

**THE PERFORMANCE OF POTASSIUM PERMANGANATE  
AND HYDROGEN PEROXIDE OXIDATION AND/OR  
ALUM COAGULATION IN THE REMOVAL OF  
COMPLEXED FE(II) FROM DRINKING WATER**

by

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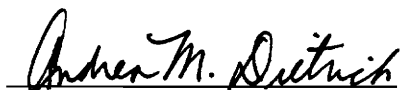
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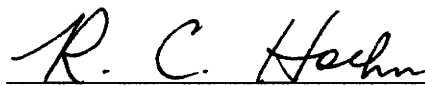
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**Dr. William R. Knocke**

**Environmental Sciences and Engineering**

**(ABSTRACT)**

The influence of solution pH, DOC concentration, the relative molecular weight distribution of DOC, and the source of DOC were investigated for their effects on the removal of complexed Fe(II) by alum coagulation and/or  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  oxidation. The differentiation between particulate, colloidal, and soluble iron species was achieved through the use of 0.2  $\mu\text{m}$  filters and 100K ultrafilters.

Results from oxidation and ultrafiltration studies indicated incomplete complexation of the Fe(II) by DOC in solution. Following the addition of either oxidant, uncomplexed Fe(II) was oxidized to Fe(III) which was either complexed by high molecular weight DOC or formed colloidal iron oxides, both of which were efficiently removed by alum coagulation. Alum coagulation alone, however, was ineffective for removing Fe(II) in the presence of DOC.

Results revealed the formation of particulate iron species to be a function of DOC source. The formation of colloidal iron was dependent upon DOC concentration and DOC source. The adsorption of DOC by iron oxides was observed to accompany the formation of colloidal iron species.

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## Chapter I

### INTRODUCTION

Iron in drinking water is considered a problem for numerous reasons: (1) staining of laundered items and plumbing fixtures; (2) discoloration of drinking water; (3) encrustation of pipes by iron precipitants; and (4) taste and odor problems caused by the presence of iron reducing bacteria. For these reasons, which are purely aesthetic in nature, the United States Environmental Protection Agency (USEPA) has established a secondary maximum contaminant level (MCL) of 0.3 milligrams per liter (mg/L) for iron.

In the absence of significant amounts of dissolved organic carbon (DOC), iron removal methods typically involve the oxidation of ferrous iron (Fe(II)) followed by liquid-solid separation. The oxidation of Fe(II), either by dissolved oxygen ( $O_2(aq)$ ) or the addition of alternative oxidants, results in the formation of ferric hydroxide ( $Fe(OH)_3(s)$ ) precipitants which are readily removed from drinking water by filtration.

The presence of significant DOC can reduce the efficiency of Fe(II) oxygenation. Also, recent studies by Knocke *et al.* (1990) have indicated that alternative oxidants such as potassium permanganate ( $KMnO_4$ ) and hydrogen peroxide ( $H_2O_2$ ) have less than satisfactory performance when trying to promote complexed Fe(II) removal.

The fate of complexed Fe(II) during the coagulation process is also of interest. Several studies have evaluated the efficiency of DOC removal via alum coagulation by investigating such variables as concentration and relative molecular weight distribution of DOC as well as the solution pH. However, the fate of complexed Fe(II) during DOC removal has not been adequately investigated.

This study addressed these issues with the objectives of the research being to:

1. Evaluate the degree of Fe(II) complexation in waters containing significant DOC;
2. Evaluate how the concentration and the relative molecular weight distribution (MWD) of DOC present in water affects the ability of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  to oxidize complexed Fe(II);
3. Evaluate the fate of complexed Fe(II) during alum coagulation, including an assessment of how the addition of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  might affect the removal of iron during alum coagulation.



## **Chapter II**

### **LITERATURE REVIEW**

#### **Overview**

This chapter addresses the following topics:

- 1) Isolation and characterization of aquatic humic substances;
- 2) Oxidation of ferrous iron;
- 3) Complexation of iron by aquatic humic substances;
- 4) Removal of iron and organics by alum coagulation.

#### **Isolation and Characterization of Aquatic Humic Substances**

Many terms can be used to describe the organic carbon which is present in natural water. Thurman (1985) utilized the following terminology to describe organic carbon: total organic carbon (TOC), particulate organic carbon (POC), and dissolved organic carbon (DOC). POC is defined as the organic carbon which is retained on a 0.45 micron (um) filter, while DOC is defined as the organic carbon which passes a 0.45 um filter. TOC is the organic carbon which comprises both DOC and POC. Thurman's definition of DOC includes colloidal organic carbon, which is species between the sizes of 0.45 um and 1 nanometer (nm).

DOC is typically the measure of most interest to researchers because it represents the fraction of organic carbon which is chemically more reactive because it is in the dissolved state. The concentration of DOC varies depending on the type of water. In most surface waters the DOC concentration varies from 2.2 to 12 mg/L, while concentrations in marshes and bogs range from 10 to 60 mg/L (Thurman, 1985).

Aquatic humic substances comprise 40 to 60 percent of the DOC present in natural waters, while the rest of the DOC is made up of hydrophilic acids, amino acids and carbohydrates (Thurman, 1985). Aquatic humic substances are complex in their composition because they are products of vegetative, soil, and/or aquatic processes. They are hydrophobic in nature with an elemental composition of approximately 50 percent carbon, 4 to 5 percent hydrogen, 35 to 40 percent oxygen, 1 to 2 percent nitrogen, and less than 1 percent sulfur and phosphorus. No general structure for aquatic humic substances exists; however, they are characterized by the following functional groups: carboxyl, phenolic hydroxyl, carbonyl, and hydroxyl groups. Information regarding the characteristics and composition of aquatic humic substances is available in the literature; Thurman (1985) and Liao *et al.* (1982) are two such sources.

Aquatic humic substances are composed of two fractions, humic and fulvic acid. In most surface waters, approximately 30 to 50 percent of the DOC is fulvic acid, while only 10 percent of the DOC is humic acid (Thurman, 1985). Humic acid

is the fraction which is insoluble at pH 2.0 or below. They generally have a molecular weight between 100,000 atomic mass units (AMU) and 2000 AMU. Humic acids have fewer carboxyl groups than fulvic acids; therefore, they (humic acids) are less soluble and can precipitate. Fulvic acid is that fraction which remains soluble regardless of solution pH and has a molecular weight between 500 and 2000 AMU (Thurman, 1985).

Humic substances can also be differentiated by specific absorbance values measured at 254 nm. The specific absorbance of fulvic acids ranges from 3 to 4.3 liters per centimeter-milligram of carbon ( $L/(cm * mg-C)$ ), while humic acids have specific absorbance values between 4.8 to 7.4  $L/cm * mg-C$  (Reckhow *et al.*, 1990). In most surface waters, approximately 30 to 50 percent of the DOC is fulvic acid, while only 10 percent of the DOC is humic acid (Thurman, 1985).

### **Isolation of Humic Substances**

In order to study aquatic humic substances they must be separated from other organic and inorganic constituents. Precipitation, freeze drying, reverse osmosis, ultrafiltration, and liquid extraction are examples of isolation procedures for aquatic humic substances.

Thurman and Malcolm (1981) developed an adsorption procedure which can isolate humic substances from large volumes of water. The procedure involves the adsorption of humic substances (at a pH near 2) onto a nonionic macroporous XAD-8

resin, followed by extraction with an alkaline solution. The "hydrophobic effect" is the principal driving force for sorption on nonionic macroporous resins; at low pH the weak acids are protonated and adsorbed onto resin while at a high pH the weak acids are ionized, resulting in desorption (Aiken, 1985). This method is considered to be the most efficient as well as widely used isolation technique (Aiken, 1988).

There are, however, several disadvantages involved when using this isolation technique. Resins contain monomers, artifacts from the manufacturing process, which require removal by Soxhlet extraction prior to the utilization of the resin for isolation. Chemical alteration of the aquatic humic substances can also occur as a result of the extreme pH values involved in the isolation procedure. These chemical alterations include acid and base catalyzed hydrolysis reactions which are irreversible (Aiken, 1988).

### **Molecular Weight Fractionation by Ultrafiltration**

Ultrafiltration, centrifugation, gel permeation chromatography, and x-ray scattering are all common methods utilized to determine the relative molecular weight fractions of DOC. Ultrafiltration is favored by many researchers because of its versatility, usefulness towards most types of water, simplicity of method, rapidness, and ability to separate various groups with different molecular weights (Buffle, 1978). The author reported that fractionation by ultrafiltration is not greatly influenced by changes in solution pH, pressure, or the concentration of electrolytes.

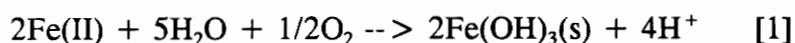
Ultrafiltration separates macromolecules according to molecular size by filtration through a membrane under an applied hydrostatic pressure. These membranes are manufactured with a variety of molecular weight exclusion size values; however, these exclusion sizes are not very distinct. In general, a membrane will retain 90 percent of the spherical, uncharged solute molecules of its quoted molecular weight exclusion size (Leenheer, 1985).

There are a number of problems associated with the ultrafiltration technique. Buffle (1978) reported that the variations in results involving fractionation by ultrafiltration were due to reactions between humic acid and fulvic acid which resulted in their aggregation. Wershaw and Aiken (1985) reported that the leakage of high molecular weight species through the membrane increased as the concentration of larger molecular size solutes increased. They also reported that the filtrate obtained from ultrafiltration can be dependent on the molecular charge of aquatic humic substances, since charge to charge interactions between solute and membrane can interfere with the ultrafiltration process.

The use of ultrafiltration to fractionate DOC only provides an index of the molecular weight distribution (MWD) of DOC that should only be used for relative comparisons (Collins *et al.*, 1986). Major trends in values collected from experimentation should be emphasized, rather than absolute values when using this technique.

### **Oxidation of Ferrous Iron by Alternative Oxidants**

The most common method of removing iron from water supplies involves aeration followed by filtration which removes the resulting  $\text{Fe}(\text{OH})_3(\text{s})$  precipitant. The oxidation of ferrous iron ( $\text{Fe}(\text{II})$ ) to ferric hydroxide ( $\text{Fe}(\text{OH})_3(\text{s})$ ) by aeration occurs according to the following:



In this reaction two electrons are transferred, and 0.14 mg of oxygen are consumed for every mg of  $\text{Fe}(\text{II})$  oxidized.

Stumm and Lee (1961) reported that the kinetics of the oxygenation of  $\text{Fe}(\text{II})$  depend on the solution pH, temperature, concentration of dissolved oxygen, and the presence of catalysts/inhibitors. They concluded that the rate of  $\text{Fe}(\text{II})$  oxygenation is first order with respect to  $\text{Fe}(\text{II})$  concentration and the partial pressure of oxygen; while the rate is second order with respect to hydroxide ion concentration. They reported an increase in reaction rate of up to 100 times for every unit increase in pH.

### **Oxidation by Potassium Permanganate**

Potassium permanganate ( $\text{KMnO}_4$ ) has been widely utilized by water utilities as an algicide, an oxidant for iron/manganese removal, and an oxidant for taste and odor control.  $\text{KMnO}_4$  is often used as a pretreatment step followed by filtration. It is inappropriate to use  $\text{KMnO}_4$  in the treatment of finished water because of the pink

color of the compound itself or the brown color of the manganese oxides ( $\text{MnO}_x(\text{s})$ ) formed following the reaction with  $\text{KMnO}_4$  (Culp *et al.*, 1986).

The oxidation of  $\text{Fe(II)}$  by  $\text{KMnO}_4$  is almost instantaneous (Knocke *et al.*, 1990) with the following reaction stoichiometry:

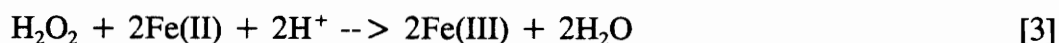


In this reaction, three electrons are transferred, and 0.94 mg of  $\text{KMnO}_4$  are consumed for every mg of  $\text{Fe(II)}$  oxidized.

### **Oxidation by Hydrogen Peroxide**

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a strong oxidizing agent that has been used as a disinfection agent for more than a century as well as a bleaching agent for textiles and wood pulp. However, use of  $\text{H}_2\text{O}_2$  has been limited by its instability and the difficulty in preparing concentrated  $\text{H}_2\text{O}_2$  solutions (Culp *et al.*, 1986).

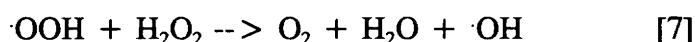
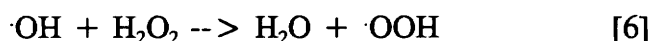
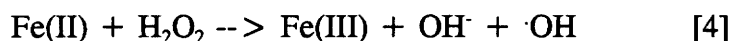
The oxidation of  $\text{Fe(II)}$  by  $\text{H}_2\text{O}_2$  corresponds to the following stoichiometric relationship:



In this reaction two electrons are transferred and 0.31 mg of  $\text{H}_2\text{O}_2$  are consumed for every mg of  $\text{Fe(II)}$  oxidized.

The decomposition of  $\text{H}_2\text{O}_2$  which accompanies the oxidation of  $\text{Fe(II)}$  has received extensive examination. If  $\text{H}_2\text{O}_2$  is present in excess, then the decomposition

of H<sub>2</sub>O<sub>2</sub> and the evolution of oxygen occurs with the oxidation of ferrous iron. The following reactions have been proposed as the mechanism for the decomposition of hydrogen peroxide:



Under conditions in which Fe(II) is in excess the first two reactions in the mechanism are important, resulting in the oxidation of two moles of Fe(II). When H<sub>2</sub>O<sub>2</sub> is in excess, however, the last two reactions in the mechanism become predominant, resulting in the consumption of three moles of H<sub>2</sub>O<sub>2</sub> for every mole of Fe(II) (Schumb *et al.*, 1955). If organic substrates are present, the hydroxyl radical formed can react with the substrate either by hydrogen abstraction or by the addition of the hydroxyl radical to an unsaturated system. The organic radicals which are generated can dimerize, be oxidized by Fe(III), or reduced by Fe(II) (Nonhebel *et al.*, 1979).

## **Complexation of Iron by Humic Substances**

### **Complexation Mechanisms**

Two mechanisms have been hypothesized to describe complexation between aquatic humic substances and iron: peptization and chelation. Peptization is the dispersion of organic molecules and ferric hydroxide resulting in a



colloidal/particulate interaction. Chelation occurs when two or more ligands coordinate a metal ion to form an internal ring structure. The chelation reaction occurs between dissolved iron and organic molecules.

Shapiro (1964) investigated the relationship between organic color and ferric iron (Fe(III)) to describe difficulties associated with iron removal in highly colored waters. He reported that the primary mechanism for the "solubilization" of iron was the result of the dispersion of  $\text{Fe}(\text{OH})_3$  due to adsorbed organic acids on the particle surface. He suggested chelation became an important mechanism at high organic color-to-iron ratios. Later research by Cameron and Liss (1984) and Eisenreich *et al.* (1980) support peptization as the primary mechanism for the complexation of iron by natural organic matter.

Studies by Ghassemi and Christman (1968), as well as Oldham and Gloyne (1969), concluded that the interaction between organic color and iron proceeds on a purely chemical basis, therefore due primarily to chelation. Jobin and Ghosh (1972) reported that organic species containing hydroxyl and carboxyl groups readily formed complexes with iron. Fulvic acids, which have a higher concentration of carboxyl groups than humic acids, have been reported to be most effective at complexing metal ions (Weber, 1988).

## **Effect of Solution pH**

Shapiro (1964) investigated the association of iron and organic color to better understand the difficulty in removing iron from highly colored waters. He reported greatest stability of Fe(III) for solution pH values between 9 and 11; however, in most natural water systems the pH is well below this range. According to Langford et al. (1983), the solutions containing high concentrations of fulvic acids at high pH values have a large number of chelation sites available for interaction with metal ions. Ghassemi and Christman (1968) also examined the relationship between iron and organic color. Their data suggested Fe(II) and Fe(III) stability was greatest at slightly acidic pH values. Oldham and Gloyna (1969) reported that complexation of Fe(II) by organic color did not occur at pH 5 but it did occur at a solution pH of 8. They attributed the Fe(II) complexation to the dissociation of humic acids at higher pH values which resulted in the presence of more ionized carboxyl groups. Through polarographic studies, Theis and Singer (1974) illustrated that the extent of complexation increased as the solution pH increased from 5 to 7.

## **Effect of Water Quality Characteristics**

The presence of inorganic anions in solution such as chloride, bicarbonate, sulfate, and nitrate had no significant effect on the ability of aquatic humic substances to stabilize Fe(III) as reported by Cameron and Liss (1984). They concluded that high concentrations of silicate did result in the stabilization of Fe(III); however, in

most natural water systems, the silicate concentration is insufficient to result in Fe(III) stabilization. In addition, concentrations of phosphate between 0.4 and 250 mg/L resulted in the stabilization of Fe(III) at pH values between 6.5 and 11. Eisenreich et al. (1980) reported an increased iron concentration in the dissolved phase as the suspended solids concentration decreased. Perdue et al. (1976) reported that the presence of other metal ions in solution could decrease the stabilization effect of aquatic humic substances for iron.

### **Extent of Complexation**

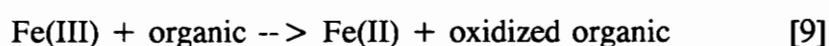
Cameron and Liss (1984) utilized humic and tannic acids as complexing agents to stabilize Fe(III). Tannic acid was used because it is composed of functional groups that are also present in humic acids. Both agents were reported to stabilize Fe(III) in solution; in particular, 1 mole of tannic acid was reported to stabilize approximately 15 moles of Fe(III) in solution. Theis and Singer (1974) reported similar results for the stabilization of Fe(II) and Fe(III) by tannic acids. They observed an increase in iron stabilized as the concentration of tannic acid was increased.

Thurman (1985) recommended a "rule-of-thumb" guideline for metal binding capacity. He suggested that for every mg of DOC in solution there is approximately 1 microequivalent (ueq) of metal binding capacity, which for iron corresponds to 0.02 to 0.03 mg of Fe per mg DOC. Theis and Singer (1973) reported that 0.005 mg of Fe(II) was stabilized by every mg of DOC present in solution as evaluated after

filtration through 0.45 um filter. Perdue et al. (1976) found from studies conducted using water obtained from the Satilla River in the southeastern portion of the U.S. that every mg of DOC stabilized 0.05 mg of iron. Trivalent metals, like Fe(III), have been found to form more stable complexes than divalent metal ions (Alberts and Giesy, 1983). These studies suggest that the complexation capacity of DOC varies from its source to the valence state of iron present in solution.

### **Behavior of Iron in the Presence of Oxygen and DOC**

Morgan and Stumm (1964) were some of the first to study the oxygenation of Fe(II) in the presence of natural organic species. They proposed that the inhibition of Fe(II) oxygenation could be attributed to a cyclic reaction involving the oxidation of Fe(II) followed by the reduction of Fe(III). The model is illustrated below:

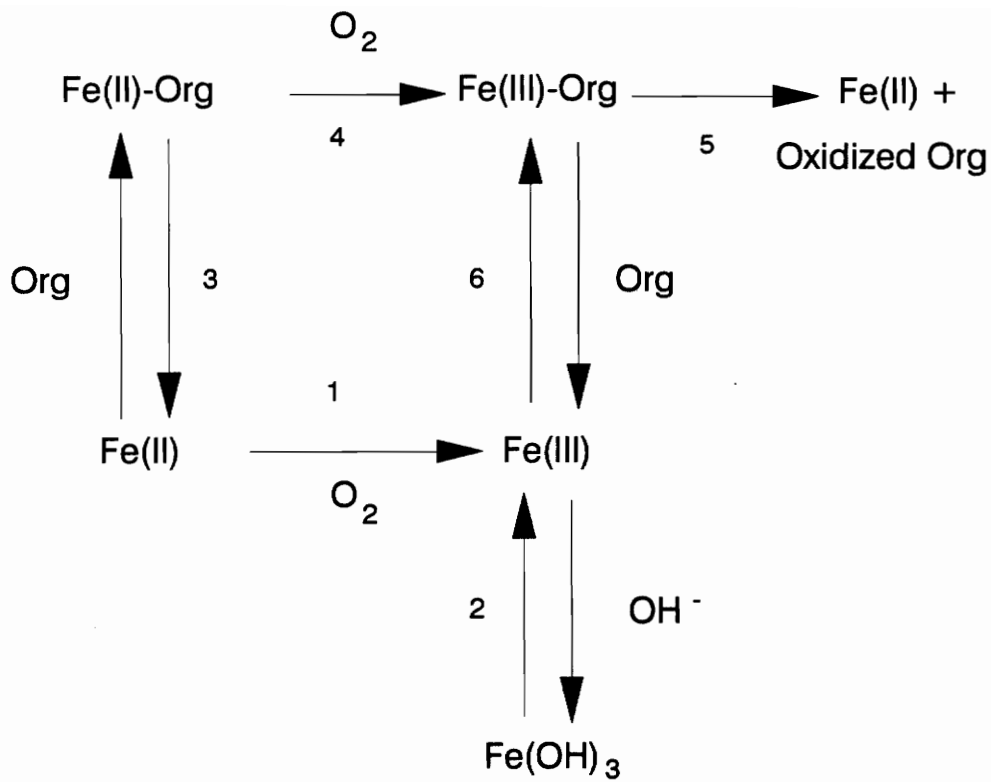


Their model predicts that a steady state concentration of Fe(II) will persist if the Fe(III) reduction step is rapid, even under oxidizing conditions, as long as organic matter is present as a reducing agent. This model suggests that the Fe(III)-Fe(II) couple acts as an electron transfer catalyst in the oxidation of organic matter by oxygen.

Jobin and Ghosh (1972) reported a significant retardation in the rate of Fe(II) oxygenation in the presence of humic acids. They observed a decrease in the oxygenation rate of Fe(II) as the humic acid concentration increased; also, they reported slower oxygenation rates for Fe(II) in the presence of tannic acid than in the presence of humic acid. The experimental results obtained from this study supported the model of Morgan and Stumm (1964).

Theis and Singer (1974) investigated the inhibition of Fe(II) oxygenation in the presence of dissolved organic species to provide a better understanding of the behavior of iron under oxic conditions in natural water systems. They observed the inhibition of Fe(II) in the presence of tannic acid, glutamine, and pyrogallol; however, the acceleration of Fe(II) oxygenation was observed in the presence of citric acid. The authors also provided a qualitative summary of kinetic rates of Fe(II) oxygenation in the presence and/or absence of various dissolved organic species. For example, an initial inhibition in oxygen consumption by tannic acid was observed in the presence of Fe(II). This was attributed to the complexation of tannic acid by Fe(II).

Theis and Singer (1974) developed a hypothetical model (shown in Figure 1) to explain the behavior of iron in the presence of dissolved organic species and oxygen. The complexation reactions appear vertically, while the redox reactions are depicted horizontally. The authors described the model as follows:



Source: Theis and Singer 1974.

Figure 1. Model depicting the behavior of iron in the presence of organic matter (Org) and dissolved oxygen ( $\text{O}_2$ ).

"In the absence of appreciable quantities of dissolved organic matter, Fe(II) is oxidized quite rapidly upon the introduction of oxygen to ferric iron which precipitates to  $\text{Fe}(\text{OH})_3$  and is removed from the system (Reactions 1 and 2). If significant concentrations of organic matter are present, the complexation reaction with ferrous iron (Reaction 3) will compete with the oxygenation reaction. The fractions of ferrous iron complexed or oxidized will depend on the pH and the quantity and type of organic matter present. Oxidation of complexed ferrous iron (Reaction 4) proceeds via a slow step to form the corresponding ferric iron complex with the organic matter. The resultant ferric iron is unstable and is reduced by the organic compound (Reaction 5). The ferrous iron is free to participate in the cycle again. The oxidized organic matter... may participate... until it is oxidized to an inert form.... An additional competition exists for ferric iron between organic species and the hydroxide (Reactions 2 and 6). Again, pH is a determining factor in regards to the relative proportions of ferric iron complexed by organic matter (Reaction 6), reduced by organic compounds (Reaction 5), or complexed by hydroxide (Reaction 2)."

This model differs from the one proposed by Morgan and Stumm (1964) in that it accounts for the complexation of iron by dissolved organic species (reactions 3 and 4). These reactions provide an explanation for the slow rate of oxygen consumption by the iron-organic system.

### **Behavior of Iron in the Presence of Alternative Oxidants and DOC**

In the presence of DOC, the oxidation of Fe(II) by  $\text{KMnO}_4$  can be inhibited. Willey and Jennings (1963) reported that longer contact times were required between permanganate application and filtration for waters containing chelated iron. They also reported that adjustment in the permanganate dose was necessary to meet the oxidant demand of organic species present.

Similar results were obtained by Knocke et al. (1990) who based iron removal on retention by a 0.2  $\mu\text{m}$  membrane filter. The authors evaluated iron removal from solutions containing fulvic acids at pH values of 6.5 and 7.5. Large  $\text{KMnO}_4$  doses (greater than 500 percent of the stoichiometric requirement) yielded less than 25 percent iron removal following a thirty minute contact period.

Knocke et al. (1990) also reported that uncomplexed  $\text{Fe(II)}$  was oxidized efficiently by  $\text{H}_2\text{O}_2$  over the pH range 5 to 7. However, for a solution with a DOC-to-iron weight ratio of 3.0, no detectable iron removal was observed following  $\text{H}_2\text{O}_2$  addition even with  $\text{H}_2\text{O}_2$  dosages as high as 625 percent of the stoichiometric requirement for  $\text{Fe(II)}$  oxidation.

### **Removal of Complexed Iron by Alum Coagulation**

Several studies have been conducted to determine the optimum conditions for the removal of organic color by alum coagulation. Organic color in natural waters results from the presence of humic substances. Humic substances are yellow to brown colored, polymeric acids which can be leached from soils and sediments, and are known to be by-products of vegetative degradation. They can be removed by coagulation via two mechanisms: 1) precipitation by cationic species or 2) adsorption on organic or inorganic solids or a combination of the two mechanisms (Dempsey et al., 1984).



Hall and Packham (1965) observed that, in general, fulvic acids required higher coagulant doses than similar concentrations of humic acids. Amy and King (1981) observed similar results between the removal of humic and fulvic acids. They also reported the optimum pH range of color removal to be between 5 and 6. Rest (1982) observed that the optimum DOC removal for alum coagulation occurred between pH 5.2 to 5.3. He also reported that high molecular weight organic species (greater than 42K) were removed more efficiently from solution by alum coagulation than low molecular weight organic species. Source related differences between natural waters can also be attributed to differences in response to coagulation as a treatment; such differences include alkalinity, pH, and the diverse nature of organic species present (Chadik and Amy, 1987).

Few studies have been conducted in which the removal of complexed iron via coagulation has been addressed. Knocke *et al.* (1990) found that iron tended to be complexed by higher molecular weight species which were efficiently removed by alum coagulation. Residual Fe(II) was found to be complexed by lower molecular weight organics which were not removed by coagulation. When potassium permanganate was added, this residual Fe(II) was reduced by 83 percent; therefore the Fe(II) complexed by lower weight organics was susceptible to chemical oxidation.

