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Chromium Oxidation by Disinfectants and Oxidants Used in Drinking Water Treatment

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CHROMIUM OXIDATION BY DISINFECTANTS AND OXIDANTS USED IN DRINKING WATER TREATMENT

by

Nathan D. Rogers

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Civil and Environmental Engineering

Approved:

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UTAH STATE UNIVERSITY
Logan, Utah

2016

ABSTRACT

Chromium Oxidation by Disinfectants and Oxidants Used in Drinking Water Treatment

by

Nathan D. Rogers, Master of Science

Utah State University, 2016

Major Professor: Dr. Laurie McNeill
Department: Civil and Environmental Engineering

The USEPA Maximum Contaminant Level (MCL) for Total Chromium in drinking water is 100 μg/L. Total chromium includes both trivalent chromium (Cr(III), a trace nutrient) and hexavalent chromium (Cr(VI), a probable human carcinogen). The State of California set a Cr(VI)-specific MCL of 10 μg/L in 2014, and USEPA is considering a new federal MCL for Cr(VI). This would have a significant impact on drinking water systems across the US, with estimated annual cost of compliance between $0.6 to 5.1 billion per year.

While Cr(VI) is the species of concern for health effects, water utilities must also consider Cr(III) since it can be oxidized to Cr(VI) by various chemicals. This oxidation has been documented for commonly used disinfectants. However, past studies were conducted with higher levels of chromium (e.g., 20 to 500 μg/L) and it is unknown if the reactions proceed at the same rate and extent at the lower concentrations relevant to most water treatment plants (< 10 μg/L).

This project, funded by the Water Research Foundation, systematically evaluated the extent of oxidation of Cr(III) by drinking water oxidants under conditions relevant to drinking water utilities. Five oxidants (chlorine, monochloramine, chlorine dioxide, potassium permanganate, and ozone) were tested. Two doses were used for each chemical with their respective reaction times reflecting the typical application of the chemical in treatment. Three different water qualities were evaluated, each at pH 5.5, 7, and 9, and at two different temperatures (5 and 16 °C).

Chlorine consistently oxidized an average of 80% of the available Cr(III), with the majority of the oxidation happening within the first 7 hours. Monochloramine did not significantly oxidize Cr(III) at any of the conditions tested. Chlorine dioxide was an effective oxidant at pH 7, with complete oxidation occurring in 6 hours, but was less effective at pH 5.5 and 9. Potassium permanganate achieved complete oxidation in 4 hours at each pH, with pH 7 experiencing the fastest oxidation. Ozone oxidized all available Cr(III) within minutes at all pH values. Quantifying the Cr(III) oxidation as a result of using these oxidants provides understanding of potential Cr(VI) addition into drinking water.

(127 pages)

PUBLIC ABSTRACT

Chromium Oxidation by Disinfectants and Oxidants Used in Drinking Water Treatment

Nathan D. Rogers

This project investigated the behavior of hexavalent chromium (Cr(VI), a potential carcinogen) in drinking water. While Cr(VI) can exist naturally, it can also be oxidized from Cr(III), a known trace nutrient. Recently, the State of California implemented a water regulation specifically for Cr(VI) at 10 parts per billion (ppb). This project completed a comprehensive evaluation of chromium behavior when in contact with common drinking water treatment chemicals including chlorine, monochloramine, chlorine dioxide, potassium permanganate, and ozone.

The results of these oxidation experiments are highly applicable to water treatment facilities. If a treatment plant is using monochloramine, there is no indication that Cr(III) oxidation would occur. When using chlorine, around 80% of Cr(III) will oxidize to Cr(VI) within 12 hours under typical treatment conditions. If chlorine dioxide is used in treatment at pH 7, complete Cr(III) oxidation can be expected within 6 hours of addition. Similarly at all pH values, potassium permanganate will cause complete Cr(III) oxidation in 4 hours. Ozone will oxidize all available Cr(III) within minutes of contact.

This information on chromium behavior when in contact with different treatment chemicals allows water utilities and regulators to make more informed decisions to protect public health and limit exposure to this potentially harmful metal species.

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Lastly, I would like to offer a special thank you to my family for providing an amazing support system: To my wife Elle, for always being there and encouraging me to be better and have confidence in myself; To my kids, who can always lift my mood and put a smile on my face; To my parents, who taught me the value of hard work and persistence, while making sure to have fun in the process.

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INTRODUCTION

Chromium in drinking water and its effects on human health have been a topic of concern for many years, but have been especially discussed over the last few decades. This concern was elevated beginning in 1991 when the U.S. Environmental Protection Agency (EPA) set an enforceable maximum contaminant level (MCL) of 100 μg/L due to concerns at the time that excessive consumption of chromium-contaminated water could lead to skin reactions (USEPA 2013).

The two oxidation states of chromium found in drinking water are trivalent (Cr(III)) and hexavalent (Cr(VI)). An intriguing aspect of chromium chemistry is that one oxidation state is known to be a trace nutrient while the other is a probable carcinogen. The Cr(III) oxidation state is a known trace nutrient, often contained in daily human health supplements. On the other hand, Cr(VI) is a known carcinogen when inhaled and a probable carcinogen when ingested (USEPA 2010). These oxidation states are interchangeable in treatment and distribution systems, which is the main driving force to understand the oxidation kinetics of chromium in drinking water systems.

Sources of chromium in drinking water come from both naturally occurring and anthropogenic sources. Depending on geographic regions, natural chromium levels vary, as chromium is the 21st most common metal found in the earth's crust (Nriagu and Nieboer 1988). There are also many mechanical and industrial processes that can lead to discharges into source water, such as leather tanning, wood preservation, and decorative plating. Another potential source of chromium in drinking water is contamination in drinking water treatment chemicals such as iron coagulants (Olsen 2014).

There is currently no federal regulation on Cr(VI) concentration in drinking water, only for total chromium (TotCr), which is the combination of both Cr(III) and Cr(VI). As previously stated, the MCL for TotCr is currently 100 μg/L (USEPA 2013). It is important to note that the MCL for chromium is measured at the entry point of the distribution system, and since both oxidation and reduction of chromium can occur in distribution system pipes, the concentration of Cr(VI) actually present at consumers' taps may differ from the entry point. There has been discussion of possible federal regulation of Cr(VI) for many years. The State of California set a revised MCL for TotCr at 50 μg/L and was the first state to create a regulation specifically for Cr(VI). Setting a possible example for federal regulation, the California Cr(VI) MCL was set at 10 μg/L and was enforced starting July 2014.

Understanding the conditions that cause chromium to change between oxidation states during treatment processes and within a distribution system is extremely important when dealing with consumer health. This project is an extension of previous projects that have looked at the oxidation potential of chromium in drinking water, and will specifically look at five common disinfectants and oxidants used in drinking water treatment: chlorine, monochloramine, chlorine dioxide, potassium permanganate, and ozone.

With a greater understanding of chromium oxidation, more informed decisions could be made pertaining to regulation. When discussing regulation, one of the many considerations taken into account is economic feasibility. While it may be ideal to set a regulation well below the concentration thought to cause health effects, the necessary chromium treatment would require additional funds ultimately provided by the customer.

Any future regulation must balance effective chromium treatment and acceptable treatment costs.

LITERATURE REVIEW

Chemistry & Speciation

In drinking water treatment plants and distribution systems, the oxidation of Cr(III) to Cr(VI) often occurs from adding treatment chemicals. Water quality factors such as pH and temperature can impact oxidation reactions (McNeill el al. 2012). A pE-pH diagram of chromium shows that at equilibrium Cr(VI) is the favored species at higher redox and pH conditions (Figure 1).

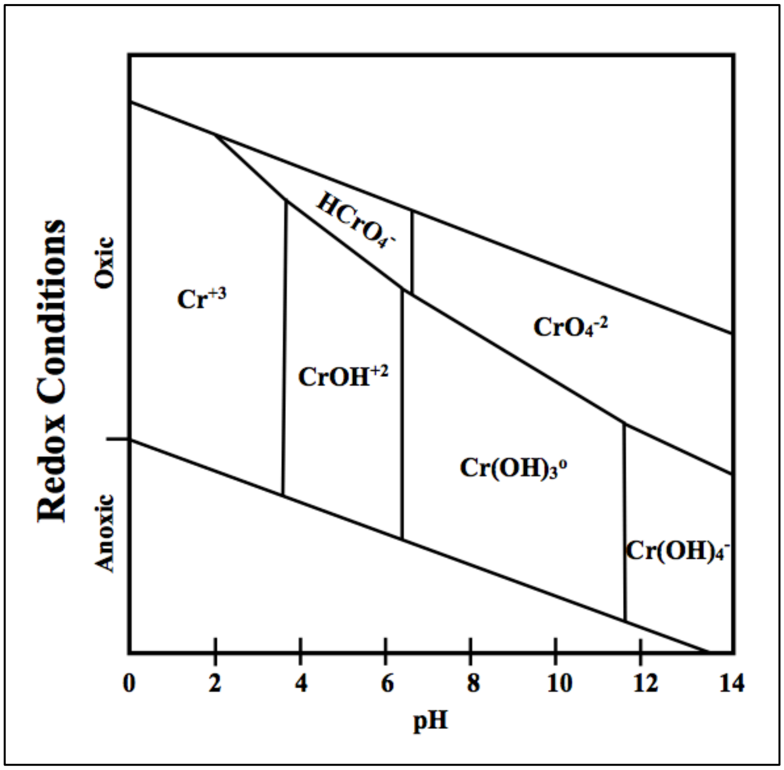


Figure 1. pE-pH diagram for speciation of aqueous chromium.

Of the aqueous species shown in Figure 1, the Cr(VI) species are given as $HCrO_4^-$ and CrO_4^{-2} while the Cr(III) species are Cr^{+3}, $CrOH^{+2}$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$. A pC-pH diagram for Cr(VI) in solution was constructed to show how the concentration of these two Cr(VI) species change, but remain soluble throughout the experiments conducted in this project (Figure 2).

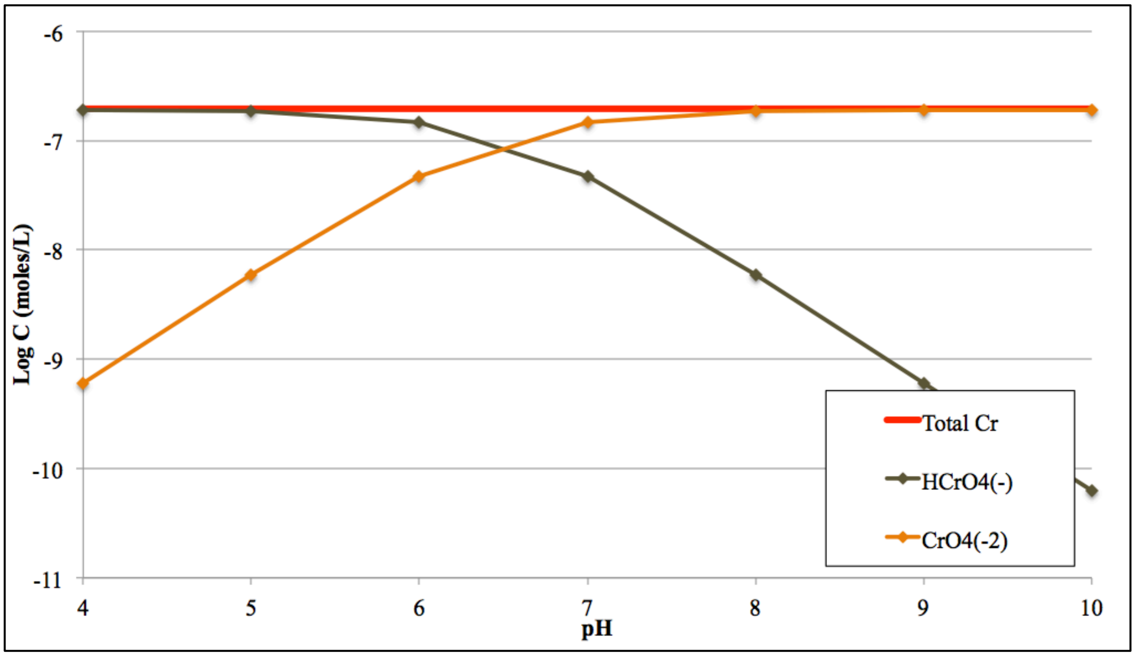


Figure 2. pC-pH diagram of various Cr(VI) species when 10 µg/L of Cr(VI) is in solution at 16 °C.

From Figure 2 the changes in concentration among the two dominant Cr(VI) species are observed while the TotCr concentration remains the same throughout. This predicts that the Cr(VI) species remain soluble and no precipitates are formed.

Previous studies have shown that there are precipitated species of Cr(III) that can form when water conditions, largely pH, favor particulate formation (Brandhuber et al. 2004; Chebeir and Liu 2016; Clifford and Chau 1988; Lai and McNeill 2006; Lee and

Hering 2005). In Figure 3, a pC-pH diagram of the aqueous Cr(III) species was created using the chemical equilibrium system software MINEQL+.

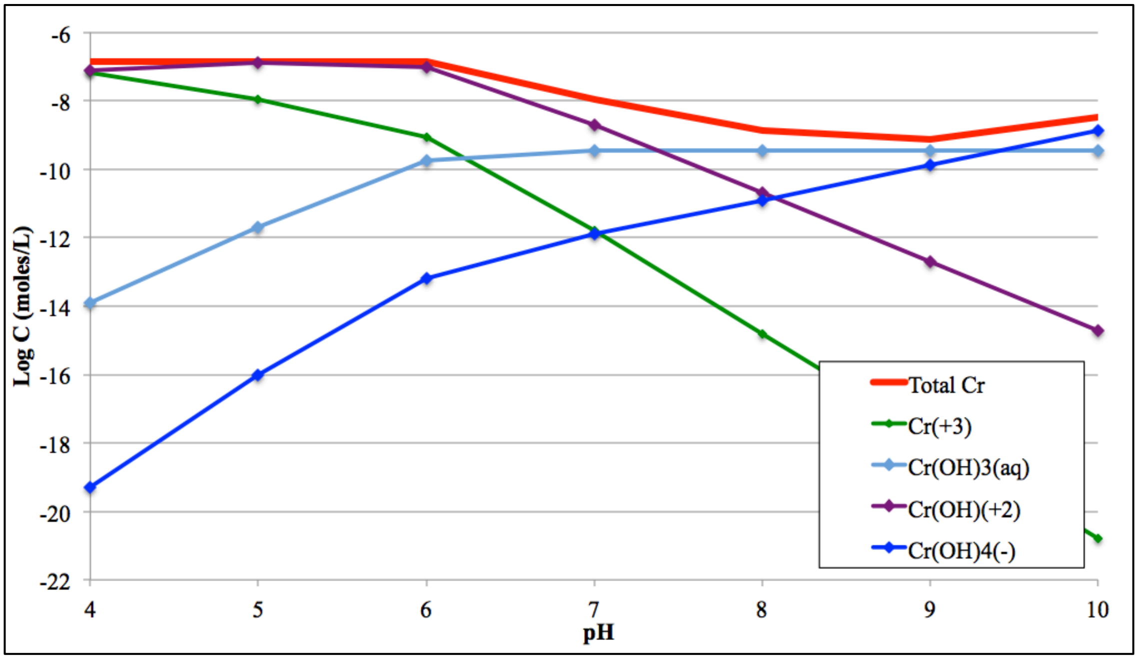


Figure 3. pC-pH diagram of various Cr(III) species when 10 µg/L of Cr(III) is in solution at 16 °C.

At pH values higher than pH 6, a drop in total chromium (all combined dissolved Cr(III) species) is observed. The decreasing total chromium is an indicator of Cr(III) precipitation. As the pH increases beyond 6, the solubility product for chromium hydroxide ($Cr(OH)_{3(s)}$, $K_{sp} = 6.3x10^{-31}$) is reached and these aqueous forms of chromium begin to form the particulate species chromium hydroxide (not directly shown in Figure 3).

These particulate species may settle out of solution. This is important for this project, as precipitation may be observed in the mid to high pH ranges, especially during the longer duration experiments, and particulates may not be included during sample collection. Particulate species may also have different behavior. It has been shown that chromium can still be oxidized when in a precipitated form (Lee and Hering 2005). The oxidation kinetics of precipitated chromium are different than aqueous chromium, but factors affecting the kinetics remain largely unknown (Chebeir and Liu 2016).

Chromium may also sorb to particulate species in drinking water. For example, McNeill et al. (2012) used a diffuse layer model to predict the amount of soluble Cr(III) and Cr(VI) as a function of pH when iron particles were present in a solution (Figure 4).

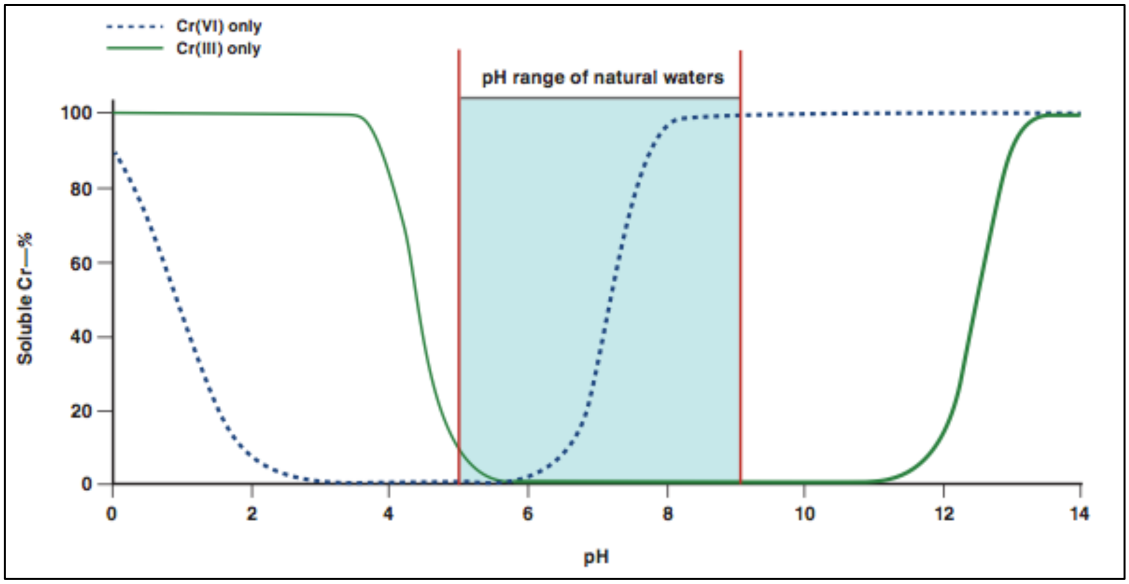


Figure 4. Model prediction of soluble Cr(III) and Cr(VI) in a drinking water sample containing iron particles (McNeill et al. 2012).

At pH values typically found in natural waters (5 – 9), Cr(III) is generally sorbed to the iron particles while Cr(VI) can be anywhere from 0-100% soluble. Lee and Hering (2005) also demonstrated that Cr(VI) can sorb to precipitated Cr(III) species at low pH. There are currently no data showing how much Cr(VI) is able to sorb to other insoluble species. Redox reactions of sorbed chromium are poorly understood (Chebeir and Liu

2016), which creates a further challenge in understanding which form of chromium is prevalent and what the oxidation potential will be.

Prevalence of Chromium

In an effort to understand the prevalence of chromium and the populations affected by chromium in drinking water, data from the Third Unregulated Contaminant Monitoring Rule (UCMR3) (USEPA 2015) were used to map chromium occurrence in the lower 48 states of the United States. Using the Esri software ArcMap, the chromium concentration data from the participating utilities were loaded into ArcMap using the linking data identifier of zip codes. Since the Cr(VI) data provided in the UCMR3 database are measured at the entry point of the distribution system, both naturally occurring and recently formed Cr(VI) (from treatment) contribute to these average amounts.

The average Cr(VI) concentrations measured at the entry point of the distribution system are displayed in Figure 5. Multiple areas within and outside of California experienced average Cr(VI) concentrations in the drinking water that were greater than the State of California's MCL of 10 μg/L. However, it should be noted that because data from UCMR3 were collected from 2013-2015, some of the data reflect conditions before the implementation of the State of California's MCL in July 2014.

While not provided in Figure 5, the UCMR3 data also documented areas that experienced maximum Cr(VI) concentrations both within and outside of California that reached higher than 50 μg/L, and in a few cases outside California that were almost

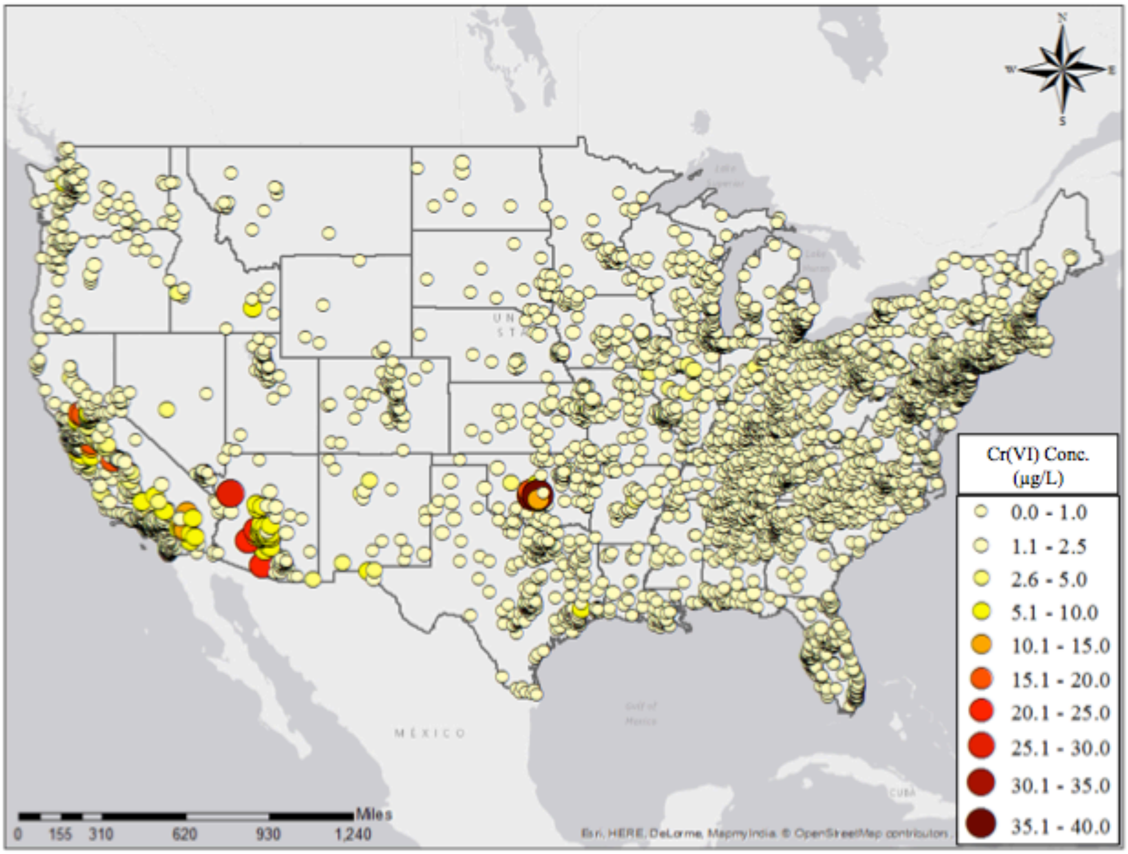


Figure 5. Average Cr(VI) concentration at the entry point to the distribution system in the lower 48 United States based on data provided by UCMR3 (USEPA 2015).

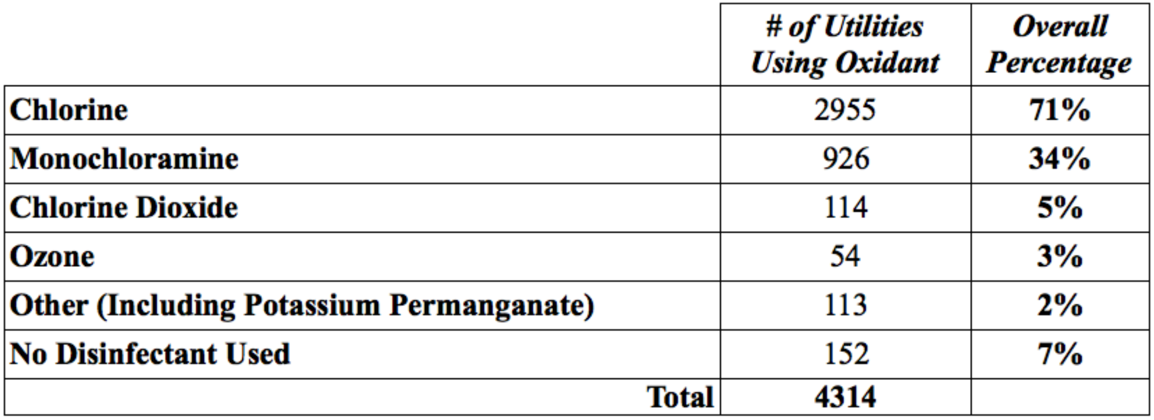
100 µg/L. However, all of them were under the current federal MCL for total chromium (100 µg/L) (USEPA 2015).

It is important to reiterate that Cr(VI) concentrations in Figure 5 are measured at the entry point to the distribution system. The Cr(VI) concentration experienced at a customer tap could increase if there is soluble Cr(III) remaining after treatment and oxidation to Cr(VI) continues as the water moves through the distribution system. Depending on the materials used in a distribution system, it is also possible for the Cr(VI) concentration to decrease between the entry point and consumer tap if Cr(VI) sorbs to Fe particles in a distribution system (Figure 4).

Prevalence of Oxidants

Oxidants are routinely used in water treatment for disinfection. There are two main types of disinfection: primary and secondary. Primary disinfection is used for the inactivation of pathogens, while secondary disinfection provides a chemical residual in a distribution system. To meet drinking water regulations, it is common for utilities to use multiple oxidants to achieve both primary disinfection and provide a residual in the distribution system. Data from the (UCMR3) provided by the EPA show the prevalence of oxidant use in more than 4300 facilities in 2151 municipalities throughout the United States (Table 1).

Table 1. Percentages of Utilities using Common Treatment Oxidants (USEPA 2015)



	# of Utilities Using Oxidant	***Overall Percentage***
Chlorine	2955	**71%**
Monochloramine	926	**34%**
Chlorine Dioxide	114	**5%**
Ozone	54	**3%**
Other (Including Potassium Permanganate)	113	**2%**
No Disinfectant Used	152	**7%**
Total	**4314**	

The majority of municipalities are using either chlorine or monochloramine (Table 1). Chlorine is chosen primarily for its ability to inactivate pathogens while also providing a residual in distribution systems to satisfy drinking water regulations. Monochloramine, a weaker oxidant, is mainly used to provide a residual in distribution systems. These residual holding times are often in the time span of several days. Even though chlorine dioxide and ozone do not provide a residual, they often provide stronger oxidation potential for primary disinfection during treatment. While not a disinfectant, potassium permanganate is also used in water treatment due to its strong oxidation potential.

Redox Equations

The oxidation of Cr(III) to Cr(VI) when in contact with oxidants used in drinking water treatment can be better understood by redox equations. For each of the investigated oxidants, Table 2 outlines the redox equations that were expected to occur. It should be noted that Cr(III) and Cr(VI) are shown as Cr^{3+} and CrO_4^{2-}, respectively.

