

**The Performance of Free Chlorine and Chlorine Dioxide
Oxidation and/or Alum Coagulation for the Removal of
Complexed Fe(II) from Drinking Water**

by

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(ABSTRACT)

Past research regarding complexed iron has focused on the resistance to and kinetics of oxidation by $O_2(aq)$ and the extent of stabilization. The 0.45 μm filter was typically used to differentiate between dissolved and particulate iron.

This research investigated Fe(II) oxidation by free chlorine and ClO_2 in the presence of DOC by varying the pH, DOC to Fe ratios, DOC sources, oxidant dosages, and contact time. Complexed iron removal by alum coagulation with and without oxidant addition was also examined. Particulate, colloidal, and soluble iron were differentiated by the use of 0.2 μm filters and 100K ultrafilters.

Ultrafiltration and oxidation studies revealed that, at the DOC-to-iron ratios used for this research, not all of the Fe(II) in solution was actually complexed. Thus, oxidation studies represented the oxidation of uncomplexed Fe(II) to Fe(III), which was then complexed by the higher molecular weight DOC.

Results indicated that particulate iron formation (as defined as retention by a 0.2 μm filter) was a function of the DOC source and oxidant used for

testing. The formation of colloidal iron (as defined by retention on 100K ultrafilter) due to oxidation was dependent upon the initial DOC-to-iron ratio and the DOC source. A correlation between DOC adsorption to iron oxide solids and the solution pH, initial DOC-to-iron ratio, and the oxidant used was also evident. Complexed Fe(II) was removed from solution by alum coagulation. Oxidant addition to alum coagulation was necessary to effectively remove uncomplexed Fe(II) (in the presence of DOC) from solution.

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TABLE OF CONTENTS

INTRODUCTION	1
LITERATURE REVIEW	3
Isolation and Characterization of Humic Substances	3
Techniques for the Isolation of Humic Substances	4
Molecular Weight Fractionation by Ultrafiltration.....	5
Complexation of Iron by Humic Substances	6
Mechanisms of Complexation	6
Effects of pH on the Complexation of Iron	7
Water Quality Characteristics	8
Extent of Complexation	8
Behavior of Iron in the Presence of O ₂ (aq) and DOC	9
Oxidation of Ferrous Iron by Alternative Oxidants	13
Oxidation by Free Chlorine	14
Oxidation by Chlorine Dioxide	15
Iron and DOC Removal by Alum Coagulation	17
Summary	18
METHODS AND MATERIALS	22
Introduction	22
Physical and Chemical Analysis	22
Total Iron Measurement	22
Dissolved Organic Carbon	23
Turbidity	23
Specific Absorbance	23
pH	23
Color Transmittance	24
Oxidant Residual	24
Temperature Considerations	26
Laboratory Procedures	26
Isolation of Humic Substances	26
Characterization of Humic Substances	28
Fractionation by Ultrafiltration	28

Specific Absorbance	29
Estimation of Relative Fraction of Humic/Fulvic Acids	29
Definition of Dissolved, Colloidal, and Particulate Species.....	30
Preparation of Water Solutions	32
Preparation of Stock Solutions	32
Ferrous Iron	32
Aluminum Sulfate	33
Sodium Bicarbonate	33
Preparation of Oxidants	33
Oxidant Demand by Humic Substances	34
Oxidation of Uncomplexed Fe(II)	34
Fractionation of Complexed Iron Solutions	35
Effect of Open Atmosphere on Complexed Iron	35
Oxidation Studies	36
Coagulation Studies	37
Ferrous Iron Detection	38
Glassware Cleaning	40
Field Experiments	40
Williams Water Treatment Plant, Durham, NC	40
EXPERIMENTAL RESULTS	41
Methods Development	41
Oxidation Experiment Methods	41
Ferrous Iron Determination	45
Chlorite Determination by Potentiometric Titration	51
Characterization of Humic Substances	53
Complexed Fe(II) Distribution in Test Solutions Used in this Research	55
Effect of Open Atmosphere on Complexed Fe(II)	58
Oxidant Demand of Humic Materials Used in this Research	61
Oxidation of Fe(II) by Free Chlorine and ClO ₂	66
Oxidation of Fe(II) by Free Chlorine	70
Free Chlorine Oxidation of Uncomplexed Fe(II)	70
Free Chlorine Oxidation of Complexed Fe(II)	70

1) Fe(II) Complexed with Dismal Swamp Humic Material	70
a) DOC Removal by 100K Ultrafilter after Oxidation by Free Chlorine	70
b) Exerted Free Chlorine Demand During Oxidation of Complexed Fe(II)	73
c) Fate of Complexed Fe(II) after Free Chlorine Oxidation	73
2) Fe(II) Complexed With Durham, NC Humic Material	76
3) Fe(II) Complexed with High Molecular Weight University of Washington Humic Material	80
4) Fe(II) Complexed with Low Molecular Weight University of Washington Humic Material	80
Oxidation of Fe(II) by ClO ₂	83
Chlorine Dioxide Oxidation of Uncomplexed Fe(II)	83
Stoichiometry of ClO ₂ Reduction during Oxidation of Complexed Fe(II)	83
Chlorite Oxidation of Complexed Fe(II)	85
Chlorine Dioxide Oxidation of Complexed Fe(II)	89
1) Fe(II) Complexed with Dismal Swamp Humic Material	89
a) DOC Removal by a 100K Ultrafilter after ClO ₂ Oxidation.....	89
b) Fate of Complexed Fe(II) after ClO ₂ Oxidation	91
2) Fe(II) Complexed with High Molecular Weight University of Washington Humic Material	91
3) Fe(II) Complexed with Low Molecular Weight University of Washington Humic Material	96
Alum Coagulation of Complexed Fe(II) in the Presence and Absence of Free Chlorine and ClO ₂	96
Alum Coagulation of Fe(II) Complexed with Dismal Swamp Humic Material	107

Alum Coagulation of Fe(II) Complexed with Durham, NC Humic Material	109
Alum Coagulation of Fe(II) Complexed with High Molecular Weight University of Washington Humic Material	109
Alum Coagulation of Fe(II) Complexed with Low Molecular Weight University of Washington Humic Material	111
DISCUSSION	115
Iron Complexation and Speciation	115
Oxidation of Complexed Fe(II)	117
Sorption of DOC onto Iron Oxide Solids	118
Alum Coagulation of Complexed Fe(II) both in the Absence and Presence of an Oxidant	123
Similar Research with KMnO_4 and H_2O_2	125
Applicability of Results to Water Treatment	126
CONCLUSIONS	128
REFERENCES	130
VITA.....	137

LIST OF FIGURES

Figure 1:	Model depicting the behavior of iron in the presence of organic matter (Org) and dissolved oxygen (O ₂).	11
Figure 2:	Removal of soluble iron and DOC by alum coagulation at pH 6.0–6.3. (DOC source–Provincial Brook humic acids)	19
Figure 3:	Removal of soluble iron and DOC by alum coagulation at pH 6.0–6.3. (DOC source–Provincial Brook fulvic acids).....	20
Figure 4:	An illustration of particulate, colloidal, and soluble iron. (free chlorine iron oxidation; pH = 6.5; DOC = 5 mg/L; reaction time = 5 minutes; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	31
Figure 5:	Oxidation of complexed Fe(II) by free chlorine at pH 7.5. (reaction time = 60 minutes; DOC source–Dismal Swamp; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	44
Figure 6:	The DOC molecular weight distribution of the Dismal Swamp, Durham, NC, and University of Washington humic sources. (Nominal DOC = 10 mg/L)	54
Figure 7:	Iron distribution within the Dismal Swamp and Durham, NC humic sources. (Nominal DOC = 10 mg/L)	56
Figure 8:	Changes in iron and DOC speciation due to exposure to O ₂ . (pH = 5.5; DOC source–Dismal Swamp)	60
Figure 9:	Free chlorine demand by Dismal Swamp humic material	62
Figure 10:	Chlorine dioxide demand by Dismal Swamp humic material	63

Figure 11:	Oxidation of complexed Fe(II) by free chlorine following 5 and 60 minute reaction periods. (DOC source–Dismal Swamp; DOC = 5.4 mg/L; pH = 5.5; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	67
Figure 12:	Free chlorine demand by Durham, NC humic material	68
Figure 13:	Oxidation of uncomplexed Fe(II) by free chlorine. (pH = 5.8; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	71
Figure 14:	Formation of colloidal iron due to oxidation by free chlorine at pH 5.5 and 6.5. (DOC source–Dismal Swamp; reaction time = 5 minutes; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	72
Figure 15:	Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 500 percent free chlorine; reaction time = 5 minutes; DOC source–Dismal Swamp; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	77
Figure 16:	Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC=10 mg/L; pH = 5.5; oxidant = 100 percent free chlorine; reaction time = 5 minutes; DOC source–Dismal Swamp; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	78
Figure 17:	Oxidation of uncomplexed Fe(II) by chlorine dioxide. (pH = 5.8; stoichiometric requirement = 0.24 mg chlorine dioxide per mg Fe)	84

Figure 18:	Chlorite oxidation of complexed Fe(II). (DOC source–Dismal Swamp; DOC = 5.4 mg/L; pH = 6.5; reaction time = 5 minutes; stoichiometric requirement = 0.3 mg chlorite per mg Fe)	88
Figure 19:	Formation of colloidal iron due to oxidation by chlorine dioxide at pH 5.5 and 6.5. (DOC source–Dismal Swamp; reaction time = 5 minutes; stoichiometric requirement = 1.2 mg chlorine dioxide per mg Fe)	90
Figure 20:	Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 500 percent chlorine dioxide; reaction time = 5 minutes; DOC source–Dismal Swamp; stoichiometric requirement = 1.2 mg chlorine dioxide per mg Fe)	93
Figure 21:	Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 100 percent chlorine dioxide; reaction time = 5 minutes; DOC source–Dismal Swamp; stoichiometric requirement = 1.2 mg chlorine dioxide per mg Fe)	94
Figure 22:	Turbidity profiles of alum coagulation without oxidant addition. (pH 5.7–6.0, DOC source–Dismal Swamp)	99
Figure 23:	Complexed Fe(II) removal by alum coagulation with and without oxidant addition. (Nominal DOC = 10 mg/L; pH 5.7–6.0; DOC source–Dismal Swamp; stoichiometric requirements = 0.64 mg as Cl ₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)	102

Figure 24:	Complexed Fe(II) removal by alum coagulation with and without oxidant addition. (Nominal DOC = 5 mg/L; pH 5.7–6.0; DOC source–Dismal Swamp; stoichiometric requirements = 0.64 mg as Cl ₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)	103
Figure 25:	Iron distribution after alum coagulation at 0, 12, and 48 mg/L alum and in the presence and absence of an oxidant. (DOC source–Dismal Swamp; Nominal DOC = 10 mg/L; pH 5.7–6.0; stoichiometric requirements = 0.64 mg as Cl ₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)	104
Figure 26:	Iron distribution after alum coagulation at 0, 12, and 48 mg/L alum and in the presence and absence of an oxidant. (DOC source–Dismal Swamp; Nominal DOC = 5 mg/L; pH 5.7–6.0; stoichiometric requirements = 0.64 mg as Cl ₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)	106
Figure 27:	The DOC distribution after alum coagulation at 0, 12, and 48 mg/L alum and in the presence and absence of an oxidant. (DOC source–Dismal Swamp; Nominal DOC = 5 mg/L; pH 5.7–6.0; stoichiometric requirements = 0.64 mg as Cl ₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)	107
Figure 28:	Complexed Fe(II) and DOC removal by alum coagulation at pH 6.8–7.3. (no oxidant addition; DOC source–Dismal Swamp)	108
Figure 29:	A comparison of the iron removal by alum coagulation with and without 200 percent free chlorine at pH 5.7–6.0. (conducted in Durham, NC; water spiked with 1 mg/L Fe; Nominal DOC = 4 mg/L; stoichiometric requirement = 0.64 mg as Cl ₂ per mg Fe)	110

Figure 30:	Effects of alum coagulation on iron and DOC at pH 5.7–6.0. (no oxidant addition; DOC source–University of Washington (100–10K))	112
Figure 31:	Effects of alum coagulation on iron and DOC at pH 5.7–6.0. (no oxidant addition; DOC source–University of Washington (<3K))	113
Figure 32:	Freundlich isotherms for DOC adsorption onto iron oxide solids after free chlorine and chlorine dioxide oxidation at pH 5.5 and 6.5	121

LIST OF TABLES

Table 1:	A comparison between the use of a jar-test apparatus and BOD bottles for iron oxidation studies	42
Table 2:	An evaluation of Fe(II) analysis methods	46
Table 3:	An evaluation of the boiling option of the bathophenanthroline procedure	48
Table 4:	A comparison between the 1,10-phenanthroline and ferrozine Fe(II) detection methods	50
Table 5:	The effects of Fe and DOC concentrations on potentiometric titration in the absence of an oxidant	52
Table 6:	Iron and DOC removal by alum coagulation of Fe(II) complexed with high molecular weight humic material (100–10K)	59
Table 7:	Summary of the free chlorine and ClO ₂ demands by Dismal Swamp humic materials	65
Table 8:	Summary of the free chlorine demand by Durham, NC humic materials	69
Table 9:	Typical DOC removals by a 100K ultrafilter after free chlorine iron oxidation	74
Table 10:	Exerted free chlorine demand during oxidation of complexed Fe(II)	75
Table 11:	Free chlorine oxidation of Fe(II) complexed with Durham, NC humic materials	79
Table 12:	Free chlorine oxidation of Fe(II) complexed with high molecular weight humic material (100–10K)	81
Table 13:	Free chlorine oxidation of Fe(II) complexed with low molecular weight humic material (<3K)	82
Table 14:	Residual chlorine species during oxidation of complexed Fe(II) by ClO ₂	86
Table 15:	Residual ClO ₂ and ClO ₂ ⁻ concentrations after ClO ₂ iron oxidation	87
Table 16:	Typical DOC removals by a 100K ultrafilter after ClO ₂ iron oxidation	92

Table 17:	Chlorine dioxide oxidation of Fe(II) complexed with high molecular weight humic material (100–10K)	95
Table 18:	Chlorine dioxide oxidation of Fe(II) complexed with low molecular weight humic material (<3K)	97
Table 19:	Typical percentages of DOC passing through a 100K ultrafilter after alum coagulation in the presence and absence of free chlorine and ClO ₂	100
Table 20:	Ratios of the changes in DOC to the changes in Fe after free chlorine and ClO ₂ oxidation of complexed Fe(II).....	119
Table 21:	Summary of the complexed iron removal by alum coagulation in the presence and the absence of an oxidant.....	124

Chapter I

INTRODUCTION

Iron in drinking water is considered a problem for several reasons: 1) staining of plumbing and laundered items; 2) encrustation of pipes by precipitated iron; 3) color and turbidity; and 4) possible taste and odor problems induced by iron bacteria. These issues, while strictly aesthetic in nature, have prompted the United States Environmental Protection Agency (USEPA) to establish a secondary maximum contaminant level of 0.3 milligrams per liter (mg/L) for iron.

Typically, iron removal in the absence of dissolved organic carbon (DOC) is achieved by oxidizing ferrous iron (Fe(II)) to ferric iron (Fe(III)) followed by solid/liquid separation. Oxidation of Fe(II) by oxygen ($O_2(aq)$) during aeration or by direct oxidant addition produces ferric hydroxide ($Fe(OH)_3(s)$) which is readily removed from drinking water. Chlorine and chlorine dioxide are two oxidants which are commonly used in water treatment for disinfection as well as iron and manganese oxidation.

When organic matter is present in natural water, iron is often complexed, becoming very resistant to oxidation. The resistance of complexed iron to oxidation by $O_2(aq)$ is well documented in the literature; however, more needs to be learned about iron complexation and the performance of various alternative oxidants in the removal of complexed iron from drinking water. The specific objectives of this study were:

1. To investigate the composition and extent of Fe(II) complexation in natural and synthetic waters;
2. To evaluate how the concentration and relative molecular weight distribution of the organic matter in water affects the ability of free chlorine and chlorine dioxide to oxidize complexed iron;
3. To evaluate the removal efficiency of complexed iron from water by alum coagulation, both in the presence and absence of an oxidant.

Chapter II

LITERATURE REVIEW

This chapter addresses the following topics:

1. Isolation and Characterization of Humic Substances,
2. Complexation of Iron by Humic Substances,
3. Oxidation of Ferrous Iron by Alternative Oxidants,
4. Iron and DOC Removal by Alum Coagulation.

Isolation and Characterization of Humic Substances

Organic species associated with natural waters have been separated into different categories. Thurman (1985) reported that total organic carbon (TOC) can be size classified as particulate organic carbon (POC, species with diameters greater than 0.45 micrometer (μm)) and dissolved organic carbon (DOC, species with diameters less than 0.45 μm). Within Thurman's DOC characterization exists a colloidal organic carbon fraction (diameters between 10 Angstroms and 0.45 μm), which is sometimes referred to as a humic substance.

Humic substances are more specifically differentiated by molecular weight ranges, functional groups, and specific absorbance. Humic substances are typically divided into two groups: fulvic acids and humic acids. Fulvic acids have a molecular weight between 500 and 2,000 atomic mass units (amu) and carboxylic and phenolic functional groups (Thurman, 1985). The ultraviolet (UV)-visible specific absorbance of fulvic acids at 254 nanometers (nm) ranges from 3 to 4.3 liter per centimeter-milligram of Carbon ($\text{L}/(\text{cm} * \text{mg}-\text{C})$)

(Reckhow et al., 1990). Humic acids, which have a molecular weight greater than 2,000 (and usually less than 100,000 amu), generally have fewer carboxylic functional groups than fulvic acids, but an equivalent number of phenolic functional groups (Thurman, 1985). The specific absorbance of humic acids ranges from 4.8 to 7.4 L/(cm * mg-C) (Reckhow et al., 1990). In surface waters, approximately 30 to 50 percent of DOC is fulvic acid, whereas approximately 10 percent of the DOC is humic acid. The remaining percentage of DOC consists of carbohydrates, carboxylic acids, hydrophilic acids, hydrocarbons, and amino acids (Thurman, 1985).

Thurman (1984) reported that 30 to 50 percent of the TOC of natural waters is aquatic humic substances. Humic substances are yellow to brown colored, polymeric acids which can be leached from soil and sediments, and are known to be natural by-products of vegetative degradation. They are comprised of carbon (generally greater than 50 percent) and varying amounts of nitrogen, oxygen, phosphorus, sulfur, and ash (Thurman, 1985). In most surface waters, the concentration of humic acids ranges from 100 micrograms per liter (ug/L) to 4 mg/L, with concentrations in bogs and marshes sometimes exceeding 100 mg/L (Thurman, 1985). Detailed information regarding the composition and characteristics of organic carbon is available in the literature; Thurman (1985) and Liao et al. (1982) are two sources which review these topics.

Techniques for the Isolation of Humic Substances

Precipitation, freeze drying, vacuum evaporation, reverse osmosis, ultrafiltration, and solvent extraction are examples of isolation/concentration

procedures that are available for researchers to attain a stock solution of humic substances. However, these methods are often not suitable for concentrating large volumes of water containing low concentrations of DOC.

Thurman and Malcolm (1981) developed an adsorption chromatography procedure which can isolate humic substances from large volumes of water. The procedure involves the adsorption of the humic species onto a macroporous XAD-8 resin, followed by a base extraction. Extensive cleaning of the resin prior to isolation is necessary to prevent organic carbon interference (Aiken, 1988). Researchers such as Aiken (1988), Dempsey *et al.* (1984), and Collins *et al.* (1986), have utilized this procedure and found it to be appropriate for the isolation of humic substances. However, chemical alteration of the organic species due to the extreme pH variations during adsorption and desorption are unavoidable. Irreversible ester hydrolysis can occur under both acidic and basic conditions; thereby altering the chemical structure of the original organic material (Aiken, 1988).

Molecular Weight Fractionation by Ultrafiltration

Ultrafiltration, small angle x-ray scattering, centrifugation, and gel permeation are four common methods for separating DOC into different molecular weight fractions. This research utilized ultrafiltration, which involved filtering samples under nitrogen pressure through ultrafilters; these ultrafilters retain and allow passage of DOC molecules, thus providing separation by apparent molecular size. Buffle *et al.* (1978) stated that the ultrafiltration cell fractionation process is not greatly effected by changes of the pH, pressure, or electrolyte concentrations. The author also concluded that variations in

analytical results involving ultrafiltration were due to humic and fulvic acid aggregation.

Collins et al. (1986) defined the fractionation of DOC by ultrafiltration as an apparent molecular weight distribution. The values collected from experimentation suggest trends in the molecular weight fractions rather than absolute values.

Complexation of Iron by Humic Substances

The complexation of iron by humic substances is well documented in the literature. Several researchers have focused on different aspects of the complexation phenomenon such as mechanisms, extent of stabilization, kinetics of and resistance to oxidation, and effects of different water quality characteristics on complexation.

Mechanisms of Complexation

Complexation of iron by organic material occurs naturally in the environment. Two mechanisms were originally hypothesized to cause complexation: peptization and chelation. Peptization involves the adsorption between organic molecules and ferric hydroxide, thus a particulate/colloidal interaction. Chelation involves a chemical reaction between iron and organic material in a dissolved form. Iron essentially "becomes" a part of the organic molecule as functional groups of the organic molecule interact with free iron.

Shapiro (1964) examined the relationships between Fe(III) and organic color to better understand the difficulties associated with iron removal in highly colored waters. He hypothesized that iron remains "soluble" due to peptization

(accompanied by moderate chelation). Later research by Ghassemi and Christman (1968), as well as Oldham and Gloyna (1969), showed that peptization does occur; however, the authors concluded that iron stability in organic-laden waters is due principally to chelation.

Further studies with complexed iron have revealed specific characteristics of chelation. Jobin and Ghosh (1972) reported that organic material with carboxylic and hydroxyl groups readily forms complexes with iron. These complexes can retard Fe(II) oxidation by $O_2(aq)$. Also, fulvic acids generally have carboxylic and hydroxyl functional groups, whereas humic acids are known to have fewer carboxylic groups (Thurman, 1985). This information helps to address the iron complexation trends with humic and fulvic acids.

Effects of pH on the Complexation of Iron

Ghassemi and Christman (1968) investigated the association of iron with organic color. Sephadex gel filtration was used to size fractionate organic matter, and to analyze the association with iron in these fractions. Data from pH variation experiments involving elution from the column revealed that Fe(II) and Fe(III) stability was greatest at a near neutral, but slightly acidic pH. However, Shapiro (1964) found greatest Fe(III) stability at a pH between 9 and 11.

Solution pH had a substantial effect on the complexation of Fe(II) with humic acids in experiments conducted by Oldham and Gloyna (1969). No complexation occurred at pH 5; however, greater complexation was detected as the pH was increased to 8. Likewise, polarographic studies undertaken by

Theis and Singer (1974) showed that the extent of Fe(II) complexation increased as the solution pH was increased from 5 to 7.

Water Quality Characteristics

Cameron and Liss (1984) found that the presence of inorganic anions such as chloride, bicarbonate, sulfate, and nitrate induced minimal stabilization of Fe(III). At high concentrations, silicate stabilized Fe(III); however, the silicate concentration in natural waters is usually not great enough to enhance stabilization of Fe(III). Also, phosphate concentrations between 0.4 and 250 mg/L almost completely stabilized Fe(III), especially in the pH range between 6.5 and 11.

Extent of Complexation

Cameron and Liss (1984) investigated different iron complexation mechanisms found in fresh water systems. Humic and tannic acids were the two organic complexing agents used; both were able to stabilize Fe(III) in solution. Tannic acid (which is structurally similar to humic acid) was found to stabilize approximately 15 moles of Fe(III) for every mole of tannic acid in solution. Similar results were observed by Theis and Singer (1974) who concluded that, for Fe(II) and Fe(III), the extent of iron complexation increases as the tannic acid to iron ratio increases. Cameron and Liss (1984) also reported that humic acids completely complexed Fe(III) at a DOC-to-iron ratio of <3.4:1. The 0.45 μm filter was used to remove the particulate iron from the 'dissolved' iron.

The generalization that every mg/L of DOC in solution has approximately 1 microequivalents per liter (ueq/L) of metal-binding capacity was reported as "a rough rule of thumb" by Thurman (1985). This corresponds to an iron binding capacity of approximately 0.02 to 0.03 mg Fe per mg DOC. Theis and Singer (1973) observed that 0.005 mg Fe(II) was stabilized by each mg of DOC in solution. This result was based on filtration through a 0.45 μm filter. Perdue *et al.* (1976) indicated that iron stabilization in the Satilla River of south-eastern United States occurred at approximately 0.05 mg Fe per mg DOC. The filtration method of this study was not mentioned. The nature of iron (Fe(III) or Fe(II)) also influences the stability of the iron complex. Trivalent metals, such as Fe(III), form more stable complexes with organic matter than divalent metals, such as Fe(II) (Alberts and Giesy, 1983). From these studies, it was evident that the complexation ability of iron by DOC varies with the type of DOC present and the nature of iron (Fe(II) or Fe(III)) in solution.

Behavior of Iron in the Presence of $\text{O}_2(\text{aq})$ and DOC

One of the earlier studies on complexation/oxygenation of iron was conducted by Jobin and Ghosh (1972). The presence of humic acids retarded the oxidation rate (by $\text{O}_2(\text{aq})$) of Fe(II), with increased humic acid concentration yielding poor Fe(II) oxidation by $\text{O}_2(\text{aq})$. Also, the rate of oxidation (by $\text{O}_2(\text{aq})$) for Fe(II) complexed with tannic acid was slower than the oxidation rate for Fe(II) complexed with humic acid.

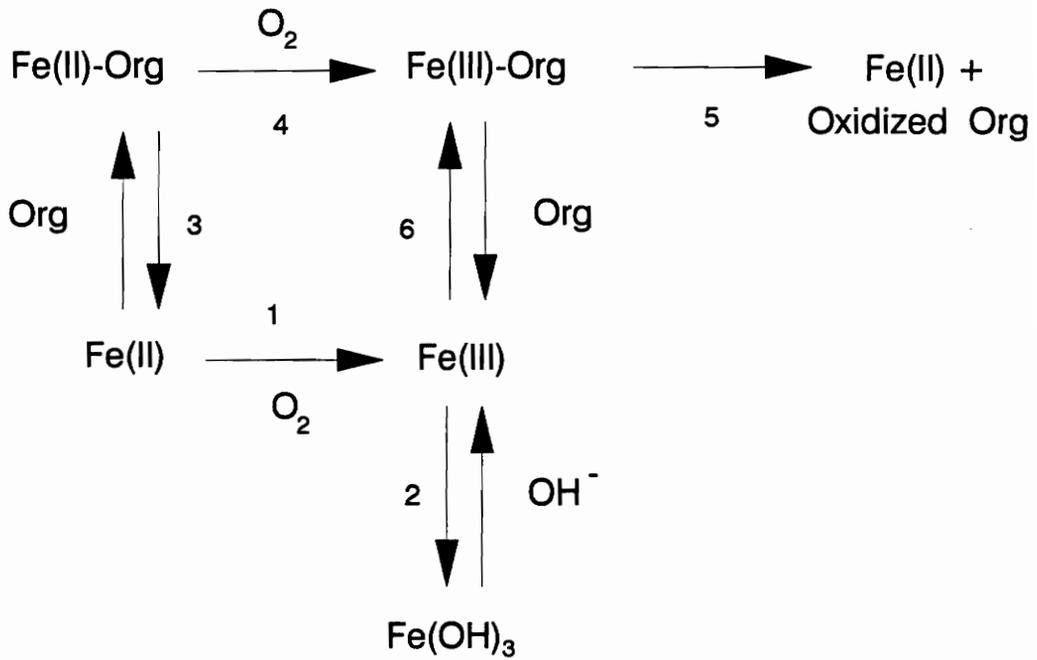
Theis and Singer (1974) also investigated how the presence of different types of DOC affected Fe(II) oxidation by $\text{O}_2(\text{aq})$. Ferrous iron oxidation was completely inhibited when Fe(II) was complexed with tannic acid, glutamine,

and pyrogallol. The authors also provided a qualitative summary regarding the kinetic rates of Fe(II) oxidation by $O_2(aq)$ in both the presence and absence of DOC. The Fe(II) oxidation by $O_2(aq)$ rate was found to be partially or completely retarded when in the presence of organic species. However, it was accelerated when in the presence of an oxidation enhancer such as citric acid.

As seen throughout the literature, researchers have worked to better understand the different aspects regarding iron complexation. Hem (1960) found that Fe(III) was reduced to Fe(II) in the presence of tannic acid (5 mg/L) at pH values less than 4. Stumm and Singer (1966) suggested that there exists a Fe(II)–Fe(III) couple which acts as a catalyst for the oxidation of organic matter. Also, because of the cyclic reactions between Fe(II), Fe(III), and organic material, Jobin and Ghosh (1972) noted that organic compounds both retard and catalyze Fe(II) oxidation. Theis and Singer (1974) observed a steady–state concentration of Fe(II) during the oxidation by $O_2(aq)$ of a Fe(II)–tannic complex. It was hypothesized that tannic acid was oxidized by $O_2(aq)$ prior to any Fe(II) oxidation. This indicates the formation of an oxidation resistant complex between Fe(II) and tannic acid.

Theis and Singer (1974) outlined a model (shown in Figure 1) which represents the interactive reactions between Fe(III), Fe(II), and DOC. This diagram shows the competitive nature of Fe(III) being reduced to Fe(II), oxidized organic matter, and the complexation of Fe(II) and Fe(III). The authors describe this model as follows:

"In the absence of appreciable quantities of dissolved organic matter, ferrous iron is oxidized quite rapidly upon the introduction of oxygen to ferric iron which precipitates as $Fe(OH)_3$ and is removed from the system (Reactions 1 and 2...). If significant



Source: Theis and Singer 1974.

Figure 1. Model depicting the behavior of iron in the presence of organic matter (Org) and dissolved oxygen (O_2).

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 the complexed ferrous iron (Reaction 4) proceeds via a slow step...to form the corresponding ferric complex with the organic matter. The resultant Fe(III) is unstable and is reduced by the organic compound (Reaction 5)...An additional competition exists for the ferric iron between the organic species and hydroxide (Reactions 2 and 6). Again, pH is a determining factor in regard to the relative proportions of ferric iron complexed by organic matter (Reaction 6), reduced by the organic compounds (Reaction 5), or complexed by hydroxide (Reaction 2)."

Recent research has focused on more specific aspects of complexation and oxidation. Eisenreich et al. (1980) conducted a study on metal transport in the upper Mississippi River. Ultrafiltration tests revealed that the iron was often retained in the higher molecular weight fractions of 25K to 100K (25,000 to 100,000 AMU) and was colloidal in nature. Also, iron in the dissolved phase increased as the suspended solids concentration decreased.

Knocke et al. (1990) analyzed Fe(II) complexed with humic acid. The authors observed that most of the Fe(II) was complexed with DOC having an apparent molecular weight greater than 30K. Solution pH greatly influenced the distribution of complexed iron within the molecular weight fractions. At a higher pH, the iron was retained by higher molecular weight organics. Also, complexed Fe(II) was not readily oxidized by oxygen or oxidizing agents like potassium permanganate, chlorine, hydrogen peroxide, and chlorine dioxide. This finding was based on iron species removal by a 0.2 um pore size membrane filter, with retention on the filter representing an oxidized iron species.

From the literature regarding complexation of iron, it is evident that pH is an important parameter. The type, concentration, and molecular weight distribution of the organic matter also influences complexation

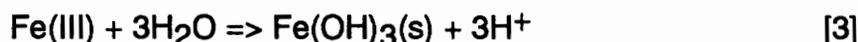
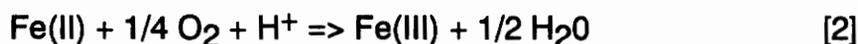
Oxidation of Ferrous Iron by Alternative Oxidants

Oxidation of Fe(II) can be achieved by aeration ($O_2(aq)$) or by the addition of oxidants such as potassium permanganate ($KMnO_4$), ozone (O_3), chlorine ($HOCl$ or OCl^-), chlorine dioxide (ClO_2), or hydrogen peroxide (H_2O_2). In water treatment operations, oxidation of Fe(II) to Fe(III) generally occurs prior to sedimentation and filtration.

