

Cr(VI) Generation and Stability in Drinking Water

Kathita Chittaladakorn

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Marc A. Edwards (Chair)

Laurie S. McNeill

Peter J. Vikesland

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ABSTRACT

The current US Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for total chromium of 100 ppb is under revision to consider a specific level for Cr(VI), which has a proposed MCL of 10 ppb in California. Cr(VI) is a suspected carcinogen, and interconverts with the other most commonly found chromium species, Cr(III). To regulate and further understand the behavior of Cr(VI) in water systems, appropriate sample preservation methods are essential for accurate measurements. The ammonia buffer (recommended by EPA) was proven to be the most effective preservation when a holding time of 14 days is considered.

Apart from proper Cr(VI) preservation, sampling at an appropriate site is important for determining the public's exposure to Cr(VI). The proposed MCL for Cr(VI) in the state of California will be monitored at the entry point of distribution systems. To the extent that Cr(VI) is formed in the distribution system or in water contacting plumbing, measurements at the treatment plant might not reflect consumer exposure at the tap. Cr(VI) can be released to drinking water from Cr present in stainless steel alloys. At the maximum residual disinfectant level (MRDL), Cr(VI) formation decreased in the order chlorine dioxide > chlorine > chloramine. Less Cr(VI) was released from stainless steel at lower pH in the presence of chlorine, but the opposite trend was observed for chlorine dioxide. Stainless steels with a higher chromium content tended to release more Cr(VI).

ATTRIBUTION

This thesis was prepared in a journal manuscript format according to the guidelines given by the graduate school and Department of Civil and Environmental Engineering at Virginia Tech.

Experiments for Chapter 1, “Evaluation of Hexavalent Chromium Stability in Drinking Water Samples” was done at the Utah Water Research Laboratory, Logan, UT under the supervision of Laurie McNeill and Joan McLean. They and Marc Edwards were involved in data interpretation and editing. The author would also like to thank the following laboratory team members for their contribution: Suzy Smith, Lindsey Stevens, Indhira Hasbun, Rahel Beyene, Tessa Guy and Joe Stewart. This study was partially funded by the Water Research Foundation project 4404.

Chapter 2, “Hexavalent chromium [Cr(VI)] formation in potable water from stainless steel components” was done at Virginia Tech, and would not be possible without support from Jody Smiley and other members of the Edwards research group. This work was done under the guidance of Laurie McNeill and Marc Edwards.

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Last but not least, the author would like to express her special thanks to Marc Edwards, Laurie McNeill, Joan McLean and members of the Edwards research group for their academic and mental support.

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Chapter 1 : Evaluation of Hexavalent Chromium Stability in Drinking Water Samples

Chittaladakorn, K., McNeill, L., McLean, J. and Edwards, M.

(In review for publication)

ABSTRACT

Currently, USEPA has a maximum contaminant level (MCL) for chromium of 100 ppb. Chromium generally exists in two oxidation states in the environment: Cr(III) and Cr(VI). Cr(III) is perceived as a micronutrient while Cr(VI) is considered unsafe for human consumption. The public health goal (PHG) set by the state of California for Cr(VI) is 0.02 ppb, and the proposed MCL is 10 ppb. When analyzing chromium-containing samples, it is critical that the samples be properly preserved so that the measurement accurately reflects the chromium speciation (Cr(III) vs. Cr(VI)) at the time the sample was collected. If successful, sample preservation can dramatically reduce shipping and analytical costs for water utilities. Currently, the average cost for Cr(VI) analysis is \$86 per sample.¹ This study systematically evaluated a variety of sample preservatives in three water qualities, to establish which preservatives are effective at maintaining chromium speciation. When a holding time of 14 days is considered, ammonia buffer is the best preservative, able to hold Cr(VI) concentrations constant in all the waters tested, with an exception of situations in which nitrifiers were present. All of the buffers, except the borate buffers (borate only and borate + ammonia), are able to hold Cr(VI) concentrations in the absence of free chlorine, NOM, and nitrifiers. The borate buffers, which are recommended by the California Department of Public Health for chromium sampling, are the least effective, and were actually equal to or less effective than the control without preservative in every case. The carbonate buffers (carbonate only and carbonate + ammonia) are able to preserve Cr(VI) better than the controls. However, the carbonate buffers could not maintain Cr speciation when chlorine or NOM was present in the water.

INTRODUCTION

Chromium is the 21st most abundant element in the earth's crust,² and can enter water sources either naturally or by industrial contamination. Chromium generally exists in two oxidation states in the environment: Cr(III) and Cr(VI). Cr(III) is believed to be a micronutrient, while Cr(VI) is considered a carcinogen. There is clear evidence of Cr(VI) carcinogenicity via inhalation. However, the understanding of Cr(VI) health effects via ingestion is not yet well established.

Currently, only total chromium (Cr(III) and Cr(VI) combined) is regulated. The federal maximum contaminant level (MCL) set by USEPA is 100 µg/L,³ while the MCL is 50 µg/L in the state of California.¹ Since Cr(VI) is the primary oxidation state of concern, there have been thoughts of setting standards specifically for the compound. California had already set a public health goal (PHG) for Cr(VI) as 0.02 µg/L,¹ and recently proposed a new MCL for Cr(VI) as 10 ppb.¹

If a regulation for Cr(VI) were to be implemented, analysis specifically for Cr(VI) has to be done. Nitric acid is used to preserve samples for total chromium analysis. However, nitric acid usage converts all chromium in solutions to Cr(III), and is therefore not appropriate to be used as a preservative prior to Cr(VI) analysis. An appropriate preservative should prevent Cr(VI) conversion to Cr(III) and vice versa.

Several preservatives have been used in prior research. The National Chrome and Boron Occurrence Survey⁴ used a carbonate buffer, while the California Department of Public Health recommended using a borate buffer.⁵ The USEPA Method 218.6, however, suggested using an ammonia buffer.⁶ Method 218.6 was used at the beginning of this study, before the new USEPA Method 218.7 was released. The same ammonia buffer continued to be used after the new method was applied to the study, since the two methods recommended the same preservative.^{6,7}

Chromium Redox Chemistry

To assess which of these buffers is the most appropriate for Cr(VI) preservation in most conditions, an understanding of chromium redox chemistry is essential. Cr(III) commonly exists as Cr³⁺, Cr(OH)²⁺, Cr(OH)₃ and Cr(OH)₄⁻, while Cr(VI) is commonly found as HCrO₄⁻ and

CrO_4^{2-} . Chromium speciation depends on the potential and pH, and the general trend is that Cr(VI) is preferred at higher potential and higher pH. In natural aerated waters, Cr(VI) is favored (Figure 1-1). However, kinetics also have to be considered when predicting chromium speciation since natural waters are rarely in equilibrium.

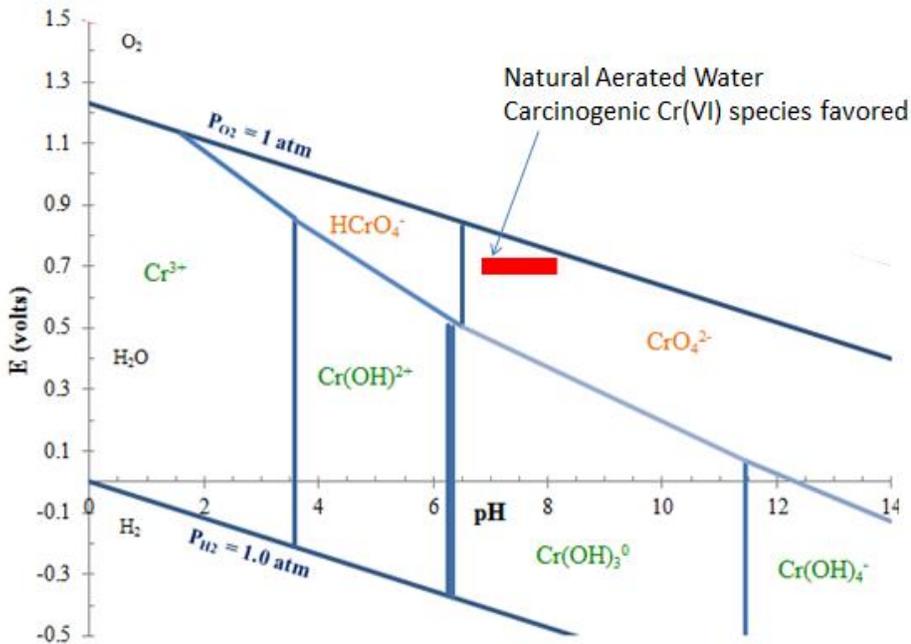
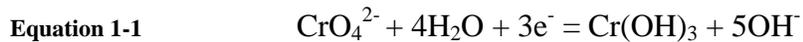


Figure 1-1: Potential vs pH diagram of chromium speciation : orange font represents Cr(VI) compounds, green font represents Cr(III) compounds

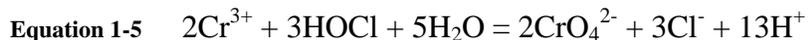
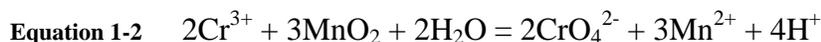
Effect of pH

As pH increases, there is higher tendency for chromium to remain in the +6 oxidation state (Figure 1-1 and Equation 1-1). Buffers used for Cr(VI) preservation raise pH of solutions to prevent Cr(VI) conversion to Cr(III).



Effect of Oxidizing Agents

Oxidizing agents can convert Cr(III) to Cr(VI). Oxidizing agents commonly found or used in drinking water treatment include MnO_2 solids (Equation 1-2), H_2O_2 (Equation 1-3), KMnO_4 (Equation 1-4), chlorine (Equation 1-5) and monochloramine (Equation 1-6).

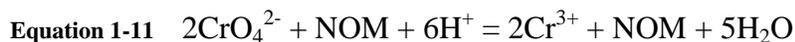
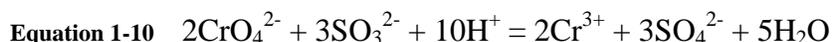
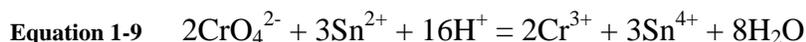
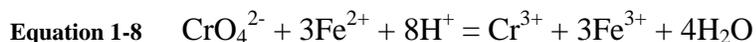


The rate chloramine oxidizes Cr(III) is much slower than chlorine.⁸ To decrease Cr(III) oxidation rate when chlorine is present, EPA Methods 218.6 and 218.7 require adding ammonium which combines with free chlorine to form chloramine (Equation 1-7).



Effect of Reducing Agents

Reducing agents can reduce Cr(VI) to Cr(III), thus giving a false negative when analyzing for Cr(VI). Reducing agents commonly found in natural waters and water treatment systems include Fe(II) (Equation 1-8), stannous chloride (Equation 1-9), sulfites (Equation 1-10) and natural organic matter (NOM, Equation 1-11).



Effect of Microbial Activities

Microbes can affect chromium speciation either directly or indirectly. Some microbes can reduce Cr(VI) to Cr(III),⁹ while some change other chemical compounds which in turn influences chromium speciation. An example of indirect microbial impact is nitrification. In this process, ammonium added for Cr(VI) preservation can serve as a food source for nitrifiers. The decrease

in ammonium concentration can affect the buffer's performance, especially in binding with free chlorine to form chloramine. Nitrifiers oxidize ammonium to nitrite, then nitrate. Nitrite and nitrate may in turn reduce Cr(VI).

The objective of this research was to compare the performance of different buffers used for Cr(VI) preservation and test if temperature has an effect on the ammonium buffer's ability to preserve Cr(VI).

EXPERIMENTAL DESIGN

Water Sources

Three water sources were tested in these experiments: double deionized water (DDW), surface water from Utility A, and a groundwater from Utility B (Table 1-1). For both of the utilities, the water was collected before any treatment. The waters have native Cr(VI) concentrations of 0.05 µg/L and 0.18 µg/L respectively (Table 1-1). The 18MΩ DDW was generated from a Barnstead Nanopure deionization unit in the Utah Water Research Laboratory (Logan, UT).

Table 1-1: Water sources

	Utility A	Utility B
Water Source	Surface Water	Ground Water
Treatment of collected water	Coagulation with ferric chloride, sedimentation, sand filtration	Chlorination
pH	7.7	8.0
Alkalinity (mg/L CaCO ₃)	140	185
Cr(VI) concentration (µg/L)	0.05	0.18

Buffers

Ammonium, carbonate, and borate buffers were tested. In waters with chlorine present, ammonium will combine with free chlorine to form chloramine, which oxidizes Cr(III) much slower. The carbonate and borate buffers are not expected to react with free chlorine, so buffer performance is expected to be worse than the ammonium buffer. To determine whether adding

ammonium buffer to the carbonate and borate buffers would enhance the two buffers' efficiency, a set of samples were also made for these conditions (Table 1-2).

On collection dates, the buffers were brought in coolers to Utilities A and B and were added to the waters on-site. The containers used to store the buffers and collect water samples were rinsed with 50% HNO₃ before use.

Table 1-2: Buffers used

Buffer	Concentration	Reference
No buffer	-	N/A
Ammonium	2.5 mM (NH ₄) ₂ SO ₄ + 10 mM NH ₄ OH	USEPA method 218.6 ⁶ and USEPA method 218.7 ⁷
Carbonate	12 mM Na ₂ CO ₃	National chrome and boron occurrence survey ⁴
Carbonate + Ammonium	12 mM Na ₂ CO ₃ 2.5 mM (NH ₄) ₂ SO ₄ + 10 mM NH ₄ OH	N/A
Borate	1 mM Na ₂ B ₄ O ₇ ·10H ₂ O + 13.4 mM KHCO ₃ + 4.7 mM Na ₂ CO ₃	California Department of Public Health ⁵
Borate + Ammonium	1 mM Na ₂ B ₄ O ₇ ·10H ₂ O + 13.4 mM KHCO ₃ + 4.7 mM Na ₂ CO ₃ 2.5 mM (NH ₄) ₂ SO ₄ + 10 mM NH ₄ OH	N/A

Treatments

Experiments were set up one day after the utilities were sampled and the same day of DDW generation. Five-hundred ml of buffered water was poured into amber bottles and dosed with one of four treatments: no treatment (control), chlorine, natural organic matter (NOM) or nitrifiers (Table 1-3). Sodium hypochlorite (Clorox®) was added to obtain chlorine in the solution. NOM used is Suwannee River fulvic acid Standard #2 from the International Humic Substances Society (IHSS, St. Paul, MN). The VitaStim Nitrifier solution used was purchased from Aquafix Inc. (Madison, WI) and was diluted 1:500 in the reactors. The reactors were prepared in

triplicate for each water source, buffer and treatment combination. With six buffers and four treatments, the total number of reactors per water source was 72.

Table 1-3: Treatments used

Treatment	Stock concentration	Added volume	Diluted concentration
Control	-	-	-
Cl ₂	6% NaOCl	0.03 ml	4 mg/L
NOM	500 mg C/L	5 ml	5 mg C/L
Nitrifier	N/A	1 ml	N/A

After addition of buffer and treatment, each reactor was dosed with 0.5 µg/L Cr(III) and 0.5 µg/L Cr(VI) from CrCl₃·6H₂O and K₂Cr₂O₇ salts, respectively. The reactors were kept in the dark at 4 °C and sampled over 4 time intervals (days 0, 1, 5, and 14).

Temperatures

The ammonia buffer was tested at two temperatures: 4°C and 20°C. Constant temperature was maintained by storing reactors in temperature-controlled rooms. Note that this study was done prior to the release of EPA Method 218.7⁷, which defines chilled temperature as 6°C and ambient as 25°C.

SAMPLING

In the 4 °C experiments, reactors were removed from 4 °C storage and sampled at room temperature (about 20 °C) at each sampling event. The reactors were then returned to cold storage right away. The temperatures of the samples were not monitored, but sampling was done immediately after reactors were removed from storage. Collected samples (40 mL) were filtered through 0.2 µm nylon syringe filters (product# SF020N, Environmental Express, Charleston, SC) before analysis. For the NOM treatments, an additional 30 mL of sample was removed and filtered for DOC analysis. In the 20°C experiments reactors were sampled in the constant-temperature room at each time interval.

LABORATORY ANALYSES

All of the samples were analyzed for Cr(VI), total Cr, and pH. Appropriate additional analyses were also done for some sets of samples (Table 1-4). All of the analyses were performed at the Utah Water Research Laboratory in Logan, UT (Table 1-5).

