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**Fluoride, Natural Organic Matter, and Particles: The Effect of Ligand
Competition on the Size Distribution of Aluminum Precipitates in
Flocculation**

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by

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Thesis

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Abstract

Fluoride, Natural Organic Matter, and Particles: The Effect of Ligand Competition on the Particle Size Distribution of Aluminum Precipitates in Flocculation

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Fluoride occurs at elevated concentrations naturally in surface and ground waters around the world. If consumed at low concentrations in drinking water (< 1.5 mg/L), fluoride is shown to reduce the occurrence of dental caries and the Centers for Disease Control and Prevention named fluoridation of public water systems one of the 10 Great Public Health Achievements of the 20th Century (CDC, 1999). However, prolonged exposure to high concentrations of fluoride (> 2.0 mg/L) causes adverse health effects to teeth and bones. For this reason the United State Environmental Protection Agency (USEPA) enacted a maximum contaminant level (MCL) for fluoride at 4.0 mg/L. This rule is currently under review following a recent risk assessment and may be lowered. If the MCL were lowered, water systems previously meeting treatment standards would suddenly find themselves out of compliance and will need to implement additional treatment to meet the new standard.

Defluoridation by alum coagulation is a proposed defluoridation method. However, the interaction between fluoride and natural organic matter (NOM) and their effects on the particle size distribution of aluminum precipitates is not well understood. Because the particle size distribution of aluminum precipitates is an important parameter in the efficiency of sedimentation and filtration systems, a thorough understanding of these interactions and their potential effect on sedimentation and filtration is needed to inform the implementation of defluoridation by alum coagulation.

This work utilized a series of jar tests on synthetic surface water to determine the effect of fluoride and NOM on the particle size distribution of aluminum precipitates. It was found that fluoride caused the volume distribution of aluminum precipitates to shift toward smaller particle sizes. However, NOM caused the formation of a larger number of aluminum precipitates, which resulted in a dramatic increase in the total volume of precipitates. When both fluoride and NOM were in the system, a combination of the two effects was observed: the volume distribution shifted toward smaller particle sizes but the peak of the distribution shifted toward a greater volume, indicating both smaller particles were being formed and a greater overall volume of particles precipitated.

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Chapter 1: Introduction

1.1 BACKGROUND

Coagulation/flocculation systems at drinking water plants are designed to destabilize and aggregate particles for their removal by sedimentation and filtration. These methods are traditionally used to remove colloidal particles (i.e., turbidity) and natural organic matter (NOM) from drinking water. One parameter used to determine the effectiveness of flocculation systems is the particle size distribution of particles (flocs) formed in the process. If the number of large particles is great, then they are more likely to be removed by settling or filtration. If the particles are small, then they are less likely to be removed by either process. However, coagulation and flocculation are heavily dependent upon the chemical nature of the water being treated, and the resultant particle size distribution of flocs can be affected by the chemistry of the aqueous system in which they form.

One compound being investigated for removal by coagulation is fluoride. Fluoride occurs naturally in groundwater and surface water around the world. Throughout the United States, many public water systems add small amounts of fluoride (< 1.0 mg/L) to public drinking water for the dental health benefits it provides. The ingestion of low concentrations in drinking water promotes healthy tooth development in children and healthy enamels in adults. Nevertheless, long term consumption of fluoride at levels above 2.0 mg/L results in deleterious effects to teeth and bones. For this reason, in the 1980s the United States Environmental Protection Agency (USEPA) set a maximum contaminant level (MCL) for fluoride in drinking water at 4.0 mg/L to prevent the occurrence of the most serious effects of excessive fluoride intake.

However, after a National Research Council (NRC) study recommended the lowering of the USEPA's maximum contaminant level goal (MCLG) for fluoride, the USEPA is now reviewing the fluoride rule as part of its third 6-year review. Since the MCLG is the basis for where the MCL is set, following the completion of the 6-year review, the USEPA might reduce the MCL from its current level. Should the MCL be reduced, many public water systems that are currently meeting the MCL for fluoride would suddenly find themselves out of compliance and need to perform additional treatment to meet a lower limit. Lowering the MCL would disproportionately affect small water systems that do not have the resources, both financial and labor, to quickly change treatment schemes.

The main processes for defluoridation are adsorption, ion exchange, membrane removal, and coagulation (Ayoob et al., 2008). Coagulation and flocculation using aluminum sulfate (alum) is already widely used in the US to remove turbidity and NOM, and aluminum and fluoride are known to interact strongly based on their aqueous complexation chemistry. If alum coagulation can be optimized to remove fluoride at treatment systems already using alum, then these utilities can potentially avoid the installation and associated costs of a completely new treatment system. Nevertheless, the knowledge of how the interaction between fluoride and NOM affects the particle size distribution of aluminum precipitates is lacking. A better understanding of the interaction between fluoride and NOM and its effect on this important flocculation parameter is needed to inform the development of a robust treatment scheme.

1.2 OBJECTIVES

The main objective of this research was to explore the interactions among fluoride, NOM, and alum during the coagulation process and how those interactions

affect the particle size distribution of aluminum precipitates. Experiments were conducted at the bench scale using synthetic surface water created in the laboratory. The specific objectives of the research were as follows:

1. Determine the effect of fluoride and/or NOM on the particle size distribution of aluminum precipitates in a simulated coagulation/flocculation treatment system,
2. Relate residual aluminum concentration, fluoride and NOM removal to the observed particle size distributions and elucidate any implications it has for fluoride impacted treatment systems.

The remainder of this report is organized to give the reader a comprehensive overview of issues surrounding fluoride and NOM as contaminants and their removal by coagulation processes. Chapter 2 includes a brief overview of the history of fluoride in the environment and drinking water, the regulations governing fluoride and NOM, alum coagulation as a means of removing both constituents, and the physical and chemical mechanisms involved in this process. Chapter 3 outlines the methods and materials used in this experimental portion of this work. Experimental results are presented in Chapter 4, along with discussions of the mechanisms behind the results and any implications of the findings. A final summary and overall conclusions are contained in Chapter 5.

Chapter 2: Literature Review

2.1 FLUORIDE IN DRINKING WATER AND THE ENVIRONMENT

2.1.1 Fluoride in Drinking Water

Fluoride was not known to be in water until the early 1900s, when dentist Frederick McKay began looking into the causes of brown staining, mottling, and pitting of the teeth of residents of Colorado Springs, CO (McKay and Black, 1916; Douglas, 1959). While this staining was first described in 1901, it was not until 1931 that fluoride was discovered to be the cause when H.V. Churchill, a chemist with the Aluminum Company of America (ALCOA), discovered elevated fluoride levels in drinking water sources around Bauxite, Arkansas (Mullen, 2005). Until Churchill's discovery, fluoride was not known to exist in water (Douglas, 1959). Working with Churchill, McKay found all Colorado communities affected by dental staining had similar concentrations of fluoride in the water. The link was clear and a new term, dental fluorosis, was coined to describe the staining and mottling of teeth previously known as Colorado brown stain.

At the time that researchers were looking for the cause of the staining, population studies were conducted that indicated people who had dental fluorosis had lower rates of dental caries (Douglas, 1959; Mullen, 2005). After the link between fluoride and fluorosis was established, epidemiological studies were conducted to understand that relationship quantitatively. One of the most prominent researchers in this area, Dr. Henry Dean, established 1 mg/L fluoride in water as sufficient to prevent cavities in most of the population while not resulting in the negative symptoms of dental fluorosis (Dean and Elvove, 1935; Dean et al., 1941; Dean et al., 1942). It was mainly a result of his research and a positive test case of fluoridation in Grand Rapids, MI that fluoridation of public water supplies became common (Arnold, 1957).

2.1.2 Fluoride Presence in the Environment

Fluoride occurs naturally in both aquatic and terrestrial environments around the world. Generally, fluoride is associated with regions where marine sediments were deposited near mountainous areas, areas with ongoing or past volcanic activity, or where formations defined by calcium-poor igneous and metamorphic rocks like granites or gneisses occur (Edmunds and Smedley, 1996; Gordon et al., 2004; D'Alessandro, 2006; Fawell et al., 2006). Fluoride can occur in both groundwater and surface water with average concentrations being in the range of 1-10 mg/L and less than 0.5-1 mg/L, respectively (Tebbutt, 1983; Hem, 1985; Fawell et al, 2006). In groundwater, concentrations depend on the nature of the surrounding rocks and the presence or absence of fluoride-bearing minerals. Positive correlations have been made between elevated fluoride concentrations and thermal groundwaters with high pH (7.6-8.6) and bicarbonate concentrations (Handa, 1975; Hem, 1985; Edmonds and Smedley, 1996). Low concentrations are typically associated with areas absent of fluoride-bearing minerals, where circulation of groundwater is rapid, or where significant concentrations of calcium occur in an aquifer (Handa, 1975; Hem, 1985).

Anthropogenic sources also contribute to fluoride occurrences in the environment. Some fertilizers, pesticides, and pharmaceuticals contain fluoride and are introduced into water supplies by direct application or stormwater runoff (Handa, 1975; NRC, 2006a). Fly ash and the combustion of fossil fuels results in the release of fluoride into natural waters as the ash and combustion gases partition into rainfall or solubilize into surface waters after settling (Churchill et al., 1948; Brindha and Elango, 2011). Industrial activities like alumina production, ore processing, and brick and ceramic manufacturing also contribute to the anthropogenic release of fluoride into the environment (Haidouti, 1991; WHO, 2002).

2.2 HEALTH EFFECTS OF FLUORIDE

Human exposure to fluoride comes from its presence in the air, dietary intake, and dental products. However, the primary contributor to fluoride intake is considered to be drinking water because its bioavailability from mineral water is greater than that of many solid foods (Murray, 1986; USIM, 1997; Trautner and Siebert, 1986). The most well-known health effects of excessive fluoride intake are dental, but other effects have also been documented.

The effects of fluoride on cavity prevention and dental fluorosis are well documented. The benefits of fluoride are realized at early ages during tooth development and tooth eruption from the gums. Fluoride ions replace hydroxyl groups in the hydroxyapatite structure of the teeth, creating a less soluble mixed crystalline structure resembling fluoroapatite (Moreno et al., 1977; Ten Cate and Featherstone, 1991; Driessens, 1982). Continued topical exposure to fluoride later in life helps by decreasing enamel solubility, repairing softened tooth enamel, and promoting faster remineralization of enamel should caries begin to form (Wefel et al., 1984; Loesche, 1986; Featherstone, 1999; Glenn, 2002). These dental health benefits are realized without the risk of dental fluorosis at drinking water fluoride concentrations of 0.7 to 1.2 mg/L (Dean et al., 1941; Dean et al. 1942; Galagan and Vermillion, 1957; USPHS, 1991; Heller et al., 1997; Tylenda et al., 2003). For this reason, continued topical exposure to low fluoride levels through mediums such as drinking water is recommended to decrease susceptibility in teeth for developing caries (Ten Cate and Featherstone, 1991). The United States Public Health Service recommends public water fluoridation at concentrations of 0.7 mg/L to provide the best balance of protection from dental caries while limiting adverse health effects of excessive fluoride intake (USDHHS, 2015). This recent recommendation (which lowered the previous recommendation of 1.0 mg/L) followed studies conducted

by the NRC and new data on human exposure to other fluoride sources, e.g., fluoridated toothpaste, dental rinses, fluoride supplements, and professionally applied fluoride compounds (USDHHS, 2015).

However, when fluoride concentrations in water are greater than 2.0 mg/L, dental fluorosis can occur. The most severe cases can occur after prolonged exposure to concentrations greater than 4.0 mg/L (NRC, 2006b). The severity of the condition depends on demographic, diet, and climactic conditions (Murray, 1986; USIM, 1997).

Excessive fluoride intake over time can also lead to other, more severe, health impacts. Chronic exposure to high concentrations (> 4.0 mg/L) of fluoride in drinking water can lead to an increased likelihood of bone fractures as well as bone pain and tenderness in adults; a condition known as skeletal fluorosis (NRC 2006b; USEPA, 2015). This condition, if undetected, can progress with the skeleton continuously accumulating fluoride until ligaments in the neck and vertebra can eventually calcify creating crippling deformities. This condition is commonly accompanied by muscle wasting and compression of nerves and spinal cord, i.e., radiculopathy and myelopathy, which causes pain, weakness and other conditions (Reddy, 2009). In children, fluoride concentrations greater than 2 mg/L can cause damage to liver and kidney functions (Xiong et al., 2007). Researchers are also looking into possible links between exposure to high concentrations of fluoride and the neurodevelopment of children (Choi et al., 2012; Choi et al., 2015).

2.3 REGULATION OF FLUORIDE IN DRINKING WATER

Fluoride was first identified as a potential drinking water contaminant that should be regulated in 1974 when the Safe Drinking Water Act was enacted. However, the current enforceable maximum contaminant level (MCL) was set at 4.0 mg/L in 1986

(NRC, 2006). Additionally, the EPA set the non-enforceable secondary MCL at 2.0 mg/L to prevent the worst of the cosmetic effects of dental fluorosis and set a maximum contaminant level goal (MCLG) at 4.0 mg/L to protect against crippling skeletal fluorosis (USEPA, 2015).

Following a comprehensive study of new clinical data dealing with exposure to fluoride in drinking water, the National Research Council (NRC) recommended that the USEPA's MCLG should be lowered to prevent severe dental fluorosis and long term exposures that can lead to skeletal fluorosis (2006a). They did not, however, make any recommendation to change the SMCL of 2 mg/L. Nevertheless, a lower MCL might be possible in the future as indicated by announcements by the EPA (Jones, 2010), the department of Health and Human Services (Isa, 2011), and the fact that the EPA is reviewing current drinking water standards for fluoride as part of the third Six-Year Review.