The half-cell reaction equation for iron is as follows:



Oxidation of Fe(II) to $Fe(OH)_3(s)$ by aeration occurs as follows:



The summation of these two reactions yields Equation 4:



Stumm and Lee (1961) concluded that the oxidation rate of Fe(II) by O_2 is first-order with respect to the Fe(II) concentration and the partial pressure of oxygen. Also, the authors found that increases in solution pH, alkalinity, and temperature accelerate the Fe(II) oxidation rate.

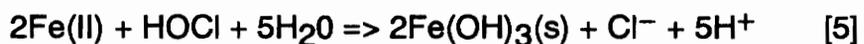
Jobin and Ghosh (1972) also evaluated the kinetics of iron oxidation/reduction. Their results regarding the kinetics of Fe(II) oxidation by O_2 and the effects of buffer intensity on Fe(II) oxidation correlated well with those of Stumm and Lee (1961).

Sung and Morgan (1980) investigated the kinetics of Fe(II) oxidation by O_2 in aqueous systems, providing information about temperature effects, pH effects and the influence of anions on the oxidation rate. Apparently, an increase in the ionic strength yields a decrease in the rate of Fe(II) oxidation by $O_2(aq)$. This is also true in the presence of anions like nitrate, chloride, bromide, iodide, and sulfate. Tests with varied alkalinity revealed no trend in altering the reaction kinetics except for the additional ionic strength which was introduced to the experiment.

Oxidation by Free Chlorine

For years, chlorination has been employed by water utilities for disinfection along with iron and manganese oxidation, taste and odor control, prevention of algal growths, and other water treatment facility controls. It is estimated that chlorination of water at treatment facilities began near the turn of the century, and that since that time, nearly all facilities in the United States which disinfect their water have used chlorine (White, 1972).

Free chlorine readily oxidizes Fe(II) when organic material is not present (Nordell, 1961). The equation for Fe(II) oxidation by chlorine is as follows:



In this reaction, two electrons are transferred, and 0.64 mg as Cl_2 of hypochlorous acid (HOCl) is consumed for every 1.0 mg Fe(II) oxidized. The predominant chlorine species within the pH range of experimentation (5.5 to 7.5) for this research is HOCl (Snoeyink and Jenkins, 1980), and will henceforth be addressed as 'free chlorine.'

In the presence of DOC, Fe(II) is not readily oxidized by free chlorine. Nordell (1961) reported the inability of free chlorine to oxidize chelated iron. Two separate waters having iron concentrations of 3.5 and 12 mg/L were tested by adding free chlorine (dosages as high as 48 mg/L), but no substantial iron removal was achieved. Similar results were reported by Knocke *et al.* (1990) who based iron removal on retention by a 0.2 μm pore size membrane filter. The authors reported no iron removal after free chlorine oxidation from solutions containing fulvic acids at pH values of 6 and 7.5.

An additional issue regarding free chlorine oxidation is the decrease in the oxidizing capacity of free chlorine when water treatment facilities apply free chlorine to organic-laden water. Noack and Doerr (1978) investigated the free chlorine demand by humic acids and found an initial second-order reaction followed by a decreased rate over time. At a solution pH of 6.0, the free chlorine demand was 0.46 mg Cl_2 /mg humic acid. This oxidant demand by humic substances must be accounted for to ensure adequate oxidation by free chlorine.

Oxidation by Chlorine Dioxide

Chlorine dioxide is used in water treatment for disinfection, taste and odor control, and iron and manganese oxidation (Aieta and Berg, 1986). It is a highly soluble, greenish-yellow gas which has an intense, distinct odor (Rosenblatt, 1978). Chlorine dioxide is extremely volatile because it remains as a dissolved gas when placed in solution rather than hydrolyzing (Aieta and Berg, 1986). Water treatment facilities usually apply ClO_2 to raw-water, before settling, before filtration, and/or after filtration at dosages ranging from 0.1 to 5

mg/L (Aieta and Berg, 1986). In recent years, the use of ClO_2 as an alternative disinfectant has been vigorously investigated due to the formation of trihalomethanes (THM's) in waters treated with chlorine. Unlike chlorine, ClO_2 does not react with organic substances to form THM's (Rav-Acha, 1984).

There are two possible reaction equations for the oxidation of Fe(II) by ClO_2 . If ClO_2 is reduced to chloride (Cl^-), the following equation applies:



At a pH of 7, five electrons are transferred in the reduction of ClO_2 to Cl^- . Only 0.24 mg of ClO_2 are required to oxidize 1.0 mg Fe(II).

If ClO_2 is reduced to chlorite (ClO_2^-), the following reaction equation applies:



In this reaction, only one electron is transferred, thus requiring 1.2 mg of ClO_2 to oxidize 1.0 mg of Fe(II). This study will investigate each possibility to determine which of the above mentioned stoichiometric relationships exists for the oxidation of complexed Fe(II) by ClO_2 . However, Rosenblatt (1978) stated that when ClO_2 oxidizes an electron-rich substance, like amines or organic substances, ClO_2^- is formed; thus, less oxidizing capability is available.

Knocke *et al.* (1991) reported that the oxidation of uncomplexed Fe(II) by ClO_2 occurs within seconds of contact time at pH values greater than 5.5. Also, when oxidizing Fe(II)-humic acid complexes, ClO_2 oxidized only 10 percent of the original Fe(II) in the test solution at pH values of 6.5 and 8.0. In these studies, oxidized iron was represented by retention by a 0.2 μm pore size membrane filter.

As with chlorine, there exists a ClO_2 demand by humic materials. Noack and Doerr (1978) measured a ClO_2 demand of 0.92 mg ClO_2 /mg humic acid at pH 6.0. Likewise, Knocke *et al.* (1990) reported that a 10 mg/L humic acid solution reduced the ClO_2 concentration from 5 to 2 mg/L within one minute of contact time at pH 6.3.

Iron and DOC Removal by Alum Coagulation

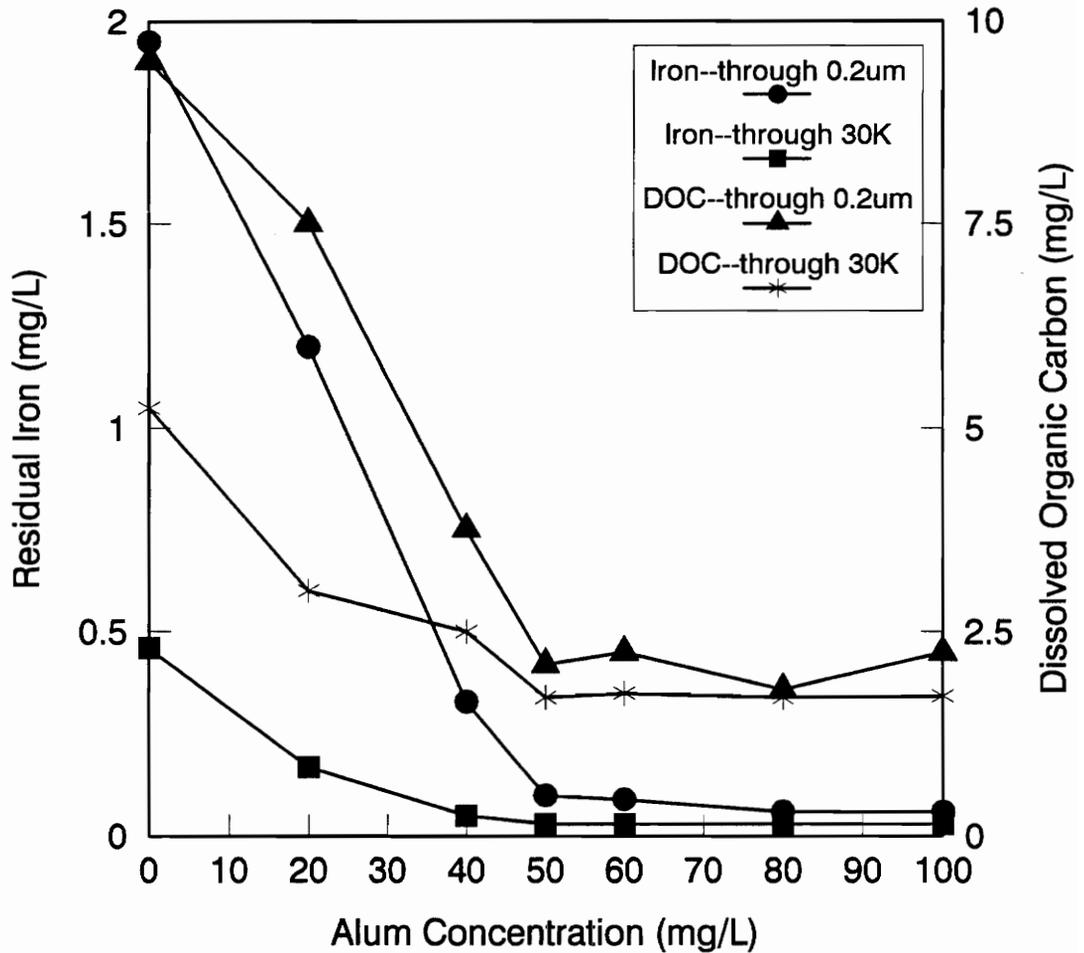
Many studies have been conducted to determine the optimum conditions and the mechanisms for the removal of organic color by alum coagulation. The mechanisms of humic substances removal by alum coagulation are hypothesized to be either precipitation by the dissolved aluminum species, adsorption of humic substances onto aluminum solid species, or a combination of the two mechanisms (Dempsey *et al.*, 1984). Optimum pH and coagulant dose are site specific; the type and concentration of organic species, and the pH buffering capabilities of the water greatly influence the efficiency of coagulation by alum (Dempsey *et al.*, 1984).

Black and Willems (1961) analyzed two different waters and found that in general, the optimum pH range for color removal by alum coagulation in these waters was between 4.8 and 5.5, with increased alkalinity improving color removal. Hall and Packam (1965) found that fulvic acids are more difficult to remove by alum coagulation than humic acids. Rest (1982) concluded that the best DOC removal by alum coagulation was achieved at a pH between 5.2 and 5.3. High molecular weight organic compounds (greater than 42K) were more readily removed by alum coagulation than lower molecular weight compounds.

Few detailed studies have been conducted using alum coagulation for the removal of complexed iron. Alum coagulation at a pH near 6.5 reduced the iron concentrations in the two water sources cited by Nordell (1961) to 0.1 and 0.3 mg/L. Knocke *et al.* (1990) also conducted alum coagulation studies with complexed iron and further investigated the relationship between iron and DOC. Ferrous iron tended to complex with the higher molecular weight compounds. This complexed Fe(II) was then efficiently removed by alum coagulation (Figure 2). Coagulation tests with fulvic acids (Figure 3) yielded a residual Fe(II) concentration of 0.6 mg/L. This residual Fe(II) was found to be complexed by the lower molecular weight fractions (<30K) of DOC. As shown by Figures 2 and 3, the apparent molecular weight of the DOC influenced the iron removal efficiency by alum coagulation. Knocke *et al.* (1990) also reported that the addition of 2.5 mg/L KMnO_4 to the test solution of Figure 3 resulted in a residual soluble iron concentration of 0.1 mg/L. Thus, the Fe(II) complexed by lower molecular weight organics was susceptible to chemical oxidation.

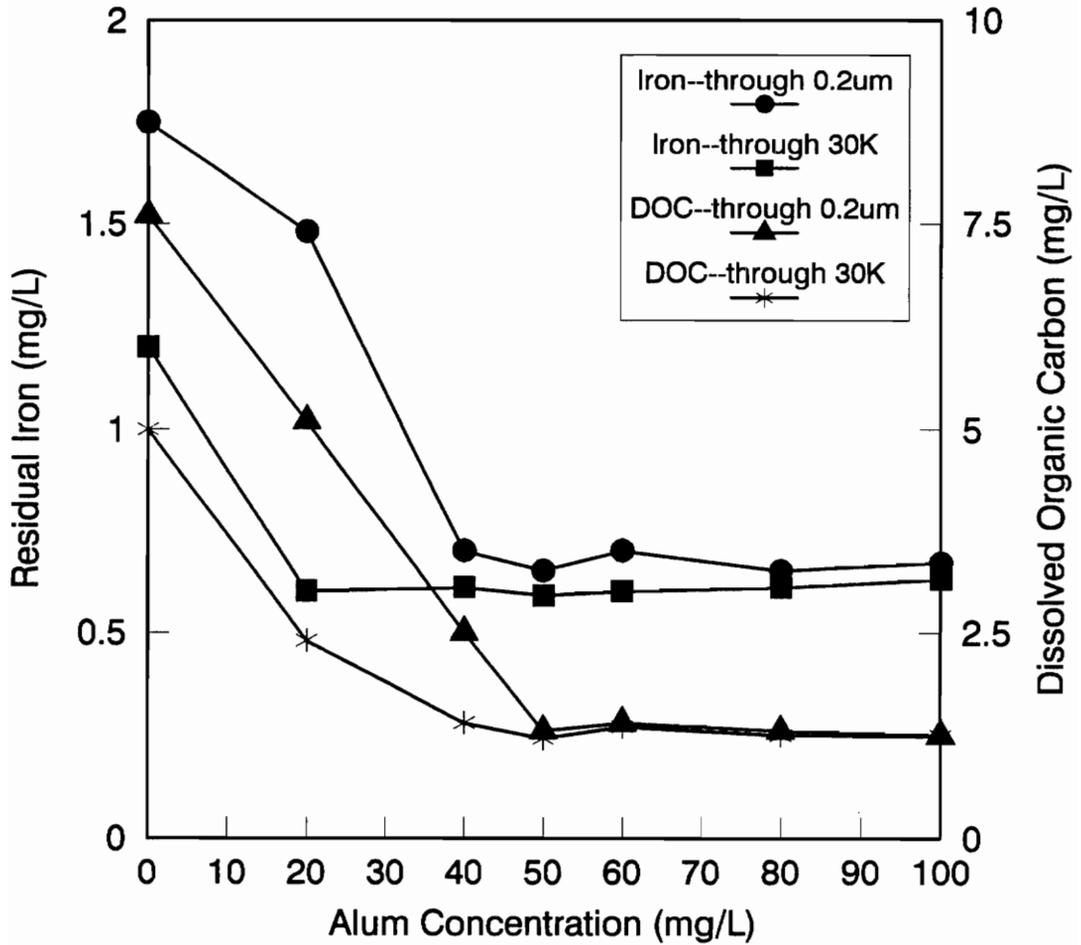
Summary

From the literature, it is evident that a thorough investigation of Fe(II) complexed by humic substances is necessary to understand the influences of different water quality characteristics on Fe(II) removal by oxidation and alum coagulation. Obviously, solution pH is an important parameter which can effect both the extent of Fe(II) complexation and the oxidation capacity of oxygen (and possibly free chlorine and ClO_2). The only research regarding the oxidation of complexed Fe(II) to date focuses on iron speciation by a 0.2 μm pore size membrane filter and a 30K ultrafilter. Further fractionation of complexed iron



Source: Knocke et al. 1990.

Figure 2. Removal of soluble iron and DOC by alum coagulation at pH 6.0 - 6.3. (DOC source - Provincial Brook humic acids)



Source: Knocke et al. 1990.

Figure 3. Removal of soluble iron and DOC by alum coagulation at pH 6.0 - 6.3. (DOC source - Provincial Brook fulvic acids)

solutions could reveal trends in iron speciation due to oxidation and alum coagulation. Also, no literature addressed the differentiation between Fe(II) and Fe(III) in complexed iron solutions which were oxidized or coagulated. The effects of pH, oxidation by free chlorine and ClO₂, and alum coagulation on iron speciation (between Fe(II) and Fe(III)) could reveal important characteristics about the behavior of iron under these conditions.

The literature citations presented here also provide information that will help to develop the methodology for experimentation. A stock humic substance from a natural aqueous environment can be obtained by the isolation procedure of Thurman and Malcolm (1981). Ultrafiltration and specific absorbance tests will help to characterize the humic material. Variations in solution pH, and the type and concentration of organic matter will be monitored to evaluate their effects on the oxidation of complexed Fe(II) by free chlorine and ClO₂. Also, the influence of different pH ranges, DOC concentrations, and molecular weight distributions of DOC on iron removal by alum coagulation, both in the presence and absence of an oxidant, will be evaluated.

Chapter III

METHODS AND MATERIALS

Introduction

The three main sections of this chapter are: (1) Physical and Chemical Analysis, which explains the analytical methodology used for each different water quality characteristic; (2) Laboratory Procedures, which addresses the methodology for all laboratory experiments; and (3) Field Experiments, which outlines the purpose and procedures for all off-campus experiments.

Physical and Chemical Analysis

Total Iron Measurement

Total iron concentrations were determined by a Perkin-Elmer Model 703 (Norwich, CT) atomic absorption spectrophotometer (AAS). Instrument settings included a wavelength of 248.3 nm and a slit width of 0.3 millimeters (mm). The detection limit for iron detection was 0.03 mg/L. The concentrations of the Fe(II) standards that were used for instrument calibration were 1.0 mg/L, 5.0 mg/L and 8.0 mg/L. Samples were collected in glass test tubes and acidified with 1–2 drops of concentrated HNO₃.

Samples containing complexed iron were digested to determine if digestion was necessary before iron analysis by AAS. An EPA experiment (Methods for Chemical Analysis of Water and Wastes, 4.1.4, Chapter 6,7) which involved the addition of concentrated HCl followed by evaporation of the sample, proved that digestion was not necessary.

Dissolved Organic Carbon

Dissolved organic carbon concentrations were quantified using a Dohrmann Carbon Analyzer, Model DC-80 (Xertex, Santa Clara, CA). Manufacturer recommendations were followed for operation and sample preservation. The instrument had calibrations at 10, 400, and 2000 mg/L DOC. Samples for DOC determination were collected in glass vials and acidified to approximately pH 2 with 85 percent phosphoric acid.

Turbidity

Samples (25 mL) were removed from the test vessels by pipet and placed in glass cuvetts for turbidity analysis with a Hach Model 2100A Turbidimeter. Standards used for the calibration of the instrument were 0.2, 1, 10, 100, and 1000 nephelometric turbidity units (NTU).

Specific Absorbance

The UV absorbance by solutions containing humic substances was measured with a Beckman DU-6 UV Spectrophotometer (Irvine, CA). A wavelength setting of 254 nm was used (Reckhow et al., 1990).

pH

Solution pH was determined with a Fisher Accumet pH meter (Model #610A). The meter was calibrated with standard buffers (pH 4, 7, and 10).

Color Transmittance

The three ferrous iron detection methods required measurement of solution transmittance which was accomplished with a Bausch & Lomb Spectronic 20 Colorimeter. Wavelength settings were test-specific and are discussed in the Ferrous Iron Detection section of this chapter. Three standards of known concentration and a blank were used to produce a standard curve. Typical R^2 values for the standard curves ranged from 0.95 to 0.98.

Oxidant Residual

Chlorine, ClO_2 , ClO_2^- , and ClO_3^- concentrations were quantified with a Fisher Scientific Computer-Aided Titrimeter (Model 465) (Pittsburgh, PA) which utilized potentiometric titration with 0.00564 N phenylarsine oxide (PAO). The Aieta et al. (1984) titration procedure for free chlorine and ClO_2 concentrations was modified as follows:

1) For free chlorine studies: Residual free chlorine analysis involved PAO titration of a 100 mL sample containing 1 mL phosphate buffer (pH 7) and approximately 1 g of potassium iodide (KI). Aieta et al. (1984) stated that this analysis determined free chlorine + $1/5 \text{ClO}_2$; however, since no ClO_2 was added to the prepared chlorine solutions, the ClO_2 concentration was assumed to be 0.0 mg/L. The free chlorine concentration was calculated as follows:

$$\text{Cl}_2 \text{ (mg/L)} = \frac{\text{PAO (mL)} * 0.00564 \text{ (eq/L)} * 35.450 \text{ (mg/eq)}}{\text{mL sample}} \quad [9]$$

2) For ClO_2 studies: Because ClO_2 solutions disproportionate over time, it was necessary to quantify all of the chlorine species present in solution.

Analyses of free chlorine, ClO_2 , ClO_2^- , and ClO_3^- were required and these analyses involved several separate titrations. Chlorate determination, as outlined by Aieta *et al.* (1984), produced negative results, so ion chromatography was used instead.

During ClO_2 oxidation studies, minimal amounts of free chlorine were present; therefore, the free chlorine concentration was assumed to be 0.0 mg/L. The procedure for free chlorine titration was also used for ClO_2 determination. The ClO_2 concentration was determined as follows:

$$\text{ClO}_2 \text{ (mg/L)} = \frac{5 * \text{PAO (mL)} * 0.00564 \text{ (eq/L)} * 13.490 \text{ (mg/eq)}}{\text{mL sample}} \quad [10]$$

Chlorite and ClO_3^- concentrations were quantified using a Dionex Ion Chromatograph (IC) (Sunnyvale, CA) with a Dionex IonPac AS9 anion column. The method for ClO_2^- and ClO_3^- analysis (as described by Ledder, 1991) utilizes a flow rate of 2 mL/min, and a specific suppressant and eluant. The suppressant was used to suppress the conductance of the background ions and enhance the conductivity of the analytes. The suppressant had a concentration of 0.025 N H_2SO_4 . The eluant was comprised of 0.4 mM NaHCO_3 and 2.8 mM Na_2CO_3 . Three standards of known concentration (between 0 and 15 mg/L for ClO_2^- , and between 0 and 2 mg/L for ClO_3^-) and a blank established a standard curve with typical R^2 values ranging from 0.95 to 0.99. This procedure was also used for Cl^- concentration determination during ClO_2 oxidation studies.

Temperature Considerations

The temperature of the test solutions did not fluctuate during experimentation. Temperatures were maintained between 20 to 22°C.

Laboratory Procedures

Isolation of Humic Substances

Isolation of humic substances onto an XAD-8 Amberlite resin (obtained from Rohm & Haas, Philadelphia) was performed according to the procedure outlined by Thurman and Malcolm (1981), while incorporating modifications presented by Thurman (1984). The granular resin required extensive cleaning. An initial saturation and rinsing with 0.1 N sodium hydroxide (NaOH) was followed by sequential 24-hour Soxhlet extractions with methanol, hexane, acetonitrile, and methanol, in that order. The resin was stored in methanol in amber glass containers.

In March, 1991, approximately 350 liters (L) of water were collected from the Jerico Ditch in Dismal Swamp, located near Suffolk, Virginia. The swamp water had an initial DOC of 106 mg/L, turbidity of 1.2 NTU, and a pH of 3.3.

Approximately 377 cubic centimeters (cm³) of resin was thoroughly rinsed with Milli-Q, carbon-free, water before it was packed into the column. Glass wool was inserted into a glass column to prevent leakage of the resin. For this procedure, the glass column had a top and bottom port, along with a side port near the top of the column which helped to establish a constant hydraulic head across the resin. The diameter of the column was 4 cm, and the length was 60 cm. After the resin was packed into the column, 50 bed volumes (a bed volume equals the volume of the resin in the column) of Milli-Q water

was passed through the resin. Next, a bed volume of 0.1 N NaOH was passed through the column. This was followed by a bed volume rinse with 0.1N hydrochloric acid (HCl). Two additional base-followed-by-acid rinses were conducted; thus, the resin in the column was acidic after the final rinse.

The water which was processed for DOC isolation was initially acidified to pH 2 to 2.5 with concentrated HCl. Since the initial turbidity of the swamp water was low, filtration through a sand filter was not necessary. This water was then passed through the resin at a rate of approximately 15 bed volumes per hour. The resin became discolored by the sorbed humic substances. The DOC of the effluent was monitored until a satisfactory "break through" point was established. When this occurred, processing was terminated. Next, five void volumes (a void volume of the XAD-8 resin equals 60 percent of the bed volume) of 0.1 N NaOH was pumped through the resin in a countercurrent direction. A flow rate of five bed volumes per hour was used. The 0.1N NaOH released the humic material from the resin. The eluate was collected in an amber glass bottle, acidified to a neutral pH with nitric acid (HNO₃), and purged with nitrogen gas. The humic material was stored in the refrigerator at 4 to 5°C. Approximately 11 liters of stock humic substances were produced having an average DOC concentration of 1180 mg/L. The measured iron concentration in the Dismal Swamp stock DOC solution was <0.01 mg Fe per mg DOC.

In August, 1991, isolation of humic substances was conducted at the terminal reservoir of the Williams Water Treatment Plant in Durham, NC. During the isolation, raw-water DOC concentrations ranged from 3.8 to 6 mg/L. The extraction yielded approximately 4 liters of stock humic substances with a

composite DOC concentration of 160 mg/L. The Durham, NC DOC source contained <0.02 mg Fe per mg DOC.

A third humic source was obtained from the University of Washington. Humic substances from Lake Pleasant, near Seattle, Washington were adsorbed onto iron oxide solids at pH 3.8 (Benjamin, 1991). The initial TOC of the lake water was 45 mg/L; the adsorption procedure that was used involved dilution (10:1) of the lake water prior to adsorption. The humic substances were extracted from the iron oxide solids with 0.5 N NaOH. This DOC source was separated by ultrafiltration into two separate molecular weight fractions: between 100–10K (66 mg/L DOC) and <3K (135 mg/L DOC), so that comparative analyses could be performed. The measured iron concentrations in these two stock solutions was <0.01 mg Fe per mg DOC.

Characterization of Humic Substances

Fractionation by Ultrafiltration: Ultrafiltration for the fractionation of water samples was performed with an Amicon ultrafiltration cell apparatus (Model 8200, Amicon Div., W. R. Grace & Co., Danvers, MA). Most humic and fulvic acids found in natural waters have a molecular weight less than 25,000 amu (Theis and Singer, 1973). For this reason, ultrafilters that retained molecules with molecular weights of 100K (100,000 amu), 30K, 10K, 3K, and 1K were used during experimentation. The samples were filtered through ultrafilters under a nitrogen gas pressure of 40 pounds per square inch (psi). The volume of each ultrafiltration cell was approximately 200 milliliters (mL), and all but 40 to 50 mL of the sample was passed through the ultrafilter.

New ultrafilters required a 24-hour saturation in Milli-Q water prior to use. Used ultrafilters were stored in a one percent HNO₃ solution. Prior to each ultrafiltration test, approximately 200 mL of organic-free water was passed through the ultrafilter. Ultrafilters were cleansed after each filtration by lightly rubbing a finger tip across the top of the ultrafilter with a dilute soap (commercial liquid soap) solution.

The DOC molecular weight distribution was evaluated by ultrafiltration of a 10 mg/L DOC solution. The 100K, 30K, 10K, 3K, and 1K ultrafilters were used. This was conducted in a parallel system; samples were passed through each ultrafilter separately. The DOC passing through each ultrafilter was measured to help establish the molecular weight distribution of the humic material.

Specific Absorbance: The specific absorbance of the extracted humic substances was determined by measuring the UV absorbance at 254 nm with a UV spectrophotometer. The following equation was used to calculate the specific absorbance:

$$\text{Specific Absorbance} = \frac{\text{Absorbance (1/cm)} * 100}{\text{DOC (mg/L)}} \quad [8]$$

(L/(cm * mg-C))

Reckhow et al. (1990) stated that the specific absorbance of humic and fulvic acids is between 3 and 7.3 L/(cm * mg-C). Each stock humic solution was analyzed for specific absorbance.

Estimation of Relative Fraction of Humic/Fulvic Acids: The Thurman and Malcolm (1981) procedure for the separation of humic acids from fulvic

acids by precipitation was conducted. A 50 mL sample of the stock solution was acidified to pH 1 with concentrated HCl. After a 24-hour settling period, the sample was centrifuged with a Beckman Model J21C centrifuge for 30 minutes at 14,000 revolutions per minute (rpm). The supernatant (primarily fulvic acids) was decanted from the precipitate (primarily humic acids). The relative amounts of humic and fulvic acids in each stock DOC solution were quantified by measuring the DOC concentration of the supernatant.

Definition of Dissolved, Colloidal, and Particulate Species

For this study, iron was separated into three classifications: dissolved, colloidal, and particulate fractions. Dissolved iron was defined as the iron that passed through a 100K ultrafilter. Colloidal iron was defined as the iron that passed through a 0.2 μm pore size membrane filter but was retained by a 100K ultrafilter. Particulate iron was defined by retention on a 0.2 μm pore size membrane filter.

Dissolved organic carbon was defined as the organic carbon that passed through a 100K ultrafilter, whereas colloidal organic carbon was defined as that retained by a 100K ultrafilter. The 0.2 μm pore size membrane filter was not used for the classification of organic carbon because the filters contributed DOC to solution (sometimes as much as 2.3 mg/L).

Figure 4 illustrates the particulate, colloidal, and soluble iron speciation that exists in solution after oxidation by free chlorine. These data were collected from an experiment that was conducted at pH 6.5. This method of representation will be used throughout this thesis.

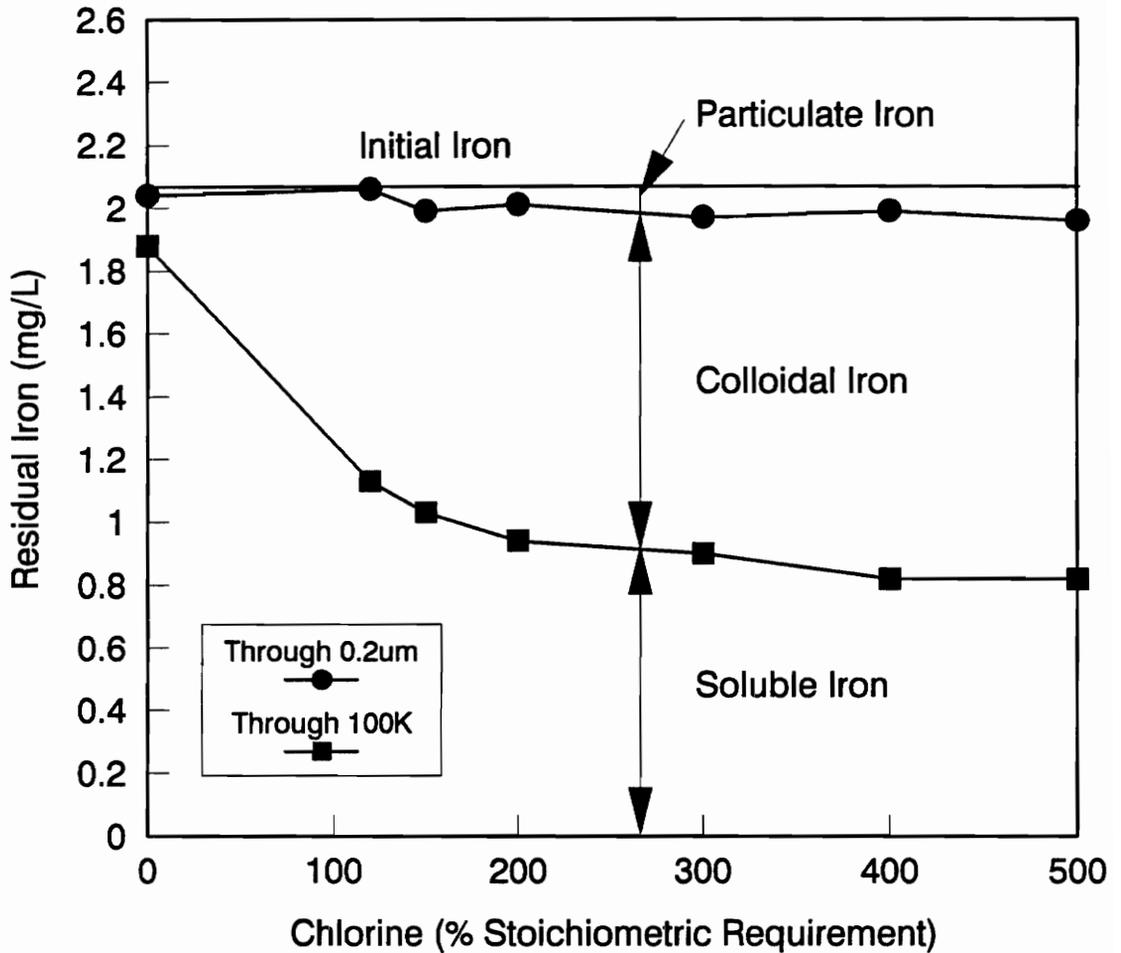


Figure 4. An illustration of particulate, colloidal, and soluble iron. (free chlorine iron oxidation; pH = 6.5; DOC = 5 mg/L; reaction time = 5 minutes; stoichiometric requirement = 0.64 mg as Cl_2 per mg Fe)

Preparation of Water Solutions

Water solutions for all oxidation, coagulation, and oxidant demand studies were prepared as follows:

1. An appropriate amount of the stock humic solution was added to distilled, deionized, and carbon-filtered water from a Milli-Q ion exchange system (Millipore Corp., Milford, MA) (<0.4 mg/L DOC).
2. Calcium chloride and sodium sulfate served as the background ions. These salts were added to the solutions to yield concentrations of 1 milli-equivalent per liter (meq/L) and 0.25 meq/L, respectively.
3. Next, 1 meq/L of sodium bicarbonate (NaHCO_3) was added to solution.
4. For coagulation studies, a defined quantity of a kaolinite suspension was added to create an initial turbidity of 4 to 6 NTU.
5. The water was then deaerated by purging it with nitrogen for at least 15 minutes, and immediately sealing the vessel from the atmosphere with Parafilm. Dissolved oxygen measurements revealed that a trace amount of oxygen (0.6 mg/L) still remained in solution after purging.
6. The pH was adjusted to 5.5 with concentrated HNO_3 .
7. Next, the appropriate amount of Fe(II) as FeSO_4 was added.
8. If the experiment involved complexed iron, a contact time of at least 12 hours was provided to ensure adequate time for complexation between the DOC and Fe(II).