Table 1-4: Additional analyses done for each set of samples

	No Treatment	Cl ₂	NOM	Nitrifiers
Control		Free/Total Cl ₂	DOC	
Ammonium	NH ₄ ⁺	NH ₄ ⁺ , Free/Total Cl ₂	NH ₄ ⁺ , DOC	NH ₄ ⁺ , NO ₂ ⁻ , NO ₃ ⁻
Carbonate		Free/Total Cl ₂	DOC	
Carbonate + Ammonium	NH ₄ ⁺	NH ₄ ⁺ , Free/Total Cl ₂	NH ₄ ⁺ , DOC	NH ₄ ⁺ , NO ₂ ⁻ , NO ₃ ⁻
Borate		Free/Total Cl ₂	DOC	
Borate + Ammonium	NH ₄ ⁺	NH ₄ ⁺ , Free/Total Cl ₂	NH ₄ ⁺ , DOC	NH ₄ ⁺ , NO ₂ ⁻ , NO ₃ ⁻

Table 1-5: Analytical methods

Analysis	Method	Method Detection Limit	Minimum Reporting Level
Cr(VI)	218.6 ⁶	0.0121 µg/L	0.05 µg/L
Cr(VI)	218.7 ⁷	0.0067 µg/L	0.02 µg/L
Total Cr	200.8 ¹⁰	0.05 µg/L	0.3 µg/L
NO ₃ ⁻	300.0 ¹¹	0.02 mg/L	N/A
NO ₂ ⁻	300.0 ¹¹	0.02 mg/L	N/A
NH ₄ ⁺ -N	Dionex Application Note 141 ¹²	0.05 mg/L	N/A
Free Cl ₂	HACH Method 8021 ¹³	0.02 mg/L	N/A
Total Cl ₂	HACH Method 8167 ¹³	0.02 mg/L	N/A
DOC	EPA Method 415.1 ¹⁴	0.12 mg/L	N/A

Hexavalent Chromium

Ion chromatography with post column derivatization and UV-visible spectroscopic detection was used to analyze for Cr(VI). Utility B samples, all samples with borate and borate plus ammonium buffers, and the 20°C experiments were analyzed using a Dionex ICS-1600 (Sunnyvale, CA) following USEPA Method 218.7.⁷ All other samples were analyzed using a Dionex DX-320 with AD25 UV-Vis detector following USEPA Method 218.6.⁶ Per Methods 218.6 and 218.7, all samples that did not already contain the ammonium buffer had 0.05 ml of the concentrated buffer added just prior to analysis, to ensure proper speciation of any Cr(VI) present.

Chromatograms for reactors with nitrifiers suggest that there was a matrix interference in these samples. The nitrifiers solution contained a high concentration of molybdenum, a micronutrient for microbes, which interferes with the colorimetric method used.¹⁵ To account for this interference, a 1:500 dilution of the nitrifier solution in deionized water was used to generate the chromatogram baseline, instead of a laboratory reagent blank.

Total Cr

Total chromium was analyzed using ICP-MS (Agilent 7500c) using a modified version of USEPA Method 200.8.¹⁰ The instrument was run in collision-cell mode with helium as the collision gas. Some samples were also acid digested using the procedure outlined in USEPA guidance for chromium sampling in UCMR3.¹⁶ Cr(III) concentrations were calculated as the difference between Total Cr and Cr(VI) in each sample.

NO₃⁻, NO₂⁻, NH₄⁺

Nitrate and nitrite were analyzed using a Dionex ICS-3000 ion chromatograph. USEPA Method 300.0¹¹ was modified by using a 30 mM sodium hydroxide eluent with a AS11-HC guard and analytical column. Ammonium was also analyzed using the ICS-3000 with a CS12A guard and analytical column with a 15mM sulfuric acid eluent. Nitrate and nitrite were measured in samples with nitrifiers. Ammonium was measured in samples with ammonium buffers (ammonium, carbonate plus ammonium, and borate plus ammonium) added (Table 1-4).

Chlorine Residual

Free chlorine and total chlorine were determined using HACH methods 8021 and 8167¹³ using a HACH DR2800 spectrophotometer (Loveland, CO). Chlorine residuals were only monitored for samples with chlorine added (Table 1-4).

Dissolved Organic Carbon

Dissolved organic carbon was analyzed in reactors with the fulvic acid added (Table 1-4). The samples were preserved with H₃PO₄ and bubbled with nitrogen for 10 minutes prior to analysis. Total organic carbon was then analyzed using Dohrmann – Teledyne Tekmar DC-180 (Cincinnati, OH) following USEPA Method 415.1¹⁴.

pH

All samples were measured for pH using a Corning 313 pH/Temperature probe (Corning, NY).

STATISTICAL ANALYSES

Two statistical tests were done on each set of data: regression analysis and relative standard deviation. The Cr(VI) concentration change over time is deemed significant only when both of the following analyses indicate so.

Regression Analysis

R version 2.13.1 was used to perform regression analyses. A linear model was fit to each set of data with the same buffer and treatment. Time is the independent variable while Cr(VI) concentration is the dependent variable. Results with $p < 0.05$ indicate that the slope of the regression line is significantly different from zero, and there is a change in Cr(VI) concentration over time.

Relative Standard Deviation

Microsoft Excel was used to find relative standard deviation (RSD) from each set of triplicates. The average for each set of triplicate reactors at each sampling time was then subtracted from the same set of samples at time 0. Then, the percent change was found by dividing the difference by the initial average concentration. If the difference is greater than three times the average RSD (21%), the Cr(VI) concentrations at those time intervals are considered different from the initial condition (time 0). This analysis was used as a second-level screen because although a statistical analysis may show significant differences based on $p < 0.05$, some differences fall within analytical variability and are thus not truly significant in the context of these experiments.

RESULTS AND DISCUSSION

Maintaining Preservation pH

The purpose of the buffers is to raise the pH of the samples to at least pH of 8. At $\text{pH} > 8$, the rates of redox reactions of chromium are greatly reduced. Without any buffer, the samples' pH values are lower than 8 (Figure 1-2). All of the buffers raised the pH for all systems tested to $\text{pH} > 8$ (Figure 1-3). The pH was held constant over time for all buffered systems and there was no treatment effect on pH. Details on pH measurements can be found in Appendix B (Table B-1).

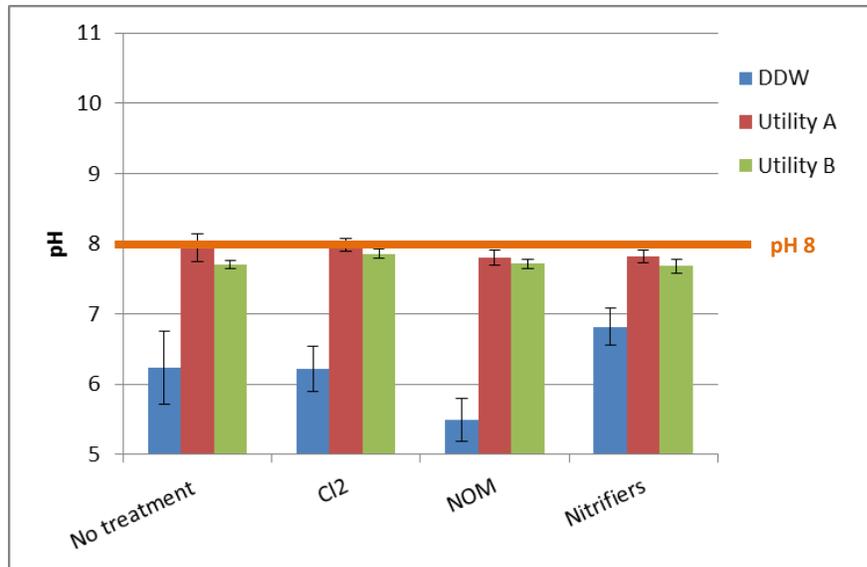


Figure 1-2: pH values for samples without buffer added; error bars show 95% confidence interval. Orange horizontal line represents pH value of 8

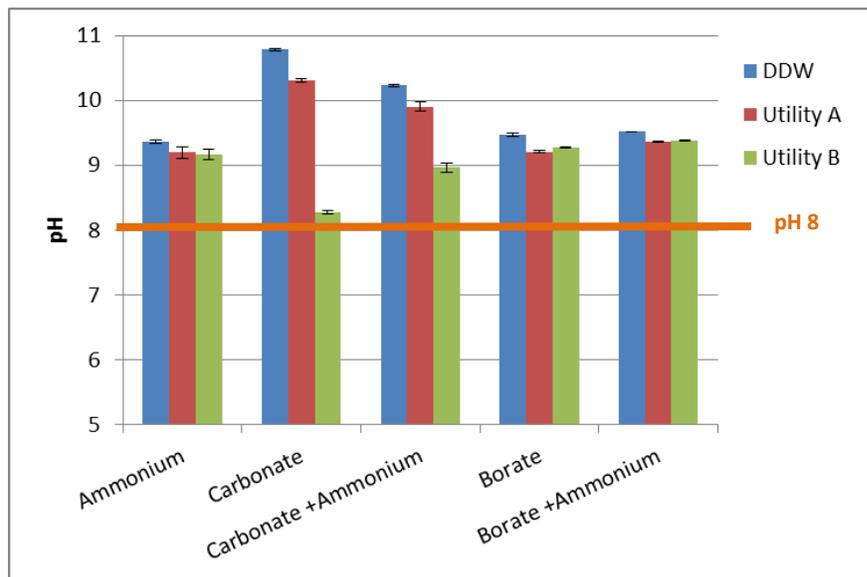


Figure 1-3: pH values for samples with buffer added; error bars show 95% confidence interval. Orange horizontal line represents pH value of 8

Ammonium Concentrations in Ammonium Buffered Samples

Ammonium was monitored in samples with ammonium buffer added (ammonium, carbonate + ammonium, and borate + ammonium). Ammonium added was 100 times the stoichiometric requirement to convert all chlorine to chloramine, and the concentration did not change over time in all cases (Appendix B, Tables B-2 to B-4).

Chlorine Concentrations

Free and total Cl_2 were measured for chlorine treated samples (Appendix B, Tables B-5 and B-6). No decrease in free and total chlorine concentrations over time was observed. The addition of ammonium to each of the buffers tested promoted the formation of chloramines, slowing the oxidation of Cr(III) to Cr(VI). Representative results from Utility B show that free and total chlorine concentrations are essentially the same in samples with no ammonium addition, while samples with ammonium added have very little free chlorine (Figure 1-4). This is expected given that ammonium added to these solutions is 100 times more than needed to convert all chlorine to chloramine according to the stoichiometry (Equation 1-7). The low levels (<0.3 mg/L) of free chlorine detected are consistent with false positives from the DPD method used¹⁷.

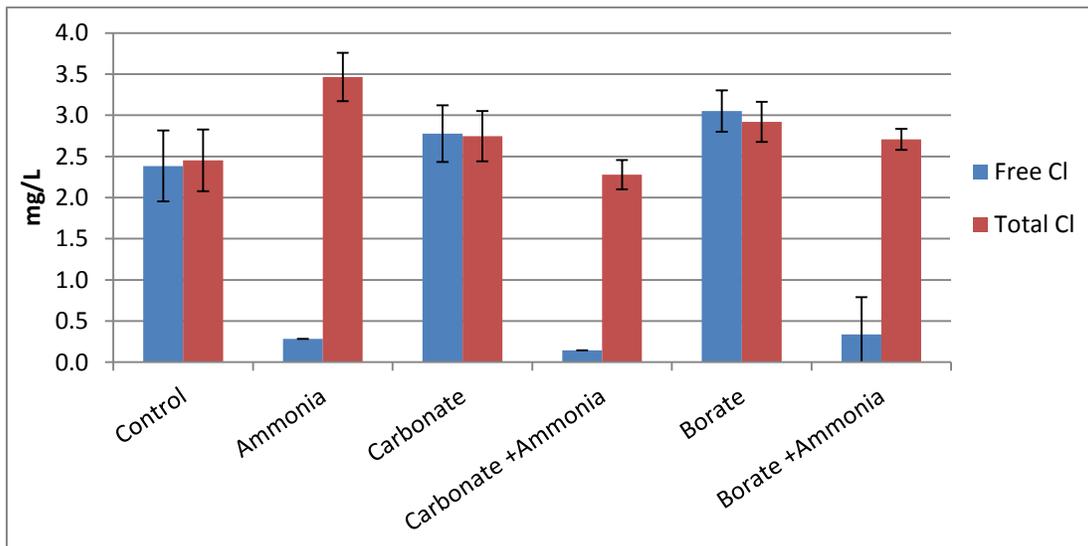


Figure 1-4: Chlorine concentrations in Utility B samples, error bars show 95% confidence interval

Hexavalent Chromium Stability

In the majority of cases, the total chromium concentration remained unchanged ($1 \mu\text{g/L} \pm 0.2 \mu\text{g/L}$) over the course of the study. There was no observed loss of chromium due to sorption to the containers or during sample processing.

Cr(VI) concentrations were stable over time in all waters only when ammonium buffer was used. Surprisingly, the borate buffer and borate buffer with ammonium added are less effective than not adding any preservatives at all (Tables 1-6 and 1-7).

Table 1-6: Water source where Cr(VI) concentration for each preservative and treatment combination was constant over 14 days

Treatment	Preservative					
	No buffer	Ammonium	Carbonate	Carbonate + Ammonium	Borate	Borate + Ammonium
No Treatment	DDW	DDW	DDW	DDW		
	Utility A	Utility A	Utility A	Utility A		
	Utility B DDW	Utility B DDW	Utility B DDW	Utility B	Utility B	
Cl ₂		Utility A	Utility A	Utility A		
		Utility B DDW		Utility B		
NOM	Utility A	Utility A	Utility A	Utility A		
	Utility B	Utility B DDW	Utility B	Utility B DDW	Utility B	Utility B
Nitrifier		Utility A	Utility A	Utility A	Utility A	
		Utility B		Utility B	Utility B	Utility B

Table 1-7: Combination of preservative and treatment that holds Cr(VI) concentration to 14 days for all water types

Preservative	Treatment			
	No treatment	Cl ₂	NOM	Nitrifier
No buffer (Control)	√			
Ammonium	√	√	√	√
Carbonate	√			
Carbonate + Ammonium	√			√
Borate				
Borate + Ammonium				

Controls (No Treatment Addition)

When no treatment was added to reactors, Cr(VI) was stable in the control, ammonia, carbonate and carbonate + ammonia buffers for 14 days (Table 1-6 and Figure 1-5). When the borate buffer was used in Utility B water, Cr(VI) was also stable (Figure 1-5c). However, the borate buffer was not efficient in DDW (Figure 1-5a) and Utility A (Figure 1-5b). The borate + ammonia buffer did not hold Cr(VI) constant in any of the waters.

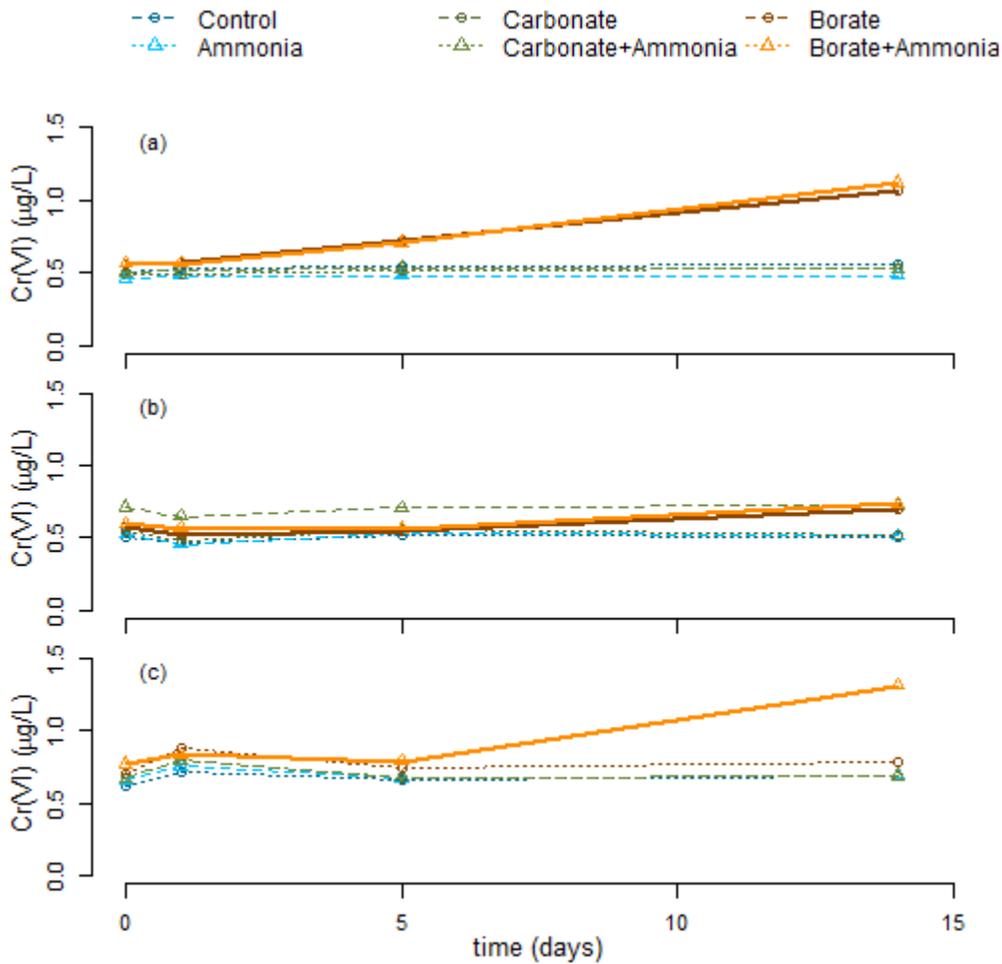


Figure 1-5: Cr(VI) concentrations in no treatment reactors over time in a) DDW, b) Utility A, c) Utility B. Solid lines signify sets of data where change over time is significant

Effect of Chlorine Treatment

When no buffer was added to solution, Cr(VI) was stable in DDW (Figure 1-6a). Ammonium buffer alone is the only buffer which can preserve Cr(VI) in all of the waters tested when chlorine is added (Figure 1-6 and Table 1-6). Carbonate preserved Cr(VI) in DDW (Figure 1-6a) and Utility A waters (Figure 1-6a), while carbonate + ammonium works only in Utility A and Utility B waters (Figure 1-6). The borate and borate + ammonia buffers did not preserve Cr(VI) in any of the waters. Adding ammonium to the carbonate or borate buffers does not improve the buffers' performance.

