

**HEXA VALENT CHROMIUM (Cr(VI)) IN WI
GROUNDWATER: IDENTIFYING FACTORS
CONTROLLING THE NATURAL CONCENTRATION AND
GEOCHEMICAL CYCLING IN A DIVERSE SET OF
AQUIFERS**

**Patrick Gorski
Martin Shafer
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Zana Sijan
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Patrick Gorski, Ph.D
WI State Laboratory of Hygiene
University of Wisconsin-Madison

Martin Shafer, Ph.D
WI State Laboratory of Hygiene and Water Science and Engineering
University of Wisconsin-Madison

James Hurley, Ph.D
Aquatic Sciences Center and Civil and Environmental Engineering
University of Wisconsin-Madison

Zana Sijan
Water Science and Engineering
University of Wisconsin-Madison

James Swarthout
WI State Laboratory of Hygiene
University of Wisconsin-Madison

Administered by:
University of Wisconsin Water Resources Institute

Funded by:
State of Wisconsin Groundwater Research and Monitoring Program

(2015)

This project was also supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

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a diverse set of aquifers.**

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Title: Hexavalent Chromium (Cr(VI)) in WI Groundwater: identifying factors controlling the natural concentration and geochemical cycling in a diverse set of aquifers.

Project ID: WRI Project Number WR12R005

Investigators:

Principal Investigators:

Gorski, Patrick, PhD, Assistant Scientist, Univ. of WI – Madison, WI State Laboratory of Hygiene

Shafer, Martin, PhD, Associate Scientist, Univ. of WI – Madison, Water Science & Engineering

Laboratory and WI State Laboratory of Hygiene

Hurley, James, PhD, Associate Professor, Univ. of WI – Madison, Aquatic Sciences Center and Civil and Environmental Engineering

Research Assistant:

Sijan, Zana, Graduate Student, Univ. of WI – Madison, Water Science & Engineering

Limited Term Employee (LTE):

Swarthout, James, LTE, Univ. of WI – Madison, WI State Laboratory of Hygiene

Period of Contract: July 1, 2012-July 30, 2014

Background/Need: The level of concern about hexavalent chromium (Cr (VI)) contamination in groundwater was heightened due, in-part, to a highly publicized report by the Environmental Working Group (www.ewg.org/chromium6-in-tap-water) in 2010, which documented the widespread occurrence of Cr (VI), a known carcinogen, in drinking water across the nation and in WI. Since there are almost one million private wells in WI and many public drinking water utilities have groundwater sources, it is critical to more fully understand naturally occurring Cr (VI) concentrations and sources. We hypothesized that the Cr (VI) present in groundwater is naturally occurring and proposed to identify factors controlling natural concentrations and geochemical cycling in WI aquifers than contain high levels of mineralization.

Objectives: The goal of this project is to characterize aquifers material of WI as to their natural background concentrations and identify factors associated with release rates of total chromium (Cr) and hexavalent (Cr(VI)) chromium into groundwater.

Methods: Cuttings of aquifer solids were obtained from edges of the three major geologic basins in WI during the well drilling process of new or replacement wells. On the day of collection, solids were placed in clean zip lock bags and transported in coolers to the laboratory. Solids were later rinsed, sieved placed in Mylar bags, purged with nitrogen gas and stored frozen. Aquifer solids for further study were selected based on their geologic formation and concentration gradient for total Cr, Mn and Fe after analysis for 52 different trace metals and elements.

Oxidation state specific release rates of Cr from natural aquifer materials were evaluated in controlled laboratory experiments using batch reactors. All equipment and materials used followed trace metal clean techniques and experiments were conducted in a glove box to maintain anoxia (dissolved oxygen <1 mg L⁻¹). Experiments were performed in filter-sterilized buffered (pH 7) reference ground water and an aquifer solid suspension density of 2 g L⁻¹. The batch reactors were placed on a shaker table, in the dark, at 25 °C, and subsampled on days 0, 1, 7, 14, and 21 for bulk chemistry, pH, dissolved oxygen, temperature, chromium speciation, Fe speciation and sulfide.

Results and Discussion:

Seven contrasting aquifer solid samples were selected based on their concentrations of Cr and levels of other metals that literature suggests may be associated with Cr redox cycling (i.e. Fe and Mn). A positive linear relationship ($R > 0.93$) was observed between solid-phase chromium ($Cr_{(s)}$) and solid-phase aluminum ($Al_{(s)}$) and $Cr_{(s)}$ and solid-phase iron ($Fe_{(s)}$) in the aquifer solid, suggesting that $Cr_{(s)}$ is associated with either Al-bearing and/or Fe-bearing clay minerals. A linear relationship between $Cr_{(s)}$ and $Mn_{(s)}$ was not clear due to variability between samples.