2.4 REGULATIONS GOVERNING NATURAL ORGANIC MATTER

Natural Organic Matter (NOM) is the product of plant and biological decay and is present in all natural waters. The composition varies spatially and temporally and depends on the origin (e.g., autochthonous, allochthonous, wastewater), age, fate, and season and is present as dissolved, colloidal, and organic detrital states (Aiken et al., 1992; Prakash and MacGregor, 1983). Because NOM reacts with common disinfectants to produce a range of potentially carcinogenic disinfection by-products, including the regulated trihalomethanes (THMs) and haloacetic acids (HAAs) and many unregulated compounds, the EPA started requiring treatment of NOM in the 1998 Disinfectant/Disinfection By-Product Rule (D/DBP) (Richardson, 1998; Arora et al., 1997). The D/DBP rule specifically targets total organic carbon (TOC) in drinking water

sources. As shown in Table 2.1, utilities are required to reduce TOC by a fixed percentage according to a matrix dependent upon the raw water TOC and alkalinity. An exception to this rule is allowed if they reach the “point of diminishing returns,” defined as less than 0.3 mg/L TOC removal per 10 mg/L addition of alum or its equivalent amount of iron salt (USEPA 815-R-99-012, 1999). Another constituent in the water may impart a demand on the coagulant used for treatment, so that the point of diminishing returns might be reached at a lower coagulant concentration than if that constituent was not present in the water. This case might be especially true in the case of fluoride, as fluoride has a high affinity for forming aqueous aluminum-fluoride bonds, thereby reducing the available aluminum for NOM interactions (Hao and Huang, 1986; Lopez Valdiviesco et al., 2006).

Table 2.1: Required Removal of Total Organic Carbon by Coagulation for Systems Using Conventional Treatment. (USEPA 815-R-99-012, 1999)

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO ₃)		
	0-60	60-120	>120
2.0-4.0	35%	25%	15%
4.0-8.0	45%	35%	25%
>8.0	50%	40%	30%

2.5 ALUM COAGULATION AND FLOCCULATION FOR WATER TREATMENT

Coagulation and flocculation are treatment processes used in many drinking water treatment plants to remove particles and NOM. Although the terms coagulation and flocculation are often used interchangeably, the two processes are subtly different. Coagulation is the chemical process of destabilizing particles or the adsorption or precipitation of soluble materials. Flocculation is the process of aggregating small particles into larger particles to aid in their removal via sedimentation or filtration. Aluminum based coagulants act in two main ways: (1) charge neutralization of negatively

charged particles by the positively charged metal hydrolysis species followed by the aggregation of the destabilized particles and (2) sweep flocculation by which contaminants or particles are enmeshed in or adsorbed onto precipitated aluminum hydroxide particles (Benjamin and Lawler, 2013 Shin et al., 2008). In general, water with low turbidity is considered collision-limited and requires a higher concentration of aluminum coagulant to induce the formation of $\text{Al(OH)}_{3(s)}$, i.e., sweep flocculation). However, turbid waters require lower concentrations of aluminum coagulant in order to neutralize the surface charges of particles to achieve destabilization (Shin et al., 2008).

This work is focused on the effect of ligand substitution on the coagulation and flocculation process. As discussed in Sections 2.6.2 and 2.7, different ligands can change the process of particle destabilization by changing the overall surface charge of the solid or by complexation with aluminum hydrolysis species. As will be seen, these effects can be either beneficial or detrimental to the process. The focus of this research is on alum coagulation to remove fluoride from surface water. Since surface water typically has some fraction of NOM, this work includes studying the interaction of these two constituents (fluoride and NOM) and their effect on alum coagulation/flocculation processes. More specifically, the effect of the presence of these two constituents on the particle size distribution of alum flocs is explored in this research to try to gain insight into the potential implications for treatment systems utilizing coagulation/flocculation as a means of particle removal. The remainder of this chapter focuses on these interactions to provide insight into the experimental results in this work.

2.6 ALUMINUM PRECIPITATES AND NOM

2.6.1 NOM Structure and Characterization

The phrase natural organic matter is used to describe all organic compounds found in nature other than living organisms and those of man-made origin. These compounds are derived from the remains of organisms and plant matter as well as their waste products. Compounds that make up NOM include carbohydrates, proteins, lignins, organic acids, and other compound classes (Hur et al., 2006). These compounds can vary in their complexity, but dissolved organic carbon (DOC) is commonly used to describe the amount of NOM in water. DOC is generally defined as the fraction of NOM that can pass through a 0.45 μm pore filter. Particulate organic carbon is the fraction remaining on the filter (Edzwald, 1993). While the most common way to classify DOC is as either fulvic acids or humic acids, Buffle suggests that fulvic and humic acids should be considered as two ‘extremes’ in a continuum of compounds and the proportions of each can vary seasonally in a given ecosystem (1990). Humic acids have a higher degree of aromaticity, undergo more condensation and adsorption reactions, have a higher molecular weight, and are traditionally known to precipitate at $\text{pH} < 2.0$ (Rodriguez and Nunez, 2011; Buffle, 1990). Fulvic acids have a lower molecular weight and its aliphatic chains are more oxidized, resulting in higher carboxylic content, charge, and solubility (i.e., it remains soluble at $\text{pH} < 2.0$) (Rodriguez and Nunez, 2011; Buffle, 1990).

As indicated earlier, one way to assess the amount of NOM in water is to analyze the amount of organic carbon present. Another useful way to determine the amount of NOM in water is to measure a sample’s absorbance of ultraviolet light at the wavelength of 254 nm (measured in m^{-1}). UV_{254} is useful because its measurement is simple and it can be an indication of how effective coagulation will be in removing NOM. An important difference between TOC measurements and UV_{254} is that TOC measures all of the

organic carbon in a sample but UV_{254} measures only the organic content that absorbs light at this wavelength, e.g., the aromatic portion of organic carbon. Additionally, UV_{254} absorbance has little value for studying the functionality in DOC and cannot be used for direct determination of functional groups (MacCarthy and Rice, 1985). However, when divided by the DOC concentration (in mg/L), it can give an indication of the aromatic fraction of the NOM in the water (Equation 2.1). The resulting value is called the specific UV_{254} absorbance ($SUVA_{254}$).

$$SUVA_{254} = \frac{(UV_{254nm} \text{ in } cm^{-1}) \times 100 \frac{cm}{m}}{(DOC \text{ in } mg/L)} \quad (2.1)$$

Chin et al. demonstrated that a strong positive correlation exists between the molar absorptivity, total aromaticity, and the weight average molecular weights of humic substances (1994). This means that, as the aromatic fraction and weight average molecular weight of DOC increases, its molar absorptivity increases. Therefore, higher $SUVA_{254}$ values indicate greater aromaticity, larger molecular weights, and greater hydrophobicity while low $SUVA_{254}$ values indicate a greater aliphatic fraction, lower molecular weights, and generally lower hydrophobicity (Edzwald and Benschoten, 1990; Chin et al., 1994). $SUVA_{254}$ values not only help one to ascertain the nature of the NOM, but they can provide insight into how effective coagulation might be for NOM removal.

The efficacy of alum coagulation to remove NOM is dependent on the character of the compounds that make up NOM. In this regard, the SUVA value can be useful in determining how effective alum coagulation is likely to be at removing NOM from a particular water. It has been shown that coagulation processes are best at removing NOM with high SUVA values (Edzwald, 1993; White et al., 1997; Edzwald and Kaminski, 2008). Table 2.2 outlines expected NOM removal by coagulation based on SUVA values.

Table 2.2: Effect of Nature of NOM on Coagulation*

SUVA	NOM composition	Coagulation Impact
< 2	Mostly non-humic Low hydrophobicity Low molecular weight Mostly aliphatic	Poor DOC removal NOM has little influence on coagulant dosages
2 - 4	Mixture of aquatic humics and other NOM Mixture of hydrophobic and hydrophilic NOM Mixture of molecular weights Mixture of aliphatic and aromatic	Fair to good DOC removal NOM may influence coagulant dosages
> 4	Mostly humic High hydrophobicity High molecular weight Mostly aromatic	Good DOC removal NOM controls coagulant dosages

*Table derived from Edzwald and Van Benschoten, 1990 and Pernitsky and Edzwald, 2006.

2.6.2 NOM as Organic Ligand in Aluminum Complexation

The removal of NOM by alum coagulation proceeds by two main mechanisms, adsorption to aluminum hydroxide solids and direct precipitation with aluminum (Dempsey et al., 1984; Edzwald, 1993; Dennett et al., 1996). Fulvic acid can even enhance the rate of particle growth by neutralizing the positive charge of $\text{Al}(\text{OH})_{3(s)}$ particles or acting as a polymer to provide a physical bridge between two $\text{Al}(\text{OH})_{3(s)}$ particles (Snodgrass et al., 1984). Conducting experiments with humic acid, Huang and Shiu (1996) found that, after the hydrolysis of aluminum in water, mononuclear and polynuclear Al(III) species are present. These aluminum species induce a complexation reaction with humic acid, with the latter functioning as a strong organic ligand for Al(III). The positively charged aluminum species can also neutralize the negatively charged sites on humic acid, subsequently forming aluminum humate (Huang and Shiu, 1996). Once the overall charge balance of the two species is satisfied, precipitation can occur.

As previously stated, negatively charged organic ligands will cause strong electrostatic based complexation reactions with positively charged aluminum species. Even under conditions when adsorption of NOM onto amorphous $\text{Al}(\text{OH})_{3(s)}$ occurs, the NOM can still be complexed to some degree with aluminum that is not part of the sorbent (Edzwald, 1993). Edzwald argues that, under neutral or acidic pH conditions, humic acid and fulvic acid organic ligands complex aluminum, creating a demand for aluminum that must be satisfied before precipitation of $\text{Al}(\text{OH})_{3(s)}$ can occur (1993). Van Benschoten and Edzwald presented a complexation model for alum reactions with fulvic acid from pH 5 to 7 (1990a). Accounting for aluminum speciation, they found that aluminum complexed with fulvic is hydrolyzed to a ligand number of 2.7 ($n = 2.7, \text{OH}/\text{Al}_T$) (Van Benschoten and Edzwald, 1990a). In other words, the aluminum species complexing with fulvic acid was $\text{Al}(\text{OH})_{2.7}^{+0.3}$. Edzwald builds on this information to argue that minimizing hydrolysis of aluminum will mean less aluminum is required for complexation and charge neutralization (1993). That is to say, with no hydrolysis Al^{+3} has a charge of +3 per atom, which is more effective than AlOH^{+2} at complexing negatively charged fulvic acid (Edzwald, 1993). This argument suggests that coagulation of organics is more efficient at a lower pH because there is less hydroxide competing with the organics for aluminum complexation.

The groups involved with bonding as well as the nature of the bonds helps to understand the pH dependence of this process. Conducting ATR-FTIR experiments on aluminum hydroxides with various organic acids, Guan et al. (2006) confirmed that carboxylic groups govern the adsorption of NOM at acidic pH while phenolic groups govern this process at alkaline pH. Additionally, at acidic pH, chelate formation involving a carboxylic group and *ortho*-phenolic-oxygen was found to be important for the adsorption of dihydroxybenzoic acid (Guan et al., 2006). Conducting additional

experiments with benzoate and salicylate, Guan et al. (2007) proposed that a combination of bridging and monodentate complexes are formed at acidic pH while bridging complexes predominated at alkaline pH. The additional bonding options at acidic pH can help explain why coagulation is more effective in this range.

The formation and growth of alum flocs can also be accelerated by the presence of NOM. Shin et al. found the overall alum dose needed to remove turbidity was reduced if multivalent anionic moieties such as those found in NOM are present in the water (2008). The mechanism proposed is that complexation of multivalent anionic moieties with positively charged aluminum species (or between microflocs) is responsible for enhanced floc formation in the presence of NOM (Shin et al. 2008). One proposed mechanism for this phenomenon is the formation of mononuclear chelate complexes with carboxylic groups in NOM (Hagvall et al., 2015).

However, at high concentrations of NOM, the overall size of flocs start to be negatively affected. Work by Ho and Newcombe showed that flocs formed in surface water with DOC of 12.6 mg/L formed smaller flocs than the same surface water diluted to have a DOC of 4.6 mg/L (2005). The ionic strength, turbidity, and alkalinity of the two waters were controlled to be the same. This result suggests that if the concentration of NOM gets too high, the NOM can start to have a negative effect on the overall size of the flocs. These data suggest Al/DOC ratios play an important role in the size of the floc, with larger flocs forming as the ratio increases (2005). This result also agrees with that of other researchers (Gregory and Rossi, 2001; Chakraborti et al., 2003). Ho and Newcombe also suggest that the size, or molecular weight (MW), of the NOM played an important role in the size of alum flocs (2005). In the same study they found that larger flocs were formed when higher MW NOM was present. Both findings mean that the makeup of the NOM in water can work for or against the formation of larger flocs.

To summarize, the complexation of NOM with aluminum is complex even without the presence of competing ligands, and it is important to know the nature of the NOM to be able to optimize coagulation/flocculation processes.

