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Sources of naturally occurring chromium in bedrock aquifers underlying Madison, Wisconsin

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- report and figures (PDF)
- 2 appendices (tab-delimited text files, Excel spreadsheets)

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Abstract

This study evaluated the potential for bedrock aquifers in Madison, Wisconsin to provide a naturally occurring source of Cr (VI) to groundwater. Three hundred thirty five solid-phase samples from drill cuttings of the Mount Simon, Eau Claire, Wonewoc, and Tunnel City Formations were analyzed for total digestible Cr and other trace elements from four City of Madison water supply wells. Groundwater from thirteen monitoring wells was sampled for total Cr and Cr(VI). Results show Cr present in all solid-phase samples—with concentrations typically around 5 ppm. However, the Mount Simon-Precambrian contact interval and the Eau Claire Formation are consistently enriched relative to other intervals. Cr concentrations typically follow very similar trends to those of iron. Well 19 differs from all other wells studied in having Cr and Fe concentrations several times higher, especially in the Mount Simon. Although these results indicate that Cr is present in all bedrock formations, aqueous Cr (VI) in highest in groundwater from the upper bedrock aquifer (i.e., above Mount Simon). Wells completed in the Tunnel City and Wonewoc Formations contain 1 to 2 µg/L Cr(V). Groundwater sampled from the Mt Simon aquifer ranges from less than detection (< 0.02 µg/L) to 0.24 µg/L. These result support the conclusion that naturally occurring chromium is present in the aquifer rocks and is a potential source of Cr(VI) to Madison's groundwater system. However it appears that only geochemical conditions in the upper bedrock aquifer promote the mobility of aqueous Cr (VI).

Introduction

Chromium is a naturally occurring element that exists in water in trivalent (III) and hexavalent (VI) forms. Although Cr (III) is an essential trace nutrient at low concentrations, Cr (VI) is a suspected carcinogen through inhalation and ingestion. The National Primary Drinking Water Regulations, which are federal standards that apply to all public water systems, currently limit total chromium (the sum of Cr III and Cr VI) to a maximum contaminant level (MCL) of 100 µg/L. However, an EPA sponsored toxicological review of Cr (VI) is expected to be released in 2013 and may drive the development of a standard for Cr (VI) in drinking water (http://water.epa.gov/drink/info/chromium/index.cfm). The State of California recently established a Public Health Goal (PHG) of 0.02 µg/L for Cr (VI) in drinking water (Pesticide and Environmental Toxicology Office, 2011). It is important to note that California's PHGs are not regulatory requirements; they are based on public health considerations and do not consider economic or technical factors relevant to public water supply systems.

The Madison Water Utility initiated sampling of the City's municipal wells for Cr (VI) in water in 2011. Concentrations of Cr (VI) range from less than the detection limit, 0.02 µg/L, to 2.04 µg/L. In light of these findings, the Water Utility requested assistance from the Wisconsin Geological and Natural History Survey (WGNHS) to determine if there is a naturally occurring source of chromium in the bedrock formations within the groundwater system. The WGNHS also provided assistance in sampling Madison-area groundwater monitoring wells for Cr (VI). The primary objective of this investigation is to determine if the observed concentrations of Cr (VI) in groundwater could result from naturally occurring chromium from primary constituents of the bedrock formations.

Hydrogeologic setting and groundwater supply

The hydrostratigraphy in Dane County, Wisconsin includes a discontinuous sand and gravel aquifer overlying upper and lower bedrock aquifers (figure 1). Within the City of Madison, the upper bedrock aquifer generally consists of the Tunnel City Group and Wonewoc Formation (figure 2). The sandstone of the Mount Simon Formation constitutes the deep aquifer. The Eau Claire aquitard separates the shallow and deep aquifers. It is absent to the northeast and in the lake basins (Bradbury et al., 1999). Pumping from municipal wells completed in the Mount Simon aquifer has created a cone of depression in the greater Madison region that in some areas induces downward vertical flow across the Eau Claire, as illustrated in Figure 1 (Krohelski et al., 2000).

The City of Madison Water Utility operates 22 supply wells that are drilled into bedrock formations (figure 3). Fourteen of the wells are cased into the upper bedrock aquifer. These multi-aquifer wells draw water from both the upper and deep aquifers, as shown in figure 4. Eight wells are cased into the Eau Claire aquitard and presumably pump water from the deeper, confined Mount Simon Formation.

Methods

Bedrock investigation

Rock samples available from four Madison area municipal wells were analyzed for Cr content (figure 3). These wells were selected based on the concentrations of aqueous Cr (VI) in groundwater samples. Groundwater from two wells, 6 and 14, had some of the highest Cr(VI) concentrations while the other two, 19 and 24, had less than detectable concentrations of Cr(VI). Sets of rock cuttings from the drilling of these wells are archived at the WGNHS and were utilized in this study. The wells do not all start in the same formation, nor did the casings end in the same formation. However, all of the wells are completed to the base of the Mount Simon. All rock intervals penetrated by these wells were sampled, including the Cambrian Mount Simon, Eau Claire, Wonewoc, and Tunnel City. A previous study of rock cuttings from Well 29 showed elevated Cr values in the Eau Claire, Wonewoc and Tunnel City (Montgomery Associates and RMT, Inc., March 2007). Thus, a sampling protocol was developed that reflected this stratigraphic variation. Cuttings samples were taken at 5-foot intervals in these upper units and in the uppermost and lowermost Mount Simon. The remaining Mount Simon was sampled at 20-foot intervals (figure 5).

All cuttings sets were analyzed using qualitative techniques. 335 samples were submitted to the ALS Minerals, Reno Nevada laboratory. Sample preparation included grinding to a fine powder and homogenizing prior to analysis. Sample powders were then partially dissolved in an Aqua Regia solution, liberating the acid-leachable component for analysis. Sample solutions were analyzed using atomic emission spectroscopy (AES; Appendix A). This technique has a detection limit of 1 ppm for Cr.