Preparation of Stock Solutions

Ferrous Iron: The Fe(II) solution was prepared by dissolving ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in acidified (0.1 mL concentrated HNO_3

per 100 mL solution), deaerated Milli-Q water. The Fe(II) concentration in the stock solution was 1 mg/mL. This solution was prepared daily and stored in an amber glass bottle.

Aluminum Sulfate: Aluminum sulfate, a coagulant commonly called alum, was prepared by dissolving the appropriate amount of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ into Milli-Q water. The solution concentration was 1 mg/mL $\text{Al}_2(\text{SO}_4)_3$ and was stored in an amber glass bottle.

Sodium Bicarbonate: The sodium bicarbonate solution, used for pH control in coagulation studies, was prepared by dissolving the appropriate amount of NaHCO_3 in Milli-Q water. The concentration of this solution was 10,000 mg/L, and it was stored in an amber glass bottle.

Preparation of Oxidants

Stock free chlorine solutions were prepared by a dilution of common bleach, which contained approximately 5.25 percent sodium hypochlorite, (NaOCl). Dilution was based on the assumption that the density of the bleach was 1 gram per milliliter (g/mL); thus, the bleach had a concentration of approximately 50,000 mg/L as Cl_2 . The titre of the stock free chlorine solution was measured prior to each experiment.

Chlorine dioxide was generated by the procedure outlined in Standard Methods (Method 4500-B). This method utilized the addition of sulfuric acid to a sodium chlorite (NaClO_2) solution and the collection of the ClO_2 gas that was generated by this reaction. Recommendations from White (1986) were also followed for the generation of ClO_2 . The suggestions included chilling the collection vessel (10°C) and doubling the amount of NaClO_2 in the reactor flask

to 20 g. When ClO_2 generation was completed, the pH of the stock solution was adjusted to approximately 6.0 with NaHCO_3 to help prevent disproportionation. The stock ClO_2 solution was then poured into amber glass bottles and stored in the refrigerator.

This generation procedure yielded a stock ClO_2 solution with the following concentrations: 750 mg/L ClO_2 ; 80 mg/L ClO_2^- ; <9 mg/L chlorate (ClO_3^-); 15 mg/L Cl_2 ; and <30 mg/L Cl^- . Over time, the separate bottles of stock partially disproportionated, and each constituent (excluding ClO_3^- and Cl^-) was measured prior to each experiment.

Chlorite as an alternative oxidant for complexed Fe(II) oxidation was also investigated. Stock ClO_2^- solutions were prepared by dissolving NaClO_2 crystals in Milli-Q water. The stock solution concentration was 1000 mg/L ClO_2^- . The titre of the stock solution was determined by ion chromatography.

Oxidant Demand by Humic Substances

The oxidant demand of the Dismal Swamp and Durham, NC humic materials was evaluated; free chlorine and ClO_2 were added to prepared water solutions that contained varying concentrations of DOC. Solutions containing 3, 5, and 10 mg/L DOC were each dosed with either 2, 5, or 10 mg/L oxidant. Residual oxidant was measured over time until the rate of depletion approached zero.

Oxidation of Uncomplexed Fe(II)

Two studies were conducted to determine if the theoretical stoichiometry for Fe(II) oxidation by free chlorine and ClO_2 was achieved under laboratory

conditions. Solutions containing approximately 2 mg/L Fe(II) were oxidized for 5 minutes. Oxidant dosages ranged from 0 to 150 percent of the stoichiometric requirement for Fe(II) oxidation. Based on the stoichiometry for free chlorine reaction with Fe(II), 0.64 mg as Cl₂ is required for each mg Fe(II) in solution. In comparison, 1.2 mg ClO₂ is required per mg Fe(II) if ClO₂ is reduced to ClO₂⁻; and 0.24 mg ClO₂ per mg Fe(II) if ClO₂ is reduced to Cl⁻. The water solutions were oxidized for 5 minutes in 300-mL BOD bottles while being mixed by magnetic stirrers. Samples were passed through a 0.2 um pore size membrane filter and through a 100K ultrafilter to differentiate between particulate, colloidal, and dissolved iron.

Fractionation of Complexed Iron Solutions

Two prepared water samples (water #1: 10 mg/L DOC, 2 mg/L Fe(II); water #2: 5 mg/L DOC, 2 mg/L Fe(II)) were fractionated to determine the DOC-to-iron ratios in each DOC molecular weight fraction. The 0.2um, 100K, 30K, 10K, 3K, and 1K filters were used for analysis. Iron and DOC concentrations in samples fractionated at pH 5.5 and 6.5 were determined.

Effect of Open Atmosphere on Complexed Iron

The extent of oxidation of complexed Fe(II) by oxygen was evaluated by sampling a complexed Fe(II) solution (2 mg/L Fe, 10 mg/L DOC) that was exposed to open atmosphere for 48 hours, while simultaneously monitoring a sealed complexed Fe(II) solution. The solutions were not mixed. Iron concentrations passing through a 100K and 0.2 um pore size membrane filter,

along with the DOC concentrations passing a 100K ultrafilter, were measured over the 48-hour period.

Oxidation Studies

In an attempt to simulate water treatment facility operations, oxidation studies were conducted with free chlorine, ClO_2 , and ClO_2^- at pH values ranging from 5.5 to 7.5. Ferrous iron concentrations ranged from 1 to 2 mg/L, and DOC concentrations ranged from 2 to 10 mg/L. The filters used for fractionation were the 0.2 μm , 100K, 30K, 10K, 3K, and 1K filters. Oxidant dosages ranged from zero to 500 percent of the stoichiometric requirement for Fe(II) oxidation. Also, high and low molecular weight humic substances were tested.

Originally, oxidation studies were conducted in an open jar-test apparatus. Solutions were mixed for one hour, and samples were withdrawn after 5 and 60 minutes. The solution pH increased during the 60 minute mixing period, most probably because carbon dioxide ($\text{CO}_2(\text{aq})$) was released during mixing. Modifying the test procedure to the use of mixing with a magnetic stirrer in 300-mL BOD bottles helped maintain the desired pH (see Experimental Results, Chapter IV). Oxidation studies were also conducted in 130-mL amber glass bottles for studies with the University of Washington humic source, because a limited quantity of the stock humic materials was available.

Actual operation of the oxidation studies was as follows:

1. After pH adjustment by HNO_3 or NaHCO_3 , prepared water solutions were carefully poured (to minimize O_2 transfer) into the testing bottles.

2. Oxidant was added by pipet at time zero, and the solutions were placed on a magnetic stirrer.
3. After 5 minutes, the bottles were removed from the magnetic stirrers, and the solution was poured into an Amicon ultrafiltration cell. Samples to be analyzed for oxidant residual, soluble iron, and DOC were collected from the filtrate that passed through a 100K ultrafilter. The remaining water in the testing bottle was filtered through a 0.2 um pore size membrane filter so that the particulate iron fraction could be determined.
4. A second test was conducted using the same procedures except for the use of a 60 minute reaction period.

Fractionations of oxidized complexed iron solutions aided in the determination of the molecular weight fraction in which iron was complexed. A water sample containing the specified background ions was dosed with a specified amount of either free chlorine or ClO_2 , allowed to react for one hour, and fractionated through 0.2 um, 100K, 30K, 10K, 3K, and 1K filters. Both the iron and DOC concentrations were measured.

Coagulation Studies

Alum coagulation of complexed iron was conducted in a conventional jar-test apparatus (Phipps & Bird, Inc. Model 300, Richmond, VA) which had six circular, paddle-stirred containers. Samples were rapidly mixed for 90 seconds, flocculated first for 15 minutes at 50 rpm, flocculated for 15 minutes at 20 rpm, and allowed to settle for one hour. When the experiment involved oxidation and coagulation, the oxidant and alum solutions were poured from 50

mL beakers into the jars. If the volume added was less than 10 mL, the volume was dispensed from a pipet. Oxidant addition preceded alum addition in these experiments. Maintenance of the desired pH was accomplished by adding an appropriate amount of a 10,000 mg/L NaHCO₃ solution immediately following the coagulant and oxidant addition.

Alum doses ranged from 0 to 60 mg/L; the pH ranges used for testing were 5.5 to 6.0 and 6.8 to 7.3. Samples were analyzed for pH, residual DOC, turbidity, total iron, particulate iron, colloidal iron, and, on occasion, DOC molecular weight distribution. Turbidity samples were withdrawn by placing a 25 mL pipet at the volumetric center of the test solution. The remaining samples were withdrawn with 25 mL syringes.

For certain studies, samples were withdrawn after alum coagulation and passed through 0.2 µm, 100K, 30K, 10K, 3K, and 1K filters. These data were used to determine the molecular weight fraction that continued to complex iron. Samples were analyzed for iron and DOC concentrations.

Ferrous Iron Detection

In an attempt to differentiate between complexed Fe(III) and complexed Fe(II), it was necessary to establish a reliable method for Fe(II) detection.

Three methods were evaluated and are described as follows:

- 1) 1,10-phenanthroline: The Tamura *et al.* (1974) method, which was a modification to the original phenanthroline procedure in Standard Methods (Method 3500-C), utilized 1,10-phenanthroline and an ammonium fluoride masking agent for Fe(III). A stable complex was formed between Fe(II) and 1,10-phenanthroline. The resulting red-to-pink color was then related by

spectrophotometry (at a wavelength of 510 nm) to the Fe(II) concentration. A standard curve comprised of three standards (typically 0.5, 1.0, and 2.0 mg/L Fe(II)) and a blank was always used.

2) Bathophenanthroline: Lee and Stumm (1960) reported that this procedure was more sensitive and had fewer interferences than the original phenanthroline procedure described by Standard Methods (Method 3500–C). Bathophenanthroline complexed with Fe(II) yields a stable red-to-pink solution that can be related to the Fe(II) concentration by spectrophotometry at a wavelength of 533 nm. The authors suggested boiling an acidified sample (1 mL of concentrated HCl per 25 mL of sample) before the bathophenanthroline procedure if organic material is present. However, Theis and Singer (1974) claimed that such boiling may alter the Fe(II) to Fe(III) ratio. The authors suggested that the sodium acetate addition should release the iron from the organic complex. A standard curve comprised of three standards (typically 0.5, 1.0, and 2.0 mg/L Fe(II)) and a blank was always used.

3) Ferrozine: The chelating agent, ferrozine, (from Hach Chemical Co.), forms a stable, purple-colored complex with Fe(II). Spectrophotometric measurements (at a wavelength of 564 nm) related the color to the Fe(II) concentration (Gibbs, 1979). A standard curve comprised of three standards (typically 0.5, 0.75, and 1.0 mg/L Fe(II)) and a blank was always used.

Several studies were conducted with each of these methods, along with the modifications, to determine which method produced reliable, reproducible results. The selected method of Fe(II) detection was then used to quantify the Fe(II) concentration in select oxidation studies by both free chlorine and ClO₂.

Glassware Cleaning

Glassware was washed in a one percent HNO₃ acid bath and rinsed with organic-free water. This acid bath was used to remove any iron or organic residue that might interfere with other experiments.

Field Experiments

Williams Water Treatment Plant, Durham, NC

The objectives of this sampling trip were to: (1) conduct studies to evaluate the applicability of laboratory-scale studies involving complexed iron to actual water treatment plant operations, and (2) collect and concentrate humic materials from the influent water supply to the plant.

At the time of the study, the Williams Water Treatment Plant treated approximately 30 million gallons per day. Typical DOC and iron concentrations in the raw-water were 7 to 10 mg/L and 0.0 to 1.5 mg/L, respectively. The Williams Water Treatment Plant used 28 mg/L alum for coagulation. First- and second-stage flocculation (each with a retention time of 30 minutes) was followed by a 4-hour settling period. The water was then filtered and disinfected with 6.5 mg/L chlorine.

Coagulation tests (with and without free chlorine oxidation) were conducted using the same procedures as those previously described. Isolation of humic substances was performed. Approximately 1500 L of raw-water were passed through the XAD-8 resin.

Chapter IV

EXPERIMENTAL RESULTS

This chapter presents the results from the experiments that were previously described in the Methods and Materials chapter. First, the validation of three experimental methods is discussed: (1) oxidation experiment methods, (2) ferrous iron determination, and (3) chlorite determination by potentiometric titration. Results from experiments that investigate the interactions of humic materials, iron and oxidant are then discussed.

Methods Development

Oxidation Experiment Methods

Oxidation studies were originally conducted in a conventional jar-test apparatus, which allowed the test solutions to be exposed to the atmosphere. An undesirable increase in the solution pH (increases as high as 0.7 pH units) during this mixing period prompted the use of a sealed container. The use of 300-mL glass-stoppered BOD bottles allowed the solution pH to be maintained within +/- 0.15 pH units throughout the mixing period.

Two tests, which were previously conducted by the jar-test method, were repeated in BOD bottles. Representative data regarding iron removal following free chlorine oxidation at pH 5.5 are shown in Table 1. The differences observed when using the two solution vessels were minimal; therefore, the repetition of all previous tests was not necessary.

Iron oxidation studies were conducted at pH 5.5, 6.5, and 7.5. However, at pH 7.5, Fe(II) oxidation and subsequent precipitation to colloidal Fe(OH)₃(s)

Table 1

A comparison between the use of a jar-test apparatus and BOD bottles for iron oxidation studies

Jar-Test Apparatus			BOD Bottles		
Cl ₂ Dosage (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	Cl ₂ Dosage (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)
0.00	1.01	0.95	0.00	0.98	0.97
1.53	0.99	0.55	1.28	0.90	0.48
1.92	1.06	0.52	1.92	0.89	0.38
2.56	0.98	0.49	2.56	0.93	0.49

Note: DOC = 3 mg/L, Fe = 1 mg/L, pH = 5.5, Reaction time = 60 minutes, DOC source – Dismal Swamp

was often detected in the control samples (no oxidant addition; see representative results in Figure 5). For the 0.0 mg/L (zero percent) free chlorine dose in the 5 mg/L DOC sample, only 0.5 mg/L Fe (25 percent of the original Fe concentration) passed through the 100K ultrafilter, while for the 10 mg/L sample, 1.5 mg/L Fe remained soluble. In comparison, greater than 95 to 98 percent of the iron added passed the 100K ultrafilter in the pH 5.5 and 6.5 control samples.

The loss of soluble iron in the pH 7.5 control samples was attributed to Fe(II) oxidation by trace quantities of $O_2(aq)$ that remained following solution stripping with $N_2(g)$. Several test solutions were analyzed for $O_2(aq)$ concentration following 15 minutes of $N_2(g)$ stripping. Results indicated that the average, residual $O_2(aq)$ concentration was near 0.5 mg/L. Theoretical reaction stoichiometry indicates that 0.14 mg O_2 are required to oxidize 1 mg Fe(II). Thus, it was hypothesized that the combination of trace quantities of $O_2(aq)$ and the elevated pH resulted in a solution condition that was kinetically favorable for Fe(II) oxidation by $O_2(aq)$.

Stumm and Lee (1961) reported that the oxidation of uncomplexed Fe(II) by $O_2(aq)$ was kinetically rapid at pH values above 6.5. The fact that a portion of the Fe(II) apparently could be oxidized by $O_2(aq)$ indicated that not all of the Fe(II) added to solution was being complexed by the DOC. This was also shown by the increased oxidation of Fe(II) in the 5 mg/L sample when compared to the 10 mg/L sample (Figure 5). The 10 mg/L DOC sample would complex more iron than the 5 mg/L DOC sample because the DOC-to-iron ratio is higher in the 10 mg/L DOC sample. Data from later ultrafiltration studies confirmed this hypothesis.

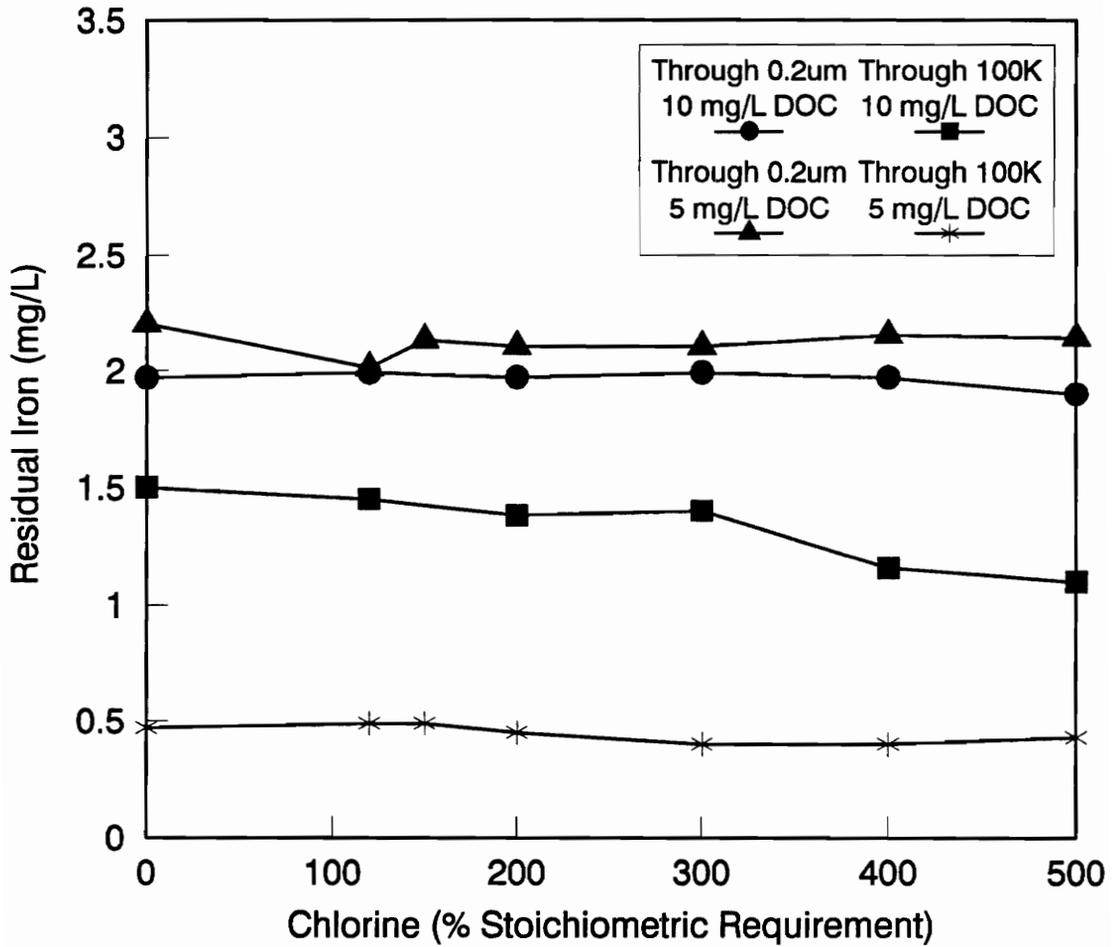


Figure 5. Oxidation of complexed Fe(II) by free chlorine at pH 7.5. (reaction time = 60 minutes; DOC source - Dismal Swamp; stoichiometric requirement = 0.64 mg as Cl₂ per mg Fe)

A more costly, high purity $N_2(g)$ was investigated as a means of overcoming the potential problem associated with residual trace quantities of $O_2(aq)$ in pH 7.5 test solutions. While the use of this high purity $N_2(g)$ did help reduce the Fe(II) oxidation problem, it did not eliminate it. Ultimately, it was decided that the testing at pH 7.5 would be discontinued and an emphasis would be placed on the examination of Fe(II) oxidation at the lower pH values.

Ferrous Iron Determination

Initially, it was not known whether the bathophenanthroline (Lee and Stumm, 1960), 1,10-phenanthroline (Tamura *et al.*, 1974), or ferrozine (Gibbs, 1978) methods for Fe(II) analysis would accurately measure the Fe(II) concentrations in samples containing 3, 5, and 10 mg/L DOC. Several tests were conducted with each method to measure the Fe(II) concentration in complexed Fe(II) samples, both in the absence and presence of an oxidant.

Each method was first used to analyze solutions containing unoxidized, complexed Fe(II) at pH 5.5. Because oxidation kinetics are considerably slower at pH values less than 6.5 (Stumm and Lee, 1961), iron oxidation by trace quantities of $O_2(aq)$ would be negligible, and approximately 100 percent Fe(II) recovery by each method was expected. Representative results from different tests, including the acidified/boiled option for the bathophenanthroline method (Bathophen./Boiled), are presented in Table 2. The 'Total Fe' column denotes the total iron concentration (Fe(II) and Fe(III)) in solution as quantified by atomic absorption spectrophotometry. Recall that the acidified/boiled option of the

Table 2

An evaluation of Fe(II) analysis methods

Method	Total Fe* (mg/L)	Fe(II) (mg/L)	Nominal DOC (mg/L)
Bathophenanthroline	2.0	0.6	10
Bathophenanthroline	2.0	0.7	5
Bathophenanthroline	1.0	0.3	3
Bathophen./Boiled	2.1	2.4	10
Bathophen./Boiled	2.3	2.5	5
Bathophen./Boiled	1.1	1.2	3
1,10-phenanthroline	2.1	1.7	10
1,10-phenanthroline	2.2	2.0	5
1,10-phenanthroline	1.0	0.9	3
Ferrozine	2.0	2.0	10
Ferrozine	2.0	1.9	10
Ferrozine	2.0	2.0	10

Note: pH = 5.5, DOC source – Dismal Swamp

Bathophenanthroline, Lee and Stumm (1960); Bathophen./Boiled, Lee and Stumm (1960); 1,10-phenanthroline, Tamura *et al.* (1974); and Ferrozine, Gibbs (1978)

* data determined by atomic absorption spectrophotometry

bathophenanthroline procedure required acidification of a complexed iron solution (1 mL concentrated HCl per 25 mL sample) prior to boiling for 5 minutes.

The bathophenanthroline procedure alone was deemed inadequate because the average Fe(II) recovery was only 30 percent. The acidified/boiled modification of this procedure appeared satisfactory, but further tests were needed to determine if the acidification and boiling processes altered the Fe(II)–to–Fe(III) ratio of the test solutions. The 1,10–phenanthroline and ferrozine procedures achieved approximately 86 and 100 percent recovery of Fe(II), respectively. It should be noted that the standard curve for the ferrozine procedure was found to be linear only between 0.0 and 1.0 mg/L Fe(II).

To further investigate the acidified/boiled option of the bathophenanthroline method, uncomplexed Fe(II) solutions were oxidized with 65 and 100 percent KMnO_4 on a stoichiometric basis. Samples were analyzed by both the bathophenanthroline and the acidified/boiled bathophenanthroline (Bathophen./boiled) methods. Results are shown in Table 3. The iron concentration passing through the 0.2 μm pore size membrane filter was the concentration that was expected to be detected as soluble Fe(II) by each method. The elevated Fe(II) concentrations detected by the acidified/boiled option of the bathophenanthroline method (when compared to the iron concentrations that passed through the 0.2 μm pore size membrane filter), indicated that approximately 15 to 20 percent of the Fe(III) was converted to Fe(II) during the acidified/boiled process. Because of this error, the acidified/boiled option of the bathophenanthroline method was not used.

Table 3

An evaluation of the boiling option of the bathophenanthroline procedure

	Total Fe*	KMnO ₄ Dosage	Fe* Through 0.2 um	Fe(II)
	(mg/L)	(percent)	(mg/L)	(mg/L)
Bathophenanthroline	1.84	100	0.05	<0.1
Bathophen./Boiled	2.11	100	0.05	0.5
Bathophenanthroline	1.91	65	0.60	0.3
Bathophen./Boiled	2.23	65	0.60	0.9

Note: DOC = <0.4 mg/L, stoichiometric requirement = 0.94 mg KMnO₄ per mg Fe

* data determined by atomic absorption spectrophotometry

An additional study was conducted to differentiate between the ferrozine and the 1,10-phenanthroline methods by quantifying Fe(II) in oxidized complexed Fe(II) solutions. Complexed Fe(II) samples were oxidized with 40 to 100 percent of the stoichiometric requirement of KMnO_4 for Fe(II) oxidation. Data presented in Table 4 show satisfactory results by both methods when the iron concentrations that passed the 0.2 μm pore size membrane filter are compared to the measured Fe(II) concentrations. The ferrozine procedure required no physical separation of reagents, had a one minute reaction time, required no solution dilution after reagent addition, and it produced a stable, purple-colored solution. For these reasons and the apparent experimental accuracy, the ferrozine method was chosen for further use in this research.

Detection of Fe(II) in the presence of substantial concentrations of DOC has not been thoroughly investigated in the published literature. Each Fe(II) detection method is based on the complexation of the Fe(II) by chelating agents. Specific details regarding the capability of these chelating agents to complex Fe(II) in the presence of DOC are not known. However, ferrozine tests conducted for this research with unoxidized, complexed Fe(II) achieved nearly 100 percent Fe(II) recovery, while studies with oxidized complexed Fe(II) solutions achieved nearly 0 percent recovery. These results suggest that the ferrozine method does accurately detect Fe(II) in the presence of DOC; however, results from ferrozine tests should be considered more qualitative than quantitative.

Table 4

A comparison between the 1,10-phenanthroline and ferrozine Fe(II) detection methods

	Total Fe*	KMnO ₄ Dosage	Fe* Through 0.2 μ m	Fe(II)
	(mg/L)	(percent)	(mg/L)	(mg/L)
1,10-phenanthroline	1.84	100	0.05	<0.1
1,10-phenanthroline	1.91	65	0.60	0.7
Ferrozine	1.95	80	0.37	0.2
Ferrozine	1.92	40	1.18	1.1

Note: DOC = 5 mg/L, Fe = 2 mg/L, pH = 5.5, DOC source – Dismal Swamp, stoichiometric requirement = 0.94 mg KMnO₄ per mg Fe

* data determined by atomic absorption spectrophotometry

Chlorite Determination by Potentiometric Titration

One objective of this research was to determine if ClO_2 is reduced to ClO_2^- or Cl^- during the oxidation of complexed Fe(II). The use of potentiometric titration for ClO_2^- determination, as outlined by Aieta *et al.* (1984), requires two, separate titrations, which they referred to as "A" and "B." The "A" titration, which represents free chlorine + $1/5 \text{ClO}_2$, was performed at a near neutral pH after the addition of approximately 1 mL of pH 7.0 buffer and 1 g KI to the sample. After the "A" titration, the pH was adjusted to approximately pH 2 with 2.5 N HCl, and the sample was placed in the dark for at least 5 minutes. Titration of this sample represented $4/5 \text{ClO}_2 + \text{ClO}_2^-$.

In the control sample of the oxidation studies (in which no ClO_2 was added nor ClO_2^- was present) the "B" titration consistently yielded a positive response. Theoretically, no titrant response should have been observed due to the absence of ClO_2 or ClO_2^- . Instead, the volume of the "B" titration was greater than the detection limit of 0.1 mL for potentiometric titration.

Tests were conducted to investigate the possible interferences of the "B" titration by varying the ratios of DOC to Fe in complexed Fe(II) solutions. Subtle trends were observed in these studies (Table 5). As the iron concentration was increased from <0.03 to 3.4 mg/L with respect to the DOC concentration (approximately 10.3 mg/L), the "B" titration volume also increased. No apparent trend was observed as the DOC concentration was increased with respect to the iron concentration. Also, when no iron was present in solution, no interference was detected due to the DOC alone. Because no method was available to remediate these interferences, it was decided that ClO_2^- concentrations would be quantified by IC rather than potentiometric titration.

Table 5

The effects of Fe and DOC concentrations on potentiometric titration in the absence of an oxidant

DOC (mg/L)	Total Fe (mg/L)	"A"* (mL)	"B"* (mL)
10.5	0.10	<0.1	0.39
10.3	0.94	<0.1	0.53
10.4	1.85	<0.1	0.57
10.2	3.40	<0.1	0.58
7.7	0.93	<0.1	0.27
6.6	0.99	<0.1	0.33
4.4	0.83	<0.1	0.20
2.6	0.96	<0.1	0.25
0.8	0.88	<0.1	0.13
10.7	<0.03	<0.1	0.16
5.4	<0.03	<0.1	0.13
3.6	<0.03	<0.1	0.19

Note: DOC source – Dismal Swamp

* "A" and "B" represent two separate titrations as explained by Aeita *et al.* (1984)

Characterization of Humic Substances

Three different humic substances were obtained for this research. Humic substances were isolated by XAD-8 resin adsorption from water of the Dismal Swamp, Virginia, and the terminal reservoir at the Williams Water Treatment Plant in Durham, NC. The third source was extracted at the University of Washington by adsorption onto iron oxide solids and subsequent alkaline extraction (Benjamin, 1991).

Each of the stock humic solutions was characterized by ultrafiltration fractionation through 100K, 30K, 10K, 3K, and 1K ultrafilters. The DOC molecular weight fractionation of a 10 mg/L solution of each humic source is shown in Figure 6. It was evident that each stock solution had approximately the same DOC molecular weight distribution. The Dismal Swamp molecular weight distribution presented in Figure 6 is an average of several fractionations which were performed over a six month period.

A pH 1 humic acid precipitation was performed with the Durham, NC, and Dismal Swamp stock humic solutions to further differentiate the relative fractions of fulvic and humic acids. This experiment was not performed with the University of Washington humic material due to a limited quantity of the stock solution. The DOC concentration of the supernatant after centrifugation was found to be 92 percent and 89 percent fulvic acids for the Durham, NC, and Dismal Swamp stock solutions, respectively. These data further supported the previous observation that the humic sources had relatively similar DOC molecular weight distributions.