2.7 ALUMINUM COMPLEXATION WITH FLUORIDE AND OTHER LIGANDS

2.7.1 Aluminum and Fluoride Complexation

Fluoride is known to form soluble, inorganic compounds with aluminum in water undergoing coagulation with aluminum salts (Matijevic et al., 1969; Sung and Rezanian, 1985; Driscoll and Letterman, 1988; Van Benschoten and Edzwald, 1990b; Gong et al. 2012). Furthermore, some of these fluoro-aluminum complexes are non-adsorbable (Matijevic et al, 1969). The amount of fluoro-aluminum complexation is pH dependent. Gong et al. (2012) found that at pH values less than 5.0, almost all fluoride existed as fluoro-aluminum complexes, which inhibited its removal by coagulation. The opposite was true at pH values > 8.0 with fluoride existing almost exclusively as free fluoride (Gong et al. 2012). These data indicate that hydroxide ions have a greater affinity for aluminum at a higher pH. Hu et al. (2005) found that the optimum molar ratio of hydroxide to fluoride ($[OH^-]/[F^-]$) is greater than 2.4 for sufficient fluoride reduction in a coagulation system. A lower ratio resulted in fluoride interfering with the formation of aluminum hydroxide precipitates.

Fluoride can also be incorporated into a mixed fluoro-aluminum solid. Hu et al. proposed a general formula for this precipitate: $Al_nF_m(OH)_{3n-m}$ (2005). The main mechanism is by replacement of hydroxide with fluoride in the aluminum precipitate. The proposed hydrolytic reactions for the formation a mixed aluminum hydroxide precipitate with incorporated fluoride is shown in Table 2.3. However, Alfredo (2012)

found that the required [Al]:[F] ratio to observe co-precipitating effects is 1:1.5. This is outside of the range of [Al]:[F] used in this work, which is closer to 1:0.86.

Table 2.3: Hydrolytic Reactions* for the Formation of an Aluminum Hydroxide and Mixed Precipitate Incorporating Fluoride

Reaction
$\text{Al}^{3+} + 3 \text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_{3(s)} + 3 \text{H}^+$
$\text{Al}^{3+} + 3 \text{OH}^- \leftrightarrow \text{Al}(\text{OH})_{3(s)}$
$\text{AlF}_2^+ + \text{OH}^- \leftrightarrow \text{AlF}_2(\text{OH})_{(s)}$
$\text{AlF}(\text{OH})^+ + \text{OH}^- \leftrightarrow \text{AlF}(\text{OH})_{2(s)}$
$\text{AlF}^{2+} + 2 \text{OH}^- \leftrightarrow \text{AlF}(\text{OH})_{2(s)}$

*Adapted from Pommerenk and Schafran, 2002 and Gong et al. 2012

In looking at the impact of pre-fluoridation (fluoridating water prior to treatment), Pommerenk and Schafran found that a significantly higher alum dose was required to achieve appreciable turbidity removal via charge neutralization (2002). A similar trend was found with regard to DOC removal where more alum was required to remove the same amount of DOC in water with fluoride than in water without fluoride (Pommerenk and Schafran, 2002). In both cases, the effect was attributed to the reduced formation of an amorphous aluminum solid phase. They were able to make this conclusion not only because of the observed increase in the residual aluminum concentration in water treated with alum (2002), but also because the adsorption of fluoride to amorphous $\text{Al}(\text{OH})_{3(s)}$ does not seem to affect the ζ -potential of the solid (Pommerenk and Schafran, 2005). If the ζ -potential is changed by fluoride, then a charge reversal effect would be possible, resulting in the restabilization of particles and an increase in turbidity or DOC of treated water. The way in which fluoride does not affect the ζ -potential of solids is explained by a ligand exchange reaction where hydroxide is replaced by fluoride and the overall charge of the surface group is not affected (Hao and Huang, 1986). This reaction is also the proposed mechanism by which fluoride adsorbs to aluminum solids. Nevertheless, if a

hydroxide ion is released in the proposed ligand exchange reaction, the pH should rise. This mechanism might not be as relevant if the system is buffered as it is in this work.

While a number of researchers looked at the effect of NOM on alum flocs (Section 2.6.2), little work has looked into the effect fluoride has on the particle size distribution of flocs. Alfredo (2012) showed that the PSD of alum flocs might shift toward smaller particles in the presence of fluoride. This work on the effect of fluoride on PSDs was limited in scope and warrants further exploration.

2.7.2 Aluminum and Other Ligands

The presence of sulfate ions in alum may also accelerate particle growth by forming outer-sphere complexes with Al hydrolysis species and act to balance the positive charge of the cation, creating an overall neutral charge balance (de Hek et al., 1978). This charge neutralization accelerates the formation of polynuclear complexes and better enables them to form a solid lattice and settle out of suspension. However, recent work suggests that even stronger bonds are being formed between sulfate and aluminum. Looking at the effect of sulfate on the ζ -potential of $\text{Al}(\text{OH})_{3(s)}$, Pommerenk and Schafran found a significant decreases of the ζ -potential but not a charge reversal (2005). They attribute this effect to the specifically adsorbed ions forming inner-sphere complexes. In other words, the process of adsorption onto the surface by forces other than electrical potential (e.g., covalent bonding) (Pommerenk and Schafran, 2005).

2.8 SUMMARY

Fluoride is naturally occurring in surface and ground waters around the world. In public water systems with little or no naturally occurring fluoride, fluoridation to a concentration of 0.7 mg/L is recommended by the United States Department of Health and Human Services (2015). This practice is recommended to promote the beneficial

aspects of fluoride intake such as prevention of dental caries. However, due to the concerns of fluoride consumption at high concentrations (> 4.0 mg/L), the USEPA set the MCL for fluoride at 4.0 mg/L. The MCL might be lowered, however, taking into account new information published in an NRC report indicating that the severe forms of dental fluorosis can occur if fluoride concentrations in drinking water exceed 2.0 mg/L (2006). Public water systems currently in compliance with the fluoride rule would suddenly find themselves out of compliance and would be required to implement a treatment method to comply with a lowered fluoride rule.

Alum coagulation is one method proposed to help water systems meet a lowered fluoride MCL. Alum coagulation is traditionally used to remove turbidity and NOM from drinking water. It works by (1) destabilizing particles in suspension by charge neutralization and then aggregation of the destabilized particles and (2) sweep flocculation by which contaminants or particles are enmeshed in or adsorbed onto precipitated aluminum hydroxide particles (Benjamin and Lawler, 2013; Shin et al., 2008).

Alum removes NOM through the adsorption of NOM directly to precipitated aluminum solids and direct precipitation with aluminum (Dempsey et al., 1984; Edzwald, 1993; Dennett et al., 1996). NOM has been shown to enhance the rate of particle growth, cause the formation of larger flocs, and cause the formation of a greater volume concentration of flocs (Snodgrass et al., 1984; Huang and Shiu, 1996; Ho and Newcombe, 2005). Nevertheless, the ratio of Al/DOC seems to be important in determining the size of the formed flocs, with the flocs getting larger as the ratio increases (Ho and Newcombe, 2005; Gregory and Rossi, 2001; Chakraborti et al., 2003). The efficiency of NOM removal is pH dependent with greater removal occurring at lower

pH when there is less hydroxide in competition with NOM (Van Benschoten and Edzwald, 1990a; Edzwald, 1993).

Fluoride removal by alum occurs by co-precipitation with aluminum solids or adsorption to the surface of preformed aluminum solids (Hu et al., 2005; Pommerenk and Schafran, 2002; Gong et al., 2012). However, fluoride also makes soluble fluoro-aluminum complexes, some of which are non-adsorbable to aluminum solids (Matijevic et al. 1969; Sung and Rezania, 1985; Driscoll and Letterman, 1988; Van Benschoten and Edzwald, 1990b; Gong et al., 2012). Fluoride can also reduce the removal of other contaminants. For example, turbidity and NOM removal by alum coagulation was shown to decrease when fluoride was present; this was attributed to the role of fluoride in inhibiting aluminum hydroxide precipitation (Pommerenk and Schafran, 2002; Pommerenk and Schafran, 2005). Finally, fluoride was also shown to shift the PSD of aluminum solids toward smaller particles, indicating an inhibition of flocculation (Alfredo, 2012). This work, however, was limited in scope and so this interaction between fluoride and aluminum precipitates warrants further study.

To date, a number of studies have reported on the effect of NOM on the particle size and PSD of alum flocs. With regard to fluoride, one researcher looked at fluoride and how it affects the PSD of alum flocs. However, to the knowledge of the author, no one has studied how the interactions of both fluoride and NOM simultaneously affect the PSD of aluminum precipitates. This work aims to contribute to filling this research gap and will draw on the knowledge summarized in this chapter to inform the interpretation of the experimental results.

Chapter 3: Methods and Materials

To accomplish the objectives outlined in this study, a series of experiments using jar tests was conducted. Jar tests simulate the treatment conditions found in a flocculation/sedimentation treatment system at a water treatment plant. To study the effect of ligand substitution on aluminum hydroxide precipitation, four different conditions were studied:

- Alum with no additional ligands
- Alum with fluoride
- Alum with NOM
- Alum with fluoride and NOM

All jar tests were conducted using synthetic waters made in the laboratory with de-ionized water and chemical reagents. NOM used in the jar tests was isolated and concentrated from a surface water sample taken from Lake Austin, TX.

3.1. CHEMICALS AND REAGENTS

All chemicals and reagents used were of analytical grade or higher. The synthetic water solution was made from a recipe of de-ionized water, calcium chloride dihydrate (Calcium Chloride Dihydrate, CaCl_2 , Certified ACS, Fisher Scientific), and sodium bicarbonate (Sodium Bicarbonate, NaHCO_3 , Certified ACS, Fisher Scientific) such that a hardness of 3.0 meq/L and alkalinity of 3.0 meq/L resulted. Sodium chloride (Sodium Chloride, NaCl , ACS, Alpha Aesar) was added to adjust the ionic strength in the synthetic waters. The ionic strength varied between 0.01 and 0.017 M due to the addition of hydrochloric acid or sodium hydroxide for pH adjustment. Synthetic water solutions were made in 4 L batches and acidified with 1 N hydrochloric acid made from concentrated hydrochloric acid (Hydrochloric Acid 36.5-38.0% V/V, HCl , ACS, EMD

Millipore). Acidification prevented the nucleation of aluminum precipitates when jars were dosed with alum coagulant. A stock of 1000 mg/L fluoride solution was made in 100 mL batches from de-ionized water and sodium fluoride (Sodium Fluoride, NaF, Certified ACS, Fisher Scientific). This stock was used to dose jars to an initial concentration of 5 mg/L fluoride.

Alum (Aluminum Sulfate Hydrate, $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{H}_2\text{O})_{14-18}$, 98%, Aldrich Chemical Company) was used as the coagulant in the jar tests and dosed from a stock solution of 13.32 g/L alum acidified with 4 mL of 1 N hydrochloric acid. Alum stock solutions were made in 200 mL batches. Sodium hydroxide (1 N) was used to adjust pH during coagulant dosing and was made from concentrated sodium hydroxide (Sodium Hydroxide, NaOH, 10.0N, BDH).

Natural organic matter was isolated and concentrated from a sample of surface water sourced from Lake Austin, Texas. Approximately 3000 L of water from Lake Austin was passed through 5.0 μm and 0.5 μm filters in series. This filtration removed essentially all suspended solids from the lake water sample and resulted in the sample containing only dissolved organic matter and other free ions. The filtrate was then passed through a strong acid cation resin (CG8-H, Hydrogen Form, 8% Crosslinked Gel, ResinTech) to remove metals such as Ca^{2+} and Mg^{2+} . After passing through the resin, the filtrate was pumped into two HDPE storage tanks. After all of the water underwent filtration and ion exchange, it was passed through a reverse osmosis membrane (BW30-4040, Dow Filmtech) with approximately 90% permeate flux. The permeate was discarded while the concentrate was pumped back into the storage tanks. The water was concentrated in this manner until approximately 20 L of water remained. Further description of this process can be found in Ingenloff (2011). The chemical analysis of the isolated and concentrated NOM is shown in Table 3.1. Two items in this chemical

analysis warrant comment. The first is the presence of aluminum in the concentrated NOM solution. The concentration may seem high but the solution was stored at a pH less than 3.0. At this pH, the solubility of aluminum is quite high and accounts for this elevated concentration. The second item requiring comment is the lack of information regarding the concentration of sulfate in the NOM solution. When analyzing the concentration of anions by ion chromatography, tailing in the chloride peak masked the sulfate peak. To measure the sulfate requires adjusting the eluent profile to separate the peaks and this procedure was not performed prior to this report being written.

Nevertheless, the concentration of sulfate is expected to be high in the concentrate since it will get concentrated along with the NOM (Serkiz and Perdue, 1990; Pressman et al., 2010). For example, a similar method used by Pressman et al. (2010) concentrated NOM by 165 % and resulting sulfate concentrations were > 3500 mg/L. Sulfate is not expected to be as high in the NOM solution used in this work because the NOM was only concentrated 50-60 times (4-5 mg/L initial DOC concentrated to ~250 mg/L). Because the NOM was concentrated from a sample taken from Lake Austin, which is the source water for the Davis Water Treatment Plant, one can assume that the sulfate concentration of the sample used for concentrating the NOM in this work has a similar sulfate concentration as the raw water treated at the Davis Water Treatment Plant. The average raw water sulfate concentration at the time when this sample was taken was approximately 36.1 mg/L (City of Austin Water Utility, 2015). Assuming an initial sulfate concentration of 36.1 mg/L and no loss of sulfate in the concentration process, the sulfate concentration in the concentrated NOM solution could be upwards of 2166 mg/L. However, once diluted to achieve a DOC concentration of ~5.0 mg/L, the sulfate concentration will be only 42 mg/L without a dose of 100 mg/L alum and about 85 mg/L after alum addition.

