
SUMMARY REPORT

UNIT WELL 29 MANGANESE ASSESSMENT

PREPARED FOR

CITY OF MADISON WATER UTILITY
MADISON, WISCONSIN

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IN COLLABORATION WITH
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SUMMARY REPORT

UNIT WELL 29 MANGANESE ASSESSMENT

1. INTRODUCTION

1.1 Project Background

The City of Madison water supply has in recent years encountered undesirable water quality, with organic and inorganic constituents in the raw water of some unit wells. Inorganic constituents, whether natural or contaminants, have included nitrate, iron and manganese. Wells most significantly affected by these constituents include unit wells (UW) UW 10 (manganese), UW 3 (VOCs and manganese) and UW 29 (manganese) (see Figure 1 for well locations). The City of Madison water utility is actively maintaining high water quality standards and pursuing remedies for water quality issues when they occur.

The water supply wells with unacceptable manganese concentrations are widely distributed across the City, with many acceptable wells in between. Further, both older wells (which allow entry of water from both the upper and lower bedrock aquifers) as well as a newer well (which has steel casing installed to a much greater depth to allow water entry only from the lower bedrock aquifer) have been affected.

Montgomery Associates and RMT, Inc. were retained by the City of Madison Water Utility to assess the potential source and cause of manganese at UW29 in a scope of services described in a proposal dated October 25, 2006. We reviewed well construction data and water quality in the Madison area which led to several observations and hypotheses regarding the occurrence of manganese in the City of Madison wells. The observations include:

- The most likely source of manganese in the aquifer is manganese oxides that are present in the rock matrix of the aquifer. These oxides are probably distributed throughout the upper and lower bedrock aquifers in the Madison area, although local concentrations could be expected to vary widely.
- Simply having an available source of manganese in the aquifer does not mean that manganese will be present in well water. Conditions must be present to dissolve the manganese for it to be present in the water delivered to the system.
- Manganese dissolution in groundwater is controlled by the pH and oxidation/reduction potential (Eh) of the groundwater. The oxidation/reduction potential, often referred to as "redox" potential, is critical to predicting whether manganese will exist as immobile, solid oxides or as mobile, dissolved manganese ions.

- Iron is more abundant in the aquifer rocks than is manganese. Iron acts in a similar way as manganese regarding dissolution, but generally does not dissolve substantially until the redox potential is even lower than that which will dissolve manganese oxides. Additionally, at very low redox potential iron combines with sulfur to create iron sulfide, known as pyrite. Pyrite is known to occur in bedrock in the Madison area.
- Reducing conditions that can lead to solution of manganese can be due to either natural causes or due to human activity. An example of a natural cause of reducing conditions that could dissolve manganese oxides is the oxidation of existing in situ iron sulfide (pyrite). Another cause could be degradation of organic loading from lake or wetland deposits.
- Reducing conditions produced by organic contamination due to human activity typically involves biodegradation of the organic loading to the groundwater as assisted by microbes. The source of the organic materials could be from landfills, leaking underground storage tanks, or sanitary sewers. Near a source of organic contamination, strongly reducing conditions exist which diminish with distance. Oxygen, nitrate, manganese oxides, iron oxides and iron hydroxides, and sulfate are reduced progressively as reducing conditions intensify near the source. These reducing conditions can also change with time, as the source is gradually degraded.
- In many areas within the Madison area, there is a downward hydraulic gradient from the upper bedrock aquifer to the lower bedrock aquifer. The aquifers are separated by a relatively thin, low permeability bedrock unit known as the Eau Claire shale throughout most of the Madison area. However, the Eau Claire shale is occasionally absent or thin in places.
- One of the wells most significantly affected by manganese, UW 10, is open to both the upper and lower bedrock aquifers. Data showing reductions in manganese concentration as the well is pumped suggest that manganese concentrations in both aquifers are not uniform. It is possible that reducing conditions produced in the upper aquifer could be creating elevated manganese concentrations.
- Another of the significantly affected wells, UW 29, is open only to the lower bedrock aquifer. However, it is relatively near to an abandoned landfill site which could be a source of biological activity producing reducing conditions.

Consideration of these observations led us to develop two working hypotheses that could guide action to control high manganese levels encountered at several of the City of Madison wells:

1. **Natural Source and Cause** – If the source of the manganese is from aquifer minerals and the cause for it to be dissolved is naturally occurring and widely distributed, then future water quality is likely to be similar to that currently experienced.
 - In this case, applying manganese treatment designed to achieve target potable water quality criteria given a reasonable range around current raw

water quality conditions could be a reliable long-term solution for control of manganese concentrations.

- Re-drilling the well at a nearby location would have uncertain results with respect to potential manganese concentrations. This uncertainty is due to the lack of data on the distribution of the mineral source of manganese and the cause of the manganese to be dissolved from the aquifer solids.

2. **Anthropogenic Cause** – If dissolution of manganese from the aquifer solids is caused by a human (anthropogenic) impact, then future water quality at the well would be much more uncertain, both with respect to manganese concentration and other potential constituents of concern, such as other constituents of concern (e.g., VOCs).

- In the case of an anthropogenic cause for reducing conditions, significant questions could complicate the design of the treatment system: will the manganese concentrations increase, decrease, or stay the same? Will other constituents of concern affect the well in the future, such as iron or sulfur, VOCs, taste and odor, etc. Thus, in this case, the treatment system design would have to accommodate the potential for significant changes in raw water quality.
- In contrast, re-drilling the well at a nearby location, outside the influence of the impacts of the human activity, would likely avoid the reducing conditions producing higher manganese concentrations. If manganese were encountered at the re-drilled well location controlled by natural conditions, well head treatment would provide more certain long term water quality.

Discussion of these observations and hypotheses with Water Utility staff produced a scope of investigation focused on UW 29. This well has unacceptable manganese concentrations and has been shut down, and a well head treatment design is undergoing pilot testing. The scope of work focused on UW 29 was developed with Water Utility staff and a proposal dated October 25, 2006, was approved by the Water Utility Board in November 2006 and authorized by the City Council in December. Work on the project took place in December 2006 through March 2007.