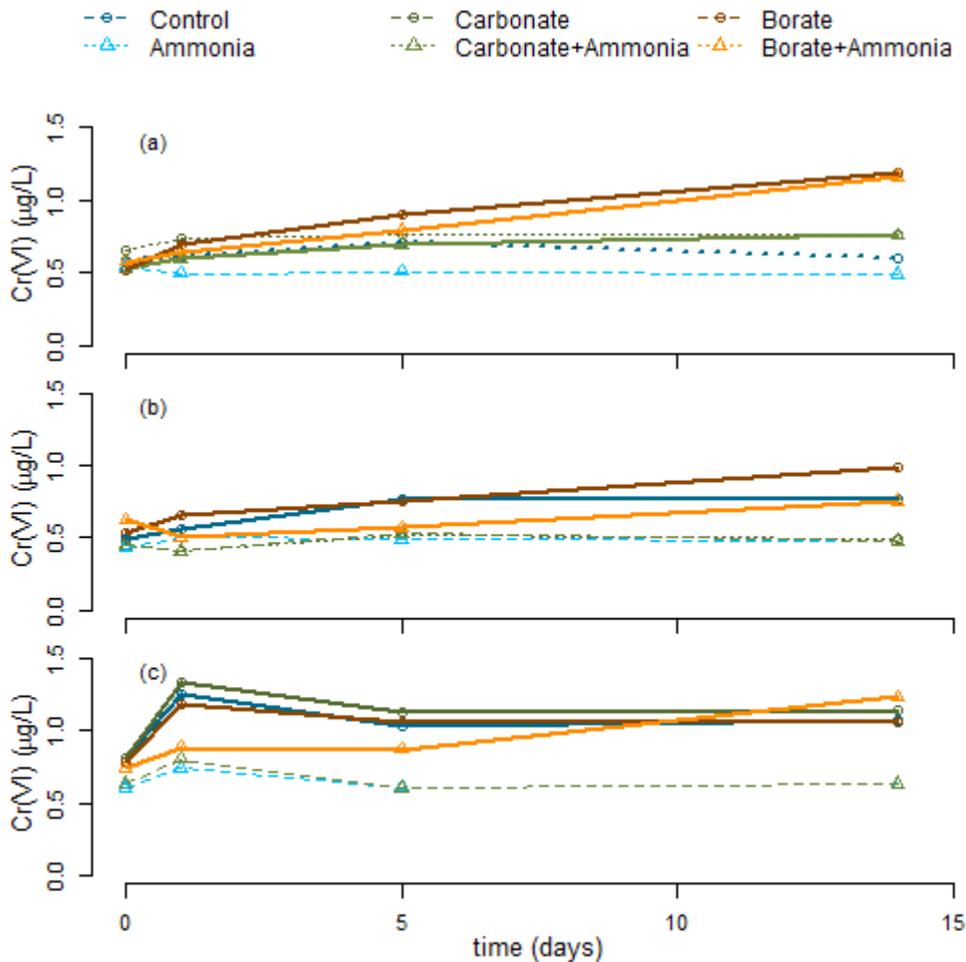


Figure 1-6: Cr(VI) concentrations in chlorine treatment reactors over time in a) DDW, b) Utility A, c) Utility B. Solid lines signify sets of data where change over time is significant

Effect of NOM Treatment

Only the ammonium buffer was efficient in preserving Cr(VI) for this condition. In DDW samples (Figure 1-7a), Cr(VI) was reduced when no buffer was added, resulting in decreasing Cr(VI) with time. When buffers other than ammonium were added, Cr(VI) concentration increased over time, implying that Cr(III) was oxidized to Cr(VI) (Figure 1-7a). It is speculated that the pH of solutions might be correlated to these results. The pH of reactors with no buffer added was 5.22-5.89. The pH of reactors with ammonium added was 9.22-9.42, and the pH of samples with other buffers added was 9.49-10.85. The pH differences between the ammonium buffer and other buffers suggest that Cr(III) oxidation in these buffers is correlated to the higher pH in solutions.

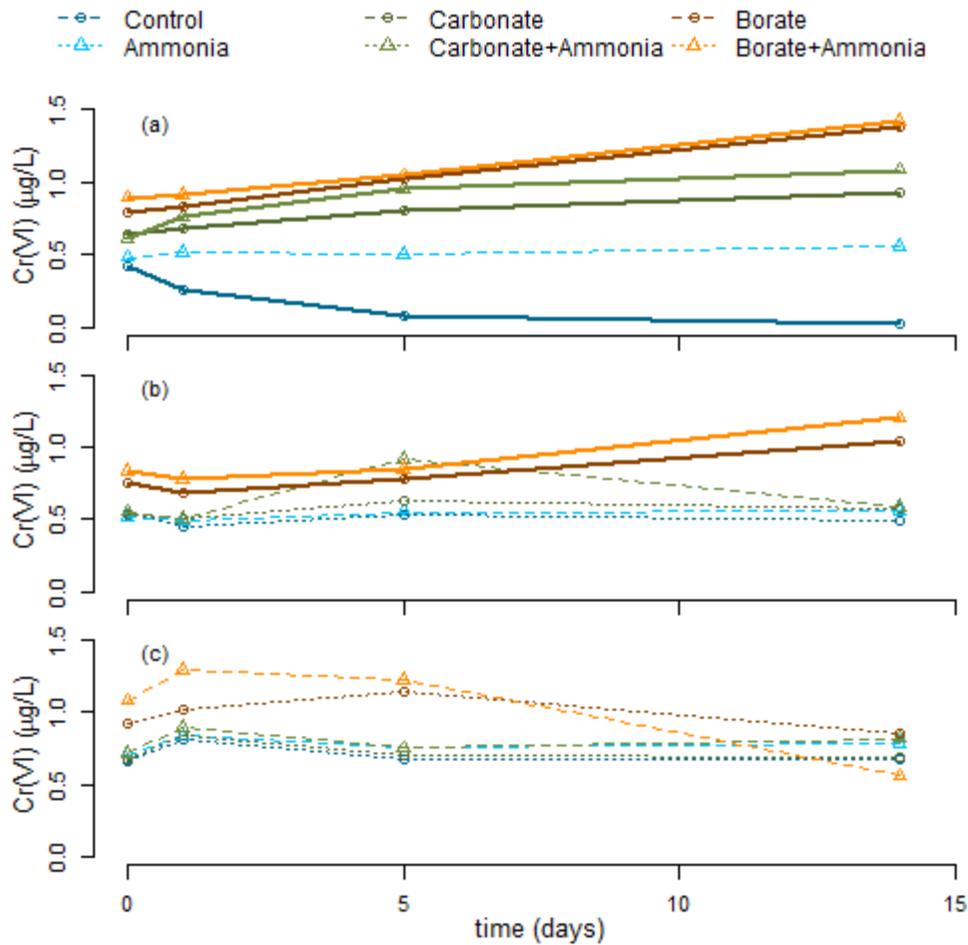


Figure 1-7: Cr(VI) concentrations in NOM treatment reactors over time in a) DDW, b) Utility A, c) Utility B. Solid lines signify sets of data where change over time is significant

Effect of Nitrifiers Treatment

Cr(VI) was stable in the ammonium buffer and carbonate + ammonium buffer in all waters (Figure 1-8). In the carbonate, borate, and borate + ammonia buffers reactors, Cr(VI) behavior was mixed, sometimes increasing and sometimes decreasing with time. Nitrite and nitrate concentrations did not change over time in any of the samples, except in DDW with carbonate + ammonium added (Tables B-7 and B-8). However, Cr(VI) did not change in these samples (Figure 1-8a) indicating that any change in Cr(VI) concentration is not a result of nitrification.

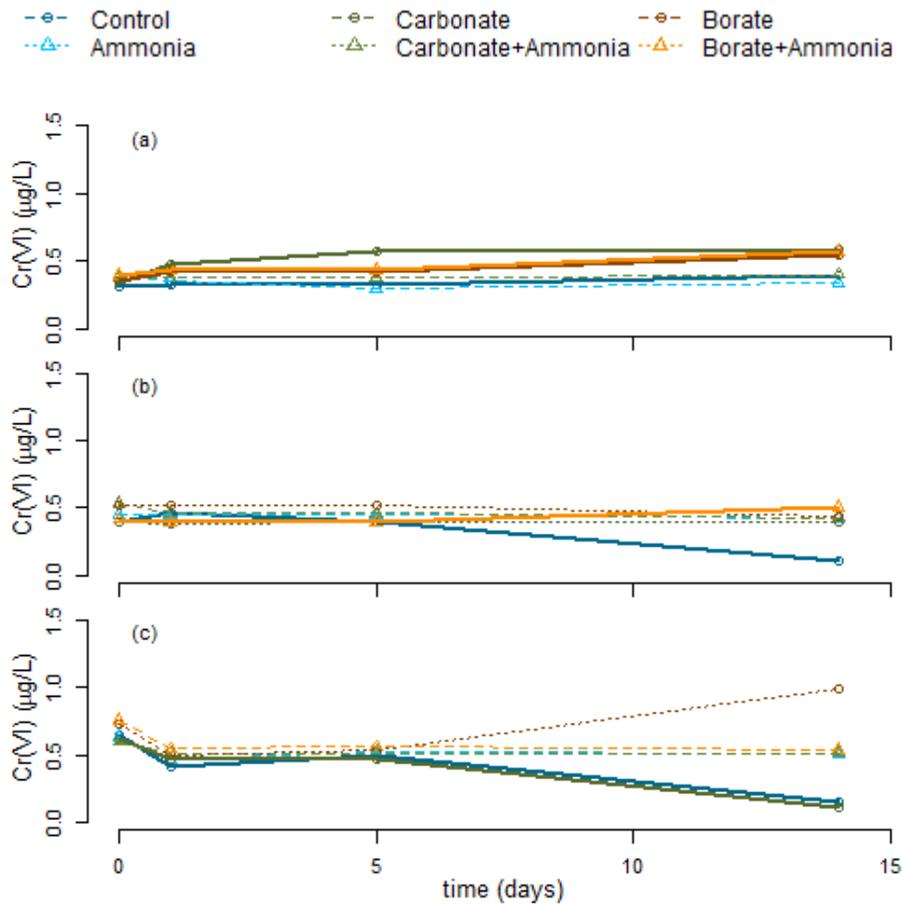


Figure 1-8: Cr(VI) concentrations in nitrifiers treatment over time in a) DDW, b) Utility A, c) Utility B. Solid lines signify sets of data where change over time is significant

Effect of Temperature in Ammonium Buffers Samples

The study was repeated using the ammonium buffer at 20 °C. Cr(VI) was stable in the three water sources for all treatments over the 14 day study, with the exception of NOM treatment of DDW and Utility B and nitrifier treatment of Utility A (Table 1-8). For the two NOM treatments, Cr(VI) increased by 30%. The addition of nitrifiers to Utility A resulted in the complete removal of Cr(VI) from solution (Figure 1-9). Total Cr also decreased. Utility A samples with the nitrifiers were difficult to filter due to microbial growth. The decrease in Cr concentration may be due to Cr sorbing to the microbes that are removed from the sample with filtration prior to analysis.

Table 1-8: Conditions where Cr(VI) concentration was constant over 14 days in ammonium buffer at different temperatures

Treatment	4 °C			20 °C		
	DDW	Utility A	Utility B	DDW	Utility A	Utility B
No Treatment	√	√	√	√	√	√
Chlorine	√	√	√	√	√	√
NOM	√	√	√		√	
Nitrifiers	√	√	√	√		√

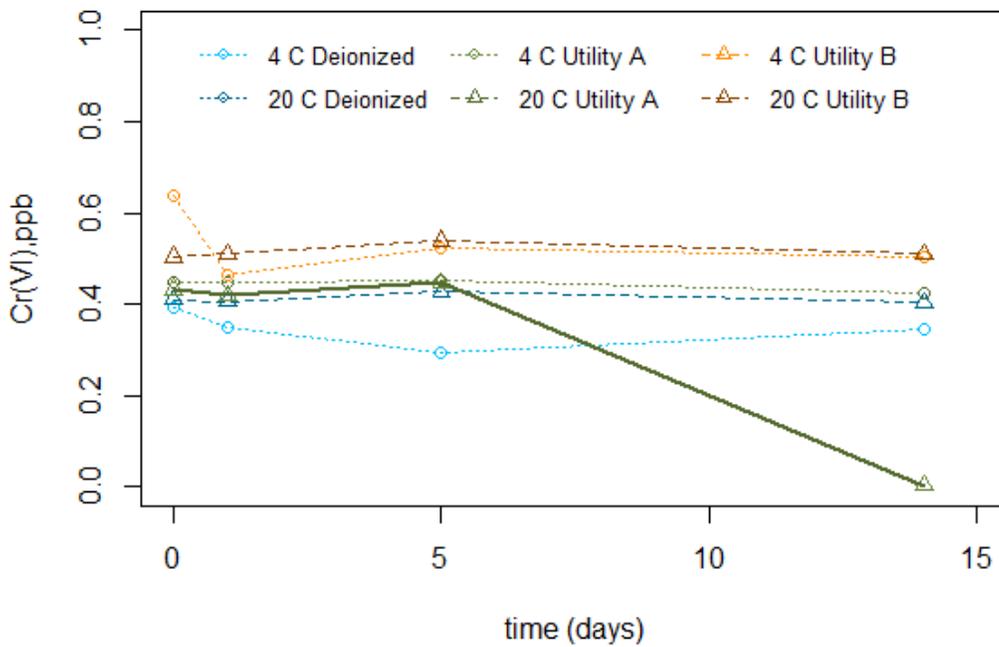


Figure 1-9: Average Cr(VI) concentrations in ammonium buffers samples treated with nitrifiers at different temperatures. Solid line signifies set of data where change over time is significant

COMPARISON WITH PRIOR STUDIES

The effectiveness of the ammonium buffer in four other water qualities at 6°C and 25°C was evaluated by the USEPA as part of the development of Method 218.7⁷. Parameters for the water used in the USEPA study are presented in Table 1-9. The treatment and Cr fortifications in this

study can be found in Table 1-10. For all of the samples fortified with Cr(III), the Cr(III) to Cr(VI) conversion in 14 days was less than 5% of the Cr(III) added. For the rest of the samples, the Cr(VI) recoveries at day 14 were within +/- 20% of the value at day 0⁷. This indicates that the ammonium buffer was also effective in other water sources.

Table 1-9: Waters evaluated by EPA

Water Source	TOC (mg/L)	pH	Total hardness (mg/L as CaCO ₃)	Free chlorine (mg/L)	Total chlorine (mg/L)
Surface water	3.1	6.77	120	1.2	1.52
Groundwater	n.a.	7.94	252	0.03	0.64
Groundwater	n.a.	7.66	322	0.84	0.84
Surface water	n.a.	n.a.	96	1.12	1.22

n.a. = not analyzed

Table 1-10: Experimental matrix

Treatment	Fortification (µg/L)
None	None
None	1.0 Cr(VI)
None	1.0 Cr(III)
3 mg/L Cl ₂	1.0 Cr(III)
Ambient storage	None

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Chapter 2 : Hexavalent chromium [Cr(VI)] formation in potable water from stainless steel components

Chittaladakorn, K., McNeill, L. and Edwards, M.