The method described above is relatively inexpensive and allows for the development of a large data set. However, it is not fully quantitative and does not measure non-acid leachable minerals in samples. In order to provide a comparison of methods, five samples from rock cores DN1466 and DN1467, obtained from the WGNHS Nine Springs Research Site (figure 3) in 2003, were analyzed to assess the relationship between qualitative and quantitative results. Utilization of rock core was also sought as it is superior to rock cuttings; it provides a continuous undisturbed subsurface record, allowing the discrimination of primary versus secondary mineralization and original depositional features. These cores penetrate the Tunnel City through uppermost Mount Simon formations, and contain several intervals with high concentrations of intergranular cements with mineralogies rarely seen in other parts of the Wisconsin bedrock succession. Preliminary examination of these mineralized zones suggested the presence of iron- and phosphate-bearing minerals, rather than the more ubiquitous calcite/dolomite and quartz cements found elsewhere. The five mineralized horizons sampled include one sandstone sample from uppermost Mount Simon; one shale sample from the base of the Eau Claire; and three sandstone samples from the bottom, middle, and top of the Tunnel City. Most of the Wonewoc Formation was not recovered in these cores. Each sample was ground to a powder and homogenized. The samples were then split into thirds and analyzed for their elemental composition using Aqua Regia AES, lithium borate fusion ICP-MS, and pressed pellet XRF, the latter two being considered quantitative techniques.

Groundwater sampling

Monitoring wells are typically constructed with relatively short screens, on the order of five to ten feet, and provide water samples over a discrete interval of the groundwater system. The thirteen monitoring wells sampled during this study are completed at a variety of depths (Table 1) and are located across the City (figure 3). With the exception of the Nine Springs 3 and the Sentry Well, wells were purged and sampled with a submersible stainless steel pump. The Nine Springs 3 well and the Sentry Well contain FLUTe™ systems, which are multi-level sampling devices. Dedicated gas displacement pumps are used to purge and collect samples from each sample depth within the FLUTe™, which is referred to as a "port".

Samples were speciated for Cr(VI) in the field immediately following sample collection using a method that relies on selective retention of Cr (III) on a cation exchange cartridge (Gorski et al., 2012). The groundwater sample is split and an unfiltered portion is placed on ice and transported to the laboratory for acidification. This split is analyzed for total chromium. A 20 mL aliquot of the sample is field- filtered (0.45 micron) and passed through the cartridge. The effluent is presumably Cr(VI), while Cr(III) is retained on the cartridge. Samples collected in this manner were preserved on ice and transported to the Wisconsin State Laboratory of Hygiene for analysis by sector field inductively coupled plasma mass spectrophotometer (SF-ICP-MS).

Field measurements included pH, conductivity, and temperature. Samples for tritium analysis were collected from monitoring wells that had not been previously sampled for this constituent.

Information on water quality at each monitoring well was compiled from Water Utility records and from data available from previous studies at the WGNHS. These data include analyses for major ions such as chloride, manganese, iron and nitrate.

Table 1. Monitoring well construction and water quality

Monitoring Well	**Hydrogeologic Unit Sampled**	**Depth of Screened interval (ft)**	**Total Chromium μg/L**	**Cr (VI) μg/L**	**Percent of total Cr as Cr(VI)**	**Tritium, TUs**
PP556 (near Unit Well 6)	Tunnel City	63	1.72	1.49	87	5.7
Nine Springs 2[1]	Tunnel City	125	4.12	2.71	66	7.4
Merrill Springs (SW932)	Tunnel City	144	2.08	2.01	97	1.7
Sentry Well[2], Port 1	Tunnel City	92	1.27	1.14	90	6.7
Sentry Well[2], Port 2	Wonewoc	209	0.93	0.92	98	1.3
DN-1481 (Lake Edge Park)	Wonewoc	235	0.37	0.22	59	1.3
Nine Springs 3[3], Port 1	Wonewoc	275	0.35	< 0.02	--	< 0.8
Sentry Well[4], Port 3	Wonewoc/Eau Claire contact	270	0.82	0.74	91	< 0.8
Nine Springs 3[3], Port 6	Mount Simon	305	0.76	< 0.02	--	< 0.8
Sentry Well[2], Port 4	Mount Simon	302	0.27	0.24	89	8.4
Sentry Well[2], Port 5	Mount Simon	410	0.30	< 0.02	--	< 0.8
Sentry Well[2], Port 6	Mount Simon	460	0.12	0.05	37	< 0.8
DN-1482 (Lake Edge Park)	Mount Simon	268	8.04	< 0.02	--	< 0.8

[1] Nine Springs 2 = DN-1366

[2] Sentry Well = DN-6008

[3] Nine Springs 3 = DN-1367

Results

Bedrock geochemistry

The Cr content is variable between the studied wells (figure 5). In general Cr concentration is near 5 ppm throughout most of the Mount Simon Formation and Tunnel City Group. Some intervals are consistently enriched relative to this trend—the Mount Simon-Precambrian boundary interval (>30 ppm) and Eau Claire Formation (>20 ppm) show elevated concentrations in all wells. Other intervals show inconsistent concentrations. The Wonewoc Formation shows concentrations ranging from less than 5 ppm in some wells, while in others it is as high as 30 ppm. As noted above, the Tunnel City Group typically has concentrations of about 5 ppm, but in some wells it is in part greater than 20 ppm.

Trends in Cr concentration show no consistent pattern with regard to the base or the top of the studied succession. Concentrations of Cr are highly variable throughout the stratigraphy, as noted above. The variability does not show a consistent increase toward the top or the bottom of the study interval. For example, Well 24 contains a series of concentration spikes that increase, in a stepped manner, upward from the upper Mount Simon, through the Eau Claire and Wonewoc to the top of the bedrock surface. However, the pattern is reversed at Well 19, with concentrations decreasing upward toward the buried top of bedrock surface.

The highest Cr concentrations in all formations are at Well 19 samples. Well 19 differs from the other wells studied, having high (on the order of 20 ppm) Cr concentrations in the Mount Simon Formation at approximately four times that of the other wells.