This summary report describes the results of the investigation of UW 29, and presents an approach for evaluating future wells for the City of Madison.

1.2 Study Objectives

Based on the background conditions at UW 29 the following objectives were developed for this project:

- Assess the probable cause of manganese dissolution and probable migration pathways to Well 29;

- Provide recommendations on whether manganese treatment or re-drilling UW 29 at a nearby location will provide the greater likelihood for providing a reliable source of water with acceptable manganese concentrations; and
- Develop a draft protocol for siting new wells and for well investigation and analysis that could help identify conditions with low potential for manganese production.

1.3 Activities Performed

The completed activities that were described in our scope of work for this project, including approved modifications include the following:

- Review of UW 29 pumping and drawdown records;
- Review of the Wellhead Protection Plan for UW 29 and other data to identify contaminant sources that have the potential to affect UW 29;
- Review of the literature on elevated manganese in groundwater from other states;
- Review of geologic logs, well construction report and downhole videos for UW 29;
- Review of well construction reports for the UW 29 area;
- Review of aquifer hydraulic parameters developed by the Wisconsin Geological and Natural History Survey, the University of Wisconsin, and other researchers;
- Collaboration with WGNHS to select and analyze rock cuttings taken during well drilling for selected and organic parameters;
- Groundwater flow modeling and particle tracking analysis focused on potential contaminant source areas relevant to UW 29;
- Review of existing water quality data for UW 29;
- Review of available water quality data for the Sycamore Landfill;
- Collection of composite (well head) samples at UW 29, and analysis for field parameters and detailed laboratory analyses. Data collected in the field included pH, dissolved oxygen, temperature, conductivity and oxidation-reduction potential (referred to as “redox”). Laboratory analyses included major ions, total organic carbon, total dissolved solids, redox-related water quality parameters (Mn, Fe, Nitrate-N, Total Kjeldahl-N, and ammonia-N), bromide and iodide, low level Volatile Organic Compounds, tritium, and stable isotopes of water, including hydrogen (δD) and oxygen ($\delta^{18}O$).

As the project was conducted, additional out-of-scope work elements were identified that had the potential to significantly increase the understanding of the occurrence of manganese at UW 29. This out-of-scope work was anticipated to be relatively low-cost and high-value with respect to project objectives, and included analysis of water quality at UW 30 and UW 12 which were compared to water quality at UW 29, and water level monitoring at the Sycamore Landfill

during pilot testing of the possible manganese treatment for UW 29 to aid in the evaluation of potential impacts of landfill-derived contaminants. This work was discussed and agreed-upon with the water utility prior to being conducted, and was performed without a formal change order. These out-of-scope activities included:

- Analysis of field parameters (pH, dissolved oxygen, temperature, conductivity and redox) at UW 30 and UW 12 during normal production pumping operations;
- Review of well construction reports and water level data for monitoring wells installed at Sycamore Landfill;
- Coordination with the City Health Department for the removal of permanent water quality sampling pumps and temporary installation of pressure transducers at two Sycamore Landfill monitoring wells; and
- Review and analysis of iron and manganese groundwater concentrations at UW 29 during the well pumping for pilot testing for manganese treatment conducted by Earth Tech in January and February 2007.

2. RESULTS OF DATA COLLECTION AND ANALYSIS

2.1 Background Literature Review

Manganese concentrations in groundwater exceeding the US EPA Secondary Maximum Contaminant Level (SMCL) have been reported from other states, particularly from those in the northeast and midwest. Reports from the states of Minnesota, Iowa, Ohio, Michigan and Connecticut were reviewed with selected results from these studies are presented below.

- Manganese and other metals in groundwater were associated with lower redox potential and low nitrate concentrations in surficial aquifers at some locations. (Reduction of nitrate is consistent with the progression of chemical changes expected under decreasing redox potential.) Studies from Minnesota indicated that once reducing conditions exist, manganese distribution is affected by dissolved solids, particularly organic matter within the aquifer (MPCA, 1998).
- In Minnesota, the median manganese concentration in the Mt. Simon Formation was reported to be 100 ug/L (MPCA, 1998). Studies from southwest Minnesota indicated that manganese concentrations were highest in samples from deep aquifers. In these aquifers, there was no correlation between manganese concentrations and oxidation-reduction potential. The distribution of manganese was associated with the parent material and residence time resulting in increased dissolution. In contrast to the deep aquifers, there was a strong correlation between manganese concentrations and oxidation-reduction potential for the shallow bedrock aquifers and the surficial Quaternary aquifer (MPCA, 1999).
- Studies in Ohio speculate that pockets of elevated manganese in the groundwater occur regionally and are related to the manganese content in bedrock and glacial till, Eh and pH values, and the presence of iron and manganese reducing bacteria (Ohio Division of Drinking and Ground Water, 1995).
- In Connecticut, recent groundwater manganese concentrations in bedrock wells have increased up to a maximum of about 25,000 ug/L and may be attributed to development activities including site excavation and construction, and rock-blasting, which result in lowering the Eh or pH conditions and increasing solubility (Robbins, 2007).
- In the northeast, the variability of manganese concentrations in groundwater by lithochemical groups was related to variability in manganese concentrations in the rock solids and the abundance of manganese which reacts with groundwater (Ayotte, et al., 1999).

Additionally, the American Water Works Association Research Foundation in collaboration with US EPA conducted a study to evaluate the occurrence of manganese in drinking water by completing a literature review, surveying 242 utilities and sampling selected distribution systems (Kohl and Medlar, 2006). The results of their study focused on treatment technologies and found that elevated manganese concentrations are widespread in ground and surface waters throughout the world. Addressing the cause of elevated concentrations of manganese in drinking water, the study reported that no strong correlations between manganese occurrence and other water quality parameters were found in source waters or in distribution systems. Additional findings were related to manganese in distribution systems and treatment technologies.