Batch reactor studies showed Cr (VI) was by far the dominant aqueous species, averaging 77% of total Cr (Cr_{Tot}) in the reactors and continually increased in concentration, while the other species of chromium, Cr (III), decreased for majority of the samples. At the end of the 21 days, Cr_{Tot} and Cr (VI) concentrations ranged from 0.23 to 1.39 $\mu\text{g L}^{-1}$ and 0.22 to 1.23 $\mu\text{g L}^{-1}$ which is similar to field measurements and below the current EPA drinking water standard for Cr_{Tot} of 100 $\mu\text{g L}^{-1}$, as well as below the California EPA standard for Cr (VI) of 10 $\mu\text{g L}^{-1}$. Within a multi-depth site, final concentration of aqueous Cr (VI) in the reactor decreased with depth, which followed the $Cr_{(s)}$ concentration and is similar to field studies. But, surprisingly a significant positive correlation between $Cr_{(s)}$ and Cr (VI) concentration in the reactors was not found due to variability.

To examine the influence specifically of Cr content of the solid on release rates, we normalized Cr (VI) release rate specifically to $Cr_{(s)}$ and the rate ranged from 8.0×10^{-5} to 2.9×10^{-3} $\mu\text{g Cr (VI)} \mu\text{g } Cr_{(s)}^{-1} \text{ day}^{-1}$. The $Cr_{(s)}$ concentration is a factor in release, but since our sample with the highest $Cr_{(s)}$ concentration has the lowest release rate and low Cr (VI) suggesting other factors are involved. This sample had the highest $Fe_{(s)}$ concentration and further study revealed an inverse exponential relationship was between Cr (VI) release rates and $Fe_{(s)}$ as well as $Al_{(s)}$. The relationship between aqueous Cr (VI) and $Mn_{(s)}$ was unclear.

Conclusions/Implications/Recommendations: Natural release rates of Cr from aquifer solids are scarce in literature; this study is one of the first and these rates could be used for further modeling. This study indicated that naturally occurring, solid phase Cr is present throughout the Tunnel City, Mt. Simon, Platteville and Wonewoc bedrock formations of WI and Cr (VI) can be released into surrounding water at low levels on time scales of days to weeks. We found Cr content of the solid plays a large role in the Cr (VI) release rates but it is not the sole factor. With our limited data set we were unable to identify factors which may predict Cr (VI) release rates in specific geologic formations across the state. However, this study helped us improve our overall understanding of Cr (VI) fate and behavior in natural aquifer systems and more laboratory study would be required to attain sufficient sample size to determine the sensitivity of the Cr release rates upon changes to the natural aquifer matrices (i.e., pH, oxygen, presence of Fe, Mn, and Al bearing minerals) and across different geological formations.

Related Publications: No peer-reviewed scientific publications to date, but one Water Resources Institute web article: <http://www.wri.wisc.edu/pressroom/Details.aspx?PostID=1179>

Key Words: Groundwater, drinking water, chromium, hexavalent chromium,

Funding: Water Resources Institute, WI State Laboratory of Hygiene.

INTRODUCTION

Chromium (Cr) is a naturally occurring element found in both surface and groundwater, with the two main states being trivalent (Cr (III)) and hexavalent (Cr (VI)). Cr (III) is an essential dietary nutrient involved in glucose metabolism, while Cr (VI) is considered toxic and is a known carcinogen. Concern about hexavalent chromium contamination in groundwater has been heightened due, in-part, to a highly publicized report by the Environmental Working Group (www.ewg.org/chromium6-in-tap-water) in 2010, which documented the widespread occurrence of Cr (VI) in drinking water. The US EPA Maximum Contaminant Levels (MCL) drinking water standard for total Cr, which includes both Cr (III) and Cr (VI), is 100 $\mu\text{g L}^{-1}$ and CA currently has a MCL of 10 $\mu\text{g L}^{-1}$ explicitly for Cr (VI).

Two thirds of WI's population relies on groundwater as its main source of drinking water, making it crucial to understand the naturally present concentrations of both total chromium (Cr_{Tot}) and Cr (VI) in WI aquifers to limit Cr (VI) exposure. Previous studies have measured Cr_{Tot} in groundwater up to 180 $\mu\text{g L}^{-1}$, whereas Cr_{Tot} from anthropogenic sources have been measured up to 220,000 $\mu\text{g L}^{-1}$ (Ball and Izbicki 2004; Fantoni et al. 2002; Lelli et al. 2014; Robles-Camacho and Armienta 2000; Tziritis et al. 2012; Tarcan, Akıncı, and Danişman 2010; Ramesh, Nagendra Prakash, and Sivapullaiah 2013; Rao et al. 2011). Although naturally occurring Cr (VI) has been reported in groundwater, only recently study (Gotkowitz, et al. 2012) has looked at naturally occurring Cr in bedrock formations of WI's aquifers as a possible source of Cr (VI) to groundwater. Since Cr (III) can oxidize to Cr (VI), with this conversion depending on pH, oxygen concentration, and the presence of key oxidants, such as manganese oxides, these components are important to consider in a groundwater system. Cr (III) and Cr (VI) can also adsorb onto clay minerals containing iron (Fe), manganese (Mn), and aluminum (Al).

The geology of WI encompasses the edges of three basins (Michigan, Illinois, and Forest City) where high levels of metals and minerals have been reported in groundwater (Wisconsin State Laboratory of Hygiene (WSLH) data, unpublished). Also, high levels of sulfide minerals and arsenic have been documented in the St. Peter sandstone formation along the edge of the Michigan basin in Eastern WI (Schreiber, Simo, and Freiberg 2000). The goal of this study was to better understand Cr (VI) release from natural aquifers within mineralized edges of the three major geological basins. We hypothesize that the basin edges, which tend to have high occurrences of minerals, and their corresponding aquifers, may be ideal sites for the release of total Cr_{Tot} and oxidation of Cr (III) to Cr (VI).

