EVALUATION OF SEASONAL VARIATIONS OF DISSOLVED ORGANIC MATTER AND HALIDE CONCENTRATIONS IN THE ST. JOHNS RIVER, FL, USA: RELATIONSHIP TO ION EXCHANGE TREATMENT POTENTIAL

By

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To my daughter, Amber, thank you for always being there
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LIST OF ABBREVIATIONS

Br⁻  Bromide
Cl⁻  Chloride
DI   Deionized
DOC  Dissolved organic carbon
DOM  Dissolved organic matter
EEM  Excitation-emission matrix
FI   Fluorescence index
FL   Florida
I⁻   Iodide
MIEX Magnetic ion exchange
MIEX-Cl Magnetic ion exchange in chloride-form
MIEX-HCO₃ Magnetic ion exchange in bicarbonate-form
NO₃⁻ Nitrate
SEM  Scanning electron microscope
SJR  St. Johns River
SJRWMD St. Johns River Water Management District
SO₄²⁻ Sulfate
SUVA₂₅₄ Specific ultraviolet absorbance at 254 nm
TDN  Total dissolved nitrogen
TDS  Total dissolved solids
USGS United States Geological Survey
UV₂₅₄ Ultraviolet absorbance at 254 nm
EVALUATION OF SEASONAL VARIATIONS OF DISSOLVED ORGANIC MATTER AND HALIDE CONCENTRATIONS IN THE ST. JOHNS RIVER, FL, USA: RELATIONSHIP TO ION EXCHANGE TREATMENT POTENTIAL

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This work has two overall objectives; the first to evaluate the seasonal variation in dissolved organic matter and halide (chloride and bromide) chemistry and concentrations, the second to evaluate the treatment potential of magnetic ion exchange resins. Both were accomplished through the ten month sampling of the St. Johns River, near Astor, FL. The concentrations of dissolved organic carbon varied from 12 to 26 mg/L, while the fluorescence index and specific ultraviolet absorbance both indicate the organic matter was of terrestrial origin. Halide chemistry also varied greatly through the year and are comparable to other large scale studies of bromide and chloride from different parts of the world. The data collected in this study have showed that the St. Johns River has high concentrations of dissolved organic matter, chloride and bromide throughout the year and could prove difficult to treat to drinking water standards.

To evaluate a treatment potential for the St. Johns River, the anion exchange resin, MIEX was used in two different forms. The first form was the traditional chloride resin (MIEX-Cl), utilizing chloride as the mobile counter ion, and the other form, MIEX-HCO₃ was regenerated to have bicarbonate as the mobile counter ion. For this work the removal of dissolved organic
carbon, ultraviolet absorbance at 254 nm, bromide and sulfate removals were compared for both resins through the entire year. Both resins showed similar removal potentials for all but bromide and sulfate. By the final regeneration sulfate removal differences between the two resins was 33%, with the MIEX-Cl showing the best removal. MIEX-Cl resin differed greatly from MIEX-HCO₃ in that the resin released bromide into the receiving waters. This phenomenon was further investigated with jar tests simulating halides in the St. Johns River. All resins were also imaged with scanning electron microscopy to describe both resins after fourteen regenerations and compare those to virgin resin. Overall, the work revealed MIEX-HCO₃ has the potential to be used in water treatment, even under the variable conditions of a river like the St. Johns River.
CHAPTER 1
INTRODUCTION

The St. Johns River Water Management District (SJRWMD) is one of five water management districts in the state of Florida and encompasses 12,300 square miles in northeast to east-central Florida (SJRWMD, 2006). The district is responsible for meeting the current and future ground and surface water demands (SJRWMD, 2010b). These demands have historically been met by groundwater sources from the surficial, intermediate, and Floridan Aquifers (SJRWMD, 2006). The SJRWMD is expecting the population to increase to 5.9 million by 2020, which will mean an increase in water demand (SJRWMD, 2006). To meet these demands many alternatives have been explored, e.g., water reclamation, water conservation, desalination, and surface water withdrawals (SJRWMD, 2006). Five projects along the St. Johns River (SJR) are being evaluated for drinking water supplies by the SJRWMD and two sites are currently removing water from the SJR (SJRWMD, 2006). It is currently estimated that a total of 262 million gallons per day could be withdrawn from the SJR to provide drinking water to the district (SJRWMD, 2006, 2010a).

The SJR is unique, it originates in the east-central Florida near Indian River County, FL and flows northward to Jacksonville, FL where it flows into the Atlantic Ocean (SJRWMD, 2006). It is also a very wide and slow moving river, the width averaging 2 miles across and the elevation change from the headwaters to the mouth is ~30 ft (Thoburn, 2002). This slow movement and low gradient means that at periods of low-flow at the northern end of the river can be influenced by tides from the ocean as far upstream as Lake George (SJRWMD, 2006). Although studies have been conducted on the SJR to understand the effects of withdrawals on the environment, little has been done to evaluate the water quality parameters as they pertain to drinking water treatment.
2.1. St. Johns River Overview

Although there are previous studies conducted on the SJR, FL, USA to evaluate the effects of surface water withdrawals on ecological and biogeochemical outcomes (SJRWMD, 2010a), there is a gap in knowledge pertaining to the chemistry of halides and dissolved organic matter (DOM). Moreover, new research findings on halides and DOM would complement existing studies on the river. In particular, it is not known how the concentration of bromide varies with respect to chloride. This is important because understanding the speciation of bromide relative to chloride is expected to provide new insights into the hydrology and geochemistry of the river (Magazinovic et al., 2004; Alcala and Custodio, 2008; D'Alessandro et al., 2008). In addition, bromide is a precursor to harmful disinfection byproducts that can be formed during water treatment (Hua et al., 2006). Although the concentration of DOM in the SJR is known, there is very little information on the chemistry of DOM. Understanding the chemistry of DOM is fundamental to understanding the numerous reactions that DOM takes part in, such as oxidation-reduction, photochemistry and light attenuation, contaminant binding, and impact on engineered water treatment processes.

Bromide and chloride are natural constituents found in surface waters at various levels (Magazinovic et al., 2004). According to Stumm and Morgan (1996), seawater ratios of chloride to bromide are approximately 300:1 (w/w). Several studies, at various locations around the world, have been conducted looking at the spatial spread of bromide and chloride levels in surface waters. These studies have determined a wide range of chloride to bromide (Cl\(^-\)/Br\(^-\)) ratios, depending upon the location (Magazinovic et al., 2004; Alcala and Custodio, 2008; D'Alessandro et al., 2008). The Cl\(^-\)/Br\(^-\) ratio has been used previously as a tracer to determine the
origin and evolution of groundwater, surface water, and brines in oil and gas exploration (Alcala and Custodio, 2008). It can also be very important for understanding the ecology of a given water and revealing anthropogenic influences on that water. For example, previous research has shown that waters from areas where Br-based pesticides are used in agriculture have Cl⁻/Br⁻ ratios of 275 – 718 (mol/mol), while leaching of septic wastes into water has a ratio of ~463 (mol/mol) (Alcala and Custodio, 2008).

Studying the changes in the DOM in the SJR is important to understanding the ecosystem of the river. This understanding is important because plant and soil-derived DOM represents a significant part of terrestrial carbon budgets and is a dominant linkage between terrestrial and aquatic ecosystems (Jaffe et al., 2008). Also, DOM is the largest pool of detrital organic carbon, in fact dissolved organic carbon (DOC) is the most important intermediate in the global carbon cycle (Battin et al., 2008). DOC concentrations in a body of water are not only a reflection of the nature of the watershed but are also influenced by seasonal variation (Leenheer and Croue, 2003).