2.2 Summary of UW 29, UW 30, and UW 12 Well Construction

Data and Geologic Logs

Unit Wells 29 and 30 are constructed similarly and are open to the lower sandstone aquifer. The geology at both sites is similar with approximately 25 to 40 feet of glacial till overlying approximately 250 feet of bedrock including the Jordan Formation, Black Earth Member, Tunnel City Group, Wonewoc Formation and Eau Claire Formation. A thin (less than ten feet) layer of Eau Claire shale separates the upper bedrock aquifer from the lower bedrock aquifer consisting of approximately 500 feet of the Mt. Simon Formation. A review of the detailed geologic logs indicates that at UW 30 pyrite, pyritic cement and green shale were identified throughout the Mt. Simon Formation to a depth of approximately 725 feet below ground surface (bgs). Although not reported on the geologic log for UW 29, pyrite may be present in the Mt. Simon Formation at that location as well.

Unit Well 29 was constructed to a depth of 815 feet bgs, cased through the Eau Claire shale to a depth of 342 feet and open to lower sandstone aquifer. The open borehole has a diameter of 29 inches from 342 feet to 500 feet bgs and a diameter of 24 inches from 500 feet to 812 feet bgs. The design capacity of the well is approximately 2,200 gallons per minute.

Unit Well 30 was constructed to a depth of 800 feet bgs, cased through the Eau Claire shale to a depth of 312 feet and open to lower sandstone aquifer. The open borehole has a diameter of 29 inches from 312 feet to 458 feet bgs and a diameter of 24 inches from 458 feet to 800 feet bgs. The design capacity of the well is approximately 2,200 gallons per minute.

The older Unit Wells 10 and 12 are constructed similarly and are open to both the upper (Wonewoc/Eau Claire) and lower sandstone aquifers (Mt. Simon). The geologic logs for UW 10 and 12 indicate that they were developed by blasting several times to increase specific capacity.

Although the Eau Claire shale is present at all four wells, it is relatively thin. At UW 29 and 30, the Eau Claire shale has a thickness of 5 and 7 feet, respectively, while at UW 10 and 12 it has a

thickness of 15 and 16 feet, respectively. A comparison of well construction details for all four wells is presented in the following Table.

Table 1. Unit Wells 29, 30 12 and 10 Construction

	Depth	Casing Depth (feet bgs)	Formation Exposed in Open Interval	Thickness of Eau Claire Shale (feet)	Depth of Eau Claire Shale (feet bgs)
Well 29	812	342	Mt. Simon	5	290 - 295
Well 30	800	312	Mt. Simon	7	290 - 297
Well 12	986	260	Wonewoc, Eau Claire, Mt. Simon	16	404 - 420
Well 10	1000	270	Wonewoc, Eau Claire, Mt. Simon	15	420 - 435

2.3 Well Construction Reports Review

A review of the well construction reports from several databases was completed to identify wells that were constructed in the vicinity of UW 29. The number and general location of wells are shown in Figure 2. Most of the well records indicated that wells were shallow. The status of these wells is unknown, however many of these wells have probably been abandoned as homes were connected to the city utilities. A few records indicated that relatively deep wells were installed to approximately 300 - 400 feet below ground surface within one mile of UW 29. One of these well records is for the church (340 feet depth) located southeast of UW 29. Based on the well log for UW 29, the church well likely draws water from the deep aquifer. The other deep wells are commercial or residential wells that are drawing water from the upper aquifer but may also extend to the top of the deep aquifer.

2.4 Rock Sample Analyses from UW 29, UW 30 and UW 12

Samples of the bedrock cuttings were selected from UW 29, UW 30, UW 12 and UW 10 by reviewing the samples to look for obvious coatings on the sand grains, differences in mineralogy and locations of fracture zones as indicated in the downhole videos of UW 29. The selected samples were analyzed for a suite of metals (which includes the targets iron and manganese) and sulfur and sulfides. A total of 51 samples were analyzed. Results are shown in Table 2. The results generally show that there are significant concentrations of manganese throughout the sandstone (ranging from 31 ppm to 1440 ppm). The concentration of iron in the sandstone ranges from 9,187 ppm to 142,591 ppm. This is much greater than the manganese concentrations in the rock.

Profiles of manganese, sulfides, and the ratio of manganese dioxide to iron hydroxides are shown in Figures 3 and 4. Figure 3 shows that the highest manganese concentration in the sandstone occurs in UW 29 at a depth of 475 ft to 485 ft. However, detailed comparisons are limited by the fewer number of samples composited over a longer interval from UW 30 and UW 12. In general, the concentration of manganese in UW 30 appears to be greater than at UW 29. Although UW 30 does not have a high “spike” in manganese concentration, it may not be evident due to the longer intervals between composited samples at UW 30 than at UW 29.

The ratio of iron hydroxides to manganese dioxide may be an important control in the availability of manganese dioxide to groundwater. The ratio of these constituents are shown in Table 2 and plotted on Figure 4 assuming that all of the Mn is manganese dioxide and all of the Fe is iron hydroxide. The ratio of iron hydroxide to manganese dioxide at UW 29 typically exceeds 100:1, although in the samples composited between 455 to 475 ft and 475 ft to 485 ft depths, the ratio drops to 16 and 6 respectively. In contrast, this ratio at UW 30 is in the range of 16 to 21 from the 286 ft to 650 ft depths.

Sulfides in the sandstone probably consist primarily of the mineral pyrite (an iron sulfide). The sulfide concentrations in the sandstone range from <100 ppm to 11,500 ppm (1.15%). The higher sulfides are generally coincident with the higher manganese concentration zones.

2.5 Well Head Field Parameters at UW 29, UW 30, and UW 12

The methods used to collect field parameter data are described in Appendix A with results summarized in Table 3. Of particular note are the dissolved oxygen (DO), pH, and reduction oxidation potential as reported as Eh.

The DO at UW29 and UW30, the deep wells, are both essentially zero, indicating that there is little communication with surficial groundwater. In contrast, UW 12’s DO is 3.42 mg/L, which probably represents a combination of the deep groundwater with nearly 0 mg/L and surficial groundwater that has nearly 8 mg/L.