PROCEDURES AND METHODS

Location, Collection and Storage of Aquifer Material

Table 1: Aquifer solid sample depth, location, formation or group, and description of material composition across all sites.

Sample	Depth (ft)	Well Location Latitude/Longitude (Decimal Degrees)	Group or Formation	Description
Verona	260-300	43.0038/ -89.5706	Tunnel City Group (TCG)	Much gray-green dolomite, little sand, with glauconite and green clay
Pulaski	264-270	44.6675/ -88.3731	Mt. Simon Formation (MSF)	Sandstone poorly sorted and red shale
La Crosse	360-380	43.8049/ -91.1607	Tunnel City Group (TCG)	Sandstone, much dolomite with glauconite and green shale
Appleton	60-95	44.3240/ -88.3968	Platteville Formation (PLT)	Much buff tan to gray green dolomite, little chert
Dane A	185-230	43.2606/ -89.4911	Tunnel City Group (TCG)	Sandstone, trace dolomitic cement, glauconite
Dane B	350-370	43.2606/ -89.4911	Wonewoc Formation (WWF)	Sandstone, trace red gray shale, trace brown shale, white chert
Dane C	370-418	43.2606/ -89.4911	Wonewoc Formation (WWF)	Sandstone, trace brown shale, trace dolomitic cement, trace white chert

Aquifer solids were obtained from edges of three major geologic basins: Michigan, Illinois and Forest City. Fresh core cuttings were obtained during the well drilling process of new or replacement wells in La Crosse, Pulaski, Appleton, Verona and Dane, WI. Solids were collected in clean zip lock bags every five feet, stored in a cooler and transported to the laboratory on the same day of collection. Solids were then rinsed with Type 1 water in a non-metallic fine meshed sieve (125 μm) to remove loose dirt and organic matter. Finally, the moist solids were placed in Mylar bags, purged with nitrogen gas and stored frozen. Aquifer solids used in the study were selected based on their geologic formation (Table 1) and concentration gradient for total Cr, Mn and Fe (Table 2, below). This study used stereomicroscopic observation of sedimentary features to provide qualitative mineral identification for the aquifer materials. The geologic units that include these aquifers are well known to vary in lithology (basic rock type) and mineralogy over very short distances in areal extent and stratigraphic intervals. A listing of basic minerals commonly found in generic sedimentary rock types provides a resource for describing the aquifer materials.

Batch Reactor Study

All equipment and materials used followed trace metal clean techniques to minimize metal contamination. Subsamples of the aquifer cuttings were ground to a diameter of $<250 \mu\text{m}$ using a ball mill. Reactor experiments were conducted in a glove box to maintain anoxia (dissolved oxygen $<1 \text{ mg L}^{-1}$). Experiments were performed in 250 mL LDPE bottles with reference ground water and an aquifer solid suspension density of 2 g L^{-1} . Each experiment consisted of eight sample reactors and four controls (two sample duplicate and two blank reactors). The batch reactors were placed on a shaker table, in the dark, at $25 \text{ }^\circ\text{C}$, and subsampled on days 0, 1, 7, 14, and 21 for: bulk chemistry, pH, dissolved oxygen, temperature, Cr speciation, Fe speciation and sulfide.

Preparation of Reference Ground Water. Fresh deep aquifer ground water was collected (Madison, WI, Well #19) and used as reference ground water. The reference water was passed through a pre-cleaned sodium-form chelex resin (Bio Rad, CA, USA) column to remove metals associated with Cr redox processes. The reference ground water was buffered at pH 7 with 24mM TRIS-Maleate and filtered ($0.2 \mu\text{m}$) to remove any bacteria. Sterile conditions were maintained throughout the 21 day experiments. Anoxic conditions ($<1 \text{ mg L}^{-1}$ dissolved oxygen) were obtained by bubbling the reference water with ultra-high purity nitrogen.

Solid-Phase Characterization:

Aquifer solids were completely solubilized by automated microwave-aided mixed acid (HNO_3 , HCl , HF) digestion (Milestone Ethos+). Following dilution and internal standard addition, fifty two elements were determined by high resolution (magnetic-sector field) inductively coupled plasma mass spectrometry (SF-ICPMS). The reported concentration values have been corrected for the reagent blanks in the digestion batch, and the error has been expanded to account for the variation in the sample, the reagent blanks and the digestion recovery of the certified reference materials.

Solution-Phase Characterization:

Bulk Chemistry. Time-specific reactor subsamples were filtered ($0.22 \mu\text{m}$), acidified with HNO_3 , and quantified by SF-ICPMS for trace elements as done with solid bulk samples.

Cr Speciation. To chemically and physically separate the two significant Cr species, Cr (III) and Cr (VI), a cation exchange column (CEC) technique was applied to our samples (Ball and McCleskey 2003) and analyzed by SF-ICPMS. Total Cr and Cr (VI) concentration values were corrected for reactor blanks, and error was propagated to account for variation in the sample, uncertainty in reagent blanks and reactor blanks. Cr (III) concentration was determined by difference (Total Cr – Cr (VI)).