Table 3.1: Chemical Analysis of Concentrated Lake Austin Surface Water

Analyte	Concentration (mg/L)
DOC	248.9
Cl ¹⁻	136.5
NO ₂ ¹⁻	0.0
NO ₃ ¹⁻	0.5
PO ₄ ³⁻	8.4
Ca ²⁺	35.0
Mg ²⁺	1.7
K ¹⁺	1.5
Na ¹⁺	8.0
Al ³⁺	1.0

3.2. JAR TESTS

Jar tests were used to simulate a flocculation system found in a drinking water treatment plant. Experiments were performed using a Phipps and Bird PB-700 Jartester with custom-made, rectangular, acrylic jars. For each run, a jar was filled with 200 mL of synthetic water and dosed with the desired amount of ligand(s). The jar was then dosed with the desired amount of alum and rapid mixed for a period of 3 min. to allow for dispersal of alum throughout the solution; all experiments reported in this thesis were performed at a dose of 100 mg/L of alum, equivalent to 0.15 mM alum and 0.30 mM aluminum. During rapid mixing, the pH was adjusted to 6.5 with sodium hydroxide (1 N) or hydrochloric acid (1 N). This sequence of ligand and alum dosing ensured that co-precipitation of ligand(s) and amorphous aluminum hydroxide precipitates occurred simultaneously.

Following rapid mixing, a 30 min. period of slow mixing occurred at a speed of 18-20 rpm (estimated to yield a mean velocity gradient, G , value of 12-15 s⁻¹) (Cornwall and Bishop, 1983). Precipitation (or co-precipitation) is likely initiated during the brief rapid mx period, but the particle growth and completion of the precipitation occurs

primarily during the longer slow mixing period. During jar tests, samples are allowed to settle for 40 min after the slow mixing period. However, because the objective in the experiments reported herein was to observe aluminum precipitates *in situ*, samples of the supernatant were taken immediately after 30 min of slow mixing while the precipitates were still suspended. These samples were analyzed for particle size distribution, pH, ligand residual, and aluminum residual.

3.3. EXPERIMENTAL SYSTEMS

3.3.1. Jar Tests Without Ligands

Jar tests were performed with synthetic water solutions and only alum to observe precipitate characteristics without the interference or substitution of competing ligands. These observations served as the baseline to which successive experiments were compared.

3.3.2. Single Ligand Jar Tests

Synthetic water solutions containing only fluoride or NOM were classified as single ligand systems. Single ligand systems allowed the observation of the change in aluminum hydroxide precipitates, as well as changes in solution characteristics, as a result of ligand substitution into the aluminum hydroxide matrix. It was expected that the presence of each ligand would result in a change in the particle size distribution of aluminum hydroxide precipitates.

3.3.3. Dual Ligand Jar Tests

Synthetic water solutions containing both fluoride and NOM were classified as dual ligand systems. Dual ligand systems allowed the observation of the change in aluminum hydroxide precipitates and solution residuals as a result of competing ligands.

A change in the particle size distribution relative to the single ligand jar tests was expected and was expected to show either an average particle size in between the two sizes shown in the single ligand tests or an average particle size smaller than what was seen in the two single ligand tests.

3.4. EXPERIMENTAL WATERS

Synthetic waters were made in 4 L batches in the laboratory using reagents and de-ionized water. Table 3.2 contains the exact recipe for synthetic water experiments. This water was intended to mimic a simplified and controlled version of a natural water.

Table 3.2: Synthetic Water Recipe (4 L Batches)

Reagent	Quantity	Unit	Contribution
CaCl ₂	672	mg	Hardness
NaHCO ₃	1008	mg	Alkalinity
NaCl	x (varies)	mg	Ionic strength adjustment
HCl (1 N)	12	mL	Acidification
H ₂ O	3.988	L	Background solute

3.5. ANALYSIS OF AQUEOUS CONSTITUENT CONCENTRATIONS

Water samples were taken after the period of slow mixing during a jar test experiment. Depending on the parameter of interest, different methods and materials were used for analysis.

3.5.1. pH Sampling and Analysis

Measurements of pH were taken at the beginning of the jar tests prior to alum dosing, during pH adjustment, and at the end of each experiment. An Orion Ross Ultra pH/ATC Triode Combination Electrode (Thermo Scientific) was used for pH measurements. Hach pH 4, 7, and 10 buffer solutions were used to calibrate the probe

daily. Buffer solutions were replaced every three to four weeks and the probe was maintained using Ross storage and filling solutions.

3.5.2. Fluoride Sampling and Analysis

Fluoride samples were collected at the end of each jar test experiment and were measured immediately after sample collection. All fluoride samples were handled using plastic labware. Fluoride samples contained 10 mL of solution and were filtered through a 25 mm diameter, 0.45 μm pore nylon syringe filter (VWR International) prior to analysis. From the filtrate, 8 mL of sample were removed and placed in a clean plastic beaker. This extracted filtrate was mixed with 8 mL of TISAB II with CDTA buffer. The TISAB II with CDTA provided pH adjustment and ionic strength consistency. It also prevented background aluminum interference with the sample during the analysis and broke up any fluoride complexes in the sample. An Orion Ionplus Sure-Flow Solid State Combination Fluoride electrode (Thermo Scientific) was used for fluoride measurements. Measurements were read as relative milli-volts and converted into mg/L using a fluoride standard calibration curve. A calibration curve for fluoride, similar to the example shown in Figure 3.1 was made after each jar test and before measuring. Because of the tendency of the fluoride probe readings to drift over time, the meter was re-zeroed after every two samples to prevent any misreading. In addition, a fluoride standard was measured after every seven samples.

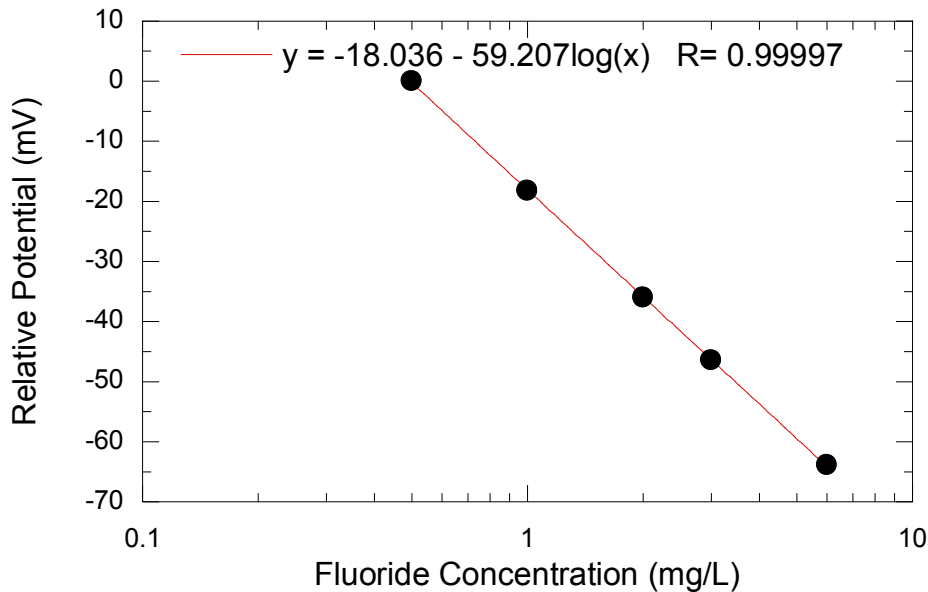


Figure 3.1: Typical fluoride standard curve

3.5.3. Organic Sampling and Measurement

Samples for analysis of organic matter were collected at the end of each jar test experiment and measurement occurred immediately after sample collection or samples were preserved for analysis at a later date depending on the analysis method.

Approximately 100 mL of sample were filtered through a 25 mm diameter, 0.45 µm pore syringe filter (VWR International) prior to analysis.

All samples were measured for dissolved organic carbon. 40 mL of filtrate to be analyzed for TOC were preserved with concentrated phosphoric acid according to Standard Method 5310 (TOC – High Temperature Combustion Method). Samples were then refrigerated at 4.0 °C until they were analyzed. Analyses were done using a Shimadzu TOC-L total organic carbon analyzer (Shimadzu Corporation) in non-purgeable organic carbon (NPOC) mode. NPOC standards were made from powdered potassium hydrogen phthalate (Potassium Hydrogen Phthalate, C₈H₅KO₄, Sigma-Aldrich)

dissolved in de-ionized water. A sample calibration curve is presented in Figure 3.2. For quality control, a standard was measured after every 8 to 10 samples. Samples were not held longer than three weeks prior to analysis.

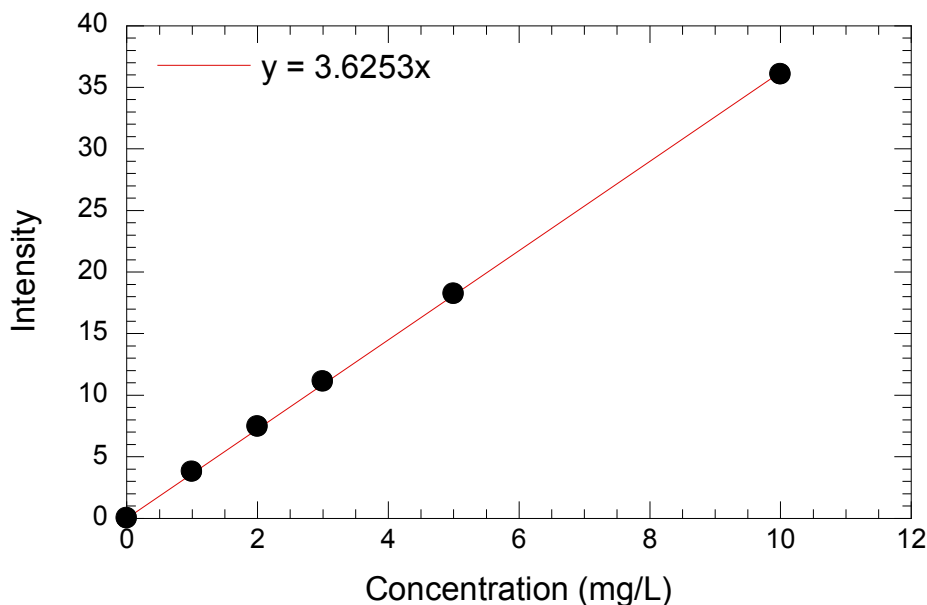


Figure 3.2 NPOC calibration curve

An Agilent 8453 spectrophotometer was also used to measure organic content by measuring the amount of light absorbed by samples at 254 nm. UV-254 is a common water parameter used to describe the amount of organic material in natural water. A quartz cell with a 1 cm path length was used.

3.5.4. Residual Aluminum Sampling and Analysis

Samples to measure residual aluminum were collected at the end of each jar test experiment. Sample volumes of 10 mL were filtered through a 25 mm diameter, 0.45 μm pore nylon syringe filter (VWR International) prior to analysis. Concentrated nitric acid (OmniTrace Nitric Acid, HNO_3 , 67-70% V/V, ACS, EMD Millipore) was added to each

sample at a ratio of 100 μL nitric acid to 10 mL filtered sample to acidify and preserve each sample. A Varian 710-ES Inductively Coupled Plasma (ICP) Optical Emission Spectrometer and Autosampler with 2% concentrated nitric acid mobile phase was used to measure aluminum residual concentrations in the supernatants of the jar tests.

Aluminum standards were made from an aluminum ICP stock solution (Aluminum ICP Standard, Ricca Chemical Company). A sample calibration curve is presented in Figure 3.3. For quality control, a standard was measured every eight to ten samples. Residual aluminum samples were stored at 4°C following acidification if they were not immediately measured. Samples were not held for more than three weeks prior to analysis.

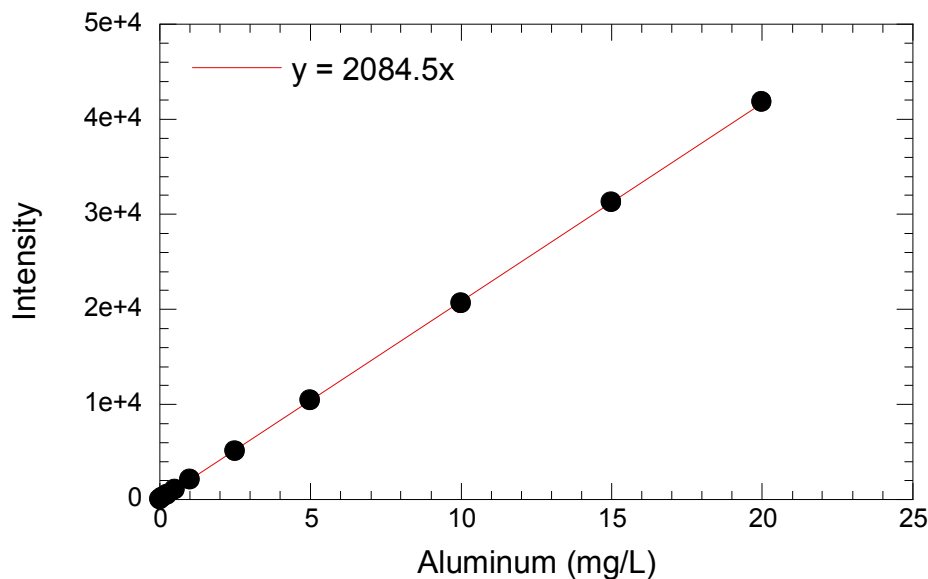


Figure 3.3 Aluminum standard curve

3.6. SUSPENSION CHARACTERIZATION

Measurements of particle size distributions were made using a Coulter Counter (Multisizer III, Beckman Coulter), an instrument for counting and measuring particles in

suspension. A Coulter Counter is an instrument that utilizes the electrical sensing zone principle, where a constant electrical current is passed through a micro-channel in a glass tube separating a clean electrolyte solution and the sample (in the same electrolyte) being measured. The sample solution is drawn through the micro-channel, or aperture, and each time a particle passes through the aperture, the resistance increases and results in a voltage spike. The magnitude of the voltage spike is proportional to the volume of the particle. In this manner, the number and size of the particles can be measured. For more details on the theory and operation of electrical sensing zone instruments, see Van Gelder et al. (1999) and Chowdhury et al. (2000).