The pH at each location is within the same range of 7.2 to 7.3, which is typical for the hard water groundwater in the City. The Eh range is from around 115 mv at UW 29 and UW 30 to 298 mv at UW30. The best presentation method for pH and Eh is on an Eh-pH diagram for manganese (Figure 5) and iron (Figure 6). These diagrams indicate whether manganese or iron is stable in solution or in a mineral form.

The Eh-pH diagram for manganese indicates that each well plots within the Mn²⁺ zone, indicating that manganese is soluble in the groundwater from each well. This diagram illustrates that, at equilibrium, common manganese minerals (e.g., manganese dioxide, manganese carbonate, etc.) would dissolve into the groundwater at UW12, UW29, and UW 30.

The Eh-pH diagram for iron indicates that the water from well UW12 is well inside of the $\text{Fe}(\text{OH})_3$ zone, indicating that iron is stable in the solid, iron hydroxide form at UW12. Water from wells UW29 and UW 30 are also in the $\text{Fe}(\text{OH})_3$ zone, but are at the boundary with the soluble Fe^{2+} form. This indicates that with a small reduction in Eh could result in dissolution of iron.

2.6 Other Chemical Analyses of UW 29 Samples

Samples were collected from well UW 29 on January 8, 2007, during a test pumping period of the well for chemical analysis as described in Appendix A. Analyses included the following:

- I. Field parameters using a recording flow through cell including DO, Redox, pH, and Conductivity.
- II. General Water Chemistry
 1. Major ions – Ca, Mg, Na, K, Cl, Alkalinity, SO_4
 2. Total Organic Carbon (TOC)
 3. TDS
 4. Redox parameters – Mn, Fe, Nitrate-N, Total Kjeldahl-N, and ammonia-N,
- III. Bromide and Iodide
- IV. VOCs

These data are summarized in Table 4 and lab data sheets are included in Appendix A. These data were collected to characterize the general geochemical character of the water, especially in the event that there was indication of a human activity influence at the well. The data were collected through time to determine if there was a difference between water near the well borehole and at distance from the well bore.

Based on the results of these analyses and the isotope data, there does not appear to be an effect on the water quality from a human related contaminant source, such as the Sycamore Landfill, sanitary sewers, etc. In addition, there are apparently not significant differences in the iron and manganese concentrations during the pumping period that is worthy of note.

2.7 Radiological Analysis of UW 29 Samples

Two water samples from UW 29 were analyzed for tritium and stable isotopes of water, δD (deuterium, which is a stable, naturally occurring isotope of hydrogen) and $\delta^{18}\text{O}$ (which is a stable, naturally occurring isotope of oxygen). These samples were collected and analyzed from the very beginning of the pumping period and at the end of the pumping period to determine the character of the water at the beginning and end of the test. Both samples yielded virtually the same results.

The tritium analysis showed that there was less than 1 tritium unit in the water samples, indicating that at least 90% of the water was recharged to the aquifer prior to about 1960. This analysis

interpretation is based on the known presence of a significant concentration of tritium in rain water following the atmospheric testing of nuclear weapons, which began in the 1940s and extended through the early 1960s. Rain water around the world, after the beginning of atmospheric nuclear testing, contains significant concentrations of tritium, and would be expected to currently contain on average 10 tritium units. Therefore, the groundwater at UW29, with less than 1 tritium unit, indicates that the water is generally old and probably recharged more than 30 years ago.

The stable isotopes δD and $\delta^{18}O$ were collected and analyzed to help evaluate the history of the water in the near surface. Rainfall naturally contains δD and $\delta^{18}O$ and the concentrations generally depend on the temperature at which the rain condenses from atmospheric moisture (i.e., the δD and $\delta^{18}O$ fractionates from the atmospheric moisture). Therefore, rainfall δD and $\delta^{18}O$ concentrations fall along what is referred to as a “meteoric water line”. After rainfall occurs, the δD and $\delta^{18}O$ can fractionate due to surface processes. In particular, if the water moves through a surface water body and is subject to evaporation, the lighter hydrogen and oxygen are preferentially removed. In this case the δD and $\delta^{18}O$ falls below the meteoric water line. If the water moves through a landfill, the methanogenic conditions preferentially uses the heavier isotopes and shifts the δD and $\delta^{18}O$ concentrations to above the meteoric water line.

Figure 7 is the local meteoric water line for Madison (Swanson, et. al., 2006). This line together with plots of δD and $\delta^{18}O$ results from UW 29 indicates that the water analyzed entered the groundwater without significant fractionization of these isotopes.

The isotope data indicate that rainfall recharge to the aquifer occurred prior to about 1960 (i.e., prior to atmospheric nuclear weapons testing) and the rainfall did not move through a process that would affect the δD and $\delta^{18}O$ concentrations, such as moving through a surface water body or a methanogenic process such as a landfill or wetland.

2.8 Comparison of Iron and Manganese at Selected Wells

Iron and manganese concentrations available at wells UW29, UW30, UW 12, and UW 10 were compared to assist in determining the potential cause(s) of manganese dissolution. Only a small set of samples or over a short period of time were available for some wells. Furthermore, UW 10 and UW 12 have shallow casings and are open to both the upper and lower aquifers, whereas UW 29 and UW 30 are cased through the Eau Claire shale and are open only to the lower aquifer. Therefore, the following assessment should be considered a preliminary evaluation.

The available iron and manganese concentrations are presented in Table 5 and compared on Figure 8. This figure illustrates that there appears to be a general correlation between manganese and iron concentrations at well UW 10, with higher manganese concentrations occurring with higher iron concentrations. Iron and manganese concentrations at UW 12 and UW 30, although low, are generally consistent with the trend observed at UW 10. However, the iron – manganese concentrations at UW 29 are not consistent with those observed at UW 10. In particular, the iron concentration at UW 29 is much lower than would be predicted at UW 10 for the same manganese concentration.

The comparison of iron and manganese concentrations at UW 10 and UW 29 shown on Figure 8 suggests a different cause of manganese dissolution at these two wells. Eh and pH data are not available for the water at UW 10, so the position of this water with respect to the iron and manganese eH-pH diagrams is not known. However, the high iron and high manganese concentrations at UW 10 may suggest that dissolution of iron is related to conditions making manganese dioxide available for dissolution (e.g., dissolution of iron hydroxide makes manganese dioxide available for dissolution).