## Summary

After review of the literature, it appears that an investigation into the effects of oxidation (by  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$ ) and/or alum coagulation on the removal of complexed  $\text{Fe(II)}$  is necessary. Factors such as solution pH, source of DOC, and concentration of DOC have been reported to effect the complexation capacity of humic substances as well as the oxygenation kinetics of  $\text{Fe(II)}$ . Optimum removal of organic color and DOC has been reported to occur at pH values between 5.5 and 6.0; in addition, higher molecular weight species have been reported to be removed preferentially over lower molecular weight species. This study addresses these issues with regards to complexed  $\text{Fe(II)}$  removal by alum coagulation and/or oxidation by  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$ .

## **Chapter III**

### **METHODS AND MATERIALS**

#### **Overview**

This chapter is divided into three main sections which address the following issues: (1) Laboratory Procedures, which discusses the procedures followed for all laboratory experiments; (2) Physical/Chemical Analysis, which addresses the analytical techniques involved for determining water quality characteristics; and (3) Field Experiments, which explains procedures utilized in all off-campus experiments.

#### **Laboratory Procedures**

##### **Isolation of Humic Substances**

Humic substances were isolated onto an XAD-8 Amberlite resin (Rohm & Haas, Philadelphia, PA) according to the procedure of Thurman and Malcolm (1981), with modifications by Thurman (1984). The resin was cleaned according to the recommended process. First, it was saturated and rinsed with 0.1 N sodium hydroxide (NaOH), followed by consecutive, 24 hour Soxhlet extractions with methanol, hexane, acetonitrile, and methanol, in that order. The resin was stored in brown glass containers in methanol until needed.

The methanol was decanted off of the resin prior to the resin being packed into the column. This was followed by several washes of the resin with distilled, carbon-filtered water from a Milli-Q ion exchange system (Millipore Corporation, Milford, MA). The resin (volume = 430 mL; bed volume equals volume of resin) was then packed into a glass column. Glass wool was inserted in the bottom of column to prevent the resin from leaking out. Once the resin was packed in the column, the resin was rinsed with Milli-Q water to remove any remaining trace amounts of methanol. The packed column was then rinsed three times, alternating from 0.1 N NaOH to 0.1 N hydrochloric acid (HCl); leaving the resin saturated with the acidic solution.

Approximately 350 liters (L) of water were obtained from the Jerico Ditch in the Great Dismal Swamp, located in southeastern Virginia, in March, 1991. The swamp water had the following characteristics: DOC of 106 mg/L, turbidity of 1.2 nephelometric turbidity units (NTU), and a pH of 3.3.

The water obtained from the Great Dismal Swamp was acidified with concentrated HCl to a pH between 2 and 2.5 prior to being applied to the packed column. It was not necessary to filter the water through a sand filter prior to application to the resin since the initial turbidity was so low. The water was applied to the resin in a down-flow manner at a flow rate of 15 bed volumes per hour as recommended by Thurman and Malcolm (1981). Operations continued until a "breakthrough" value of DOC was reached in the effluent from the column. This

breakthrough value was arbitrarily set at between 40 and 45 mg/L of DOC. The column was then eluted in an upflow manner with 0.1 N NaOH with a flow rate of 5 bed volumes per hour. The eluate (from all adsorption passes) was collected in brown, glass jars, acidified to pH 7 with concentrated nitric acid ( $\text{HNO}_3$ ), and purged with nitrogen gas ( $\text{N}_2$  (g)) prior to storage at 4 to 5 degrees Celsius ( $^{\circ}\text{C}$ ). The process yielded 11 L of a stock humic substances solution with an average DOC concentration of 1180 mg/L. The iron concentration of the stock solution, determined by atomic absorption spectrophotometry, was less than 0.01 mg Fe per mg of DOC.

Humic substances were also isolated from the raw water source at the Williams Water Treatment Plant in Durham, NC, in August, 1991. The isolation method described previously was again utilized. The water was obtained from the terminal reservoir serving the treatment plant, with DOC concentrations prior to isolation in the range of 3.8 to 6 mg/L. Approximately 4 L of stock humic substances were obtained following resin adsorption, with an average DOC concentration of 160 mg/L. Iron was present in this stock solution in an amount less than 0.02 mg Fe per mg DOC.

A third source of humic substances was obtained from Dr. Mark Benjamin (University of Washington). These humic substances had been previously adsorbed onto iron oxide solids and subsequently extracted with an alkaline solution. This source was separated into two molecular weight fractions by ultrafiltration: between 10K and 100K (66 mg/L DOC) and less than 3K (135

mg/L DOC). Iron was present in these stock solutions in an amount less than 0.01 mg Fe per mg DOC.

## **Characterization of Humic Substances**

**Fractionation by Ultrafiltration:** The fractionation of stock DOC solutions was performed with an Amicon stirred-cell ultrafiltration apparatus (Model 8200, Amicon Division, W.R. Grace & Company, Danvers, MA). According to Theis and Singer (1984), most humic acids and fulvic acids found in natural waters have a molecular weight less than 25,000 AMU. For this reason the following nominal molecular weight exclusion size ultrafilters were chosen for use in this study: 100K, 30K, 10K, 3K, and 1K. Samples were filtered under a  $N_2(g)$  pressure of 40 pounds per square inch (psi). Each ultrafiltration cell had a volume of approximately 200 mL and all but 40 to 50 mL of sample was filtered for each fractionation test.

Each new ultrafilter was soaked in Milli-Q water for 24 hours. Approximately 200 mL of Milli-Q water was passed through each ultrafilter prior to filtration. Ultrafilters were cleaned after use by gently rubbing a dilute soap solution across the filter surface, followed by rinsing the filter surface with Milli-Q water. Between studies, ultrafilters were stored in a 1 percent solution of  $HNO_3$ ; for extended periods of storage, however, ultrafilters were stored in a sodium azide solution to reduce bacterial growth.

Relative MWD of DOC solutions were determined by passing a 10 mg/L DOC solution through the ultrafilters. The ultrafilters were set up in a parallel configuration, meaning the solution was passed through each ultrafilter separately. The DOC of each filtrate was then measured to determine the relative MWD. This test was conducted on each of the stock solutions of humic substances.

**Specific Absorbance:** Specific absorbance of the stock humic substances solutions was determined by measuring UV absorbance at 254 nm with a Beckman DU-6 UV Spectrophotometer (Fullerton, CA). The specific absorbance was calculated using the following relationship:

$$SA = \frac{Abs(100)}{DOC} \quad [11]$$

$$\begin{aligned} SA &= \text{Specific Absorbance (L/(cm * mg-C))} \\ Abs &= \text{Absorbance (1/cm)} \\ DOC &= \text{Dissolved organic carbon (mg-C/L)} \end{aligned}$$

Reckhow et al. (1990) reported the specific absorbance of humic acids and fulvic acids to be between 3 and 7.3 L/(cm \* mg-C).

**Estimation of Relative Fraction of Humic and Fulvic Acids:** Humic acid is the fraction of aquatic humic substances which is insoluble at pH 2.0 or less; therefore, the humic acid fraction can be separated from the fulvic acid fraction at extremely low pH values. A 50 mL sample of the stock solution of humic substances was acidified to a pH of 1 with concentrated HCl and subsequently allowed to settle for a 24 hour period, according to the method described by Thurman and Malcolm

(1981). The sample was then centrifuged in a Beckman Model J21C Centrifuge (Fullerton, CA) for 30 minutes at 40,000 revolutions per minute (rpm). The supernatant was decanted off of the precipitant, and the DOC of the supernatant was measured. By comparing the DOC of the supernatant to the DOC of the stock solution of humic substances, an estimate of the relative fraction of humic acids and fulvic acids can be determined.

### **Definition of Species in Solution**

The following classifications were utilized throughout the study with regards to iron speciation: particulate iron, colloidal iron, and soluble iron. Particulate iron was defined as that fraction of iron retained on a 0.2  $\mu\text{m}$  pore size membrane filter. Colloidal iron was defined as that fraction of iron which passed a 0.2  $\mu\text{m}$  membrane filter but was retained on a 100K ultrafilter. Soluble iron was defined as that fraction that passed through a 100K ultrafilter. Figure 2 illustrates the species of iron that were typically present after oxidant addition.

Similar classifications were used with regards to organic carbon. DOC was defined as the organic carbon passing a 100K ultrafilter, while colloidal organic carbon was defined as the fraction of organic carbon retained on a 100K ultrafilter. The 0.2  $\mu\text{m}$  membrane filter was not used for organic carbon speciation because it was found to contribute to DOC.



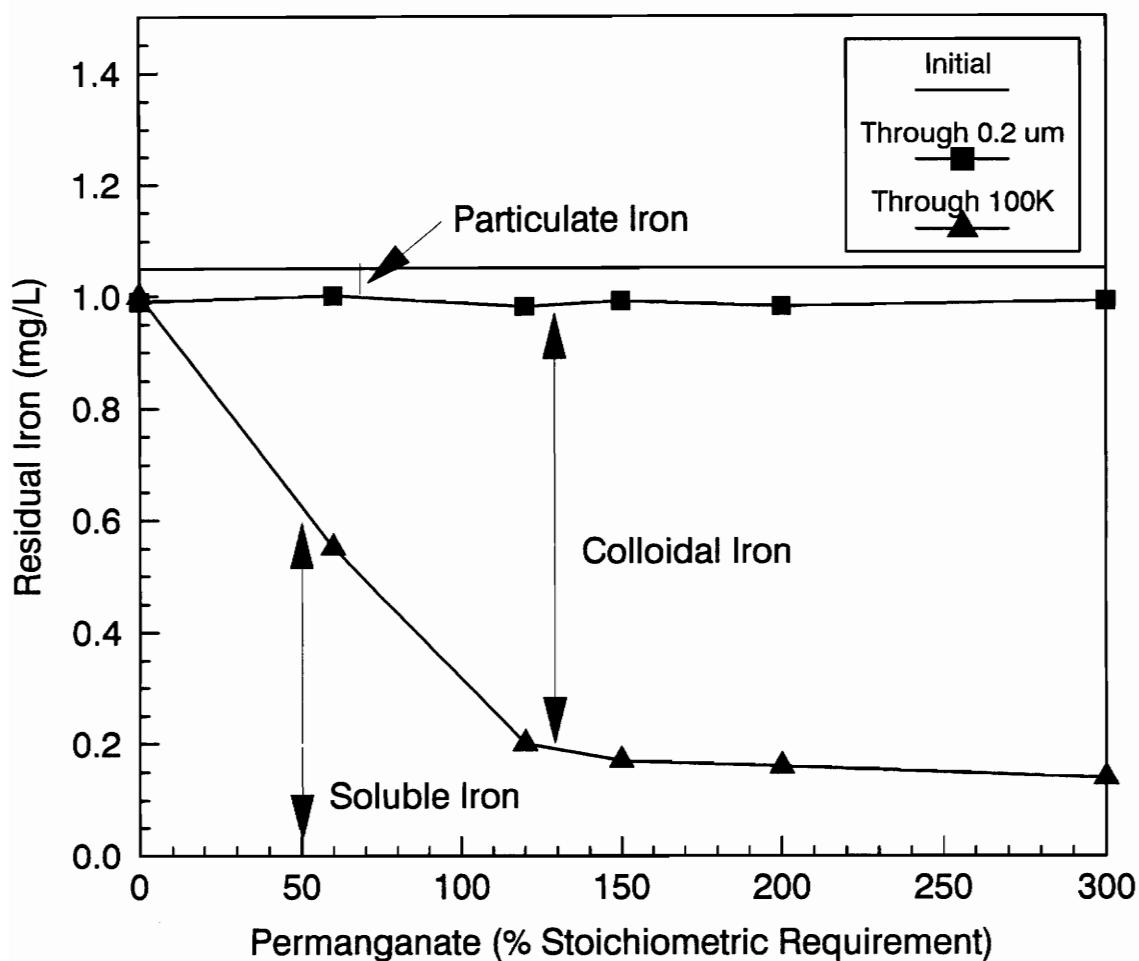


Figure 2. An illustration of particulate, colloidal, and soluble iron. (pH = 6.5; DOC = 3 mg/L; DOC source - Dismal Swamp; reaction time = 5 minutes; stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe)

## Preparation of Water Solutions

Experimental studies were conducted using a "natural" water that was prepared as follows:

1. The "natural" water was prepared using Milli-Q water with a DOC concentration of less than 0.4 mg/L.
2. The following background ions were added to simulate freshwater conditions: 0.25 meq/L of sodium sulfate, 1.0 meq/L of calcium chloride, and 1.0 meq/L of sodium bicarbonate.
3. An appropriate amount of the stock humic substances was added to establish the desired solution DOC concentration.
4. For coagulation studies, an appropriate amount of kaolinite (added as a slurry) was added to create an initial turbidity between 4 to 6 NTU.
5. The water was deaerated (for O<sub>2</sub> stripping) by bubbling with N<sub>2</sub>(g) for 20 minutes.
6. The pH of the water was then adjusted to 5.5 by dropwise additions of concentrated HNO<sub>3</sub>.
7. An appropriate amount of Fe(II) stock solution was added to achieve the desired initial Fe(II) concentration.
8. The vessel containing the water was sealed with Parafilm to reduce interferences resulting from atmospheric oxygen.

9. If the experiment involved complexed Fe(II), the solution was allowed to sit for at least 12 hours prior to use to insure adequate time for complexation between DOC and Fe(II) to occur.
10. The pH of the water was adjusted as necessary by the addition of sodium bicarbonate.

Two solutions were prepared to examine the extent of oxygenation of complexed Fe(II) during the 12 hour complexation period. One solution was allowed to remain open to the atmosphere, while the other solution remained covered with Parafilm. Both solutions were monitored for the formation of colloidal iron species over a 48 hour period. Data presented in Figure 3 illustrate changes in iron and DOC speciation during the monitoring period. From these data, it was concluded that the complexation period of 12 hours (in a sealed vessel) did not result in the formation of any appreciable amounts of colloidal species.

### **Preparation of Stock Solutions**

**Ferrous Iron:** The Fe(II) stock solution was prepared by adding a sufficient amount of ferrous sulfate heptahydrate crystals ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) to Milli-Q water to obtain a concentration of 1 mg/mL. The Milli-Q water used in the preparation of this solution was deaerated for a minimum of 15 minutes and acidified to a pH near 2 (0.1 mL concentrated  $\text{HNO}_3$  per 100 mL solution) prior

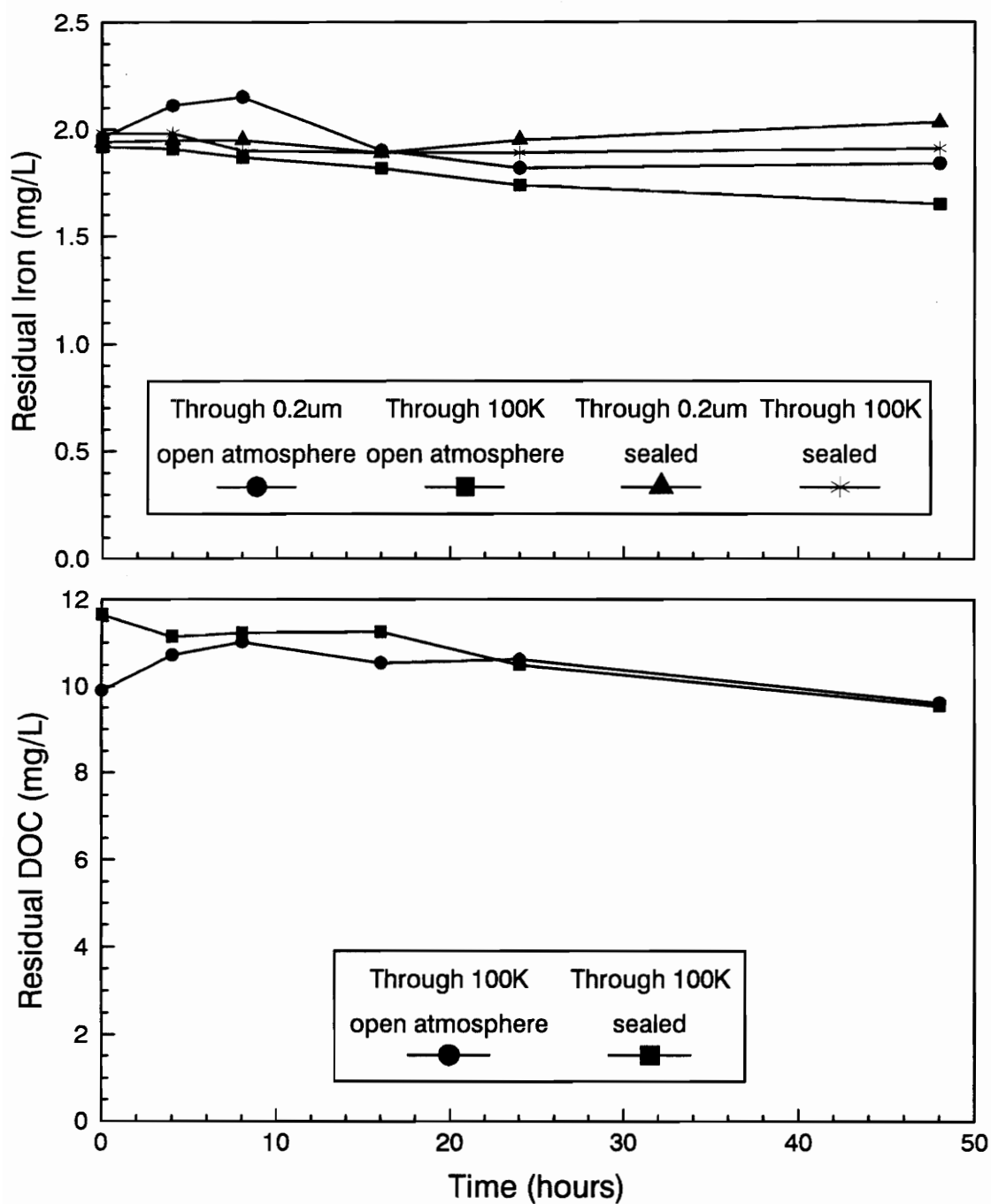


Figure 3. Changes in iron and DOC speciation during complexation period. (pH = 5.5; DOC source- Dismal Swamp)

to Fe(II) addition. This solution was only stable for approximately 24 hours, so it was prepared prior to each experiment.

**Aluminum Sulfate:** An aluminum sulfate (alum) solution was prepared by dissolving a sufficient amount of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  into Milli-Q water to obtain a concentration of 1 mg/mL.

**Sodium Bicarbonate:** The sodium bicarbonate stock solution was prepared by dissolving a sufficient amount of sodium bicarbonate ( $\text{NaHCO}_3$ ) in Milli-Q water to obtain a concentration of 10 mg/mL. This solution was used for pH maintenance in coagulation studies.

### **Preparation of Oxidant Stock Solutions**

**Potassium Permanganate:** Stock solutions of potassium permanganate ( $\text{KMnO}_4$ ) were prepared by dissolving reagent grade  $\text{KMnO}_4$  in Milli-Q water to create solutions with 1 mg/mL and 4 mg/mL concentrations as  $\text{KMnO}_4$ . These stock solutions were stored in brown, glass bottles under dark refrigerated conditions (4 to 5 °C). The titre of the stock solution was measured by potentiometric titration prior to use in each study.

**Hydrogen Peroxide:** The stock solution of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was purchased as a 3 percent USP-grade solution. The stock solution was stored in a brown bottle at room temperature. The stock solution was diluted with Milli-Q water

prior to use to an appropriate working concentration. The titre of the stock solution was determined by potentiometric titration prior to each study.

### **Oxidant Demand of Humic Substances**

The oxidant demand of humic substances was determined by adding oxidant (2 to 10 mg/L) to water solutions containing varying concentrations of DOC (3, 5, or 10 mg/L). Residual oxidant concentrations were then monitored as a function of time until the rate of oxidant depletion approached zero.

### **Oxidant Demand of Uncomplexed Fe(II)**

Water solutions were prepared to contain 2 mg/L of Fe(II) and background ions in the absence of DOC. They were each dosed with oxidant dosages ranging from 0 to 150 percent of the stoichiometric requirement (0.94 mg  $\text{KMnO}_4$  per mg Fe; 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe) for Fe(II) oxidation. Samples were withdrawn after a contact period of five minutes and (1) filtered through a 0.2  $\mu\text{m}$  membrane filter and acidified for residual iron analysis, (2) filtered through a 100K ultrafilter and acidified for residual iron analysis, and/or (3) filtered for residual oxidant analysis. These data were useful for comparing the actual, experimental reaction stoichiometry to that predicted by the balanced chemical oxidation-reduction reaction.

## **Fractionation of Complexed Fe(II) Solutions**

Two complexed Fe(II) solutions (10 mg/L DOC, 2 mg/L Fe(II); and 5 mg/L DOC, 2 mg/L Fe(II)) were fractionated by ultrafiltration to determine the DOC-to-iron weight ratios in each relative molecular weight fraction. The following ultrafilters were used in this study: 100K, 30K, 10K, 3K, and 1K. The 0.2  $\mu$ m membrane filter was also used for analysis of any particulate iron. Fractionation studies were conducted for the two complexed Fe(II) solutions at pH 5.5 and 6.5.

## **Oxidation of Complexed Fe(II)**

Studies were conducted to evaluate the ability of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  to oxidize complexed Fe(II) over a pH range of 5.5 to 7.5. The concentration of soluble Fe(II) ranged from 1 to 2 mg/L, while the DOC concentration ranged from 2 to 10 mg/L.

Initially, oxidation studies were conducted using a jar-test apparatus which was open to the atmosphere. The pH of the solution was found to increase during the course of the study, sometimes as much as 2 pH units. This pH increase can probably be attributed to the loss of carbon dioxide ( $\text{CO}_2(\text{aq})$ ) from solution due to mixing. The test procedure was modified by utilizing 300-mL BOD bottles which were sealed from the atmosphere with a glass stopper. This modification helped to eliminate fluctuations in pH ( $\pm 0.15$  pH units).

Initially, oxidation studies were conducted over the pH range 5.5 to 7.5; however, for studies conducted at pH 7.5 the formation of colloidal iron species was

observed in control solutions (no oxidant addition). Representative results from studies conducted at pH 7.5 are illustrated in Figure 4. For the control solution (zero percent oxidant) in the 5 mg/L DOC sample, approximately 1.6 mg/L Fe (80 percent of the original iron concentration) were retained on the 100K ultrafilter; while in the 10 mg/L DOC control solution only 0.3 mg/L Fe (15 percent of the original iron concentration) were retained on the 100K ultrafilter. In comparison only 4 to 8 percent of the original iron concentration was retained on a 100K ultrafilter for pH 5.5 and 6.5 control solutions.

The formation of colloidal iron species in the pH 7.5 control solutions was attributed to Fe(II) oxidation by trace quantities of  $O_2$  that remained in solution after deaeration. Test solutions were analyzed for  $O_2(aq)$  concentrations following solution purging with  $N_2(g)$  for twenty minutes. It was determined that on average 0.5 mg/L of  $O_2(aq)$  remained in solution. From the reaction stoichiometry, 0.14 mg/L of  $O_2(aq)$  are required to oxidize every mg Fe(II) present; therefore, it was hypothesized that the excess stoichiometric amount of  $O_2(aq)$  present coupled with the elevated pH condition resulted in an environment which kinetically favored Fe(II) oxygenation.

Experimental modifications, such as the use of an oxy-trap and high purity  $N_2(g)$ , were investigated as methods to eliminate interferences resulting from residual  $O_2(aq)$  in pH 7.5 test solutions. Although these modifications did reduce the oxygenation of Fe(II), they did not eliminate it. It was concluded that testing at pH 7.5 should be eliminated from the experimental matrix, since the



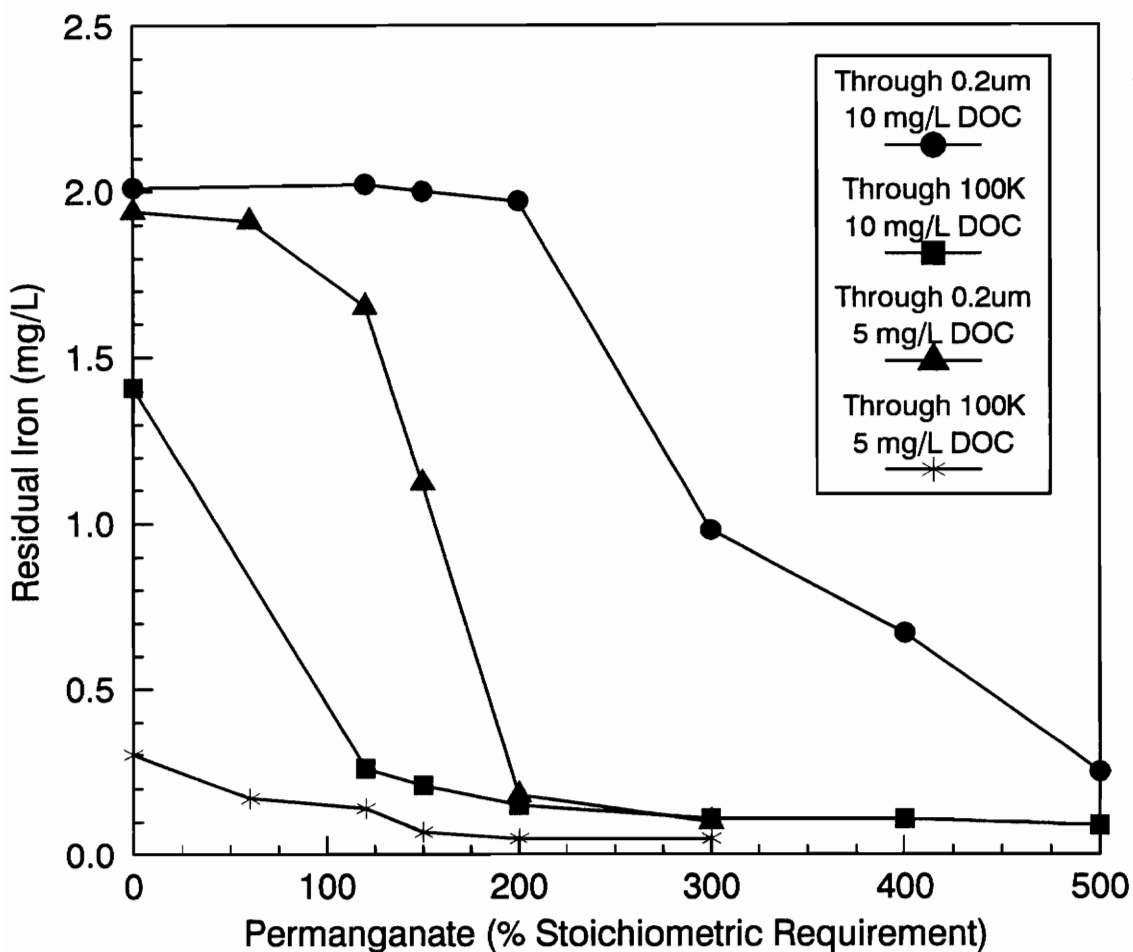


Figure 4. Oxidation of complexed Fe(II) by potassium permanganate at pH 7.5. (reaction time = 60 minutes; DOC source - Dismal Swamp; stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe)

effectiveness of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  on the oxidation of complexed  $\text{Fe(II)}$  could not be fully evaluated due to competitive  $\text{Fe(II)}$  oxidation by  $\text{O}_2(\text{aq})$ .

