

**Final Report**

**Evaluation of the potential for Arsenic release in two cones of depression in northeastern Wisconsin**

Report prepared for the Wisconsin Department of Natural Resources

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# INTRODUCTION

## Project Objectives

This study is a collaboration between the University of Wisconsin – Green Bay (UWGB) and the Wisconsin Geological and Natural History Survey (WGNHS) which is part of UW – Madison Division of Extension. This study focuses on evaluating groundwater management strategies associated with two cones of depression in the Green Bay – Fox Cities region, which is part of the Northeast Groundwater Management Area (GMA). In the northern part of the GMA, drawdown in the confined sandstone aquifers has been recovering since the late 2000s, as a result of the villages surrounding Green Bay transitioning municipal water sources from groundwater to surface water. In the southern part of the GMA, continued groundwater use has sustained a cone of depression near the Fox Cities, including Kimberly and Kaukauna. The overall goal of this study is to evaluate how groundwater recovery or continued drawdown impacts groundwater quality in these two regions of the GMA, with a focus on metals concentrations. This project builds upon previous studies in the confined sandstone aquifer, but takes a unique focus evaluating water quality at a downdip portion of the aquifer farther from the recharge area, within cones of depression that may have (historically or currently) dewatered portions of the Ansell Group. Project deliverables include installation of a monitoring well in the southern region of the GMA, a summary of groundwater chemistry in the region, an evaluation of the aquifer dewatering in the region, and results from a suite of batch leaching experiments with well cuttings. Results from this 18-month study lay the groundwork for continued evaluation of groundwater resources and water quality in the Northeast GMA.

The main objectives of this study include:

1. Facilitate improved monitoring in the southern cone of depression in the Northeast Wisconsin Groundwater Management Area (GMA) by installing an additional monitoring well
2. Determine potential water quality risks associated with oxidative metals mobilization through analyzing well water chemistry and conducting batch experiments with aquifer materials
3. Evaluate aquifer water connectivity using water chemistry data from existing well data and 19 additional wells sampled in this study
4. Evaluate areas of the GMA at risk of dewatering and potential arsenic and other metals release

## Relation to Other Projects

Previous research related to metals mobilization in aquifers of northeast Wisconsin has focused on arsenic release from iron sulfide minerals in the sulfide cement horizon (SCH) near the recharge zone updip in the aquifer. This zone of sulfide mineralization has been observed at the top of the Ansell Group and parts of the Prairie du Chien Group where the Ansell is absent, near the recharge area to the west and deeper in the aquifer further east. The present study focuses on regions of the GMA that have historically or are projected to dewater the Ansell Group due to groundwater pumping in the region, expanding upon previous work focused further west in the GMA that showed evidence for elevated arsenic concentrations (Plank et al., 2020; Schreiber et al., 2000). Current understanding of arsenic mobility in groundwaters of this region

is most strongly associated with iron-sulfide mineral oxidation (Gotkowitz et al., 2004; Schreiber et al., 2000; Thornburg and Sahai, 2004). The present study expanded to include not only arsenic, but also other relevant metals such as cobalt and nickel that can also be released due to oxidative dissolution of iron sulfide minerals. This expanded focus was prompted by results from batch leaching experiments discussed later in the report.

Previous studies have shown that arsenic and other metals are closely associated with Mississippi Valley-type (MVT) mineralization in Cambrian-Devonian rocks of eastern Wisconsin (Luczaj et al., 2016). The presence of these metals is not restricted to areas near the outcrop belt, but rather it extends down-dip, as evidenced by drill cores, cuttings analysis, and scanning electron microscopy (SEM) investigation. Additional evidence of down-dip mineralization containing arsenic, nickel, cobalt, and other metals can be inferred from unintended water-rock interactions in the City of Green Bay (Dickoff, 2010; Johnson) and the Village of Bellevue (Luczaj, 2022). In the case of Green Bay's Well #10, a planned Aquifer Storage and Recovery (ASR) injection of treated surface water mobilized significant amounts of arsenic and nickel due to MVT mineral oxidation. In the case of the Village of Bellevue, an inadvertent leak through a backflow valve allowed oxygenated and chlorinated potable water to enter the well over several years, resulting in the slow injection of millions of gallons of water. Mobilization of arsenic above the EPA MCL, as well as significant Ni and Co (above NR 140 ES) led the utility to pump over 4 million gallons to waste in an effort to reduce concentrations (Luczaj, 2022; ongoing research).

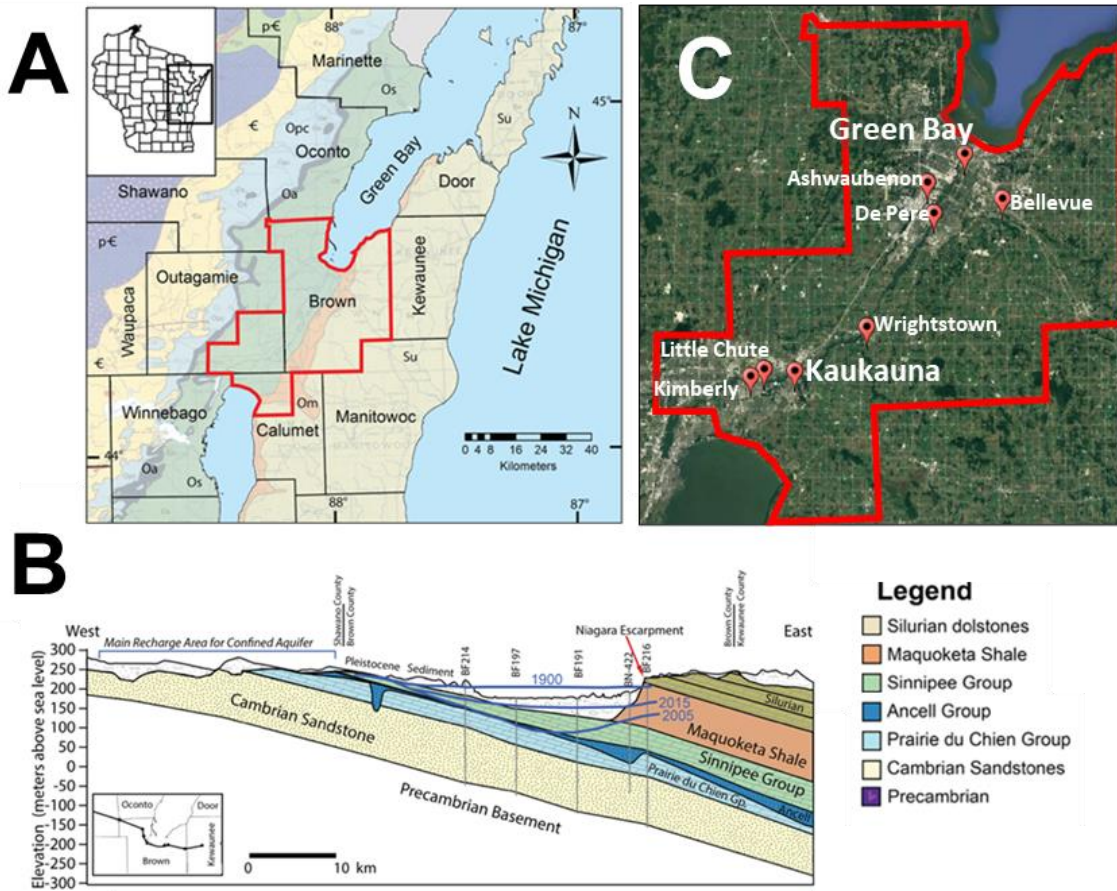
## Background

### *The Confined Cambrian-Ordovician Combined Sandstone Aquifers*

The bedrock geology of eastern Wisconsin consists of eroded Precambrian crystalline rocks, overlain by Paleozoic marine rocks that can be up to 2,300 feet (700 m) thick. Figure 1 shows how the strata in the GMA dip eastward away from central Wisconsin, toward the Michigan basin. Younger Pleistocene glacial, glaciofluvial, and glaciolacustrine sediments range in thickness from 0 feet to over 330 feet (0 m to 100 m) and are important confining layers in parts of the region (Conlon, 1998; Krohelski, 1986).

Paleozoic strata in the Northeast-GMA are separated major hydrostratigraphic groups. The lowermost groups include the Cambrian-Ordovician sandstone and dolostone units that are informally known as the "confined sandstone aquifer" in the region, and it is these strata that are targeted as the focus of the Northeast Groundwater Management Area (GMA). The Cambrian units are about 400 feet (120 m) thick, high conductivity quartz sandstones, with lesser amounts of shale and dolomitic and glauconitic sandstone. The overlying Prairie du Chien and Ancell groups constitute the remainder of the Cambrian-Ordovician sandstone aquifer. The Prairie du Chien Group is comprised of a mixed carbonate – clastic sequence of sediments, with multiple thin quartz sandstone interbeds. The Ancell Group is dominated by the St. Peter Sandstone, a mature quartz sandstone that fills a network of ancient paleovalleys up to 300 feet (~100 m) deep (Mai and Dott, 1985). The top of the St. Peter Sandstone includes a zone referred to as the sulfide-bearing secondary cement horizon (SCH) – also called the sulfide cement horizon, though sulfide mineralization occurs throughout the Cambrian-Ordovician strata. Together, this 600 ft (~180 m) thick sequence of Cambrian-Ordovician rocks represents a single confined aquifer (Krohelski, 1986; Luczaj et al., 2017). The Ordovician Sinnipee Group (dolostone) and Maquoketa Group (mainly shale) are two significant low permeability units that overlie the Cambrian-Ordovician sandstone aquifer and together act as a regional confining layer along with clay-rich Pleistocene tills and lake sediments

(Conlon, 1998; Krohelski, 1986). As a result, the confined sandstone aquifer is poorly connected to surface water bodies located in the Northeast GMA (e.g., the Fox River, Lake Winnebago, or Green Bay) (see cross section in Figure 1B).



**Figure 1.** Geology of Northeast Wisconsin from Luczaj et al. (2017). Northeast Wisconsin GMA indicated by red polygon in map view (A), Cambrian-Ordovician combined aquifers shown in cross-section (B) dipping toward the east, and important cities and villages in the region (C). Blue lines in 1B indicate the approximate position of the potentiometric surface for the confined aquifer in 1900, 2005, and 2015.

### *Northeast Wisconsin Groundwater Management Area and History of Groundwater Use*

Wisconsin groundwater quantity legislation, 2003 Act 310, addresses the largest drawdowns by designating areas with drawdowns greater than 150 feet as Groundwater Management Areas (GMAs) (Wisconsin State Legislature, 2004). Act 310 requires the Wisconsin Department of Natural Resources (WDNR) to “assist local governmental units and regional planning commissions in groundwater management areas designated in par. (a) by providing advice, incentives, and funding for research and planning related to groundwater management.” Act 310 also contains language to aid the WDNR in administration of GMAs, with the advice of the groundwater coordinating council, to conduct monitoring and research related to characterization of the interaction of groundwater and surface water, characterization of groundwater resources, and strategies for managing water. One of the regions in Wisconsin that satisfies the 150-foot drawdown criterion, is the Northeast GMA in parts of Brown,

Outagamie, and Calumet Counties. Luczaj et al. (2017) provide a detailed history of water use during the 20<sup>th</sup> and early 21<sup>st</sup> centuries.

#### *Potentiometric Surface Monitoring Over Time*

The Northeast GMA contains two major cones of depression in the Cambrian-Ordovician confined sandstone aquifer, and each cone is centered near cities that have used groundwater for over 100 years. The potentiometric surface showed a large cone of depression in the early 2000s in the northern portion of the GMA (northern cone), centered on Green Bay, which has since partially recovered due to decreased groundwater pumping after a shift to most municipal water being sourced from surface water. The second cone of depression, located farther south near the cities of Kimberly, Kaukauna, and Little Chute (southern “Fox Cities” cone), has seen progressive drawdown during the late 20th and early 21<sup>st</sup> centuries (Luczaj et al., 2017), resulting from continued pumping. While the southern cone appears less dramatic than drawdown observed for the northern cone in the early 2000s, the drawdown still indicates significant depression of the potentiometric surface (~150-177 ft) which has implications for aquifer oxidation.

#### *Potential for Metals Release with Drawdown*

Iron sulfide mineral oxidation can promote the release of sulfide-associated metals. The historical cone of depression in the northern region of the GMA and more recent expansion of the southern cone of depression could cause oxidation of sulfide-rich stratigraphic sequences. Metals such as arsenic, cobalt, nickel, and others can be associated with iron sulfide minerals such as pyrite and marcasite through isomorphous substitution. Upon oxidative dissolution of the iron sulfide minerals, these associated metals are also released to groundwater. To evaluate potential for metals release in different portions of the Cambrian-Ordovician combined sandstone aquifer, the potentiometric surface of the aquifer can be compared to a structure contour map of the base of the Sennepsee Group that would overlay the iron-sulfide rich Ancell group. When the potentiometric surface declines below the base of the Sennepsee, it is possible that iron sulfide minerals in the Ancell group could become oxidized.

## **METHODS**

### **Potentiometric Surface Mapping**

An updated potentiometric surface map for the Northeast Wisconsin Groundwater Management Area (GMA) was developed using information from well reports and municipal datasets. Previous research presents methods for map development (Luczaj et al., 2017), and a preliminary 2019-2020 map presented by Luczaj and Koester (2021) served as the foundation for a new map. Depth to water (DTW) in GMA wells between 2023-2024 were collected from the publicly accessible Wisconsin Department of Natural Resources (WDNR) Well Construction Information System, municipal well reports, and well construction and abandonment reports from Brown, Outagamie, Calumet, Oconto, Kewaunee, and Winnebago counties. Additional data were available from the WDNR for selected municipal wells, along with the Green Bay Water Utility data for their wells. Only wells deep enough to reach the confined Cambrian-Ordovician sandstone aquifer were included. LIDAR maps were used to determine land surface elevation for any wells missing this information, and water level elevations were determined by subtracting DTW from land surface elevations (plus casing stick up as appropriate). The map was developed using ArcGIS Pro (ESRI), with inverse distance weighting techniques, and Adobe Illustrator for tracing and color matching the final maps.

### **Hydrographs from GMA**

Static water level data from wells with adequate time-series data and relevant proximity to the GMA were compiled from three main sources. These included:

1. Limited USGS monitoring wells in the GMA that penetrate the confined sandstone aquifer (4 total; 3 remain active).
2. Municipal water level records reported to WDNR by municipal water utility operators. See Luczaj et al. (2017) for accuracy concerns.
3. The Green Bay Water Utility also keeps records of water levels in its municipal wells, but they are apparently not supplied to WDNR. A full compilation of available data has been completed through 2024.

Ground level elevations were obtained from Geologic Logs or the USGS website, and data were plotted in Microsoft Excel.

### **Dewatering of the Ancell Group**

A preliminary structure contour map was made for the GMA and additional areas beyond using approximately 515 well construction reports and geologic logs by co-PI Luczaj and a UW-Green Bay student as part of an independent study project. The ground surface elevations were collected from geologic logs or LiDAR data, and the depth to the base of the Sinipee Group was interpreted from Well Construction Reports or WGNHS Geologic Logs. The calculated elevations for the base of the Sinipee Group were contoured using ArcGIS Pro to generate raster data for the structure contour map. Using the “Raster Calculator” in the Spatial Analyst tools, raster data showing the potentiometric surface in the confined aquifer for various dates were subtracted from the raster data representing the base of the Sinipee Group. Values  $\geq 0$  were plotted in GIS and traced in Adobe Illustrator. Three maps contained sufficient well coverage and data quality to generate regions in which at least part of the Ancell Group (i.e., St. Peter Sandstone) was dewatered.

## New Monitoring Well (ABQ564) Drilling, Cuttings Sampling, and Logging

The new monitoring well site selection was evaluated in collaboration with the City of Kaukauna Water Utility and Department of Public Works. There was interest in monitoring water level elevations east of the existing United States Geological Survey monitoring well (AAJ872, OU-21/18E/23-1900) in La Follette Park, Kaukauna. A parcel owned by the City of Kaukauna (parcel number 325112704) on County Highway CE near Haas Road was identified as a location that would provide monitoring data valuable for both the project and the City of Kaukauna. Well construction reports for existing wells within a mile of the site for the proposed monitoring well showed stratigraphic units with high sulfide content, providing some evidence that the selected site could also offer a well that would intersect the secondary sulfide cement horizon in the Ancell Group.

After obtaining an easement for the well site location from the City of Kaukauna and a variance approval from the Wisconsin Department of Natural Resources (Appendix A), Hintzke Well Drilling drilled monitoring well ABQ564 in November 2023. Mud rotary was used to minimize oxidation to stratigraphic intervals with reduced minerals and the well was not chlorinated, per variance approval (Ben Degner). The well was developed to remove any residual drilling mud by pumping in water from a water truck, and then surging with a steel bailer, followed by pumping the well until the water conductivity increased to that expected from formation water. The new monitoring well (ABQ564) was installed with 6" steel casing to 144 ft and an open borehole from 144-400 ft; full details on well construction are included in the well construction report (WCR) in Appendix B. After well construction and development in November 2023, the depth to water from top of casing was measured at 151 ft. A Solinst Levellogger 5 (M30) and Barrologger 5 were then installed in the well to monitor elevation of the potentiometric surface over time.