3.6.1. Electrolyte Preparation

Coulter Counter operation relies on the solution being electrically conductive. To this end, samples must be diluted into an electrolyte solution prior to measurement. High-purity electrolyte was prepared following the methods outlined in Broyan (1996) and Chowdhury et al. (2000).

The electrolyte solution used in this research was made from sodium chloride, which provided electrical conductivity, and sodium azide (Sodium Azide, NaN_3 , High Purity, VWR), which prevented microbial growth in the filtration apparatus. Previous work shows that 1 to 8 % (weight/volume) sodium chloride solutions provide the appropriate range of aperture resistance (Lines, 1992). A 2 % (weight/volume) concentration was used in this research, but after dilution, the concentration decreased slightly. However, the concentration never dropped below 1.4 %. The sodium azide concentration was 0.1 % (weight/volume) and was chosen based on previous work (Nason, 2006). Aside from omitting CaCl_2 and increasing the mass of sodium azide from 2 to 4 grams, this worked followed the same procedure for electrolyte preparation as that

outlined in Nason (2006). The purity of the electrolyte was checked prior to every experiment to ensure that the number of counts in the electrolyte was acceptable (Table 3.3).

Table 3.3: Acceptable Electrolyte Background Counts

Aperture Diameter (μm)	Maximum permissible total count for blank
30	< 500
100	< 300
200	< 100

3.6.2. Coulter Counter Operation

Because of the broad range of particle sizes in the suspensions in this research, multiple apertures were used to capture the entire distribution of aluminum precipitates in solution. According to the Coulter manuals, each aperture is capable of measuring particles with diameters from 2% to 60% of the aperture diameter; experience in this laboratory suggests that the upper limit, when measuring flocs that contain a high amount of water, is approximately 20% of the aperture diameter. The approximate upper and lower bounds and operating conditions for the three apertures used are shown in Table 3.3.

Table 3.4 Aperture Dimensions, Particle Size Limits, and Operating Conditions

Aperture Diameter (μm)	Measurable Size Range (μm)	Current (μA)	Gain (-)
30	0.7* – 6	800	8
100	2.0 – 20	3200	1
200	4.0 – 40	1600	2

*The lower limit of the 30 μm aperture was limited by electrical noise

As described above, samples must be diluted in electrolyte prior to measurement. This dilution not only maintains the appropriate conductivity but also ensures a

reasonable concentration of particles in the resulting suspension. As the concentration increases, the probability of coincidence (i.e., two particles passing through the aperture at the same time and being counted as one) increases. Additionally, particle concentrations that are too high can result in clogging of the aperture. However, low particle concentrations will result in scattered data and a reduction in the statistical significance of the measured distribution. These two factors result in an acceptable range of particle concentrations for each aperture. The recommended sample volumes (times) and particle counts used throughout this research are shown in Table 3.4.

While all reasonable measures were taken to remove all particles from the electrolyte solution, complete removal was not achieved. To account for these particles in the electrolyte, background samples containing only the electrolyte were measured as “blanks”. Blank counts were subtracted from samples to determine the actual particle size distribution. Acceptable counts from blank solutions are shown in Table 3.4.

Table 3.5 Guidelines for Sample Volumes (Times) and Acceptable Particle Counts During Coulter Counter Operation

Aperture diameter (μm)	Sample volume (mL)	Sample time (s)	Recommended range of total count for sample
30	0.05*	~16	11,000-16,000
100	2.0*	~50	10,000-18,000
200	9.31	60*	9,000-13,000

*Indicates controlling variable. The 30 and 100 μm apertures are operated using a volumetric metering pump. The 200 μm aperture is operated using a vacuum pump. The calibration of the 200 μm aperture with respect to volume is described in Section 3.6.3.

3.6.3. Coulter Counter Calibration

The Coulter Counter was calibrated using uniform diameter latex microspheres (Beckman Coulter). The Multisizer III software was operated in logarithmic mode with

the lower size range set to a value just above that of the background noise. This size was typically 2.0-2.5% of the aperture diameter. Setting the number of logarithmically spaced size bins to 128, the upper limit of the size range was calculated such that the logarithmic interval for each channel ($\Delta\log(dp)$) is 0.01. In logarithmic mode, the response of the instrument is linear with respect to the logarithm of the particle volume. When the size range is set to result with a bin spacing of $\Delta\log(dp) = 0.01$, the slope of the line is 0.03 $\log(vp)/\text{channel}$.

Each aperture is calibrated using four different size particles between 2 and 40% of the aperture diameter. The smallest particle was diluted into clean electrolyte and a measurement taken. Particles of each larger size were added with measurements taken after each subsequent addition. The response of the instrument was determined by recording the channel into which the maximum number of the particles of a particular size fell. Best-fit lines with slope 0.03 were fit to the calibration data on a plot of the logarithm of particle volume versus channel number, yielding an intercept. Figure 3.4 shows an example calibration curve. The slope and intercept of the calibration curve were used to convert raw counts (# vs. channel) into the particle size distribution. Calibration was periodically verified using one of the particle size standards.

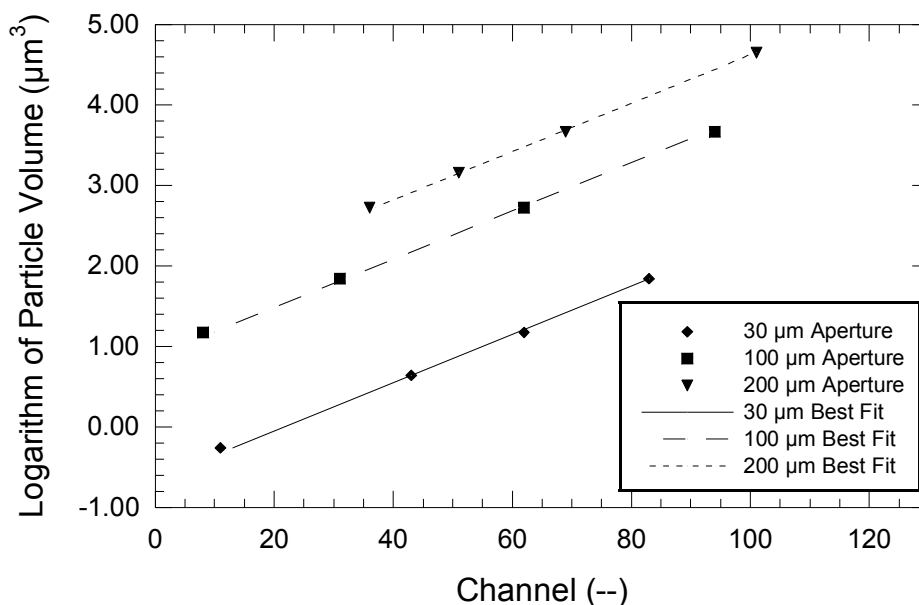


Figure 3.4 Coulter Counter calibration curve

Samples can be drawn through the aperture by a volumetric metering pump or by a vacuum pump. Smaller apertures (30 and 100 µm) were operated using the volumetric metering pump. In this case, the desired analytical volume is set and the instrument measures particles while exactly that volume is pulled through the aperture. However, the metering pump can only pull a maximum of 2000 µL. This volume is typically not enough to achieve the target particle counts with the larger apertures (200 µm). This problem can be overcome by switching the sampling method to the internal vacuum pump and sampling time is the controlling variable. In this case, when using the 200 µm aperture, the suspension is sampled for 60 s. The volume of sample drawn during that time is determined by measuring the change in mass of clean electrolyte drawn for 60 s. This procedure was repeated 5 times and averaged. This average was then converted to volume using the measured density of the electrolyte.

3.6.4. Sample Preparation

Alum flocs are prone to breakup and subject to numerous steps during sampling and measurement. For this reason, utmost care was taken to prevent this breakup and ensure the original particle size distribution was maintained.

Sampling

Samples were drawn from the center of the jars at the end of the 30 min slow-mix period to ensure a representative sample. A wide-mouth pipette (i.e., a pipette with the tapered end cut off) and bulb were used to reduce the velocity of the flow into the pipette and reduce breakup. Samples were drawn into the pipette very slowly; for example, a sample of 5 mL would take approximately 7-10 s. The choice of pipette size depended on the size of the sample desired, so that the volume could be measured quite accurately. Graduated pipettes were used, and the volume drawn into the pipette was greater than the desired sample volume, so that the sample was dispensed from a starting point to an ending point on the pipette. The dispensing was also done extremely slowly to avoid breaking up flocs.

Dilution and Mixing

60 mL graduated bottles with Teflon lined caps (Quorpak) were used to make the dilutions. These bottles were cleaned with a 2% solution of Liqui-Nox (Alconox, Inc.), soaked in a 10% nitric acid solution, thoroughly rinsed with deionized water, and dried upside down. Each bottle was rinsed with clean electrolyte prior to use and the same electrolyte was used to rinse 5 different bottles. The bottles were then filled with 40 mL of clean electrolyte. The sample was then released directly into the electrolyte by holding the tip of the pipette just above the water level and allowing the sample to slowly flow into the electrolyte. To minimize any error in the volume dispensed into the electrolyte, a small amount of sample was wasted onto the laboratory bench following the method

outlined in Lawler (1979). The bottles were then capped and mixed using the same method outlined in Lawler (1979); in this method, the bottles are attached non-axially to a cylinder rotating at 6 rpm, so that the suspension undergoes a gentle rocking and rolling motion that mixes the sample into the electrolyte without breaking the flocs.

Measurement

Following mixing, the bottle was placed on the Multisizer III sample tray and raised to immerse the external electrode and aperture tube. Measurement was then performed according to the guidelines outlined above.

At times, the aperture became clogged with particles. If this clogging occurred, the blockage was removed by reversing the flow of electrolyte through the aperture. If this step was not successful, a brush was used to unclog the aperture. If this blockage still persisted, the aperture was removed and briefly sonicated and/or water was forced through the aperture at high pressure by pressing a rubber stopper into the top of the water filled aperture tube.

Measurements With Multiple Apertures

Samples were first taken and measured with the 200 μm aperture. After measurement, the aperture was changed to the 100 μm aperture. Because larger flocs tended to clog the 30 μm aperture, the samples for the 30 μm aperture were taken, diluted and set aside while the samples for the 100 μm aperture were taken and measured immediately. After measurement with the 100 μm aperture, the apertures were changed and the second sample was measured with the 30 μm aperture. The time between measurements was on the order of 4-5 minutes which ensured sufficient settling of particles larger than those to be measured in the 30 μm aperture to prevent blockage by larger precipitates.

3.7 REPRESENTATION AND ANALYSIS OF PARTICLE SIZE DISTRIBUTION DATA

Raw data from the Coulter Counter are the number of particles counted in each channel or bin (128 bins in this research). These raw data can be converted into many useful forms for presentation and analysis. This section outlines the ways in which data are presented in this work.

3.7.1 Representation of the PSD

In many particle processes, suspensions are characterized with respect to the number and size of particles. These particle suspensions are often quite heterodisperse and are characterized by broad and nearly continuous particle size distributions (PSDs) (Nason, 2006). PSDs can be represented in many ways and detailed discussions of these methods can be found elsewhere (Friedlander, 1977; Benjamin and Lawler, 2013). The following discussion introduces some common representations, all of which were used in this research.

Particle size distributions were measured by the Coulter Counter on the basis of particle number and particle volume (see Section 3.6). Nevertheless, they are presented in a number of ways to facilitate analysis. Particle size is always presented in terms of equivalent spherical diameter, d_p . Defining particle volume as v_p , the equivalent spherical diameter is the diameter of a sphere of volume v_p .

$$d_p = \left(\frac{6v_p}{\pi} \right)^{1/3} \quad (3.1)$$

The amount of material in a given size (i.e., a small size interval) is presented in terms of number and volume at various points throughout this work.

The cumulative distributions are not particularly useful when trying to analyze particle distributions (Benjamin and Lawler, 2013; Nason, 2006). Because of this, it is

more common to analyze differential distributions. The particle size distribution function (PSDF) is defined as follows:

$$n(d_p) = \frac{\Delta N(d_p)}{\Delta(d_p)} = \frac{dN(d_p)}{d(d_p)} \quad (3.2)$$

Equation 3.2 shows both the discrete and continuous formulations of the PSDF.

Oftentimes, the numerical values of the PSDF vary over several orders of magnitude for a particular suspension. To display the information in a meaningful way, the log of the PSDF is plotted in this work. Additionally, the abscissa (particle diameter) is generally displayed in terms of the log of the particle diameter, consistent with the fact that the Coulter Counter was set up to measure at equal intervals of log diameter. A linear scale would compress the data for small sizes and spread out the data for larger sizes, relative to their importance. For example, the differences in behavior and concentration between the 0.5, 1.0, and 2.0 μm (diameter) particles are far different than the behavior between the 100.5, 101.0, and 102.0 μm particles, but using a linear scale would suggest they have the same importance (Benjamin and Lawler, 2013). Utilizing a logarithmic scale ensures that this problem is avoided.