To date, no information is available on the correlation between bromide and chloride in the SJR. To add to the lack of knowledge regarding halide chemistry, iodide (presented in Appendix A) is rarely studied in natural waters and it is not known if there is a correlation between iodide and chloride. Many studies have looked at the temporal and spatial characteristics of DOM to understand the ecology of surface water(s) (Jaffe et al., 2008). Few studies have been dedicated to one location through an entire course of seasons to understand the impact of seasonal changes on DOM. This study is aimed at filling some of these gaps in knowledge.

The overall goal of this work is to study the concentration and speciation of halides and DOM in the SJR. The specific objectives of this work are: (1) to evaluate the temporal trends in
the ratios of Cl-/Br⁻; (2) to evaluate the temporal trends in the specific ultraviolet absorbance (SUVA) and fluorescence excitation-emission matrix (EEM) spectra of DOM; and (3) to discuss the implications of the chemistry of halides and DOM on natural and engineered processes.

2.2. Materials and Methods

2.2.1. Sampling Location

All samples were collected from the SJR at Astor, FL, which is located 204 km upstream from the mouth of the river (US Geological Survey (USGS), 2009). Sources of recharge for the river are groundwater, stormwater runoff, and rainfall. The sampling location was chosen because it is near proposed locations of surface water withdrawal (SJRWMD, 2010a) and has a USGS gage station (02236125) that monitors gage height, discharge, water temperature, dissolved oxygen, turbidity, and specific conductance. The location of the gage station is latitude 29°10′00″ and longitude 81°31′20″. The drainage area for the gage station is 8,352 km² (SJRWMD, 2009). There are no wastewater treatment plants within 8 km radius of the sample location (SJRWMD, 2009). The land use for the drainage area is wetland (32%), agriculture (24%), forest (16%), urban (13%), and other (15%) (SJRWMD, 2009). The SJR is characterized by high salt content (median chloride is 235 mg/L) and contains a high organic matter content (median total organic carbon is ~17 mg C/L) (SJRWMD, 2009).

2.2.2. Sample Collection

Samples were collected twice a month by the SJRWMD or author, for a 10 month period starting in October 2009. Samples collected by the author were taken from either the east or west bank, from a dock ~12 ft from the shore. Samples collected by the SJRWMD were collected from the side of a boat roughly in the middle of the river, by a kalawasi tube ~7 ft long and blended in a plastic container before being dispensed into sample bottles. Samples were
delivered to the Department of Environmental Engineering Sciences, University of Florida within 24 hr of collection and stored at 4°C. Samples were analyzed within 2 weeks of receipt.

2.2.3. Analytical Methods

All standards were prepared from ACS grade chemicals and deionized (DI) water. Dry materials were weighed on a Mettler AE 160 analytical balance. The pH of all samples was measured with an Accumet AP71 pH meter with an Ag/AgCl pH/ATC probe that was calibrated using pH 4, 7, and 10 buffer solutions. All subsequent analyses were performed on samples that were filtered through a 0.45 µm nylon membrane filter (Millipore). All filters were pre-rinsed with 500 mL of DI water and ~20 mL of sample. DOC was measured on a Shimadzu TOC-VCPH total organic carbon analyzer, utilizing combustion at 680°C for analysis, equipped with an ASI-V autosampler. The stock standard for DOC was made from potassium hydrogen phthalate.

Chloride and bromide were measured on a Dionex ICS-3000 ion chromatograph equipped with IonPac AG22 guard column, AS22 analytical column and ARS-4mm suppressor running 4.8 mM Na₂CO₃/1.0 mM NaHCO₃ eluent with 100 µL sample loop and a flow rate of 1.5 ml/min, following manufacturer’s recommendations. Temperature of the column and detector compartments was set to 35°C and the suppressor current was set at 40 mA. Stock standards for chloride were prepared from sodium chloride and stock standards for bromide were prepared from sodium bromide.

All DOC, chloride, and bromide measurements were made in duplicate and averaged. Each run on the TOC-VCPH and ICS-3000 were monitored using calibration check standards (4, 40 and 400 mg/L for chloride; 0.025, 0.25 and 2.5 mg/L for bromide; and 1, 5, 10, 15 and 20 mg/L for DOC) to ensure that the measured concentration fell within 10% of the known value. Ultraviolet absorbance at 254 nm (UV₂₅₄) was measured a Hitachi U-2900 spectrophotometer in a 1 cm quartz cuvette. Specific UV₂₅₄ absorbance (SUVA₂₅₄) was calculated by dividing UV₂₅₄
by DOC. Fluorescence excitation-emission (EEM) spectra were collected on a Hitachi F-2500 fluorescence spectrophotometer using a 1 cm quartz cuvette. Samples were scanned at 5 nm increments over an excitation of 220–400 nm and 2 nm increments over an emission of 250–500 nm. For the measurement excitation slit was set at 5.0 nm, emission slit was set at 2.5 nm and scan speed was set at 1500 nm/min. The raw fluorescence EEMs were processed in MATLAB using an in-house program (Comstock et al., 2010; Appel and Boyer, 2010). The fluorescence index (FI) is defined as the ratio of fluorescence intensity at emissions of 470 nm and 520 nm at an excitation of 370 nm (Cory and McKnight, 2005), and was calculated using the in-house MATLAB program. All data presented in this thesis will be the average for the entire sampling period ± the standard deviation for the entire sampling period.

2.3. Results and Discussion

2.3.1. Hydrology and General Water Quality

The hydrology and general water quality parameters of the river for the entire sampling period are shown in Figures 2-1a–c and 2-2 a–d. Solid black lines represent the data collected by the USGS gage station (2009) except for pH which was measured in the laboratory, and the red line, when present, represents the 13 year median data reported by the SJRWMD (2009). The SJRWMD (2009) rates the Astor site as having good water quality. Over the course of the study period the gage height of the river has been variable, the highest point registering 2 ft and lowest point at 0.25 ft (Figure 2-1a). The river is also characterized by a variable discharge rate, at times even flowing in reverse (Figure 2-1b). The specific conductance for the river has the lowest reading at 600 µS/cm to the highest at ~1,200 µS/cm, nearly double the lowest point (Figure 2-1c). In terms of total dissolved solids (TDS), this represents a range of 400–800 mg/L using the estimator that TDS is $0.75 \times$ the specific conductance (Fishman and Friedman, 1989), for comparison brackish water has a TDS of ~1000 mg/L and seawater a TDS of ~3,500 mg/L.
(Hem, 1985). Interestingly, the period of highest conductance does not correlate with the periods of negative discharge. As stated in the Introduction, the SJR flows from south to north, where it meets the Atlantic Ocean. The negative discharge would suggest that water is flowing in reverse, and one would think this corresponds to a surge of water from the north (i.e., the Atlantic Ocean). The TDS for these periods of negative discharge do not support this theory, the TDS measures ~600 mg/L, which is not near brackish water, and so no saltwater is present in the surge.

Figures 2-2 a–d provide further insight into the quality of the water at the sampling site. Dissolved oxygen (DO) (Figure 2-2a) content follows an inverse of winter/summer trend as temperature, with DO highest in the winter season and lowest in the summer season. The pH of the water (as measured in the laboratory) was on average 7.3 ± 0.4, with the lowest reading at 6.3 and the highest at 8 (Figure 2-2b). The turbidity (Figure 2-2c) of the water ranged from 1 FNU to 8 FNU, which is below the level of biological impact threshold of 25 FNUs (Klein, 2008). Figure 2-2d shows the sampling period’s seasonal variation in the temperature of the water, with the coldest period starting in December 2009 through March 2010 and the warmest period starting in June 2010 and continuing through September 2010. This data follows the typical trend in winter/summer seasons for this portion of Florida.