Table 2. Redox Equations for Investigated Oxidants

Oxidant	**Chromium Redox Equation**
Chlorine	$2Cr^{3+} + 3HOCl + 5H_2O = 2CrO_4^{2-} + 3Cl^- + 13H^+$
Monochloramine	$2Cr^{3+} + 3NH_2Cl + 8H_2O = 2CrO_4^{2-} + 3NH_3 + 3Cl^- + 13H^+$
Chlorine Dioxide	$Cr^{3+} + 3ClO_2 + 4H_2O = CrO_4^{2-} + 3ClO_2^- + 8H^+$
	$5Cr^{3+} + 3ClO_2 + 14H_2O = 5CrO_4^{2-} + 3Cl^- + 28H^+$
Potassium Permanganate (as Permanganate)	$5Cr^{3+} + 3MnO_4^- + 8H_2O = 5CrO_4^{2-} + 3Mn^{2+} + 16H^+$
	$Cr^{3+} + MnO_4^- + 2H_2O = CrO_4^{2-} + MnO_2 + 4H^+$
Ozone	$2Cr^{3+} + 3O_3 + 5H_2O = 2CrO_4^{2-} + 3O_2 + 10H^+$

Some of the oxidants in Table 2 have multiple redox equations that could occur when in contact with Cr(III). For example, during the reaction chlorine dioxide (ClO_2) may be reduced to chlorite (ClO_2^-) or even further to chloride (Cl^-). It should also be noted that due to the Cr(III) and oxidant concentrations being investigated in this project, there is a stoichiometric excess of oxidant.

Previous Chromium Oxidation Studies

The current study is an extension of previous studies that investigated the oxidation of Cr(III) by dissolved oxygen, chlorine, monochloramine, potassium permanganate, and hydrogen peroxide (Brandhuber et al. 2004; Lai and McNeill 2006). These oxidants were dosed into three different water types containing 100 μg/L Cr(III) and monitored under controlled conditions to observe the oxidation of Cr(III) to Cr(VI). The water types previously investigated were 18-MΩ high purity deionized water with $NaNO_3$ added as a background electrolyte, a laboratory generated synthesized water, and a source water obtained from a water utility in California. These experiments were conducted at a controlled temperature of 15 °C and at pH values of 5, 7, and 9 (Lai and McNeill 2006). Those results, as well as other studies' conclusions, are summarized below according to the various oxidant used.

Dissolved Oxygen

The experiments conducted by Lai and McNeill (2006) confirmed that dissolved oxygen (DO) did not appreciably oxidize Cr(III) to Cr(VI) over the given time period of 50 hours, even though Cr(VI) is thermodynamically favored in a well-oxygenated system (Eary and Rai 1987; Figure 1). Other studies also showed the kinetics to be extremely slow (Chittaladakorn 2013; Schroeder and Lee 1975). Even though this project will not be looking at DO as an oxidant, it should be noted that all experiments began with water saturated with DO.

Chlorine

Since chlorine (Cl_2) is the most common oxidant used in drinking water treatment (Table 1), multiple experiments have been conducted to evaluate its chromium oxidation potential (Bartlett 1997; Brandhuber et al. 2004; Clifford and Chau 1988; Lai and McNeill 2006; Lindsay et al. 2012; Saputro et al. 2011; Sorg 1979; Ulmer 1986). Many of these studies observed variation in Cr(III) oxidation at different pH values. For example, Lai and McNeill (2006) showed that when using a common residual dose of 1 mg/L chlorine in deionized water, the oxidation of 100 μg/L Cr(III) to Cr(VI) varied depending on the pH of the solution. Over a 24-hour period, greater oxidation (roughly 50%) occurred at pH 5.5, compared to only 19% oxidation at a pH of 9. The same trends were noticed when using different water qualities and starting chromium concentrations (Lai and McNeill 2006). Clifford and Chau (1988) and Saputro et al. (2011) also observed more oxidation occurring at a lower pH.

Due to production of H^+, the redox equation for chlorine predicts that oxidation would be favored at higher pH values (Table 2), which is the opposite of trends observed in past Cr(III) oxidation studies. With changes in pH, both chromium and chlorine speciation can change, and chlorine speciation is known to have a significant impact on its oxidation potential (Copeland and Lytle 2014). The pKa value for free chlorine (HOCl) is 7.43, so HOCl dissociates at higher pH values to form the hypochlorite ion

(OCl^-) which is not as strong an oxidant. This causes the oxidation trends to favor lower pH values, which was observed during previous Cr(III) oxidation studies.

Clifford and Chau (1988) and Bartlett (1997) also observed that when organic carbon from natural organic matter (NOM) was present in the water, the Cr(III) did not oxidize as quickly as when the experiments were conducted in deionized water. It was proposed that the humate anions in NOM complexed the Cr(III) to prevent oxidation normally observed when the NOM was not present. It is known that NOM has a free chlorine demand, which also reduces the potential of chromium oxidation due to lower free chlorine concentrations (Clifford and Chau 1988).

In previous experiments, it was noticed that regardless of the water type used, when the experiment was conducted at a pH of 9 the total chromium concentration slowly dropped. This was explained by possible precipitation and settling of the chromium in solution (Lai and McNeill 2006; Figure 3). To provide adequate quality control in the current study, at the end of each experiment a mass accounting was performed for all the chromium used.

Brandhuber et al. (2004) evaluated the use of various chemicals to fully oxidize all chromium present in a water to the Cr(VI) oxidation state, which could then be removed using an anion exchange resin. Evidenced by the multiple experiments discussed above, chlorine was unable to completely oxidize Cr(III) to Cr(VI) within a reasonable time frame. While chlorine is not an effective treatment to provide complete oxidation of chromium, it does still significantly affect chromium speciation.

Monochloramine

Another widely used oxidant in drinking water treatment is monochloramine (NH_2Cl), as it provides a stable residual in a distribution system. Previous experiments have shown that while monochloramine can oxidize chromium, the kinetics are extremely slow compared to chlorine. The study done by Lai and McNeill (2006) showed that even after a period of 200 hours, very little oxidation of Cr(III) was recorded at any of the pH values and water types investigated. Other studies confirmed these slow oxidation kinetics and added that even under the most ideal conditions of pH and chloride concentration, monochloramine would not be an effective oxidizer of Cr(III) (Clifford and Chau 1988, Brandhuber et al. 2004).

Recently, a study was conducted in Glendale, California that included bench and pilot scale experiments and full-scale implementation tests. Contrary to other studies, the results of their experiments showed that monochloramine was an effective oxidant of chromium. During their experiments, it was observed that while using monochloramine doses of 0.5, 1.0 and 2.0 mg/L, the Cr(VI) concentration almost doubled from 28 to 52 μg/L within two days of oxidant addition (Blute and Wu 2013). While this study used similar oxidant doses and water quality as previous studies, the reason for the discrepancies in chromium oxidation potential is unknown.

Chlorine Dioxide

Chlorine dioxide (ClO_2) is generally considered to be effective disinfectant over a wide range of pH values, with slightly better disinfection as the pH increases (Clarke and

Bettin 2006). The redox equations for chlorine dioxide (Table 2) also show that at higher pH values, ClO_2 should be more effective as an oxidant.

While there have been no studies looking specifically at aqueous chromium oxidation by chlorine dioxide (ClO_2) in drinking water systems, Chittaladakorn (2013) studied the effects of chlorine dioxide in contact with stainless steel. While aqueous Cr(VI) formation was observed, it was unclear whether it was leached directly from the stainless steel, or whether Cr(III) was released from the steel and subsequently oxidized to Cr(VI) (Chittaladakorn et al. 2013). This current project will examine the ability of chlorine dioxide to directly oxidize aqueous Cr(III) to Cr(VI).

Potassium Permanganate

Of the oxidants being investigated in this study, it is important to remember that potassium permanganate ($KMnO_4$) is not a disinfectant, but it is used as an oxidant in drinking water treatment. Previous experiments using potassium permanganate showed much faster Cr(III) oxidation times than observed with free chlorine, with nearly complete oxidation within an hour at pH 7 and 9. At pH 5.5, the oxidation of Cr(III) was slower, but still achieved complete oxidation within 4 hours (Lai and McNeill 2006). These trends favoring oxidation at higher pH values agree with the redox equations for $KMnO_4$ (Table 2).

The Brandhuber et al. (2004) study also looked at using potassium permanganate to oxidize all available Cr(III) to Cr(VI). Once in the Cr(VI) oxidation state, an anion exchange resin would effectively capture the chromium. While potassium permanganate would probably be more effective for this type of Cr(VI) removal, difficulties in verifying this technique arose. These difficulties are discussed in greater detail in the Methods and Materials section.

Ozone

There are no reported studies that investigated oxidation of Cr(III) by ozone (O_3). Ozone is a very strong oxidant, so it is expected to oxidize Cr(III) effectively.

Experiment Durations

Using the information and knowledge gained in the previous studies in the literature, a list of expected oxidation times (to reach >85% oxidation) and experiment duration for each of the chosen oxidants under investigation was created (Table 3).

Table 3. Expected Oxidation Times & Experiment Durations for each Oxidant

Oxidant	Doses	Expected Oxidation Time	Duration of Experiment
Chlorine	1 & 4 mg/L	2 Days	5 Days
Monochloramine	1 & 4 mg/L	5 Days	5 Days
Chlorine Dioxide	0.4 & 0.8 mg/L	1-2 Hours	8 Hours
Potassium Permanganate	1 & 5 mg/L	5 Hours	8 Hours
Ozone	1 mg/L	30 Minutes	1 Hour

The duration of the experiments in Table 3 is considerably longer than the expected oxidation times in order to match expected contact times observed in drinking water systems. For example, if chlorine and monochloramine are used to provide a residual in a distribution system, the maximum contact time could be up to 5 days. Since chlorine dioxide is not used to provide a residual in a distribution system, it usually has a maximum residence time of 8 hours in a treatment plant. An 8-hour residence time was also chosen for potassium permanganate, as it is not a disinfectant and is only used within the treatment plant. Ozone was given the lowest duration simply because of the short amount of time it is used in a treatment plant due to its extremely short half-life. Only one dose was chosen for ozone given the extremely fast oxidation at 1 mg/L during preliminary experiments.

OBJECTIVES

The overall objective of this project was to quantify the rate and extent of chromium oxidation over relevant time periods at conditions found in drinking water treatment plants and distribution systems.

Two concentrations of five commonly used oxidants were chosen to represent doses that are typically used in water treatment systems (Table 3). While chromium oxidation has been studied for chlorine, data for both chlorine dioxide and ozone are lacking. There are also few data for Cr(III) oxidation when using monochloramine or potassium permanganate as an oxidant. Bench scale batch experiments for each of these oxidants were conducted under controlled conditions to monitor the oxidation of 10 μg/L Cr(III). This concentration was chosen considering the implementation of California's 10 μg/L MCL for Cr(VI) and the likelihood that federal regulation will be similar. The overall objective was achieved by completing the five specific objectives explained below.

The first objective of this project was to determine the change in chromium oxidation kinetics at the pH values of 5.5, 7, and 9. The values of 5.5 and 9 were chosen to show a range of pH values while the middle value of pH 7 was chosen as a more realistic pH value that would be observed at any given utility.

The second objective of this project was to determine if the oxidation kinetics of chromium are impacted within a range of temperatures (5-16 °C) typically found in drinking water treatment plants and distribution systems.

The third objective of this project was to determine if oxidant dose would affect the oxidation kinetics of chromium. Two doses typically used in drinking water treatment plants and distribution systems were chosen for each investigated oxidant. This objective did not apply to the experiments investigating ozone, since only one dose was investigated.

The fourth objective of this project was to observe the chromium oxidation in a natural water and laboratory generated water qualities. The laboratory generated water qualities were used to provide a baseline for the oxidation experiments, which was compared to the oxidation observed in the natural water quality. Another factor investigated as a part of this fourth objective is how chromium oxidation is affected by the addition of natural organic matter (NOM) into a laboratory generated water.

The fifth and last objective of this project was to investigate the effect of initial Cr(III) concentration. Experiments were conducted with chlorine, monochloramine, and potassium permanganate at a starting Cr(III) concentration of 100 μg/L instead of 10 μg/L. This also allowed for comparisons between the current experiments and previous studies performed with 100 μg/L Cr(III). Completing these objectives provided additional data to allow for a more informed regulation of chromium in drinking water systems.

MATERIALS & METHODS

Bench Scale Experiment Plan

This project investigated the effects that pH (5.5, 7, 9), ambient temperature (5 and 16 °C), varying oxidant doses, water quality (3 different types), and initial Cr(III) concentration have on the oxidation of Cr(III) to Cr(VI) when in contact with the chosen oxidants. These parameters provided a range of conditions that could be experienced in treatment plants and distribution systems.

The bench scale experiments were separated into four separate sets, each focusing on a different initial Cr(III) amount with the other parameters varying as needed to provide a comprehensive list of potential conditions found in drinking water treatment (Table 4).

Table 4. Bench Set Design Plan

Parameter	**Values**			
	Bench Set 1	**Bench Set 2**	**Bench Set 3**	**Bench Set 4**
Oxidant	Cl_2, NH_2Cl, ClO_2, $KMnO_4$, O_3	Cl_2, NH_2Cl, $KMnO_4$	Cl_2	Cl_2
Cr(III) Concentration	10 µg/L	100 µg/L	10 µg/L + 5 mg/L DOC	10 µg/L
pH	5.5, 7, 9	7, 9	7	Ambient
Temperature	5 & 16 °C	16 °C	16 °C	16 °C
Water Quality	DI, Synthesized	Synthesized	Synthesized	Delran

Bench set 1 generated the main workload of this project because all variations of each parameter were examined (Objectives 1, 2, and 3). Bench set 2 extended the understanding of oxidation of Cr(III) at the higher 100 μg/L concentration (Objective 5) and verified the previous oxidation experiments (Lai and McNeill 2006). Bench set 3 also mirrored a previous experiment looking at oxidation with the presence of NOM (5 mg/L DOC), but with the smaller starting Cr(III) amount of 10 μg/L (Objective 4). Bench set 4 experiments were conducted as a joint effort to understand full-scale chromium oxidation in water obtained from American Water's Delran Water Treatment Facility (Objective 4).

Experiment Conditions

pH Monitoring

To provide a broad range of pH conditions experienced in drinking water treatment, the Bench Set Design Plan (Table 4) called for each oxidant to be tested at pH values of 5.5, 7, and 9. Throughout each of the experiments, the pH was monitored periodically to verify that it remained near the desired value for each individual experiment (Table 5).

For the chlorine, monochloramine, and potassium permanganate experiments, the desired pH was maintained within 0.1 or 0.2 pH units. Ozone had slightly more variation, up to 0.4 pH units. In contrast, the average pH values reported for the experiments conducted using chlorine dioxide experienced significant drift throughout the experiments, resulting in large standard deviations. This will be discussed more thoroughly in the chlorine dioxide section in the next section.

Table 5. Average pH for each Oxidant During Experiments

Oxidant	Desired pH	Average pH
Chlorine	5.5	5.5 ± 0.2
	7	7.2 ± 0.1
	9	8.9 ± 0.1
Monochloramine	5.5	5.6 ± 0.2
	7	7.2 ± 0.1
	9	8.9 ± 0.1
Chlorine Dioxide	5.5	6.9 ± 1.4 [a]
	7	7.7 ± 0.5 [b]
	9	8.5 ± 0.3 [c]
Potassium Permanganate	5.5	5.6 ± 0.1
	7	7.1 ± 0.0
	9	8.9 ± 0.1
Ozone	5.5	5.7 ± 0.3
	7	7.3 ± 0.4
	9	8.9 ± 0.0

At experiment start [a]5.6 ± 0.2; [b]7.3 ± 0.2; [c]8.7 ± 0.3

Temperature

Each of the oxidants was tested at 5 and 16 °C to provide a realistic temperature range associated with water treatment and distribution. The 5 °C experiments were performed in a walk-in refrigerator (960 ft^3) at the Utah Water Research Laboratory (UWRL). The water qualities used for the 30-minute ozone experiments were pre-equilibrated in the refrigerator prior to the addition of ozone to ensure the desired water temperature was achieved. The sampling for the ozone was conducted at room temperature due to the short duration of the experiments. A constant temperature room was used for the experiments conducted at 16 °C. Temperatures were monitored in all experiments using a HOBO U23 Pro v2 Temperature/Relative Humidity Data Logger (Bourne, MA) set to collect data in 30-minute intervals (Figure 6).

Figure 6. HOBO Pro v2 external temperature/relative humidity data logger.

All the temperature data that were gathered from the data logger over a 16-week period were combined to show the actual temperature experienced during the oxidation experiments (Table 6).

Table 6. Average Temperature Data for all Oxidation Experiments

Desired Temperature (°C)	Average Temperature (°C)
5	4.69 ± 1.00
16	16.9 ± 5.6

Water Quality

Three water types were investigated. The first was 18-MΩ high purity deionized water with Na_2CO_3 (0.001 M) added to provide background ionic strength and alkalinity (0.106 g/L Na_2CO_3). The second water type was a laboratory generated synthesized water with a high total dissolved solids concentration. This was the same water quality that was used in the previous study (Lai and McNeill 2006) and is made by adding specific chemicals to deionized water (Table 7).

Table 7. Recipe and Concentrations for Synthesized Water

Chemical	Amount Added (g/L)	Concentration (mM)	Contribution to Alkalinity (mg $CaCO_3$/L)
$CaCO_3$	0.1	0.999	100
Na_2CO_3	0.094	0.887	88.7
NaCl	0.078	1.335	n/a
$MgSO_4$	0.149	1.238	n/a

For the bench set 3 experiments, the Suwanee River Fulvic Acid Standard II was purchased from the International Humic Substances Society (St. Paul, MN) and added to the synthesized water. A stock solution of 380 mg/L DOC was used to dose approximately 33 mL into the containers to achieve the necessary 5 mg/L of dissolved organic carbon (DOC), which was the source of the NOM for the experiment. Prior to dosing the fulvic acid into the cubitainers, it was filtered to prevent any complication during Cr(VI) analysis.

The third water type was treated water provided from American Water's Delran (NJ) Water Treatment Facility. This water was investigated because American Water used this same water to conduct pipe loop studies to monitor Cr(III) oxidation in a simulated distribution system. The existing water quality constituents that are present in the treated Delran water can be seen in Table 8.

Table 8. Water Quality Details for Delran Water

pH	Total Organic Carbon (mg/L)	Hardness (Carbonate) (mg $CaCO_3$/L)	Alkalinity (mg $CaCO_3$/L)
6.97	1.29	84.9	30.1

Experiment Setup

Multiple types of plastic and glass containers were tested to find an adequate container that minimized the off-gassing of the oxidants. It was decided to use low-density polyethylene (LDPE) collapsible cubitainer containers (Hedwin; Baltimore, Maryland) (Figure 7). These cubitainers have fairly malleable characteristics, which allowed the containers to collapse as samples were withdrawn. This along with the low permeability of LDPE plastic provided a way to minimize air headspace to reduce off-gassing of chlorine and monochloramine. They also provided the option of connecting a quick-serve tap to make sampling easier.

Figure 7. Hedwin cubitainer with Quick-Serve tap.

To ensure the containers provided a demand-free environment for the oxidant being tested, containers were rinsed with a solution containing the water being tested as well as the same oxidant dose as the experiment being conducted. This minimized organics or sorbed materials that may have exerted an oxidant demand.

For each of the oxidation experiments, either 10 or 100 μg/L of Cr(III) was added (depending on the experiment) into separate cubitainers with specific oxidant doses and the desired water type (the "sample" container). The oxidation of Cr(III) to Cr(VI) was monitored at specific times by taking samples that were preserved to halt any further reactions prior to sample analysis. To ensure that the oxidant residual remained at a high enough concentration to continue oxidizing Cr(III) throughout the time period of the experiment, a separate container containing only the oxidant in the same water type (indicated as the "residual" container) was monitored alongside the sample container. A "control" container with Cr(III) but no oxidant was also monitored in the same water quality to verify the amount of TotCr and Cr(VI) in the absence of the oxidant. An illustration of the experiment setup can be seen in Figure 8, which details the steps taken to set up an experiment that used deionized water (DIW) as the water type with bleach (chlorine) as the oxidant.

Experiments with the different water types and oxidants were set up in a similar manner as Figure 8. The process began with a clean high-density polyethylene (HDPE) plastic bucket filled with 9 liters (L) of DIW. To add a background concentration of alkalinity to the DIW, 0.1 M of Na_2CO_3 (0.106 g/L) was added. The pH of the DIW was then adjusted to the desired pH value by bubbling CO_2 gas into the DIW using a diffuser. The CO_2 gas was used to lower the pH without decreasing the alkalinity of the solution.

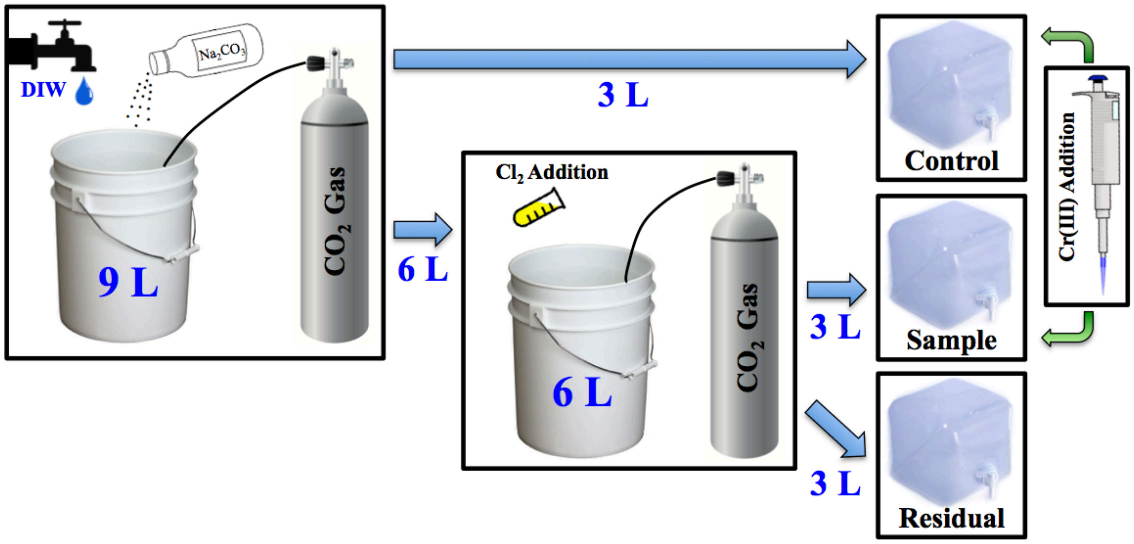


Figure 8. Experiment setup flow-chart using deionized water as the water type and bleach (chlorine) as the oxidant.

Once the pH has been adjusted, 3 L of the water went into the control container. The remaining 6 L of water was dosed with chlorine to meet the desired dose concentration of oxidant for the experiment. During the chlorine and monochloramine experiments, the addition of the oxidant affected the pH, so it was re-adjusted with the CO_2 gas to again reach the desired pH value. Once this was completed, 3 L was poured into the sample container and the remaining 3 L volume was poured into the residual container. The last step of the process was the addition of the 10 μg/L Cr(III) into the control and sample containers, made from chromium(III) chloride hexahydrate salt from Acros Organics (Morris Plains, NJ). At the moment the Cr(III) was added to the sample container, the reaction time clock began.

In order to ensure adequate quality control of the experiments, the process detailed in Figure 8 was repeated three times to provide triplicate sampling, yielding a total of 9 containers for each experimental run. Once the containers were filled, samples were taken at the pre-determined time intervals to monitor the oxidation of Cr(III). An overview of the sampling process can be seen in Figure 9.

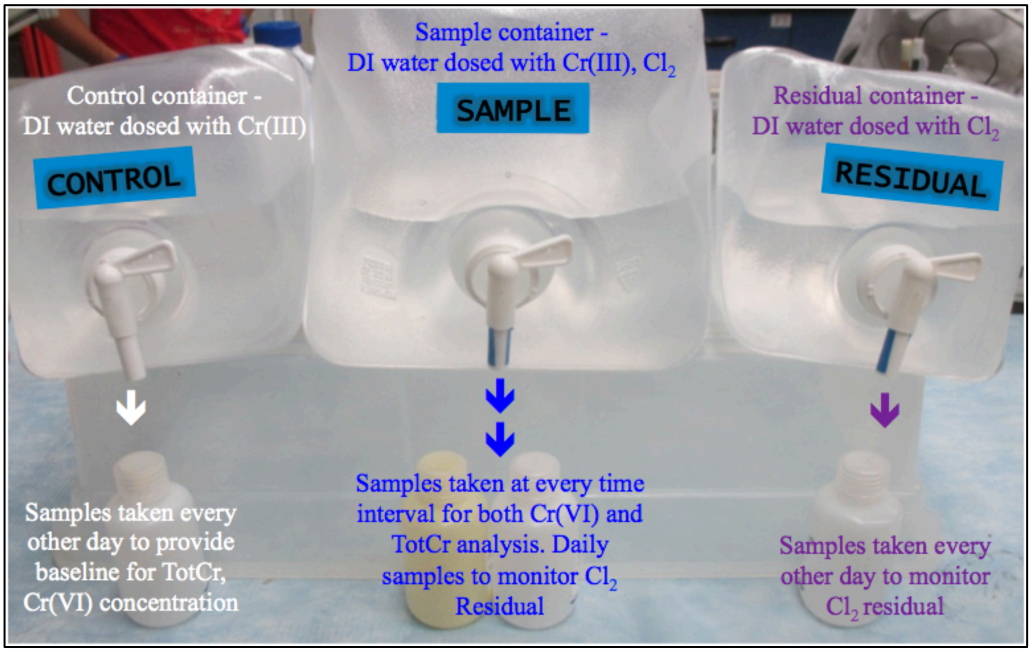


Figure 9. Filled containers for experiment using deionized water as the water quality and bleach (Cl_2) as the oxidant.

The residual container contained only the DIW and the specific chlorine dose. To ensure adequate residual, samples from this residual container were taken on a specific schedule tailored for each oxidant (for example, chlorine residual was monitored every other day). The control container contained only DIW and the desired Cr(III) dose. Samples from the control container were also taken on a specific schedule that was customized for each oxidant (during chlorine experiments, samples were also taken every other day). These control samples were taken to provide baseline concentrations of Cr(VI) and TotCr throughout the experiment. While the residual and control containers did not contribute to understanding the oxidation kinetics, they did provide invaluable data used for quality control to ensure there was adequate residual within the other parameters of the experiment. Other quality control measures are detailed later in this thesis.

The sample container was the most important of the three containers as it was where the actual oxidation of Cr(III) to Cr(VI) occurred. Once the Cr(III) was added into the container already dosed with chlorine, samples were taken at specified time intervals and analyzed for Cr(VI) and TotCr concentrations. Samples were also taken periodically from the sample container to verify that the residual amount of chlorine was adequate for continued oxidation throughout the duration of the experiment (Table 3).

The containers were continuously mixed at the 125-speed setting on a ThermoScientific MaxQ 430 Orbital Shaker Table (Santa Clara, California). When samples were not being taken from the containers, a black cover was put on top of the shaker to help simulate the dark conditions that are present in a distribution system (Figure 10).

Figure 10. ThermoScientific MaxQ 430 HP Orbital Shaker tables. Left - Uncovered with cubitainers. Right - Covered to exclude ambient light.

Materials to Prepare Oxidants & Analytical Methods

Free chlorine from household bleach was utilized to provide the chlorine for the experiments. To reach the desired doses of 1 and 4 mg/L, 8 mL of 1:100 diluted bleach and 8 mL of 1:25 diluted bleach was used to provide the dose in the containers (sample and residual containers only). The household bleach was used within one month from its purchase date to prevent problems caused by the diminishment of free chlorine. Free chlorine concentrations were analyzed using Hach method 8021 and the Hach DR2800 Spectrophotometer. This method has a minimum reporting limit (MRL) of 0.02 mg/L as Cl_2 and a maximum range of 2.0 mg/L as Cl_2 (Hach 2014a). As such, dilutions of at least 1:2 were necessary for the experiments that required the larger 4 mg/L dose.

Concentrated ammonium hydroxide (14.5 M NH_4OH) was added (31.7 mL) to 100 mL of diluted household bleach (1:100) to create a monochloramine (NH_2Cl) solution. The addition of NH_4OH converted the available free chlorine in solution into monochloramine. Similar to the chlorine dosing, 8 mL of 1:100 NH_2Cl solution and 8 mL of 1:25 NH_2Cl was used to provide the 1 and 4 mg/L dose in the containers (sample and residual containers only). The solution must be mixed and dosed quickly as chlorine can escape as a gas once mixed with NH_4OH. The same working time of one month with the bleach pertained to the preparation of monochloramine. Monochloramine was measured by using the same 8021 Hach method for free chlorine as well as the 8167 Hach method for total chlorine. The final monochloramine concentration was found by subtracting the free chlorine from the total chlorine. The MRL for the 8167 Hach method for total chlorine is also 0.02 mg/L, but the maximum range is also 2.0 mg/L and also required dilutions of at least 1:2 for the higher monochloramine dose of 4 mg/L (Hach 2014b).