Another way of representing the PSD is the number distribution. While it is not used in this work, it is the basis for deriving the volume distribution that is used in this work. The number distribution is found by dividing the incremental number concentration ΔN by the logarithmic increment of particle diameter, $\Delta \log d_p$, associated with each bin.

$$\text{Number Distribution} = \frac{\Delta N}{\Delta \log d_p} \quad (3.3)$$

From this distribution, the volume distribution is derived. The volume distribution gives useful information when looking at coagulation/flocculation systems since this process is concerned with the aggregation of small particles to large particles. While

coagulation/flocculation may not show a dramatic change in the number distribution, a considerable effect can be seen on the volume distribution as a greater number of large particles are formed, showing that the volume concentration is primarily associated with the larger diameter particles. Again, the volume concentration is calculated assuming the particles are spherical.

$$\text{Volume Distribution} \quad \frac{\Delta V_i}{\Delta \log d_p} = \frac{\Delta N_i}{\Delta \log d_p} \left(\pi \frac{d_{p,i}^3}{6} \right) \quad (3.4)$$

The volume distribution is the primary means by which the data are represented in this work. The PSDF is also used to further gain insight into the observations from the volume distributions presented.

3.7.2 Data Manipulation and Combining Data from Multiple Apertures

The data were converted to the various representations of the PSD following the method outlined by Nason (2006). The only difference was that the number of bins in this work was 128, not 130.

Data from the 30 μm , 100 μm , and 200 μm apertures were combined in a similar manner outlined in Nason (2006). In general, counts were removed from the lower end of the size range of each aperture due to excessive background counts. Counts from the upper end were also removed where counts were too low to ensure statistical validity. This method ensured that all of the zero counts were removed from the data (vertical lines in Figure 3.5a). Finally, the combined raw data were smoothed using a 5-point centered running average. Figure 3.5 represents raw (a), combined (b), and averaged (c) PSDFs from the Alum Only experiment. The averaged data were used to make the statistical analyses outlined later in this chapter.

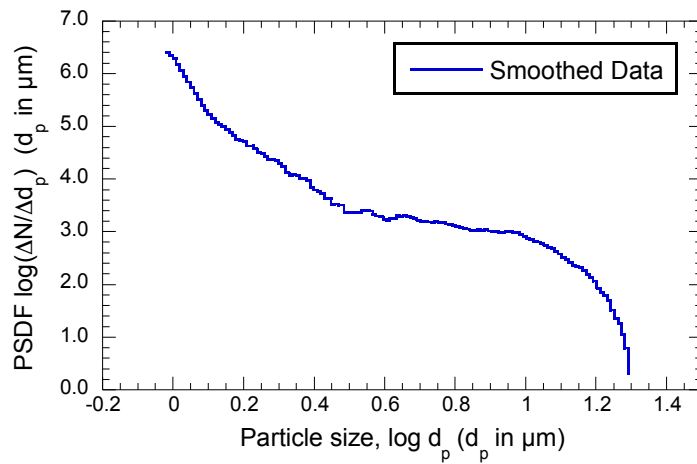
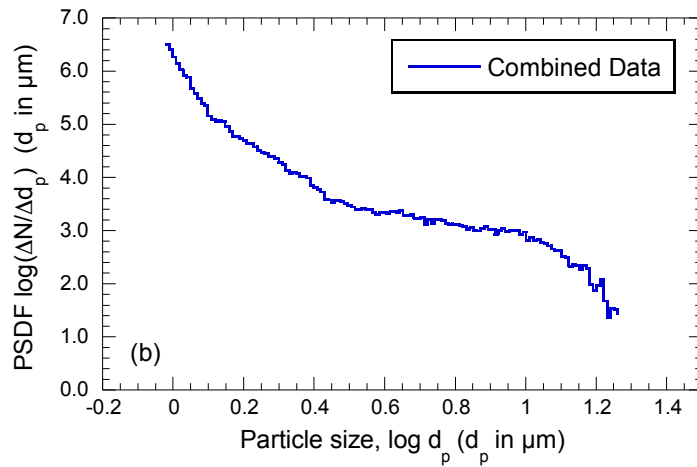
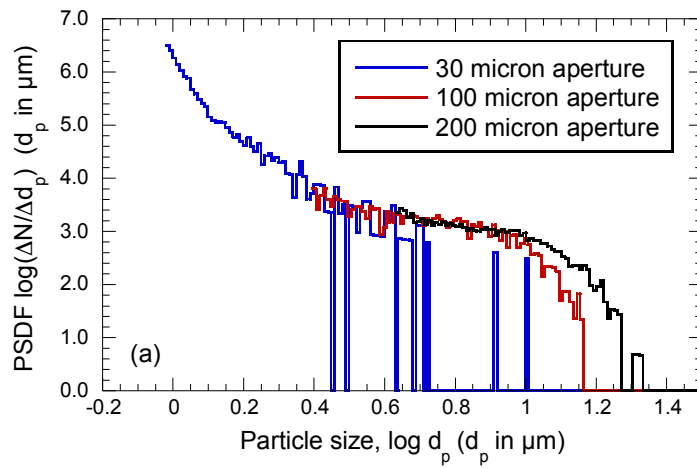


Figure 3.5: Raw (a), combined (b), and averaged (c) data from the Alum Only experiment to create a single PSDF distribution

3.7.3 Quantifying Changes in PSD

While examining the full PSD yields the highest resolution picture of the change in particle characteristics as a result of ligand substitution, a set of summary statistics is useful for examining these effects. A number of metrics were used to quantify the trends in particle size distribution data.

Moments

The i^{th} moment of a generalized probability density function $f(x)$ is defined as follows:

$$m_i = \int_0^{\infty} x^i f(x) dx \quad (3.5)$$

A number of authors described the relevance of moment transformation of the PSDF for aerosol, particulate and crystallization processes (Friedlander, 1977; Ramkrishna, 2000; Mersmann, 2001; Tavaré, 2001). When the probability density function is the PSDF, the moments characterize several physical aspects of the system. The zeroth moment is equal to the total number of particles.

$$m_0 = \int_0^{\infty} n(d_p) d(d_p) \quad (3.6)$$

The cube root of the third moment divided by the zeroth moment gives the volume average diameter.

$$\bar{d}_{pV} = \left(\frac{m_3}{m_0} \right)^{1/3} = \left(\frac{\int_0^{\infty} d_p^3 n(d_p) d(d_p)}{\int_0^{\infty} n(d_p) d(d_p)} \right)^{1/3} \quad (3.7)$$

Similar to the method utilized by Nason (2006), the total particle number is calculated in this work by summing the discrete concentrations in each bin (i.e., integrating).

Full-Width at Half Maximum

Another means of comparing different volume distributions is by characterizing the width or spread of the distribution. This spread can be characterized in a number of

ways (e.g. standard deviation, quartiles), but many can be biased by the choice of the measured standard size range and can be influenced by the influx of new particles into the measured size range via nucleation (Nason, 2006). In this work, the width of the volume distribution was quantified using the full-width at half maximum (FWHM). The FWHM is defined as the distance (here, $\Delta \log d_p$) between points on the curve at which the function reaches half its maximum value.

Chapter 4: Experimental Results and Discussion

Experimental results from jar tests are presented in this chapter and have been divided into three main sections. The first section summarizes the aqueous constituent concentrations of the jar tests, including the measured residual aluminum, fluoride, and DOC concentrations and the calculated SUVA values. The next two sections compare the precipitate characteristics observed in each of the three systems: no ligands, one ligand (i.e., fluoride or NOM), and two ligands (both F and NOM). These characteristics are related back to the aqueous constituent concentrations to better explain the observations. A summary of the results from all jar tests concludes the chapter.

4.1 AQUEOUS CONSTITUENT CONCENTRATION SUMMARY

4.1.1 Residual Aluminum

The results of the residual aluminum analysis are presented in Table 4.1. Each jar test was conducted with a control without alum (labeled herein Fluoride Only). With two notable exceptions, the residual aluminum concentrations were all quite low (generally well below 0.1 mg/L). When fluoride was present in the system with alum, the residual aluminum increased markedly to above 0.20 mg/L. This increase is important as it indicates that fluoride is likely complexing with aluminum to make a soluble fluoro-aluminum complex. Furthermore, it also means that the SMCL of 0.20 mg/L for aluminum is exceeded when fluoride is present. The aluminum in the NOM Only and Fluoride + NOM Only controls are a result of the presence of aluminum in the concentrated Lake Austin NOM solution.

Table 4.1: Residual Aluminum* Concentrations in Jar Tests

Jar Test	Residual Aluminum	
	(mg/L)	(mM/L)
Alum Only	0.017	6.41E-04
Fluoride Only	ND	ND
Alum + Fluoride	0.244	9.08E-03
NOM Only	0.021	7.92E-04
Alum + NOM	0.058	2.15E-03
Fluoride + NOM Only	0.020	7.50E-04
Alum + Fluoride + NOM	0.265	9.85E-03

*Recall alum doses in all jars (except for two controls) were 100 mg/L, equivalent to 8.0 mg/L and 0.30 mM of aluminum

4.1.2 Fluoride Removal

Table 4.2 outlines the fluoride removal from the two experiments that had both fluoride and alum. While removals were similar between the two systems, the presence of NOM caused a small but measurable decrease in the fluoride removal from 50.1% to 45.8%.

Table 4.2: Summary of Fluoride Removals

Jar Test	[F ⁻] Initial	[F ⁻] Final	Removal (%)
	(mg/L)	(mg/L)	
Alum + Fluoride	5.12	2.55	50.1%
Alum + Fluoride + NOM	5.08	2.75	45.8%

4.1.3 NOM Removal

The NOM removal in each experiment is shown in Table 4.3. In addition to showing the DOC removal, the SUVA values are summarized. In contrast to the small decrease of fluoride removal in the presence of NOM, NOM removal was greatly reduced by the presence of fluoride. This result indicates that fluoride is apparently outcompeting NOM for complexation with aluminum or adsorption to aluminum solids. Though the scope of this work was not to determine the effect fluoride has on the dose response of

NOM removal using alum coagulation, these results show that in an otherwise identical system, if fluoride is present an equivalent dose of alum resulted in decreased NOM removal. This reduced removal indicates that the point of diminishing returns provision of the D/DBP rule will be reached at a lower alum dose in a water with fluoride present than one without. The reduction in SUVA values for both experiments indicates that the larger, more aromatic, and more hydrophobic compounds making up the NOM are being preferentially removed by coagulation.

Table 4.3: Summary of NOM Removal

Jar Test	DOC Initial (mg/L)	DOC Final (mg/L)	Removal (%)	SUVA Initial (L mg ⁻¹ m ⁻¹)	SUVA Final (L mg ⁻¹ m ⁻¹)	ΔSUVA (L mg ⁻¹ m ⁻¹)
Alum + NOM	6.02	3.90	35.2%	2.37	1.20	-1.17
Alum + Fluoride + NOM	5.69	4.47	21.4%	2.38	1.37	-1.01

4.2 SINGLE LIGAND JAR TESTS – PRECIPITATE CHARACTERISTICS

4.2.1 Alum with Fluoride

Figure 4.1 shows the volume distributions (a) and particle size distribution functions (b) of aluminum precipitates with and without fluoride present.

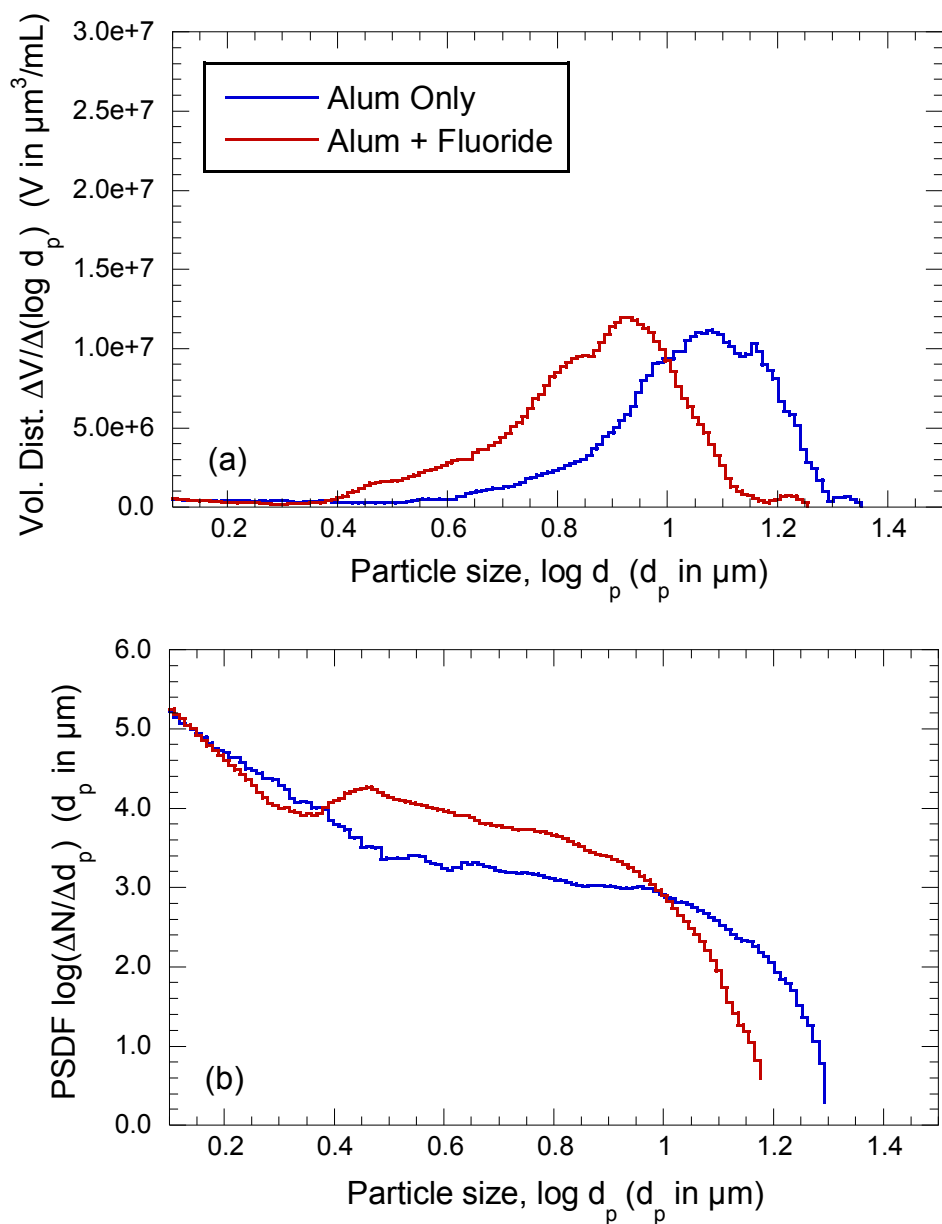


Figure 4.1: Volume distributions (a) and PSDFs (b) of aluminum precipitates formed in the Alum Only vs. Alum + Fluoride experiments

