexes which form the compounds, however, is too expensive and time consuming using existing analytical procedures. No method currently exists to isolate, identify, and measure all organic solutes in the aquatic environment. The goal of current isolation procedures is to bridge the gap between DOC as a whole and specific compound identification.

As mentioned earlier, DOC was first separated into three separate fractions based on its solubility in acidic and basic solutions. Other fractionation procedures include vacuum distillation, freeze concentration, liquid extraction, carbon adsorption, ultrafiltration, charcoal, and the use of synthetic resins. Vacuum distillation occurs at low temperatures preventing changes in chemical properties due to thermal effects, but all organic solutes are concentrated requiring further extraction (Aiken, 1985). Like vacuum distillation, freeze concentration concentrates all organic solutes present (Aiken, 1985).

Liquid-liquid extraction may appear to be a suitable isolation procedure for DOC in natural waters, but several inherent limitations exist. First, liquid-liquid extraction involves the use of a nonpolar solvent like methanol to remove nonpolar DOC. Unfortunately, highly polar solutes aren't removed and these constitute a major fraction of DOC in natural waters (Leenheer and Huffman, 1976). Leenheer (1981) reported that liquid-liquid extraction isolates only approximately 10% of the organic solutes. Second, the loss of volatile organic solutes occurs during solvent removal. Third, research has shown that the partition coefficient of an organic solute between two immiscible liquids varies with solute concentration (Leenheer and Huffman, 1976). This problem is magnified at the low concentrations of organic solutes found in natural waters.

Carbon adsorption also appears to be a feasible fractionation procedure, but it also has limitations. First, research has shown desorption of organic solutes from activated carbon to be incomplete (Leenheer and Huffman, 1976). Second, adsorption of the organic solutes is also not quantifiable. Third, activated carbon has been shown to alter the chemistry of organic solutes during adsorption (Aiken *et al.*, 1979).

Table 1 summarizes the advantages and limitations of various fractionation procedures. Table 1 illustrates that no one technique is completely effective in fractionating DOC with respect to both size and chemical properties. However, an analytical procedure can be developed by combining various techniques to isolate, concentrate, and quantify DOC through chemical and physical fractionation.

### **Synthetic Resin Adsorbents**

Much research has been performed in analyzing the usefulness of synthetic resins to chemically fractionate DOC. Synthetic resins address all concerns associated with any fractionation procedure such as quantification, irreversible adsorption, elution, and chemical alteration of organic solutes. The advantages of synthetic resins to fractionate DOC are numerous.

- 1) Fractionation procedures are relatively simple. Columns are packed with resin and water samples pass through the resin either by gravity flow or pumps. After the sample has passed through the resin, the organic material is eluted from the resin by either application of an acid, base, or solvent.
- 2) Resins not only fractionate the DOC but concentrate it. Elution procedures remove organic solutes in much less volume than the water

Table 1. Advantages and limitations of various isolation procedures for humic substances.

Method	Advantages	Disadvantages
Precipitation	None.	Fractionates sample, not specific for humus, slow on large volumes.
Freeze concentration	All DOC concentrated.	Slow, tedious procedure, concentrates inorganics.
Liquid extraction	Visual color removal.	Not quantified by DOC, slow for large volumes.
Ultrafiltration	Also separates by molecular weight.	Slow.
Strong anion-exchange	Efficient sorption.	Does not desorb completely.
Charcoal	Efficient sorption	Does not desorb completely.
Weak anion-exchange	Adsorbs and desorbs efficiently.	Resin may physically break down indicated by an increase in DOC.
XAD resin	Adsorbs and desorbs efficiently.	Resin must be cleaned to minimize physical break down.

from Thurman (1985)



sample passed through the column making storage of the fractions less space consuming. Also, diluting the fractions for further study can be easily accomplished from the concentrated organic fractions.

- 3) Resin fractionation can process large volumes of water due to the large surface areas and the resulting high adsorptive capacities of the resin.
- 4) Resin fractionation is ideally suited for the low levels of solute concentration typically encountered in natural waters.
- 5) Unlike activated carbon, synthetic resins are easy to regenerate through simple application of either acid or base.
- 6) Resin absorbents give reproducible results. One can be sure that alteration of the chemistry of synthetic resin matrix does not occur over time.
- 7) The use of synthetic resins is a low energy process. As natural waters pass through resin columns, no phase change occurs as the organic solutes adsorb to the resin. The solute is still in an aqueous environment and less energy is involved since the solute did not have to cross a liquid-liquid interface to adsorb to the resin.
- 8) The low temperature and high vapor pressure that exist in resin columns (samples are passed through the resin columns at room temperature) minimizes the loss of volatile solutes.
- 9) A wide variety of resins are available making adsorption selective. Depending on the chemistry and polymerization technique, selective

adsorption of organic solutes will take place. The polymerization techniques will effect the pore size and surface area of the resin.

### **Nonionic Resins**

In 1972, Simpson (1972) advocated the use of macroreticular nonionic polymeric adsorbents (XAD resins) to separate organic chemicals from water. These macroreticular adsorbents or resins are characterized by having very large surface areas. The advantages of macroreticular nonionic resins became immediately apparent. Prior to the introduction of nonionic resins, researchers had used ion-exchange resins. Ion-exchange resins remove hydrophilic compounds, leaving most hydrophobic substances behind in the water sample unconcentrated. Hydrophobic substances are typically 50% of the DOC in an average water sample while 75-90% for swamps (Thurman, 1985). Also, humic substances adsorbed to ion-exchange resins are more difficult to elute (Thurman, 1985). Immediately researchers began investigating the performance of nonionic resins to fractionate DOC in natural waters (Aiken et al., 1979; Kim et al., 1976; Thurman et al., 1978a). Researchers have concluded that the XAD series of macroreticular nonionic polymeric resins (specifically XAD-8) offer the best adsorptive characteristics for hydrophobic substances in natural waters (Aiken et al., 1979; Malcolm et al., 1977; Simpson, 1972).

The four resins which have received the most attention from researchers are XAD-8, XAD-7, XAD-4, and XAD-2. XAD-4 and XAD-2 resins have a styrene divinylbenzene matrix of high nonpolarity while XAD-8 and XAD-7 resins have an acrylic ester matrix of intermediate polarity. Aiken et al. (1979) found XAD-8 resin to have higher recoveries of organic solute than XAD-4 resin. They also discovered slow

diffusion-controlled adsorption and the formation of charge-transfer complexes which hinders elution when using XAD-4 resin. Also, the mechanism of adsorption to XAD-8 resin is by weak physical forces, allowing solutes to desorb quickly and easily upon elution (Thurman, 1985). XAD-8 resin was initially developed to adsorb the lignosulfonic acids present in kraft pulp mill wastewater. Lignosulfonic acids are very similar in nature to fulvic acids found in natural waters. Aiken (1985) reported that XAD-8 resin has a higher adsorptive capacity and more efficient elution properties than a styrene divinylbenzene resin like XAD-4 when fulvic acids are the solutes of interest. XAD-8 and XAD-7 resins absorb more water than XAD-4 and XAD-2 resins. This causes the XAD-8 and XAD-7 resins to swell, thereby increasing their surface area and adsorptive sites for organic solutes (Aiken *et al.*, 1979). XAD-7 (another acrylic ester resin similar to XAD-8 resin) has high organic bleed problems associated with NaOH which is typically used to elute fulvic acid (Aiken *et al.*, 1979). Therefore, XAD-8 is the nonionic resin of choice. Adsorption of organic solutes on XAD-8 resin involves van der Waals' forces incorporating many types of interactions such as hydrophobic bonding, dipole-dipole interaction, and hydrogen bonding (Simpson, 1982).

Organic matter binding to XAD-8 resin will be nonionic and low to intermediate in polarity (hydrophobic). Typically, samples are acidified to pH 2 before application to XAD-8 resin, causing hydrophobic organic acids to become protonated and assume a neutral charge. Since hydrophobic organic acids represent most humic substances (i.e. humic and fulvic acids), XAD-8 resin will generally adsorb most of the DOC in rivers (Thurman, 1985). Organic color is generally associated with humic and fulvic acids, and Thurman (1985) found 85% of organic color to be removed by XAD-8 resin. The

hydrocarbon portions of organic solute molecular structure will repel water and attract to the hydrocarbon surfaces of XAD-8 resin. Organic material passing through the XAD-8 resin will be hydrophilic (highly polar) in nature. Therefore, a hydrophobic/hydrophilic break is determined by organic solutes that will adsorb to XAD-8 resin and organic solutes that will not adsorb to XAD-8 resin (Malcolm et al., 1977).

Many researchers have developed capacity factors for various organic solutes on XAD-8 resin based on the aqueous solubility of the organic solute (Thurman et al., 1978b). A capacity factor is defined as the mass of solute adsorbed on the resin divided by the mass of solute in the void volume of the column. Unfortunately, the DOC of natural waters contain literally thousands of organic solutes each having a unique capacity factor. By assuming a capacity factor, however, one can size a resin column to completely adsorb those humic substances with capacity factors greater than the selected capacity factor.

Humic substances assume a new definition when using XAD-8 resin. Schnitzer (1972) defined humic substances as those substances soluble at pH 12 while Thurman (1985) termed them to be organic solutes retained on XAD-8 resin. Elution of humic substances from XAD-8 resin occurs by application of base, thereby ionizing the adsorbed humic substances. The resulting negatively charged humic substances are no longer nonionic and desorb from XAD-8 resin. One documented problem with XAD-8 resin is resin "bleed" or the physical break down of the resin resulting in an increase in DOC concentration most common during elution. XAD-8 is a synthetic material containing residual monomers, artifacts of the polymerization pathway, and some chemical preservatives. Resin "bleed" from XAD-8 resin will contain methyl acrylic acid

(Aiken, 1988). Extensive Soxhlet extraction with various organic solvents will minimize resin bleed.

### **Ion-Exchange Resins**

Although the advent of macroporous nonionic resins shifted the focus away from ion-exchange resins, they are still crucial in chemically fractionating DOC. Malcolm et al. (1977) found 50% of organic solutes to be hydrophilic (hydrophilic since not retained by XAD-8 resin). Thurman (1985) reported that approximately 30% of the DOC are organic acids not retained on the XAD-8 resin. These hydrophilic acids represent a substantial amount of organic material that needs to be isolated and concentrated. Anion exchange resins have been shown to be successful in separating hydrophilic organic acids from natural waters (Leenheer, 1981; Thurman, 1985). Ion-exchange resins are available in both the microporous and macroporous forms, although macroporous resins provide more surface area for adsorption.

Two types of anion exchange resins have been studied: strong base ion-exchange and weak base ion-exchange resins. Strong base resins commonly have quaternary ammonium functional groups while weak base resins commonly have secondary amine functional groups. Common resin matrices for either resin are styrene divinylbenzene or phenol formaldehyde. The exchange of organic solutes occurs at the functional groups; therefore, the nature of the functional groups determines the behavior of the resins. With strong base anion exchange resins, the quaternary ammonium functional group can be in a hydroxide or chloride form while the secondary amine group of a weak base anion exchange resin can be in a free base or acid chloride

form. Kim et al. (1976) reported similar capacities with either the strong base or weak base resin but irreversible sorption on the strong base resin.

In addition to reporting a high capacity for weak base resin, Aiken (1988) also advocated the phenol formaldehyde resin matrix. The phenol formaldehyde resin matrix is more hydrophilic than the styrene divinylbenzene resin matrix making the phenol formaldehyde matrix more amenable to hydrophilic acids. A-7, a weak base anion exchange resin with a phenol formaldehyde resin matrix, is the particular anion exchange endorsed by researchers (Aiken, 1988; Kim et al., 1976; Leenheer, 1981). Kim et al. (1976) found the free base form of Duolite A-7 to have the highest resin capacity for the weak organic acid P-nitrophenol which is similar in chemistry to hydrophilic acids.

The mechanisms of organic solute adsorption to A-7 resin is both very different and less understood than adsorption to XAD-8 resin. Water samples are applied to the A-7 resin at an acidic pH. At pH 2, hydrophilic acids will be protonated and possess a net neutral charge; however, the end of the acid containing the proton will possess a positive charge. Kim et al. (1976) believed adsorption occurs via hydrogen bonding to the free amine group at acidic pHs. Aiken (1988) suggested both hydrogen bonding and ion exchange as adsorption mechanisms. The adsorption mechanism is pH dependent. Since the A-7 resin adsorbs protons, hydrophilic acids are also competing with the hydrochloric acid used to acidify the sample and any inorganic ions. Elution of the A-7 resin is performed by application of base which deprotonates the hydrophilic acids and inorganic anions. This makes them incapable of forming hydrogen bonds thereby, eluting the hydrophilic acids and also unfortunately, the inorganic anions.

Desalting of the hydrophilic acids via vacuum distillation will remove unwanted inorganic anions. Another disadvantage of the A-7 resin is resin bleed at high pH values (e.g. pH 10). A-7 resin is a synthetic material containing residual monomers, artifacts of the polymerization pathway, and some chemical preservatives. Resin bleed from the A-7 resin will contain amino phenols, formic acid, and formaldehyde (Aiken, 1988). Extensive Soxhlet extraction with solvents, however, will minimize the organic bleed.

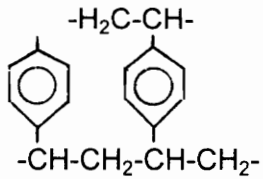
Thurman (1985) found 75-80% of the DOC to be fulvic, humic, and hydrophilic acids and the remaining 20-25% to include carboxylic acids, amino acids, carbohydrates, and volatile hydrocarbons. Thurman (1985) endorsed cation exchange resins to adsorb amino acids and some polypeptides. Leenheer (1984) suggested the use of MSC-1 cation exchange resin which is a strong acid, sulfonated, polystyrene macroporous ion-exchange resin. The principal of adsorption is purely ion-exchange. MSC-1 resin is protonated by application of hydrochloric acid. The acidified water sample contains protonated bases containing a net positive charge which compete with other cations (e.g. sodium) for exchange sites by displacing hydrogen protons. Elution occurs via application of base which deprotonates the adsorbed organic bases. Figure 1 contains schematics of the matrices and functional groups of the MSC-1 and A-7 resins.

### **Synthetic Resin Fractionation Procedures**

Aiken (1988) reported that both the lack of a universally accepted or standard method of isolating DOC and an operational definition of the DOC fractions are the two basic problems associated with characterizing DOC. Furthermore, the lack of a standard procedure makes direct comparison of fractionation results difficult. Even with

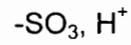
## Dowex MSC-1 Resin

Matrix



polystyrene

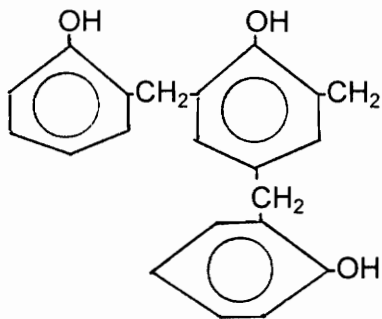
Cation Exchange  
Functional Group



strong acid sulfonate group  
hydrogen ion form

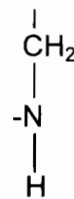
## Duolite A-7 Resin

Matrix

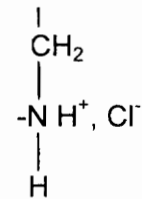


phenol-formaldehyde

Anion Exchange  
Functional Group



free base form



acid chloride form

weak base secondary amine group

Figure 1. Ion-exchange resins.

from Kim *et al.* (1976)



the development of synthetic resin adsorbents, many procedures have been developed regarding the selection and sequence of the adsorbents. Four of the more popular synthetic resin fractionation procedures will be described since data presented later for comparison purposes all result from these four procedures except one. Comparison of the results are meaningless unless differences in the chemistry of the organic fractions resulting from the chosen fractionation procedure are considered.

Generally, all synthetic resin fractionation procedures for natural waters utilized in the literature include XAD-8 resin (Bose, 1993; Leenheer, 1981; Malcolm *et al.*, 1977; Thurman, 1985). The first procedure only incorporates XAD-8 resin. An acidified water sample is passed through the resin adsorbing hydrophobic acids (humic and fulvic acids) to the XAD-8 resin. Since humic and fulvic acids constitute the majority of DOC in rivers, the literature contains many studies utilizing this fractionation procedure (Aiken *et al.*, 1979; Collins *et al.*, 1986; Stepan and Smith, 1977).

The second procedure incorporates passing the acidified water sample through the XAD-8 resin followed by another XAD resin (XAD-4 or XAD-2). Croué *et al.* (1993) used XAD-8 resin followed by XAD-4 resin to fractionate hydrophobic and hydrophilic acids, respectively. As mentioned earlier, XAD-4 resin is highly nonpolar making Croué *et al.*'s use of XAD-4 resin or hydrophilic acids suspect. Aiken *et al.* (1979) also found XAD-4 resin to possess poor elution characteristics.

The third procedure incorporates passing unacidified water sample through XAD-8 resin followed by MSC-1 and A-7 resins in sequential order. The XAD-8 resin removes hydrophobic bases, weak hydrophobic acids, and hydrophobic neutrals since the water sample is at neutral pH. The hydrogen saturated MSC-1 resin has a dual role.

MSC-1 resin adsorbs hydrophilic bases but is also necessary to acidify the water sample before application to the A-7 resin. Finally, the A-7 resin adsorbs strong hydrophobic and hydrophilic acids. Strong hydrophobic acids are not adsorbed on XAD-8 resin since the water sample is not acidified prior to application to the XAD-8 resin. Aiken (1985), Leenheer and Noyes (1984), and Edzwald (1993) have fractionated natural water samples using this procedure.

The fourth procedure also incorporates XAD-8 resin followed by MSC-1 and A-7 resins, however, the water sample is passed through the XAD-8 resin twice. The first XAD-8 resin pass is at neutral pH removing hydrophobic bases and hydrophobic neutrals. After elution of the bases, the water sample is acidified and passed through the XAD-8 resin again removing hydrophobic acids (humic and fulvic acids). The MSC-1 resin removes hydrophilic bases while the A-7 resin removes hydrophilic acids. The remaining water sample contains the hydrophilic neutral fraction. This procedure developed by Leenheer (1981) is the most comprehensive synthetic resin fractionation procedure. The procedure fractionates DOC into six fractions: hydrophobic acid, base, and neutral and hydrophilic acid, base, and neutral. The main disadvantages of this procedure are it is both time and labor intensive. Table 2 contains a summary of the four synthetic resin fractionation procedures described. Figure 2 contains schematics of the four fractionation procedures.

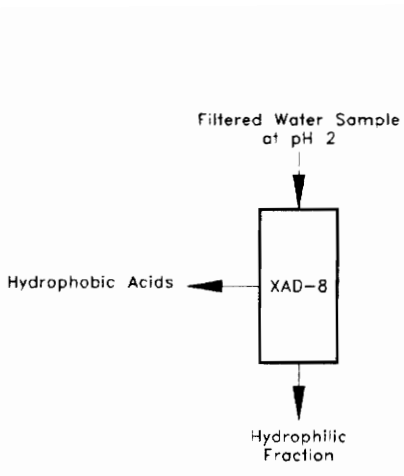
Sinsabaugh et al. (1986) developed an innovative procedure based on Leenheer's procedure. The authors utilized a strong cation exchange resin and a strong anion exchange resin. Water samples were first passed through the anion exchange resin and then the resin was eluted. Next, the water samples were passed through the

Table 2. Summary of the four synthetic resin fractionation procedures.

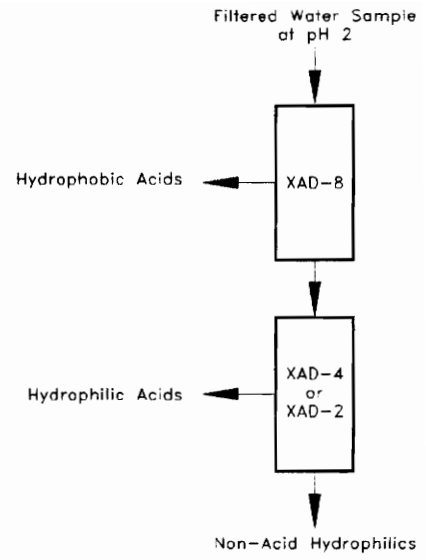
<b>Procedure Number and Resin Sequence</b>	<b>Organic Fractions</b>	<b>Distinguishing Features</b>
1. XAD-8	humic and fulvic acids, HPI DOC not adsorbed	sample acidified prior to application to resin
2. XAD-8, XAD-2 or XAD-4	HPO acid and HPI acid fractions	sample acidified prior to application to resins, XAD-8 adsorbs HPO acids while XAD-2 or XAD-4 adsorbs HPI acids
3. XAD-8, MSC-1, A-7	strong and weak HPO acid, HPO base and neutral, HPI acid, base, and neutral	sample not acidified prior to application to XAD-8, strong HPO acids adsorb to A-7 with HPI acids
4. XAD-8, MSC-1, A-7	HPO acid, base, and neutral and HPI acid base and neutral	two passes through XAD-8, first time neutral and second time acidified, most comprehensive resin fractionation procedure

HPO = hydrophobic

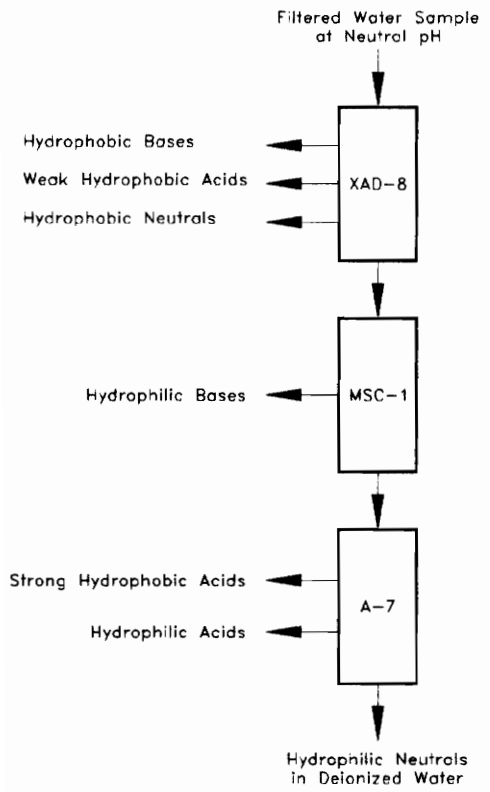
HPI = hydrophilic



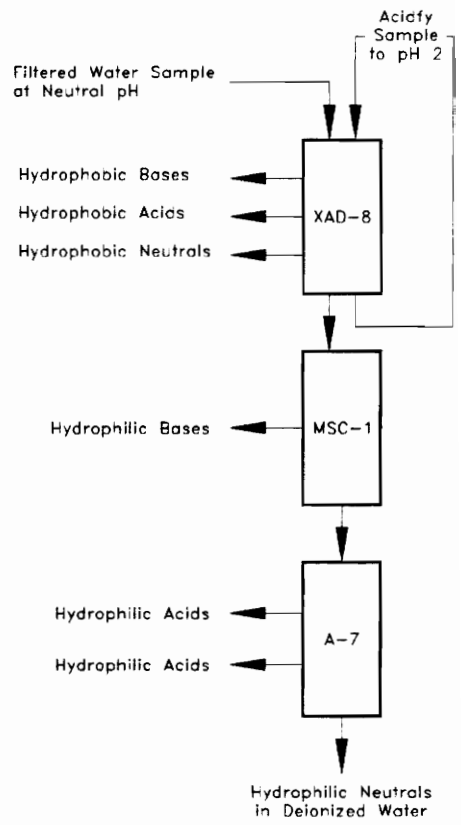
Fractionation Procedure A



Fractionation Procedure B



Fractionation Procedure C



Fractionation Procedure D

Figure 2. Synthetic Resin Adsorbent Fractionation Procedures.

cation exchange resin and then the resin was eluted. The anion exchange eluant contained the acid fraction, the cation exchange eluant contained the base fraction, and the water sample exiting the cation exchange resin contained the neutral fraction. Each fraction was subsequently analyzed by reverse-phase high performance liquid chromatography (HPLC). HPLC divided the acid, base, and neutral fractions into philic, mesic, and phobic fractions. The authors concluded that the phobic and most of the mesic fractions would most likely be included in the hydrophobic fraction as defined by Leenheer's method. The resins fractionated the water based on charge while HPLC fractionated the water based on solubility.

In addition to the resin matrix, research has shown that molecular size, pH, ionic strength, and sample flow rate also effect organic solute adsorption (Curtis and Rogers, 1984; Simpson, 1972; Stepan and Smith, 1977). Organic solutes that are large in size will be unable to penetrate the pores of the macroporous resins. The pH will define which organic solutes will adsorb to the resin. For example, at pH 2, hydrophobic acids will adsorb to XAD-8 resin while at neutral pH hydrophobic bases and neutrals will adsorb to XAD-8 resin. An increase in solution ionic strength will increase the adsorptive capacity of the resin and vice versa. The flow rate can greatly affect adsorption. If the flow rate is too high, organic solutes which should adsorb to the resin column will pass through the column.

Despite the numerous advantages of synthetic resin adsorbents several areas of concern regarding the resins need to be addressed. A major problem is there is no consensus as to the definitions of the organic fractions. The traditional definition for humic substances is those organic compounds soluble at pH 12. Thurman (1985)

defined aquatic humic substances (i.e. humic and fulvic acids) as those organic solutes which upon acidification to pH 2 have a column distribution coefficient greater than 50 on the XAD-8 resin at 50% breakthrough. Leenheer (1981), however, defined those organic solutes as hydrophobic acids. Another issue is the separation of the fractions is not sharp, that is, overlap exists. Aiken (1985) reported potential overlap of hydrophilic acid in the hydrophobic acid fraction. He also stated the possibility of the hydrophobic acids solubilizing hydrophobic neutrals if the hydrophobic acid concentration is high preventing hydrophobic neutral adsorption to the XAD-8 resin. Aiken (1985) also discouraged the use of organic solvents to elute XAD-8 resin. The solvents elute both the hydrophobic neutral and acid fractions from XAD-8 resin. The use of base and acid prevents this paired elution. If the water sample is not adjusted to pH 2 before application to the XAD-8 resin, Aiken (1985) found approximately 20% crossover of the humic-like compounds into the hydrophilic acid fraction.

Besides procedural concerns, chemical alteration of the organic fractions due to extreme pH shifts is also a concern. First, ester hydrolysis can occur in both acidic and basic solutions. When eluting with base, ester hydrolysis is rapid (Aiken, 1988). The net effect is the fractionated organic material is not representative of the original organic material in the unfractionated water. Also, organic solute contact with alcohol can cause methanolysis or alcoholysis reactions (Aiken, 1988). Finally, if ammonium hydroxide is used as the base for elution, aminolysis can occur with organic esters,  $\text{NH}_3$  interaction with phenols, and nonexchangeable adsorption of nitrogen to humic acids (Aiken 1988). To counter these effects sodium hydroxide is used for base elutions and eluted samples are quickly adjusted to neutral pH.

## Chemistry of Synthetic Resin Absorbent Fractions

Although specific compound identification is currently not possible both technically and economically, the chemical reactivity of the compounds within the synthetic resin fractions are similar. As mentioned earlier, the general chemistry of DOC is dependent on the resin fractionation procedure used. Regardless of the procedure, the chemical and physical properties of organic solutes are largely governed by the solute's major functional groups (Thurman, 1985). The solubility of the functional groups seems to govern the types of functional groups present in DOC (Thurman, 1985). The functional groups not only affect the interaction of DOC compounds with one another but also with metals and coagulants.

Table 3 contains the important functional groups of DOC. As Table 3 illustrates, carboxylic acids are the most prevalent functional group on DOC. Carboxylic acids contribute both aqueous solubility and acidity to organic molecules. Organic acids exist as ions at pH 6-8 (the pH of most natural waters) and are the most abundant of DOC compounds (Thurman, 1985). The solubility and chemical and biological stability of the carboxylic anion is the main reason carboxylic acids are ubiquitous in DOC. Carboxylic acids include aliphatic acids, aromatic acids, aliphatic dicarboxylic acid, hydroxyacid, and aromatic dicarboxylic acid. The location of these functional groups affect the acidity of the compound. Phenols are another important acidic functional group. These acidic functional groups would be found on fulvic and humic acids and on the hydrophobic and hydrophilic acid eluants from synthetic resin fractionation procedures A, B, C, and D.

The important neutral functional groups are hydroxyl, ether, ketone, aldehyde, ester, and lactone. Due to the presence of oxygen in these functional groups, they form

Table 3. Important functional groups of DOC.

Functional Group	Structure	Where found
<b>Acidic Groups</b>		
Carboxylic acid	R-CO <sub>2</sub> H	90% of all DOC
Enolic hydrogen	R-CH=CH-OH	Aquatic humus
Phenolic OH	Ar-OH	Aquatic humus, phenols
Quinone	Ar=O	Aquatic humus, quinones
<b>Neutral Groups</b>		
Alcoholic OH	R-CH <sub>2</sub> -OH	Aquatic humus, sugars
Ether	R-CH <sub>2</sub> -O-CH <sub>2</sub> -R	Aquatic humus
Ketone	R-C=O(-R)	Aquatic humus, volatiles, keto-acids
Aldehyde	R-C=O(-H)	sugars
Ester, lactone	R-C=O(-OR)	Aquatic humus, tannins, hydroxy acids
<b>Basic Groups</b>		
Amine	R-CH <sub>2</sub> -NH <sub>2</sub>	Amino acids
Amide	R-C=O(-NH-R)	Peptides

Where R is a aliphatic backbone, and Ar is an aromatic ring

from Thurman (1985)



hydrogen bonds with water, thereby increasing their solubility. The hydroxyl functional group imparts the greatest solubility. These neutral functional groups are found on humic substances (fulvic and humic acids) but impart the largest impact on the neutral compounds (organic solutes neutrally charged at both acidic and basic pHs). Hydrophobic and hydrophilic neutral fractions from synthetic resin fractionation procedures C and D contain most of these functional groups.

The basic functional groups are amines and amides. These functional groups are found on humic substances, amino acids, and polypeptides. Like the neutral functional groups, the basic functional groups are most prevalent on basic compounds (organic solutes with a positive charge at acidic pH). Amino acids and peptides are important in that they make up approximately 2-3% of the DOC in natural water (Thurman, 1985). Hydrophobic and hydrophilic basic fractions from synthetic resin fractionation procedures C and D contain most of these functional groups.

Table 4 contains a summary of the location of functional groups in DOC fractions. The strong hydrophobic acid fraction would be included with the A-7 resin eluant for fractionation procedure C while it would be included with the XAD-8 resin eluant for fractionation procedure D.

### **Apparent Molecular Weight Distribution**

In order to fully characterize DOC, determination of apparent molecular weight is necessary for physical characterization. Molecular weight is important for three main reasons (Wershaw and Aiken, 1985). First, molecular weight information helps establish approximate molecular formulas of organic solutes along with other means of characterization (e.g. synthetic resin fractionation). Second, molecular weight

Table 4. DOC fractions and functional groups.

<b>Fraction</b>	<b>Functional Groups</b>
<u>Hydrophobic</u>	
<u>Acids</u>	
Strong	Humic and fulvic acids, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids
Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acids
<u>Bases</u>	Proteins, aromatic amines, high MW alkyl amines
<u>Neutrals</u>	Hydrocarbons, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furans, pyrole
<u>Hydrophilic</u>	
<u>Acids</u>	
	Hydroxy acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids
<u>Bases</u>	Amino acids, purines, pyrimidines, low MW alkyl amines
<u>Neutrals</u>	Polysaccharides, low MW alkyl alcohols, aldehydes, and ketones

MW = molecular weight

from Edzwald (1993)

information helps establish approximate stoichiometric relationships between organic solutes and other chemical species. Third, and most importantly, molecular weight aids in comparing results with organic fractions extracted from other natural waters.

Apparent molecular weight determination methods include: ultracentrifugation, viscometry, colligative property measurements, small-angle X-ray scattering, gel-permeation chromatography (GPC), and ultrafiltration. Actually, small-angle X-ray scattering, GPC, and ultrafiltration measure molecular size while the other methods measure apparent molecular weight. A strong correlation between apparent molecular weight and molecular size exists, however. Since DOC is mainly composed of carbon, oxygen, and hydrogen (Thurman, 1985), any increase in molecular weight will generally correspond to an increase in molecular size. Small-angle X-ray scattering, GPC, and ultrafiltration estimate apparent molecular weight by comparing obtained results to model compounds of known molecular weight and composition. For this reason, the sizes of DOC are referred to as apparent molecular weight distributions although the term molecular weight distribution is also used. The two most popular apparent molecular weight determination methods are gel-permeation chromatography and ultrafiltration.

### **Gel-Permeation Chromatography**

Gel-permeation chromatography operates based on size-exclusion chromatography which is based on the size of the molecule. Apparent molecular weight data can only be estimated by calibrating the gel with appropriate standards. A concentrated sample is applied to the top of the chromatography column. Smaller organic solute molecules penetrate into the gel pores by molecular diffusion while larger

molecules are excluded. During elution, large molecules have a short retention time while small molecules have a long retention time. By measuring the DOC or specific absorbance of the column effluent, a continuous apparent molecular weight distribution is developed.

A major problem associated with GPC is the potential of chemical interaction between the sample and column packing. Also, there is the possibility of an interaction between solute molecules leading to flocculation of humic substances (fulvic and humic acids) (Amy et al., 1987). The flocculation problem can be avoided by applying the sample at basic pH although Amy et al. (1987) reported electrostatic expansion of humic substances through ionization of acidic functional groups, causing high apparent molecular weight overestimation.

Natural waters must be concentrated prior to column application to permit dilution during the elution procedure. At high concentration levels, organic solutes (particularly humic substances) will tend to aggregate, leading to skewed high apparent molecular weight distributions. Also, it may not be feasible to obtain sufficient material in some of the organic fractions (e.g. hydrophilic bases) for GPC. The gel composition presents a problem as the gel may contain carboxyl functional groups which can retard positively charged molecules and repel negatively charged molecules at low eluant ionic strength (Amy et al., 1987). Since DOC surface water samples at neutral pH generally contain a large number of negatively charged organic acids, an overestimation of molecular size can result. Finally, Kwak et al. (1977) and Thurman (1985) both reported instances of irreversible adsorption of large amounts of organic material. In summary, a

longer retention time of organic solutes does not necessarily point to lower apparent molecular weight in gel-permeation chromatography.

### **Ultrafiltration**

Ultrafiltration operates on the principal of selective rejection of DOC via convective flow through a membrane. Unlike gel-permeation chromatography which gives a continuous apparent molecular weight distribution, ultrafiltration gives a discrete distribution. That is, the distribution results by passing samples through membranes of specific sizes. Organic solutes larger than the membrane size are rejected and retained in the retentate while smaller organic solutes pass through the membrane into the permeate. The apparent molecular weight distribution is a collection of distinct data points equivalent to the membrane sizes selected. Flow through the membrane is a combination of advective flow and molecular diffusion. Flux is directly related to membrane size, cell pressure gradient, and solution pH, ionic strength, and concentration.

Like GPC, several areas of concern exist with regard to ultrafiltration. First, the water sample concentration affects resulting apparent molecular weight distributions. Buffle et al. (1978) reported an increase in high apparent molecular weight fractions and a decrease in low apparent molecular weight fractions as water sample DOC concentration increased. Second, a deposition of large-sized organic material on the membrane surface (concentration polarization) can form a gel layer resulting in gel-layer diffusion rather than membrane diffusion (Amy et al., 1987). Amy et al. (1987) also reported on the Donnan effect (membrane rejection) where the membrane acquires a

potential through organic solute deposition which retards the flow of organic solutes of similar size.

Another item for concern is that the stated apparent molecular weight cutoffs (MWC) of membranes are nominal (NMWC). That is, DOC larger than the NMWC will pass through the membrane while some DOC smaller than the NMWC will be retained by the membrane. Sinsabaugh et al. (1986) reported that polymeric or charged molecules were rejected by the ultrafiltration membranes not based on molecular weight alone. Therefore, the actual molecular distributions are most likely shifted toward lower molecular weights. Finally, like gel-permeation chromatography, ultrafiltration results also depend on organic solute interactions with other solution constituents such as pH, ionic composition, and polyvalent cations. The aforementioned areas of concern can be minimized by using dilute samples, tracking membrane performance by monitoring pure water flux through the membrane, selecting proper membranes, and continuous stirring of the sample. Also, parallel processing of samples negates the synergistic effect of concentration polarization that would result from series processing of samples.

Logan and Jiang (1990) developed a simple method to address the membrane rejection problem. The rejection of a ultrafiltration membrane for organic solutes is a function of the solute concentration at the membrane surface. The authors observed an increase in permeate DOC concentrations in proportion to sample volume processed for lower apparent molecular weight membranes. Likewise, underestimation of DOC smaller than the membrane size up to 70% was reported, resulting from failure to account for membrane rejection. Using a mass balance around a batch ultrafiltration cell, Logan and Jiang defined a permeation coefficient. This permeation coefficient is a

function of the instantaneous permeate concentration and the instantaneous retentate concentration. By sampling the permeate at specific intervals, the permeation coefficient and the true DOC of the sample can be determined. Unfortunately, this procedure is time and labor intensive due to the necessity of processing multiple samples. Also, permeation coefficients vary from water sample to water sample necessitating multiple samples for each sample processed (Owen *et al.*, 1993). Failure to follow Logan and Qiang's method, however, will result in underestimation of lower apparent molecular weight ranges.

Ultrafiltration has several advantages over gel-permeation chromatography. First, samples do not need to be concentrated for ultrafiltration as is required for gel-permeation chromatography. In fact, it is better for samples to be dilute which is generally the case for natural waters for ultrafiltration. Second, Amy *et al.* (1987) reported gels may contain carboxyl groups which possess a negative charge. The result is the repulsion of negatively charged organic solutes, and the retardation of positively charged molecules. The end result is that negatively charged organic solutes will travel through the gel column faster, resulting in an overestimation of molecular size. Third, large volumes of sample can be processed more quickly with ultrafiltration than with GPC.

### **Apparent Molecular Weight Distribution of DOC**

The apparent molecular weight distributions of water sources is varied and is dependent on climate, geography, topography, and the relative contributions of soil organic material and aquatic organic material to the total natural organic material. One may expect similar water sources like river water to have similar apparent molecular

weight distributions. Amy et al. (1987) found approximately 77% of the DOC for the Colorado River to be less than 5,000 atomic mass units (amu) while approximately 37% of the DOC for the Grasse River was less than 5,000 amu. Approximately 42% of the DOC for the Floridian Aquifer (a groundwater) was less than 5,000 amu. Collins et al. (1985) found approximately 77% of the DOC for the Colorado River to be less than 5,000 amu while approximately 95% of the DOC for the Floridian Aquifer was less than 5,000 amu. Collins found the 5,000 amu results to differ greatly for the Colorado River and Grasse River. Both Collins and Amy used the same type ultrafiltration membrane although sampling locations and season of the year are not known. The 5,000 amu results were the same for the Colorado River but varied greatly for the Floridian Aquifer. These results illustrate that apparent molecular weight distributions of water sources vary between types of source (e.g. Colorado River and Floridian Aquifer), between same types of water sources (e.g. Colorado River and Grasse River), and within the same source (e.g. Floridian Aquifer)

Much like water sources, the apparent molecular weight distribution of the different DOC fractions (e.g. hydrophobic, hydrophilic, fulvic acids, and humic acids) are varied; however, some generalities do exist. The most popular DOC fraction for determination of apparent molecular weight distributions are humic substances (humic and fulvic acids). The apparent molecular weight distributions are partially a function of the DOC fractionation procedure. The results of Thurman (1985) are most often reported in the literature. Using the simple acid and base precipitation fractionation procedure described earlier, Thurman (1985) found the aquatic fulvic acids' MW range to be 1,000-2,000 amu and the aquatic humic acids to be larger than 2,000-5,000 amu



and often colloidal in size (X-ray scattering method). Table 5 shows the results of a number of apparent molecular weight distribution studies of aquatic humic substances using ultrafiltration (extraction procedures unknown). The results indicate that the apparent molecular weight of the majority of humic and fulvic acids was less than 10,000 amu. Gjessing, however, found 85% of the humic substances to have apparent molecular weights greater than 20,000 amu.

Using synthetic resin fractionation procedure A, Thurman et al. (1982) fractionated humic substances from a number of water sources. Separation into humic and fulvic acids was achieved at pH 1 following fractionation. The apparent molecular weight distributions of the humic and fulvic acids are presented in Table 6.

These results illustrate that fulvic acid apparent molecular weight is generally less than 2,000 amu while humic acid apparent molecular weight ranges from 1,000 amu - colloidal in size. Apparent molecular weight distributions of the hydrophilic fractions are rare in the literature. Bose (1993) performed apparent molecular weight distributions of both the hydrophobic and hydrophilic fractions of a water source. Sinsabaugh et al. (1986) performed apparent molecular weight distributions on untreated and treated waters. After performing the apparent molecular weight distributions, he further fractionated the fractions based on charge and solubility. The results will be discussed later.

Table 5. Apparent molecular weight of aquatic humic substances using ultrafiltration.

<b>Researchers</b>	<b>Membrane Size amu (% less than membrane)</b>
Andrew and Harriss (1975)	500 (90%)
Tuschall and Brezonik (1980)	10,000 (50%)
Giesy and Briese (1977)	500 (70%)
Buffle and others (1978)	10,000 (81%)
Mauer (1976)	10,000 (85%)
Schindler and others (1972)	10,000 (25%)
Gjessing (1970)	20,000 (15%)
Moore and others (1979)	10,000 (78%)
Ogura (1974)	10,000 (73%)
Wheeler (1976)	30,000 (75%)
Wilander (1972)	10,000 (71%)
Brown (1975)	10,000 (97%)

from Thurman et al. (1982)

Table 6. Apparent molecular weights of humic substances isolated from water and determined by small-angle X-ray scattering.