Chlorine dioxide (ClO_2) solution (3000 mg/L) was obtained from CDG Environmental (Bethlehem, PA). A working stock solution of 100 mg/L ClO_2 was made by dosing 34 mL of the concentrated ClO_2 solution into 1 L of deionized water. In order to achieve the desired doses (0.4 and 0.8 mg/L) of ClO_2, 0.2 and 0.4 mL of the working stock solution were added to the sample containers. Chlorine dioxide concentrations were monitored using Hach method 10126 and the Hach DR2800 Spectrophotometer. The MRL for this method is 0.04 mg/L as ClO_2 and the maximum range is 5.0 mg/L as ClO_2, so there was no need for dilutions since the largest dose that was investigated was 0.8 mg/L ClO_2 (Hach 2014d).

Potassium permanganate ($KMnO_4$) solutions were made using potassium permanganate salt, which when in solution has a pink color. Permanganate (MnO_4^-) is the oxidation state of manganese that oxidizes chromium. When permanganate reacts, it is reduced to either Mn^{+2} or Mn^{+4} and loses its pink color. This is helpful when monitoring the residual of $KMnO_4$. Even though there is not a specific residual monitoring method, it is recommended by Hach to measure total manganese (Mn) and absorbance values at a wavelength of 530 nm and apply a conversion equation (Hach 2015). In this study, total Mn concentrations were measured by inductively coupled plasma-mass spectroscopy (ICP-MS, Agilent 7700x) and MnO_4^- was monitored using a Shimazdu UV-1700 Spectrophotometer (Columbia, MD) at a wavelength of 530 nm (Figure 11).

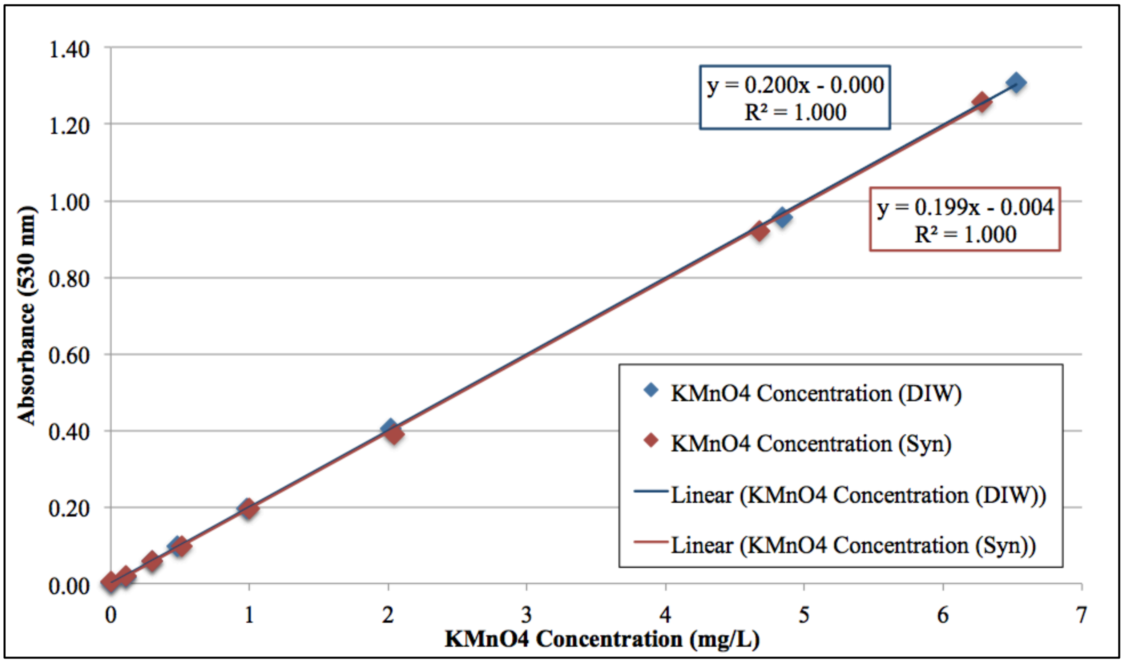


Figure 11. Potassium permanganate ($KMnO_4$) absorbance curve at 530 nm in both deionized and synthesized water qualities.

The absorbance was tested in both the deionized and synthesized water qualities and compared to the total Mn concentration that was verified by ICP-MS analysis. From Figure 11 it is observed that both water qualities yielded the same equation, so the absorbance was not affected by water quality.

Ozone (O_3) was dosed into solution using a Clear Water Tech, Inc. (San Luis Obispo, CA) ozone gas generator (Figure 12). This generator requires the use of pure oxygen and has the capability to generate aqueous ozone concentrations as high as 20 mg/L O_3.

Ozone was directly bubbled into the cubitainers in order to reach the desired concentration of 1 mg/L O_3. Preliminary experiments were conducted at each of the pH values in both water qualities to find the exact amount of time O_3 would need to be

Figure 12. Clear Water Inc. ozone generator.

bubbled to reach the desired concentration. With the ozone generator set to the highest power setting and the flow of oxygen at 1 L/min, it required 3-7 seconds to reach the desired concentration of 1 mg/L O_3 in each of the water qualities.

The concentration of ozone was measured using Hach method 8311 (Hach 2014c). This method uses a vacuum-sealed vial (AccuVac Ampul) with potassium indigo trisulfonate dye, which creates an indigo color. When this dye comes in contact with ozone, the dye pigments are scavenged and the sample becomes more and more colorless and the absorbance decreases, depending on the concentration of the ozone. The high range for this method was used, which has an MRL of 0.1 mg/L O_3 with a maximum concentration of 1.5 mg/L O_3.

Residual Monitoring

Each oxidant was measured at the start and periodically through the experiment to verify enough oxidant remained. In some cases, the oxidant concentration decreased over the duration of the experiment. To illustrate these changes, Figure 13 displays the average changes in chlorine (Cl_2) residual that were monitored during the experiments.

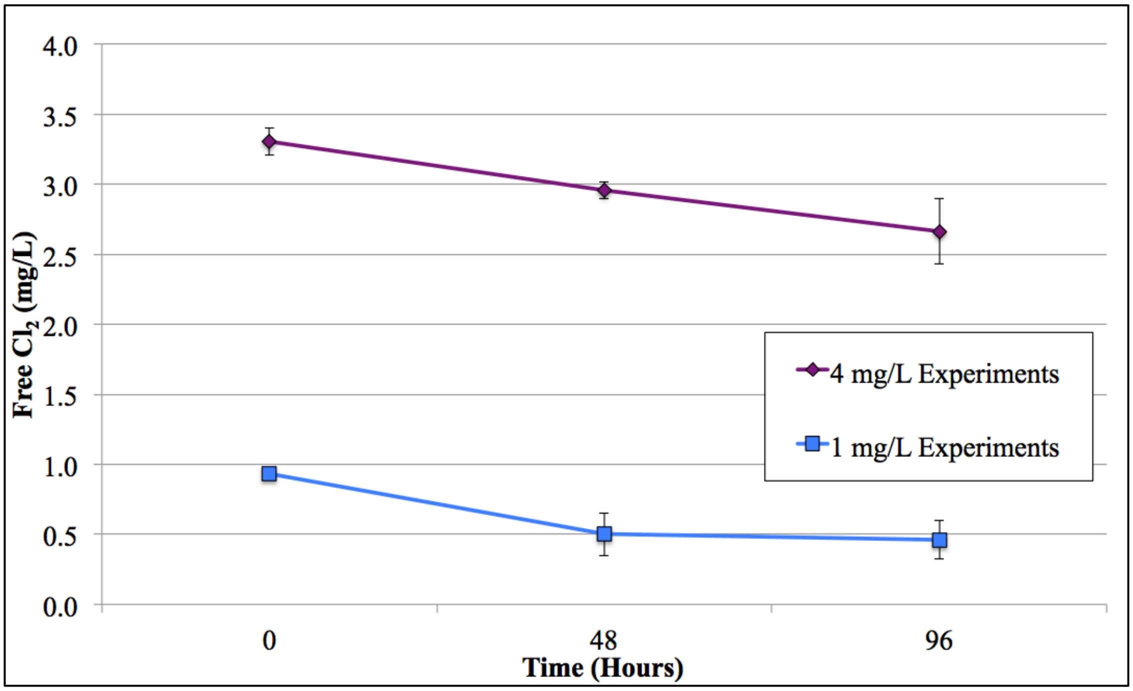


Figure 13. Chlorine residual results for both experiment doses. Error bars are standard deviation of all measurements.

Over the duration of the chlorine experiments, the residual in the 4 mg/L Cl_2 experiments dropped more than 20%. This is even more pronounced in the 1 mg/L Cl_2 experiments, where the residual dropped approximately 50% from its original starting concentration. Even considering the observed decrease in Cl_2, there was still significantly more oxidant than soluble Cr(III) to allow oxidation to continue.

The initial and average concentration of each investigated oxidant is shown in Table 9. There were no significant differences in residual as a function of pH, temperature, or water quality, so values for all experiments at each oxidant dose are combined.

Table 9. Average Residual Data for each Oxidant During all Experiments

Oxidant	**Desired Residual (mg/L)**	**Average Starting Residual (mg/L)**	**Average Residual Over Experiment Duration (mg/L)**
Chlorine	1	0.9 ± 0.1	0.6 ± 0.3
	4	3.3 ± 0.5	3.0 ± 0.3
Monochloramine	1	0.9 ± 0.1	0.9 ± 0.1
	4	2.7 ± 0.2	2.6 ± 0.1
Chlorine Dioxide	0.4	0.4 ± 0.0	0.2 ± 0.2
	0.8	0.7 ± 0.1	0.4 ± 0.4
Potassium Permanganate	1	0.9 ± 0.0	0.9 ± 0.0
	5	Not Studied	Not Studied
Ozone	1	1.3 ± 0.3	0.4 ± 0.5

The drop in oxidant residual could be caused by many factors including autocatalytic degradation, off gassing, loss from demand in containers, and the actual chromium oxidation occurring that consumes residual. These changes created some variation in the residual averages, but detectable residual was maintained throughout each experiment, and residual concentrations were always in excess of the stoichiometric amount required for oxidation (Table 2).

The higher dose of potassium permanganate (5 mg/L) was not investigated as it caused interference and compromised the ability to confidently analyze Cr(VI) in the samples. This interference will be discussed later in this section.

Chromium Analysis

Since this project required extensive knowledge of the concentrations of each chromium oxidation state throughout each experiment, it was necessary to determine concentrations of Cr(III), Cr(VI), and total chromium (TotCr) in the sample solution. There is currently no approved method by the EPA for Cr(III) analysis, so concentrations of Cr(III) were determined by the difference between TotCr analysis and Cr(VI) analysis. When possible, experiment samples were collected into pre-preserved bottles as discussed below.

All sampling equipment was carefully cleaned and rinsed in an acidic cleaning solution (1:2:9 nitric acid:hydrochloric acid:deionized water), rinsed thoroughly with deionized water, and air-dried. All chemicals used for preservation or analyses were trace metal grade. Filtered deionized water (18.3 MΩ) was used as reagent water for standards and other sampling processes to limit contamination or interference.

TotCr Analysis

TotCr samples were preserved by the addition of a concentrated nitric acid solution to the sample water (1% v/v) to establish a pH less than 2. This provided a holding time of 6 months to complete analysis. All TotCr concentrations were measured using a collision-cell mode modification to EPA Method 200.8 (USEPA 1994) using an Agilent 7700x Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Figure 14). This ICP-MS was equipped with a helium collision-cell mode to reduce polyatomic interferences and some matrix effects. The calculated MRL for this procedure is 0.2 μg/L.

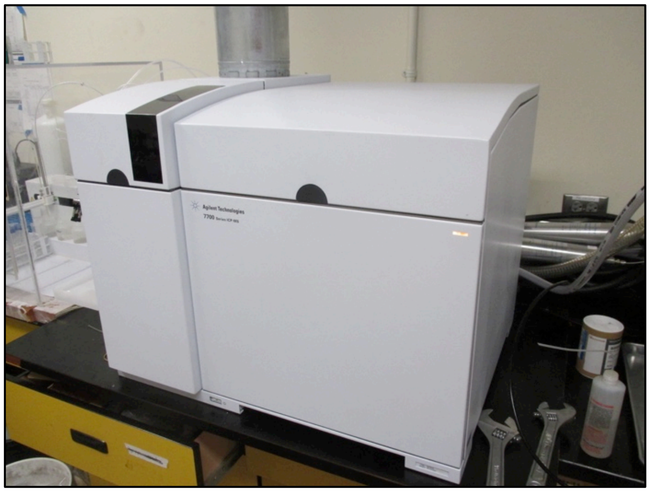


Figure 14. Agilent 7700x ICP-MS.

Samples from the chlorine, monochloramine, chlorine dioxide, and potassium permanganate experiments were digested prior to ICP-MS analysis. This digestion was done using an adaptation of EPA Standard Method 3050B, which uses concentrated nitric acid to ensure any particulate chromium will solubilize. After 0.5 mL of concentrated nitric acid is added to the 50 mL sample (1% by volume), it is heated with a hotplate (~ 90°C) to allow digestion to occur. The sample remained on the hotplate until the volume was reduced to between 2-10 mL (roughly 6-8 hours). The sample was then cooled and brought back to the original volume (50 mL) with deionized water (APHA et al. 1992). The sample was then ready to be analyzed using the ICP-MS. For the ozone experiments, the TotCr samples did not undergo the same digestion process. This was due to logistical concerns due to the short half-life of ozone as well as large volume requirements (50 mL for each sample). Instead, the TotCr samples for the ozone experiments were pre-preserved with concentrated nitric acid (5% v/v). This was done to lower the pH to a value less than 2, which helps to keep the chromium species in solution. To ensure that the chromium remained in solution, these ozone samples were also soaked in a hot water bath (75°C) for 30 minutes.

Cr(VI) Analysis

During the chlorine and monochloramine experiments, the Cr(VI) samples were preserved by adding an ammonia buffer to sample water (1% v/v) to establish a pH range 9 - 9.5 and slow down the reaction kinetics (USEPA 2011). During the O_3 experiments, 0.1 M NaOH (5% v/v) was used to quench the ozone in the sample. The use of NaOH as a quenching agent was effective in both stopping the chromium oxidation in the sample and preventing O_3 from causing interference in the Cr(VI) analysis. All Cr(VI) concentrations were measured using EPA Method 218.7 using a Dionex ICS-1600 ion chromatography instrument (Figure 15).

Figure 15. Dionex ICS-1600 Ion Chromatography instrument.

This instrument employs a post-column reaction where the exiting sample mixes with 1,5-diphenylcarbazide, which is a dye that complexes with Cr(VI) to create a pink color. Following the mixing, the absorbance is read by a spectrophotometer using the UV-Vis detector at a wavelength of 530 nm to quantify the Cr(VI) (USEPA 2011). The established MRL for this procedure is 0.02 µg/L and according to the method, the preservation only provides a holding time of 14 days from the time of sampling.

Potassium permanganate ($KMnO_4$) presented some complications for Cr(VI) analysis because $KMnO_4$ in solution has a pink color similar to the Cr(VI) complex with the diphenylcarbazide indicator (Appendix A). To overcome this issue, previous studies created Cr(VI) calibration curves with varying concentrations of potassium permanganate. The individual concentrations from these calibrations were then used to create a correction factor that could be applied to absorbance values measured on the spectrophotometer (Lai and McNeill 2006).

In this current study, because samples containing permanganate could not be analyzed for Cr(VI) using ion chromatography, samples were instead directly analyzed on a spectrophotometer with a 10 cm path-length cell (Shimazdu UV-1700 Spectrophotometer, Figure 16). This was done by adding 5 mL of the liquid diphenylcarbazide solution (0.5 g diphenylcarbazide dissolved into 100 mL of methanol and mixed with 1 L of 2.8% v/v H_2SO_4) to 20 mL of the sample to allow the reaction to occur. This reaction, which creates the aforementioned pink color, was then monitored for absorbance at a wavelength of 530 nm.

The spectrophotometer in Figure 16 was chosen for its capability to read absorbance values from a 10 cm path-length cell. This longer path length allowed for samples with lower concentration of Cr(VI) to be measured. The MRL of this method using this spectrophotometer was calculated to be 0.8 μg/L Cr(VI).

Figure 16. Shimazdu UV-1700 PharmaSpec UV-Visible Spectrophotometer instrument with 10 cm path-length cells.

Calibration curves with Cr(VI) standards were made in the two investigated water qualities alone, and then with additions of 1 and 5 mg/L of $KMnO_4$. The calibration done in the deionized water quality can be seen in Figure 17 while the calibration performed in the synthesized water is displayed in Figure 18.

In both the deionized (Figure 17) and synthesized (Figure 18) water qualities, the higher concentration of 5 mg/L $KMnO_4$ caused significant suppression of absorbance, falsely decreasing the measured Cr(VI) concentration. This was assumed to be caused by interference between the 5 mg/L dose of $KMnO_4$ and the diphenylcarbazide used to complex the Cr(VI). In the Lai and McNeill (2006) study, a correction factor was used to compensate for the suppression.

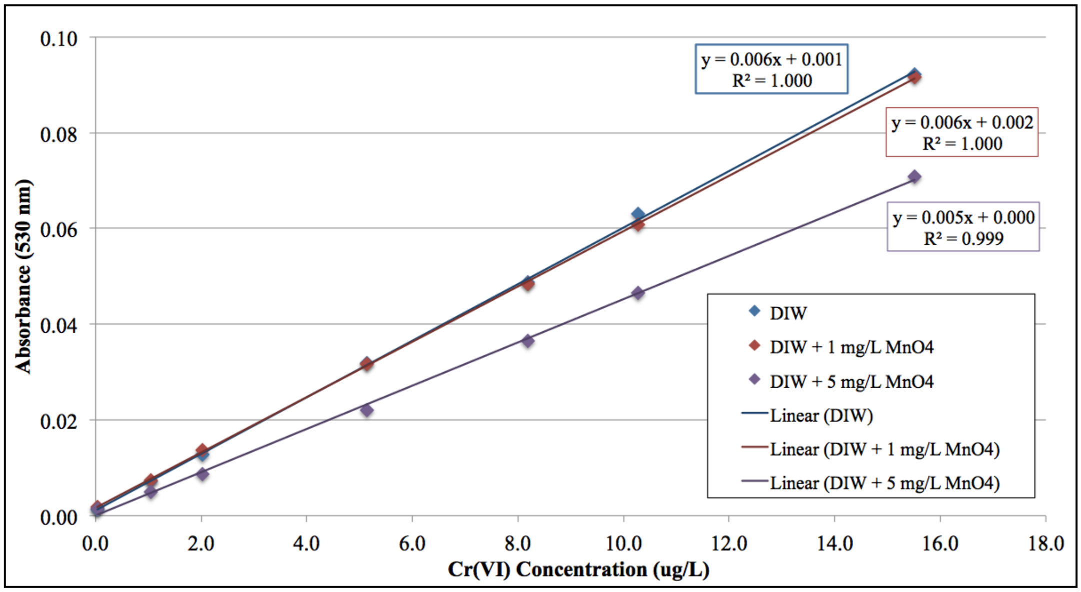


Figure 17. Calibration for Cr(VI) in the deionized water (DIW) quality in the presence of 1 and 5 mg/L $KMnO_4$.

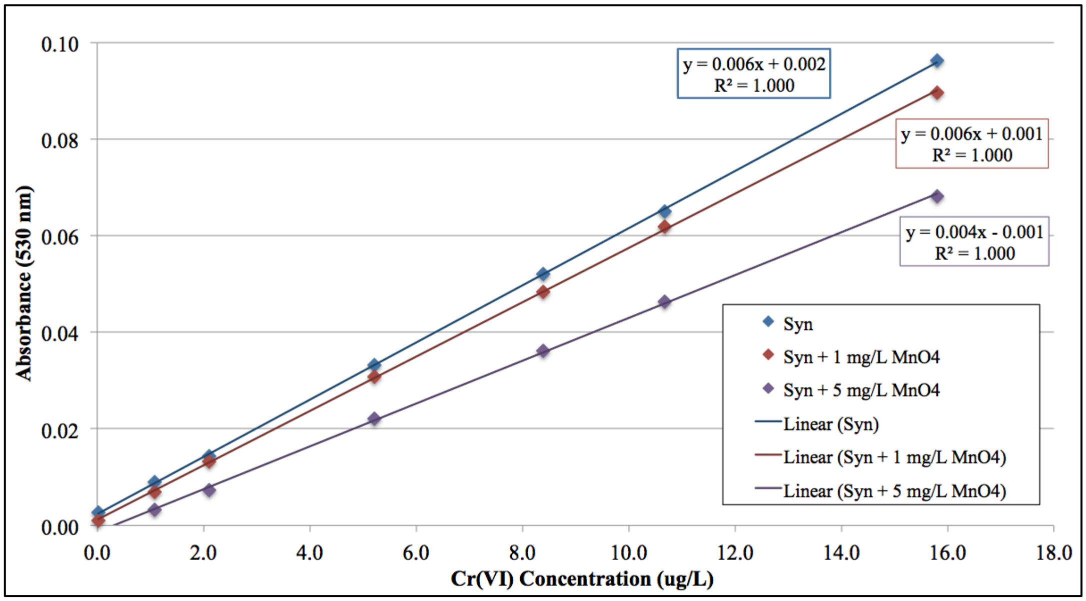


Figure 18. Calibration for Cr(VI) in the synthesized water quality in the presence of 1 and 5 mg/L $KMnO_4$.

However, for the lower Cr(VI) concentrations used in this current study, it was determined that 5 mg/L $KMnO_4$ caused too great of an interference and compromised the analytical confidence. Accordingly, only the 1 mg/L $KMnO_4$ dose was used in the experiments.

Similar to the analytical issues of $KMnO_4$, preliminary experiments showed that chlorine dioxide (ClO_2) also caused interference when attempting to analyze Cr(VI) by ion chromatography. Using the same method outlined above, calibration curves with Cr(VI) standards were made in the two investigated water qualities alone, and then with additions of 0.4 and 0.8 mg/L of ClO_2. The same ratio of 5 mL diphenylcarbazide solution to 20 mL sample was then added to each of the standards to complex with the Cr(VI) and measure the absorbance at 530 nm. The calibrations done for ClO_2 in the deionized water quality can be seen in Figure 19 while the calibration performed in the synthesized water is displayed in Figure 20.

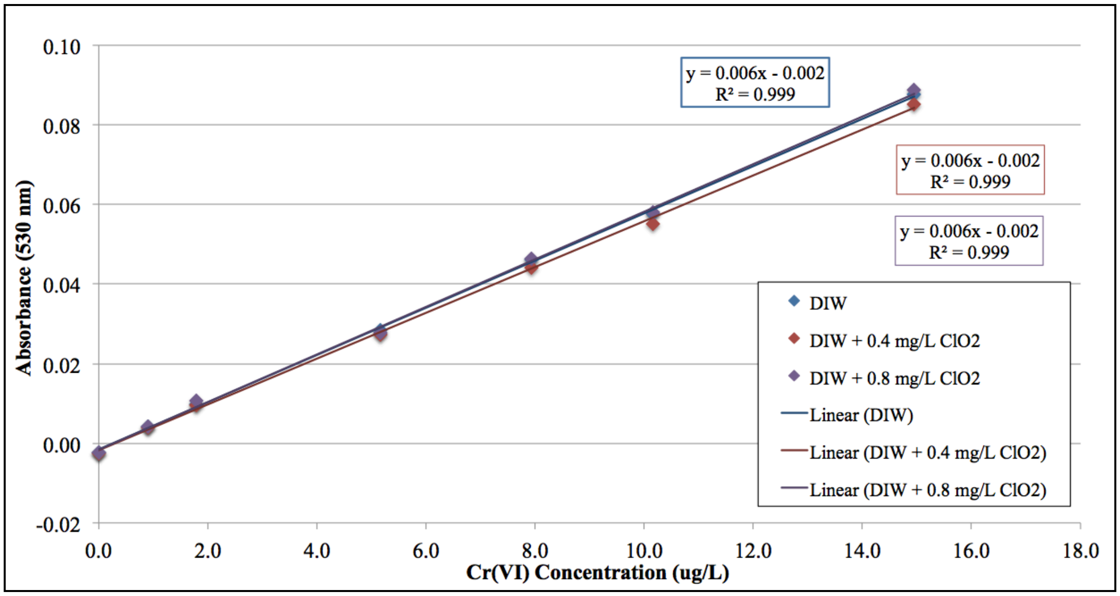


Figure 19. Calibration for Cr(VI) in the deionized water (DIW) quality in the presence of 0.4 and 0.8 mg/L ClO_2.

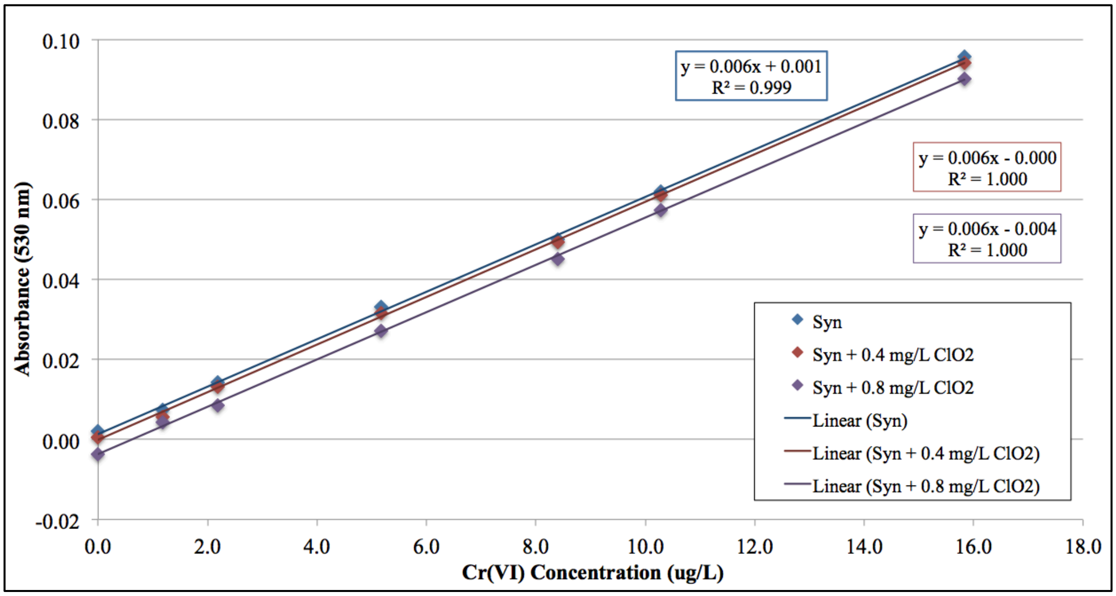


Figure 20. Calibration for Cr(VI) in the synthesized water quality in the presence of 0.4 and 0.8 mg/L ClO_2.

The calibrations generated in the different ClO_2 dose scenarios in Figure 19 all provided the same equation. As such, it is assumed that these two doses do not affect the spectrophotometric analysis of the chromium by using diphenylcarbazide. In the calibrations performed in the synthesized water quality (Figure 18), each dose scenario yielded the same slope, but had slightly varied intercepts. These variations were not far from the intercept value found for the calibration completed without the addition of ClO_2, providing the confirmation that both dose scenarios would be acceptable for experimentation.

Quality Assurance & Quality Control

To verify that the data gathered in the analyses of Cr(VI) and TotCr concentrations are statistically viable, all instrument processes and data went through strict quality control and quality assurance measures. Both the IC and ICP-MS had routine calibrations conducted each time the instrument was used with at least 5 concentration levels. In order for the calibration to be used for analyses, the R^2 was always at or above 0.999. The IC was also periodically checked with a lab-generated standard to ensure that the MRL (0.02 μg/L) was accurately measured.