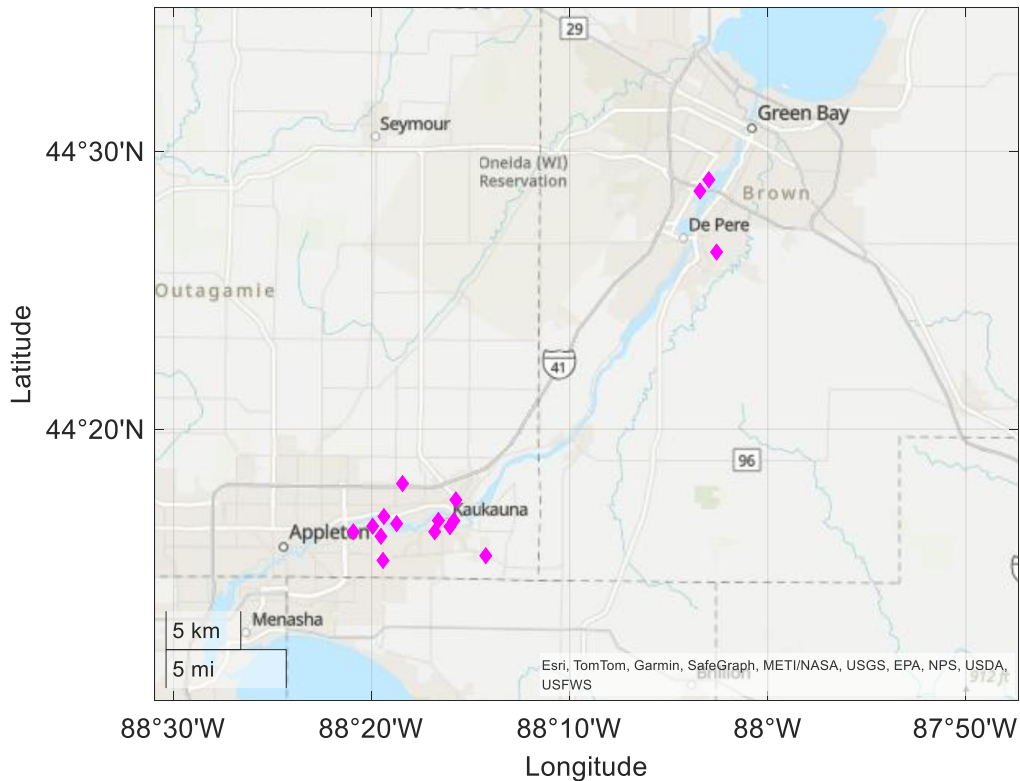
During monitoring well construction, rock cuttings were collected for lithographic characterization and batch leaching experiments. Representative samples from each 5-ft depth interval were collected. A separator was used to remove most of the bentonite drilling mud from the cuttings. At the drilling site, lower priority samples from the upper dolomite of the Sinnipee Group were washed with water from the drilling truck and higher priority samples from the lower Sinnipee Dolostone near the contact with the St. Peter Sandstone were washed with anoxic, dechlorinated tap water. Water was dechlorinated by filtering through a granular activated carbon filter, and anoxic conditions were achieved by purging water with nitrogen gas to achieve <0.1% dissolved oxygen which was confirmed with an optical dissolved oxygen sensor (Pyroscience). High priority samples were transported in coolers with ice back to the laboratory and washed again in anoxic, dechlorinated tap in the anaerobic glove bag (Coy Laboratories) water to remove residual bentonite drilling mud, and then frozen. Small, representative splits of each interval were kept unfrozen for mineral characterization. This treatment of well cuttings was necessary to preserve mineralogy and minimize oxidation for additional characterization and batch experiments.

Mineral characterization of the well cuttings was done via microscopy. Optical observations (Leica S9i binocular microscope) were used to describe the dominant rock type and minerals, color, shape/size, and relevant anomalies, including fossils. These observations were used to construct a detailed log of the monitoring well stratigraphy of the well, which. This log was then used to assist in targeting zones of interest for further geophysical investigation and batch experiments.

The new monitoring well, ABQ564, was also logged by Pete Chase at the Wisconsin Geological and Natural History Survey. Initial logging was conducted a week after well drilling, and measurements included caliper, gamma, resistivity, temperature, flow spinner, and optical borehole imagery. Instrumentation was lowered down the well on a winch mounted in the WGNHS well logging van. The well log is included in Appendix C. The OBI data indicated the locations of a few fractures in the borehole and the gamma-log aligned with higher measurements in shale-rich stratigraphy. The OBI data was also valuable for validating that the ABQ564 was well-developed, with minimal remaining drilling mud. Negligible flow with the flow spinner promoted follow up measurements with the heat pulse flow meter, which confirmed negligible vertical flow in AQB564.

### Groundwater Sampling and Analysis

To evaluate differences in groundwater chemistry across the GMA, 19 wells were selected for water chemistry analysis. Wells were selected from municipal, industrial, irrigation, and monitoring wells that penetrate the confined sandstone aquifer. Well locations are shown in Figure 2, indicating the focus on the southern region of the GMA near Kaukauna and Appleton. A Thermo Scientific Orion Star multiparameter meter equipped with a ROSS Ultra Triode pH/ATC electrode, DuraProbe 4-cell conductivity sensor, and RDO optical DO sensor was used to measure pH, temperature, conductivity, and dissolved oxygen. Each well was sampled for general chemistry (major cations, anions, metals, and alkalinity), water isotopes, and sulfur and <sup>14</sup>C (radiocarbon) isotopes.



**Figure 2.** Well locations for wells included in the water quality sampling. The southern region of the GMA near Appleton and Kaukauna was prioritized and includes 15 of the 19 wells sampled. Map developed using Geoscatter function in MATLAB.

Two different groundwater sampling approaches were utilized to collect samples for water chemistry analysis. Wells with pumps installed were sampled directly from the wellhead tap, prior to any treatment or storage and after a minimum of one well volume had been pumped. Monitoring wells without pumps were sampled with a low flow bladder pump at discrete depths using a van-mounted winch with support from Pete Chase at the Wisconsin Geological and Natural History Survey. Heat pulse flow measurements on monitoring wells ABQ564, AAJ872 (OU-21/18E/23-1900), and BN\_435 (WGNHS Well ID: 5000435) indicated negligible vertical flow which allowed discrete samples to be generally representative of formation water at sampled depths. Water samples were collected in 250 mL high density polyethylene (HDPE) bottles (preserved with nitric acid for metals) and sent to the state-certified Clean Water Testing laboratory in Appleton, WI for evaluation of major cations, anions, and metals. Metals sample duplicates were sent to the University of Wisconsin-Milwaukee’s School of Freshwater Science for concentration verifications. Isotope samples were collected under low flow conditions with no headspace to limit exchange with the atmosphere. Sulfur and radiocarbon isotope samples were each collected in new 1L HDPE bottles and were analyzed at the University of Waterloo Environmental Isotope Laboratory. Water isotope samples were taken in 30 mL HDPE bottles and analyzed at the University of Wisconsin-Milwaukee’s School of Freshwater Science.

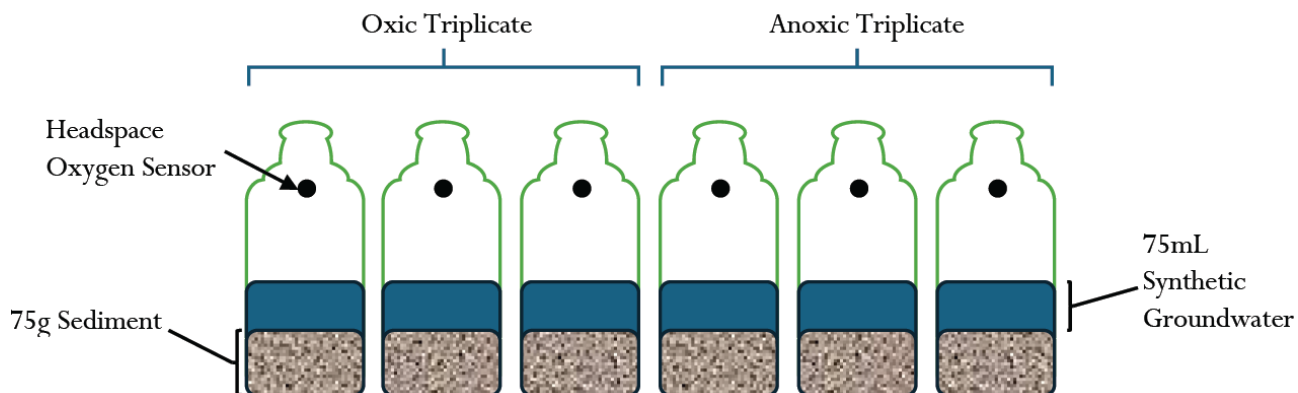
### Batch Experiments for Metals Leaching

Batch experiments were conducted with well cuttings from ABQ5564 to evaluate the potential for metals leaching under oxic and anoxic conditions. Well cuttings were selected from depth intervals that were observed to have iron sulfide minerals during optical microscopy characterization. Two depth intervals were selected: Saint Peter sandstone and dolomite (335-340 ft) and Prairie du Chien sandstone (depth 345-350 ft). The first depth interval with the St. Peter sandstone represents the contact of the Sinipee Group (Platteville Formation) and the St. Peter Sandstone of the Ancell group, and the second depth interval represents a lens of sulfide rich sandstone and dolomite within the Prairie du Chien Group. Cuttings from each depth were added to 160 mL serum bottles with synthetic groundwater and crimp sealed with butyl rubber stoppers. As shown in the schematic in Figure 3, each bottle included of 75 grams of well cuttings and 75 mL of synthetic groundwater (detailed below). Batch experiments were prepared in triplicate for both oxic and anoxic conditions resulting in a total of 12 batch experiments which are summarized in Table 1. For each depth interval, 600g of well-mixed cuttings were split using a sediment splitter into six representative samples of 75g and added to each serum bottle. Anoxic experiments were prepared inside an anaerobic glove bag (COY Laboratories) with synthetic groundwater that had been deoxygenated by sparging with N<sub>2</sub> gas for 30 minutes. Oxic experiments utilized the same groundwater recipe, but water was not degassed with N<sub>2</sub>. After initial setup, batch experiments were stored in an incubator at 25°C and inverted twice each week to ensure an exchange of pore space water with supernatant water. Water samples were taken regularly from each experimental bottle throughout the four-month experiment.

**Table 1.** Summary of sample sets for batch leaching experiments. Parentheses indicate shorthand for each experimental condition.

Sample Set	Replicates
Saint Peter Oxic (SO)	3
Saint Peter Anoxic (SA)	3
Prairie du Chien Oxic (PO)	3
Prairie du Chien Anoxic (PA)	3

The batch experiments were monitored for oxygen and sampled for metals. For both oxic and anoxic conditions, two of the three triplicates were outfitted with an optical oxygen sensor dot (Pyroscience), and the headspace oxygen content was monitored. Figure 3 shows the placement of the sensor dots on the portion of the batch serum bottles. When the headspace of the oxic condition bottles was measured to be below 18% O<sub>2</sub>, the headspace of each bottle was circulated with air from a gas tank (Airgas, Zero Air). Anoxic experiments remained at 0% O<sub>2</sub>, and this was confirmed using the sensor dots. Throughout the batch leaching experiments, water was removed and analyzed for metals concentrations. Samples were taken from each batch experiment at eight different timepoints during the four-month experiment using a needle and syringe (pre-filled with N<sub>2</sub> gas). Each 2 mL sample was diluted 2x with 4% trace metal grade nitric acid (HNO<sub>3</sub>) to achieve 2% HNO<sub>3</sub> for ICP-MS analysis. After each sample was taken, and the bottle mass was recorded to account for the volume of water removed at each sampling timepoint. Batch experiment samples were then stored in 15 mL conical tubes and refrigerated (4°C) until ICP-MS analysis at the University of Wisconsin-Milwaukee's School of Freshwater Sciences. Metals that were measured included Al, As, B, Co, Cu, Fe, Pb, Mn, Ni, Sr, and Zn. A synthetic groundwater sample control and a Millipore water blank control were also sent for analysis with each sample set to assure quality control and inform baseline concentrations.



**Figure 3.** Batch experiment schematic for well cuttings under oxic and anoxic conditions.

To better simulate the chemical composition of regional groundwater and to prevent the rapid release of soluble minerals in the well cuttings into a low ionic strength water, synthetic groundwater was prepared for the experiments. The synthetic groundwater chemistry was informed by water analyzed from the Kaukauna monitoring well. Since the regional groundwater is at or above saturation for some mineral species, the synthetic groundwater had decreased concentrations (60%) of alkalinity and calcium to allow for complete dissolution of the constituents in the synthetic groundwater. The synthetic groundwater used NaHCO<sub>3</sub>, CaSO<sub>4</sub>•2H<sub>2</sub>O, NaCl, MgCl•6H<sub>2</sub>O, KCl, Sr(OH)<sub>2</sub>•8H<sub>2</sub>O, NaF, and MgSO<sub>4</sub> to achieve ionic concentrations of 0.154 mM Sr<sup>2+</sup>, 2.096 mM Ca<sup>2+</sup>, 1.56 mM Na<sup>+</sup>, 1.403 mM Mg<sup>2+</sup>, 0.088 mM K<sup>+</sup>, 0.968 mM Cl<sup>-</sup>, 0.105 mM F<sup>-</sup>, 3.362 mM SO<sub>4</sub><sup>2-</sup>, and 1.599 mM HCO<sub>3</sub><sup>-</sup>. This synthetic groundwater was used for all batch experiments and as a control for metals leaching analysis.

## RESULTS AND DISCUSSION

### Updated Potentiometric Surface Map for NE WI GMA

The updated potentiometric surface map for 2023-2024 provides a comparison to previous regional potentiometric surface maps, and will be a valuable tool for GMA groundwater planning and management. Figure 4 shows a timeseries of potentiometric surface maps for the Northeast Wisconsin GMA that compare analyses previously conducted by Luczaj et al. (2017) and Luczaj and Koester (2021). In Figure 4A, the historical cone of depression around Green Bay is visible in 2004-2005 when the villages around Green Bay used groundwater as a municipal water source. Figure 4B and 4C indicate recovery of the potentiometric surface after the villages shifted to a surface water drinking water source. The present study developed the potentiometric surface map in Figure 4D to evaluate changes in the potentiometric surface in more recent history. In the northern region of the GMA, the potentiometric surface has been stable from 2019-2024 with no evidence of a regional-scale cone of depression. A transect across Brown County from Northwest to Southeast shows a gradual decline from groundwater elevations at 230 m to 170 m. In contrast, the southern region of the GMA shows evidence for a regional cone of depression, with a steep gradient in the potentiometric surface in southeastern Outagamie County. While the cone of depression in the southern region of the GMA is not as extreme as the cone in the northern region in 2004-2005 (Figure 4A), it does persist from 2019-2024 and provides evidence that continued use of groundwater for municipal water supplies in the region will maintain a significant local depression in the potentiometric surface. The updated potentiometric surface maps will support decision-making by water managers in the Northeast Wisconsin GMA and can be used in conjunction with hydrograph data from specific wells in the region.