<b>Source of Aquatic Humic Substance</b>	<b>Molecular Weight (amu)</b>
<u>Fulvic Acid</u>	
Arvada, Colorado, tap water	500 - 1,000
Deer Creek, Montezuma, Colorado	500 - 1,000
Groundwater, Biscayne aquifer, Miami, Florida	800 - 1,000
Suwannee River, Georgia	1,000 - 1,500
Yampa River, Yampa, Colorado	1,000 - 1,500
<u>Humic Acid</u>	
Arvada, Colorado, tap water	5,000 - Colloidal
Groundwater, Biscayne aquifer, Miami, Florida	1,500 - 2,000
Suwannee River, Georgia	5,000 - 10,000
Trona ground water, Rock Springs, Wyoming	5,000 - 10,000
Water from coal field, western South Dakota	1,000 - 10,000

from Thurman et al. (1982)

## Removal of Natural Organic Material by Coagulation

### Overview

Coagulation refers to the water treatment process of particle aggregation.

Coagulation aims to destabilize both turbidity causing material (e.g. clay minerals, POM) and DOC and remove them by flocculation and sedimentation or direct filtration. Failure to remove turbidity and DOC has aesthetic and health effects as described earlier.

Coagulation incorporates addition of the coagulant, flocculation, and sedimentation.

It is well known that DOC is stable in natural waters. The four generally accepted theorized destabilization and removal mechanisms for DOC are double layer compression, adsorption for charge neutralization, enmeshment in a precipitate, and adsorption for interparticle bonding (Amirtharajah and O'Melia, 1990). The two coagulation mechanisms associated with metallic salts (e.g. alum and ferric chloride) are adsorption for charge neutralization and enmeshment in a precipitate (Dempsey et al., 1984; Edzwald, 1993; Edzwald and Van Benschoten, 1990). Adsorption for interparticle bonding occurs with polymers functioning as flocculant aids.

The removal of DOC during coagulation is a function of both operating conditions (e.g. pH, type of coagulant, coagulant dose, temperature, mixing velocity) and the character of DOC itself. The character of DOC most influential in terms of coagulation are functional groups and molecular weight. First, however, a brief discussion of the solubility of metals is necessary. The solubility of aluminum will be discussed since alum is the most widely used coagulant and alum was used in this research. Iron solubility is similar to aluminum except the pH of minimum iron solubility is higher than aluminum and fewer and smaller iron polymers are formed.

## Aluminum Speciation

Upon alum addition to water, aluminum reacts to form monomers (e.g.  $\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3$ ), polymers (e.g.  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_3(\text{OH})_4^{5+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ), and solid  $\text{Al}(\text{OH})_{3(s)}$  precipitate. Dempsey *et al.* (1984) found formation of monomers ( $t_{1/2} < 10^{-4}$  seconds) to be very fast while polymer formation to be much slower. Van Benschoten and Edzwald (1990a) found little evidence of aluminum polymers following addition of alum to deionized water. The concentrations of aluminum monomers and polymers is pH dependent. Figure 3 illustrates the solubility of the predominant aluminum species in water at equilibrium with amorphous  $\text{Al}(\text{OH})_3$  as a function of pH. The pH of most natural waters is from 5 to 7 where positively charged monomeric and polymeric aluminum species dominate. The charge on the  $\text{Al}(\text{OH})_{3(s)}$  surface becomes more positive with decreasing pH, leading to increased adsorptive capacity for negatively charged species (Edzwald and Van Benschoten, 1990).

## DOC/Aluminum Interactions

It is well documented that DOC controls the coagulant dose and not turbidity. The cation exchange capacity of a clay mineral ranges from 0.1 to 1  $\mu\text{eq}/\text{mg}$  while the total charge on fulvic acid is 10 to 15  $\mu\text{eq}/\text{mg}$  due to carboxylic functional groups (Edzwald, 1993). Also, humic substances can adsorb to certain clays, thereby increasing their particle stability. The net effect is greater coagulant doses to remove both DOC and turbidity. Edzwald (1993) demonstrated this fact by performing jar tests on Missouri River water near St. Louis and water from the Intercoastal Waterway near Myrtle Beach. The highly turbid, low DOC Missouri River water required three times

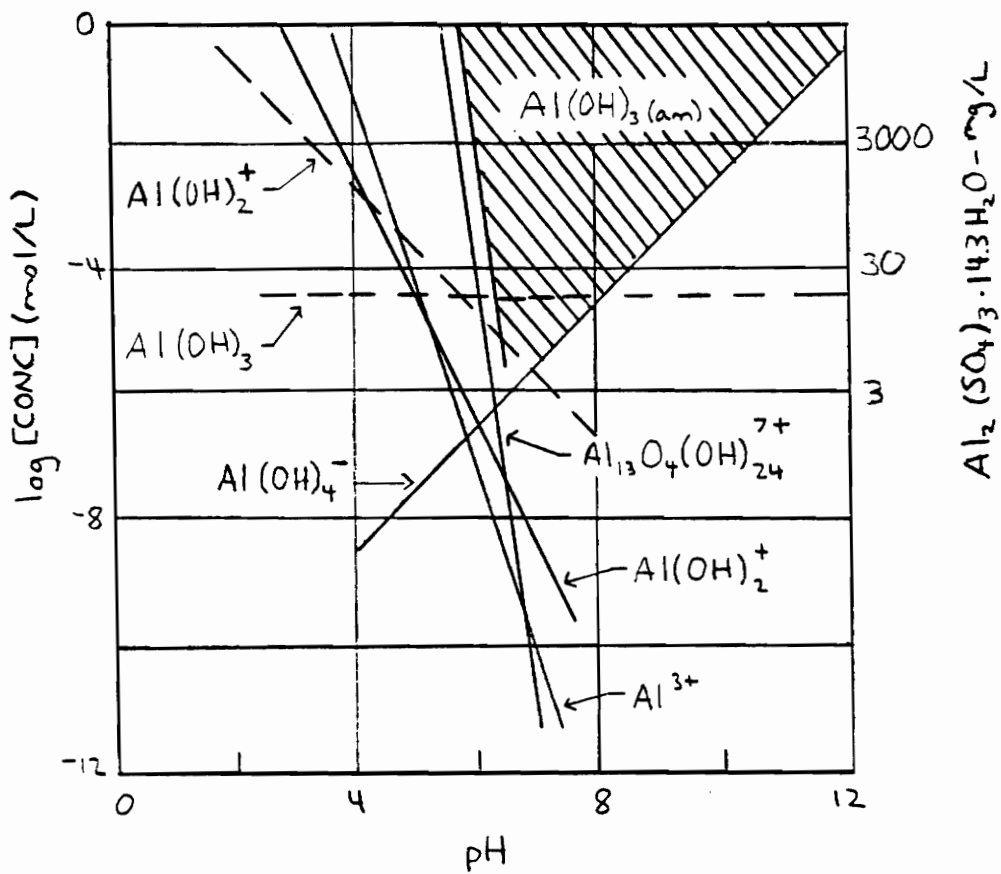


Figure 3. Solubility of aluminum at equilibrium with amorphous  $\text{Al}(\text{OH})_3$ .  
 from Amirtharajah and O'Melia (1990)

less coagulant for good turbidity and DOC removal than the low turbidity, high DOC Intercoastal Waterway water.

Most current coagulation research pertains to humic substances while often ignoring the hydrophilic fractions since humic substances commonly represent the majority of DOC in natural waters (Collins et al., 1986; Dempsey, 1989; Dempsey et al., 1984). Collins et al. (1986) advocated the need to study hydrophilic compounds since they often contribute significantly to both the DOC and THMFP. Unfortunately, very few studies have focused on or even investigated the hydrophilic fractions. When comparing coagulation studies in the literature, one must also be careful to identify the source of the humic substances. Often, humic substances have been extracted from soil (peat) or purchased commercially. Soil humic substances are usually extracted using acid and base solubility and not by synthetic resin fractionation. Commercially purchased fulvic and humic acids may be extracted from soil or natural waters. Regardless of the fractionation procedure, Davis (1980) found inherent chemical differences between aquatic organic material and soil organic material.

Interactions between chemical coagulants and DOC are either based on electrostatic attraction or physi-sorption. Metal monomers and polymers interact with DOC based on electrostatic attraction. Metal solids (e.g.  $\text{Al}(\text{OH})_3$ ), however, interact with DOC based on direct physi-sorption.

Hydrophobic acids (fulvic and humic acids) contain many carboxylic acid functional groups which are ionized (negatively charged) at pH 5 to 7. Fulvic and humic acids are also hydrophobic making them more amenable to adsorption to aluminum hydroxide precipitate. Finally, humic acids have large molecular size, increasing the

probability of contact with aluminum monomers and polymers. Therefore, humic and fulvic acids would be preferentially removed over the hydrophilic fractions during coagulation along with increased removal of large molecular weight compounds over small molecular weight compounds. Edzwald and Van Benschoten (1990) found DOC removals of 50-70% in waters high in humic substances while DOC removals of <50% in waters low in humic substances. Due to the ubiquity of ionized organic acids in natural waters, coagulation studies of pH vs. DOC removed often follow aluminum solubility diagrams. Figure 4 illustrates the possible removal mechanisms for DOC.

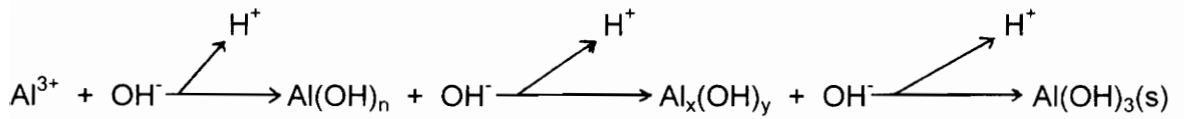
The following section presents studies which examined the effects of DOC chemistry and molecular weight on removal. Chemistry and molecular weight are not separate issues but are related in that the hydrophobic fractions tend to be higher in molecular weight. A combination of DOC chemistry and molecular weight most likely effects DOC removal. The effect of pH on DOC removal is also presented.

### **DOC Chemistry and Molecular Weight Effects**

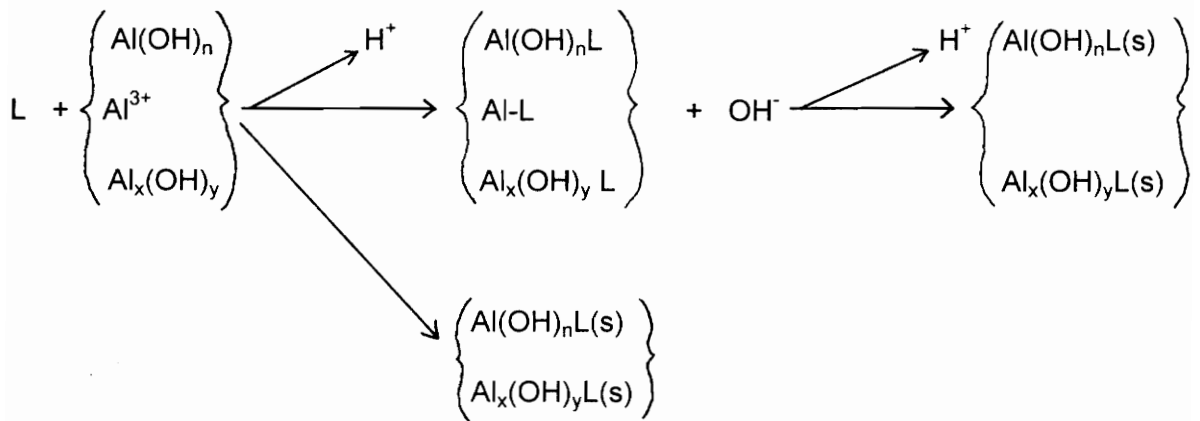
Collins et al. (1985) used ultrafiltration to separate DOC by molecular weight from four water sources. All treatment methods (e.g. direct filtration, conventional treatment) designed to remove high levels of turbidity also removed the high molecular weight material. None of the treatment methods were effective at removing DOC of extremely low apparent molecular weight (<500 amu). Like Collins, Croué et al. (1993) and Semmens and Staples (1986) reported preferential removal of high apparent molecular weight DOC. Semmens and Staples (1986) suggested removal of low molecular weight DOC by association of “neutralized” metal-organic complexes with larger molecular weight species during flocculation.



## HYDROLYSIS



## COMPLEXATION / PRECIPITATION



## ADSORPTION ON COAGULANT FLOC

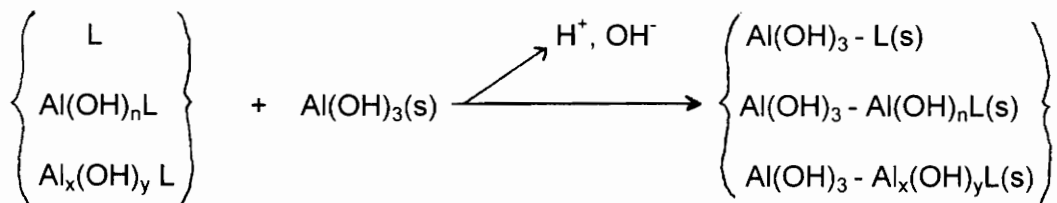


Figure 4. Schematic of chemical reactions between natural organic material and aluminum.

from Edzwald and Benschoten (1990)

Croué et al. (1993) found the hydrophobic fraction obtained from the XAD-8 resin using fractionation procedure B to be more amenable to coagulation than the hydrophilic fraction for various natural waters. Collins et al. (1986) obtained hydrophobic acids via fractionation procedure A and found the carboxylic content of hydrophobic acids to be inversely proportional to molecular weight. That is, hydrophobic acids with the highest carboxylic content were lowest in apparent molecular weight and therefore required additional coagulant for destabilization Collins et al. (1986). The poor removal of fulvic acids in relation to humic acids can be explained by the increased alum doses needed to destabilize the high negative charge density associated with the high carboxylic acidity of fulvic acids. Like Collins, Dempsey et al. (1984) found the need for higher coagulant doses with an increase in carboxylic acidity.

In two separate papers (Dempsey et al., 1984; Dempsey, 1989), Dempsey reported on the coagulation mechanisms between alum and fulvic acid. Dempsey's water sample was from the Jerico Ditch in the Dismal Swamp. Dempsey et al. (1984) followed fractionation procedure A but collected the elute in four distinct fractions by slowly increasing the pH. The elute may be better termed hydrophobic acids although Dempsey named it fulvic acids. Dempsey (1989) followed fractionation procedure A but separated the humic acids from the fulvic acids by centrifugation at pH 1 following fractionation. Dempsey (1989) found the adsorption of hydrophobic acids on  $\text{Al}(\text{OH})_{3(s)}$  to be a much stronger reaction than complexation with monomeric aluminum. This prediction held for the entire pH range for which the removal of hydrophobic acids occurred.

Hydrophobic acids actually enhanced the formation of  $\text{Al}(\text{OH})_{3(s)}$  at  $\text{pH} \leq 5$ . Dempsey et al. (1984) found direct precipitation of hydrophobic acids by aluminum monomers at  $\text{pH} < 5$  and adsorption of hydrophobic acids and hydrophobic acid/aluminum complexes onto  $\text{Al}(\text{OH})_{3(s)}$  at  $\text{pH} > 7$ . At  $\text{pH} 5-6$  the mechanism of removal was dependent on coagulant dosage. At low dosage, precipitation occurred via precipitation with aluminum polymers and at high dosage, precipitation occurred via adsorption on  $\text{Al}(\text{OH})_{3(s)}$ . Dempsey et al. (1984) also found strong hydrophobic acid/aluminum complexation to hinder the removal of hydrophobic acids where polymers of aluminum or  $\text{Al}(\text{OH})_{3(s)}$  are necessary for removal ( $\text{pH} > 5$ ). However, strong hydrophobic acid/aluminum complexation enhanced the removal of hydrophobic acids by aluminum monomers ( $\text{pH} < 5$ ).

Van Benschoten and Edzwald (1990b) obtained hydrophobic acids by following fractionation procedure C. Removal of hydrophobic acids occurred by charge neutralization at  $\text{pH} 5$  while aluminum complexation increased as coagulant dose increased. Apparent competition between hydrophobic acids and  $\text{OH}^-$  for aluminum existed at  $\text{pH} 7$  while aluminum complexation decreased as coagulant dose increased. Van Benschoten and Edzwald (1990b) also found removal of hydrophobic acids at  $\text{pH} 7$  can exceed removal at  $\text{pH} 5.5$  but at the expense of higher coagulant doses. The sorbed species to  $\text{Al}(\text{OH})_{3(s)}$  may be aluminum/hydrophobic acid complexes at  $\text{pH} > 5.5$ . Finally, Van Benschoten and Edzwald (1990b) suggested the  $\text{pH}$  of optimum DOC removal may be decreased by the presence of other anions to substitute for  $\text{OH}^-$ .

Sinsabaugh et al. (1986) studied water from the Harwood's Mill Reservoir in Virginia. They found most of the DOC to be less 5,000 amu. Upon coagulation with

ferric sulfate, most of the large apparent molecular weight DOC (>5,000 amu) was removed. Following ultrafiltration, Sinsabaugh et al. fractionated the <1,000 amu, 1,000-5,000 amu, and 5,000-10,000 amu DOC fractions using synthetic resin adsorption followed by high performance liquid chromatography as described earlier. They found the charged fractions (i.e. acids and bases) to be removed during coagulation unlike the neutral fractions. They attributed the removal of charged organic compounds to their ability to interact with positively charged iron species and form insoluble complexes. Neutral compounds were theorized to be removed by enmeshment in floc. Surprisingly, the hydrophilic fraction was better removed than the hydrophobic fraction while the mesic compounds were poorly removed.

### **Phase-Change Behavior of DOC and Aluminum**

During alum coagulation, DOC may undergo three possible phase change pathways. First, DOC may bind with  $\text{Al}(\text{OH})_{3(s)}$  thereby proceeding directly from a dissolved state to a solid state. Second, DOC may bind with aluminum monomers and/or polymers entering a colloidal state until the floc is large enough to reach a particulate state and settle. Third, the DOC may bind with aluminum monomers and polymers and enter a colloidal state but proceed no further. DOC in the colloidal state will not precipitate. A colloid is no longer in a dissolved state, but it is not settleable. Shorney (1992) and Bellamy (1992) witnessed this colloidal state phenomenon.

When performing jar tests for DOC removal, coagulated samples are typically passed through 0.45  $\mu\text{m}$  to 1  $\mu\text{m}$  glass fiber filters to remove aluminum/DOC precipitate. Shorney (1992) found iron/DOC complexes were not sufficiently removed during coagulation at low alum doses. Coagulated samples were passed through both 0.2  $\mu\text{m}$

glass fiber filters and 100K membranes. Residual iron measurements indicated a distinct gap between the 0.2  $\mu\text{m}$  and 100K residual iron levels. This gap indicated the presence of a DOC/aluminum colloidal phase. At high alum doses the gap closed as sufficient alum was added to effectively remove the complexed DOC/iron. A typical filter size used for jar tests (e.g. 0.45  $\mu\text{m}$ ) would possibly have indicated an even larger gap. Shorney (1992) found that the 100K residual iron levels remained the same as alum dose increased. That is, a low alum dose sufficiently removed the DOC/iron complexes in terms of the 100K membrane. The DOC/iron/aluminum complexes are no longer dissolved but exist in a colloidal state at low alum doses. Knocke et al. (1990) found the same trend in terms of both DOC and residual iron.

### **Summary**

From the literature, it is evident that much research into the nature of DOC has been accomplished, but only in selected areas. Researchers have thoroughly studied hydrophobic acids (humic and fulvic acids) while almost totally disregarding the hydrophobic bases, neutrals, and the hydrophilic fractions. In many instances, the hydrophilic fractions contribute a significant amount of the total DOC. Hydrophilic compounds also have a THMFP. Another issue is the lack of standard procedures to fractionate and characterize DOC. The results of past research into the nature of DOC are difficult to compare since DOC extraction procedures influence the chemical behavior of the DOC fractions. Only two studies to date (Bose et al., 1993; Sinsabaugh et al., 1986) have thoroughly fractionated, quantified, and analyzed DOC. Future research needs to follow the precedent set by Bose and Sinsabaugh. The most thorough chemical fractionation procedure currently available appears to be fractionation

procedure D while the best physical fractionation procedure appears to be ultrafiltration for reasons previously explained.

In terms of the coagulation of DOC fractions, much of the literature has focused on humic and fulvic acids. Individual hydrophilic fractions have either been totally disregarded or studied together as one fraction. Bose *et al.* (1993) did not study the response of the different fractions to coagulation. Research needs to be performed in this area to better understand the response of all DOC fractions, particularly the hydrophilic fractions to coagulation.

The phase-change behavior of organic material is a relatively new area of research. Shorney (1992), Bellamy (1992), and Knocke *et al.* (1990) have demonstrated insufficient removal of colloidal DOC/iron/aluminum complexes at low alum doses. Research into the use of polymers as flocculant aids at low alum doses appears to be a suitable option. Polymers may successfully remove colloidal DOC/aluminum complexes thereby achieving adequate DOC removal to meet DBP regulations at lower alum doses.

## CHAPTER III

### METHODS AND MATERIALS

This chapter details the all laboratory equipment utilized and experiments performed throughout the research. The main sections are: 1) Experimental Overview, 2) General Laboratory Procedures, and 3) Specific Experiments. The Experimental Overview section summarizes the remainder of the chapter. The General Laboratory Procedures section covers topics ranging from pH measurement to the chemical fractionation procedure, whereas the Specific Experiments section describes experimental procedures specific to this research.

#### **Experimental Overview**

The two water samples used in the characterization of DOC were from Lake Drummond near the outfall of the Jerico Ditch (both water bodies partially contained in the Great Dismal Swamp Refuge Area in Suffolk, Virginia) and the Chickahominy River near Providence Forge, Virginia (where route 155 crosses the Chickahominy River). The water sample used in the study of the DOC fractions and the aluminum, iron, and aluminum/polymer study was from Lake Drummond. Ten carboys (approximately 189 liters) of Lake Drummond water were obtained on August 24, 1995, while two carboys (approximately 19 liters) of Chickahominy River water were obtained on December 9, 1995. Both water samples were filtered through a Poly-Bio-Marine, Inc., Model PSM-1 0.45  $\mu\text{m}$  submicronic filter to remove both particulates, particulate organic material, fungi, and most bacteria. All carboys were refrigerated at 5°C throughout the study to inhibit biodegradation of DOC.

Both water samples were chemically fractionated into six organic fractions (hydrophobic acid, base, neutral and hydrophilic acid, base, neutral) using synthetic resin fractionation procedure D as described in the Literature Review. The DOC within each fraction was then quantified. Jar test studies were performed on the untreated Lake Drummond water at a constant coagulant dose while varying the pH to determine the pH of optimum organics removal. Next, jar test studies were performed on the untreated Lake Drummond water at the optimum pH while varying the coagulant dose to determine the enhanced coagulant dose for organics removal. The definitions of both optimum pH and enhanced coagulant dose were as follows:

**Optimum pH** - The pH at which the most DOC is removed from a water (no further significant DOC removal observed for added coagulant).

**Enhanced Dose** - The coagulant dose where a 10 mg/L increase in coagulant dose does not produce greater than a 0.3 mg/L decrease in DOC (EPA definition).

Four of the six chemically fractionated organic fractions (hydrophobic acid, hydrophobic neutral, hydrophilic acid, and hydrophilic neutral) from Lake Drummond were coagulated at the enhanced dose to measure the removal of DOC in each fraction at varying pHs.

Apparent molecular weight distributions were determined for the untreated and coagulated Lake Drummond water, untreated Chickahominy River water, and all six organic fractions obtained from Lake Drummond using ultrafiltration cells. Therefore, the whole Lake Drummond and Chickahominy River waters were characterized both chemically (through synthetic resin fractionation) and physically (through ultrafiltration).

The Lake Drummond hydrophobic acid and hydrophobic neutral fractions were then combined in varying concentrations, coagulated, and passed through the XAD-8



resin. The goal was to identify any synergistic or antagonistic removal effects the fractions had on each other during coagulation. Next, two separate diluted solutions of the Lake Drummond hydrophobic acid were passed through the XAD-8 resin to determine if the hydrophobic acid fraction would fail to adsorb to the XAD-8 resin at pH 6.3. Similarly, two separate coagulated solutions of the Lake Drummond hydrophobic neutral fraction were passed through the XAD-8 resin to determine if the hydrophobic neutral fraction would completely adsorb to the resin at pH 6.3. Finally, a diluted solution of Lake Drummond hydrophobic neutral fraction was passed through the XAD-8 resin at pH 6.3. These experiments were to verify or negate the results of the mixtures of hydrophobic acid and hydrophobic neutral solutions coagulated and passed through the XAD-8 resin previously.

Lake Drummond hydrophobic acids which were <10,000 (<10K) atomic mass units (amu) were then studied to determine the performance of alum, ferric chloride, and alum/polymer as coagulants in removing DOC. The <10K amu hydrophobic acid fraction was coagulated in separate experiments using alum and ferric chloride as coagulants. By using variously sized filters and membranes, an operational definition defining particulate, colloidal and dissolved organic material was established.

**particulate organic material** - organic material retained on a 1  $\mu\text{m}$  filter

**colloidal organic material** - organic material passing through 1  $\mu\text{m}$  filter and retained on a 100,000 nominal molecular weight membrane

**dissolved organic material** - organic material passing through a 100,000 nominal molecular weight membrane

A pH study followed by a dose study was performed using alum as the coagulant. For comparison purposes, a dose study was performed using ferric chloride. By monitoring the residual DOC, aluminum, and iron concentrations from the both the filter and membrane effluents, the presence of a colloidal size organic fraction was definitively measured. Following identification of a colloidal size organic fraction, studies were initiated using a nonionic polymer flocculant aid in an attempt to identify chemical addition conditions that removed this colloidal fraction. Table 7 summarizes the studies performed on each water sample and the organic fractions.

### **General Laboratory Procedures**

#### **Chemicals and Solutions**

Deionized, distilled and carbon-filtered (Milli-Q) water was used for all resin rinses and dilutions (e.g. 12.1 N hydrochloric acid to 1 N hydrochloric acid). The water was obtained by first passing tap water through a deionization cartridge followed by distillation. The deionized-distilled water was then passed through cartridges manufactured by the Millipore Corporation (Norwalk, CT) to remove any remaining ions and to filter out organic carbon. The chemicals used in the research are summarized in Appendix A, Table A-1.

#### **Glassware Preparation**

All new glassware was washed by coating the inside of the glassware with chromic acid. The chromic acid was removed, and the glassware sat overnight. The next day the chromic acid washed glassware was rinsed with tap water three times and then soaked in a 10% nitric acid bath for a minimum of one hour. The glassware was then rinsed with tap water three times followed by soaking the glassware in a 0.1%

Table 7. Summary of studies performed on water samples.

Sample	pH Optimization	Dose Enhancement w/ alum	Chemical Fractionation Raw Water	Chemical Fractionation Coagulated Water	Apparent Molecular Weight Distribution	pH Study w/ alum	Dose Study w/ alum	Dose Study w/ FeCl3	Dose Study w/ alum and polymer
Lake Drummond	X	X	X	X	X				
Chickahominy River			X	X	X				
L.D. HPO Base					X				
L.D. HPO Acid					X	X	X		
L.D. HPO Neutral					X	X	X		
L.D. HPI Base					X				
L.D. HPI Acid					X	X	X		
L.D. HPI Neutral					X	X	X		
L.D. <10K HPO Acid						X	X	X	X

Key: L.D. = Lake Drummond  
HPI = Hydrophilic  
HPO = Hydrophobic

chlorine bath for a minimum of one hour. Following the chlorine bath, the outside of the glassware was rinsed with tap water while the inside was rinsed three times with deionized-distilled water and three times with Milli-Q water. Used glassware was washed using either Alconox (New York, NY) biodegradable detergent or Fisher Scientific (Springfield, NJ) Sparkleen biodegradable detergent. The glassware was then rinsed three times with tap water, three times with deionized-distilled water, and three times with Milli-Q water. All washed and rinsed glassware was placed in a drying oven.

### **pH Measurements**

The pH of all water samples, solutions, and organic fractions was measured using a Fisher Scientific (Springfield, NJ) pH meter, model 620. The meter was calibrated with standard buffers at pH 4 and 7.

### **Ionic Strength**

The ionic strength of all water samples, solutions, and organic fractions was quantified using a YSI (Yellow Springs Instrument, Yellow Spring, Ohio) conductance meter, model 32. Conductance meter readings were given in either  $\mu\text{mhos/cm}$  or  $\text{mmhos/cm}$ . The conductance readings were converted to ionic strength measurements by the following formula:  $\text{ionic strength} = \text{conductance } (\mu\text{mhos/cm}) * 1.6 \times 10^{-5}$ . This formula was derived based on ionic strength measurements from over 70 surface waters as published in Snoeyink and Jenkins (1980).

### **Sodium Ion Measurements**

Sodium ion measurements for water samples, sodium chloride standard solutions, and the MSC-1 resin effluent were measured using a Fisher Scientific (Springfield, NJ) sodium ion probe, model 13-620-500. An Orion (Cambridge, MA)

single junction reference electrode probe, model 90-01 was filled with Fisher Scientific (Springfield, NJ) 4 M KCl saturated with AgCl (solution SP135). The supplied sodium ion ionic strength adjuster solution (triethanolamine) packaged with the sodium ion probe was added at a volume of 0.5 mL solution per 10 mL sample to adjust the ionic strength of samples prior to undertaking the sodium measurement. The sodium probe was connected to a Fisher Scientific (Springfield, NJ) pH meter, model 620, and measurements were in terms of millivolts. A calibration curve was prepared using sodium chloride solutions at five different concentrations (0.1 M, 0.01 M, 0.001 M, 0.0001 M, and 0.00001 M). Sodium ion measurements in samples were compared to this calibration curve to determine sodium ion concentrations.

### **Organic Carbon Determinations**

DOC concentrations were measured using a Dohrmann Carbon Analyzer, Model DC-80 (Xertex, Santa Clara, CA) or a Shimadzu, Model TOC-5000A (Kyoto, Japan). The Dohrmann analyzer operates by chemically oxidizing organic carbon to carbon dioxide via ultra-violet promoted persulfate oxidation. The Shimadzu analyzer measures organic matter by combusting the organic matter to carbon dioxide.

All samples were collected in 40 mL amber vials and sealed with Teflon lined plastic caps. Samples analyzed using the Dohrmann analyzer were acidified at the time of collection with 85% phosphoric acid since chloride ions present in hydrochloric acid have a profound effect on the oxidation rate of organics in the ultra-violet persulfate system (Aiken, 1992). Samples processed through the Shimadzu analyzer were acidified with 3 N hydrochloric acid since phosphoric acid will destroy the platinum catalyst present in this analyzer. All samples were sparged with oxygen (Dohrmann) or

compressed air (Shimadzu) to remove any inorganic carbon present. Phthalic acid standards (10 mg/L and 400 mg/L DOC) were prepared by diluting a known concentration (2000 mg/L) standard with Milli-Q water. Duplicate injections per sample were analyzed by the Dohrmann analyzer unless the values were greater than 0.1 mg/L DOC apart in value in which triplicate injections were performed. A maximum of five injections were performed on the Shimadzu unless the coefficient of variation was less than 1% or the standard deviation was less than 100. DOC measurements were made following the manufacturers' procedures.

## **Residuals Analysis**

### **Aluminum**

Aluminum concentration was measured using a Perkin Elmer Model 5100 PC (Norwalk, CT) graphite furnace atomic absorption spectrophotometer. Samples were first acidified with nitric acid prior to aluminum measurement following the manufacturer's recommendations.

### **Iron**

Iron was measured using either a Perkin Elmer Model 703 (Norwalk, CT) flame atomic absorption spectrophotometer or a Perkin Elmer Model 5100 PC (Norwalk, CT) graphite furnace atomic absorption spectrophotometer. The instrument utilized depended on the concentration of iron in the sample. For iron samples at concentrations in the mg/L range the Perkin Elmer Model 703 was used while the Perkin Elmer Model 5100 was used at concentrations in the  $\mu\text{g/L}$  range. Samples measured on the Perkin Elmer Model 5100 were first acidified with nitric acid prior to iron measurement following the manufacturer's recommendations.

## **Chemical Fractionation of Organic Material**

Chemical fractionation of DOC followed synthetic resin fractionation procedure D as described in the Literature Review. This procedure was developed by Jerry A. Leenheer of the United States Geological Survey (Leenheer, 1981). A few minor refinements and modifications to the procedures were made during the course of this study as deemed necessary. These changes are noted in the text. Appendix B contains a numbered list of the steps contained in the following description. Figure 5 contains a schematic of the chemical fractionation procedure.

### **Resin Cleaning**

One nonionic and two ion-exchange resins were utilized to chemically fractionate the Lake Drummond and Chickahominy River water samples. Each resin required preparation which involved sieving and Soxhlet extraction with one or more solvents to remove organic resin contaminants. The nonionic and anion exchange resins selected for the study were the same resins used by Leenheer in his 1981 study while the cationic exchange resin selected was the same resin used by Leenheer and Noyes in their 1984 study.

Amberlite XAD-8, a nonionic, nonpolar, macroporous methylmethacrylate copolymer resin, manufactured by Supelco Separation Technologies (Bellefonte, PA) was used as the nonionic resin. The XAD-8 resin was sieved using No.30 (600- $\mu\text{m}$ ), 40 (300- $\mu\text{m}$ ), 50 (300- $\mu\text{m}$ ), 60 (300- $\mu\text{m}$ ), and 70 (300- $\mu\text{m}$ ) sieves to remove small and large resin beads to attain a relatively uniform bead size. The large beads and fines were discarded while the remaining XAD-8 beads were soaked in 0.1 N NaOH for 24 hours. Next, the XAD-8 beads were Soxhlet extracted with methanol for 24 hours followed by

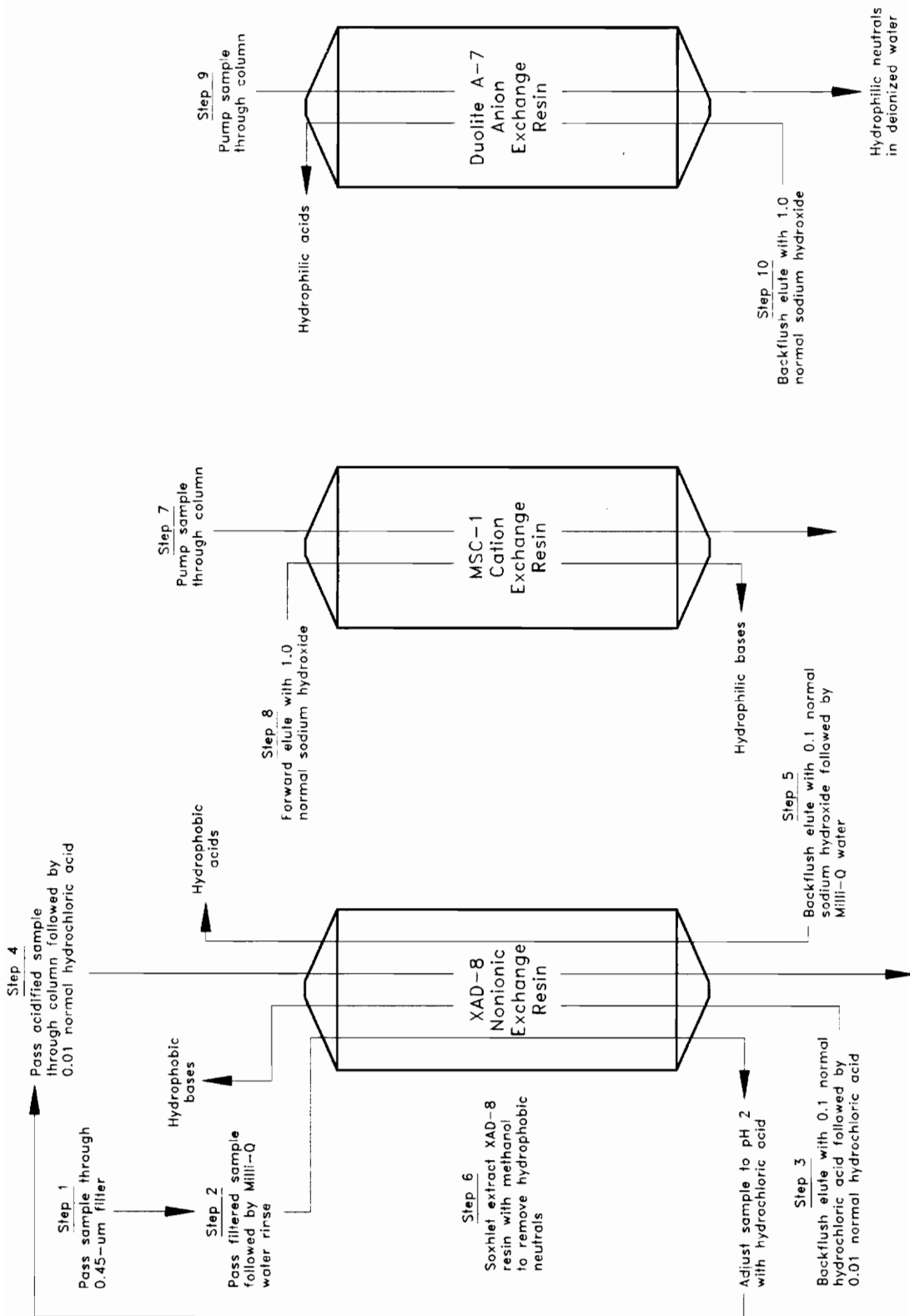


Figure 5. Chemical Fractionation Procedure (Sample Application and Elution).



Soxhlet extraction with acetonitrile (six hours) and methylene chloride (six hours). Gas chromatography analysis of both acetonitrile and methylene chloride for XAD-8 resin monomers showed that the six-hour Soxhlet extraction times were adequate in lieu of the 24 hour Soxhlet extraction suggested by Leenheer (1981). The Soxhlet extracted resin was air-dried overnight and packed into a glass resin column and stored in methanol.

Dowex Macroporous MSC-1 (a strong acid, sulfonated, polystyrene macroporous ion-exchange resin manufactured by Dow Chemical Company (Midland, Michigan)) served as one of the ion-exchange resins. The MSC-1 resin was sieved using No. 30 (600- $\mu\text{m}$ ) and No. 50 (300- $\mu\text{m}$ ) sieves to remove both large and small resin beads to attain a relatively uniform bead size. The large beads and fines were discarded while the remaining MSC-1 beads were Soxhlet extracted with methanol for 24 hours. The Soxhlet extracted resin was air dried overnight to aid in removal of the methanol and then slurried with Milli-Q water in six, 600 mL beakers. The slurries were stirred for five minutes with a jar test stirrer, allowed to settle, and the Milli-Q water was discarded. This stirring process was repeated until the DOC of the Milli-Q water containing the resin was less than 1 mg/L. MSC-1 resin beads were then packed into a glass resin column and stored in Milli-Q water.

Duolite A-7 (a weak base, secondary amine group, phenol-formaldehyde macroporous ion-exchange resin, manufactured by Rohm and Haas (Philadelphia, PA)) served as the other ion-exchange resin. The A-7 resin was sieved using No. 14 (1.4-mm) and No. 50 (300- $\mu\text{m}$ ) sieves to remove both large and small resin flakes to attain a relatively uniform flake size. The large flakes and fines were discarded while the

remaining A-7 flakes were Soxhlet extracted with acetone for 24 hours. The Soxhlet extracted resin was air dried overnight to aid in removal of the methanol and then slurried with Milli-Q water in six, 600 mL beakers. The slurries were stirred for five minutes with a jar test stirrer and the Milli-Q water discarded. This stirring process was repeated until the DOC of the Milli-Q water containing the resin was less than 1 mg/L. A-7 resin beads were then packed into a glass resin column and stored in Milli-Q water.

### **Resin Columns**

Three different sized resin or chromatography columns were used during the study: a 23.5 mL column, a 343 mL column, and a 1650 mL column. The 23.5 mL column served as pilot column for the three resins to determine the exchange capacities and elution profiles of the resins. The purpose of the 343 mL column was to quantify the amount of organic matter in each whole water sample (i.e. Lake Drummond and Chickahominy River). Three columns were made; one for each resin. The 23.5 mL column proved too small to accurately quantify the DOC while the 1650 mL column proved too large. The purpose of the 1650 mL column was to provide large quantities of each organic fraction while minimizing time-consuming resin elution and regeneration procedures due to organic carbon breakthrough. Three columns were made; one for each resin.

The 23.5 mL column was 1 cm in diameter by 30 cm in length and was fitted with a frit and Teflon stopcock at one end and a ground glass female fitting at the other end. The 343 mL column was 41 mm in diameter by 26 cm in length and was fitted with a frit and Teflon stopcock at one end and a ground glass female fitting at the other end. The

1650 mL column was manufactured by Kontex and was tapered at both ends to prevent short-circuiting and to ensure uniform flow across the diameter of the resin column.

Two separate 500 mL and 2000 mL glass reservoirs (each fitted with a Teflon stopcock and ground glass male fitting) were used to contain the water sample for the 23.5 mL and 343 mL columns, respectively. Flow through the column proceeded via gravity flow by placing the glass reservoir above the column. However, flow through the 1650 mL columns proceeded via pressurized carboys in which air lines within the lab were used to pressurize a carboy to force the water samples through the columns. A miniature filter/regulator (Arrow Pneumatics, Inc., Lake Zurich, IL), a pressure gauge (Ashcroft, Berea, KY), and a disposable in-line filter/dryer (Arrow Pneumatics, Inc., Lake Zurich, IL) were attached to the air line to control air pressure and remove oil aerosols. Due to the large size of the columns, pressurized air was selected over gravity flow or pumps to pass the water through the columns. Gravity flow would not provide an adequate flow rate while pumps would provide a pulsed flow. Pressurized air provided an adequate flow rate and pulseless flow. The large size of these columns provided high adsorptive capacities, permitting large volumes of water to be passed through the columns before reaching organic carbon breakthrough.