2.3.2. Chloride and Bromide

Figure 2-3a–b represents the concentrations of chloride and bromide in the river for the entire sampling period. The x-axis is in months and spans the entire sampling period. The y-axis is measured in mg/L for chloride (Figure 2-3a) and µg/L for bromide (Figure 2-3b). All data were generated from analysis of collected samples. Figure 2-3a shows the concentration of chloride in the river has changed greatly (nearly doubled from low to peak concentration) through the course of the year, generally increasing from October 2009 through March 2010 and
then began to decrease until May 2010. The average chloride concentration was 195 ± 35 mg/L. The specific conductance also increased during this time period (Figure 2-1c) and recall the corresponding TDS range was 400–800 mg/L.

The bromide concentration has varied through the study period, again with the maximum concentration (>1,000 µg/L) more than double the minimum concentration (~500 µg/L) (Figure 2-3b) with an average of 768 ± 175µg/L. As a note, von Gunten (2003) reports a typical bromide concentrations range of 2–700 µg/L in U.S. and European waters, while research by Kroening (2004) shows a historical range in the SJR of 190–17,000 µg/L. It should also be noted that bromide concentrations over 100 µg/L will form problematic concentrations of disinfection byproducts (DBP’s) (von Gunten, 2003). Chloride and bromide peaks, while not exactly aligning, do seem to follow a similar trend. Other research in the SJR found disagreement with chloride and bromide concentrations (Kroening, 2004) and was able to better link bromide concentrations with negative discharge periods. Bromide concentrations are influenced by multiple factors including geology and anthropogenic influences (Magazinovic et al., 2004; Alcala and Custodio, 2008; D'Alessandro et al., 2008). Recent research has focused on understanding the relationships between chloride and bromide levels and relating those to their potential sources (Magazinovic et al., 2004; Alcala and Custodio, 2008; D'Alessandro et al., 2008). Data from this study was plotted and compared with this recent research to understand the influences at the sample site.

The Cl-/Br⁻ ratio is used by many researchers to predict the concentration of bromide in a water given only the chloride and also as an indication of upstream activities in the river that will influence the biogeochemistry of that river (Alcala and Custodio, 2008). Figure 2-4 shows the Cl'/Br⁻ ratio trend, on a molar basis, for this study averages 582 ± 84. The ratio increases from
October 2009 to February 2010, which agrees with the increase in chloride concentration for the same time period (Figure 2-3a).

Figure 2-5 compares studies from three different countries, with the results from this study. This study is less variable than the previous work, owning mostly to this work’s focus on a single location, in contrast to the other work focused across a country/region (Magazinovic et al., 2004; Alcala and Custodio, 2008; D'Alessandro et al., 2008). It can also be seen that the results from the current study align more closely with the study in Spain (Alcala and Custodio, 2008), and is only slightly similar to the lower results from the other two countries (Magazinovic et al., 2004; D'Alessandro et al., 2008). Although these studies were conducted over a period of 1–4 years depending on location, the data discussed were representative of that entire time period (Magazinovic et al., 2004; Alcala and Custodio, 2008; D'Alessandro et al., 2008). So, it is likely the difference seen when comparing data, are due to the differences in geology in these countries.

2.3.4. DOM

Figure 2-6 a–c represents the DOC, SUVA$_{254}$, and FI for the entire year of the sampling period. The x-axis of both figures is represented in months, the y-axis is presented in different units; part (a) is measured in mg/L, part (b) in L/mg m and part (c) is unitless. All data were generated from collected samples analyzed in the laboratory.

Total organic carbon (TOC) measurements are used to quantify organic matter present in a body of water, and TOC can be split into two fractions: particulate organic carbon and DOC (Leenheer and Croue, 2003). Because DOC represents >90% of TOC (Leenheer and Croue, 2003), it is often used as a surrogate for the concentration of organic matter (Croue et al., 2000). For the SJR the concentration of DOC (Figure 2-6a) changes through the sampling period, starting out at its highest point in October 2009 to reaching its lowest point in August 2010.
Jaffe et al. (2008) collected data from a 10 different locations in North America and found a DOC range of 1–30 mg/L, with most surface waters being less than 6 mg/L. The SJR has an average concentration of 18.9 ± 3.4 mg/L, well above the 6 mg/L but within the range of the Jaffe et. al. (2008) study.

To further the understanding of the DOM, SUVA is used to determine the quality of the DOM (Owen et al., 1993). For the sampling period the SUVA$_{254}$ remained constant, at ~4 ±0.3 L/mg m (Figure 2-6b), which indicates a terrestrially derived organic matter (Croue et al., 2000; Leenheer and Croue, 2003). Fluorescence is also used to determine the quality of organic matter (Croue et al., 2000). A high FI indicates microbial organic matter, while a low FI indicates terrestrial organic matter (Croue et al., 2000; Cory and McKnight, 2005; Hur et al., 2007). The fluorescence method utilized in the laboratory is uncorrected, unlike those often reported in literature. To better understand the data presented, the FI was determined for known DOM (Suwannee River Natural Organic Matter Reverse Osmosis isolate from International Humic Substances Society and a natural spring water from the Ichentuckee Springs river run with DOM of microbial origin), and data presented in Figure 2-6c was scaled between these two points. For the study period FI (Figure 2-6c) was fairly constant at 1.90 ± 0.03, which falls within the range of terrestrial organic as determined by the lab comparison study. The data generated from the SUVA$_{254}$ and FI are in agreement, the organic matter present in the SJR through the course of the sampling period is of terrestrial origin. When considering a source for drinking water it is important to understand the concentration of organic matter present and also the origin of the organic matter. This is important because terrestrial organic matter will form DBP’s during water treatment (Hua and Reckhow, 2007; Sani et al., 2008).
2.4. St. Johns River Summary

The SJR is a dynamic system undergoing various changes in the chemistry of the river throughout the year. Chloride and bromide concentrations have both doubled in the year, going from 130–270 mg/L and 500–1,000 µg/L respectively. The concentration of bromide in the river is high. Comparing the Cl-/Br\(^-\) ratio coincides well with other reported data and provides an important understanding of comparing temporal and spatial variations. The DOC of the river has also undergone extreme changes, again more than doubling from 12–27 mg/L and is much higher than the typical range for surface waters. Finally, the two parameters used to determine the quality of the organic matter, SUVA\(_{254}\) and FI, have remained fairly constant through the year and in agreement that the organic matter is of terrestrial origin.

Looking at all of this data together provides a detailed picture of the water treatment hurdles present in the SJR. The concentrations of DOC and bromide are both high and fluctuate considerably during the year. The organic matter is of terrestrial origin, as SUVA and FI indicate, and as such will form DBP’s during water treatment. Finally, knowing that high bromide will lead to problematic DBP’s, it is obvious that treatment of these waters to meet drinking water standards will be a challenge.