### Water Level Monitoring in the Northeast GMA

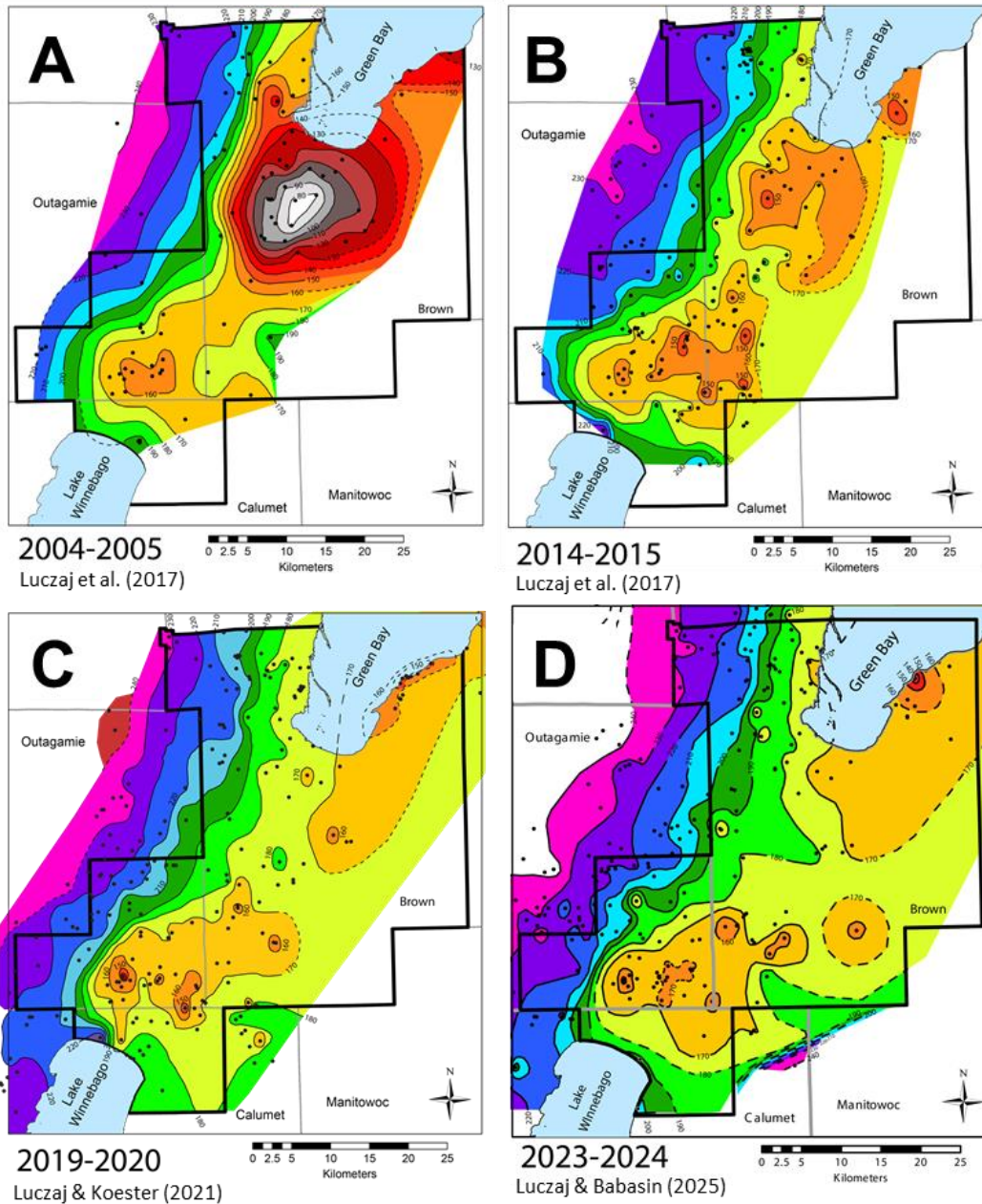
Most water level data available in the Northeast GMA come from either municipal wells during non-pumping conditions or from private well installations and abandonment logs, which do not yield time-series data. These records also have water level accuracy challenges (Luczaj et al., 2017), and for many municipalities, air lines used to measure water levels are no longer functioning after water level recovery in Central Brown County (aka the northern cone), resulting in a lack of data since about 2010.

There are only a few dedicated monitoring wells in the confined sandstone aquifer of the Northeast GMA in Wisconsin. More precise water level data are available from the USGS Active Bedrock Monitoring Network, which includes three wells at present, one of which was a replacement for the only long-term monitoring well in the GMA that was recently abandoned. Two of these wells are in the northern part of the GMA, while only one is near the southern cone at the Fox Cities. Several municipalities have also recorded static water levels in their wells (see below), which were typically supplied to WDNR. In addition, the Green Bay Water Utility has been taking static water level data since the early 20<sup>th</sup> century and were compiled previously (Luczaj et al., 2017) and through 2024 as part of this project. Table 2 summarizes trends in water levels in municipal and monitoring wells across the GMA.

Contour Interval = 10 m  
 (meters above sea level)

<80 m	100-110 m	130-140 m	160-170 m	190-200 m	220-230 m
80-90 m	110-120 m	140-150 m	170-180 m	200-210 m	230-240 m
90-100 m	120-130 m	150-160 m	180-190 m	210-220 m	>240 m

Potentiometric Levels



**Figure 4.** Potentiometric surface changes over time in NE WI GMA. Potentiometric surface in 2004-2005 (A), 2014-2015 (B), 2019-2020 (C), and 2023-2024 (D). Maps previously presented in Luczaj et al. (2017), Luczaj and Koester (2021), and this study (Luczaj et al. (2025)). Panels C and D indicate limited changes in the potentiometric surface, providing evidence of relatively stable conditions between 2020-2024, especially in the northern cone. Maps developed in ArcGIS and modified using Adobe Illustrator.

**Table 2.** Summary of hydrograph trends for the northern and southern regions of the Northeast GMA

<b>Northern Region of Northeast GMA</b>				
<b>Municipality</b>	<b>Well #</b>	<b>WUWN/ID</b>	<b>Trend (upward, downward, steady)</b>	<b>Rate (m/year) since 2020</b>
Green Bay	3	BF190	steady	steady
Green Bay	5	BF192	slight decline	1.6 meters/year
Green Bay	6	BF193	steady	steady, but variable
Green Bay	7	BF194	slight decline	1.6 meters/year
Green Bay	8	BF195	slight increase	0.4 meters/year
Green Bay	9	BF196	steady	steady
Green Bay	10	BF197	steady	steady
Pulaski	1	BF220	steady	steady
Pulaski	2	BF221	steady	steady
USGS-443035088045501		BN_0099	slight decline	< 0.2 meters/year, sinusoidal
USGS-442859088025801	NRRM-1	BN_0435	steady	steady, sinusoidal seasonally
<b>Southern Region of Northeast GMA</b>				
<b>Municipality</b>	<b>Well #</b>	<b>WUWN/ID</b>	<b>Trend (upward, downward, steady)</b>	<b>Rate (m/year) since 2020</b>
Brillion	1	BF249	steady, except upward since 2022	2.4 meters/year since 2022
Darboy	1	DG402	slight decline	≤ 1 meter/year
Darboy	3	HW895	slight decline	≤ 1 meter/year
Forest Junction	1	BF257	steady	steady
Forest Junction	2	WG311	steady	steady
Holland	2	CL048	slight increase	0.5 meters/year
Kaukauna	4	BG574	slight decline	0.93 meter/year
Kaukauna	5	BG575	slight decline	0.93 meter/year
Kaukauna	8	HJ196	slight decline	1.0 meter/year
Kaukauna	9	BG578- AY326	slight decline	0.63 meter/year
Kaukauna	10	BG576	slight decline	1.0 meter/year
Kimberly	1	BG579	variable (step decrease, then step increase)	step change
Kimberly	2	BG580	slight decline	step change
Kimberly	3	BG581	step increase	step change
Little Chute	1	BG582	step increase; mostly lower than long-term	variable
Little Chute	3	BG584	variable (step decrease, then step increase)	little overall; step changes
Little Chute	4	NG591- NQ265	decline, variable long term	2.26 meters/year
Kaukauna	-	ABQ564*	decline	> 2.72 meters/year
USGS-441642088163801	OU-21	AAJ872	decline	1.52 meters/year

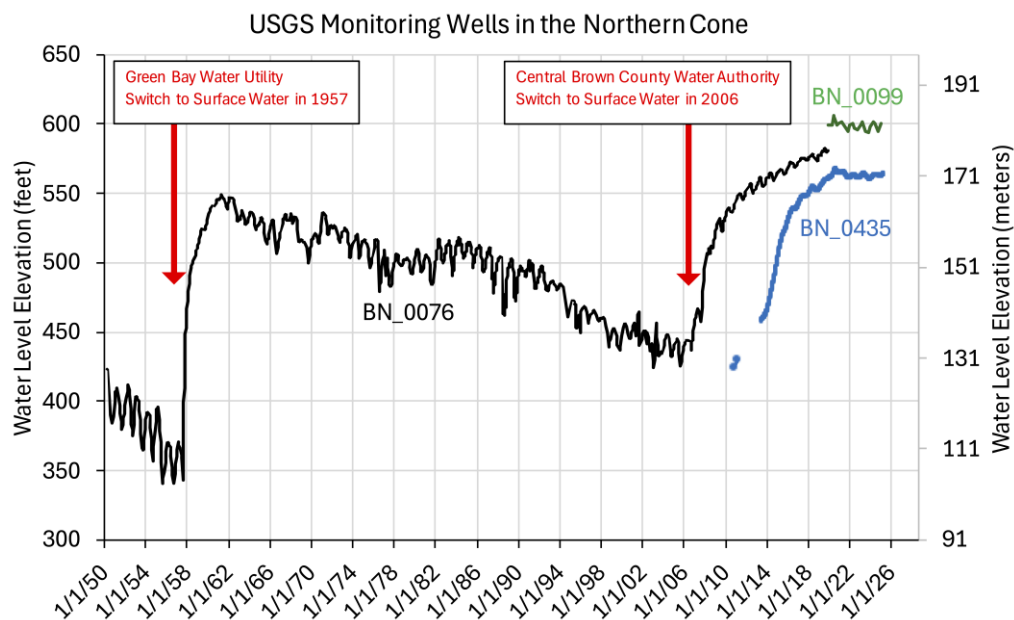
\* Indicates the new monitoring well drilled for this study that includes less than one year of monitoring data

### ***Northern Cone Hydrographs***

The northern cone of depression is located in Central Brown County, between Green Bay and De Pere, Wisconsin. Of the three wells in the northern portion of the GMA that were or are part of the USGS Active Groundwater Monitoring Network, only one provided a robust record of the two drawdown and recovery cycles that affected central Brown County during the 20<sup>th</sup> century (Luczaj et al., 2017) Figure 5. Historically, BN-24/20E/24-0076 - 443228088003101 was a well near the mouth of the Fox River at Green Bay with an excellent record from 1950 through the end of 2019 until it was abandoned. Though not in the center of the cone, it still reflected the major changes and annual water level fluctuations associated with seasonal

pumping variations. The replacement for this well, BN-24/20E/33-0099 - 443035088045501, which shows a similar trend, albeit with a small decline  $< 0.2$  m/year) since 2020 and stable water levels since 2021. One well near the northern border of the GMA in Suamico, Wisconsin (BN-25/20E/14-0890 - 443833088021801) is only 56 feet deep (open to the Sinnipee Group), but despite its similar long-term record, it does not likely have full communication with the confined sandstone aquifer and is therefore not included in this study.

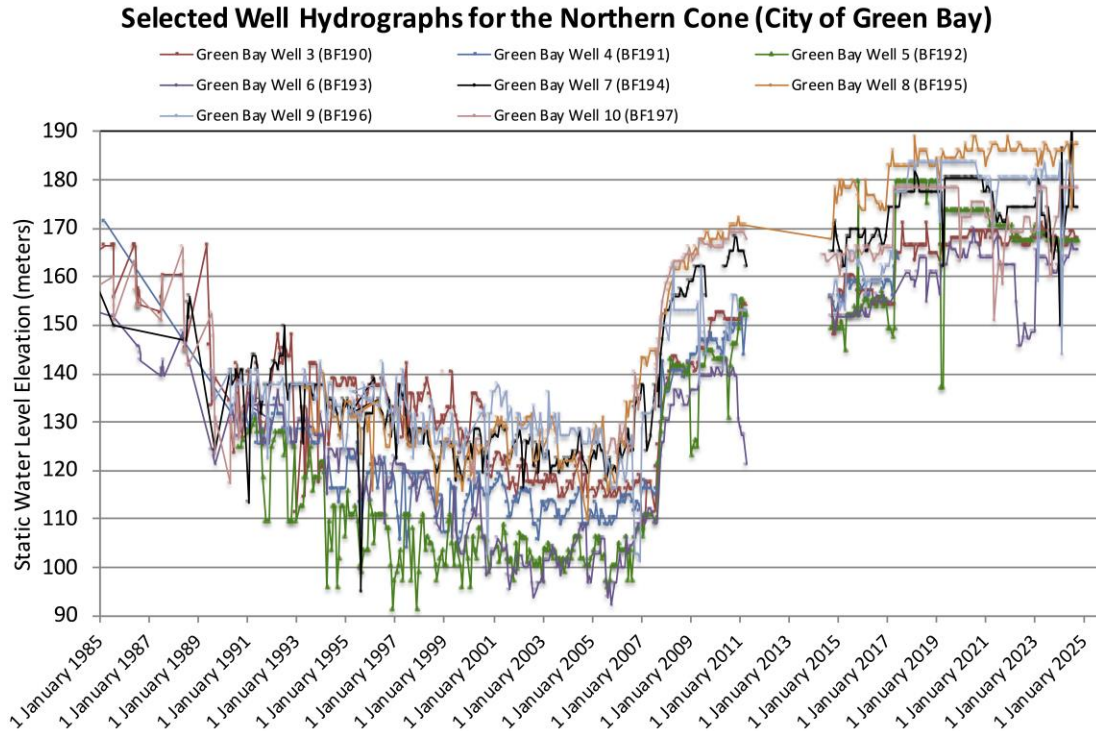
Near the center of the northern cone, a newer monitoring well penetrates the confined sandstone aquifer at the National Railroad Museum (BN-23/20E/10-0435 - 442859088025801), drilled as part of a county-wide bedrock monitoring project (Luczaj, 2011). This well was installed after the majority of water level recovery had occurred after the 2006-2007 switch to surface water, but a substantial amount (~46 m or 150 feet) of recovery continued until at peak in July 2020, after which, water levels have been roughly stable (Figure 5).



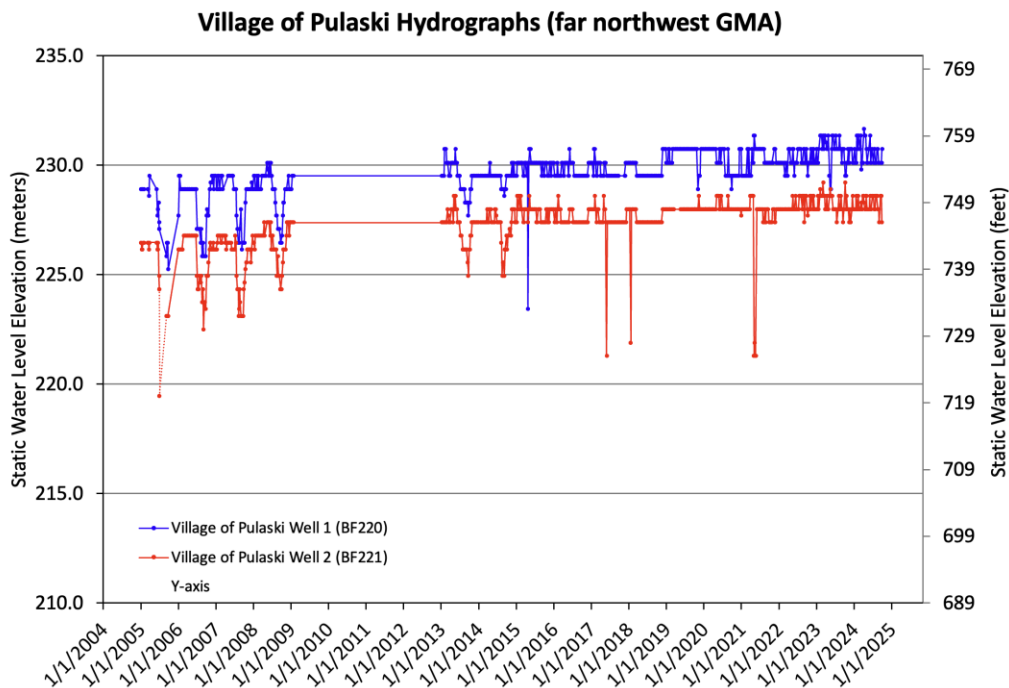
**Figure 5.** Hydrographs for three current and historic USGS Monitoring Wells in Central Brown County.

Eight wells owned by the Green Bay Water Utility are on emergency backup status, and their water levels are monitored monthly by the utility. A robust set of hydrographs shows relatively similar behavior (Figure 6) following the post-2006-2007 recovery. These wells also show mostly stable water levels since about 2020. Numerous additional municipal wells in the confined sandstone aquifer of central Brown County can no longer be monitored due to well abandonment or lack of water level monitoring capabilities. Additional data can be seen in Luczaj et al. (2017) and references therein. The Village of Pulaski (northwest corner of the GMA) is the only remaining well with a long-term water level record (Figure 7).

Numerous reports of flowing artesian wells have occurred in the northwestern part of the northern cone, beginning in 2009 with a municipal well in the Village of Howard. In addition, three confined aquifer wells at Barkhausen Nature Preserve flow, at least seasonally, and numerous private wells have been reported and observed to be flowing northwest of Green Bay. Three of Green Bay's wells (#5, BF192, #9, BF196, #10, BF197) have had water levels at or above ground level episodically in 2017-2019, 2023 and 2024. Of these 3, only wells #9 and #10 have continued this trend in 2023-2024.