It was desired to have stock humic solutions with either relatively high or low molecular weight DOC so comparative oxidation studies could be

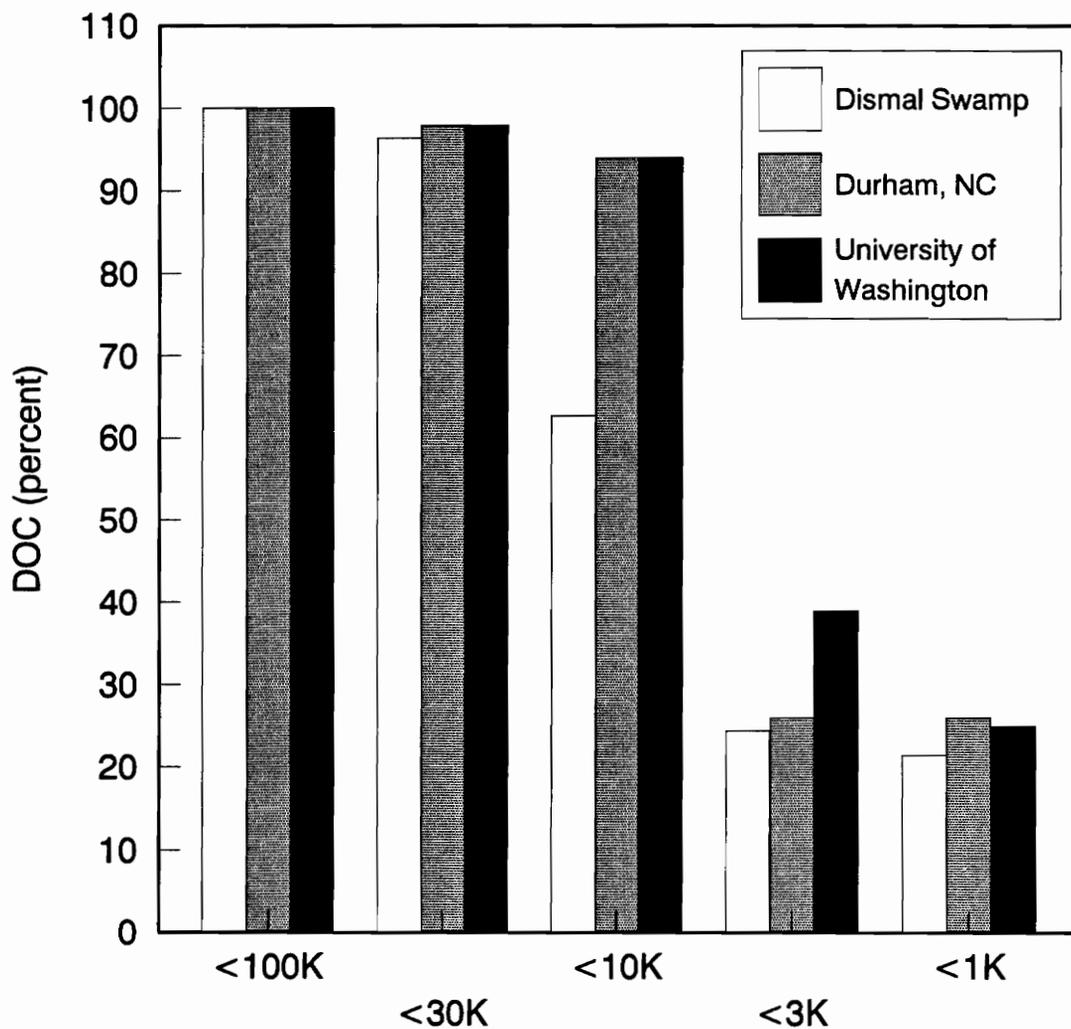


Figure 6. The DOC molecular weight distribution of the Dismal Swamp, Durham, NC, and University of Washington humic sources. (Nominal DOC = 10 mg/L)

performed. From these analyses, the three sources seemed to have similar molecular weight distributions of DOC, and it was decided that the University of Washington humic source would be separated by ultrafiltration. Two specific fractions were prepared: between 100K and 10K and less than 3K. These fractions were used to represent extremely high and low molecular weight DOC species.

The specific absorbance of each stock solution was also determined to verify that the organic material of each source had a humic and fulvic acid composition. The specific absorbances 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 correspond well with the characterization of humic and fulvic acids by Reckhow *et al.* (1990).

Complexed Fe(II) Distribution in Test Solutions Used in this Research

Complexed Fe(II) solutions were separated into molecular weight fractions to reveal the complexed iron distribution for the Dismal Swamp and Durham, NC humic materials. Data contained in Figure 7 show that approximately 65 percent of iron in solution passed through the 1K ultrafilter. When comparing this to the <1K DOC concentrations in Figure 6, it appeared that not all of the Fe(II) in solution was being complexed by the humic material. From these data, DOC-to-iron ratios through the 1K ultrafilter were

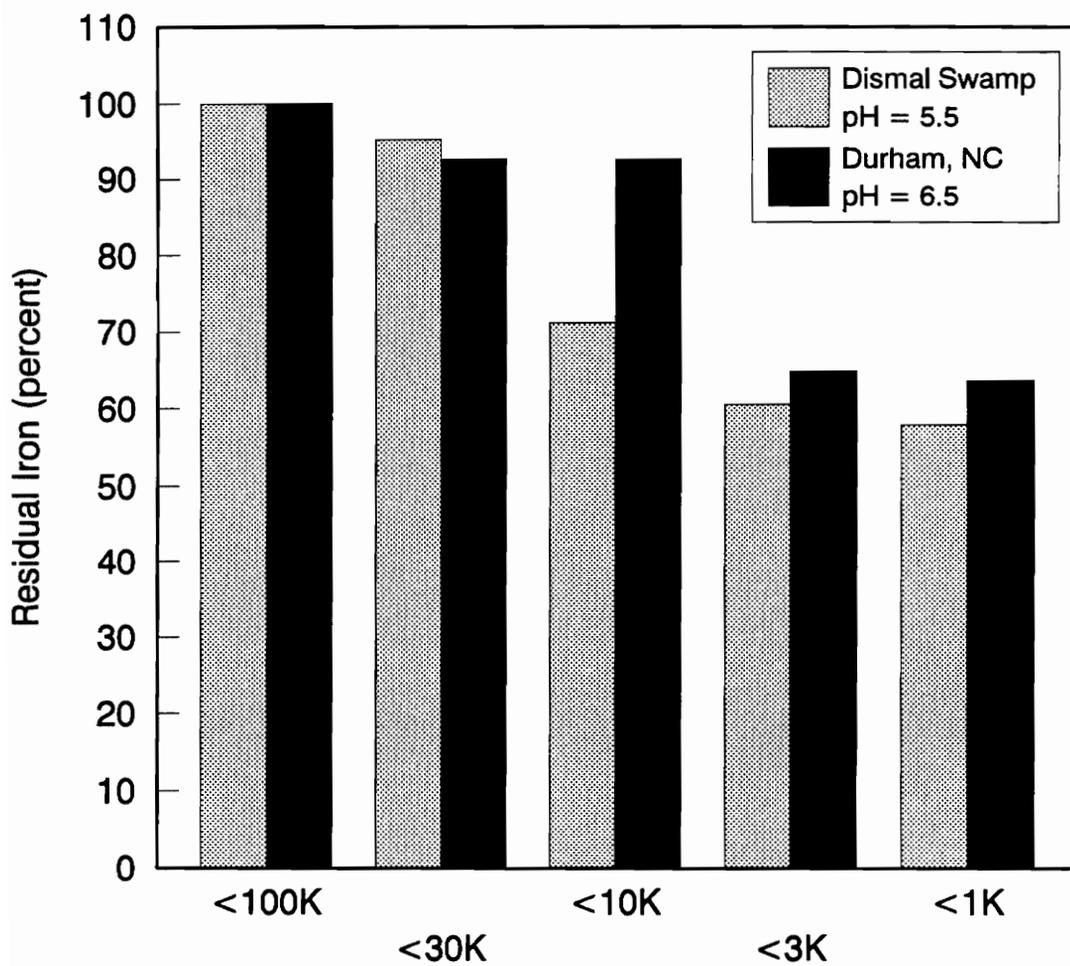


Figure 7. Iron distribution within the Dismal Swamp and Durham, NC humic sources. (Nominal DOC = 10 mg/L)

approximately 1:1 to 2:1 for the Dismal Swamp and Durham, NC humic sources.

The data presented in Figure 5 also support the hypothesis that not all of the iron was being complexed by the Dismal Swamp humic material. Control samples (which received no oxidant addition) experienced some colloidal iron formation, possibly due to the kinetically favorable conditions for Fe(II) oxidation by $O_2(aq)$ at pH 7.5. From these results, it appeared as though only 0.5 mg/L Fe was complexed by the 5 mg/L DOC in solution. The remaining 1.5 mg/L Fe was hypothesized to have been oxidized by the trace $O_2(aq)$ and removed from solution by a 100K ultrafilter as colloidal iron.

Because of the low DOC-to-iron ratio in the water passing through the 1K ultrafilter and the pH 7.5 precipitation of colloidal iron, it was hypothesized that the Fe(II) in solution was not completely complexed by the humic material.

These data allow for an analysis of the iron complexation capability of the Dismal Swamp humic source. Approximately 0.1 to 0.2 mg Fe(II) was complexed by each mg of DOC in solution.

A solution (pH = 6.5, 6.8 mg/L DOC, and 1.74 mg/L Fe(II)) containing the lower molecular weight (<3K) DOC of the University of Washington was prepared and passed through a 1K ultrafilter. Residual concentrations were 0.82 mg/L Fe and 1.6 mg/L DOC. Again, it appeared that the DOC-to-iron ratio within this molecular weight fraction was too small to support complete complexation. The lower molecular weight humic material, even at 2 to 3 times the initial concentration of the Fe(II) in solution, failed to complex all of the Fe(II).

The supply of the high molecular weight (100–10K) humic material from the University of Washington was limited; therefore, no fractionations were performed. However, an investigation of the data from a coagulation experiment (Table 6) shows that after alum coagulation of a test solution containing 1.88 mg/L Fe and 4.2 mg/L DOC, 1.3 mg/L soluble iron and only 0.9 mg/L DOC remained in solution. This low DOC-to-iron ratio suggests incomplete complexation of the Fe(II) in solution by the higher molecular weight humic material.

The DOC-to-iron ratios which were used for testing were 5:1, 3:1, and 2.5:1. At these ratios, the humic sources used for this research were unable to complex all of the Fe(II) in solution. Oxidation of complexed Fe(II) solutions in this research is believed to be an oxidation of the uncomplexed Fe(II) to Fe(III), which is then complexed with the solution DOC. However, for this thesis, solutions containing Fe(II) and DOC will be referred to as 'complexed Fe(II) solutions.'

Effect of Open Atmosphere on Complexed Fe(II)

Data presented in Figure 8 compare changes in iron and DOC speciation over a 48-hour period in complexed Fe(II) solutions contained in sealed and open containers. Little transfer (<15 percent) of iron between the soluble, colloidal, and particulate fractions occurred in either the sealed or open containers. Also, the colloidal and soluble DOC fractions remained relatively constant over time. Thus, it was decided that complexation in a sealed container for at least 12 hours was satisfactory for the testing solutions used in this research.

Table 6

Iron and DOC removal by alum coagulation of
Fe(II) complexed with high molecular weight
humic material (100–10K)

Alum Dosage (mg/L)	Fe Through 0.2 um (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

Note: pH 5.7–6.0, DOC source – University of Washington

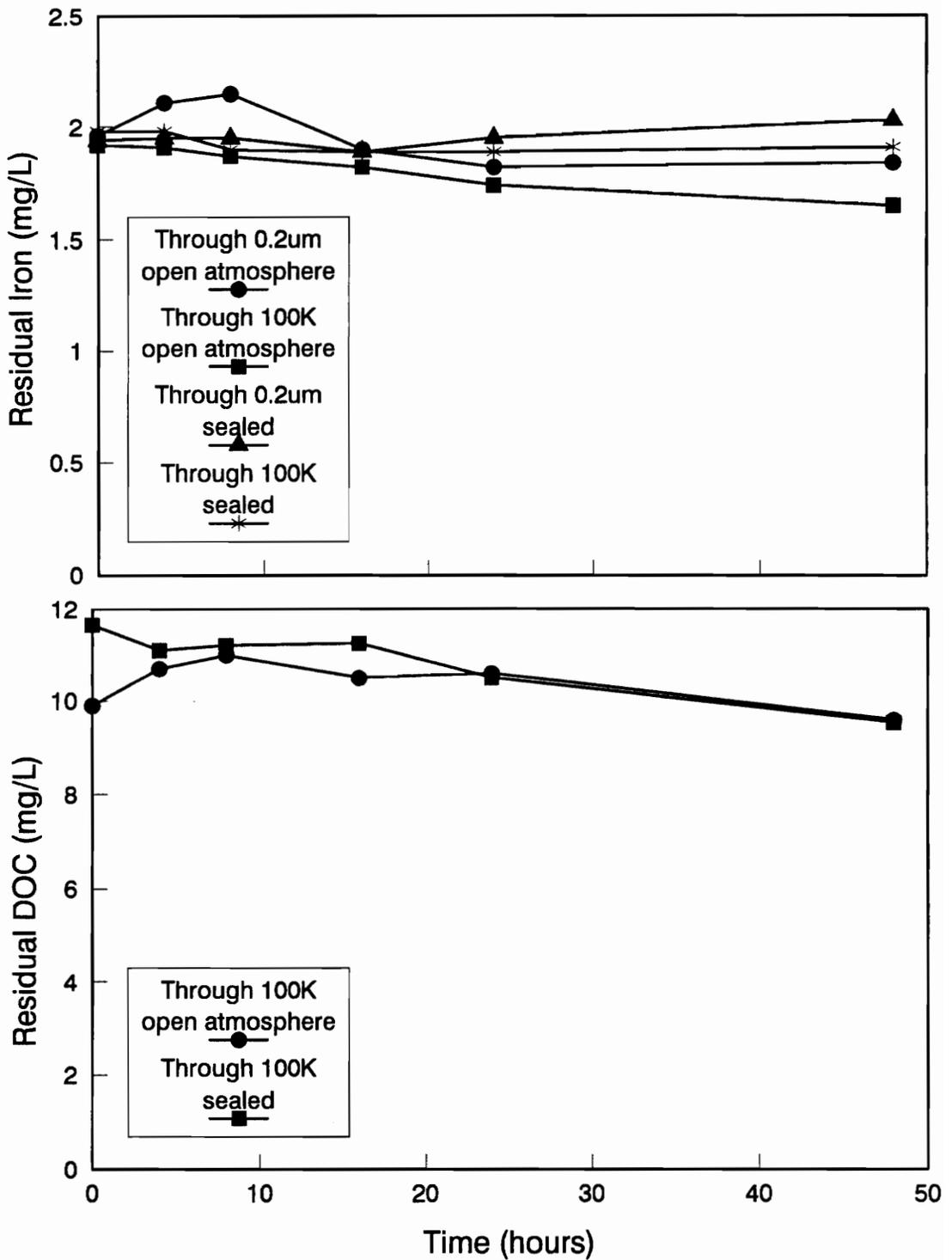


Figure 8. Changes in iron and DOC speciation due to exposure to O_2 . (pH = 5.5; DOC source - Dismal Swamp)

Oxidant Demand of Humic Materials Used in this Research

Humic materials are known to be oxidized when in the presence of free chlorine and ClO_2 . Thus, the presence of DOC represents a potential competitive oxidant demand when considering Fe(II) oxidation. To quantify this oxidant demand of the humic materials, test solutions of varying DOC (Dismal Swamp) concentrations were exposed to different concentrations of free chlorine or ClO_2 . The residual oxidant concentrations were measured over time; representative data are shown in Figures 9 and 10.

Contact between the Dismal Swamp humic material and the oxidants caused the residual concentrations of both free chlorine and ClO_2 to be reduced. As the DOC concentrations in solution increased, the residual oxidant concentrations decreased. As seen in Figure 9, the 10 mg/L dosage of free chlorine had residuals which persisted in each DOC solution. However, lower free chlorine dosages were consumed to <0.2 mg/L in the presence of DOC.

Chlorine dioxide was rapidly depleted to <0.4 mg/L within 8 minutes of contact time in samples that contained 10 mg/L DOC (Figure 10). Higher ClO_2 residuals were detected in solutions with 5 and 3 mg/L DOC, but in general, the ClO_2 available for Fe(II) oxidation was greatly reduced in the presence of DOC.

For Fe(II) oxidation studies, it was necessary to overcome the oxidant demand of the humic materials to ensure sufficient oxidant concentrations for Fe(II) oxidation. Thus, oxidant dosages in excess of the oxidant demand were required before sufficient oxidant was available for Fe(II) oxidation. For Fe(II) oxidation by free chlorine, 0.64 mg as Cl_2 are required per each mg Fe. For ClO_2 oxidation, Iatrou (1991) reported that each mg of uncomplexed Fe(II) consumes 0.24 mg ClO_2 . This stoichiometry is based on the reduction of ClO_2

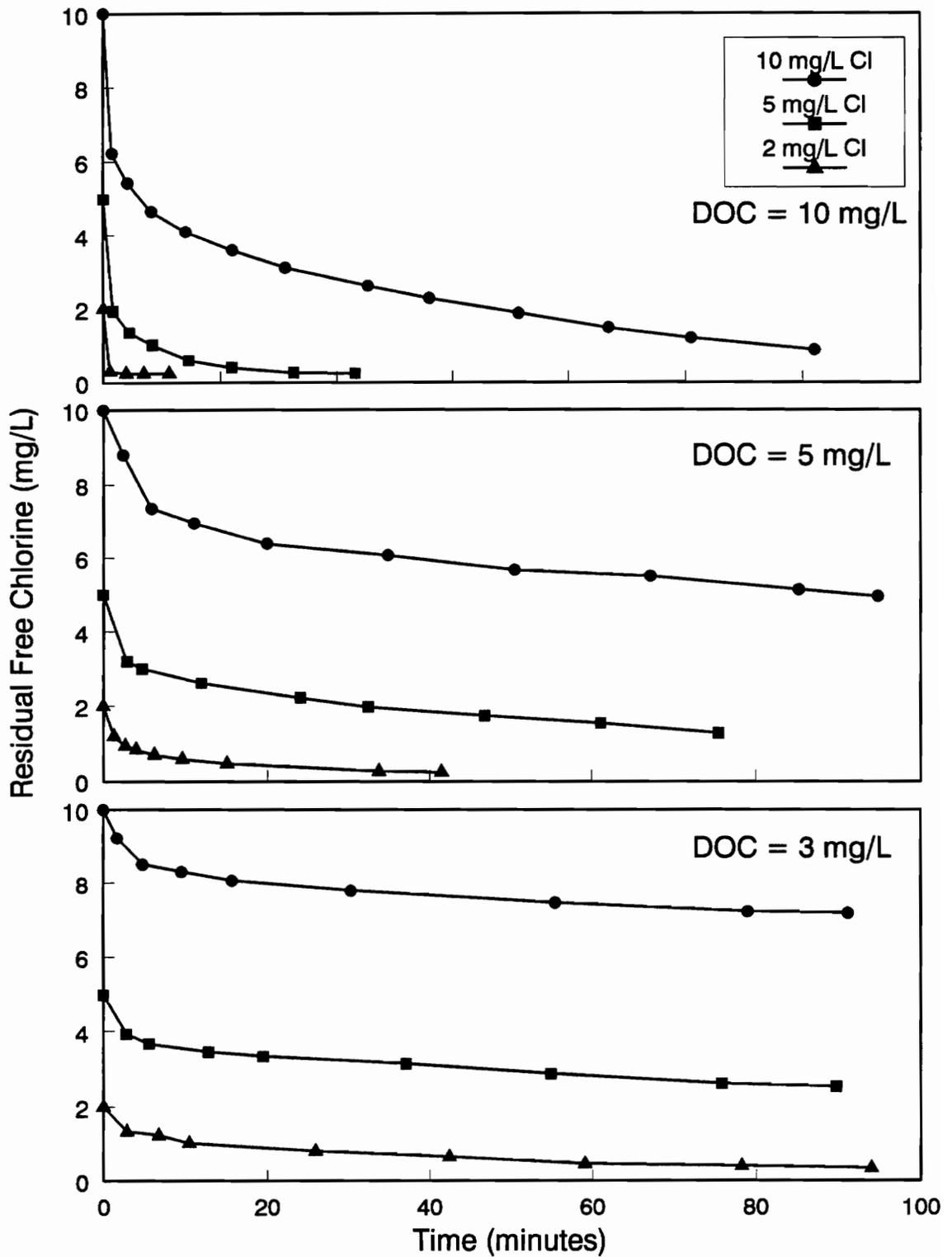


Figure 9. Free chlorine demand by Dismal Swamp humic material.

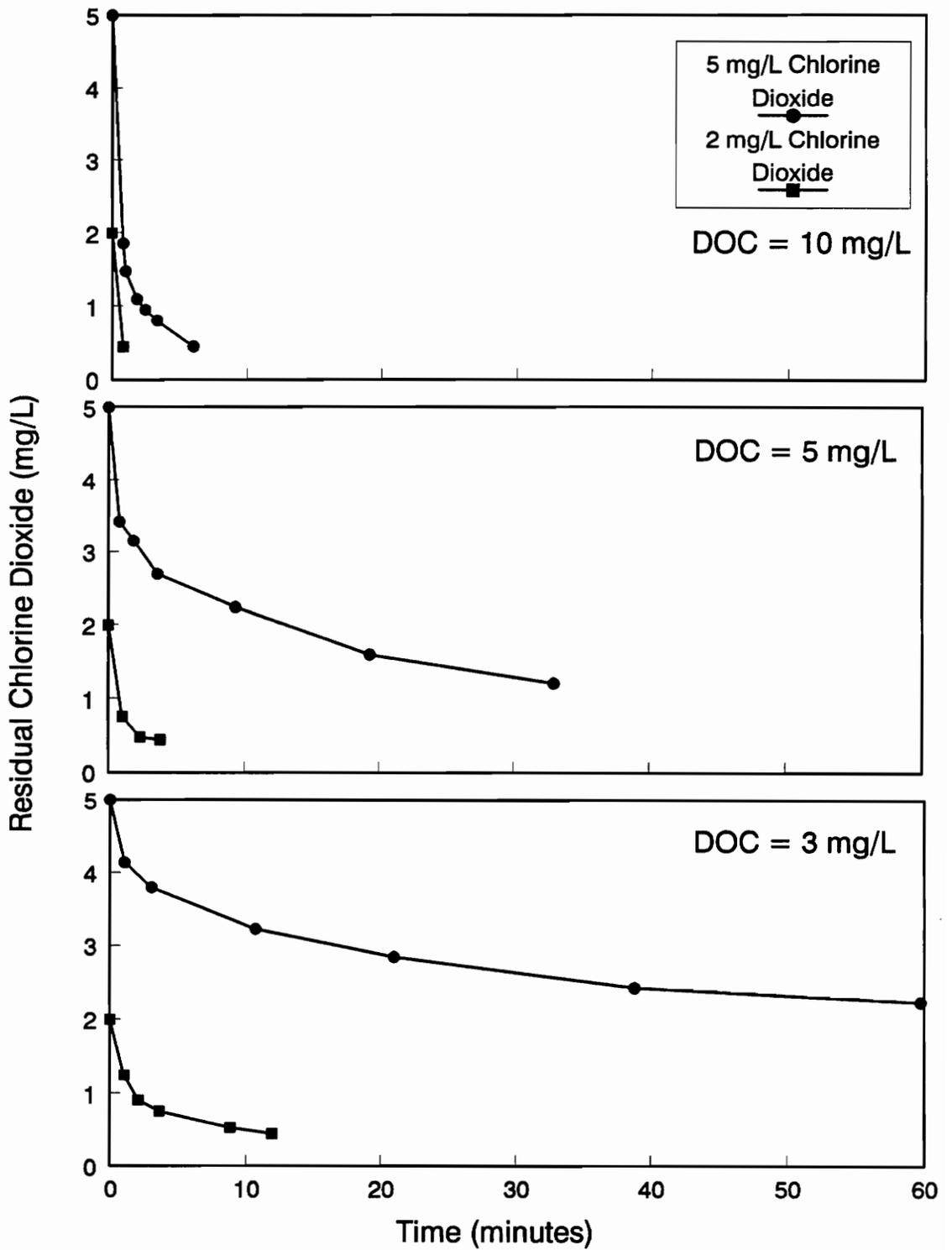


Figure 10. Chlorine dioxide demand by Dismal Swamp humic material.

to Cl^- . However, if ClO_2 reduces only to ClO_2^- , 1.2 mg ClO_2 are required to oxidize each mg Fe.

A summary of the competitive oxidant demands of the Dismal Swamp humic material is presented in Table 7. Interpretation of these results is explained by the following testing conditions. For free chlorine oxidation of a 2 mg/L Fe(II) solution, a 500 percent oxidant dose is 6.4 mg/L as Cl_2 , and 1.28 mg/L as Cl_2 are needed to oxidize Fe(II). From Table 7, in a 10 mg/L DOC sample, 0.36 to 0.47 mg oxidant are consumed per mg DOC in solution during a 5 minute reaction time. This calculates to 3.6 to 4.7 mg/L as Cl_2 being consumed during the first 5 minutes of reaction. Thus, after 500 percent free chlorine was added to solution, a residual of 2.8 to 1.7 mg/L as Cl_2 persisted in solution and were available for Fe(II) oxidation. Further analysis of the exerted oxidant demands per mg DOC suggests that oxidant dosages ranging from 0 to 500 percent of the stoichiometric requirement for Fe(II) oxidation (by free chlorine and both stoichiometries of ClO_2) would provide sufficient oxidant residuals for complexed Fe(II) oxidation.

Another aspect of the competitive oxidant demand is the reaction time for Fe(II) oxidation. Knocke *et al.* (1990) reported that ClO_2 instantaneously oxidizes uncomplexed Fe(II), and free chlorine oxidation of Fe(II) occurs within 15 seconds of contact time (even at pH values as low 5.0). Thus, oxidation of Fe(II) occurs quickly once the oxidant is introduced to solution, and the oxidant demand within this time period, as seen by the low oxidant demands within 5 minutes contact time, would not deplete the oxidant concentration to below the stoichiometric requirement for Fe(II) oxidation.

Table 7

Summary of the free chlorine and ClO₂ demands by
Dismal Swamp humic materials

DOC (mg/L)	Oxidant	Oxidant Dosage (mg/L)	Reaction Time	
			5 min.	60 min.
			Exerted Demand (mg oxidant/mg DOC)	
9.9	Cl ₂	10	0.47	0.80
4.8	Cl ₂	10	0.48	0.94
3.2	Cl ₂	10	0.46	0.81
10.0	Cl ₂	5	0.36	--
4.9	Cl ₂	5	0.43	0.71
3.0	Cl ₂	5	0.42	0.73
10.3	Cl ₂	2	--	--
4.9	Cl ₂	2	0.25	--
3.1	Cl ₂	2	0.23	0.48
10.9	ClO ₂	5	0.41	--
5.3	ClO ₂	5	0.45	--
3.3	ClO ₂	5	0.40	0.85
11.0	ClO ₂	2	--	--
6.2	ClO ₂	2	--	--
4.6	ClO ₂	2	0.28	--

Note: '--' represents oxidant residuals below the detection limit for
potentiometric titration

Cl₂ titrations performed at pH 7

Results from free chlorine and ClO_2 oxidation studies also indicated that Fe(II) oxidation in the presence of Dismal Swamp DOC occurred within the first 5 minutes of reaction time. Data of Figure 11 show iron removal by a 0.2 μm pore size membrane filter and a 100K ultrafilter after free chlorine oxidation. Minimal differences in iron removal after the 5 and 60 minute contact times by the two filters were observed. Thus, oxidation of Fe(II) occurred within the first 5 minutes of contact time. Results from free chlorine oxidation studies with the Durham, NC humic source indicate reaction time did influence the iron removal by the 0.2 μm pore size membrane filter. This will be discussed in a later section. For data representation (from experiments using the Dismal Swamp humic material) in this thesis, only the 5 or 60 minute oxidation data will be presented.

The Durham, NC humic source was also exposed to 10, 5, and 2 mg/L free chlorine (Figure 12). The oxidant demands per mg DOC in Table 8 show that the Durham, NC source had a weaker oxidant demand than the Dismal Swamp humic material. This information helps to address the differences witnessed in the Fe(II) oxidation studies with these two DOC sources.

Oxidation of Fe(II) by Free Chlorine and ClO_2

Oxidation of complexed Fe(II) by free chlorine and ClO_2 was conducted at pH 5.5 and 6.5. Prepared water solutions were dosed with varying percentages of the stoichiometric requirement for Fe(II) oxidation of each oxidant: 0.64 mg free chlorine per mg Fe, and either 1.2 mg ClO_2 per mg Fe if ClO_2 reduced to ClO_2^- or 0.24 mg ClO_2 per mg Fe if ClO_2 reduced to Cl^- . The solutions were then allowed a contact time of 5 and 60 minutes.