Quality control and assurance measures were also taken during manual spectrophotometer analysis for the chlorine dioxide and potassium permanganate experiments. To verify that the spectrophotometer was reading similar values to what was found during the calibration process, throughout each experiment the absorbance of a lab generated standard of 1 μg/L Cr(VI) was checked.

To verify that the IC and ICP-MS instruments generated accurate data, a purchased external reference solution of 1 μg/L Cr (High Purity Standards, Charleston SC) was used to verify that the concentrations measured were within ±15 % of the certified standard concentration. During each analysis run, a continuing calibration verification (CCV) of two selected calibration standards was run between every 10 samples as independent samples to verify the continuing accuracy of the instrument.

To aid in the analyses of samples, every 10 samples contained a spiked sample (done in duplicate), which consisted of a known concentration of chromium spiked into the chosen samples. This spiked sample was verified with duplicates of a blank sample spike (BSS). These BSS samples were created by spiking a known concentration of chromium into a known volume of laboratory certified deionized water. Once the BSS and spiked samples were run, they were verified with both percent recovery (85 - 115%) and relative percent difference (<15%) equations. The spiked samples were also checked to verify that the percent recovery and relative percent difference equations were acceptable and the data generated were acceptable.

Data Analysis and Statistics

First Order Kinetics

The oxidation kinetics of Cr(III) to Cr(VI) can be modeled mathematically using differential equations. Models using zero order reactions were done by Lee and Hering (2005), but were created primarily to investigate chromium dissolution, not oxidation. Other studies investigating chromium oxidation had success using first-order reactions to model the Cr(III) oxidation and to predict the concentrations of Cr(III) and Cr(VI) with respect to time (Bartlett 1997; Lai 2004; Lindsay et al. 2012). Second order reactions have also been used to model Cr(III) oxidation (Lai 2004).

For this project, because the oxidant concentration remained in excess, the decrease in Cr(III) is assumed to follow pseudo first order kinetics with a rate constant, k (1/time). Equation 1 describes the rate where C is the concentration of Cr(VI) (μg/L).

$$dCr(III)/dt = -kCr(III) \tag{1}$$

This equation can then be integrated to find the Cr(III) concentration with respect to time (Equation 2).

$$Cr(III) = Cr(III)_{initial} * e^{-kt} \tag{2}$$

Since there is not an analytical method to measure Cr(III), and TotCr is defined as the summation between Cr(III) and Cr(VI), Equation 2 can be rearranged to reflect the Cr(VI) concentration (Equation 3).

$$Cr(VI) = TotCr(1 - e^{-kt}) \qquad (3)$$

Using this first order equation and the rate constant k, the expected trends of Cr(III) and Cr(VI) concentration with respect to time for a generic oxidation experiment can be seen in Figure 21. Time zero is defined as the time when Cr(III) comes in contact with an oxidant.

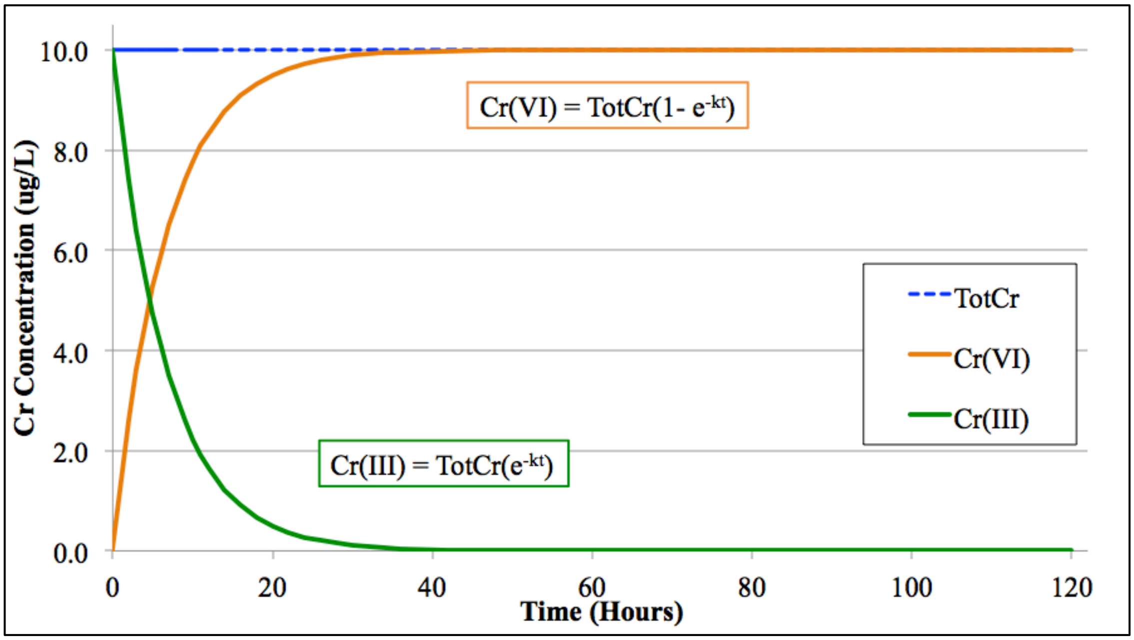


Figure 21. Expected chromium concentrations vs. time when in the presence of an oxidant.

However, the model in Figure 21 that was generated using Equation 3 is only valid when the TotCr concentration remains constant (at the initial Cr(III) concentration). At higher pH values, precipitation of Cr(III) as $Cr(OH)_{3(s)}$ may decrease the measured TotCr amount. Considering the maximum Cr(VI) concentrations ($Cr(VI)_{max}$) observed during the experiments were within one standard deviation of the Cr(VI) concentration plateau observed at the end of the experiments, this $Cr(VI)_{max}$ value was used instead of the TotCr concentration (Equation 4). This solved the problem caused by the precipitation observed in some of the experiments.

$$Cr(VI) = Cr(VI)_{max}\,(1 - e^{-kt}) \tag{4}$$

This is similar to the approach of Lindsay et al. (2012), who used the observed plateau of the maximum Cr(VI) during each experiment as the upper bound asymptote of the equation (modeled in Figure 22).

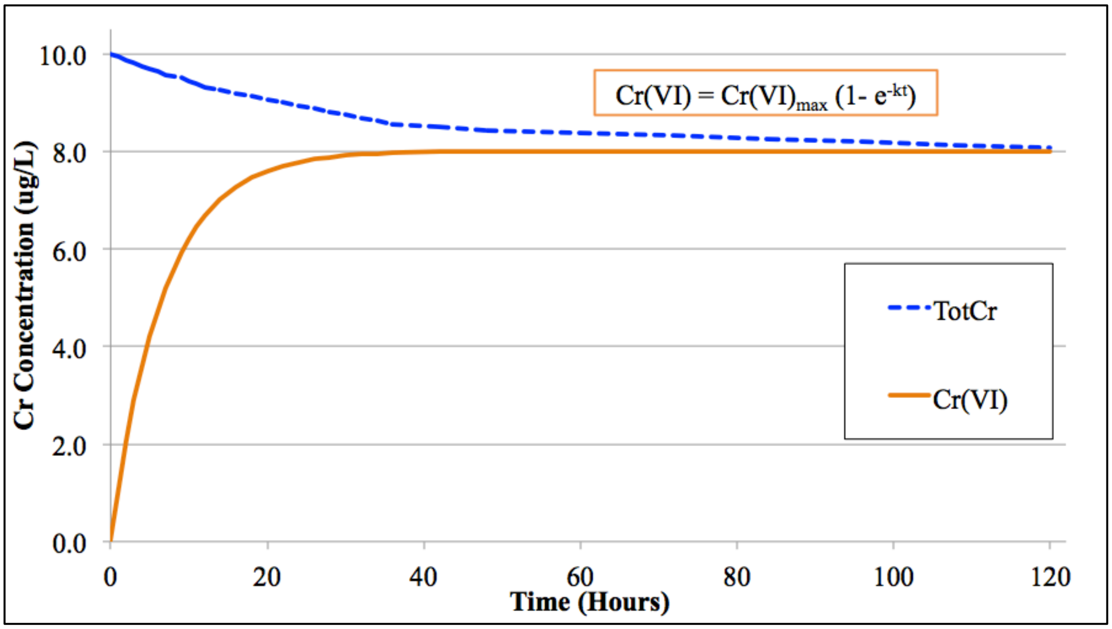


Figure 22. Expected Cr(VI) concentration vs. time when precipitation of TotCr is present.

Using the observed Cr(VI) and TotCr data at each time interval, the rate constant k was found by algebraically rearranging and log transforming Equation 4 to linear form, shown in Equation 5.

$$-kt = \ln\,(1 - (Cr(VI) / Cr(VI)_{max}) \tag{5}$$

With the Cl_2 experiments, the majority of the Cr(III) oxidation occurred during the first six measurements (0-7 hour) of each experiment. As a result, the triplicate data for these first six measurements were plotted according to Equation 5 and a linear regression was performed. Varying amounts of data were used for each of the other investigated oxidants, depending on how fast the oxidation kinetics were. For each linear regression, the y-intercept was forced to zero to satisfy the assumption that there was no background concentration of Cr(VI) before the oxidant was added. The resultant slope of the regression was equal to the rate constant (k) of the linear transformation.

Statistical Analysis

To check for significant differences in rate constants and chromium concentration, further analyses on the data were conducted using the statistical software, R. When applicable, triplicate data were analyzed using Welch two sample t-tests to determine if there was a statistically significant difference between data points. A p-value ≤ 0.05 was used to determine significance.

For the experiments that used rate constants to create models of Cr(VI) formation, R was used to generate qqnorm plots to verify that the data were in fact normally distributed. To verify that the residuals were normally, identically, and independently distributed (NIID), residual plots were also generated using R for each set of data (Appendix B).

Using R, 95% confidence intervals were calculated for the rate constant (k) found for each applicable experiment. Overlap of 95% confidence intervals was used as a preliminary indicator that rates of Cr(VI) formation were not significantly different.

RESULTS & DISCUSSION

Oxidation Results

To explain how each objective was achieved while also explaining the oxidation trends that were observed for each parameter, the details of the experiments conducted are presented for each oxidant. The objectives that were accomplished are detailed during the discussion of each oxidant.

Chlorine

Chlorine (Cl_2) is widely used in water treatment (Table 1) especially as a disinfectant residual in distribution systems. The potential for chromium oxidation as a result of chlorine addition is of great interest as it could result in the increase of a probable carcinogen in drinking water.

To summarize the chlorine experiments that were conducted with the lower Cr(III) starting concentration of 10 μg/L, tables for the deionized water (Table 10) and synthesized water (Table 11) are shown. These tables consist of the rate constant (k) values with their respective 95% confidence intervals, the maximum Cr(VI) concentration, and the total chromium remaining at the end of each experiment. The maximum Cr(VI) concentration that is indicated for each experiment is the value that was used in Equation 3 in place of the TotCr value.

Table 10. Oxidation Summary for Chlorine in Deionized Water

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (µg/L)	Total Chromium Remaining (µg/L)
5 °C Temperature	4 mg/L	pH 5.5	0.058	0.055 ~ 0.060	7.9 ± 0.2	9.0 ± 0.2
		pH 7	0.160	0.153 ~ 0.166	7.4 ± 0.0	8.7 ± 0.2
		pH 9	0.125	0.112 ~ 0.138	5.3 ± 0.1	9.7 ± 0.5
	1 mg/L	pH 5.5	0.031	0.028 ~ 0.034	2.6 ± 0.1	8.8 ± 0.1
		pH 7	0.038	0.034 ~ 0.042	4.4 ± 0.9	9.0 ± 0.3
		pH 9	0.145	0.126 ~ 0.164	2.6 ± 0.2	8.7 ± 0.6
16 °C Temperature	4 mg/L	pH 5.5	0.090	0.087 ~ 0.093	9.3 ± 0.4	8.9 ± 0.3
		pH 7	0.249	0.228 ~ 0.271	8.2 ± 0.1	8.0 ± 0.1
		pH 9	0.155	0.138 ~ 0.171	7.6 ± 0.3	7.9 ± 0.5
	1 mg/L	pH 5.5	0.023	0.022 ~ 0.024	4.1 ± 0.1	5.5 ± 0.4
		pH 7	0.105	0.090 ~ 0.120	3.5 ± 0.1	4.8 ± 0.7
		pH 9	0.132	0.122 ~ 0.141	5.4 ± 0.4	7.1 ± 0.3

Table 11. Oxidation Summary for Chlorine in Synthesized Water

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (µg/L)	Total Chromium Remaining (µg/L)
5 °C Temperature	4 mg/L	pH 5.5	0.143	0.138 ~ 0.147	9.6 ± 0.2	9.8 ± 0.1
		pH 7	0.233	0.218 ~ 0.249	9.8 ± 0.3	9.8 ± 0.2
		pH 9	0.190	0.170 ~ 0.210	3.7 ± 0.5	8.5 ± 0.2
	1 mg/L	pH 5.5	0.047	0.041 ~ 0.052	6.1 ± 1.1	9.1 ± 0.1
		pH 7	0.106	0.100 ~ 0.111	7.3 ± 0.4	9.3 ± 0.4
		pH 9	0.151	0.136 ~ 0.166	4.2 ± 0.2	8.4 ± 0.7
16 °C Temperature	4 mg/L	pH 5.5	0.288	0.279 ~ 0.297	9.6 ± 0.1	9.9 ± 0.1
		pH 7	0.249	0.235 ~ 0.263	9.9 ± 0.5	10.1 ± 0.5
		pH 9	0.199	0.182 ~ 0.216	3.3 ± 0.3	9.1 ± 0.5
	1 mg/L	pH 5.5	0.062	0.058 ~ 0.065	9.3 ± 0.2	9.7 ± 0.3
		pH 7	0.115	0.098 ~ 0.132	8.0 ± 0.5	9.6 ± 0.3
		pH 9	0.160	0.141 ~ 0.179	3.3 ± 0.2	3.5 ± 0.4

The rate constants provided in these summaries were used to model the amount of Cr(VI) concentration at any time (within the 120-hr experiment) for each experiment.

The observed experiment data and these models were then used to accomplish the objectives of this project as described below.

Effect of pH

A typical experimental result for Cr(III) oxidation in deionized water at the warmer temperature and higher dose of Cl_2 is shown in Figure 23, along with the modeled results using values from Table 10.

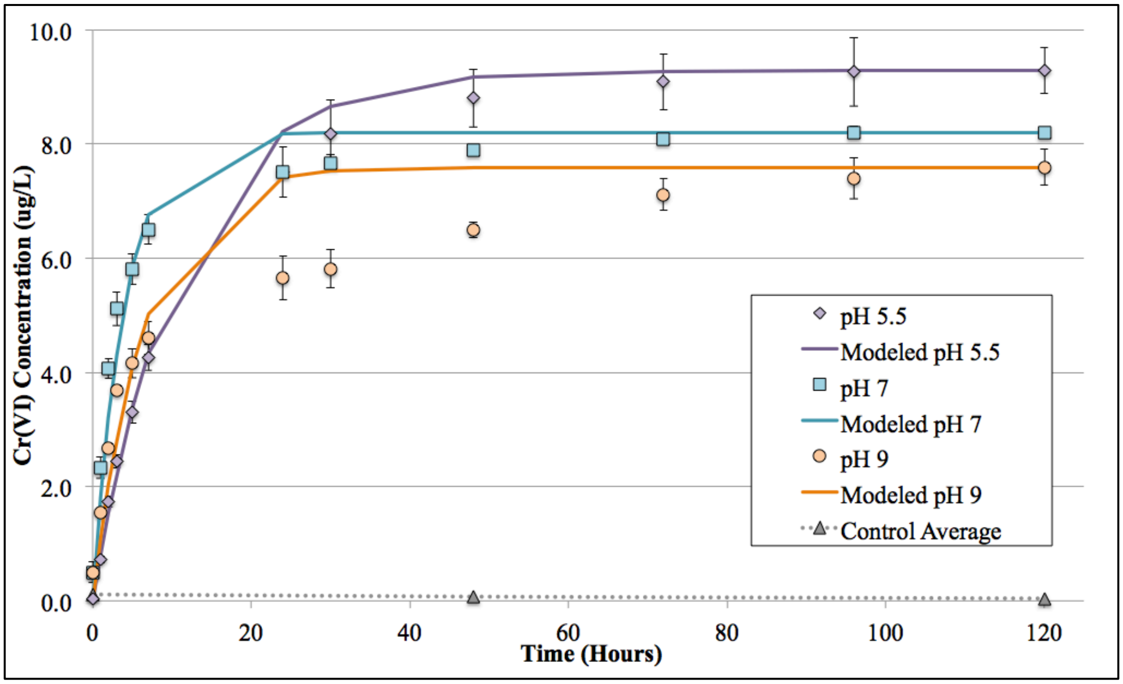


Figure 23. Cr(VI) results & modeling for 4 mg/L Cl_2 in deionized water at 16 °C. Error bars are standard deviation of triplicate measurements.

To verify there was no Cr(VI) formation in the absence of chlorine, the average concentration of Cr(VI) monitored in the control cubitainer during each of the pH experiments is shown to be less than 0.1 μg/L Cr(VI). For each of the pH values in Figure

23 the corresponding models are accurate for the first 7 hours of the experiments. This is expected as the first six measurements were used to generate the rate constants to create these models. Since $Cr(VI)_{max}$ was used as the upper bound asymptote of the model (Equation 3), each of the models is also accurate for the last 40 hours of the experiment. However, these models are not as accurate at the “knee of the curve” between the 8-80 hour time values.

During the first 7 hours, the Cr(III) oxidation rates (Table 10) show that the Cr(VI) formation was fastest during the experiments conducted at pH 7 with pH 9 being slower and pH 5.5 being the slowest. However, the trends from the oxidation rates did not match the Cr(VI) concentration observed at the end of the experiment.

While the Cr(III) oxidation rate was fastest at pH 7, the Cr(VI) concentration eventually leveled off around 8.2 μg/L, which was not the highest concentration of Cr(VI) observed among the different pH values. The highest concentration of 9.3 μg/L Cr(VI) occurred at pH 5.5 while the experiments at pH 9 had the lowest maximum Cr(VI) concentration (7.6 μg/L). This was as expected; the lower pH values had the higher total oxidation. This was initially attributed to the speciation of chlorine, with the less effective OCl^- species being dominant at pH 9 (Copeland and Lytle 2014). However, an important factor to take into account is precipitation.

With the increase in pH, Cr(III) can precipitate as $Cr(OH)_{3(s)}$, even in the deionized water quality (Figure 3). To illustrate the effect precipitation can have on chromium oxidation at higher pH values, Figure 24 displays the same pH 9 data from Figure 23, while also including the total chromium (TotCr) that was monitored.

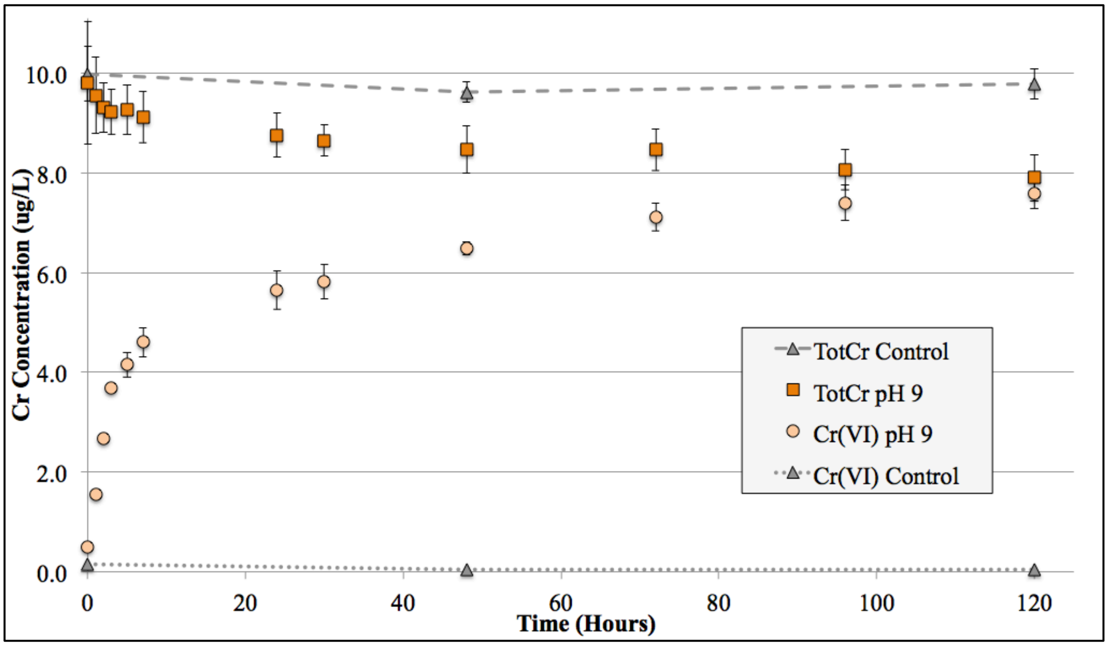


Figure 24. Cr(VI) results for 4 mg/L Cl_2 in deionized water at 16 °C at pH 9. Error bars are standard deviation of triplicate measurements.

The amount of Cr(VI) production at pH 9 was ultimately limited by the amount of soluble Cr(III) available, which decreased over time as a result of precipitation. After 120 hours, essentially all of the soluble Cr(III) had been oxidized to produce 7.6 μg/L of Cr(VI). Thus, both the speciation of chlorine and precipitation must be taken into account when discussing the oxidation potential as a function of pH.

It should be noted that when soluble Cr(III) precipitates as $Cr(OH)_{3(s)}$, the potential for oxidation changes dramatically and depends largely on the strength of the oxidant being used. This project did not specifically investigate which oxidants were capable of oxidizing precipitated chromium, but consistent with previous work (Chebeir and Liu 2016), it appears that precipitated forms of Cr(III) were not as effectively oxidized as soluble forms.

In the data summaries for deionized (Table 10) and synthesized (Table 11) water, the column for the amount of total chromium remaining was included to show when precipitation was a factor. These summaries show that precipitation was present in nearly every chlorine experiment conducted in the deionized and synthesized water. While there was no significant trend in precipitation for a given pH in the deionized water, all of the pH 9 experiments conducted in the synthesized water had the lowest remaining TotCr concentration of the pH values.

It is also possible that more precipitation was occurring than what was indicated by decreasing TotCr concentrations. All the TotCr analyses performed during this study were on samples that were unfiltered. If some precipitated $Cr(OH)_3$ was suspended in solution (a likely scenario considering the constant mixing), some of these precipitates could have been sampled along with the aqueous species of Cr. With the TotCr analysis requiring a digestion, these sampled precipitates would have re-solubilized and been quantified as TotCr.

This potential sampling of precipitates was confirmed by filtered and unfiltered TotCr analysis performed by Brandhuber et al. (2016) on the same Delran WTP water used during this project. Performing a similar experiment with a starting Cr(III) concentration of 10 μg/L, it was observed that after 220 hours, the unfiltered TotCr decreased to 8 μg/L while the filtered TotCr was between 3-4 μg/L. This indicates that between 4-5 μg/L TotCr was in a precipitated form, but had not settled out of solution and was sampled (Brandhuber et al. 2016).

For this project, since there was a drop in total chromium over the 120-hour experiment duration (attributed to precipitation), a mass balance procedure was conducted at the end of each experiment to account for all the chromium in the system. Nitric acid (10% v/v) was added to the remaining volume in the container to cause any particulates to re-solubilize into solution. After the nitric acid addition, the container was shaken for 20 minutes to remove any potentially sorbed chromium. Samples from the containers were then analyzed by ICP-MS for total chromium and a mass balance was conducted. This mass balance procedure recovered 97 ± 0.1% of the initial Cr used during the chlorine experiments.

To compare the baseline oxidation trends that were observed in deionized water (Figure 23), the same set of experiments that were conducted in the synthesized water quality are shown in Figure 25 along with their oxidation models created using the rate constants in Table 11.

When comparing the observed Cr(VI) measurements to the modeled approximations for each of the investigated pH values in the synthesized water (Figure 25), the corresponding models are more accurate than what was modeled in the deionized water (Figure 23). This is especially evident during the 8-80 hour "knee of the curve" time span. For this experiment, the rate constant decreased significantly at pH 9 with the maximum Cr(VI) concentration being much lower ($Cr(VI)_{max}$ = 3.3 μg/L) than pH 5.5 or 7. The rate constants at pH 5.5 and 7 were not significantly different and the $Cr(VI)_{max}$ values were the same at pH 5.5 and 7 with essentially complete oxidation by the end of the experiment (Table 11). However, at other conditions in synthesized water, there was no clear trend in rate constants as a function of pH.

The pH 9 experiment had the most significant change between water qualities, with the Cr(VI) concentration only reaching approximately 3.3 μg/L by the end of the

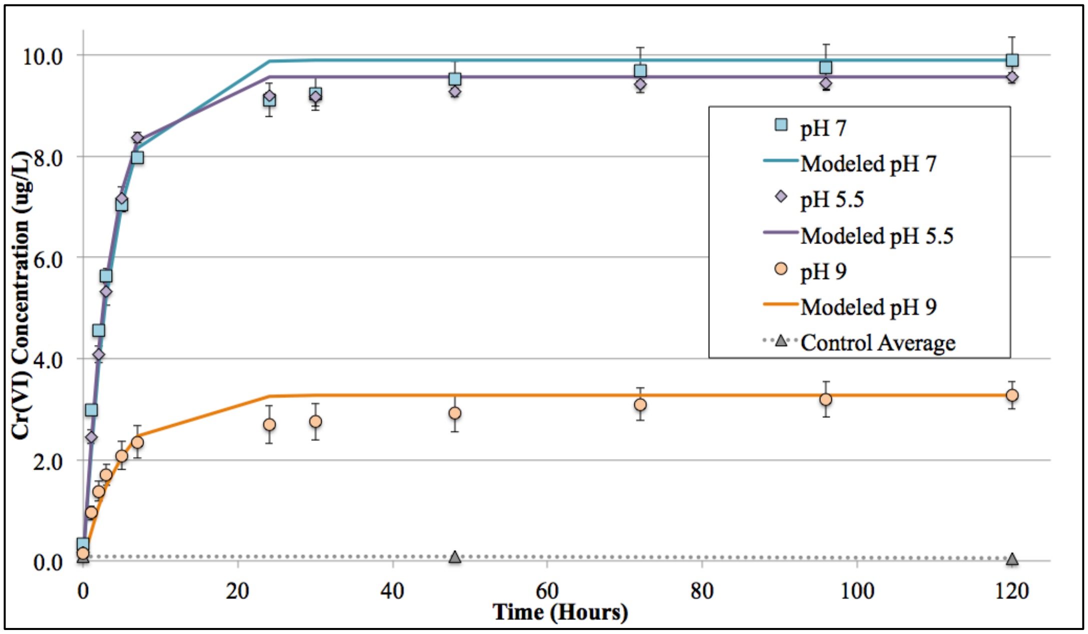


Figure 25. Cr(VI) results & modeling for 4 mg/L Cl_2 in synthesized water at 16 °C. Error bars are standard deviation of triplicate measurements.

synthesized water experiment, despite most of the TotCr (9.1 μg/L) still remaining in solution. There are multiple factors that could cause less oxidation of the experiment conducted at pH 9. One factor observed was the chemicals used to create the synthesized water quality did not all dissolve into solution at pH 9. This could have resulted in precipitates which may have provided sites for the soluble Cr(III) to sorb to, slowing or preventing the oxidation to Cr(VI). The second factor, which was previously discussed (Figure 3), is the potential for Cr(III) to form $Cr(OH)_{3(s)}$ precipitates at higher pH values. However, the synthesized water summary (Table 10) indicates that 9.1 ± 0.5 μg/L of total chromium remained at the end of the experiment. Chromium was likely precipitating at this high pH, but it is possible the cubitainer was mixed enough that the precipitates were suspended in solution and were sampled. A third possibility is that Cr(VI) may have sorbed to some of the aforementioned precipitates (solids in the synthesized water or

$Cr(OH)_{3(s)}$; Lee and Hering 2005) and was not quantified due to sample filtration prior to IC analysis.