The following procedures were utilized during oxidation studies:

1. If necessary, the initial pH of the test solution was adjusted by adding either  $\text{HNO}_3$  or  $\text{NaHCO}_3$ .
2. The solution was carefully poured into the 300 mL BOD bottle to minimize interferences caused by atmospheric oxygen.
3. Samples were dosed at time zero with a known amount of the oxidant stock solution.
4. After the appropriate contact time (5 minutes or 60 minutes), samples were withdrawn and (1) filtered through a 0.2  $\mu\text{m}$  membrane filter and acidified for residual iron analysis, (2) filtered through a 100K ultrafilter and acidified for residual iron and DOC analysis, and/or (3) filtered through 100K ultrafilter for residual oxidant analysis.

Some solutions from oxidation studies (contact time = 60 minutes) were chosen for analysis of their MWD by fractionation through ultrafilters. The following filters were utilized: 0.2 $\mu\text{m}$ , 100K, 30K, 10K, 3K, and 1K. Both iron and DOC concentrations were analyzed.

## Determination Of Fe(II)

A method was desired which could detect Fe(II) when complexed with organic carbon. The method would be utilized for Fe(II) detection both before and after the addition of an oxidant. It was desired that the method produce reproducible data.

According to Lee and Stumm (1960), the bathophenanthroline method was more sensitive for ferrous iron analysis than the 1,10-phenanthroline method described in Standard Methods (Method 3500-C). This method involves complexation of Fe(II) by bathophenanthroline. The formation of the Fe(II)-bathophenanthroline complex results in a pale-pink to deep red color. The concentration of Fe(II) is directly proportional to the color produced. The Fe(II)-bathophenanthroline complex is extracted from the sample by hexane. The percent transmittance of the complex is determined by spectrophotometry at a wavelength of 533 nm.

For natural water samples, Lee and Stumm (1960) suggested boiling the sample in the presence of acid to free ferrous iron from organic matter. Theis and Singer (1974), however, noted that the addition of acid could interfere with the ferric/ferrous iron ratio. They felt that the addition of sodium acetate buffer was effective at releasing ferrous iron from organic matter and recommended that the acidification step be avoided.

The Tamura et al. (1973) 1,10-phenanthroline method was a modification of the 1,10-phenanthroline method described in Standard Methods (Method 3500-C).

This method includes the addition of ammonium fluoride as a masking agent for Fe(III). A complex between Fe(II) and 1,10-phenanthroline forms, resulting in a pale-peach to reddish orange color. The complex is stable in diffuse sunlight for up to one hour. The percent transmittance of the colored complex is determined by spectrophotometry at a wavelength of 510 nm.

Ferrozine also forms a complex with Fe(II) (Gibbs, 1978). The formation of the complex results in a lavender to deep purple color. The complex is stable in diffuse sunlight for up to 24 hours. The percent transmittance of the colored complex is determined by spectrophotometry at a wavelength of 564 nm.

Each method involved the detection of a colored complex by spectrophotometric methods. For each method, the percent transmittance of the sample was determined with a Bausch & Lomb Spectronic 20 Colorimeter at a specified wavelength. Transmittance values were converted to absorbance values. Using the Beer-Lambert law, a regression line plotted for Fe(II) concentration (from standards with 0-2 mg/L of Fe(II)) versus absorbance could be obtained. This relationship was then used to estimate the concentration of Fe(II) present in the samples.

The three methods (along with any suggested modifications) were examined for Fe(II) determination. Each method was used to measure Fe(II) in samples containing reduced and oxidized Fe. These results will be discussed in detail at the beginning of the next chapter.

## **Removal of Complexed Fe(II) by Alum Coagulation**

Coagulation studies were conducted using a conventional jar-test apparatus (Phipps & Bird, Inc., Model 300, Richmond, VA) with six paddle-stirred containers. Samples were rapidly mixed (max speed) for 90 seconds, flocculated for 15 minutes at 50 rpm and then 15 minutes at 20 rpm, and settled for one hour. Certain tests involved the addition of an oxidant; in such cases, the oxidant was added prior to coagulant during the rapid mix phase. The pH was maintained during coagulation studies by the addition of appropriate amounts of  $\text{NaHCO}_3$  solution following oxidant and coagulant addition during rapid mix. After sedimentation, samples were withdrawn and analyzed for pH, turbidity, residual iron (particulate, colloidal, and soluble), and residual DOC.

The following variables were examined for their effect on the removal of complexed Fe(II) via alum coagulation:

1. Alum dose: The concentration ranged from 0 to 60 mg/L, values typically utilized in full-scale treatment facilities.
2. pH: Two pH ranges were examined: 5.5 to 6.0 and 6.8 to 7.3. The former corresponds to the optimum pH range for color and DOC removal (Dempsey *et al.*, 1984), while the latter corresponds to the range often used by treatment facilities.

3. Oxidant dose: Control studies were conducted in which no oxidant was added, while companion studies were conducted to evaluate the effect of oxidant addition.

Certain solutions from coagulation studies were chosen for analysis of their MWD after sedimentation. The following filters were used: 0.2um, 100K, 30K, 10K, 3K, and 1K. Both residual iron and DOC were analyzed.

### **Temperature Control**

Fluctuations in solution temperature were not observed during the course of the study, nor was temperature a primary variable in the study. Instead, solution temperature remained relatively constant (20 to 22 °C) for all studies.

### **Glassware Washing**

Glassware was washed in a one percent HNO<sub>3</sub> bath and rinsed with Milli-Q water. This technique was designed to remove any residual iron or organic matter which might result in experimental or analytical interferences.

## **Physical/Chemical Analysis**

### **Residual Iron**

Residual soluble iron concentrations were determined using an atomic absorption spectrophotometer (AAS) (Perkin-Elmer, Model 703, Norwich, CT).

Samples were collected in glass test tubes and acidified with 1 to 2 drops of concentrated  $\text{HNO}_3$  prior to analysis. The following instrument settings were used for iron analysis: a wavelength of 248.3 nm and a slit width of 0.3 mm. At these settings, the detection limit for iron was 0.03 mg/L and the procedure was linear up to iron concentrations of 10 mg/L. Standards used for instrument calibration contained 1, 5, and 8 mg/L Fe.

### **Dissolved Organic Carbon**

DOC concentrations were determined using a Total Organic Carbon Analyzer (Dohrmann Carbon Analyzer DC-80, Santa Clara, CA). Samples were collected in glass vials and acidified to pH 2 with 2 to 3 drops of 85 percent phosphoric acid. The instrument was operated using the manufacturer's recommendations. The instrument was calibrated with solutions containing 10, 400, and 2000 mg/L DOC.

### **Turbidity**

Solution turbidity was determined using a Hach Model 2100A Turbidimeter (Loveland, CO). Samples (25 mL) were removed from test vessels by a volumetric pipet placed just below the water surface in the center of the solution. Standards used for instrument calibration were 0.2, 1, 10, 100, and 1000 NTU.

## **Solution pH**

Solution pH was determined with a Fisher Accumet pH meter (Model #610A; Pittsburg, PA). The meter was calibrated using standard buffer solutions (pH 4, 7, and 10).

## **Oxidant Residual**

The concentrations of residual oxidant were determined using a Fisher Scientific computer-aided titrimeter (Model #465; Pittsburg, PA). This technique is based on the potentiometric titration of the sample with 0.00564 N phenylarsine oxide (PAO). Sample titration involves a programmable titrator and a platinum combination electrode. The endpoint of the titration is determined by the detection of a sign change in the second derivative of the titration curve.

**Potassium Permanganate:** Residual  $\text{KMnO}_4$  analysis involved PAO titration of a 100 mL sample. Each sample was buffered with 1 mL of a pH 7 phosphate buffer followed by the addition of 1 gram (g) of potassium iodide (KI) to fix the residual oxidant. The sample was then placed in the dark for at least ten minutes prior to titration. The  $\text{KMnO}_4$  concentration was calculated as follows:

$$\text{KMnO}_4(\text{mg/L}) = \frac{\text{PAO (mL)} * 0.00564 (\text{eq/L}) * 45150 (\text{mg/eq})}{\text{sample volume (mL)}} \quad [12]$$

It should be noted that 3.5, as recommended by Hair (1987), was the value used for electron transfer instead of 3.



As a comparative study, standard solutions (2 mg/L and 5 mg/L as  $\text{KMnO}_4$ ) were analyzed on both the titrimeter for  $\text{KMnO}_4$  concentration and AAS for manganese (Mn) concentration. Excellent agreement was observed between the two methods. The results are compiled in Table 1.

**Hydrogen Peroxide:** A slight modification was made to determine residual  $\text{H}_2\text{O}_2$  concentration. In addition to the phosphate buffer and KI, 1 g of ammonium molybdate was also added to the 100 mL sample. The kinetics of the reaction between  $\text{H}_2\text{O}_2$  and KI are extremely slow without the addition of ammonium molybdate (Knocke *et al.*, 1990). The sample was placed in the dark for at least ten minutes prior to titration. The  $\text{H}_2\text{O}_2$  concentration was calculated as follows:

$$\text{H}_2\text{O}_2 \text{ (mg/L)} = \frac{\text{PAO (mL)} * 0.00564 \text{ (eq/L)} * 17000 \text{ (mg/eq)}}{\text{sample volume (mL)}} \quad [13]$$

### Field Experiments

In August 1991, a sampling trip was made to the Williams Water Treatment Plant in Durham, NC. At that time, the plant was treating approximately 30 million gallons per day. The raw water had DOC and iron concentrations of 3.8 to 6 mg/L and 0 to 1.5 mg/L, respectively. The water was treated with 28 mg/L of alum. After flocculation (total retention time 1 hour) and sedimentation (4 hours), the water was filtered and disinfected with chlorine.

Table 1

Comparison between AAS and potentiometric titration to  
determine  $\text{KMnO}_4$  concentrations

Potentiometric Titration (mg/L $\text{KMnO}_4$ )	AAS (mg/L $\text{KMnO}_4$ )
1.97	1.93
1.94	1.93
4.89	4.84
4.82	4.84

Note:

- a) AAS quantifies manganese (Mn) concentration; to convert to  $\text{KMnO}_4$  multiply by 2.88.

Coagulation studies were conducted using water obtained from the terminal reservoir serving the facility. Tests were conducted using the procedures described previously. Tests were conducted both with and without the addition of  $\text{KMnO}_4$ .

## **Chapter IV**

### **RESULTS**

#### **Overview**

This chapter contains the results of the experiments described in the Methods and Materials chapter. First, the results used to determine which Fe(II) analysis method would be utilized are presented, followed by the characterization of humic substances utilized throughout the study. Next, the results concerning the oxidation of complexed Fe(II) by  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  are presented. Finally, results from studies involving the coagulation of complexed Fe(II) in the presence and absence of oxidant addition are considered.

#### **Determination of Fe(II)**

Tests were conducted to establish which of the following three methods (along with any recommended modifications) would be utilized for analyzing Fe(II) in the presence of DOC: bathophenanthroline, 1,10-phenanthroline, and ferrozine. Several studies were conducted where each method was utilized to analyze Fe(II) concentrations. Solutions were prepared with various concentrations of Fe(II) and DOC, which were representative of DOC-to-iron weight ratios used in the oxidation studies.

First, each method was used to analyze unoxidized, complexed Fe(II) solutions at pH 5.5. Near 100 percent Fe(II) recovery was anticipated because oxygenation kinetics are considerably slower at pH values less than 6.5 (Stumm and Lee, 1961). Representative results are summarized in Table 2. It should be noted that the acidified/boiled method refers to the recommendation of Lee and Stumm (1960) that natural water samples should be acidified (1 mL of concentrated HCl to 25 mL of sample) and boiled for five minutes prior to Fe(II) analysis. From this study the bathophenanthroline procedure alone was deemed inadequate, due to the low Fe(II) recovery from complexed Fe(II) solutions. The 1,10-phenanthroline and ferrozine procedures resulted in average Fe(II) recovery values of 86 and 96 percent, respectively. The acidified/boiled modification also appeared to be satisfactory, with an average Fe(II) recovery of 100 percent. Further tests, however, were required to insure that this modification did not result in the alteration of the Fe(II)-to-Fe(III) ratio in test solutions.

An auxillary study was conducted to determine whether samples which were acidified and boiled contained Fe(III) which had been converted to Fe(II). Uncomplexed Fe(II) solutions were dosed with 65 and 100 percent of the stoichiometric requirement of  $\text{KMnO}_4$  and each solution was analyzed for Fe(II) concentration by both the bathophenanthroline and the acidified/boiled bathophenanthroline methods. Results are depicted in Table 3. It was expected that the Fe concentrations in the 0.2  $\mu\text{m}$  filtrate would be equivalent to the Fe(II)

Table 2

## Evaluation of Fe(II) analysis methods

Total Fe (mg/L)	Nominal DOC (mg/L)	Fe(II) Analysis Method	Fe(II) (mg/L)	Fe(II) Recovery (%)
2.00	10	Bathophenanthroline	1.54	74
2.22	5	Bathophenanthroline	1.73	79
0.99	3	Bathophenanthroline	0.57	57
2.22	10	Acidified/Boiled	2.22	100
2.27	5	Acidified/Boiled	2.38	105
1.05	3	Acidified/Boiled	1.07	102
2.08	10	1,10-phenanthroline	1.70	82
2.22	5	1,10-phenanthroline	1.95	87
0.99	3	1,10-phenanthroline	1.88	88
2.00	10	Ferrozine	1.90	95
1.01	3	Ferrozine	0.98	97

## Notes:

- a) test conducted at pH = 5.5; DOC source - Dismal Swamp;
- b) 'Total Fe' quantified by AAS; 'Nominal DOC' refers to DOC concentration at which test solutions were prepared, although values were not measured;
- c) 'Acidified/Boiled' refers to modification of Lee and Stumm (1960) for the bathophenanthroline procedure.

Table 3

Comparison between bathophenanthroline and acidified/boiled  
bathophenanthroline procedures

KMnO <sub>4</sub> Dose (%)	Total Fe (mg/L)	Fe Through 0.2 $\mu$ m (mg/L)	Fe(II) Analysis Method	Fe(II) (mg/L)
100	1.84	0.05	Bathophenanthroline	0.1
100	2.11	0.05	Acidified/Boiled	0.5
65	1.91	0.60	Bathophenanthroline	0.3
65	2.23	0.60	Acidified/Boiled	0.9

## Notes:

- a) test conducted at pH = 5.5; DOC = <0.4 mg/L;
- b) 'Total Fe' and 'Fe Through 0.2  $\mu$ m' quantified by AAS;
- c) 'Acidified/Boiled' refers to modification of Lee and Stumm (1960) for the bathophenanthroline procedure;
- d) stoichiometric requirement = 0.94 mg KMnO<sub>4</sub> per mg Fe.

concentrations measured by both methods. From the elevated Fe(II) values obtained when using the acidified/boiled modification, it was concluded that this modification resulted in the conversion of some fraction of the Fe(III) to Fe(II). concentrations measured by both methods. From the elevated Fe(II) values obtained when using the acidified/boiled modification, it was concluded that this modification resulted in the conversion of some fraction of the Fe(III) to Fe(II). Also, the bathophenanthroline procedure alone failed to yield 100 percent Fe(II) recovery even in the absence of DOC. Due to these inefficiencies, neither bathophenanthroline procedure was utilized for Fe(II) analysis.

A final comparative study was conducted to differentiate between the 1,10-phenanthroline and ferrozine methods by measuring Fe(II) in complexed Fe(II) solutions oxidized with  $\text{KMnO}_4$ . The results presented in Table 4 illustrate that both methods yielded satisfactory Fe(II) recovery values. As in the previous study, measured Fe(II) values were compared to the Fe concentration in the 0.2  $\mu\text{m}$  filtrate after oxidation. The ferrozine method was chosen as the method for Fe(II) analysis for the following reasons: (1) it did not require liquid extraction of Fe(II) complex; (2) it did not require dilution after addition of reagents; (3) it required only one minute to form the colored Fe(II)-ferrozine complex; and finally (4) it produced a purple colored Fe(II)-ferrozine complex which was stable for up to 24 hours. It should be noted, however, that the standard curve obtained when using this procedure was linear only up to Fe(II) concentrations of 1.0 mg/L.



Table 4

Comparison between 1,10-phenanthroline and ferrozine procedures for Fe(II) analysis

KMnO <sub>4</sub> Dose (%)	Total Fe (mg/L)	Fe Through 0.2 $\mu$ m (mg/L)	Fe(II) Analysis Method	Fe(II) (mg/L)
100	1.84	0.05	1,10-phenanthroline	0.1
65	1.91	0.60	1,10-phenanthroline	0.7
80	1.95	0.37	Ferrozine	0.2
40	1.92	1.18	Ferrozine	1.1

Notes:

- a) test conducted at pH = 5.5; DOC = 5 mg/L; DOC source - Dismal Swamp;
- b) 'Total Fe' and 'Fe Through 0.2  $\mu$ m' quantified by AAS;
- c) stoichiometric requirement = 0.94 mg KMnO<sub>4</sub> per mg Fe.

## Characterization of Humic Substances

Three sources of humic substances were utilized for this research project. Humic substances were isolated onto an XAD-8 resin from water obtained from the Great Dismal Swamp, Virginia, and the terminal reservoir at the Williams Water Treatment Plant in Durham, North Carolina. The third group of humic substances was obtained from Dr. Mark Benjamin (University of Washington). Dr. Benjamin adsorbed natural DOC onto iron oxide solids and extracted it with an alkaline solution. The Dismal Swamp source was the principal source of study, while the other sources were utilized in comparative studies.

Fractionation with nominal molecular weight exclusion size ultrafilters (100K, 30K, 10K, 3K, and 1K) was performed to characterize each of the stock humic solutions. The relative MWD of DOC present in these stock solutions is presented in Figure 5. The humic stock solutions appear to have relatively similar MWD with regards to DOC; with a majority of the DOC located in the smaller molecular weight fractions (less than 10K). The MWD of DOC for the Dismal Swamp humic solution represents an average of seven fractionations which were performed over a six month period.

The precipitation of humic acids at pH 1 was performed with the Dismal Swamp and Durham stock humic solutions to evaluate the relative fractions of humic acids and fulvic acids present in the stock solutions. After centrifugation the supernatant had a DOC concentration of 92 percent and 88 percent of the original

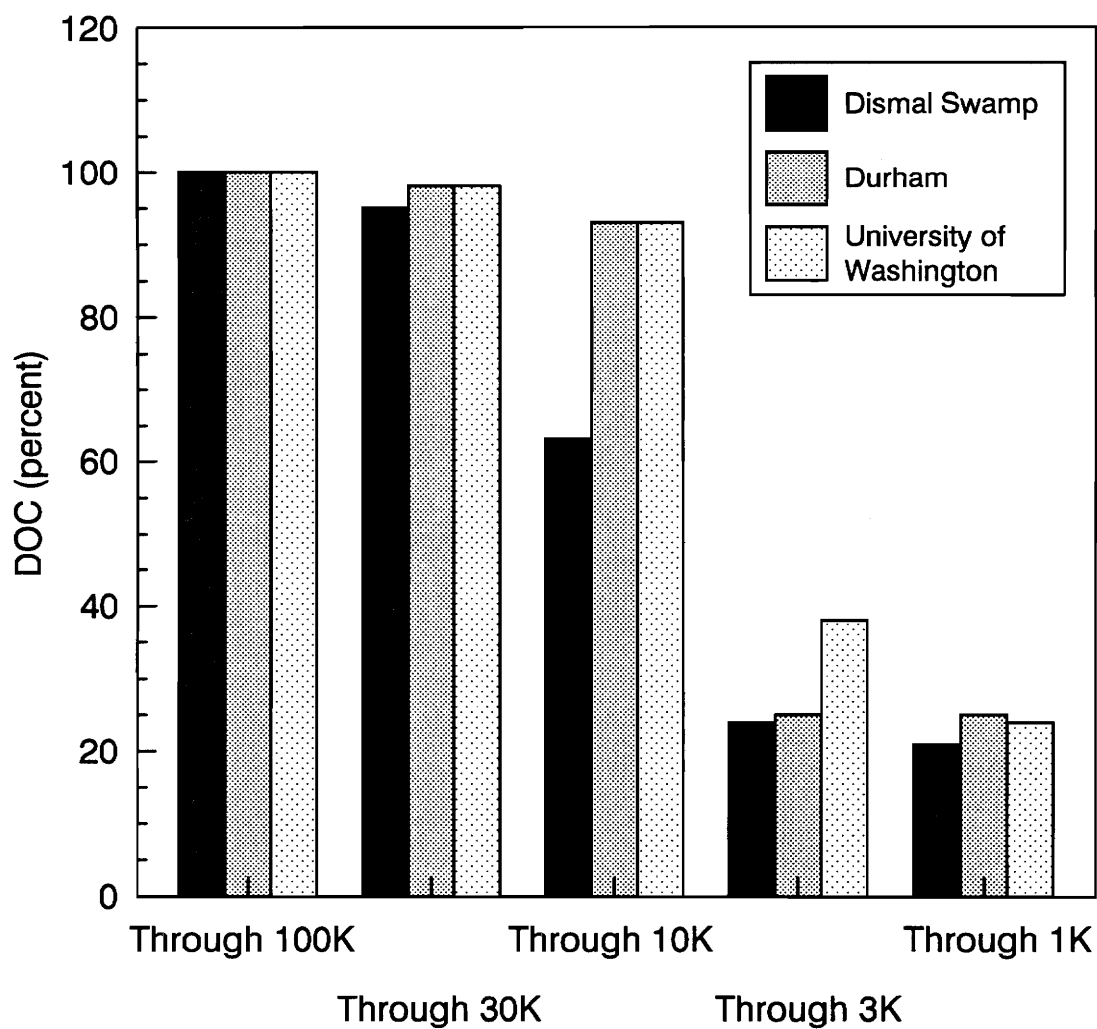


Figure 5. DOC molecular weight distributions of the Dismal Swamp, Durham, and University of Washington humic material. (DOC = 10 mg/L)

DOC concentration for the Durham and Dismal Swamp humic stock solutions, respectively. These values supported the observations from the MWD of DOC which indicated that the DOC was primarily composed of fulvic acids.

The specific absorbance was determined for each stock humic solution so that the presence of humic acids and fulvic acids could be confirmed. The specific absorbances for each stock humic solution were as follows:

Dismal Swamp	4.7 L/(cm * mg-C)
Durham, NC	4.6 L/(cm * mg-C)
University of Washington	3.2 L/(cm * mg-C)

These values corresponded to the ranges of values for humic and fulvic acids reported by Reckhow et al. (1990): fulvic acids - 3 to 4.3 L/(cm \* mg-C) and humic acids - 4.8 to 7.4 L/(cm \* mg-C). It appears from these specific absorbance values obtained for each of the three humic sources that each source was composed of predominantly fulvic acids.

### **Distribution of Complexed Fe(II) In Test Solutions**

Complexed Fe(II) solutions were prepared and fractionated to determine the relative amounts of iron and DOC present in each molecular weight fraction using the following molecular weight exclusion size ultrafilters: 100K, 30K, 10K, 3K, and 1K.

Data in Figure 6 illustrate the MWD of iron and DOC in each complexed Fe(II) solution prepared with the Dismal Swamp humic stock solution at three

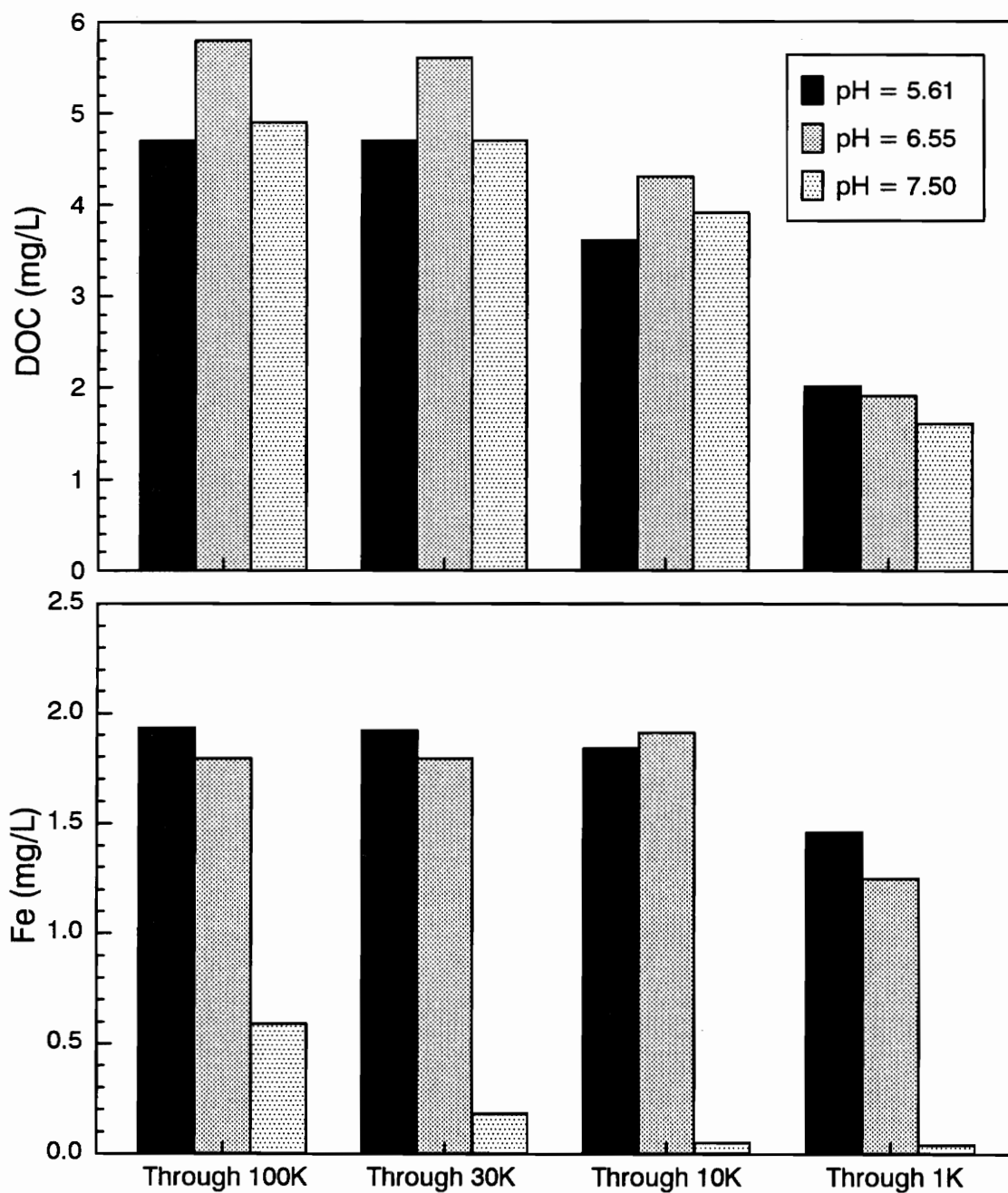


Figure 6. Molecular weight distribution of complexed Fe(II) test solutions at different pH values. (DOC source - Dismal Swamp)

different pH values. Approximately 73 percent and 67 percent of the soluble Fe(II) present in solution passed through the 1K ultrafilter for the pH 5.5 and 6.5 test solutions, respectively. In comparison, the DOC concentration passing the 1K ultrafilter was approximately 40 percent and 32 percent for the pH 5.5 and 6.5 test solutions. From these data, DOC-to-iron weight ratios in the solutions passing through the 1K ultrafilter were determined to be approximately 1.5 mg DOC:1 mg Fe for both the pH 5.5 and 6.5 test solutions. It appears, therefore, that not all of the Fe(II) in the solution was being complexed due to the large amount of iron in this 1K filtrate compared to DOC in the same fraction.