(In review for publication)

ABSTRACT

The state of California recently proposed a maximum contaminant level (MCL) for hexavalent chromium [Cr(VI)] at 10 ppb as measured at the entry point to the distribution system. To the extent that Cr(VI) is formed in the distribution system or in water contacting plumbing, measurements at the treatment plant might not reflect consumer exposure at the tap. Cr(VI) can be released to drinking water from Cr present in stainless steel alloys. At the maximum residual disinfectant level (MRDL), Cr(VI) formation decreased in the order chlorine dioxide > chlorine > chloramine. Cr(VI) release increases at lower pH in chlorine, but the opposite trend was observed for chlorine dioxide. More Cr(VI) is also generated from stainless steel with a higher percentage of Cr in the alloy.

INTRODUCTION

Of the two common forms of chromium [Cr(III) and Cr(VI)], only Cr(VI) is considered toxic via ingestion,¹ with a 0.02 ppb Public Health Goal (PHG) and a maximum contaminant level (MCL) of 10 ppb Cr(VI) now under consideration in California.² The estimated cost for implementing the new MCL is \$156 million annually in California.²

Cr(VI) will be monitored at the point of distribution system entry.² An improved understanding of Cr(VI) formation pathways will inform analysis of health risks, monitoring protocols, interpretation of occurrence data and development of treatment techniques. For instance, lead was once regulated at 50 ppb in water leaving the treatment plant, which did virtually nothing to protect public health because the vast majority of lead in water was derived from lead-bearing plumbing in service lines and homes. There would be similar concerns if Cr(VI) was also formed from reactions with plumbing or in the distribution system. In natural aerated water, Cr(VI)

formation is thermodynamically favored from Cr(III), although kinetics are considered very slow without strong oxidants³ (Figures 2-1 and 2-2). Disinfectants are usually oxidizers, and their presence increases the potential of waters. Cr(VI) dominance generally increases with higher potential, and is therefore expected to be more favored in disinfected waters.

The most commonly used residual disinfectants in potable water are chlorine (68%) and chloramine (29%).⁴ Chlorine dioxide is also gaining popularity in some applications.⁵ Chlorine dioxide tends to form fewer disinfection by-products than chlorine,^{5,6} and is also gaining favor as a proven *Legionella* control in building plumbing systems⁷ which could receive additional impetus given a proposed *Legionella* standard by American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE).⁸ Chlorine is known to increase the kinetics of Cr(III) oxidation to Cr(VI)⁹ (Figure 2-1), due to direct reactions but also possibly due to its role as a disinfectant, which reduces microbial rates of reduction.^{10,11} Chloramine is generally reported to have little ability to increase rates of Cr(III) oxidation to Cr(VI), and the impacts of chlorine dioxide have not been reported.

The redox potential of some chlorine dioxide species are higher than free chlorine (Figures 2-1 and 2-2).¹² In one study of drinking water, chlorine dioxide reacted to form 70% chlorite and 30% chlorate/chloride.⁶ The proportion of chlorite/chlorate formed is highly pH dependent, with more chlorite formed at higher pH.^{13,14} Chlorate is more stable than chlorite⁶ and has been reported to inhibit aspects of stainless steel corrosion in short term laboratory tests in pulp mill waters.¹⁵

Stainless steel is an important alloy of iron, chromium and nickel, which is gaining popularity in premise plumbing¹⁶ due to its reduced cost relative to copper pipe¹⁷ and perceived corrosion resistance.¹⁸⁻²¹ Stainless steel has been used as a plumbing material since at least 1965.^{20,21} Alloys of stainless steel commonly used in water distribution systems are 304, 304L, 316, 316L and 2205 (Table 2-1)^{16,19,20,22}. Each type of stainless steel has different chemical composition, and those with higher chromium content tend to be more corrosion resistant. These stainless steel types pass extraction standards for metallic contaminants established by NSF International and are certified as safe for use in US and European potable water applications.^{23,24} Distribution

systems using stainless steel have been installed in Germany, Japan, Korea, Canada, Italy and New York City.^{19-21, 25}

Despite the general perception of its corrosion resistance, there have been occasional reports of stainless steel failures.¹⁸ Studies show that disinfectants, pH, temperature and chloride concentration have an effect on stainless steel corrosion, although other studies suggest that drinking water chemistry has little effect on stainless steel type 316 corrosion.²⁶

The formation of Cr(VI) from Cr in stainless steel alloys is not reported in the literature, although it can be hypothesized to occur via a stepwise corrosion reaction (Equation 2-1) followed by further oxidation of the released Cr(III) to Cr(VI) in the bulk water, or directly at the pipe surfaces (Equation 2-2):



Disinfectants are known to accelerate corrosion of stainless steel^{27, 28} and given previous discussion of redox, it is logical to expect that disinfectants would accelerate any Cr(VI) generation from stainless steel due to a higher rate of corrosion and a faster rate of Cr(VI) formation.

This work will attempt to examine whether Cr(VI) is generated from stainless steel pipes under conditions found in potable water distribution systems, and if so, how Cr(VI) formation rates are controlled by disinfectant type and dose, pH, temperature, chloride, and the type of stainless steel alloy.

Table 2-1: Typical chemical composition for types of stainless steel commonly used in potable water
 (AK Steel, Stainless Steel Comparator. West Chester, OH, 2007. Used under fair use, 2013)

Type	Cr (%)	Ni (%)	C (%)	Mo (%)
304	18	8	0.06	-
304L	18	9	0.02	-
316	16.5	10.5	0.05	2
316L	16.5	10.8	0.02	2
2205	22	5.5	0.02	3

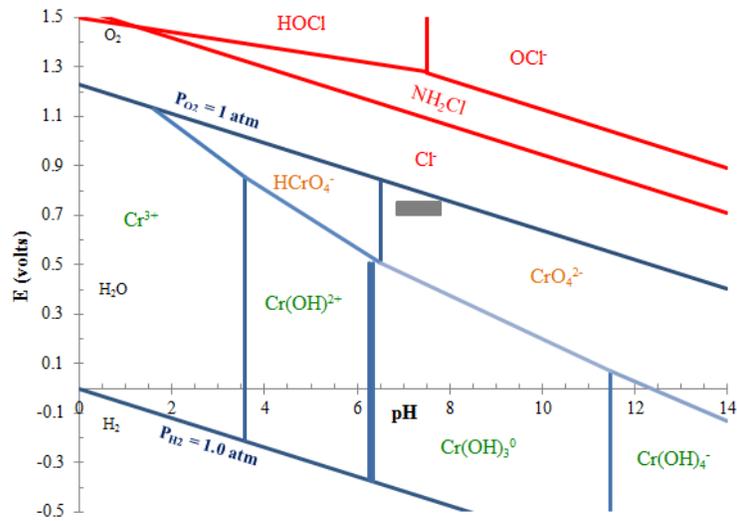


Figure 2-1: Potential vs pH diagram of chromium speciation : orange font represent Cr(VI) compounds, green font represent Cr(III) compounds. Red lines and fonts represent disinfectants (10^{-4} M chlorine and 10^{-4} M chloramine). Grey box represents natural waters.

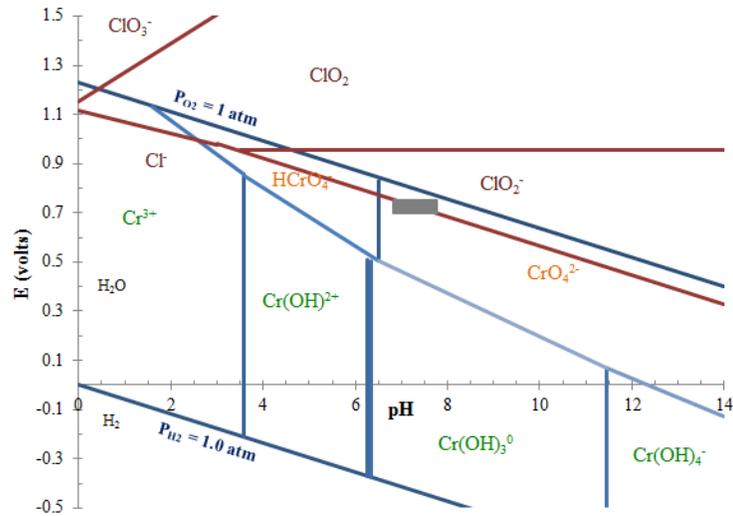


Figure 2-2: Potential vs pH diagram of chromium speciation : orange font represent Cr(VI) compounds, green font represent Cr(III) compounds. Red lines and fonts represent disinfectant (10^{-5} M chlorine dioxide). Grey box represents natural waters.

MATERIALS AND METHODS

Replication of Schroeder and Lee (1974) Experiments

To test the rate and extent of Cr(III) conversion to Cr(VI) by dissolved oxygen at different pH (7, 8.5 and 9) and temperatures (24°C and 50°C), amber glass reactors (250 ml) with 100 ppb Cr(III) solution were incubated for 398 days. NaCl (0.5 mM) was added to all of the conditions to add ionic strength. NaHCO_3 , Na_2CO_3 and CO_2 gas were used for pH adjustment. Controls (pH 8.5 without any Cr(III) addition) were also constructed for both temperatures. Triplicates were made for all conditions tested.

Reactors and Exposure Conditions

Stainless steel sheets (51 mm x 51 mm x 1.2 mm) were submerged in target waters up to 36 hours to quantify the effect of chemistry on Cr(VI) generation. The surface area of the stainless steel sheets to the water volume in reactors ratio is comparable to a 13 inch diameter pipe. Reactors were glass bottles (450 ml) placed on a shaker table at 60 rpm and 24.5°C unless otherwise noted. The stainless steel sheets were polished with 400 grit resin-coated sandpaper

and held upright with custom plastic supports. Controls, where no stainless steel was added, were done for some conditions.

Comparison of Different Disinfectants

Type 304 stainless steel was exposed to disinfectants commonly used in potable water including chlorine, chloramine, and chlorine dioxide and no disinfectant. Chlorine was dosed from a sodium hypochlorite concentrate and a chloramine concentrate (90 mg/L as Cl₂) was made in the laboratory by combining sodium hypochlorite and 28-30% w/w reagent ammonium hydroxide solution (4:1 molar ratio Cl₂:NH₃). Concentrated chlorine dioxide (500 mg/L) was generated from Selectocide® 2L500 pouch from Selective Micro Technologies, LLC (Columbus, OH). Disinfectants were diluted to a residual concentration of 4 mg/L in reactors as confirmed by Standard Methods 4500-Cl and 4500-ClO₂²⁹. Target levels of chloride in tests were obtained using reagent grade sodium chloride. Two pH values (6.5 and alkalinity of 34 mg/L CaCO₃; 9.5 and alkalinity of 67 mg/L CaCO₃) were also tested by appropriate adjustment of sodium carbonate, sodium bicarbonate and carbon dioxide gas. Reactors were made in triplicate, including a set of control experiments (no stainless steel sheet added) for the condition with no disinfectant, pH 6.5 and 20 mg/L chloride.

Effect of pH, Temperature and Chloride

Effects of pH 7.0, 7.5, 8.0, 8.5, 9.0 and 9.5 on Cr(VI) release in the presence of chlorine dioxide at the EPA maximum residual disinfectant level (MRDL) of 0.8 mg/L and a chloride level of 20 mg/L were examined at 24.5°C after 36 hours of exposure for type 304 stainless steel. The same tests with the same conditions were also done for pH 7.5 only at 48°C and 60°C. Effects of chloride (20 and 200 mg/L) at pH 9.5 were tested for type 304 stainless steel sheets in the presence of 4 mg/L chlorine and 0.8 mg/L chlorine dioxide for 24 hours.

Effect of Stainless Steel Type

Various types of stainless steel sheets (2205, 316, 316L, 304, 304L) were exposed to chlorine (4 mg/L) and chlorine dioxide (0.8 mg/L) for 8 hours at pH 6.5 and 9.5 in the presence of 200 mg/L chloride. Tests were performed in duplicate except types 316 and 316L at pH 6.5 in chlorine and chlorine dioxide conditions where no replicate was constructed. Type 2205 stainless steel sheets was also tested using chloramine and no disinfectant at pH 9.5.

Sampling Reactors

Targeted levels of disinfectant and pH were achieved at $t = 0$ and 8 hours by addition of appropriate acid/base or disinfectant stock solutions outside of the incubator and constant mixing. Samples collected at 8 hours had a minimum of 5 hours of mixing at the target temperature (adjustments at ambient temperature are always < 3 hours). Mixing time at the target incubation temperature is at least 19 hours for samples collected at 24 hours and a minimum of 31 hours for samples collected at 36 hours (adjustment time is always < 5 hours).

Laboratory Analyses

Samples for Cr(VI) analysis were filtered through 0.2 μm nylon filter before analysis by EPA method 218.7³⁰. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure for metals (including iron, nickel and chromium) and chloride (Table 2-2).

Table 2-2: Analytical methods

Analysis	Method	Minimum Reporting Level
Cr(VI)	218.7 ³⁰	0.02 ppb
Cr	200.8 ³¹	0.2 ppb
Fe	200.8 ³¹	50 ppb
Ni	200.8 ³¹	0.2 ppb
Cl ⁻	Adapted from McCamley ³² and Tagami ³³	200 ppb

Statistical Analyses

Analysis of variance was quantified using R 3.0.1 and Tukey's HSD was then used to determine differences between conditions. For other parameters, 95% confidence intervals using a student t-test are reported.

RESULTS AND DISCUSSION

After replicating and verifying results of Schroder and Lee³, who found relatively rapid conversion of Cr(III) to Cr(VI) in the presence of oxygen alone, the possible production of hexavalent chromium from stainless steel was examined.

Replication of Schroeder and Lee Results

Schroeder and Lee³ found 3% of 100 ppb Cr(III) converted to Cr(VI) after 30 days (room temperature) in the presence of dissolved oxygen at pH 8.6, while only 10-11 days or 3 days was required for 3% conversion at 35°C and 48°C, respectively. The relatively high conversion of Cr(III) to Cr(VI) reported in this early research was deemed of high interest in this work, since recent short-term studies did not find detectable conversion of Cr(III) to Cr(VI) in potable water unless strong oxidants such as chlorine were present. The results from this study (Appendix C, Figure C-1) verified the trend in Schroeder and Lee although the magnitude of the effect was different. Specifically, three percent of Cr(III) conversion to Cr(VI) occurred in only one of three replicate samples after 398 days at room temperature, and at 50°C three percent conversion occurred after 28 days in only one of three replicate samples. The highest rates of conversion observed in this research (3% conversion in 28 days) are about ten times slower than observed by Schroeder and Lee (3% in less than 3 days), and the rates were much lower in 2 of 3 replicates. The highest Cr(VI) observation in this work after 398 days is 67% of the added Cr(III). Because replicates varied by a factor of up to 25 times from one another (i.e., 67% conversion vs. < 2.7% after 13 months), uncontrolled variables that might include microbial ecology in laboratory samples (even under nutrient poor conditions using reagent grade water) or other factors were influential. Clearly, appreciable [> 0.02 ppb Cr(VI)] conversion from Cr(III) does occur in the presence of oxygen in some natural waters over the timespan of weeks, months or years. Although water tested in this set of experiments is slightly different from that used in the research that follows (Appendix C, Table C-1), detecting some Cr(VI) in reactors with Cr(III) is expected.

Stainless Steel

Effect of Type of Disinfectant

Insignificant levels of Cr(VI) were detected in the control reactors (no stainless steel sheet added). But in the presence of chlorine and especially chlorine dioxide at 4 mg/L, much more Cr(VI) was formed in 24 hours than in the presence of chloramine and oxygen (Figure 2-3). In samples with chlorine addition, Cr(VI) generation after 24 hours is 75 times higher for 200 mg/L chloride at pH 6.5 than in all other conditions with chlorine, chloramine and control (only

oxygen, no disinfectant). Excluding the unusually high Cr(VI) concentration in one chlorine sample at pH 6.5, Cr(VI) released from stainless steel chlorine dioxide solutions is 500 times the average Cr(VI) measured in comparable conditions with chlorine, chloramine and no disinfectant. Ranking of the average Cr(VI) detected after 24 hours is 4 mg/L chlorine dioxide > 4 mg/L chlorine \approx 4 mg/L chloramine > no disinfectant (Figure 2-3).

Effect of Chlorine Dioxide Concentration

The concentration of chlorine dioxide greatly influenced Cr(VI) release in solutions. At pH 9.5 and 20 mg/L chloride, Cr(VI) release at 4 mg/L (Figure 2-3) is 15 times the Cr(VI) released at 0.8 mg/L chlorine dioxide.