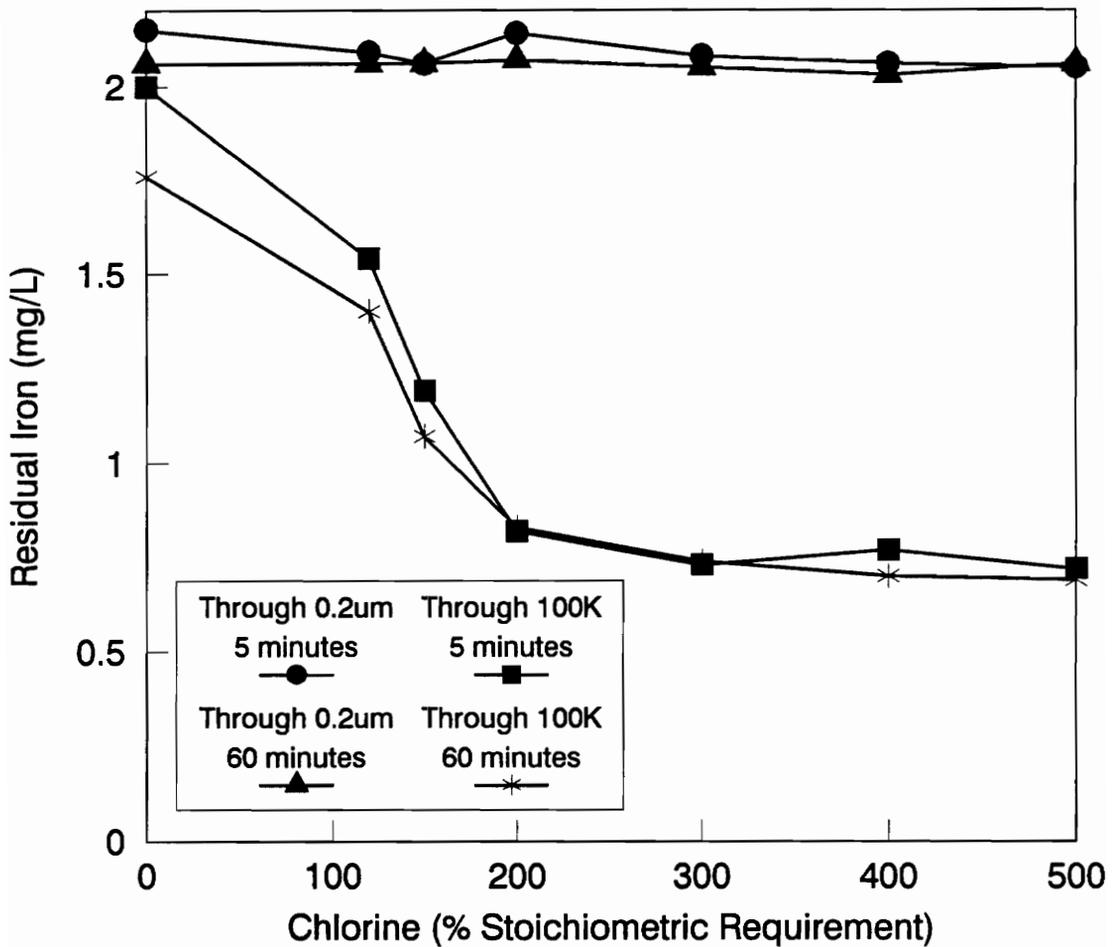


Figure 11. Oxidation of complexed Fe(II) by free chlorine following 5 and 60 minute reaction periods. (DOC source - Dismal Swamp; DOC = 5.4 mg/L; pH = 5.5; stoichiometric requirement = 0.64 mg as Cl₂ per mg Fe)

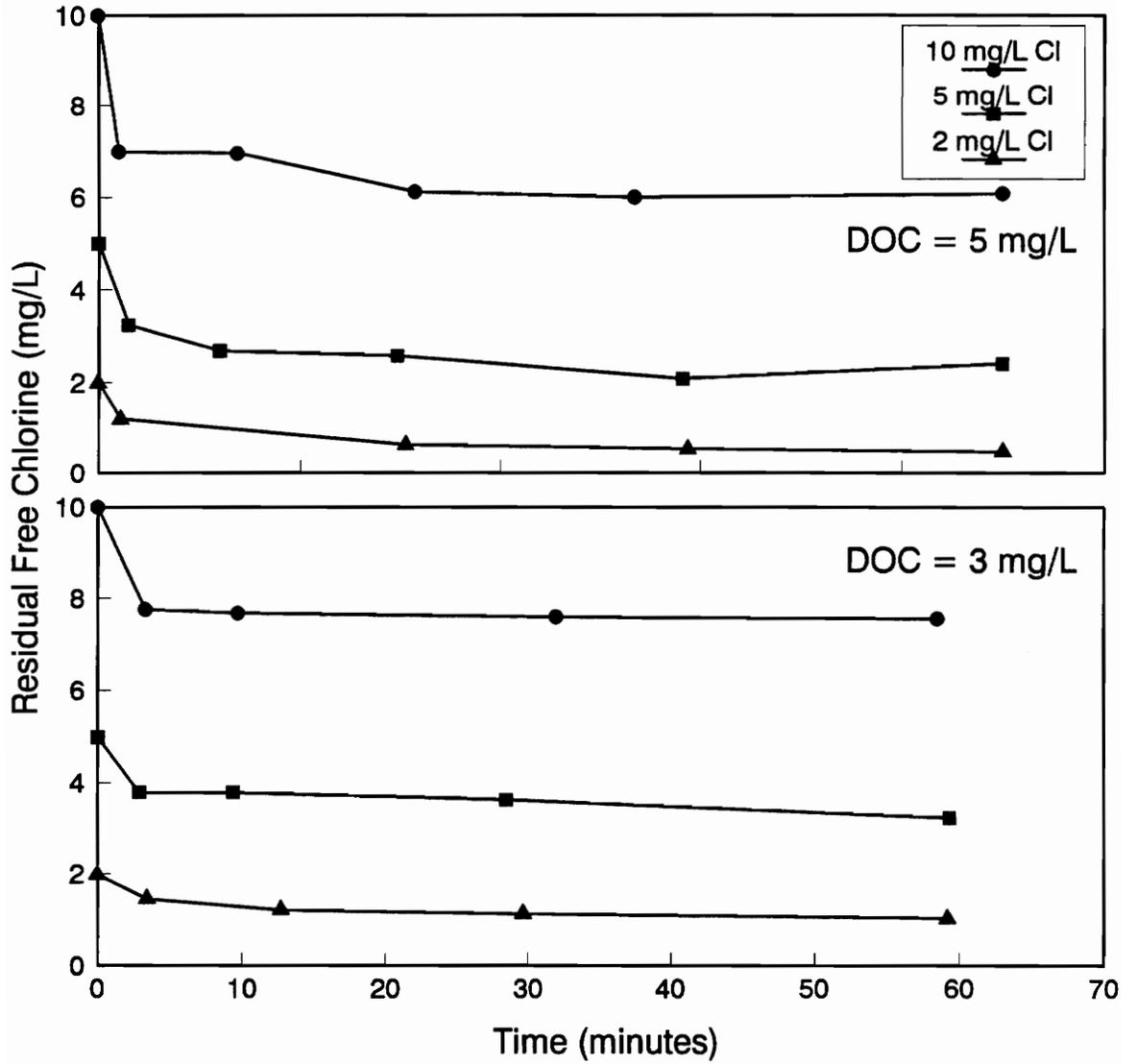


Figure 12. Free chlorine demand by Durham, NC humic material.

Table 8

Summary of the free chlorine demand by
Durham, NC humic materials

DOC (mg/L)	Oxidant	Oxidant Dosage (mg/L)	Reaction Time	
			2-4 min.	60 min.
Exerted Demand (mg oxidant/mg DOC)				
5.0	Cl ₂	10	0.60	0.78
3.2	Cl ₂	10	0.70	0.76
5.0	Cl ₂	5	0.35	0.58
3.4	Cl ₂	5	0.35	0.53
5.3	Cl ₂	2	0.15	0.28
3.1	Cl ₂	2	0.17	0.30

Note: Cl₂ titrations performed at pH 7

Oxidation of Fe(II) by Free Chlorine

Free Chlorine Oxidation of Uncomplexed Fe(II): Free chlorine oxidized uncomplexed Fe(II) to Fe(OH)₃(s) at a stoichiometric requirement of 0.64 mg free chlorine per mg Fe. Data presented in Figure 13 show the particulate iron removal by the 0.2 um pore size membrane filter and the 100K ultrafilter. Laboratory results correlated well with theoretical predictions for Fe(II) oxidation.

Free Chlorine Oxidation of Complexed Fe(II): Free chlorine was used to oxidize Fe(II) which was complexed by DOC from each humic source. The following sections present the trends which were observed in iron and DOC speciation after free chlorine oxidation for each DOC source.

1) Fe(II) Complexed with Dismal Swamp Humic Material: Data presented in Figure 14 show that free chlorine was not effective in oxidizing Fe(II) into a particulate form (based on retention by a 0.2 um pore size membrane filter). Further, an average of only 60 percent of the soluble Fe(II) was oxidized into the colloidal fractions in test solutions containing 5 and 3 mg/L DOC. The 10 mg/L DOC solutions retarded colloidal iron formation, with only 11 percent being oxidized to colloidal iron. The solution pH did not greatly influence the performance of free chlorine at dosages greater than 300 percent of the stoichiometric requirement for Fe(II) oxidation. However, from 0 to 200 percent free chlorine, more colloidal iron was formed at pH 6.5 than at pH 5.5.

a) DOC Removal by 100K Ultrafilter after Oxidation by Free Chlorine: The DOC concentrations in water which passed through the 100K ultrafilter were effected by oxidation and solution pH. The DOC removal by a 100K ultrafilter for test solutions after free chlorine oxidation is presented in

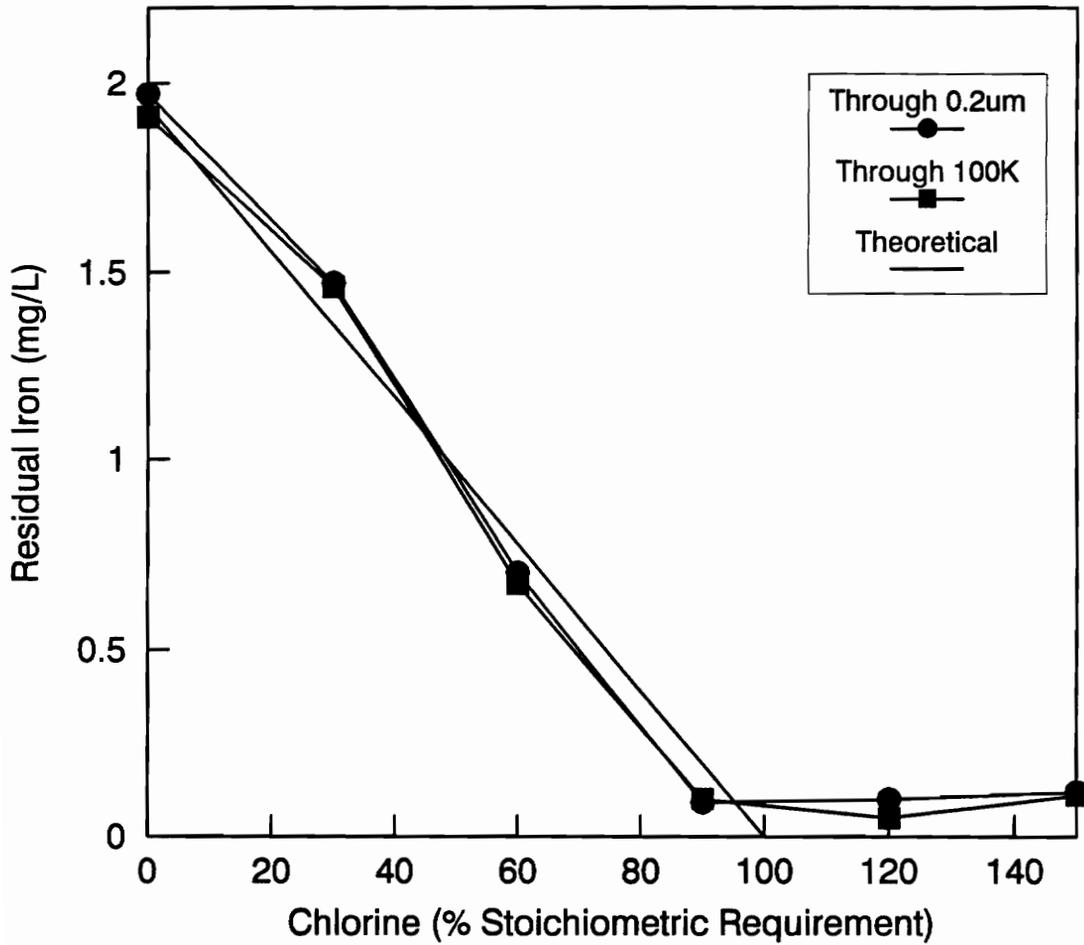


Figure 13. Oxidation of uncomplexed Fe(II) by free chlorine.

(pH = 5.8; stoichiometric requirement = 0.64 mg as Cl₂ per mg Fe)

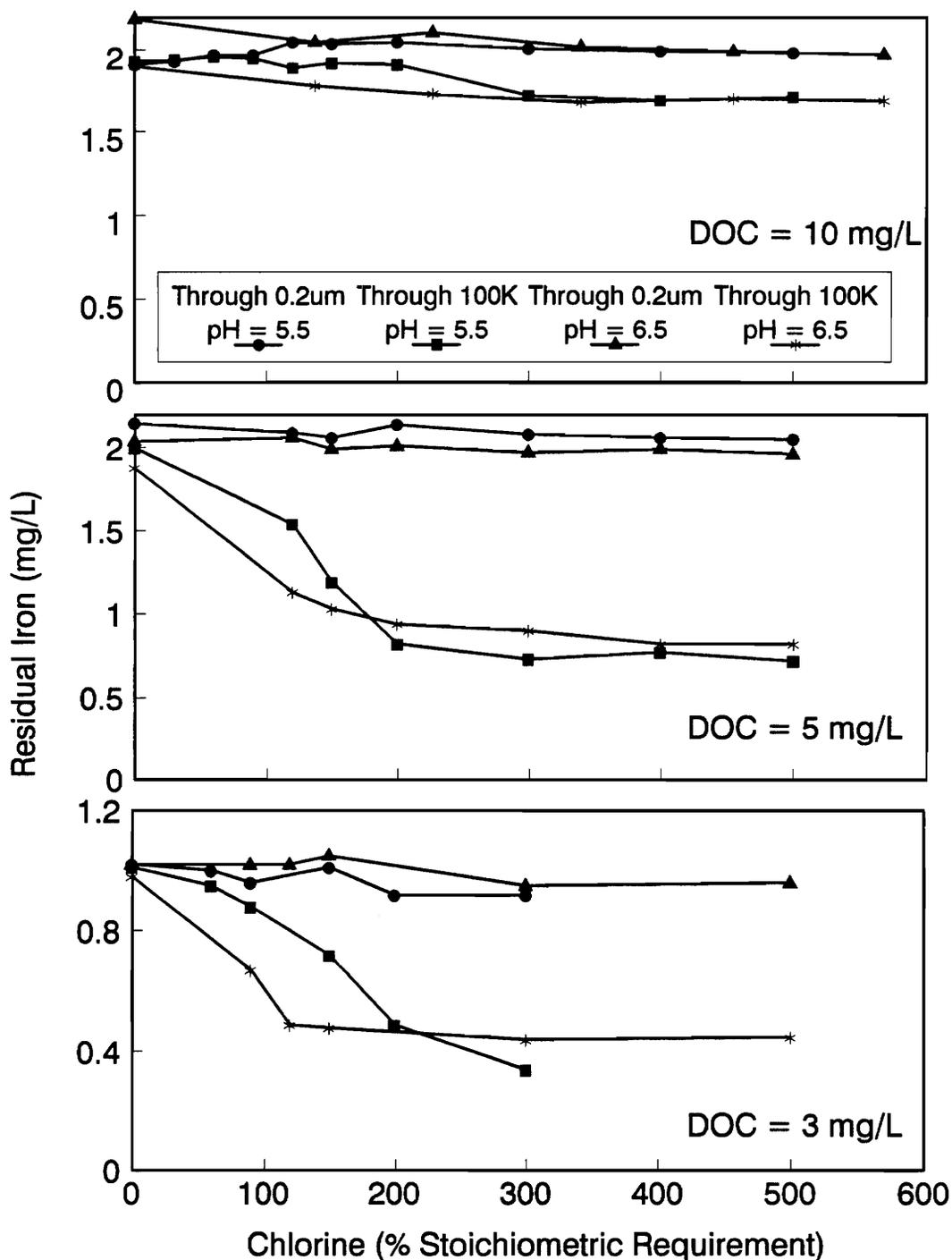


Figure 14. Formation of colloidal iron due to oxidation by free chlorine at pH 5.5 and 6.5. (DOC source - Dismal Swamp; reaction time = 5 minutes; stoichiometric requirement = 0.64 mg as Cl_2 per mg Fe)

Table 9. Note that higher removals were observed at pH 5.5 than at pH 6.5, and the highest DOC removals (26 and 18 percent) were in test solutions having a DOC-to-iron ratio of 2.5:1.

Removal of DOC by a 100K ultrafilter was also found to be related to the iron removal by a 100K ultrafilter. This increase in the particle molecular size is hypothesized to be a result of DOC adsorption onto iron oxide solids which were produced during oxidation. These trends, as well as the ratios relating changes in the DOC concentrations to changes in the iron concentrations, are addressed in the Discussion chapter.

b) Exerted Free Chlorine Demand During Oxidation of Complexed Fe(II): Monitoring the residual chlorine concentration after oxidation revealed that free chlorine dosages ranging between 0 and 500 percent provided sufficient oxidant residuals for Fe(II) oxidation. Data of Table 10 show the free chlorine demands that were measured after 5 minutes of free chlorine oxidation in test solutions containing 2 mg/L Fe and 5 mg/L DOC. At the lower free chlorine dosages, the residual oxidant concentration was completely depleted, however, at free chlorine dosages greater than 2.7 mg/L, oxidant residuals persisted in solution. Thus, within the initial 5 minute reaction time, enough oxidant should be available for Fe(II) oxidation.

c) Fate of Complexed Fe(II) after Free Chlorine Oxidation: The fate of Fe(II) during oxidation by free chlorine was investigated by fractionating unoxidized and oxidized complexed Fe(II) solutions and quantifying the Total Fe (representing Fe(III) and Fe(II)) and Fe(II) concentrations in each molecular weight fraction. Fractionation data for two

Table 9

Typical DOC removals by a 100K ultrafilter after
free chlorine iron oxidation

Original DOC (mg/L)	pH	Δ Fe (mg/L)	Δ DOC (mg/L)	DOC retained by 100K ultrafilter (percent)
9.6	6.5	0.21	0.3	2.8
5.0	6.5	1.06	0.9	17.6
3.6	6.5	0.53	0.4	10.6
9.6	5.5	0.22	0.5	5.6
5.4	5.5	1.28	1.4	25.8
3.7	5.5	0.29	<0.1	2.4

Note: DOC source – Dismal Swamp, free chlorine dosages between 300
and 600% of the stoichiometric requirement for Fe(II) oxidation,
Reaction time = 5 minutes

' Δ ' denotes changes in concentration

Table 10

Exerted free chlorine demand during oxidation
of complexed Fe(II)

Cl ₂ Dosage (mg/L)	pH	Consumed Cl ₂ * (mg/L)
0.0	5.5	--
0.8	5.5	>0.5
1.3	5.5	>1.1
1.9	5.5	>1.7
2.7	5.5	1.9
3.2	5.5	1.9
0.0	6.5	--
0.9	6.5	>0.7
1.5	6.5	>1.3
2.2	6.5	>2.0
2.9	6.5	2.6
3.6	6.5	2.8

Note: DOC source – Dismal Swamp, Nominal DOC = 10 mg/L, Nominal Fe = 2 mg/L, Reaction time = 5 minutes

* detection limit for Cl₂ residual analysis by potentiometric titration = 0.2 mg/L

solutions of Fe(II) complexed with Dismal Swamp humic material are shown in Figure 15. Solution 1 was unoxidized, while Solution 2 was oxidized for 5 minutes with 500 percent free chlorine. Note that more than 50 percent of the initial Fe(II) in solution passed through the 1K ultrafilter in the unoxidized solution. This iron was also detected almost entirely as Fe(II). However, when oxidized by free chlorine, nearly all of the iron was retained in the molecular weight fractions greater than 10K. Also, the iron was oxidized to Fe(III), as shown by the lower Fe(II) concentrations in this oxidized solution.

To further analyze the ability of the free chlorine to oxidize Fe(II) in the presence of DOC, a companion experiment, identical to the one previously described, was performed using only 100 percent free chlorine. Under these conditions, the oxidant demand by the humic material could dominate and deplete the free chlorine concentration prior to Fe(II) oxidation. The higher Fe(II) concentrations presented in Figure 16 show that the oxidant demand by the humic material did inhibit Fe(II) oxidation, indicating that DOC was competing with Fe(II) for reaction with free chlorine. Thus, free chlorine doses greater than the theoretical stoichiometry are necessary for complete Fe(II) oxidation in the presence of DOC.

2) Fe(II) Complexed With Durham, NC Humic Material: Free chlorine oxidation studies were performed with the Durham, NC stock humic solution. The results were quite different from the results obtained with Dismal Swamp humic material. Nearly 60 and 83 percent of the soluble Fe(II) became particulate iron after 60 minutes contact time with 3.2 and 6.4 mg/L free chlorine, respectively, at pH 6.5 (Table 11). No particulate iron was formed after only 5 minutes of contact time.

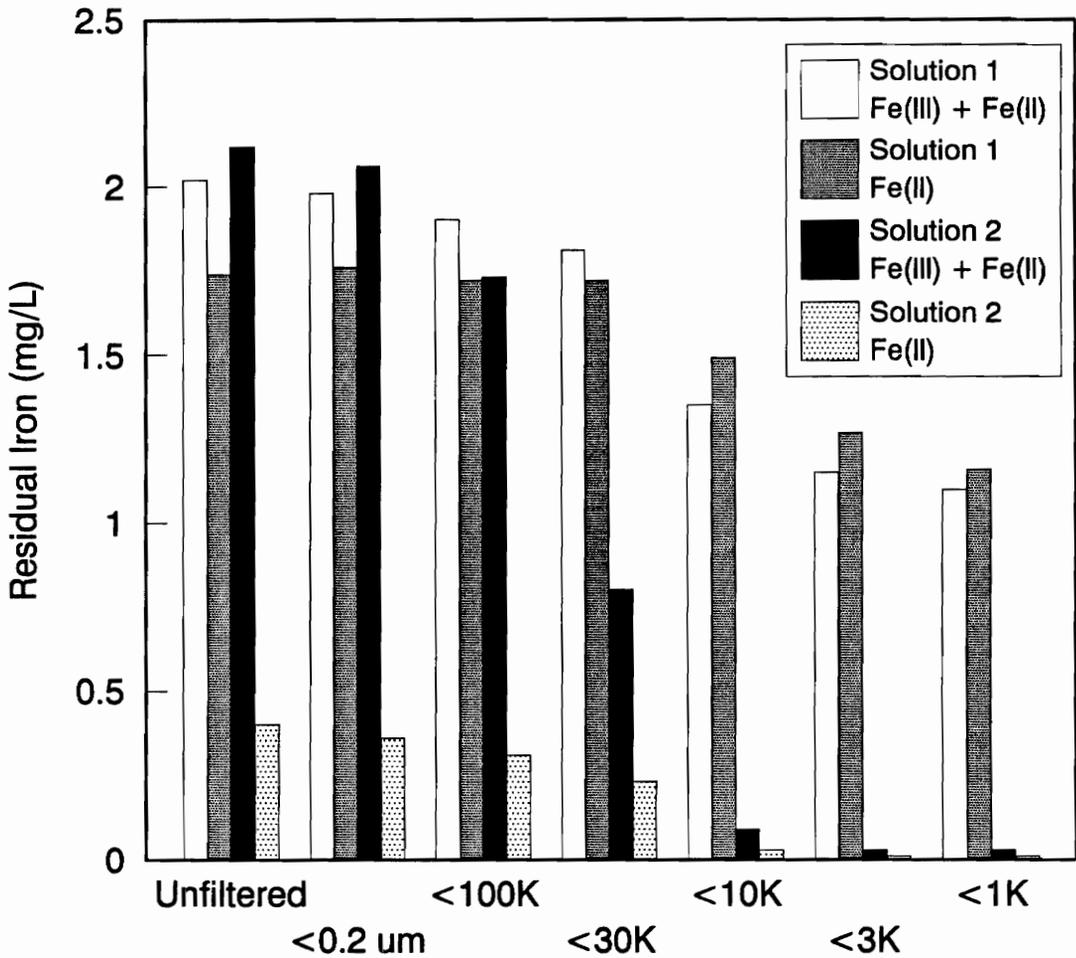


Figure 15. Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 500% free chlorine; reaction time = 5 minutes; DOC source - Dismal Swamp; stoichiometric requirement = 0.64 mg as Cl₂ per mg Fe)

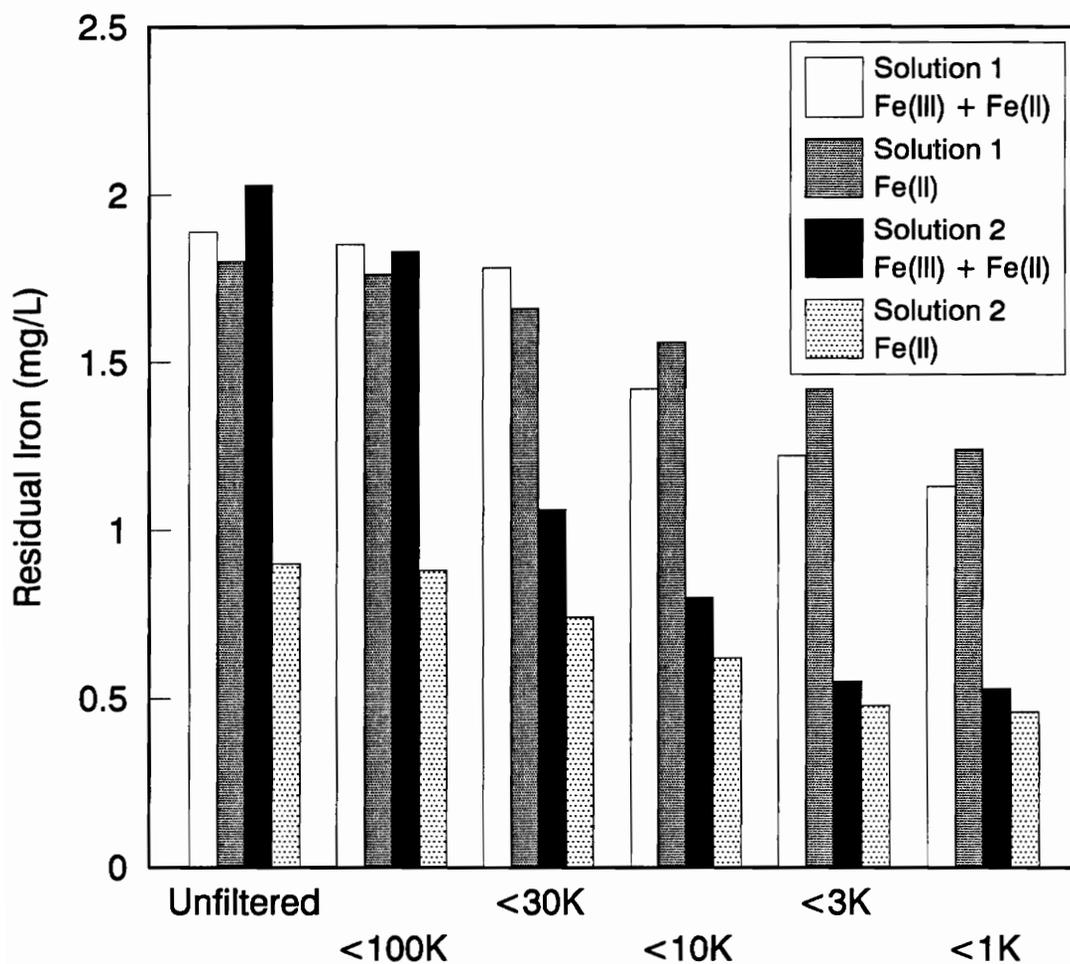


Figure 16. Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 100% free chlorine; reaction time = 5 minutes; DOC source - Dismal Swamp; stoichiometric requirement = 0.64 mg as Cl₂ per mg Fe)

Table 11

Free chlorine oxidation of Fe(II) complexed with
Durham, NC humic material

Cl ₂ Dosage (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)
0.00	0.93	0.87	3.4
0.96	0.94	<0.03	3.3
3.20	0.93	<0.03	3.5

Note: pH = 6.5, Reaction time = 5 minutes, Fe = 1.1 mg/L, DOC = 3.4 mg/L

Cl ₂ Dosage (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)
0.00	0.94	0.82	3.7
0.96	0.85	<0.03	3.4
3.20	0.38	<0.03	3.3

Note: pH = 6.5, Reaction time = 60 minutes, Fe = 1.1 mg/L, DOC = 3.4 mg/L

The DOC removal (as quantified by the 100K ultrafilter) was minimal in all solutions, indicating little interaction between the organic species and the iron colloids formed by oxidation. This indicates that even with similar molecular weight distributions and DOC concentrations, different trends in DOC adsorption onto iron oxide solids exist for the Durham, NC and Dismal Swamp humic material. Thus, the differences in chemical characteristics of each DOC source influenced the behavior of organics under oxidized conditions.

3) Fe(II) Complexed with High Molecular Weight University of Washington Humic Material: Oxidation studies were conducted with the higher molecular weight DOC (100K–10K) from the University of Washington humic source. Free chlorine was used to oxidize complexed Fe(II) at pH 6.5. Results in Table 12 show that at a 1.0 mg/L (100 percent) dosage of free chlorine, approximately 50 percent of the iron was retained by the 100K ultrafilter. (Percentage dosages for this experiment were based on the iron concentration that passed through a 100K ultrafilter in the 0.0 mg/L control sample.) At the higher dosages, almost all of the iron was colloidal. Relatively low percentages of DOC were removed by the 100K ultrafilter, and in the presence of a 100 percent oxidant dosage, approximately 100 percent of the iron in solution was detected as Fe(III). This indicated little competitive oxidant demand from the organics.

4) Fe(II) Complexed with Low Molecular Weight University of Washington Humic Material: Results from oxidation studies with the <3K DOC molecular weight fraction of the University of Washington humic source are shown in Table 13. These experiments were performed at pH 6.5 and allowed a 5 minute contact time. Nearly 82 percent soluble iron conversion to

Table 12

Free chlorine oxidation of Fe(II) complexed with high molecular weight humic material (100–10K)

Cl ₂ Dosage (mg/L)	Fe Through 0.2 um (percent)	Fe Through 100K (percent)	DOC Through 100K (percent)	Fe(II) Through 100K (mg/L)
0.0	100	100	100	1.0
1.0	100	51	81	0.2
2.6	100	15	98	<0.1
5.1	96	15	93	<0.1

Note: pH = 6.5, Reaction time = 5 minutes, Nominal Fe = 2 mg/L, Nominal DOC = 5 mg/L, free chlorine dosages based on Fe through 100K in the 0.0 mg/L control sample, DOC source – University of Washington

Table 13

Free chlorine oxidation of Fe(II) complexed with
low molecular weight humic material (<3K)

Cl ₂ Dosage (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)
0.0	1.79	1.74	6.8
1.3	1.73	0.86	5.3
2.6	1.74	0.44	4.8
6.4	1.75	0.32	5.0

Note: pH = 6.5, Reaction time = 5 minutes, DOC source – University of Washington

colloidal iron was achieved by 6.4 mg/L free chlorine. The DOC retained by the 100K ultrafilter at these oxidant dosages was approximately 26 percent of the original DOC concentration.

Iron removals by the 0.2 μm pore size membrane filter and the 100K ultrafilter for the high and low molecular weight DOC experiments were similar. However, the DOC retention by the 100K ultrafilter for the low molecular weight DOC was appreciably more than that for the high molecular weight DOC. The DOC adsorption trends will be addressed in the Discussion chapter.

Oxidation of Fe(II) by ClO_2

Chlorine Dioxide Oxidation of Uncomplexed Fe(II): Characterization of ClO_2 oxidation required an investigation into the stoichiometry of ClO_2 reduction during Fe(II) oxidation. Uncomplexed Fe(II) was oxidized to a particulate form with only 0.24 mg/L ClO_2 per mg Fe (based on ClO_2 reduction to Cl^-) (Figure 17). Ferric hydroxide solids were retained by the 100K ultrafilter. This indicated that laboratory results correlated well with theoretical Fe(II) oxidation predictions. Further, the $\text{Fe}(\text{OH})_3(\text{s})$ formed in the absence of DOC grew sufficiently large to be retained by the 0.2 μm pore size membrane filter.