Overall, it seems clear that precipitates were present during the synthesized water experiments (from solids in the synthesized water or precipitated $Cr(OH)_{3(s)}$), but they did not behave uniformly. Some pH 9 experiments experienced lower total chromium remaining concentrations while others remained near the starting concentration of 10 µg/L. Overall, the role of precipitates was a confounding factor in the interpretation of these experiment results.

Effect of Temperature

Since the second objective of this project was to determine whether water temperature affects the oxidation kinetics of chromium, a comparison of the various pH experiments in synthesized water completed at different temperatures and their respective models can be seen in Figure 26.

Initial observations would suggest that at pH 7 in the synthesized water, there is no difference in oxidation at 1 mg/L Cl_2 in the different temperatures. The rate constants confirm that temperature was not a significant factor in Cr(III) oxidation for pH 7 in synthesized water (overlapping confidence intervals, Table 11). Similarly, the t-tests performed on the maximum Cr(VI) concentration at 5 vs 16 °C confirmed that temperature was not a significant factor in the chromium oxidation at pH 7 ($p=0.21$).

This was also the case for the experiments done with the same parameters but with 4 mg/L Cl_2 (not shown). In contrast, using this same method of analysis showed that

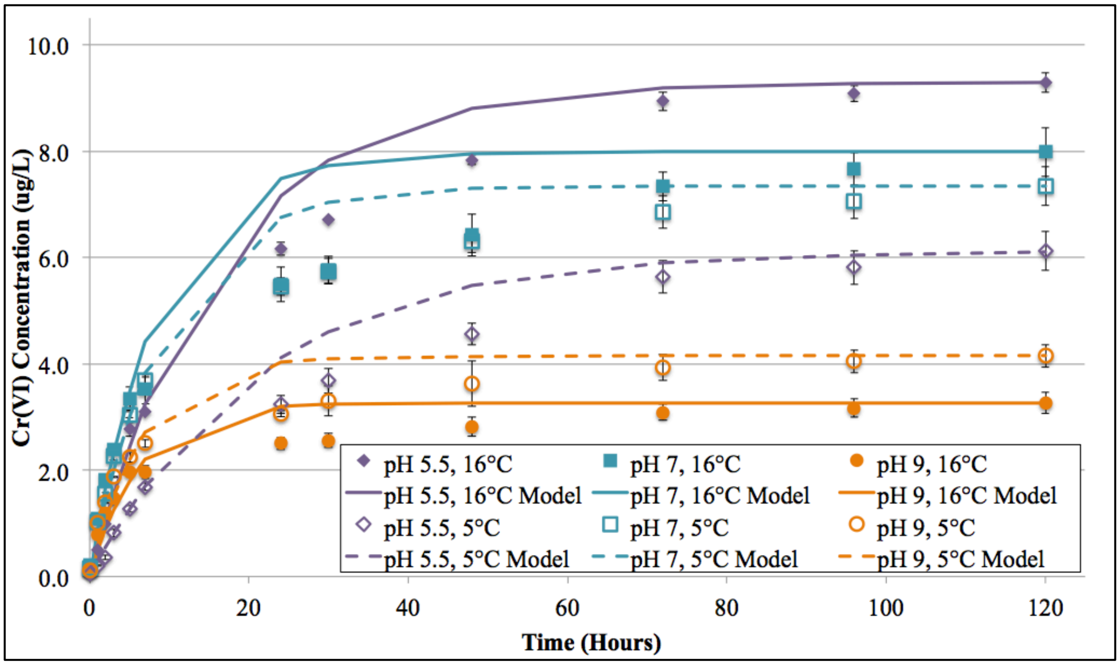


Figure 26. Temperature effects on oxidation by 1 mg/L Cl_2 in synthesized water at pH 5.5, 7, & 9. Error bars are standard deviation of triplicate measurements.

in deionized water, rate constants were significantly higher at 16 °C for the pH 7 experiments with both 1 and 4 mg/L Cl_2.

At the lower pH value of 5.5, temperature had a significant effect in all experiments. Using 1 mg/L Cl_2 in the synthesized water, kinetics were significantly faster at 16 °C compared to 5 °C (Figure 26); a similar trend was found for 4 mg/L Cl_2 in both deionized (Table 10) and synthesized (Table 11) water. However, the rate constant at 5 °C was slightly higher than 16 °C using 1 mg/L Cl_2 in the DI water.

At pH 9, there was no significant difference in rate constants with temperature found in either chlorine dose for the experiments performed in both the deionized and synthesized water.

Comparisons of the extent of maximum Cr(VI) concentration were made between temperature experiments that did experience a significant difference in rate constants. These comparisons showed that during the experiments conducted in the warmer temperature, the extent of oxidation of Cr(III) was faster. Further observation of Figure 26 showed the pH 9 experiments conducted at 5 °C experienced a higher maximum Cr(VI) concentration (4.2 µg/L) than those pH 9 experiments conducted at 16 °C (3.3 µg/L). While this was unexpected, the oxidation rates between these experiments were not significantly different. The difference in the Cr(VI) concentration may have been caused by sorption of recently formed Cr(VI) to precipitates which are more prevalent at pH 9.

Effect of Oxidant Dose

To complete the third objective of this project, the variations in oxidation caused by the different chlorine doses were also investigated. It was assumed that higher 4 mg/L Cl_2 dose would have a significant effect on the Cr(III) oxidation simply due to the increased amount of oxidant. During the 1 mg/L Cl_2 dose experiments, residuals monitoring showed slight drops in Cl_2 residual (Figure 13) that were attributed to off gassing and potential oxidant demand of the container itself, although detectable residual was maintained at all times. With the increased amount of oxidant (Cl_2) dose in the 4 mg/L experiments, these residual losses would not affect the Cr(III) oxidation as much as the 1 mg/L Cl_2 experiments and the Cr(VI) formation would be greater (Figure 27).

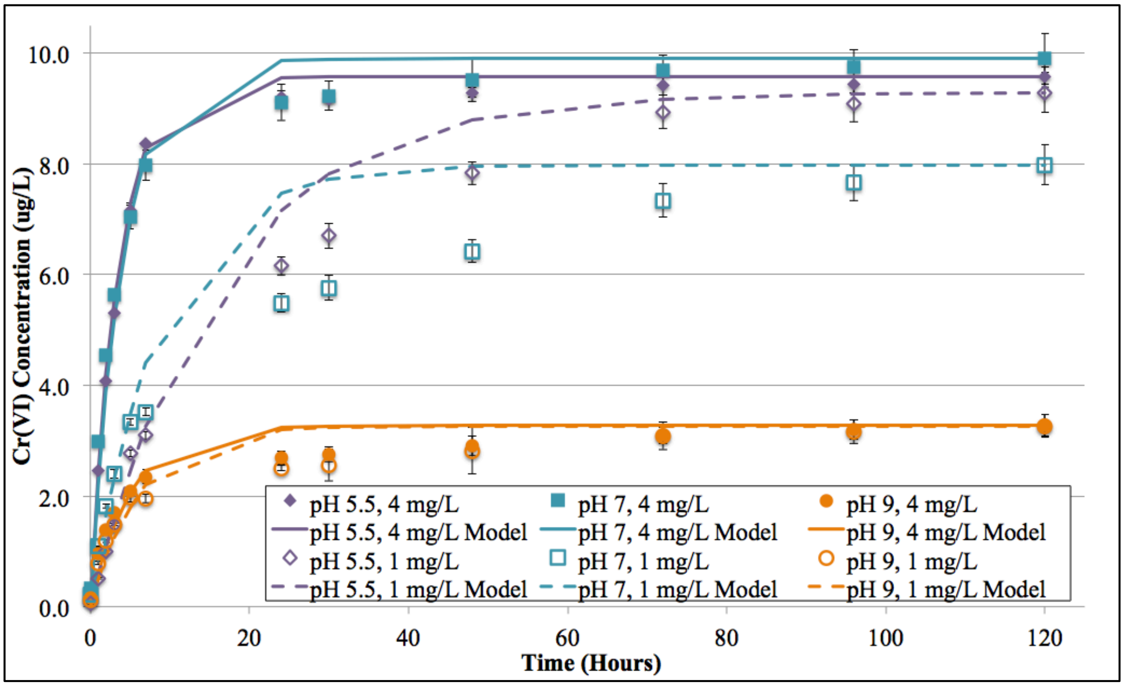


Figure 27. Chlorine dose effects on oxidation in synthesized water at pH 5.5, 7, & 9 at 16 °C. Error bars are standard deviation of triplicate measurements.

For the experiments conducted at pH 5.5 and 7, the 4 mg/L Cl_2 dose had significantly faster Cr(III) oxidation rates in the deionized (Table 10) and synthesized (Table 11) water at both temperatures. Initial observation of Figure 27 would suggest that Cl_2 dose did not have a significant effect on the pH 9 experiments. However, the confidence intervals of the rate constants did not overlap indicating that the oxidation rates were significantly different with faster oxidation occurring at the higher dose. This was also true at the 5 °C temperature in the synthesized water. In contrast, chlorine dose did not affect oxidation rates at pH 9 in the deionized water at either temperature.

There was a greater maximum Cr(VI) concentration with higher Cl_2 dose for every experiment parameter that was investigated except for the pH 9 experiments performed in synthesized water, which showed no significant difference with chlorine dose. Since precipitation is more likely at higher pH values, this may have significantly affected the extent of oxidation for these experiments. Overall, these analyses confirmed the initial assumption that there is a significantly faster Cr(III) oxidation rates achieved at the higher (4 mg/L) chlorine dose.

Effect of Water Quality

When the experiments for the fourth objective were conducted using the synthesized water (Figure 25), initial observations show the oxidation trends in the pH 5.5 and 7 experiments were similar to those done in the deionized water quality. However, by comparing the values for deionized (Table 10) and synthesized (Table 11) water, differences in rate constants and extent of oxidation between the water qualities can be seen. Overall, the experiments conducted in the synthesized water had an equal or greater oxidation rate than the experiments conducted in the deionized water.

For example, the rates of oxidation between the two water qualities at 16 °C, 4 mg/L Cl_2, and pH 5.5 were significantly different (deionized, 0.090 hr^{-1}; synthesized, 0.288 hr^{-1}), but the extent of oxidation was not significantly different (deionized, 9.3 ± 0.4 μg/L Cr(VI); synthesized, 9.6 ± 0.1 μg/L Cr(VI)). In contrast, the rate constants for the same parameters during the pH 7 experiments were the same (0.249 hr^{-1}) between the two water qualities, but the $Cr(VI)_{max}$ of the two pH 7 experiments were significantly different (deionized, 8.2 ± 0.1 μg/L Cr(VI); synthesized, 9.9 ± 0.5 μg/L Cr(VI)).

To compare the oxidation trends in the different water qualities being investigated, data from Bench Set 4 (treated water from the American Water Delran

Treatment Facility) were compared to the Bench Set 1 data (both deionized water and synthesized water) with the same parameters in Figure 28.

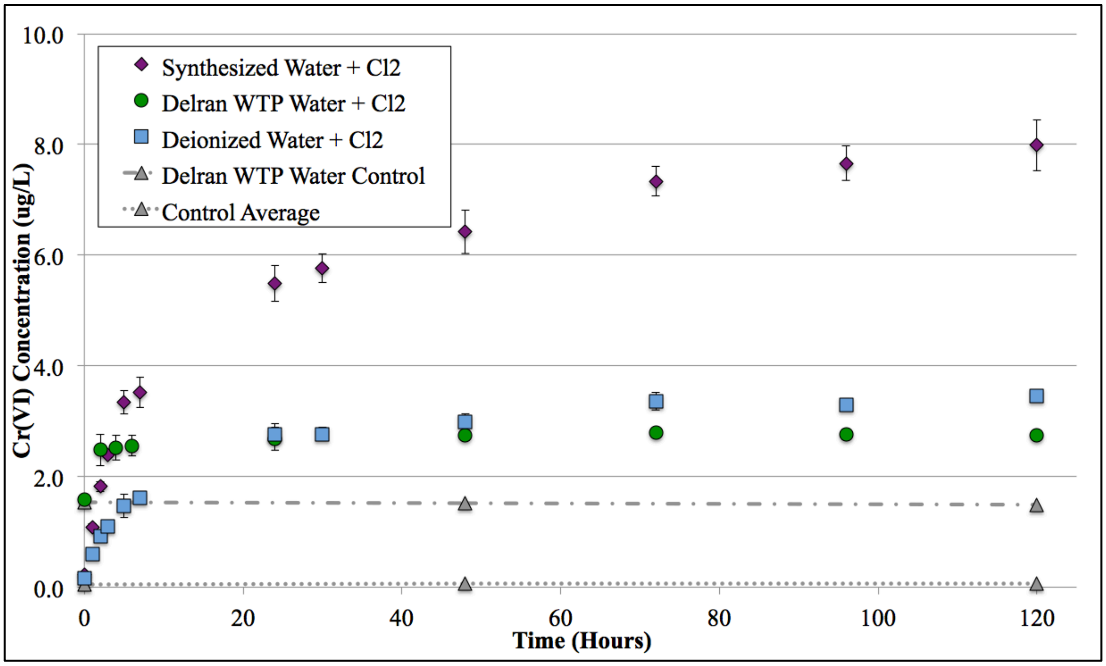


Figure 28. Cr(VI) results with different water qualities with 1 mg/L Cl_2 at pH 7 at 16 °C. Error bars are standard deviation of triplicate measurements.

The synthesized water quality had the greatest Cr(VI) production over the 120-hour experiment. The deionized water experiment had less ultimate oxidation than the synthesized water quality but greater than the water provided from the Delran Water Treatment Facility (WTP), especially considering that the Delran water started with a background Cr(VI) concentration of 1.5 μg/L.

This lack of oxidation in the Delran WTP water was likely caused by the presence of NOM. The Delran WTP water contained 1.28 mg/L of total organic carbon (TOC) (Table 8). NOM can complex Cr(III) as well as take up some available chlorine residual in the water so chromium oxidation could not occur (Clifford and Chau 1988). The chlorine residual during these Delran WTP water experiments dropped more dramatically (from 0.8 mg/L on day 0 to 0.2 mg/L on day 2) than those conducted using the deionized and synthesized water qualities. This confirms that NOM does have a significant chlorine demand.

To verify the changes in chromium oxidation as a result of the presence of NOM, controlled bench scale experiments were conducted in bench set 3 (Table 4) to simulate conditions in the Delran WTP water experiments. NOM was added (5.5 ± 0.3 mg/L DOC) into the synthesized water quality and oxidation experiments were conducted with both the 1 and 4 mg/L Cl_2 doses (Figure 29).

This was the only experiment during this project that was dosed with additional oxidant (Cl_2) after the experiment had begun, indicated by the dashed blue line in Figure 29. From the time that the Cl_2 was dosed into the container to the time the residual Cl_2 was monitored (20 minutes), a significant drop (~ 75%) was observed in both dose experiments. On the second day of these experiments, there was no longer detectable Cl_2 residual. This was attributed to the chlorine demand exhibited from the NOM (Clifford and Chau 1988; Bartlett 1997). As a result, an additional dosing of chlorine (1 and 4 mg/L, respectively) was performed on the second day of the experiment (~ 48 hours).

The supplemental chlorine dosing caused additional oxidation in the 4 mg/L experiments after the 48 hour observation time, although no further oxidation was observed in the 1 mg/L experiments (Figure 29). Only 20 minutes after the supplemental chlorine dosing, there was no chlorine residual present in the 1 mg/L experiments and

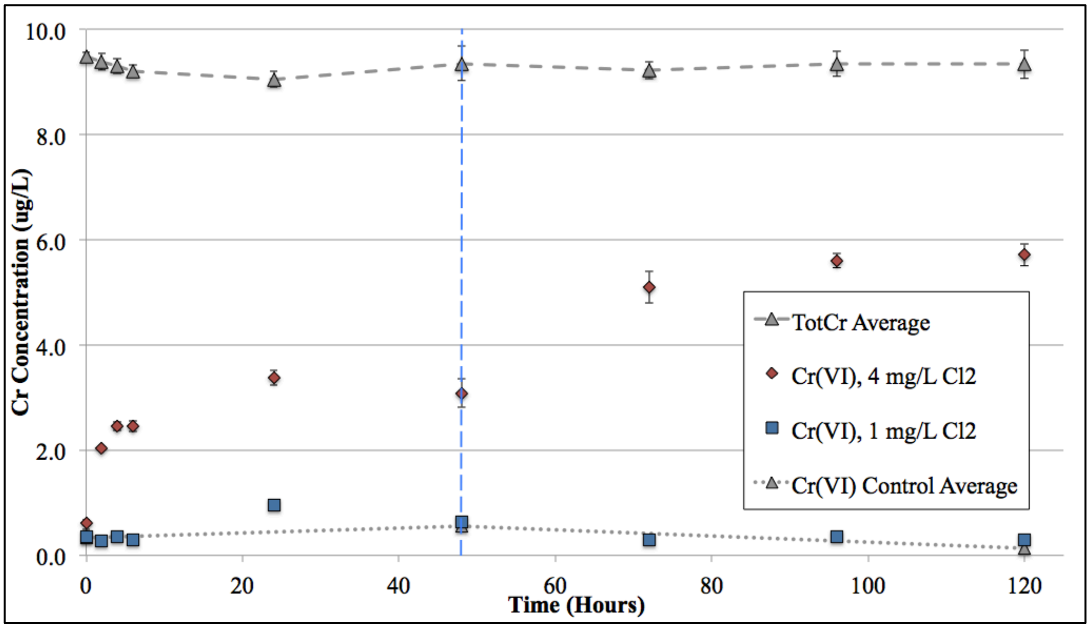


Figure 29. Effect of 5 mg/L DOC on oxidation by chlorine in synthesized water at pH 7, 16 °C. Dashed blue line indicates time of second oxidant dosing. Error bars are standard deviation of triplicate measurements.

less than 1 mg/L Cl_2 in the 4 mg/L experiments. It appears that the NOM had a much stronger Cl_2 demand than that of chromium oxidation, and the presence of NOM can significantly change the chromium oxidation reaction.

The second factor to consider when looking at the oxidation of the Delran WTP water is that of the total remaining chromium, because significant precipitation of TotCr was observed. A complete chromium concentration summary of the experiment conducted with the Delran WTP water with 1 mg/L Cl_2 added is shown in Figure 30.

It should be noted that the beginning TotCr amount in Figure 30 was slightly higher (12.2 ± 0.6 μg/L TotCr) than previous experiments. This was due to the additional 10 μg/L Cr(III) added to the pre-existing background concentration of 1.5 μg/L Cr(VI) in the Delran WTP water. The total chromium dropped rapidly to the same level of maximum Cr(VI) concentration, signaling a strong possibility of particulates. The TotCr control average (Delran water with no oxidant) also showed the same decline in TotCr. Neither of these decreases were present in the controlled experiments containing NOM (Figure 29), which also suggests that precipitation was more likely in the treated source water of the Delran WTP compared to the laboratory generated synthesized water.

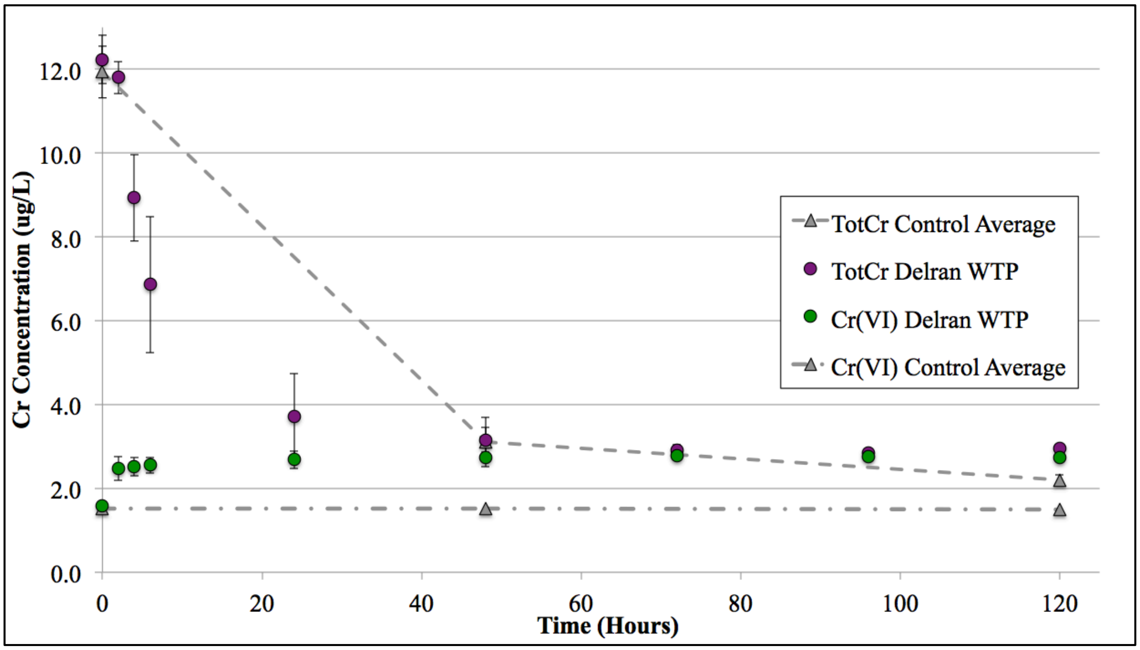


Figure 30. Cr(VI) results with 1 mg/L Cl_2 in Delran WTP water at pH 7 at 16 °C. Error bars are standard deviation of triplicate measurements.

The maximum Cr(VI) concentration of the Delran WTP water was 2.8 ± 0.1 μg/L. Since the majority of the oxidation that occurred in the Delran WTP water (Figure 28) occurred between the first two samples and then leveled off, those two samples were used to find the rate constant (k) of 0.48 hr^{-1}. This rate constant was higher than any other observed in the chlorine experiments (Table 10, Table 11), although confidence in the value is low since it was obtained from only two data points. Ultimately, the initial observation (Figure 28) that less than 10% oxidation of the available 10 μg/L Cr(III) occurred in the Delran WTP water is likely due to most of the chromium precipitating and chlorine residual being consumed by NOM. Had the Cr(III) remained soluble and NOM not been present, the extent of oxidation could have been much higher.

Effect of Initial Cr(III) Concentration

The chlorine experiments that were conducted with the higher initial Cr(III) concentration of 100 μg/L (Bench Set 2, Table 4) were done in synthesized water to investigate the effect that initial Cr(III) concentrations had on chromium oxidation (Table 12). The observed Cr(VI) formation along with the models generated from the rate constants that were found during this study are shown in Figure 31.

Table 12. Oxidation Summary for Chlorine in Bench Set 2 Experiments (100 μg/L Initial Cr(III) Concentration in Synthesized Water)

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (μg/L)	Total Chromium Remaining (μg/L)
16 °C Temperature	4 mg/L	pH 7	0.204	0.178 ~ 0.230	86.3 ± 3.90	95.7 ± 1.44
		pH 9	0.078	0.067 ~ 0.090	26.2 ± 1.50	33.1 ± 13.0
	1 mg/L	pH 7	0.283	0.207 ~ 0.358	19.5 ± 8.01	59.0 ± 15.5
		pH 9	0.095	0.076 ~ 0.113	10.7 ± 2.09	10.9 ± 1.85

Looking at the rate constants in Table 12 it can be observed Cr(III) oxidation was faster during the pH 7 experiments. It can also be observed that Cl_2 dose did not have a significant effect on oxidation with overlapping confidence intervals for both the 1 and 4

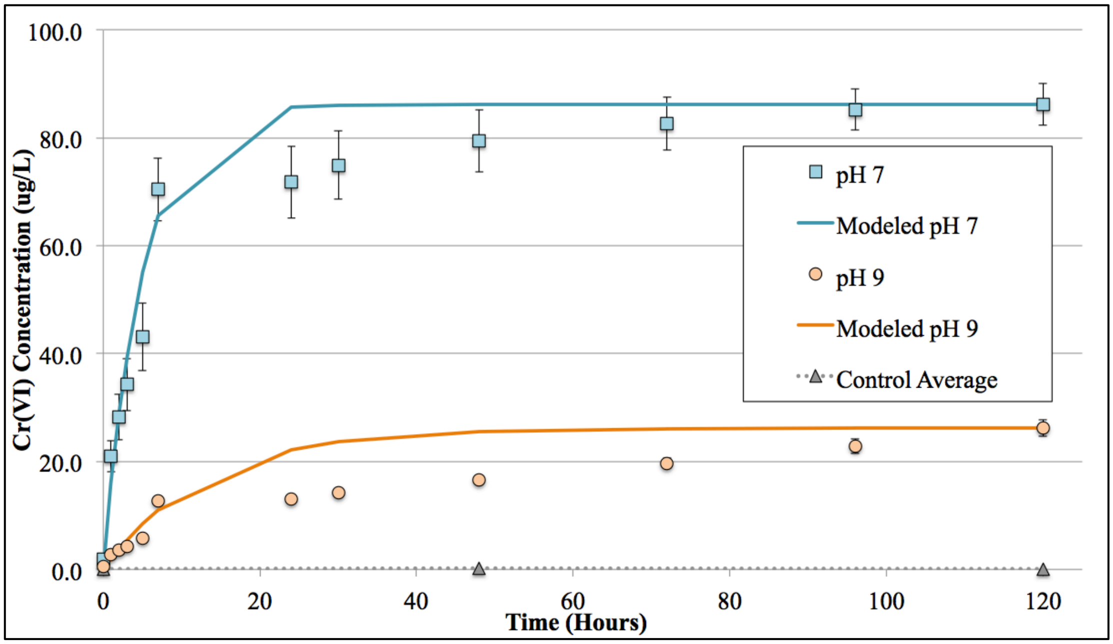


Figure 31. Cr(VI) results & modeling for 4 mg/L Cl_2 in synthesized water at 16 °C. Error bars are standard deviation of triplicate measurements.

mg/L Cl_2 doses for both pH values. There was also a significant amount of precipitation in all of the experiments with the exception of the pH 7 experiment with 4 mg/L Cl_2 which did not have as much precipitation. As a result of the precipitation, the maximum amount of Cr(VI) observed during the experiments was limited.

When comparing the rate constants from these experiments to those in Table 11 (10 μg/L initial Cr(III) concentrations in synthesized water), the 95% confidence intervals do not overlap. This was a preliminary indication that initial Cr(III) concentration was a significant factor. Due to the dependence on initial Cr(III) concentration, first order kinetics may not be the best model for Cr(VI) formation. However, since the first order kinetics were used only as a preliminary tool and they adequately modeled the observed data, they were still used. This project was not set up as a kinetic study, and in order to more accurately fit a mechanistic model more experiments would have to be done looking at initial Cr(III) concentrations to verify it as an independent factor.

The range of rate constants found by Lindsay et al. (2012) was significantly higher (0.10-3.15 hr^{-1}) than those observed during these experiments (Table 12). This was likely due to the different Cr(III) concentrations (3500-5200 μg/L) and higher doses of Cl_2 being investigated (1-100 mg/L Cl_2) by Lindsay et al. (2012). While the range of rate constants found by Bartlett (1997) was more similar to those observed during these experiments (0.01-0.70 hr^{-1}), they were found when a dose of 20 mg/L Cl_2 was being investigated with an initial Cr(III) concentration of 1000 μg/L.

The Cr(VI) formation observed was compared to the previous chlorine experiments conducted by Lai and McNeill (2006) using 1 mg/L chlorine in the same synthesized water quality. Lai and McNeill (2006) did not account for precipitation in the first order reaction equation (they used TotCr) and used second order kinetics, which did not allow for the comparisons between rate constants. The Cr(VI) formation trends did not show similar results to the previous study that investigated the same parameters, with the pH 7 and pH 9 experiments reaching maximum Cr(VI) concentrations of approximately 75 and 18 μg/L by 120 hours (Lai and McNeill 2006).