2.5. Supplementary Material

Appendix A presents additional details into the chemistry of the SJR. The concentrations of nitrogen, sulfate, and iodide in the SJR during the sampling period are reported. All measurement techniques and data are included and discussions of each are presented in this section.
Figure 2-1. St. Johns River hydrology for Astor, FL site from October 2009 to August 2010. Figures presented are (a) gage height, (b) discharge, and (c) specific conductance. Dashed line, when present, represents the 13 year median reported by the St. Johns River Water Management District (2009). All data were collected from U.S. Geological Survey online database (2009).
Figure 2-2. St. Johns River water quality for Astor, FL site collected from October 2009 to August 2010. Figures represent: (a) dissolved oxygen (DO), (b) pH, (c) temperature, and (d) turbidity. Dashed line, when present, represents 13 year median (SJRWMD, 2009). All data, except for pH, were collected from U.S. Geological Survey online database (2009).
Figure 2-3. Absolute concentrations in water of (a) chloride, reported in mg/L, and (b) bromide, reported in µg/L, from St. Johns River Astor, FL site. Error bars represent standard deviation for each sample. Data in parenthesis represents the average concentration and standard deviation for the entire year.
Figure 2-4. Ratio of Cl⁻/Br⁻ (mol/mol) for St. Johns River at Astor, FL site. The y-axis is measured in (mol/mol) and the months of the study are on the x-axis. Error bars represent the standard deviation for each sample. Data in parenthesis represents the average and standard deviation.
Figure 2-5. Box and whisker plot comparison of Cl⁻/Br⁻ (mol/mol) data across different spatial and temporal scales (Magazinovic et al., 2004 (Australia); Alcala and Custodio, 2008 (Spain); D'Alessandro et al., 2008 (Sicily)). The vertical lines represent the range of the data, horizontal lines represent the median of the data. The boxes represent the median of the upper and lower quartiles of the data.
Figure 2-6. Absolute concentrations in St. Johns River waters of (a) dissolved organic carbon (DOC), measured in mg/L, (b) SUVA$_{254}$, presented in L/mg m and (c) fluorescence index (FI), unitless ratio of intensity at emission of 370 nm over intensity at emission of 520 nm both at excitation of 370 nm. Error bars, not included for fluorescence index, represent standard deviation for each sample. Data in parenthesis represents the average and standard deviation for the entire year. SUVA$_{254}$ is scaled between microbial organic matter (1) and terrestrial organic matter (5) and fluorescence index is scaled between terrestrial (1.8) and microbial (2.1) to better understand the data.
CHAPTER 3
ROBUSTNESS OF MIEX TREATMENT: EFFECT OF SEASONAL CHANGES IN WATER QUALITY AND REGENERATION EFFICIENCY

3.1. Magnetic Ion Exchange Overview

The SJR located in FL, USA, has very high concentrations of DOM and bromide. The water quality in the SJR is important because the river is being considered as an alternative drinking water source, and is estimated to supply 262 million gallons per day by 2020 (SJRWMD, 2010a). It is well known that DOM affects water treatment processes and finished water quality. For example, DOM adds color, taste and odor to raw drinking water (Leenheer and Croue, 2003); forms DBPs during water treatment (Hua and Reckhow, 2007; Sani et al., 2008); exerts a demand on oxidation and coagulation chemicals (Sharp et al., 2006; Sani et al., 2008); fouls membranes (Lozier et al., 2008); and contributes to biological growth in distribution systems (Clement et al., 2003). Also during water treatment, bromide is oxidized to hypobromous acid by free chlorine and other oxidants, and then reacts with DOM to form brominated DBPs (Cowman and Singer, 1996; Liang and Singer, 2003; von Gunten, 2003; Hua and Reckhow, 2007; Richardson et al., 2008; Krasner, 2009; Hsu and Singer, 2010). Thus, advanced processes, such as ion exchange, nanofiltration, and reverse osmosis, will be required to effectively treat water from the SJR to produce high-quality drinking water.

Magnetic ion exchange (MIEX), using chloride as the mobile counter ion, has been shown in previous research to be an effective process for removing DOM and to a limited extent bromide (Tan et al., 2005; Kabsch-Kobutowicz et al., 2008; Zhang et al., 2008; Hsu and Singer, 2010), and has been shown to be as effective as or more effective than activated carbon adsorption and enhanced coagulation (Singer and Bilyk, 2002; Humbert et al., 2008; Jarvis et al., 2008; Drikas et al., 2009; Bond et al., 2010). A few studies have evaluated MIEX treatment as a function of source water quality and regeneration efficiency using pilot plant studies (Singer et...
al., 2007; Drikas et al., 2009) and through multiple regenerations in bench-scale experiments (Mergen et al., 2008). Other studies have looked at spatially diverse waters and compared the MIEX removal capabilities (Singer and Bilyk, 2002; Kitis et al., 2007; Boyer and Singer, 2008). A major limitation of previous MIEX research is that its long-term performance due to changing water quality and regeneration efficiency has not been systematically studied.

A disadvantage of MIEX treatment, and anion exchange in general, is the production waste regenerant brine that is difficult to dispose. One potential solution is to use a different, more benign mobile counter ion such as bicarbonate. Previous work by Holl and Kiehling (1981), Jelinek et al. (2004), and Matosic et al. (2000) have demonstrated the use of bicarbonate as a mobile counter ion in anion exchange reactions. Recent work by Rokicki and Boyer (2010) demonstrated that MIEX resin with the bicarbonate mobile counter ion (MIEX-HCO₃) performed very similar to traditional MIEX resin with chloride as the mobile counter ion (MIEX-Cl). No work has been done to evaluate the long-term performance of MIEX-HCO₃ resin due to changing water quality or to compare its long-term performance with MIEX-Cl resin.

The goal of this work is to evaluate the robustness of MIEX treatment with respect to seasonal changes in water quality for a river high in DOM and bromide. The specific objectives of this work are: (1) to quantify the differences between MIEX-Cl and MIEX-HCO₃ resins for DOM removal; (2) to quantify the differences between MIEX-Cl and MIEX-HCO₃ resins for bromide removal; (3) to assess the viability of regenerating MIEX-Cl and MIEX-HCO₃ resins multiple times; (4) to examine the physical structure of MIEX resin; and (5) to study the performance of MIEX resin under conditions of rapidly changing water quality. This work is also expected to provide insights into water quality and treatment as a result of climate change.
3.2. Materials and Methods

3.2.1. Sampling Location

All samples were collected from the SJR at Astor, FL, which is located 204 km upstream from the mouth of the river (USGS, 2009). Sources of recharge for the river are groundwater, stormwater runoff, and rainfall. The sampling location was chosen because it is near proposed locations of surface water withdrawal (SJRWMD, 2010a) and has a USGS gage station (02236125) that monitors gage height, discharge, water temperature, dissolved oxygen, turbidity and specific conductance. The location of the gage station is latitude 29°10’00″ and longitude 81°31’20″. The drainage area for the gage station is 8,352 km² (SJRWMD, 2009). There are no wastewater treatment plants within 8 km radius of the sample location (SJRWMD, 2009). Land use for the chosen site’s drainage area is wetland (32%), agriculture (24%), forest (16%), urban (13%), and other (15%) (SJRWMD, 2009). The SJRWMD (2009) identifies the river as having a high salt content (median chloride concentration of 235 mg/L) and a high DOM content (median total organic carbon concentration of 17 mg C/L).

Samples were collected twice a month by the SJRWMD or the author, for a 12 month period starting in October 2009. Samples collected by the author were taken from either the east or west bank, from a dock ~12ft from the shore line. Samples collected by the SJRWMD were collected from the side of a boat at roughly the center of the river, by a kalawasi tube ~7ft long and blended in a plastic container before being dispensed into sample bottles. Samples were delivered to the Department of Environmental Engineering Sciences, University of Florida within 24 hr of collection and stored at 4°C. Samples were analyzed within 2 weeks of receipt.

3.2.2. Materials

MIEX resin from Orica Watercare was used in this work. Two mobile counter ions: bicarbonate (HCO₃⁻) and chloride (Cl⁻) were evaluated based on previous research by Rokicki
and Boyer (2010). MIEX-HCO₃ resin was originally produced from virgin MIEX-Cl resin, and both MIEX-Cl and MIEX-HCO₃ resins were regenerated after every experiment, as described in Section 3.2.4.

3.2.3. SJR Jar Tests

All experiments were conducted at ambient laboratory temperature and open to the atmosphere. Jar tests were performed using a Phipps & Bird PB-700 jar tester with 2 L jars. One liter of sample water was used in all jar tests. A MIEX resin dose of 10 mL was measured as the volume of wet settled resin in a graduated cylinder. The jar tests were conducted at 100 rpm for 20 min and the resin was allowed to settle for at least 5 min before samples were decanted from the jar (Boyer and Singer, 2005). MIEX resin was then rinsed two times with DI water as outlined below, covered and stored until regeneration. All jar tests were performed in duplicate and the data shown are the average of duplicate samples.