Other measurements. Inside the glove box, subsamples at each time point were also processed for other analysis, such as Fe speciation, sulfide, pH, temperature and dissolved oxygen. Dissolved Fe (II) was measured colorimetrically using the ferrozine method (Stookey 1970). Fe (III) was determined by difference from Fe_{Tot} and Fe (II). Dissolved sulfide was measured colorimetrically using the methylene blue method (Cline 1969).

Cr (VI) Release Rate

Blank corrected dissolved Cr (VI) concentration was analyzed in reactors for each time point. The Cr (VI) concentration was multiplied by the water volume in each reactor for each time point to account for periodic subsampling and to determine time-specific mass of dissolved Cr (VI). Next, the time-specific dissolved Cr (VI) mass was normalized either by the reactor-specific mass of sample solid or by the concentration of Cr in the solid. Normalized data was transformed to determine the order of the reaction (i.e. concentration versus time, ln(concentration) versus time, and inverse concentration versus time). A linear regression analysis was applied for each sample and release rate (i.e. slope of the linear fit), standard deviation of the release rate (standard deviation from the linear fit) and coefficient of determination was obtained for each sample. Similar calculations were used to determine Cr (III) release.

RESULTS AND DISCUSSION

Characterization of Aquifer Solids

Seven contrasting aquifer solid samples (Table 1, above) were selected based on their concentrations of Cr and levels of other metals that literature suggests may be associated with Cr redox cycling (i.e. Fe and Mn, Table 2). Solid-phase concentrations of Cr (Cr_(s)) ranged from 0.7 to 42.1 µg g⁻¹, from 12.2 to 853 µg g⁻¹ Mn and from 162 to 62,400 µg g⁻¹ Fe. The La Crosse sample had the highest concentrations of solid phase Cr and Fe, and highest Fe:Cr and lowest Mn:Cr molar ratios. The Verona sample had the highest concentration of Mn and highest Mn:Cr molar ratio. Overall, the Dane samples had the lowest metal concentrations, but high Mn:Cr and low Fe:Mn molar ratios. A positive linear relationship (R>0.93) was observed between Cr_(s) and solid-phase aluminum (Al_(s)) and Cr_(s) and solid-phase iron (Fe_(s)) in the aquifer solid, suggesting that solid Cr is potentially associated with

Table 2. Summary of aquifer solid composition for select metals and molar ratios for solid phase iron, manganese and chromium across all sites. See Table 1 for geological formation abbreviations.

	(TCG) Dane A (µg/g)	(WWF) Dane B (µg/g)	(WWF) Dane C (µg/g)	(PLT) Appleton (µg/g)	(MSF) Pulaski (µg/g)	(TCG) Verona (µg/g)	(TCG) La Crosse (µg/g)
Metal							
Al	6930	4710	1710	10500	31129	7820	46000
As	0.77	0.08	0.27	1.34	3.77	6.29	28.3
Ca	40200	631	373	177000	19400	115000	20900
Co	0.75	0.38	0.14	2.34	14.8	4.94	14.6
Cr	4.43	1.26	0.72	9.91	14.9	10.8	42.1
Cu	1.87	1.16	0.59	3.33	57.5	4.18	5.18
Fe	1900	588	162	3490	5640	4410	62400
Mg	16400	320	108	53900	2070	27000	12800
Mn	222	75.4	12.2	357	56.9	853	344
Ni	0.95	1.29	0.17	3.66	27.5	9.62	20.5
S	31.0	<30	<30	3400	675	2280	3720
Molar Ratios							
Fe:Mn	8.46	7.67	13.06	9.65	97.51	5.09	178
Fe:Cr	399	435	209	329	352	380	1380
Mn:Cr	47.22	56.64	16.04	34.10	3.61	74.76	7.73

either Al-bearing clay minerals, Fe-bearing minerals, and/or adsorbed to Fe-oxyhydroxides, or all three of these phases. Gotkowitz et al. (2012) observed the same high positive correlation between $Cr_{(s)}$ and $Fe_{(s)}$ for the Dane County aquifer samples. A linear relationship between $Cr_{(s)}$ and $Mn_{(s)}$ was not clear due to variability between samples.