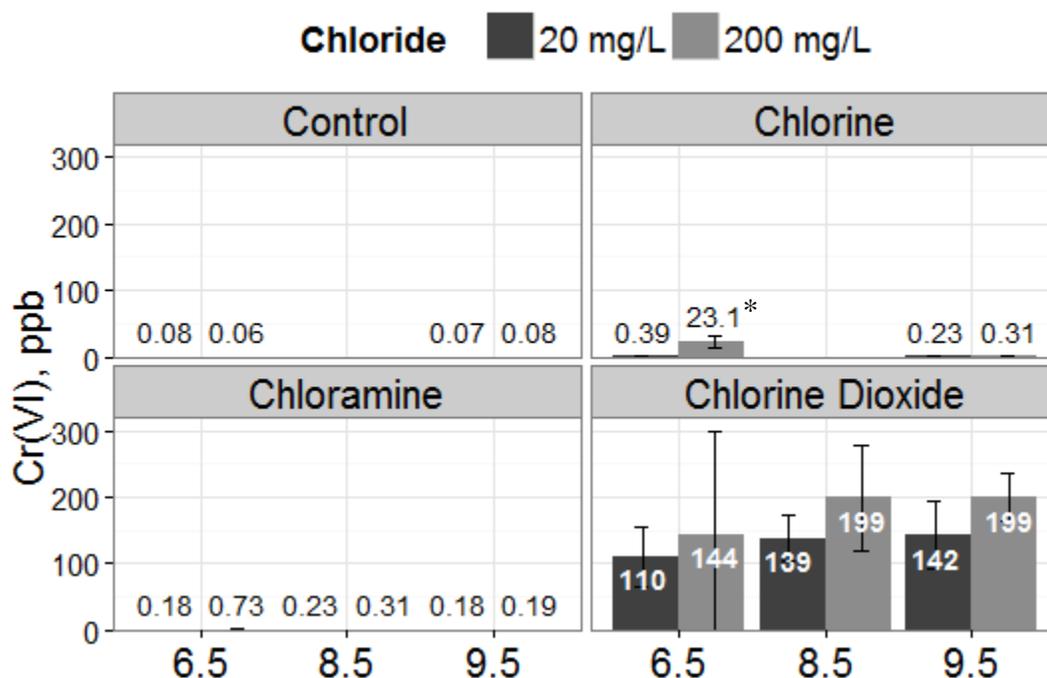


Figure 2-3: Average Cr(VI) concentration at 24 hours in 24.5°C, different disinfectants (4 mg/L) and chloride concentrations. Type 304 stainless steel was used. Error bars denote 95% confidence intervals in triplicates.

*Attempts to reproduce results for the chlorine samples in 200 mg/L chloride and pH 6.5 conditions have been unsuccessful.

Effect of pH on Cr(VI) Formation

Previous work on chlorine dioxide in paper industry bleaching processes found that stainless steel corrosion rates increased at lower pH in chlorine dioxide solutions,^{34, 35} for conditions that

were different from those used in this work including pH 3-5 (vs. 6.5-9.5 in this work) and 450-3,000 mg/L chloride (vs. 20-200 mg/L) and 35-100 mg/L chlorine dioxide (vs. 0.8-4 mg/L). But Cr(VI) formation tended to increase at higher pH in this study (Figure 2-4 and Appendix C, Figure C-2).

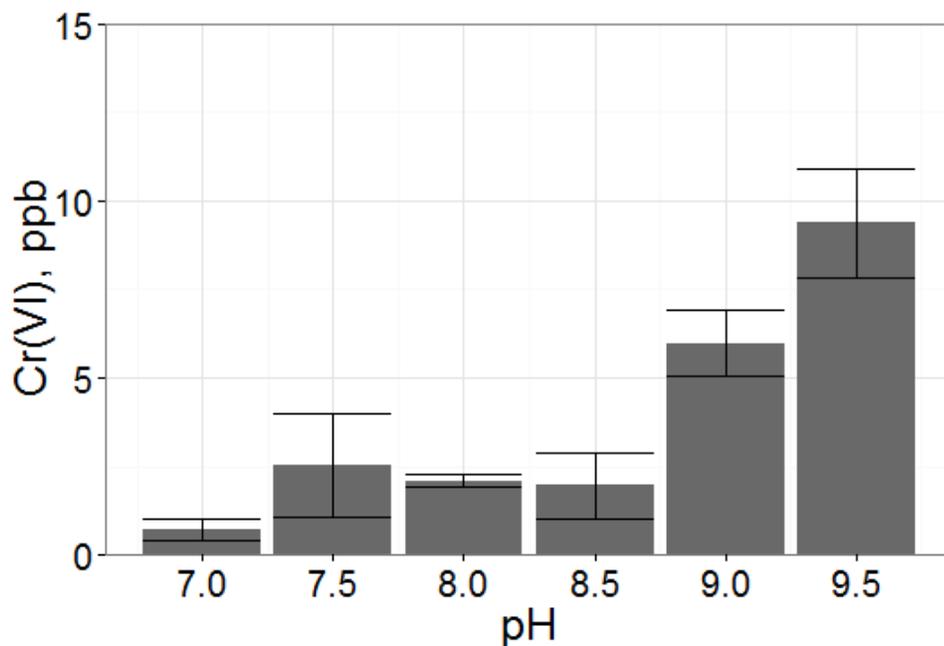


Figure 2-4: Average Cr(VI) concentration in 24.5°C and 0.8 mg/L chlorine dioxide solutions at different pH values after 36 hours (24 hours for pH 9.5). Type 304 stainless steel was used. Error bars denote 95% confidence intervals.

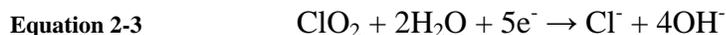
Effect of pH on Cr(VI) Formation as a Function of Disinfectant Consumption

The chlorine dioxide consumption in pH 7 and pH 9 samples are different from their controls (no stainless steel sheet addition) with p-values 0.02 and 0.003 respectively, indicating that reactions with the type 304 stainless steel sheets increases chlorine dioxide consumption (Appendix C,

Table C-2). The consumption in reactors with stainless steel sheets are not statistically different between the two pH values (p-value = 0.06 based on a t-test). The increase in Cr(VI) generation from pH 7 to pH 9 (Figure 2-4) indicates that the production of Cr(VI) per unit disinfectant increases with pH.

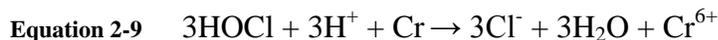
The stoichiometry of Equation 2-5 from adding Equations 2-3 and 2-4 suggests that up to 0.83 moles of Cr(VI) could be produced per mole of chloride dioxide consumed. However, the maximum observed experimental ratio of 0.008 mole Cr(VI) per mole of ClO₂ (Appendix C,

Figure C-3) is much lower than the stoichiometric ratio, indicating that chlorine dioxide was also undergoing other reactions with the stainless steel including corrosion of other alloying metals including iron. The total Cr(VI) measured in solutions of chlorine dioxide was also close to the total chromium measured (Appendix C, Figure C-4), suggesting that a limiting factor for Cr(VI) generation is the total chromium available in the solution or that Cr(VI) is formed directly from the stainless steel.



Studies show that chlorate is formed to a greater extent from chlorine dioxide decay at lower pH while chlorite formation is higher at higher pH,^{14, 36, 37} and it is possible that higher chlorate generated at lower pH might be inhibiting stainless steel corrosion and reactions favoring Cr(VI) in this research.¹⁵ This might explain the counterintuitive trend (Equation 2-5) of more Cr(VI) produced at higher pH.

In water, chlorine hydrolyzes to form HOCl (Equation 2-6). HOCl can further dissociate into ClO^- , with a pKa of about 7.5 (Equation 2-7).⁶ HOCl is often a more effective oxidant than OCl^- . Consistent with this expectation, Cr(VI) formation in the presence of 4 mg/L chlorine is higher at lower pH. Stoichiometrically up to 0.3 mole Cr(VI) could be generated per mole of chlorine addition (Equation 2-9 from combining Equations 2-4 and 2-8). However, Cr(VI) measurements were much lower than this value (Appendix C, Table C-3), suggesting that chlorine was also involved in other reactions as was observed for chlorine dioxide. There was five times higher Cr(VI) to chlorine yield (Appendix C, Table C-3) at lower pH than higher pH.



Effect of Temperature on Cr(VI) Formation

In samples with 4 mg/L chlorine addition, the Cr(VI) concentration after 24 hours is three times higher at 60°C than at 48°C and 24.5°C (95% confidence), and Cr(VI) at 48°C is twice than at 24.5°C but not at 95% confidence ($p = 0.07$) (Appendix C, Figure C-5). Previous studies suggest that higher temperatures result in more corrosion of stainless steel in chlorine dioxide solutions and therefore more Cr(VI) is not unexpected.³⁸ No statistical difference was measured in 0.8 mg/L chlorine dioxide samples at the different temperatures in this study (Appendix C, Figure C-5) due to high variability amongst replicates, although the maximum Cr(VI) observed in the replicates increased at higher temperature (Appendix C, Figure C-5). Chlorine dioxide consumption in 60°C samples is 0.35 mg/L/day higher than the control, and 0.39 mg/L/day higher than samples at 24.5°C (Table C-4).

Effect of Chloride on Cr(VI) Formation

In stainless steel grade selection for potable water use, chloride content is considered the most important parameter for crevice corrosion.²¹ Crevice corrosion is rare at chloride concentrations < 200 mg/L for 304/304L and < 1000 mg/L for 316/316L stainless steel types.¹⁹ The chloride contents tested in this study were 200 mg/L and lower. Although not statistically different (Appendix C, Figure C-6), higher chloride in solution did tend to increase Cr(VI) release (Figure 2-3). Thus, the trend is consistent with previous studies showing that chloride is a factor in stainless steel corrosion.^{34, 38, 39}

Effect of Type of Stainless Steel

In testing with a range of stainless steels, despite the lower MRDL and target residual dose, chlorine dioxide produced more Cr(VI) than chlorine in all conditions (Figure 2-5). The production of Cr(VI) in chlorine dioxide solution was also more sensitive to pH, and again increased at higher pH, whereas Cr(VI) production in the presence of chlorine was statistically lower at higher pH with 4 mg/L chlorine samples ($p < 0.05$; consistent with earlier results).³⁴

The type of stainless steel had no significant effect on the rate at which chlorine dioxide was consumed. Stainless steel with higher %Cr in the alloy released more Cr(VI) in all waters tested (Figure 2-5 and Appendix C, Table C-5). Cr(VI) formation is highest for type 2205 (highest %Cr tested), and the Cr(VI) measured is roughly equal to total chromium in every condition tested for

type 2205 (Appendix C, Figure C-7). At pH 9.5, total Cr was also roughly equal to the Cr(VI) for every type of stainless steel tested with chlorine dioxide (Appendix C, Figure C-8). But at pH 6.5 the percentage of total Cr as Cr(III) was as high as 48% for chlorine dioxide (Appendix C, Figure C-8). A significant fraction of the total Cr (>10%) was present as Cr(III) with chlorine at pH 6.5 and pH 9.5 (Appendix C, Figure C-9).

Individual and total metal released from stainless steel (Cr, Fe, Ni) to water (Appendix C, Figures C-12 to C-17) indicated that release of each (Cr, Fe, Ni) tended to increase roughly in proportion to overall metals, and that dealloying (i.e., selective leaching) was not occurring. But even though total chromium release was roughly proportional to total metal release, the fraction of total Cr present as Cr(VI) was highly variable (Appendix C, Figures C-10 and C-11). Total metals (Cr, Fe, Ni) release in chlorine dioxide solution is nine times the value in chlorine solution at pH 6.5 ($p = 0.01$) and six times the value at pH 9.5 ($p = 0.004$, p -value from paired t -test using average values for each type of stainless steel). Compared with the same conditions (pH 9, type 2205), total metals release in 0.8 mg/L chlorine dioxide reactors is 150 times that of 4 mg/L chloramine (0.2 ppb) solutions, and 300 that of no disinfectants (0.1 ppb).

The pH did not have an effect on total metals release in either disinfectant ($p = 0.98$ [chlorine] and $p = 0.19$ [chlorine dioxide]) (Figure C-18). This is consistent with results from earlier tests (Figure C-19).

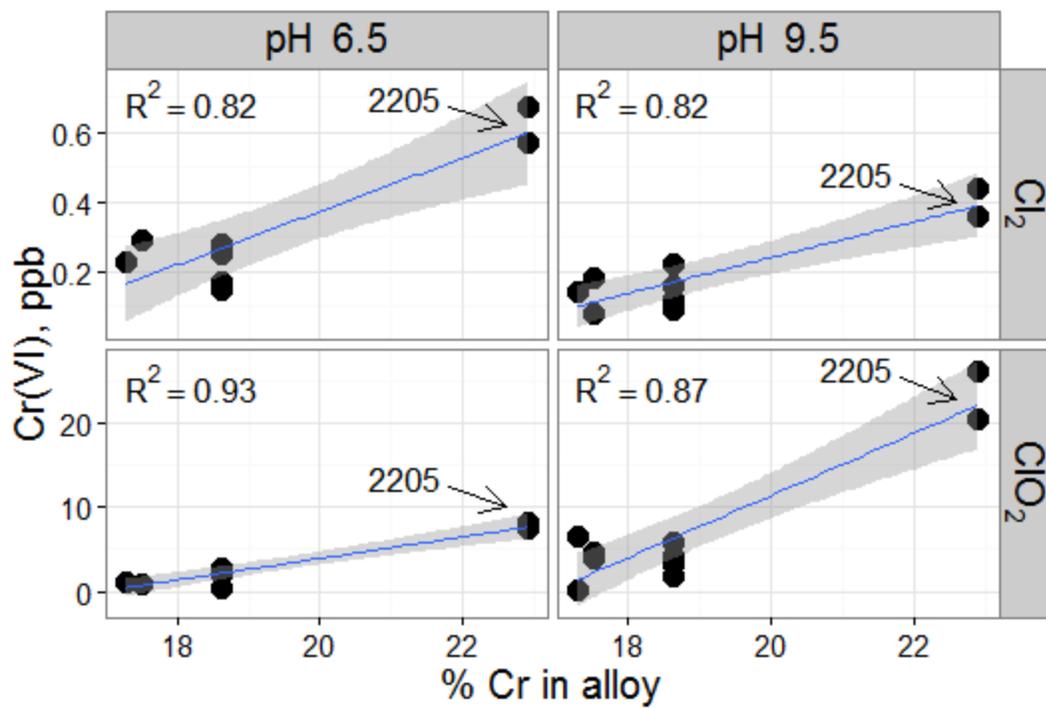


Figure 2-5: Cr(VI) concentration at 8 hours in 24.5°C as a function of %Cr in different types of stainless steel fitted with linear model, shaded areas denote 95% confidence intervals based on all measurements plotted. Four mg/L chlorine and 0.8 mg/L chlorine dioxide were used.

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Appendix A: Engineering Significance

New regulations specifically for Cr(VI) in drinking water are under revision to protect public health. To achieve this goal, Cr(VI) measured and regulated must accurately reflect the public's exposure to the compound. When samples are taken at the point of entry of distribution systems, as suggested by the proposed Cr(VI) MCL in the state of California, Cr(VI) concentration in water samples may change before measurement in the following ways:

- Change in chromium speciation: Cr(III) and Cr(VI) interconvert. Depending on the water condition, either species can be favored. To prevent change in chromium speciation, appropriate preservation, holding time and storage temperature prior to analysis were investigated in this study. Ammonium buffer, as suggested by EPA Method 218.7, was the best preservative tested. In general, the holding time and storage temperature suggested by the method also appear to be appropriate. The only discrepancy this study has with the method suggestion is Cr(VI) stability in ammonium buffer at higher temperature after 14 days.
- Cr(VI) generation from stainless steel piping: If stainless steel piping is used anywhere from the point of distribution system entry to the tap, there is a potential for Cr(VI) formation. This study confirmed that Cr(VI) generation can occur in the presence of stainless steel after as short as 8 hours. Amounts higher than the proposed Cr(VI) MCL of 10 ppb were also observed in some conditions. Therefore, Cr(VI) concentration measured at the point of entry of distribution systems does not necessarily represent the amount consumers are drinking at the tap. It is perhaps more logical to monitor Cr(VI) at the tap if the compound were to be regulated at all.