2.9 Groundwater Modeling to Identify Potential Contaminant Sources

The Dane County Regional Groundwater Flow Model (Krohelski et al., 2000) was used to simulate groundwater flow conditions in the vicinity of UW 29. The regional model was constructed using the U.S. Geological Survey groundwater flow model code, MODFLOW (McDonald and Harbaugh, 1988). The four layer regional model was constructed to represent the upper glacial and bedrock aquifers (layers 1 and 2), the Eau Claire shale (layer 3) and the lower sandstone aquifer (layer 4). The square grid cells have dimensions of 1312.4 feet on a side. To represent the area more accurately, the telescopic mesh refinement (TMR) approach (Ward et al., 1997) was used to reduce the square grid spacing to 301 feet on a side. The new model has 100 rows and 100 columns and covers an area of approximately 32 square miles. Except for the reduction in the grid spacing, model parameters remained the same. The model was run for steady state conditions, that is, the input parameters do not change with time. Model details and output are presented in Appendix C.

A review of potential contaminant sources in the vicinity of UW 29 indicated that the most likely source of potential contaminants was the Sycamore Landfill located approximately 1500 feet west of UW 29 (see Figure C2). The primary objective of the modeling was to assess the likelihood that groundwater impacted from Sycamore Landfill would be captured by UW 29. The model code MODPATH (Pollock, 1994) was used to track particle movement from the landfill. Results of the modeling include: 1) In general, groundwater flow is from east to west; the model confirms that the capture zone for UW 29 extends to the northeast (Figure C1); 2) The operation scenario in which UW 29 was pumping at a rate one-half of design capacity (1,050 gpm) did not result in particle capture from the Sycamore Landfill (Figure C3); and 3) Particles emanating from the landfill would not be captured unless UW 29 were pumped at a rate of 2,000 gpm for approximately 25 years, the confining layer were breached or the particles were already in the deep aquifer (Figures C5 – C8).

2.10 Synthesis and Interpretation of Data

The data collection described above provided a great deal of information, and the inclusion of data for UW 30 and UW 12 substantially increased the complexity of data to be reviewed. Not all of the data fit into any single cause-effect mechanism for manganese release to the aquifer. Significant observations on the data include the following:

- **Old Water at UW 29** – The isotope data indicate that at least 90% of the water being produced from well UW 29 is older than about 1960 and recharged the aquifer without moving through a surface water body or other feature (e.g., a landfill or wetland).
- **Low Redox associated with Pyrite in Aquifer** – Naturally occurring reducing conditions are indicated by and may be due to the presence of pyrite (iron sulfide) and/or other reduced minerals present in the aquifer solids. The Eh of the water is relatively low at wells UW 29 and UW 30. In addition, detailed mineralogical observations of cuttings from the borehole collected by WGNHS shows that certain zones have fresh, unoxidized pyrite that could shift the Eh/pH conditions in the water to more reducing and/or acidic conditions. Other zones have oxidized pyrite (e.g., iron oxide shown in the boring log for the Larkin test well as “limonite after pyrite”) indicating that the reducing potential of this zone has decreased from the very reducing conditions under which pyrite is stable to less reducing conditions over time. These observed conditions could also exist at UW 29. The Eh/pH conditions of any interval of groundwater may be dependent on the abundance and availability of unoxidized pyrite in the zones where groundwater is flowing.
- **Availability of Manganese for Dissolution** – Iron probably occurs within the aquifer predominantly as coatings of iron hydroxides as coatings around the sand grains, creating the yellow/orange color of the sandstone. The two most common forms of iron and manganese are iron hydroxides [Fe(OH)₃] and manganese dioxide (MnO₂). The manganese dioxides probably occur with the iron hydroxides in the coatings around the sand grains. As measured in this study at UW 29, UW 30, UW 10, and UW 12 the ratio of Fe(OH)₃:MnO₂ ranges from approximately 10:1 to over 400:1 and typically near 100:1. These ratios are approximate assuming that all Fe is as iron hydroxide and Mn is manganese dioxide. Therefore, since the water in the aquifer can dissolve manganese oxides, but typically not iron hydroxides, the available manganese oxides may have been dissolved over the millennia of groundwater flow, leaving behind a coating of iron hydroxides over what is a now manganese oxides.
- **UW 29 Development** – UW 29 required sufficient development to achieve its desired production capacity, using several forms of well development, including blasting. Final development activity achieved its production goal, and sufficiently disturbed the rock matrix that approximately 8,000 ft³ of sand was dislodged from the rock matrix, flowed into the well and was removed. This development action was effective at strongly disturbing the aquifer solids in the vicinity of UW 29 to increase its well yield to the desired capacity. The well continued to produce sand, so an Aquiscreen was installed to reduce the sand production, which is largely successful, although some amount of sand production continued during operation. This development and movement of the sand may also have disturbed the coatings on the sand grains that had been established over the long term groundwater flow through the aquifer.
- **Results of UW 29 Development** – Movement of the sand grains of the aquifer could potentially disturb the soft iron hydroxide coatings and expose manganese oxides and

unoxidized pyrite in the aquifer that had been unavailable to groundwater by a coating of iron hydroxides. The results of these minerals becoming available to dissolution in groundwater around well UW 29 could produce the observed differences between UW 29 and UW 30.

- **Duration of Manganese Concentrations at Well 29** – The duration of manganese concentrations in excess of those observed at UW 30 is dependent on the duration that manganese oxides are available to migrating groundwater captured by well UW 29. This duration is dependent on the rate of manganese dissolution, the area and mass of available manganese oxides, the rate of groundwater migration, and whether iron hydroxides are dissolved (i.e., residual iron hydroxides are critical to create a coating over manganese oxides to make them unavailable). The total mass of manganese around UW 29 can be calculated using the results of the rock analyses and the assumption that these analyses are representative of the area. To determine the duration of manganese availability for dissolution would require knowing how much manganese oxide became available for dissolution and over what horizontal and vertical zone. However, there are no known methods to determine how much manganese became available even if we knew the zone of availability. In light of these uncertainties, a simple calculation using some assumptions provides a general indication. If the zone of manganese availability was 50 ft by 50 ft by 400 ft (the length of open hole), the rate of manganese decline when pumping water at a rate of 2,000 gpm continuously, would drop the manganese concentration by approximately 10 ppm/yr. Given an average concentration of manganese in the rock of approximately 300 ppm, would require 30 years to deplete the available manganese. However, pumping would not occur at this rate continuously but the amount of manganese available is probably less than the total. While this calculation is very approximate, the best estimate of the duration of manganese availability at UW 29 is that it is much longer than a few years and probably longer than 10 to 20 years.