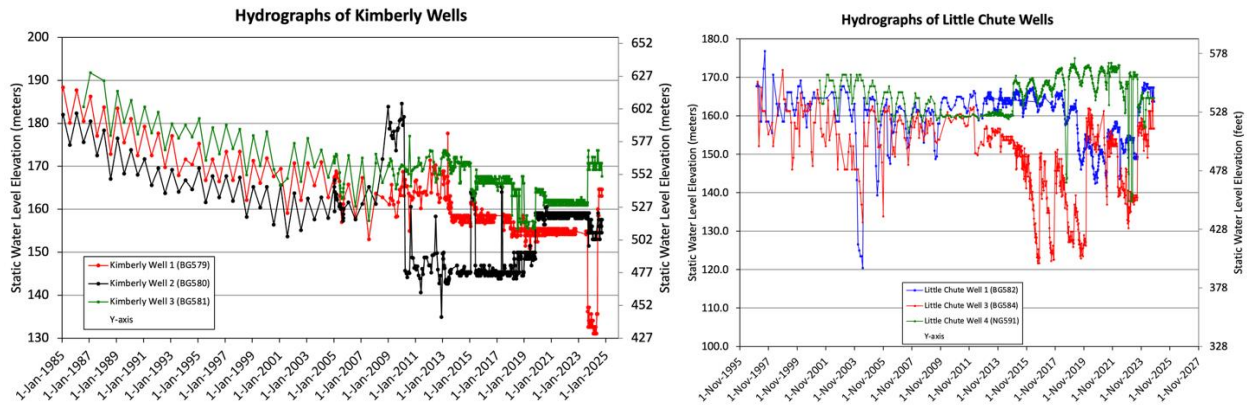
**Figure 6.** Well hydrographs for Green Bay Water Utility municipal wells (on emergency backup status) in central Brown County (Northeast GMA). The post-2006 water level recovery is clearly documented, as a result of neighboring municipalities switched to surface water in 2006-2007 (CBCWA), 2011 (Hobart), and 2015 (Wrightstown). Water levels have been roughly stable since 2020.



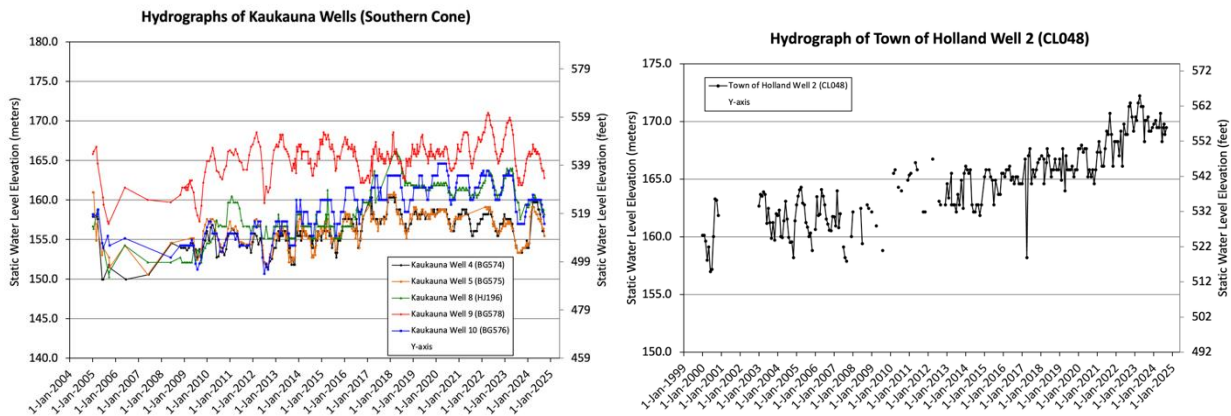
**Figure 7.** Well hydrographs for Pulaski, Wisconsin (northwest corner of the GMA). Water levels are stable or slightly increasing over time and are far enough away that they showed little change due to the 2006-2007 switch to surface water by the CBCWA.

## Southern Cone Hydrographs

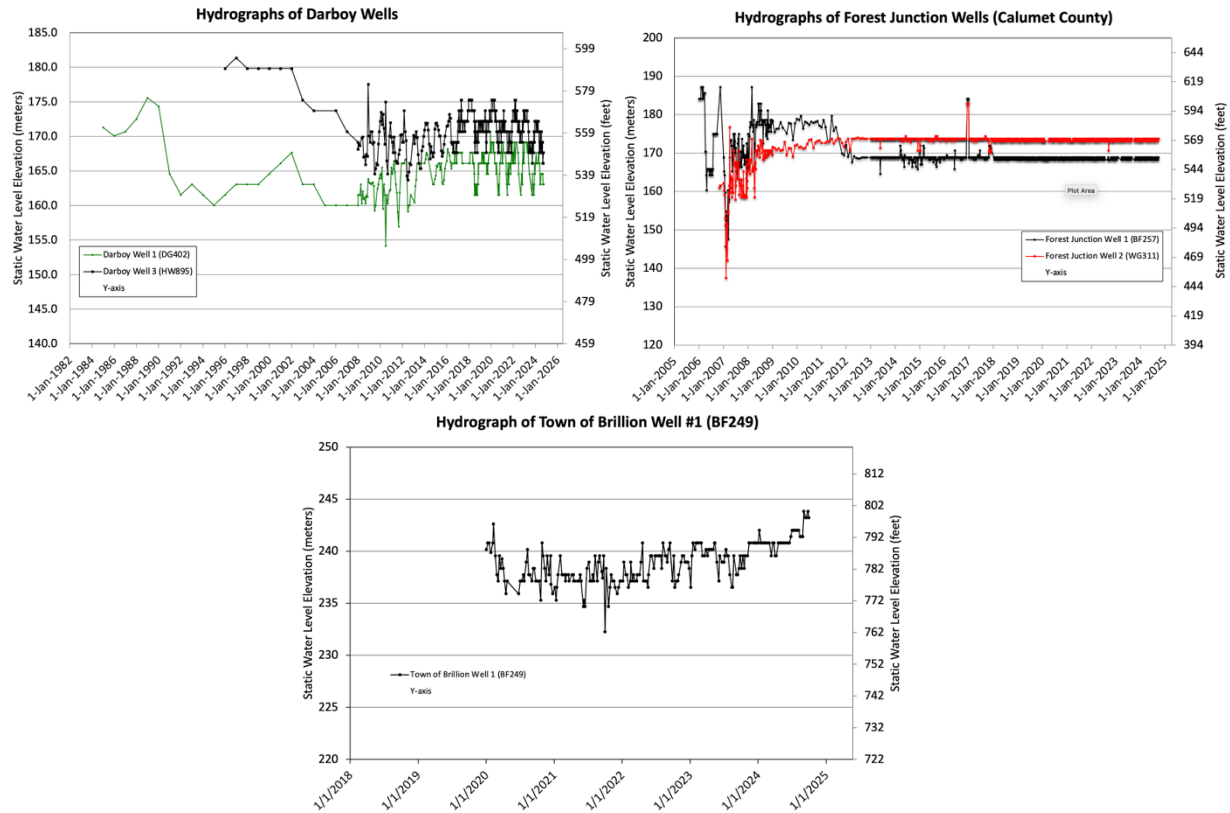
The southern cone of the Northeast GMA is located near the Fox Cities (e.g., Kaukauna, Kimberly, Little Chute, etc.). Most of what is known about water levels in this part of the GMA comes from available municipal water level data and newly installed private wells. Only one recently installed monitoring well is part of the USGS Water Level Monitoring Network in the southern half of the GMA (AAJ872), which has been recording water levels since 2022. Hydrographs were made for 17 municipal wells in the southern half of the Northeast GMA (Figures 8-10). Wells show a variety of conditions, but mostly stable to falling water levels near the southern cone, suggesting an unsustainable condition there.



**Figure 8.** Well hydrographs for the villages of Kimberly (left) and Little Chute (right). Wells show considerable variability, possibly due to variation in pumping. Kimberly wells have reached new lows during the past decade (now nearly 20-years after the CBCWA switch) and generally show long-term declining water levels. Little Chute wells are more variable but also show new lows during the past decade. In both, figures, water level fluctuations/declines are as much as 13 to 35 m since about 2010.

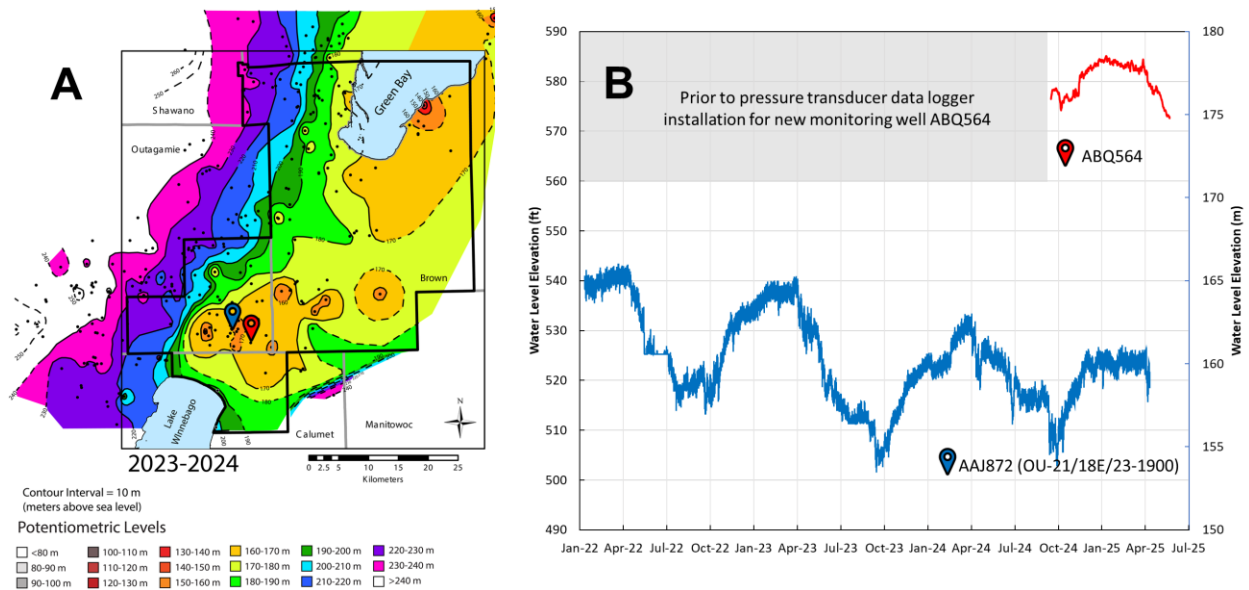


**Figure 9.** Well hydrographs for the Village of Kaukauna (left) and Town of Holland (right). These two wells exhibit relatively stable water levels in some wells, with others (HJ196, BG576, and CL048) showing marked increases, particularly since about 2015. This may be due to the close proximity of these two communities to the Village of Wrightstown, which switched from groundwater to surface water supplies (via Green Bay Water utility) in 2015. However, these water level recoveries are all < 10 m, so the magnitude of change is less than shown in the figure above.



**Figure 10.** Well hydrographs for the Village of Darboy (upper left), Forest Junction (upper right), and Brillion (lower center). The wells for Darboy and Forest Junction exhibit relatively stable water levels over time. In the case of Forest Junction, stability is likely due to the relative distance from the center of the cone. For the City of Brillion, water levels have been mostly stable, showing a rise of several meters in the past few years, likely due to local water use changes that are unrelated to the regional cone of depression.

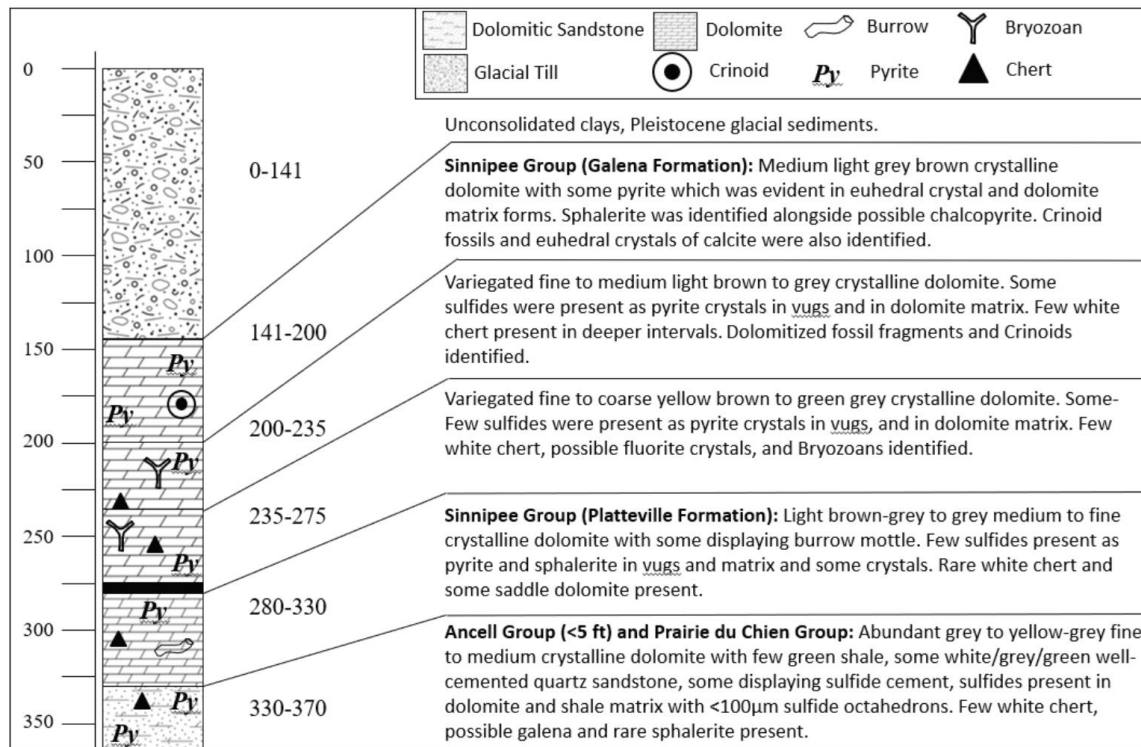
Figure 11 shows the two dedicated monitoring wells now present in the southern half of the Northeast GMA. One USGS Monitoring Network well located in La Follette Park in Kaukauna (OU-21/18E/23-1900 – 441642088163801) has a continuous water level record since 2022. In addition, this WDNR funded project involved the installation of a second monitoring well in late 2023 (WUWN: ABQ564), which has enhanced the monitoring capabilities of the southern part of the GMA. Although the new well does not yet have a complete year of data, both wells appear to show the same seasonal cyclicality in water levels relating to seasonal changes in confined aquifer pumping (see Luczaj et al., 2017).



**Figure 11.** Groundwater levels in monitoring wells in southern cone in NE WI GMA. The new potentiometric surface map from 2023-2024 with markers for well locations (A), water levels from monitoring well AAJ 872 (OU-21/18E/23-1900 – 441642088163801) in La Follette Park, Kaukauna the new monitoring well ABQ564 on County Road CE near Haas Road in Buchanan (B). Grey coloring in B indicates time prior to data collection for ABQ564. Data from AAJ872 is from United States Geological Survey and is only available through April 15<sup>th</sup>, 2025.

## New Monitoring Well Cuttings Characterization and Water Levels

During the installation of the new monitoring well (ABQ564), the driller indicated unconsolidated clays and gravel-bearing clays overlying the Sinnipee, Ancell, and Prairie du Chien groups. Casing was set the day before bedrock drilling and cuttings observations were conducted. Cuttings of bedrock were collected every 5 feet in large sealable plastic bags, with selected intervals collected in 5-gallon buckets. The well was drilled to a depth of 397 feet (driller reports 400 feet, but they measured from top of casing). The first bedrock encountered was brown to gray dolostone, which is interpreted to be part of the Galena Formation. Dolostone continued, as expected into the Platteville Formation, reaching base of the Platteville at approximately 330 feet below ground level where quartz sandstone was observed in the cuttings (with some pyrite-cemented sandstone). Because of the abundance of dolomite in samples immediately below this layer, and the presence of oolitic chert observed in the 333-338 foot sample, we interpret that the Ancell Group is likely < 5 feet thick at this location and most of what was intercepted is the Prairie du Chien Group mixed carbonate-clastic system. Although dominantly dolostone, the Prairie du Chien Group has abundant thin sandstone layers throughout, based on observations of cores and outcrops elsewhere in northeastern Wisconsin. Some layers (353-358 feet and 363-368 feet) contained abundant sandstone. Although there is some evidence of sulfide cement horizon mineralogy, and the thickness of the Ancell group was significantly smaller than thicknesses indicated on WCRs from other nearby wells, it is important to note that pyrite and other sulfides were observed in most of the bedrock intervals encountered in the well. Despite the thin layers of sandstone in the Ancell and Prairie du Chien groups, these layers appear to be in communication with the sandstone aquifer, based upon the similarity in the pattern of seasonal water levels for the southern cone and the close match to water levels expected nearby (Figure 11B).