Of the 35 analyzed elements, Fe concentration is most closely correlated to Cr (figures 6 and 7). Fe concentrations are in the range of 1% through most of the samples analyzed. As with Cr, there are more highly concentrated intervals at the Mount Simon-Precambrian boundary (>5%) and to a lesser extent in the Eau Claire (up to nearly 3%). As with Cr, Fe concentrations in Well 19 are elevated relative to other wells, most notably in the Mount Simon where they are typically in the range of 3-5%. Some intervals show a slight enrichment of Cr over Fe relative to the average proportion (>0.1%; figure 7). Again, these are typically near the base of the Mount Simon and in the Eau Claire. Macroscopic analysis of the samples shows a general dominance of iron cements where Fe and Cr are elevated.

Comparison of qualitative (AES) versus quantitative (ICPMS and XRF) Cr results from samples of the Nine Springs core show similar profiles (figure 8). AES results match closely those obtained for similar positions in the stratigraphy from Well 6 cuttings samples. ICPMS and XRF results from the Nine Springs samples were almost identical. ICPMS and XRF results were always higher than the AES results. In general, the ICPMS and XRF results for Cr were typically twice the concentration given by AES.

Distribution of aqueous chromium in groundwater

Unit wells were sampled for Cr and Cr(VI) by the Madison Water Utility two or three times in 2011. Total Cr ranges from 0.02 to 2.12 μg/L in these wells and is primarily in the hexavalent state (figure 9). These results indicate consistent Cr(VI) concentrations over time (figure 10). Cr(VI) concentrations exceed the detection limit of 0.02 μg/L in 13 of the 14 multi-aquifer wells and range up to just over 2 μg/L at Unit Wells 6 and 14. None of the eight confined aquifer wells contain detectable levels of Cr(VI).

The results from monitoring wells are consistent with those from unit wells, indicating higher aqueous chromium in the upper aquifer. Monitoring wells screened across the Tunnel City Formation generally have greater total Cr and Cr (VI) than wells completed in deeper hydrostratigraphic units (Table 1; figure 11). Monitoring well DN1482 is an exception to this with a Cr concentration of 8 μg/L. Samples collected for total Cr were not filtered in the field, and this result could be attributable to particulate matter retained in the sample from DN1482.

Discussion

Cr is typically present in bedrock as a component of minerals, iron oxyhydroxides and adsorbed to grain surfaces. It is thought to be liberated into solution through redox and desorption reactions. Generally, naturally occurring Cr (VI) contamination of groundwater (10-100s μg/L) is associated with alkaline and oxidizing conditions (Rai et al., 1987).

In the samples studied here, the positive correlation of solid phase Cr and Fe suggests that most Cr is bound to iron minerals or is adsorbed to iron oxyhydroxides and is likely not bound in or on a carbonate or clay mineral. The increase in Cr together with Fe suggests presence of greater concentration of iron oxy-hydroxides throughout the Unit Well 19 section. However, the source of chromium to groundwater cannot be determined conclusively without sufficient knowledge of the redox conditions in each hydrogeologic unit. For example, because the observed aqueous Cr is very low, trace Cr related to minerals other than oxyhydroxides could contribute to the aqueous Cr measured in wells completed in these units. Those intervals that show enrichment of Cr over Fe relative to the average of ~0.1% are likely indicative of Cr adsorbed to other phases—the Eau Claire and base of Mount Simon.

Groundwater samples from water supply wells and monitoring wells show that Cr is present in the upper bedrock aquifer across the greater Madison area. Wells open to the Tunnel City Group have the greatest Cr(VI) at concentrations on the order of 1 to 3 μg/L. Cr and Cr(VI) concentrations are lower in wells completed in deeper formations. At all locations sampled during this study and those sampled previously by the Water Utility, chromium is two orders of magnitude lower than the federal and state drinking water limit of 100μg/L.

The strong positive correlation between aqueous Cr and wells open to the upper bedrock aquifer, and the geographic extent of these wells, suggest that the mineralogic residence of Cr and the upper aquifer geochemical conditions support the mobility of Cr in the groundwater environment. The geographic extent of monitoring wells with detectable Cr(VI) suggests a non-point source, such as the aquifer solids, rather than a series of anthropogenic, point sources across the study area. Although solid phase chromium is present in the Mt Simon Formation, with relatively high concentrations in Well 19, conditions in the deep aquifer do not appear to favor the release of Cr to solution. Younger groundwater (as indicated by tritium concentration) is associated with higher Cr(VI), supporting the conclusion that more recently recharged groundwater geochemically favors the release of chromium from rock to water.

Conclusions and Recommendations

Results of this study indicate that naturally occurring, solid phase chromium is present throughout bedrock formations in the Madison area. The highest concentrations of aqueous chromium in the groundwater system are in the Tunnel City Group in the upper bedrock aquifer. Groundwater from wells in the Mount Simon aquifer contain very low concentrations of total chromium and Cr(VI), although solid phase Cr is present in this formation. This suggests that the geochemical conditions and/or the mineralogic residence of the chromium in the upper aquifer promote the mobility of Cr(VI), but conditions are not similar in the deep aquifer.

The widespread spatial distribution of chromium in the bedrock formations of the groundwater system strongly support the conclusion that naturally occurring chromium is the source of Cr(VI) to groundwater. Additional research could shed light on the hydrogeochemical conditions leading to mobilization of Cr(VI) within the various hydrostratigraphic units and on the mineralogic residence of chromium. Additional groundwater sampling should include use of a flow-through cell to continuously measure redox indicators such as pH, dissolved oxygen and Eh. Bench scale experiments of core or well cuttings could use sequential extractions to target various mineral phases of chromium.