3.2.4. Resin Regeneration

MIEX resin was regenerated to alter the mobile counter ion available for exchange on the resin. All resins were regenerated with 1 L of salt solution (sodium chloride or sodium bicarbonate), which contained the desired mobile counter ion. The regeneration concentration was based upon the equivalent capacity of MIEX-Cl resin, which was previously determined to be 0.52 meq/mL (Boyer and Singer, 2008). Previous experiments also showed that a regeneration solution with 10 times the equivalent capacity of the resin dose would be sufficient to fully regenerate the resin (Rokicki and Boyer, 2010). The MIEX resin was mixed in the regeneration solution using a Phipps & Bird PB-700 jar tester for 20 min to allow for exchange of ions. The resin was allowed to settle for 5 min before the supernatant liquid was decanted. To ensure that there was no remaining regeneration solution, the resin was washed with DI water by adding 1 L of DI water, mixing for 10 min, and settling for 5 min before decanting the
supernatant liquid. This washing was repeated a second time before the resins were covered and stored in DI water.

The SJR jar test, resin regeneration, and washing of the resin was repeated for every sample collection from October 2009 through August 2010, leading to 17 regenerations of MIEX-Cl and MIEX-HCO₃ resin. Table 3-1 lists the dates that SJR water was collected and the corresponding regeneration number.

3.2.5. Bromide Release Jar Tests

A set of jar tests were conducted to determine if MIEX resin could be retaining a removed anion and then releasing it later in the presence of a more preferable anion. To begin, a large batch of virgin MIEX-Cl resin was converted to MIEX-HCO₃ resin. One jar was used for the entire experiment, which contained 10 mL of resin. For each cycle, 1 L of synthetic water was added containing a pre-determined concentration of anions, as shown in Table 3-2. The composition of the synthetic water was based on halide and sulfate levels in the SJR. After each jar test, 1 mL of partially exhausted MIEX-HCO₃ resin was removed and 1 mL of fresh MIEX-HCO₃ resin was added. This was to simulate how a full-scale MIEX treatment plant is operated, with a small portion of the resin being removed and replaced with freshly regenerated resin (Kitis et al., 2007; Hsu and Singer, 2009; Neale and Schafer, 2009). The concentration of anions in the synthetic water was altered to simulate periods of low and high concentrations of sulfate.

3.2.6. Analytical Methods

All standards were prepared from ACS grade chemicals and DI water. Dry materials were weighed on a Mettler AE 160 analytical balance. All samples were vacuum-filtered with a 0.45 µm nylon membrane (Millipore) to remove any MIEX resin particles and to ensure only dissolved species were analyzed. Filtered samples were analyzed for DOC, ultraviolet absorbance at 254 nm (UV₂₅₄), chloride, bromide, and sulfate. DOC was measured on a
Shimadzu TOC-V\textsubscript{CPH} total organic carbon analyzer, utilizing combustion at 680°C for analysis, equipped with an ASI-V autosampler. The stock standard for DOC was made from potassium hydrogen phthalate. Chloride, sulfate, and bromide were measured on a Dionex ICS-3000 ion chromatograph equipped with IonPac AG22 guard column, AS22 analytical column and ARS-4mm suppressor running 4.8 mM Na\textsubscript{2}CO\textsubscript{3}/1.0 mM NaHCO\textsubscript{3} eluent with 100 µL sample loop and a flow rate of 1.5 ml/min, following manufacturer’s recommendations. Temperature of the column and detector compartments was set to 35°C and the suppressor current was set at 40 mA. Chloride stock standards were made from sodium chloride, sulfate stock standards were made from potassium sulfate, and bromide stock standards were made from sodium bromide.

All DOC, chloride, sulfate, and bromide measurements were made in duplicate and averaged. Each run on the TOC-V\textsubscript{CPH} and ICS-3000 were monitored using calibration check standards to ensure that the measured concentration fell within 10% of the known value. UV\textsubscript{254} was measured a Hitachi U-2900 spectrophotometer in a 1 cm quartz cuvette. Data presented in this paper represents the average for the entire sampling period ± the standard deviation for the entire sampling period.

Virgin MIEX-Cl, regenerated MIEX-Cl, and regenerated MEX-HCO\textsubscript{3} resins were characterized using a field emission scanning electron microscope (SEM) (JEOL JSM-6335F). The regenerated MIEX-Cl and MIEX-HCO\textsubscript{3} resins were sampled after 14 regeneration cycles. Each MIEX resin was prepared for microscopy by lyophilizing ~0.1 mL of wet resin to prevent any distortion of the resin during drying. The resin samples were then mounted to the pedestal with carbon tape and analyzed. Resin surface morphologies were characterized without coating using an accelerating voltage of 5.0 kV and a ~15 mm working distance in order to minimize
charging, enhance surface features, and observe the resin at magnifications ranging from 40 to 5,000×.

3.3. Results and Discussion

3.3.1. DOM Removal

Figures 3-1a and c show the DOC concentration and UV$_{254}$ absorbance, respectively, for raw and MIEX-treated (i.e., MIEX-Cl and MIEX-HCO$_3$) water. The DOC concentration of the SJR was at its maximum value (26 mg/L) at the beginning of the study (October 2009), and varied between 15–21 mg/L for a majority of the study. The corresponding DOC concentrations for MIEX-Cl and MIEX-HCO$_3$ treated waters maintained a concentration of 4.5 ± 0.7 mg/L and 5.1 ± 0.7 mg/L, respectively, for the duration of the study, despite the changes in the DOC concentration of the SJR. When evaluating the overall removal of DOC (see Figure 3-1b), both MIEX-Cl and MIEX-HCO$_3$ resins begin with ~90% removal and continue to have similar removal efficiencies with an average efficiency of 75% and 72%, respectively. Mergen et al. (2008) compared multiple MIEX-Cl resin single-use removal studies (i.e., regeneration 0 in this study), and reported a DOC removal range of 40–93%. One difference is that the DOC range of the raw waters in the Mergen et al. (2008) work was 1.6–5.1 mg/L, well below the concentration of this study. The UV$_{254}$ absorbance of the SJR water and MIEX-treated waters (Figure 3-1c and d) followed a nearly identical pattern as DOC (Figure 3-1a and b). The UV$_{254}$ concentration is reduced to ~0.1 ± 0.2 1/cm by both resins, which equates to a ~85% removal. Other studies have reported a UV$_{254}$ removal range of 80–95% (Humbert et al., 2007; Kitis et al., 2007). For both MIEX-Cl and MIEX-HCO$_3$ treated waters, the DOC concentrations and UV$_{254}$ absorbance behaved similarly. This illustrates that bicarbonate-form anion exchange has the same DOC and UV$_{254}$ removal efficiency as chloride-form anion exchange, and regeneration with sodium bicarbonate is able to achieve the same regeneration efficiency as regeneration with sodium bicarbonate.
chloride. Also, Figure 3-1 illustrates the robustness of the MIEX process in terms of fluctuating DOC and UV$_{254}$ (Figure 3-1a and c). Both resins show great efficiency at removing the aromatic organic carbon content, as seen by the reduction of UV$_{254}$ absorbance, but for DOC there still remains 5 mg/L. This remaining DOC is likely a combination of the non-aromatic DOC, which is not favorably removed by MIEX resin (Ates et al., 2007) and/or competition by other anions for exchange sites (Kitis et al., 2007; Neale and Schafer, 2009; Hsu and Singer, 2010).