### **Pilot Column Testing**

Prior to purchasing the 343 mL and 1650 mL resin columns, extensive pilot column tests were performed using the 23.5 mL resin column to determine the exchange capacities and elution profiles of all three resin types. A decision was made to size all resin columns the same to maintain uniformity. Since the hydrophobic acid fraction is typically the largest DOC fraction in surface waters, especially in the

Chickahominy River and Lake Drummond samples, the columns had to be sized based on the XAD-8 resin. The XAD-8 resin would be the first resin to experience organic carbon breakthrough due to the abundance of the hydrophobic fraction. The XAD-8 resin was also the most expensive resin so oversizing the other columns was not important from an economical standpoint. A capacity factor of 100 was chosen, meaning organic solutes with capacity factors <100 would initially be adsorbed on the XAD-8 resin than desorb (Leenheer, 1981). Effectively, those organic solutes would simply pass through the column. Using the resin sizing equation (Leenheer, 1981), the amount of resin (including void volume) necessary to process 200 L of water sample was determined to be 1520 mL as shown below.

$$\begin{aligned} V_{0.5r} &= 2V_o(1 + k'_{0.5r}) & [2] \\ 200 \text{ L} &= 2V_o(1 + 100) \\ V_o &= 990 \text{ mL} \end{aligned}$$

$$V = V_o/0.65 = 990 \text{ mL}/0.65 = 1520 \text{ mL} \quad (\text{void volume of XAD-8 resin is 65\% of its bulk volume (Leenheer, 1981)})$$

where:  $V_{0.5r}$  = volume of water sample  
 $k'_{0.5r}$  = capacity factor  
 $V_o$  = volume of XAD-8  
 $V$  = bulk volume of XAD-8 (void volume plus volume of XAD-8)

Kontes, a resin column manufacturer, did not produce a chromatography column at 1520 mL so a 1650 mL column was purchased. Since 189 L of Lake Drummond water was to be passed through the XAD-8 resin, the column was more than adequate for a capacity factor of 100. The 1650 mL columns were used for the MSC-1 and A-7 resins simply to have uniform column sizes. Although the columns were sized adequately theoretically, extensive pilot column studies were performed with each resin to determine their true exchange capacity and elution profiles.

Elution profiles determined the volume of base or acid necessary for elution completion. Selected organic carbon breakthrough and elution curves from the pilot studies are in Appendix A, Figures A-1 through A-6. Results from the pilot studies were simply scaled up to the larger resin columns in terms of bed volumes. Also, the larger resin columns were less susceptible to short circuiting of the water sample than the pilot column. The results of the pilot studies are summarized in Table 8 based on processing 200 L of resin. Therefore, all resin columns were of adequate size to process the water samples.

### **Sample Preparation**

Aiken (1988) established that the DOC of the water samples should be no more than 20 mg/L for the adsorptive capacities of the resins to perform properly. The Lake Drummond sample had a DOC of approximately 40 mg/L. Therefore, the Lake Drummond water sample was diluted to 10 mg/L DOC with Milli-Q water before resin column application. Conversely, the DOC of the Chickahominy River water was approximately 7 mg/L and no dilution was required. Due to the large number of carboys (ten) of Lake Drummond water passed through the 1650 mL resin columns, uniform pH and ionic strength conditions were desired among the carboys. The pH was adjusted using a sodium carbonate solution while ionic strength adjustments were made using a sodium chloride solution.

### **Resin Preparation, Sample Application to Resin Columns, and Elution**

The following description follows the chemical fractionation procedure in chronological order as performed in the lab so the entire procedure may be repeated with the utmost of ease. At this point, all three glass resin columns (either the 343 mL

Table 8. Summary of pilot column results.

<b>Resin</b>	<b>Exchange Capacity</b>	<b>Resin Required</b>	<b>Resin Provided</b>
XAD-8	100 (capacity factor)	1520 mL	1650 mL
MSC-1	2.9 meq/g	270 g	1300 g
A-7	23 meq/g	34 g	1080 g

equations to determine resin required from (Leenheer, 1981)

or 1650 mL columns) were packed with cleaned XAD-8, MSC-1, and A-7 resins as described in the Resin Cleaning section.

Milli-Q water was passed through the XAD-8 resin until the effluent DOC from the resin column was within 0.1 mg/L of the influent Milli-Q water. Next, the XAD-8 resin was rinsed with one bed volume of 0.1 N sodium hydroxide (NaOH) followed by one bed volume of 0.1 N hydrochloric acid (HCl). The rinses were performed to elute any hydrophobic bases or hydrophobic acids that may have been adsorbed to the XAD-8 resin. Milli-Q water was rinsed through the resin to flush out any residual 0.1 N HCl.

The pH of the water sample was adjusted to 6.3 before application of the sample to the column. At neutral pH, the XAD-8 resin adsorbed both hydrophobic bases and hydrophobic neutral organic matter. The flow rate was maintained at 10 bed volumes (BV) per hour (Simpson, 1972; Thurman *et al.*, 1978). A bed volume is the total volume of resin including void spaces. Effluent samples were obtained periodically and the DOC measured to ensure that breakthrough had not occurred. After passing the water sample through the column, 2.5 BV of Milli-Q water was passed to displace the water sample remaining in the column. The 1650 mL columns were backflushed with 0.25 BV of 0.1 N HCl followed by 1.5 BV of 0.01 N HCl to elute the hydrophobic bases while the 23.5 mL and 343 mL columns were forward eluted due to being gravity flow fed. Collection of the elution occurred immediately upon application of the 0.25 BV of 0.1 N HCl. Approximately 1.25 BV after HCl breakthrough the desorption of the hydrophobic base fraction was complete. Milli-Q water was passed after the 0.1 N HCl to ensure elution of the hydrophobic bases. The eluted hydrophobic base fraction was refrigerated in 1 L glass amber jars at pH 2 to prevent loss of DOC by volatilization.

Next, the water sample was acidified to pH 2 with 1 N HCl before application to the XAD-8 resin a second time. The acidified water sample permitted adsorption of the hydrophobic acid fraction by the resin. The flow rate was maintained at 10 BV/hour. Effluent samples were obtained periodically and the DOC measured to ensure that DOC breakthrough had not occurred. After passing the water sample through the column, 1 BV of 0.01 N HCl was passed to displace the water sample remaining in the column. The 1650 mL columns were backflushed with 0.25 BV of 0.1 N NaOH followed by 1.5 BV of Milli-Q water to elute the hydrophobic acids while the 23.5 mL and 343 mL column were forward eluted due to being gravity flow fed. The hydrophobic acid fraction was rich in color; therefore, collection of the eluant was stopped when visible elution of the acid fraction had ended. Collection of the eluant commenced immediately upon application of the 0.1 N NaOH and, additional Milli-Q water was passed to ensure elution of the hydrophobic acids. The hydrophobic acid fraction was refrigerated in 1 L glass amber jars at neutral pH. Neutral pH was obtained by the addition of hydrochloric acid.

The XAD-8 resin, now devoid of both the hydrophobic acid and base fractions, contained only the hydrophobic neutral fraction. The resin was unpacked and Soxhlet extracted with methanol for at least one hour. The hydrophobic neutral fraction was removed from the methanol by vacuum distillation using the Brinkmann Instruments, Inc. Büchii Rotavapor (Westbury, NY), Model R110. Vacuum distillation was possible since methanol is not azeotropic with water. The hydrophobic neutral fraction was refrigerated in a 1 L glass amber jar at neutral pH. The XAD-8 resin was repacked in the glass column.



Next, the water sample was passed through the MSC-1 resin to remove the hydrophilic bases. First, 3 BV of 1 N NaOH was passed through the MSC-1 resin column to remove any hydrophilic bases. Next, 4 BV of 2 N HCl were passed through the column to hydrogen saturate the MSC-1 resin. Milli-Q water was then passed through the resin until the specific conductance in the column effluent was less than 10  $\mu\text{mhos/cm}$ . The water sample then was applied to the column at a flow rate of 10 BV/hr. Effluent samples were obtained periodically and the DOC and sodium ion concentration measured to ensure that DOC breakthrough had not occurred. After passing the water sample through the column, 1 BV of 0.01 N HCl was passed to displace the water sample remaining in the column. This step was not included by Leenheer (1981) but was deemed necessary to displace the water sample from the column before elution. All columns (23.5 mL, 343 mL, and 1650 mL) were forward eluted with 1 N NaOH. Collection of the elute commenced immediately upon application of the 1 N NaOH and continued until breakthrough of NaOH occurred. The hydrophilic base fraction was refrigerated in 1 L glass amber jars at neutral pH. Neutral pH was obtained by the addition of hydrochloric acid.

The water sample was finally passed through the A-7 resin to remove the hydrophilic acids. First, 1 N HCl was passed through the A-7 resin column until the DOC of the exiting HCl was less than 1 mg/L. This step ensured that organic bleed from the resin would not occur when the acidified water sample was passed through the resin. Next, 1 N NaOH was passed through the column to place the A-7 resin in the free-base form. Milli-Q water was then passed through the resin until the specific conductance of the column effluent was less than 10  $\mu\text{mhos/cm}$ . The water sample was

applied to the column at a flow rate of 10 BV/hr. Effluent samples were obtained periodically and the DOC and conductance measured to ensure that DOC breakthrough had not occurred. After passing the water sample through the column, 1 BV of Milli-Q water was passed to displace the water sample remaining in the column. The 1650 mL columns were backflushed with 1 N NaOH to elute the hydrophilic acids while the 23.5 mL and 343 mL columns were forward eluted due to being gravity flow fed. Collection of the eluant commenced immediately upon application of the 1 N NaOH and continued until visible bleed from the resin occurred. The hydrophilic acid fraction was refrigerated in 1 L glass amber jars at neutral pH. Neutral pH was obtained by the addition of hydrochloric acid.

The hydrophilic neutral fraction now remained in the water sample. The Lake Drummond hydrophilic neutral fraction was concentrated by vacuum distillation. A conventional still was converted into a vacuum still. The reduced boiling temperature caused by pulling a vacuum hopefully prevented changes in the chemistry of the hydrophilic neutral fraction due to high temperatures. Approximately 189 L of hydrophilic neutral fraction was concentrated to approximately 2.5 gallons. The hydrophilic neutral fraction was refrigerated in a carboy at neutral pH.

### **Apparent Molecular Weight Distributions**

The AMWD of organic matter was determined for the Lake Drummond and Chickahominy River water samples using five ultrafiltration cells manufactured by Amicon, Inc. (Beverly, MA), model 8200. In addition, AMWD data were determined for all six organic fractions obtained from the Lake Drummond water sample. Five ultrafiltration membranes manufactured by Amicon, Inc. (Beverly, MA) with nominal

molecular weight cutoffs of 30,000 (30K) (YM-30), 10,000 (10K) (YM-10), 3,000 (3K) (YM-3), 1,000 (1K) (YM-1), and 500 (0.5K) (YC-05) atomic mass units (amu) were used. Five magnetic stir plates (one for each ultrafiltration cell manufactured by Corning, (Corning, NY)) rotated the stir bar in each cell to prevent build-up of organic material on the membranes.

The ultrafiltration cells were cleaned by washing the cells in the same detergent used for the glassware. However, the membranes were first soaked in Milli-Q water for at least thirty minutes. After inserting the membranes into the ultrafiltration cells, the cells were filled with 200 mL of Milli-Q water and pressurized to 45 pounds per square inch (psi) using nitrogen gas. Milli-Q water was passed through the membranes until the effluent DOC was deemed equivalent to Milli-Q water.

Sample volumes of 200 mL were typically used and were processed in parallel through the five ultrafiltration cells. The first 80 mL of each cell's effluent were captured in 10 mL increments in eight 40 mL amber vials. The samples were acidified with 3 N HCl and the DOC of each vial was measured on the Shimadzu TOC-5000A. Eight samples were obtained from each cell to account for variances in the DOC during sample collection caused by concentration polarization. The eight DOC values from the eight vials were used to determine a true DOC value using a mass balance approach developed by Logan and Jiang (1990).

After 80 mL of sample had passed through the membrane, the nitrogen gas to the cell was shut off and the cell vented to depressurize the cell. With flow through the membrane stopped, the stir bar continued stirring for approximately fifteen minutes to permit any organic material on the membrane to dissolve back into solution. The cell

was depressurized and the sample discarded. Next, 200 mL of Milli-Q water with 5 mL of 1 N NaOH was added to the cell and approximately 150 mL passed through the membrane to lyse any microorganisms and to clean the membrane. Then, 200 mL of Milli-Q water with 5 mL of pH 7 phosphate buffer were added to the cell and approximately 150 mL passed through the membrane to neutralize the base. Finally, 150 mL of Milli-Q water was passed through the membrane.

### **Jar Testing**

Jar tests were performed on both the Lake Drummond and Chickahominy River water samples, four of the Lake Drummond organic fractions, mixtures of the hydrophobic acid and hydrophobic neutral fractions, and the <10K hydrophobic acid fraction. Alum was used in all experiments except for the <10K hydrophobic acid fraction in which both alum and ferric chloride was used. The same jar test procedures were followed regardless of the samples being studied and the chosen coagulant. All jar tests were performed to analyze the removal of DOC as a function of pH, coagulant dose, or type of coagulant.

First, the samples were diluted with Milli-Q water to a targeted DOC value, if necessary. For example, all four of the Lake Drummond organic fractions tested were diluted to 5 mg/L DOC before jar testing so coagulation results could be compared. Next, 300 mL, 500 mL, or 1 L of sample were poured into rectangular, glass jar testing jars. Either NaOH or HCl was added using a Fisher Scientific Pasteur pipette (Springfield, NJ) model 13-678-20C to adjust the pH of the samples to the desired value. Next, the jars were placed under a Phipps and Bird six-paddle stirrer (Richmond, VA) model 300. The samples were stirred for approximately 10 minutes at 100 revolutions

per minute (rpm) to allow equilibrium with the atmosphere. NaOH and HCl were added to make any minor adjustments to achieve the desired solution pH. During the ten minute stirring time, 40 mL amber vials were filled with a stoichiometric amount of 0.1 N NaOH to neutralize the acidic effect of the coagulant dose that would be added to each jar.

The jar tests consisted of five stages: rapid mixing, three flocculation stages, and sedimentation. Rapid mixing was at a speed of 100 rpm for two minutes during which coagulant and base addition occurred. The coagulant was added using either a 1 mL or 5 mL automatic pipette. Base was added from the 40 mL vials. Following simultaneous coagulant and base addition minor pH adjustments were made using NaOH or HCl to maintain the initial pH values using NaOH or HCl. The total amount of acid, base, and coagulant added was less than 3% of the original sample volume to minimize dilution effects. First stage flocculation occurred at a speed of 40 rpm for ten minutes during which pH adjustment sometimes occurred. Second- and third-stage flocculation were for ten minutes each at speeds of 30 and 20 rpm, respectively. After third-stage flocculation the jar test stirrer was turned off, and the paddles were removed from the samples. Sedimentation occurred for one hour.

Following sedimentation, the water samples were passed through either a Whatman 934-AH (Whatman International Ltd., Maidstone, England) glass microfibre filter or a Gelman Sciences 61631 (Ann Arbor, MI) 1  $\mu\text{m}$  glass fibre filter to remove solid, precipitated aluminum/organic or iron/organic material. The filters were held in a Gelman Sciences 4201 (Ann Arbor, MI) vacuum filter holder which was placed on a 1 L filter flask. A Fisher Scientific (Springfield, NJ) vacuum pump supplied the vacuum. All

filters were cleaned to remove any organic material by passing 1 L of Milli-Q water through the filters prior to processing the water samples. Experiments determined that 1 L of Milli-Q water was sufficient to remove all organic material from the filters. A separate filter was used for each water sample with as many as four filters required for some samples due to filter fouling. The filter flask and vacuum filter holder were rinsed three times with Milli-Q water between samples. The DOC of the filtered samples were measured using the Dohrmann DC-80 or the Shimadzu TOC-5000A.

## **Specific Experiments**

### **pH Optimization**

As mentioned earlier, the pH of optimum organics removal with alum from the Lake Drummond water sample was determined through jar testing. The pH range evaluated was from 5.5-6.5 using pH increments of 0.1. The coagulant dose selected was less than the expected enhanced dose to ensure that organics removal was dependent on pH and not the dose. The pH of optimum organics removal was then used to determine the enhanced dose. The optimum pH was used in the coagulation of the Lake Drummond and Chickahominy River samples and mixtures of the hydrophobic acid and hydrophobic neutral fractions.

### **Dose Enhancement**

Jar tests were performed with alum on the Lake Drummond water sample to determine the enhanced alum dose for organics removal. Using the optimum pH, coagulant doses from 25 mg/L to 150 mg/L were used. The coagulant dose increments were initially 25 mg/L and then 10 mg/L followed by 5 mg/L as the enhanced dose range narrowed through subsequent experiments. The enhanced dose was used in the

coagulation of the Lake Drummond and Chickahominy River samples, the four Lake Drummond organic fractions, and the mixture of hydrophobic acid and hydrophobic neutral fractions.

### **Characterization of Lake Drummond and Chickahominy River Water**

Both the Lake Drummond and Chickahominy River waters were fractionated and the fractions quantified using the 300 mL resin columns as described previously. Next, both water samples were coagulated at the optimum pH and enhanced alum dose as described previously. Following coagulation, the samples were passed through the resin columns to fractionate and quantify the residual organic matter present. The AMWD of the DOC present in the untreated Lake Drummond and Chickahominy River water samples and the coagulated Lake Drummond water sample was determined as described previously.

### **Study of Lake Drummond Organic Fractions**

The hydrophobic acid, hydrophobic neutral, hydrophilic acid, and hydrophilic neutral fractions used for jar testing were obtained by passing the Lake Drummond water through the 1650 mL resin columns. The effect of pH on the removal of organic material at the enhanced alum dose was performed on all four fractions by performing jar tests at various pH values. AMWD for all six chemically fractionated organic fractions were performed as described previously.

### **Coagulation of Hydrophobic Acid and Hydrophobic Neutral Mixtures**

From analysis of the results, it was decided to study the effect that the hydrophobic acid and hydrophobic neutral fractions had on each other in terms of organic removal during coagulation. Solutions of varying ratios of hydrophobic acid

fraction to hydrophobic neutral fraction were prepared (all containing approximately 5 mg/L DOC) and coagulated at the optimum pH and enhanced dose as described in the jar test procedure. The coagulated samples were passed through the XAD-8 resin in the 23.5 mL column at pH 6.3. The hydrophobic neutral fraction should be adsorbed at pH 6.3 while the hydrophobic acid fraction should pass through the resin column. Following measurement of the DOC of the XAD-8 resin column effluent, the amount of organic material remaining in both fractions was quantified through mass balance calculations.

### **Hydrophobic Acid and Hydrophobic Neutral Fractions through the XAD-8 resin**

The results of passing the mixtures of hydrophobic acid and hydrophobic neutral coagulated solutions through the XAD-8 resin led to the premise of possible incomplete adsorption of the hydrophobic neutral fraction and partial adsorption of the hydrophobic acid fraction onto the XAD-8 resin. At pH 6.3, all of the hydrophobic acid fraction should pass through the XAD-8 resin with no adsorption while the hydrophobic neutral fraction should completely adsorb to the XAD-8 resin.

In the first experiment, 70 mL of diluted hydrophobic acid fraction was passed through the resin column at pH 6.3. Continuous 10 mL samples of the effluent were collected, and the DOC of these samples quantified. Next, 300 mL of diluted hydrophobic acid fraction was passed through the resin column at pH 6.3. Every 30 mL, 10 mL samples of the effluent were collected, and the DOC was monitored. In the third experiment, 90 mL of previously coagulated then filtered (<1  $\mu\text{m}$ ) hydrophobic neutral fraction was passed through the resin column at pH 6.3 while in a subsequent experiment 90 mL of previously coagulated then filtered (<30K) hydrophobic neutral



fraction was passed through the resin column at pH 6.3. In both experiments 10 mL samples were collected continuously and the DOC and residual aluminum were monitored. Finally, 90 mL of diluted hydrophobic neutral fraction was passed through the resin column at pH 6.3, 10 mL samples were collected continuously, and the DOC was monitored.

### **Phase-Change Behavior of DOC, Aluminum, and Iron**

As described earlier, at lower doses of alum, the literature suggests the presence of colloidal organic material following coagulation. A pH and dose study were performed using alum to determine the pH and dose where the presence of colloidal organic material occurs. 1  $\mu\text{m}$ , 100K amu (YM-100), and 30K amu (YM-30) filters and membranes were used to establish the operational definitions of particulate, colloidal, and dissolved organic material previously mentioned. The Lake Drummond hydrophobic acid organic fraction was selected to be studied since it was both most prevalent in the Lake Drummond water and the most amenable to coagulation.

First, the Lake Drummond hydrophobic acid fraction was passed through a 10K nominal molecular weight membrane using the ultrafiltration procedure defined earlier. The 10K membrane ensured the presence of any organic material in the operationally defined colloidal fraction (30K to 100K) would be the result of coagulation only. During the study, the <10K hydrophobic acid fraction was diluted to approximately 5 mg/L with Milli-Q water for all jar tests.

All jar tests were performed according to the procedure previously defined. Following sedimentation, samples were passed through a 1  $\mu\text{m}$  filter. The 1  $\mu\text{m}$  filtrate was split and passed through 100K and 30K nominal molecular weight membranes.

The measurement of DOC from eight different vials to identify the true DOC value as performed during the apparent molecular weight distributions was deemed unnecessary. Experiments showed that the DOC did not vary greatly in the ultrafilter effluent when 100K and 30K membranes were used. The variation in DOC values occurred when using membrane sizes less than 30K as in the apparent molecular weight distributions. Following ultrafiltration, 100 mL of effluent was collected from both the 100K and 30K membranes. Approximately 10 mL of sample was poured into separate 40 mL amber vials for DOC and aluminum analysis. Separate vials were used since the DOC samples were acidified with  $H_3PO_4$  which was incompatible with metals' analytical equipment. DOC samples were measured on the Dohrmann DC-80 while the residual aluminum and iron were determined as previously described.

The first experiment consisted of a constant alum dose of 50 mg/L over a pH range from 4.5-7.5 in 0.5 pH increments. The DOC and residual aluminum of the 1  $\mu$ m filter, 100K membrane and 30K membrane effluents were measured to identify pH values at which the presence of colloidal organic matter was observed. The second experiment used a constant pH of 5.8 while varying the alum dose from 5-50 mg/L in 5 mg/L increments. The pH 5.8 value was selected since that is in the general range of the pH of minimum aluminum solubility. Again, the DOC and residual aluminum of the 1  $\mu$ m filter, 100K membrane and 30K membrane effluents were measured to identify alum doses where colloidal organic matter was present. For comparative purposes, the third experiment used ferric chloride as the coagulant. The ferric chloride doses were varied while maintaining a constant pH of 5.5. The ferric chloride doses were equivalent to the alum doses on a aluminum:iron molar basis.

Information gained from the second experiment was used to determine the alum dose for the fourth experiment. The alum dose used was the dose where the largest generation of colloidal organic material occurred. A coagulant aid in the form of a nonionic polymer, POL-E-Z 652 (manufactured by Calgon Corporation (Pittsburgh, PA), was added during the first stage flocculation step. Polymer addition was studied to evaluate the ability of polymer to remove colloidal organic material following coagulant addition. DOC and residual aluminum concentration were measured on coagulated samples to determine the polymer dose that minimized the production of colloidal organic material.

## Chapter IV

### EXPERIMENTAL RESULTS

This chapter presents the results from the experiments described in the Methods and Materials chapter. The outline of the chapter is as follows:

1. Lake Drummond pH Optimization and Dose Enhancement
2. Lake Drummond and Chickahominy River Fractionation Results and Apparent Molecular Weight Distributions
3. Apparent Molecular Weight Distributions and Coagulation of Organic Fractions
4. Hydrophobic Acid and Hydrophobic Neutral Coagulation Study
5. Phase-Change Behavior of Organic Material

#### **Lake Drummond pH Optimization and Dose Enhancement**

The pH of optimum organics removal and the dose of enhanced organics removal were determined for the Lake Drummond water. The results of these experiments were used to establish uniform jar testing conditions. For example, both the Lake Drummond and Chickahominy River water samples were coagulated at the same pH and alum dose.

The alum dose for the pH optimization experiment was arbitrarily set at a suboptimum value of 25 mg/L to ensure observed DOC removal was a function of pH and not dose alone. A large dose would have negated the pH effect by swamping the water sample with alum. Data presented in Figure 6 illustrate that the pH of optimum

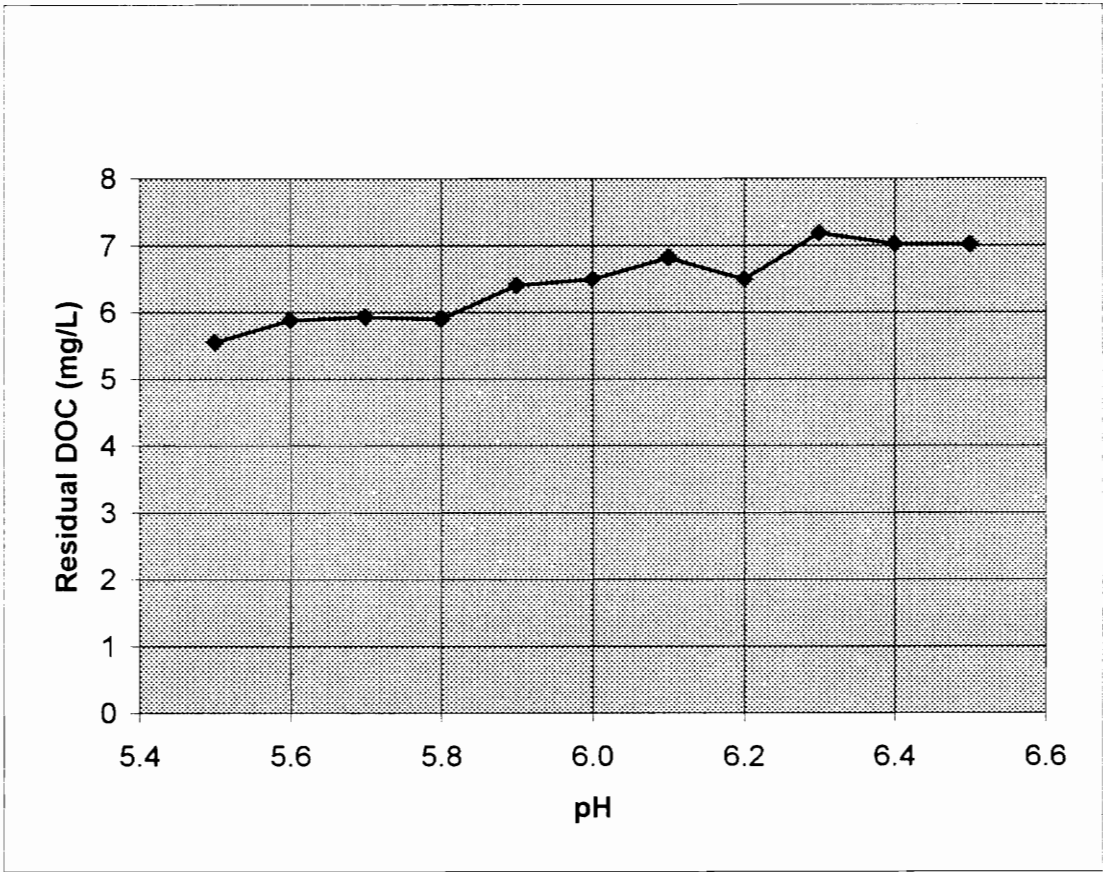


Figure 6. Results of coagulation of Lake Drummond water with a constant alum dosage (alum = 25 mg/L) at various pHs. (original DOC = 10.0 mg/L)

organics removal was 5.5 for the pH range tested. Lower pH values were not tested since utilities rarely treat waters under such acidic conditions for various reasons (i.e. aggressive nature of low pH waters on basins, increased residual Al content in treated water). Results of dose enhancement studies (Figure 7) show a 50 mg/L alum dose satisfied the criteria for this water.

### **Lake Drummond and Chickahominy River Fractionation Results**

The untreated Lake Drummond and Chickahominy River samples were chemically and physically fractionated to characterize the DOC. Untreated and coagulated samples were chemically fractionated using synthetic resin adsorption. Apparent molecular weight distributions using ultrafiltration were performed to physically characterize the untreated and coagulated water samples except for the coagulated Chickahominy River water. As discussed earlier, adsorption characteristics of synthetic resins are influenced by pH, ionic strength, and flow rate. Therefore, the pH and ionic strength of the untreated and coagulated Lake Drummond water samples were adjusted to similar values prior to application to the resin columns as were the untreated and coagulated Chickahominy River water samples. The flow rate through the resins was maintained at 10 BV/hr for all samples. The DOC of all samples varied slightly but were sufficiently dilute (i.e. DOC  $\approx$ 10 mg/L) to negate any adverse concentration effects (Aiken, 1988). Dilution of the Lake Drummond water sample with Milli-Q water was necessary to achieve a DOC of approximately 10 mg/L. Table A-2 summarizes the pertinent fractionation conditions.

The DOC of water samples prior to coagulation were essentially the same as the untreated water samples. The pH and ionic strength differences between all samples

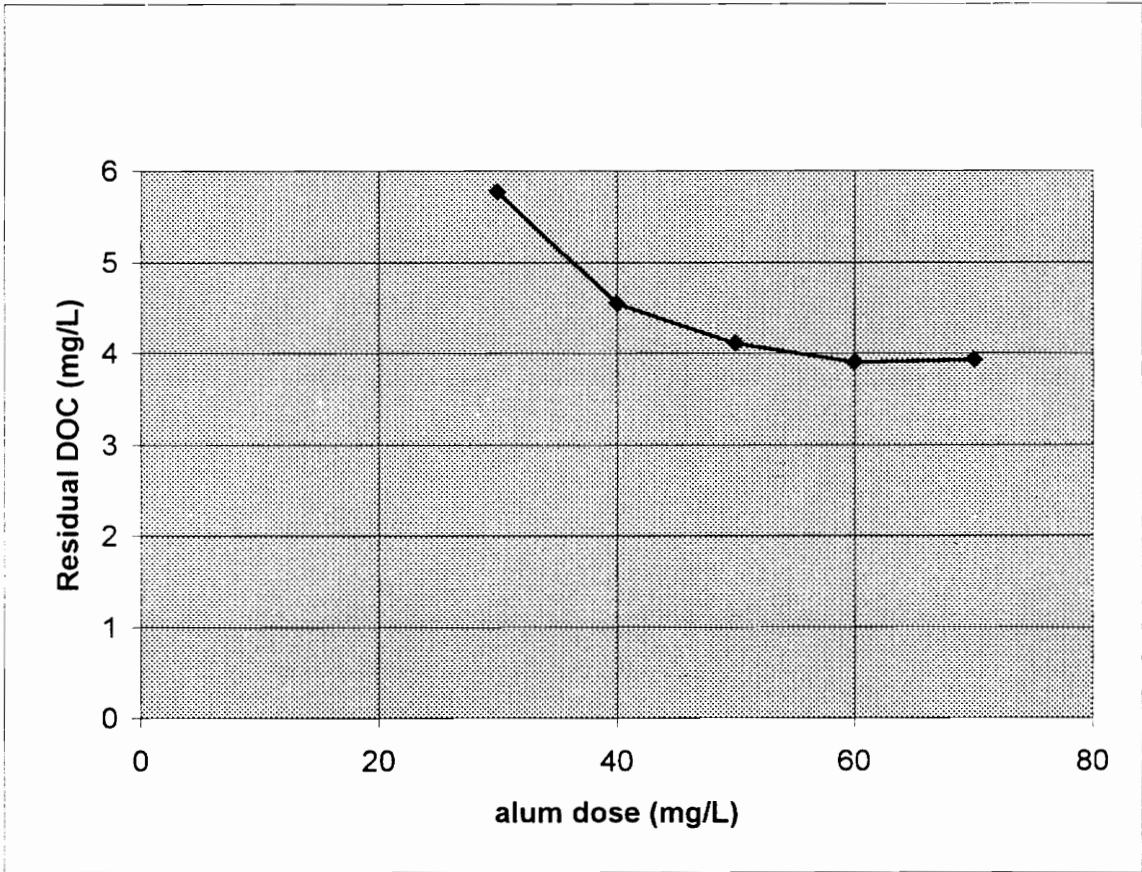


Figure 7. Results of coagulation of Lake Drummond water with varying alum dosages at pH 5.5. (original DOC = 9.9 mg/L)

were minimal making the results between all samples comparative (Thurman et al., 1978). Samples were coagulated at the optimum pH (5.5) and the enhanced dose (50 mg/L). Chemical fractionation of the samples was performed as described in the Methods and Materials chapter. Mass balance calculations were performed on the desorbed fractions rather than on the adsorbed fractions since the DOC was concentrated in a much smaller volume, allowing for fewer DOC measurements and minimizing volume errors (Leenheer and Huffman, 1976). Mass balance calculations on the adsorbed fractions would have involved measuring the DOC of the column effluent after each resin pass to quantify the organic carbon adsorbed on the resin column.

### **Lake Drummond Fractionation Results**

The DOC of Lake Drummond water was approximately 45 mg/L giving it a distinct, brown-like, tea color (dilution of the sample to  $\approx 10$  mg/L DOC was necessary for resin application). The hydrophobic acids were the predominant organic fraction representing 72% of the total DOC (Figure 8 and Table A-3) in the untreated Lake Drummond water sample. This result is not surprising as color is typically a result of humic and fulvic acids (hydrophobic acids); those acids that adsorb to XAD-8 resin at pH 2 (Thurman, 1985). Furthermore, the pH of Lake Drummond was 4.5 indicating a high concentration of organic acids. Finally, much of the organic carbon in Lake Drummond originates from the surrounding swamp. The swamp water DOC is predominately from allochthonous (soil organic matter) sources, and soil is very high in organic acids.

The next largest organic fraction was the hydrophilic neutrals totaling 11% of the DOC. Bose et al. (1993) reported 22% of the DOC in Forge Pond to be hydrophilic



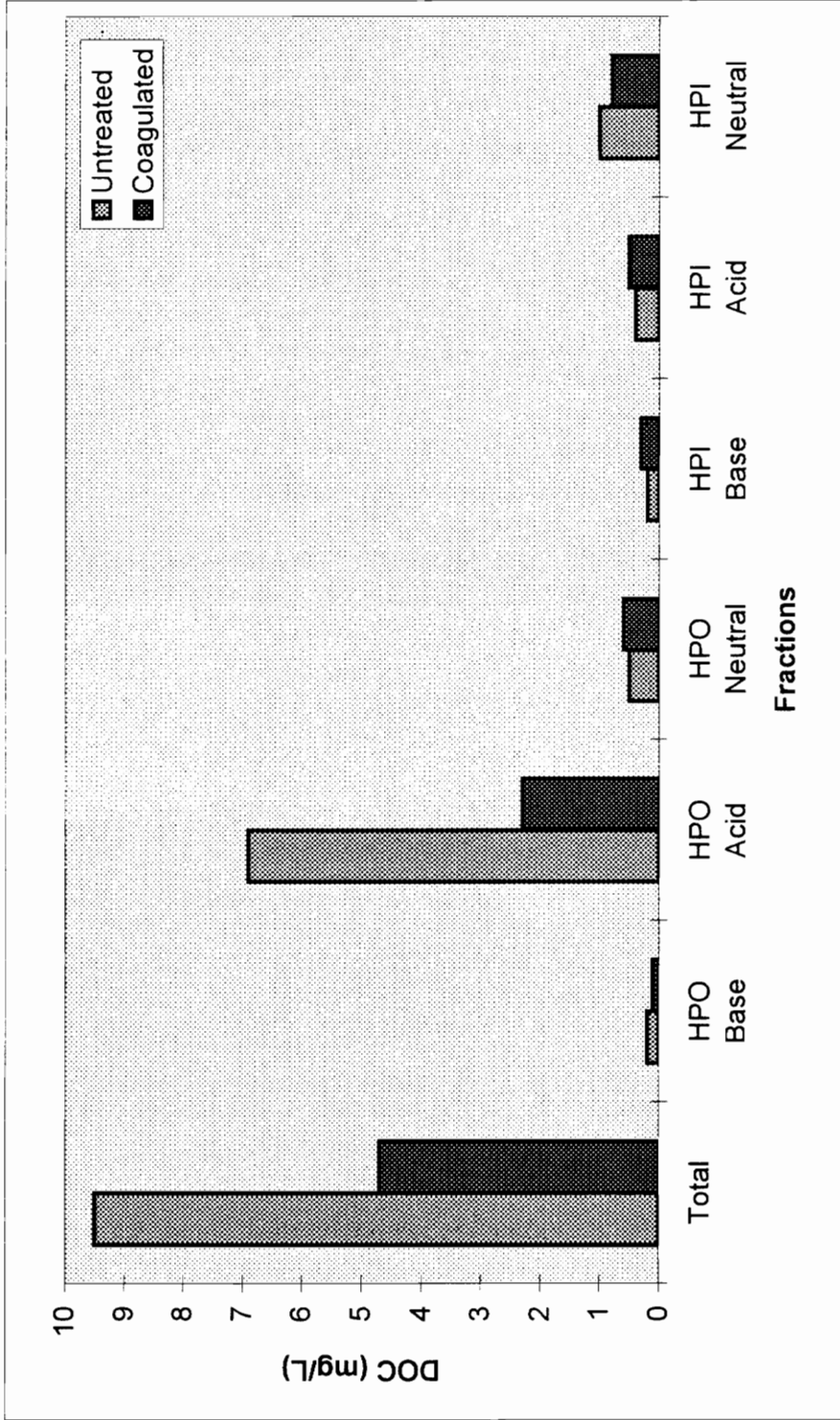


Figure 8. Comparison of the relative amounts of DOC in each organic fraction in untreated and alum coagulated Lake Drummond water. (untreated sample DOC = 9.5 mg/L, coagulated sample DOC = 4.3 mg/L)

neutrals. Bose used fractionation procedure C which is almost identical to fractionation procedure D; however, care must be taken when comparing fractionation results between studies due to variability in both fractionation procedures and water sources. Hydrophobic and hydrophilic base fractions were small for Lake Drummond which is always the case for natural waters since natural waters are generally devoid of basic functional groups (Thurman, 1985).

Recovery of organic solutes from the resins was 96% which demonstrates that the resins definitely provided quantifiable results. Any error in measurement was probably either in the hydrophobic acid or hydrophilic neutral fraction. The hydrophobic acid DOC concentration was so large (66 mg/L) that any error would magnify itself. The hydrophilic neutral fraction was the only unconcentrated fraction and any volume measurement error would greatly manifest itself in the mass balance calculation.

The hydrophobic acids were the largest organic fraction of the coagulated Lake Drummond water representing 50% of the total DOC (Table A-3). The hydrophilic neutral fraction was the next largest fraction measuring 18% of the DOC. Figure 8 illustrates the changes in organic carbon concentration between the untreated and coagulated Lake Drummond water samples. The hydrophilic base fraction underwent the largest change based on percent (110%), but a small change in terms of concentration (0.18 mg/L DOC). Obviously, coagulation removed more of the hydrophobic acid fraction than any other fraction. Hydrophobic acids are more amenable to coagulation due to their hydrophobic nature, large number of sites for potential complexation, and negative charge at pH 5.5 (Bose, 1993). Positively charged aluminum monomers, polymers, and  $\text{Al}(\text{OH})_{3(s)}$  are the predominate aluminum species

at pH 5.5 and bind readily with the negatively charged hydrophobic acids. Coagulated Lake Drummond water sample DOC recovery from the resins (101%) was deemed quite acceptable.

Apparent molecular weight distributions were performed on both the untreated and coagulated Lake Drummond water samples and the AMWD results are shown in Figure 9 and Table A-4. The untreated Lake Drummond AMWD indicates that a significant amount of the organic material in the untreated water (20%) was greater than 30,000 amu. The majority of the organic material (54%) was larger than 3,000 amu. Due to the large molecular weight of hydrophobic acids, the AMWD was on the high end since 72% of the untreated water DOC was hydrophobic acids. The AMWD of the treated water indicates that coagulation removed the high molecular weight material (Croué *et al.*, 1993; Semmens and Staples, 1986). The majority of the coagulated water DOC was less than 1,000 amu and effectively no DOC was larger than 30,000 amu. Overall, coagulation removed 53% of the DOC (untreated water DOC was 10.0 mg/L). Over 50% removal of DOC is very good, but it is expected since most of the DOC was amenable to coagulation (i.e. initially present as hydrophobic acids).

