

**LONG-TERM ALTERATIONS IN GROUNDWATER CHEMISTRY INDUCED BY
MUNICIPAL WELL PUMPING**

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TABLE OF CONTENTS

Project Summary	3
Introduction	5
Procedures and Methods – Physical Flow Modeling	8
Results and Discussion – Physical Flow Modeling	8
Procedures and Methods – Geochemical Modeling	10
Results and Discussion – Geochemical Modeling	11
Conclusions and Recommendations	13
References	14
Appendix A	15

LIST OF FIGURES

Figure 1. Confined aquifer, multi-aquifer, and monitoring well diagrams	5
Figure 2. Aqueous chromium, iron, and manganese concentrations in Madison wells	7
Figure 3. Compiled illustration of particle tracking results	9
Figure 4. Conceptual model for PHREEQC mobilization and sorption simulations	10
Figure 5. Simulated mobilization of manganese under varying dissolved oxygen	13

PROJECT SUMMARY

Title: Long-term Alterations in Groundwater Chemistry Induced by Municipal Well Pumping

Project ID: WR15R002

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Period of Contract: March 1, 2016 – February 28, 2017

Background:

Dane County, Wisconsin, hosts a number of high-capacity, multi-aquifer wells that were drilled through the regional Eau Claire aquitard and draw from both the confined and unconfined aquifers. These wells are excellent study sites in which to test hypotheses related to pumping-induced changes in redox conditions and mobilization of trace elements. Simulations with a recently revised county-scale flow model indicate that the presence of multi-aquifer wells and drawdown in the confined aquifer generated by decades of pumping have changed interactions between the confined and unconfined aquifers and between the surface and groundwater systems. Additionally, historical groundwater sampling of Madison Water Utility wells has revealed elevated hexavalent chromium, iron, and manganese in the groundwater from certain wells.

Objectives:

Objectives of this study were to further explore the impacts of pumping on induced mixing of groundwater from shallow and deep aquifers and to identify geochemical processes resulting from such mixing.

Methods:

A variety of MODFLOW simulations, coupled to particle tracking with MODPATH, were performed that focused on determining the impact of municipal pumping and drawdown on groundwater flowpaths and mixing of water from different sources. PHREEQC was used to model the various geochemical scenarios caused by pumping, focusing on the mobilization of hexavalent chromium, manganese, and iron.

Results and Discussion:

The results of physical flow modeling, particle tracking and mass balance analyses indicate that the long-term, high capacity pumping occurring in Dane County is impacting the surface and

groundwater systems. Groundwater flow rates are accelerated under current conditions and have been redirected toward the pumping-induced cones of depression along the Isthmus. Downward migration of oxic groundwater across the Eau Claire aquitard has increased throughout Dane County and is further enhanced at multi-aquifer wells. Groundwater contributions to surface waters are declining, and gradient reversals have resulted in portions of Lake Mendota and Lake Monona recharging the groundwater system rather than receiving groundwater discharge. These findings helped inform geochemical modeling that examined the possibility of mobilization of trace metals under varying pumping scenarios. Concentrations of hexavalent chromium measured in groundwater from multi-aquifer wells in the study area exceed those measured in confined aquifer wells. Conversely, manganese and iron values are higher in groundwater from confined aquifer wells with aqueous manganese concentrations highest near the boundary between oxic and anoxic conditions and iron most prevalent under completely anoxic conditions. Geochemical model simulations indicate that while chromium mobilization may be occurring in the confined system, aqueous chromium concentrations are limited by the sorption potential of iron in the Mount Simon formation. Additionally, whether the chromium is adsorbed onto the surface of sand grains or, instead, bound within the mineral structure may impact mobilization and release rates in the confined Mount Simon aquifer. Cumulatively, these findings suggest that in this hydrogeologic setting, pumping practices and alterations to redox conditions are impacting the mobility of hexavalent chromium, manganese, and iron.

Conclusions/Implications/Recommendations:

Public water managers need strategies to address water quality impacts of long term pumping. Because iron mobilization is restricted to purely anoxic conditions, introducing oxygen to the confined system should result in a slight decline in iron concentrations over time. Manganese, however, is less predictable. Because aqueous manganese values are highest near the boundary between oxic and anoxic conditions, water managers will need to know when that boundary is approaching a high-Mn_(s) portion of the Mount Simon. For chromium mobilization, multi-aquifer wells and increased drawdown create the greatest concerns, as they accelerate downward flow across the Eau Claire aquitard, oxygenating the confined system. Water managers in Dane County could try to spatially balance withdrawals more evenly across the county to reduce the worst cones of depression. This could potentially have a marginal benefit. However, based on current withdrawal rates, it is unlikely that drawdowns will reverse in the near future. Aqueous chromium concentrations in municipal water supplies could be significantly reduced by using only confined aquifer wells, limiting Cr_(aq) inputs from the shallow aquifer and mobilization from the Mount Simon at multi-aquifer wells, but this would likely make iron and manganese issues more prevalent and lead to even greater drawdown in the Mount Simon. Ultimately, there is no single solution that addresses all the concerns, so operating cost or water quality concessions will likely need to be made in the future.