Appendix B: Evaluation of Hexavalent Chromium Stability in Drinking Water Samples

pH Measurements

Table B-1: pH measurements

Source	Buffer		pH		
			Averaged across time and treatments	Standard Deviation	
DDW	No buffer	No treatment	6.2	0.91	
		Cl ₂	6.2	0.57	
		NOM	5.5	0.54	
		Nitrifier	6.8	0.47	
		Ammonium		9.4	0.09
		Carbonate		10.8	0.06
		Carbonate +Ammonium		10.2	0.04
		Borate		9.5	0.08
		Borate +Ammonium		9.5	0.02
	Utility A	No buffer		7.8	0.24
Ammonium		9.2	0.29		
Carbonate		10.3	0.09		
Carbonate +Ammonium		9.9	0.26		
Borate		9.2	0.06		
Borate +Ammonium		9.4	0.04		
Utility B	No buffer		7.7	0.15	
	Ammonium		9.2	0.28	
	Carbonate		8.3	0.10	
	Carbonate +Ammonium		9.0	0.26	
	Borate		9.3	0.03	
	Borate +Ammonium		9.4	0.04	

Ammonium Measurements

Table B-2: Ammonium concentrations in DDW

Buffer	Treatment	Average NH ₄ -N (mg/L)	SD (mg/L)
Ammonium	No treatment	233	NS
	Cl ₂	236	NS
	NOM	228	NS
	Nitrifiers	239	NS
Borate + Ammonium	No treatment	168	NS
	Cl ₂	170	NS
	NOM	167	NS
	Nitrifiers	171	NS
Carbonate + Ammonium	No treatment	175	NS
	Cl ₂	173	NS
	NOM	182	NS
	Nitrifiers	173	NS

SD = standard deviation

NS = no significant change over time

Table B-3: Ammonium concentrations in Utility A

Buffer	Treatment	Average NH ₄ -N (mg/L)	SD (mg/L)
Ammonium	No treatment	200	NS
	Cl ₂	214	NS
	NOM	216	NS
	Nitrifiers	224	NS
Borate + Ammonium	No treatment	191	NS
	Cl ₂	192	NS
	NOM	190	NS
	Nitrifiers	190	NS
Carbonate + Ammonium	No treatment	169	NS
	Cl ₂	170	NS
	NOM	190	NS
	Nitrifiers	173	NS

SD = standard deviation

NS = no significant change over time

Table B-4: Ammonium concentrations in Utility B

Buffer	Treatment	Average NH ₄ -N (mg/L)	SD (mg/L)
Ammonium	No treatment	191	NS
	Cl ₂	205	NS
	NOM	211	NS
	Nitrifiers	243	NS
Borate + Ammonium	No treatment	200	NS
	Cl ₂	187	NS
	NOM	180	NS
	Nitrifiers	175	NS
Carbonate + Ammonium	No treatment	200	NS
	Cl ₂	152	NS
	NOM	168	NS
	Nitrifiers	149	NS

SD = standard deviation

NS = no significant change over time

Chlorine Measurements

Table B-5: Chlorine measurements for chlorine-treated samples with no ammonium

Source	Buffer	Free Cl ₂		Total Cl ₂	
		Mean	SD	Mean	SD
DDW	No buffer	3.61	NS	3.66	NS
	Borate	2.36	0.88	2.52	0.60
	Carbonate	3.32	NS	3.34	NS
Utility A	No buffer	1.63	NS	1.77	NS
	Borate	1.28	NS	1.49	NS
	Carbonate	2.09	NS	2.24	NS
Utility B	No buffer	2.40	NS	2.47	NS
	Borate	3.07	NS	2.89	NS
	Carbonate	2.72	NS	2.74	NS

SD = standard deviation

NS = no significant change over time

Table B-6: Chlorine measurements for chlorine-treated samples, with ammonium

Source	buffer	Free Cl ₂		Total Cl ₂	
		Mean	SD	Mean	SD
DDW	Ammonium	0.50	NS	3.98	NS
	Borate + Ammonium	0.20	NS	2.70	NS
	Carbonate + Ammonium	1.08	NS	3.89	NS
Utility A	Ammonium	0.26	NS	3.61	NS
	Borate + Ammonium	0.24	NS	1.98	NS
	Carbonate + Ammonium	0.68	NS	3.11	NS
Utility B	Ammonium	0.28	NS	3.59	NS
	Borate + Ammonium	0.34	NS	2.81	NS
	Carbonate + Ammonium	0.20	NS	2.33	NS

SD = standard deviation

NS = no significant change over time

Nitrite and Nitrate Measurements

Table B-7: Nitrite concentrations

Source	Buffer	NO ₂ -N (mg/L)	
		mean	SD
DDW	Ammonium	3.83	NS
	Carbonate + Ammonium	4.57	0.77
	Borate + Ammonium	3.89	NS
Utility A	Ammonium	4.50	NS
	Carbonate + Ammonium	4.60	NS
	Borate + Ammonium	4.30	NS
Utility B	Ammonium	3.77	NS
	Carbonate + Ammonium	4.07	NS
	Borate + Ammonium	3.96	NS

SD = standard deviation

NS = no significant change over time

Table B-8: Nitrate concentration

Source	Buffer	NO ₃ -N (mg/L)	
		mean	SD
DDW	Ammonium	0.36	NS
	Carbonate + Ammonium	0.39	0.08
	Borate + Ammonium	0.37	NS
Utility A	Ammonium	0.37	NS
	Carbonate + Ammonium	0.39	NS
	Borate + Ammonium	0.41	NS
Utility B	Ammonium	0.44	NS
	Carbonate + Ammonium	0.42	NS
	Borate + Ammonium	0.46	NS

SD = standard deviation

NS = no significant change over time

Appendix C: Hexavalent chromium [Cr(VI)] formation in potable water from stainless steel components

Replication of Schroeder and Lee

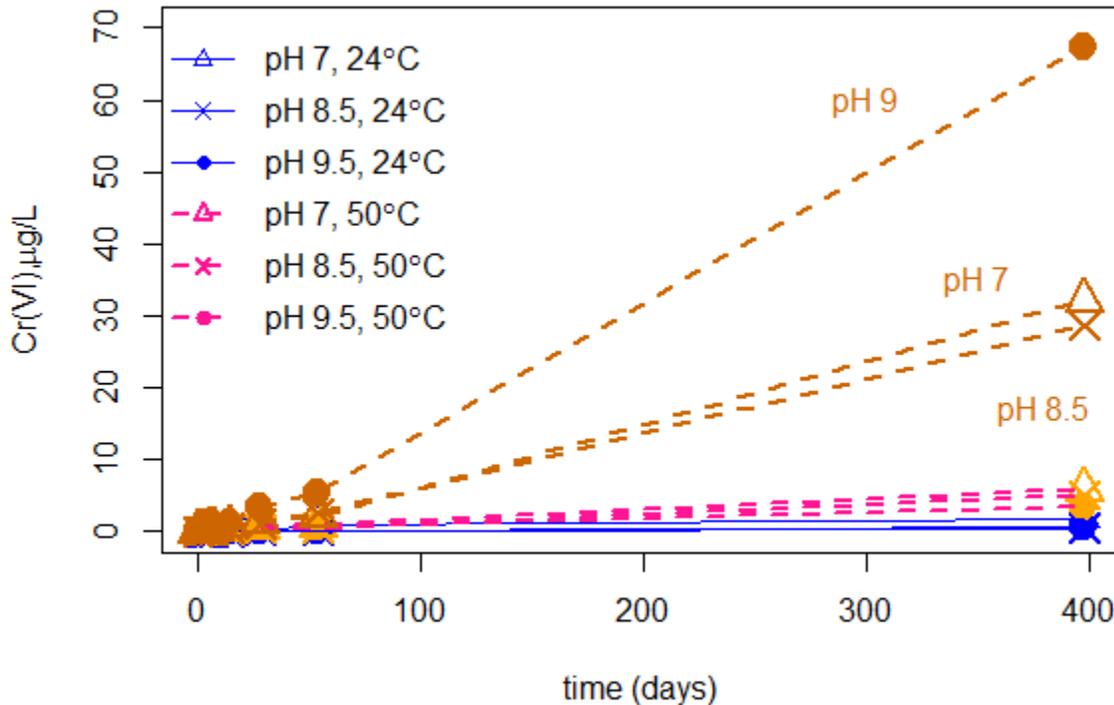


Figure C-1: Cr(VI) concentration over time in different pH and temperatures. Brown points indicate samples where Cr(VI) concentration at the last time interval is considerably higher than their replicates (all are 50°C samples). Other points are the average Cr(VI) concentrations in the rest of the samples.

Table C-1: Comparison of alkalinity between Cr(III) to Cr(VI) by dissolved oxygen experiment and Cr(VI) leachate from stainless steel sheets experiment in this study

pH	Alkalinity (mg/L CaCO ₃)	
	DO experiment	Sheets experiment
6.5	NA	34
7	122	NA
8.5	163	NA
9	110	NA
9.5	NA	67

Chloride concentration for DO experiment = 29 mg/L

Chloride concentration for stainless steel sheets experiment = 20 or 200 mg/L

Effect of pH on chlorine dioxide samples

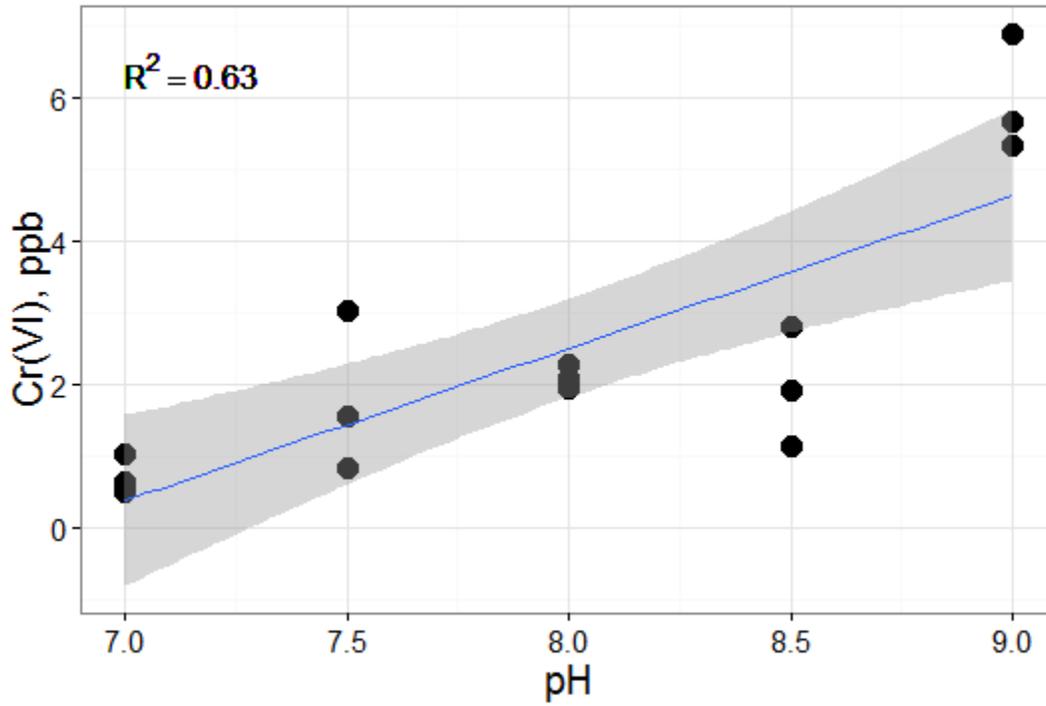


Figure C-2: Cr(VI) vs pH after 36 hours in 24.5°C samples with 0.8 mg/L chlorine dioxide, 20 mg/L chloride and 304 stainless steel sheets, fitted with linear model. Shaded area represents 95% confidence interval based on all measurements plotted, and the p-value for the slope is 0.000399.

Table C-2: Chlorine dioxide consumption rate in 24.5°C samples with type 304 stainless steel sheets compared with their controls (no stainless steel sheet addition). Target chlorine dioxide value is 0.8 mg/L.

	Consumption (mg/L/day)	
	pH 7	pH 9
Samples	0.71	0.60
Control	0.30	0.40

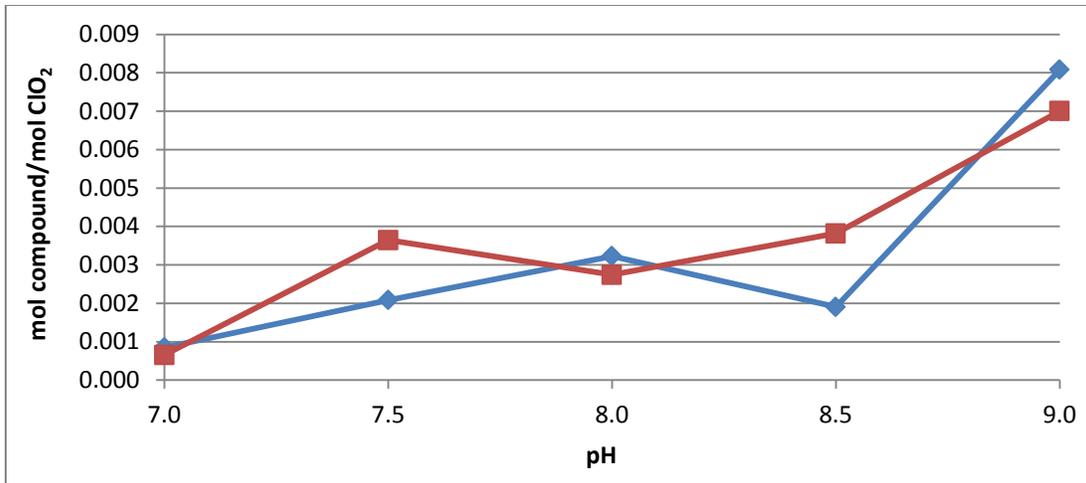


Figure C-3: mole of Cr(VI) (red line) and mole of total Cr (blue line) generated per mole of chlorine dioxide consumed in 0.8 mg/L chlorine dioxide and 20 mg/L chloride. Type 304 stainless steel sheets and temperature of 24.5°C were used.

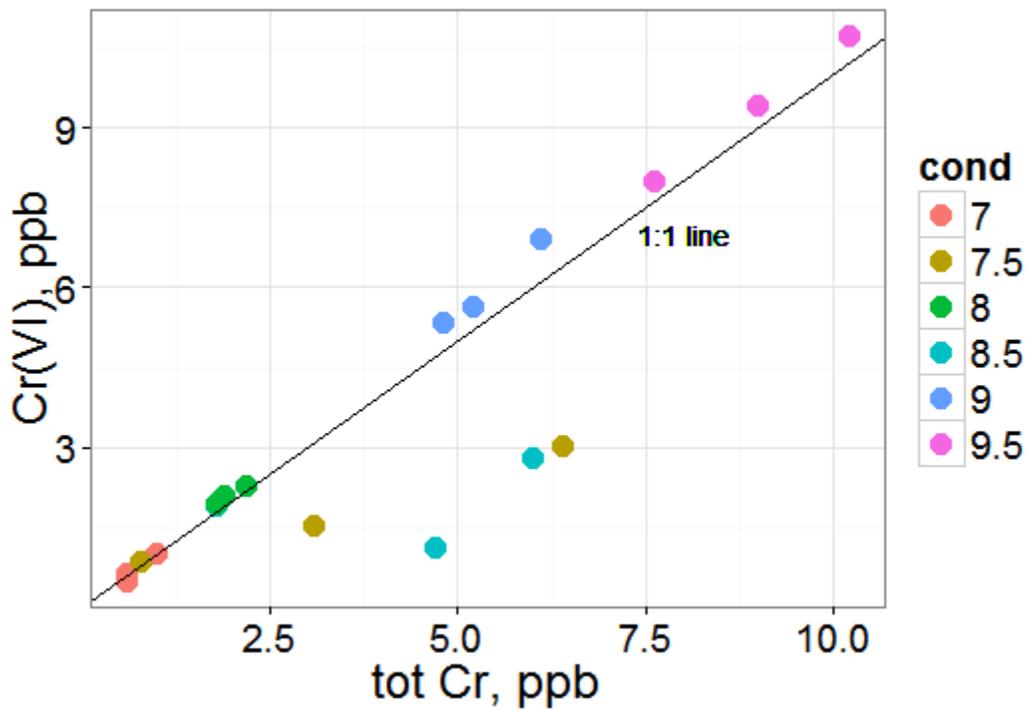


Figure C-4: Cr(VI) vs total chromium concentration after 36 hours in samples in 0.8 mg/L chlorine dioxide, 20 mg/L chloride and 304 stainless steel sheets. Type 304 stainless steel sheets and temperature of 24.5°C were used

Table C-3: Cr(VI) and total Cr generation per mole of chlorine consumed in 4 mg/L chlorine and 20 mg/L chloride. Type 304 stainless steel sheets and temperature of 24.5°C were used

pH	mol Cr(VI)/mol Cl ₂	mol total Cr/mol Cl ₂	Cr(VI)/total Cr
6.5	0.0008	0.0137	6%
9.5	0.0002	0.0003	64%

Effect of Temperature

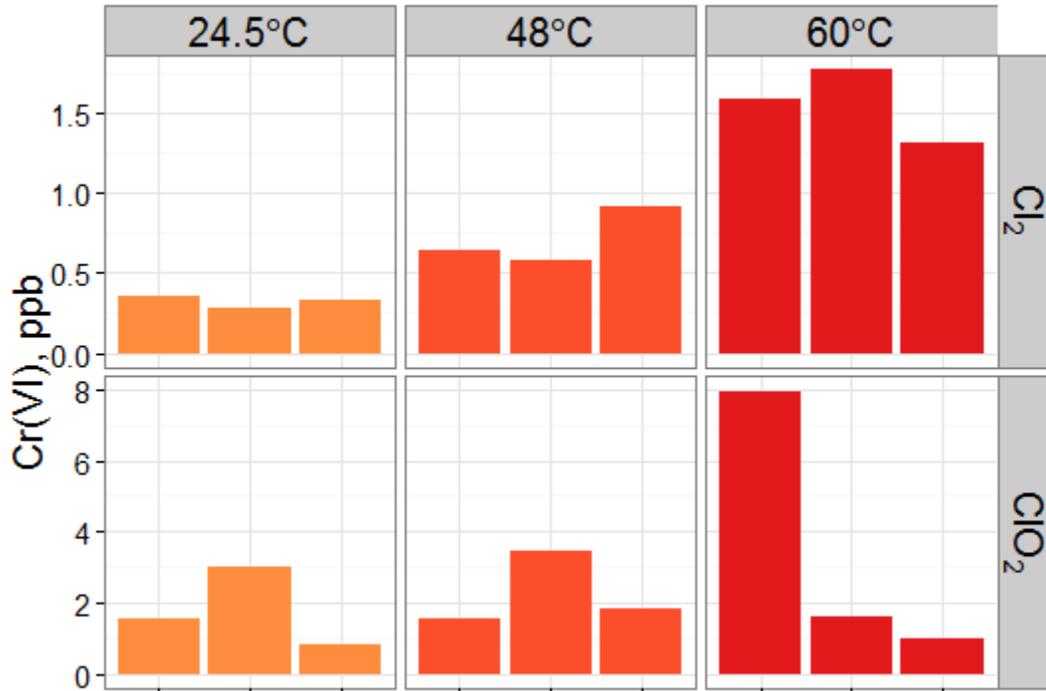


Figure C-5: Cr(VI) concentrations at 36 hours in 0.8 mg/L chlorine dioxide solution and at 24 hours in 4 mg/L chlorine at different temperatures in type 304 stainless steel sheets. From left to right: 24.5 °C, 48 °C and 60 °C.