When plotted in this way, the area under the volume distribution is the total volume concentration of particles with the measured size range; the volume distributions in Figure 4.1a have essentially the same particle volume concentration but it is distributed

quite differently. The qualitative observation regarding nearly identical total particle volumes is confirmed when the total volumes are calculated. The volumes of solids produced with Alum Only vs. Alum + Fluoride are 3.91 and 4.14 ppmv, respectively. As is evident in the figure, a discernible shift in the $\log d_p$ value associated with the peak of the volume distribution from approximately 1.072 without fluoride present to approximately 0.925 in the presence of fluoride. These values correspond to particle diameters of 11.8 μm and 8.4 μm , respectively. The shift indicates that, while a similar volume of particles is produced, the particles are concentrated at smaller particle diameters when fluoride is present. The corresponding volumetric mean $\log d_p$ values are 0.698 (4.99 μm) and 0.667 (4.65 μm), respectively. This shows that the particle diameter about which the total volume of particles is centered, i.e., the centroid, shifted in the presence of fluoride to a smaller diameter. The FWHM ($\Delta \log d_p$) value for the Alum Only system is 0.30 while that of the Alum + Fluoride system is 0.31. These values are essentially identical, so the two distributions (as can be seen visually) have very similar distribution of particle volume around the peak value, at least on a log diameter basis. Table 4.4 summarizes the summary statistics of both distributions.

Table 4.4: Summary Statistics Comparison Between the Alum Only and Alum + Fluoride Distributions

	Approx. Peak Volume Particle Diameter		FWHM	Total Vol. of Solids (ppmv)	Vol. Mean Diameter (log d_p (d_p in μm))
	log d_p (d_p in μm)	d_p (μm)			
	Alum	1.072	11.80	0.30	3.91
Alum + F ⁻	0.925	8.42	0.31	4.14	0.667

To gain more insight into the differences of the two distributions, the log of the particle size distribution function (PSDF) is shown in Figure 4.1b for both experiments.

As can be seen in this figure, in the range of $0.4 < \log d_p < 1.0$ (or $2.5 \mu\text{m} < d_p < 10.0 \mu\text{m}$), the PSDF of the Alum Only experiment is below that of the experiment with fluoride. This means that when fluoride is present, a greater number of particles with diameters $< 10 \mu\text{m}$ form than if fluoride was not present. However, in the range of $\log d_p > 1.0$, the PSDF of Alum Only is above that of the experiment with fluoride. This means that when fluoride is present, fewer particles with diameters $> 10 \mu\text{m}$ are formed than if fluoride was not present.

These observations in this experiment could be the result of a number of different factors. Because both areas under the volume distributions are essentially the same, the total volume concentration of particles is nearly identical in both experiments. This observation indicates that fluoride must be inhibiting flocculation in some way by acting as a stabilizing agent or inhibiting precipitation. Work by Liu et al. (2013) suggests fluoride can affect the ζ -potential of a suspension at neutral pH but this effect was only seen at high fluoride to aluminum ratios of 3:1. This work looked at a fluoride to aluminum ratio of less than one. Additionally, Pommerenk and Schafran (2005) found fluoride affects the ζ -potential of aluminum hydroxide solids very little, but this work was strictly looking at the adsorption of fluoride onto preformed amorphous aluminum hydroxide. However, ζ -potential is not the only interaction that matters in flocculation and precipitation. Fluoride could be preventing further growth of precipitates by inhibiting the natural interaction between hydroxide and nearby particles during particle growth. Recall that fluoride can replace hydroxide in aluminum hydroxide solids (Hao and Huang, 1986). While fluoride has the same charge as hydroxide ions, it is a different size, which might be disrupting the continued formation of aluminum hydroxide complexes. Further precipitation may be inhibited by this mechanism as well. Soluble aluminum that would otherwise precipitate by complexing with hydroxide on a solid

surface might not precipitate if fluoride replaces hydroxide on the solid surface. While these fluoro-aluminum complexes do not reduce the total volume of precipitate, they might inhibit aggregation, resulting in the formation of smaller particles and an increased residual aluminum concentration.

Regarding the particle sizes themselves, the measurements in this work are smaller than what is reported by other researchers (Ho and Newcombe, 2005; Liu et al. 2013). This discrepancy is explained by recalling the way the Coulter Counter measures particles size. The Coulter Counter measures the volume of electrolyte displaced by the particle passing through the aperture. If a porous particle with a large fraction of electrolyte entrained in its bulk volume passes through the aperture, only the solid fraction of the particle is measured as the entrained electrolyte has the same conductivity of the background electrolyte. Alum flocs are suspected to be subject to this phenomenon, where the Coulter Counter measures only aluminum hydroxide precipitates and the measured particle sizes are much smaller than what is reported in the literature by researchers using different methods of particle counting (e.g., Ho and Newcombe, 2005; Liu et al., 2013).

It should also be noted that it was difficult to get a good measurement with the 30 μm aperture in the range just below the detection limit of the 100 μm aperture. For this reason, there is erratic behavior and a dip in some of the PSDFs (e.g., Alum + Fluoride). This erratic behavior continues until $\log d_p$ around 0.4-0.45, corresponding to measurements taken with the 100 μm . Because the size range we are most concerned about is found at $\log d_p$ values above 0.4, these erratic measurements were disregarded as not affecting the overall analysis.

4.2.2 Alum with NOM

Figure 4.2 shows the volume distributions (a) and PSDFs (b) of the aluminum precipitates formed with and without NOM present.

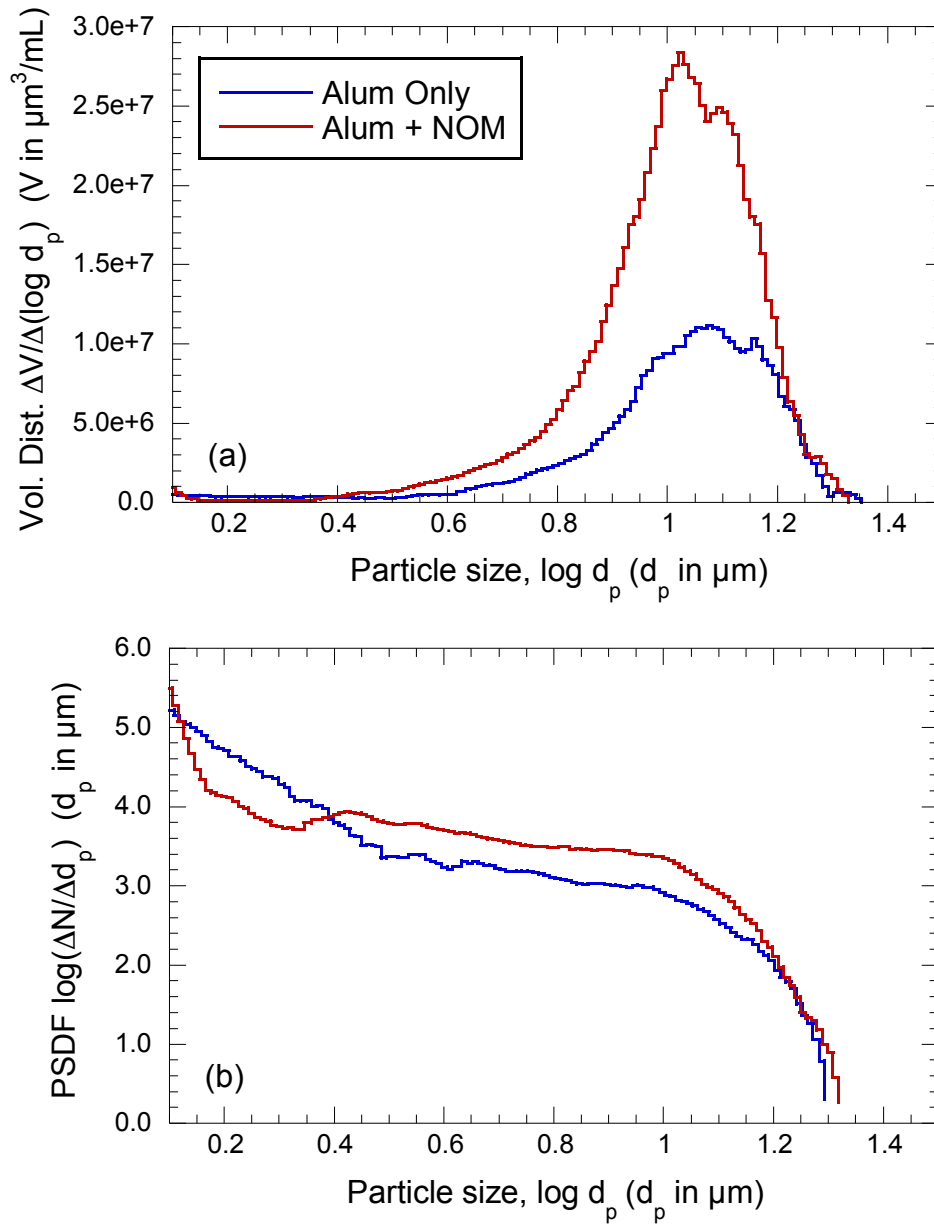


Figure 4.2: Volume distributions (a) and PSDFs (b) of aluminum precipitates formed in Alum Only vs. Alum + NOM experiments

Table 4.5 displays the differences in the summary statistics between the two systems. In contrast to the experiment with fluoride, instead of a dramatic shift to smaller particles, the distribution shifts vertically. This upward shift indicates that, while similar particle diameters are present, a greater number (Figure 4.2a) and a greater overall total volume of particles is formed in the presence of NOM. The volume shift is also indicated by the total volume calculation: 3.91 ppmv and 8.59 ppmv for the Alum Only vs. the Alum + NOM experiments, respectively. These results are similar to results by Snodgrass et al. (1984) where, in the presence of NOM, the total volume of precipitates formed increased by two to five times.

Table 4.5: Summary Statistics Comparison Between the Alum Only and Alum + NOM Distributions

	Approx. Peak Volume Particle Diameter		FWHM	Total Vol. of Solids (ppmv)	Vol. Mean Diameter (log d_p in μm)
	log d_p (d_p in μm)	d_p (μm)			
			$\Delta \log d_p$ (d_p in μm)		
Alum	1.072	11.80	0.30	3.91	0.698
Alum + NOM	1.019	10.44	0.27	8.59	0.820

The log d_p associated with the peak of the volume distribution of the aluminum precipitates formed in the presence of NOM is 1.02, or 10.4 μm . This value is also slightly smaller than the log d_p value in the Alum Only experiment (1.07 or 11.8 μm). The volumetric mean log d_p increased from 0.698 (4.99 μm) to 0.82 (6.61 μm). This increase may seem counter intuitive but is accounted for by the fact that a greater total volume of particles forms in the larger diameters which then pulls the centroid of the volume distribution to a larger particle diameter. The FWHM values are similar between the two systems with the NOM system being less heterodisperse than the Alum Only system.

The difference in the PSDF curves is characterized by the Alum + NOM distribution being shifted to a greater number of particles being formed than in the Alum Only experiment. This observation further provides evidence for the greater number of particles as well as the increase in peak height seen in the volume distribution. In the PSDF figure, the somewhat low and erratic values described in Section 4.2.1 are present in the Alum + NOM distribution at $\log d_p$ values less 0.4. As in the previous case, the more important information is found at $\log d_p$ values greater than 0.4 and do not affect the overall conclusion to be made.