Keywords: multi-aquifer wells, municipal pumping, chromium, manganese, iron, trace metal mobilization, gradient reversal

Related Publications: This work is the subject of a M.S. thesis in Geoscience that will be submitted in June 2017. Preparation of a journal article based on that work is anticipated in the future

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INTRODUCTION

Municipalities in Dane County, Wisconsin, have been using groundwater to meet public demand for more than a century. As populations have grown, the rate of withdrawal has greatly increased. Madison alone now pumps 10 billion gallons of groundwater each year from a network of 22 supply wells (Madison Water Utility, 2016). This pumping has resulted in significant alterations to groundwater gradients. The confined Mount Simon aquifer, from which all the municipal, high-capacity wells draw water to some extent, has experienced substantial drawdown, particularly at the Madison Isthmus, where municipal pumping is most concentrated (Bradbury et al., 2013). As a stacked aquifer system, these changes in gradient have a direct impact on groundwater interactions throughout Dane County.

Of the 22 Madison Unit wells operated by the Madison Water Utility, 8 are confined aquifer wells that pump exclusively from the Mount Simon (Fig. 1). The other 14 are multi-aquifer wells that were drilled through the regional Eau Claire aquitard, often all the way to the top of the Precambrian basement, but only cased through part of the upper aquifer. This creates a borehole connection between the upper and lower aquifers, which results in wells drawing from both the confined and unconfined systems and downward flow during periods of non-pumping.

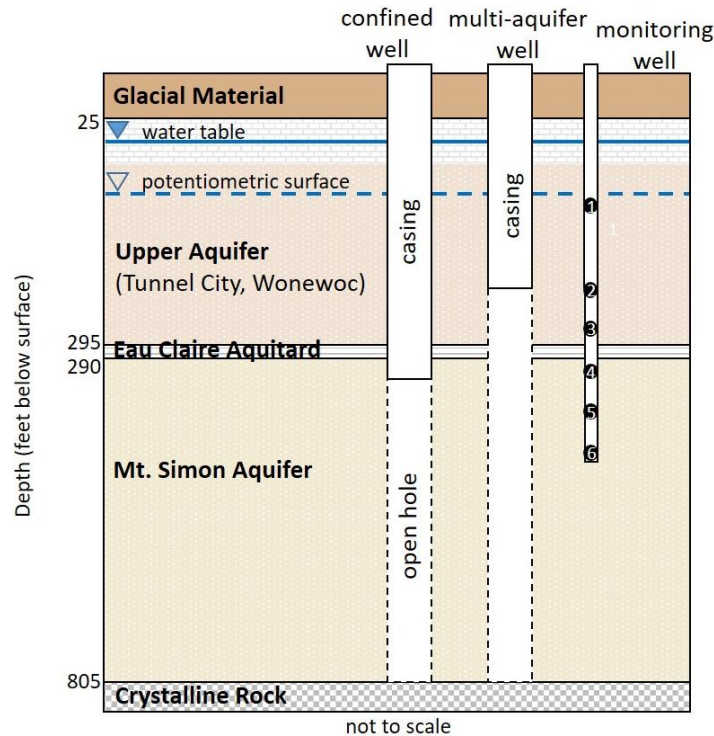


Figure 1. Construction diagrams of confined aquifer, multi-aquifer, and monitoring wells

Mixing groundwater from distinct sources creates new geochemical environments, which impact the potential for mobilization of naturally-occurring trace metals from the aquifer matrix (Ayotte et al., 2011). This is evidenced in the Madison wells by variations in chromium (Gotkowitz et al., 2012), manganese, and iron concentrations between confined aquifer and multi-aquifer wells (Personal communication with M.B. Gotkowitz, 2015a). While chromium is typically below detection limits in groundwater sampled from confined-aquifer wells (Fig. 2), it is commonly observed in groundwater from multi-aquifer wells. As aqueous chromium

concentrations are higher in the unconfined system, simply mixing groundwater from the shallow aquifer with the groundwater from the confined system could lead to higher chromium concentrations in multi-aquifer wells. However, in Dane County, the introduction of oxic water into the anoxic, confined system may further exacerbate the problem by mobilizing additional chromium, known to be present in the mineral phase in the Mount Simon (Personal communication with M.B. Gotkowitz, 2017).

Iron, by contrast, is typically mobile under anoxic conditions (Fig. 2), and primarily observed in confined aquifer wells in Dane County (Personal communication with M.B. Gotkowitz, 2015a). Manganese is also generally detected at higher concentrations in confined wells in Dane County (Fig. 2), but has also been an issue in a few multi-aquifer wells (Personal communication with M.B. Gotkowitz, 2015a). Research in a meromictic lake, containing layers of water that remain unmixed, in Norway found that aqueous manganese mobilization was less impacted than iron by increases in dissolved oxygen (Hongve, 1997). This likely explains the presence of aqueous manganese and lack of iron in groundwater from some multi-aquifer wells in Dane County. The variability of concentrations of chromium, manganese, and iron suggest that a range of geochemical conditions is being created in Dane County municipal wells.