**Figure 12.** Well cuttings characterization summary. Full characterization information included in Appendix C.

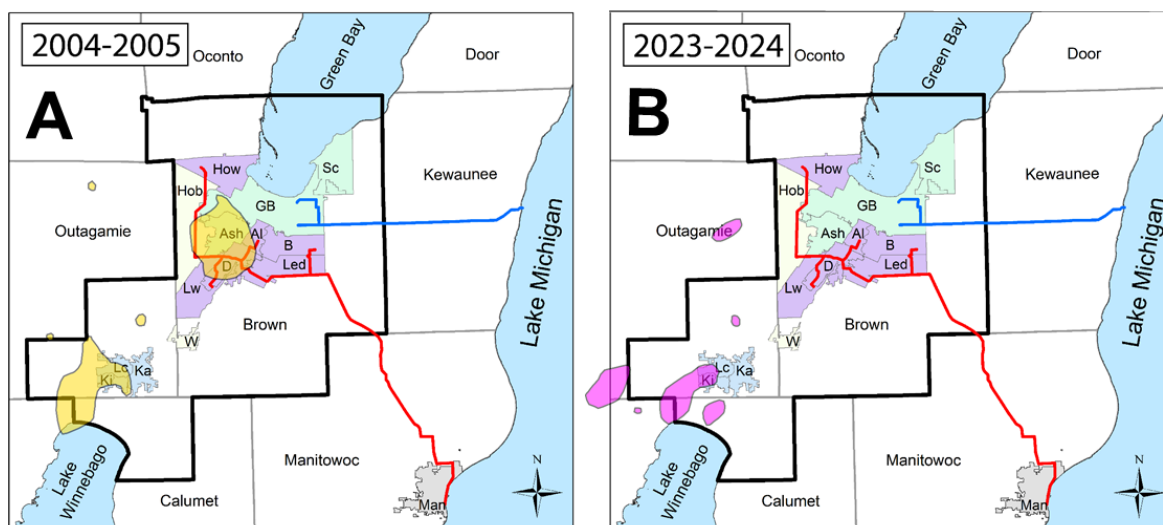
One of the main objectives for the new monitoring well, ABQ564, was to improve monitoring of the potentiometric surface in the southern region of the GMA. An existing USGS monitoring well, AAJ872, in La Follette Park, Kaukauna is further west than ABQ564 (Figure 11A) and has shown a declining trend in water elevations over the past three years (Figure 11B). Recent monitoring of water level elevations in ABQ564 show water level fluctuations over time that mirror AAJ872, but with less drawdown. This is expected, as ABQ564 was drilled at a site further from the center of the cone of depression in the southern region of the GMA. The seasonal increase in groundwater levels from October 2024 to April 2025 are observed in both monitoring wells, which could be evidence that ABQ564 is in the same aquifer system as AAJ872, as expected, just farther east. Data is not yet available for AAJ872 in May 2025, but ABQ564 shows continued water level decline from April into May 2025. Water level elevations in ABQ564 are also slightly higher (~10-20 ft) than that predicted from the potentiometric surface map (Figure 4D), but it is likely that summer water levels will continue to decrease and show better agreement with the potentiometric surface map from 2023-2024. Future continued monitoring of the water levels in both monitoring wells will provide information that will help water managers evaluate if the southern region of the GMA is experiencing continued drawdown.

### Potential for Dewatering of the Ansell Group

Using a preliminary Structure Contour Map for the base of the Sinnipee Group (See Appendix E), water level maps for 2004-2005 and 2023-2024 were used to generate regions where the potentiometric surface in the Cambrian-Ordovician confined sandstone aquifer is below the Base of the Sinnipee Group (Figure 13). This is a way to show where the Ansell Group has been “dewatered”, and therefore where the most mineralized portion of the secondary

sulfide cement horizon (SCH) may be susceptible to oxidation. Figure 13A shows a significant part of the northern cone to be dewatered in central Brown County, along with regions near the western Fox Cities (i.e., Kimberly, Appleton, Menasha) and sporadic areas west of the GMA. Unplanned confirmation of dewatering of the St. Peter Sandstone in central Brown County was made using a down-hole camera during late 2010 after installation of BN\_0435 at the National Railroad Museum. Following the recovery of the switch to surface water by the CBCWA, the dewatered area is no longer present in Figure 13B.

The southern cone near the Fox Cities has had a prolonged period of dewatering. A map generated for the year 2000 (not shown here) shows a small area near Kimberly, Wisconsin to have dewatered Ancell Group, but by 2004-2005, this had reached a more significant footprint (Figure 13A). The region of dewatered Ancell Group has remained roughly similar through 2023-2024 (Figure 13B).



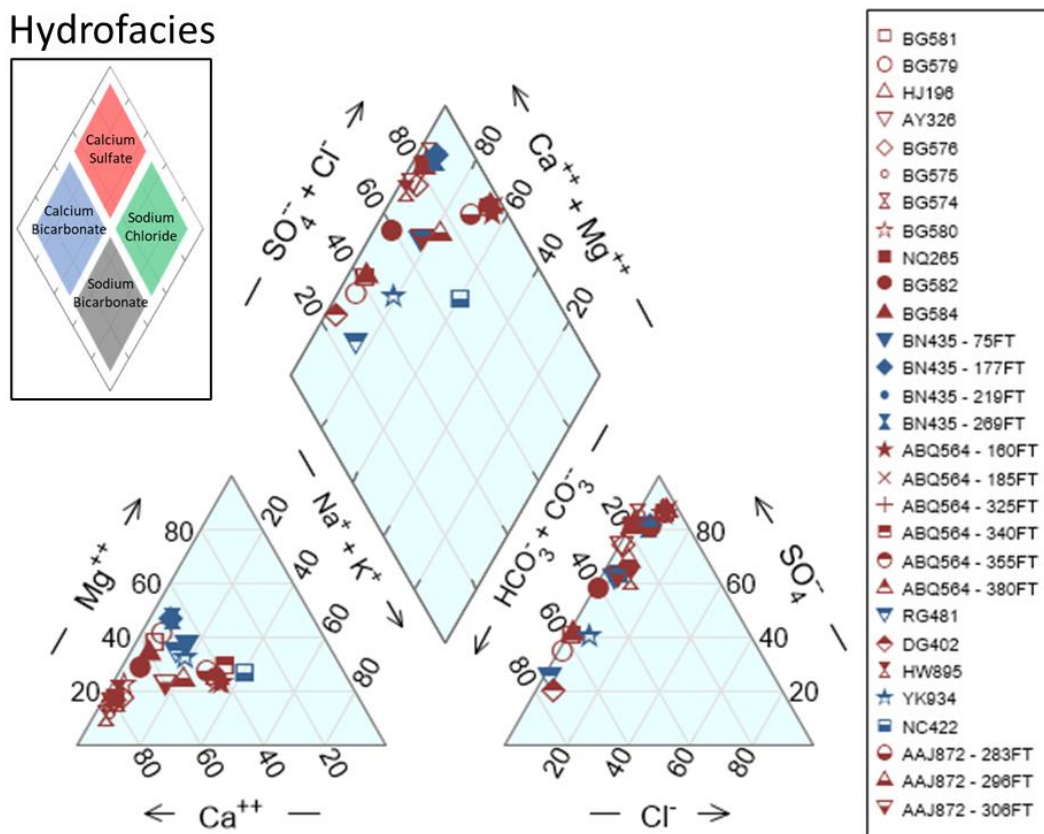
**Figure 13.** Regions of potential Ancell Group dewatering based on comparison between structure contours of base of Sinnipee (Appendix E) and potentiometric surface maps (Figure 4). Possible regions of dewatering in the Northeast GMA in 2004-2005 are shown with polygons shaded in bright yellow (A) and in 2023-2024 are shown in polygons shaded in bright pink (B).

It is important to note that these regions of dewatering that are drawn in Figure 13 are minimum, conservative estimates, especially for the southern cone region. There are several reasons for this. First, water level elevations for municipal wells (near the center of these cones) are averages of static water levels recorded in the 2024 data. Significant ups and downs of some wells would put static water levels somewhat lower during certain episodes of variable pumping, etc. In addition, data supplied by WDNR for these wells indicates that active pumping conditions result in water levels that are 80 – 175 feet lower than the static water levels used to generate the hydrographs shown in this report. As a result, the actual size of the dewatered Ancell region may be somewhat larger than shown in Figure 13.

### Well Water Chemistry Across the GMA

Water chemistry in the 19 wells sampled in this study show most waters are calcium sulfate to calcium carbonate waters with some clustering of cations for the northern GMA and southern GMA waters. Figure 14 shows a piper diagram for the water chemistry in the sampled wells. Some of the northern GMA wells, indicated with blue markers, cluster as being more

magnesium rich in the cation ternary, but many more samples would be required for a comparison in water quality with statistical power. One major limitation of this representation is that it does not include strontium concentrations. The majority of samples in this study have relatively high strontium concentrations, with only three being below the EPA lifetime health advisory limit of 4 mg/L. Only 6 of the 19 wells sampled had arsenic detections, including wells in the southern (Kimberly, Kaukauna, and Little Chute) and the northern (Green Bay) regions of the GMA. A full summary of ion concentrations and water quality field measurements can be found in Appendix D.

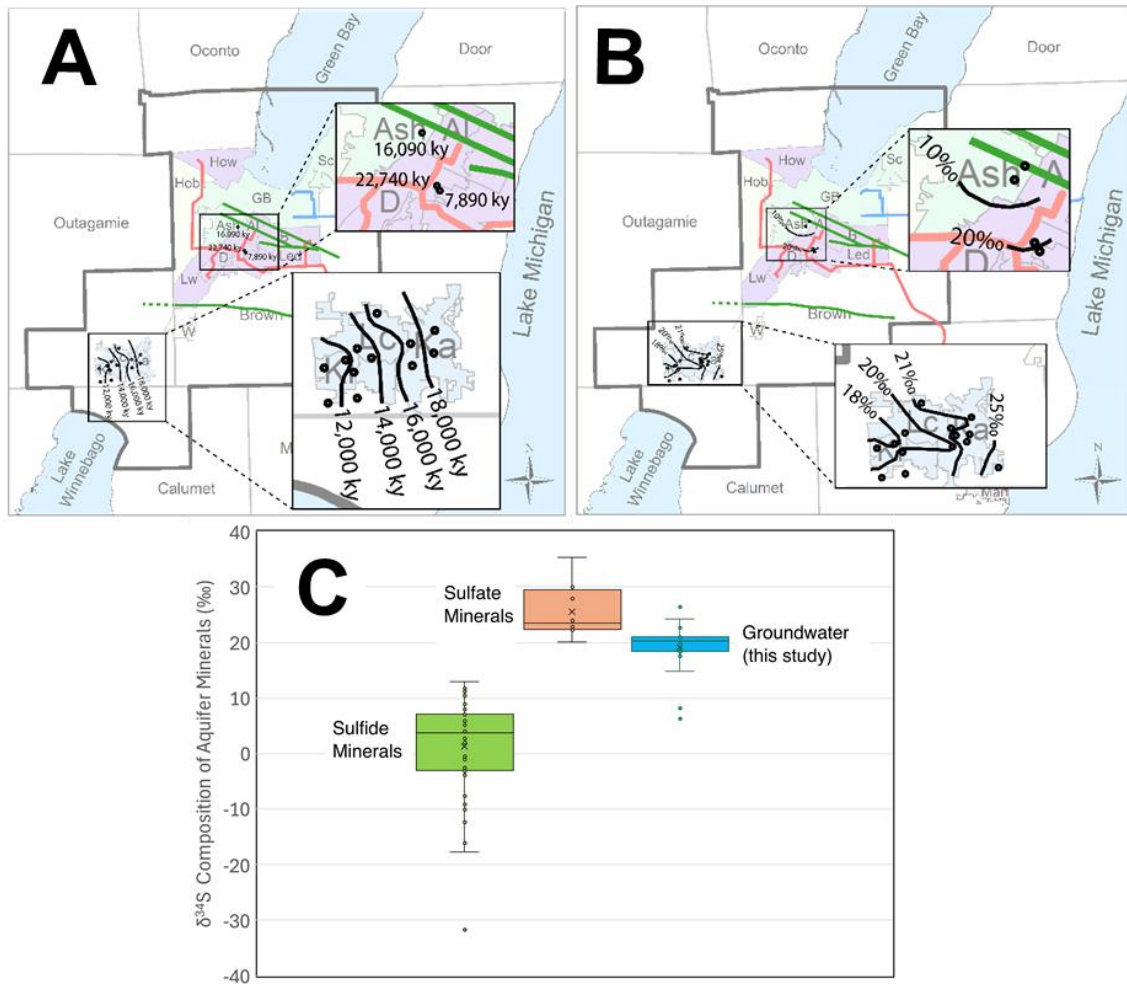


**Figure 14.** Piper diagram indicating relative amounts of major cations and anions in wells sampled in the NE WI GMA for this project. Blue markers indicate samples from the northern region of the GMA, and red markers indicate samples from the southern region of the GMA. Representation developed using Geochemist's Workbench.

In addition to general chemistry and trace metals, the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  composition of groundwater in the confined sandstone aquifer was analyzed from 19 wells to place the waters into a regional water isoscape under development by co-PI Luczaj (Luczaj et al., 2021). Samples were also analyzed for stable isotopic compositions of sulfur and oxygen of dissolved sulfate. Radiocarbon age dates on DIC (dissolved inorganic carbon) were obtained for wells that could be appropriately sampled by removing at least one well volume of water prior to sampling without atmospheric interference. These results are summarized in Appendix D, Table D3.

Radiocarbon age dating of DIC (uncorrected results presented here – future published results will model all regional data), coupled with  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopes for water, reveals that the aquifer contains considerably old water, consistent with previous research in the northern portion of the GMA that suggests subglacial groundwater recharge as the source of Pleistocene

age water in the confined aquifer beneath the GMA (Grundl et al., 2013; Luczaj et al., 2021). The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  composition of groundwater in the confined sandstone aquifer was analyzed from 19 wells to place the waters into a regional water isoscape under development by co-PI Luczaj (Luczaj et al., 2021). Although the data appear generally consistent with existing regional data, some wells (Darboy and Kimberly, specifically) appear to contain water that is isotopically slightly heavier than expected. A strong inverse correlation ( $R^2 = 0.78$ ) between the uncorrected radiocarbon ages and their  $\delta^2\text{H}$  isotopic compositions, as expected due to climate changing across the late Pleistocene-Holocene boundary. Wells farther west and south in the GMA (e.g., Kimberly and Darboy) have slightly younger ages than Kaukauna's wells that are farther down-dip.



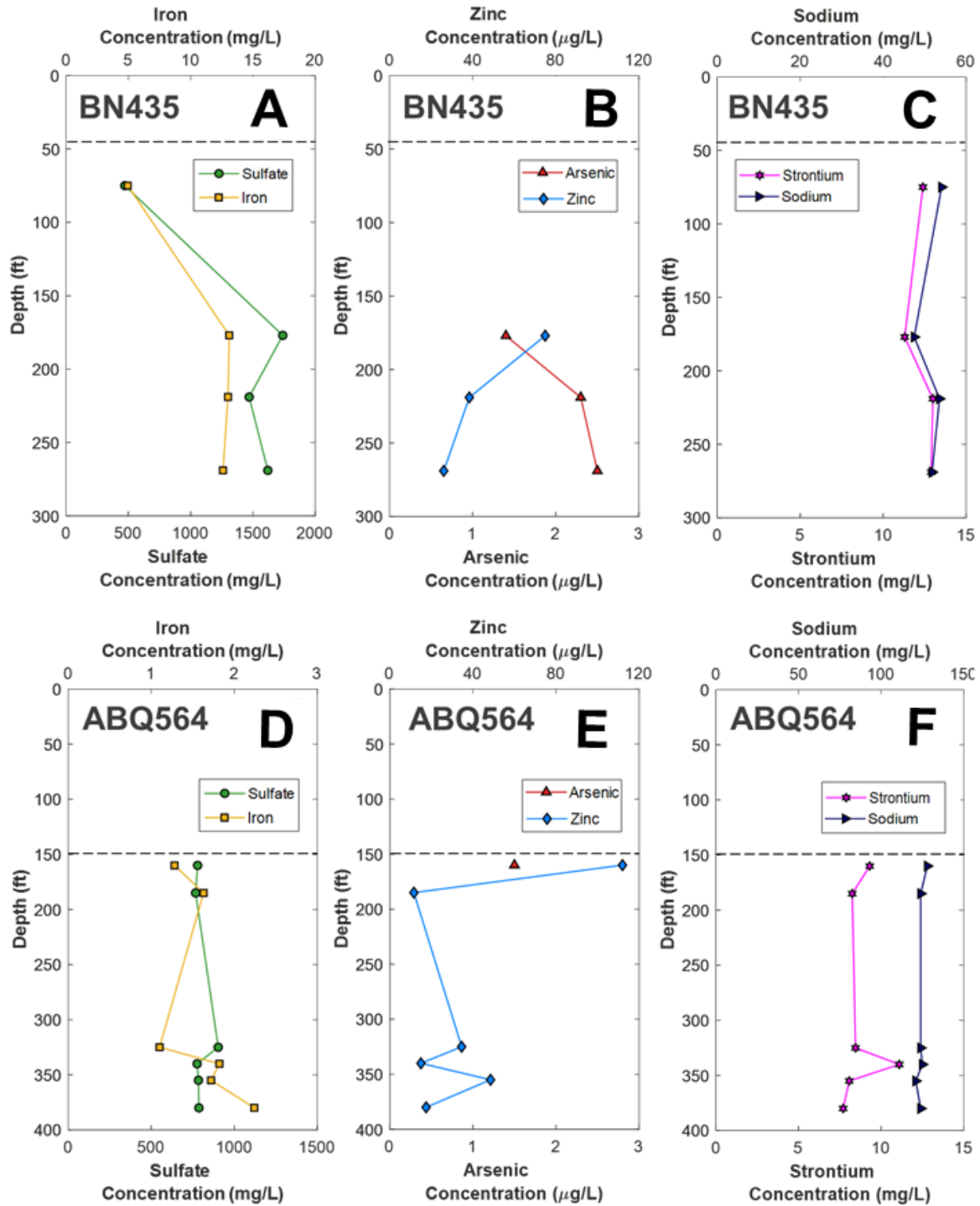
**Figure 15.** Regional trends in radiocarbon and sulfur isotopes. The uncorrected Radiocarbon age dates for dissolved inorganic carbon (DIC) in groundwater (A), the  $\delta^{34}\text{S}$  composition of groundwater across the GMA (B), and typical  $\delta^{34}\text{S}$  isotope composition for different sulfur minerals (C). Inset maps in 15A and 15B show expanded areas for each study area. For  $\delta^{34}\text{S}$ , values in the northern cone show significantly lighter isotopes ( $\ll 20\text{‰}$ ) toward the center of the cone, though data are limited. In the southern cone, a clear regional progression toward heavier  $\delta^{34}\text{S}$  values toward the east is consistent with unpublished data for other wells. Wells farthest west (i.e., Kimberly) show a greater contribution from sulfide-derived sulfate because their  $\delta^{34}\text{S}$  composition is  $< 20\text{‰}$ . Data in 15C for the  $\delta^{34}\text{S}$  composition of northeastern Wisconsin sulfide minerals is from Luczaj (2006), Luczaj and Huang (2018), and Luczaj (unpublished).