Acknowledgements

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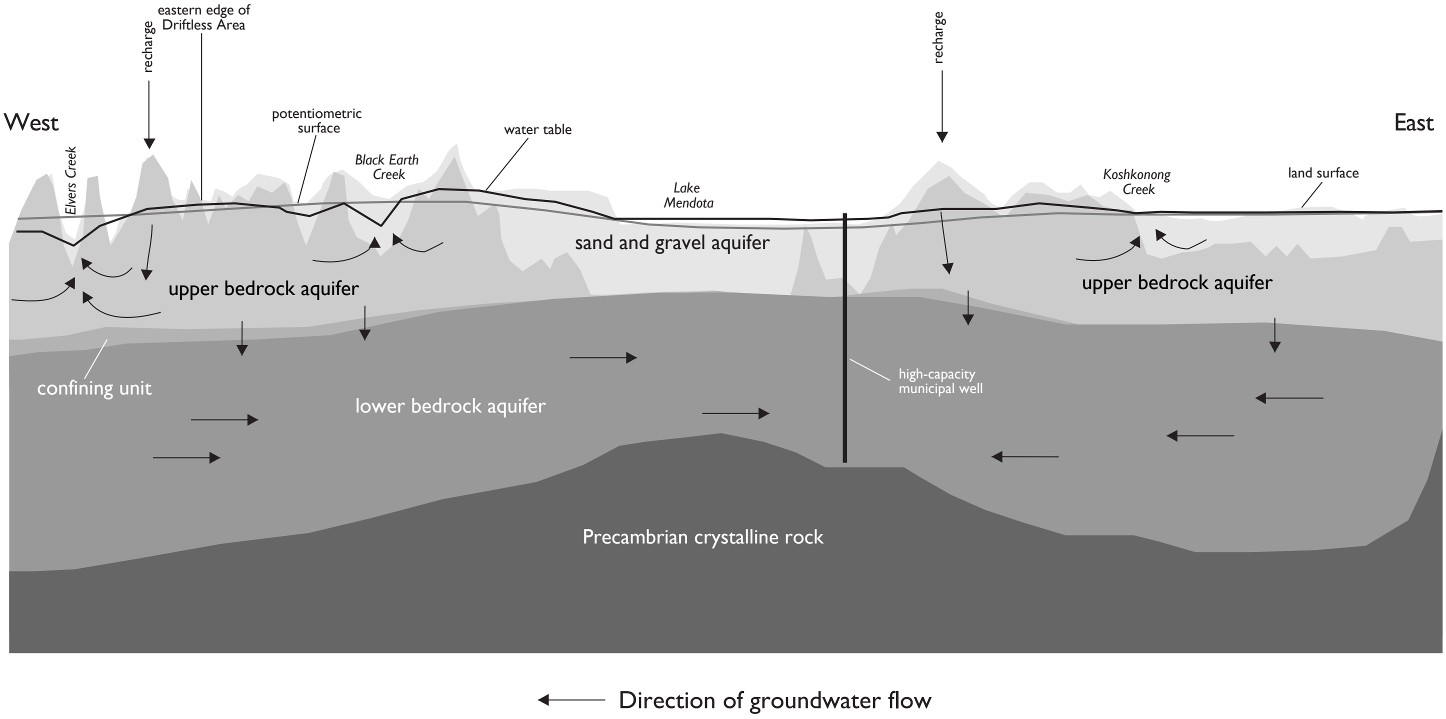

Figure 1. Hydrostratigraphy of Dane County, Wisconsin. Note the relative positions of the water table and potentiometric surface with arrows indicating the vertical direction of hydraulic gradients in the region. Adapted from Krohelski et al. (2000).

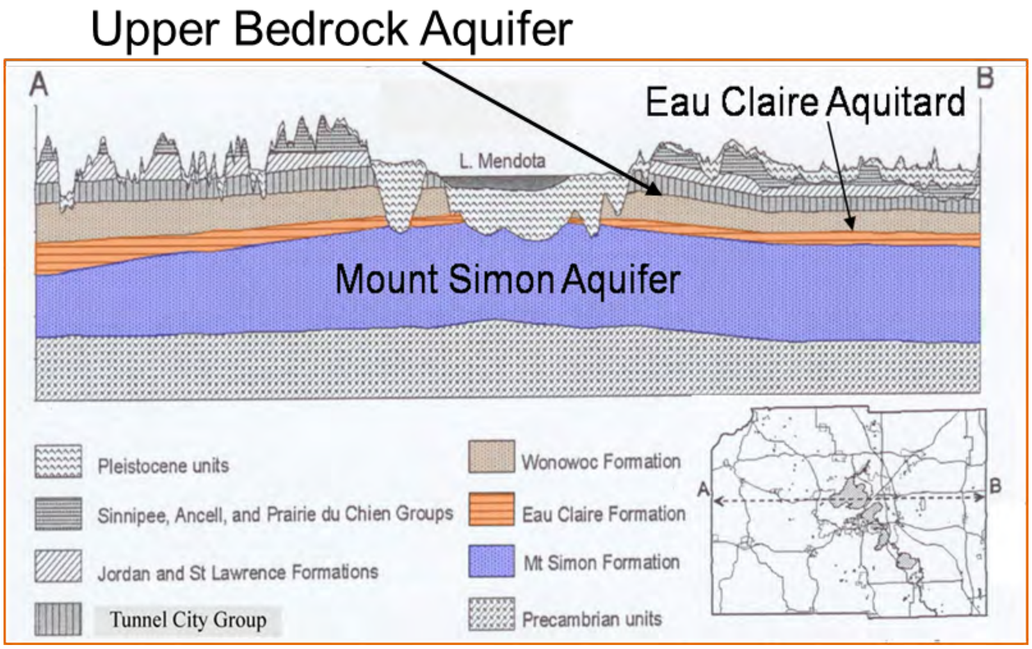

Figure 2. Bedrock stratigraphy and the groundwater system. Adapted from Massie Ferch et al. (1997).