Impacts of pumping in Dane County extend beyond the aquifer system. Substantial changes have occurred in the baseflow to streams and springs as well as discharge to Lakes Mendota and Monona, particularly along the Madison isthmus, where vertical hydraulic gradients have actually reversed from predevelopment conditions in which groundwater discharged to the lakes, to current conditions in which lake water infiltrates to the aquifer in some areas of the lake beds (Bradbury et al., 2013). The regional Eau Claire aquitard is thought to be partially absent in parts of central Dane County where a pre-glacial bedrock valley extended into the Mount Simon Sandstone (Swanson et al., 2001). This includes the area beneath the lakes of the Yahara watershed (Bradbury et al., 1999). Gradient reversals in the areas where the aquitard is absent have a magnified impact on groundwater-surface water interactions.

In assessing the situation in Dane County, this project focused on three primary objectives: evaluating how pumping-induced changes in gradient have impacted interactions between the unconfined and confined aquifers and between the surface water and groundwater systems, determining if the new geochemical environments created by these interactions impact aqueous chromium, manganese, and iron concentrations, and investigating the mobilization potential of these trace metals in the groundwater system. These issues were examined using a combination of modeling and lab-based techniques. A variety of MODFLOW simulations were performed that focused on determining the impact of municipal pumping and drawdown on groundwater flowpaths and mixing of water from different sources. These simulations helped inform geochemical modeling that examined the possibility of mobilization of trace metals under varying pumping scenarios, emphasizing the potential issue of mobilization of aqueous chromium from the Mount Simon aquifer in the presence of shallow, oxic groundwater. Mobilization potentials of chromium, manganese, and iron were further investigated by performing laboratory extractions on samples from the Tunnel City, Wonewoc, and Mount Simon formations to assess total metals concentrations (Results are pending, and therefore, not included in this report). These studies provided valuable insight into the current and future issues municipalities will need to consider if current pumping practices continue.