Stoichiometry of ClO_2 Reduction during Oxidation of Complexed Fe(II): Initial ClO_2 oxidation of complexed Fe(II) studies revealed that ClO_2 reduced to ClO_2^- rather than Cl^- . The residual ClO_2 , ClO_2^- , ClO_3^- , and Cl^- concentrations, as well as iron and DOC concentrations, were monitored during a ClO_2 oxidation study at pH 6.5. The testing solution had an initial DOC concentration of 5.6 mg/L and an initial Fe(II) concentration of 2.2 mg/L

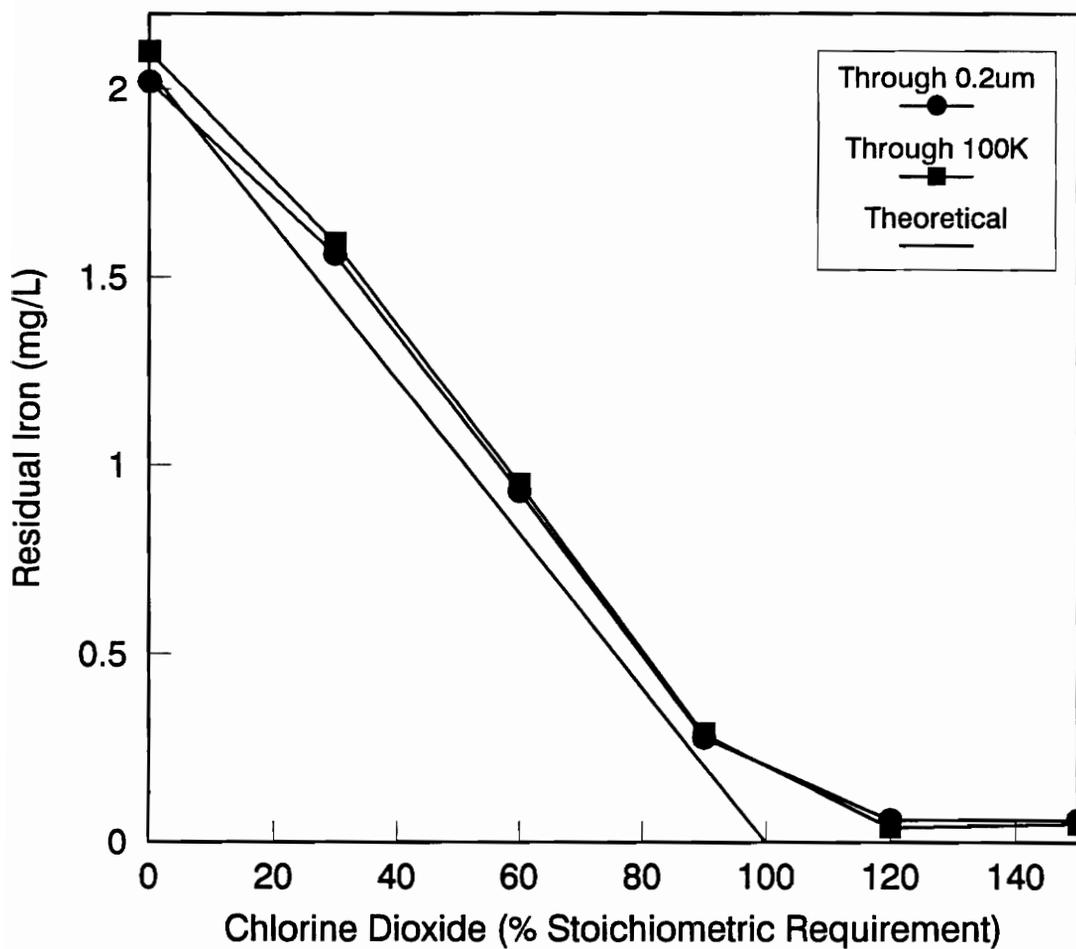


Figure 17. Oxidation of uncomplexed Fe(II) by chlorine dioxide. (pH = 5.8; stoichiometric requirement = 0.24 mg chlorine dioxide per mg Fe)

(DOC-to-Fe ratio of 2.5). Chlorite, Cl^- , and ClO_3^- concentrations were quantified by IC, while ClO_2 was analyzed by potentiometric titration.

Results (shown in Table 14) revealed no change in Cl^- or ClO_3^- concentrations due to chemical reaction. Instead, solution concentrations of these two species correlated to the concentrations that were introduced from the stock ClO_2 solution. The ClO_2^- concentration, however, increased during oxidation. (Values are reported as changes (Δ) in concentration to account for the concentrations which were added to solution from the stock ClO_2 solutions.) However, a mass balance of the chlorine species revealed a positive interference. This interference was found to be a result of residual ClO_2 in solution during ClO_2^- analysis with the IC.

An experiment was conducted to better quantify ClO_2 and ClO_2^- concentrations after ClO_2 oxidation. Samples were stripped of ClO_2 by 15 minutes of purging with $\text{N}_2(\text{g})$. Results in Table 15 show the residual ClO_2 and the changes in the ClO_2^- concentrations after oxidation of 2 mg/L Fe(II) in the presence of 10 mg/L DOC. An improved mass balance was achieved, but it was believed that a loss of ClO_2 due to volatilization occurred during the pouring of the samples for analysis. These data suggest that ClO_2 reduces to ClO_2^- during the oxidation of complexed Fe(II), thus having a stoichiometry which required 1.2 mg ClO_2 per mg Fe(II) in solution.

Chlorite Oxidation of Complexed Fe(II): Because of the high ClO_2^- residuals detected during ClO_2 oxidation studies, it was necessary to quantify the potential capacity of ClO_2^- to oxidize complexed Fe(II). A complexed Fe(II) solution (5.4 mg/L DOC, 2.0 mg/L Fe) was exposed to ClO_2^- for 5 minutes at pH 6.5 (Figure 18). Less than 5 percent of the soluble iron was oxidized into the

Table 14

Residual chlorine species during oxidation of
complexed Fe(II) by ClO₂

ClO ₂ Dosage (mg/L)	Fe Through 100K (mg/L)	ClO ₂ (mg/L)	Δ ClO ₂ ^{-**} (mg/L)	Δ ClO ₃ ⁻ (mg/L)	Δ Cl ⁻ (mg/L)
0.0	1.89	<0.4	(<0.1)	<0.04	<0.1
2.4	1.66	0.5	(1.2)	<0.04	<0.1
4.8	1.37	2.4	(2.3)	<0.04	<0.1
7.2	1.27	5.1	(2.7)	<0.04	<0.1
12.0	1.14	10.0	(5.0)	<0.04	<0.1

Note: pH = 6.5, DOC = 5 mg/L, DOC source – Dismal Swamp, Reaction time = 5 minutes

* 'Δ' denotes changes in concentration

** ClO₂⁻ concentrations are erroneous due to an interference by ClO₂ during analysis by ion chromatography

Table 15

Residual ClO_2 and ClO_2^- concentrations after
 ClO_2 iron oxidation

ClO_2 Dosage (mg/L)	Residual ClO_2 (mg/L)	ΔClO_2^- ** (mg/L)
4.8	1.6	2.9
7.2	<2.3*	3.8
12.0	4.4	5.0

Note: pH 6.5, DOC source – Dismal Swamp, DOC = 10.0 mg/L, Fe = 2.1 mg/L, Reaction time = 5 minutes.

* Due to excessive dilution, ClO_2 analysis at detection limit for potentiometric titration

** ' Δ ' denotes changes in concentration

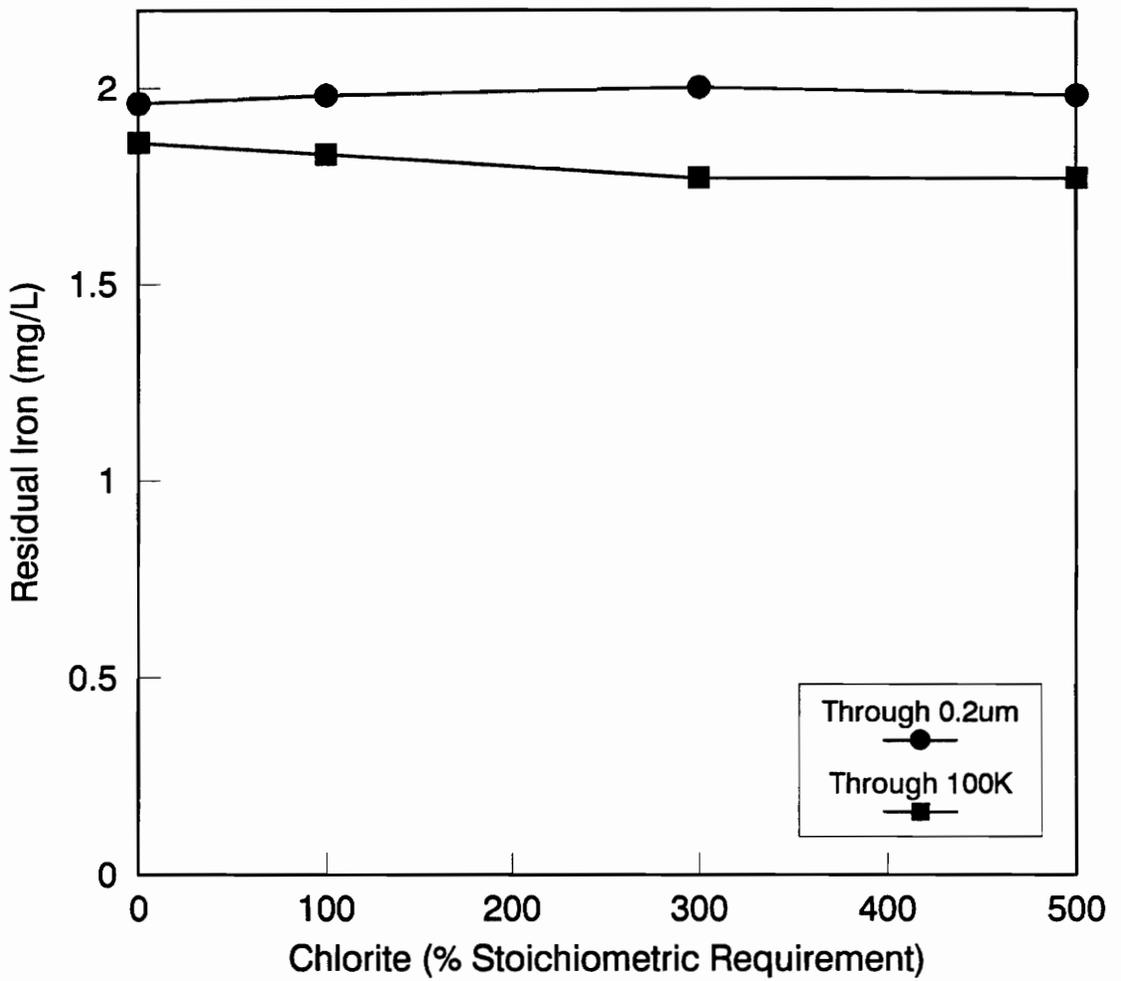


Figure 18. Chlorite oxidation of complexed Fe(II). (DOC source - Dismal Swamp; DOC = 5.4 mg/L; pH = 6.5; reaction time = 5 minutes; stoichiometric requirement = 0.3 mg chlorite per mg Fe)

colloidal form. Thus, it was concluded that ClO_2^- residuals in test solutions provided minimal additional oxidizing capability during the ClO_2 studies. Additional studies with ClO_2^- revealed that oxidant dosages in excess of stoichiometric requirement for Fe(II) oxidation converted almost 100 percent of the Fe(II) to Fe(III).

Chlorine Dioxide Oxidation of Complexed Fe(II):

1) Fe(II) Complexed with Dismal Swamp Humic Material: As seen by the data of Table 14, complexed Fe(II) is fairly resistant to removal by ClO_2 oxidation. At the 12 mg/L dosage of ClO_2 , 10.0 mg/L ClO_2 remained in solution; no particulate iron was formed; and 1.14 mg/L Fe remained soluble. The changes in iron speciation from soluble to colloidal iron due to ClO_2 oxidation however, were affected by the DOC-to-Fe ratio (Figure 19).

No particulate iron was removed by the 0.2 um pore size membrane filter in any of the test solutions. Approximately 10, 40, and 3 percent conversion of soluble iron to colloidal iron was observed at pH 6.5 in the 10, 5, and 3 mg/L DOC test solutions, respectively. This conversion was more pronounced in the 5 mg/L DOC samples than in the 10 and 3 mg/L DOC samples. The largest DOC-to-Fe ratio (10 mg/L DOC, 2 mg/L Fe) was the most resistant to colloidal formation by ClO_2 oxidation. Also, these studies revealed minimal differences in iron removal by a 100K ultrafilter for pH 5.5 and 6.5. In general, ClO_2 was ineffective in converting Fe(II) to colloidal or particulate iron in the presence of DOC, even with ClO_2 dosages as high as 12 mg/L.

a) DOC Removal by a 100K Ultrafilter after ClO_2 Oxidation:

As with free chlorine oxidation, oxidation of complexed Fe(II) by ClO_2 caused

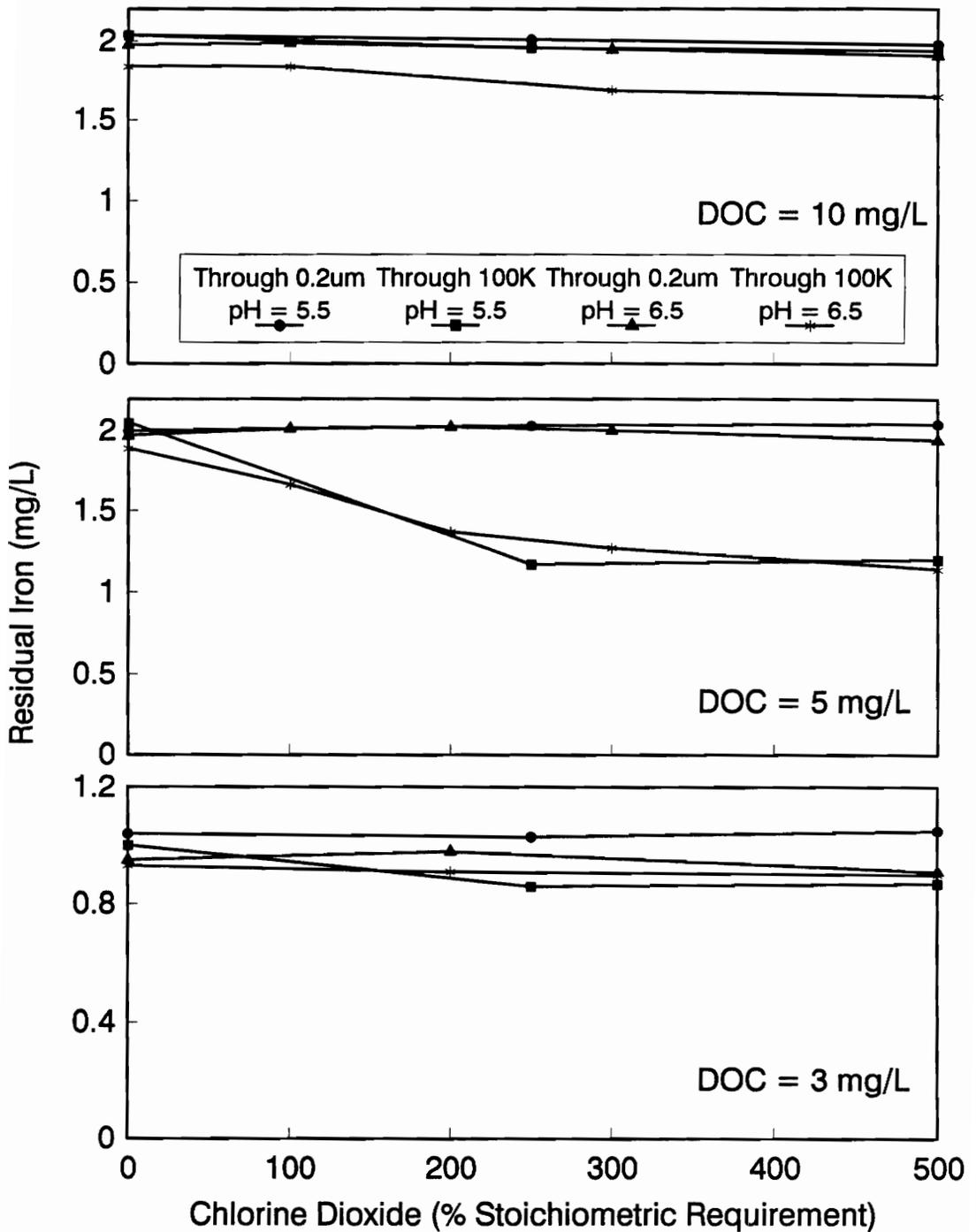


Figure 19. Formation of colloidal iron due to oxidation by chlorine dioxide at pH 5.5 and 6.5. (DOC source - Dismal Swamp; reaction time = 5 minutes; stoichiometric requirement = 1.2 mg chlorine dioxide per mg Fe)

DOC to be removed from solution by a 100K ultrafilter. The DOC removals for ClO_2 oxidation studies are presented in Table 16. In general, DOC removals were larger for ClO_2 oxidation than for free chlorine oxidation. Trends regarding DOC-to-iron ratios and DOC retention on the 100K ultrafilter were similar for both oxidants; higher DOC retention was observed in the solutions with DOC-to-iron ratios near 2.5:1.

b) Fate of Complexed Fe(II) after ClO_2 Oxidation: A

complexed Fe(II) solution was exposed to 100 and 500 percent ClO_2 at a solution pH of 5.5. These solutions were fractionated by ultrafiltration and analyzed for total iron (Fe(III) and Fe(II)) and Fe(II). Figures 20 and 21 display these results as well as a molecular weight fractionation of an unoxidized complexed Fe(II) sample. Results for the 500 percent ClO_2 dosage are similar to those from the free chlorine fractionation study. The oxidized iron species were retained by the >10K DOC. However, no Fe(II) was detected in any of the molecular weight fractions. This suggests that ClO_2 is a stronger oxidant than free chlorine.

Data from the 100 percent ClO_2 experiment (Figure 21) reveal that almost all of the iron in solution was Fe(III). This is very different from the 100 percent free chlorine experiment, where substantial iron was detected at Fe(II). Chlorine dioxide appeared to oxidize the Fe(II) without any interference by the oxidant demand of the Dismal Swamp humic material.

2) Fe(II) Complexed with High Molecular Weight University of Washington Humic Material: Chlorine dioxide oxidation studies were conducted at pH 6.5 with the higher molecular weight DOC (between 100K and 10K) from the University of Washington humic source. Data of Table 17 show

Table 16

Typical DOC removals by a 100K ultrafilter after
ClO₂ iron oxidation

Original DOC (mg/L)	pH	Δ Fe (mg/L)	Δ DOC (mg/L)	DOC retained by 100K ultrafilter (percent)
10.7	6.5	0.19	0.9	8.1
5.7	6.5	0.75	0.9	15.8
3.2	6.5	<0.03	--	--
9.4	5.5	0.10	0.9	9.7
4.8	5.5	0.85	1.2	25.4
3.0	5.5	0.13	0.4	12.1

Note: DOC source – Dismal Swamp, Reaction time = 5 minutes, ClO₂ dosages at 500% of the stoichiometric requirement for Fe(II) oxidation

'--' denotes minimal differences in concentration

' Δ ' denotes changes in concentration

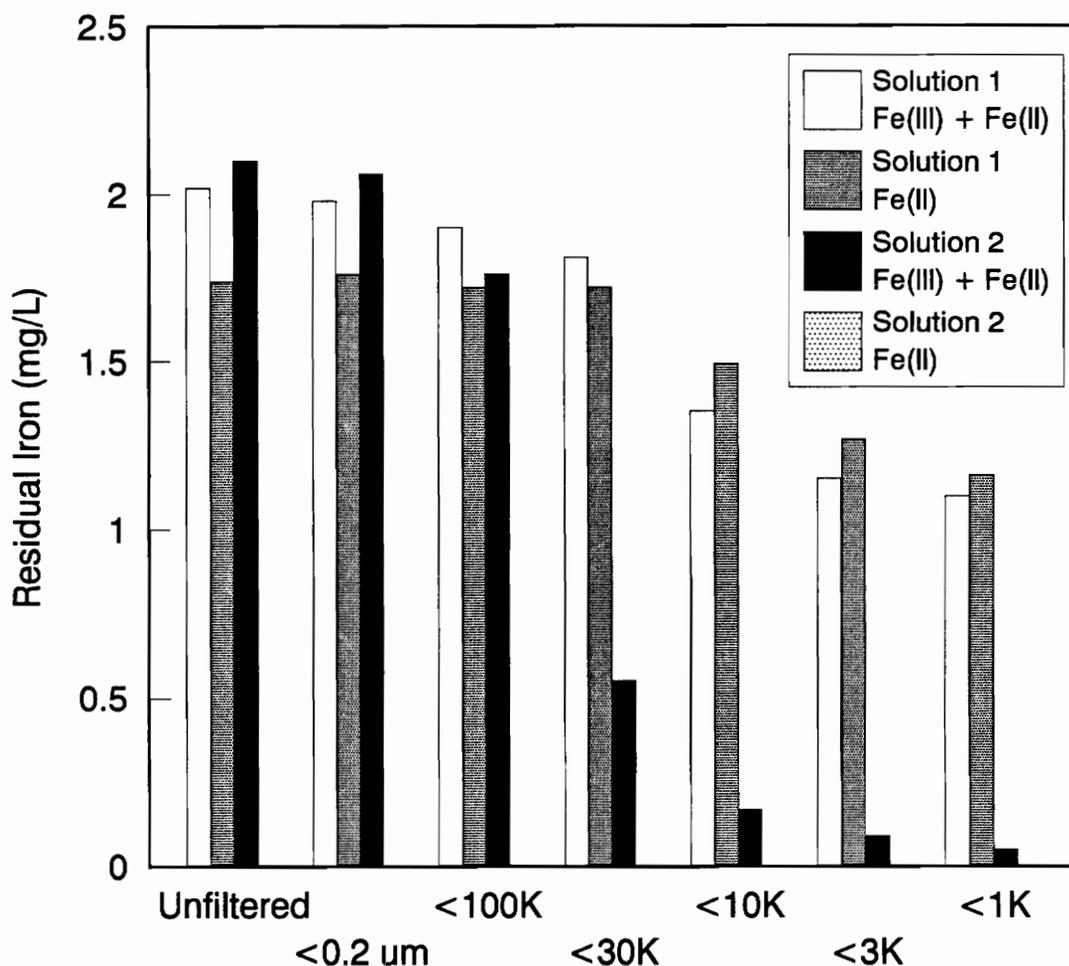


Figure 20. Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 500% chlorine dioxide; reaction time = 5 minutes; DOC source - Dismal Swamp; stoichiometric requirement = 1.2 mg chlorine dioxide per mg Fe)

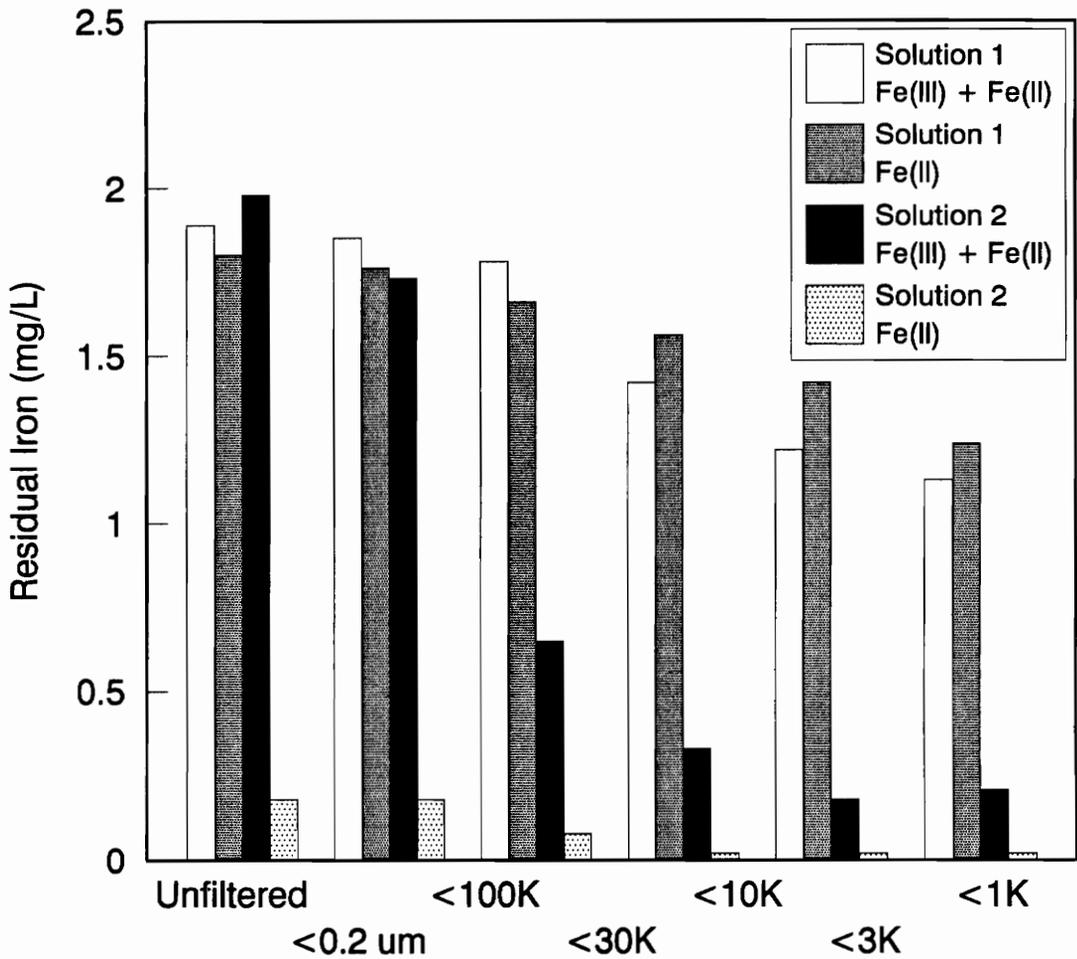


Figure 21. Distribution of iron in two test solutions: 1) total and ferrous iron of an unoxidized solution, 2) total and ferrous iron of an oxidized solution. (DOC = 10 mg/L; pH = 5.5; oxidant = 100% chlorine dioxide; reaction time = 5 minutes; DOC source - Dismal Swamp; stoichiometric requirement = 1.2 mg chlorine dioxide per mg Fe)

Table 17

Chlorine dioxide oxidation of Fe(II) complexed with
high molecular weight humic material (100–10K)

ClO ₂ Dosage (mg/L)	Fe Through 0.2 um (percent)	Fe Through 100K (percent)	DOC Through 100K (percent)	Fe(II) Through 100K (mg/L)
0.0	100	100	100	1.0
1.9	100	46	79	<0.1
3.6	98	16	88	<0.1
7.2	97	13	92	<0.1

Note: pH = 6.5, Reaction time = 5 minutes, Fe = 2 mg/L, DOC = 5 mg/L,
ClO₂ dosages based on Fe through 100K in the 0.0 mg/L control
sample, DOC source – University of Washington

that at a 1.9 mg/L dosage of ClO_2 , approximately 50 percent of the iron was retained by the 100K ultrafilter. At the higher ClO_2 dosages, almost all of the iron became colloidal. No substantial particulate iron was formed. Only about 10 percent of the DOC was retained by the 100K ultrafilter. In the presence of 100 percent oxidant, approximately 100 percent of the iron in solution was detected as Fe(III).

3) Fe(II) Complexed with Low Molecular Weight University of Washington Humic Material: Results from oxidation studies with the <3K DOC molecular weight fraction of the University of Washington humic source are shown in Table 18. These experiments were performed at pH 6.5 with a 5 minute oxidant contact time. Nearly 70 percent soluble iron conversion to colloidal iron was achieved by the 12 mg/L (500 percent) ClO_2 dosage. The DOC retained by the 100K ultrafilter at these oxidant dosages was approximately 30 percent of the original DOC concentration.

Slightly more iron was converted to a colloidal form in the high molecular weight DOC studies, than in the low molecular weight DOC experiments. As seen with free chlorine, more DOC became colloidal with the low molecular weight DOC than with the high molecular weight DOC.

Alum Coagulation of Complexed Fe(II) in the Presence and Absence of Free Chlorine and ClO_2

Coagulation studies with water containing the three humic sources were conducted, both with and without oxidant addition. The complexed iron speciation of these studies will be addressed following a discussion regarding

Table 18

Chlorine dioxide oxidation of Fe(II) complexed with
low molecular weight humic material (<3K)

ClO ₂ Dosage (mg/L)	Fe Through 0.2 um (mg/L)	Fe Through 100K (mg/L)	DOC Through 100K (mg/L)
0.0	1.79	1.74	6.8
2.4	1.75	0.42	4.6
4.8	1.77	0.43	4.5
12.0	1.75	0.51	4.7

Note: pH = 6.5, Reaction time = 5 minutes, Fe = 1.9 mg/L, DOC = 6.4 mg/L,
DOC source – University of Washington

the trends in solution turbidity and DOC removals which were observed during alum coagulation experimentation.

First, turbidity profiles for these studies followed expected trends. As shown by the representative results in Figure 22, turbidity increased as the alum dosage increased from 0 to approximately 12 and 24 mg/L. This represents the charge restabilization phenomenon that occurs when particles have accepted charges, beyond charge neutralization, causing repulsion between particles. When this occurred, the coagulation/flocculation process failed to produce settleable particles. However, as the alum dose was increased to greater than 36 mg/L, residual turbidity decreased due to the sweep floc mechanism. The results presented in Figure 22 are representative of all turbidity profiles observed in this research. Graphical representation of turbidity, therefore, will not be presented for all coagulation studies.

It is well documented in the literature that substantial DOC removal can be achieved by alum coagulation. This was observed in the coagulation studies at pH 5.7–6.0 with the Dismal Swamp humic material. The variations in the percentages of DOC passing through a 100K ultrafilter for the 12 and 48 mg/L alum dosages are shown in Table 19. In the 12 mg/L alum dose data, it was evident that oxidant addition improved colloidal species formation, with ClO_2 addition yielding superior DOC removal by a 100K ultrafilter. However, at the 48 mg/L alum dosage, oxidant addition appeared to not influence the amount of residual DOC in solution.

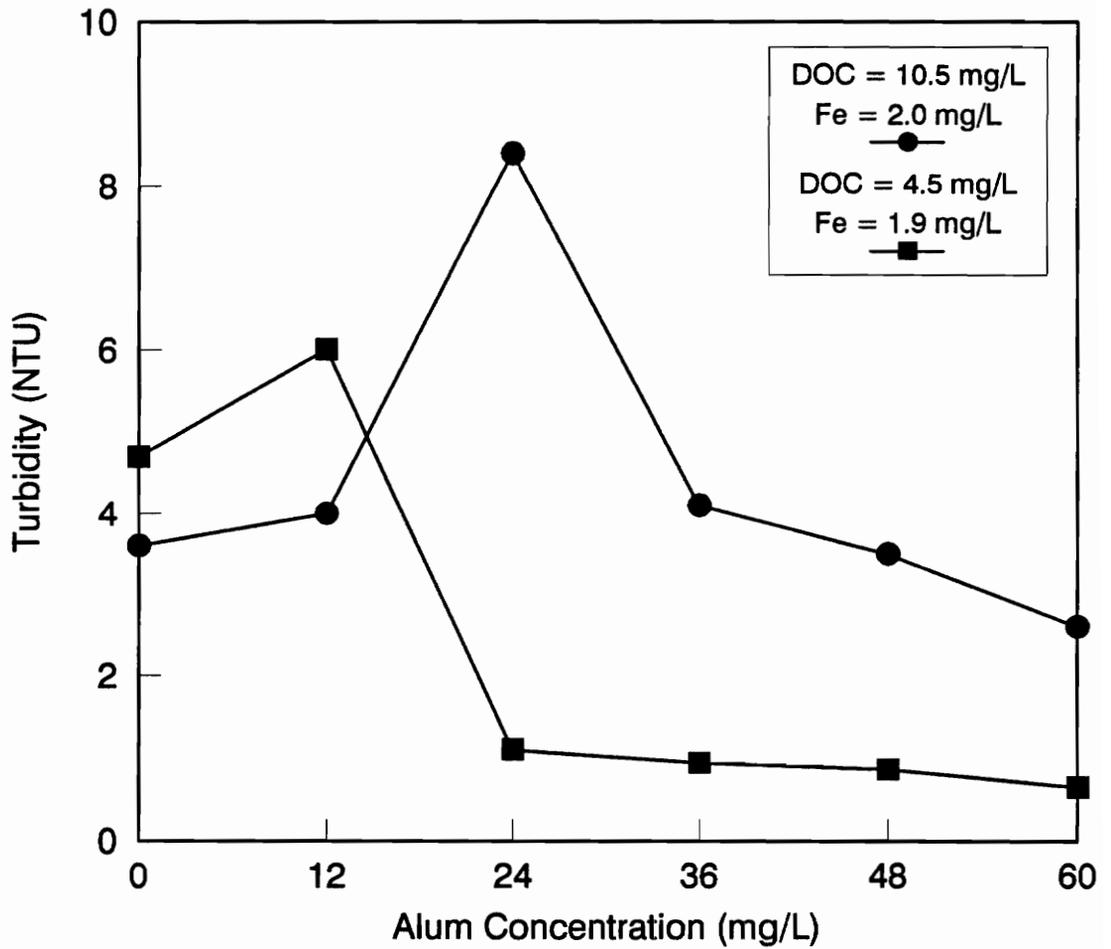


Figure 22. Turbidity profiles of alum coagulation without oxidant addition. (pH 5.7-6.0, DOC source - Dismal Swamp)

Table 19

Typical percentages of DOC passing through a 100K ultrafilter after alum coagulation in the presence and absence of free chlorine and ClO₂

Experimental Conditions	Original DOC (mg/L)	Alum Dose	
		12 mg/L	48 mg/L
		DOC (<100K)	
		(percent)	(percent)
No oxidant	10.5	71	23
100% as Cl ₂	9.4	65	19
100% ClO ₂	8.9	54	20
No oxidant	5.0	58	20
100% as Cl ₂	4.9	45	29
100% ClO ₂	4.5	40	23

Note: pH 5.7–6.0, DOC source – Dismal Swamp, Nominal DOC = 10, 5 mg/L, stoichiometric requirements = 0.64 mg as Cl₂ per mg Fe, and 1.2 mg ClO₂ per mg Fe

Alum Coagulation of Fe(II) Complexed with Dismal Swamp Humic Material

Alum coagulation, in the absence of an oxidant, was ineffective in the removal of Fe(II) from solutions containing DOC. Data of Figure 23 show that approximately 85 percent of the original iron concentration remained in solution after alum coagulation. (These test solutions contained 10 mg/L DOC and 2 mg/L Fe.) The addition of 100 percent free chlorine (center graph) to alum coagulation achieved nearly 50 percent colloidal iron formation at the 12 mg/L alum dosage, but yielded a soluble residual iron concentration of 0.6 mg/L at the 48 mg/L alum dose. Alum coagulation in the presence of 100 percent ClO₂, however, reduced the residual iron concentration to 0.2 mg/L.