During the previous study, precipitation was shown to be a significant factor in the pH 9 experiment (25 ± 13 μg/L unfiltered TotCr), limiting the amount of oxidation that could occur, although a mass balance indicated 105% recovery of that total chromium (Lai and McNeill 2006). The total remaining chromium at the end of this current experiment (10.9 ± 1.9 μg/L TotCr) also indicated the presence of precipitation, with 93 ± 0.04% recovery of the total chromium at the conclusion of the experiment.

Monochloramine

While monochloramine (NH_2Cl) is not as widely used in water treatment as chlorine (Table 1), it is still prevalent as a disinfectant residual in distribution systems. It was hypothesized that adding monochloramine will have a similar effect to the addition of the ammonia preservative to chlorinated samples to slow down the reaction kinetics (USEPA 2011). As such, the use of monochloramine as an oxidant was not expected to oxidize Cr(III) to Cr(VI) during the over the 5-day experiment period.

Summaries were created of the maximum Cr(VI) concentration observed over the duration of each experiment and total chromium remaining at the end of each experiment for deionized (Table 13) and synthesized water (Table 14). Since there was no significant formation of Cr(VI), rate constants were not calculated for the monochloramine experiments.

After completing all of the monochloramine experiments, it was apparent that less than 0.5% of the Cr(III) was oxidized to Cr(VI) and there was no significant change in Cr(VI) formation at any condition. To illustrate these results, the experiment with parameters that were expected to favor chromium oxidation (16 °C, 4 mg/L NH_2Cl) can be seen in Figure 32.

Not only did the Cr(III) oxidation to Cr(VI) never exceed 0.5% for each of the different pH values the duration of the experiment, but it can also be seen that there was no oxidation in the control containers. This proved that there was no contamination or unexpected oxidation in the containers (Figure 32).

From the summary tables for deionized (Table 13) and synthesized (Table 14) water, it can also be seen that the “Total Chromium Remaining” values were less than the

Table 13. Oxidation Summary for Monochloramine in Deionized Water

Parameters			Maximum Cr(VI) Concentration (μg/L)	Total Chromium Remaining (μg/L)
5 °C Temperature	4 mg/L	pH 5.5	0.1 ± 0.0	7.3 ± 0.3
		pH 7	0.2 ± 0.1	8.3 ± 0.4
		pH 9	0.3 ± 0.1	9.5 ± 0.3
	1 mg/L	pH 5.5	0.2 ± 0.0	8.8 ± 0.2
		pH 7	0.1 ± 0.0	8.4 ± 0.2
		pH 9	0.1 ± 0.1	9.1 ± 0.3
16 °C Temperature	4 mg/L	pH 5.5	0.2 ± 0.0	6.4 ± 0.3
		pH 7	0.2 ± 0.0	6.8 ± 0.7
		pH 9	0.4 ± 0.1	8.7 ± 0.1
	1 mg/L	pH 5.5	0.1 ± 0.0	7.4 ± 0.3
		pH 7	0.3 ± 0.1	7.3 ± 0.4
		pH 9	0.3 ± 0.0	7.2 ± 0.4

Table 14. Oxidation Summary for Monochloramine in Synthesized Water

Parameters			Maximum Cr(VI) Concentration (μg/L)	Total Chromium Remaining (μg/L)
5 °C Temperature	4 mg/L	pH 5.5	0.2 ± 0.1	8.9 ± 0.2
		pH 7	0.2 ± 0.1	9.1 ± 0.1
		pH 9	0.3 ± 0.1	9.0 ± 0.2
	1 mg/L	pH 5.5	0.1 ± 0.0	8.9 ± 0.8
		pH 7	0.1 ± 0.0	9.6 ± 0.2
		pH 9	0.2 ± 0.0	7.2 ± 0.7
16 °C Temperature	4 mg/L	pH 5.5	0.2 ± 0.1	8.4 ± 0.6
		pH 7	0.2 ± 0.0	9.0 ± 0.6
		pH 9	0.3 ± 0.1	7.4 ± 0.6
	1 mg/L	pH 5.5	0.2 ± 0.1	8.5 ± 0.5
		pH 7	0.1 ± 0.0	9.0 ± 0.2
		pH 9	0.2 ± 0.1	5.1 ± 0.6

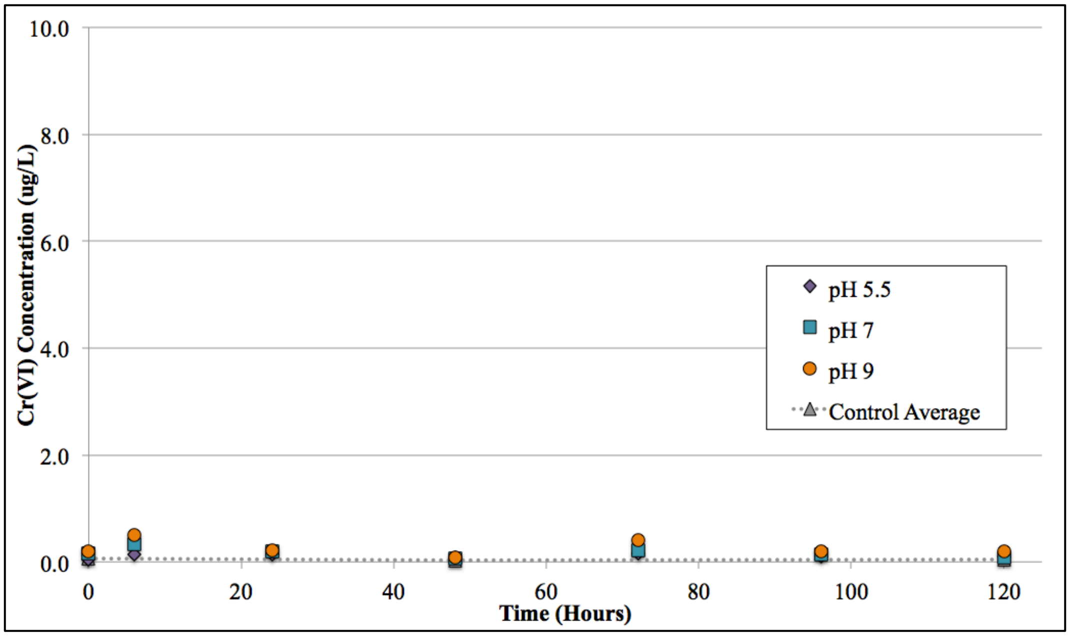


Figure 32. Cr(VI) results & modeling for 4 mg/L NH_2Cl in synthesized water at 16 °C. Error bars are standard deviation of triplicate measurements (typically <0.1 μg/L, not visible outside of data markers).

initial value of 10 μg/L. This was an indication that precipitation was present in almost every experiment and was even observed at the lower pH value of 5.5, especially in the deionized water.

Due to the precipitation of total chromium, it was necessary to digest the remaining volume in the containers at the end of each experiment to provide an accounting for all the total chromium. This was done following the same process that was done for the chlorine experiments. Throughout the monochloramine experiments, 93 ± 0.1% of the initial Cr was recovered using this process. Due to the lack of Cr(VI) formation during the monochloramine experiments, there was no further investigation into the objectives investigating the effects of pH, water temperature, or water quality.

Effect of Initial Cr(III) concentration

For the monochloramine experiments conducted with a higher initial Cr(III) concentration of 100 μg/L, the maximum Cr(VI) concentration observed was less than 1% indicating that no oxidation was occurring through the duration of the experiment (data not shown here). This confirmed observations from previous studies that showed over a time period of 200 hours, monochloramine was not an effective oxidant for chromium (Clifford and Chau 1988; Lai and McNeill 2006).

Chlorine Dioxide

Chlorine dioxide (ClO_2) is the first of two oxidants investigated by this project that had previously never been investigated for their effects on chromium oxidation. Although only 5% of utilities use ClO_2 in water treatment (Table 1), it is a strong oxidant that could potentially oxidize chromium. Thus, multiple experiments were conducted using the deionized and synthesized water to provide a basis of chromium oxidation under controlled conditions. In the bench set design plan (Table 4), it was proposed to run these ClO_2 experiments for 8 hours (maximum time ClO_2 could be involved in treatment). For logistical reasons, the duration was changed to 6 hours.

During the early stages of experimentation, there was an unexpected trend in the pH for each of the experiments that affected the average pH of the experiment duration (Table 5). For both of the water qualities investigated (deionized and synthesized) at both the investigated doses (0.4 and 0.8 mg/L ClO_2), the pH in every experiment experienced significant drift towards the approximate pH value of 8.5, despite the use of CO_2 gas to ensure that each experiment began at the desired pH (5.5, 7, and 9). This drift occurred faster in the deionized water quality, potentially explained by the lower buffering capacity (total alkalinity, Table 7) compared to the synthesized water quality.

To confirm these observations, a control experiment was conducted to monitor the pH with 0.4 and 0.8 mg/L ClO_2 dosed into the deionized and synthesized water containing no chromium (Table 15).

Table 15. pH Effects as a Result of Chlorine Dioxide Addition

Parameters		Desired pH	pH Monitoring Times (hours)			
			0	4	8	24
Deionized Water Quality	0.8 mg/L	5.5	5.5 ± 0.2	5.9 ± 0.5	7.0 ± 0.4	8.5 ± 0.3
		7	7.0 ± 0.4	7.8 ± 0.2	8.0 ± 0.5	8.2 ± 0.4
		9	9.1 ± 0.2	8.6 ± 0.4	8.4 ± 0.3	8.5 ± 0.0
	0.4 mg/L	5.5	5.4 ± 0.3	6.1 ± 0.5	7.4 ± 0.7	8.3 ± 0.6
		7	7.1 ± 0.1	7.6 ± 0.3	7.8 ± 0.4	8.6 ± 0.2
		9	9.1 ± 0.1	8.9 ± 0.2	8.9 ± 0.4	8.7 ± 0.1
Synthesized Water Quality	0.8 mg/L	5.5	5.5 ± 0.4	5.7 ± 0.8	6.7 ± 0.5	8.5 ± 0.2
		7	7.3 ± 0.2	7.4 ± 0.3	7.7 ± 0.3	8.5 ± 0.4
		9	9.0 ± 0.3	8.6 ± 0.5	8.6 ± 0.3	8.5 ± 0.2
	0.4 mg/L	5.5	5.3 ± 0.1	5.9 ± 0.4	7.1 ± 0.6	8.2 ± 0.4
		7	6.9 ± 0.2	7.3 ± 0.5	7.6 ± 0.4	8.6 ± 0.3
		9	9.0 ± 0.0	9.0 ± 0.3	8.8 ± 0.3	8.6 ± 0.2

Over the 24-hour monitoring duration of the control experiment in Table 15 there was significant drift in both the pH 5.5 and 7 experiments. The half reaction of ClO_2 reduction in water (Equation 5) shows the creation of OH^- (Copeland and Lytle 2014).

$$ClO_2 + 2H_2O + 5e^- = Cl^- + 4OH^- \qquad (5)$$

However, the complete balanced redox equation for ClO_2 (Table 2) shows the production of H^+ rather than OH^-, which would cause a decrease in pH. From the observed data, the pH increase to 8.5 was difficult to explain. It was noted that during the experiments that the higher dose of 0.8 mg/L ClO_2 did not cause the drift to occur faster. Another factor that remains unexplained was that during the pH 9 experiments, both water qualities in the control experiment did not see an increase in pH. This normally indicates the use of a pH buffer, but the manufacturer confirmed that there was no pH buffer added to the stock ClO_2 solution (Dean Gregory, personal communication, March 8, 2016).

Overall, the cause for the drift experienced during the oxidation experiments was attributed to unknown changes in the aquatic chemistry of the water qualities as a result of ClO_2 addition. To better understand this pH drift, future investigation of the effects of ClO_2 on the aquatic chemistry would be required.

Taking into account the large drift in the pH 5.5 experiments (>1 pH unit), especially at the 8-hour time period, there was not enough confidence in the pH 5.5 experiments to report the Cr(VI) formation that occurred during those experiments. The experiments conducted at pH 7 also experienced greater pH change than desired, but given the large variation in replicates most of those pH changes are not statistically significant with time, so the data are still reported.

To outline the chromium oxidation behavior in the ClO_2 experiments as well as provide rate constants for those experiments that experienced oxidation, summaries are shown for each ClO_2 experiment done in the deionized water quality (Table 16) and the synthesized water quality (Table 17).

The rate constants were generated using the same first order equation method that was used in the Cl_2 analysis. Due to the unique maximum Cr(VI) concentration trends

Table 16. Oxidation Summary for Chlorine Dioxide in Deionized Water

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (μg/L)	Total Chromium Remaining (μg/L)
5 °C Temperature	0.8 mg/L	pH 7	0.628	0.435 ~ 0.820	2.2 ± 0.2	9.0 ± 0.6
		pH 9	0.855	0.662 ~ 1.048	1.7 ± 0.1	8.9 ± 0.2
	0.4 mg/L	pH 7	1.941	1.464 ~ 2.418	10.3 ± 0.3	10.1 ± 0.2
		pH 9	n/a	n/a	< 0.8 [a]	9.9 ± 0.1
16 °C Temperature	0.8 mg/L	pH 7	1.139	1.070 ~ 1.208	10.2 ± 0.8	9.3 ± 0.3
		pH 9	0.745	0.572 ~ 0.918	4.8 ± 0.5	9.6 ± 0.5
	0.4 mg/L	pH 7	1.098	0.927 ~ 1.270	8.2 ± 1.0	9.0 ± 0.6
		pH 9	2.814	2.480 ~ 3.148	1.8 ± 0.2	9.0 ± 0.3

[a] Cr(VI) oxidation concentrations were below the MRL (0.8 μg/L)

Table 17. Oxidation Summary for Chlorine Dioxide in Synthesized Water

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (μg/L)	Total Chromium Remaining (μg/L)
5 °C Temperature	0.8 mg/L	pH 7	1.695	0.313 ~ 3.077	1.7 ± 0.1	9.7 ± 0.2
		pH 9	2.195	1.127 ~ 3.264	2.2 ± 0.3	9.9 ± 0.1
	0.4 mg/L	pH 7	0.688	0.502 ~ 0.874	3.4 ± 0.4	8.5 ± 1.0
		pH 9	1.714	1.063 ~ 2.365	2.1 ± 0.3	10.0 ± 0.3
16 °C Temperature	0.8 mg/L	pH 7	0.888	0.681 ~ 1.096	7.7 ± 1.2	9.3 ± 0.6
		pH 9	n/a	n/a	< 0.8 [a]	8.8 ± 0.3
	0.4 mg/L	pH 7	1.149	0.895 ~ 1.403	9.7 ± 0.1	10.0 ± 0.0
		pH 9	0.536	0.458 ~ 0.614	2.5 ± 0.1	10.0 ± 0.1

[a] Cr(VI) oxidation concentrations were below the MRL (0.8 μg/L)

that were observed during the ClO_2 experiments, the upper bound asymptote value (Equation 3) was not necessarily the Cr(VI) concentration at the last measured point since there were experiments that experienced significant Cr(VI) decreases with time. Rather than always using the same number of measurements (first six as was done with Cl_2 experiments) to determine the rate constants, each ClO_2 experiment was observed to find suitable points, with the first four measurements (0-2 hour) most often being used.

Effect of pH

It was immediately apparent that the Cr(VI) formation observed during some ClO_2 experiments was different than what was observed during the Cl_2 experiments. Formation of Cr(VI) over time during the pH 7 experiment was similar to observations from the Cl_2 experiments, and the kinetic model adequately described the measured data (Figure 33).

However, the trend of Cr(VI) formation during the pH 9 experiment was different. During the first two hours of the experiment, the Cr(VI) concentration increased as expected, but the following measurement indicated a significant drop in Cr(VI) concentration at 4 hours. In this case, the Cr(III) oxidation model generated by the rate constant was not adequate. The design of pseudo first-order reaction models can not account for a decrease in Cr(VI) concentration, regardless of what caused the decrease.

Due to the observed decreases in Cr(VI) concentration during some of the experiments, the first order equation used to generate these models could not account for those decreases as evidenced in the pH 9 experiments (Figure 32). The model could be altered to instead use the Cr(VI) concentration observed at the end of the experiment as the upper bound asymptote of Equation 2, but the decreasing Cr(VI) concentration

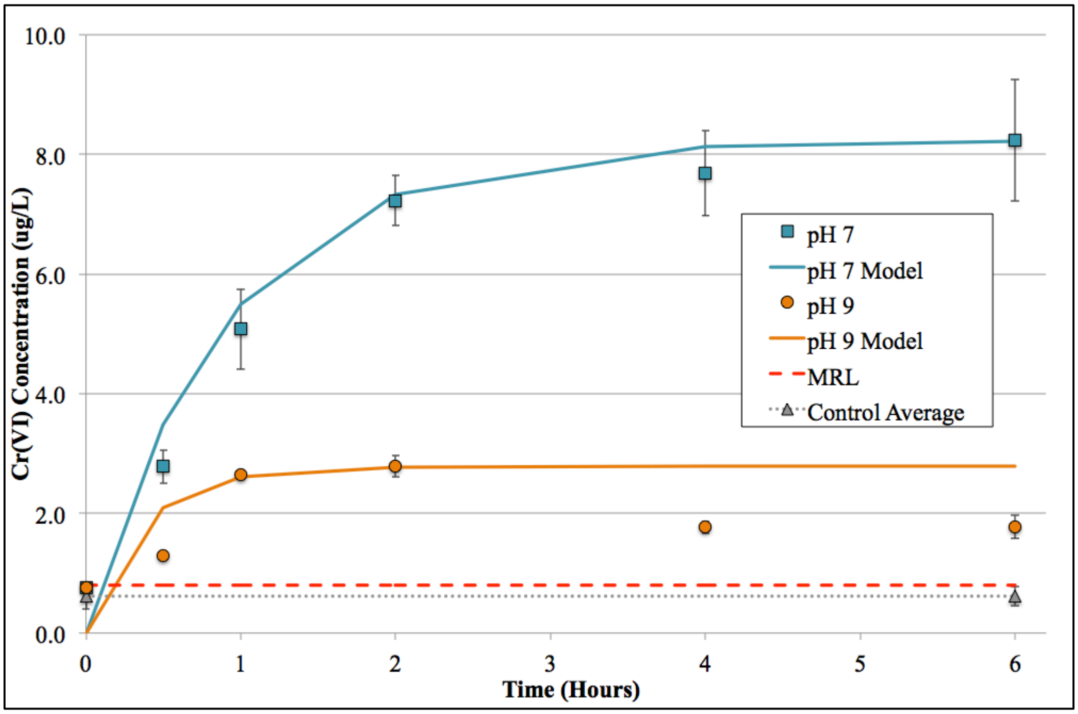


Figure 33. Cr(VI) results & modeling for 0.4 mg/L ClO_2 in deionized water at 16 °C. MRL was 0.8 μg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

would not be included in the model. While this project did not focus on creating complete mechanistic kinetics models of the Cr(III) oxidation, the presence of Cr(VI) sorption would significantly complicate the modeling process regardless of different models being utilized to more accurately predict the Cr(VI) concentration.

There have been studies showing that Cr(VI) will sorb onto $Cr(OH)_{3(s)}$ if present, but this more commonly occurs at pH values lower than 5.5 (Lee and Hering 2005), which does not adequately explain the decrease during the pH 9 experiments. The total chromium (TotCr) concentration in the pH 7 and 9 experiments in the deionized water decreased only slightly (average of 9%) (Table 16), indicating that minimal precipitation occurred. This was also the same for experiments conducted in the synthesized water and was expected given the short duration of the experiment.

Effect of Temperature

The effects that water temperature (5 and 16 °C) had on Cr(VI) formation with 0.4 mg/L ClO_2 in synthesized water are illustrated in Figure 34.

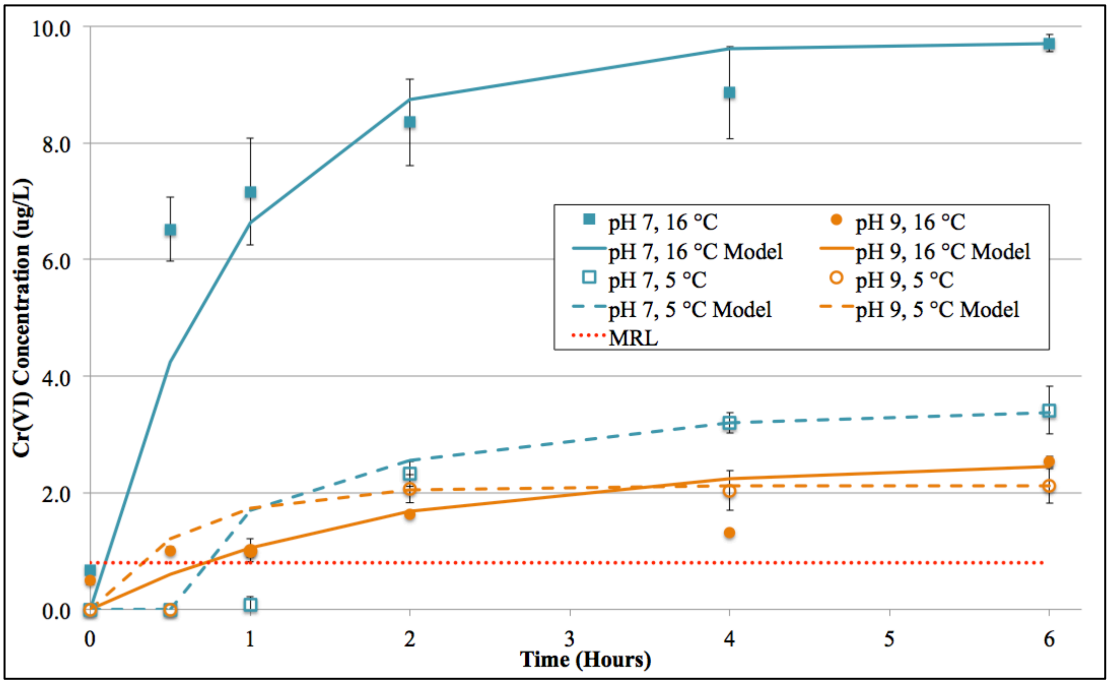


Figure 34. Cr(VI) results & modeling for 0.4 mg/L ClO_2 in synthesized water. MRL was 0.8 µg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

At pH 7 in synthesized water, the warmer 16 °C experiments had faster kinetics and greater extent of oxidation. In fact, the rate constants for the ClO_2 experiments showed a significant difference with water temperature for both the investigated doses at both the deionized (Table 16) and synthesized (Table 17) water qualities. However, the observed trends were not consistent. This was evident in the pH 7 experiments, where at the lower ClO_2 dose the oxidation rates were faster at the 5 °C temperature, but at the higher ClO_2 dose, the oxidation rates were faster at the 16 °C temperature. Overall, for both the pH values that were investigated, the oxidation trends were not consistent.

Effect of Oxidant Dose

An experiment with the same parameters as Figure 33, but with the higher ClO_2 dose of 0.8 mg/L is shown in Figure 35 to highlight the dose effects on the formation of Cr(VI).

Contrary to Cr(III) oxidation trends observed during the Cl_2 experiments, when the concentration of ClO_2 was increased, faster rates of oxidation and larger maximum Cr(VI) concentrations were not consistently observed during the experiments. When oxidation did occur, the rate constants at the larger 0.8 mg/L ClO_2 dose either decreased or were not significantly different. This was partially caused by the large confidence intervals attributed to the decreases in Cr(VI) concentrations which cause the measured Cr(VI) values to deviate from the first order model. As a result, conclusions based on the oxidation rate for the various experiment parameters were difficult to make.

It was proposed that increasing the ClO_2 dose caused unknown effects on the aquatic chemistry and as a result the overall Cr(III) oxidation. Due to these unknown effects, it was difficult to determine clear trends in both the oxidation rates and the extent of maximum Cr(VI) concentration.

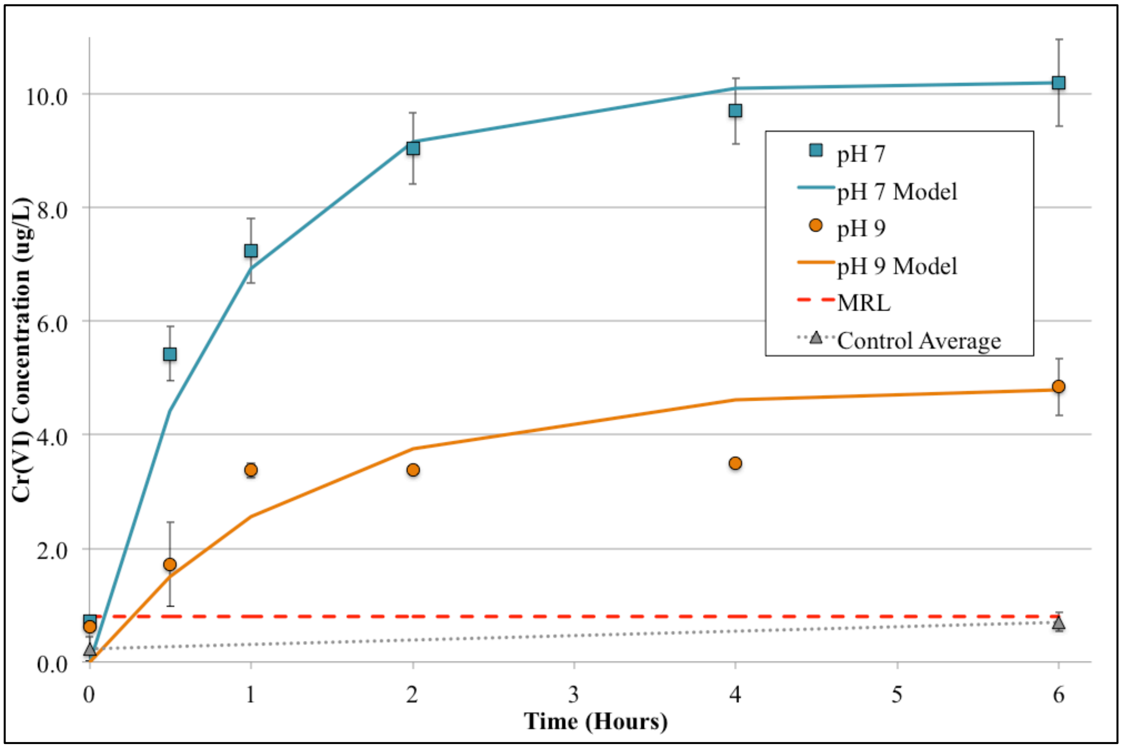


Figure 35. Cr(VI) results & modeling for 0.8 mg/L ClO_2 in deionized water at 16 °C. MRL was 0.8 μg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

Effect of Water Quality

An observation of the rate constants for both the deionized water (Table 16) and synthetic water (Table 17) qualities revealed some unusual results. There were two experiments at pH 9 where there was no oxidation observed throughout the duration of the experiment (deionized water, 0.4 mg/L ClO_2 at 5 °C; synthesized water, 0.8 mg/L ClO_2 at 16 °C). These results are difficult to explain because these no-oxidation scenarios occurred in both investigated doses, in both water qualities, and at both temperatures, but not consistently at any condition. There was not an immediate predictable trend that explains when the Cr(III) oxidation would not occur.

There were also some significant changes in Cr(III) oxidation when the experiments conducted in the deionized water were compared to those conducted in the synthesized water, although there were no consistent trends with water quality. The synthesized water experiments illustrated in Figure 36 have the same parameters as those conducted in deionized water (Figure 33).