Table C-4: Chlorine dioxide consumption rate in 24.5°C and 60°C samples.

Type 304 stainless steel sheets were used, and the target chlorine dioxide concentration in samples is 0.8 mg/L

replicate	ClO ₂ consumption (mg/L/day)	
	24.5 °C	60 °C
1	0.71	1.18
2	0.75	0.77
3	0.75	1.08
average	0.74	1.01
Control	NA	0.78

Using t-test, ClO₂ consumption in 60 °C samples are higher than in 24.5 °C (p = 0.08 when including all data, p = 0.03 when excluding replicate 2 in 60 °C)

Effect of Chloride Concentration

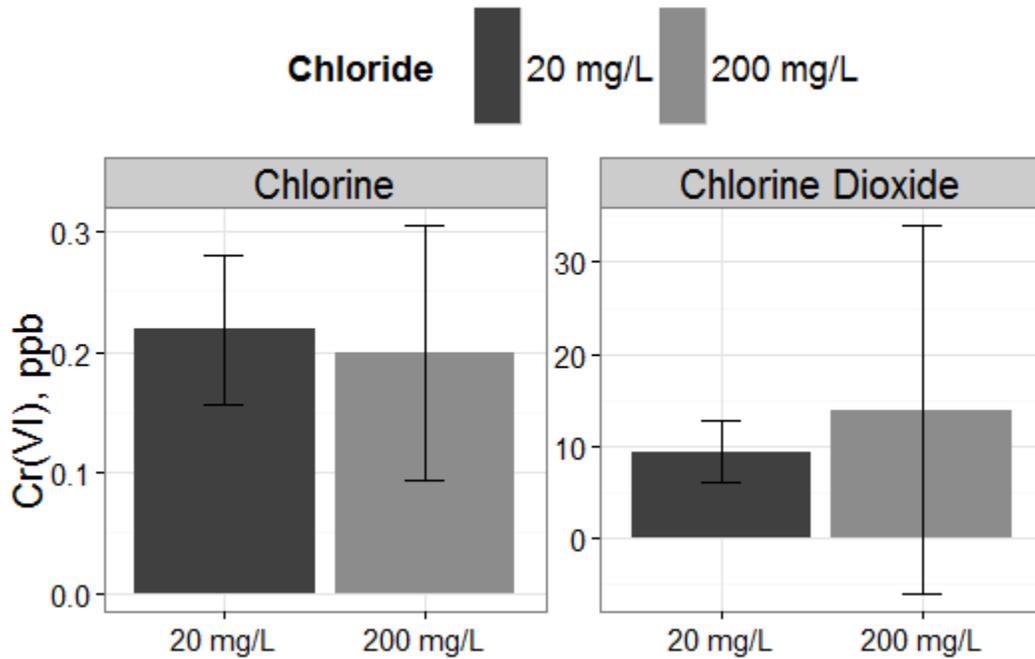


Figure C-6: Average Cr(VI) concentration in 20 mg/L and 200 mg/L chloride in 4 mg/L chlorine solutions (left) and 0.8 mg/L chlorine dioxide solutions (right). Type 304 stainless steel was used, and test was done in 24.5°C. Error bars denote 95% confidence intervals based on triplicates

Effect of Different Types of Stainless Steel

Table C-5: Intercepts and slopes for linear model fitted Cr(VI) concentration vs %Cr in alloy graphs at 24.5°C. Dosages used are 4 mg/L for chlorine and 0.8 mg/L for chlorine dioxide. Significance codes (p-values, $p < 0.05$ is considered significant): 0 ***, 0.001 ** and 0.01*

Disinfectant	pH	Intercept	slope
Chlorine	6.5	-1.158**	0.0765**
	9.5	0.00288**	0.000776***
Chlorine Dioxide	6.5	-21.726***	1.283***
	9.5	-62.520***	3.698***

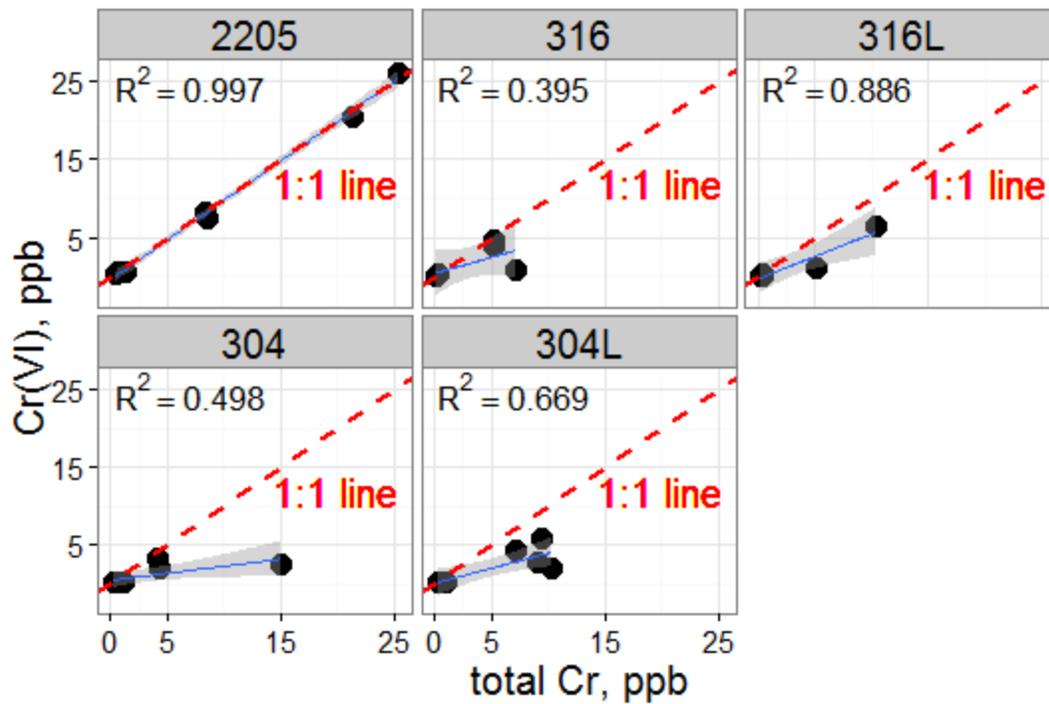


Figure C-7: Cr(VI) concentration after 8 hours at 24.5°C as a function of total chromium in different types of stainless steel fitted with linear model. Shaded areas denote 95% confidence intervals based on all observations (all pH and disinfectants conditions) plotted.

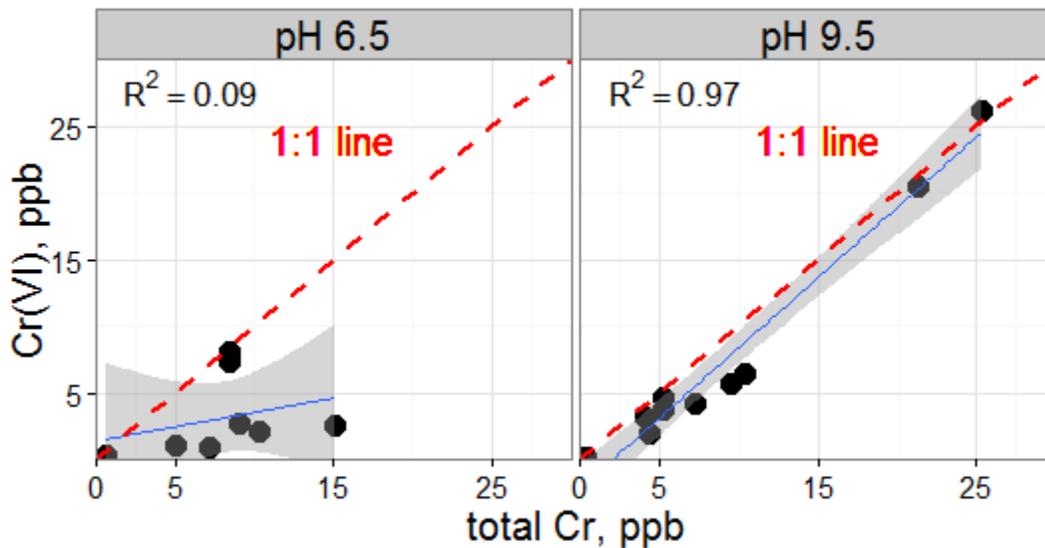


Figure C-8: Cr(VI) concentration after 8 hours as a function of total chromium at 24.5°C and 0.8 mg/L chlorine dioxide solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all measurements plotted.

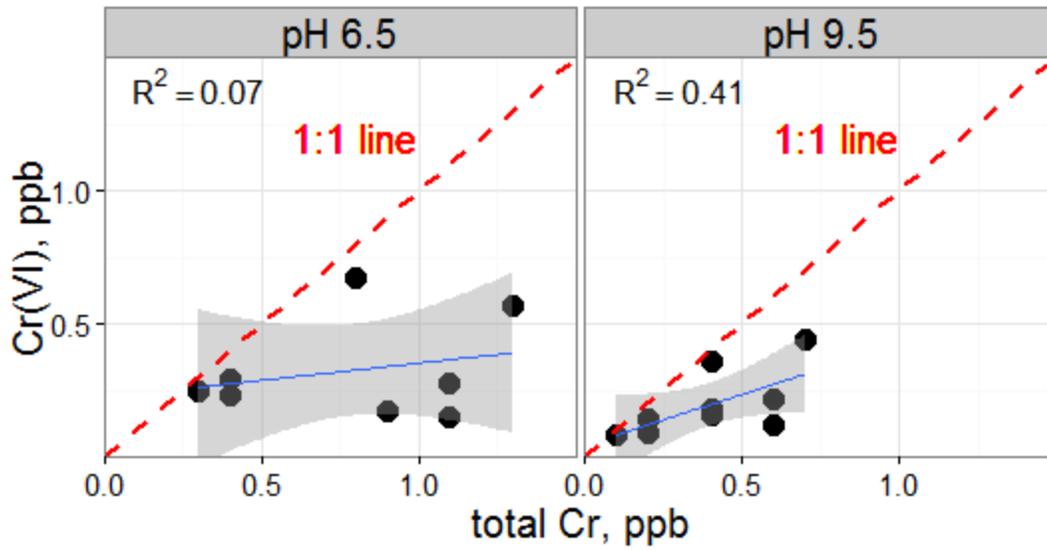


Figure C-9: Cr(VI) concentration after 8 hours as a function of total chromium at 24.5°C and 4 mg/L chlorine solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all measurements plotted.

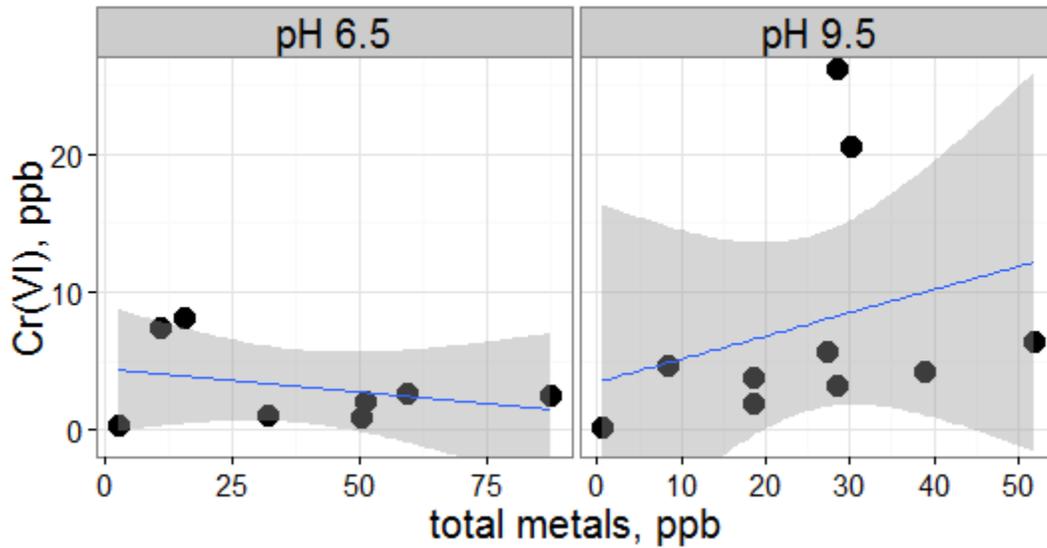


Figure C-10: Cr(VI) concentration after 8 hours as a function of total metals (Cr, Fe, Ni) at 24.5°C and 0.8 mg/L chlorine dioxide solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

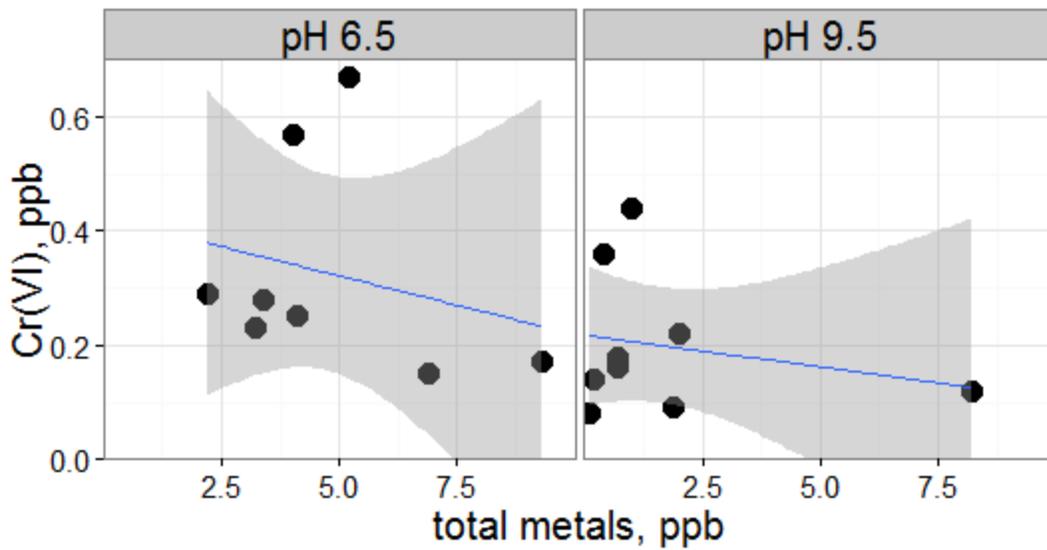


Figure C-11: Cr(VI) concentration after 8 hours as a function of total metals (Cr, Fe, Ni) at 24.5°C and 4 mg/L chlorine solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