This theory was supported by the MWD of iron and DOC present in the complexed Fe(II) solution at pH 7.5. The MWD of DOC for this test solution was analogous to those conducted at pH 5.5 and 6.5; however, the iron distribution was not. Approximately 70 percent of the iron present in solution was removed as colloidal iron. The iron which remained in solution was located mostly in the molecular weight fraction between 100K and 30K; essentially, no iron remained in the 1K filtrate. Similar results were observed in control solutions (no oxidant addition) in the oxidation studies. Representative results were presented in the Methods and Materials chapter, Figure 4. As discussed previously, the formation of colloidal iron species was attributed to Fe(II) oxidation by trace quantities of  $O_2(aq)$ .

Stumm and Lee (1961) found that the oxidation of uncomplexed Fe(II) was kinetically rapid at pH values above 6.5. From the results presented in Figures 4 and

6, it appears that the iron which was oxidized at the kinetically favorable conditions of pH 7.5 was not initially complexed by the Dismal Swamp humic materials. The iron remaining in solution at pH 7.5 was assumed to be complexed by the DOC present in solution. Analysis of these data yielded an iron complexation capacity for the Dismal Swamp humic source of approximately 0.1 to 0.2 mg of iron complexed by each mg of DOC presence in solution.

Figure 7 illustrates the MWD of iron and DOC in a complexed iron solution at pH 6.5 prepared using the Durham humic source. The MWD of both iron and DOC is analagous to the MWD observed for the Dismal Swamp humic source. Approximately 1.0 mg/L (53 percent) of the iron passed a 1K ultrafilter while only 2.0 mg/L (23 percent) of the DOC was located in this less than 1K fraction. The DOC-to-iron weight ratio of 2 mg DOC:1 mg Fe indicated that there was not enough DOC present to complex the iron in solution.

A solution containing the the less than 3K fraction of the University of Washington humic material (pH 6.5, DOC = 6.8 mg/L, 1.74 mg/L of Fe(II)) was prepared and passed through a 1K ultrafilter. The concentrations of DOC and iron in the 1K filtrate were 1.6 mg/L and 0.82 mg/L, respectively. Again, the DOC-to-iron weight ratio was found to be approximately 2 mg DOC:1 mg Fe which corresponds to the ratios obtained for the Dismal Swamp and Durham humic materials.

The supply of the 100K-10K fraction of the University of Washington humic material was limited; therefore, no fractionations were performed. An examination of

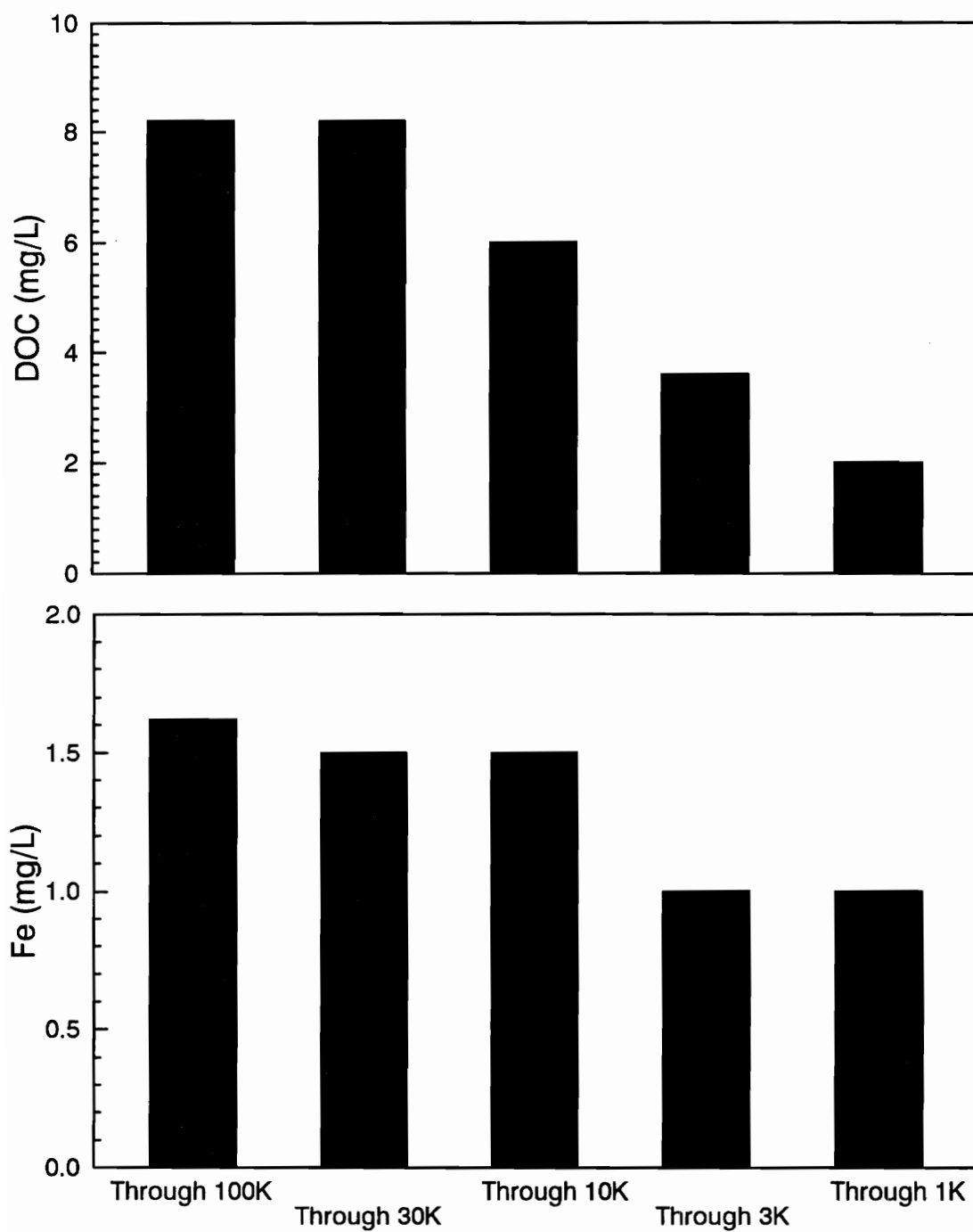


Figure 7. Molecular weight distribution of iron and DOC for Fe(II) complexed with Durham humic material. (pH = 6.5)



the results from a coagulation study (Table 5) reveal that after the alum coagulation of a 4.3 mg/L DOC and 1.99 mg/L Fe(II) solution only 1.3 mg/L residual iron and 0.9 mg/L DOC remained in solution. This low DOC-to-iron weight ratio (0.69 mg DOC:1 mg Fe) likewise suggests incomplete complexation of Fe(II) in solution.

The following initial DOC-to-iron weight ratios were utilized in the experiments: 5:1, 3:1, and 2.5:1. The humic sources utilized in this research were unable to complex all of the Fe(II) at these ratios; however, throughout this document solutions containing Fe(II) in the presence of DOC will be referred to as "complexed Fe(II) solutions."

### **Oxidant Demand of Various Humic Materials**

Humic acids and fulvic acids are composed of many functional groups and sub-units which are prone to oxidation; therefore, their presence in solution can potentially exert an oxidant demand. Test solutions were prepared with various concentrations of DOC and their  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$  residual concentration was monitored.

Figures 8 and 9 illustrate data representative of contact between Dismal Swamp humic material and  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$ . From these results, it appears that the Dismal Swamp humic material exerted a slight demand for  $\text{KMnO}_4$  and little or no demand was exerted for  $\text{H}_2\text{O}_2$ . The slight demand indicated initially for  $\text{H}_2\text{O}_2$  was most likely an artifact of dilution due to the inability to measure the initial oxidant dose.

Table 5

Residual iron and DOC concentrations after alum coagulation of  
Fe(II) complexed with high molecular weight  
humic material (100K - 10K)

Alum Dose (mg/L)	Fe Through 0.2 $\mu$ m (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)
0	1.88	1.61	4.2
12	1.80	1.09	1.7
24	1.38	1.37	1.0
48	1.27	1.27	0.9

## Notes:

- a) test conducted at pH = 5.5 to 6.0;
- b) DOC source - University of Washington.

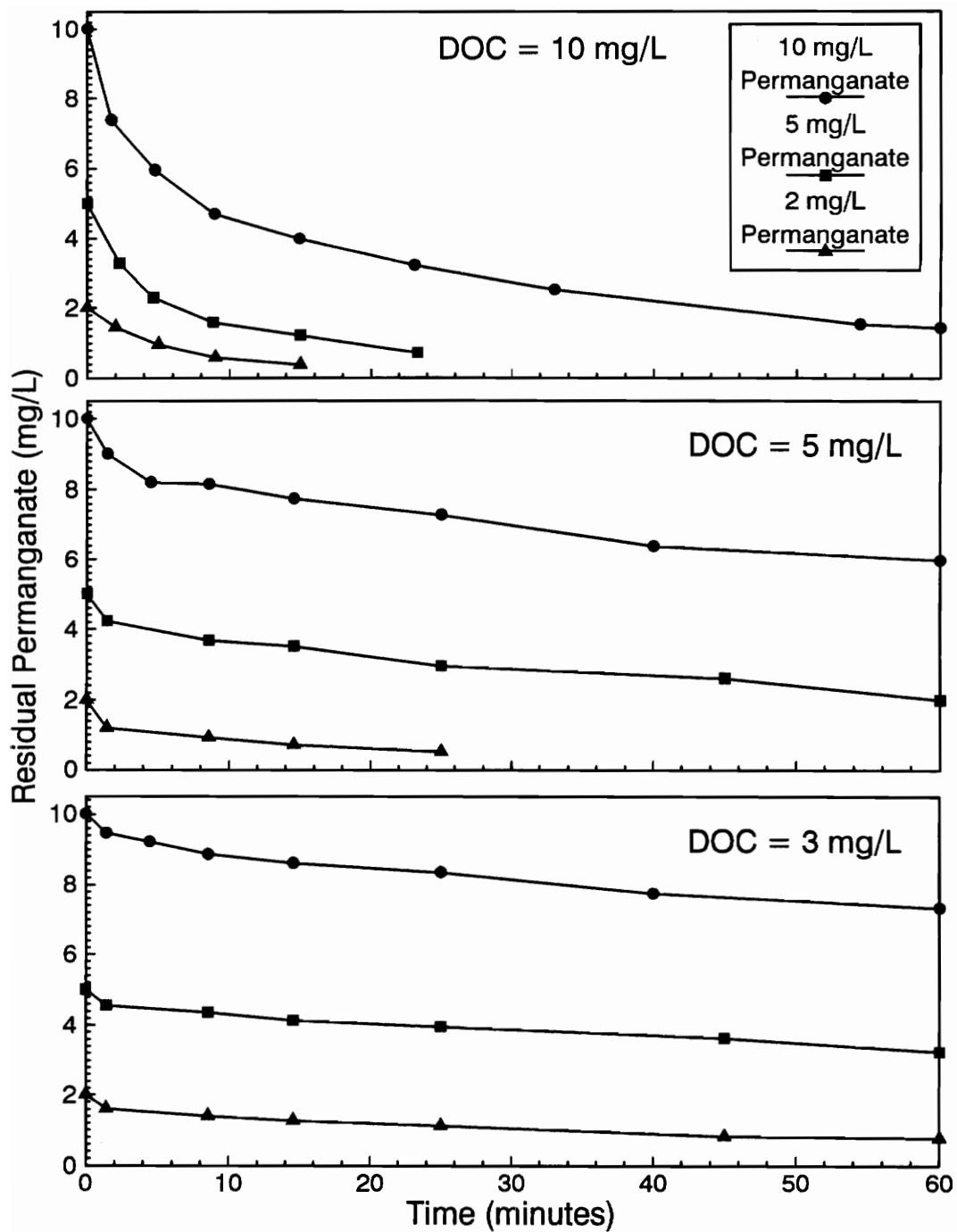


Figure 8. Permanganate demand of Dismal Swamp humic material.

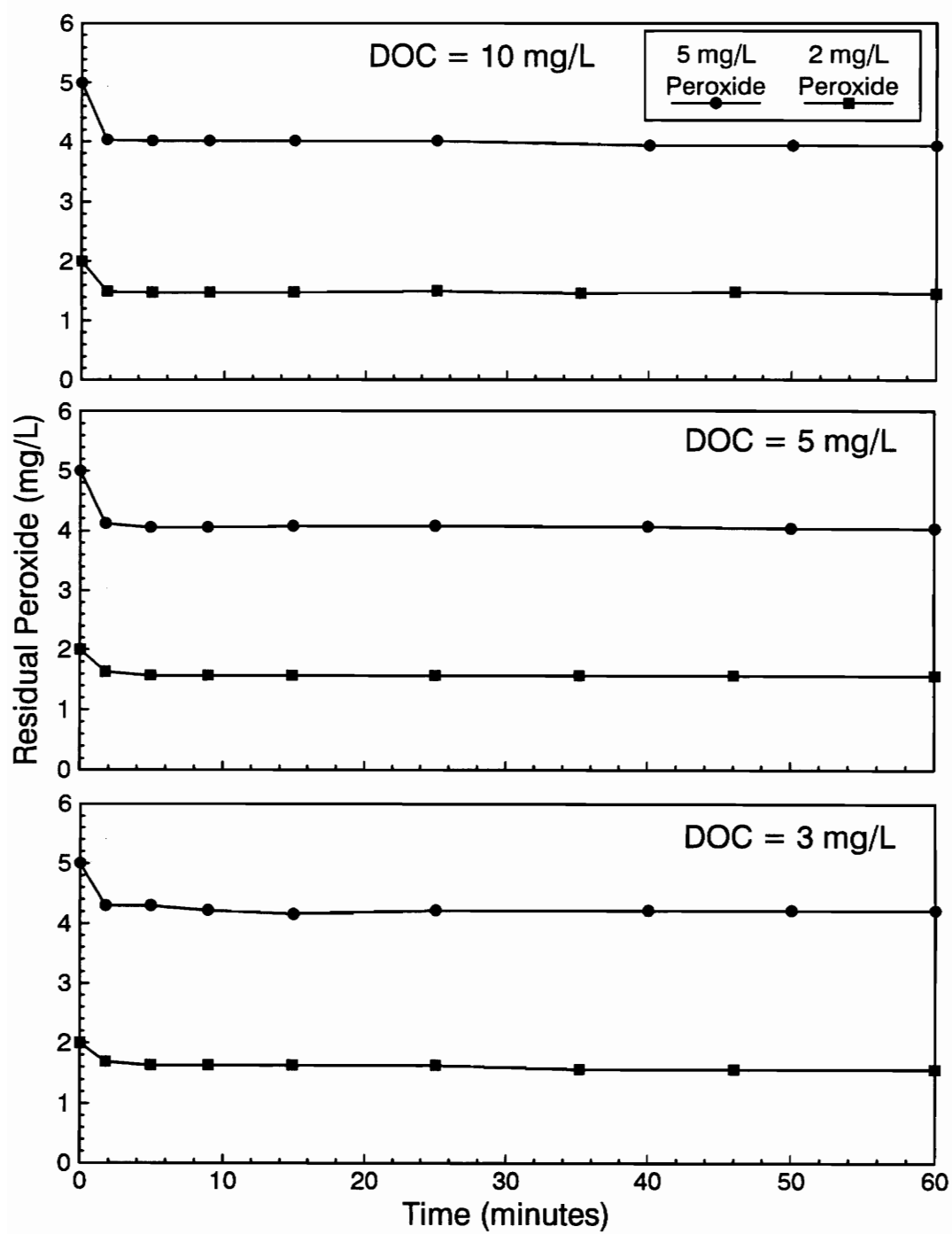


Figure 9. Peroxide demand of Dismal Swamp humic material.

Figure 10 depicts the data illustrating contact between the Durham humic material and  $\text{KMnO}_4$ . It appears from this representation that the permanganate demand exerted by the Durham humic material was similar to the demand exerted by the Dismal Swamp humic material.

### **Oxidation of Fe(II) by $\text{KMnO}_4$ and $\text{H}_2\text{O}_2$**

Oxidation studies for complexed Fe(II) solutions were conducted at pH 5.5 and 6.5; pH 7.5 was eliminated from the experimental matrix due to kinetically favorable conditions for Fe(II) oxygenation existing at this solution pH. The solutions were dosed with varying percentages of the stoichiometric amount of oxidant required for Fe(II) oxidation (0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe; 0.94 mg  $\text{KMnO}_4$  per mg Fe). Solutions were allowed contact periods of 5 and 60 minutes.

### **Oxidation of Fe(II) by $\text{KMnO}_4$**

**Oxidation of Uncomplexed Fe(II):**  $\text{KMnO}_4$  oxidized Fe(II) to  $\text{Fe}(\text{OH})_3(\text{s})$  at the near stoichiometric requirement. In Figure 11, the formation of particulate iron species is indicated by retention on a 0.2  $\mu\text{m}$  filter and a 100K ultrafilter. The experimental results correlated well to the theoretical predictions for Fe(II) oxidation.

**Oxidation of Complexed Fe(II):** Oxidation studies were conducted in which  $\text{KMnO}_4$  oxidized Fe(II) in the presence of DOC from each humic source. Trends observed for each DOC source after oxidation are addressed in the following sections.

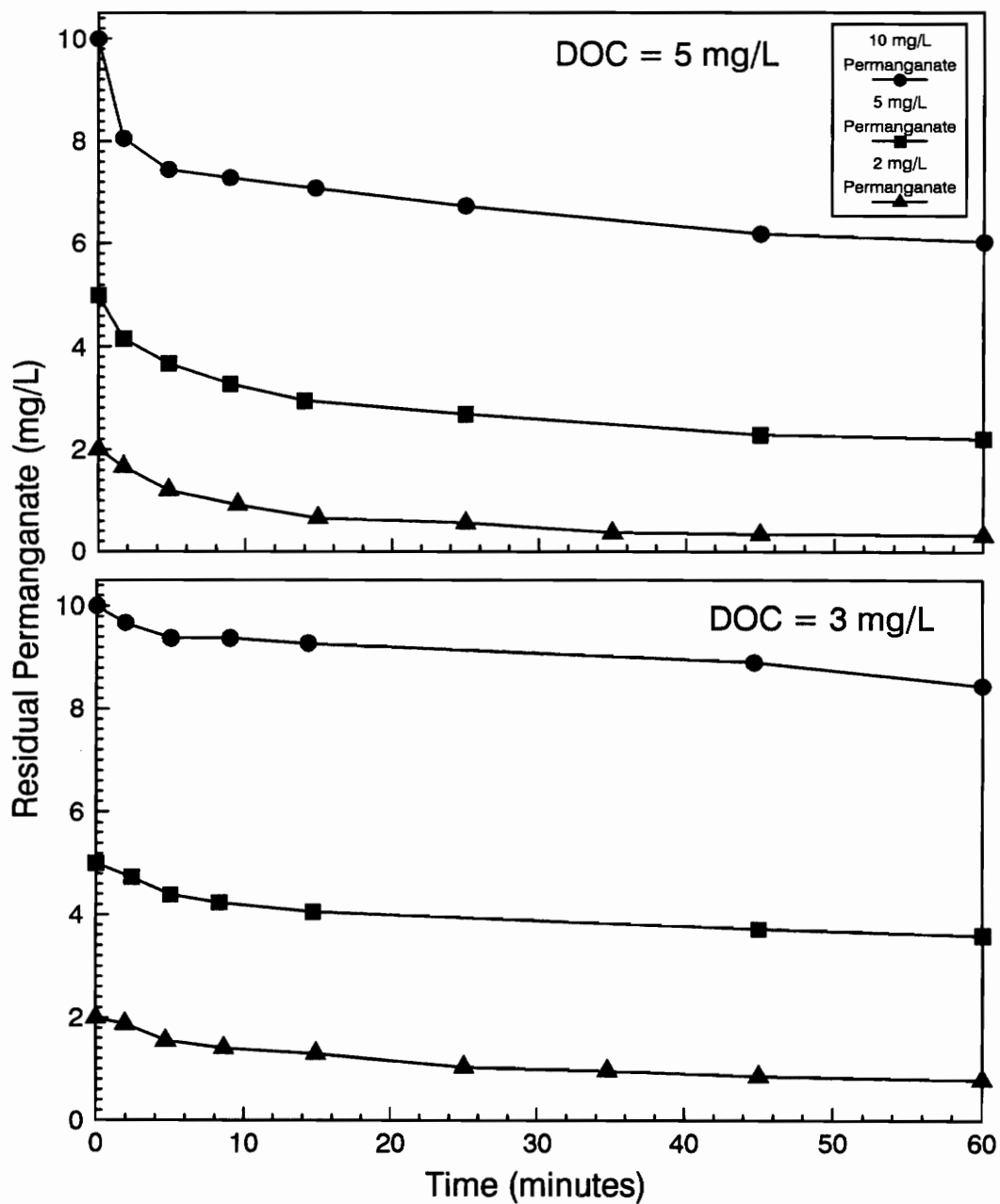


Figure 10. Permanganate demand of Durham humic material.

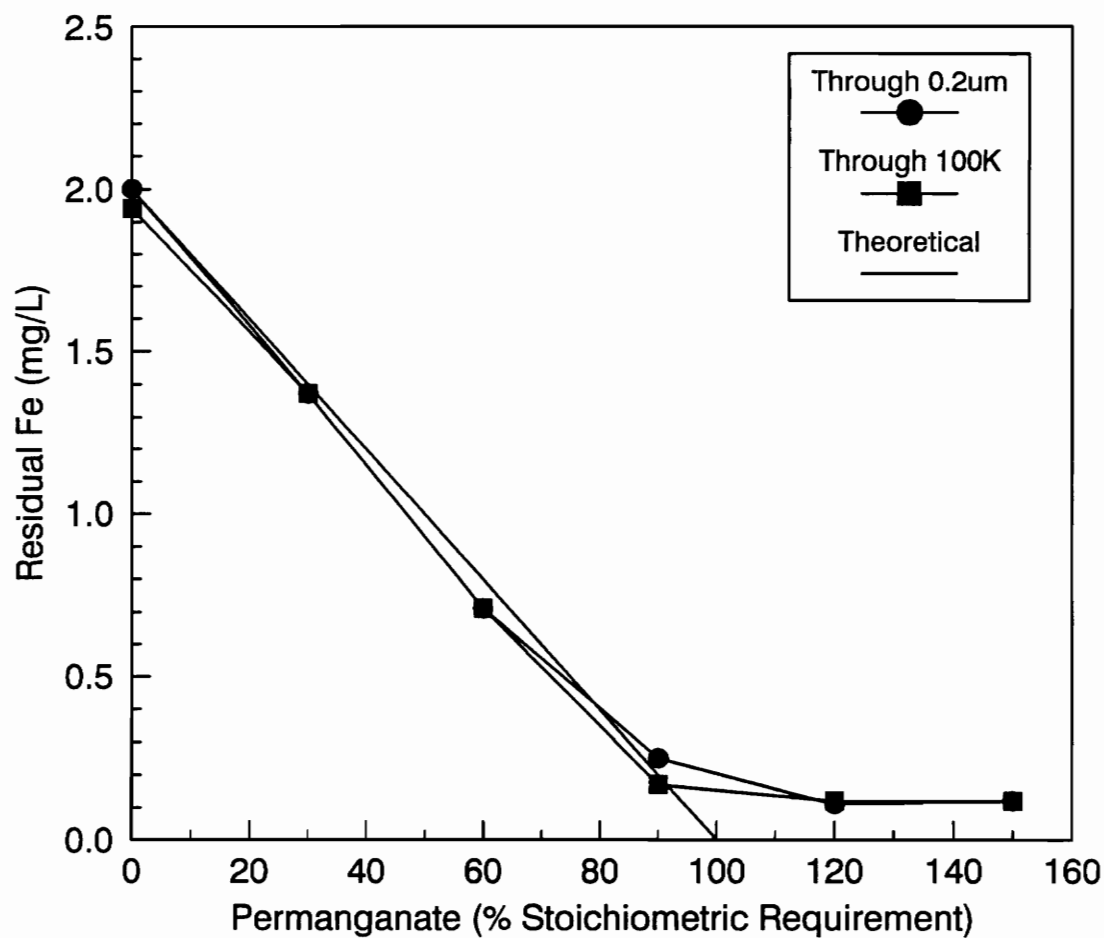


Figure 11. Oxidation of uncomplexed Fe(II) by potassium permanganate. (pH = 5.5; stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe)

**1) Fe(II) Complexed With Dismal Swamp Humic Material:** Data presented in Figure 12 depict the results obtained from oxidation studies at pH 5.5 and 6.5 after a contact period of five minutes. The data indicate that  $\text{KMnO}_4$  was not effective at oxidizing Fe(II) into particulate species. On average, between 0.25 and 0.10 mg/L (88 and 90 percent) of soluble Fe(II) were oxidized into the colloidal fraction in test solutions containing 3 and 5 mg/L DOC for  $\text{KMnO}_4$  doses exceeding 150 percent of the stoichiometric requirement. For solutions containing 10 mg/L DOC, only approximately 1.3 mg/L (60 to 70 percent) of the soluble Fe(II) was oxidized to colloidal iron for  $\text{KMnO}_4$  doses greater than 150 percent of the stoichiometric amount. The pH of the test solution did not appear to effect the performance of  $\text{KMnO}_4$ ; however, slightly more colloidal iron was formed at pH 6.5 in comparison to pH 5.5.

Results were also obtained from the oxidation studies after a contact period of 60 minutes at pH 5.5 and 6.5. Data depicted in Table 6 show residual iron values following oxidant contact periods of five minutes and 60 minutes. These data are representative of oxidation studies involving complexed Fe(II) prepared with Dismal Swamp humic material oxidized with  $\text{KMnO}_4$ . In general, no appreciable difference in iron removal (as colloidal species) occurred in solutions with a contact period of 60 minutes. For this reason, most of the remaining discussion will emphasize results from studies using a five minute contact period.