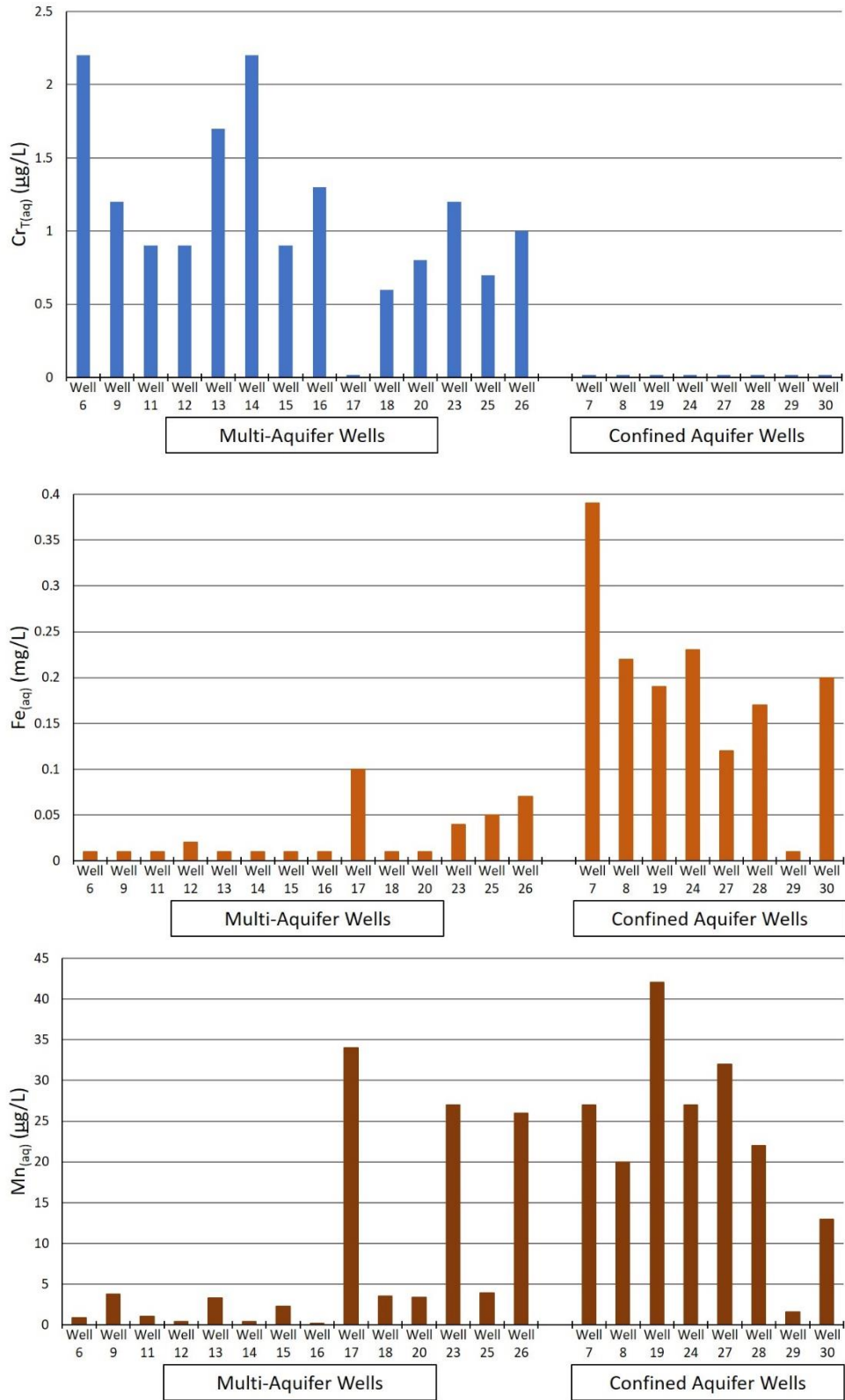


Figure 2. Comparison of aqueous chromium, iron, and manganese concentrations in Madison Water Utility multi-aquifer and confined aquifer supply wells, as measured in 2013

PROCEDURES AND METHODS – PHYSICAL FLOW MODELING

The 2016 Groundwater Flow Model for Dane County, Wisconsin (Parsen et al., 2016) was utilized to run steady-state MODFLOW simulations under current and pre-development conditions. All wells were active for simulations of current conditions and deactivated for pre-development simulations. Comparisons of the two scenarios were made using backward particle tracking in MODPATH. Broad particle releases were used to examine flow variations in the Mount Simon aquifer around and below Lake Mendota, as well as along the Isthmus. Particles were released from the top and bottom of model layer 12 (Mount Simon) to examine flow across the Eau Claire aquitard and in the deep Mount Simon. Broad and feature-focused mass balances were used to examine changes in volumetric groundwater flow rates across the aquitard, as well as changes in groundwater contributions to surface waters.

Focused particle releases in the areas surrounding municipal wells were used to evaluate local scale flow dynamics caused by high-capacity pumping. Madison Unit Wells 15, 23, 6, and 25 were selected for particle releases, as they represent a range of $Cr_{(aq)}$ concentrations observed at multi-aquifer wells during a 2013 sampling round. At each of the four identified wells, particle circles of 6 particles were released at the top, middle, and bottom of the Mount Simon in the area immediately surrounding the well and then backward-traced for varying travel times. Particle travel paths were then compared under current and pre-development conditions.

RESULTS AND DISCUSSION – PHYSICAL FLOW MODELING

Particle releases in the Mount Simon along the Madison Isthmus and Lake Mendota area reveal that pumping practices have significantly accelerated and shifted flow in the deep aquifer toward the Isthmus. Under pre-development conditions, Lake Mendota was the primary groundwater discharge point in the area and groundwater recharge along the Isthmus discharged to Lake Mendota (Fig. 3). Additionally, groundwater from the middle and upper portions of the confined system flowed upward across the aquitard near the Isthmus. These flow dynamics were significantly altered when pumping was introduced to the system. Under current conditions, pumping-induced drawdown has reversed vertical gradients, causing Lake Mendota water to flow into the groundwater system. Groundwater flow in the middle and upper portions of the confined system near the Isthmus is now also downward. This shift in flowpaths and intrusion of surface water into the groundwater system was further confirmed by mass balance analysis.

Previous studies found that, under pre-development conditions, the model estimated that streams contributed approximately 4 million gallons to the groundwater system and received approximately 402 million gallons from the groundwater system each day (Parsen et al., 2016), resulting in a net stream recharge of approximately 398 million gallons of groundwater per day in Dane County. Under current conditions, stream contributions to groundwater were approximately 6 million gallons per day, and groundwater flow to streams was approximately 361 million gallons per day (Parsen et al., 2016), resulting in a net groundwater discharge to streams in Dane County of roughly 355 million gallons per day. Lakes in the model area showed a similar trend and were even more significantly impacted. Under pre-development conditions, approximately 5 million gallons of lake water flowed into the groundwater system compared to 19 million gallons of groundwater flowing into lakes (Parsen et al., 2016), resulting in a net groundwater discharge to lakes in Dane County of approximately 14 million gallons per day. Under current conditions, lake contributions to the groundwater system increased and groundwater discharge to the lakes decreased. Simulations estimated 6 million gallons of lake

water flowing into the groundwater system and 12 million gallons of groundwater discharging daily to lakes (Parsen et al., 2016), resulting in a net groundwater discharge to lakes in Dane County of approximately 6 million gallons per day. That is a reduction of over 40% in net discharge to lakes under current pumping conditions.