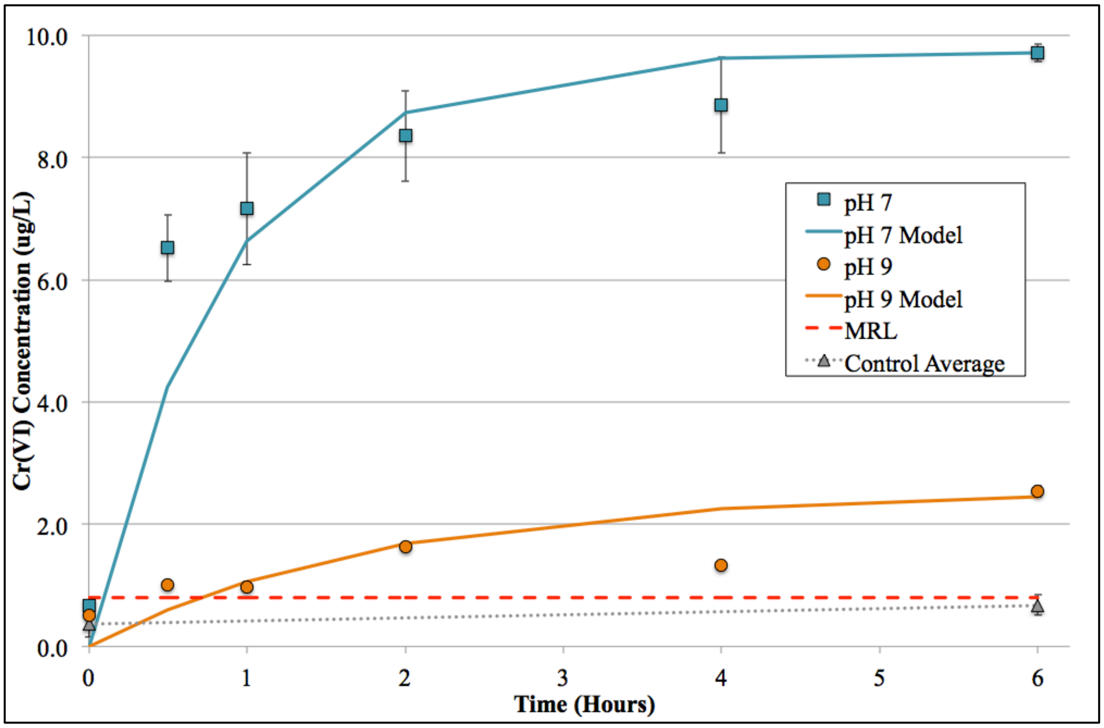


Figure 36. Cr(VI) results & modeling for 0.4 mg/L ClO_2 in synthesized water at 16 °C. MRL was 0.8 μg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

In the synthesized water at 16 °C, there was a significant increase in maximum Cr(VI) concentration for both the pH 7 and pH 9 experiments (1.5 and 0.7 μg/L, respectively) compared to deionized water. However, there was no significant difference in the rate of oxidation between water qualities for the pH 7 experiments and the rate of oxidation was significantly slower in the synthesized water for the pH 9 experiments. In contrast, at the 5 °C temperature Cr(III) oxidation at pH 7 was faster and the Cr(VI) concentration was greater in deionized water than in synthesized water.

There was not as much Cr(VI) decrease observed in the pH 9 experiments conducted in the synthesized water. To reiterate, this was possibly explained by the greater buffering capacity of the synthesized water. Since there was not as much Cr(VI) decreasing after the initial oxidation, the models created for the experiments conducted in the synthesized water followed closer to the measured values. While there are still Cr(VI) concentrations decreasing when compared to previous measurements, the error bars (standard deviation of triplicate measurements) of the measured data points are within the modeled Cr(VI) concentration (with the exception of one value at 0.5 hours for both pH 7 and 9 and another at 4 hours for pH 9). Overall, comparisons between the modeled and measured Cr(VI) concentration were more accurate in the synthesized water than the deionized water.

Effect of Initial Cr(III) concentration

Experiments were not conducted for chlorine dioxide using the 100 µg/L Cr(III) concentration, so the effect of the initial Cr(III) concentration (Objective 5) was not investigated.

Potassium Permanganate

Of the five oxidants investigated in this project, potassium permanganate ($KMnO_4$) is not classified as a disinfectant, though it is a strong oxidant. Due to coloration interference (Appendix A), these experiments required the use of a manual spectrophotometer method to analyze Cr(VI). This Cr(VI) analysis method was not as precise and had a higher MRL of 0.8 μg/L (same as the ClO_2 experiments).

Since the higher proposed dose of 5 mg/L $KMnO_4$ caused too great of an interference that compromised the analytical confidence of the experiments in both the deionized (Figure 17) and synthesized (Figure 18) water, the summary in Table 18 is only for the experiments conducted with 1 mg/L $KMnO_4$. Rate constants were generated using the same methods as those done in the chlorine analysis, with the exception of using only the first four measurements (0-2 hours).

Table 18. Oxidation Summary for Potassium Permanganate

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (μg/L)	Total Chromium Remaining (μg/L)
Deionized Water	**16 °C**	**pH 5.5**	0.431	0.309 ~ 0.553	9.7 ± 0.2	9.4 ± 0.3
		pH 7	4.082	3.595 ~ 4.570	9.5 ± 0.5	9.3 ± 0.6
		pH 9	1.891	1.792 ~ 1.991	9.8 ± 0.1	9.3 ± 0.4
	5 °C	**pH 5.5**	0.525	0.489 ~ 0.561	10.3 ± 0.3	10.0 ± 0.4
		pH 7	2.703	2.503 ~ 2.903	9.6 ± 0.5	9.8 ± 0.1
		pH 9	3.027	2.559 ~ 3.494	9.3 ± 0.1	9.3 ± 0.2
Synthesized Water	**16 °C**	**pH 5.5**	1.096	1.012 ~ 1.180	7.8 ± 0.2	9.6 ± 0.2
		pH 7	1.253	1.086 ~ 1.421	9.5 ± 0.1	9.8 ± 0.2
		pH 9	0.753	0.720 ~ 0.786	9.2 ± 0.1	9.2 ± 0.2
	5 °C	**pH 5.5**	0.600	0.547 ~ 0.653	9.1 ± 0.2	9.3 ± 0.1
		pH 7	2.206	1.845 ~ 2.566	7.8 ± 0.3	9.9 ± 0.3
		pH 9	1.581	1.353 ~ 1.809	7.5 ± 0.2	10.2 ± 0.3

When observing the extent of Cr(VI) formation, all the experiments reached complete oxidation with the exception of three cases in synthesized water where the maximum Cr(VI) was 7.8, 7.8, and 7.5 μg/L (pH 5.5 at 16 °C, pH 7 at 5 °C; pH 9 at 5 °C, respectively).

The total chromium remaining concentrations (Table 18) confirmed that precipitation was not a factor over these shorter time frame experiments. Since the majority of the $KMnO_4$ experiments neared complete oxidation by the end of the 4-hour experiment duration, statistical analysis did not show any significant differences in the maximum Cr(VI) concentration between the different parameters investigated.

For the pH 7 and 9 experiments, the Cr(VI) concentration models generated by the rate constants for the various $KMnO_4$ experiments were generally good representations of the chromium oxidation when compared to the measured Cr(VI) concentrations, especially the experiments conducted in the synthesized water. The oxidation models representing the pH 5.5 experiments were adequate only for the experiments conducted in the synthesized water.

Effect of pH

To provide a basis of chromium oxidation by $KMnO_4$ under controlled conditions, an experiment expected to favor chromium oxidation is shown in Figure 37. During the Cl_2 experiments pH 9 consistently experienced less oxidation, which was attributed to both the speciation of chlorine with respect to pH and the increased potential for precipitation. For the $KMnO_4$ experiments, all the pH values (including pH 9) were expected to reach complete oxidation since the concerns of precipitation or oxidant speciation were not the same for this oxidant.

Although most of the $KMnO_4$ experiments eventually reached complete Cr(III) oxidation (considering total chromium remaining), pH 5.5 experienced a slower rate of oxidation than the experiments conducted at pH 7 and 9. Interestingly, the first-order model does not provide a very good fit to the pH 5.5 data (Figure 37).

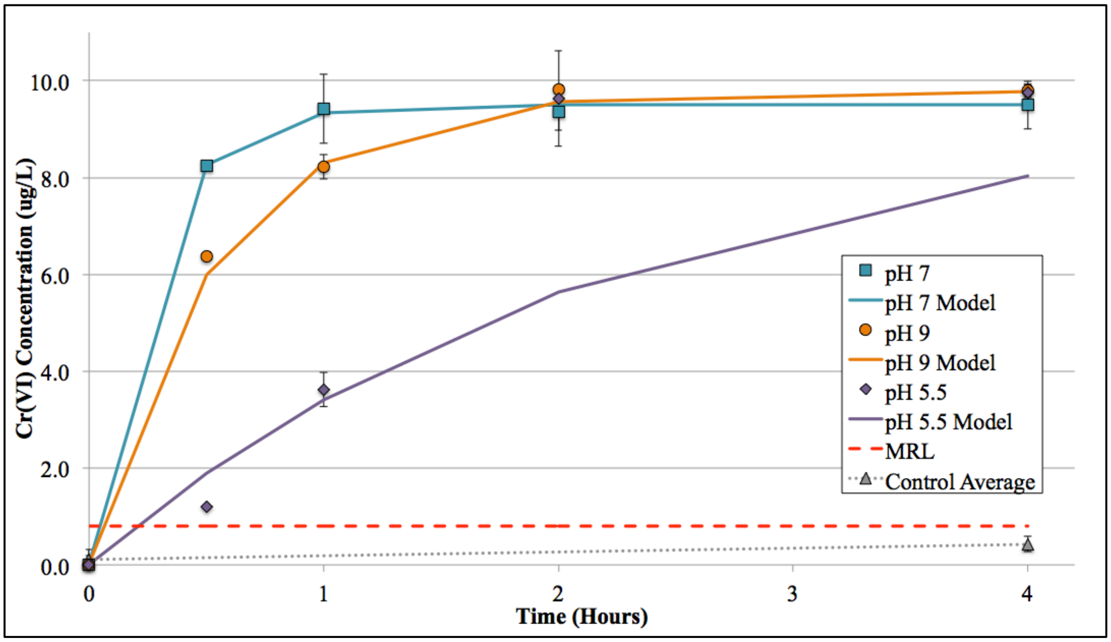


Figure 37. Cr(VI) results & modeling for 1 mg/L $KMnO_4$ in deionized water at 16 °C. MRL was 0.8 µg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

There were two instances where the 95% confidence intervals for the oxidation rate overlapped between two pH values in the same water quality and temperature, indicating no significant difference (deionized water, pH 7 & 9, 5 °C; synthesized water, pH 5.5 & 7, 16 °C). Further statistical analysis (t-tests) on the maximum Cr(VI) concentration for these two sets of experiments indicated that even though the oxidation rates were not significantly different, one of the cases was still significant (synthesized water, p=0.002). In this case, the pH 7 had a higher maximum Cr(VI) concentration (9.5 ± 0.1 µg/L).

Another observation was that of the four sets of pH experiments, there were three instances where the pH 5.5 results had the slowest oxidation rate. However there was no clear trend showing which experiments (pH 7 or 9) experienced the faster oxidation rate.

Effect of Temperature

Temperature comparisons of the rates of oxidation for each pH value and water quality showed there were some significant differences (Table 18). However, the colder temperature of 5 °C did not always slow down the oxidation kinetics when compared to the corresponding 16 °C experiment.

Effect of Oxidant Dose

Since only one dose (1 mg/L) of KMnO4 was investigated, it was not possible to determine any trends as a result of different oxidant doses.

Effect of Water Quality

During the synthesized water experiments, there were some significant changes in Cr(III) oxidation, especially for the pH 5.5 experiments. These synthesized water experiments are illustrated in Figure 38 and have the same parameters as those conducted in deionized water (Figure 37).

For the 16 °C experiments that were conducted in the synthesized water (Figure 38), the rates of oxidation in each of the pH values was significantly different from their deionized water counterpart. However, the pH 7 and 9 experiments conducted in the synthesized water were slower than the experiments conducted in the deionized water quality while the pH 5.5 experiments were faster in the synthesized water. In the synthesized water the pH 5.5 experiments also experienced less maximum Cr(VI) production over the 4-hour duration than those in the deionized water. Despite these differences in rates, from Figure 38 it can be observed that significant Cr(III) oxidation will occur within 4 hours of $KMnO_4$ addition at all pH values.

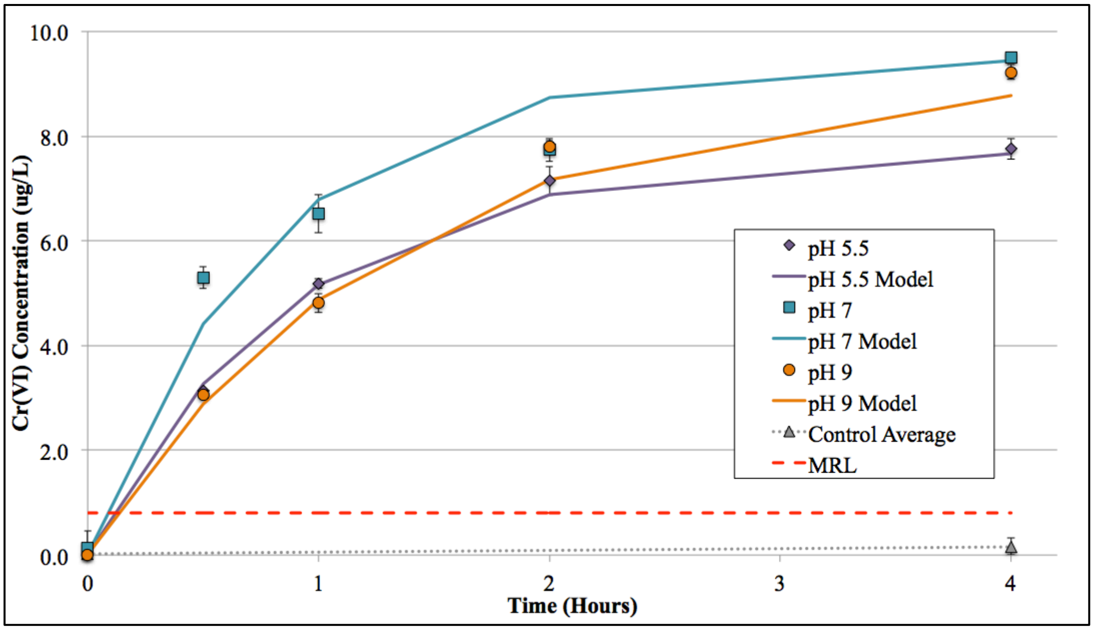


Figure 38. Cr(VI) results & modeling for 1 mg/L $KMnO_4$ in synthesized water at 16 °C. MRL was 0.8 μg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

Effect of Initial Cr(III) Concentration

To satisfy the fifth objective of this project, $KMnO_4$ experiments were also conducted with a higher starting Cr(III) concentration of 100 μg/L to compare to the lower starting Cr(III) concentration and to compare the Cr(III) oxidation experiments previously conducted.

In the original bench set design plan (Table 4), pH 7 and 9 were to be investigated. After observing the Cr(III) oxidation in the experiments with the lower Cr(III) starting concentration in bench set 1, both pH 7 and 9 exhibited similar Cr(III) oxidation trends while pH 5.5 was significantly slower. The slower Cr(III) oxidation in the pH 5.5 experiments was also observed in a previous study (Lai and McNeill 2006). As a result, pH 5.5 and 7 were investigated instead of pH 7 and 9. The rate constants and the overall experiment summary for these experiments can be seen in Table 19.

Table 19. Oxidation Summary for Potassium Permanganate; Bench Set 2 Experiments (100 µg/L starting Cr(III) in Synthesized Water at 16 °C)

Parameters			Rate Constant k (hr^{-1})	95% Confidence Interval for k (hr^{-1})	Maximum Cr(VI) Concentration (µg/L)	Total Chromium Remaining (µg/L)
Synthesized Water	1 mg/L	pH 5.5	0.910	0.604 ~ 1.215	97.1 ± 1.30	95.6 ± 2.20
		pH 7	3.193	3.009 ~3.376	98.0 ± 0.60	95.8 ± 2.56

For the experiments conducted at pH 5.5, there was no significant difference in oxidation rate based on initial Cr(III) concentration (k = 0.910 hr^{-1} compared to 1.096 hr^{-1} for 10 µg/L Cr(III), Table 18). At the higher starting Cr(III) concentration, the experiments conducted at pH 7 did see a significant increase in oxidation rate (3.193 hr^{-1} vs 1.253 hr^{-1}, Table 18). Both the pH experiments reached complete oxidation and the total chromium remaining indicated that precipitation was not likely a factor during these experiments. The Cr(VI) formation that occurred during these experiments can be seen in Figure 39.

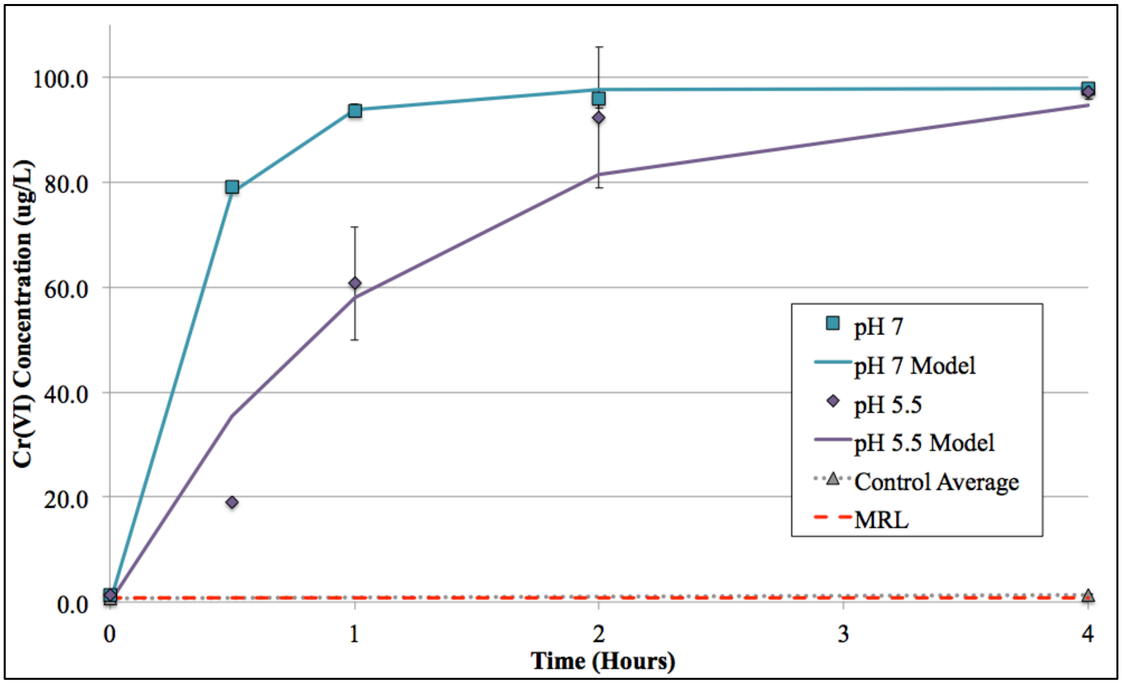


Figure 39. Cr(VI) results & modeling for 1 mg/L $KMnO_4$ in synthesized water at 16 °C. MRL was 0.8 µg/L for modified Cr(VI) analysis. Error bars are standard deviation of triplicate measurements.

The observed Cr(VI) concentration in the pH 7 experiments was similar to the previous experiment conducted, with complete oxidation of Cr(III) (Lai and McNeill 2006). However, it was not possible to determine exact comparisons of the Cr(VI) concentrations due to differences between sampling times. The same trend was also observed of slower kinetics at pH 5 (Lai and McNeill 2006) and pH 5.5 (this study) compared to pH 7.

Ozone

Ozone (O_3) was the second of two oxidants chosen for this project that had never been investigated in terms of chromium oxidation. The assumption was that due to the strong nature of O_3 as an oxidant, it would oxidize all available Cr(III) to Cr(VI) faster than any of the previous oxidants that were investigated. This assumption was immediately confirmed during every variation of the 1 mg/L O_3 experiments (Table 20).

In every experiment, complete oxidation was observed by the first sampling time (2 minutes). It is possible that the O_3 could have oxidized the available Cr(III) to Cr(VI) faster than the observed 2 minutes, but it was not logistically possible to sample the Cr(VI) concentration any faster. A typical result in synthesized water at 16 °C is shown in Figure 40.

Table 20. Oxidation Summary for Ozone with 1 mg/L O_3

Parameters			**Maximum Cr(VI) Concentration (μg/L)**	**Total Chromium Remaining (μg/L)**
Deionized Water	**16 °C**	**pH 5.5**	9.6 ± 0.2	9.5 ± 0.1
		pH 7	9.9 ± 0.6	9.8 ± 0.4
		pH 9	10.0 ± 0.2	9.7 ± 0.2
	5 °C	**pH 5.5**	9.8 ± 0.2	9.5 ± 0.3
		pH 7	10.0 ± 0.2	9.6 ± 0.3
		pH 9	9.9 ± 0.4	9.8 ± 0.4
Synthesized Water	**16 °C**	**pH 5.5**	10.2 ± 0.5	10.4 ± 0.3
		pH 7	10.2 ± 0.1	9.8 ± 0.3
		pH 9	12.0 ± 0.3	11.6 ± 0.4
	5 °C	**pH 5.5**	10.0 ± 0.5	9.6 ± 0.4
		pH 7	11.6 ± 0.3	11.3 ± 0.2
		pH 9	11.6 ± 0.8	11.1 ± 01

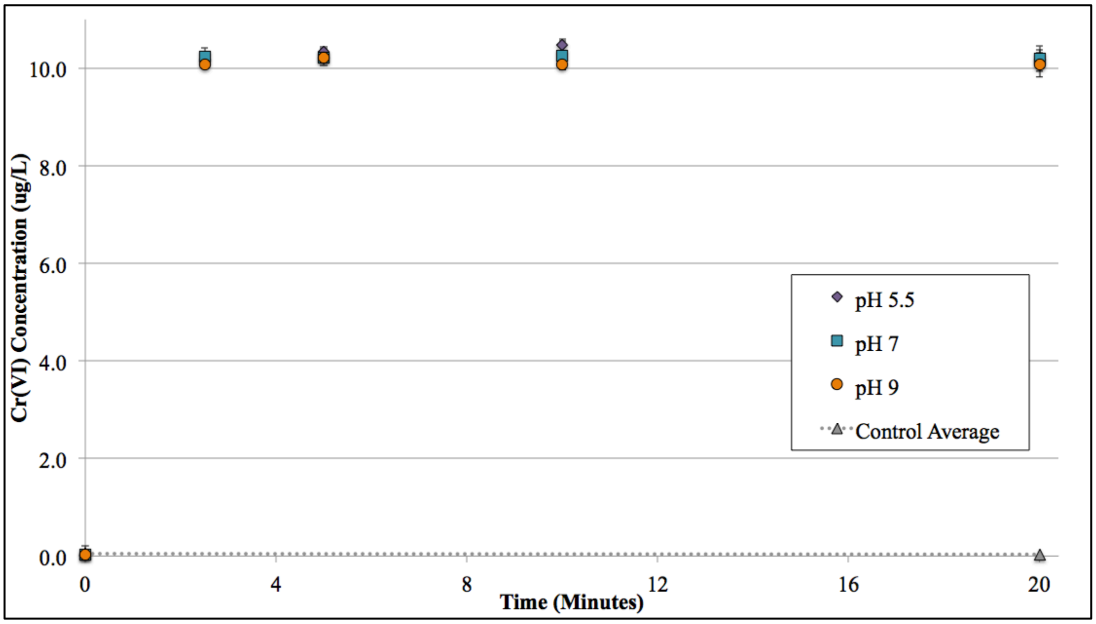


Figure 40. Cr(VI) results for 1 mg/L O_3 in synthesized water at 16 °C. Error bars are standard deviation of triplicate measurements (typically <0.1 µg/L, not visible outside of data markers).

Due to these fast kinetics, rate constants could not be determined for ozone, but it was clear that ozone caused Cr(VI) formation more rapidly than the other oxidants tested. During the experiments, the maximum Cr(VI) concentration that was observed was equal to that of the total chromium remaining at the end of the experiment and there was no indication that precipitation was occurring, likely due to the short duration of the experiments.

Since ozone oxidized Cr(III) so quickly to Cr(VI) for each condition investigated, there was no further investigation into the effects of pH, water temperature, water quality, and initial Cr(III) concentration.

CONCLUSION

This study investigated the ability of five common drinking water oxidants (chlorine, monochloramine, chlorine dioxide, potassium permanganate, ozone) to oxidize Cr(III) to Cr(VI). Considering the recent implementation of California's MCL for Cr(VI), investigating the lower starting Cr(III) concentration of 10 μg/L has provided more insight into chromium oxidation at a concentration that may also be considered for federal regulation.

The Cr(VI) formation observed for each oxidant provided the data to quantify the extent of Cr(III) oxidation over the specific time periods chosen for each oxidant. These observations led to the development of rate constants used in a first order equation. These rate constants along with summaries of maximum Cr(VI) formation and total chromium remaining after each experiment provided a basis for comparisons between the different parameters investigated throughout this project.

Overall Summary of Oxidant Performance

From the various experiments, it was shown that chlorine (Cl_2) would oxidize Cr(III) to Cr(VI) at the pH values of 5.5, 7, and 9 in both the laboratory generated deionized and synthesized water qualities over the duration of the 120 hour experiments. However, Cl_2 did not completely oxidize all soluble Cr(III) over the same 120 hour duration. The maximum Cr(VI) concentration was always greater when the higher 4 mg/L Cl_2 dose was used. The rates and extent of oxidation were generally faster at the higher 4 mg/L dose (one exception was pH 9 in deionized water), with an observed range of 0.015-0.288 hr^{-1} for all the experiments. Similar to previous experiments, the majority of the chromium oxidation as a result of Cl_2 addition occurred within the first 12 hours of the experiment, which is a realistic residence time for most distribution systems.

As expected, monochloramine (NH_2Cl) was not an effective oxidant under any of the investigated conditions.

With no previous studies having investigated oxidation to Cr(VI) as a result of using chlorine dioxide (ClO_2), this project provided data on Cr(VI) production and also provided methods to analyze Cr(VI) when using ClO_2 since the suggested method of post column reaction with ion chromatography proved to be difficult. The oxidation results were difficult to analyze, as ClO_2 had an as-yet unexplained effect on solution pH and in some cases there was a decrease in Cr(VI) with time. At the smaller ClO_2 dose of 0.4 mg/L, experiments conducted in both the deionized and synthesized water qualities at pH 7 showed nearly complete Cr(III) oxidation within the 6 hour experiment duration with observed oxidation rates of 0.430-2.814 hr^{-1}. At pH 5.5 and 9, results were more variable, but oxidation was generally slower and less complete. Large variations in results at the dose of 0.8 mg/L ClO_2 precluded analysis of water quality or temperature effects.

Due to coloration interference, the experiments investigating Cr(III) oxidation by potassium permanganate ($KMnO_4$) were challenging. Utilizing a Cr(VI) analysis method which required manual spectrophotometry, the larger dose of 5 mg/L $KMnO_4$ (more color) created complications with the indicator solution (diphenylcarbazide) used to monitor Cr(VI). These complications prevented the continuation of the $KMnO_4$ experiments using the larger 5 mg/L dose. At the smaller dose of 1 mg/L, $KMnO_4$ was shown to oxidize all available Cr(III) to Cr(VI) for all the investigated parameters within 4 hours, with oxidation rates of 0.431-4.082 hr^{-1} being observed. With limited data on the oxidation potential of $KMnO_4$, the data collected during this project verified its ability to oxidize Cr(III) to Cr(VI) within time durations common for water treatment.

This project was the first to provide data on Cr(VI) by ozone (O_3). Confirming initial assumptions that O_3 was a strong oxidant, complete oxidation of Cr(III) to Cr(VI) was observed within 2 minutes in every experiment at each investigated condition.

Objective 1: Effect of pH

The first objective of this project was to determine the change in chromium oxidation at the pH values of 5.5, 7, and 9. The values of 5.5 and 9 were chosen to show an extreme range of pH values while the middle value of pH 7 was chosen as a more realistic pH value that would be observed at any given utility.