Figure 24 displays data from coagulation studies with solutions containing 5 mg/L DOC and 2 mg/L Fe. Results similar to those of the 10 mg/L DOC coagulation experiments were observed, with oxidant addition decreasing the residual iron concentration. Nearly 93 percent of the initial Fe(II) concentration was removed from solution by alum coagulation in the presence of 100 percent ClO₂. Free chlorine was less effective.

Fractionation of coagulated waters into the 100K, 30K, 10K, and 1K molecular weight fractions revealed the molecular weight fractions in which iron was being retained with respect to alum dosages. The iron distribution within each molecular weight fraction of a 10 mg/L DOC, pH 5.7–6.0 alum coagulation study is displayed in Figure 25. The dosages of alum were 0, 12, and 48 mg/L and each dose was exposed to 100 percent free chlorine and 100 percent ClO₂.

Without oxidant or coagulant addition, iron was retained in the <30K fractions. As seen in the previous data from the fractionations of oxidized complexed Fe(II) solutions (Figures 15 and 21), the presence of 100 percent

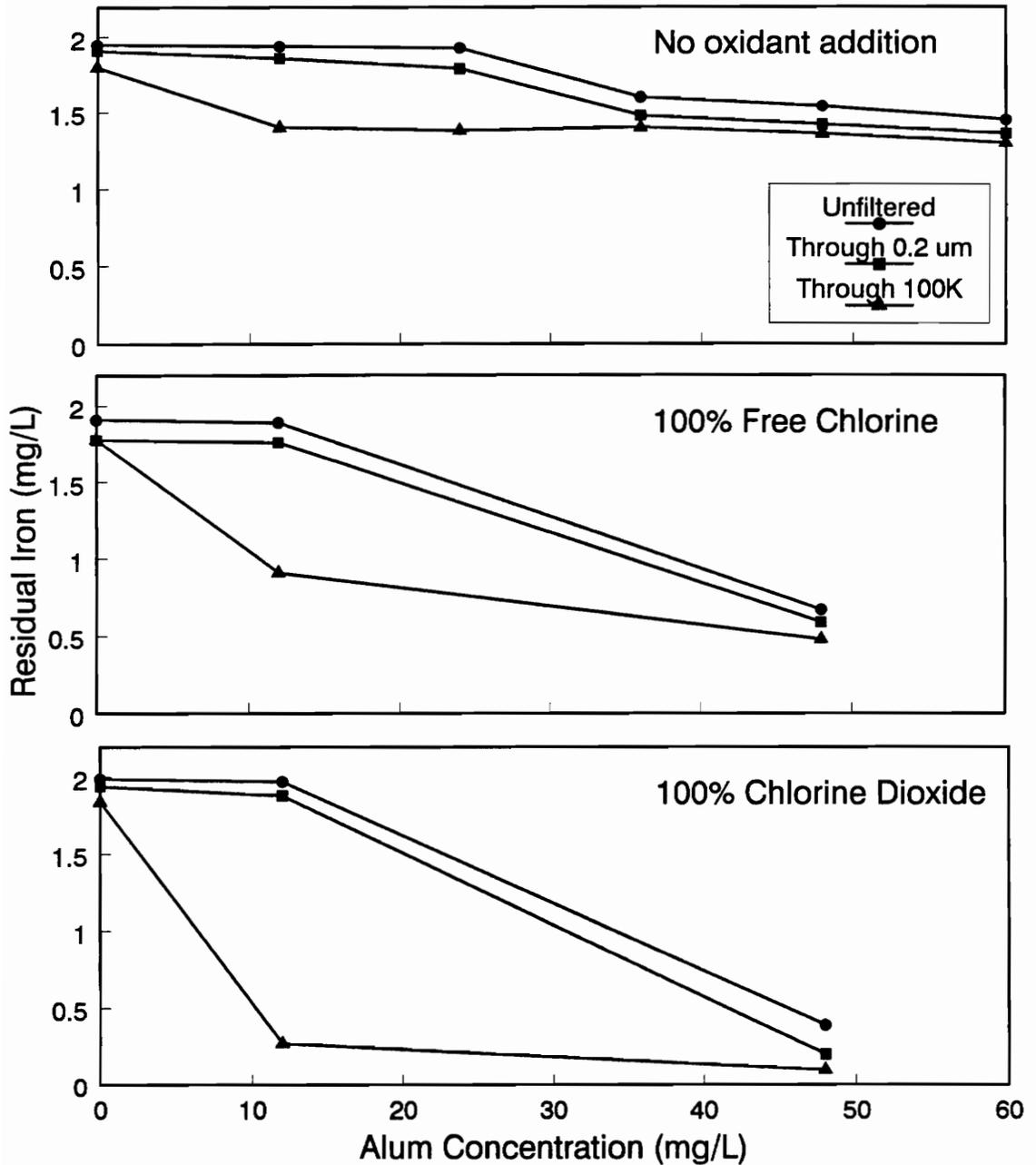


Figure 23. Complexed Fe(II) removal by alum coagulation with and without oxidant addition. (Nominal DOC = 10 mg/L; pH 5.7-6.0; DOC source - Dismal Swamp; stoichiometric requirements = 0.64 mg as Cl₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)

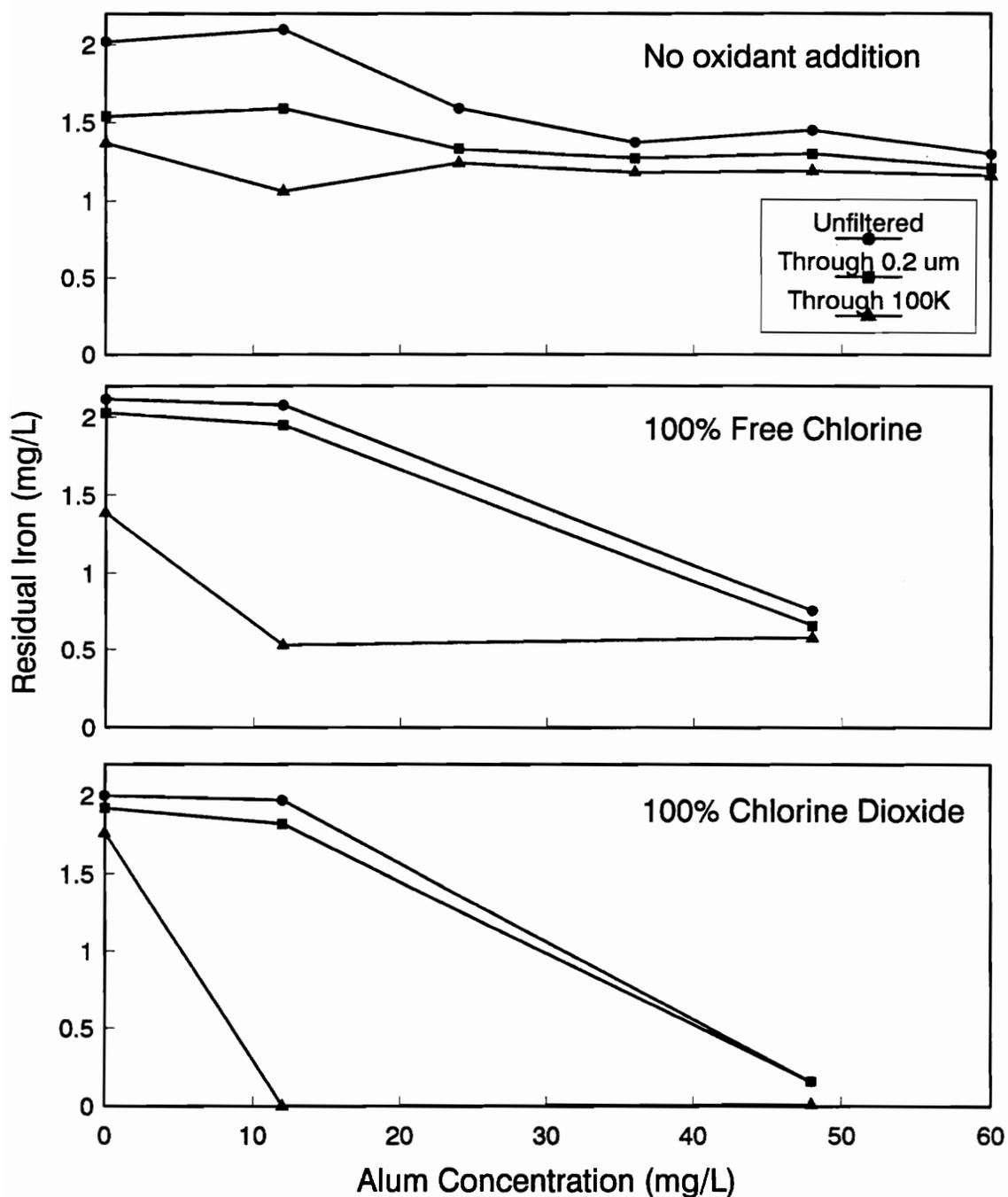


Figure 24. Complexed Fe(II) removal by alum coagulation with and without oxidant addition. (Nominal DOC = 5 mg/L; pH 5.7-6.0; DOC source - Dismal Swamp; stoichiometric requirements = 0.64 mg as Cl₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)

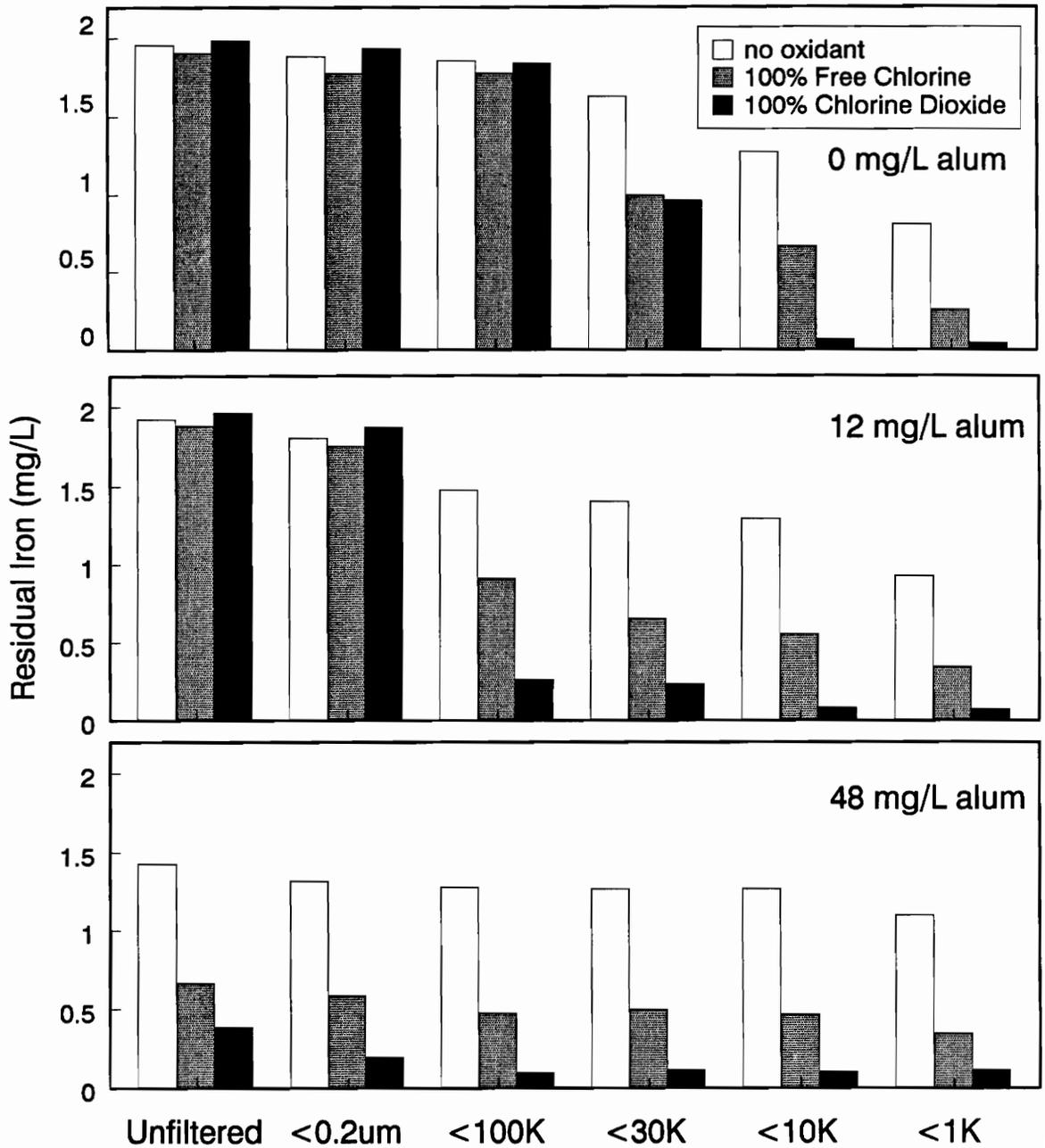


Figure 25. Iron distribution after alum coagulation at 0, 12, and 48 mg/L alum and in the presence and absence of an oxidant.

(DOC source - Dismal Swamp; Nominal DOC = 10 mg/L; pH 5.7-6.0; stoichiometric requirements = 0.64 mg as Cl_2 per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)

free chlorine and ClO_2 caused the iron to be complexed in the higher molecular weight fractions.

Alum coagulation alone did not greatly alter the iron distribution within these molecular weight fractions, and residual iron concentrations greater than 1 mg/L persisted in solution. However, alum coagulation with 100 percent free chlorine addition reduced the iron concentration through the 1K ultrafilter to 0.4 mg/L. The presence of 100 percent ClO_2 caused nearly 80 percent of the iron in solution to be retained by the 100K ultrafilter; this iron was then more amenable to removal by alum coagulation.

Similar results were obtained from alum coagulation experiments involving 5 mg/L DOC test solutions (Figure 26). Alum alone, and alum in the presence of 100 percent free chlorine yielded the same iron complexation trends as did the 10 mg/L DOC coagulation studies. Chlorine dioxide as a coagulant aid achieved nearly 100 percent soluble iron removal.

The DOC molecular weight distributions of 5 mg/L DOC test solutions are presented in Figure 27. This DOC distribution confirms the hypothesis that higher molecular weight DOC is removed from solution by alum coagulation. Note that only 20 percent of the initial DOC passed through the 1K ultrafilter. Recall that nearly 85 percent of the initial Fe(II) was also detected in this molecular weight fraction. The DOC-to-iron ratio within this fraction was approximately 1:1, which further supports the belief that the Dismal Swamp humic material failed to complex all of the Fe(II) in solution.

A higher pH range of 6.8–7.3 was also used for coagulation studies. The representative results of Figure 28 indicate that nearly 100 percent of the iron became colloidal in the presence of alum alone. Obviously, at the higher pH

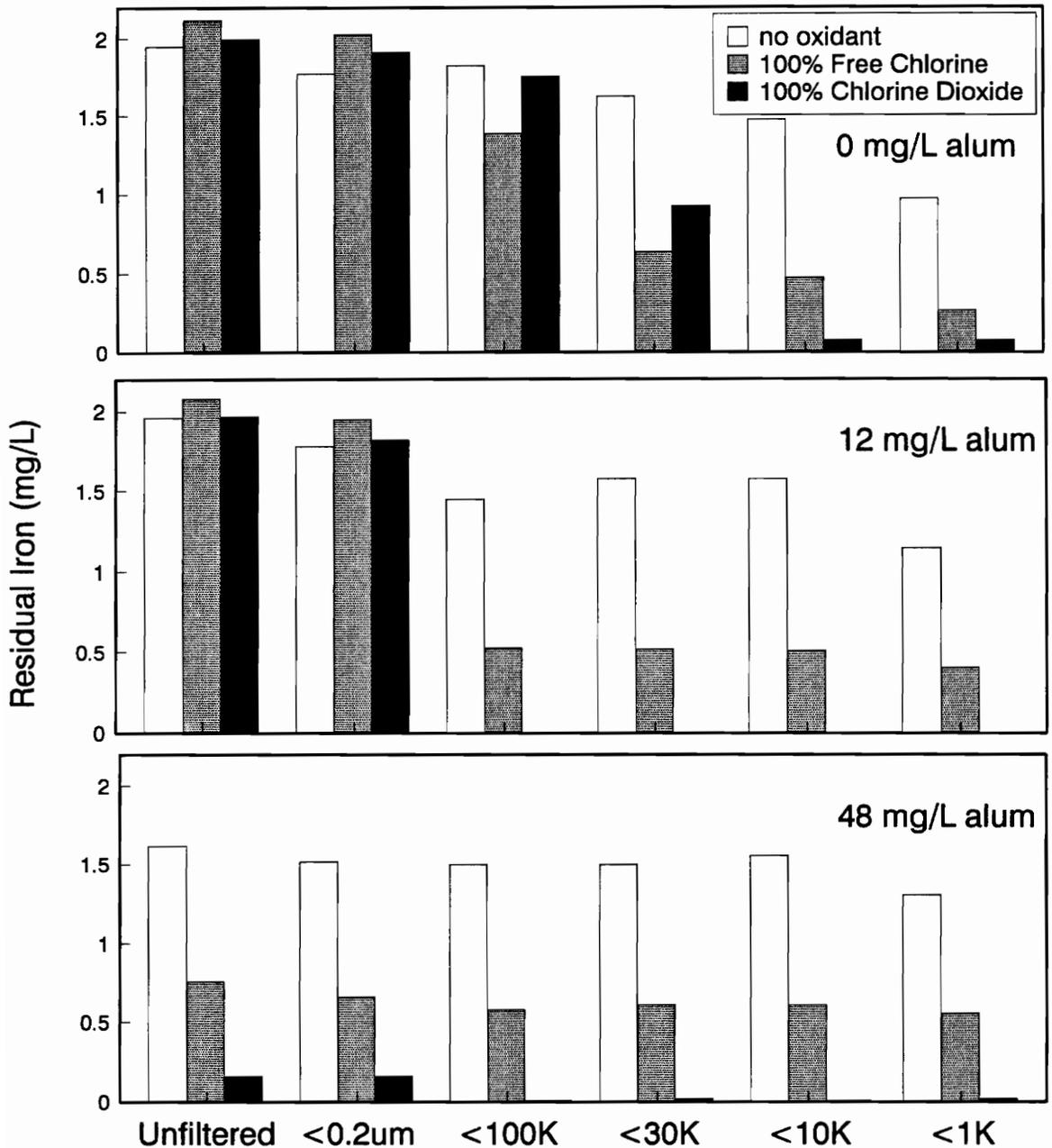


Figure 26. Iron distribution after alum coagulation at 0, 12, and 48 mg/L alum and in the presence and absence of an oxidant. (DOC source - Dismal Swamp; Nominal DOC = 5 mg/L; pH 5.7-6.0; stoichiometric requirements = 0.64 mg as Cl₂ per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)

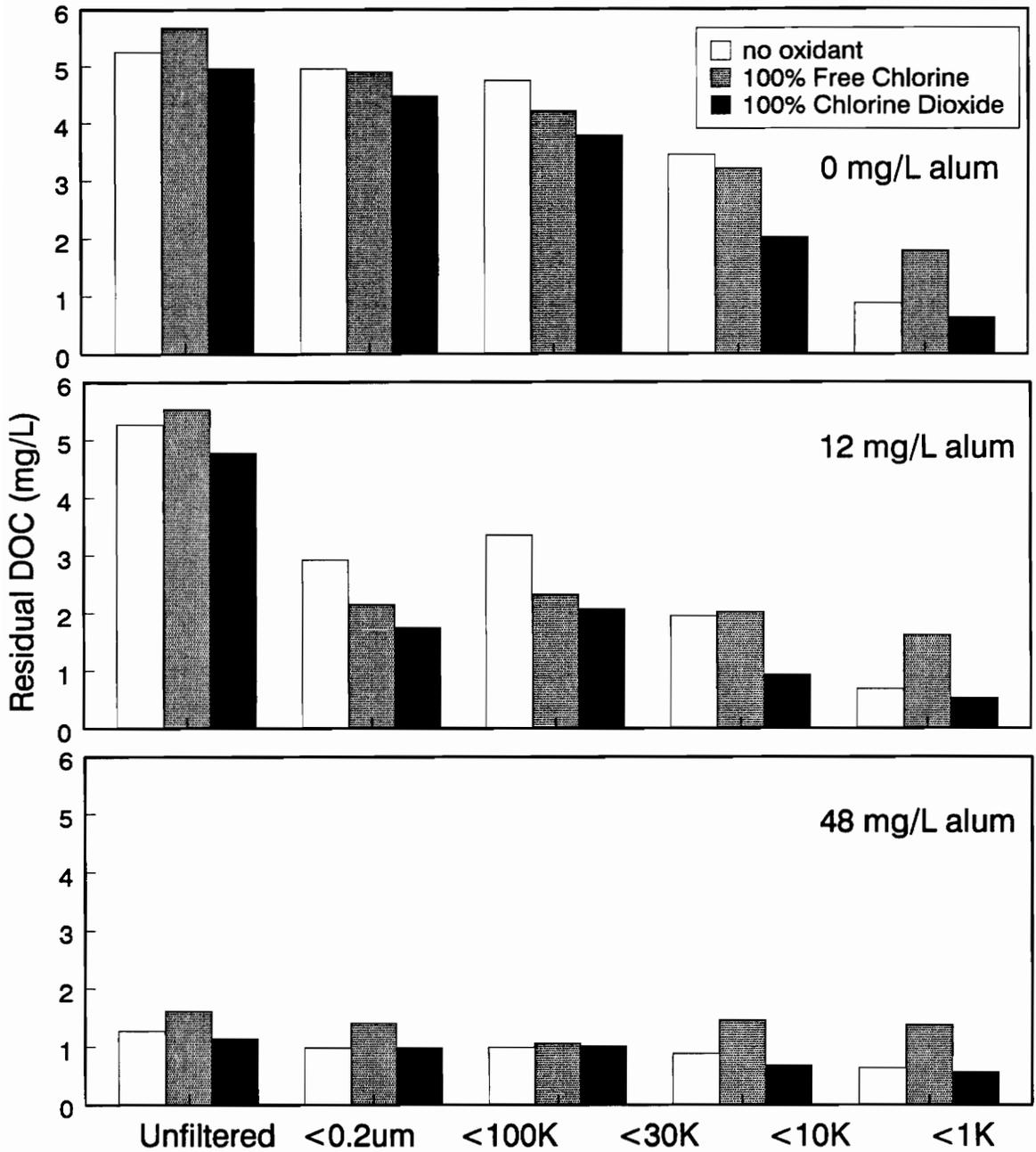


Figure 27. The DOC distribution after alum coagulation at 0, 12, and 48 mg/L alum and in the presence and absence of an oxidant.

(DOC source - Dismal Swamp; Nominal DOC = 5 mg/L; pH 5.7-6.0; stoichiometric requirements = 0.64 mg as Cl_2 per mg Fe, and 1.2 mg chlorine dioxide per mg Fe)

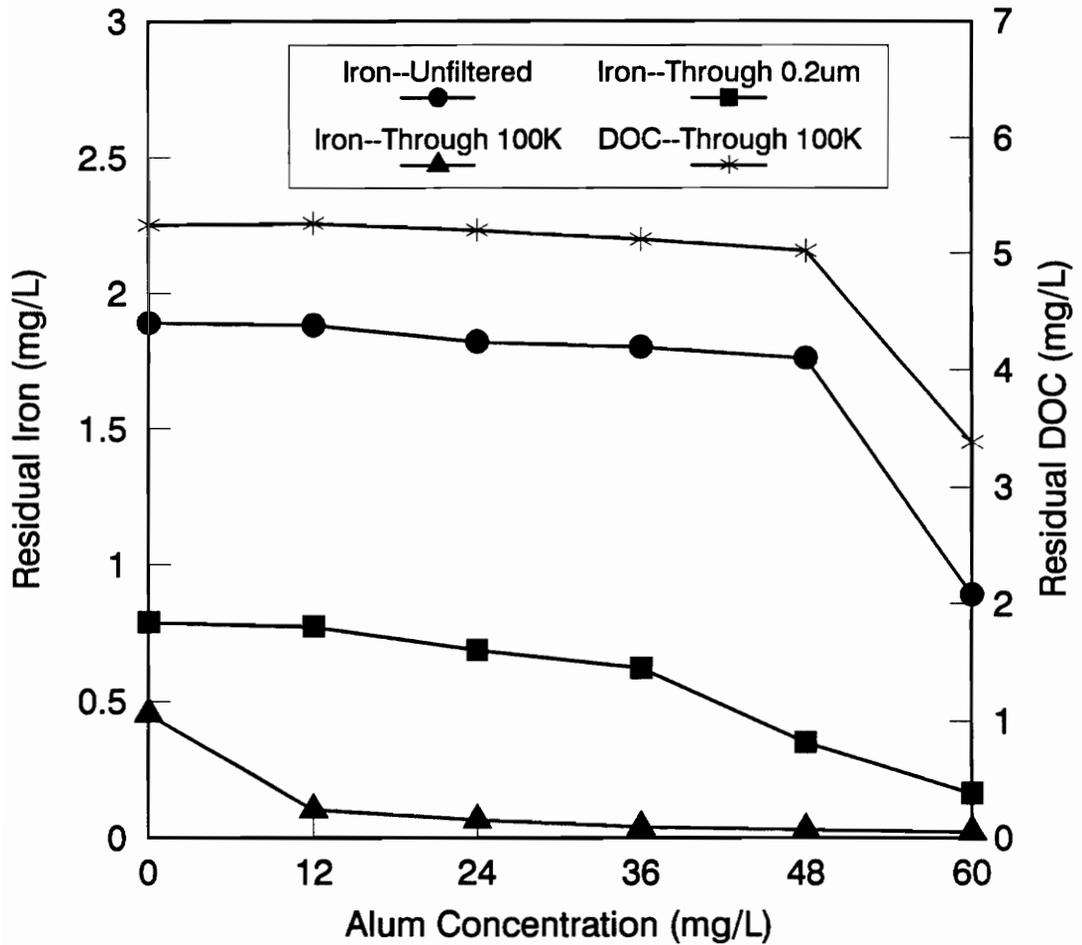


Figure 28. Complexed Fe(II) and DOC removal by alum coagulation at pH 6.8-7.3. (no oxidant addition; DOC source - Dismal Swamp)

range, kinetically favorable conditions existed for Fe(II) oxidation by O₂(aq) and subsequent colloidal iron removal by alum coagulation.

Alum Coagulation of Fe(II) Complexed with Durham, NC Humic Material

Coagulation studies were performed in the Williams Water Treatment Plant of Durham, NC, using intake water from the terminal reservoir. Initial tests revealed that iron and DOC concentrations at the time of the study were approximately 0.35 and 5 mg/L, respectively. Ferrous iron was added to the intake water and allowed a complexation reaction time prior to alum coagulation. Data presented in Figure 29 show that alum coagulation alone experienced colloidal iron residuals of approximately 0.5 mg/L. In the presence of 200 percent of the stoichiometric requirement of free chlorine for Fe(II) oxidation, however, nearly all of the iron was removed from solution in the presence of >12 mg/L alum.

Alum Coagulation of Fe(II) Complexed with High Molecular Weight University of Washington Humic Material

Alum coagulation experiments were also performed using the high molecular weight fraction (100–10K) of the University of Washington humic material. Better DOC removal was expected in these studies because alum coagulation has been proven to be very effective at removing higher molecular weight DOC (Rest, 1982). Also, in the presence of an oxidant, as previous coagulation studies have shown (Figures 16 and 21), complexed iron tended to be retained in the higher molecular weight DOC, thus more susceptible to removal by alum coagulation. The changes in the iron and DOC speciation due

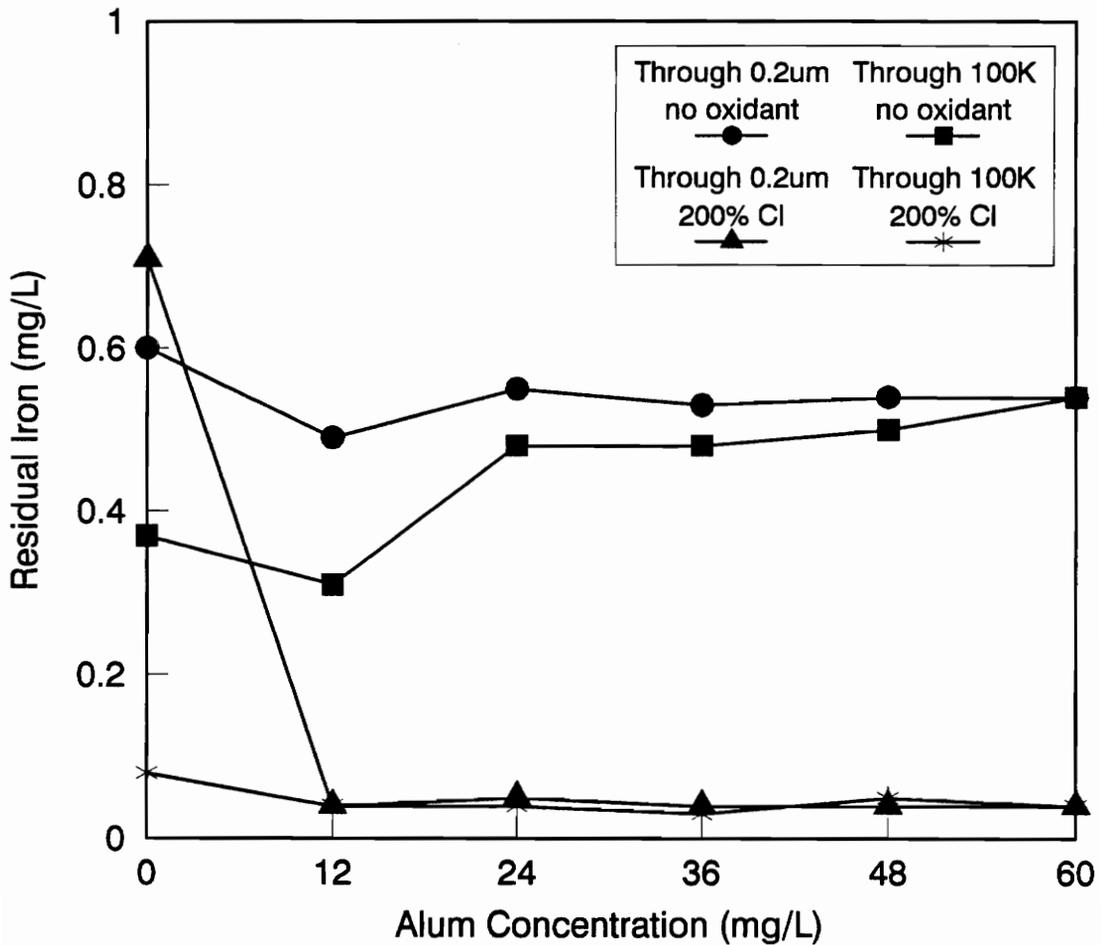


Figure 29. A comparison of the iron removal by alum coagulation with and without 200% free chlorine at pH 5.7-6.0. (conducted in Durham, NC; water spiked with 1 mg/L Fe; Nominal DOC = 4 mg/L; stoichiometric requirement = 0.64 mg as Cl₂ per mg Fe)

to alum coagulation are shown by the data presented in Figure 30. A soluble residual iron concentration of 1.3 mg/L remained in solution, while approximately 80 percent of the DOC was removed from solution at the 48 mg/L alum dose. Due to a limited quantity of stock humic material within this higher molecular weight fraction, only solutions containing 12 mg/L alum dosages were oxidized by 100 percent free chlorine and 100 percent ClO_2 . In the presence of free chlorine, 75 percent of the soluble iron became colloidal; with ClO_2 , 95 percent. Nearly 45 and 40 percent of the DOC passed through a 100K ultrafilter after free chlorine and ClO_2 oxidation, respectively. These results regarding colloidal DOC formation were similar to those observed with the Dismal Swamp humic material.