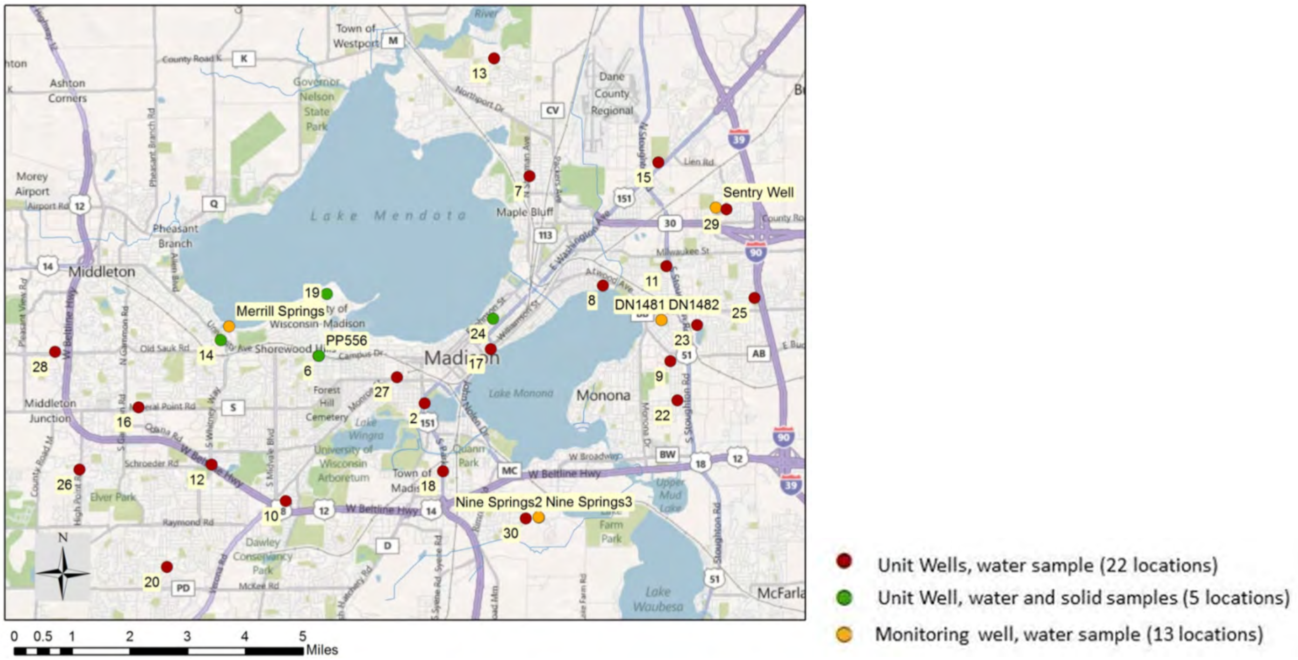

Figure 3. Groundwater and solid-phase sampling locations.

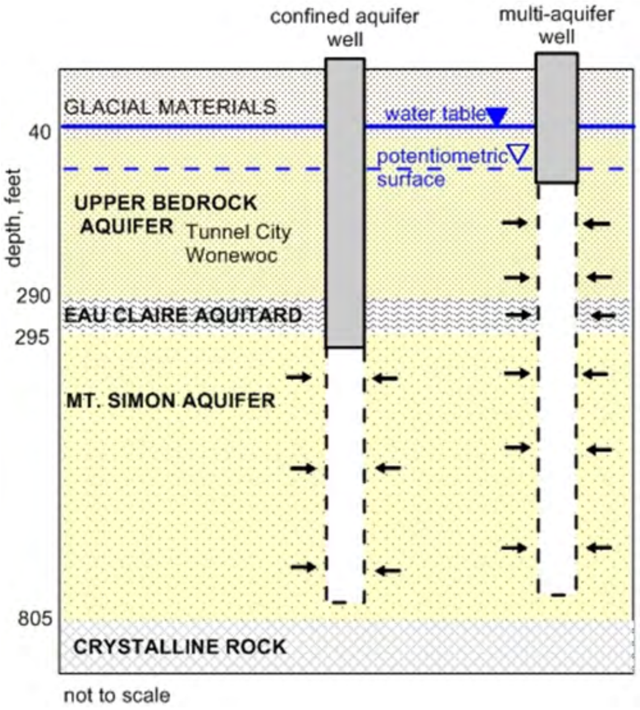

Figure 4. Construction of multi-aquifer and confined water supply wells.