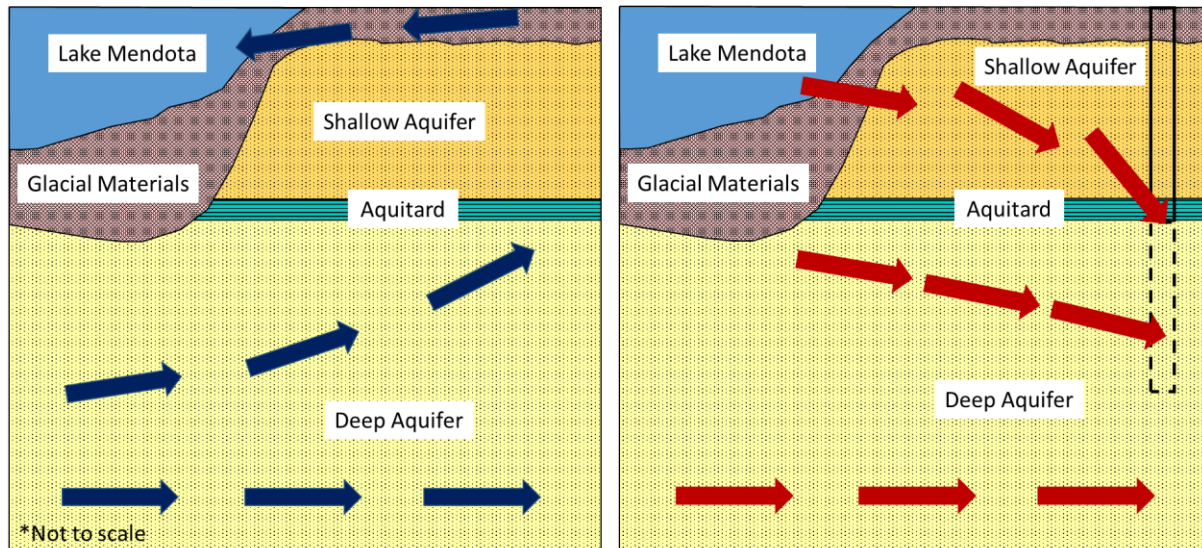


Figure 3. Compiled illustration of pre-development (blue arrows) and current groundwater flow conditions (red arrows) near the Madison Isthmus based on simulation results

Impacts to Lake Mendota are a primary component of the trend of declining groundwater inputs to Dane County lakes. Mass balance simulations that targeted Lake Mendota estimated that Lake Mendota received 5.9 million gallons of groundwater per day and made no contribution to the groundwater system under pre-development conditions. This shifted under current conditions, with approximately 0.5 million gallons of lake water intruding into the groundwater system. Additionally, groundwater contributions to Lake Mendota declined to approximately 1.2 million gallons per day, with a net discharge of groundwater to Lake Mendota of roughly 0.7 million gallons per day.

Mass balance results also demonstrated that volumetric flow across the Eau Claire aquitard is impacted by pumping practices. Increased downward flow, across the aquitard, was visible throughout Dane County in simulations under current conditions and was particularly noticeable along the Madison Isthmus. Under pre-development conditions, approximately 150 million gallons of groundwater per day flowed downward through the Eau Claire aquitard into the confined system. Under current conditions, approximately 174 million gallons of groundwater per day reach the confined system.

Locally-focused particle tracking at Madison Unit Wells 15, 23, 6, and 13 showed similar impacts on groundwater flowpaths from pumping. At Unit Well 15, located northeast of the Isthmus, groundwater flow under pre-development conditions was relatively straight and slow, traveling less than half a mile in a hundred years. Flow was nearly horizontal with a slight upward gradient in the shallow and middle portions of the Mount Simon under pre-development conditions. Under current conditions, flow is still horizontal at the base of the Mount Simon, but is downward throughout the middle and upper portions of the confined system. This results in groundwater migration from shallow system that did not occur before pumping. Flowrates are

also significantly higher in all layers in the area around Unit Well 15 under current conditions and flowpaths are curved. Simulations at Unit Wells 23, 6, and 25 show similar patterns of accelerated flow rates and disturbed, curved flowpaths under current pumping conditions, confirming that migration of oxic groundwater from the unconfined aquifer across the Eau Claire aquitard is enhanced under current pumping.

PROCEDURES AND METHODS – GEOCHEMICAL MODELING

Mixing Simulations

Madison Unit Wells 15 and 23 were chosen as target wells for the first round of geochemical simulations. Unit Well 15 is considered a relatively low $Cr_{(aq)}$ multi-aquifer well ($Cr_{(aq)} < 1 \mu\text{g/L}$), and Unit Well 23 is considered to have moderate $Cr_{(aq)}$ for a multi-aquifer well ($1 \mu\text{g/L} < Cr_{(aq)} < 2 \mu\text{g/L}$). To assess the likelihood of chromium mobilization from the deep aquifer, PHREEQC was utilized to create a straightforward equilibrium model to determine if it is possible to achieve the chromium concentrations observed in Unit Wells 15 and 23 simply by mixing water from the unconfined and confined units without mobilizing any additional chromium from the sandstone in the confined aquifer. To do this, simple batch-reactions were run in PHREEQC with six mixing solutions based on values observed at a Madison monitoring well, referred to as the Sentry Well (Fig. 1), capable of depth-discrete monitoring. Chloride and sodium were used to estimate shallow system contributions and functioned with chromium, iron, and manganese as primary calibration parameters for the simulations.