### **Chickahominy River Fractionation Results**

Like Lake Drummond, hydrophobic acids constituted the largest portion of the Chickahominy River DOC at 66% (Figure 10 and Table A-5). Similarly, the hydrophilic neutral fraction represented the second largest fraction of the DOC at 14%. Unlike Lake Drummond (which resides in a swamp), it is somewhat unusual for the hydrophobic acid fraction to be this large for a river. Malcolm *et al.* (1977) reported that Leenheer found the hydrophobic acids for Evacuation Creek near Bonanza, Utah to have a hydrophobic

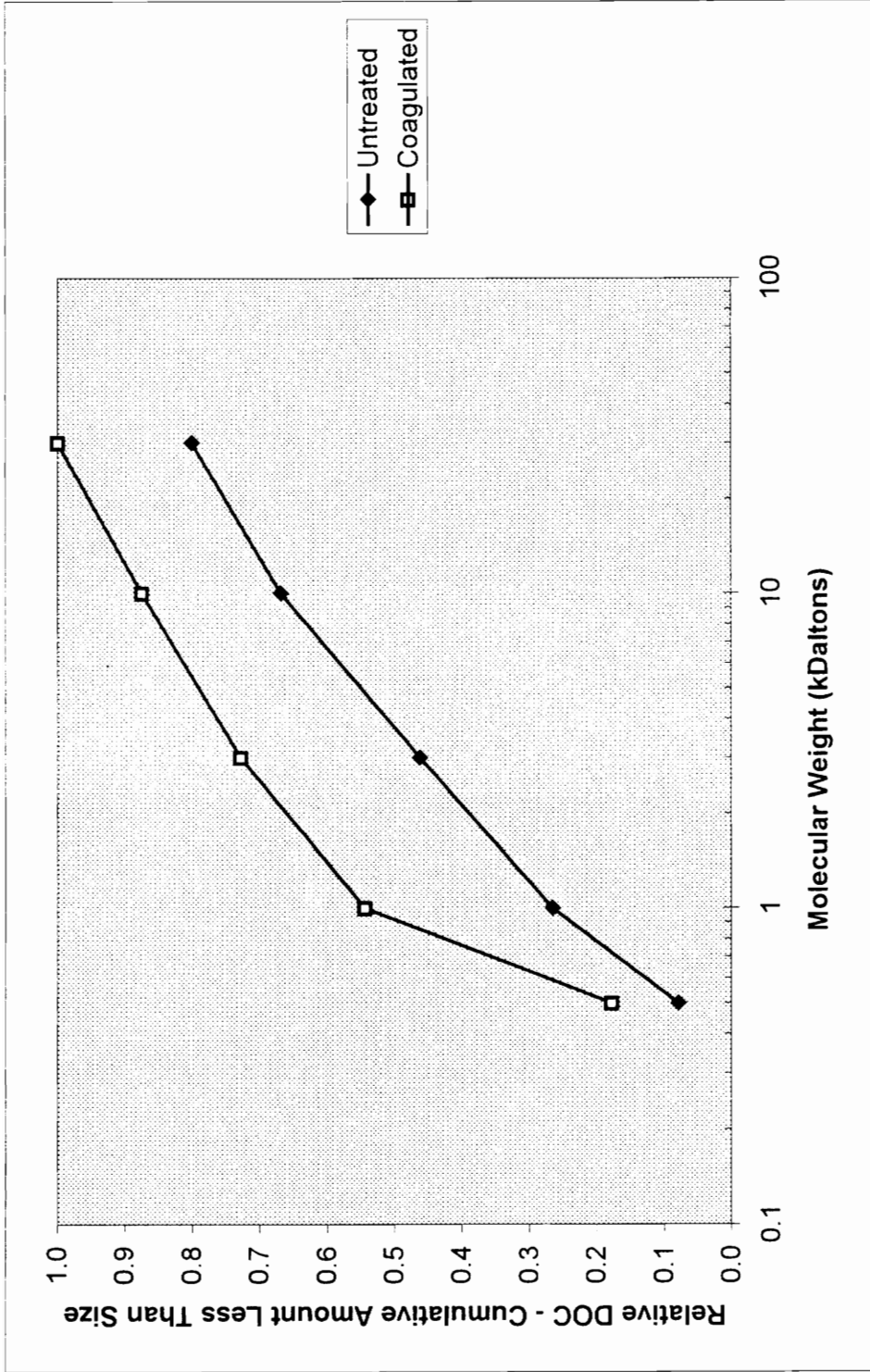


Figure 9. Untreated and coagulated Lake Drummond apparent molecular weight distributions. (untreated sample DOC = 10.0 mg/L, coagulated sample DOC = 4.8 mg/L)

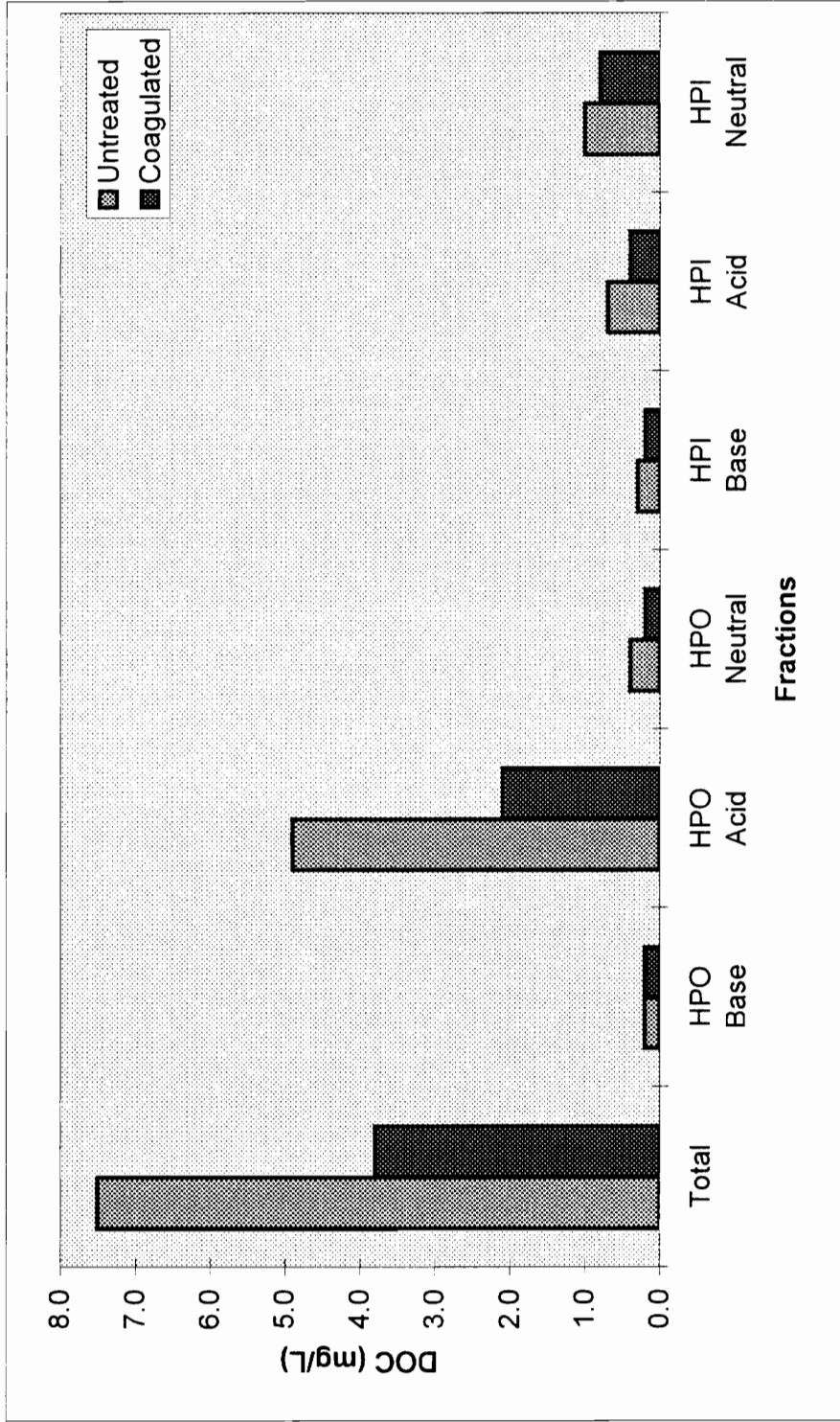


Figure 10. Comparison of the relative amounts of DOC in each organic fraction in untreated and alum coagulated Chickahominy River water. (untreated sample DOC = 7.5 mg/L, coagulated sample DOC = 3.8 mg/L)

acid content of 40% using fractionation procedure C. Leenheer (1981) found the South Platte River near Denver, Colorado to have a hydrophobic acid content of only 16% using fractionation procedure D. Thurman (1985) stated humic substances typically contribute 30-50% of the DOC in natural waters while 50-90% of the DOC in colored waters. These results indicate that organic content is highly dependent on the topography, climate, and geology of the area surrounding the water source. The Chickahominy River sampling location does have approximately the same climate, topography, and geology as Lake Drummond, and the results from the studies mentioned above indicate the speciation of DOC varies greatly between water bodies.

The concentration of hydrophobic base and neutral fractions and the hydrophilic base and neutral fractions were approximately the same for both the Lake Drummond and Chickahominy River waters. Organic solute recovery from the fractionation process was an acceptable 101%. Sources of measurement error of the organic fractions were the hydrophobic acid and hydrophilic neutral fractions as discussed earlier.

The coagulated Chickahominy River fractionation results indicate removal to some degree of all organic fractions except for the hydrophobic base fraction. The hydrophobic base fraction represented such a minimal amount of the total DOC that the observed slight increase may be considered negligible. The largest fraction removed was the hydrophobic acid fraction with 57% removed. The hydrophobic acid fraction still constituted over 50% of the DOC remaining, however. The recovery of organic fractions was 102%.

The AMWD of the untreated Chickahominy River sample is shown in Figure 11 and Table A-6. Only 7% of the DOC was larger than 30,000 amu compared with 20% of

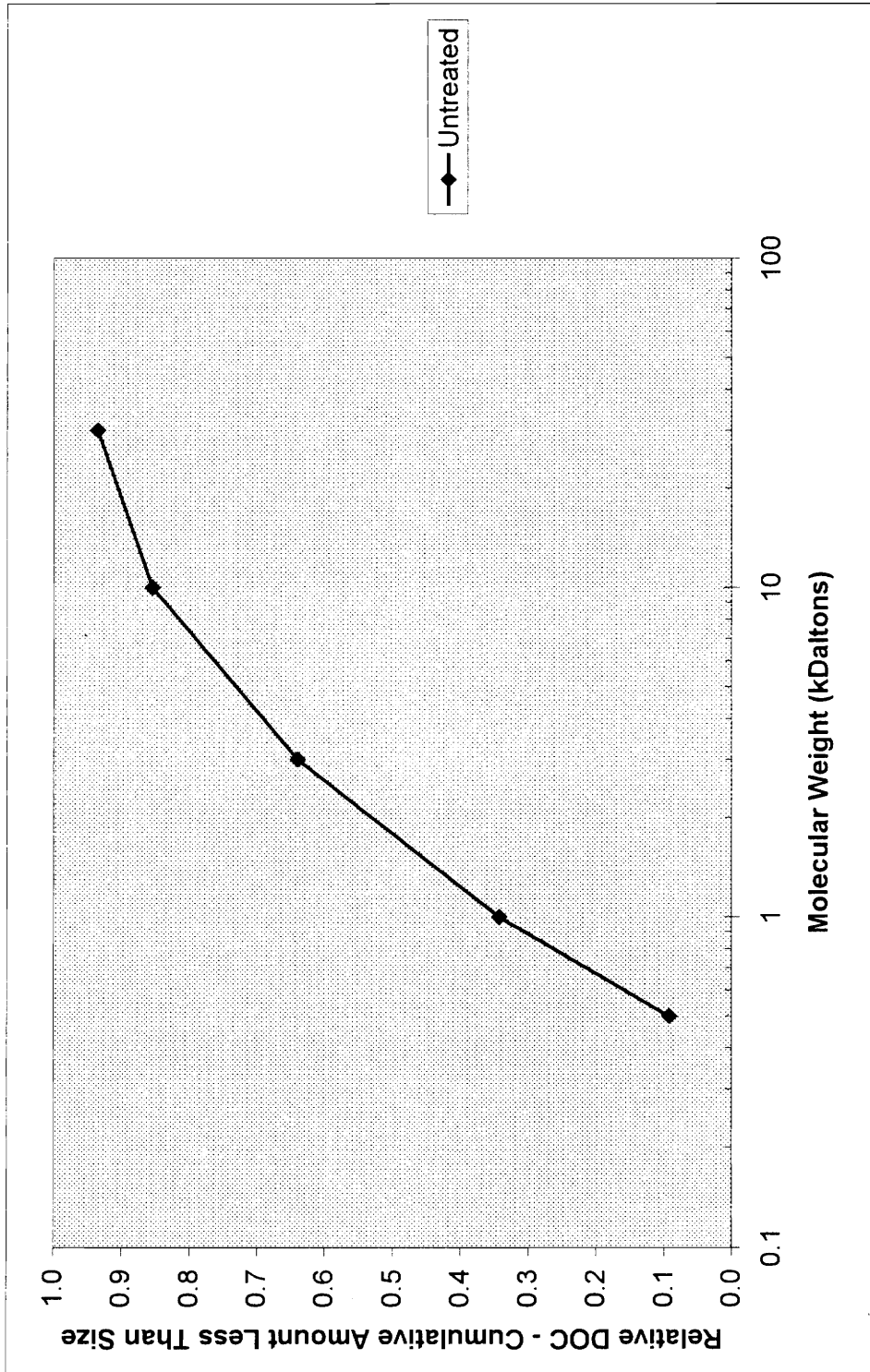


Figure 11. Untreated Chickahominy River apparent molecular weight distribution. (untreated sample DOC = 8.1 mg/L)

the Lake Drummond DOC. Also, 64% of the Chickahominy River DOC was less than 3,000 amu while 46% of the Lake Drummond DOC was less than 3,000 amu. Swamps will have generally more hydrophobic acids (especially humic acids which have large molecular weights) than rivers (Thurman, 1985). Even though the majority of organic solutes in the Chickahominy River were hydrophobic acids, they were smaller in molecular weight than the Lake Drummond hydrophobic acids. Most likely the Chickahominy River contained more fulvic acids than humic acids while Lake Drummond contained more humic acids than fulvic acids. An AMWD of the coagulated Chickahominy River sample was not performed.

### **Organic Fractions Apparent Molecular Weight Distributions and Coagulation Studies**

This study involved performing AMWDs and coagulation studies on the individual Lake Drummond organic fractions. AMWDs were determined for all six DOC fractions while coagulation studies were performed on the hydrophobic acid, hydrophobic neutral, hydrophilic acid, and hydrophilic neutral fractions. Coagulation studies were not performed on either base fraction due to a lack of sufficient mass of organic material.

#### **Apparent Molecular Weight Distributions**

Figures 12 and 13 and Table A-7 contain the AMWDs of the six Lake Drummond organic fractions in both graphic and tabular form. A general synopsis of the results indicates that the hydrophilic fractions had AMWDs smaller in size than their hydrophobic counterparts (except for the base fractions). The hydrophobic and hydrophilic base fractions had very similar AMWDs. As expected the hydrophobic acid fraction had the largest AMWD with a median size somewhere between 3,000 amu and



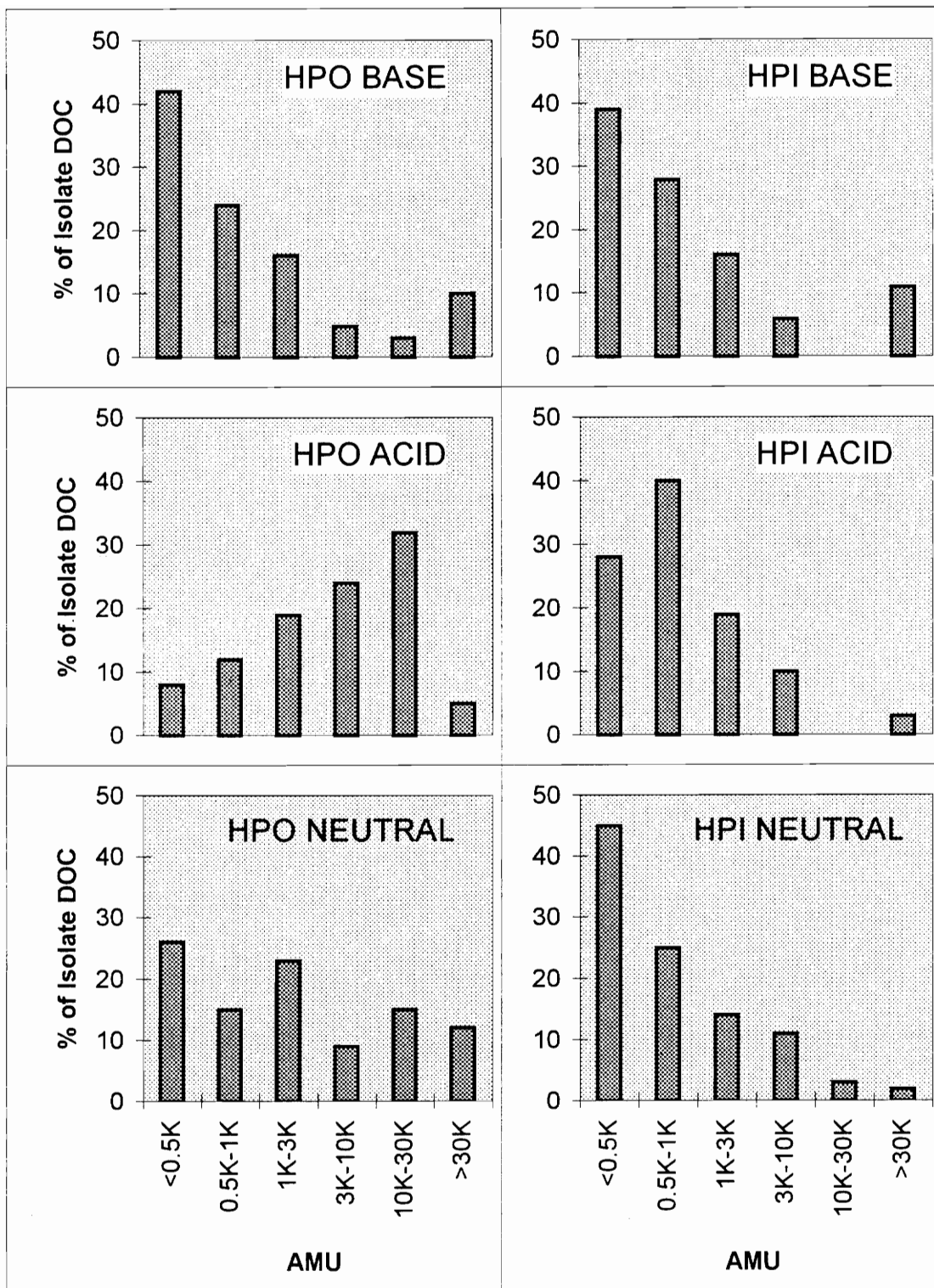


Figure 12. Lake Drummond organic fractions apparent molecular weight distributions. (HPO = hydrophobic, HPI = hydrophilic)

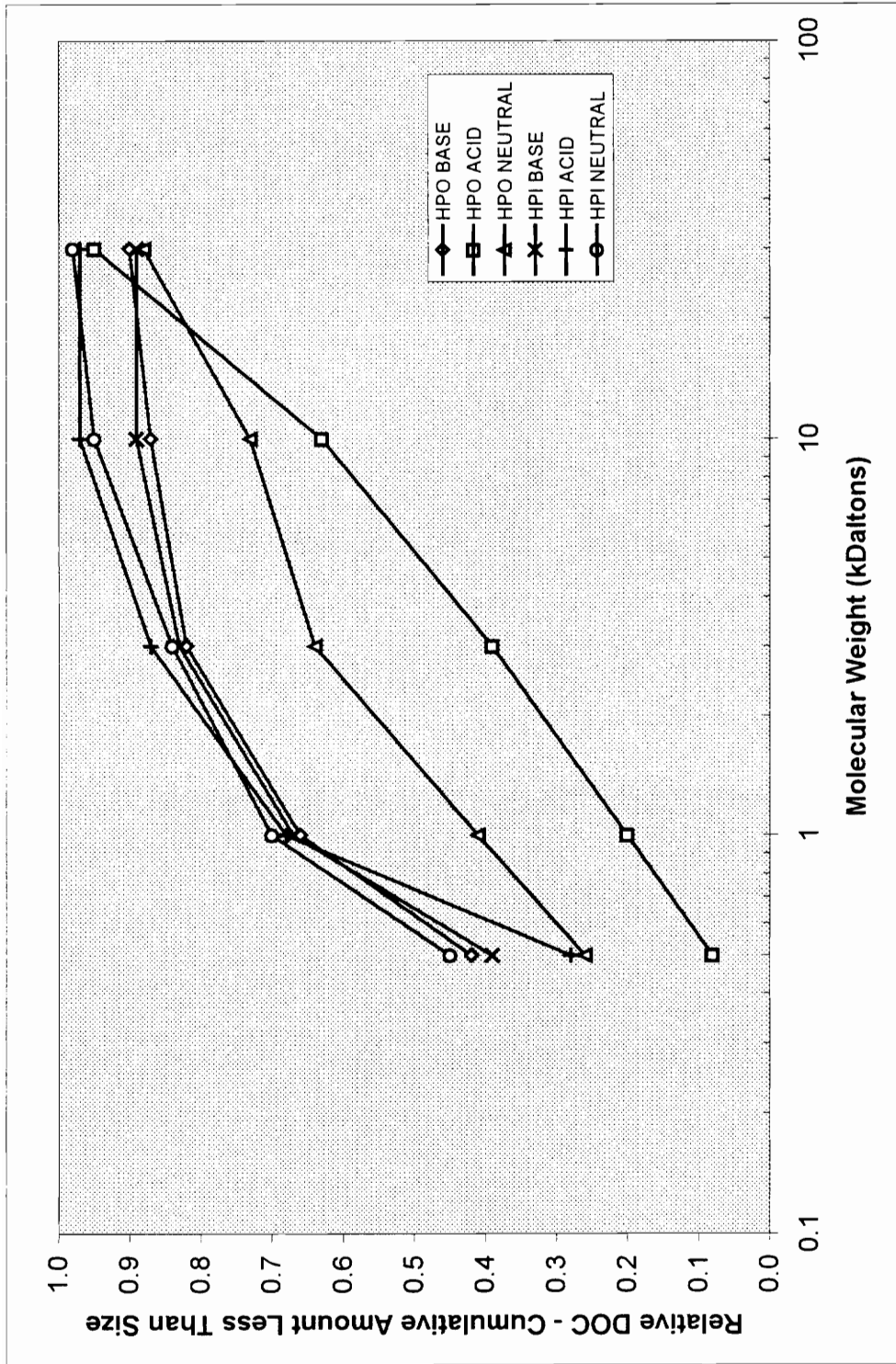


Figure 13. Lake Drummond organic fractions apparent molecular weight distributions.

10,000 amu. The median size of the base fractions, hydrophilic acid fractions, and hydrophilic neutral fraction were all between 500 amu and 1,000 amu. The median size of the hydrophobic neutral fraction was between 1,000 and 3,000 amu. The smallest AMWDs were the hydrophilic base fraction, hydrophobic base fraction, and hydrophilic neutral fraction. The large molecular size of the hydrophobic acid fraction directly correlates to its excellent DOC removal during coagulation.

Bose et al. (1993) determined AMWDs for all organic fractions from Forge Pond except the hydrophobic base fraction due to a lack of sufficient amount of organic material. In addition, Bose also separated the hydrophobic acid fraction into humic, fulvic, and weak hydrophobic acids. As expected, Bose found the humic acids to be much larger in size than the fulvic acids with the weak hydrophobic acids in the middle. Table 9 compares the Lake Drummond organic fraction AMWDs with those of Forge Pond. The Lake Drummond hydrophobic acid fraction most closely resembles the Forge Pond humic acid fraction based on a comparison of fractionation procedures. The Lake Drummond hydrophobic acid fraction most likely contained more humic acids than fulvic acids due to the surrounding Dismal Swamp. As Table 9 shows, the majority of the hydrophobic acid fraction in both waters is larger than 3,000 amu. Also, over 60% of the hydrophilic neutral fraction is less than 1,000 amu. The AMWDs of the remaining three fractions (hydrophobic neutral, hydrophilic base, hydrophilic acid) differ, however. This difference is indicative of the wide range of molecular sizes found within specific organic fractions. In summary, the AMWDs of the Lake Drummond organic fractions agree well with literature reported values.

Table 9. Comparison of Lake Drummond organic fractions AMWDs with Forge Pond organic fractions AMWDs.

Apparent Molecular Weight Distribution Ranges	Lake Drummond (% of Isolate DOC)	Forge Pond (% of Isolate DOC) *
		Hydrophobic Acid **
<500 amu	8	17
500 - 1,000 amu	12	10
1,000 - 3,000 amu	19	7
>3,000 amu	61	66
		Hydrophobic Neutral
<500 amu	26	59
500 - 1,000 amu	15	9
1,000 - 3,000 amu	23	12
>3,000 amu	36	20
		Hydrophilic Base
<500 amu	39	24
500 - 1,000 amu	28	17
1,000 - 3,000 amu	16	21
>3,000 amu	17	38
		Hydrophilic Acid
<500 amu	28	50
500 - 1,000 amu	40	9
1,000 - 3,000 amu	19	16
>3,000 amu	13	25
		Hydrophilic Neutral
<500 amu	45	40
500 - 1,000 amu	25	18
1,000 - 3,000 amu	14	19
>3,000 amu	16	23

\* The values for Forge Pond were estimated from a bar graph.

\*\* The Lake Drummond hydrophobic acid fraction compared to the Forge Pond humic acid fraction.

from Bose *et al.*, (1993)

## Coagulation Studies

Coagulation studies performed on the hydrophobic acid, hydrophobic neutral, hydrophilic acid, and hydrophilic neutral fractions were to determine the effect of pH on removal of DOC in each of the four fractions. To conserve limited organic material and for comparison purposes, each fraction was diluted with Milli-Q water to a DOC value between 4 and 5 mg/L C. The alum dose was the enhanced dose (50 mg/L alum) previously determined for the untreated Lake Drummond water sample. Table A-8 contains the data from each coagulation pH study in tabular form.

### Hydrophobic Acid Fraction

Figure 14 illustrates the pH of maximum hydrophobic acid removal was between 5.5 and 6.0; maximum DOC removal observed was 67%. The 67% removal in the hydrophobic acid solution is essentially equivalent to the 66% removal observed for the hydrophobic acid fraction of the coagulated Lake Drummond water sample (Table A-3) while a 57% removal was observed for the hydrophobic acid fraction of the coagulated Chickahominy River water sample. At pH values 5.0-7.5, the hydrophobic acids will be ionized and possess a net negative charge. The aluminum speciation curve (Figure 3) shows at pH values 5.0-7.0 positively charged aluminum monomers and polymers predominate and the concentration of amorphous  $\text{Al}(\text{OH})_{3(s)}$  is largest around pH 6.5. In this pH region, hydrophobic acids are very amenable to removal by adsorption and/or direct chemical precipitation. Above pH 7.0, positively charged aluminum monomers and polymers are essentially nonexistent and the charge on  $\text{Al}(\text{OH})_{3(s)}$  is negative leading to poor removal of hydrophobic acids. The combination of charge and

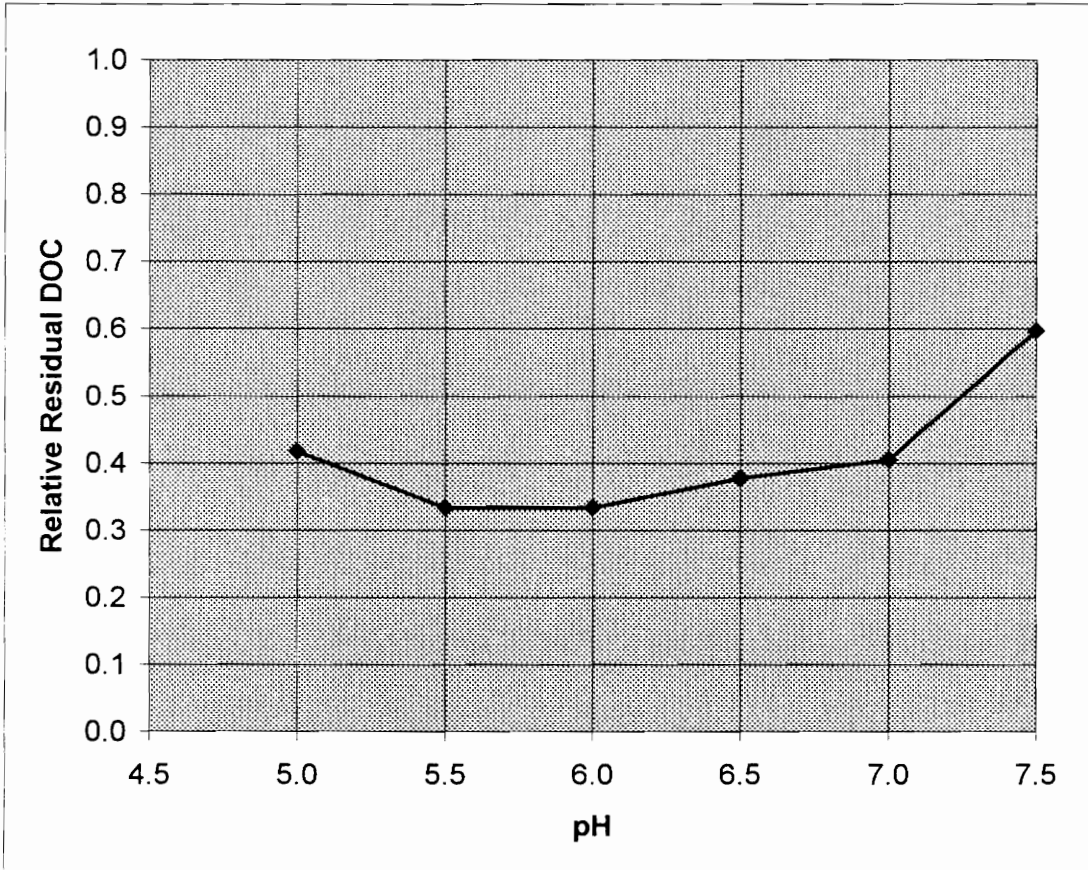


Figure 14. Results of coagulation of Lake Drummond hydrophobic acid fraction with a constant alum dosage (alum = 50 mg/L) at various pHs. (original DOC = 4.9 mg/L)

concentration of aluminum species help explain the observed hydrophobic acid coagulation results.

### **Hydrophobic Neutral Fraction**

The hydrophobic neutral DOC removal was constant ( $\approx 40\%$ ) from pH 5.0-7.5 as shown in Figure 15. Upon initial review, it may seem unusual that the DOC removal was constant across the entire pH range tested. The net charge on the hydrophobic neutral fraction was zero, however. Therefore, pH would not have an effect on DOC removal in terms of charged aluminum species. Removal of the hydrophobic neutral fraction was most likely the result of adsorption on  $\text{Al}(\text{OH})_{3(s)}$  and not to charge neutralization/precipitation due to the neutral charge of the organic fraction.

Unlike the excellent DOC removal of the hydrophobic acid fraction, the hydrophobic neutral fraction actually increased in concentration for the coagulated Lake Drummond water sample (Figure 8). Better DOC removal with the hydrophobic neutral fraction raised the question of possible interference of the hydrophobic acid fraction on the hydrophobic neutral fraction during coagulation of the Lake Drummond water sample. A separate experiment was designed to investigate this phenomenon.

### **Hydrophilic Acid Fraction**

The pH range for the hydrophilic acid solution coagulation study was 3.0-7.5. The hydrophilic acid solution had a maximum DOC removal of 30% at pH 5.5 (Figure 16). The hydrophilic acid fraction of the coagulated Chickahominy River water sample had a similar DOC removal of 40% while no removal was observed for the coagulated Lake Drummond water sample. The observed ratio of hydrophilic acids to hydrophobic acids in the untreated Chickahominy River water sample was much larger (0.14) than

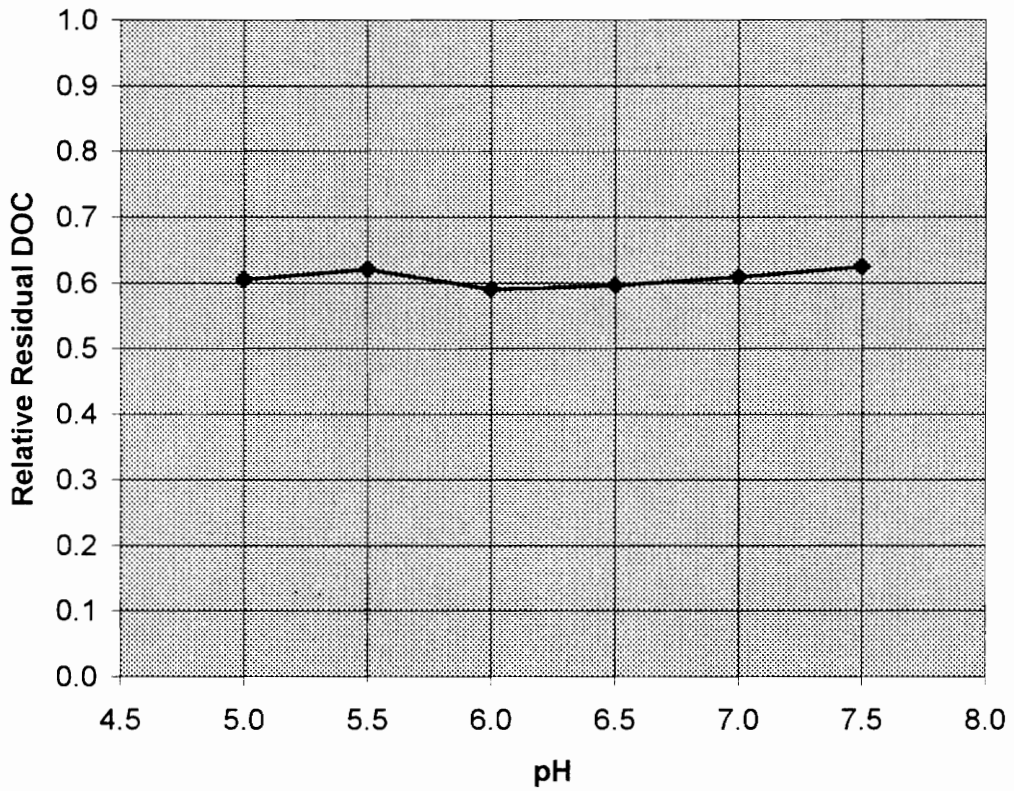


Figure 15. Results of coagulation of Lake Drummond hydrophobic neutral fraction with a constant alum dosage (alum = 50 mg/L) at various pHs. (original DOC = 5.0 mg/L)



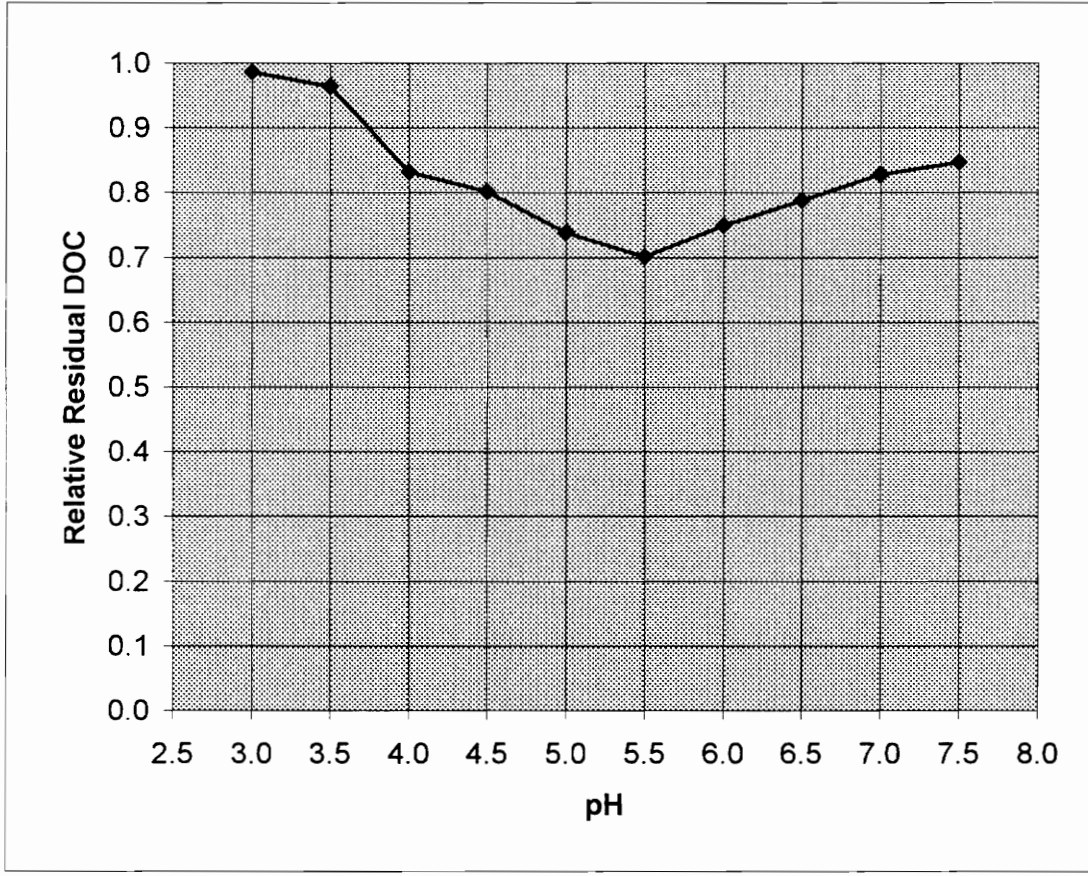


Figure 16. Results of coagulation of Lake Drummond hydrophilic acid fraction with a constant alum dosage (alum = 50 mg/L) at various pHs. (original DOC = 4.9 mg/L)

for the untreated Lake Drummond sample (0.06). This supports the notion of competitive effects; that is, the competition between hydrophobic and hydrophilic acids for aluminum species. This phenomena will be discussed later.

The hydrophilic acid coagulation results in Figure 16 closely follow the hydrophobic acid coagulation results in Figure 14. Like the hydrophobic acids, the hydrophilic acids will possess a net negative charge in the test pH range (3.0-7.5). The combination of charge and concentration of aluminum species (as discussed in the hydrophobic acid section earlier) helps explain the observed hydrophilic acid coagulation results. At the pH extremes (<5 and >7), the concentration of aluminum monomers, polymers, and  $\text{Al(OH)}_{3(s)}$  are very small when compared to pH 5.0-7.0. Likewise, positively charged aluminum species will be abundant from pH 5.0-7.0.

### **Hydrophilic Neutral Fraction**

Like the hydrophobic neutrals, the removal of hydrophilic neutrals was constant ( $\approx 10\%$ ) across the pH test range (Figure 17). DOC removal for the hydrophilic neutral fraction of the coagulated Lake Drummond water sample was 20% and 28% for the coagulated Chickahominy River water sample. The net charge on the hydrophilic neutral fraction was zero meaning pH would not have an effect on DOC removal in terms of charged aluminum species. Removal of the hydrophobic neutral fraction was therefore most likely the result of adsorption on  $\text{Al(OH)}_{3(s)}$  and not to charge neutralization/precipitation due to the neutral charge of the organic fraction.

The hydrophobic neutral solution had a much higher DOC removal ( $\approx 40\%$ ) than the hydrophilic neutral solution for two reasons. First, the hydrophilic neutral fraction is more difficult to remove than the hydrophobic fraction because hydrophilic compounds

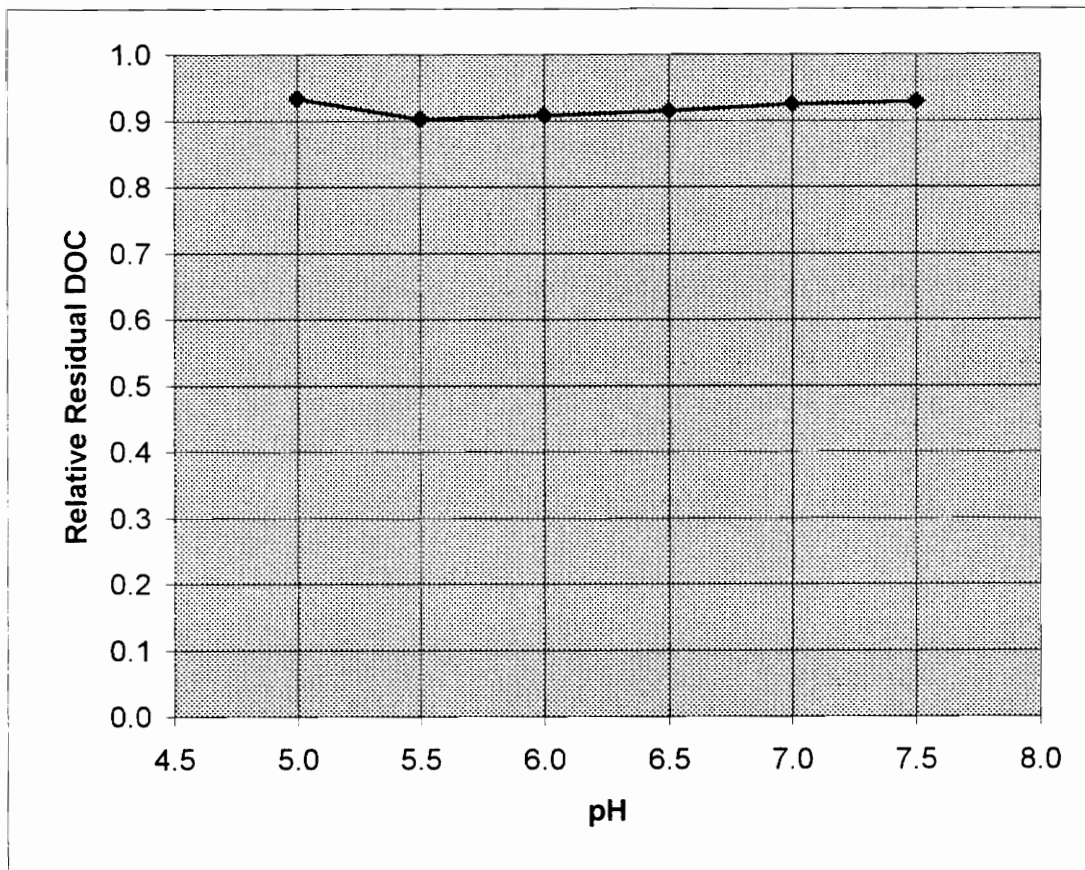


Figure 17. Results of coagulation of Lake Drummond hydrophilic neutral fraction with a constant alum dosage (alum = 50 mg/L) at various pHs. (original DOC = 4.9 mg/L)

are more water soluble. Second, the hydrophilic neutral fraction's AMWD was much smaller than the hydrophobic neutral fraction.