The  $\delta^{34}\text{S}_{\text{VCDT}}$  composition of dissolved sulfate in wells can be used as a fingerprint to determine whether sulfide oxidation has occurred because the isotopic composition of sulfide and sulfate minerals in the aquifer is totally different. The  $\delta^{34}\text{S}$  composition of dissolved sulfate in wells was also determined for water samples from across the Northeast GMA (Grundl et al., 2013; Luczaj et al., 2021; Luczaj, unpublished). Overall, most samples analyzed fit well into the existing regional  $\delta^{34}\text{S}$  isoscape developed by Luczaj et al. (2021), indicating a two-source system for sulfate that includes sulfide oxidation near the recharge area to the west, along with a progressive sulfate dissolution source as water migrates eastward down-dip in the confined aquifer (Figure 15). In the 2024 sample set, most water samples from municipal and other high-capacity wells behaved as expected, with a few exceptions. Two wells showed some distinctly different  $\delta^{34}\text{S}$  values that might be indicative of anomalous sulfide oxidation in the northern cone of depression near Green Bay. Specifically, the  $\delta^{34}\text{S}_{\text{VCDT}}$  values for two wells (RG481 and National Railroad Museum Observation Well (USGS 442859088025801 BN-23/20E/10-0435)) yielded values of 8.13‰ and 6.27‰, respectively. These  $\delta^{34}\text{S}$  values are considerably lower than expected and overlap with values expected for sulfide oxidation as a source of dissolved sulfate. In the case of the National Railroad Museum observation well, elevated sulfate concentrations are consistent with this interpretation, as are observations made by co-PI Luczaj during the 2010-2011 field season in which dewatering of the St. Peter Sandstone was directly observed in the well. In addition, Kimberly #1 and #3 wells appear to have somewhat lower  $\delta^{34}\text{S}$  compositions than other wells in the southern portion of the GMA. Their values (17.66‰ and 18.39‰, respectively) are below the reported  $\delta^{34}\text{S}$  range for sulfate minerals (minimum 20‰) (Figure 15). These wells fall within the dewatered area (Figure 13B), which is consistent with at least some sulfide oxidation contributing to the dissolved sulfate in the aquifer.

Radiocarbon age dates are presented as unmodeled and uncorrected ages. The ages in the southern cone show a clear progression toward older ages moving eastward, consistent with Grundl et al. (2013) and unpublished data. Ages in the northern cone are too limited to contour but show a younger age for an irrigation well that is open to the St. Peter Sandstone. The other two wells are cased deeper and are only open to the Cambrian.

The three monitoring wells in this study allowed for development of water chemistry depth profiles. The approach to use discrete depth sampling was a shift from the initial proposed work to use a down well water quality sonde that is capable of evaluating continuous profiles of pH, ORP, conductivity, and other parameters. This rental equipment was unavailable due to damage during the proposed study timeframe, so discrete depth samples were evaluated instead. Discrete depth samples were only informative because borehole vertical flow was deemed negligible using a heat pulse flow meter in all three monitoring wells: ABQ564, AAJ872 (OU-21/18E/23-1900), and BN435 (WGNHS Well ID: 5000435). It was assumed that water sampled at the discrete depths represents formation water associated with those stratigraphic layers, but this can be confounded by variability in hydraulic conductivity of different stratigraphic layers and mixing in the borehole. Despite these limitations, the low flow pump did provide samples that showed evidence of variations in water chemistry with depth (Figure 11). Changes in iron and sulfate concentrations (Figures 11A & 11D) indicate depths where iron sulfide mineralogy may be more relevant. For example, in well BN435 (USGS-442859088025801), elevated arsenic (Figure 11B) is associated with increases in sulfate and iron concentrations. The depth profiles may also provide evidence for stratigraphic units where higher levels of strontium may be sourced (Figure 11F). As sodium remains relatively constant for ABQ564 at a depth of 340 ft,

the strontium increases. This could be initial evidence for stratigraphic layers that are important controls on well water chemistry.



**Figure 16.** Depth profiles of dissolved ions in discrete depth water samples from monitoring wells BN435 in Green Bay (A-C) and ABQ564 in Buchanan (D-F).

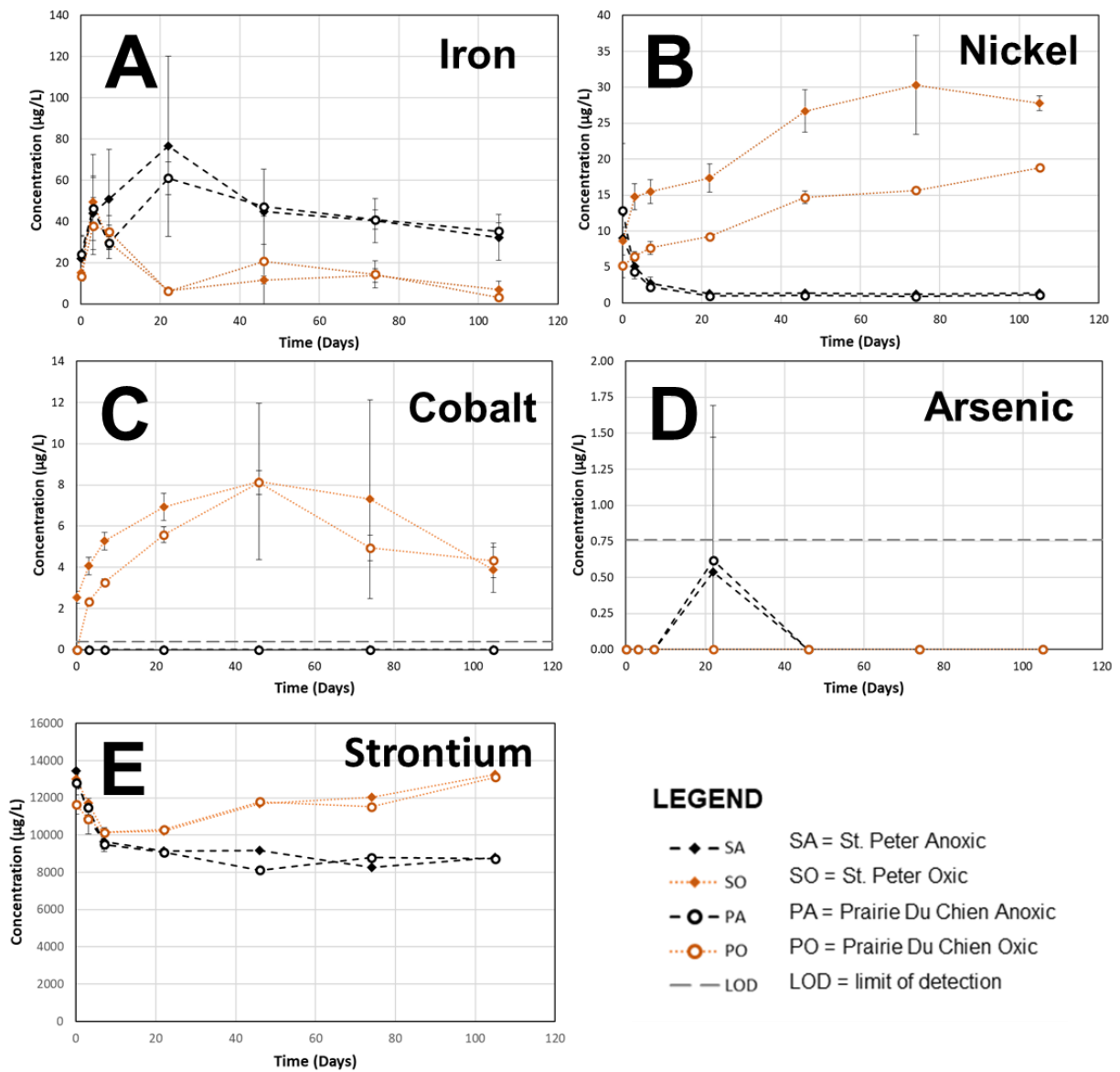
## Batch Leaching Experiments Time Series

A suite of batch leaching experiments with well cuttings from ABQ564 were evaluated for changes in dissolved metals concentrations under both oxic and anoxic conditions. Only the metals that showed changes over time that differed for oxic and anoxic conditions are presented in Figure 17. Relatively higher iron concentrations were observed for both sediment types (St. Peter and Prairie Du Chien) under anoxic conditions (Figure 17A). This was expected, as oxic experiments are more likely to form iron oxides, decreasing aqueous iron concentrations. Nickel and cobalt (Figures 17B and 17C) increased over time for the oxic experiments, with cobalt decreasing at later experimental times potentially indicating precipitation of cobalt starting after day 45. The St. Peter oxic experiments also had significantly higher nickel leaching than the Prairie du Chien (Figure 17B). Anoxic experiments showed only decreases in nickel and cobalt over time. The higher observed concentrations of nickel and cobalt under oxic conditions is important evidence for evaluating the potential for metals release when aquifers shift from anoxic to oxic conditions. Schreiber et al. (2000) also observed increases in nickel and cobalt in their oxic leaching experiments from oxidative dissolution of iron sulfide minerals in the secondary sulfide cement horizon (SCH). While concentrations of cobalt and nickel in this study are considerably lower, this is likely because cuttings from well ABQ564 had less sulfide mass than SCH samples from Schreiber et al. (2000).

Arsenic was intended to be the focus of this study, but cuttings from ABQ564 showed negligible arsenic release over time in the batch leaching experiments. Anoxic experiments may have shown a small increase in arsenic at day 22 (Figure 17D), but these concentrations were below the limit of detection (LOD). Previous research has shown that arsenic can be released from iron minerals under oxic and anoxic conditions (Gotkowitz et al., 2004; Schreiber et al., 2003; Schreiber et al., 2000), and that released arsenic can readily readsorb onto iron oxide minerals (Schreiber et al., 2000). The batch leaching experiments in the present study could have captured temporal variations in arsenic with an experimental design with more frequent sampling; as conducted, the experiments did not show evidence for arsenic release under either oxic or anoxic conditions. Limited arsenic was also expected, as the water chemistry for ABQ564 showed low concentrations of arsenic (1.5 µg/L) and only at the very top of the well (Figure 16E); water deeper in the well showed arsenic below detection limits (Appendix D). Samples are also being evaluated for initial metals concentrations in the well cuttings. It is possible that the stratigraphic layers used for the batch experiments had sulfides with limited isomorphous substitution of arsenic.

Changes in strontium concentrations were also observed in the batch leaching experiments. Both oxic and anoxic experiments showed an initial decrease in strontium, but at later times the oxic experiments showed an increase in strontium while anoxic experiments continued to decline (Figure 17E). The mechanism controlling this difference is uncertain, but future geochemical equilibrium speciation simulations in PHREEQC will likely provide insight.

Two additional sets of aquifer sediments were used for a second suite of oxic and anoxic batch leaching experiments. Cuttings and rock samples selected for the additional leaching experiments are from regions with higher sulfide content, and will be used as a comparison to the cuttings from well ABQ564. These additional batch leaching experiments are ongoing, and results will be presented in the graduate student's Master's thesis upon graduation.



**Figure 17.** Concentrations of selected metals from batch leaching experiments. Concentrations of iron (A), nickel (B), cobalt (C), arsenic (D), and strontium (E) are presented over time for the 105-day experiment.

## CONCLUSIONS AND FUTURE WORK

Updated potentiometric surface maps and hydrographs for available municipal and monitoring wells in the GMA indicate that the northern cone (central Brown County) has now stabilized since about 2020, while the southern cone (Fox Cities) ranges from slightly expanding and deepening to stable, depending on the specific area of the southern GMA. Our installation of a new monitoring well in the southern cone of the GMA was successful, and the well should provide an important long-term monitoring point.

Water quality and isotopic data suggest that, despite evidence for dewatering of the Ancell Group near both cones of depression, there is no evidence for oxidative release of heavy metals (As, Ni, Co, etc.) that would exceed regulatory limits in the aquifer at the present time for the wells analyzed. Radiocarbon ages for dissolved inorganic carbon yielded old (>10,000 years) ages consistent with the rest of the confined aquifer in northeastern Wisconsin. This suggests that there has been limited recharge across the Sinipee-Pleistocene aquitard in the GMA, at least up to this point. However, there is evidence for limited oxidative release in the northern cone, based upon Sulfur-isotope data and dissolved arsenic that was coassociated with iron. This part of the GMA experienced multiple dewatering episodes (1950s and 2000s) that persisted for a longer period of time, compared to the southern cone near the Fox Cities. In the wells we targeted in the southern cone, wells closer to the dewatered region (i.e., Kimberly) showed the lightest Sulfur-isotopes that were consistent with at least some oxidatively-sourced sulfate.

Batch leaching experiments conducted on monitoring well cuttings from the new monitoring well yielded low concentrations of cobalt and nickel, with negligible arsenic. The release of metals only occurred in oxic experiments, supporting the idea that the release of these metals is associated with sulfide oxidation. The reasons for the limited arsenic release are unclear, but resorption of the As onto oxide minerals is a likely explanation. This could be because the cuttings we used had As-poor Fe-sulfide mineralization, but additional batch experiments on cuttings from other wells and whole-rock digestions of well cuttings are ongoing to answer this question.

Future research will synthesize data from this study and the previous studies to further characterize the aquifer system. The data acquired during this grant research will be used in conjunction with other unpublished data to evaluate regional groundwater quality trends, aquifer connectivity and fault compartmentalization, and groundwater flow histories.

We recommend continued monitoring of water levels and metals concentrations across the GMA, especially near the southern cone. The fact that there are significant areas with potentially dewatered Ancell Group and/or Prairie du Chien Group sulfide mineralization suggests that the release of metals is a real possibility and future concern, especially if conditions become more oxic in the future. For now, groundwater ages remain old in most of the cone areas, indicating breakthrough/leakage through the confining layer (Sinipee Group) has been limited thus far.

## **ACKNOWLEDGEMENTS**

UW-Green Bay graduate student Sean Babasin was responsible for evaluating well cuttings, conducting batch leaching experiments, and collecting Levelogger data from the new monitoring well. He helped write some of the methods for this report. We would like to thank Sean for his commitment and hard work on this project and forthcoming thesis.

We would like to thank Pete Chase (WGNHS) for field logging and assistance with well sampling. We are also deeply appreciative of the access provided by well owners (municipal and non-municipal) to allow sampling of their wells for this project. Water Utility operators and other well owners supported this project by allowing access to water samples, without which, this project would not have been possible. The Village of Kaukauna allowed for the installation of well ABQ564 on their property to provide access for a long-term monitoring point in the southern portion of the GMA. Dave Johnson (WDNR) provided valuable advice and insight on drilling, arsenic contamination, and other hydrogeological information that was valuable for this project. Ben Degner (WDNR) supported getting the variance in place for the new monitoring well. Aaron Pruitt (WDNR) provided historic municipal water level data used to construct hydrographs and some potentiometric surface maps. The Green Bay Water Utility also provided water levels that allowed for historic hydrographs and potentiometric surface maps to be constructed. Kristal VandenElzen Benson contributed effort toward the structure contour map (base of Sinnipee Group) that was used to calculate dewatered portions of the Ancell Group.