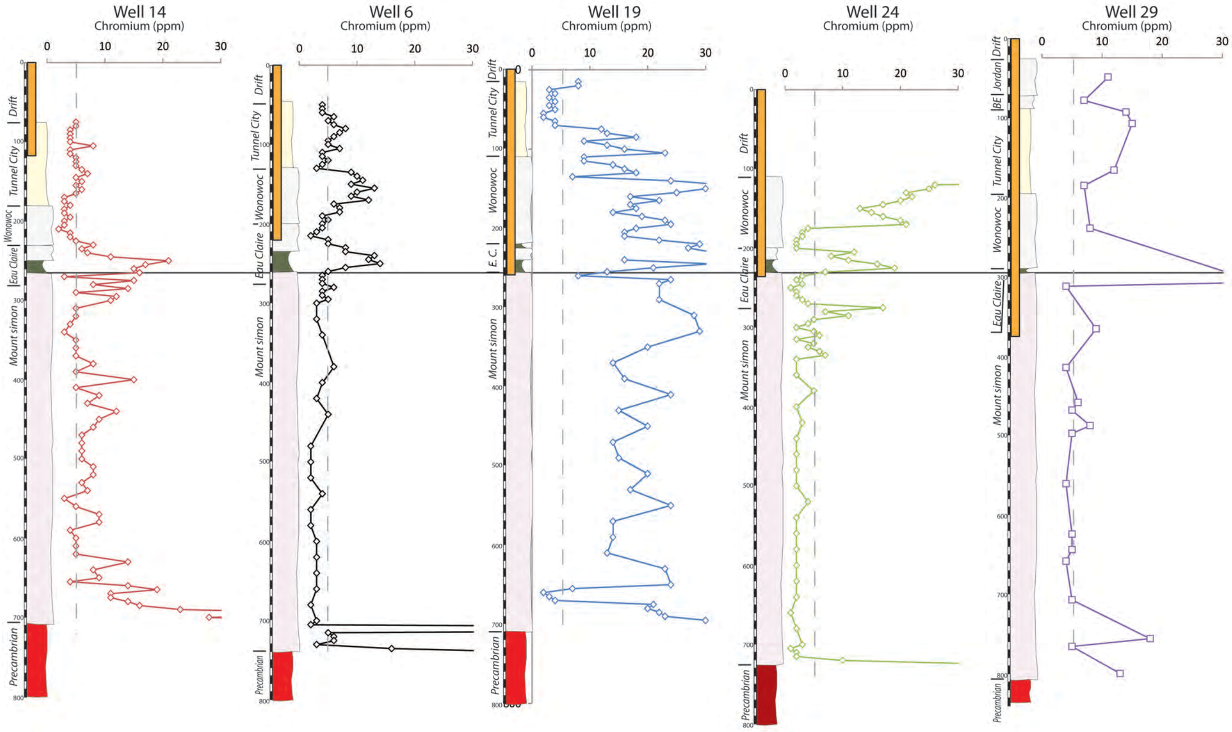

Figure 5. Stratigraphic plot of qualitative (AES) results for total chromium (ppm). Footage is marked in hundreds of feet. Orange bars at the top of each well represents casing position. Lithostratigraphic units in italics. Sections are correlated by the base of the Eau Claire shale. Cr detection limit is 1 ppm. Results shown for Well 29 are from a previous study (Montgomery Associates and RMT, Inc., March 2007).

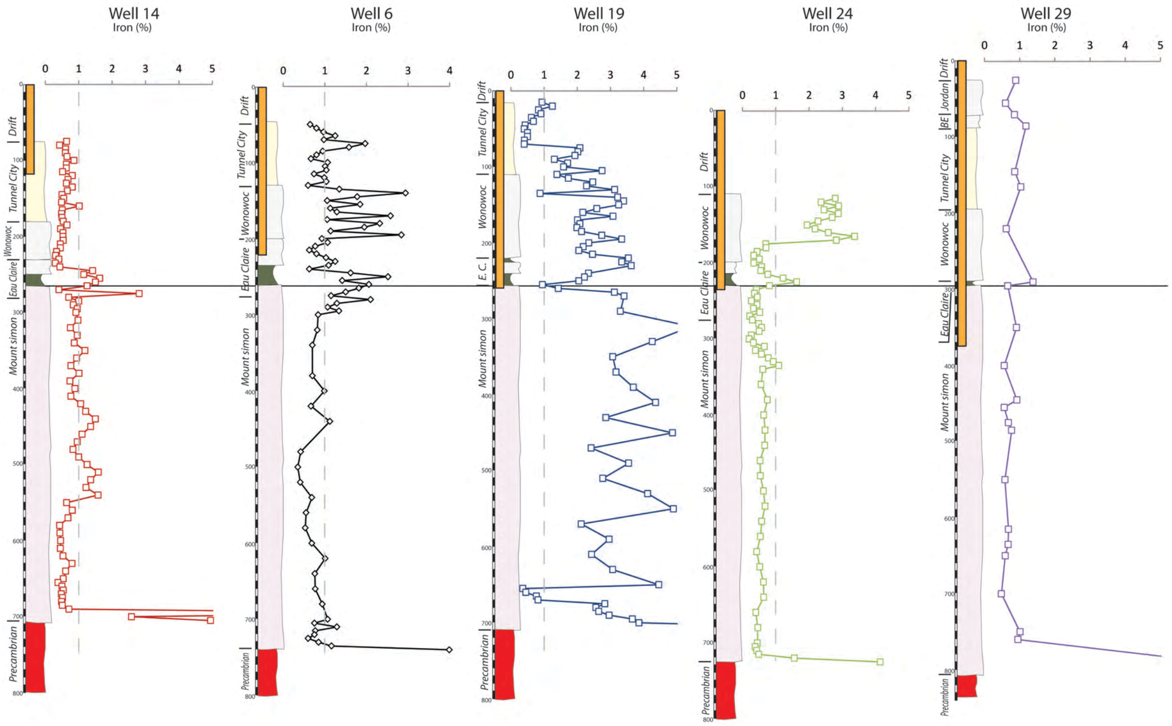

Figure 6. Stratigraphic plot of qualitative (AES) results for iron (ppm). Note similarity to Cr trends.