### **Hydrophobic Acid and Hydrophobic Neutral Coagulation Study**

The results of both the hydrophobic neutral fraction and hydrophilic acid fraction coagulation pH study prompted the need to study the competition between different fractions for aluminum species. The two fractions chosen for this study were the hydrophobic acid fraction and hydrophobic neutral fraction. Coagulation of the hydrophobic neutral fraction yielded approximately 40% removal across the entire pH test range while essentially no removal of the hydrophobic neutral fraction occurred with the coagulated Lake Drummond water sample (Figure 8). The presence of the hydrophobic acid fraction was believed to interfere with removal of the hydrophobic neutral fraction. An experimental procedure was developed to test this hypothesis.

#### **Method Development**

The goal of the experiment was to determine any synergistic or antagonistic effects the hydrophobic acids had on the removal of the hydrophobic neutrals and vice versa. The method developed incorporated jar tests and the XAD-8 resin. Mixtures of the hydrophobic acid and hydrophobic neutral fractions were made at two DOC ratios: 3 mg/L hydrophobic neutral:2 mg/L hydrophobic acid and 4 mg/L hydrophobic acid:1 mg/L hydrophobic neutral. The 300 mL samples of the mixtures were coagulated at either pH 5.5 or 7.5 using an alum dose of 50 mg/L. The coagulated solutions were filtered through 1 µm glass fiber filters and then passed through XAD-8 resin (following adjustment to pH 6.3) using the 23.5 mL pilot test column with a 15 mL bed volume.

The resin preparation, sample application, and elution procedures are described in the Methods and Materials chapter.

The 23.5 mL column was selected since the water sample volume was very small and also to minimize dilution effects. At pH 6.3 most of the hydrophobic acid fraction should adsorb to the XAD-8 resin while the hydrophobic neutral fraction should adsorb to the XAD-8 resin. The effluent DOC from the XAD-8 resin was measured and adjusted back to the actual coagulated sample to obtain the hydrophobic acid DOC. The first 10 mL of effluent collected from the XAD-8 resin was primarily Milli-Q water due to void volume space. After passing the coagulated sample through the column, 2.5 BV of Milli-Q water (37.5 mL) was passed through the column to displace the coagulated sample. The net effect was dilution of the coagulated effluent from the XAD-8 resin. The true DOC of the coagulated XAD-8 effluent (hydrophobic acid DOC) was determined by the following equation:

$$\text{true DOC of the coagulated XAD-8 effluent} = \text{measured DOC} \times \frac{\text{effluent volume}}{\text{coagulated sample volume}} \quad [3]$$

where: measured DOC = DOC of the effluent from the XAD-8 column  
 effluent volume = coagulated sample volume + Milli-Q water in void spaces and for sample displacement  
 coagulated sample volume = 300 mL

The hydrophobic neutral DOC was determined by simply subtracting hydrophobic acid DOC from the coagulated sample DOC.

### Experimental Results

The first experiment was at a hydrophobic neutral to hydrophobic acid ratio of 3:2. The actual ratios and experimental results are illustrated graphically in Figure 18

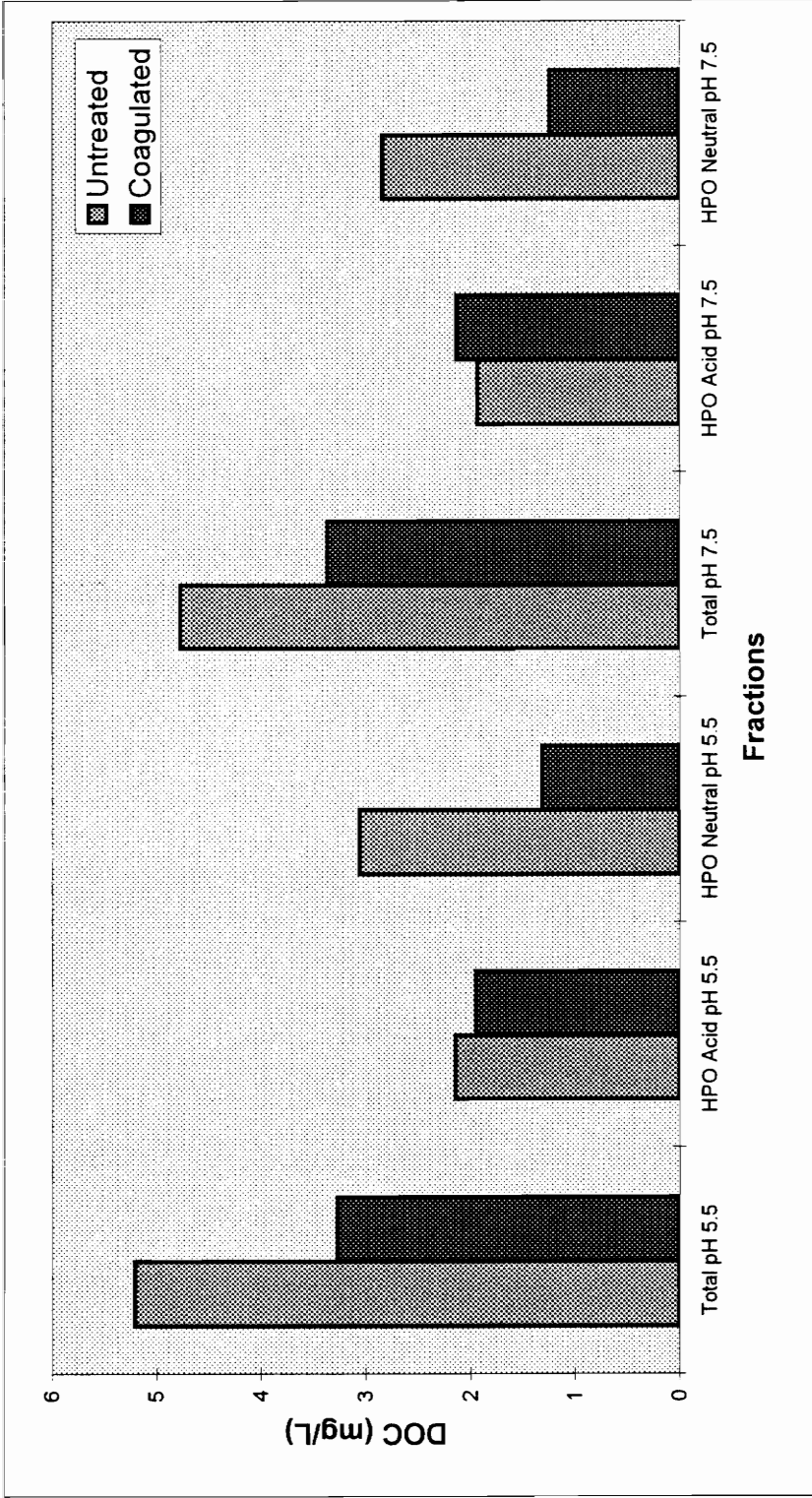


Figure 18. Comparison of the relative amounts of the hydrophobic acid and hydrophobic neutral fractions present in untreated and alum coagulated Lake Drummond hydrophobic acid/hydrophobic neutral mixtures. (alum = 50 mg/L, hydrophobic neutral to hydrophobic acid ratio = 3:2, untreated pH 5.5 sample DOC = 5.3 mg/L, coagulated pH 5.5 sample DOC = 3.3 mg/L, untreated pH 7.5 sample DOC = 4.8 mg/L, coagulated pH 7.5 sample DOC = 3.4 mg/L)

and listed in Table A-9. Although a ratio of this magnitude would be rather rare in natural waters (due to the ubiquity of hydrophobic acids), this ratio tested the possibility of the hydrophobic neutral fraction adversely affecting the removal of the hydrophobic acid fraction in hopes that the results can be related to other fractions.

At pH 5.5, 57% of the hydrophobic neutral fraction was removed in relation to 9.1% of the hydrophobic acid fraction. This can be explained by the fact that there were 1.5 times more hydrophobic neutrals than hydrophobic acids. Also, there was the possibility of negatively charged hydrophobic acid molecules binding with positively charged aluminum species creating a neutrally charged molecule that did not settle during sedimentation. This neutrally charged hydrophobic acid/aluminum complex would have adsorbed to the XAD-8 resin at pH 6.3. However, the resin adsorption procedure is designed to remove hydrophobic neutral compounds. Unfortunately, both hydrophobic neutral compounds and neutrally charged hydrophobic acid/aluminum complexes may have been removed by the XAD-8 resin. Therefore, the hydrophobic acid/aluminum complexes would appear to be in the hydrophobic neutral fraction meaning more of the hydrophobic acid fraction may have been removed than the 9.1% measured.

At pH 7.5, 56% of the hydrophobic neutral fraction was removed while the hydrophobic acid fraction actually increased in concentration by 10% over the initial hydrophobic acid concentration. The increase in hydrophobic acid fraction can be explained by the predominant aluminum speciation charge. As the pH increases, aluminum species tend to be negatively charged. Negatively charged aluminum species (including  $\text{Al}(\text{OH})_{3(s)}$ ) may have binded with hydrophobic neutral molecules creating a

negatively charged molecule that was not removed by either sedimentation or filtration. The negatively charged hydrophobic neutral/aluminum complex would have passed through the XAD-8 resin and thus appear in the hydrophobic acid fraction.

The second experiment was conducted at a hydrophobic acid to hydrophobic neutral ratio of 4:1. The actual ratios and experimental results are illustrated graphically in Figure 19 and listed in Table A-10. This ratio tested the possibility of the hydrophobic acid fraction adversely affecting the removal of the hydrophobic neutral fraction. At pH 5.5, 52% of the hydrophobic acid fraction was removed in relation to 9.1% of the hydrophobic acid fraction in the first experiment. This increase can be explained by the increased presence of hydrophobic acids in relation to hydrophobic neutrals. The removal of the hydrophobic neutral fraction was 56% which is similar to the 57% removal in the first experiment; however, removal was actually less on a mass basis.

At pH 7.5, 56% of the hydrophobic acid fraction was removed compared to a removal of 10% in the first experiment. This increase can be explained by the increased presence of hydrophobic acids in relation to hydrophobic neutrals. The hydrophobic acid removal was approximately the same at pH 7.5 (56%) as at pH 5.5 (52%). The hydrophobic neutral fraction increased in concentration by 6.7% at pH 7.5.

In summary, both experiments indicated that the greater presence of hydrophobic acids interfered with the removal of hydrophobic neutrals and vice versa. Also, shifts between fractions due to coagulation process may have occurred resulting in one fraction "appearing" as the other fraction following separation by the XAD-8 resin. For example, negatively charged hydrophobic acid molecules may bind with positively charged aluminum species creating a neutrally charged molecule. To the XAD-8 resin,



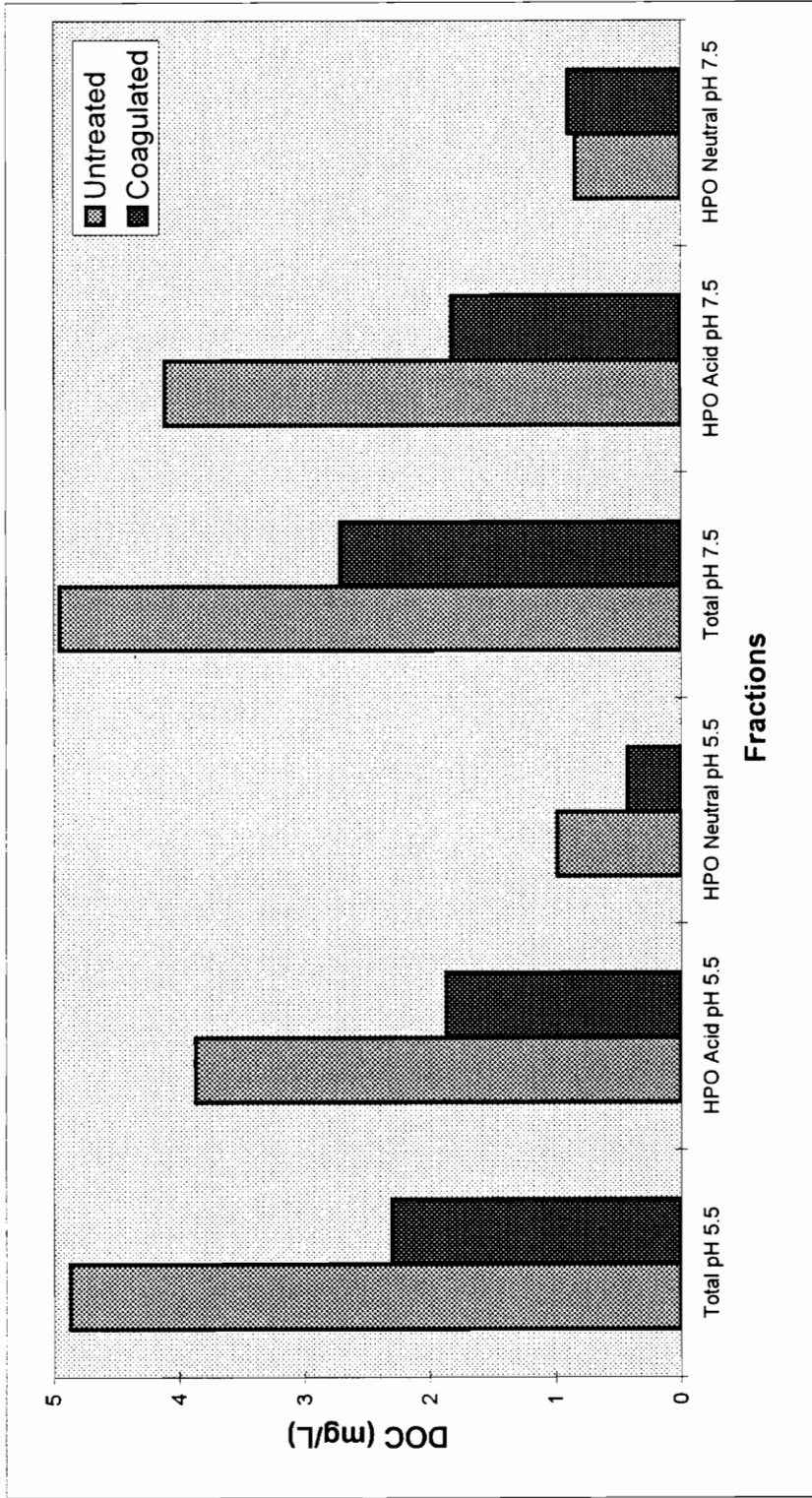


Figure 19. Comparison of the relative amounts of the hydrophobic acid and hydrophobic neutral fractions present in untreated and alum coagulated Lake Drummond hydrophobic acid/hydrophobic neutral mixtures. (alum = 50 mg/L, hydrophobic neutral to hydrophobic acid ratio = 1:4, untreated pH 5.5 sample DOC = 4.9 mg/L, coagulated pH 5.5 sample DOC = 2.3 mg/L, untreated pH 7.5 sample DOC = 5.0 mg/L, coagulated pH 7.5 sample DOC = 2.7 mg/L)

this hydrophobic acid/aluminum complex would adsorb to the XAD-8 resin at pH 6.3 even though it is an acid.

### **XAD-8 Resin Adsorption Study**

The results of the hydrophobic acid/hydrophobic neutral study prompted concern about the performance of the XAD-8 resin. XAD-8 resin is typically used to fractionate natural waters but rarely fractionated organic fractions. Thurman and Malcolm (1981) developed a fractionation procedure using XAD-8 resin whereby the acidified sample (pH 2) was passed through XAD-8 resin to remove humic substances. The eluant was acidified to pH 1 to separate the fulvic acids from the humic acids, and then the fulvic acid fraction was applied to the XAD-8 resin to purify the fulvic acid. Leenheer (1981) applied the hydrophilic acids to XAD-8 resin following elution from A-7 to desalt the fraction. In theory, hydrophobic acids applied to XAD-8 resin at pH 6.3 should not adsorb to the resin column while hydrophobic neutrals should. A series of simple experiments were designed to test the theory.

Three hydrophobic neutral water samples were passed through the XAD-8 resin at pH 6.3 (23.5 mL resin column volume). The resin preparation, sample application, and elution procedures are described in the Methods and Materials chapter. All water sample sizes were 90 mL; larger sizes were not used due to the lack of hydrophobic neutral organic material. Figure 20 and Table A-11 contain the results of the three experiments. The first sample was 90 mL of hydrophobic neutral organic material at a DOC of 3.8 mg/L. Figure 20 illustrates that hydrophobic neutral DOC breakthrough peaked at 34%, that is, 34% of the hydrophobic neutrals did not adsorb to the XAD-8 resin after 5 BV. The first 2 BV or 30 mL of sample effluent contained Milli-Q water from

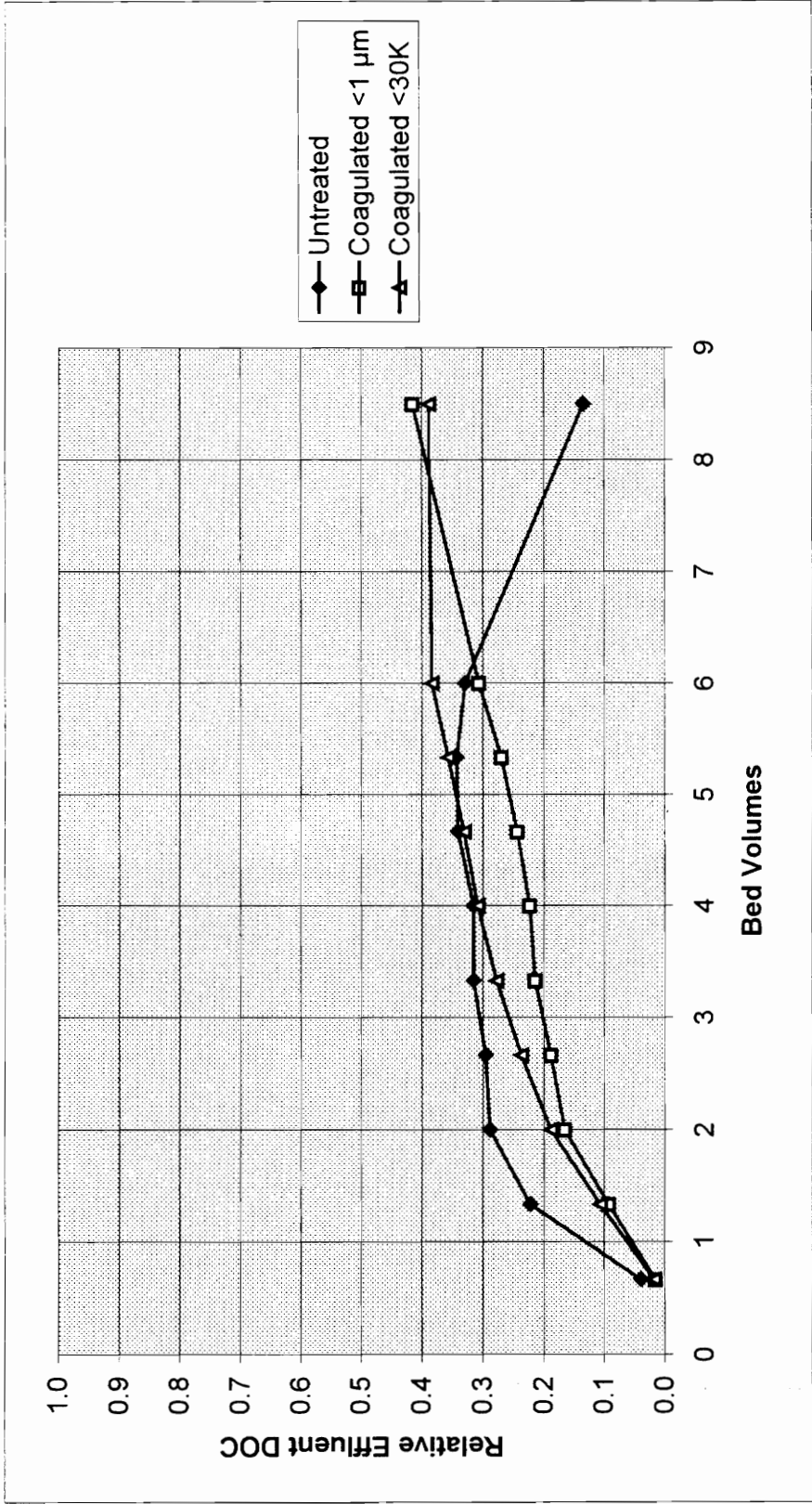


Figure 20. Results of passing Lake Drummond hydrophobic neutral fraction through the XAD-8 resin at pH 6.3. (1 bed volume = 15 mL, untreated sample DOC = 3.8 mg/L, coagulated <1 μm sample DOC = 3.6 mg/L, coagulated <30K sample DOC = 3.4 mg/L)

the void spaces prior to sample application. Also, mixing of sample occurred in the column; the sample did not pass through as a slug. Short circuiting may have also occurred due to the small column size. The tailing effect at 8.5 BV was due to the Milli-Q water used to displace the hydrophobic neutral sample.

The second and third samples were coagulated prior to XAD-8 resin application and had DOC values of 3.6 mg/L and 3.4 mg/L, respectively. Prior to resin application the second sample was filtered through a 1  $\mu\text{m}$  filter (typical jar test procedure) while the third sample was filtered through a 1  $\mu\text{m}$  filter and a 30,000 amu membrane. The 30,000 amu membrane filtered any "large" hydrophobic neutral/aluminum species remaining from the 1  $\mu\text{m}$  filter. Figure 20 indicates the 30,000 amu membrane had a distinct effect on the 1  $\mu\text{m}$  XAD-8 resin effluent results. A 7% DOC separation between the 30,000 amu and 1  $\mu\text{m}$  XAD-8 effluents indicates that some of the 1  $\mu\text{m}$  filtered sample may have been mechanically filtered by the XAD-8 resin.

The 8.5 BV results indicate no dilution of either the 1  $\mu\text{m}$  or 30,000 amu XAD-8 resin effluent caused by Milli-Q water. This indicates possible mixing of the coagulated hydrophobic neutral samples in the column whereby the Milli-Q water simply flushed out the sample. The 30-40% DOC breakthroughs observed for the 30,000 amu and 1  $\mu\text{m}$  filtered samples suggest the possibility of negatively charged hydrophobic neutral/aluminum species which would pass through the XAD-8 resin although the untreated hydrophobic neutral experiment casts doubt on this hypothesis. In summary, adsorption of the hydrophobic neutral fraction on XAD-8 was not complete as between 30% and 40% DOC breakthroughs were observed for the three hydrophobic neutral samples tested.

Next, two hydrophobic acid samples were passed through the XAD-8 resin at pH 6.3 (23.5 mL resin column volume). Both samples were made by diluting the hydrophobic acid fraction with Milli-Q water and neither sample was coagulated. Figure 21 and Table A-12 contain the results of the two experiments. The first sample was 70 mL of hydrophobic acid at a DOC of 4.7 mg/L. Figure 21 shows that the DOC breakthrough peaked at 75%, that is 75% of the hydrophobic acid passed through the column at 4.7 BV. The first 2 BV were probably diluted by Milli-Q water that remained in the XAD-8 resin void spaces prior to sample application. The results of this experiment suggested the need for a larger sample as breakthrough was not reached.

A 300 mL sample was selected for the second experiment which was equivalent in volume to those used for the hydrophobic neutral/hydrophobic acid study and had a DOC of 5.1 mg/L. Figure 21 shows that 100% DOC breakthrough occurred at approximately 13 BV. Probable mixing of the sample occurred in the column initially causing the low DOC effluent readings. The greater than 100% DOC readings also suggest mixing in the column and final flushing of accumulated hydrophobic acids at 14 BV. The tailing effect at 22.5 BV was due to dilution by Milli-Q water used to displace the hydrophobic acid sample. In summary, the 300 mL hydrophobic acid sample did pass through the XAD-8 resin with minimal adsorption and mixing.

The final conclusions from the XAD-8 resin study are that hydrophobic acids did not adsorb to the XAD-8 resin at pH 6.3. However, approximately 30% breakthrough of hydrophobic neutrals occurred. In light of these results, another explanation of the hydrophobic acid/hydrophobic neutral mixtures results can be added. Some of the coagulated hydrophobic neutral/aluminum species may have passed through the XAD-8

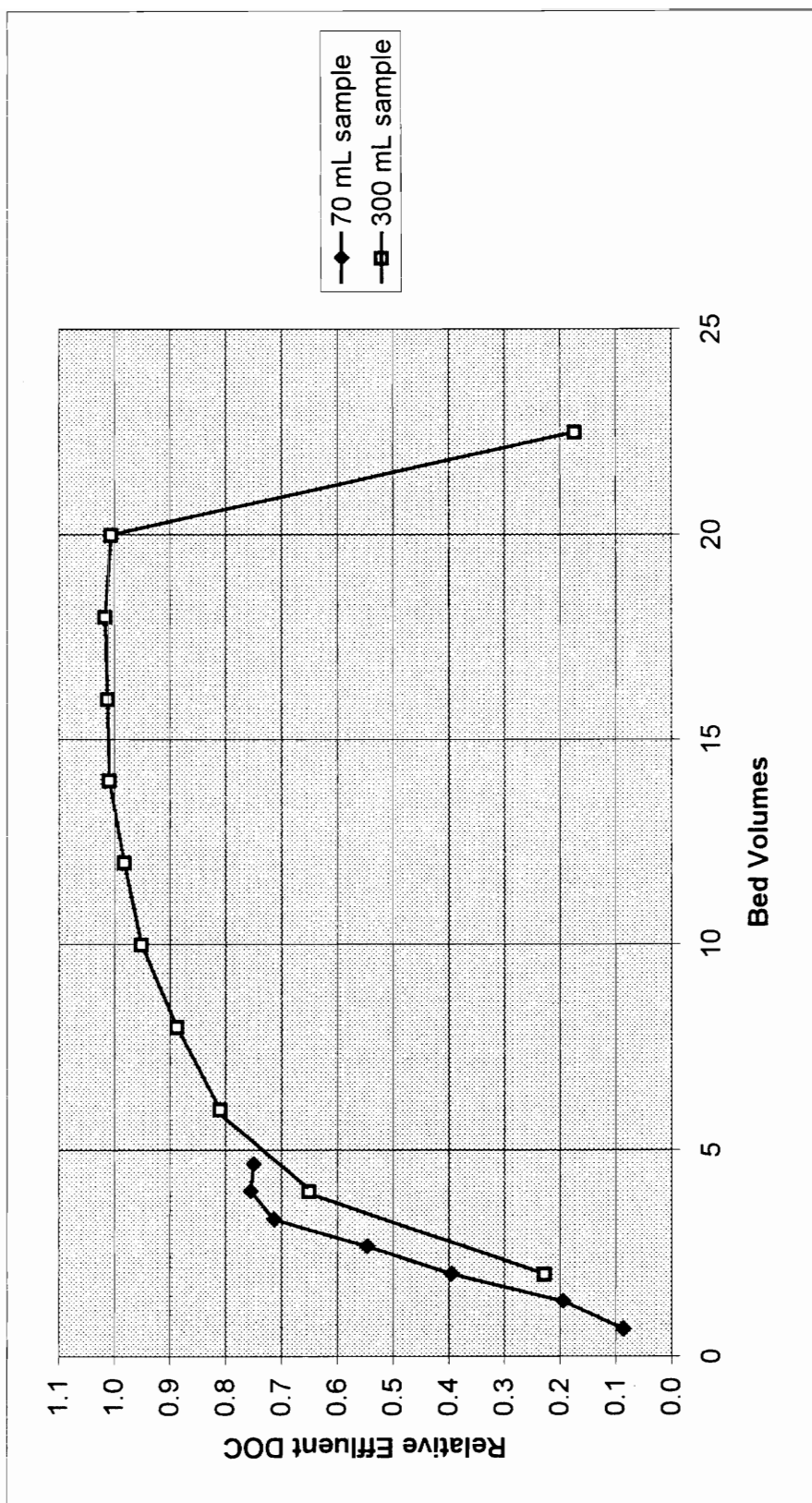


Figure 21. Results of passing Lake Drummond hydrophobic acid fraction through the XAD-8 resin at pH 6.3. (1 bed volume = 15 mL, 70 mL sample DOC = 4.7 mg/L, 300 mL sample DOC = 5.1 mg/L)

resin although they still maintained a neutral charge. The XAD-8 resin study, however, does not provide conclusive evidence to refute the results obtained by the hydrophobic acid/hydrophobic neutral study.

### **Phase-Change Behavior of Organic Material**

The results of Knocke et al. (1990) and Knocke et al. (1994) suggested the need to further study the phase-change behavior of organic material under conditions of chemical coagulation. The goal was to identify the alum doses where the presence of colloidal aluminum bound organic material occurred and to investigate the use of a nonionic polymer to remove the colloidal material. The investigation involved four separate experiments: a pH study with alum, a dose study with alum, a dose study with ferric chloride, and a dose study with both alum and a nonionic polymer to remove the colloidal organic material. All experiments were performed using fractionated hydrophobic acids (<10,000 amu) from Lake Drummond water. The ferric chloride dose study was performed for comparison with the alum dose study. Both DOC and residual aluminum or residual iron were monitored during each experiment.

### **Method Development**

The first issue in developing a method was to determine a definition of colloidal organic material. Throughout the research, coagulated samples were passed through 1  $\mu\text{m}$  filters prior to DOC and/or residual aluminum measurements, however, Knocke et al. (1994) found significant DOC measurement differences between 0.2  $\mu\text{m}$  filters and 100,000 amu membranes. The authors attributed the measurement differences to the formation of iron colloids which had significant amounts of adsorbed DOC.

To maintain consistency with earlier experimental procedure, coagulated samples were first filtered through 1  $\mu\text{m}$  filters to remove precipitated aluminum/organic complexes. Next, 100 mL of the filtered sample was passed through a 100,000 amu membrane while a separate 100 mL of the filtered sample was passed through a 30,000 amu membrane. The DOC and residual aluminum or residual iron concentrations were measured for the 1  $\mu\text{m}$ , 100,000 amu, and 30,000 amu filtrates. The 1  $\mu\text{m}$ , 100,000 and 30,000 amu membranes were used to establish a colloidal organic material definition. Significant differences between the 100,000 amu and 30,000 amu membrane DOC measurements did not exist as shown in Figure 22. The operational definitions for the phase-change behavior of organic material study were as follows:

**particulate organic material** - organic material retained on a 1  $\mu\text{m}$  filter

**colloidal organic material** - organic material passing through 1  $\mu\text{m}$  filter and retained on a 100,000 amu membrane

**dissolved organic material** - organic material passing through a 100,000 amu membrane

The second issue was selection of a water sample. This issue was twofold: molecular size and sample. Since a 30,000 amu membrane was used for a portion of the analysis, it was desired that all DOC in the untreated sample be less than 30,000 amu; therefore, a 10,000 amu membrane was selected to ensure the <30,000 amu condition. Two options were available for sample selection: a natural water or an organic fraction. An organic fraction was chosen for repeatability of results. The chemistry of natural waters vary from location to location, but organic fractions have comparative chemistry provided the same fractionation procedure is utilized.



Hydrophobic acids were the organic fraction selected for three main reasons. First, hydrophobic acids represent the largest organic fraction in most natural waters. Therefore, results obtained from the hydrophobic acids could be better applied to the whole waters than any other organic fraction. Second, there was a more than ample supply of hydrophobic acid materials available from the Lake Drummond organic fractionation studies. Third, the hydrophobic acid fraction was concentrated. Since the liquid flow rate through a 10,000 amu membrane is slow, a concentrated organic fraction could be processed more quickly. Over 18 L of <10K, 5 mg/L DOC hydrophobic acid solution was needed for the experiments. Concentrated hydrophobic acids ( $\approx$  65 mg/L DOC) passing through a 10,000 amu membrane quickly obtained the required 90 mg of organic carbon.

The final issue was the experiments. All jar tests were performed on <10,000 amu hydrophobic acid solution at 5 mg/L DOC. The first experiment was to monitor the phase-change behavior as a function of pH. The enhanced alum dose of 50 mg/L was used at a pH range of 4.5-7.5. The results were also used to determine the colloidal organic material size cutoff definition as described previously. DOC and residual aluminum were measured for sample filtrates from 1  $\mu$ m filters, 100,000 amu membranes, and 30,000 amu membranes.

The second experiment was to monitor the phase-change behavior as a function of coagulant dose. The pH was set at 5.8 with a coagulant dose range of 0-50 mg/L alum. DOC and residual aluminum were measured for sample filtrates from 1  $\mu$ m filters, 100,000 amu membranes, and 30,000 amu membranes.

The third experiment was a comparison dose study using ferric chloride. The pH was set at 5.5 with a coagulant dose range of 0-35 mg/L ferric chloride. Most of the ferric chloride doses were equivalent to the alum doses on a molar basis. DOC and residual iron were measured for sample filtrates from 1  $\mu\text{m}$  filters, 100,000 amu membranes, and 30,000 amu membranes.

Finally, the fourth experiment was to remove colloidal organic material at low alum doses using a nonionic polymer. The pH was 5.8 with an alum dose of 12.5 mg/L and a polymer dose ranging from 0.1-0.5 mg/L. DOC and residual aluminum were measured for sample filtrates from 1  $\mu\text{m}$  filters, 100,000 amu membranes, and 30,000 amu membranes. All jar tests and ultrafiltrations were performed as described in the Material and Methods chapter.

### **Experimental Results**

Figures 22 and 23 contain the results of the alum coagulation pH experiment. The pH range was from 4.5-7.5 in 0.5 increments with the pH 5.8 result included from the coagulation dose study with alum. For consistency with previous jar test experiments, the alum dose was 50 mg/L. Table A-13 contains the raw data from this experiment. At pH values below 5.8, a separation existed between the 1  $\mu\text{m}$  and 100,000 amu or 30,000 amu residual DOC values, indicating the presence of colloidal aluminum bound organic material.

Figure 23 illustrates a good correlation between colloidal aluminum bound organic material and colloidal residual aluminum at pH values below 5.8. One possible explanation is fewer aluminum species exist at neutral pHs (i.e. pH 6.5-7.5). That is, aluminum bound organic material existed in this pH range; however, the organic

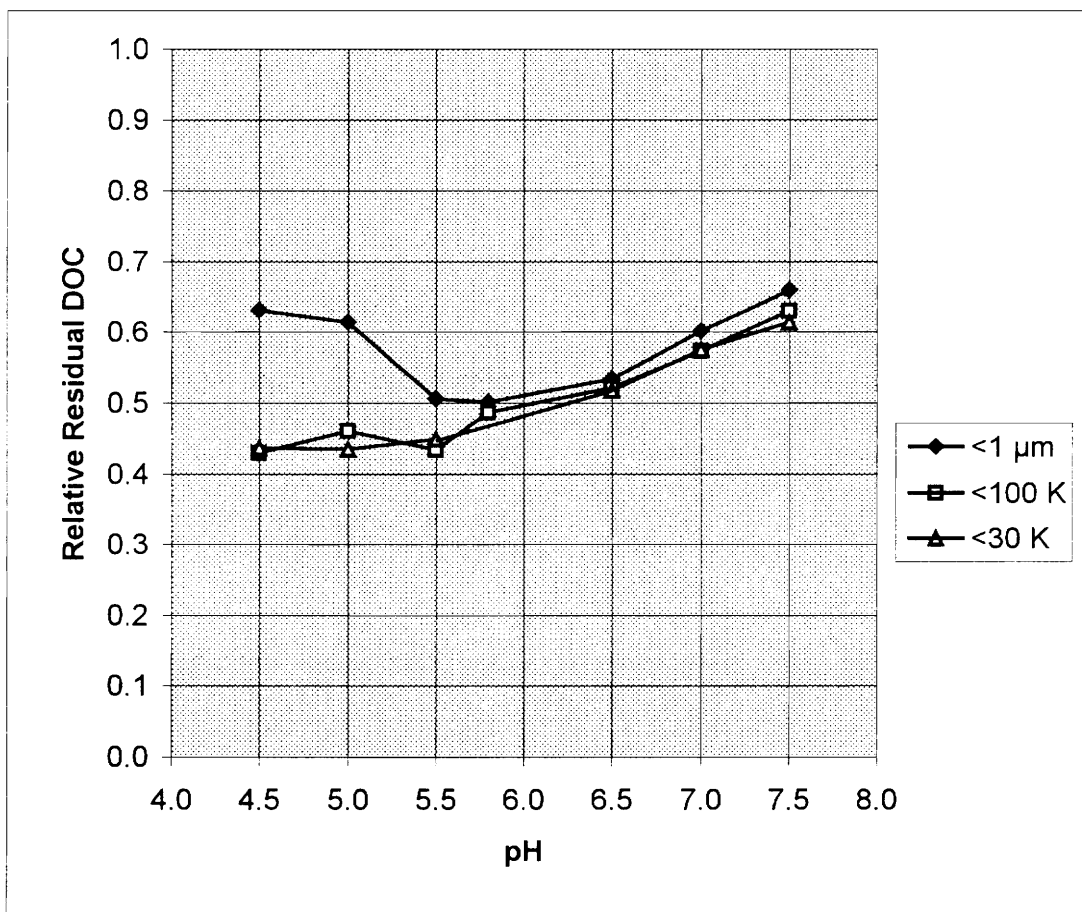


Figure 22. Relative residual DOC results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with a constant alum dosage (alum = 50 mg/L) at various pHs. (original DOC = 4.9 mg/L)

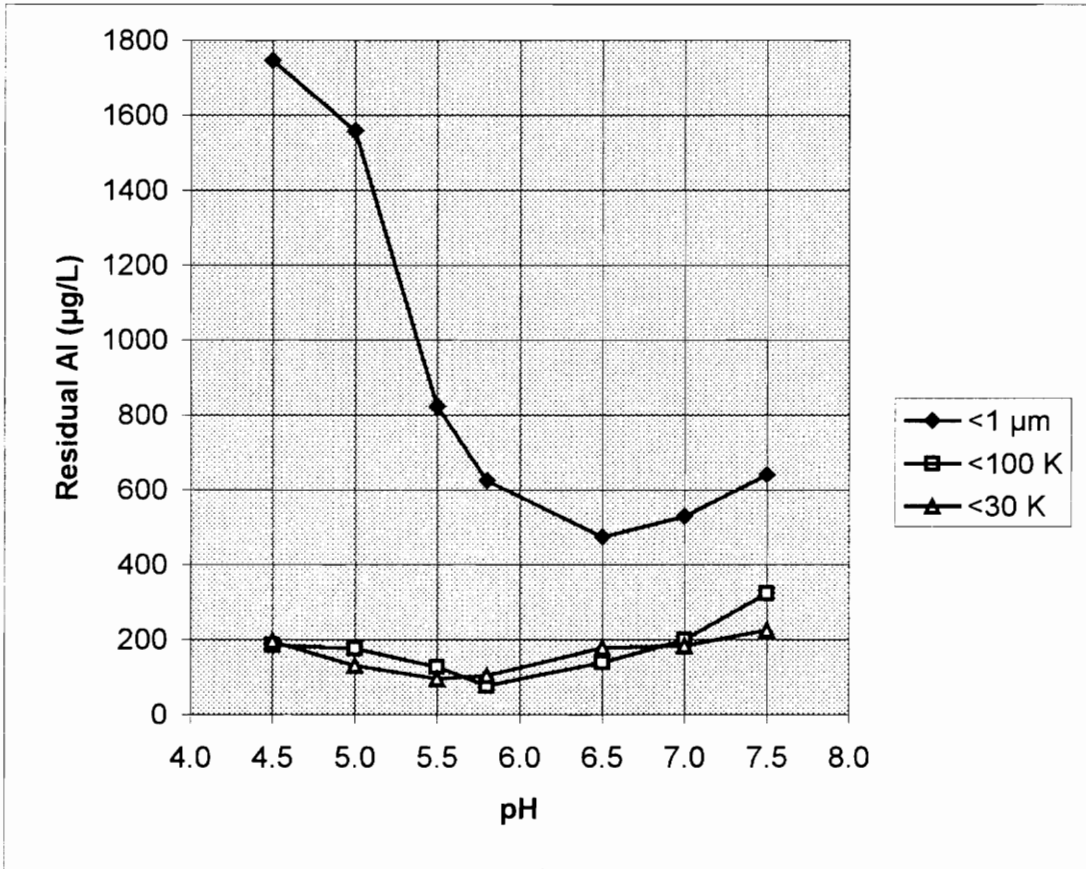


Figure 23. Residual aluminum results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with a constant alum dosage (alum = 50 mg/L,  $Al_T = 4499 \mu\text{g/L}$ ) at various pHs.

material was most likely bound to smaller, monomeric aluminum species than the larger, polymeric aluminum species present at lower pHs and was thus not filtered by the 1  $\mu\text{m}$  filter. Also, the concentration of  $\text{Al}(\text{OH})_{3(s)}$  decreases in the neutral pH range as pH increases.