3.3.2. Inorganic Anion Removal

The bromide and sulfate concentrations in the SJR vary greatly through the year (see Figure 3-2a and c). The bromide concentration starts at ~600 µg/L and increases through the sampling period with occasional fluctuations (April – May 2010), with an average concentration of 768 ±175 µg/L. The bromide concentration reaches its highest value in August 2010. Sulfate also starts the sampling period at its lowest concentration, ~20 mg/L, and increases to nearly 120 mg/L in April 2010, then begins to decline and has an average of 55 ± 24 mg/L. Figures 3-2b and d, show that both MIEX-Cl and MIEX-HCO$_3$ resins have the highest removals of bromide and sulfate at regeneration 0. Bromide removals for MIEX-Cl and MIEX-HCO$_3$ range from 10–50% and 25–60%, respectively, with an average removal of 30 ± 28% and 37 ± 11%, respectively, for each resin. Other researchers evaluating bromide removal by MIEX-Cl resin reported 10–90% bromide removal (DOC range 0–25 mg/L and initial concentration bromide range 10–300 µg/L) depending upon the MIEX resin dose and additional anions in the water (Singer and Bilyk, 2002; Neale and Schafer, 2009; Hsu and Singer, 2010). Results from this work, for both virgin and regenerated MIEX-Cl and MIEX-HCO$_3$ resins, fall within the published data. Note that MIEX-Cl resin experiences periods of bromide release (see Figure 3-2b), which are shown by the negative removal periods. This is likely due to the resin not being fully regenerated and releasing bromide in the presence of more favorable anions, such as sulfate.
or DOM (Kitis et al., 2007; Neale and Schafer, 2009). This idea is further explored in the bromide release experiments discussed in Section 3.3.4. Sulfate is always removed by both forms of MIEX resin, between 60–96% for MIEX-Cl and 40–95% for MIEX-HCO₃ depending on the number of regenerations. Kitis et al. (2007) reported 9–24% sulfate removal, with a similar sulfate concentration to this study and low DOC (2.6–4.3 mg/L). This work showed a much higher removal, with both MIEX-Cl and MIEX-HCO₃, with the average removal for each being 77 ± 11% and 65 ± 17%, respectively. Unlike DOC and UV₂⁵₄ performance, the MIEX-HCO₃ appears to not be as effective as MIEX-Cl at removing sulfate over numerous regenerations, with a 33% difference between the two resins at the end of the sampling term. This phenomenon could explain why the MIEX-Cl resin releases bromide (Figure 3-2b), i.e., the MIEX-HCO₃ resin does not have as high a preference for sulfate as the MIEX-Cl resin. Another possibility is that the MIEX-Cl is performing better at sulfate removal because it is releasing excess bromide to take on sulfate, the preferred ion (Neale and Schafer, 2009). Comparing DOC and UV₂⁵₄ removal (Figure 3-1b and d) with the removal efficiency of bromide and sulfate (Figure 3-2b and d), there is an obvious disparity, the resin efficiency decreases over time for both inorganic anions while it remains constant for DOM. This could be caused by the resin retaining DOM, sulfate, and/or bromide during regeneration, thus limiting the number of available removal sites for subsequent jar tests. It could also be a preference for DOM over the inorganic anions when the resins encounter high concentrations of each.

3.3.3. MIEX Resin Characteristics

MIEX resin is a polyacrylate macroporous polymer with strong-base quaternary ammonium functional groups for ion exchange and magnetic iron oxide incorporated into the resin structure to aid in settling. There is very little published information on the physical characteristics of MIEX resin. For example, Neale et al. (2010) shows an SEM image of MIEX
resin, however, the history of the resin or how it was prepared are not clear. Furthermore, over numerous regeneration cycles in this study, it was noted that the regenerated MIEX-Cl and MIEX-HCO₃ resins used in the SJR jar tests began to behave differently. Regenerated MIEX-HCO₃ resins began to agglomerate and clump to the bottom of the jar during mixing and the efficiency of sulfate removal by regenerated MIEX-HCO₃ resin began to decrease. Therefore, SEM images of regenerated MIEX-Cl and MIEX-HCO₃ resins were compared with a sample of virgin MIEX-Cl resin to provide new insights into the physical structure of MIEX resin (see Figure 3-3 and Figure B-1a–e in appendix B). Figure 3-3a shows multiple regenerated MIEX-Cl resin beads in the field of view and illustrates that even with numerous regenerations there does not appear to be any mechanical attrition of the resin beads. Comparing all three resins at 40× magnification, (Figure 3-3a, Figure B-1a and c) all appear to have the same range of bead diameters, <10 µm to over 200 µm, but the virgin MIEX-Cl resin (Figure B-1c) has a larger portion of fine particles than the other two. Figure 3-3b is a magnified image of regenerated MIEX-Cl resin. Comparing Figure 3-3b with Figures B-1b and d in Appendix B shows that the regenerated MIEX-HCO₃ resin is slightly different from the virgin and regenerated MIEX-Cl resins. In general, the surfaces of the regenerated MIEX-HCO₃ resin have both a greater number and more variability in surface features than do the regenerated and virgin MIEX-Cl resins. The regenerated and virgin MIEX-Cl resins are more similar in surface appearance, with a much smoother look. Figure 3-3c shows a cross-section of a regenerated MIEX-Cl resin bead and a cross-section of the virgin MIEX-Cl resin is also shown in Figure B-1e in Appendix B. Looking at both images it is obvious that the internal structures of the resin beads are very complex and allow for interactions not only on the surface but within the resin. The darker features are assumed to be pores, as the structure is known to be porous, but could be a result of how the bead
was sheared. Pore-like features have a size range from 10 μm to < 1 μm and appear consistent between the two resins.

3.3.4. Bromide Release Jar Test

MIEX-Cl resin released bromide at different points during the SJR jar tests (see discussion in Section 3.3.2). Ishii and Boyer (2010) saw similar results in a full scale MIEX-Cl water treatment plant, where sulfate was released into treated waters when the raw water supply was switched from a well with a high sulfate concentration to a well with a low sulfate concentration. A series of jar tests were conducted to investigate the possible cause for bromide release as illustrated in Figures 3-4a–c. During regenerations 1–10, MIEX-HCO₃ resin removed chloride and bromide from the synthetic water, and removal plateaued at 12% and 20%, respectively. To understand this consider that MIEX resin has a limited potential for removal (i.e., 0.52 meq/mL of charge sites; Boyer and Singer, 2008). Taking this and considering only chloride, for simplicity, 10 mL of MIEX-HCO₃ has the potential to remove 182 mg/L of chloride. The synthetic water is dosed with 200 mg/L of chloride, so at first the resin is capable of removing nearly all the chloride. In each cycles after the initial, only 1 mL of exhausted resin is removed and replaced by 1 mL fresh resin (capable of removing ~18 mg/L of chloride). As the experiment continues the resin becomes saturated with chloride more easily and is unable to take on any more chloride. In the actual experiment, synthetic waters also contained other competing anions (bromide and sulfate). During regenerations 11–15, 50 mg/L of sulfate was added to the synthetic water and the removal of bromide and chloride decreased as sulfate is the more preferred anion (Neale and Schafer, 2009). In fact, the resin released chloride (regeneration 11) and bromide (regenerations 12–15). The bromide is the least favorable anion, as is seen in Figure 3-4b, and resin releases nearly 1.5 times the initial concentration at regeneration 14. This provides strong evidence for the potential of MIEX resin to sequester
anions and then exchange the anions into receiving waters when a more preferred anion is present. To further prove this point, when the synthetic water was returned to its initial condition the residual sulfate is released through the last five regenerations (Figure 3-4c). At the same time, chloride exchange (Figure 3-4a) reaches a plateau at the same level as seen in regenerations 5–10. The bromide concentration for the final five regenerations, (Figure 3-4b) has a low removal and is even released into the treated waters again at regeneration 19, possibly due to bromide being held on the resin and being released again in the presence of sulfate. This shows that the performance of MIEX resin depends not only on the concentrations of anions but more importantly which anions are present, as MIEX has a greater affinity for some anions (sulfate) over others (bromide).