Snodgrass et al. (1984) proposed the reason for this significant increase in the total number of particles as well as the total volume of particles formed is a result of the formation of an “aluminum fulvate” (their experiments looked at fulvic acid as the organic ligand). They suggest the extra volume is due to the fact that fulvic acid molecules are much larger than the hydroxyl ion. These experiments were conducted at pH ~5.5, which is lower than the pH in this work (~6.5). Nevertheless, Dempsey et al. (1984) proposed that adsorption of fulvic acid or aluminum-fulvic acid complexes on aluminum hydroxide solids is an important mechanism at the pH and alum dose used in this work. Shin et al. (2008) also proposed that the anionic moieties of NOM molecules play an important role by complexing with positively charged aluminum species and promoting their aggregation and coagulation. It seems a combination of both phenomenon occurred in the experiments conducted in this work: aluminum organic complexes are forming that incorporate molecules that are much larger and complex than the hydroxyl ions that typically complex with aluminum to form $\text{Al}(\text{OH})_{3(s)}$. Furthermore, the aggregation and precipitation of aluminum precipitates is being promoted by negatively charged organic moieties complexing with positively charged aluminum species. One other possibility is that NOM compounds are acting as bridging molecules

between particles and facilitating aggregation. The small increase in residual aluminum in the Alum + NOM experiment may lead some to conclude otherwise; that more aluminum is in solution and so a greater absolute number of aluminum solids cannot be formed. However, two factors can account for this observation. The first is the presence of a small amount of aluminum in the concentrated NOM solution added to the jars. Some of this aluminum may have been already been bound up in soluble aluminum NOM complexes and contributes to the total aluminum in solution. The second is that due to the detection limit of the Coulter Counter, one cannot account for the absolute number of particles formed in suspension. It could be that a similar number of particles were formed in both systems, but aggregation played a larger part bringing a larger number of particles into the detection range of the Coulter Counter.

4.3 DUAL LIGAND JAR TESTS – PRECIPITATE CHARACTERISTICS

Figure 4.3 shows the volume distributions (a) and PSDFs (b) of aluminum precipitates formed with and without fluoride and NOM present. The volume distributions reflect both trends of the experiments with each ligand alone—an increase in the total volume concentrations in the presence of NOM and an overall decrease in the floc sizes in the presence of fluoride.

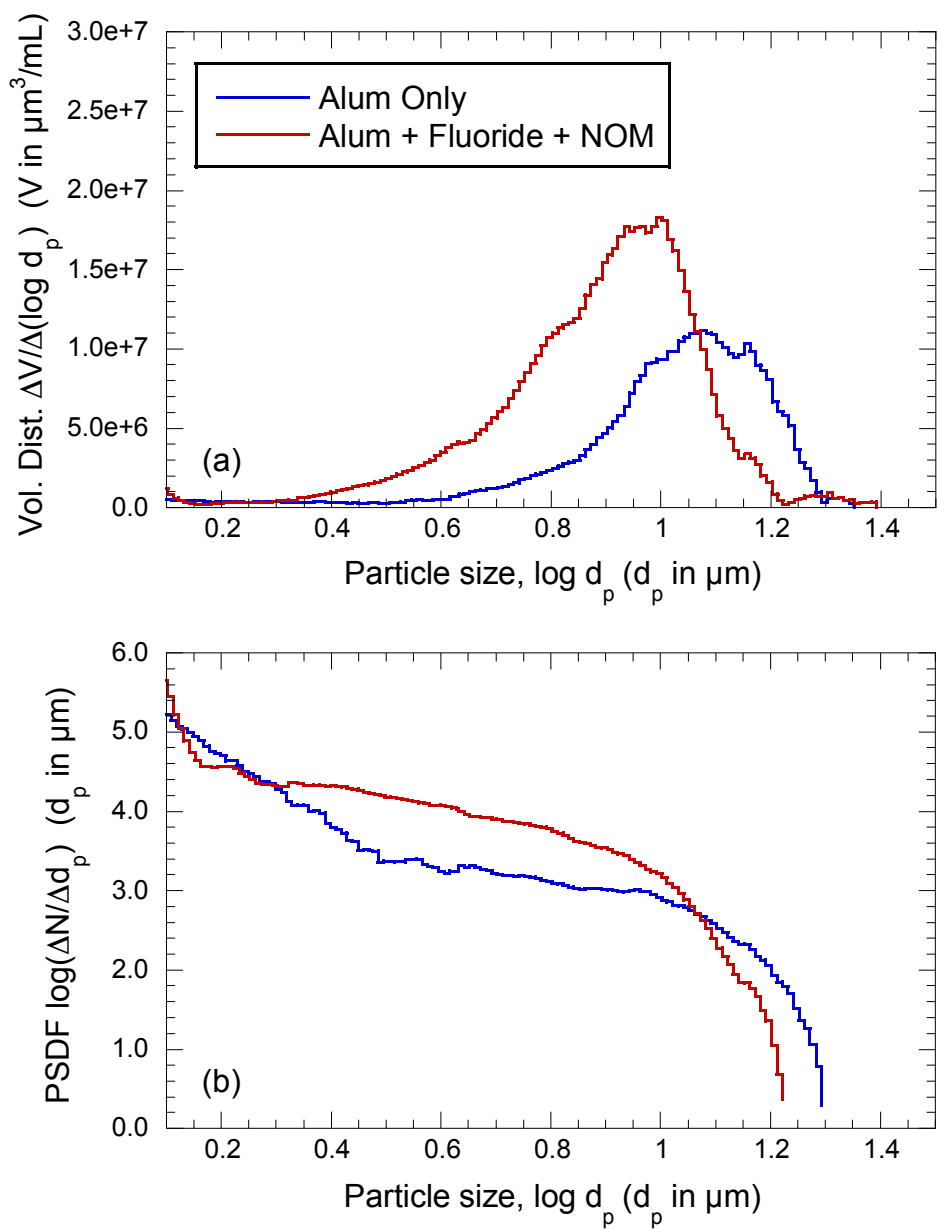


Figure 4.3: Volume distributions (a) and PSDFs (b) of aluminum precipitates formed in the Alum Only vs. Alum + Fluoride + NOM experiments

Table 4.6 displays the summary statistics for the two systems. In this experiment, the particle diameter at the peak of the volume distribution shifts to smaller sizes in comparison to the alum only case and the total volume concentration of particles (the area

under the volume distribution graph) shifts upward, indicating a larger volume of particles being formed. The total volume of the Alum Only vs. Alum + Fluoride + NOM systems are 3.91 ppmv and 6.56 ppmv, respectively. The FWHM of the distribution broadens slightly and the volumetric mean diameter also decreases slightly. The decrease is not as dramatic as seen in the experiment with Alum + Fluoride because a large number of particles still formed in the range above the centroid. In other words, while the particle diameter associated with the peak of the volume distribution decreased, the significant number of particles in the large particle diameters greatly reduced the shift in the centroid of the distribution.

Table 4.6: Summary Statistics Comparison Between the Alum Only and Alum + Fluoride + NOM Distributions

	Approx. Peak Volume Particle Diameter		FWHM	Total Vol. of Solids (ppmv)	Vol. Mean Diameter (log d _p (d _p in μm))
	log d _p (d _p in μm)	d _p (μm)			
			Δlog d _p (d _p in μm)		
Alum	1.072	11.80	0.30	8.32	0.698
Alum + F ⁻ + NOM	0.992	9.82	0.32	6.30	0.693

It seems the mechanisms observed in the previous two (single ligand) systems are working together to produce a trend in between the two. Soluble fluoro-aluminum complexes are likely being formed as indicated by the increased residual aluminum concentration. Additionally, fluoro-aluminum complexes are disrupting aluminum hydroxide formation and inhibiting the aggregation of aluminum precipitates. The inhibited aggregation results in the formation of smaller particles similar to the results of the Alum + Fluoride experiment. Furthermore, aluminum organic complexes may be forming, which are contributing to a greater number of large particles as seen in the

experiment with Alum + NOM. This results in the increase in the peak (and total) volume seen in this experiment.

4.4 SUMMARY

Table 4.7 displays a compiled form of the summary statistics describing all four of the distributions observed in this work. The effect of ligand substitution on the particle size distributions of aluminum precipitates was investigated through jar tests in synthetic water. Results showed that a noticeable effect on the particle distributions is seen when fluoride and NOM are present. In the presence of fluoride alone, the particle diameter associated with the peak of the volume distribution is shifted toward smaller particles, indicating that particle formation and aggregation is inhibited by the presence of fluoride. When NOM is present in the system, however, a noticeable increase in the total volume of particles occurs. This increased volume indicates the formation of aluminum organic precipitates that contribute to the total volume of suspended particles. When both fluoride and NOM are present in the system, a combination of the two effects occurs: a shift in the volume distribution toward smaller particles and an increase in the total volume of particles. This observation indicates that while fluoride is inhibiting the formation or aggregation of particles resulting in a larger number of smaller particles, the NOM is also complexing with the aluminum to create aluminum organic precipitates, resulting in a larger volume concentration of particles. Despite the significant shifts described among the four distributions, all had quite similar spreads as indicated by the logarithmic FWHM values.

Table 4.7: Summary Statistics Comparing All Four Distributions

	Approx. Peak Volume Particle Diameter		FWHM	Total Vol. of Solids (ppmv)	Vol. Mean Diameter
	log d_p	d_p	$\Delta \log d_p$		log d_p
	(d_p in μm)	(μm)	(d_p in μm)	(d_p in μm)	
Alum	1.072	11.80	0.30	3.91	0.698
Alum + F ⁻	0.925	8.42	0.31	4.14	0.667
Alum + NOM	1.019	10.44	0.27	8.59	0.820
Alum + F ⁻ + NOM	0.992	9.82	0.32	6.56	0.693

Chapter 5: Conclusions

Fluoride naturally occurs in surface and ground waters throughout the United States. Recent research by the NRC prompted the USEPA to review its MCL (4 mg/L) and MCLG (4 mg/L), and it is possible that the USEPA will enact more stringent regulations on fluoride concentrations in drinking water in the near future. A lower MCL for fluoride will cause many water systems in the United States that were meeting the MCL to be suddenly out of compliance, and they will need to implement additional treatment to meet a more stringent fluoride rule.

Alum coagulation has the potential to enable water systems to meet treatment goals for fluoride while still removing other contaminants (i.e., turbidity and NOM). One potential drawback is that fluoride may affect the settling and filtration characteristics of the precipitated solids by changing the particle size distribution of these solids. However, the present knowledge of how fluoride affects the size distribution of flocs is thin. Extensive work has been done on how NOM changes particle sizes and only minimal work on how fluoride affects the particle size distribution. To the author's knowledge, no studies have looked at the way fluoride and NOM interact together to change the particle size distribution in a system. This work was aimed at contributing to this knowledge and aiding in the determination of the implications fluoride has on the settling characteristics of aluminum precipitates. Specifically, the objectives of this work were:

3. Determine the effect of fluoride and/or NOM on the particle size distribution of aluminum precipitates in a simulated coagulation/flocculation treatment system,

4. Relate residual aluminum concentration, fluoride and NOM removal to the observed particle size distributions and elucidate any implications it has for fluoride impacted treatment systems.

Experiments for this study utilized jar tests to simulate an alum coagulation and flocculation system at the bench scale. Synthetic water was made in the laboratory and was meant to mimic the characteristics of surface water under carefully controlled conditions. A jar test with alum and no interfering or competing ligands was performed to determine the baseline particle size distribution of alum flocs. This experiment was followed by single and dual ligand jar tests to determine how the presence of fluoride and NOM affect the baseline particle size distribution, which was the first objective of this work. The NOM was isolated from a natural source, serving as a model organic compound encountered at a water treatment plant, to determine how fluoride interacts with organic matter. To complete the second objective, the residual aluminum concentrations in addition to the fluoride and NOM removal were measured to better understand the mechanisms by which these changes were occurring.

5.1 CONCLUSIONS

Results from this study confirmed that the particle size distribution of aluminum precipitates change when fluoride and NOM are present in treated water. Specific conclusions to be made from this work are as follows:

1. The presence of fluoride causes the particle size distribution of aluminum precipitates to shift towards smaller particles by inhibiting flocculation, acting as a stabilizer or inhibiting precipitation,
2. Elevated residual aluminum concentrations in the fluoridated water treated with alum suggest the formation of soluble fluoro-aluminum complexes,

3. The presence of NOM causes the total volume of aluminum precipitates to increase, as seen in the upward shift in the peak of the volume distribution and the overall increase in the area under the curve of the volume distribution, a measure of the total particle volume concentration,
4. The upward shift in both the volume distribution and the PSDF suggests the formation of a greater number of precipitates through the formation of aluminum NOM complexes that have a greater MW than aluminum hydroxides,
5. The presence of both fluoride and NOM causes a particle size distribution that reflects both trends with each ligand alone—the production of smaller particles due to the presence of fluoride and an increase in the total volume concentration due to the precipitation of alumino-organics (e.g., aluminum humate),
6. Fluoride and NOM compete for complexation with aluminum or adsorption to aluminum precipitates, as indicated by the decrease in removals for both when they are concurrent in a system, but fluoride is preferentially removed as indicated by the smaller decrease in its removal,
7. Though fluoride pulls the particle size distribution toward smaller particles, NOM acts to counteract this process by increasing the number of particles in the larger particle sizes.

5.2 FUTURE WORK

This research partially fills a knowledge gap in the realm of the interaction of fluoride, NOM, and other ions in coagulation and flocculation but much has yet to be understood. Concurrent work by researchers at The University of Texas at Austin suggest

that silica can play an important role in ligand exchange processes of precipitated aluminum hydroxides in drinking water. Further tests are needed to better understand this process and to determine if the size distributions of the particles are affected by silica. Additionally, the alum dose used in this work is higher than what is typically used in a treatment plant. Future work should explore the effect of fluoride, NOM and silica on the particles formed in an alum treatment system utilizing lower dosages (e.g., 25 and 50 mg/L alum).

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