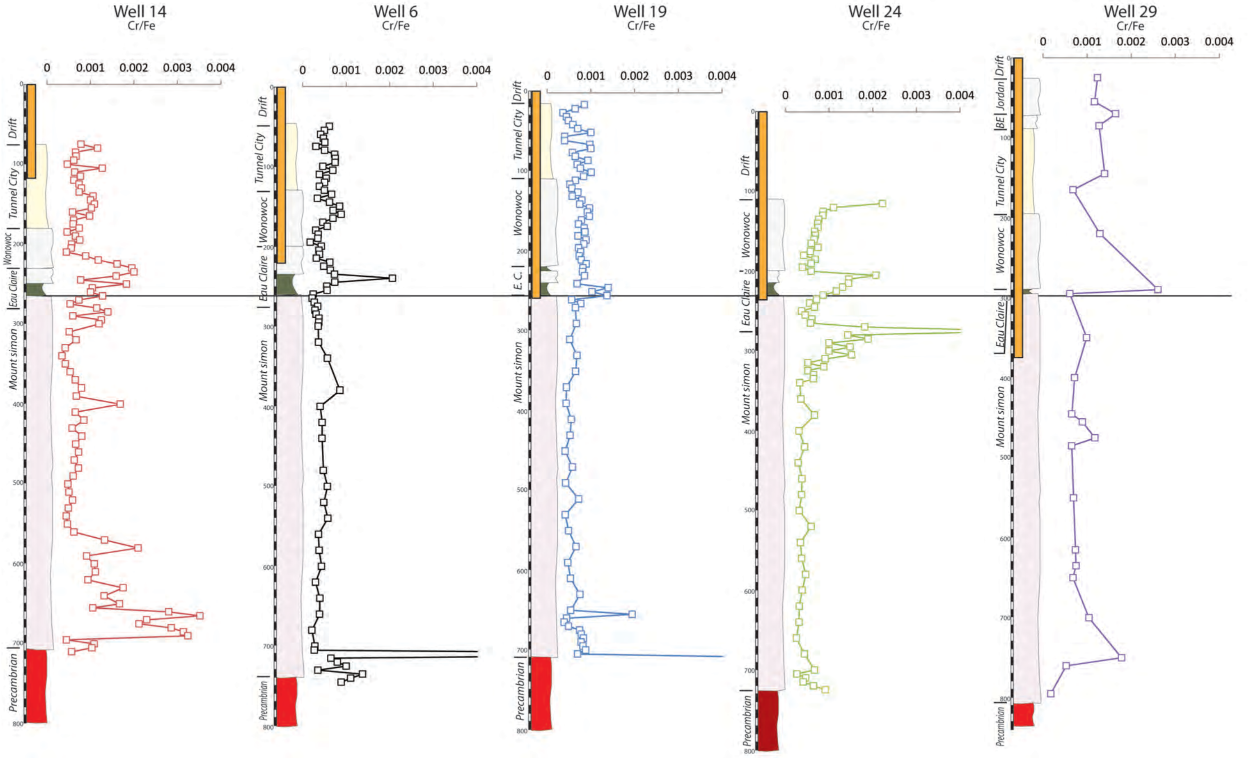

Figure 7. Stratigraphic plot of the difference in chromium vs. iron concentration (Cr/Fe). Note that this relationship shows is nearly constant except in the a few narrow stratigraphic intervals where Cr is relatively enriched.

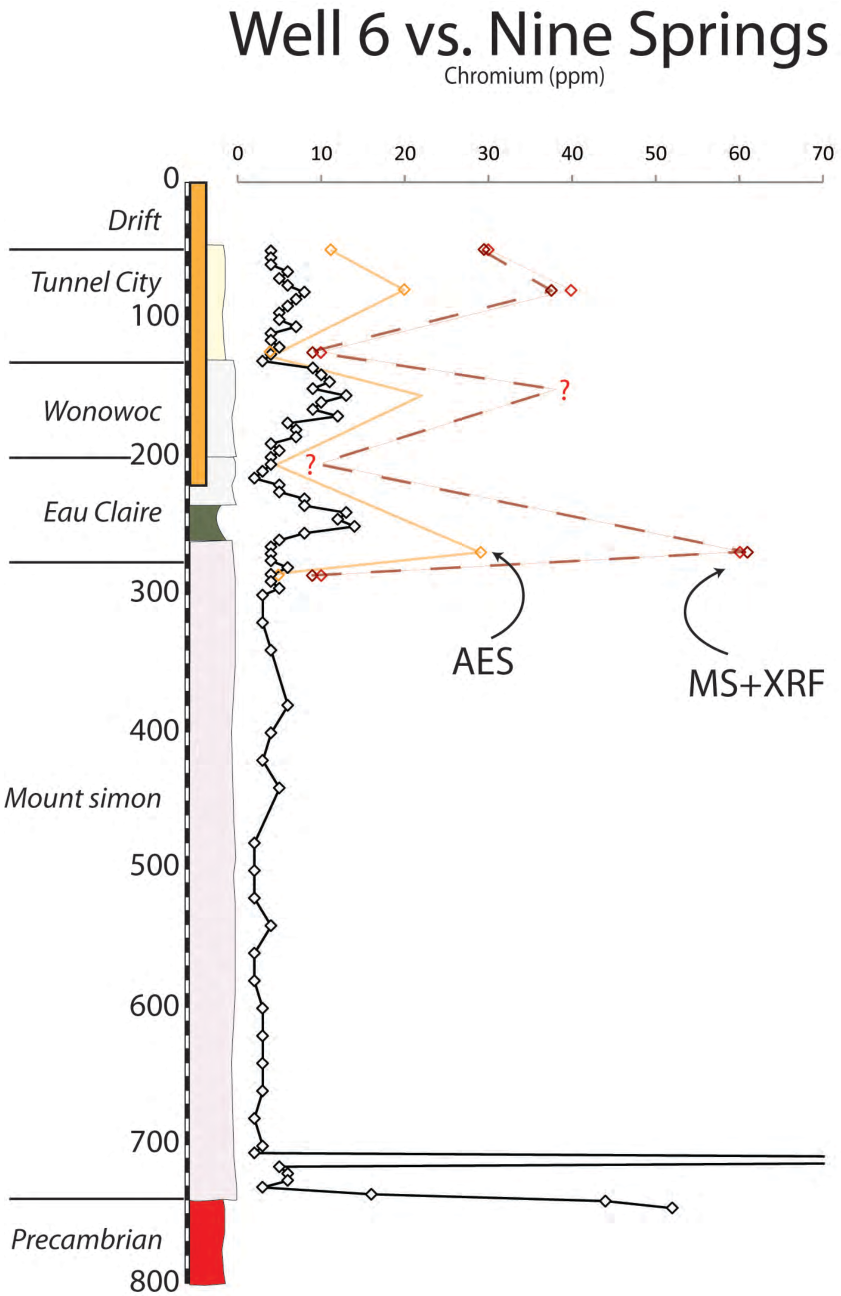

Figure 8. Stratigraphic plot of qualitative (AES) results for total chromium from Well 6 cuttings (black diamonds) versus quantitative Cr results (XRF and ICPMS; colored diamonds) from the Nine Springs core. Samples were taken from similar lithologies in the same parts of the formations to facilitate direct comparison of results between the core and well cuttings.