Mobilization and Sorption Simulations

For the second round of simulations, Madison Unit Wells 6 and 25 were used as the target wells. Unit Well 6 is considered a relatively high $Cr_{(aq)}$ multi-aquifer well ($2 \mu\text{g/L} < Cr_{(aq)}$). The $Cr_{(aq)}$ concentration of $2.2 \mu\text{g/L}$ measured at Unit Well 6 was tied for the highest concentration observed in any multi-aquifer well during the 2013 sampling (personal communication from M.B. Gotkowitz, 2015a). Unit Well 25 is a relatively low $Cr_{(aq)}$ multi-aquifer well ($Cr_{(aq)} < 1 \mu\text{g/L}$). It has very low chloride and sodium concentrations, indicating it represents a multi-aquifer well with a lesser input from the unconfined aquifer. To more accurately mimic the complexities of the actual groundwater system, chromite, goethite, and manganese dioxide were added as equilibrium phases for a model that included sorption and dissolution processes (Fig. 4). The simulations mimic the downward migration of shallow groundwater in the borehole into the confined system that occurs when multi-aquifer wells are not pumping. This is represented by the mixing of waters from ports 1-5. That mixed composite

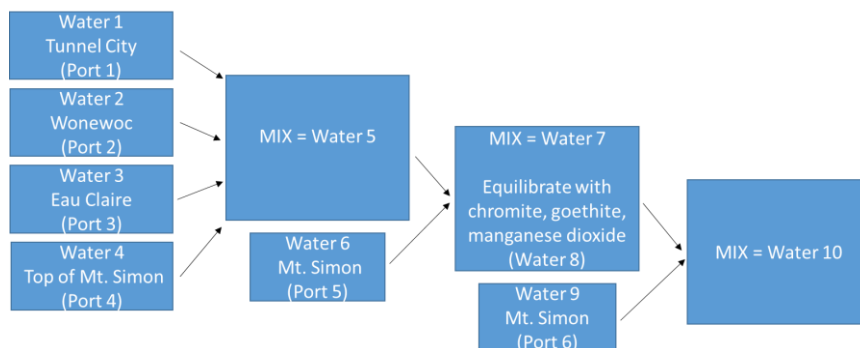


Figure 4. Conceptual model for PHREEQC chromium mobilization and sorption simulations

is then equilibrated with the chromite, goethite, and manganese dioxide, simulating the potential to mobilize trace metals by dissolution or desorption from the confined aquifer when shallow groundwater adds oxygen to the previously anoxic environment. Finally, water from port 6 is added to the mix to simulate groundwater from the deep Mount Simon that remains under anoxic conditions until it is withdrawn along with the overlying oxygenated groundwater when the well resumes pumping. Rock analysis data from Madison Unit Well 29, the nearest municipal well to the Sentry Well, had been collected in a previous study (Montgomery Associates and RMT, Inc., 2007). These data were used to determine goethite and manganese dioxide input concentrations for the simulations. The Madison Unit Well 29 study did not include chromium values, so chromite input for initial simulations was based on a separate 2012 WGNHS analyses. The input concentration was gradually reduced until simulated values more closely matched concentrations observed in multi-aquifer wells. To simulate potential chromate adsorption, goethite was defined as a surface species and given surface properties.

Manganese Simulations

Manganese concentrations in groundwater from port 5 of the monitoring well (Fig. 1) have consistently been significantly higher than values from samples at any other port. Iron concentrations were more variable than manganese over time. Port 5 is near the boundary of anoxic and oxic conditions in the confined aquifer. To examine the impact of DO on manganese mobilization in the confined aquifer, simulations were run using groundwater values from only port 5 (water 5 in figure 4) with aqueous manganese initially removed. The solution was equilibrated with chromite, goethite, and manganese dioxide, using the previous experimentally defined and calculated values for those solid phases, under concentrations of DO ranging from 0 to 9 mg/L. To focus exclusively on the impact of DO on manganese mobilization, nitrate was also removed from the system. Final aqueous manganese values were then plotted against DO.

RESULTS AND DISCUSSION – GEOCHEMICAL MODELING

Mixing Simulations

Madison Utility Well 15, considered a relatively low chromium multi-aquifer well at 0.9 µg/L, was the first well modeled. Through a process of trial and error, a composite mixture of 25% port 1, 20% port 2, 15% port 3, 15% port 4, 15% port 5, and 10% port 6 (25/20/15/15/15/10) was found to generate results similar to those observed from Madison Utility Well 15. Simulated results approximated the primary match parameters except manganese, which was off by roughly an order of magnitude. Based on these results, it seems plausible that relatively low (~1 µg/L) chromium concentrations observed in multi-aquifer wells could be produced without mobilizing any additional chromium from the confined aquifer.

The second mixing simulation modeled an intermediate $Cr_{(aq)}$ value of 1.2 µg/L, as observed in Madison Unit Well 23. After a variety of simulations, a $Cr_{(aq)}$ value of 1.21 µg/L was obtained using a composite mix of 55/20/10/10/5/0. While chromium matches well, using port 1 as the majority contributor results in simulated chloride and sodium values that are too high. Additionally, manganese and iron, which are higher in the confined aquifer, are underestimated by this model. These are all indications that it is necessary to include additional contributions from the confined aquifer in the model to more closely simulate conditions at Well 23. However, incorporating more groundwater from the deep aquifer reduces simulated $Cr_{(aq)}$. Thus, a reasonable composite for Well 23 cannot be created using the mixing model alone.