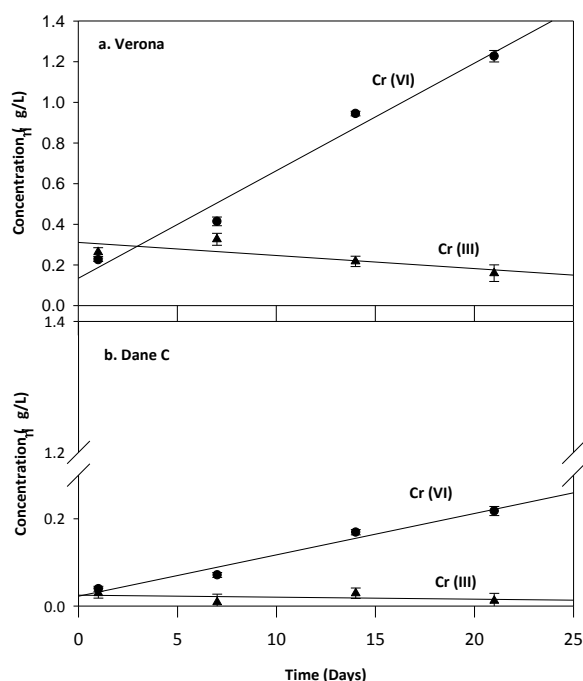
Time Course Analysis of Cr Speciation

Subsamples were obtained at Day 1, 7, 14, and 21 to determine kinetics and speciation of soluble Cr over time. Soluble Cr (III) and Cr (VI) concentrations for the Verona and Dane C represent the two main patterns of Cr release and speciation (Figure 1). In both examples, Cr (VI) was by far the dominant species in the reactors and continually increased in concentration, while Cr (III) concentration slightly decreased for majority of the samples. For the Verona sample, Cr (III) was initially the dominant species but within the first week Cr (VI) became the dominant species and continued to increase in concentration while the Cr (III) species decreased over time (Figure 1a). In the Dane C sample, Cr (VI) was the dominant species from the beginning (Figure 1b).

Typically, Cr (III) is the dominant species in Cr-bearing minerals, therefore we hypothesize that Cr (III) was initially leached from the solid into the reactor solution. Then, over time Cr (III) may precipitate as $Cr(OH)_3$, since precipitation is favored under neutral or basic conditions (our reactors had a pH=7), thus decreasing the aqueous Cr (III) concentration in the reactor (Lin 2002). Secondly, the observed decrease of Cr (III) may be due to adsorption of Cr (III) onto the surface of the cuttings or to the surface of the reactor walls.

Lastly, the decrease of Cr (III) and increase of Cr (VI) concentrations in the reactors may be due to the oxidation of Cr (III) to Cr (VI) by Mn oxides naturally present in the cuttings. The oxidation of Cr (III) has been extensively studied (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Kim et al., 2002; Trebien et al., 2011; Weaver and Hochella, 2003). However, the oxidation of Cr (III) can be limited by the concentration of dissolved Cr (III), pH, initial available surface area and ionic strength. We observed a high positive correlation ($R= 0.702$) between concentrations of aqueous Cr (VI) and aqueous Mn_{Tot} as well as high positive correlation ($R= 0.91$) between concentrations of aqueous Cr (VI) and Mn in the solid. As shown in Table 2, the Mn concentration in the solids ranged from 12 to $360 \mu g g^{-1}$ and soluble total Mn concentrations increased over time for all the sites, with final concentration ranges from 16 to $280 \mu g L^{-1}$ (data not shown). However, the speciation of soluble Mn in the reactors was not determined in this study. Also, the Verona sample had a low Fe to Mn molar ratio of 5.09 and exhibited a decrease in Cr

Figure 1. Comparison of soluble Cr (III) and Cr (VI) concentrations over time in the reactor study for two representative sites: a. Verona, b. Dane C.



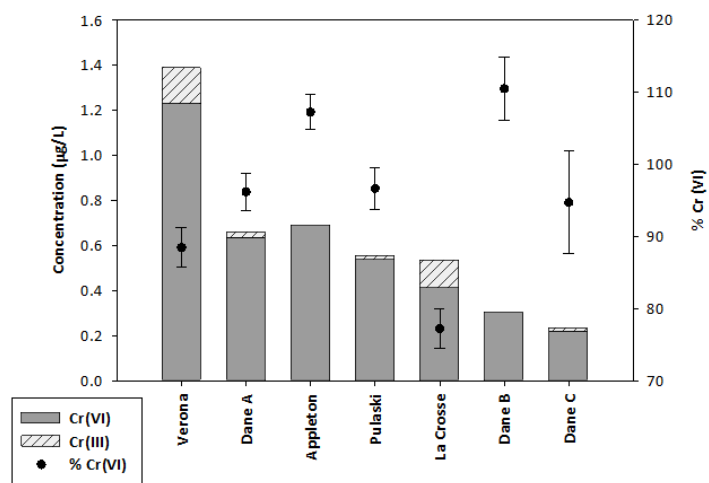
(III) concentration over time while the La Crosse sample exhibited a slight increase in Cr (III) concentration and had a high Fe to Mn molar ratio of 178 (Table 2).

Dissolved Cr Concentration and Speciation

At the end of the 21 days, Cr_{Tot} and Cr (VI) concentrations ranged from 0.23 to 1.39 µg L⁻¹ and 0.22 to 1.23 µg L⁻¹ (Figure 2) which is within the range of Cr_{Tot} concentrations for Dane County municipal wells found by Gotkowitz et al. (2012). Our observed concentrations were well below the

current EPA drinking water standard for Cr_{Tot} of 100 µg L⁻¹, as well as below the California EPA standard for Cr (VI) of 10 µg L⁻¹. The dominant Cr species was Cr (VI), averaging 77% of Cr_{Tot} present as Cr (VI) across sites, with five sites (i.e., Dane A, Dane B, Dane C, Pulaski, and Appleton), at over 90% Cr (VI). Our findings agree with numerous studies which found that the majority of the aqueous Cr_{Tot} in ground water is present as Cr (VI) (Bourotte et al. 2009; Gonzalez, Ndung'u, and Flegal 2005; Lelli et al. 2014; Ball and Izbicki 2004; Fantoni et al. 2002). The dominant presence of Cr (VI) likely is a result of the low solubility of Cr (III) in water at circumneutral pH and potentially favorable oxidizing conditions, allowing for release, oxidation and mobility of Cr (VI).