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# APPENDICES

## Appendix A: New Monitoring Well Location Easement and Variance

<b>GROUND WATER MONITORING STATION EASEMENT</b>	
Document Name	
<p><b>THIS GROUNDWATER MONITORING STATION EASEMENT</b> (“Easement”) made by and between the City of Kaukauna, a Wisconsin Municipal Corporation (“Grantor”), and the Board of Regents of the University of Wisconsin doing business as the University of Wisconsin-Green Bay and the Wisconsin Geological and Natural History Survey (“Grantee”).</p> <p><b>RECITALS</b></p> <p><b>WHEREAS</b>, Grantor and Grantee enter into this Easement to cooperatively collect groundwater level and geochemical data to fulfill Grantee’s research objectives through the State of Wisconsin Joint Solicitation for Groundwater Research and Monitoring.</p> <p><b>WHEREAS</b>, Grantee desires to install a monitoring station in order to collect said data;</p> <p><b>WHEREAS</b>, Grantee requests an easement allowing access over and upon Grantor’s property to collect groundwater data by constructing, installing, operating, and maintaining a monitoring station containing one groundwater well; and</p> <p><b>WHEREAS</b>, the portion of Grantor’s property subject to this Easement (“Premises”) is described below and more particularly shown on Exhibit “A”:</p> <p>Being a part of Lot Two (2) of Certified Survey Map No. 5866 as recorded in Volume 34 of Certified Survey Maps on Page 5866 as Document No. 1809521, and being located in the Southwest Quarter (SW1/4) of the Southeast Quarter (SE1/4) of Section Thirty (30), Township Twenty-One (21) North, Range Nineteen (19) East, City of Kaukauna, Outagamie County, Wisconsin containing 1,500 square feet (0.034 acres) of land and being described by:</p> <p>Commencing at the South Quarter Corner of said Section 30; thence S88°-44’-41”E 1479.50 feet along the south line of the SE1/4 of said Section 30 to the southeast corner of said Lot 2; thence N01°-15’-35”W 51.45 feet along the west line of said Lot 2 to a point on the south line of County Highway CE; thence N60°-45’-40”W 115.87 feet along said south line of County Highway CE to the point of beginning; thence S29°-14’-20”W 25.00 feet; thence N60°-45’-40”W 60.00 feet; thence N29°-14’-20”E 25.00 feet to a point on the south line of County Highway CE; thence S60°-45’-40”E 60.00 feet along said south line of County Highway CE to the point of beginning. Being subject to any and all easements and restrictions of record.</p> <p><b>NOW, THEREFORE</b>, Grantor hereby conveys to Grantee and its assigns, a non-exclusive perpetual easement to access and use the Premises for purposes of accessing, constructing, installing, operating, repairing, removing, replacing, and maintaining a monitoring station drilled and/or placed on the above-described Premises, along with activities directly related to groundwater sampling and testing as required to collect long-term groundwater level and geochemical data (“Easement Purpose”).</p>	<p>Recording Area</p> <p>Name and Return Address:</p> <p>City of Kaukauna 144 W 2nd Street PO Box 890 Kaukauna, WI 54130</p> <p><u>325112704</u> Parcel Identification Number</p>

IN WITNESS WHEREOF, Alexandria Roe, Sr. Associate Vice President, Capital Planning and Budget, Board of Regents of the University of Wisconsin System, 2420 Nicolet Drive, Green Bay, WI 54311 hereby accepts and consents to the terms and conditions of this Easement this 20th November, 2023.

Board of Regents of the University of Wisconsin System

By Alexandria Roe (SEAL)  
Alexandria Roe

State of Wisconsin )  
                                  ) ss.  
County of Dane )

Personally came before me this 20th day November, 2023, the above named, Alexandria Roe, to me known to be the person who executed the foregoing instrument and acknowledged that he executed and delivered the same as and for the act and deed of Grantee.

E. W. Rosner  
\* Ellen W. Rosner  
Notary Public, State of Wisconsin  
My Commission (expires) (is) 5/22/2027

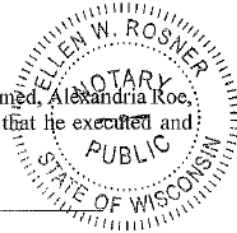
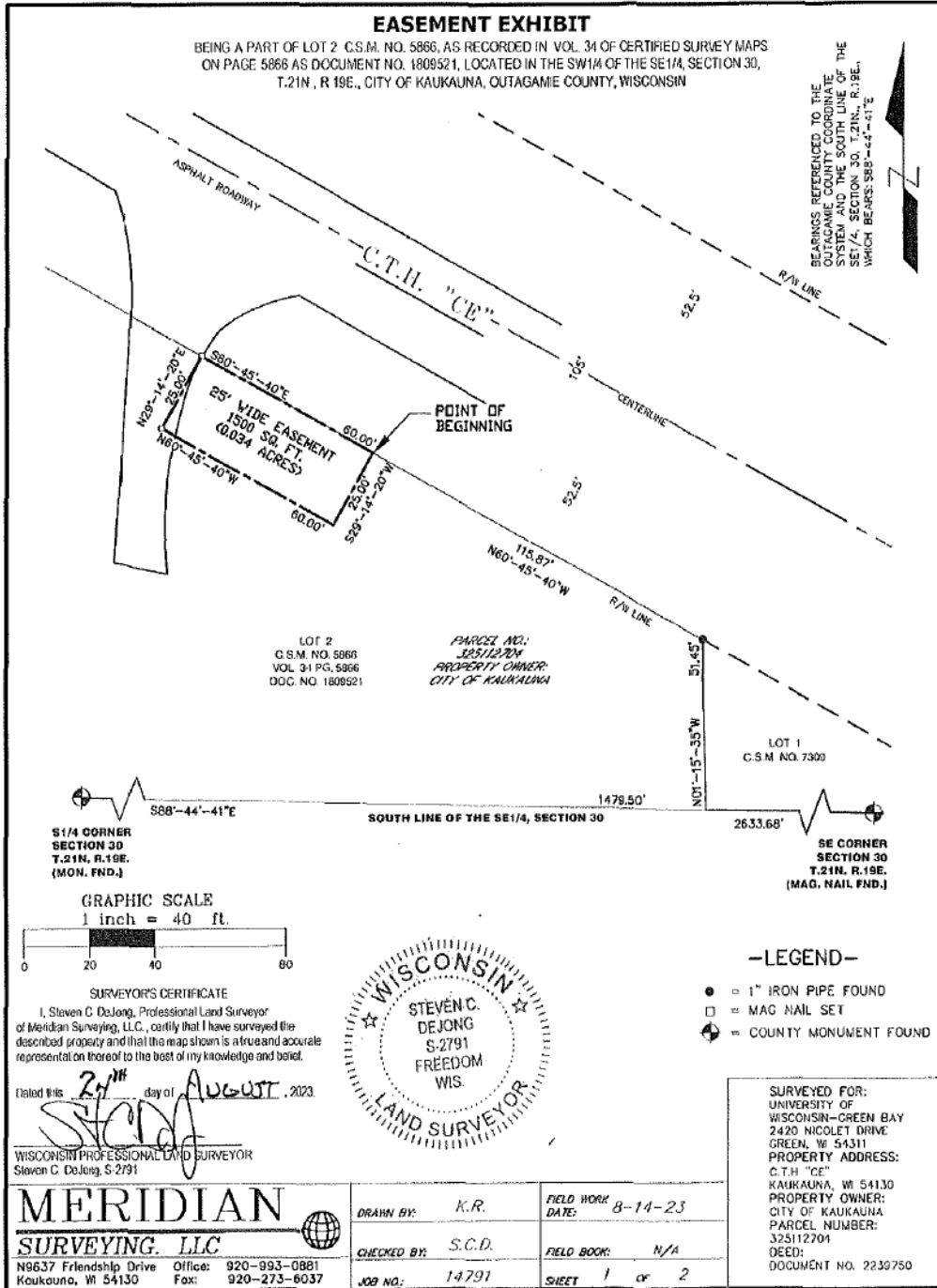


EXHIBIT A



**EASEMENT EXHIBIT**

BEING A PART OF LOT 2 C.S.M. NO. 5866, AS RECORDED IN VOL. 34 OF CERTIFIED SURVEY MAPS  
ON PAGE 5866 AS DOCUMENT NO. 1809521, LOCATED IN THE SW1/4 OF THE SE1/4, SECTION 30,  
T.21N., R.19E., CITY OF KAUKAUNA, OUTAGAMIE COUNTY, WISCONSIN

Legal Description:

Being a part of Lot Two (2) of Certified Survey Map No. 5866 as recorded in Volume 34 of Certified Survey Maps on Page 5866 as Document No. 1809521, and being located in the Southwest Quarter (SW1/4) of the Southeast Quarter (SE1/4) of Section Thirty (30), Township Twenty-One (21) North, Range Nineteen (19) East, City of Kaukauna, Outagamie County, Wisconsin containing 1,500 square feet (0.034 acres) of land and being described by:

Commencing at the South Quarter Corner of said Section 30; thence S88°-44'-41"E 1479.50 feet along the south line of the SE1/4 of said Section 30 to the southeast corner of said Lot 2; thence N01°-15'-35"W 51.45 feet along the west line of said Lot 2 to a point on the south line of County Highway CE; thence N60°-45'-40"W 115.87 feet along said south line of County Highway CE to the point of beginning; thence S29°-14'-20"W 25.00 feet; thence N60°-45'-40"W 60.00 feet; thence N29°-14'-20"E 25.00 feet to a point on the south line of County Highway CE; thence S60°-45'-40"E 60.00 feet along said south line of County Highway CE to the point of beginning. Being subject to any and all easements and restrictions of record.

SURVEYED FOR:  
UNIVERSITY OF  
WISCONSIN-GREEN BAY  
2420 NICOLET DRIVE  
GREEN, WI 54311  
PROPERTY ADDRESS:  
C.T.H. "CE"  
KAUKAUNA, WI 54130  
PROPERTY OWNER:  
CITY OF KAUKAUNA  
PARCEL NUMBER:  
325112704  
DEED:  
DOCUMENT NO. 2239750

**MERIDIAN**  
**SURVEYING, LLC**



N9637 Friendship Drive Kaukauna, WI 54130 Office: 920-993-0881 Fax: 920-273-6037

DRAWN BY:	K.R.	FIELD WORK DATE:	8-14-23
CHECKED BY:	S.C.D.	FIELD BOOK:	N/A
JOB NO.:	14791	SHEET	2 OF 2



October 23, 2023

UNIVERSITY OF WISCONSIN GREEN BAY  
2420 NICOLET DR  
GREEN BAY, WI 54311

Subject: **VARIANCE APPROVAL** for a new well located at PARCEL 325112704, City of Kaukauna, in Outagamie County, SW 1/4 SE 1/4 Sec. 30 T21N R19E; **Variance ID 47633**.

Dear UNIVERSITY OF WISCONSIN GREEN BAY :

The Department of Natural Resources (the Department) has reviewed your request received by the Department on October 13, 2023 for a variance to the requirements of s. NR 812.22, 812.12, Wis. Adm. Code, which requires NR812.12(3) requires that a driller or well constructor shall provide for greater depth of well casing pipe in special well casing depth areas designated by the department where well histories show contamination extends to a greater depth. In some of these areas, department approval shall be obtained for each well prior to construction. Special well casing depth area for Outagamie and Winnebago counties (#79) Option A - Galena-Platteville Dolomite Aquifer wells no deeper than 294 feet.

NR812.22 requires batch chlorination. All of the following requirements apply to the batch chlorination of a water system by a well driller or well constructor:

- (a) The entire water system shall be thoroughly disinfected with a chlorine solution having a concentration of at least 100 mg/L, prepared according to Table D.
- (b) The volume of chlorine solution shall be equal to or greater than the volume of water standing in the well.
- (c) The chlorine solution shall be brought into contact with the entire inside of the well casing pipe by continuous circulation from the water system.
- (d) A contact time of at least 12 hours shall be provided for the disinfectant.
- (e) The well and water system shall be thoroughly flushed. The Department has determined that your variance meets the requirements of NR 812.43, Wis. Adm. Code, and the variance is approved, subject to the following:

#### CONDITIONS

The following construction or installation features for the well and water supply system shall be complied with to protect human health and groundwater comparable to strict code compliance:

1. An upper enlarged drill hole and casing pipe shall extend a minimum of 100 feet below ground surface.
2. The lower drill hole shall extend to 400 feet below ground surface.
3. The well shall be grouted with high solids bentonite using the Bradenhead method.
4. The well is constructed to meet all other applicable requirements in NR 812, Wis. Adm. Code.
5. A copy of this variance must be provided to any potential buyer at least 10 - days prior to the closing of any sale of this property. All subsequent owners must also comply with this condition.
6. If construction of the well has not commenced within 2 years of the date on this letter, the approval is void.
7. The well may not be used for potable purposes and must be abandoned following NR 812 guidelines when it is no longer in use.
8. The well must be marked with signage indicating the well cannot be used for potable water purposes.

Failure to comply with the conditions of this variance or any other applicable requirements of ch. NR 812 voids the variance approval.

Please note that groundwater flow, the surrounding land uses and the physical condition of your well will change over time. The changes can affect the groundwater quality of your well. To investigate for changes in groundwater quality, the Department recommends at least annual sampling for bacteria and nitrate.

# Appendix B: Well Construction Report ABQ564

Well Construction Report WISCONSIN UNIQUE WELL NUMBER				ABQ564		Drinking Water and Groundwater - DG/5 Department of Natural Resources, Box 7921 Madison WI 53707				Form 3300-077A				
Property Owner CITY OF KAUKAUNA, UW GREEN BAY				Phone #		1. Well Location				Fire # (if avail.)				
Mailing Address 120 E FOURH ST						City of KAUKAUNA				5866				
City KAUKAUNA				State WI		Street Address or Road Name and Number				COUNTY CE				
County Outagamie		Co. Permit #		Notification # 9294645203		Completed 11-15-2023		Subdivision Name		Lot #	Block #			
Well Constructor (Business Name) HINTZKE WELL DRILLING INC				Lic. # 267	Facility ID # (Public Wells)	Latitude / Longitude in Decimal Degree (DD)				Method Code				
Address N5072 HINTZKE RD NEW LONDON WI 54961-9802				Well Plan Approval #		SE SE		Section 30	Township 21 N	Range 19 E				
Hicap Permanent Well #		Common Well #		Specific Capacity 0		2. Well Type New Well				of previous unique well # constructed in				
3. Well serves 1 # of STUDY WELL NOT FOR WATER				Hicap Well ? No		Reason for replaced or reconstructed well ?								
Private, non-potable				Hicap Property ? No		Construction Type Drilled								
Heat Exchange ___ # of drillholes				Hicap Potable ? No										
4. Potential Contamination Sources - ON REVERSE SIDE														
5. Drillhole Dimensions and Construction Method						8. Geology								
Dia. (in.)	From (ft.)	To (ft.)	Upper Enlarged Drillhole			Lower Open Bedrock	Geology Codes		8. Geology Type, Caving/Noncaving, Color, Hardness, etc...		From (ft.)	To (ft.)		
6	Surface	400	<u>No</u> Rotary - Mud Circulation .....			<u>Yes</u>	R	C	R-RED C-CLAY		Surface	135		
			<u>Yes</u> Rotary - Air .....			<u>No</u>	T	Z	T-TAN/BROWN Z-CLAY & GRAVEL		135	142		
			<u>No</u> Rotary - Air & Foam .....			<u>No</u>	T	L	T-TAN/BROWN L-LIMESTONE/DOLOMITE		142	330		
			<u>Yes</u> Drill-Through Casing Hammer				U	X	L	H	U-BLUE X-LENSED/STREAKED/LAYERED L-LIMESTONE/DOLOMITE H-SHALEY		330	350
			<u>No</u> Reverse Rotary				T	X	L	H	T-TAN/BROWN X-LENSED/STREAKED/LAYERED L-LIMESTONE/DOLOMITE H-SHALEY		350	400
			<u>No</u> Cable-tool Bit ___in. dia...			<u>No</u>								
			<u>No</u> Dual Rotary .....			<u>No</u>								
			<u>No</u> Temp. Outer Casing ___in. dia											
			<u>No</u> Removed? ___depth ft. (If NO explain on back side)											
6. Casing, Liner, Screen														
Dia. (in.)	Material, Weight, Specification Manufacturer & Method of Assembly				From (ft.)	To (ft.)								
6	US NUCORE PE 280 WALL A53 WELD				Surface	144								
Dia. (in.)	Screen type, material & slot size				From (ft.)	To (ft.)								
7. Grout or Other Sealing Material														
Method MOUNDED														
Kind of Sealing Material		From (ft.)	To (ft.)	# Sacks Cement										
GRANULAR BENTONITE		Surface		2 S										