The fractionation of oxidized and unoxidized complexed Fe(II) solutions was performed to investigate the fate of Fe(II) during oxidation. The fractionation data



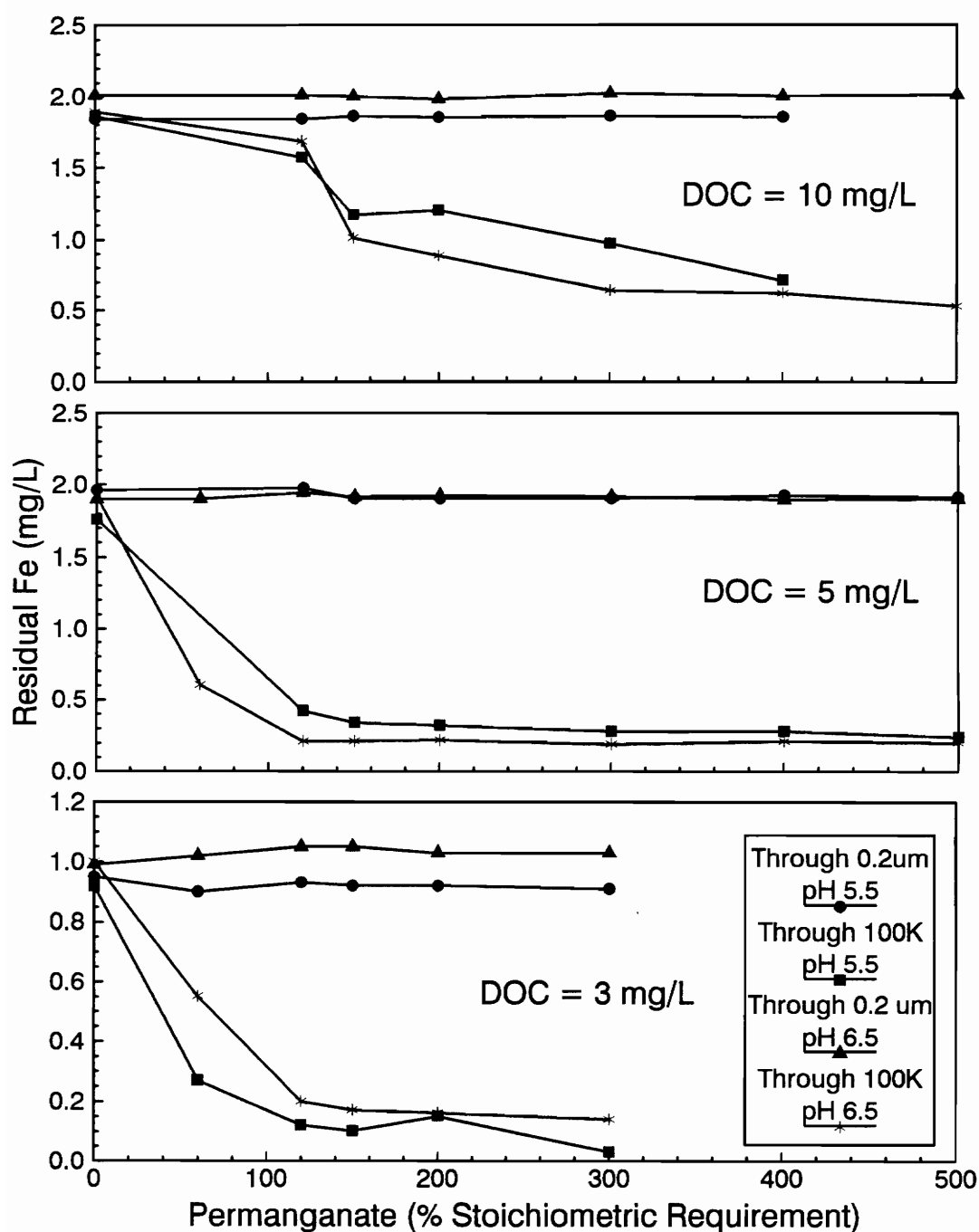


Figure 12. Oxidation of complexed Fe(II) by potassium permanganate at pH 5.5 and 6.5. (DOC source - Dismal Swamp; reaction time = 5 minutes; stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe)

Table 6

Residual iron concentrations after 5 minute and 60 minute  
contact periods

KMnO <sub>4</sub> Dose (%)	5 minute Fe Through 0.2um (mg/L)	5 minute Fe Through 100K (mg/L)	60 minute Fe Through 0.2 um (mg/L)	60 minute Fe Through 100K (mg/L)
0	1.84	1.86	1.82	1.80
120	1.84	1.57	1.78	1.48
150	1.86	1.17	1.80	1.24
200	1.85	1.20	1.79	1.24
300	1.86	0.97	1.79	0.98
400	1.85	0.71	1.79	0.75

Notes:

- a) test conducted at pH=5.5;
- b) DOC = 10 mg/L; DOC source - Dismal Swamp;
- c) stoichiometric requirement = 0.94 mg KMnO<sub>4</sub> per mg Fe.

for the two solutions of complexed Fe(II) (DOC = 10 mg/L, Fe = 2 mg/L) are illustrated in Figure 13. For the unoxidized test solution, 92 percent of the soluble Fe was present as Fe(II), and more than 50 percent of the total soluble iron was located in the less than 1K fraction, all of which was present as Fe(II). For the solution dosed with 120 percent of the stoichiometric amount of  $\text{KMnO}_4$ , only 12 percent of the total soluble iron was present as Fe(II). In this solution, most of the total soluble iron was located in either the colloidal iron fraction (30 percent) or in the complexed fraction greater 30K (80 percent).

The removal of iron, as well as the pH of test solutions, appeared to affect the amount of DOC removed from solution as indicated by the data compiled in Table 7. In general, higher DOC removal was observed for solutions at pH 5.5 than at 6.5; furthermore, the highest DOC removal occurred in test solutions involving DOC-to-iron weight ratios of 2.5 mg DOC:1 mg Fe. The removal of DOC corresponded to retention of colloidal iron species on a 100K ultrafilter. The correlation is believed to be the result of adsorption of DOC onto iron oxides formed during oxidation. These trends will be addressed in more detail in the Discussion chapter.

A parallel study was conducted in which solutions containing 10 mg/L DOC in the absence of Fe(II) were dosed with varying amounts of  $\text{KMnO}_4$ . The purpose of this study was to evaluate if the observed DOC removal could be attributed to colloidal ferric oxides or colloidal manganese oxides, by-products of oxidation with  $\text{KMnO}_4$ . These data depicted in Table 8 illustrate that only a very small percentage

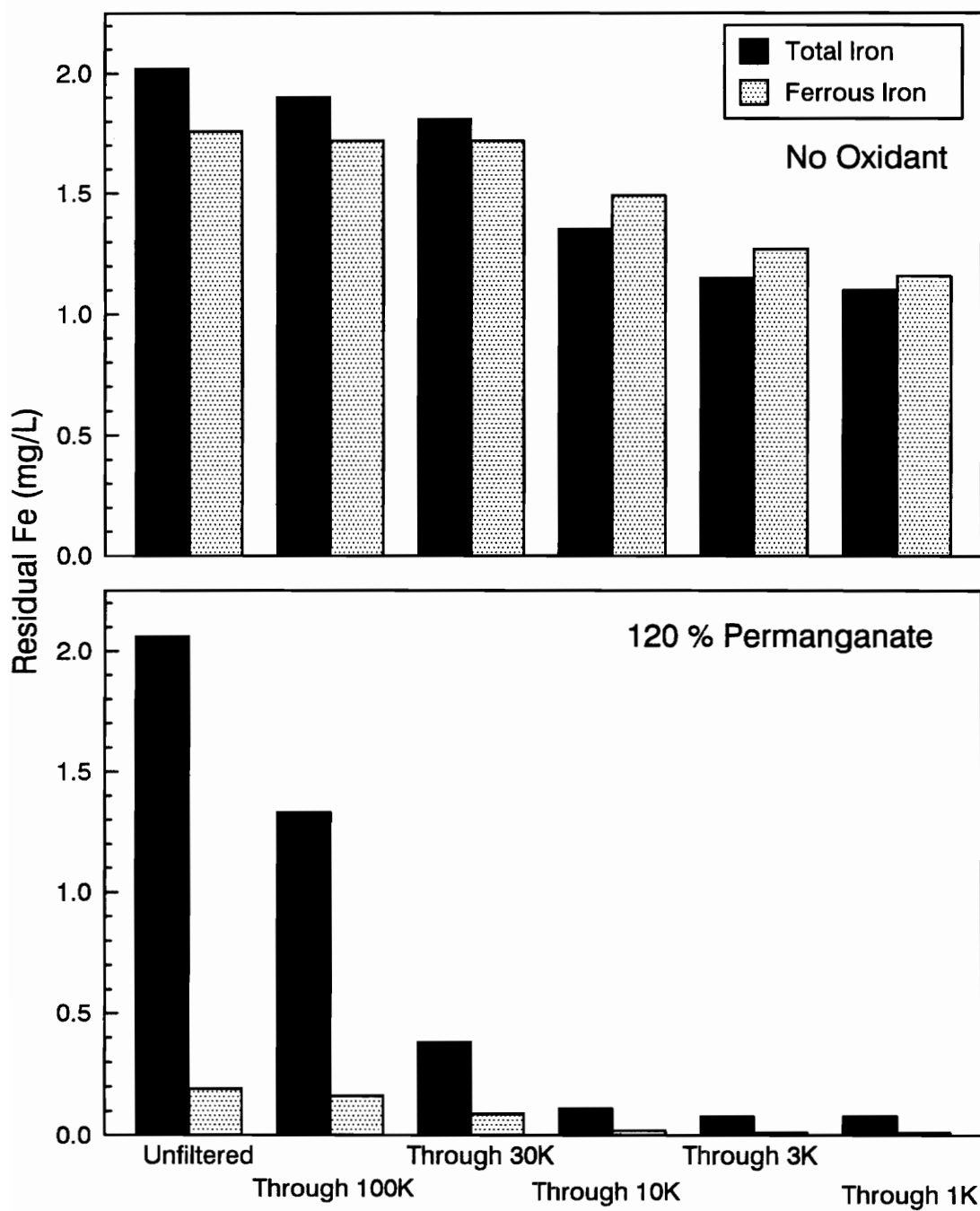


Figure 13. Distribution of Total Fe and Fe(II) in test solutions. (DOC = 10 mg/L; DOC source - Dismal Swamp; pH = 5.5; reaction time = 5 minutes; stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe)

Table 7

Typical residual DOC concentrations following  $\text{KMnO}_4$   
oxidation of complexed Fe(II) test solutions

pH	Initial		Residual		$\Delta\text{DOC}$ (mg/L)	$\Delta\text{Fe}$ (mg/L)	DOC retained by 100K (%)
	DOC (mg/L)	Fe (mg/L)	DOC (mg/L)	Fe (mg/L)			
5.5	9.7	1.86	7.9	0.71	1.8	1.15	19
5.5	5.5	1.76	2.9	0.24	2.6	1.52	47
5.5	3.9	0.92	2.6	0.03	1.3	0.89	33
6.5	9.8	1.89	7.6	0.53	2.2	1.36	22
6.5	5.5	1.92	3.8	0.21	1.7	1.71	31
6.5	3.5	1.00	2.8	0.17	0.7	0.83	20

Notes:

- a) DOC source - Dismal Swamp;
- b) ' $\Delta$ ' denotes changes in concentrations after a 5 minute contact period;
- c) dosages between 200 and 500 percent of the stoichiometric requirement (0.94 mg  $\text{KMnO}_4$  per mg Fe).

Table 8

Residual DOC concentrations after the addition of  
KMnO<sub>4</sub> in the absence of Fe(II)

KMnO <sub>4</sub> Dose (mg/L)	DOC Through 100K (mg/L)	DOC Removed (%)
0	10.3	--
2.3	10.1	2
2.8	9.8	5
3.8	10.2	1
5.6	9.8	5
7.5	9.7	6
9.4	9.3	9

Notes:

- a) test conducted at pH = 5.5;
- b) DOC source - Dismal Swamp.

(less than 10 percent) of DOC was removed from a 10 mg/L DOC solution dosed with various amounts of  $\text{KMnO}_4$ . This indicates that the observed DOC removal was due to the presence of colloidal ferric oxides and not manganese oxides.

Residual  $\text{KMnO}_4$  concentrations were measured to insure the presence of sufficient oxidant residuals for Fe(II) oxidation. Data contained in Table 9 show residual  $\text{KMnO}_4$  concentrations measured five minutes after oxidant addition to test solutions. At doses less than 300 percent of the stoichiometric amount, essentially all  $\text{KMnO}_4$  was consumed; at doses of 300 percent and greater, however, residual oxidant was measured. These data, coupled with the data presented previously regarding Fe(II) concentrations after  $\text{KMnO}_4$  oxidation (Figure 13), indicate that sufficient quantities of  $\text{KMnO}_4$  are present to oxidize Fe(II) in the presence of DOC concentrations used in this study.

**2) Fe(II) Complexed With Durham Humic Material:** Results obtained from oxidation studies on a complexed Fe(II) solution prepared with Durham humic material were quite different from results obtained from studies involving the Dismal Swamp humic material (Table 10). Essentially all of the iron became colloidal in nature after five minutes; after a contact period of 60 minutes all of the iron became particulate (even at a dose less than 100 percent of the stoichiometric requirement). DOC removal was minimal in the solution prepared with the Durham humic material. This indicates little if any interaction between DOC and ferric oxides formed during the oxidation of Fe(II).

Table 9

Residual  $\text{KMnO}_4$  concentrations after oxidation of  
complexed Fe(II)

$\text{KMnO}_4$ Dose (mg/L)	pH	Residual $\text{KMnO}_4$ (mg/L)
0	5.5	--
2.3	5.5	<DL
2.8	5.5	<DL
3.8	5.5	<DL
5.6	5.5	<DL
7.5	5.5	0.9
9.4	5.5	2.3
0	6.5	--
2.3	6.5	<DL
2.8	6.5	<DL
3.8	6.5	<DL
5.6	6.5	1.1
7.5	6.5	1.9
9.4	6.5	3.2

**Notes:**

- a) reaction time = 5 minutes; DOC = 10 mg/L; DOC source - Dismal Swamp;
- b) 'DL' denotes detection limit; detection limit = 0.25 mg/L  $\text{KMnO}_4$



Table 10

Residual iron and DOC concentrations after  $\text{KMnO}_4$  oxidation  
of Fe(II) complexed with Durham humic material

$\text{KMnO}_4$ Dose (mg/L)	5 minutes			60 minutes		
	Fe Through 0.2 $\mu\text{m}$ (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)	Fe Through 0.2 $\mu\text{m}$ (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)
0.0	0.89	0.73	3.0	0.87	0.62	3.0
0.56	0.88	<0.03	3.0	0.09	<0.03	2.8
1.13	0.25	<0.03	2.9	<0.03	<0.03	2.8

Notes:

a) test conducted at pH = 6.5;

b) Fe = 1.01 mg/L; DOC = 3.4 mg/L.

### **3) Fe(II) Complexed With High Molecular Weight Fraction of Humic**

**Material Obtained From the University of Washington:** The high molecular weight fraction (between 100K and 10K) obtained from the the University of Washington was utilized to conduct complexed Fe(II) oxidation studies. The oxidation of complexed Fe(II) was conducted at pH 6.5 with a contact time of five minutes. Dosages for this experiment were based on the iron concentration passing a 100K ultrafilter in the control solution (no oxidant addition).

Results from this study are compiled in Table 11. For the 120 percent  $\text{KMnO}_4$  dose, approximately 73 percent of the iron was retained on a 100K ultrafilter. At a dose of 200 percent  $\text{KMnO}_4$ , almost all of the iron in solution was present in the colloidal form as Fe(III). The formation of particulate iron was not observed. DOC removal accompanying the removal of colloidal ferric oxides at both doses of oxidant was approximately 33 percent of the original DOC concentration.

### **4) Fe(II) Complexed With Low Molecular Weight Fraction of Humic**

**Material Obtained From the University of Washington:** Oxidation studies were conducted with the less than 3K fraction from the University of Washington humic source at pH 6.5 with a contact time of five minutes. Results are depicted in Table 12. Nearly all of the soluble iron was converted to colloidal iron (present as Fe(III)) at a dose of 120 percent of the stoichiometric requirement. Approximately 30 percent of the DOC originally in solution was removed following the addition of 120 percent of the stoichiometric requirement of  $\text{KMnO}_4$  to oxidize complexed Fe(II).

Table 11

Residual iron and DOC concentration after  $\text{KMnO}_4$  oxidation  
of Fe(II) complexed with high molecular weight  
humic material (100K - 10K)

$\text{KMnO}_4$ Dose (mg/L)	Fe Through 0.2 $\mu\text{m}$ (mg/L)	Fe Through 100K (mg/L)	Fe(II) Through 100K (mg/L)	DOC Through 100K (mg/L)
0.0	1.83	1.62	1.56	4.8
1.8	1.79	0.44	0.03	3.3
3.0	1.72	0.22	0.03	3.2

## Notes:

- a) test conducted at pH = 6.5;
- b) reaction time = 5 minutes;
- c) Fe = 1.88 mg/L; DOC = 4.8 mg/L; DOC source - University of Washington;
- d) stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe.

Table 12

Residual iron and DOC concentrations after  $\text{KMnO}_4$   
oxidation of Fe(II) complexed with low molecular weight  
humic material (less than 3K)

$\text{KMnO}_4$ Dose (%)	Fe Through 0.2 $\mu\text{m}$ (mg/L)	Fe Through 100K (mg/L)	Fe(II) Through 100K (mg/L)	DOC Through 100K (mg/L)
0	1.95	1.94	1.78	4.5
60	1.95	0.83	0.09	4.0
120	1.93	0.09	0.08	3.8
200	1.94	0.03	0.07	3.6

## Notes:

- a) test conducted at  $\text{pH} = 6.5$ ;
- b) reaction time = 5 minutes;
- c)  $\text{Fe} = 1.97 \text{ mg/L}$ ;  $\text{DOC} = 4.6 \text{ mg/L}$ ; DOC source - University of Washington;
- d) stoichiometric requirement =  $0.94 \text{ mg KMnO}_4$  per mg Fe.

## **Oxidation of Fe(II) by H<sub>2</sub>O<sub>2</sub>**

**Oxidation of Uncomplexed Fe(II):** H<sub>2</sub>O<sub>2</sub> oxidized uncomplexed Fe(II) to Fe(OH)<sub>3</sub>(s) as depicted in Figure 14 by the retention of particulate iron species on a 0.2  $\mu$ m filter and a 100K ultrafilter. The experimental results did not correlate well with the theoretical predictions. This could be attributed to the decomposition of H<sub>2</sub>O<sub>2</sub> when peroxide is present in excessive amounts compared to iron (Schumb *et al.*, 1955), or it could simply be a deviation from the theoretical reaction stoichiometry. All of the H<sub>2</sub>O<sub>2</sub> percent doses throughout this study were based on the theoretical reaction stoichiometry.

**Oxidation of Complexed Fe(II):** The following sections address trends observed in oxidation studies in which Fe(II) in the presence of DOC from each humic source was oxidized by H<sub>2</sub>O<sub>2</sub>.

**1) Fe(II) complexed with Dismal Swamp Humic Material:** As illustrated in Figure 15, H<sub>2</sub>O<sub>2</sub> was not effective at oxidizing complexed Fe(II) to particulate species. Approximately 0.30 mg/L (30 percent) and 1.13 mg/L (50 percent) of the soluble iron were oxidized to the colloidal fraction containing 3 and 5 mg/L DOC, respectively, for H<sub>2</sub>O<sub>2</sub> doses exceeding 300 percent of the stoichiometric requirement. The presence of 10 mg/L of DOC in solution retarded the formation of colloidal iron species, with 0.13 mg/L (10 percent of the original Fe(II)) being oxidized to colloidal iron for H<sub>2</sub>O<sub>2</sub> doses exceeding 300 percent. This indicates that the amount of colloidal iron species formed decreases as the initial DOC-to-iron weight ratio present

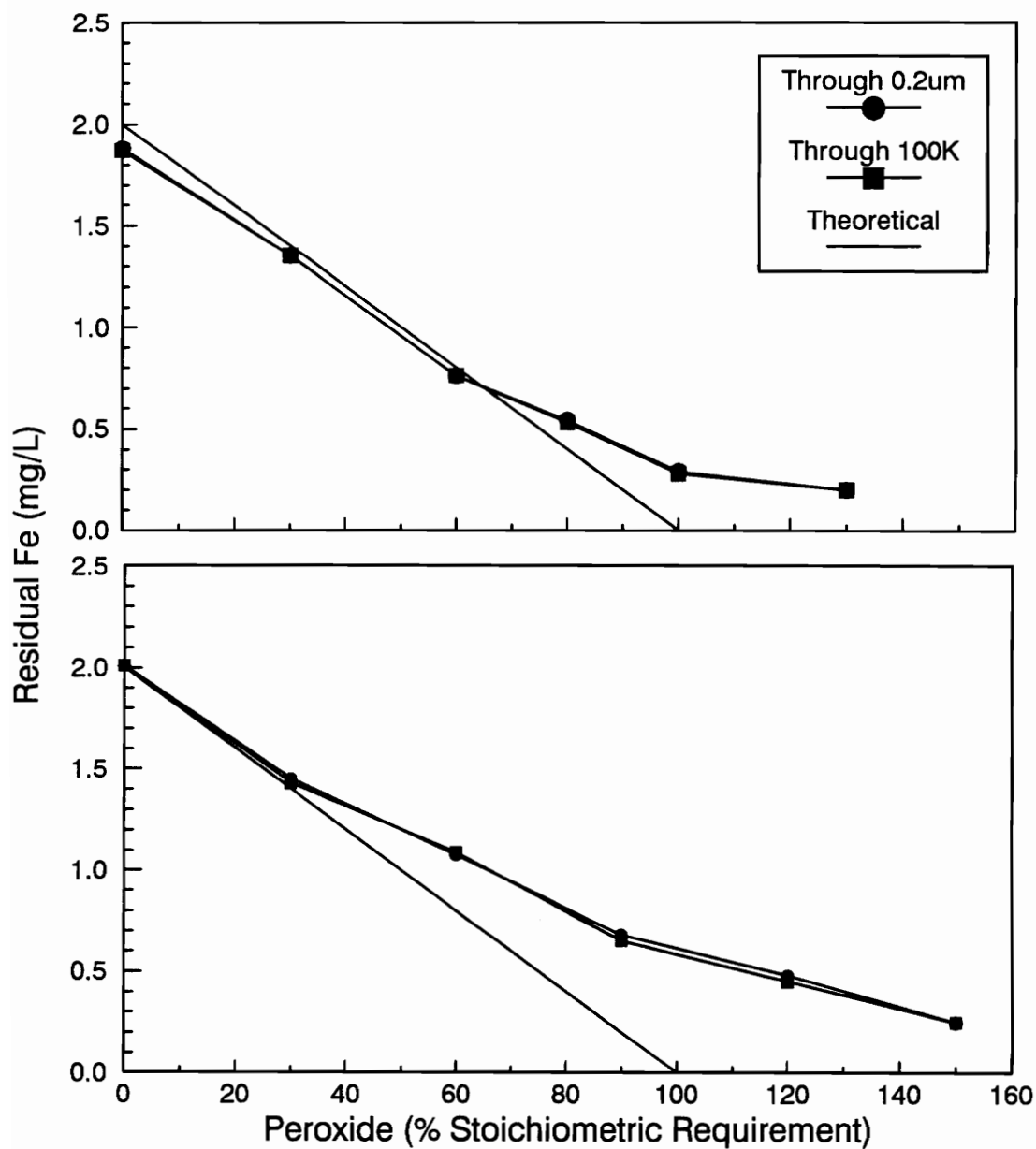


Figure 14. Replicates of the oxidation of uncomplexed Fe(II) by hydrogen peroxide. (pH = 5.5; theoretical stoichiometric requirement = 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

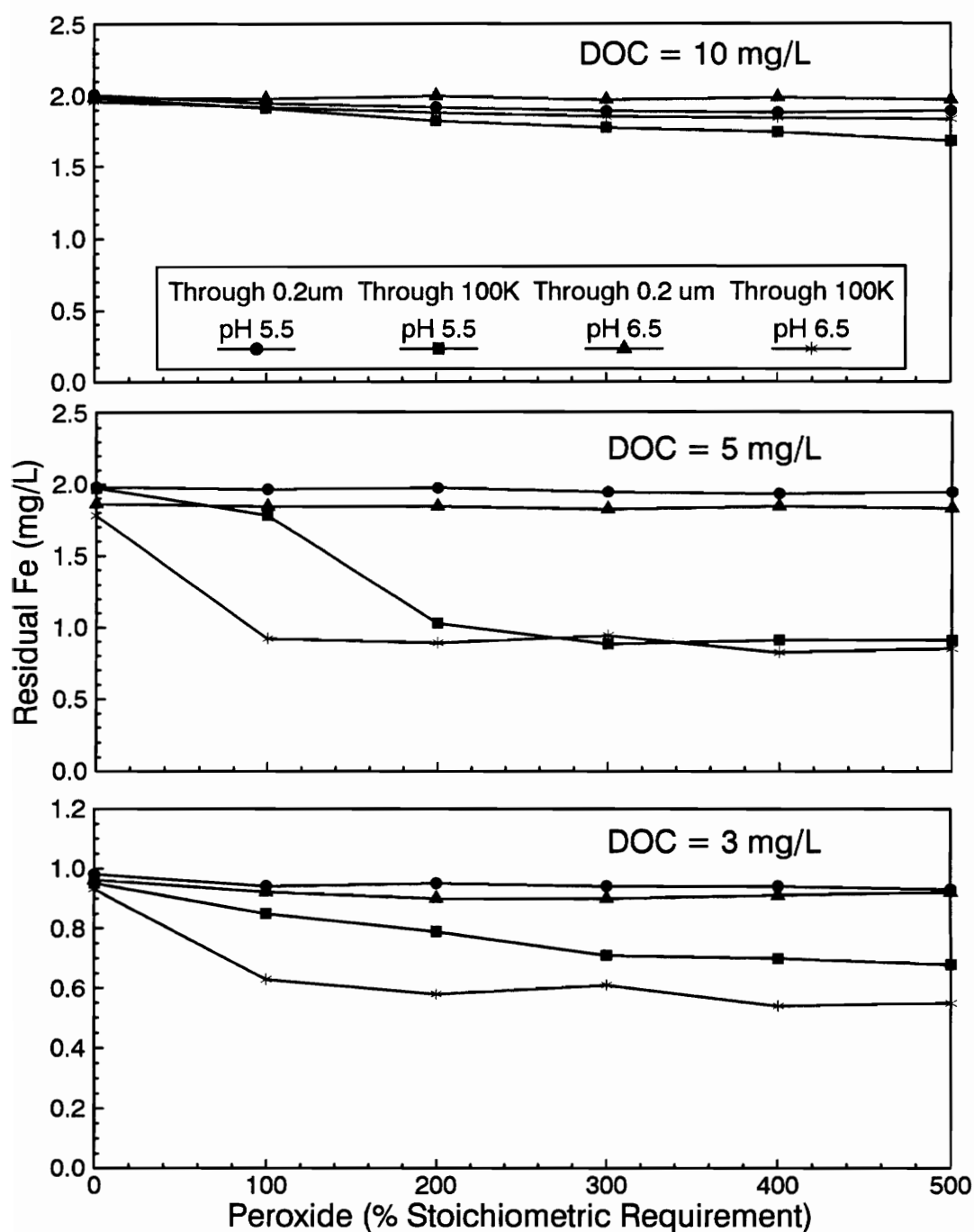


Figure 15. Oxidation of complexed Fe(II) by hydrogen peroxide at pH 5.5 and 6.5. (DOC source - Dismal Swamp; reaction time = 5 minutes; theoretical stoichiometric requirement = 0.31 mg H<sub>2</sub>O<sub>2</sub> per mg Fe)

in the test solution increases. The pH of solution did not appear to greatly influence the performance of  $\text{H}_2\text{O}_2$ .