An interesting observation was the relatively constant residual aluminum levels (<100,000 amu and <30,000 amu) throughout the pH range (Figure 23). This consistency verified the effect of pH on the presence of colloidal aluminum bound organic material. The 100,000 amu and 30,000 amu residual DOC and residual aluminum results indicated that the 100,000 amu membrane was sufficiently small to separate colloidal organic material from DOC. While it could be possible to differentiate DOC at the 100,000 amu cut-off only, both membranes were used for all further experiments except for the nonionic polymer experiment in which the 100,000 amu membrane was used.

Figures 24 through 26 and Tables A-14 and A-15 contain the results of the coagulation dose experiment with alum. At lower alum doses (10 - 25 mg/L alum) a separation existed between the 1  $\mu\text{m}$  and 100,000 or 30,000 amu residual DOC values. The existence of colloidal aluminum bound organic material at low alum doses was possibly due to the lack of sufficient alum to create a separable or filterable (1  $\mu\text{m}$ ) phase of aluminum bound organic material. Dempsey *et al.* (1984) found at low alum dosage, precipitation occurred via precipitation with aluminum polymers and at high dosage, precipitation occurred via adsorption on  $\text{Al}(\text{OH})_{3(s)}$ . Aluminum/organic complexes formed but not in sufficient amounts to flocculate to a size large enough to be retained on a 1  $\mu\text{m}$  filter.

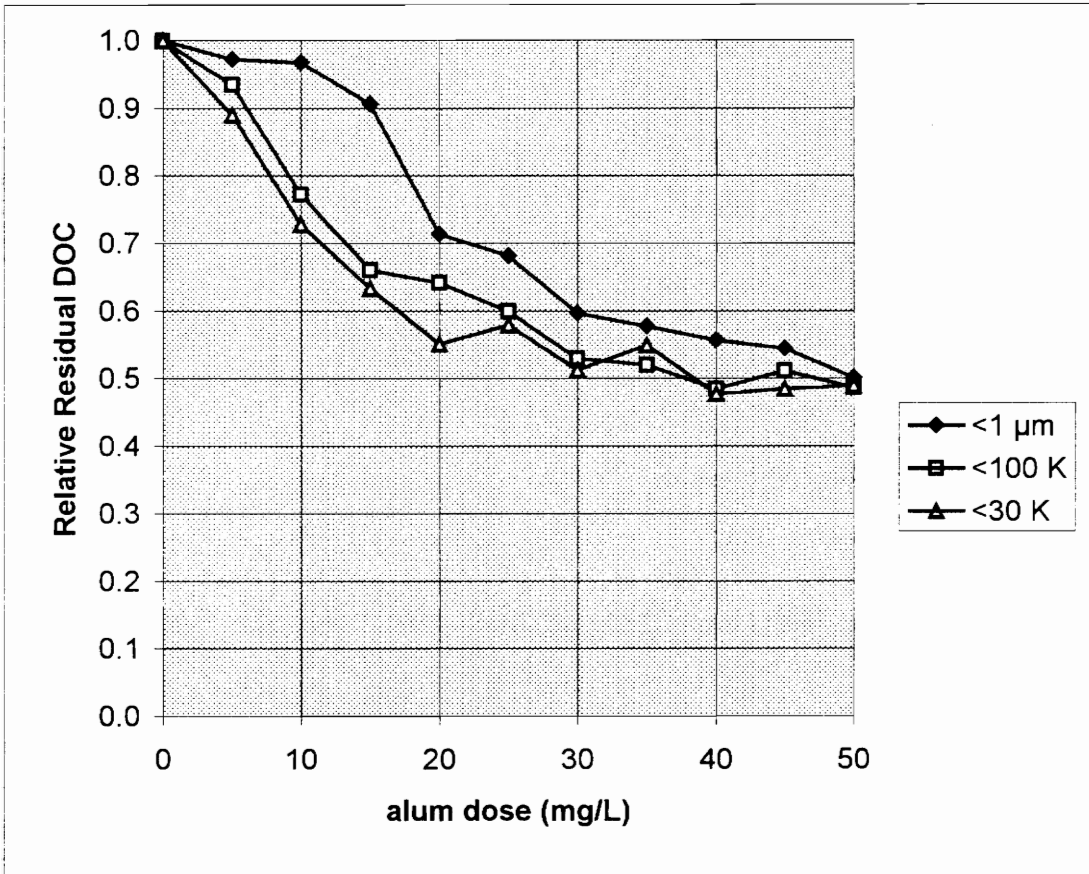


Figure 24. Relative residual DOC results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying alum dosages at pH 5.8.

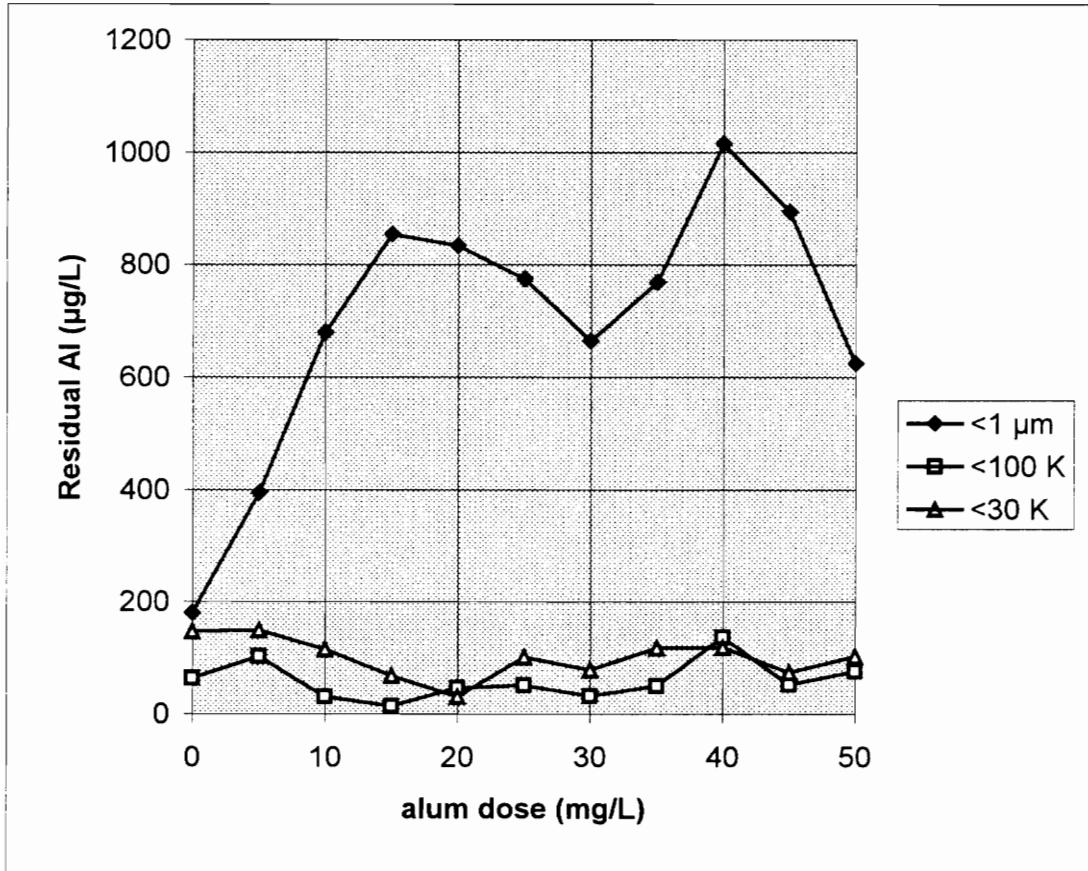


Figure 25. Residual aluminum results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying alum dosages at pH 5.8.

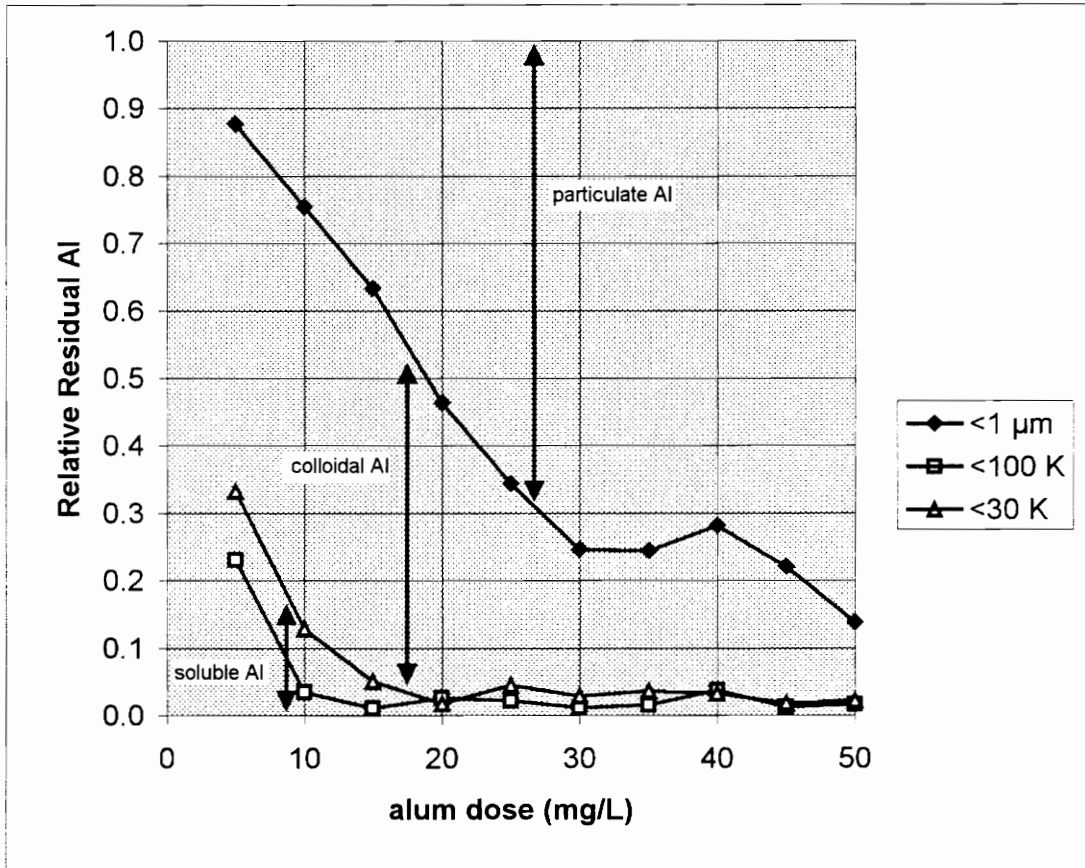


Figure 26. Relative residual aluminum results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying alum dosages at pH 5.8.



Like the coagulation pH experiment, the coagulation dose experiment had relatively constant residual aluminum values (<100,000 amu and <30,000 amu) throughout the dose range (Figure 25). Residual aluminum values in these size ranges were in fact at or below the level present in the untreated sample. A significant amount of colloidal aluminum was present throughout the dose range. Figure 26 shows the relative residual aluminum remaining following aluminum addition and coagulation. At low alum doses, aluminum was not effectively removed due to the predominance of the charge neutralization/precipitation coagulation removal mechanism.

The third experiment involved ferric chloride as a coagulant for comparison to alum in DOC removal and possible colloidal iron formation. The ferric chloride doses selected represented similar amounts of metal ion added to aluminum when calculated on a molar basis. However, the ferric chloride doses were slanted towards the lower doses to better characterize the phase-change behavior. Figures 27 through 29 and Tables A-16 and A-17 contain the results of the ferric chloride dose study.

Figure 27 indicates the presence of colloidal iron bound organic material at very low ferric chloride doses. Even at higher coagulant doses (>16.2 mg/L), there was still a significant presence of the colloidal organic material. Likewise Figure 28, illustrates a large presence of colloidal iron throughout the dose range; however, there was almost a complete lack of soluble iron (<100 K) throughout the dose range. Figure 29 shows the relative residual iron remaining following ferric chloride addition and coagulation. At low ferric chloride doses, iron was not effectively removed due to the predominance of the charge neutralization/precipitation coagulation removal mechanism.

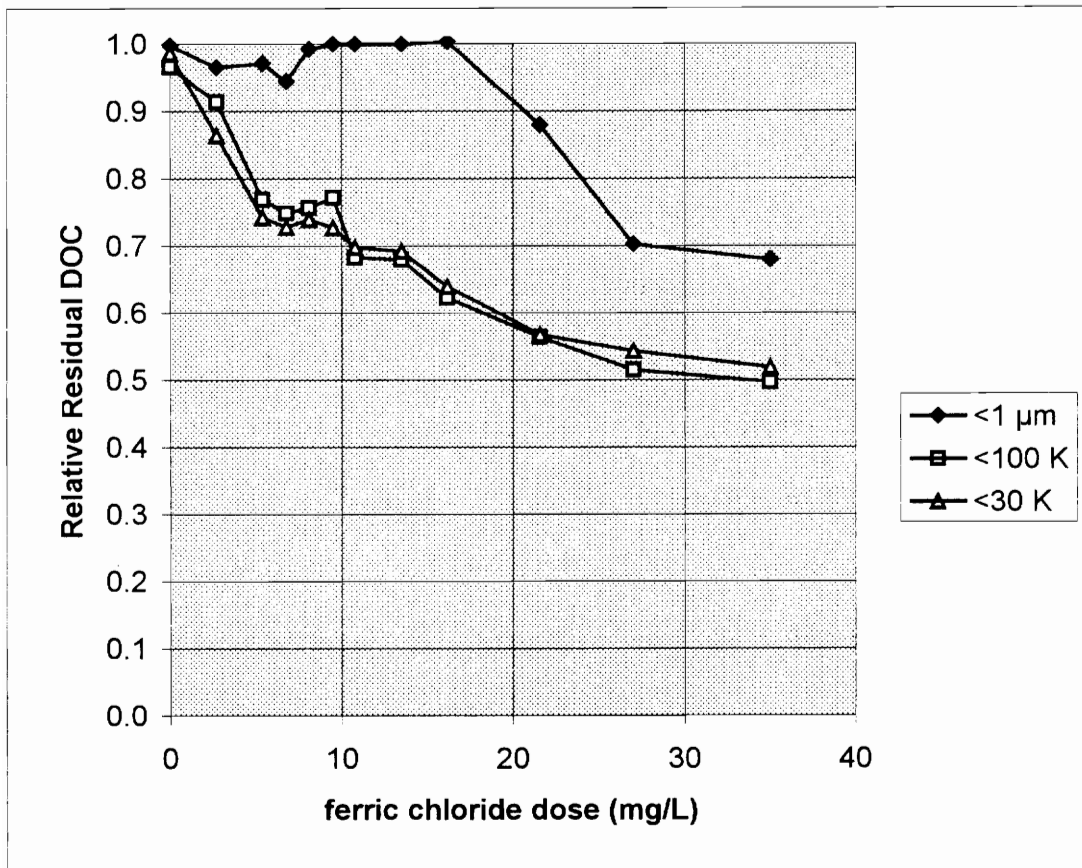


Figure 27. Relative residual DOC results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying ferric chloride dosages at pH 5.5.

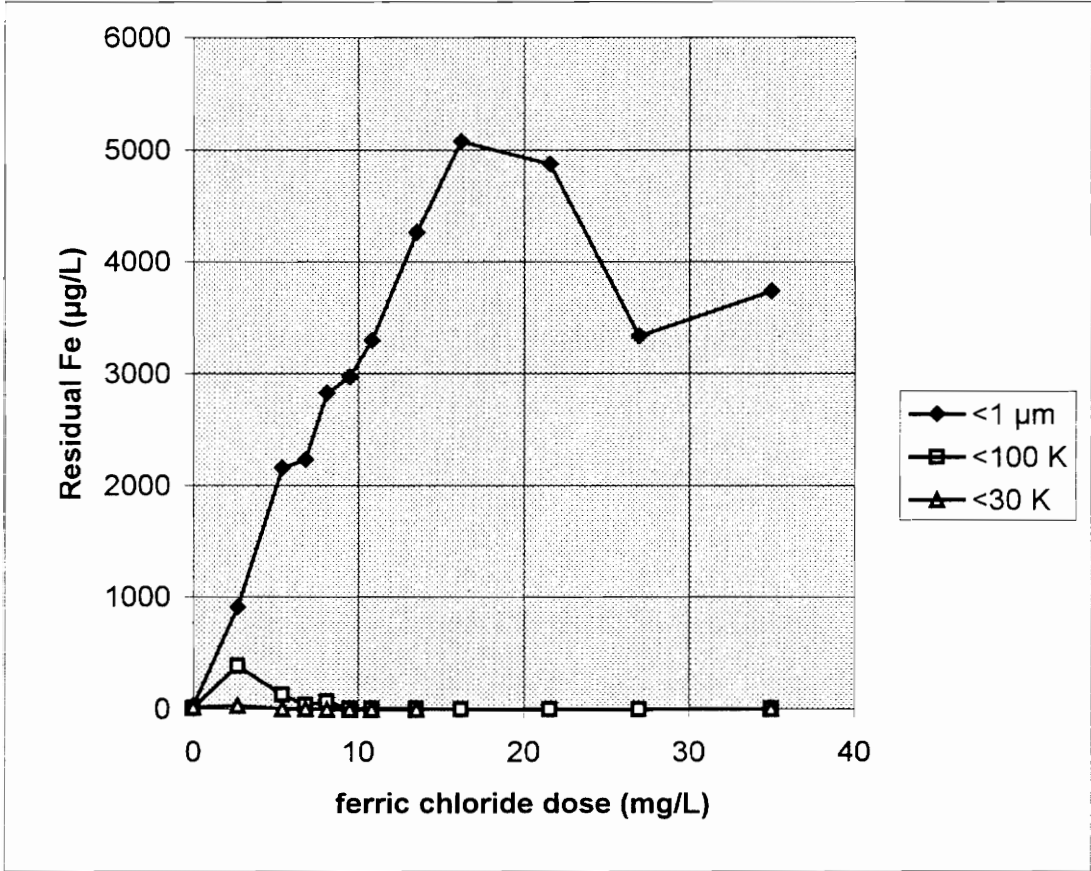


Figure 28. Residual iron results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying ferric chloride dosages at pH 5.5.

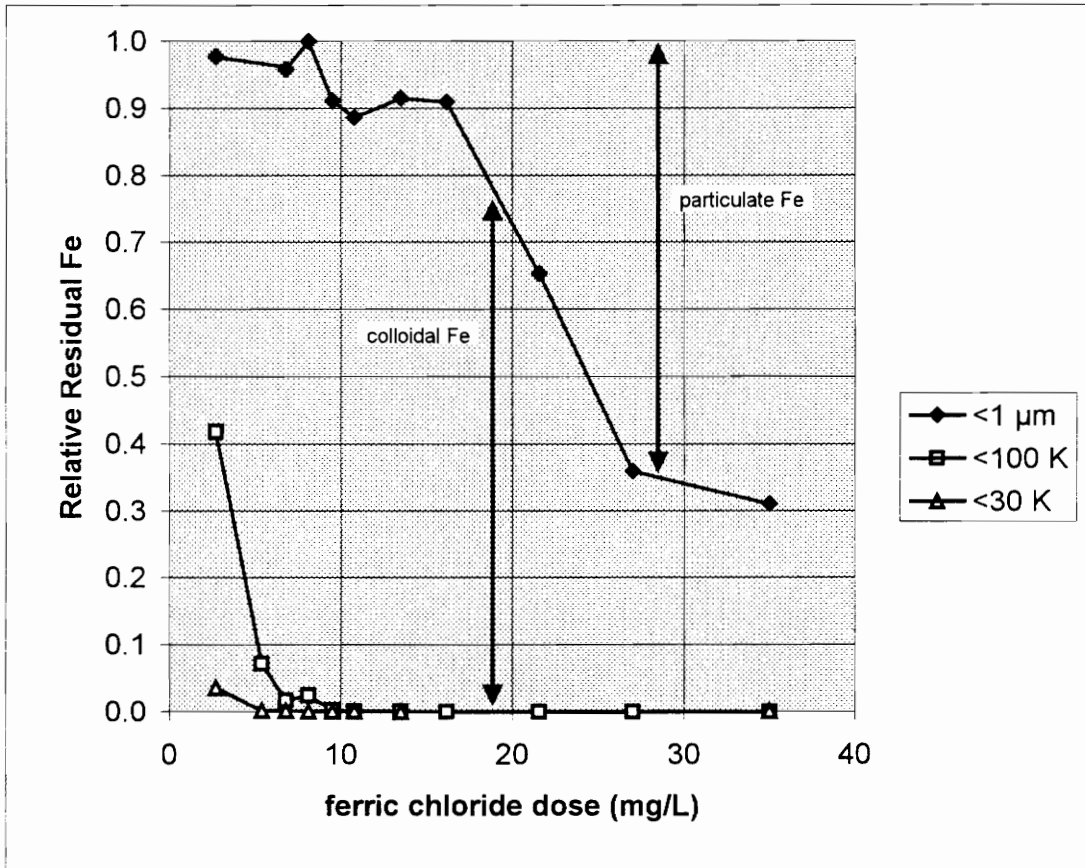


Figure 29. Relative residual iron results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying ferric chloride dosages at pH 5.5.

The fourth experiment was to remove the colloidal aluminum bound organic material present at low alum doses through the use of a flocculant aid. Calgon POL-E-Z 652 nonionic polymer was selected due to its high molecular weight and availability. Polymers are typically applied in water treatment situations at dosage less than 0.3 mg/L (Reynolds, 1982); therefore, the selected polymer dose range was 0.1-0.5 mg/L. The alum dose was 12.5 mg/L since a large presence of colloidal organic material was observed at this dose (Figure 24). Only a 1  $\mu$ m filter and 100,000 amu membrane were used for reasons described earlier. Preliminary tests evaluated polymer addition at first, second, and third stage flocculation. First stage flocculation polymer addition gave the most visible floc formation so first stage flocculation was the polymer dosing point used to generate the following experimental data.

Figures 30 through 32 and Table A-18 contain the results of the alum/nonionic polymer dose study. Figure 30 illustrates that a polymer dose of 0.3 mg/L successfully removed the colloidal aluminum organic material. Polymer doses <0.3 mg/L were insufficient to efficiently bridge the colloidal aluminum bound organic material to cause precipitation. In comparison, polymer doses >0.3 mg/L caused apparent restabilization of the colloidal aluminum bound organic material. Similar results are shown in Figure 31 where residual aluminum data are presented. Note in both Figures 30 and 31 that the relative residual DOC and residual "soluble" aluminum (as defined by the <100,000 amu ultrafilter) were essentially constant throughout the polymer dose range. This implied that the nonionic polymer was interacting only with the colloidal aluminum bound organic material in the system and not with truly soluble DOC or aluminum. This result was independently tested in an experiment where no alum was added to the DOC-containing

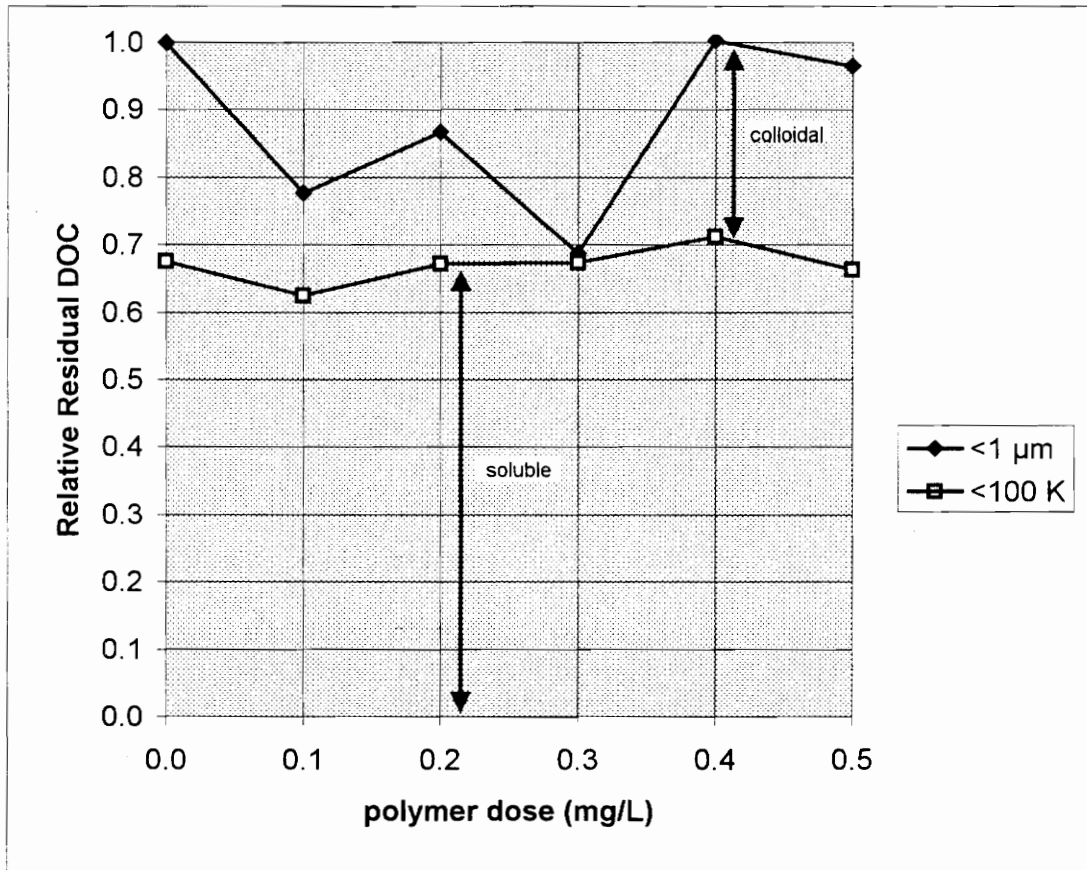


Figure 30. Relative residual DOC results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying polymer dosages at constant alum dosage (12.5 mg/L) and at pH 5.8. (original DOC = 4.7 mg/L)

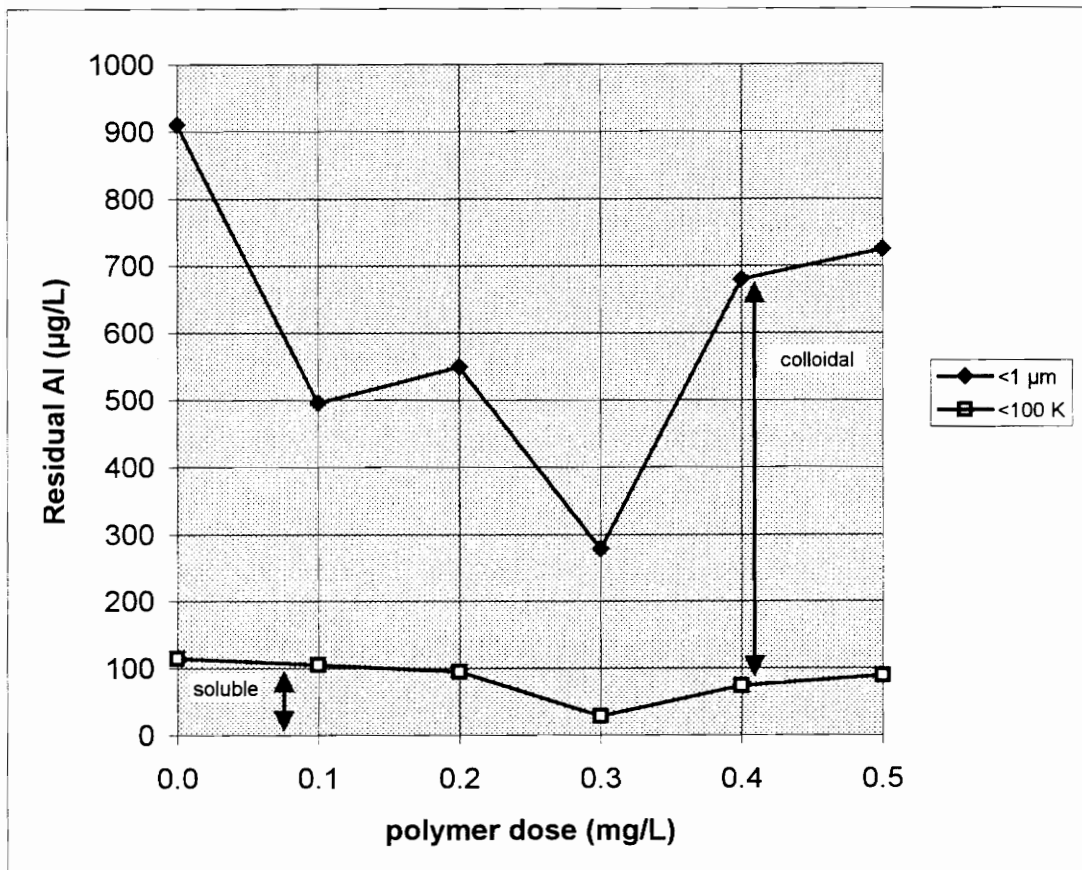


Figure 31. Relative residual aluminum results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying polymer dosages at constant alum dosage (12.5 mg/L,  $Al_T = 1125 \mu\text{g/L}$ ) and at pH 5.8.

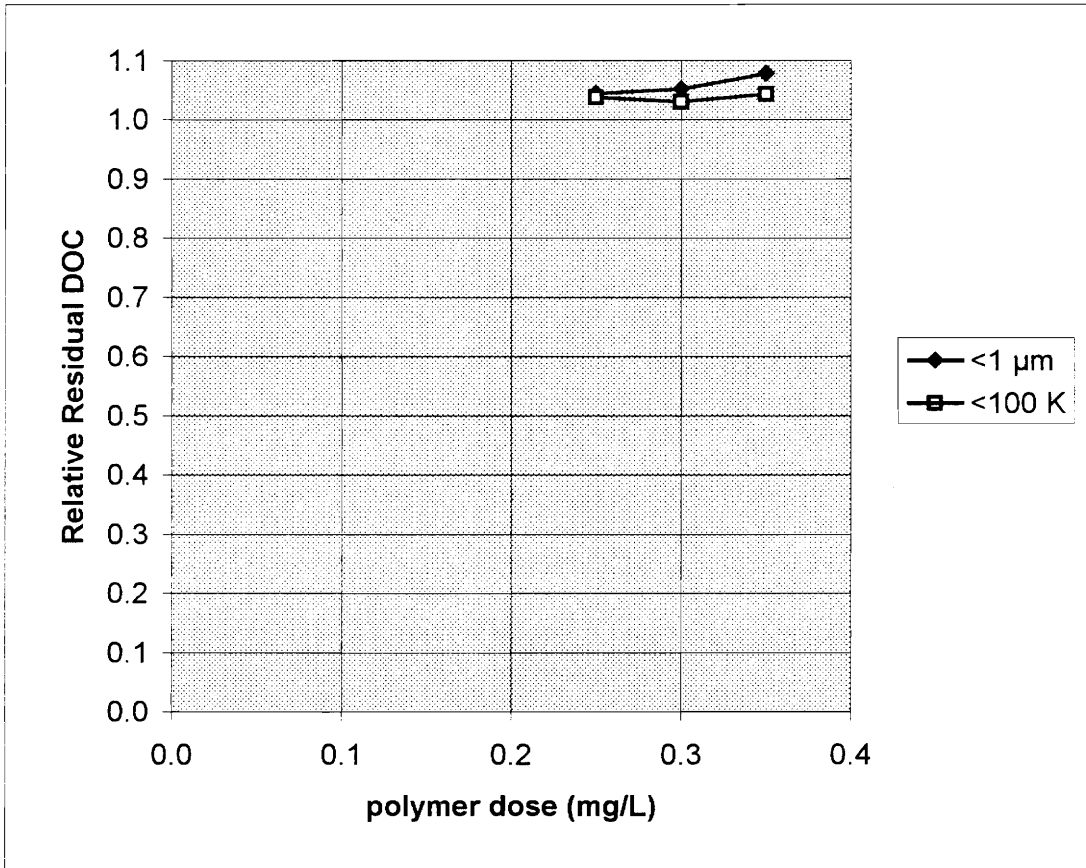


Figure 32. Relative residual DOC results of coagulation of Lake Drummond <10K amu hydrophobic acid fraction with varying polymer dosages at pH 5.8 and no alum dosage.



water sample. Instead, only nonionic polymer was added. The results (shown in Figure 32) again show no direct interaction between the polymer and the DOC present in solution.

In summary, experiments were performed on <10,000 amu hydrophobic acids to investigate the presence of colloidal metal bound organic material following coagulation. Alum coagulation experiments showed a significant amount of colloidal aluminum organic material at less than optimum pH (Figure 22) and at less than enhanced coagulant doses (Figure 24). Similarly, ferric chloride coagulation experiments indicated a significant amount of colloidal iron bound organic material at relatively low ferric chloride doses (Figure 27).

Typically, conventional jar testing procedures utilize a filter size of 0.45  $\mu\text{m}$  to differentiate between precipitated and soluble organic material. These experimental results, however, indicated that a significant amount of colloidal metal bound organic material existed that was not removed by "larger" filter sizes (e.g. 0.45  $\mu\text{m}$ ). The experiments further illustrated that organic material had interacted with the coagulant but was simply in a colloidal state. A final coagulation experiment was developed to investigate the use of a combination of metal coagulant and nonionic polymer to eliminate the colloidal fraction. That is, the premise was that a less than optimum dose of coagulant in conjunction with a nonionic polymer would effectively "push" the colloidal metal bound organic material into a particulate state thereby eliminating the colloidal fraction. Figure 30 shows that the experiment was a success as the <1  $\mu\text{m}$  and <100 K relative residual DOC values were the same.

## Chapter V

### DISCUSSION

The DOC of two natural waters, Lake Drummond and the Chickahominy River, were characterized both physically and chemically through ultrafiltration and synthetic resin adsorption, respectively. A series of synthetic resin adsorbents fractionated the waters into six organic fractions (hydrophobic acid, base, neutral and hydrophilic acid, base, neutral) based on the hydrophobicity and acidity of the DOC. Five different sized ultrafiltration membranes (30,000 amu, 10,000 amu, 3,000 amu, 1,000 amu, and 500 amu) provided apparent molecular weight distributions for the waters.

The effects of pH on coagulation performance was studied on four of the organic fractions (hydrophobic acid, hydrophobic neutral, hydrophilic acid, and hydrophilic neutral) obtained from Lake Drummond. AMWDs were performed on each of the six organic fractions obtained from Lake Drummond.

Mixtures of the hydrophobic acid fraction and hydrophobic neutral fraction were coagulated to study the effects of concentration on the removal of both fractions. In the first experiment, the concentration of the hydrophobic neutral fraction was greater than the hydrophobic acid fraction concentration while in the second experiment the reverse was true. Samples were coagulated at two different pHs in both experiments.

The phase-change behavior of DOC during coagulation was studied using the hydrophobic acid fraction obtained from Lake Drummond. During water treatment, DOC proceeds from a dissolved state to a insoluble complexed metal organic precipitate. Jar test procedures have traditionally separated floc from DOC using a 1  $\mu\text{m}$  or 0.45  $\mu\text{m}$  filter. This research investigated the possibility of the presence of colloidal aluminum

bound organic material smaller than 1  $\mu\text{m}$  or 0.45  $\mu\text{m}$ . A series of filters and membranes (1  $\mu\text{m}$ , 100,000 amu, and 30,000 amu) were used for this purpose.

### **Characterization of Lake Drummond and Chickahominy River**

Although both water sources were from distinctly different bodies of water (i.e. a lake and a river), they both exhibited similar fractionation results. Figures 8 and 10 and Tables A-3 and A-5 illustrate that the DOC of both waters were primarily hydrophobic acids. The hydrophilic neutral fraction was the next largest fraction albeit in a much smaller concentration than the hydrophobic acid fraction. As discussed earlier, the literature supports these results. Due to the ubiquity of the hydrophobic acid fraction, alum coagulation resulted in the removal of over 50% of the DOC in both waters.

Preferential removal of the hydrophobic acids was expected as hydrophobic acids are characterized by having a net negative charge at pH values above 2.0, making them susceptible to removal by the positively charged metal monomers, polymers, and precipitates. An interesting observation is that although over 55% of the hydrophobic acid fraction in both waters was removed by coagulation, over 50% of the remaining DOC in both waters following coagulation was still hydrophobic acids.

A correlation can be drawn between the acidic and neutral fractions removed in both waters. Removal of the hydrophobic acid fraction was greater for Lake Drummond while removal of the hydrophilic neutral fraction was greater for the Chickahominy River. The hydrophobic acid to hydrophilic acid DOC ratio for Lake Drummond (17.3) was much larger than for the Chickahominy River (7). Consequently, removal of the hydrophobic acid fraction was 66% for Lake Drummond but only 57% Chickahominy River (see Tables A-3 and A-5). Conversely, more of the hydrophilic acid fraction was

removed from the Chickahominy River than from Lake Drummond. The hydrophilic neutral to hydrophobic neutral DOC ratio for the Chickahominy River (2.5) was slightly larger than for Lake Drummond (2). In much the same way as for the acid fractions, removal of the hydrophilic neutral fraction was 28% for the Chickahominy River but only 20% for Lake Drummond. These ratios indicate there exists a competition by fractions of the same charge (e.g. hydrophobic and hydrophilic acid fractions) for the coagulant. The fraction with the larger concentration dominates.

Table A-3 shows that three of the Lake Drummond fractions increased in concentration following coagulation: hydrophobic neutral, hydrophilic base, and hydrophilic acid. An important concept to remember is the organic material remaining in solution following coagulation and filtration (1  $\mu\text{m}$  glass fiber filter) is 1) either dissolved ( $<100,000$  amu) or colloidal ( $>100,000$  amu but  $<1 \mu\text{m}$ ) and 2) may or may not be bound to aluminum monomers, polymers, or  $\text{Al}(\text{OH})_{3(s)}$ . Aluminum species are charged and the charge on the resulting complexes will be affected by the aluminum species. For example, hydrophobic acids which had a negative charge prior to coagulant addition may possess a neutral charge following coagulant addition due to complexation with positively charged aluminum species. Although the resulting complex has no charge and will adsorb to the XAD-8 resin as a hydrophobic neutral molecule, the organic ligand is a hydrophobic acid. This phenomena was further investigated and discussed in the Hydrophobic Acid and Hydrophobic Neutral Coagulation Study section in the previous chapter. Likewise, one hypothesis for the observed slight increase in the hydrophilic base fraction concentration would be due to a net positive charge on some aluminum/hydrophilic acid complexes that were not removed through filtration. Also, the

boundaries between fractions are not sharp as overlap exists (Aiken, 1988), thus some of the hydrophilic neutral fraction may have appeared in the hydrophilic base fraction.

Figures 9 and 11 and Tables A-4 and A-6 contain the AMWD for both waters. The Lake Drummond AMWD indicates that the DOC of Lake Drummond was much larger in physical size than the Chickahominy River. AMWD is somewhat of a misnomer as ultrafiltration actually filters based on molecular size and not weight; however, a high molecular weight usually corresponds to a large molecular size (Logan and Jiang, 1990). Incidentally, ultrafiltration membranes are calibrated with compounds of known molecular weight. Analysis of the filtrates showed 20% of the Lake Drummond DOC was greater than 30,000 amu while only 7% of the Chickahominy River DOC was greater than 30,000 amu. These results are expected as the Lake Drummond DOC is much more humic than the Chickahominy River DOC. The treated Lake Drummond water sample results (Figure 9) indicate a preferential removal by the coagulant of the larger molecular weight DOC compared to the smaller molecular weight DOC.

Collins et al. (1985) concluded that high molecular weight DOC have more reactive sites on the molecule for interaction with a coagulant than the low molecular weight DOC. The preferential removal of high molecular weight DOC over low molecular weight DOC by coagulation observed in this research agrees with the findings of Collins et al. (1986).

### **Study of Lake Drummond Organic Fractions**

An AMWD was performed on each of the six organic fractions obtained from the Lake Drummond water sample. The results are shown in Figure 12 and 13 and Table A-7. A few general observations can be made. First, the hydrophobic acid fraction was large in molecular size as compared to the other five fractions. Over 60% of the

hydrophobic acid fraction was larger than 3,000 amu. The hydrophilic neutral fraction (the second largest fraction in the Lake Drummond water sample) was small in molecular size with over 70% less than 1,000 amu. The hydrophilic acid fraction was also small in molecular size while the hydrophobic neutral fraction had a somewhat uniform AMWD. Both base fractions were small in molecular size. These data in combination with the whole water AMWD for Lake Drummond partially explains the large removal of hydrophobic acids during coagulation. Not only did the hydrophobic acids constitute the largest organic fraction in the whole water, but the hydrophobic acids were large in molecular size.

Figures 14 and 16 and Table A-8 indicate that the acid fractions were affected by pH variations during alum coagulation while Figures 15 and 17 and Table A-8 indicate that pH had no effect on the neutral fraction alum coagulation results. These results were expected as the acid fractions have negative charges at pH values above 2.0, making these fractions amenable to interactions with the positively charged aluminum monomers, polymers, and precipitates during coagulation. The presence of positively charged aluminum species decreases at pH <5 and pH >6. The neutral fractions are relatively unaffected by pH variations since the neutral fraction DOC has no net charge. The hydrophobic acid fraction had a maximum DOC removal of 67% while the hydrophilic acid fraction had a maximum DOC removal of 30%. The greater hydrophobicity of the hydrophobic acid fraction explains this phenomena. The same holds true for the neutral fractions.

In summary, the AMWDs and the coagulation study of the Lake Drummond organic fractions provided much insight into the nature of DOC. The hydrophobic acid

fraction was the largest DOC fraction of the Lake Drummond water sample, the largest in molecular size, and the most amenable of the six organic fractions to coagulation. These three facts suggest that a combination of the concentration, physical size, hydrophobicity, and acidity of an organic fraction contribute to its removal during coagulation as both chemistry and physical size appear to effect the removal of DOC.