Figure 2. Soluble Cr (VI) and Cr (III) concentrations for all sites at day 21 of the reactor study



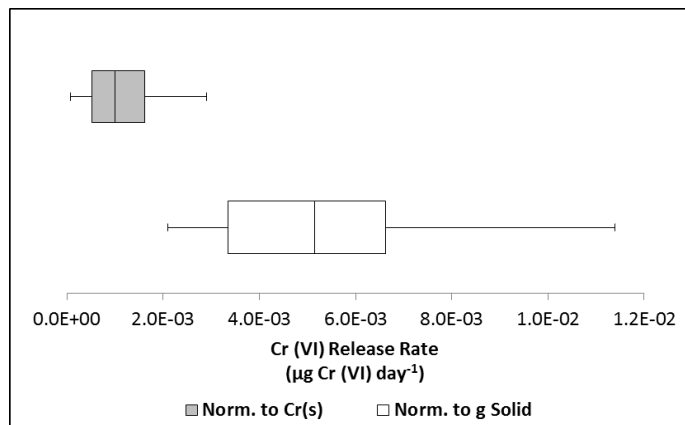
A distinct relationship between Cr_{Tot} concentration and depth was observed for the Dane well samples. Cr_{Tot} concentration decreased (0.650, 0.271, and 0.230 µg L⁻¹, respectively) with depth of 185-230 ft (A), 350-370 ft (B), and 370-418 ft (C). Other studies have also observed distinct differences in well water Cr concentrations with depth (Gonzalez, Ndung'u, and Flegal 2005; Ball and Izbicki 2004; Bourotte et al. 2009; Gotkowitz et al. 2012). Similar to our results, Gotkowitz et al. (2012) found that aqueous Cr_{Tot} and Cr (VI) concentrations were lower in wells completed in deeper formations for Dane County sites. This decreasing trend in Cr concentration also follows decreases in Cr content of the aquifer solid, as well as other metals for this site (e.g., Al, Fe and Mn, Table 2). The percent of aqueous Cr (VI) remained consistent across depths (>94%, Figure 2). Surprisingly, when comparing all sites, a significant positive correlation between Cr(s) and Cr(VI) concentration in the reactors was not found due to variability.

Making generalizations about geologic formation and Cr_{Tot} and Cr (VI) concentration was limited due to our small data set and variability within a geologic unit/formation and more samples would be needed to strengthen relationships between Cr_{Tot}, Cr (VI) and stratigraphic units. For example, the Dane A, La Crosse and Verona samples are part of the Tunnel City geologic formation, but the Verona sample had twice as much Cr_{Tot} concentrations in solution than the La Crosse and Dane A samples at 21-days.

Release Rates of Cr (VI) from Aquifer Solids

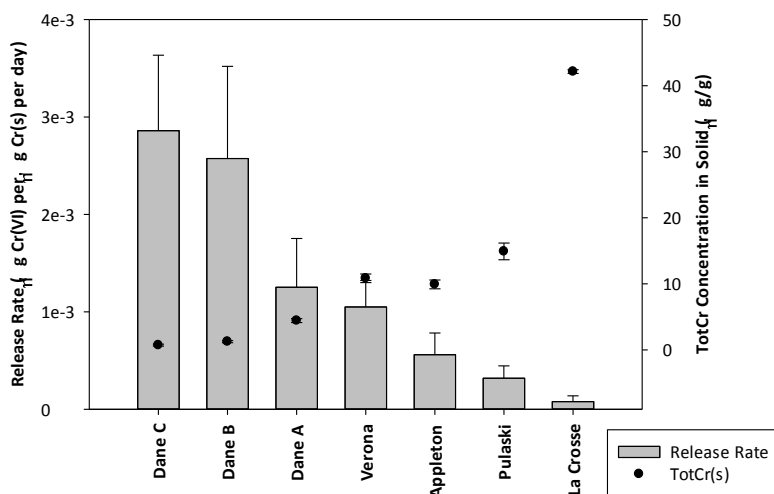
Very few reports of Cr (VI) release rates from aquifer solids are in peer-reviewed literature. The rates measured in this study are among the few ever determined. The Cr (VI) release rate of the seven aquifer solid samples, were first normalized to the mass of solid in units of micrograms of Cr (VI) per gram of solid per day (Figure 3). The Cr (VI) release rates normalized to the mass of bulk solid ranged from 2.1×10^{-3} to 1.1×10^{-2} $\mu\text{g Cr (VI) g}^{-1} \text{ day}^{-1}$ (median = 4.8×10^{-3} $\mu\text{g Cr (VI) g}^{-1} \text{ day}^{-1}$) and the variation reflects the integration of many factors that may or may not play a role in release rate. To examine the influence specifically of Cr content of the solid on release rates, we also normalized Cr (VI) release rate to the mass of only total Cr in the solid in units of $\mu\text{g of Cr (VI) per } \mu\text{g of total Cr in solid per day}$. A substantially narrower range of release rates was observed upon normalization to the Cr content of the solids, indicating that a large fraction of the variation (but not all) in Cr release was driven by Cr content.