Complexed Fe(II) solutions at pH 5.5 were exposed to 100 and 300 percent  $\text{H}_2\text{O}_2$  for five minutes and then fractionated through ultrafilters. Filtrates were analyzed for total iron by AAS and Fe(II). The results are presented in Figures 16 and 17 along with results from the fractionation of an unoxidized complexed Fe(II) solution, which were addressed previously in the discussion of Figure 13. For the solution dosed with 300 percent  $\text{H}_2\text{O}_2$ , 14 percent of the total soluble iron was present as Fe(II). Most of the total soluble iron was retained on a 30K ultrafilter (approximately 80 percent), and only 11 percent was present as colloidal iron. The test solution dosed with 100 percent  $\text{H}_2\text{O}_2$  had 40 percent of the total soluble iron present as Fe(II). Approximately 54 percent of the total soluble iron was retained on a 30K ultrafilter, while 17 percent of the total soluble iron passed a 1K ultrafilter (all present as Fe(II)). The amount of Fe(II) oxidized in the presence of DOC at 100 percent of the theoretical stoichiometric requirement corresponded to the amount of Fe(II) oxidized in the absence of DOC (Figure 14). These results indicated that complete Fe(II) oxidation requires a dosage exceeding the theoretical stoichiometric amount.

The oxidation of complexed Fe(II) by  $\text{H}_2\text{O}_2$  resulted in the removal of DOC from solution (Table 13), a result similar to that observed with  $\text{KMnO}_4$ . In general, the removal of DOC observed in studies involving  $\text{H}_2\text{O}_2$  addition was less than was



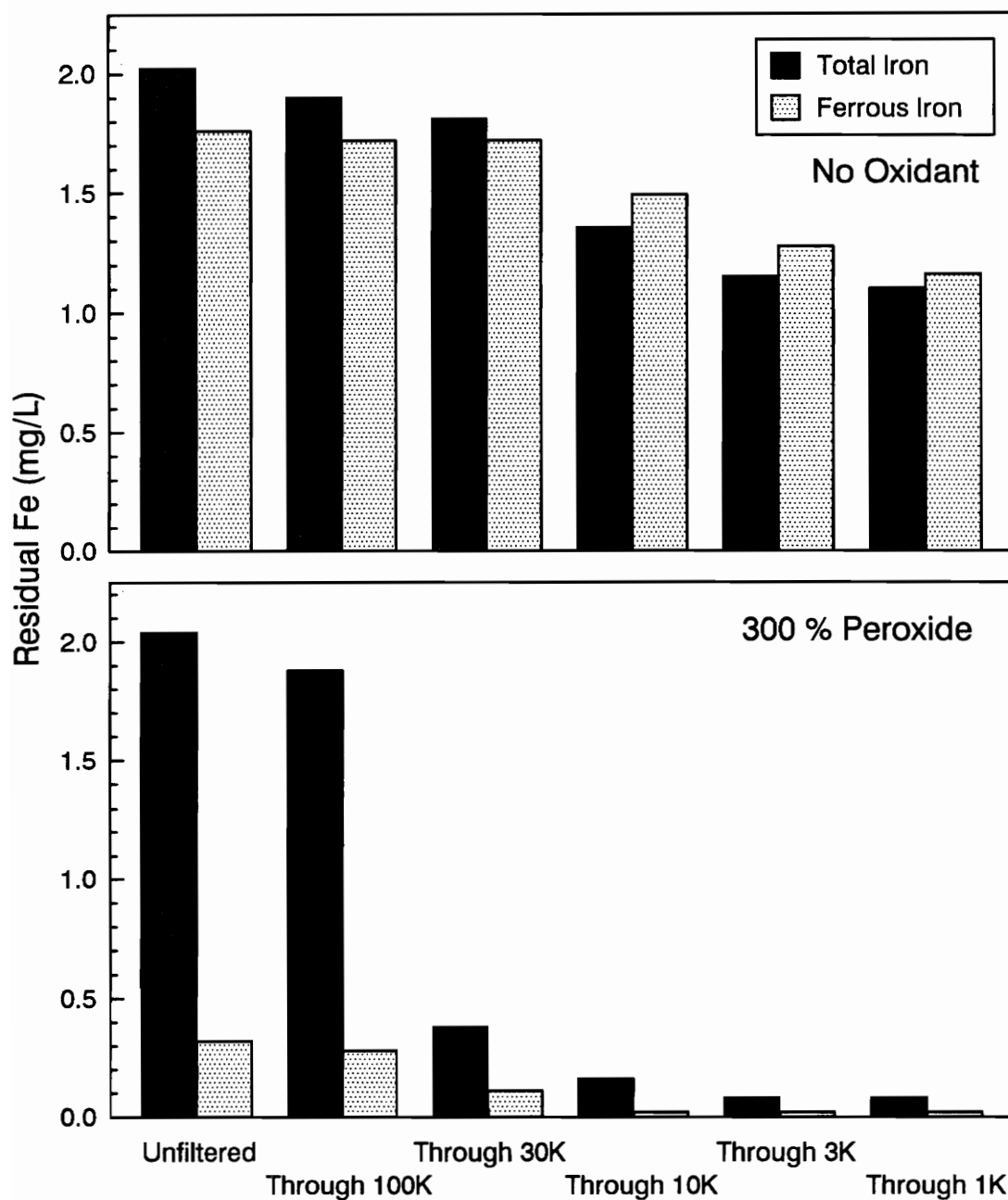


Figure 16. Distribution of Total Fe and Fe(II) in test solutions. (DOC = 10 mg/L; DOC source - Dismal Swamp; pH = 5.5; reaction time = 5 minutes; theoretical stoichiometric requirement = 0.31 mg H<sub>2</sub>O<sub>2</sub> per mg Fe)

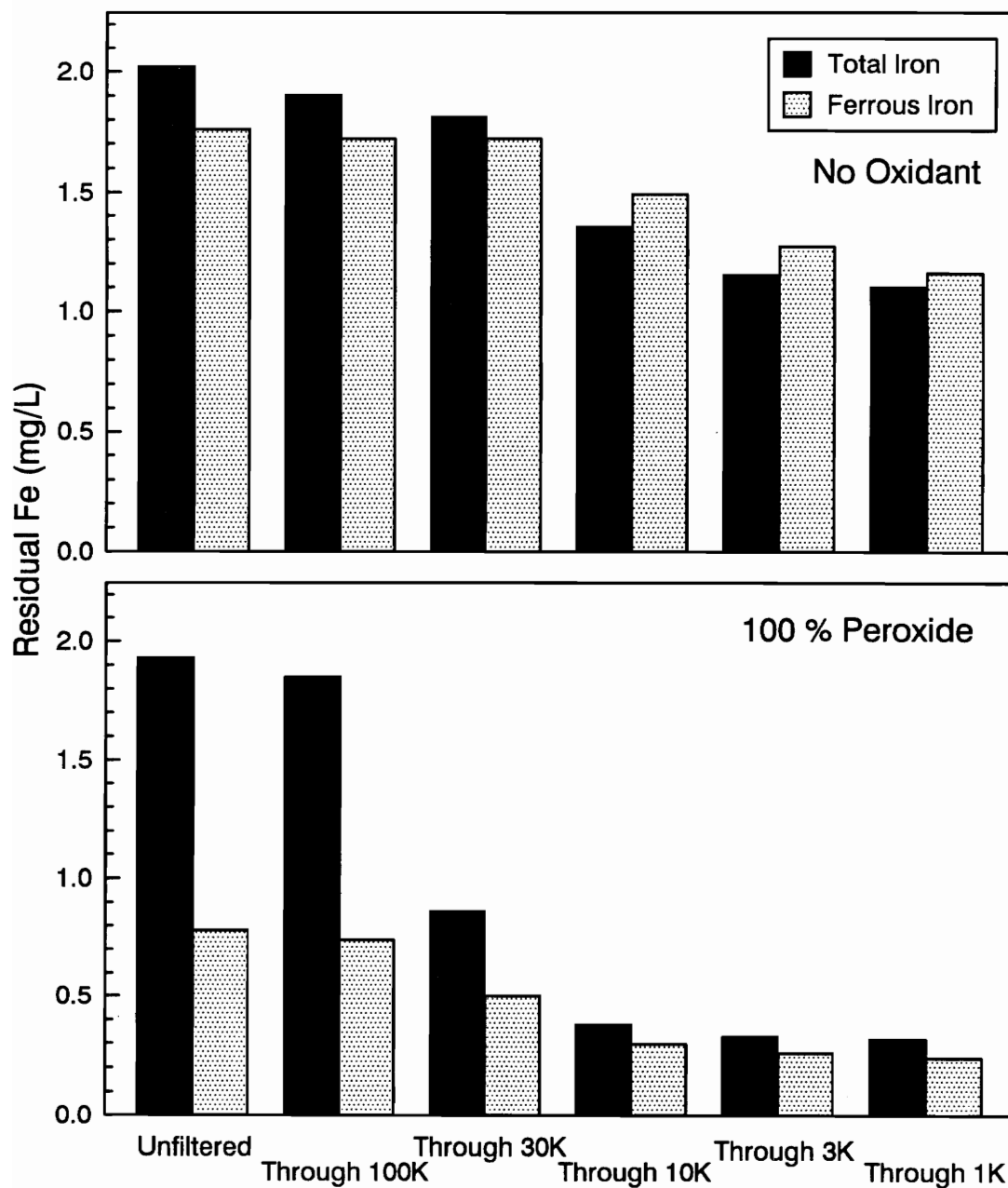


Figure 17. Distribution of Total Fe and Fe(II) in test solutions.  
 (DOC = 10 mg/L; DOC source - Dismal Swamp; pH = 5.5;  
 reaction time = 5 minutes; theoretical stoichiometric  
 requirement = 0.31 mg H<sub>2</sub>O<sub>2</sub> per mg Fe)

Table 13

Typical residual DOC concentrations following  $\text{H}_2\text{O}_2$   
oxidation of complexed Fe(II) test solutions

pH	Initial		Residual		$\Delta\text{DOC}$ (mg/L)	$\Delta\text{Fe}$ (mg/L)	DOC retained by 100K (%)
	DOC (mg/L)	Fe (mg/L)	DOC (mg/L)	Fe (mg/L)			
5.5	9.3	1.99	8.8	1.68	0.5	0.31	5
5.5	4.8	1.97	3.5	0.90	1.3	1.07	27
5.5	3.6	0.95	3.1	0.68	0.5	0.27	14
6.5	9.8	1.96	9.1	1.83	0.7	0.13	7
6.5	5.2	1.78	4.4	0.85	0.8	0.93	15
6.5	3.3	0.93	2.9	0.59	0.4	0.34	12

Notes:

- a) DOC source - Dismal Swamp;
- b) ' $\Delta$ ' denotes change in concentrations after 5 minute contact period;
- c) dosages are 500 percent of the stoichiometric requirement (0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe).

observed in studies involving  $\text{KMnO}_4$ . Increased DOC removal efficiency was also observed for solutions with lower initial DOC-to-iron ratios.

Data contained in Table 14 shows residual  $\text{H}_2\text{O}_2$  concentrations measured five minutes after oxidant addition. For solutions dosed with less than 200 percent of the stoichiometric requirement, essentially no residual oxidant was detected. Solutions in which the dose exceeded 200 percent  $\text{H}_2\text{O}_2$ , a substantial oxidant residual was measured. These data, coupled with the data presented previously with regards to Fe(II) oxidation by  $\text{H}_2\text{O}_2$ , indicate that sufficient quantities of  $\text{H}_2\text{O}_2$  were present to oxidize Fe(II) in the presence of DOC.

**2) Fe(II) Complexed with High Molecular Weight Fraction of Humic Material Obtained From the University of Washington:** Table 15 shows data obtained from  $\text{H}_2\text{O}_2$  oxidation studies at pH 6.5 with a reaction period of five minutes. The dosages were based on the iron present after the filtration of the control solution (no oxidant addition) through a 100K ultrafilter. For both  $\text{H}_2\text{O}_2$  doses, approximately 46 percent of the iron was removed by 100K ultrafiltration, while no particulate iron species were formed. In the presence of 200 percent oxidant, 91 percent of the iron in solution was present as Fe(III). Approximately 20 percent of the DOC was removed following the addition of  $\text{H}_2\text{O}_2$  for the oxidation of complexed Fe(II).

Table 14

Residual  $\text{H}_2\text{O}_2$  concentrations after oxidation of  
complexed Fe(II)

$\text{H}_2\text{O}_2$ Dose (mg/L)	pH	Residual $\text{H}_2\text{O}_2$ (mg/L)
0	5.5	--
0.6	5.5	<DL
1.2	5.5	0.2
1.8	5.5	0.6
2.4	5.5	1.1
3.1	5.5	1.5
0	6.5	--
0.6	6.5	<DL
1.2	6.5	0.6
1.8	6.5	1.1
2.4	6.5	1.7
3.1	6.5	2.2

Notes:

a) reaction time = 5 minutes; DOC = 5 mg/L; DOC source - Dismal Swamp;

b) 'DL' denotes detection limit; detection limit = 0.1 mg/L  $\text{H}_2\text{O}_2$ .

Table 15

Residual iron and DOC concentrations after H<sub>2</sub>O<sub>2</sub> oxidation  
of Fe(II) complexed with high molecular weight  
humic material (100K - 10K)

H <sub>2</sub> O <sub>2</sub> Dose (mg/L)	Fe Through 0.2 $\mu$ m (mg/L)	Fe Through 100K (mg/L)	Fe(II) Through 100K (mg/L)	DOC Through 100K (mg/L)
0.0	1.84	1.62	1.56	4.8
1.0	1.78	0.88	0.16	3.7
2.0	1.72	0.83	0.07	3.8

Notes:

a) test conducted at pH = 6.5; reaction time = 5 minutes;

b) Fe = 1.88 mg/L; DOC = 4.8 mg/L; DOC source - University of Washington.

**3) Fe(II) Complexed with Low Molecular Weight Fraction of Humic Material Obtained From the University of Washington:** Hydrogen peroxide oxidation studies were conducted at pH 6.5 with a reaction time of five minutes. Results from these studies are shown in Table 16. Approximately 50 percent of the iron was removed in the solution dosed with 100 percent  $\text{H}_2\text{O}_2$ . For the solution dosed with 500 percent oxidant, 60 percent of the iron was present in the colloidal form. The removal of DOC was approximately 10 percent of the original DOC concentration for all of the oxidant dosages tested.

#### **Alum Coagulation of Complexed Fe(II) in the Presence and Absence of $\text{KMnO}_4$ and $\text{H}_2\text{O}_2$**

Coagulation studies were conducted on solutions of complexed Fe(II) prepared with each of the different humic sources, both with and without the addition of an oxidant. The trends observed in solution turbidity will be addressed first, followed by the presentation of the results observed for the speciation of complexed iron during alum coagulation experiments.

Results presented in Figure 18 are representative of all the turbidity profiles observed throughout the study. In general, an increase in turbidity was observed as the alum dose increased from 0 to 24 mg/L for the solution containing 10 mg/L DOC and 2 mg/L Fe. For the solution containing 5 mg/L DOC and 2 mg/L Fe, the increase in the turbidity occurred as the alum dose increased from 0 to 12 mg/L.

Table 16

Residual iron and DOC concentrations after  $\text{H}_2\text{O}_2$  oxidation  
of Fe(II) complexed with low molecular weight  
humic material (less than 3K)

$\text{H}_2\text{O}_2$ Dose (%)	Fe Through 0.2 $\mu\text{m}$ (mg/L)	Fe Through 100K (mg/L)	Fe(II) Through 100K (mg/L)	DOC Through 100K (mg/L)
0	1.95	1.94	1.78	4.5
100	1.93	0.88	0.32	4.2
200	1.93	0.78	0.16	4.2
500	1.92	0.70	0.09	4.1

Notes:

- a) test conducted at pH = 6.5; reaction time = 5 minutes;
- b) Fe = 1.97 mg/L; DOC = 4.6 mg/L; DOC source - University of Washington;
- c) theoretical stoichiometric requirement = 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe.



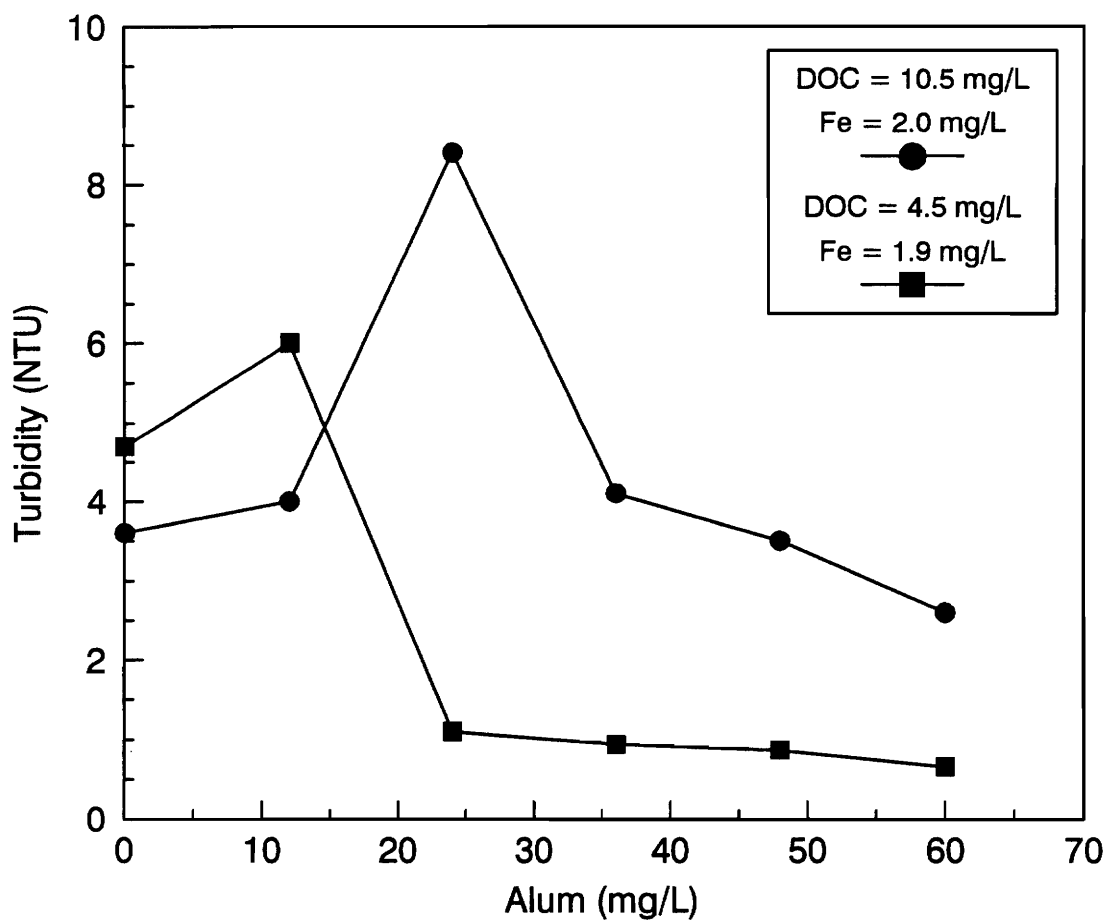


Figure 18. Turbidity profiles after alum coagulation without oxidant addition. (DOC source - Dismal Swamp; pH = 5.5 to 6.0)

These increases in turbidity were believed to result from the restabilization of charges on colloids, which prevented the aggregation of colloids to form settleable particles. Residual turbidity decreased as the alum dose was further increased, most probably due to the sweep floc mechanism and the resulting formation of  $\text{Al}(\text{OH})_3(\text{s})$ .

### **Alum Coagulation of Fe(II) Complexed With Dismal Swamp Humic Materials**

Figures 19 and 20 illustrate results from alum coagulation of test solutions containing 10 mg/L DOC and 2 mg/L Fe, both in the absence and presence of oxidant addition. Alum coagulation alone was ineffective at removing Fe(II) from solution, since approximately 85 percent of the original iron concentration remained in solution as seen in Figure 19. The addition of 100 percent oxidant resulted in a residual iron concentration of less than 0.15 mg/L. Approximately 75 percent and 90 percent of the iron were removed as colloidal species at an alum dose of 12 mg/L for  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$  addition, respectively. Data in Figure 20 illustrate that alum coagulation was effective at removing DOC from solution, since approximately 85 percent of the DOC was removed by the coagulation process. In addition, the presence of oxidants did not appear to alter the removal of DOC from solution.

Data regarding complexed Fe(II) removal for coagulation studies with solutions containing 5 mg/L DOC and 2 mg/L Fe are displayed in Figure 21. Results analogous to those of the 10 mg/L DOC solutions were observed with regards to DOC removal. In the absence of an oxidant, residuals of approximately 85 percent of

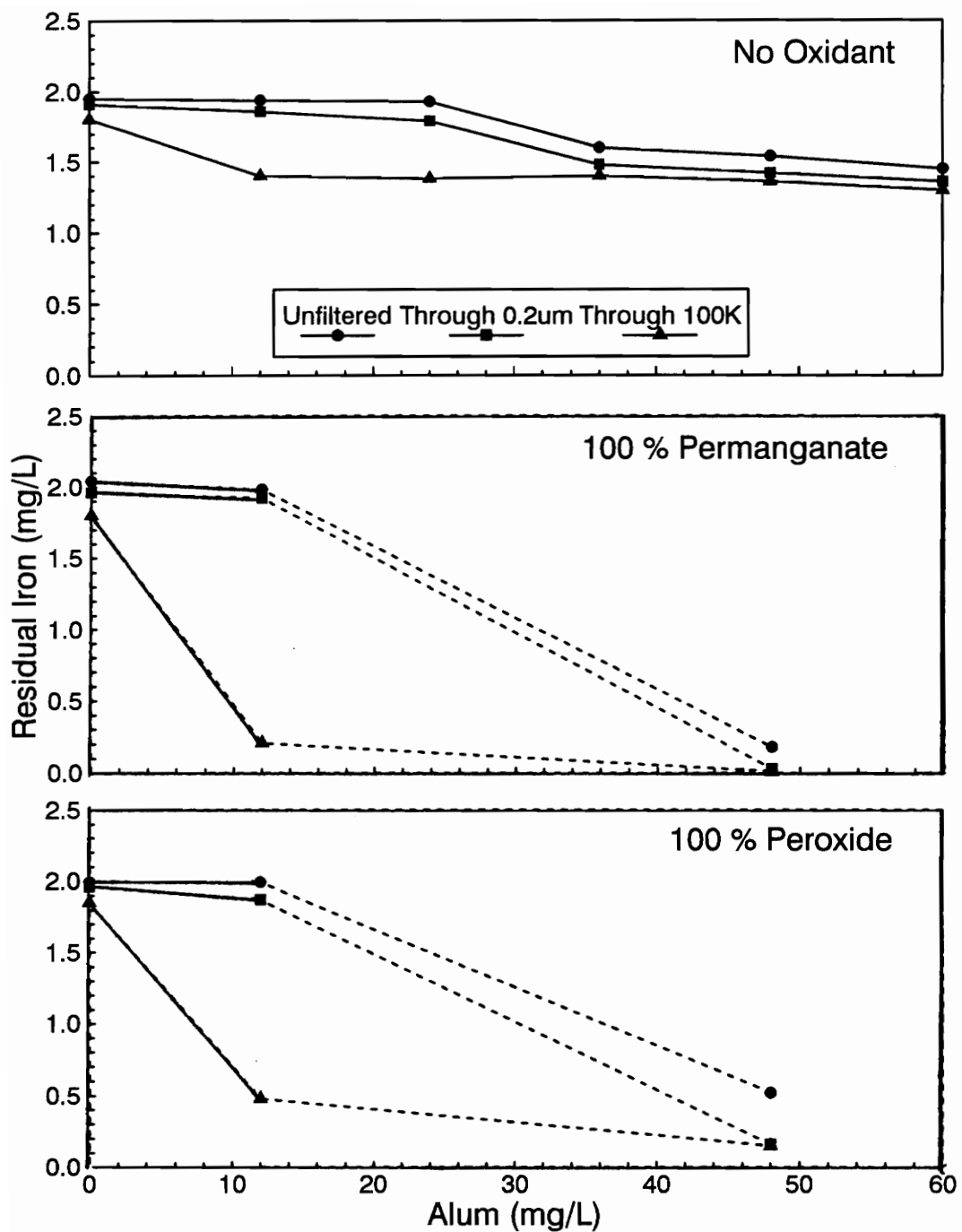


Figure 19. Complexed Fe(II) removal by alum coagulation.  
 (DOC = 10 mg/L; pH = 5.5 to 6.0; DOC source - Dismal Swamp;  
 theoretical stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per  
 mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

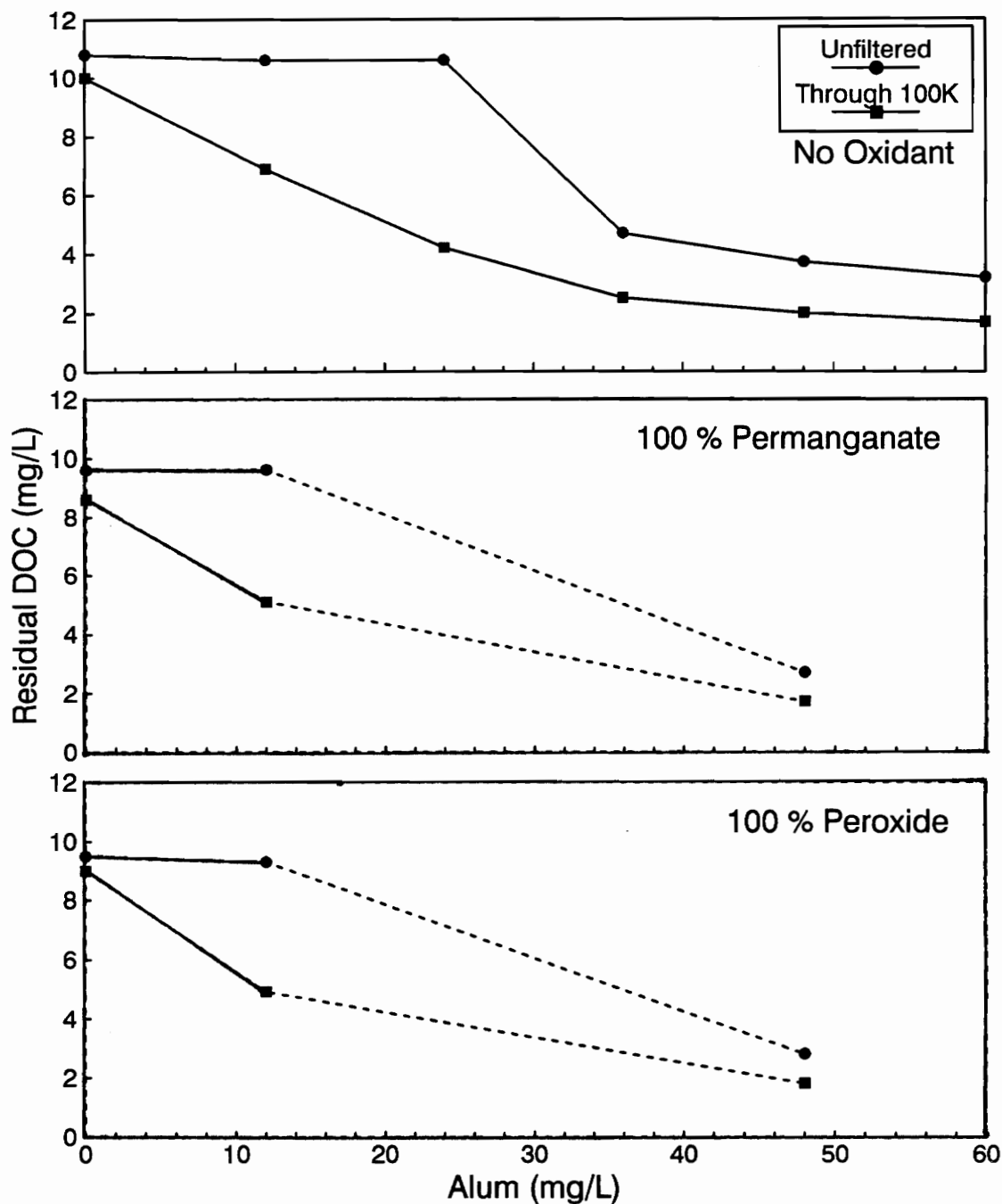


Figure 20. DOC removal in complexed Fe(II) solutions by alum coagulation. (Fe(II) = 2 mg/L; DOC source - Dismal Swamp; pH = 5.5 to 6.0; theoretical stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