2.11 Laboratory Data Reporting

Copies of the laboratory results described above are available upon request from the Madison Water Utility.

3. CONCLUSIONS

Based on the data presented in Chapter 2, the primary conclusions of this study are:

1. **The water supply aquifer for UW 29 is relatively isolated from the surface.** The aquifer supplying UW 29 (the lower sandstone aquifer, below the Eau Claire Shale) appears to be isolated from near-surface conditions. The aquifer is dominated by water older than approximately 50 years, but still of meteoric (rainfall/snowmelt) origins. The water shows no contaminant or organic loading indicative of a near-surface connection. This conclusion is based on both chemical and radiological analysis of water drawn from the well, as well as the results of pump test monitoring and groundwater modeling.
2. **Continued operation of UW 29 is not likely to be affected by surficial contamination sources.** Groundwater modeling analyses indicate that it is not likely that long-term operation of UW 29 will draw water into the well from the most significant nearby source of contamination, the Sycamore Landfill. Potential unidentified surficial sources of contamination do not appear to be likely, and do not appear to pose a significant threat, due to the isolation of the surface from the aquifer supplying UW 29. However, these conclusions must be qualified in that they are based on the results and underlying accuracy of the Dane County groundwater model.
3. **Conditions allowing release of manganese into solution from naturally occurring minerals exist at UW 29, and are expected to continue in the future.** Observed pH and oxidation/reduction conditions favor dissolution of manganese dioxide, and the aquifer contains sufficient mass of manganese dioxide to allow continued dissolution far into the future. The presence of iron sulfide in the aquifer provides a mechanism for the long-term continuation of reducing conditions that will dissolve manganese. A zone of high manganese content exists in the bedrock at a depth of approximately 480 ft, near a zone of fractures and the area of well development by blasting observed in the borehole video. These data suggest that the concentration of manganese in the well water may vary with depth in the borehole.
4. **Manganese is soluble at UW 29, UW 30 and UW 12 based on pH and redox, but concentrations are probably limited by its availability.** The rock cutting sample analyses and the composite well head pH and oxidation/reduction (Eh) data from UW 12, UW 29, and UW30 indicate that manganese is present in the aquifer bedrock, and can dissolve into the water in the aquifer. Solution of manganese into the aquifer may be limited by the isolation of manganese dioxide within the much larger mass of iron oxide that coats many of the silica sand grains of the sandstone. Elevated manganese concentrations at UW 29 suggest that near-well aquifer disturbance and variations in permeability, fractures and aquifer water chemistry may be very important in understanding the manganese levels variations from well to well.

5. **We do not have the data at this time to recommend a specific alternative location for UW 29 that will have lower manganese concentrations.** At UW 29, the water supply aquifer is isolated from the surface, and human-induced contamination impact does not control reducing conditions and hence manganese release. Aquifer geochemistry determining natural release mechanisms for the relatively low levels of manganese is complex, and we do not have data on the spatial variability of these mechanisms.
6. **A Draft Protocol for new pilot well testing has been developed based on the results of this study.** The draft recommended pilot testing protocol for new production well locations based on the observations in this project, is included in Appendix A. These recommendations could be refined in the test well /pilot well evaluation program.

4. RECOMMENDATIONS

Based on the conclusions of this study, we recommend the following:

1. **Development of a manganese treatment design for UW 29 should proceed.** Given our conclusions on water quality at UW 29, and the goal of the end of 2008 for UW 29 to be on-line with acceptable water quality, continuing design for well head water quality treatment is appropriate.
2. **A test well sampling and analysis program should be conducted.** This study identified the possibility that near-well disturbance and variations in permeability, aquifer mineralogy and water chemistry with depth in the borehole may be very important in understanding manganese levels. However, we have not been able to sample water from individual depths of the aquifer, which has limited our ability to identify the cause of the composite manganese concentrations observed at the well head. The best way to address this data gap would be by conduct of a test well drilling and sampling program at UW 29 or at another location.
3. **Assessment of additional Water Utility wells based on the conclusions and recommendations of the study should continue.** This work should include collection of field parameters as well as laboratory water quality and rock cuttings analyses, and will extend the Water Utility's understanding of sources and causes of manganese.
4. **The Water Utility should work with City Engineering to continue monitoring the Sycamore Landfill.** Although we do not expect landfill-related effects at UW 29, continuing the collection and review of periodic landfill monitoring well observations should be conducted as part of long-term operation of UW 29.

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TABLES

FIGURES

APPENDICES

APPENDIX A

FIELD INVESTIGATIONS

As part of the UW29 Manganese Assessment the following field investigation activities were completed:

- Time series sampling at UW 29
- Time series sampling of UW 12 and UW 29
- Conversion of Redox to Eh
- Water level monitoring at Sycamore Landfill

A short summary of the methods, materials, and observations during this investigation are included in this appendix.

Time Series Sampling at UW 29

On January 8, 2007, UW 29 was instrumented for sampling and then turned on for a period of approximately 5 hours for sampling. The well pump's variable frequency drive was set to its lowest setting, to pump at its slowest rate for the first 2 hours and 15 minutes of pumping. This lowest setting was used to slow down potential changes in water quality when first starting to pump the well. After this initial period, the pumping rate was increased to its maximum rate to discharge the maximum amount of water during the pumping period.