### **Coagulation of Hydrophobic Acid/Hydrophobic Neutral Mixtures**

The results of both the hydrophobic neutral fraction and hydrophilic acid fraction coagulation pH study prompted the need to study the competition between different fractions for aluminum species. An experiment was devised to investigate this phenomena. Two mixtures of the hydrophobic acid and hydrophobic neutral fraction in different ratios were coagulated with alum at two different pHs. The first mixture's ratio was at 3 mg/L hydrophobic neutral fraction to 2 mg/L hydrophobic acid fraction while the second mixture's ratio was at 4 mg/L hydrophobic acid fraction to 1 mg/L hydrophobic neutral fraction.

The first alum coagulation experiment (3:2 ratio) revealed that the increased presence of the hydrophobic neutral fraction had an antagonistic effect on the removal of the hydrophobic acid fraction (Table A-9) as compared to the Lake Drummond and Chickahominy River coagulation results (Tables A-3 and A-5, respectively). At pHs 5.5 and 7.5, approximately 57% of the hydrophobic neutral fraction was removed. However, 9% of the hydrophobic acid fraction was removed at pH 5.5 while it increased by 10% at pH 7.5. Therefore, pH effected removal of the hydrophobic acid fraction but not the removal of the hydrophobic neutral fraction.

The second alum coagulation experiment (4:1 ratio) revealed that the increased presence of the hydrophobic acid fraction had an antagonistic effect on the removal of the hydrophobic neutral fraction (Table A-10) as compared to the first experiment. At pH 5.5, 52% of the hydrophobic acid fraction was removed while 56% was removed at pH 7.5. However, 56% of the hydrophobic neutral fraction was removed at pH 5.5 while the hydrophobic neutral fraction concentration increased by 7% at pH 7.5. Therefore, pH effected the removal of the hydrophobic neutral fraction but not the removal of hydrophobic acid fraction.

In summary, the coagulation of the hydrophobic acid/hydrophobic neutral mixtures revealed that the greater presence of one organic fraction over another fraction had an antagonistic effect on the removal of the other fraction. This experiment verifies that concentration of an organic fraction in relation to the other fractions effects its removal during coagulation.

### **Phase-Change Behavior of DOC**

The Lake Drummond hydrophobic acid fraction was used to study the phase-change behavior of DOC. Knocke *et al.*, (1994) observed that iron complexed organic material not removed by a 0.2  $\mu\text{m}$  filter following jar testing. The iron complexed organic material was removed by a 100,000 amu ultrafilter. The authors concluded that a colloidal fraction of organic material existed. It was decided to investigate this phenomena using alum and ferric chloride as coagulants.

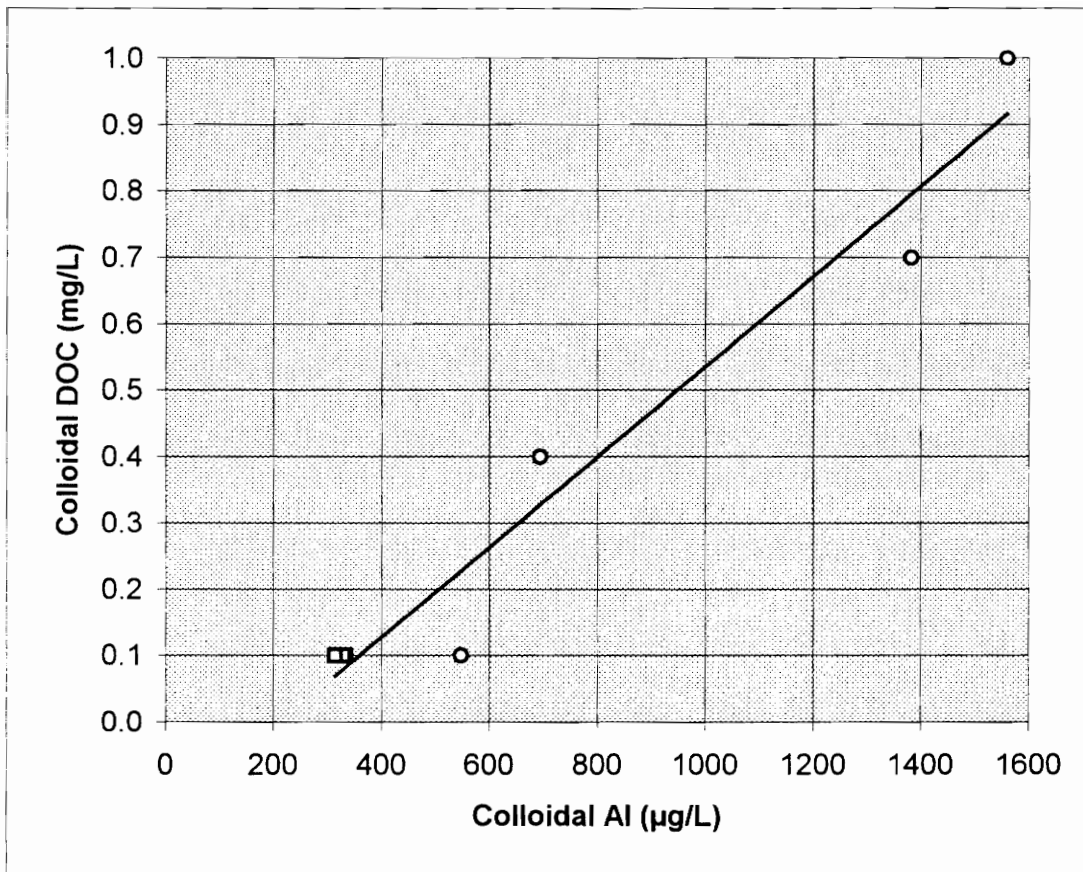
The Lake Drummond hydrophobic acid fraction was selected as the DOC fraction for the study due to its ubiquity and strong affinity for interacting with metal coagulants. The hydrophobic acid fraction was passed through a 10,000 amu



membrane to ensure the DOC was less than 30,000 amu. The hydrophobic acids were coagulated using alum and ferric chloride in separate tests. The tests were performed at varying pH doses and the DOC and residual aluminum or iron concentrations were measured after passing the sample through a 1  $\mu\text{m}$  filter, 100,000 amu membrane, and 30,000 amu membrane.

The results indicated the presence of a colloidal fraction of metal complexed organic material at less than enhanced doses for both coagulants. Traditionally, jar test procedures require a 1  $\mu\text{m}$  or 0.45  $\mu\text{m}$  filter to remove metal complexed material. It was assumed that the filtrate less than 1  $\mu\text{m}$  in size was dissolved. The EPA enhanced dose and optimum pH definitions utilize 1  $\mu\text{m}$  or 0.45  $\mu\text{m}$  filters to separate the solid metal complexed organic material from the dissolved complexed organic material. These experiments showed that truly dissolved complexed organic material is actually less than 100,000 amu.

Figure 33 illustrates the colloidal DOC and colloidal aluminum remaining following coagulation using an alum dose of 50 mg/L at various pH values. A phase-change of organic material is clearly shown in Figure 33 as the colloidal fraction was least at pH >6.0. Two mechanisms appear to be at work. First, at lower pH conditions (4.5 - 5.5), DOC removal often occurs via direct aluminum-organic material precipitation (Amirtharajah and O'Melia, 1990). Much of this aluminum bound organic material may simply be colloidal in size. At higher pH conditions, less colloidal material existed due to the absence of  $\text{Al}(\text{OH})_{3(s)}$ , however overall organic material removal was similar as at lower pH conditions (Figure 22). Second, at lower pH conditions (pH <6.0),  $\text{Al}(\text{OH})_{3(s)}$  will have a more positive surface charge than at higher pH conditions and, therefore,



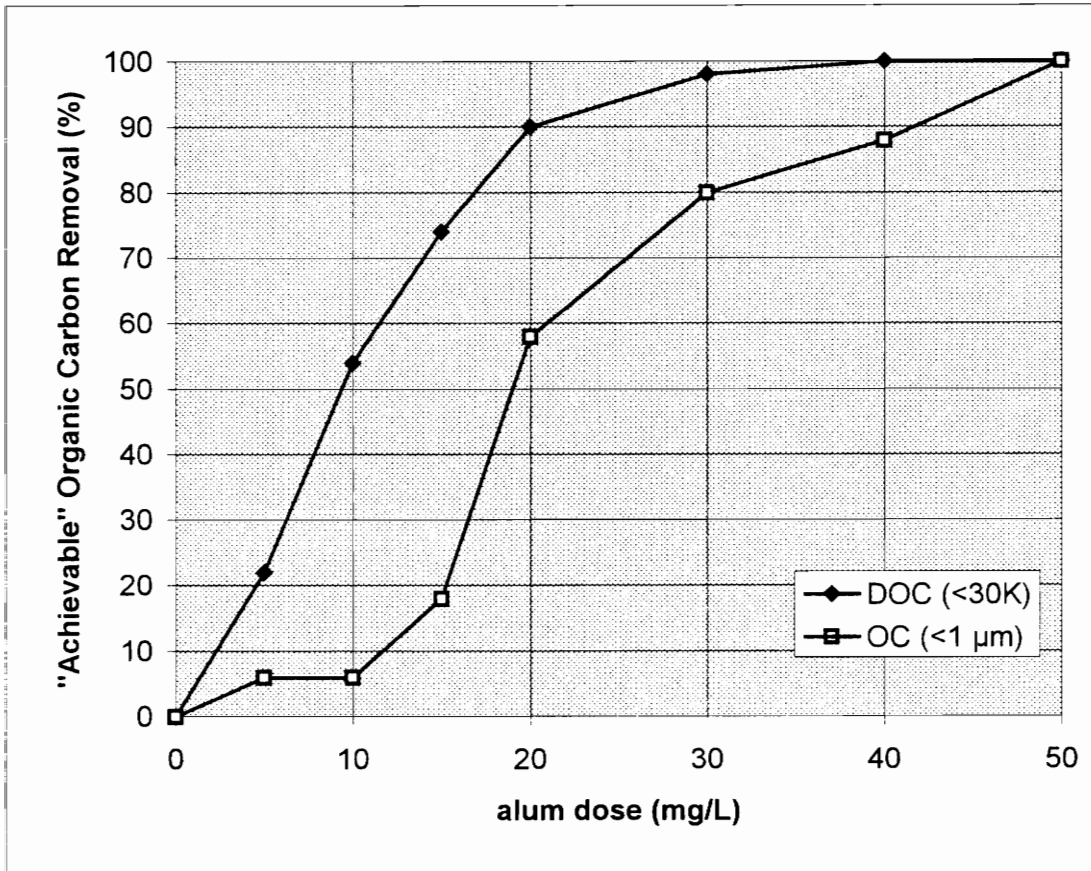
Note: Colloidal DOC = <1 µm DOC - <100 K DOC  
 Colloidal Al = <1 µm Al - <100 K Al  
 o = pH < 6.0, □ = pH > 6.0

Figure 33. Colloidal DOC and colloidal aluminum remaining following coagulation of <10K amu hydrophobic acid fraction with alum dosage of 50 mg/L at various pHs. (original DOC = 4.9 mg/L)

more difficult to aggregate to sizes greater than 1  $\mu\text{m}$  due to charge repulsion. At pH >6.0 conditions, the colloids contained far less DOC than at the lower pH conditions, that is, more of the DOC remaining in solution was dissolved than at the lower pH conditions.

Figure 34 illustrates the “achievable” organic carbon removal resulting from coagulation with alum dosages ranging from 0 to 50 mg/L at pH 5.8. “Achievable” organic carbon removal refers to the amount of organic carbon remaining based on the maximum “achievable” organic carbon removal at the 50 mg/L alum dose (2.5 mg/L DOC). DOC is defined as the organic material that is less than 30,000 amu or truly dissolved based on the operational definition used in this research. The space between DOC and OC (organic carbon) on the graph represents where DOC has been converted to colloids/small particles. OC shows when sufficient aggregation of colloids has taken place to form particle greater than 1  $\mu\text{m}$  in size.

Figure 34 identifies the additional alum dosage required to cause aggregation of aluminum/organic colloids to sizes in excess of a 1  $\mu\text{m}$  filter. For example, 90% removal of “achievable” DOC occurred at 20 mg/L alum dosage, however, 90% removal of “achievable” OC did not occur until 40 mg/L alum dosage. Hence, the additional 20 mg/L alum dosage served mainly to cause aggregation of aluminum/organic colloids already present at the 20 mg/L alum dosage. A nonionic polymer dose of 0.25-0.50 mg/L could have easily replaced the additional 20 mg/L alum dosage as shown in the Results chapter. Substituting nonionic polymer for alum would have cut the alum dose in half, thereby saving money in terms of both coagulant and sludge disposal costs.



Note: DOC (<30 K) = aluminum bound organic carbon <30 K amu  
 OC (<1 μm) = aluminum bound organic carbon <1 μm  
 DOC - OC = colloidal aluminum bound organic carbon  
 (between 1 μm and 30K amu)

Figure 34. "Achievable" organic carbon removal resulting from coagulation with varying alum dosages at pH 5.8. (based on maximum "achievable" organic carbon removal of 2.5 mg/L)

Table 10 illustrates removal of DOC and OC over seven coagulant dose ranges and the effectiveness of alum in removing both DOC and OC. For example, at a coagulant dose of 15 mg/L alum, 74% of “achievable” organic carbon removal of DOC occurred while only 18% of “achievable” organic carbon removal of OC occurred (see Figure 34). At a coagulant dose of 20 mg/L alum, 90% of “achievable” organic carbon removal of DOC occurred while 58% of “achievable” organic carbon removal of OC occurred. In Table 10,  $\Delta$  DOC refers to the DOC removal that occurred over the specified coagulant dose range in relation to the maximum “achievable” organic carbon removal of 2.5 mg/L. Therefore,  $\Delta$  DOC at the 15-20 mg/L coagulant dose range was  $(0.90-0.74) * 2.5 \text{ mg/L} = 0.40 \text{ mg/L}$  and  $\Delta$  OC was  $(0.58-0.18) * 2.5 \text{ mg/L} = 1.00 \text{ mg/L}$ .

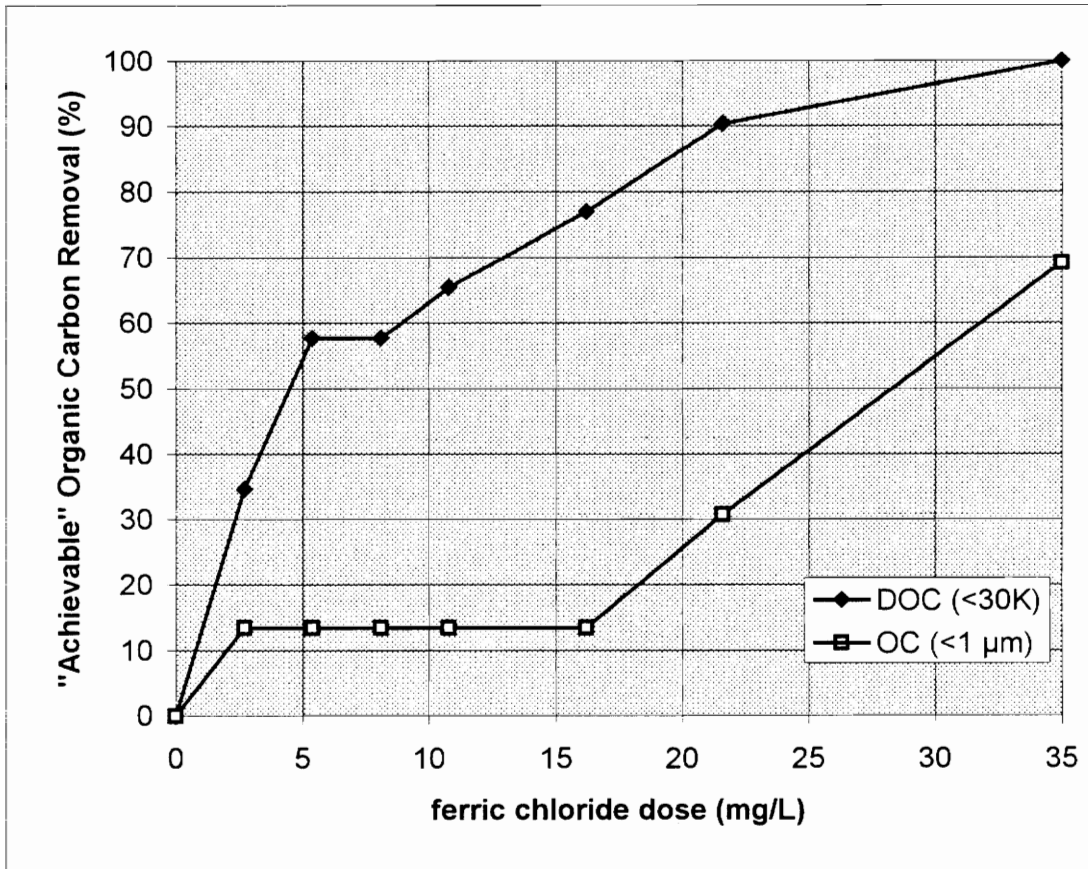
Columns three and five in Table 10 measure the effectiveness of alum at removing DOC and OC. That is, the larger the value, the more effective or efficient alum was at removing the organic carbon. The dose range at 15-20 mg/L alum was  $\Delta$  Alum = 5 mg/L. Therefore,  $\Delta$  DOC/ $\Delta$  Alum was  $0.40/5 = .080$  and  $\Delta$  OC/ $\Delta$  Alum was  $1.00/5 = 0.20$ . Table 10 clearly illustrates that the majority of the DOC was removed at low coagulant dosages (i.e. less than 20 mg/L). Alum was most effective at removing DOC at low coagulant dosages as shown by the  $\Delta$  DOC/ $\Delta$  Alum values. Table 10 supports Figure 34 by also illustrating that the higher coagulant dosages simply served to aggregate aluminum/organic colloids to sizes greater than 1  $\mu\text{m}$  that were actually already present at lower coagulant dosages but at a smaller size (30K).

Like Figure 34, Figure 35 illustrates the “achievable” organic carbon removal resulting from coagulation with ferric chloride dosages ranging from 0 to 27 mg/L at

Table 10. Removal of DOC and OC over alum dose range 0-50 mg/L at pH 5.8.

Coagulant				
Dose Range	$\Delta$ DOC (mg/L)	$\frac{\Delta \text{DOC (mg)}}{\Delta \text{Alum (mg)}}$	$\Delta$ OC (mg/L)	$\frac{\Delta \text{OC (mg)}}{\Delta \text{Alum (mg)}}$
0-5	0.55	0.11	0.15	0.030
5-10	0.80	0.16	0.00	0.00
10-15	0.50	0.10	0.30	0.060
15-20	0.40	0.080	1.00	0.20
20-30	0.20	0.020	0.55	0.055
30-40	0.05	0.005	0.20	0.020
40-50	0.00	0.00	0.30	0.030

Note: Assumed maximum "achievable" DOC and OC removal was 2.5 mg/L.



Note: DOC (<30K) = iron bound organic carbon <30K amu  
 OC (<1 μm) = iron bound organic carbon <1 μm  
 DOC - OC = colloidal iron bound organic carbon (between 1 μm and 30K amu)

Figure 35. "Achievable" organic carbon removal resulting from coagulation with varying ferric chloride dosages at pH 5.5. (based on maximum "achievable" organic carbon removal of 2.5 mg/L)

pH 5.5. The presence of iron/organic colloids is more pronounced at lower dosages and the colloids never aggregate even at the higher ferric chloride dosages as was the case in the alum study (Figure 34). A low ferric chloride dose coupled with an appropriate flocculant aid could work very well in this case.

Table 11 was derived in the same way as Table 10 except that ferric chloride was the coagulant. Like Table 10, Table 11 illustrates that the higher coagulant dosages simply served to aggregate iron/organic colloids to sizes greater than 1  $\mu\text{m}$  that were already present at lower coagulant dosages but at a smaller size (30K). Table 11 also supports the conclusions derived from Figure 35.

A comparison of alum and ferric chloride coagulation results reveals several interesting similarities and differences. Figure 27 indicates the presence of colloidal iron bound organic material at lower coagulant dosages than for identical alum dosages (Figure 24). Also, aggregation of colloidal iron organic material was never quite complete at the higher ferric chloride dosages as it was with the higher alum dosages. For example, a relative residual DOC separation of approximately 0.2 existed between the 1  $\mu\text{m}$  and 100,000 or 30,000 amu at ferric chloride dose 27 mg/L while no relative residual DOC separation existed for the corresponding alum dose of 50 mg/L. The larger relative residual DOC separation at mid-range ferric chloride doses compared to the alum doses can be explained by the small iron polymers. Aluminum polymers are much larger than iron polymers in both molecular weight and size causing aluminum floc to possibly be larger and heavier. The large aluminum polymers may both bind and precipitate with hydrophobic acids more readily than the smaller iron polymers.



Table 11. Removal of DOC and OC over FeCl<sub>3</sub> dose range 0-35 mg/L at pH 5.5.

Coagulant				
Dose	$\Delta$ DOC	$\frac{\Delta \text{DOC (mg)}}{\Delta \text{FeCl}_3 \text{ (mg)}}$	$\Delta$ OC	$\frac{\Delta \text{OC (mg)}}{\Delta \text{FeCl}_3 \text{ (mg)}}$
Range	(mg/L)		(mg/L)	
0-2.7	0.87	0.32	0.34	0.12
2.7-5.4	0.58	0.21	0.00	0.00
5.4-8.1	0.00	0.00	0.00	0.00
8.1-10.8	0.19	0.071	0.00	0.00
10.8-16.2	0.29	0.053	0.00	0.00
16.2-21.6	0.34	0.062	0.43	0.080
21.6-35	0.24	0.018	0.96	0.072

Note: Assumed maximum "achievable" DOC and OC removal was 2.5 mg/L.

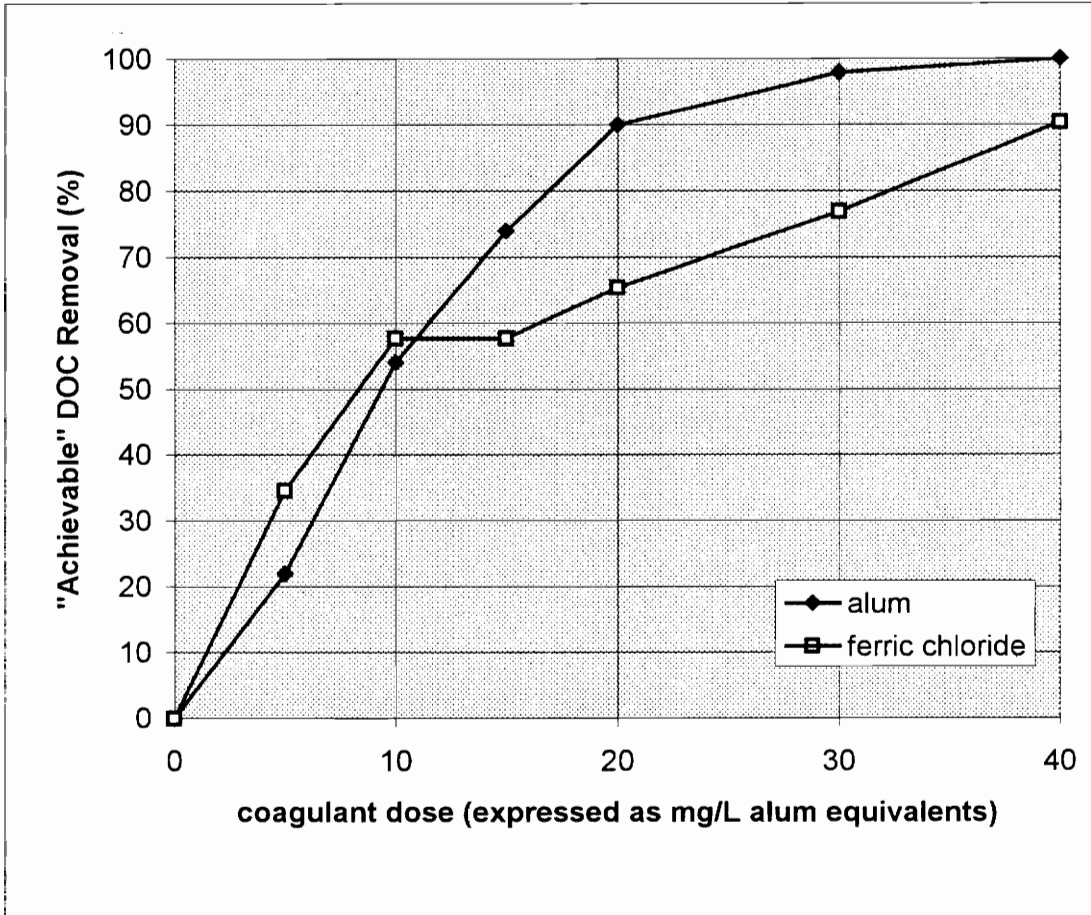
Figure 36 compares the performance of both alum and ferric chloride in terms “achievable” DOC removal, that is, DOC remaining (<30,000 amu) following coagulation. Alum shows better overall performance than ferric chloride in removal of DOC for this water.

In summary, at less than enhanced doses of both alum and ferric chloride there exists colloidal metal bound organic material. The addition of alum coupled with a nonionic polymer caused aggregation of the colloidal material. An impressive cost savings in coagulant could be realized by using a polymer in combination with the coagulant.

### **Applicability of Results to Water Treatment**

The scope of this research covered a broad range of topics concerning DOC in natural waters. A physical and chemical characterization of DOC was performed to better understand the nature of DOC. Numerous coagulation studies on the untreated Lake Drummond and Chickahominy River waters and the Lake Drummond organic fractions were performed to better understand the effects that pH and DOC have on coagulation performance. Finally, the phase-change behavior of DOC during water treatment was analyzed to understand coagulation mechanisms.

The DOC fraction most amenable to coagulation in natural waters is hydrophobic and acidic in nature. This hydrophobic acid fraction is also large in size and therefore utilizes the majority of the coagulant. If new coagulation methods could be developed, more of the non-hydrophobic acid fractions could be removed. In conventional water treatment, both alum and iron salts remove large molecular weight organic materials



Note: alum = aluminum bound organic carbon <30K amu  
 ferric chloride = iron bound organic carbon <30K amu

Figure 36. Comparison of "achievable" organic carbon removal (<30K) between alum and ferric chloride coagulation

first. Treatment methods to flocculate the smaller molecular weight organic material is one way to improve organics removal.

Finally, at less than enhanced doses of both alum and ferric chloride there exists colloidal metal complexed organic material that is not removed during coagulation. The addition of nonionic polymers as flocculant aids can remove the colloidal metal complexed organic material thereby requiring lower doses of coagulant and saving money in terms of both coagulant and sludge disposal costs. Also, traditional water treatment practices have discouraged the use of direct filtration for organic laden waters. The results of the phase-change behavior of organic material from this research suggest that direct filtration of organic laden waters may be possible when a combination of metal coagulant and nonionic polymer are used. The metal coagulant and nonionic polymer combination would effectively cause the colloids to aggregate.

## Chapter VI

### CONCLUSIONS

The purpose of the research was to physically and chemically characterize the DOC of two natural waters. The effect of pH on the coagulation of the separate DOC organic fractions was also studied. Also, the phase-change behavior of DOC during coagulation was investigated. Two natural waters were characterized for comparative purposes. The conclusions from the research were as follows:

1. The majority of the DOC in Lake Drummond and the Chickahominy River was hydrophobic ( $\approx 75\%$ ), acidic ( $\approx 75\%$ ), and greater than 3,000 amu.
2. During alum coagulation, solution pH affected the removal of the Lake Drummond acidic fractions of DOC but not the neutrally charged fractions. That is, over the pH range tested (5.0-7.5), removal of the acidic DOC fractions varied with optimal removal between pHs 5.5 and 6.0 but not for the neutral fractions. Therefore, during coagulation solution pH is more important for waters composed primarily of acidic organic fractions than for waters composed of neutral organic fractions.
3. Two properties of DOC affected its removal: hydrophobicity and physical size. Better removal of both the hydrophobic acid and hydrophobic neutral fractions was observed compared to their hydrophilic counterparts. The larger molecular weight organic material was removed in the Lake Drummond water. In addition, better removal of the organic fractions with the largest AMWDs (hydrophobic acids) was observed.

4. In prepared solutions containing only hydrophobic acid and hydrophobic neutral organic fractions, the fraction in greater concentration hindered the removal of the lesser fraction. At solution pH 7.5 and a 2:3 hydrophobic acid to hydrophobic neutral ratio, approximately 57% of the hydrophobic neutral fraction was removed while the hydrophobic acid fraction concentration increased by 10%. However, at solution pH 7.5 and a 4:1 hydrophobic acid to hydrophobic neutral ratio, approximately 56% of the hydrophobic acid fractions was removed while the hydrophobic neutral fraction concentration increased by 7%. The relative concentration of the organic fraction now only affected removal of that fraction but also interfered with removal of the other fraction.
5. At less than enhanced doses of both alum and ferric chloride there existed colloidal metal bound organic material. Low dosages of both alum and ferric chloride caused the formation of aluminum/organic colloids while additional dosages served mainly to aggregate these aluminum/organic colloids. The addition of nonionic polymer as a flocculant aid in conjunction with a metal salt successfully removed the colloidal bound organic material.
6. The traditional use of a 1  $\mu\text{m}$  or 0.45  $\mu\text{m}$  filter in jar testing was not adequate for differentiating between particulate and dissolved complexed organic material following coagulation. A 100K amu ultrafiltration membrane successfully separated colloidal organic material from truly dissolved complexed organic material, thereby allowing appropriate quantification of residual DOC in solution.

## APPENDIX A

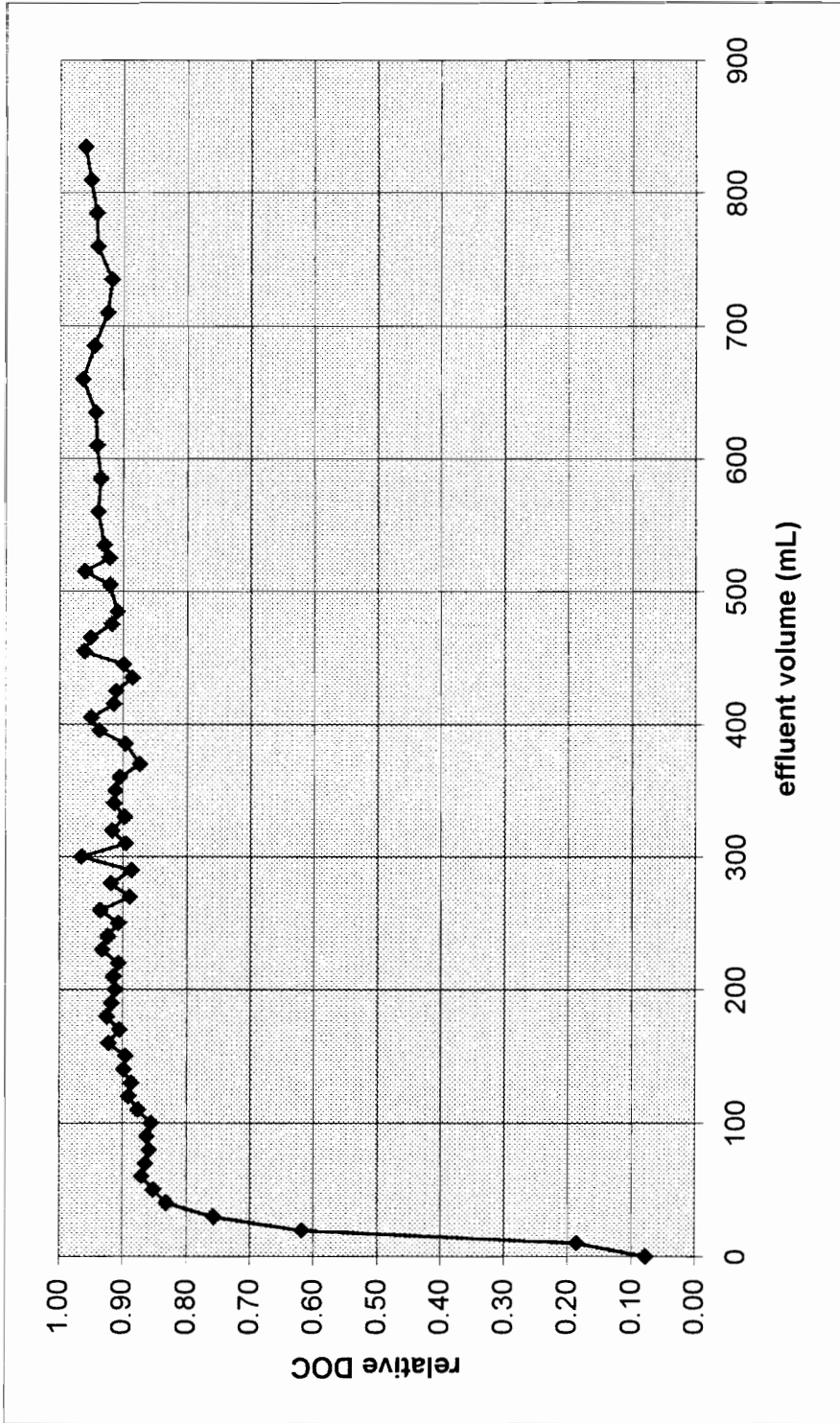


Figure A-1. Breakthrough curve for XAD-8 resin and Lake Drummond water at pH 7.0. (sample DOC = 8.5 mg/L, 1 bed volume = 16.3 mL)



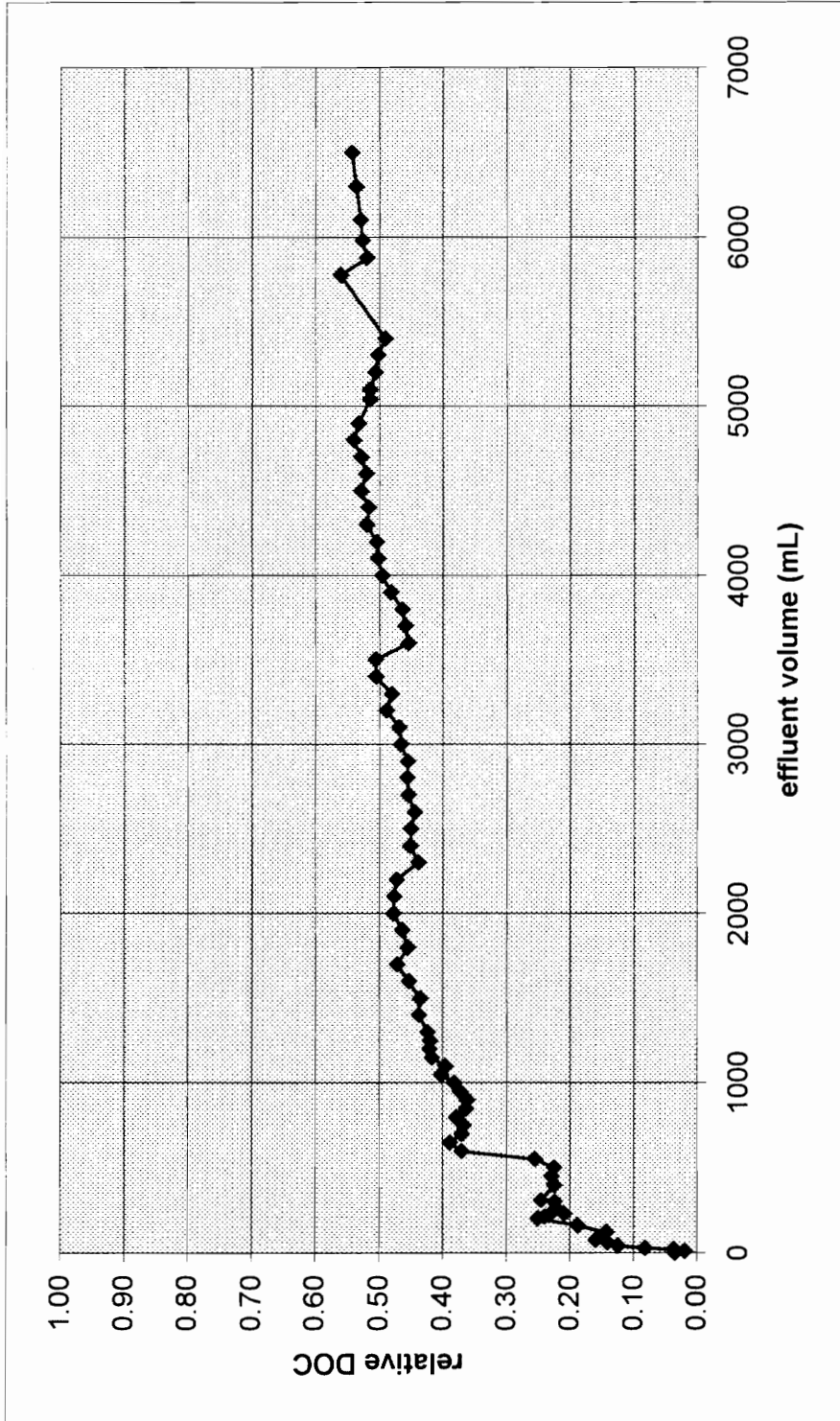


Figure A-2. Breakthrough curve for XAD-8 resin and Lake Drummond water at pH 2.0. (sample DOC = 8.3 mg/L, 1 bed volume = 16.3 mL)

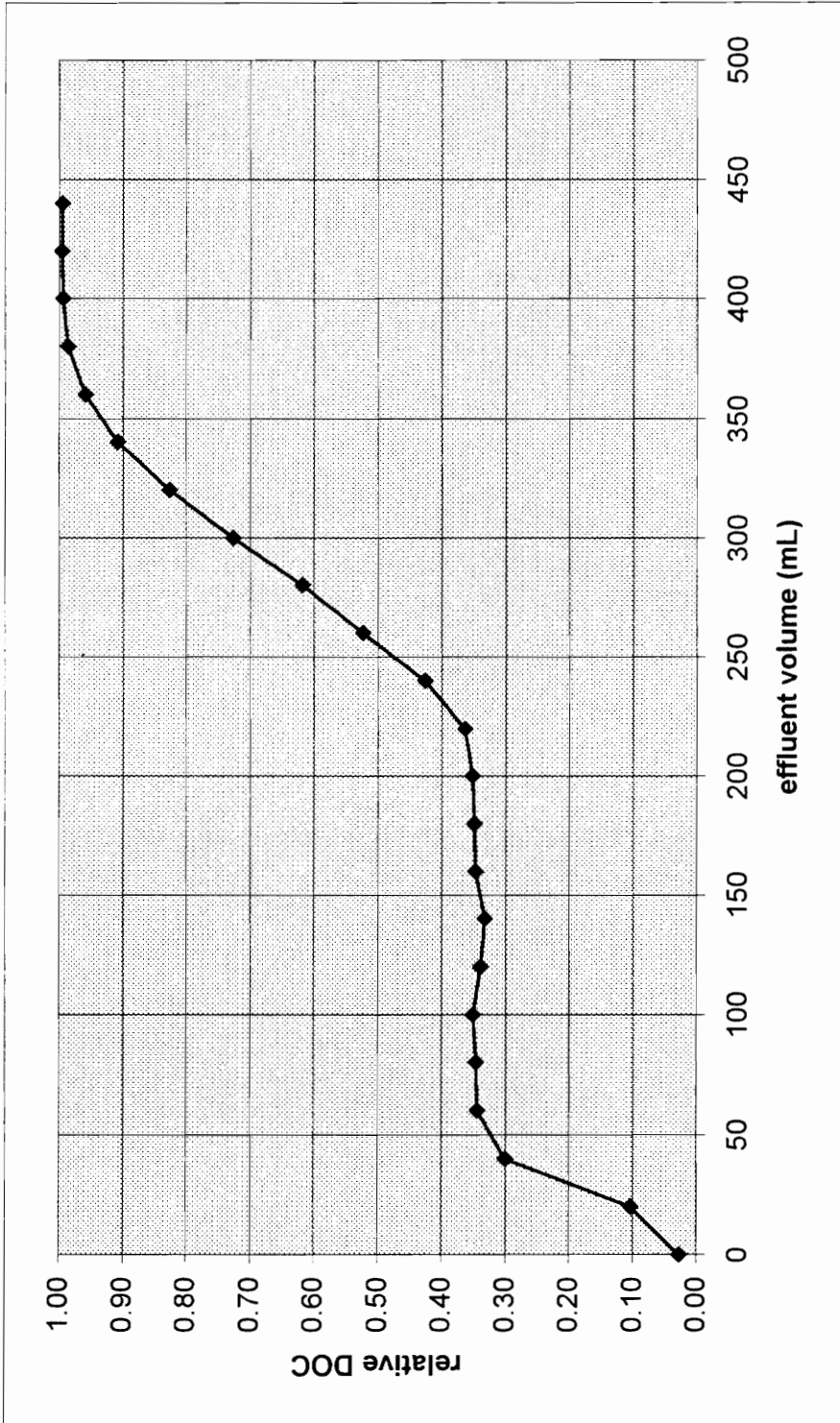


Figure A-3. Breakthrough curve for MSC-1 resin and 0.05 N NaCl at pH 2.0. (0.05 N NaCl = 194.5 mV, 1 bed volume = 9.3 mL)