Figure 3. Cr (VI) release rates normalized to aquifer solid mass ($\mu\text{g of Cr (VI) per g of solid per day}$) and by concentration of chromium in solid ($\mu\text{g of Cr (VI) per } \mu\text{g of Cr in solid per day}$) for all sites. Box plots correspond to minimum, 1st quartile, median, 3rd quartile, and maximum.



The dissolution rates of Cr (VI) most similarly followed a zero order reaction with respect to Cr in the solid and rates were determined using a linear regression. Across all samples, the Cr (VI) release rates ranged from 8.0×10^{-5} to 2.9×10^{-3} $\mu\text{g Cr } \mu\text{g Cr}_{(s)}^{-1} \text{ day}^{-1}$ (Figure 4). However, samples with the highest release rates did not translate into the highest dissolved Cr concentrations in the reactors. An inverse relationship was observed for Cr (VI) release rate and total Cr concentrations in the aquifer solid (Figure 4). For example, the La Crosse sample had the highest Cr concentration in the aquifer solid but the lowest Cr release rate, reflecting a high potential availability of Cr but the Cr did not go into solution. Overall, the Dane samples had the highest Cr (VI) release rates, and larger release rates were associated with Wonowoc Formation versus Tunnel City Group.

Figure 4. Comparison of Cr (VI) release rates ($\mu\text{g Cr (VI) per } \mu\text{g Cr}_{(s)} \text{ per day}$) as bars (left y-axis) and conc. of Cr in aquifer solid as solid points (right y-axis).



Interestingly, the Dane A and Verona samples, both belonging to the Tunnel City Group, had similar Cr release rates as well as solid phase Fe:Cr and Fe:Mn molar ratios (Figure 4, Table 2).

Variability in Cr release rates was reduced upon normalizing to $Cr_{(s)}$ indicating that Cr in the solid is a factor in release, but other factors in addition to $Cr_{(s)}$ are influencing release rates; possibly including redox conditions and redox-active metals. For example, the La Crosse sample contained the highest $Cr_{(s)}$ but exhibited the lowest Cr (VI) release rate (normalized to $Cr_{(s)}$), possibly due to the very high concentration of $Fe_{(s)}$, $62400 \mu\text{g g}^{-1}$ (Table 2). Also, the La Crosse sample had the second lowest Cr (VI) release rate when normalized to mass of solid. The reducing conditions within the La Crosse reactor with around 1.2 mg L^{-1} of dissolved Fe (II) favor the thermodynamically stable Cr (III) species thus potentially limiting the oxidation and dissolution of Cr (VI). The relationship between solid phase Fe and Mn with Cr may play a key role in Cr release. La Crosse and Pulaski samples, with the lowest Cr (VI) release rates (normalized to $Cr_{(s)}$), had the highest Fe to Mn and the lowest Mn to Cr molar ratios (Figure 4 and Table 2). Gonzalez et al. (2005) observed inverse relationships between soluble Fe_{Tot} and Cr (VI) as well as soluble Mn_{Tot} and Cr (VI) in groundwater samples. However, our data showed a positive correlation ($R > 0.70$) between soluble Cr (VI) and Fe_{Tot} as well as Fe (II) and Mn_{Tot} . Also, a high positive correlation ($R = 0.91$) was obtained between soluble Cr (VI) and $Mn_{(s)}$, which is consistent with reports that Mn (hydrated oxides) are capable of oxidizing Cr in ground water and are the most likely abiotic Cr oxidizer found naturally (Eary and Rai 1987; Rai, Eary, and Zachara 1989; Schroeder and Lee 1975; James and Bartlett 1983). Unfortunately, no single factor could be identified as largely responsible for mediating the release rates of Cr (VI) from aquifer solids. For example, an inverse exponential trend was observed between Cr (VI) release rates and $Fe_{(s)}$ as well as $Al_{(s)}$ (data not shown). However, more detailed experiments are needed in order to determine the cause of the inverse trend between Cr (VI) release rates, $Fe_{(s)}$ and $Al_{(s)}$.

Mineralogy of the formations could also determine mobility and release of Cr (VI) in the aquifer solid. Dane B and Dane C aquifer solid samples, both part of the Wonewoc formation (the “upper aquifer” in Gotkowitz et al. 2012), had the highest Cr (VI) release rates (normalized to $Cr_{(s)}$) with the lowest concentration of Cr in the solid, but had the lowest release rates when normalized to mass of solid. Both samples contain low concentrations of $Fe_{(s)}$ and $Mn_{(s)}$. Possibly, the Cr is adsorbed onto the mineral surface where oxidation may occur easier, favoring higher release rates than if the Cr was a component of the mineral structure. Unfortunately, mineralogy of our samples was not determined. In future studies, standard XRD techniques could characterize the major mineral species in the aquifer solids. Furthermore, the mineralogy of Wisconsin’s aquifers and geologic formations has not been extensively studied and geologic composition of WI may vary within a couple of meters, making wide-spread predictions difficult. Therefore, we are unable to draw specific conclusions about the influence of the mineralogy on the observed Cr release rates.