Samples were collected from the sample tap located just downstream of the well pump and gate valve. The sample tap valve was removed and replaced with a brass and Teflon tubing arrangement to split flow between a flow through cell and a valve for sample collection. A flow through cell was used for measurement of pH, conductivity, redox, and temperature. The flow through cell was maintained in a water bath of water from the well to maintain uniform temperature.

The well discharge was diverted to the hydrant adjacent to the pump house and discharge to a storm sewer by water utility personnel. Discharge of the well and the head in the well was recorded from the SCADA panel in the well house by water utility personnel. These data are recorded in Table A1.

Time series sampling was conducted to determine water quality changes as water was withdrawn from the aquifer. The volume of water contained within the well is calculated and subtracted from the total volume of water withdrawn from the well to determine how much

water is being withdrawn from the aquifer. These calculations assume that water is withdrawn from the well before water from the aquifer is withdrawn. However, mixing of water in the well and from the aquifer occurs. These calculations are approximate and used as a guide to indicate when water is being withdrawn primarily from the well and when water is withdrawn primarily from the aquifer.

The results of the field parameter monitoring is shown in Figure A1, with notes on when water was being produced from the aquifer, when the well was turned off to increase its flow rate, and the time when each sample for lab analyses were collected.

The size of the pump riser and annulus are shown in Table A1 and used to calculate the volume of water contained in these zones. The volume removed from the pump riser and annulus were calculated for the amount of drawdown that occurred in the water level in these zones. These volumes were subtracted from the total volume pumped to estimate the volume of water removed from the aquifer and the radius of capture from the sandstone aquifer. The radius of capture assumes plug flow through the entire thickness of the open zone of the aquifer (i.e., from the bottom of the casing, at 342 ft to the bottom of the aquifer, 815 ft) and an effective porosity of 10%).

Results of the analyses from the flow through cell (pH, DO, redox and temperature) are shown on Figure A1. The time series results for each parameter are affected by the pump and the meter response. Monitoring of the meter response began before water entered the flow through cell, so each probe was exposed to the air. As water entered into the flow through cell each probe began to equilibrate to the water. Within the first 10 minutes of monitoring, each probe shows a large degree of change.

The redox probe shows the largest change, dropping to a redox of approximately -250 mv before rising to a stable redox (of approximately -88mv) during the first pumping rate. The source of this large drop in redox is not known.

Over the same time frame as the redox drop and rise, the pH rose to 8.3 and then dropped to its steady state value of approximately 7.17. The source of this change in pH is also not known. The change in pH and redox approximately parallels the eH-pH diagram (see Figure A2) line between Fe^{2+} and $\text{Fe}(\text{OH})_3$, staying on the $\text{Fe}(\text{OH})_3$ side. It is of interest to note, that the samples collected and analyzed over this time frame showed little change in water quality parameters, in particular, iron changed very little, consistent with the observation that the Eh-pH stayed within the insoluble iron zone.

The DO probe shows a drop from high DO and starts to equilibrate at a value of 4.35 mg/L. This is consistent with starting the test with air in the flow through cell. The drop from a value of 4.35 mg/L to its final DO of 0.11 mg/L is probably due to the observation that there were air bubbles coming through the flow through cell for approximately 10 minutes. The fittings were re-checked to confirm they were tight, demonstrating that no air could be entering the system.

The air bubbles gradually dissipated with time. The source of the air bubbles was probably air in the riser pipe and air trapped inside part of the large gate valve. This trapped air may have been released through time. This rise and dissipation of DO was seen again after shutting down the well for approximately 40 minutes to increase its pumping rate.

Results of the time series sampling at UW 29 demonstrates that there were several changes that occurred in very early times when the well was turned on. DO changes are explained by effects of air trapped in the plumbing. The source pH and redox changes are not known, but follow the boundary between iron solubility/insolubility.

Time Series Sampling at UW 12 and UW 30

Field parameters (DO, pH, redox, and specific conductance) were measured at UW 12 and UW 30 to compare with UW 29. The same sampling arrangement was used at UW 12 and UW 30 as used at UW 29, using the same flow through cell. Data from UW 12 and UW 30 are presented in Figures A2 and A3.

The pump at UW 30 was running when the flow through cell was connected and continued running throughout the monitoring period. The pump at UW 12 was running when the flow through cell was connected, but then shut down and started again, as shown on Figure A3. It can be reasonably assumed that water quality being pumped from both these wells was not changing during the time when sampling occurred and that any changes were due to probe equalization or changes due to pump shut down (only at UW 12).

The data collected at UW 30, see Figure A3, show a gradual change in each probe to equilibrium conditions. DO is shown to require approximately 5 minutes to equilibrate from an air filled cell. Specific conductance requires a very short period of time to equilibrate. pH is shown to change quickly, but then requires more than 17 minutes to come to within 0.05 pH units of the final value. Redox is similar to pH, in that it changes dramatically early on, but then requires more than 15 minutes to come to within 20% of the final value measured at approximately 40 minutes.

The data collected at UW 12 is a combination of observations at UW 30 (i.e., a well that had been continuously pumped) and UW 29 (i.e., measurements at startup). The changes in DO initially followed the observation at UW 30, in that DO was equilibrating quickly. However, when the pump cycled off then on, the DO bounced around again, probably due to air in the lines being dissipated.

Conversion of Redox to Eh

The reduction/oxidation potential measured by the YSI probe can be converted to Eh by first correcting the values measured to the standard Zobell solution and then correction from the silver chloride solution to the standard hydrogen electrode (SHE). The standard Zobell solution was measured in the field at each well measured. The correction from the measured redox values to Eh is requires adding 185 mv to the measured redox values to obtain Eh.