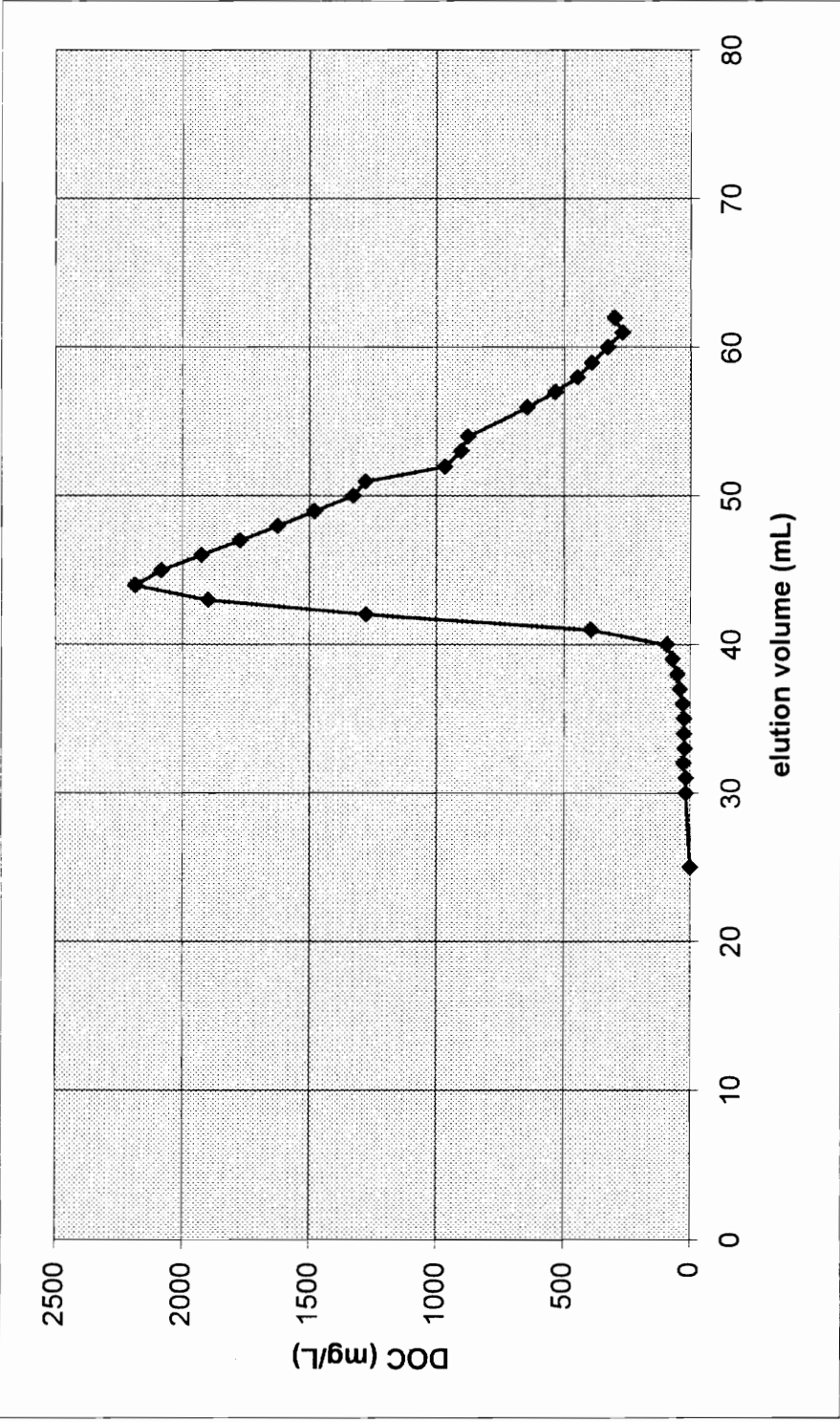


Figure A-4. Elution profile for MSC-1 resin and 100 mg/L leucine. (eluted with 1 N NaOH)

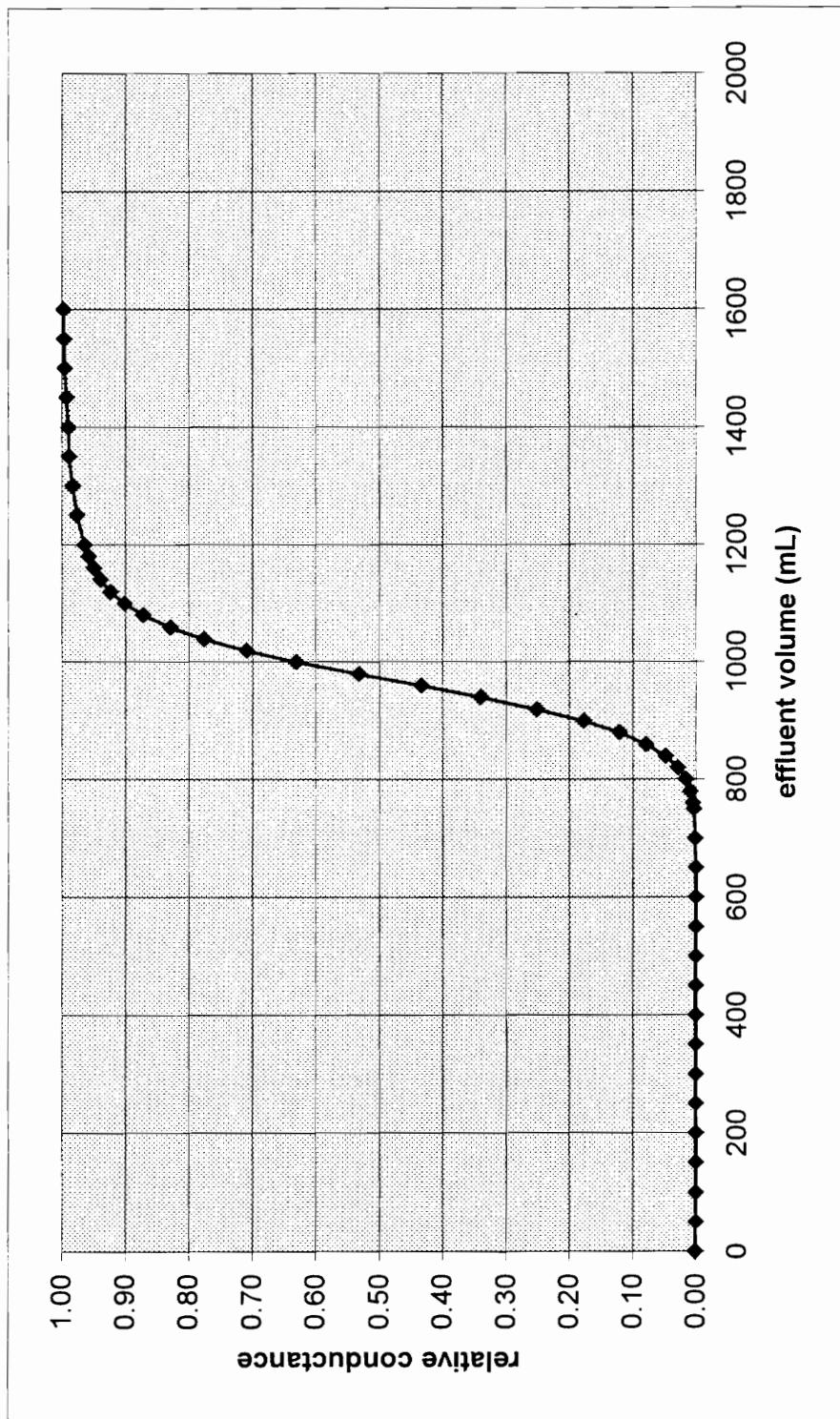


Figure A-5. Breakthrough curve for A-7 resin and 0.01 N HCl. (pH 2.0, 0.01 N HCl = 7250  $\mu$ mho/cm, 1 bed volume = 15.4 mL)

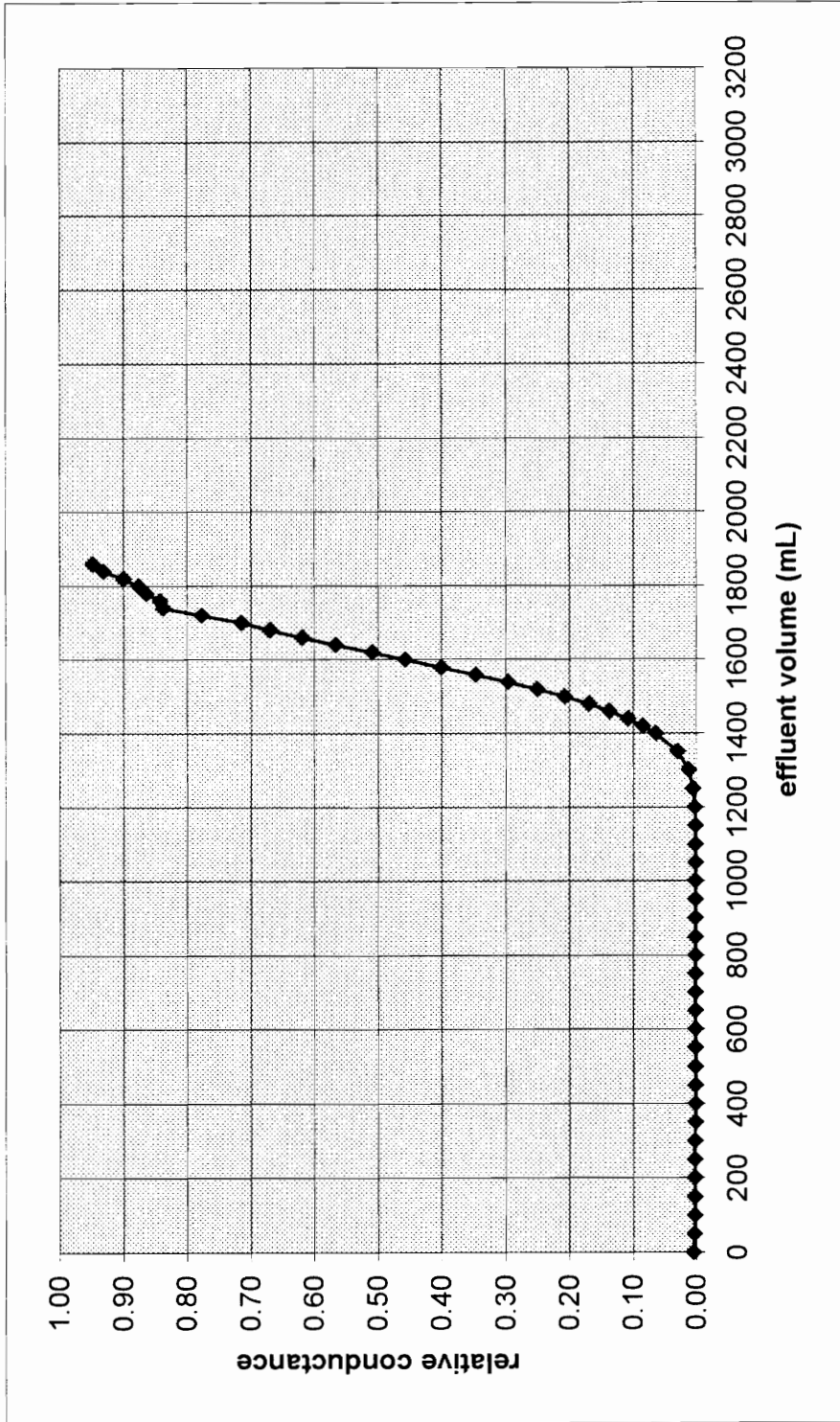


Figure A-6. Breakthrough curve for A-7 resin and 1 mg/L acetate at pH 2.0.  
 (1 mg/L acetate = 4170  $\mu\text{mho/cm}$ , 1 bed volume = 15.4 mL)

Table A-1. Chemicals and solutions.

Chemical	Supplier and Stock No.	Purity or Strength	Grade
Acetone	Fisher (A929-4)	99.6%	Optima and A.C.S.
Acetonitrile	Fisher (A21-4)	99.9%	Certified A.C.S.
Aluminum Sulfate Octadecahydrate	Aldrich (22,761-7)	98%	A.C.S.
Ammonium Hydroxide	Fisher (A-669 C)	28.0%-30.0%	Certified A.C.S. Plus
Ferric Chloride	Fisher (I-89)	100%	Purified
Hydrochloric Acid	Fisher (A144 <sup>S</sup> -212)	37.5%	Certified A.C.S. Plus
DL-Leucine	Eastman (1896)		
Methanol	Fisher (A454-4)	99.9%	Optima and A.C.S.
Methylene Chloride	Fisher (D151-4)	99.9%	Optima and A.C.S.
Nitric Acid	Fisher (A200 <sup>S</sup> 4X-212)	69.6%	Certified A.C.S. Plus
Nonionic Polymer	Calgon (POL-E-Z 652)	Emulsion	
pH 4 Buffer	Fisher (SB98-10)		Certified
pH 7 Buffer	Fisher (SB108-10)		Certified
Phosphoric Acid	Fisher (A242-500)	85%	Certified A.C.S.
Potassium Phosphate Monobasic	Fisher (P284-500)	100%	Purified
Sodium Carbonate	Fisher (261-10)	99.5%	Laboratory
Sodium Chloride	Fisher (S-271)		Certified A.C.S.
Sodium Dichromate	Fisher (S-235)	99.6%	Certified
Sodium Hydroxide	Fisher (SS410-4)	50% w/w	

Table A-1, continued

Chemical	Supplier and Stock No.	Purity or Strength	Grade
Sodium Hypochlorite	Fisher (SS290-1)	5.65-6%	Laboratory
Sodium Phosphate	Fisher (S374-500)	100.2%	Certified A.C.S.
Sulfuric Acid	Fisher (A510-212)	95.0%-98.0%	Trace Metal

Table A-2. Summary of pertinent fractionation conditions.

<b>Sample</b>	<b>DOC (mg/L)</b>	<b>pH</b>	<b>ionic strength</b>
Untreated Lake Drummond	10.0	6.31	0.0024
Coagulated Lake Drummond	4.3	6.3	0.0032
Untreated Chickahominy River	7.2	6.68	0.0018
Coagulated Chickahominy River	3.3	6.75	0.0025



Table A-3. Comparison of Lake Drummond fractionation results.

Untreated Lake Drummond

Fraction	DOC (mg/L)	Volume (L)	Mass (mg)	%	Concentration (mg/L)
Raw	9.5	12	114	100	9.5
HPO Base	2.8	0.660	1.9	1.6	0.2
HPO Acid	65.8	1.255	82.6	72	6.9
HPO Neutral	13.9	0.395	5.5	4.8	0.5
HPI Base	2.1	0.920	2.0	1.7	0.2
HPI Acid	11.7	0.450	5.3	4.6	0.4
HPI Neutral	1.0	12.980	12.4	11	1.0
Totals			110	96	9.1

Coagulated Lake Drummond

Fraction	DOC (mg/L)	Volume (L)	Mass (mg)	%	Concentration (mg/L)	% Change
Coagulated	4.7	12	56.5	100	4.7	
HPO Base	2.3	0.480	1.1	2.0	0.1	-40
HPO Acid	38.9	0.725	28.2	50	2.3	-66
HPO Neutral	28.1	0.265	7.5	13	0.6	36
HPI Base	2.3	1.815	4.1	7.3	0.3	110
HPI Acid	19.8	0.325	6.4	11	0.5	22
HPI Neutral	0.7	13.415	10.0	18	0.8	-20
Totals			57.3	101	4.8	

Note: % Change refers to the % change in concentration between the untreated and the treated fractions

Table A-4. Lake Drummond apparent molecular weight distributions.

Untreated Lake Drummond			Coagulated Lake Drummond		
total DOC = 10.0 mg/L			total DOC = 4.8 mg/L		
Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)	Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.08	0.8	0.5	0.18	0.8
1	0.27	2.6	1	0.54	2.6
3	0.46	4.6	3	0.73	3.5
10	0.67	6.7	10	0.87	4.2
30	0.80	8.0	30	1.00	4.8

Table A-5. Comparison of Chickahominy River fractionation results.

Untreated Chickahominy River

Fraction	DOC (mg/L)	Volume (L)	Mass (mg)	%	Concentration (mg/L)
Raw	7.5	6	44.8	100	7.5
HPO Base	1.7	0.665	1.1	2.5	0.2
HPO Acid	28.6	1.030	29.5	66	4.9
HPO Neutral	12.7	0.210	2.7	6.0	0.4
HPI Base	1.7	0.930	1.6	3.6	0.3
HPI Acid	12.4	0.340	4.2	9.4	0.7
HPI Neutral	0.8	7.650	6.3	14	1.0
Totals			45.4	101	7.6

Coagulated Chickahominy River

Fraction	DOC (mg/L)	Volume (L)	Mass (mg)	%	Concentration (mg/L)	% Change
Coagulated	3.8	6	23.0	100	3.8	
HPO Base	2.1	0.660	1.4	6.1	0.2	23
HPO Acid	10.7	1.195	12.8	56	2.1	-57
HPO Neutral	6.4	0.180	1.2	5.0	0.2	-57
HPI Base	1.1	0.930	1.0	4.5	0.2	-36
HPI Acid	6.5	0.390	2.5	11	0.4	-40
HPI Neutral	0.6	7.345	4.5	20	0.8	-28
Totals			23.4	102	3.9	

Note: % Change refers to the % change in concentration between the untreated and the treated fractions

Table A-6. Chickahominy River apparent molecular weight distribution.

Untreated Chickahominy River

total DOC = 8.1 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.09	0.7
1	0.34	2.8
3	0.64	5.2
10	0.85	6.9
30	0.93	7.5

Table A-7. Lake Drummond organic fractions apparent molecular weight distributions.

Hydrophobic Base

total DOC = 2.7 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.42	1.1
1	0.66	1.8
3	0.82	2.2
10	0.87	2.3
30	0.90	2.4

Hydrophilic Base

total DOC = 10.1 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.39	4.0
1	0.67	6.8
3	0.83	8.4
10	0.89	9.0
30	0.89	9.0

Hydrophobic Acid

total DOC = 10.6 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.08	0.8
1	0.20	2.1
3	0.39	4.1
10	0.63	6.7
30	0.95	10.1

Hydrophilic Acid

total DOC = 9.9 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.28	2.7
1	0.68	6.7
3	0.87	8.6
10	0.97	9.6
30	0.97	9.6

Hydrophobic Neutral

total DOC = 10.3 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.26	2.7
1	0.41	4.2
3	0.64	6.7
10	0.73	7.6
30	0.88	9.1

Hydrophilic Neutral

total DOC = 10.0 mg/L

Molecular Weight (kDaltons)	Relative DOC <membrane	DOC <membrane (mg/L)
0.5	0.45	4.5
1	0.70	6.9
3	0.84	8.4
10	0.95	9.5
30	0.98	9.8

Table A-8. Lake Drummond organic fractions coagulation results.

Hydrophobic Acid

Untreated DOC = 4.9 mg/L

pH	Relative Residual DOC	Residual DOC (mg/L)	% DOC Removed
5.0	0.42	2.1	58
5.5	0.33	1.6	67
6.0	0.33	1.6	67
6.5	0.38	1.9	62
7.0	0.41	2.0	59
7.5	0.60	2.9	40

Hydrophobic Neutral

Untreated DOC = 5.0 mg/L

pH	Relative Residual DOC	Residual DOC (mg/L)	% DOC Removed
5.0	0.61	3.0	39
5.5	0.62	3.1	38
6.0	0.59	2.9	41
6.5	0.60	3.0	40
7.0	0.61	3.0	39
7.5	0.63	3.1	37

Hydrophilic Acid

Untreated DOC = 4.9 mg/L

pH	Relative Residual DOC	Residual DOC (mg/L)	% DOC Removed
3.0	0.99	4.9	1.4
3.5	0.96	4.8	3.6
4.0	0.83	4.1	17
4.5	0.80	4.0	20
5.0	0.74	3.7	26
5.5	0.70	3.5	30
6.0	0.75	3.7	25
6.5	0.79	3.9	21
7.0	0.83	4.1	17
7.5	0.85	4.2	15

Hydrophilic Neutral

Untreated DOC = 4.9 mg/L

pH	Relative Residual DOC	Residual DOC (mg/L)	% DOC Removed
5.0	0.93	4.6	6.6
5.5	0.90	4.4	9.8
6.0	0.91	4.5	9.2
6.5	0.91	4.5	8.5
7.0	0.92	4.6	7.6
7.5	0.93	4.6	7.2

Table A-9. Hydrophobic acid / hydrophobic neutral coagulation study (2:3 ratio).

3 mg/L hydrophobic neutral / 2 mg/L hydrophobic acid

actual ratio: 1.43 HPO-N / 1 HPO-A at pH 5.5

actual ratio: 1.47 HPO-N / 1 HPO-A at pH 7.5

pH	Raw		Coag. Whole		Coag. HPO-A		Coag. HPO-N		% Removal Raw		% Removal HPO-A		% Removal HPO-N	
	DOC (mg/L)	HPO-A (mg/L)	DOC (mg/L)	HPO-A (mg/L)	DOC (mg/L)	HPO-A (mg/L)	DOC (mg/L)	HPO-N (mg/L)	DOC	HPO-A	DOC	HPO-A	DOC	HPO-N
5.5	5.2	2.1	3.1	3.3	2.0	2.0	1.3	1.3	37	37	9.1	9.1	57	57
7.5	4.8	1.9	2.8	3.4	2.1	2.1	1.2	1.2	29	29	-10	-10	56	56

Table A-10. Hydrophobic acid / hydrophobic neutral coagulation study (4:1 ratio).

4 mg/L hydrophobic acid / 1 mg/L hydrophobic neutral

actual ratio: 3.92 HPO-A / 1 HPO-N at pH 5.5

actual ratio: 4.90 HPO-N / 1 HPO-A at pH 7.5

pH	Raw		Coag. Whole		Coag. HPO-A		Coag. HPO-N		% Removal Raw		% Removal HPO-A		% Removal HPO-N	
	DOC (mg/L)	HPO-A (mg/L)	DOC (mg/L)	HPO-N (mg/L)	DOC (mg/L)	HPO-A (mg/L)	DOC (mg/L)	HPO-N (mg/L)	DOC	HPO-A	DOC	HPO-A	DOC	HPO-N
5.5	4.9	3.9	2.3	1.0	1.9	0.4	0.4	0.4	53	52	52	56	56	56
7.5	5.0	4.1	2.7	0.8	1.8	0.9	0.9	0.9	45	56	56	-6.7	-6.7	-6.7



Table A-11. Hydrophobic neutral through XAD-8 resin.

DOC of HPO NEUTRAL = 3.8 mg/L  
 DOC of coagulated <1 µm HPO NEUTRAL = 3.6 mg/L  
 DOC of coagulated <30 K HPO NEUTRAL = 3.4 mg/L

sample (mL)	bed volumes	HPO NEUT		<1 µm coag.		<30K coag.		<1 µm coag.		<30K coag.	
		Relative Effluent DOC	HPO NEUT Relative Effluent DOC	HPO NEUT Relative Effluent DOC	HPO NEUT Relative Effluent DOC	HPO NEUT Effluent DOC (mg/L)	HPO NEUT Effluent DOC (mg/L)	HPO NEUT Effluent DOC (mg/L)	HPO NEUT Effluent DOC (mg/L)		
10	0.7	0.04	0.02	0.02	0.02	0.1	0.1	0.1	0.1	0.1	0.1
20	1.3	0.22	0.09	0.11	0.11	0.8	0.3	0.3	0.4	0.4	0.4
30	2	0.29	0.17	0.19	0.19	1.1	0.6	0.6	0.6	0.6	0.6
40	2.7	0.29	0.19	0.24	0.24	1.1	0.7	0.7	0.8	0.8	0.8
50	3.3	0.31	0.21	0.28	0.28	1.2	0.8	0.8	0.9	0.9	0.9
60	4	0.32	0.22	0.31	0.31	1.2	0.8	0.8	1.0	1.0	1.0
70	4.7	0.34	0.24	0.33	0.33	1.3	0.9	0.9	1.1	1.1	1.1
80	5.3	0.34	0.27	0.36	0.36	1.3	1.0	1.0	1.2	1.2	1.2
90	6	0.33	0.31	0.38	0.38	1.3	1.1	1.1	1.3	1.3	1.3
127.5	8.5	0.13	0.41	0.39	0.39	0.5	1.5	1.5	1.3	1.3	1.3

Table A-12. Hydrophobic acid through XAD-8 resin.

DOC of HPO ACID (70 mL sample) = 4.7 mg/L

DOC of HPO ACID (300 mL sample) = 5.1 mg/L

sample (mL)	bed volumes	70 mL Relative Effluent DOC	300 mL Relative Effluent DOC	70 mL Effluent DOC (mg/L)	300 mL Effluent DOC (mg/L)
10	0.7	0.09		0.4	
20	1.3	0.19		0.9	
30	2	0.39	0.23	1.9	1.2
40	2.7	0.55		2.6	
50	3.3	0.71		3.4	
60	4	0.75	0.65	3.6	3.3
70	4.7	0.75		3.5	
90	6		0.81		4.1
120	8		0.89		4.5
150	10		0.95		4.8
180	12		0.98		5.0
210	14		1.01		5.1
240	16		1.01		5.1
270	18		1.02		5.2
300	20		1.00		5.1
337.5	22.5		0.17		0.9

Table A-13. Lake Drummond <10K hydrophobic acid coagulation pH study results.

pH	<1 µm		<100 K		<30 K		<1 µm		<30 K		<100 K		<30 K	
	Relative DOC	DOC (mg/L)	Relative DOC	DOC (mg/L)	Relative DOC	DOC (mg/L)	% Removed	DOC	% Removed	DOC	% Removed	% Removed	DOC	% Removed
4.5	0.63	3.1	0.44	2.1	0.44	2.1	37	2.1	57	2.1	56	57	2.1	56
5.0	0.62	3.0	0.44	2.3	0.44	2.1	38	2.1	54	2.1	56	54	2.1	56
5.5	0.51	2.5	0.45	2.1	0.45	2.2	49	2.2	57	2.2	55	57	2.2	55
5.8	0.50	2.5	0.55	2.4	0.55	2.7	50	2.7	51	2.7	45	51	2.7	45
6.5	0.53	2.6	0.52	2.5	0.52	2.5	47	2.5	48	2.5	48	48	2.5	48
7.0	0.60	2.9	0.58	2.8	0.58	2.8	40	2.8	43	2.8	42	43	2.8	42
7.5	0.66	3.2	0.62	3.1	0.62	3.0	34	3.0	37	3.0	38	37	3.0	38

Note: The value of <30 K relative DOC at pH 5.8 appears to be in error and is therefore not shown in Figure 22.

pH	<1 µm		<100 K		<30 K		<1 µm		<30 K		<100 K		<30 K	
	Relative AI	AI (µg/L)	Relative AI	AI (µg/L)	Relative AI	AI (µg/L)	% AI Removed	AI (µg/L)	% AI Removed	AI (µg/L)	% AI Removed	% AI Removed	AI (µg/L)	% AI Removed
4.5	0.39	1747	0.04	187	0.04	197	61	197	96	197	96	96	197	96
5.0	0.35	1560	0.03	177	0.03	132	65	132	96	132	97	96	132	97
5.5	0.18	823	0.02	128	0.02	96	82	96	97	96	98	97	96	98
5.8	0.14	625	0.02	77	0.02	104	86	104	98	104	98	98	104	98
6.5	0.11	475	0.04	140	0.04	180	89	180	97	180	96	97	180	96
7.0	0.12	530	0.04	199	0.04	185	88	185	96	185	96	96	185	96
7.5	0.14	641	0.05	325	0.05	226	86	226	93	226	95	93	226	95

Table A-14. Lake Drummond <10K hydrophobic acid coagulation dose study DOC results using alum.

alum dose (mg/L)	<1 µm Relative DOC	<100 K Relative DOC	<30 K Relative DOC	<1 µm DOC (mg/L)	<100 K DOC (mg/L)	<30 K DOC (mg/L)	<1 µm % DOC Removed	<100 K % DOC Removed	<30 K % DOC Removed
50	0.50	0.49	0.55	2.5	2.4	2.7	50	51	45
45	0.54	0.51	0.49	2.7	2.5	2.4	46	49	51
40	0.56	0.49	0.48	2.7	2.4	2.4	44	51	52
35	0.58	0.52	0.55	2.8	2.6	2.7	42	48	45
30	0.60	0.53	0.51	2.9	2.6	2.5	40	47	49
25	0.68	0.60	0.58	3.4	3.0	2.9	32	40	42
20	0.71	0.64	0.55	3.5	3.2	2.7	29	36	45
15	0.91	0.66	0.63	4.3	3.2	3.0	9.3	34	37
10	0.97	0.77	0.73	4.6	3.7	3.5	3.2	23	27
5	0.97	0.93	0.89	4.7	4.5	4.3	2.7	6.5	11
0	0.92	1.07	0.96	4.5	5.3	4.7	7.9	-6.9	4.4

Note: All relative DOC values at alum dose 0 mg/L should have a value of 1.0 and this is reflected in Figure 24. Also, the <30 K relative DOC value at 50 mg/L alum dose appear to be in error and is shown as 0.49 in Figure 24.

Table A-15. Lake Drummond <10K hydrophobic acid coagulation dose study aluminum results using alum.

alum dose (mg/L)	<1 µm Relative Al	<100 K Relative Al	<30 K Relative Al	<1 µm Al (µg/L)	<100 K Al (µg/L)	<30 K Al (µg/L)	<1 µm % Al Removed	<100 K % Al Removed	<30 K % Al Removed
50	0.14	0.02	0.02	625	77	104	86	98	98
45	0.22	0.01	0.02	895	54	75	78	99	98
40	0.28	0.04	0.03	1015	138	119	72	96	97
35	0.24	0.02	0.04	770	51	118	76	98	96
30	0.25	0.01	0.03	665	33	80	75	99	97
25	0.34	0.02	0.05	775	52	102	66	98	95
20	0.46	0.03	0.02	835	48	32	54	97	98
15	0.63	0.01	0.05	855	15	69	37	99	95
10	0.76	0.04	0.13	680	32	116	24	96	87
5	0.88	0.23	0.33	395	104	150	12	77	67
0				181	65	148			

Table A-16. Lake Drummond <10K hydrophobic acid coagulation dose study DOC results using ferric chloride.

ferric chloride dose (mg/L)	<1 µm		<100 K		Relative		<30 K		<1 µm		<100 K		<30 K		<30 K	
	Relative DOC	DOC (mg/L)	Relative DOC	DOC (mg/L)	DOC (mg/L)	DOC (mg/L)	DOC (mg/L)	DOC (mg/L)	DOC (mg/L)	% DOC Removed	% DOC Removed	% DOC Removed	% DOC Removed	% DOC Removed	% DOC Removed	% DOC Removed
35.0	0.68	3.2	0.50	2.4	0.52	2.5	3.2	2.5	32	50	48	48	48	48	48	48
27.0	0.70	3.4	0.52	2.5	0.54	2.6	3.4	2.6	30	48	46	46	46	46	46	46
21.6	0.88	4.2	0.56	2.7	0.57	2.7	4.2	2.7	12	44	43	43	43	43	43	43
16.2	1.00	4.8	0.62	3.0	0.64	3.1	4.8	3.1	-0.4	38	36	36	36	36	36	36
13.5	1.01	4.8	0.68	3.2	0.69	3.3	4.8	3.3	-0.9	32	31	31	31	31	31	31
10.8	1.02	4.9	0.68	3.3	0.70	3.3	4.9	3.3	-2.4	32	30	30	30	30	30	30
9.5	1.06	5.0	0.77	3.7	0.73	3.7	5.0	3.5	-5.7	23	27	27	27	27	27	27
8.1	0.99	4.7	0.76	3.6	0.74	3.5	4.7	3.5	0.7	24	26	26	26	26	26	26
6.8	0.94	4.5	0.75	3.6	0.73	3.5	4.5	3.5	5.5	25	27	27	27	27	27	27
5.4	0.97	4.6	0.77	3.7	0.74	3.5	4.6	3.5	2.8	23	26	26	26	26	26	26
2.7	0.97	4.6	0.91	4.3	0.86	4.1	4.6	4.1	3.4	8.5	14	14	14	14	14	14
0	1.00	4.8	0.97	4.6	0.99	4.7	4.8	4.7	0.1	3.4	1.3	1.3	1.3	1.3	1.3	1.3

Note: The <1 µm relative DOC at ferric chloride doses 9.5 - 13.5 mg/L should not have exceeded 1.0 and this is reflected in Figure 27.

Table A-17. Lake Drummond <10K hydrophobic acid coagulation dose study iron results using ferric chloride.

ferric chloride dose (mg/L)	<1 µm Relative Fe	<100 K Relative Fe	<30 K Relative Fe	<1 µm Fe (µg/L)	<100 K Fe (µg/L)	<30 K Fe (µg/L)	<1 µm % Fe Removed	<100 K % Fe Removed	<30 K % Fe Removed
35.0	0.31	0.00	0.00	3740	5	6	69	100	100
27.0	0.36	0.00		3340	2		64	100	100
21.6	0.65	0.00		4870	1		35	100	100
16.2	0.91	0.00		5080	1		9.1	100	100
13.5	0.92	0.00	0.00	4260	4	1	8.5	100	100
10.8	0.89	0.00	0.00	3300	4	2	11	100	100
9.5	0.91	0.00	0.00	2970	8	2	8.9	100	100
8.1	1.01	0.02	0.00	2830	68	2	-1.3	98	100
6.8	0.96	0.02	0.00	2230	39	4	4.2	98	100
5.4	1.16	0.07	0.00	2160	134	4	-16	93	100
2.7	0.98	0.42	0.04	910	389	34	2.3	58	96
0				31	14	17			

Note: The <1 µm relative iron value at 5.4 and 8.1 mg/L ferric chloride doses should not have exceeded 1.0. The 5.4 mg/L dose value was removed from Figure 29 while the 8.1 mg/L value is shown as 1.0.

Table A-18. Lake Drummond <10K hydrophobic acid coagulation study results using varying polymer doses and constant alum dose.

polymer dose (mg/L)	<1 $\mu$ m Relative DOC	<100 K Relative DOC	<1 $\mu$ m DOC (mg/L)	<100 K DOC (mg/L)	<1 $\mu$ m % DOC Removed	<100 K % DOC Removed
0.5	0.97	0.66	4.6	3.2	2.5	33
0.4	1.00	0.71	4.8	3.4	-1.4	28
0.3	0.69	0.67	3.3	3.2	30	32
0.2	0.87	0.67	4.1	3.2	12	32
0.1	0.78	0.62	3.7	3.0	21	37
0	1.00	0.68	4.8	3.2	-1.1	32

polymer dose (mg/L)	<1 $\mu$ m Relative Al	<100 K Relative Al	<1 $\mu$ m Al (mg/L)	<100 K Al (mg/L)	<1 $\mu$ m % Al Removed	<100 K % Al Removed
0.5	0.64	0.08	725	90	36	92
0.4	0.60	0.07	680	74	40	93
0.3	0.25	0.03	279	30	75	97
0.2	0.49	0.08	550	95	51	92
0.1	0.44	0.09	496	106	56	91
0	0.81	0.10	910	115	19	90



## **APPENDIX B**

## LISTED CHEMICAL FRACTIONATION AND JAR TESTING PROCEDURES

### CHEMICAL FRACTIONATION PROCEDURE

#### I. Resin Cleaning

##### XAD-8

1. Sieve out large and small resin beads using No. 30, 40, 50, 60, and 70 sieves.
2. Soak the resin in 0.1 N NaOH for 24 hours.
3. Soxhlet extract the resin with methanol for 24 hours followed by acetonitrile for 6 hours and then methylene chloride for 6 hours.
4. Air-dry the resin overnight, pack the column with the resin, and store in methanol.

##### MSC-1

1. Sieve out large and small resin beads using No. 30 and 50 sieves.
2. Soxhlet extract the resin with methanol for 24 hours.
3. Air-dry the resin overnight.
4. Slurry the resin with Milli-Q water, stir, and pour off Milli-Q water. Repeat until the DOC of the Milli-Q water decant is less than 1 mg/L.
5. Pack the column with the resin and store in Milli-Q water.

##### A-7

1. Sieve out large and small resin flakes using No. 14 and 50 sieves.
2. Soxhlet extract resin with acetone for 24 hours.
3. Air-dry the resin overnight.
4. Slurry the resin with Milli-Q water, stir, and pour off Milli-Q water. Repeat until the DOC of the Milli-Q water decant is less than 1 mg/L.
5. Pack the column with the resin and store in Milli-Q water.

## II. Resin Preparation, Sample Application to Resin Columns, and Elution

Follow these steps in the exact order listed.

### XAD-8

#### Preparation

1. Pass Milli-Q water through the resin column until the DOC of the column effluent is within 0.1 mg/L of Milli-Q water.
2. Rinse the resin with 1 bed volume (BV) of 0.1 N NaOH.
3. Rinse the resin with 1 BV of 0.1 N HCl.
4. Rinse the resin with Milli-Q water until the pH of the column effluent is the pH of Milli-Q water.

#### Sample Application and Elution

1. Adjust the pH of the water sample to 6.3.
2. Pass the water sample through resin at a flow rate of 10 bed volumes per hour (BV/hr). Measure the DOC of the column effluent periodically to ensure breakthrough of the hydrophobic base fraction has not occurred.
3. Pass 2.5 BV of Milli-Q water through the resin to displace the water sample.
4. Backflush the column with 0.25 BV of 0.1 N HCl followed by 1.5 BV of 0.01 N HCl if possible, otherwise forward elute. Then pass Milli-Q water through the resin to ensure elution of hydrophobic base fraction is complete. Start collecting elute immediately upon application of 0.1 N HCl to the resin.
5. Elution of the hydrophobic base fraction is complete approximately 1.25 BV after HCl breakthrough. Refrigerate the hydrophobic base fraction at pH 2.
6. Acidify the water sample to pH 2 with HCl.
7. Pass the water sample through resin at a flow rate of 10 BV/hr. Measure the DOC of the column effluent periodically to ensure breakthrough of the hydrophobic acid fraction has not occurred.
8. Pass 1 BV of 0.01 N HCl through the resin to displace the water sample.
9. Backflush the resin column with 0.25 BV of 0.1 N NaOH if possible, otherwise forward elute. Start collecting elute immediately upon application of 0.1 N NaOH to the resin.
10. Pass Milli-Q water through the resin to ensure elution of the hydrophobic acid fraction is complete. Refrigerate the hydrophobic acid fraction at neutral pH.
11. Unpack the column and Soxhlet extract the resin with methanol for at least one hour to elute the hydrophobic neutral fraction. Vacuum distillate the methanol/hydrophobic neutral fraction mixture to remove the methanol. Refrigerate the hydrophobic neutral fraction at neutral pH.

## MSC-1 Resin

### Preparation

1. Pass Milli-Q water through the resin column until the DOC of the column effluent is within 0.1 mg/L of Milli-Q water.
2. Pass 3 BV of 1 N NaOH through the resin or until have breakthrough of NaOH.
3. Pass 4 BV of 2 N HCl through the resin to hydrogen saturate the resin.
4. Rinse the resin with Milli-Q water until the specific conductance of the column effluent is <10  $\mu\text{mho/cm}$ .

### Sample Application and Elution

1. Pass the water sample through resin at a flow rate of 10 BV/hr. Measure the DOC and  $\text{Na}^+$  concentration of the column effluent periodically to ensure breakthrough of the hydrophilic base fraction has not occurred.
2. Pass 1 BV of 0.01 N HCl through the resin to displace the water sample.
3. Pass 1 N NaOH through the resin until breakthrough of NaOH occurs. Start collecting elute immediately upon application of 1 N NaOH to the resin.
4. Elution of the hydrophilic base fraction is complete when breakthrough of NaOH occurs. Refrigerate the hydrophilic base fraction at neutral pH.

## A-7 Resin

### Preparation

1. Pass Milli-Q water through the resin column until the DOC of the column effluent is within 0.1 mg/L of Milli-Q water.
2. Pass 1 N HCl through the resin until the DOC of the effluent is <1 mg/L..
3. Pass 1 N NaOH through the resin until the resin obtains a yellowish color.
4. Rinse the resin with Milli-Q water until the specific conductance of the column effluent is <10  $\mu\text{mho/cm}$ .

### Sample Application and Elution

1. Pass the water sample through resin at a flow rate of 10 BV/hr. Measure the DOC and the specific conductance of the column effluent periodically to ensure breakthrough of the hydrophilic acid fraction has not occurred.
2. Pass 1 BV of Milli-Q water through the resin to displace the water sample.
3. Backflush the resin column with 1 N NaOH if possible, otherwise forward elute. Start collecting elute immediately upon application of 1 N NaOH to the resin.
4. Continue collection of the elute until visible organic bleed from the resin occurs. Refrigerate the hydrophilic acid fraction at neutral pH.
5. The remaining water sample contains only the hydrophilic neutral fraction. Refrigerate the hydrophilic neutral fraction at neutral pH.

## JAR TESTING PROCEDURE

1. Add the desired volume of water sample to each jars.
2. Adjust the pH of each of the jars to the desired pHs using HCl and NaOH.
3. Place jars under jar test stirrer and stir paddles at approximately 100 revolutions per minute (rpm) for 10 minutes to permit water samples to equilibrate with the atmosphere.
4. Make any minor adjustments to pH with NaOH and HCl.
5. Stir water samples at 100 rpm for 2 minutes. Add coagulant and the appropriate amount of NaOH simultaneously. The NaOH serves to neutralize the acidic effect of the coagulant.
6. Stir water samples at 40 rpm for 10 minutes.
7. Stir water samples at 30 rpm for 10 minutes.
8. Stir water samples at 20 rpm for 10 minutes.
9. Turn off the jar test stirrer and allow water samples to sit for 1 hour.
10. Pass 1 L of Milli-Q water through a vacuum-pumped 1  $\mu\text{m}$  filter to remove any organic material from the filter. Pass the settled water samples through the 1  $\mu\text{m}$  filter to remove settled organic material.

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## VITA

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A handwritten signature in black ink that reads "John S. Siczka". The signature is written in a cursive style with a large initial 'J' and a distinct 'S'.