Other Metals Measurements

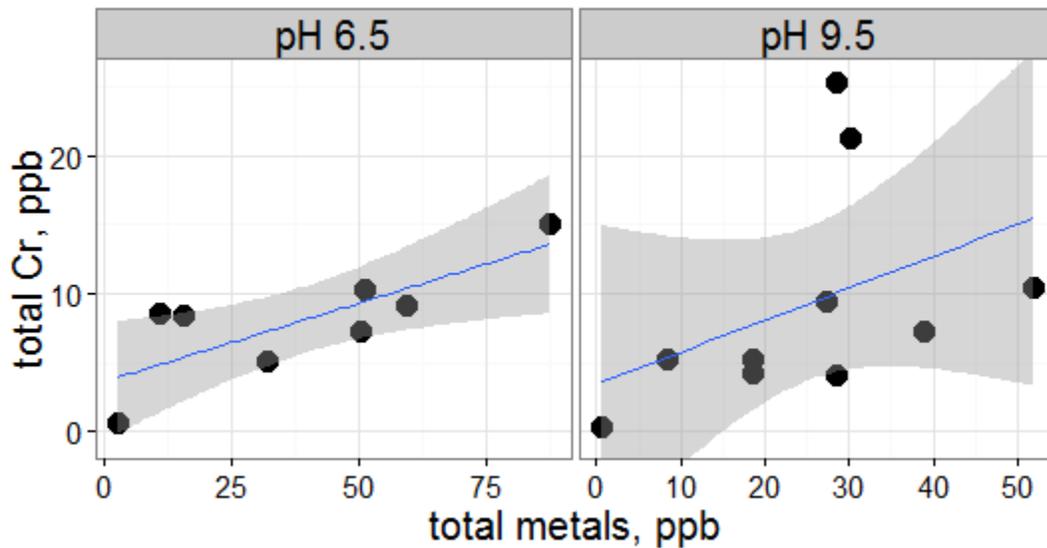


Figure C-12: Total Cr concentration after 8 hours as a function of total metals (Cr, Fe, Ni) at 24.5°C and 0.8 mg/L chlorine dioxide solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

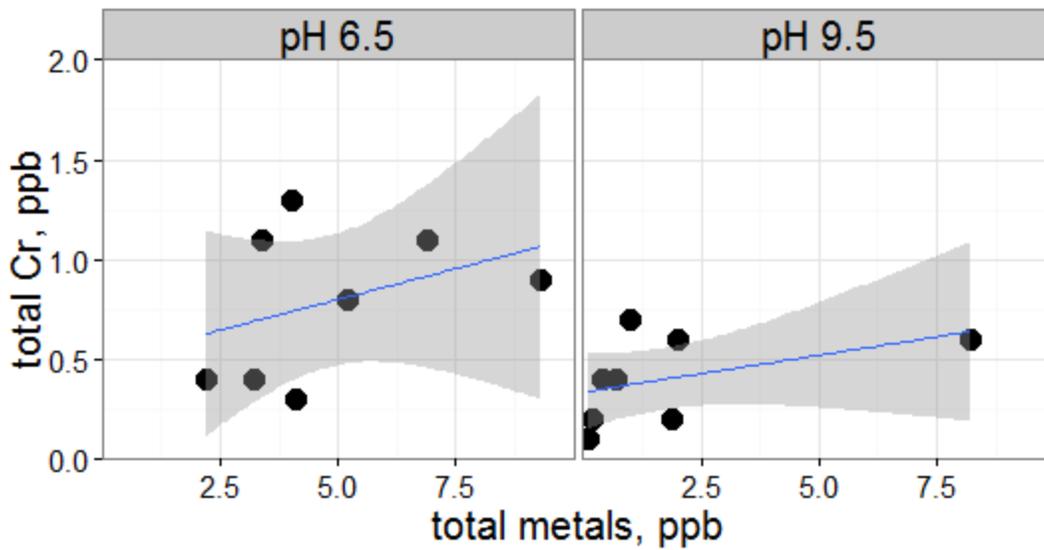


Figure C-13: Total Cr concentration as a function of total metals (Cr, Fe, Ni) at 24.5°C and 4 mg/L chlorine solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

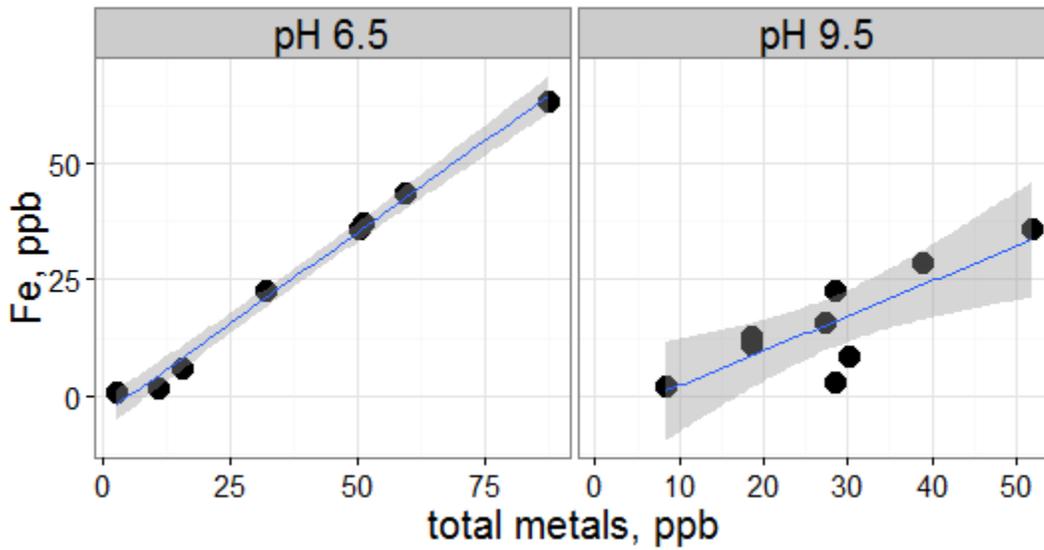


Figure C-14: Fe concentration as a function of total metals (Cr, Fe, Ni) at 24.5°C and 0.8 mg/L chlorine dioxide solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

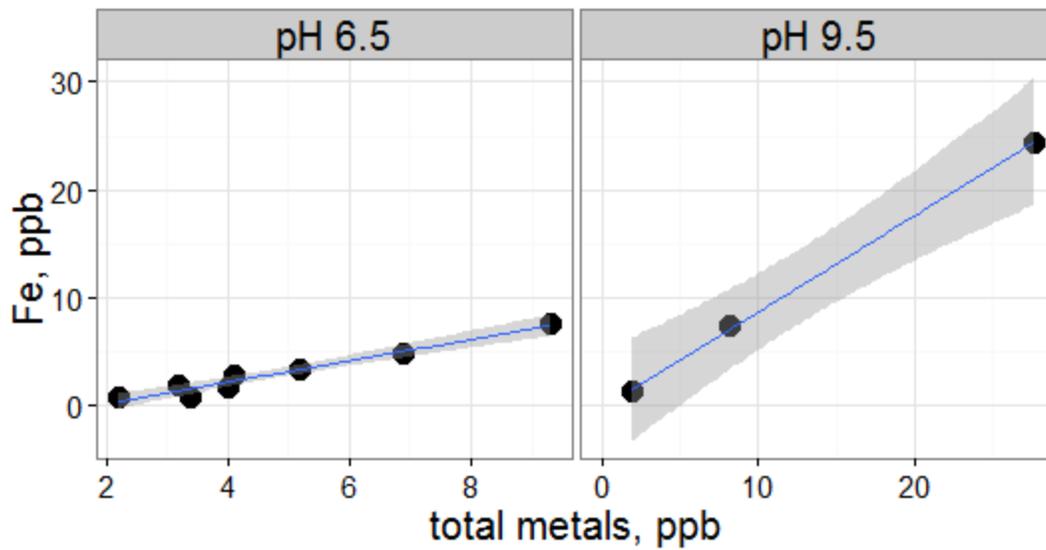


Figure C-15: Fe concentration as a function of total metals (Cr, Fe, Ni) at 24.5°C and 4 mg/L chlorine solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

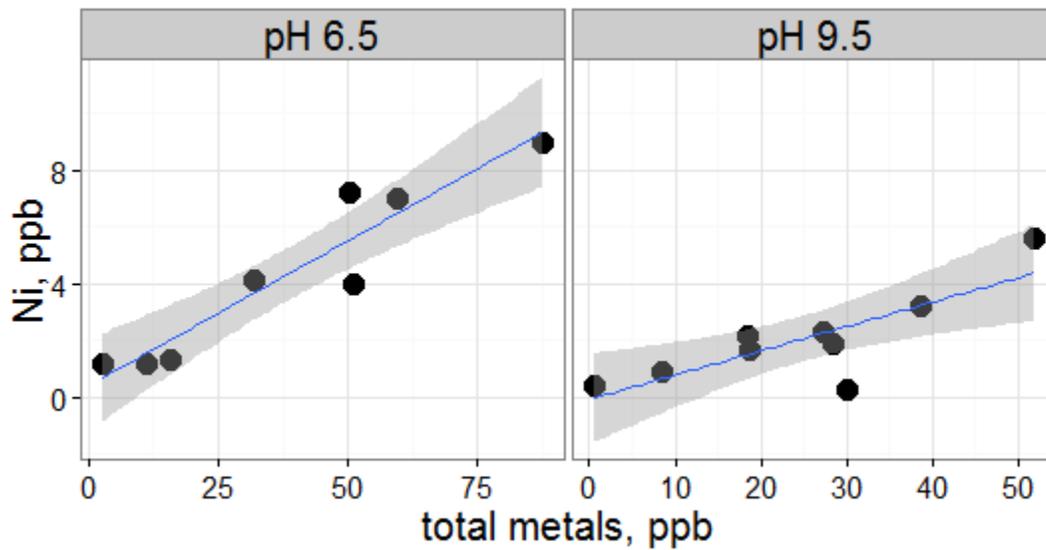


Figure C-16: Ni concentration as a function of total metals (Cr, Fe, Ni) at 24.5°C and 0.8 mg/L chlorine dioxide solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

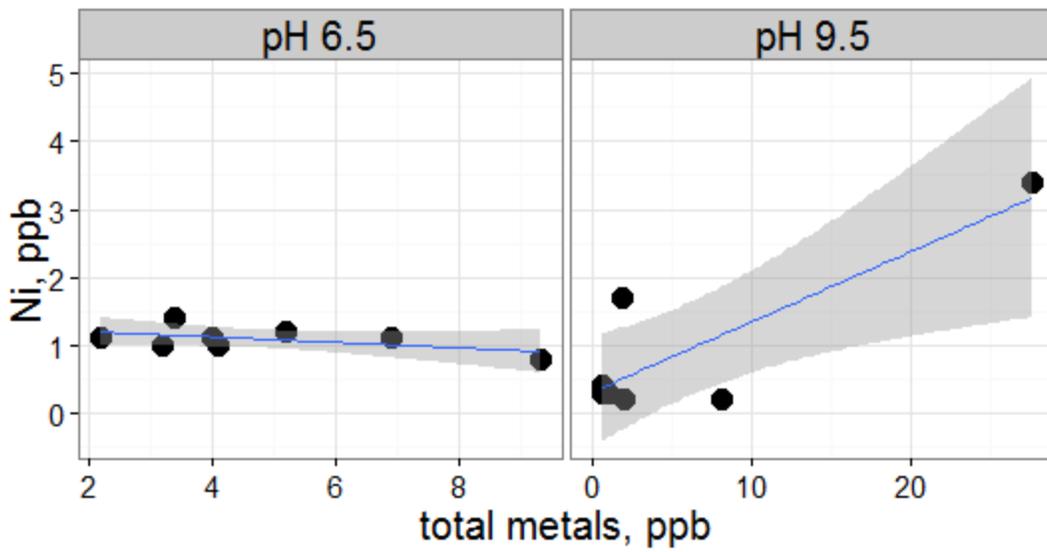


Figure C-17: Ni concentration as a function of total metals (Cr, Fe, Ni) at 24.5°C and 4 mg/L chlorine solutions in all samples (all types of stainless steel included) at pH 6.5 and 9.5. Shaded areas denote 95% confidence intervals based on all samples plotted.

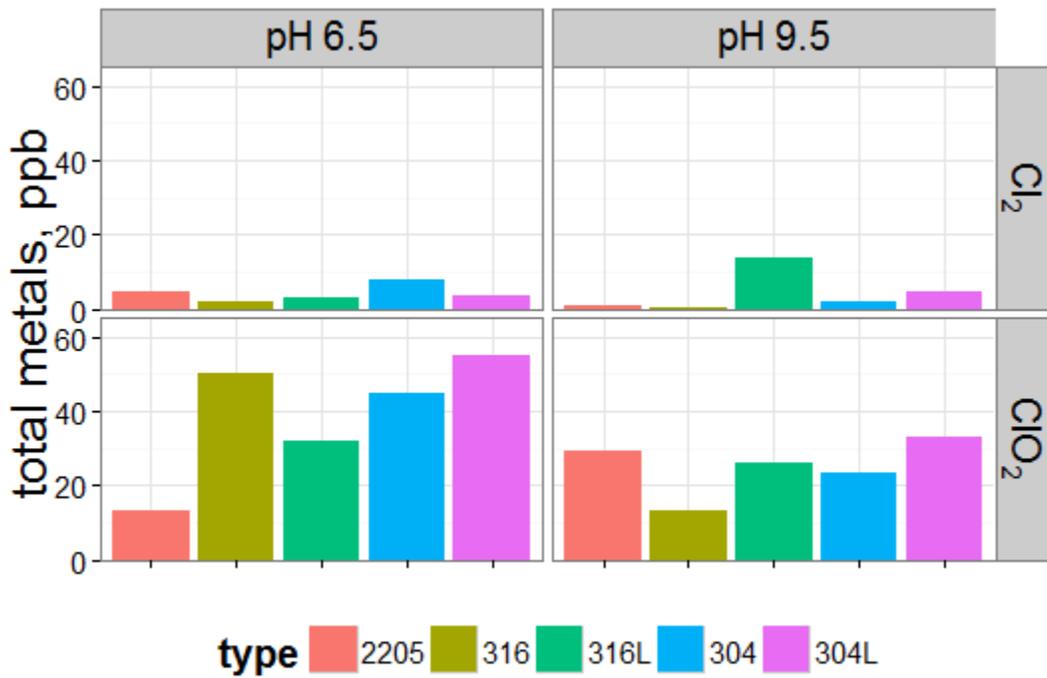


Figure C-18: Total metals (Cr, Fe, Ni) concentration after 8 hours at 24.5°C. Four mg/L chlorine and 0.8 mg/L chlorine dioxide were used.

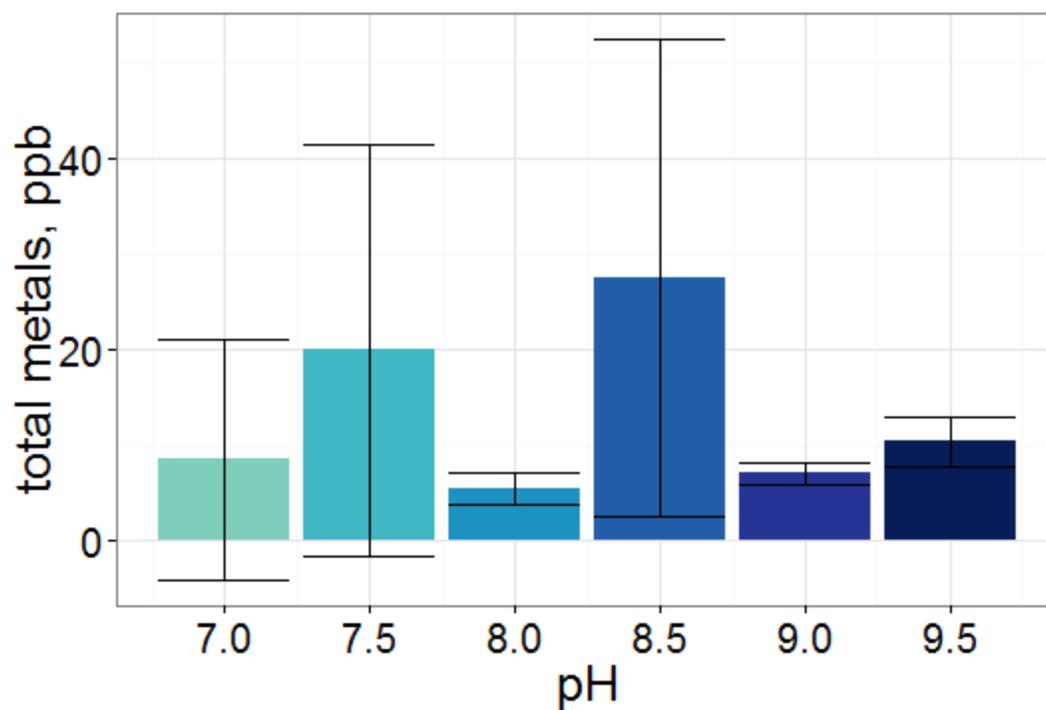


Figure C-19: Average total metals concentration (Fe, Cr, Ni) in 24.5°C and 0.8 mg/L chlorine dioxide solutions at different pH values after 36 hours (24 hours for pH 9.5). Type 304 stainless steel was used. Error bars denote 95% confidence intervals.