Mobilization and Sorption Simulations

The first mobilization and sorption model simulated conditions in Madison Unit Well 6, which had the highest $\text{Cr}_{(\text{aq})}$ concentration measured during the 2013 inorganic sampling at 2.2 $\mu\text{g/L}$. Well 6 also has relatively high concentrations of chloride and sodium at 49 mg/L and 16 mg/L, respectively. These values indicate significant contribution from the shallow system (port 1). As Well 6 is cased to near the bottom of the Wonewoc but not through the Eau Claire, the presence of shallow groundwater deeper in the system may indicate the presence of vertical fractures, which have been documented in the Wonewoc and Tunnel City units in Dane County (Gellasch et al., 2013). It is also possible that there is a leak along the casing allowing accelerated downward migration of shallow groundwater. Using a 24% contribution from port 1, the chloride value was closely matched. Contributions for ports 2 and 3 were then apportioned approximately based on transmissivity values for the upper aquifer at Well 6 in the 2016 Dane County Regional Groundwater Flow Model (Parsen et al., 2016). Contributions from the Mount Simon, ports 4-6, were then adjusted until the primary match parameters were close to those measured at Well 6. The final composite mix was 24/19/18/12/25/2. Under such conditions, the model simulated substantial mobilization of chromium from the deep aquifer, allowing the observed concentration of 2.2 $\mu\text{g/L}$ to be matched by the simulation.

An important constraint on $\text{Cr}_{(\text{aq})}$ values was adsorption to goethite, which removed more than 90% of mobilized chromium. In fact, when goethite was removed as a surface species, all added chromite was released into the groundwater system in the model simulations. This illustrates the critical role that naturally-occurring iron in the Mount Simon plays in preventing even higher $\text{Cr}_{(\text{aq})}$ in the municipal water supply. Additionally, simulations showed that either oxygen or nitrate at the concentrations measured in the shallow aquifer were individually capable of facilitating the mobilization of chromium from the confined aquifer. Simulations were initially run with a chromite input of 6.1×10^{-4} mol/L based on prior analysis, as previously mentioned. This input concentration was found to be much too high for reasonable results, so chromite input was gradually reduced. A final value of 2.4×10^{-7} mol/L, 0.04% of the calculated input, was eventually found to produce simulations that approximated observed concentrations.

The second mobilization and sorption simulation examined Madison Unit Well 25. In contrast to Well 6, Well 25 has very low chloride and sodium levels, 3.2 mg/L and 2.8 mg/L, respectively. These values indicate that there is minimal contribution of groundwater from above the Wonewoc. This is reflected in the calibrated composite of 0/0/25/5/10/60, which attributes the majority of groundwater contribution to the Mount Simon. The results closely matched all primary parameters, except for manganese, which is higher in the simulation than observed. This may be caused by the fact that port 6 of the Sentry Well is not very deep in the Mount Simon and quite close to port 5, which has high manganese concentrations. It is possible that a more accurate representation of the deeper Mount Simon would have lower manganese values due to the decrease in DO with depth.

Manganese Simulations

Simulations showed $\text{Mn}_{(\text{aq})}$ to be very responsive to changes in DO, particularly at low DO concentrations (Fig. 5). $\text{Mn}_{(\text{aq})}$ was slightly mobile under conditions measured for all tested DO values, with $\text{Mn}_{(\text{aq})}$ increasing slightly with decreasing DO. However, a significant increase in $\text{Mn}_{(\text{aq})}$ mobilization occurred at a DO concentration of 0.014 mg/L. While simulated $\text{Mn}_{(\text{aq})}$ was only 0.000213 $\mu\text{g/L}$ for a DO of 0.015 mg/L, it rose dramatically to 1.87 $\mu\text{g/L}$ when DO was

0.014 mg/L. $Mn_{(aq)}$ continued to steadily increase as DO was further reduced, with simulated $Mn_{(aq)}$ concentrations peaking at approximately 50 $\mu\text{g/L}$ for DO concentrations between 0.0001 and 0 mg/L. These results support the trend observed from sampling of port 5 of the monitoring well (Fig. 1) that indicates manganese is highly mobilizable near the boundary between oxic and anoxic conditions.