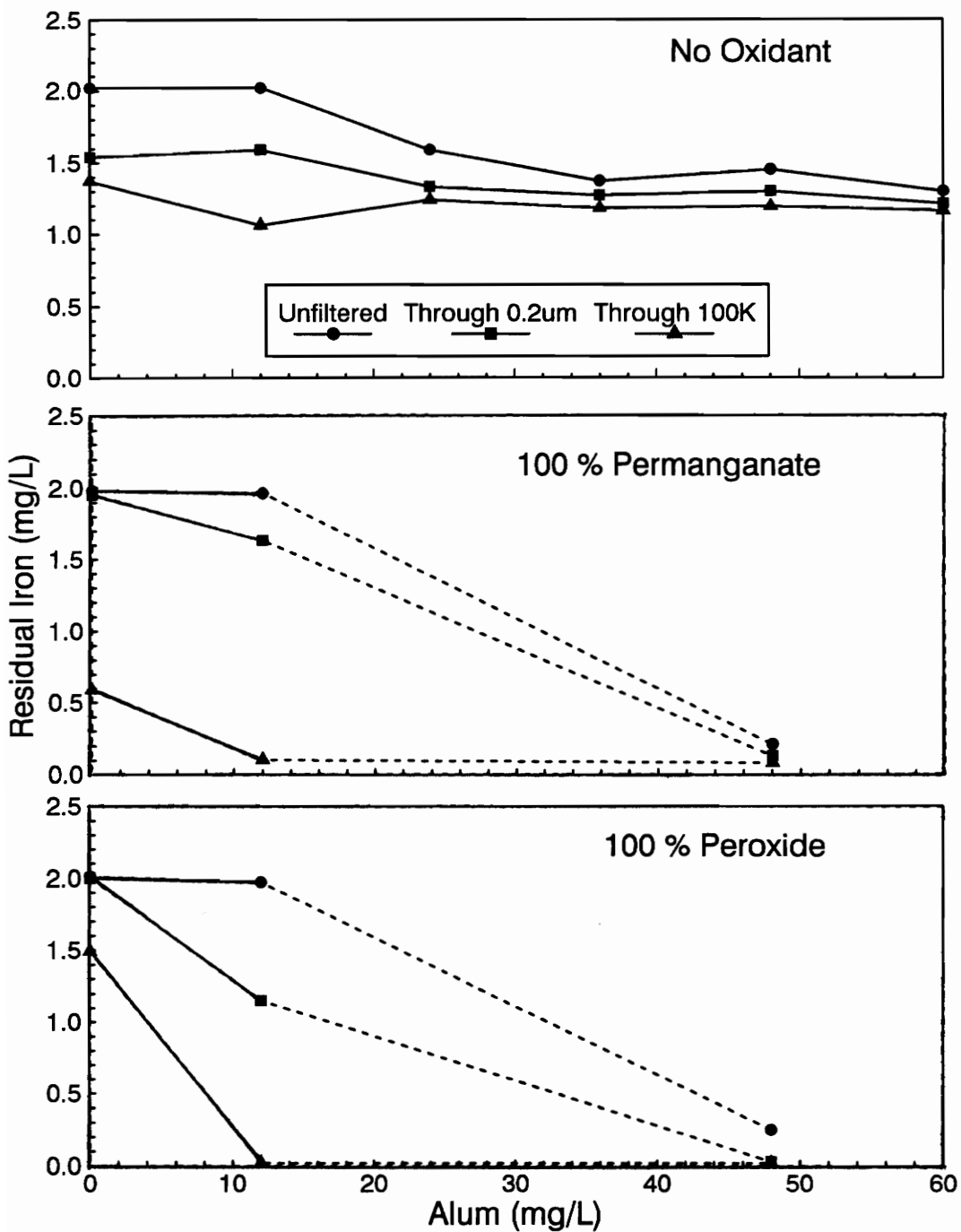


Figure 21. Complexed Fe(II) removal by alum coagulation.  
(DOC = 5 mg/L; pH = 5.5 to 6.0; DOC source - Dismal Swamp;  
theoretical stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per  
mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

the original iron concentration remained in solution. The addition of an oxidant yielded a residual iron concentration less than 0.1 mg/L after alum coagulation; therefore, the addition of either oxidant appears to result in the formation of colloidal iron species which are effectively removed by alum coagulation.

Test solutions were fractionated after alum coagulation to determine the MWD of iron and DOC. The solutions were dosed with 12 mg/L and 48 mg/L of alum, both in the absence and presence of oxidant. A control solution (no alum addition) was also fractionated, with and without the addition of an oxidant.

Figure 22 illustrates the MWD of iron from a 10 mg/L DOC test solution coagulated with alum over the pH range 5.5 to 6.0. In the absence of both an oxidant and alum, 45 percent of the iron was present in the 1K filtrate. The addition of 12 mg/L and 48 mg/L of alum resulted in the removal of 20 and 30 percent of the iron as colloidal species, respectively; however, 45 percent of the iron originally present in solution remained in the less than 1K fraction for both alum doses. The addition of an oxidant resulted in the iron being present in the higher molecular weight fraction when no coagulant was added; approximately 85 percent of the iron was present in the fractions greater than 10K for solutions dosed with 100 percent  $\text{KMnO}_4$  and 100 percent  $\text{H}_2\text{O}_2$ .

For an alum dose of 12 mg/L, 75 and 90 percent of the iron were retained on a 100K ultrafilter for solutions dosed with  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ , respectively. Solutions

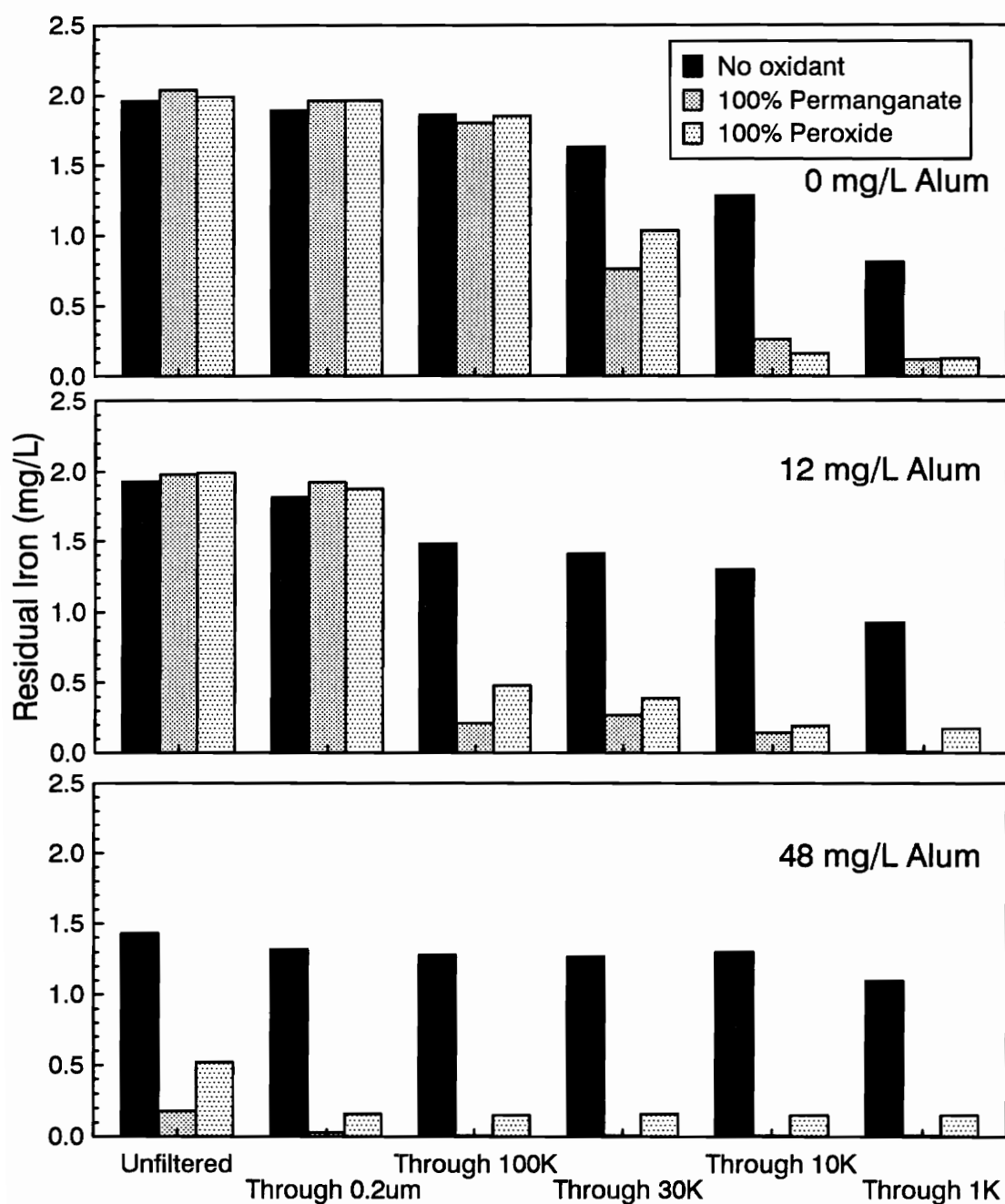


Figure 22. Distribution of iron after alum coagulation. (DOC = 10 mg/L; pH = 5.5 to 6.0; DOC source - Dismal Swamp; theoretical stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

receiving 48 mg/L of alum had 75 and 90 percent of the original iron concentration removed by sedimentation after the addition of  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ , respectively.

The MWD of the 10 mg/L DOC complexed Fe(II) test solutions are presented in Figure 23. The addition of an oxidant had little effect on the MWD of DOC remaining after coagulation. For the alum dose of 48 mg/L, a large portion of the DOC remaining in solution is located in the less than 1K fraction. This result supports findings that have shown alum coagulation to be effective at removing high molecular weight DOC (Collins *et al.*, 1986).

Results similar to those obtained from coagulation experiments involving 10 mg/L DOC are depicted in Figure 24 for experiments involving 5 mg/L DOC test solutions. The presence of alum alone was not very effective at removing Fe(II) from solution; however, the addition of 100 percent oxidant achieved 75 and 90 percent soluble iron removal for  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ , respectively. The MWD of DOC for the 5 mg/L DOC test solutions were analogous to those obtained for the 10 mg/L DOC solutions.

A coagulation study was conducted on a complexed Fe(II) solution containing 5 mg/L of DOC at a higher pH range, 6.8 to 7.3. Results from the study are shown in Figure 25. Nearly all of the iron became colloidal in nature in the presence of alum alone. At these testing conditions, the removal of iron by alum coagulation was aided by the fact that Fe(II) was oxidized to colloidal species by  $\text{O}_2(\text{aq})$ . These colloidal species were felt to be removed by alum addition. Approximately 50



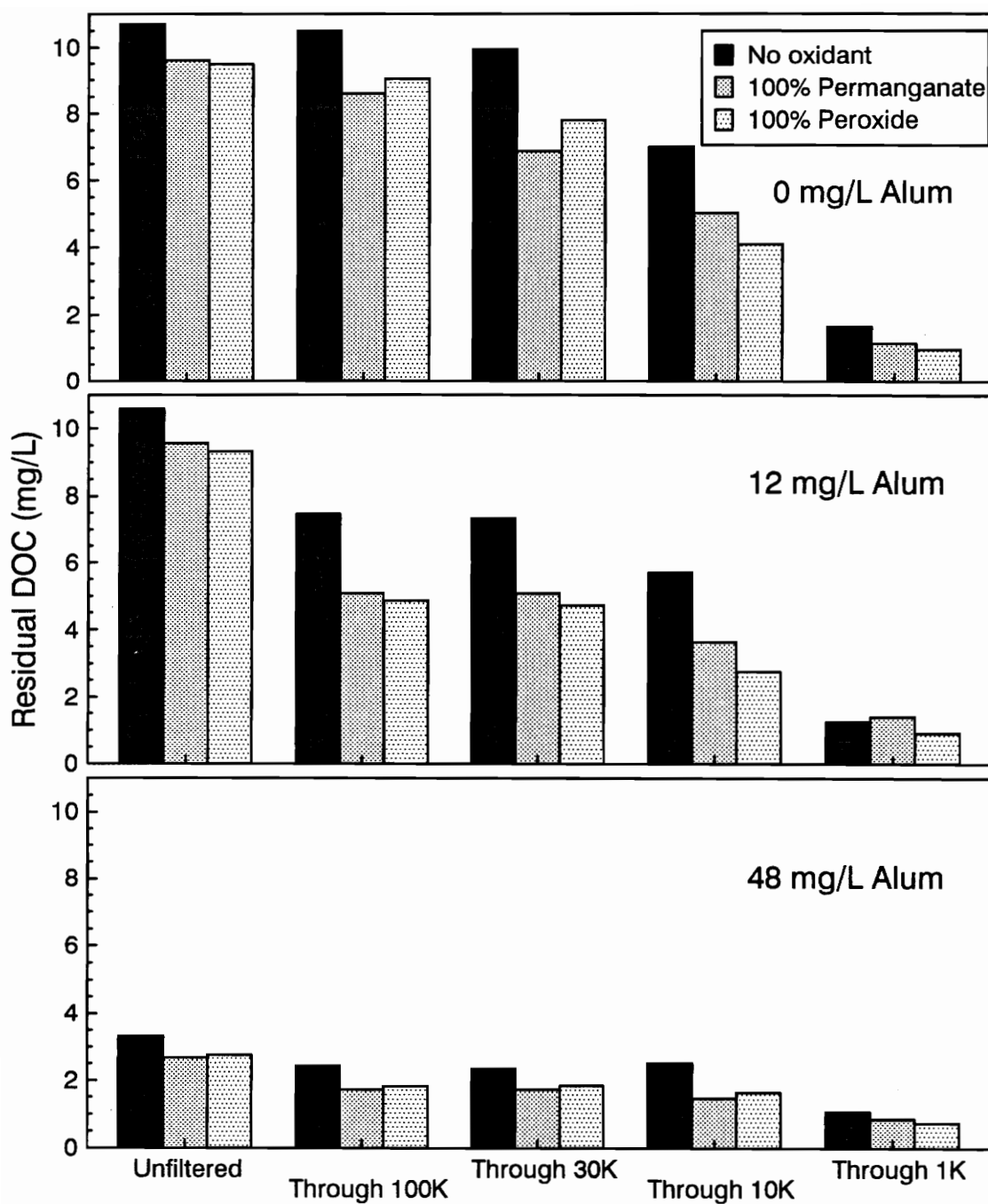


Figure 23. Molecular weight distribution of DOC after alum coagulation. (Fe(II) = 2 mg/L; pH = 5.5 to 6.0; DOC source - Dismal Swamp; theoretical stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

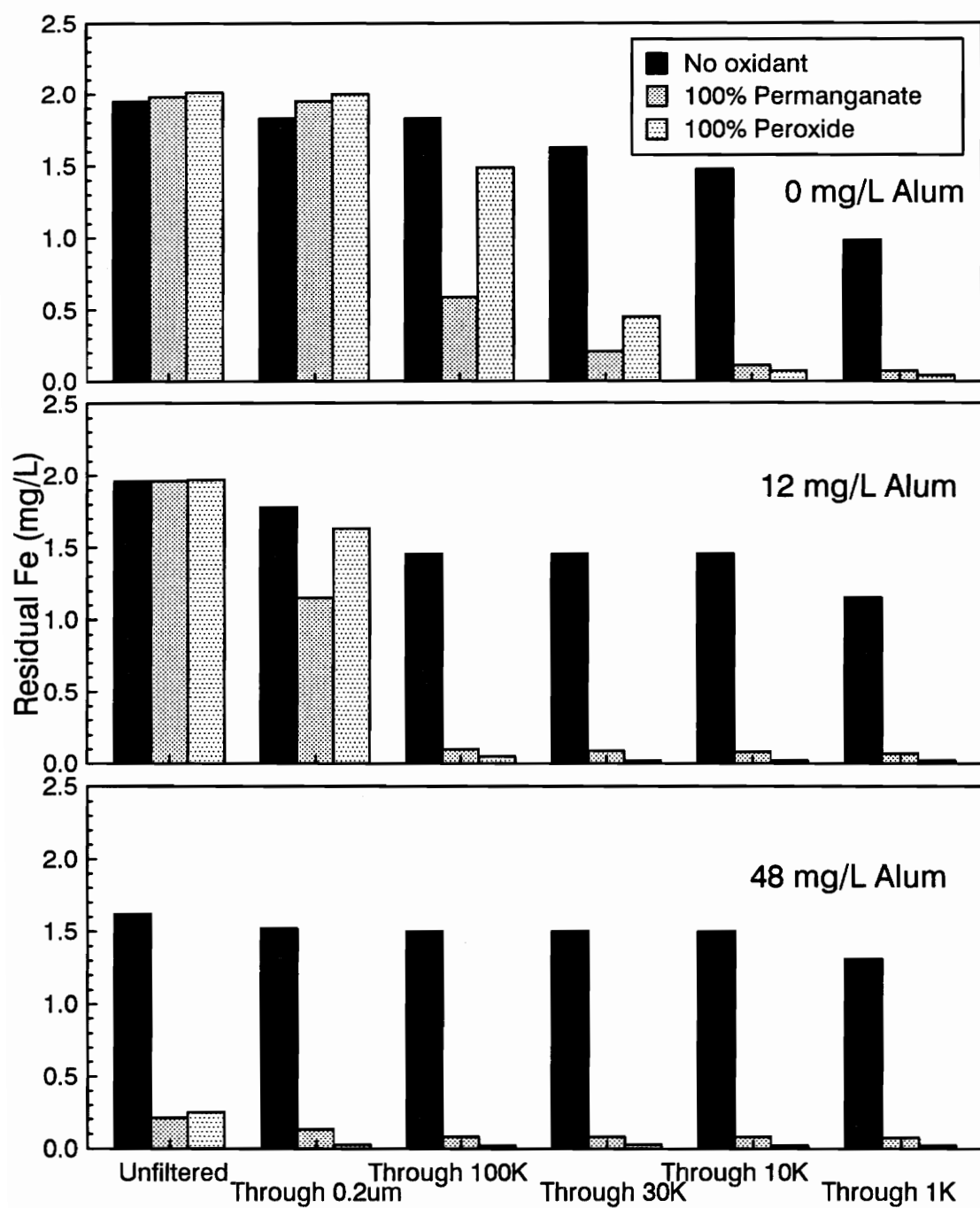


Figure 24. Distribution of iron after alum coagulation. (DOC = 5 mg/L; pH = 5.5 to 6.0; DOC source - Dismal Swamp; theoretical stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)

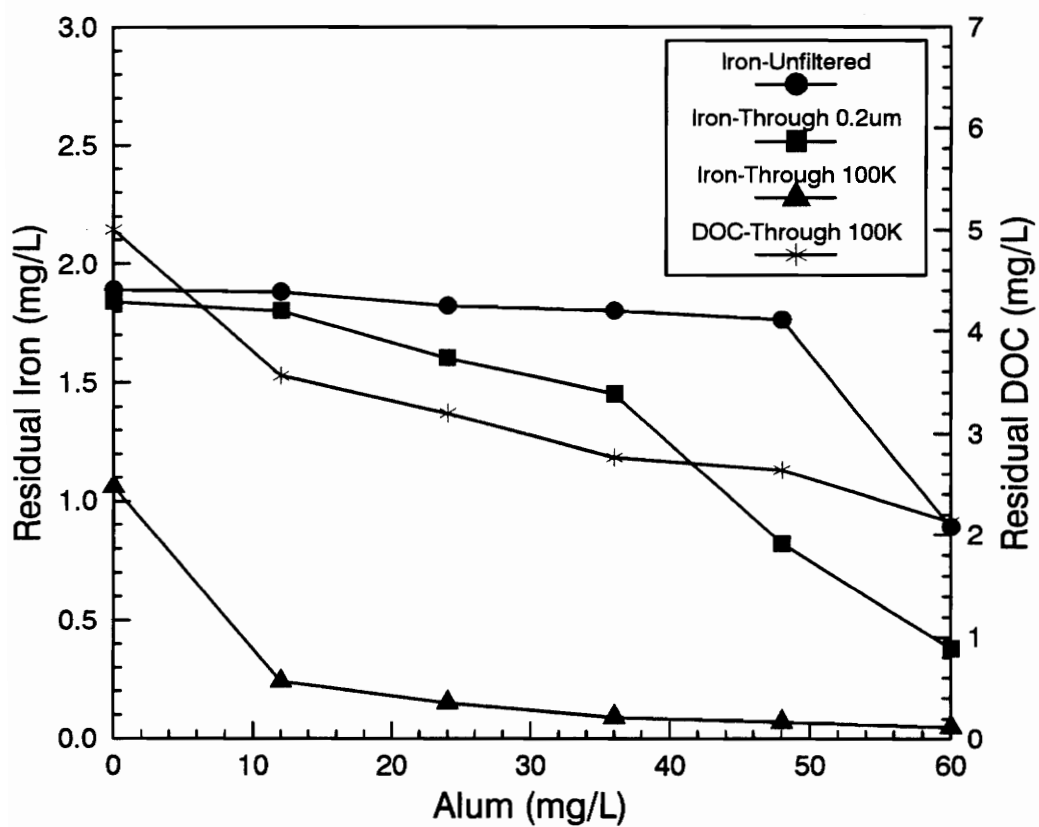


Figure 25. Complexed Fe(II) and DOC removal by alum coagulation at pH 6.8 to 7.3. (DOC source - Dismal Swamp)

percent of the DOC was removed by 100K ultrafiltration which is considerably less than the 80 percent removed under the testing conditions of pH 5.5 to 6.0.

### **Alum Coagulation of Fe(II) Complexed with Durham Humic Material**

Coagulation studies were conducted at the Williams Water Treatment Plant in Durham, NC, utilizing water obtained from the terminal reservoir. This water initially contained 0.35 mg/L Fe and 5 mg/L DOC; however, ferrous iron was added to create an initial iron concentration of 1 mg/L. Also, the water was stored for approximately 12 hours at pH 5.5 to allow time for the iron to complex with the DOC prior to coagulation.

Data in Figure 26 illustrate that alum coagulation alone was ineffective at removing iron from solution, a result similar to that seen with the Dismal Swamp DOC source. However, the addition of 100 percent  $\text{KMnO}_4$  resulted in the removal of soluble iron by sedimentation for alum doses greater than 12 mg/L. For the control solution (no alum added), essentially all of the iron became colloidal in the presence of 100 percent  $\text{KMnO}_4$ .

### **Alum Coagulation of Fe(II) Complexed With High Molecular Weight Humic Material Obtained From the University of Washington**

Alum coagulation experiments were performed at pH 5.5 to 6.0 with Fe (II) complexed by the high molecular weight fraction (100K-10K) of the University of

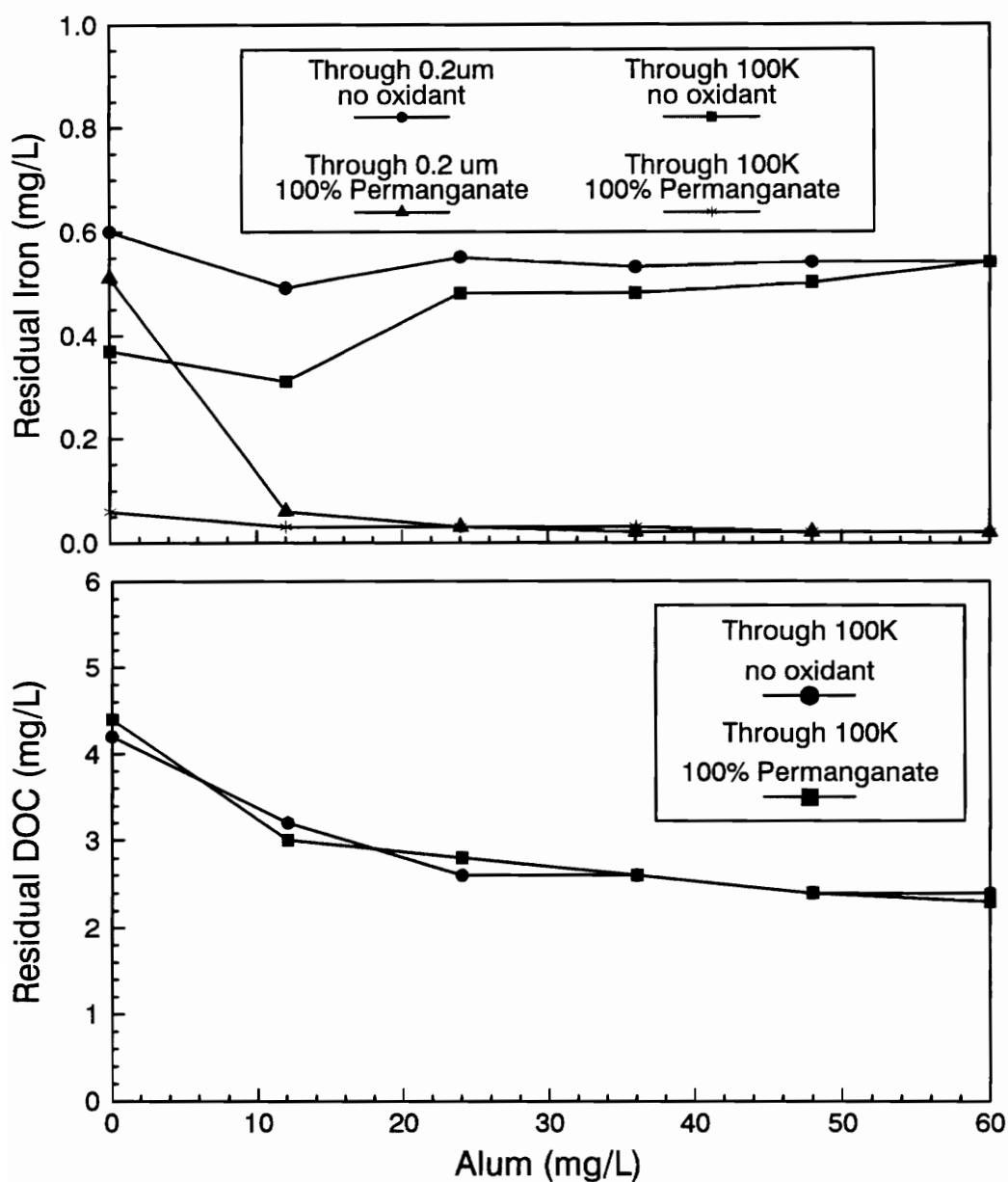


Figure 26. Complexed Fe(II) and DOC removal by alum coagulation at pH 5.5 to 6.0. (conducted in Durham, NC; water spiked with 1 mg/L Fe; stoichiometric requirement = 0.94 mg  $\text{KMnO}_4$  per mg Fe)

Washington humic material. The residual iron and DOC concentrations after alum coagulation are presented in Table 17. Approximately 70 percent of the iron remained in solution at the 48 mg/L dose of alum, while only 50 and 20 percent of the DOC remained in solution at alum doses of 12 mg/L and 48 mg/L, respectively.