During the experiments investigating Cl_2 and NH_2Cl as the oxidant, regardless of water quality, precipitation of total chromium was potentially a factor in the maximum extent of oxidation observed. Precipitation may have been a factor with the other investigated oxidants (ClO_2, $KMnO_4$, O_3), but since their respective experiment durations were much shorter (hours instead of days) it was not certain if precipitation was occurring. During the Cl_2 and NH_2Cl experiments, precipitation was apparent in all the pH values, but especially at the higher pH values (7 and 9). As a result of precipitation, the amount of soluble Cr(III) decreased and likely decreased the amount of oxidation to Cr(VI). Accordingly, the maximum Cr(VI) formed and TotCr remaining in solution are reported in the data summaries. Although precipitation was observed, mass balances at the end of each experiment recovered nearly 100% of the chromium.

The effect of pH could not be determined for NH_2Cl (no oxidation observed) and O_3 (complete oxidation at all conditions within the first sampling period). During the Cl_2 experiments, the oxidation rate at pH 5.5 was slower than at pH 7 or 9. However, the pH 5.5 experiments had the largest maximum Cr(VI) concentration at the end of the experiments; oxidation was nearly as great at pH 7 and sometimes statistically the same as pH 5.5. These trends are attributed to the chlorine speciation. The pKa value of HOCl (the source of chlorine) is 7.43, meaning HOCl dissociates at higher pH values to form the hypochlorite ion (OCl^-), which is not as strong an oxidant. The experiments conducted at pH 9 experienced the least amount of oxidation. The most precipitation was also observed at pH 9, and it appeared that precipitated chromium was not as susceptible to oxidation.

The pH trends for $KMnO_4$ were similar to those observed during the Cl_2 experiments, with pH 5.5 generally experiencing a slower Cr(III) oxidation rate. In almost every experiment, all of the soluble Cr(III) was oxidized to Cr(VI).

For the experiments investigating ClO_2 as the oxidant, the majority of the pH 7 experiments experienced effective Cr(III) oxidation during the 6 hour duration. The Cr(III) oxidation observed was faster than the oxidation rates that were seen in the Cl_2 and $KMnO_4$ experiments. However, for all the experiments there was significant change in the pH over the experiment duration. The suggested cause was that ClO_2 dose was affecting the pH and overall aquatic chemistry of the water qualities. This significant change in pH made it difficult to discern any oxidation trends associated with the pH.

Objective 2: Effect of Temperature

All experiments were conducted at both 5 and 16 °C, and it was expected that oxidation rates would be faster at the warmer temperature. Due to the rapid oxidation caused by O_3 and the lack of oxidation with NH_2Cl, temperature was not a factor for either oxidant. Statistical analyses showed there was no significant difference between temperatures for pH 7 and 9 in synthesized water during the chlorine experiments. However, oxidation kinetics were significantly faster at 16 °C during the pH 7 deionized water experiments. At pH 5.5 the kinetics were faster at 16 °C in the deionized and synthesized water qualities for all but one condition. There were significant differences with temperature for the experiments performed using chlorine dioxide and potassium permanganate, although there was not a clear trend of faster kinetics at warmer temperature.

Objective 3: Effect of Oxidant Dose

To determine if oxidant dose would affect Cr(III) concentration, two different doses were investigated for NH_2Cl, Cl_2, and ClO_2. Similar to the previous objective, the lack of oxidation with NH_2Cl led to the determination that oxidant dose was not a factor. During the ClO_2 experiments, large variations in measured Cr(VI) at the higher dose of 0.8 mg/L ClO_2 made it difficult to determine Cr(III) oxidation trends caused by oxidant dose.

During the Cl_2 experiments at pH 5.5 and 7, the higher oxidant dose caused faster Cr(III) oxidation and greater extent of Cr(VI) formation in both the deionized and synthesized water qualities. At pH 9, the higher chlorine dose caused faster oxidation in the synthesized water but did not affect extent of oxidation; in the deionized water quality the higher chlorine dose caused more Cr(VI) formation but did not affect the rate.

Objective 4: Effect of Water Quality

Conducting these experiments in the deionized water quality provided a baseline understanding of chromium oxidation under the investigated parameters of this project without effects of other water quality constituents. Performing experiments in the synthesized water quality and the actual source water from the American Water treatment facility in Delran, NJ provided a more realistic comparison to natural source waters.

Experiments performed in the synthesized water quality experienced notable changes in oxidation rates with water temperatures and oxidant doses as well as an increased presence of precipitation. These changes in oxidation included consistently higher oxidation rates in the synthesized water quality, and generally faster oxidation rates with the higher Cl_2 dose. The majority of these changes were attributed to the additional chemical constituents used in the synthesized water to create a water quality that would better reflect natural source water. These constituents allowed for closer approximation of oxidation rates found in the laboratory generated source water. These constituents also provided more potential sorption sites for Cr(III), possibly explaining the increased presence of precipitation.

NOM had a strong Cl_2 demand that ultimately decreased the amount of chromium oxidation. NOM may also complex soluble Cr(III), making it more difficult to oxidize to Cr(VI). Although NOM may decrease the amount of potentially harmful Cr(VI) formed in drinking water by Cl_2, the reaction of Cl_2 with NOM creates disinfection byproducts (DBPs), which can also be harmful in drinking water.

Objective 5: Effect of Initial Cr(III) Concentration

The last objective of this project was to complete a subset of experiments using a higher initial Cr(III) concentration (100 μg/L) for chlorine, monochloramine, and potassium permanganate as oxidants to compare to the smaller initial Cr(III) concentration (10 μg/L). These results were also compared to previous studies also conducted with the same 100 μg/L starting Cr(III) dose.

Rate constants for chlorine and permanganate were significantly different in experiments with 10 μg/L Cr(III) compared to those performed with the starting Cr(III) concentration of 100 μg/L. This was a preliminary indication that starting Cr(III) concentration was an independent factor and the use of first order reactions to model the kinetics of Cr(VI) formation could be questioned. However, since the pseudo first order reactions were used only as a preliminary modeling tool and they adequately compared to observed data, they were still used to make comparisons between experiment parameters.

Overall, this project provided necessary data on chromium behavior and oxidation under a wide range of detailed conditions that would allow operators, designers, regulators, and engineers to make more educated decisions to protect consumers from the potentially harmful effects of Cr(VI) ingestion.

ENGINEERING SIGNIFICANCE

The main purpose of this project was to expand the understanding of oxidation kinetics of chromium. The data and analyses gathered during this project provide information for drinking water utilities to better manage their systems to comply with regulations and protect public health.

Due to the health contrasts that exist between Cr(III) and Cr(VI), understanding the oxidation kinetics is crucial when discussing possible updates to drinking water regulations. Since there are no current federal regulations on Cr(VI) in drinking water, it is often unknown whether Cr(VI) concentrations are increasing after discharge from a treatment plant due to oxidation of Cr(III). To avoid the inadvertent addition of Cr(VI) into distribution systems, the first step was to understand the oxidation kinetics that create Cr(VI). All the parameters in these bench scale tests were chosen in an attempt to provide realistic, situational data that treatment plants can use and relate to their individual processes.

If a treatment plant is using monochloramine for oxidation and disinfection, there is no indication that chromium oxidation would occur. Depending on dose, pH, and residence time in a distribution system, approximately 80% oxidation of chromium will occur when using chlorine for treatment. At pH 7, if any treatment plants are using chlorine dioxide, complete chromium oxidation can be expected within 6 hours of addition. Similarly at all pH values, potassium permanganate will cause complete chromium oxidation in 4 hours. For any treatment plants utilizing ozone for water treatment, it should be expected that all available chromium would be oxidized within minutes of contact with the strong oxidant.

When discussing the possibility of new chromium regulations in drinking water, it would be ideal to measure the chromium species at the consumer tap, similar to lead and copper monitoring. Monitoring chromium at the tap would allow each water treatment plant to better understand the individual characteristics of oxidation kinetics that are occurring in the distribution system between source and actual consumption. While this idea of tap monitoring is ideal, it is not likely considering the costs that would be associated with monitoring chromium in multiple locations as opposed to just one at the entry point to a distribution system. Since tap monitoring isn’t likely due to logistical and monetary concerns, these experiments give an approximation of the extent of oxidation that will occur in different treatment and distribution systems.

Future work on this topic should focus on better understanding the role that particulate species of chromium can have on Cr(III) oxidation. Another future work topic would be a more in depth look of chromium oxidation as a result of using chlorine dioxide (ClO_2) as an oxidant. This project provided a good basis to begin looking deeper into the effects ClO_2 may have on aquatic chemistry and the oxidation kinetics of chromium. Another topic for future work is to investigate the possibility of using a cation resin to remove Cr(III). This may provide a more accurate way to monitor the different chromium species when investigating oxidants such as chlorine dioxide and potassium permanganate, which could not be analyzed for Cr(VI) using the recommended post column ion chromatography method.

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APPENDICES

APPENDIX A

Analytical Issues Related to Permanganate

Potassium permanganate ($KMnO_4$) presented some analytical complications because $KMnO_4$ in solution is a similar pink color that is manifest when Cr(VI) mixes with the diphenylcarbazide (Figure A - 1). Initially there was concern that samples containing $KMnO_4$ would cause a false positive during spectrophotometric analysis of Cr(VI) using ion exchange with the post-column reaction.

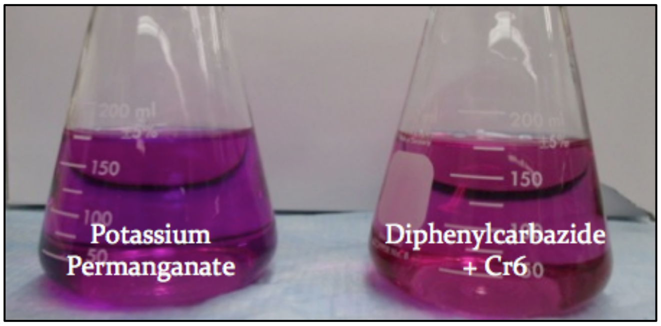

Figure A - 1. Flasks filled with potassium permanganate and diphenylcarbazide mixed with Cr(VI).

To verify this suspicion of color interference, an absorbance curve was created for the two dose concentrations of $KMnO_4$ that were proposed for the bench scale experimentation (Figure A - 2).

The curve in Figure A - 2 shows a peak absorbance at a wavelength range between 520 and 540 nm. This verifies the possibility of interference because during Cr(VI) analysis the diphenylcarbazide absorbance is measured at 530 nm. To confirm that there would be interference in the Cr(VI) analysis, a sample containing only DIW and $KMnO_4$ was run through the Dionex ICS-1600, generating the chromatogram in Figure A - 3.

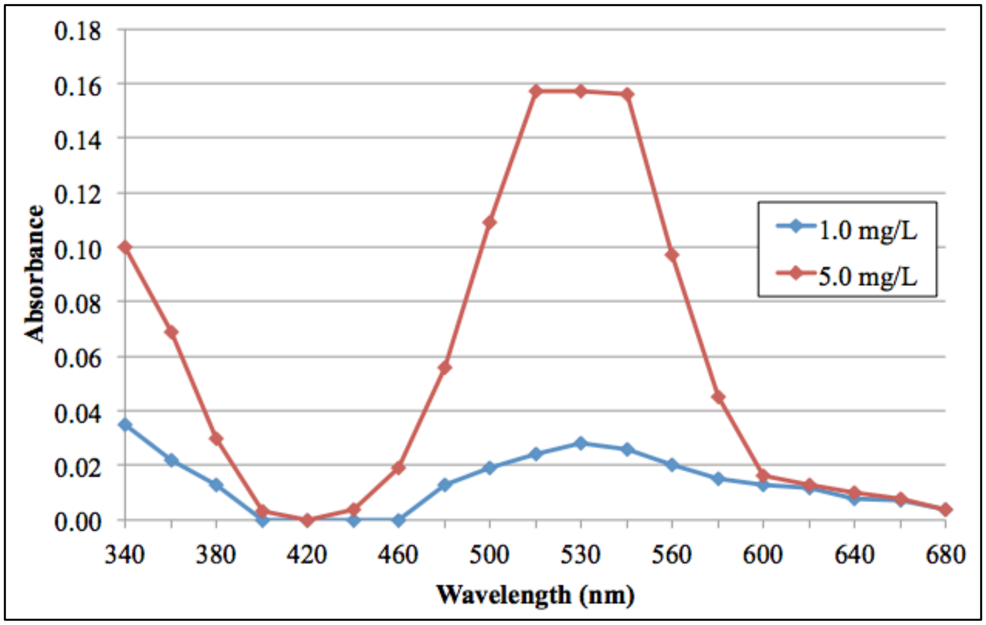

Figure A - 2. Absorbance curve for potassium permanganate at concentrations of 1.0 and 5.0 mg/L.

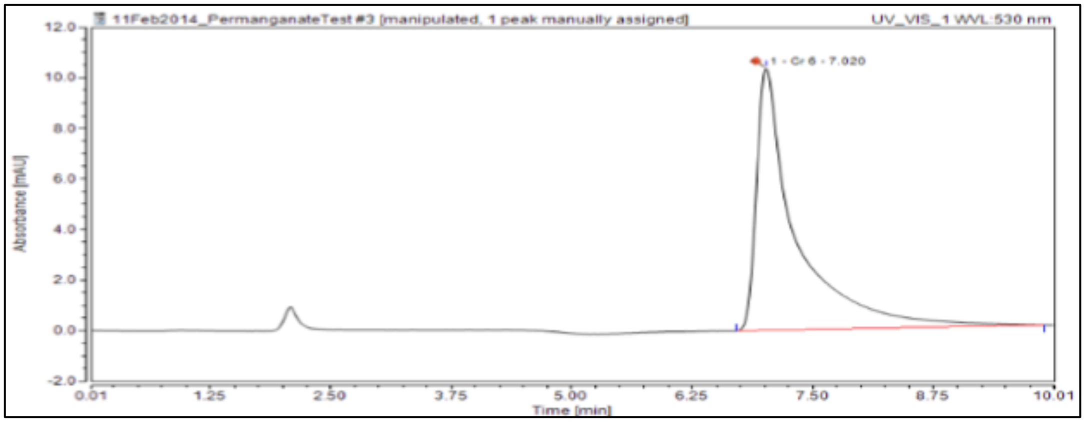

Figure A - 3. Ion chromatogram of sample containing only deionized water and potassium permanganate

This chromatogram in Figure A - 3 shows a peak that occurs around the 7 minute mark, which is the same time that Cr(VI) concentrations are detected and measured, leading to a false positive measurement of 8.5 μg/L Cr(VI).

APPENDIX B

Rate Constant Determination

This section provides an example of how the rate constants were determined using data from experiments with 1 mg/L Cl_2 in synthesized water at 16 °C.

Once a set of experiments (3 experiments were completed at the same time, one each for pH 5.5, 7, and 9) were done and the Cr(VI) and TotCr analysis was complete, the data were saved as a .csv file and uploaded into the statistical software R as one complete data frame. This data frame was then spilt into three separate data frames, one for each pH value. The triplicate Cr(VI) measurements for each of these experiments were then narrowed down to only include the first six Cr(VI) measurements (first 7 hours of the experiment) and the last Cr(VI) measurement. This last measurement was used as the maximum Cr(VI) concentration that was used in Equation 3. For each experiment, it was verified that the last Cr(VI) measurement was actually the maximum Cr(VI) concentration observed during the duration of the experiment.

The triplicate data for each data frame (corresponding to a pH value) were then linearized using Equation 4. Once this had been completed, qqnorm plots were generated for each of the data frames (pH values) to check that the data were normally distributed. An example of these qqnorm plots for the 1 mg/L Cl_2 experiments conducted in deionized water at 16 °C can be seen in Figure B - 1.

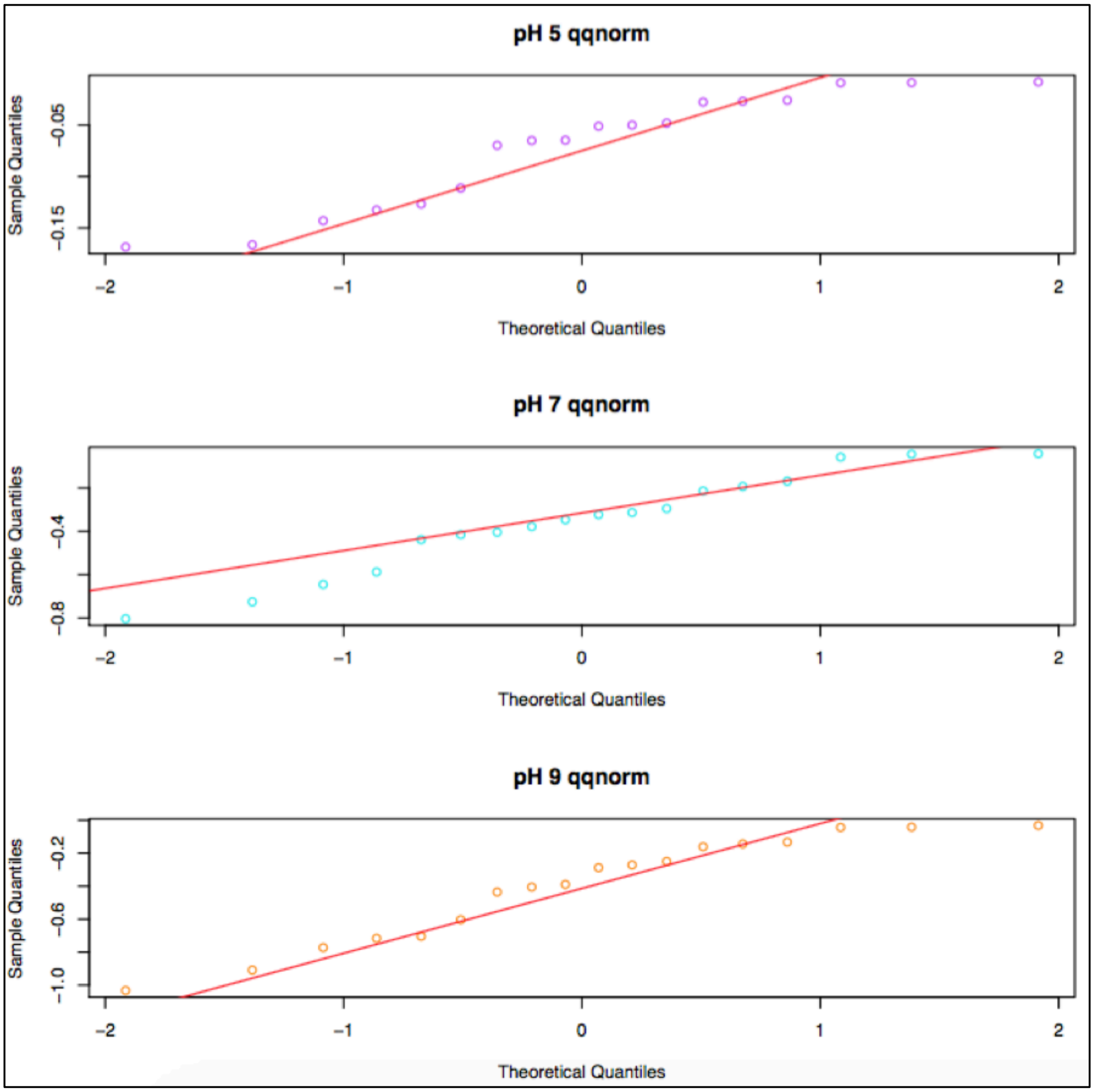

Figure B - 1. Qqnorm plots for quality control for experiments with 1 mg/L Cl_2 in synthesized water at 16 °C.

Once the qqnorm plots were verified, the residuals of these data were also plotted to check to make sure they were normally, identically, and independently distributed (NIID). These residual plots that correspond to experiments with the qqnorm plots shown in Figure B - 1 can be seen in Figure B - 2.

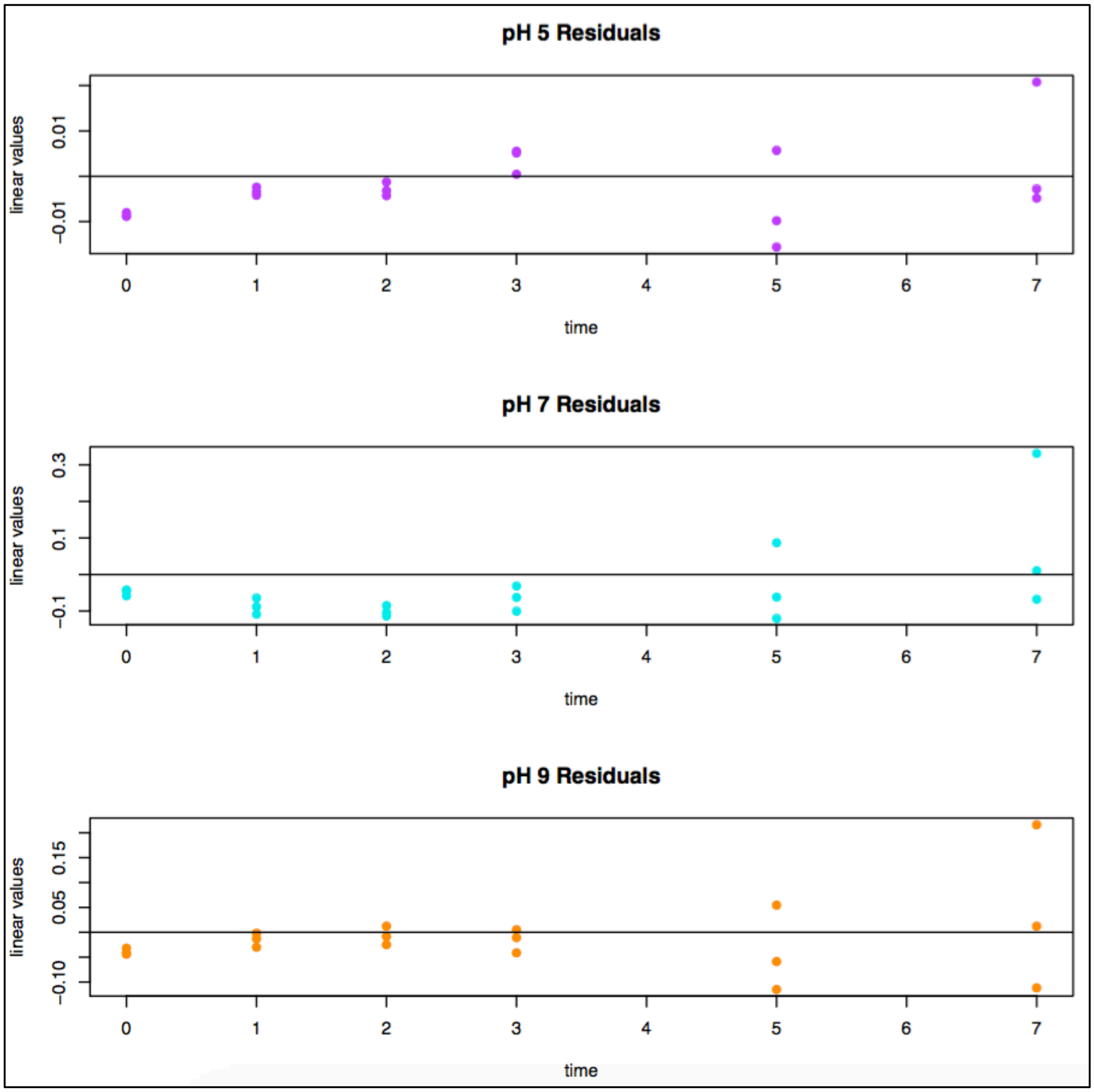

Figure B - 2. Residual plots for quality control for experiments with 1 mg/L Cl_2 in synthesized water at 16 °C.

Since the observed data were collected in triplicate, the residual plots each show three data points for each of the observed time intervals. Once the data had been verified as NIID (with the exception of the triplicate measurements), the linearized data were plotted, forcing the y-intercept to zero. The plots following the same data above are shown in Figure B - 3.

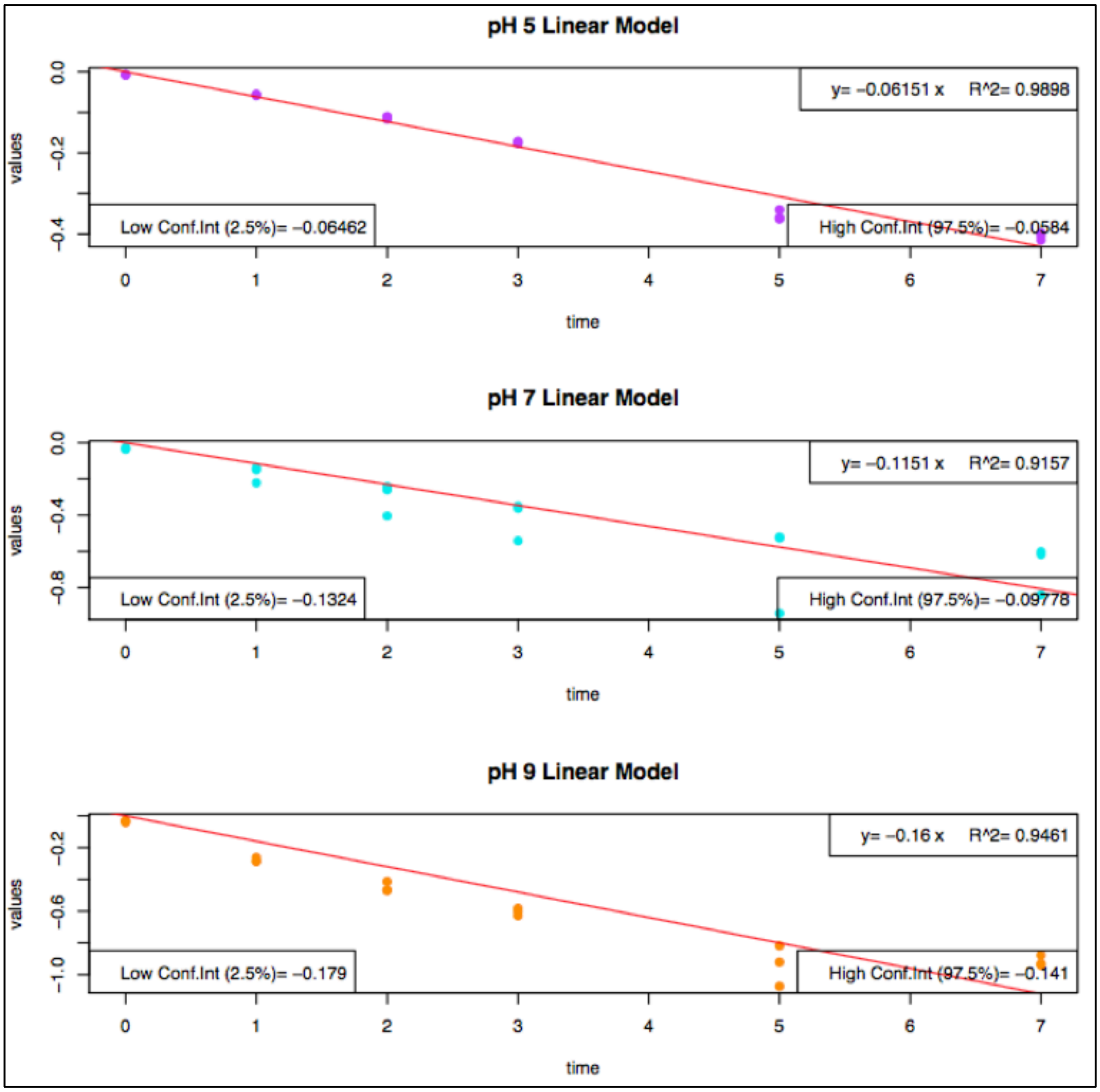

Figure B - 3. Linear plots to determine rate constants for experiments with 1 mg/L Cl_2 in synthesized water at 16 °C. Confidence intervals are included.

Once the linearized data were plotted for each of the data frames (pH values), a linear trendline was fit to the data. The slope of this line and its corresponding R^2 value were indicated in the top right corner. The 95% confidence intervals were also indicated in the bottom corners. The slope value was the equal to –*k* (Equation 5); since the slope values were already negative, the resulting positive value was the rate constant *k* that was used to create the Cr(III) oxidation models for each of the investigated parameters. This process was repeated for all other experiments.