CONCLUSIONS AND RECOMMENDATIONS

Studies looking at natural release of Cr from aquifer solids are scarce in peer-reviewed literature and this is one of the first studies to measure this process under laboratory conditions. Our results show that naturally occurring, solid phase Cr is present throughout the Tunnel City, Mt. Simon, Platteville and Wonewoc bedrock formations of WI and Cr (VI) can be released into surrounding water at low levels. Furthermore, the mineralogical association of Cr and the geochemical conditions of the ground water environment, support the mobility of $Cr_{(s)}$ on time scales of days to weeks. Under anoxic conditions and at pH 7, Cr_{Tot} and Cr (VI) concentration ranged from 0.23 to $1.39 \mu\text{g L}^{-1}$ and 0.22 to $1.23 \mu\text{g L}^{-1}$,

respectively and Cr (VI) release rates ranged from 8.0×10^{-5} to 2.9×10^{-3} $\mu\text{g Cr (VI)} \mu\text{g Cr}_{(s)}^{-1} \text{ day}^{-1}$ or 2.1×10^{-3} to 1.1×10^{-2} $\mu\text{g Cr (VI)} \text{ g}^{-1} \text{ day}^{-1}$. We found Cr content of the solid plays a large role in the Cr (VI) release rates but it is not the sole factor. An inverse exponential relationship was observed between Cr (VI) release rates and $\text{Fe}_{(s)}$ as well as $\text{Al}_{(s)}$, but Cr (VI) may be aided by $\text{Mn}_{(s)}$. Understanding whether the Cr is bound in the crystal lattice of the mineral or adsorbed onto the surface of the mineral would help us better understand these trends. With our limited data set we were unable to directly identify factors which may predict Cr (VI) release rates and link these factors to specific geologic formations across the state. However, this study helped us improve our overall understanding of Cr (VI) fate and behavior in natural aquifer systems and more laboratory study would be required to attain sample size sufficient to determine the sensitivity of the Cr release rates upon changes to the natural aquifer matrices (i.e. pH, oxygen, presence of iron and Mn bearing minerals) and across different geological formations.

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APPENDIX A:

Publications:

There have been no peer-reviewed scientific publications to date, but one Water Resources Institute web article: <http://www.wri.wisc.edu/pressroom/Details.aspx?PostID=1179>

Presentations:

Chromium 6 – Is this the new flavor of the month? Wisconsin Water Association, Regional Meeting. 2012. September. Appleton, WI. Oral Presentation. Approx. number of attendees of session: 40.

Assessing different aquifer material as possible natural sources of chromium (VI). American Water Resources Association, Regional Meeting. 2013. March. Brookfield, WI. Poster Presentation. Approx. number of attendees of session: 100.

Understanding Factors Controlling Chromium Speciation in Wisconsin Groundwater. American Water Resources Association, Regional Meeting. 2014. March. Wisconsin Dells, WI. Poster Presentation. Approx. number of attendees of session: 100.

Hexavalent Chromium in Wisconsin Groundwater. UW-Madison, Soil Science. 2014. September. Madison, WI. Invited guest lecture for section of seminar MET606. Approx. number of attendees of session: 30.

Natural Release Rates and Speciation of Chromium from Solids in Wisconsin Aquifers. American Water Resources Association, Regional Meeting. 2015. March. Oconomowoc, WI. Poster Presentation. (*Scheduled*)

Awards:

None

Student (1):

Zana Sijan, UW-Madison, MS thesis successfully defended in November, 2014. She currently has a project chemist position at the WSLH. zana.sijan@slh.wisc.edu, sijan@wisc.edu

Impact of work:

Elevator speech: Our work shows that hexavalent, which is a subset of chromium, occurs naturally at very low levels in the environment. Although hexavalent chromium is considered a carcinogen, these levels are very low - much lower than standards set by the EPA and California. These concentrations are orders of magnitude lower than what you would see if it was industrial pollution. Our work demonstrates that hexavalent chromium comes from the rock that groundwater flows through because we collected geological samples of the rocks during the well drilling process from different parts of Wisconsin and then incubated them in the lab. In our lab simulations, which is one of the first of its kind, found that the amount of hexavalent chromium is related the amount of chromium in the rocks, but also the amount of

other metals such as iron, aluminum and manganese. Some metals help the chemical process that makes hexavalent chromium and some inhibit the process. We need more samples to definitively identify all the factors involved in the natural production of hexavalent chromium, but this a great first step.

Influence of work. To our knowledge, our research has not been considered widely in management or monitoring decisions, but we have discussed our research with the members of the Madison Water Utility, Milwaukee Water Works, and Wisconsin Geological and Natural History Association, who have at least utilized our field collection techniques and test methods for Cr (VI) on a limited basis. Since this study began, Patrick Gorski has been invited and became a member of the Wisconsin Water Association (Wisconsin Section) Research Committee due to his research on Cr (VI). Patrick Gorski also has been contacted and interviewed by several media outlets (TV and radio) in regards to Cr (VI) in WI drinking water since the EWG report became public in 2010. After talking to media and research-minded individuals, the interest in Cr (VI) seems to be decreasing. The interest seems to be decreasing since the health risk concerns are minimized after putting the concentrations of Cr (VI) naturally found in ground water in perspective with industrial contaminations.