Only test solutions containing 12 mg/L of alum were dosed with 100 percent oxidant due to the limited quantity of this fraction of humic material available. In the presence of 100 percent oxidant, all of the soluble iron became colloidal species. In the presence of 100 percent  $\text{H}_2\text{O}_2$ , 50 percent of the soluble iron formed particulate species, while 75 percent became particulate species in the presence of a 100 percent stoichiometric dosage of  $\text{KMnO}_4$ . The addition of either oxidant did not appear to affect the removal of DOC by alum coagulation.

#### **Alum Coagulation of Fe(II) Complexed With Low Molecular Weight Humic Material Obtained From the University of Washington**

Alum coagulation experiments were also performed using the lower molecular weight fraction of the University of Washington humic material. Results are shown in Figure 27. Approximately 85 percent of the iron remained soluble at an alum dose of 48 mg/L. Nearly 70 percent of the DOC passed a 100K ultrafilter at 12mg/L alum, while only 30 percent of DOC passed a 100K ultrafilter at 48 mg/L alum.

The addition of 100 percent oxidant resulted in the removal of 80 percent of iron as settleable species at an alum dose of 48 mg/L. For an alum dose of 12 mg/L,

Table 17

Residual iron and DOC concentrations after alum coagulation of Fe(II)  
complexed with high molecular weight  
humic material (100K - 10K)

Alum Dose (mg/L)	Fe Unfiltered (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	DOC Unfiltered (mg/L)	DOC Through 100K (mg/L)
0	1.95	1.88	1.61	4.6	4.2
12	1.95	1.80	1.09	4.5	1.7
24	1.51	1.38	1.37	1.7	1.0
48	1.38	1.27	1.27	1.3	0.9

Alum Dose (mg/L)	Oxidant Dose (%)	Fe Unfilter (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	DOC Unfilter (mg/L)	DOC Through 100K (mg/L)
12	0	1.93	1.89	1.27	4.7	2.1
12	100 KMnO <sub>4</sub>	1.93	0.50	0.08	4.1	1.3
12	100 H <sub>2</sub> O <sub>2</sub>	1.93	1.00	0.09	4.4	1.6

Notes:

- test conducted at pH = 5.5 to 6.0; DOC source - University of Washington;
- theoretical stoichiometric requirements = 0.94 mg KMnO<sub>4</sub> per mg Fe and 0.31 mg H<sub>2</sub>O<sub>2</sub> per mg Fe.

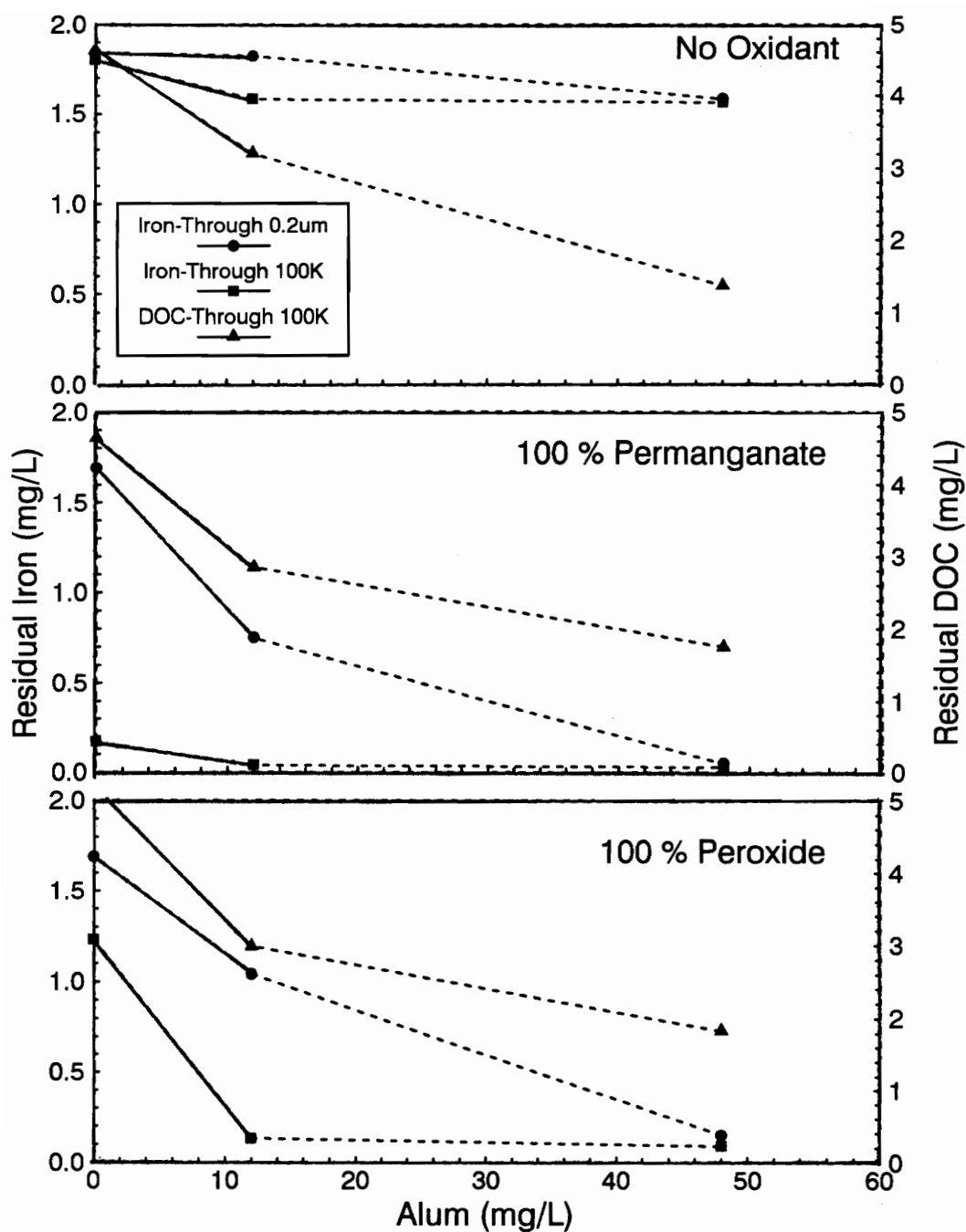


Figure 27. Complexed Fe(II) and DOC removal by alum coagulation at pH 5.5 to 6.0. (DOC source - University of Washington (less than 3K); stoichiometric requirements = 0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe)



no iron was removed by sedimentation; however, 95 percent of the initial iron was removed as colloidal species in the presence of 100 percent  $\text{KMnO}_4$  and 100 percent  $\text{H}_2\text{O}_2$ . Oxidant addition did not alter the removal of DOC.

## **Chapter V**

### **DISCUSSION**

#### **Overview**

The following variables were examined for their effects on the removal of complexed iron by alum coagulation and/or  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  oxidation: solution pH, DOC concentration, relative MWD of DOC, and the source of DOC. The MWD of iron and DOC in the absence and presence of an oxidant were also investigated; furthermore, the capacity of humic materials to complex iron was analyzed.

#### **Speciation of Iron**

It has been a common practice of past researchers to use a 0.45  $\mu\text{m}$  pore size membrane filter to differentiate between particulate and soluble iron species as indicated in the published literature regarding complexed iron. Iron present in the 0.45  $\mu\text{m}$  filtrate was assumed to be complexed by humic material. The use of a 0.45  $\mu\text{m}$  filter, however, does not allow for the determination of colloidal species, which range in size from 0.45  $\mu\text{m}$  to 1 nm (Thurman, 1985).

The use of a 0.2  $\mu\text{m}$  pore size membrane filter and a 100K ultrafilter were utilized in this research to differentiate between particulate, colloidal, and soluble species (Figure 2). Results from oxidation studies revealed that the speciation (particulate, colloidal, or soluble) of iron in the presence of DOC was altered by

the addition of an oxidant; furthermore, the species of iron present dictated the efficiency of iron removal by alum coagulation.

### **Complexation of Iron**

The following DOC-to-iron weight ratios were utilized to prepare complexed Fe(II) solutions: 5:1, 3:1, and 2.5:1. At these DOC-to-iron weight ratios the DOC (from all humic sources) was unable to complex all of the iron present in solution.

Studies conducted at pH 7.5 on complexed Fe(II) solutions prepared with the Dismal Swamp humic material revealed the formation of colloidal iron species as observed in Figures 4 and 6. These data indicate that the Fe(II) was being oxidized at pH 7.5 by trace quantities of  $O_2(aq)$ . Stumm and Lee (1961) reported that the oxidation of uncomplexed Fe(II) was kinetically rapid at pH values above 6.5; therefore, these data provided evidence that not all of the Fe(II) was being complexed by the Dismal Swamp humic material. This hypothesis is also supported by data collected from the MWD of test solutions at pH 5.5 and 6.5 (as seen in Figure 6) as well as data collected from alum coagulation studies of complexed iron (Figures 19, 20, and 21). At solution pH values of both 5.5 and 6.5, the DOC-to-iron weight ratio in the 1K filtrate was found to be 1.5 mg DOC:1 mg Fe. It appears that not all of the Fe(II) in the solution was complexed due to the presence of large quantities of iron in the 1K filtrate compared to DOC concentrations in the same fraction. Data from alum coagulation studies indicated that residual iron concentrations as high as 75

percent of the original soluble iron remained at high alum doses where 85 percent of the Dismal Swamp DOC had been removed via coagulation. The results from these studies involving the Dismal Swamp humic material suggest that on average approximately 0.1 of Fe(II) was complexed by each mg of DOC present in solution (with maximum values up to 0.2 mg Fe complexed per mg DOC).

The other DOC sources utilized throughout the study were also unable to completely complex Fe(II). Figures 7 and 26 reveal that the Durham humic material was unable to complex all of the Fe(II) present in solution as indicated by the high percentage of iron remaining in the 1k filtrate as well as after alum coagulation. Analogous results were also obtained with regards to the University of Washington fractions (Table 17 and Figure 27).

Approximate measures of the capacity of humic material to bind iron is available in the published literature. Thurman (1985) reported that 0.02 to 0.03 mg of Fe are bound for each mg of DOC present in solution. Perdue *et al.* (1976) found that each mg of DOC stabilized 0.05 mg of iron; likewise, Weber (1988) reported the iron capacity of DOC to be between 0.02 to 0.07 mg of Fe per mg of DOC.

### **Oxidation of Complexed Fe(II)**

Oxidation studies were conducted to determine the ability of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  to oxidize Fe(II) to Fe(III) in the presence of DOC. At a dose near the stoichiometric requirement,  $\text{KMnO}_4$  maintained the ability to oxidize essentially all of the Fe(II)

present in solution to Fe(III) within a 5 minute contact period, even in the presence of DOC (Figure 13). The presence of the Dismal Swamp humic material did not appear to inhibit the ability of  $\text{KMnO}_4$  to oxidize Fe(II) to Fe(III).

The oxidation of Fe(II) to Fe(III) by  $\text{H}_2\text{O}_2$  at the stoichiometric requirement resulted in the partial oxidation of Fe(II) in the presence of DOC (Figure 17). In the absence of DOC  $\text{H}_2\text{O}_2$  at the theoretical stoichiometric requirement was also unable to oxidize all of the Fe(II) present to  $\text{Fe}(\text{OH})_3(\text{s})$  as seen in Figure 14. These results indicate that  $\text{H}_2\text{O}_2$  dosages exceeding the theoretical reaction stoichiometric requirement are necessary for the complete oxidation of Fe(II) both in the absence and presence of DOC.

The relative MWD of complexed Fe(II) test solutions (10 mg/L DOC, 2 mg/L Fe) was conducted to analyze the effects of oxidant addition on the relative MWD of iron (as seen in Figures 13, 16, and 17). For control solutions (no oxidant addition) approximately 60 percent of the total soluble iron was present in the 1K filtrate as Fe(II). The addition of 120 percent of the stoichiometric amount of  $\text{KMnO}_4$  resulted in most of the iron present as colloidal species (30 percent) or in the fraction greater than 30K (80 percent). Similar results were observed for test solutions oxidized with  $\text{H}_2\text{O}_2$ ; however, considerably less colloidal iron species were formed when  $\text{H}_2\text{O}_2$  was utilized as the oxidant. Results from these studies indicate that after oxidation, the Fe(III) was either complexed by higher molecular-weight DOC or formed colloidal ferric oxide species.

The initial DOC-to-iron weight ratios present in complexed Fe(II) solutions dictated the amount of colloidal iron species formed. The formation of colloidal iron species was greatest in solutions having the lowest DOC-to-iron weight ratios, while the formation of colloids was somewhat hindered in solutions with higher DOC-to-iron weight ratios.

The formation of particulate iron species appeared to be a function of the chemical characteristics of DOC and not the MWD of DOC present in solution. Particulate iron species formed only in experiments involving  $\text{KMnO}_4$  oxidation of Fe(II) in the presence of the Durham humic material; the other DOC sources utilized throughout the study appeared to inhibit the formation of particulate iron species. Recall that all three sources of humic material had similar relative MWD with regards to DOC (Figure 5). Minimal differences were observed in the removal of iron (evaluated by 0.2  $\mu\text{m}$  filter and 100K ultrafilter) for both the high and low molecular-weight fractions extracted from the University of Washington humic material. These results indicate that factors such as the presence of particular functional groups and other differences between DOC sources dictate the interactions between iron and DOC in solution.

### **Adsorption of DOC onto Iron Oxide Solids**

DOC removal was measured during experiments involving the oxidation by both  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  of Fe(II) complexed by the Dismal Swamp humic material.

The amount of DOC removed was observed to be a function of solution pH as well as the initial DOC concentration present. The removal of DOC corresponded to the formation of colloidal iron species; therefore, the correlation was attributed to the adsorption of DOC onto iron oxides formed during the Fe(II) oxidation reaction. The adsorption capacity of the iron oxide solids was calculated by the ratio of change in DOC concentration to the change in Fe concentration after oxidation ( $\Delta\text{DOC}/\Delta\text{Fe}$ ). Values representative of this data are compiled in Table 18.

Solution pH appeared to effect the adsorption of DOC as indicated by results compiled in Table 18. In general, higher adsorption capacities were observed at pH 5.5 than at 6.5 for both  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  oxidation. These changes in adsorption capacities can be attributed to the changes in the surface charge of iron oxide solids accompanying changes in solution pH. The isoelectric or neutral point for iron oxide solids is near pH 9 (Culp *et al.*, 1986); therefore, as solution pH decreases the surfaces of iron oxide particles become more positively charged. The presence of more positively charged sites on the surfaces of iron oxides would attract more negatively charged DOC species, resulting in higher DOC adsorption.

Solutions containing higher initial DOC solution concentrations in general had higher corresponding DOC adsorption capacities (Table 18). This relationship is common of reversible physical adsorption, where equilibrium exists between DOC in solution and the DOC adsorbed on the surface of iron oxides. In general, as the

Table 18

DOC adsorption capacities after  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$   
oxidation of complexed Fe(II)

pH	Oxidant	Initial		Residual		$\Delta\text{DOC}$ (mg/L)	$\Delta\text{Fe}$ (mg/L)	Adsorption capacity (mg DOC/mg Fe)
		DOC (mg/L)	Fe (mg/L)	DOC (mg/L)	Fe (mg/L)			
5.5	$\text{KMnO}_4$	9.7	1.86	9.1	1.57	0.6	0.29	2.1
5.5	$\text{KMnO}_4$	5.5	1.76	2.7	0.24	2.8	1.52	1.9
5.5	$\text{KMnO}_4$	3.9	0.92	2.6	0.03	1.3	0.89	1.4
6.5	$\text{KMnO}_4$	9.7	1.89	7.6	0.53	2.1	1.36	1.6
6.5	$\text{KMnO}_4$	5.5	1.92	3.8	0.21	1.7	1.71	1.0
6.5	$\text{KMnO}_4$	3.5	1.00	2.9	0.14	0.6	0.86	0.7
5.5	$\text{H}_2\text{O}_2$	9.3	1.99	8.7	1.74	0.6	0.25	2.2
5.5	$\text{H}_2\text{O}_2$	4.8	1.97	3.5	0.88	1.3	1.09	1.2
5.5	$\text{H}_2\text{O}_2$	3.6	0.95	3.1	0.68	0.5	0.27	1.4
6.5	$\text{H}_2\text{O}_2$	5.2	1.78	4.0	0.72	1.2	1.06	1.2
6.5	$\text{H}_2\text{O}_2$	3.3	0.93	3.1	0.54	0.2	0.39	0.7

Notes:

- a) DOC source - Dismal Swamp; ' $\Delta$ ' denotes change in concentrations after 5 minute contact period;
- b) oxidant dosages between 100 and 500 percent of the theoretical stoichiometric requirements (0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe).



DOC concentration in solution is increased additional DOC must be adsorbed onto the iron oxides to maintain an equilibrium condition.

The DOC-to-iron ratios utilized in this study were representative of values typically encountered in surface waters. These values, however, represented a narrow concentration range over which to examine reversible physical adsorption; therefore, studies were conducted at much higher initial concentrations of DOC and Fe while maintaining the same DOC-to-iron ratios used in oxidation studies. Results from this experiment are compiled in Table 19. From this data, similar DOC adsorption capacities were obtained compared to those found in Table 18. These results were indicative of a Langmuir type response in which there is a limited surface area available for adsorption.

The results presented in Tables 18 and 19 refer to DOC extracted from the Dismal Swamp. Remarkably different results were obtained in studies where the DOC present was that of the Durham humic material. Recall that for this particular DOC source, the formation of particulate iron species was observed after a 60 minute contact period; however, minimal DOC removal was observed in these studies.

These differences in iron speciation and DOC adsorption observed between the Dismal Swamp and Durham humic material are attributed to differences in chemical characteristics between the two sources. The presence of DOC extracted from the Dismal Swamp, which adsorbed onto iron oxides, resulted in the stabilization of colloids which in turn prevented their aggregation to particulate species. For the

Table 19

DOC adsorption capacities after  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$   
oxidation of complexed Fe(II)

pH	Oxidant	Initial		Residual		$\Delta\text{DOC}$ (mg/L)	$\Delta\text{Fe}$ (mg/L)	Adsorption capacities (mg DOC/mg Fe)
		DOC (mg/L)	Fe (mg/L)	DOC (mg/L)	Fe (mg/L)			
5.5	$\text{KMnO}_4$	50.3	14.6	24.9	4.6	25.4	10.0	2.5
5.5	$\text{KMnO}_4$	99.5	34.2	44.4	8.2	55.1	26.0	2.1
6.5	$\text{KMnO}_4$	50.3	14.6	27.2	3.7	23.1	10.9	2.1
6.5	$\text{KMnO}_4$	99.5	34.2	48.9	5.0	50.6	29.2	1.7
5.5	$\text{H}_2\text{O}_2$	50.3	14.6	28.2	6.5	22.1	8.1	2.7
5.5	$\text{H}_2\text{O}_2$	99.5	34.2	46.7	11.8	52.8	22.4	2.4
6.5	$\text{H}_2\text{O}_2$	50.3	14.6	30.3	4.9	20.0	9.7	2.1
6.5	$\text{H}_2\text{O}_2$	99.5	34.2	49.9	6.8	49.6	27.4	1.8

Notes:

- a) ' $\Delta$ ' denotes change in concentrations after 5 minute contact period
- b) oxidant dosages between 100 and 300 percent of the theoretical stoichiometric requirements (0.94 mg  $\text{KMnO}_4$  per mg Fe and 0.31 mg  $\text{H}_2\text{O}_2$  per mg Fe).

Durham humic material the stabilization of colloids did not occur; therefore, after the 60 minute contact period significant particle aggregation had occurred to form particles which were retained on a 0.2  $\mu\text{m}$  filter. These findings support the hypothesis presented earlier that even with similar MWD and concentrations, different DOC sources can behave quite differently in solution.

The adsorption of DOC was also observed in studies conducted with both the high and low molecular weight fractions extracted from the University of Washington humic material. The removal of DOC was similar for both fractions as indicated in the results compiled in Tables 11, 12, 15, and 16 for both oxidants.

#### **Alum Coagulation of Complexed Fe(II) both in the Absence and Presence of an Oxidant**

Alum coagulation alone was effective at removing DOC from solution; however, it was not very efficient at removing residual iron from prepared solutions in the presence of DOC. Ultrafiltration tests revealed that the majority of iron remaining in solution after alum coagulation was located in the molecular weight fraction less than 1K. This residual iron was believed to be uncomplexed because of the low DOC-to-iron weight ratios present in this fraction.

The MWD of DOC presented in Figure 23 indicates that higher molecular weight DOC was preferentially removed by alum coagulation. Iron removal accompanying the removal of high molecular weight DOC was attributed to the

complexation of Fe(II) by these high molecular weight DOC species. In general, for the Dismal Swamp humic material, approximately 0.1 mg of Fe per mg of DOC were removed by alum coagulation alone. This value corresponds to the binding capacity calculated previously for the Dismal Swamp humic material.

The addition of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  dramatically improved the removal of soluble iron by alum coagulation. Almost 100 percent removal of iron was observed by alum coagulation after the addition of both oxidants (at dosages of the theoretical stoichiometric requirement for Fe(II) oxidation). In the presence of an oxidant the Fe(III) either formed colloidal species or was complexed by higher molecular weight DOC, thus rendering the oxidized iron to removal by alum coagulation.

### **Similar Research with Chlorine Dioxide and Free Chlorine**

Shorney (1992) conducted similar studies to analyze the ability of alum coagulation and/or chlorine dioxide ( $\text{ClO}_2$ ) and free chlorine ( $\text{HOCl}$ ) oxidation to remove complexed Fe(II). Testing conditions, sources of humic material, and experimental procedures were equivalent to the ones utilized for this research.

Free chlorine and  $\text{ClO}_2$  were found to oxidize Fe(II) in the presence of DOC, with results being similar to those observed for  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ , respectively. In general,  $\text{ClO}_2$  was reported to be a stronger oxidant than  $\text{HOCl}$ , with slightly more colloidal iron species formed in the presence of  $\text{ClO}_2$ .

The removal of iron by alum coagulation in the presence of 100 percent of the stoichiometric requirement of  $\text{ClO}_2$  was analogous to the results obtained for stoichiometric amounts of  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ . In general, soluble iron concentrations after alum coagulation in the presence of these oxidants was reduced to less than 0.15 mg/L of iron. The addition of 100 percent of the stoichiometric requirement of  $\text{HOCl}$  was reported to be less efficient with average soluble iron concentrations after alum coagulation of 0.5 mg/L of iron. This was attributed to the competitive oxidant demand exerted by the Dismal Swamp humic material for free chlorine; therefore, resulting in only the partial oxidation of  $\text{Fe(II)}$  to  $\text{Fe(III)}$ .

The results from the research conducted by Shorney (1992) coupled with the results from this research provide the information necessary to rank the oxidants according to their ability to oxidize  $\text{Fe(II)}$  in the presence of DOC in the following manner:  $\text{KMnO}_4 > \text{ClO}_2 > \text{H}_2\text{O}_2 = \text{HOCl}$ .

### **Applicability of Research to Water Treatment**

The oxidation of  $\text{Fe(II)}$  in the presence of DOC by  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  yielded the formation of colloidal iron species which resisted removal by sedimentation and filtration for all DOC sources used in this study except for the Durham humic material. Oxidation alone, therefore, does not appear to be a viable treatment for the removal of  $\text{Fe(II)}$  in the presence of DOC. The results from the study conducted with the Durham humic material indicate that in the presence of certain types of DOC,

particulate iron species can form which are amenable to removal by sedimentation or filtration. The addition of an oxidant during the rapid mix phase (prior to alum addition) resulted in the formation of iron species which were removed by the coagulation process, regardless of the type or concentration of DOC present.

The findings of this research indicate that the type of treatment method utilized to remove iron in the presence of DOC is site specific. Such factors as the chemical characteristics of DOC, concentration of DOC, the relative MWD of DOC, as well as the nature and speciation of iron dictate the type of treatment to be employed. By knowing the existing water quality characteristics, lab-scale studies can be designed to determine an effective treatment for complexed iron removal by investigating the performance of oxidation and/or alum coagulation.

## Chapter IV

### CONCLUSIONS

This research was conducted to obtain an understanding of the behavior of complexed Fe(II) in the presence of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$ . The following variables were investigated for their effects on the removal of complexed iron by alum coagulation and/or oxidant addition: solution pH, DOC concentration, relative MWD of DOC, and DOC source. From the results obtained during the course of this research, the following conclusions were formulated with respect to the previously stated research objectives:

1. The filtration of natural waters through 0.45  $\mu\text{m}$  filters distinguishes between particulate and soluble iron species. The use of a 100K ultrafilter along with a 0.2  $\mu\text{m}$  filter is necessary to distinguish particulate, colloidal, and soluble iron species from one another.
2. The capacity of the Dismal Swamp humic material was approximately 0.1 mg of Fe per mg DOC in solution. Factors such as the relative MWD and concentration of DOC affected the extent of iron complexation.
3. Potassium permanganate oxidized Fe(II) to Fe(III) both in the absence and presence of DOC at near the theoretical stoichiometric requirement;  $\text{H}_2\text{O}_2$  dosages greater than the theoretical stoichiometric requirement for Fe(II)

oxidation, however, were required in the absence and presence of DOC to achieve complete Fe(II) oxidation.

4. Adsorption of DOC by iron oxides accompanied the formation of colloidal iron (as defined by retention on a 100K ultrafilter) after Fe(II) oxidation in the presence of DOC.
5. Alum coagulation alone efficiently removed Fe(II) complexed by high molecular weight DOC. Following the addition of either oxidant, uncomplexed Fe(II) was oxidized to Fe(III) which was either complexed by high molecular weight DOC or formed colloidal species, both of which were efficiently removed by alum coagulation.



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