Alum Coagulation of Fe(II) Complexed with Low Molecular Weight University of Washington Humic Material

Alum coagulation experiments were performed at pH 5.7–6.0 with Fe(II) complexed by the lower molecular weight fraction (<3K) of the University of Washington humic material. The iron and DOC speciation following alum coagulation is displayed in Figure 31. A residual soluble iron concentration of 1.6 mg/L remained in solution after alum coagulation. Also, nearly 70 percent of the original DOC passed through a 100K ultrafilter at the 12 mg/L alum dose.

In the presence of 100 percent free chlorine, a residual soluble iron concentration of 0.43 mg/L persisted at the 48 mg/L alum dose. Also, only 44 percent of the DOC was retained by the 100K ultrafilter at the 12 mg/L alum dose. For alum coagulation with 100 percent ClO_2 addition, no residual iron

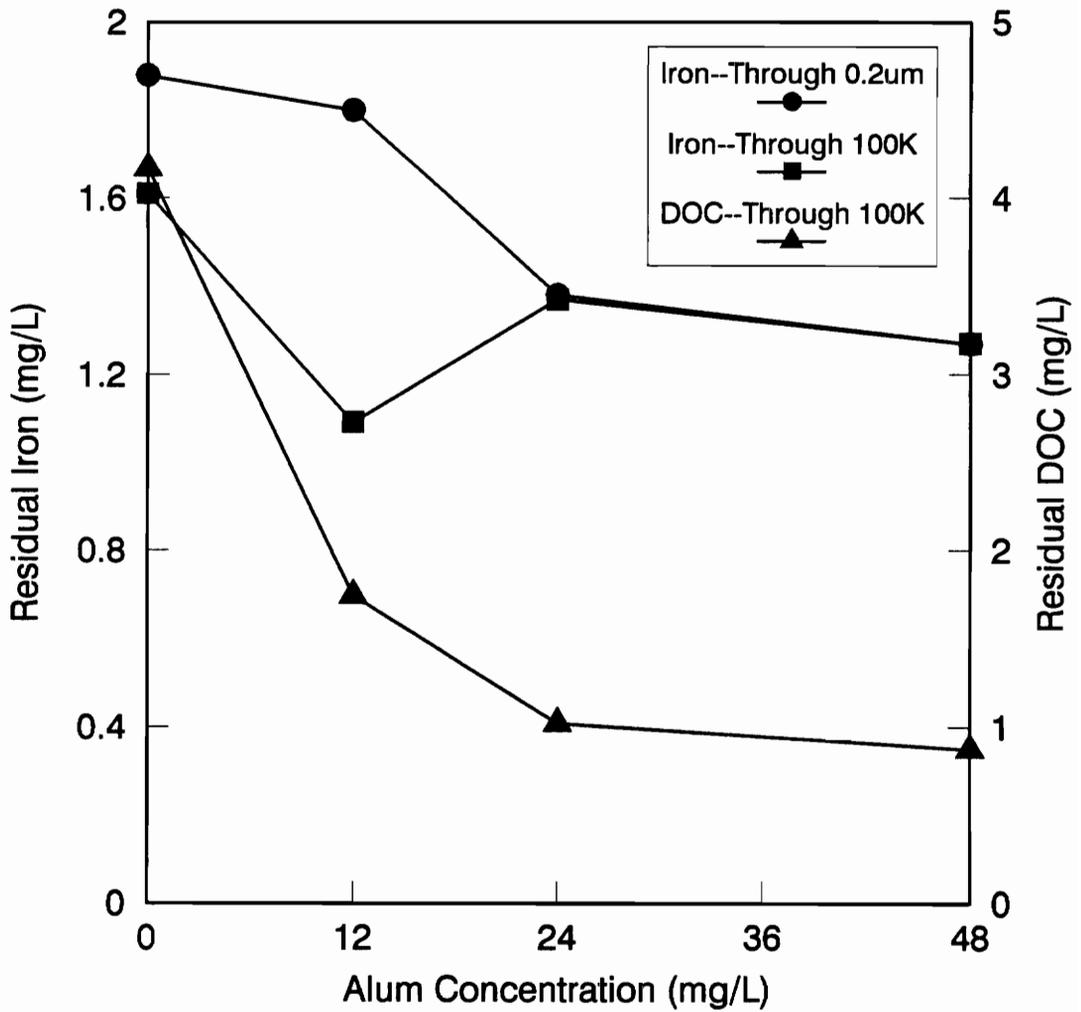


Figure 30. Effects of alum coagulation on iron and DOC at pH 5.7-6.0. (no oxidant addition; DOC source - University of Washington (100-10K))

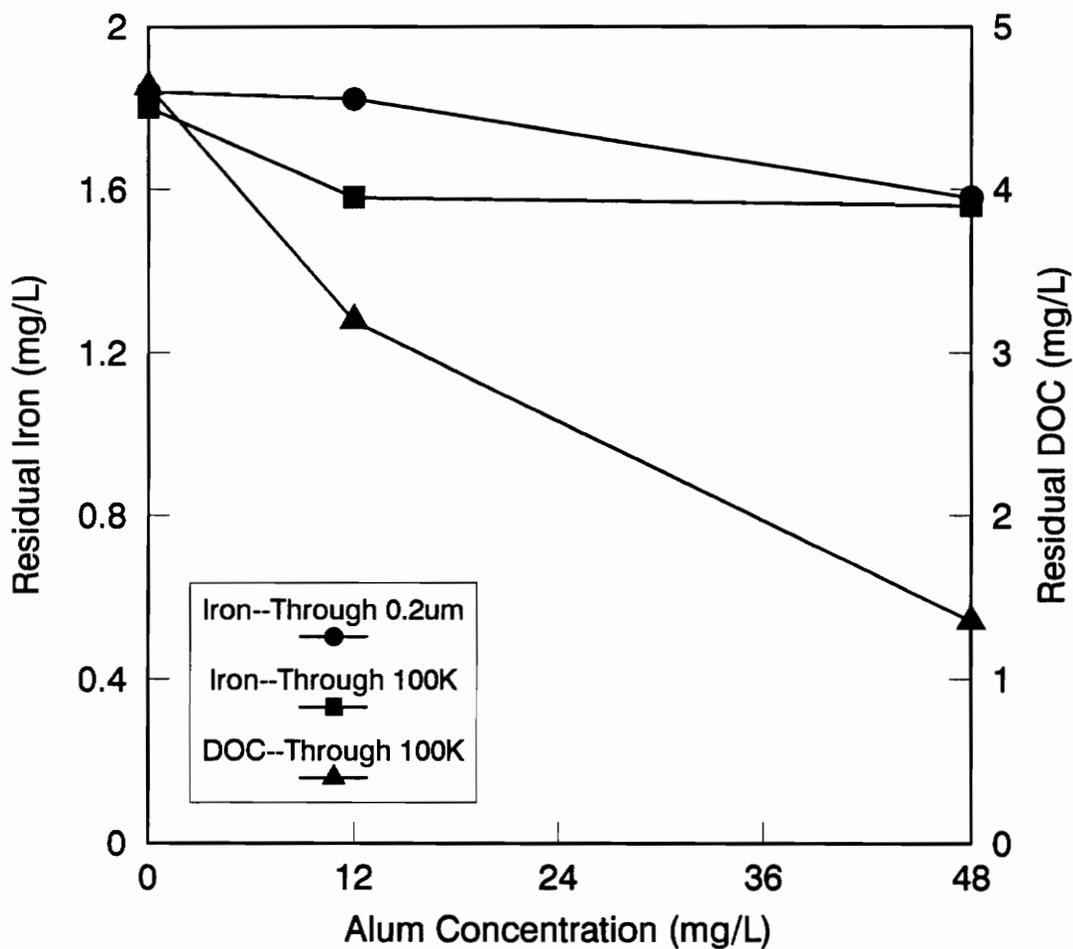


Figure 31. Effects of alum coagulation on iron and DOC at pH 5.7-6.0. (no oxidant addition; DOC source - University of Washington (<3K))

remained in solution in the presence of 48 mg/L alum, and 44 percent of the DOC was considered colloidal at the 12 mg/L alum dose.

Chapter V

DISCUSSION

Uncomplexed Fe(II) is readily oxidized to a settleable Fe(OH)₃(s) form by oxidant addition. This was shown by the retention of Fe(OH)₃(s) on a 0.2 μm pore size membrane filter after free chlorine and ClO₂ oxidation (Figures 13 and 17). However, iron that has been complexed by natural organic matter is often difficult to remove from solution because oxidation by oxidant addition usually fails to produce settleable Fe(OH)₃(s).

The effects of DOC concentration, DOC molecular weight, and DOC type on the complexed iron removal efficiencies of alum coagulation and/or free chlorine and ClO₂ oxidation were investigated. The nature and composition of complexed iron and DOC in the absence and presence of an oxidant was also studied. Further, the iron complexation capacity of humic materials was analyzed.

Iron Complexation and Speciation

Humic sources were used to complex Fe(II) at DOC-to-iron ratios between 2.5:1 and 5:1. Oxidation studies using the Dismal Swamp humic source at pH 7.5 (Figure 5) revealed a precipitation of colloidal iron in the control sample which had not received oxidant addition. This indicated that Fe(II) was being oxidized by trace quantities of O₂(aq), and provided evidence that all of the Fe(II) had not been complexed by the humic material. Data collected from these studies suggested that 0.1 to 0.2 mg of Fe(II) was actually complexed per mg of DOC in solution. Data from ultrafiltration and coagulation

studies revealed that the Durham, NC, and the two fractions of the University of Washington humic materials were also unable to complex all of the Fe(II) in the test solutions which were prepared.

Limited information regarding Fe(II) complexation by aquatic DOC is available in the published literature. Weber (1988) reported that a general range for the iron binding capacity of DOC is between 0.02 and 0.07 mg of iron bound per each mg DOC in solution. Likewise, Thurman (1985) stated that 0.02 to 0.03 mg of iron are bound per each mg DOC in solution. Perdue *et al.* (1976) observed 0.05 mg iron stabilized per mg DOC in solution. These observations provide an approximate measure of the iron binding capacity of DOC; the nature of iron in solution and the physical characteristics of DOC must be considered when analyzing the complexation of iron.

In the published literature regarding complexed iron, researchers have often used the 0.45 μm pore size membrane filter to differentiate between dissolved and particulate iron species. It was assumed that the iron which passed through the 0.45 μm pore size membrane filter was actually complexed by the humic material. However, ultrafiltration analyses performed during this study would indicate that this assumption may be invalid. Instead, it is evident that iron in the presence of DOC may be present in both a colloidal state as well as a dissolved form. Thus, iron speciation by a 0.45 μm filter alone is too general because no specific differentiation can be achieved.

In this research, the use of the 0.2 μm pore size membrane filter and the 100K ultrafilter (as well as ultrafilters with lower molecular weight differentiations) provided further size separation of iron species. Results indicated that oxidation of Fe(II) in the presence of DOC altered the state

(colloidal or soluble) of the complexed iron, and the resulting speciation dictated the performance of alum coagulation for complexed iron removal.

Oxidation of Complexed Fe(II)

The ability of free chlorine or ClO_2 to oxidize Fe(II) to Fe(III) in the presence of DOC was investigated. Chlorine dioxide (at the stoichiometric requirement for Fe(II) oxidation) was able to oxidize essentially all of the Fe(II) to Fe(III) (Figures 20 and 21) within the first 5 minutes of oxidant contact time. The humic materials did not appreciably hinder the iron oxidation. However, the oxidation capacity of free chlorine was somewhat inhibited by the competitive oxidant demand exerted by the humic materials, as shown by only partial oxidation of Fe(II) to Fe(III) (in the presence of the stoichiometric requirement for Fe(II) oxidation) (Figure 16). Thus, it appeared that ClO_2 was more aggressive at oxidizing Fe(II) than free chlorine. As a result, an oxidant dosage greater than predicted by theoretical reaction stoichiometry is required for complete Fe(II) oxidation by free chlorine.

From these studies, it was also evident that after oxidation, the Fe(III) was complexed by the higher molecular weight DOC species. This was observed for both free chlorine and ClO_2 (Figures 15, 16, 20, and 21).

Data from the oxidation experiments suggest that the characteristics of the DOC, as well as the DOC-to-iron ratio in solution, dictated the amounts of particulate and colloidal iron formed by oxidation. In this research, the only occurrence of particulate iron formation was in the free chlorine oxidation experiments involving Fe(II) which was complexed with the Durham, NC humic material; the other DOC sources inhibited particulate iron formation. Colloidal

species formation was greatest in the oxidized test solutions having the lowest DOC-to-iron ratios. In the solutions with higher DOC-to-iron ratios, colloid formation was appreciably hindered.

The high and low molecular weight DOC fractions originated from the same humic source: University of Washington. Minimal differences were observed regarding the iron removal (by the 0.2 μm pore size membrane filter and the 100K ultrafilter) when comparing the high molecular weight DOC to the low molecular weight DOC. This indicated that the behavior of complexed Fe(II) was dictated to some degree by the type of DOC; molecular weight considerations alone could not explain the observed results.

Sorption of DOC onto Iron Oxide Solids

Removal of DOC was quantified during many experiments involving free chlorine and ClO_2 oxidation of complexed Fe(II) (the Dismal Swamp source). Adsorption capacity estimates (calculated as the ratio of the change in DOC concentration to the change in iron concentration ($\Delta \text{DOC} / \Delta \text{Fe}$) after 200 to 500 percent free chlorine and ClO_2 oxidation) are shown in Table 20.

The results shown in Table 20 reveal that solution pH influenced DOC adsorption, with higher $\Delta \text{DOC} / \Delta \text{Fe}$ ratios being observed at pH 5.5 than at pH 6.5 for both oxidants. This can be explained by the variations in the surface charge of iron oxide solids with respect to pH. The isoelectric (neutral) point for iron oxide solids is near pH 9 (Culp *et al.*, 1986); as the pH decreases, the surface charge becomes more positive. Therefore, iron oxide solids at pH 5.5 would be more positive than at pH 6.5. Negatively charged DOC species would

Table 20

Ratios of the changes in DOC to the changes in Fe
after free chlorine and ClO₂ oxidation of complexed Fe(II)

Solution pH/Oxidant*	Initial		Residual**		Δ Fe (mg/L)	Δ DOC (mg/L)	Adsorption Capacity (mg DOC/mg Fe)
	DOC (mg/L)	Fe (mg/L)	DOC (mg/L)	Fe (mg/L)			
5.5/Cl ₂	5.4	2.00	4.0	0.72	1.28	1.4	1.1
5.5/Cl ₂	4.2	0.97	3.6	0.71	0.26	0.5	2.0
5.5/Cl ₂	9.6	1.93	9.0	1.71	0.22	0.6	2.7
6.5/Cl ₂	3.6	0.98	3.2	0.45	1.06	0.9	0.8
6.5/Cl ₂	5.0	1.88	4.1	0.82	0.53	0.4	0.8
6.5/Cl ₂	9.6	1.90	9.3	1.69	0.21	0.3	1.4
5.5/ClO ₂	4.8	2.05	3.6	1.20	0.85	1.2	1.4
5.5/ClO ₂	3.0	1.00	2.6	0.87	0.13	0.4	3.1
5.5/ClO ₂	9.4	2.04	8.5	1.94	0.10	0.9	9.0
6.5/ClO ₂	5.7	1.89	4.8	1.14	0.75	0.9	1.2
6.5/ClO ₂	10.7	1.84	9.8	1.65	0.19	0.9	4.7

Note: ' Δ ' denotes changes in concentration

* Comparing the changes () between concentrations before and after oxidation with at least 200 percent of the stoichiometric requirement of each oxidant

** Residual defined as passing a 100K ultrafilter

then be attracted to these positively charged iron oxide solids, with the lower pH conditions yielding higher DOC adsorption.

Also, the $\Delta \text{DOC} / \Delta \text{Fe}$ ratios after ClO_2 oxidation were greater than those after free chlorine oxidation. No specific explanation is available for the interpretation of this result. It may be hypothesized that ClO_2 reactions with DOC resulted in partially oxidized organic by-products that were more amenable to adsorption on iron oxides.

Higher DOC adsorption capacity was also observed in samples that had high solution DOC concentrations. This relationship is indicative of reversible physical adsorption. In such situations, the relationship between the amount of residual DOC in solution and the $\Delta \text{DOC} / \Delta \text{Fe}$ can be expressed by an adsorption isotherm. Two common isotherms are the Freundlich and Langmuir isotherms (AWWA, 1990). The Freundlich isotherm was used to model the data of this study as follows:

$$q_e = KC_e^{(1/n)} \quad [11]$$

Linearizing this equation by taking logarithms of both sides yields:

$$\log(q_e) = \log(K) + (1/n)\log(C_e) \quad [12]$$

where:

q_e = adsorption capacity, mg DOC/mg Fe,

C_e = residual solution DOC concentration, mg DOC/L,

K, n = constants.

Plotting data on a logarithmic scale should produce a linear relationship between residual DOC and the observed adsorption capacity.

A plot of the log adsorption capacity versus log residual DOC is shown in Figure 32. (The solid lines of Figure 32 were generated by linear regression.)

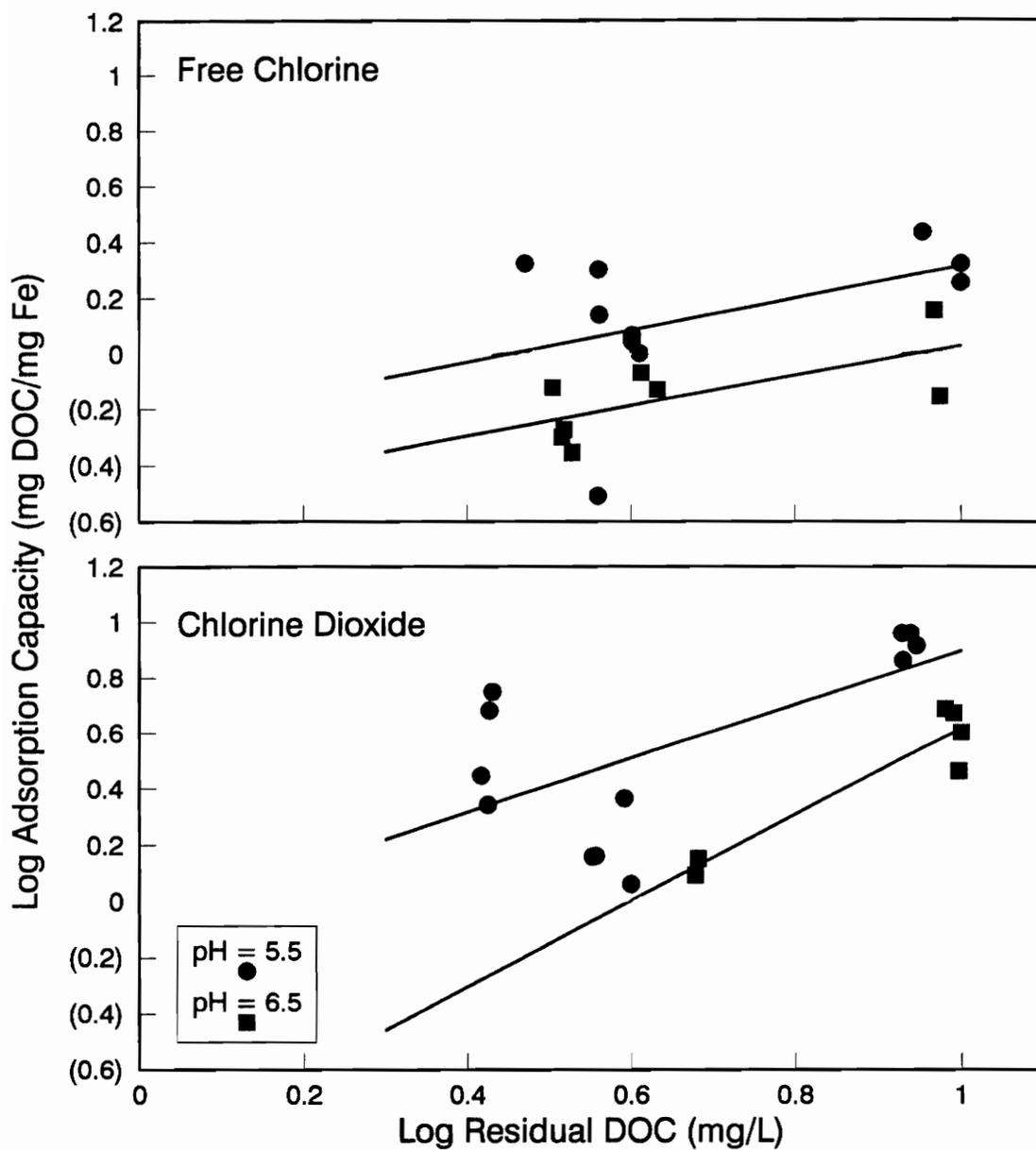


Figure 32. Freundlich isotherms for DOC adsorption onto iron oxide solids after free chlorine and chlorine dioxide oxidation at pH 5.5 and 6.5.

The patterns associated with the DOC adsorption as a function of solution pH and type of oxidant are evident. For each DOC value, the adsorption capacities were higher at pH 5.5 than at pH 6.5; again, this is a result of the greater surface charge associated with iron oxide solids at lower pH values. Also, at a given pH and residual DOC concentration, solutions oxidized with ClO_2 had higher adsorption capacities than solutions containing free chlorine. Scatter in the data is attributed to the narrow range of DOC concentrations used for testing.

The results shown in Table 20 and presented in the Freundlich isotherms were obtained in studies that used DOC extracted from the Dismal Swamp. In comparison, minimal DOC removal was observed in studies with the DOC obtained from the Durham, NC source. An interesting correlation was noted in that approximately 60 percent of the iron was retained on the 0.2 μm pore size membrane filter following 60 minutes of contact in tests with the Durham, NC source of DOC (see Table 11). These results were different from the results of oxidation studies conducted with the Dismal Swamp humic material; in tests with the Dismal Swamp DOC, no particulate iron was formed, and DOC retention by a 100K ultrafilter was sometimes as much as 30 percent of the original DOC.

It is hypothesized that the chemical characteristics of the Durham, NC organics were very different from those of the Dismal Swamp. Free chlorine apparently oxidized the Fe(II) present in solution, but did not promote the formation of colloidal DOC-Fe species.

The net result of the decreased DOC uptake was an ability of the iron oxide solids to be flocculated over time. This was evident by the greater

particulate iron removal in the Durham, NC studies after 60 minutes of mixing as opposed to after 5 minutes of mixing. The additional mixing time allowed the colloidal iron oxide particles to aggregate; thus, achieving sufficient particle size for retention by a 0.2 um pore size membrane filter. In comparison, the colloidal iron oxides formed in the oxidation of samples containing Dismal Swamp DOC were unable to aggregate efficiently. It is hypothesized that the Dismal Swamp DOC which adsorbed onto the iron oxide solids promoted colloidal stability. This strongly suggests that even with similar molecular weight distributions and concentrations, the Durham, NC and Dismal Swamp humic sources have different chemical characteristics and behave differently when exposed to free chlorine.

A DOC adsorption trend was also observed in the high and low molecular weight DOC studies (Tables 12, 13, 17, and 18). The DOC retention by the 100K ultrafilter was greater in tests with low molecular weight DOC than in studies with high molecular weight DOC. This occurred in both the free chlorine and ClO₂ oxidation studies.

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

Alum coagulation alone was unable to reduce residual iron concentrations from prepared test solutions containing Fe(II) in the presence of DOC (Table 21). Ultrafiltration revealed that Fe(II) that was complexed by the DOC was removed by alum coagulation. However, high percentages of Fe(II) were not complexed by the DOC, and alum coagulation was unable to remove this soluble iron from solution.

Table 21

Summary of the complexed iron removal by alum coagulation
in the presence and the absence of an oxidant

Humic Source (DOC/Fe)	Fe >100K after Alum Coagulation***		
	Without Oxidant (percent)	With 100% as Cl ₂ (percent)	With 100% ClO ₂ (percent)
Dismal Swamp (5)	31	73	95
(2.5)	18	58	92
High Molecular Weight DOC*			
(2.5)	21	---**	---**
Low Molecular Weight DOC*			
(2.5)	13	66	>99

* DOC source – University of Washington

** '---' denotes no data collection under these conditions

*** Alum dosages = 48 or 60 mg/L

Free chlorine and ClO_2 addition improved soluble Fe(II) removal by alum coagulation. The DOC distribution data from Figure 27 show that higher molecular weight DOC is preferentially removed from solution by alum coagulation. Recall that in the presence of each oxidant, Fe(III) tended to be complexed in the high molecular weight DOC; thus, oxidized iron which was complexed by the high molecular weight DOC was more amenable to removal by alum coagulation. Almost 100 percent iron removal was achieved by alum coagulation with ClO_2 addition (at a dosage of the stoichiometric requirement for Fe(II) oxidation). Free chlorine addition (at a dosage of the stoichiometric requirement for Fe(II) oxidation) to alum coagulation did reduce the soluble iron residuals, but not as effectively as ClO_2 . This is expected when considering the influence of the competitive oxidant demand by the humic materials during Fe(II) oxidation by free chlorine. In the presence of the stoichiometric requirement of free chlorine for Fe(II) oxidation, some of the Fe(II) in solution was not oxidized, thus not complexed by the higher molecular weight DOC and not removed from solution by alum coagulation.

Similar Research with KMnO_4 and H_2O_2

Bellamy (1992) conducted similar studies to assess the ability of KMnO_4 and H_2O_2 to oxidize complexed Fe(II). All testing conditions, DOC sources, and experimental procedures were the same as those for this research.

Ultrafiltration tests revealed that both KMnO_4 and H_2O_2 were able to oxidize Fe(II) in the presence of DOC, with results being analogous to those obtained for ClO_2 and free chlorine, respectively. In general, KMnO_4 was found to be the a strong oxidant. Potassium permanganate converted more soluble

Fe(II) to a colloidal form than free chlorine, ClO_2 or H_2O_2 . Further, KMnO_4 was able to oxidize some soluble Fe(II) to a particulate form in the presence of DOC. Iron removal by the 0.2 μm pore size membrane filter and the 100K ultrafilter after H_2O_2 oxidation was similar to that of free chlorine.

The iron removal by alum coagulation in the presence of 100 percent KMnO_4 and 100 percent H_2O_2 was similar to that with 100 percent ClO_2 for Fe(II) solutions complexed with Dismal Swamp humic material. In these studies, soluble iron concentrations were reduced from approximately 2 mg/L to <0.15 mg/L.

The results from Bellamy's research, coupled with the observations of this research indicate that the ranking of oxidants according to oxidation strength for Fe(II) oxidation in the presence of DOC is $\text{KMnO}_4 > \text{ClO}_2 > \text{H}_2\text{O}_2 = \text{Cl}_2$.

Applicability of Results to Water Treatment

In this research, oxidation of complexed Fe(II) by free chlorine and ClO_2 produced colloidal iron species that were not amenable to removal by sedimentation. Therefore, oxidation alone does not appear to be an acceptable method for complexed iron removal. However, alum coagulation in the presence of a strong oxidant like ClO_2 or KMnO_4 appears to be a viable treatment option for the removal of complexed iron from solution. Oxidant addition during rapid mix (prior to alum addition) yielded substantial reductions in soluble iron concentrations.

The findings of this research indicate that the complexation of iron, as well as the methods for complexed iron removal from drinking water, are site

specific. The type of DOC and the DOC-to-iron ratio which exists in the raw-water may dictate which treatment option provides optimum results. Water utilities experiencing difficulties with complexed iron removal must investigate the existing raw-water quality by accessing the concentrations, chemical characteristics, and the molecular weight distribution of the DOC. Also, the oxidation state and concentration of iron must be known. With this information, the performances of oxidation and/or alum coagulation can be analyzed to help develop a successful treatment methodology for complexed iron removal.

Chapter VI

CONCLUSIONS

The purpose of this research was to better understand the behavior of complexed Fe(II) in the presence of free chlorine and chlorine dioxide. Controlling and monitoring different water quality parameters provided insight about the iron removal efficiencies of oxidant addition, alum coagulation, and alum coagulation in the presence of an oxidant. Different DOC sources were used so that a comparative analysis could be performed. Conclusions regarding the various objectives of this research were formulated and are stated below:

1. The concentration and source of organic matter affect the extent of Fe(II) complexation in natural, aqueous environments. The complexation capacity of the Dismal Swamp organic material is 0.1 to 0.2 mg Fe(II) per mg DOC.
2. The oxidant demand exerted by the humic materials reduced the efficiency of Fe(II) oxidation by free chlorine. Free chlorine dosages in excess (>200 percent) of the stoichiometric requirement for Fe(II) oxidation are necessary to overcome this competitive oxidant demand.
3. Chlorine dioxide effectively oxidized Fe(II) to Fe(III) in the presence of DOC. The oxidant demand exerted by the humic materials did not inhibit Fe(II) oxidation.
4. The traditional use of a 0.45 μm filter for the differentiation between soluble and particulate iron is not an adequate representation of the iron speciation in a complexed iron solution. A 100K ultrafilter provides

further species classification by separating the colloidal fraction from the truly dissolved/complexed fraction.

5. Alum coagulation alone readily removes complexed iron from solution. When uncomplexed Fe(II) exists in the presence of DOC, improved iron removal can be achieved by the addition of free chlorine or ClO₂.
6. Colloidal iron formation by the oxidation of Fe(II) in the presence of DOC was accompanied by DOC adsorption onto iron oxide solids. The DOC adsorption capacity of the solids was a function of the solution pH, the initial DOC-to-iron ratio, and the type of oxidant.

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