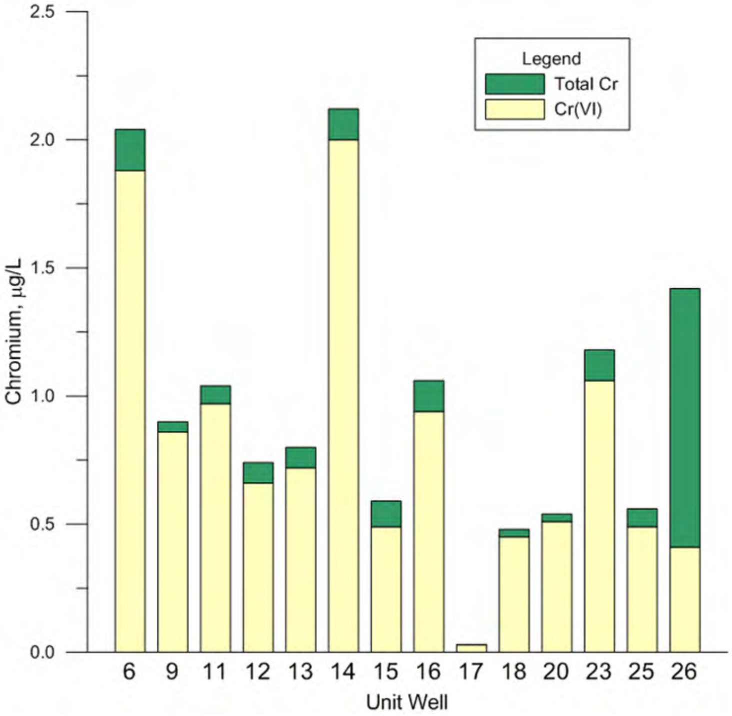

Figure 9. Total and hexavalent Cr in unit wells. Samples analyzed for total Cr were not field-filtered. Data are available at http://www.cityofmadison.com/water/waterQuality/Chromium.cfm

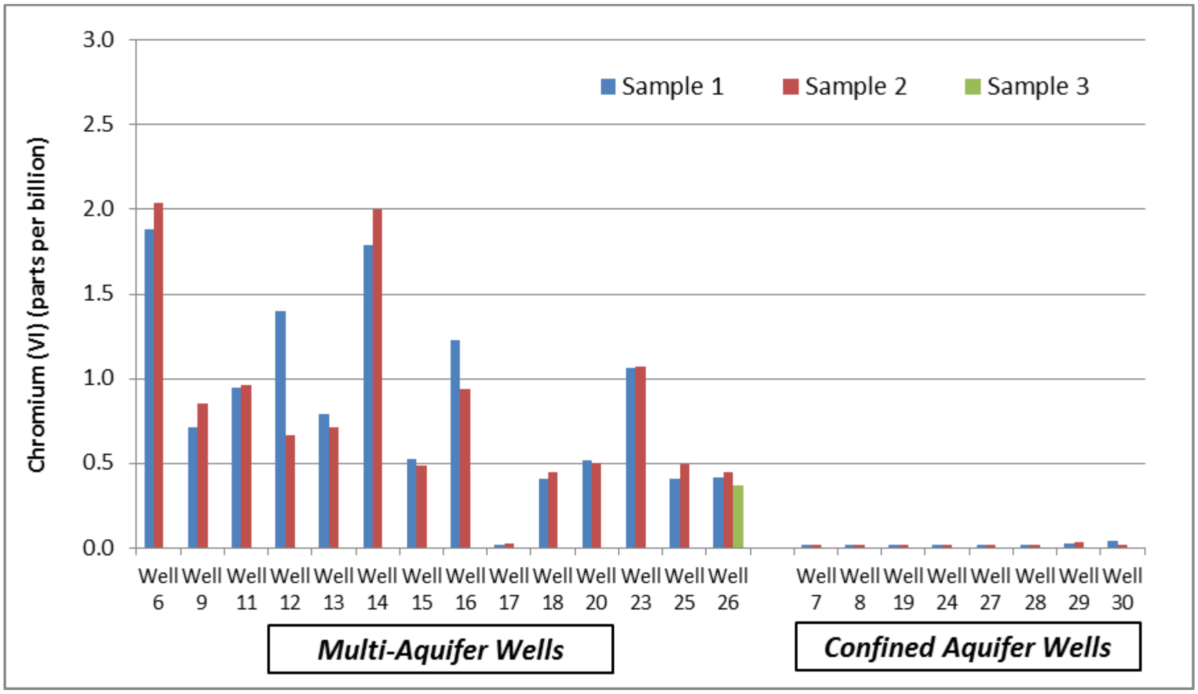

Figure 10. Cr(VI) in Unit Wells from sampling events in 2011. Data available at http://www.cityofmadison.com/water/waterQuality/Chromium.cfm

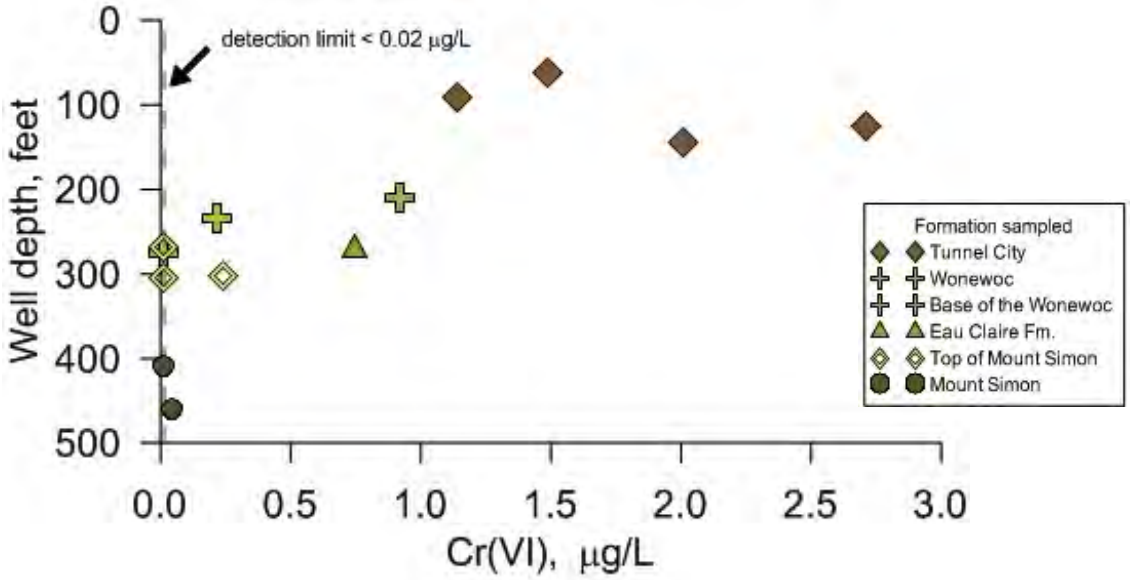

Figure 11. Depth of monitoring wells, geologic formation screened, and Cr(VI) concentrations.