3.4. Magnetic Ion Exchange Summary

MIEX-Cl and MIEX-HCO₃ resins have similar removal efficiency for DOC and UV₂₅₄, but removal is affected by different types of organic matter and competition by inorganic anions. This study has shown that both MIEX-Cl and MIEX-HCO₃ resins are capable of removing ~70% of the DOC in the SJR over variable concentrations, but consistently 30% of the DOC remains. Inorganic anions behave differently from DOM when bromide and sulfate removals are considered. In the case of bromide, overall the removal rates were similar ~30%, but the MIEX-Cl resin occasionally released bromide into the water, while the MIEX-HCO₃ resin consistently removed it. When sulfate removal is considered, MIEX-Cl resin removed more sulfate than MIEX-HCO₃ resin, with a 33% difference between the two resins at the end of the experiment. Overall the MIEX-HCO₃ and MIEX-Cl resins have a similar removal performance, which proves MIEX-HCO₃ resin could be a viable candidate to replace traditional MIEX-Cl resin for anion removal, but considerations would have to be made depending on the makeup of the water. Analysis of the regenerated MIEX-Cl and MIEX-HCO₃ resins, along with virgin MIEX-Cl resin,
show differences in the surfaces of the resins. These differences could be related to the regeneration efficiency of the resins, but further work would be required to prove this. Bromide release jar tests performed with MIEX-HCO₃ resin prove the resins preference for certain anions, such as sulfate, and also prove the resin is capable of sequestering certain anions and then releasing them later into receiving waters, as was evident with the bromide release.

Future work on MIEX-HCO₃ resins should be focused on furthering the knowledge of the resin performance, what different anions MIEX-HCO₃ is capable of removing, and if there is a breaking point where the resin can no longer be effectively regenerated. Comparisons of many different types and sources of waters should be analyzed for removal efficiency of MIEX-HCO₃. Alternative pathways for regenerating MIEX-HCO₃ resin, such as CO₂, should be evaluated in combination with resin performance studies. Further work is also needed on understanding the structure of MIEX resin. A study should be undertaken to visualize the surface changes of the resin as it goes through multiple regenerations, focus should be on characterizing the surface features. The porosity of MIEX resin should also be analyzed to determine its pore size, pore volume, and total surface area. This information would help better explain how the resin is capable of sequestering anions during regeneration and could be applicable to all MIEX resins.

**3.5. Supplementary Material**

Appendix B contains additional SEM images of virgin MIEX-Cl and regenerated MIEX-HCO₃ resins. Images were produced under the same parameters as presented in section 3.2.6 and further details are provided in the figure captions.
Table 3-1. St. Johns River jar test regeneration numbers and corresponding dates that samples were collected from the river. Regeneration 0 represents fresh resin and the start of the sampling period.

<table>
<thead>
<tr>
<th>Regeneration number</th>
<th>Date water collected</th>
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<tbody>
<tr>
<td>0</td>
<td>10/21/09</td>
</tr>
<tr>
<td>1</td>
<td>11/4/09</td>
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<tr>
<td>2</td>
<td>11/20/09</td>
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<td>12/16/09</td>
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<tr>
<td>16</td>
<td>8/6/10</td>
</tr>
<tr>
<td>17</td>
<td>8/22/10</td>
</tr>
</tbody>
</table>
Table 3-2. Synthetic waters used in bromide release jar tests. For regenerations 1–10 and 15–20 only chloride (200 mg/L) and bromide (1000 µg/L) were added to synthetic waters. Sulfate (50 mg/L) was added for regenerations 11–15 only.

<table>
<thead>
<tr>
<th>Regeneration numbers</th>
<th>Cl(^-) (mg/L)</th>
<th>Br(^-) (µg/L)</th>
<th>SO(_4^{2-}) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 10</td>
<td>200</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>11 – 15</td>
<td>200</td>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td>16 – 20</td>
<td>200</td>
<td>1000</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 3-1. Comparison of St. Johns River data for raw waters, MIEX-Cl and MIEX-HCO₃ treated waters at resin dose of 10 mL/L and contact time of 20 min. Figures are (a) absolute DOC concentration, (b) percent DOC removal, (c) absolute UV₂₅₄ and (d) percent UV₂₅₄ removal. Data presented in parenthesis are average, one standard deviation.
Figure 3-2. Comparison of St. Johns River data for raw waters, MIEX-Cl and MIEX-HCO₃ treated waters at resin dose of 10 mL/L and contact time of 20 min. Figures are (a) absolute bromide concentration, (b) percent bromide removal, (c) absolute sulfate concentration and (d) percent sulfate removal. Data presented in parenthesis are average, one standard deviation.
Figure 3-3. Field emission scanning electron microscopy images of (a) 40× magnification of regenerated MIEX-Cl resin beads (b) 250× magnification of surface of MIEX-Cl beads (c) 1,000× magnification cross section of regenerated MIEX-Cl bead collected after 14th regeneration. Samples were lyophilized and characterized without coating at an accelerating voltage of 5.0kV and ~15mm working distance.
Figure 3-4. Concentration of (a) chloride, (b) bromide, and (c) sulfate from bromide release jar tests. Resin dose was 10 mL/L and contact time of 20 min. For each regeneration 1 mL of used MIEX-HCO$_3$ resin was removed and replaced with 1 mL of fresh MIEX-HCO$_3$ resin. Stripped bar represents the concentration added into each batch of synthetic water. Black bars represent regenerations with only chloride (200 mg/L) and bromide (1000 µg/L). White bars represent the regenerations that contain sulfate (50 mg/L) in addition to chloride (200 mg/L) and bromide (1000 µg/L).
CHAPTER 4
CONCLUSIONS AND RECOMMENDATIONS

With the dwindling groundwater supplies and an ever increasing population, many water management districts in Florida are looking to other sources for drinking water. One district, the SJRWMD, has proposed the SJR as a source to supply their future needs. This study has shown that the SJR will be a complex water for treatment, with its high concentration of terrestrial DOM and bromide. The fact that these two factors together will lead to DBP problems means that special efforts should be made early in the process to remove both. This study also demonstrated the potential of using anion exchange (MIEX-Cl or MIEX-HCO₃ resin) to remove bromide and DOM from the SJR.

Future work for this research would be a longer-term study that better explains the sources of DOM, chloride and bromide in the river. The ability to track these origins would allow water treatment plant operators to better predict when treatment methods need adjustment, rather than reacting to the changes. The Br⁻/Cl⁻ ratio for the river should be further developed and studied with data from multiple sites along the river. This information would provide better predictability and identification of the sources of bromide and chloride in the SJR. Long term studies should also be combined with MIEX-HCO₃ anion exchange jar tests and pilot studies.

Research evaluating MIEX-HCO₃ resin needs to focus on understanding the failure point of the resin, when does it no longer regenerate effectively, and also study the use of alternative regenerants such as CO₂, which could be a cost savings. More focus is needed on characterizing the surface features of the MIEX resin. Analysis should be conducted on the resin from virgin resin through multiple regenerations to understand the changes occurring on the surface. Additional work, such as porosimetry, should be done to understand pore volume, size and total
surface area. All this combined could be used to explain the anion sequestering discussed in this paper.
APPENDIX A
NITROGEN, SULFATE AND IODIDE

A.1. Materials and Methods

Total dissolved nitrogen (TDN) was measured on a Shimadzu TOC-VCPH total organic carbon analyzer equipped with a TNM-1 Total Nitrogen Module and ASI-V autosampler. Nitrogen stock standards were prepared from potassium nitrate. Nitrate and sulfate were measured on a Dionex ICS-3000 ion chromatograph under the same conditions mentioned in previous sections (Chapters 2 & 3). Nitrate stock standards were made from sodium nitrate and sulfate standards were made from potassium sulfate. TDN, nitrate, and sulfate measurements were made in duplicate and averaged. Each run on the TOC-VCPH and ICS-3000 were monitored using calibration check standards (0.1, 0.5, 1, 1.5 and 2 mg N/L for TDN, 0.05, 0.5 and 5 mg N/L for nitrate, 0.5, 5 and 50 mg/L for sulfate) to ensure that the measured concentration fell within 10% of the known value. Due to iodide concentrations below the detection limit of the ion chromatography protocol, Standard Method 4500-I- C. Catalytic Reduction Method was used to determine iodide levels (Clesceri et al., 1989). The exact details of the analysis are outlined below.