APPENDIX B

NEW PILOT WELL TESTING PROTOCOL

INTRODUCTION

The program to install a new municipal well includes:

- 1) Site Selection – selecting a site for a new municipal well includes identifying, evaluating and recommending the new well site and receiving the Department of Natural Resources (DNR) approval according to Wisconsin Administrative Code section NR 811, including any appropriate variances. The site selection process will likely become more detailed than it has been in the past, and will include technical analyses of alternative sites regarding potential contaminants, geologic and groundwater flow conditions, and will also include close communication and collaboration with community stakeholders. It is also likely that the site selection process will be expanded to include evaluation of geologic and water quality characteristics of the proposed well site as determined during the pilot wells drilling and testing program, meaning that site selection will not be complete until pilot test well results have been evaluated and final DNR approval for the well site is obtained
- 2) Pilot Well – constructing and testing a pilot test well and sampling, testing and analyzing data to determine the aquifer’s production capacity and water quality, as described in the following section of this protocol;
- 3) DNR Approval for completion of the municipal well—following review and analysis of the test well data, and confirmation of acceptable expected performance, the Utility will apply for DNR approval for the new municipal well according to NR 811; and
- 4) Install and Start-Up Testing Production Well – installing the supply well, and sampling, testing and analyzing data to confirm productivity and water quality. In addition, Will startup will include startup of the monitoring program , as identified in the site selection pilot well and DNR application process, for off-site environmental variables such as monitoring wells, river or lake gauge observations, or other environmental issues identified is important to long-term operation of the water supply well.

The objectives of this recommended sampling and testing program are to complete the Pilot Test Well step listed above.

PILOT WELL INSTALLATION

The pilot test well is used to describe the site geology, delineate aquifer hydraulic properties, determine the existence and location of preferential zones of groundwater inflow, and to assess the quality of the groundwater supply.

Construction of the test well shall use similar construction techniques, although smaller diameter, as expected for the final production well, to the extent practicable. In particular, the pilot well must be installed to the same total depth, with the same length of steel casing and seals, as will be expected for the production well. Aquifer performance testing shall be conducted to establish the aquifer characteristics and verify production objectives. Several good protocols for pumping tests already exist and can be tailored for the site hydrogeology and objectives. Installation and monitoring of an observation well or utilizing nearby existing wells for monitoring water levels during the pumping test should be considered to provide additional data for analysis of hydraulic properties.

It is strongly suggested that the pilot well not be abandoned after installation, but rather remain in place, adjacent to the final production well. Having the pilot well available near the production well will allow more detailed analysis of aquifer hydraulics following completion of the production well, and will also provide an additional location, unaffected by production well installation, for water quality testing. A decision on final abandonment of the pilot well installation according to procedures in NR 811 should be made after the production well has been completed, startup procedures accomplished, and the well is in normal long-term operation.

PILOT WELL SAMPLING AND ANALYSIS

In addition to the requirement of s. NR 809, Wisconsin Administrative Code, that the groundwater at the test well be sampled for inorganic, volatile organic, synthetic organic, and radionuclide water quality parameters, we recommend the following testing program.

1. Video and Geophysical Logging – Log the well using video and geophysical logging (natural gamma, resistivity, and spontaneous potential).
2. Vertical Flow Meter – A vertical flow meter should be run with no pumping and while pumping the test well. The vertical flow meter log while at rest would be used to determine natural vertical flow in the well and would help to determine the competence of the seal if installed through a confining layer (e.g., the Eau Claire Shale). The vertical flow meter while pumping would identify the zones producing water to the pumped well. The pumping rate should be set at a rate equivalent to a pumping rate desired from the final production well. The equivalency between the pilot test pumping rate and

the final production well should be based on the actual and planned diameters of the two wells.

Have a detailed geologic log prepared using visual and microscopic evaluation (e.g., by the WGNHS) in a manner consistent with the Larkin test well. This should specifically

3. identify the presence of fresh or oxidized sulfide minerals (typically pyrite) and zones with sand grains with oxide coatings and those with no coatings on the sand grains. Based on the detailed evaluation and the downhole video, collect and analyze rock samples for metals, sulfur, and sulfides. The composite interval should be selected so that sufficient detail is available to determine if there are zones of anomalously low or high manganese or iron.
4. Based on the results of the flow meter, rock sample analyses, and video and geophysical logs, conduct water quality sampling at selected intervals in the borehole. This sampling should consist of installing a double packer and pumping from the target zone. Sampled intervals should include zones with high sulfides, high manganese or low Fe(OH)₃/MnO₂ ratios in the rock analyses, and zones with high flow based on the vertical flow meter results during pumping. Sampling and analysis should include:
 - a. Use a flow through cell to collect field parameters (pH, dissolved oxygen (DO), redox, conductivity, and temperature) while pumping from the isolated interval on a recording data logger. After stabilization of field parameters, collected samples for lab analysis.
 - b. General Water Chemistry analyses:
 - i. Major ions – Ca, Mg, Na, K, Cl, Alkalinity, SO₄
 - ii. Total Organic Carbon (TOC) – to assess potential man made and natural sources of carbon
 - iii. TDS – general character and to help in ion balance
 - iv. Redox parameters – Mn, Fe, NO₃, Nitrate-N, Total Kjeldahl-N, and ammonia-N,
 - c. Others – Low detection level bromide and iodide to assist in source characterization,
 - d. VOCs – Low level 8260B. Low detection limits to look for very low concentrations of man made or petroleum sources not detected in routine analyses,
 - e. Age Dating – low level tritium (detection limit of 1 tritium unit or less) to provide a range on the possible age of the water in the aquifer,
 - f. Isotope Characterization – δD and δ¹⁸O to characterize the source of the water.

The above data will be analyzed to evaluate:

- Well construction and development, geologic conditions, and availability of manganese for dissolution

- Existing water quality of the aquifer and potential for manganese or other constituents to impact water quality
- Preferential flow paths and zones of high hydraulic conductivity
- General age and history of the water to determine if the water supply is isolated from near-surface condition and likelihood that near-surface conditions will affect the water quality

If any water quality issues are identified, the test results will be useful for deciding on a plan of action for further assessment. More detailed groundwater and hydraulic analyses may be conducted, depending upon the results of the pilot well testing, and of the issues identified during the well site selection process.

REPORTING

The results of installation, water quality testing, and analysis of the pilot test well should be collected into a report format that includes all observational data available. This report should form the basis of confirmation or modification of the site selection process for the production well. In addition, the drilling observations, water quality, and hydraulic characteristics determined in the pilot test well will prove a valuable resource to the Utility in the future, as additional pilot test wells are constructed and analyzed.