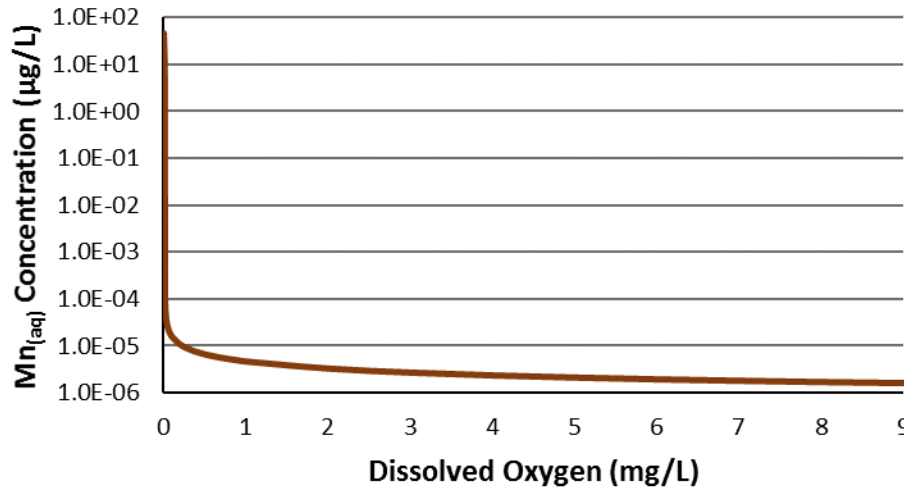


Figure 5. Simulated mobilization of $Mn_{(aq)}$ from the Mount Simon under varying DO

CONCLUSIONS AND RECOMMENDATIONS

The results of the physical flow and geochemical modeling all indicate that the long-term, high capacity pumping occurring in Dane County is impacting the surface and groundwater systems. Groundwater flow rates are accelerated under current conditions and have been redirected toward the pumping-induced cones of depression along the Isthmus. Downward migration of oxic groundwater across the Eau Claire aquitard has increased throughout Dane County and is anthropogenically enhanced at multi-aquifer wells, impacting mobilization of trace metals. Groundwater contributions to surface waters are declining, and gradient reversals have resulted in portions of Lake Mendota and Lake Monona recharging the groundwater system rather than receiving groundwater discharge.

Public water managers will need to have a strategy in place to address water quality impacts that are likely to be exacerbated by continued pumping. Because iron mobilization is restricted to purely anoxic conditions, introducing oxygen to the confined system should theoretically result in a slight decline in $Fe_{(aq)}$ concentrations over time. Manganese, however, is less predictable. Because $Mn_{(aq)}$ values are highest near the boundary between oxic and anoxic conditions, water managers will need to know when that boundary is approaching a high-Mn(s) portion of the Mount Simon, such as the interval from 540-560' below ground surface in Unit Well 6, which has over 800 mg/kg of manganese. These intervals could be avoided by adjusting pumping rates, or the resultant mobilized manganese could simply be filtered, as is the current practice.

For chromium mobilization, multi-aquifer wells and increased drawdown create the greatest concerns, as they accelerate downward flow across the Eau Claire aquitard, oxygenating the confined system. A recent study of multi-aquifer wells in Albuquerque, New Mexico, and Modesto, California, found that water quality diminished during periods of low pumping rates,

such as winter, when water supply was almost exclusively being drawn from a lower quality aquifer (Yager and Heywood, 2014). The authors concluded that balancing seasonal pumping rates could improve the situation. Rather than a temporal balance, water managers in Dane County could try to spatially balance withdrawals more evenly across the county to reduce the worst cones of depression. This could potentially have a marginal benefit. However, based on current withdrawal rates, it is unlikely that drawdowns will reverse in the near future. Aqueous chromium concentrations in municipal water supplies could be significantly reduced by using only confined aquifer wells, limiting $Cr_{(aq)}$ inputs from the shallow aquifer and mobilization from the Mount Simon at multi-aquifer wells, but this would likely make iron and manganese issues more prevalent and lead to even greater drawdown in the Mount Simon. Ultimately, there is no single solution that addresses all the concerns, so operating cost or water quality concessions will likely need to be made in the future.

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APPENDIX A

Publications

No published document has yet resulted from this study. However, it will be the basis of Joshua Olson's master's thesis, and the investigators intend to submit it for consideration for publication in the future.

Presentations

Olson, J. (April 14, 2016) Long-term alterations in groundwater chemistry induced by municipal well pumping, UW – Madison Department of Geoscience Graduate Student Symposium, Madison, WI, poster presentation

Olson, J. (September, 25, 2016) Long-term alterations in groundwater chemistry induced by municipal well pumping, GSA Annual Meeting – Denver, CO, oral presentation

Olson, J. (April 27, 2017) Long-term alterations in groundwater chemistry induced by municipal well pumping, UW – Madison Department of Geoscience Graduate Student Symposium, Madison, WI, poster presentation

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Impact

Trace metals, specifically chromium, manganese, and iron, in Dane County municipal water supplies have been an ongoing source of health concerns and treatment costs. However, the mechanisms responsible for releasing these contaminants are not sufficiently understood. This project examined the natural occurrence of trace metals in the confined and unconfined sandstone aquifers beneath Dane County. Using groundwater flow simulations, the impacts of high-capacity pumping in Dane County were examined, particularly the widespread mixing of groundwater from the confined and unconfined aquifers, as well as from surface and groundwater sources. These interactions result in altered geochemical conditions, some of which were found to increase the potential release of trace metals from the sandstone aquifers. As there are multiple metals of concern, each of which require a different management strategy to address, this project does not provide a single solution to the current issues being faced. However, it does define the problem and the variety of causes in a way that will help municipal water managers make informed decisions regarding the ramifications of chosen pumping regimes, and hopefully, lead to strategies that maximize protection of citizens and minimize treatment costs.