Reagents for iodide measurements were prepared every three months using DI water, except for ferrous ammonium sulfate which was prepared daily. All standards were prepared according to Standard Method 4500-I- C, except for arsenious acid. For arsenious acid, a step-wise addition of concentrated sodium hydroxide was required to dissolve the solid and then concentrated sulfuric acid was added to neutralize the base. 11 N sulfuric acid was used for all additions of acid. The Standard Methods 1030 E. (Clesceri et al., 1989) method detection limit was performed with DI and nanopure water to determine a detection limit of 2 µg/L. A calibration curve and check points were created using the appropriate amount of standard iodide.
solution and DI water to make up 10 mL at given points (2, 5, 10, and 12 µg/L). 10 mL of sample, calibration curve or calibration check solutions were placed in individual glass test tubes. Initially 1 mL sodium chloride, 0.5 mL arsenious acid and 0.5 mL sulfuric acid were added to each tube. Samples were then capped and placed in a water bath set to 30°C ± 0.5°C, along with the ceric ammonium sulfate. Both were allowed to equilibrate for 10–15 min. After equilibration, caps were removed and 1 mL ceric ammonium sulfate solution was added to each tube, inverted at least one time, timed for 15 min and returned to the water bath. At the 15 min point (± 0.1 min) 1 mL of ferrous ammonium sulfate was added and shaken. Immediately 1 mL of potassium thiocyanate was added to the tubes and inverted at least one time. Tubes were returned to the water bath. When all tubes were completed samples were analyzed on a Hitachi U-2900 spectrophotometer for ultraviolet absorbance at 525 nm and 510 nm. Analysis was completed within 1 hr as directed by Standard Method 4500-I C (Clesceri et al., 1989).

A.2. Results and Discussion

To better understand the ecology of the SJR, TN and nitrate concentrations were tracked through the study period (Figure A-1a and b). The x-axis spans the entire year of the study, the y-axis is in mg N/L. All data were generated from analysis of collected samples. Total nitrate concentration for the year averages 0.15 ± 0.09 mg/L, with a minimum below the detection limit of 0.05 mg/L and a maximum >0.28 mg/L (Figure A-1a), while TN averages 1.0 ± 0.2 mg/L, with a minimum of 0.7 mg/L and a maximum of 1.4 mg/L (Figure A-1b). The peak nitrate concentrations occur in November 2009 and May 2010, which does fall within typical planting periods in the area downstream of the sample site (Stephens et al., 1991).

To further understand the nitrogen present in the site waters, the nitrate/TN was plotted for the sampling period (Figure A-2). The percentage of nitrate varies through the year, ranging
from less than 5% to over 20%. On average nitrate represents 14 ± 6% of the TDN concentration.

Iodide and sulfate are other inorganic anions present in waters. Their concentrations are plotted in Figure A-3a and b. The x-axis on Figure A-3a is measured in mg/L and in Figure A-3b it is measured in µg/L. The y-axis for both figures represents the months of the study period. Sulfate concentrations were at the lowest at the start of the study, October 2009, at 24 mg/L (Figure A-3a) and the highest peaks are in February 2010 and March 2010, at >100mg/L. The average sulfate concentration in the SJR was 54.7 ± 23.6 mg/L. Comparing the trend of concentrations for sulfate (Figure A-3a) with those for chloride (Figure 2-3a) they are very similar, with peak concentrations at the same time period. Iodide concentrations were much more variable ranging from 4 – 15 µg/L, with an average of 8.8 ± 3.2µg/L. As with chloride and bromide concentrations, iodide and sulfate maximum concentrations are at least twice the minimum concentration (Figures A-3 and 2-3). Overall, data shows concentrations ranges for iodide and sulfate fluctuate throughout the sampling period.
Figure A-1. Raw absolute concentrations in St. Johns River of (a) nitrate, measured in mg/L and (b) total dissolved nitrogen, measured in mg/L for Astor, FL site. Data in parenthesis represent average and standard deviation, respectively. Error bars represent standard deviation for each sample. Nitrate measurements at 0.05 mg/L were set to the lower detection limit for experiment, actual concentration was measured at lower concentration.
Figure A-2. Percent of total dissolved nitrogen present as nitrate in the St. Johns River over sampling period. Data in parenthesis are the average and standard deviation, respectively, for the entire sampling period. Error bars represent standard deviation for each sample.
Figure A-3. Absolute concentrations of (a) sulfate and (b) iodide in the SJR for the sampling period. Data in parenthesis represents the average and mean concentrations for the year respectively. Error bars represent the standard deviation for each sample.
APPENDIX B
ADDITIONAL SEM IMAGES

SEM images were taken of MIEX-Cl and MIEX-HCO₃ resins to better understand the physical changes noted in section 3.3.3. Images were captured under the same conditions mentioned in section 3.3.3. Supplemental figure B-1a–e show the images captured and discussed in section 3.3.3. Also included in this supplemental section are additional images (supplemental figures B-2-4) taken of the regenerated MIEX-Cl, regenerated MIEX-HCO₃ and virgin MIEX-Cl resins. These images were focused more on the surfaces of the various bead and their exact descriptions are included in the figure captions.
Figure B-1. Field emission scanning electron microscopy images of (a) 40× magnification of regenerated MIEX-HCO₃ resin beads (b) 250× magnification surface view of regenerated MIEX-HCO₃ beads collected after 14th regeneration. Also included are the following images of virgin MIEX-Cl resin for comparison; (c) 40× magnification of virgin MIEX-Cl resin beads (d) 250× magnification surface view of virgin MIEX-Cl beads and (e) 1,000× magnification of cross section of virgin MIEX-Cl bead.
Figure B-2. Field emission scanning electron microscopy images of regenerated MIEX-Cl resin surfaces in greater detail. (a) 1,000× magnification of regenerated MIEX-Cl resin surface features (b) 5,000× magnification of regenerated MIEX-Cl resin surface features and (c) 15,000× magnification of regenerated MIEX-Cl resin surface features.
Figure B-3. Field emission scanning electron microscopy images of regenerated MIEX-HCO₃ resin surfaces in greater detail. (a) 40× magnification of regenerated MIEX-HCO₃ resin beads (b) 500× magnification of regenerated MIEX-HCO₃ resin bead, (c) 1,000× magnification of regenerated MIEX-HCO₃ resin surface features (d) 5,000× magnification of regenerated MIEX-HCO₃ resin surface features and (e) 20,000× magnification of regenerated MIEX-HCO₃ resin pore structure.
Figure B-4. Field emission scanning electron microscopy images of virgin MIEX-Cl resin surfaces in greater detail. (a) 1,000× magnification of virgin MIEX-Cl resin surface features (b) 5,000× magnification of virgin MIEX-Cl resin surface features and (c) 20,000× magnification of virgin MIEX-Cl resin pore structure.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Krystal Walker graduated from Eastern New Mexico University, Portales NM in July 2000, with a BS in biology and chemistry. In April 2002, she joined the United States Air Force, commissioning as a Second Lieutenant in June 2002. Since then, she has served the United States Air Force as a chemist in a variety of locations and job positions. In 2009, she was selected by the Air Force Institute of Technology to pursue her master’s degree at the University of Florida.