WISCONSIN UNIQUE WELL NUMBER ABQ564

# Appendix C: Well Logging and Well Cuttings Characterization ABQ564

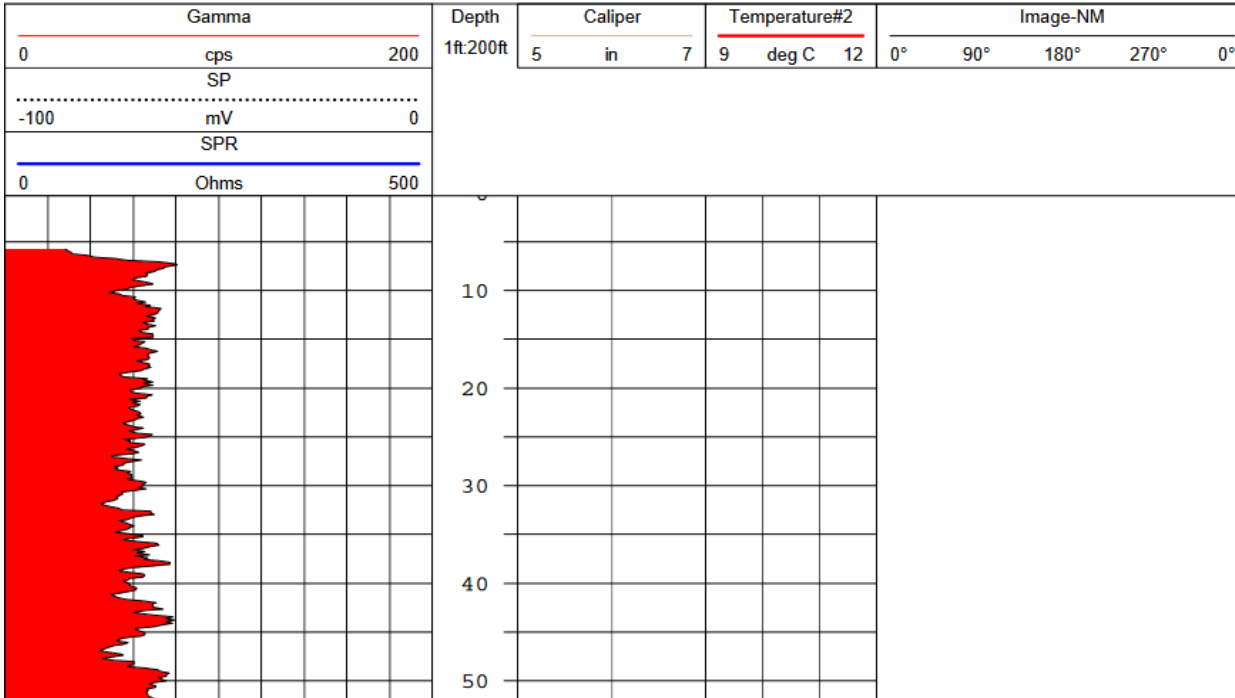
**LOGS COLLECTED:**

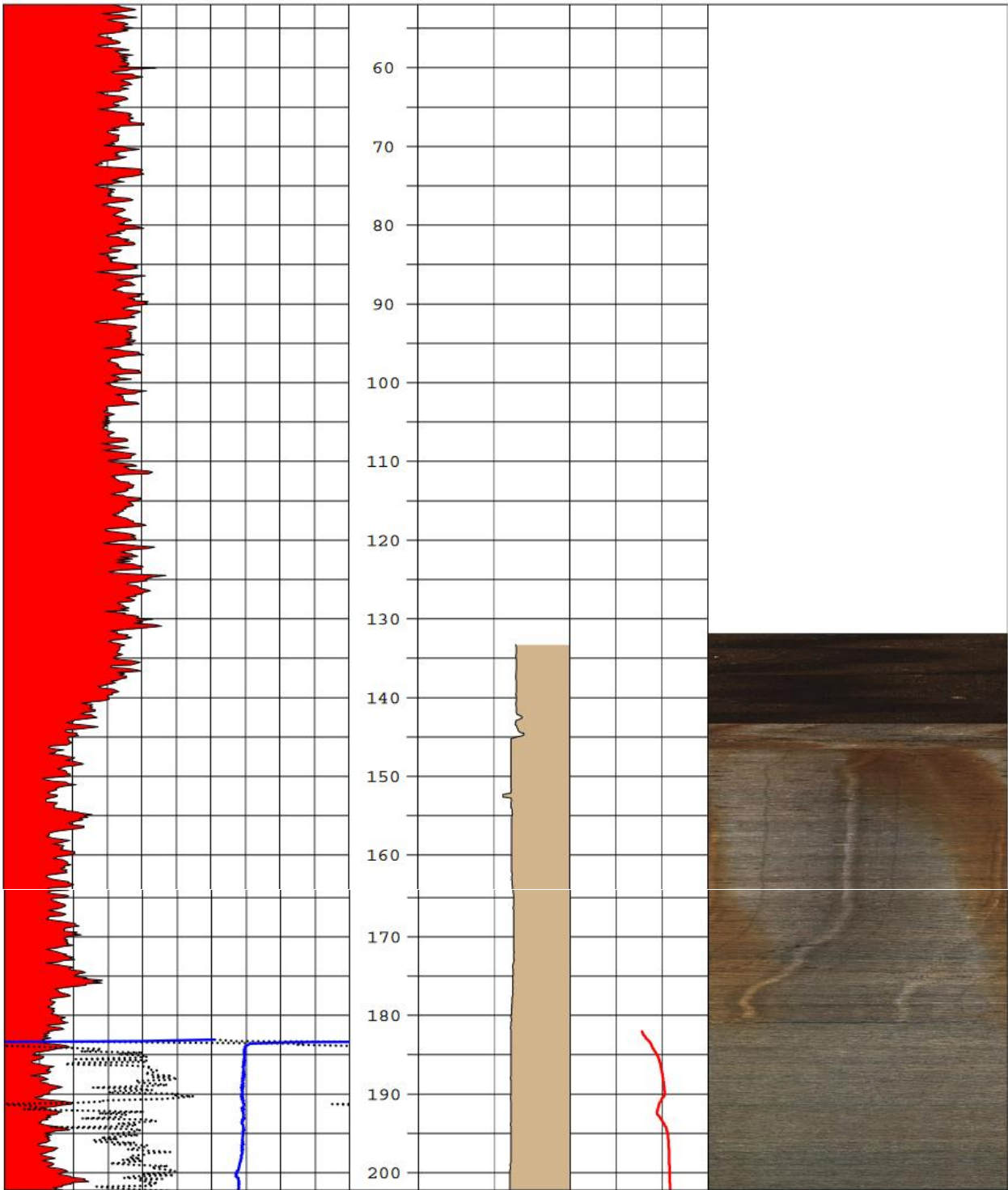
- |  |   |   |   |
|--|---|---|---|
| <input checked="" type="checkbox"/> Gamma                    | <input checked="" type="checkbox"/> Self Potential    | <input type="checkbox"/> Fluid Conductivity             | <input checked="" type="checkbox"/> Optical Borehole Imager |
| <input checked="" type="checkbox"/> Caliper                  | <input type="checkbox"/> Normal Resistivity           | <input type="checkbox"/> Flow Meter- HeatPulse          | <input type="checkbox"/> Acoustic Borehole Imager           |
| <input checked="" type="checkbox"/> Single Point Resistivity | <input checked="" type="checkbox"/> Fluid Temperature | <input checked="" type="checkbox"/> Flow Meter- Spinner | <input type="checkbox"/> OTHER                              |

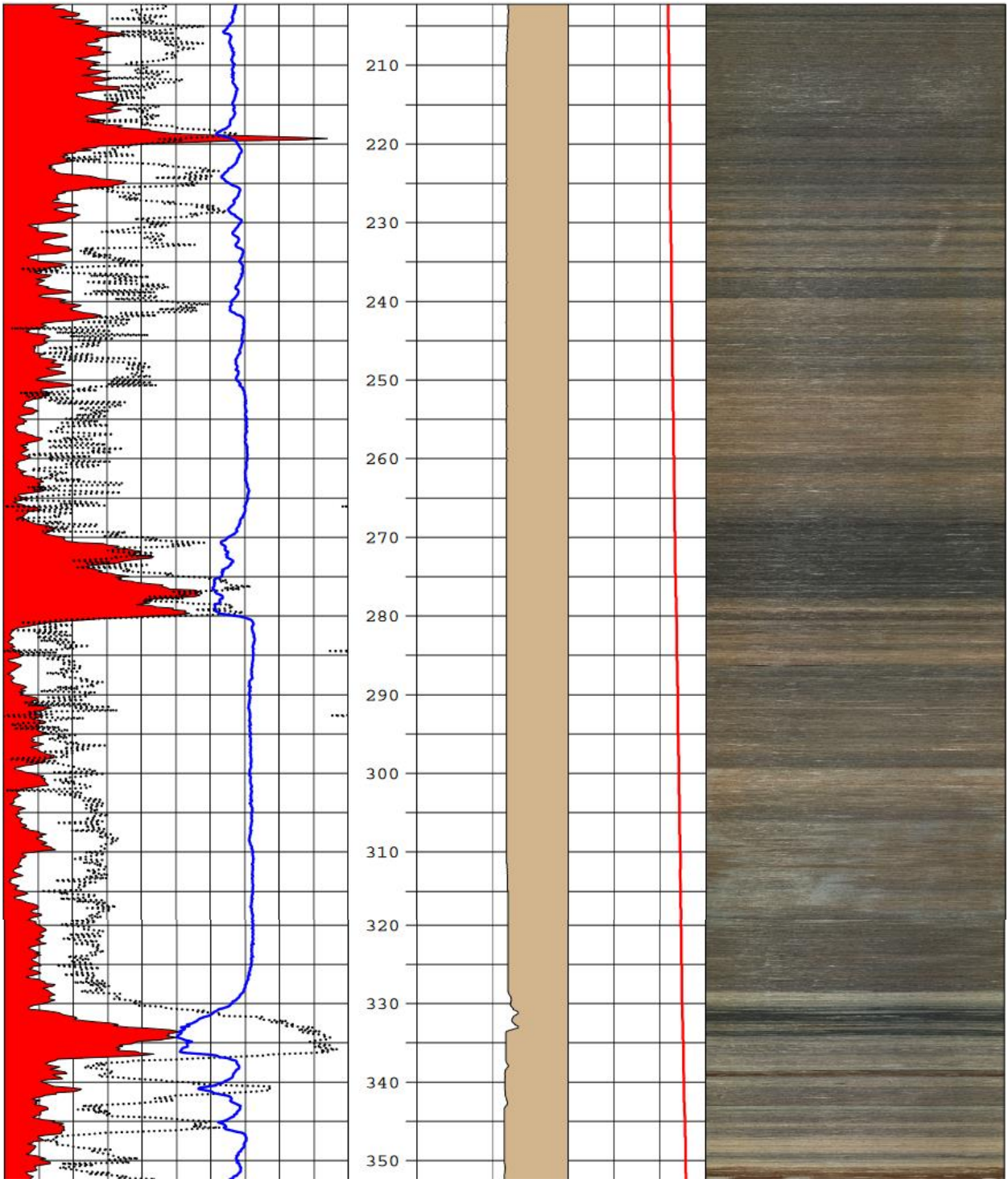
*(up is negative; down is positive)*

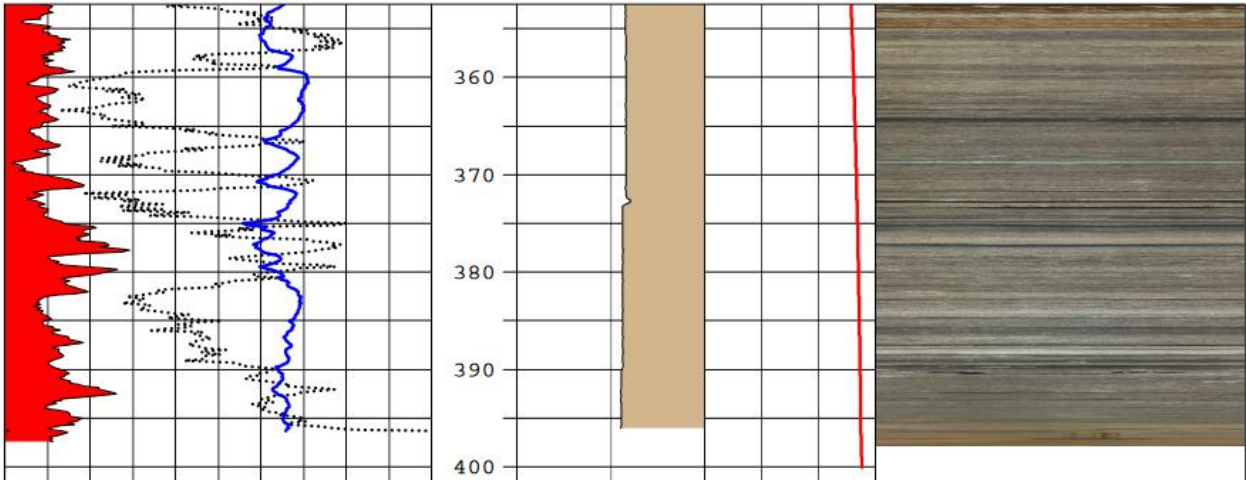
Unless noted, (1) all depths are in feet; (2) well depth, casing depth, and depth to water are interpreted from geophysical log; and (3) datum is the top of casing. For more information or to obtain collected data not shown, please contact: [data@wgnhs.wisc.edu](mailto:data@wgnhs.wisc.edu)

File Created on: 12/1/23  
By: pmc









<b>Depths (BGS)</b>	<b>Rock Type</b>	<b>Color</b>	<b>Grain Size</b>	<b>Description (Adjusted 2 feet to alter original depths from TOC to Feet below Ground Surface).</b>
				<b>Table C 1.</b> Geologic Log Created by Sean Babasin and John Luczaj; Driller – Hintzke Well Drilling, Inc. ABQ564 – Drilled on November 14-15, 2023 University of Wisconsin – Green Bay (Log Completed January 3, 2024)
0-135	Clay	Red	Fine	Driller Reports Red Clay; Pleistocene Sediments.
135-142	Clay & Gravel	Tan/Brown	Fine-Coarse	Driller Reports Tan/Brown Clay & Gravel; Pleistocene Sediments.
142	Dolomite	Light Brown	Medium	Light yellow-brown fine to medium crystalline dolomite, some crinoids, some surface contamination.
143-148	Dolomite	Light Gray Brown	Fine-Medium	Light yellow-brown fine to medium crystalline dolomite, few iron sulfides in vugs and matrix, few surface contamination (roots, gabbro, copper grease).
148-153	Dolomite	Light Gray Brown	Medium	Uniform medium light gray-brown crystalline dolomite, minor white dolomite, trace very fine grained pyrite and sphalerite minor crinoid fragments.
153-158	Dolomite	Light Gray Brown	Medium	Uniform medium light gray-brown crystalline dolomite, minor white dolomite, trace very fine-grained pyrite, few vugs with iron sulfide crystals, some crinoid fragments.
158-163	Dolomite	Light Gray Brown	Medium	Medium light gray-brown crystalline dolomite, moderate white dolomite (some saddle), trace pyrite and sphalerite some presented as sheets, few as vugs, rare glauconite pellets, rare frosted quartz sand grains, some surface contamination.
163-168	Dolomite	Light Gray Brown	Medium	Uniform light gray-brown medium crystalline dolomite, minor white dolomite, trace pyrite and possible sphalerite, few vugs, some copper grease contamination, surface contamination.
168-173	Dolomite	Light Gray Brown	Medium	Uniform light gray-brown medium crystalline dolomite, minor white dolomite, some pyrite and sphalerite, few vugs with dol and iron sulfides, some iron sulfides presented as thin sheets.
173-178	Dolomite	Light Gray Brown	Medium	Uniform light gray-brown medium crystalline dolomite, minor white dolomite, crinoid fragments, few vugs with euhedral calcite, dolomite, pyrite, and possible chalcopyrite.
178-183	Dolomite	Light Brown Gray	Medium	Medium light brown-gray crystalline dolomite, moderate white dolomite, some dark gray mottling, some pyrite and marcasite in vugs, matrix, and fractures, rare surface contamination, some fossils, crinoids, and seeds.
183-188	Dolomite	Light Brown Gray	Medium	Medium light brown-gray crystalline dolomite, minor white dolomite, some euhedral pyrite, sulfate in vugs, pyrite present in matrix, and fractures.
188-193	Dolomite	Light Brown Gray	Medium	Medium light brown-gray crystalline dolomite, minor white dolomite, some dark gray mottling, some pyrite in vugs, matrix, and fractures.
193-198	Dolomite	Light Brown Gray	Medium-Fine	Fine to medium crystalline dolomite, rare white dolomite, few black dolomitized fossils, few pyrite and dolomite in vugs.
198-203	Dolomite	Variegated	Medium-Fine	Fine-medium variegated gray to light brown crystalline dolomite, some crystalline dolomite and pyrite in vugs some copper grease contamination.
203-208	Dolomite	Variegated	Medium-Fine	Fine-medium variegated gray to light brown crystalline dolomite, some pyrite in vugs, some surface contamination.

208-213	Dolomite	Variegated	Coarse-Fine	Fine gray to coarse grained dark gray burrowed crystalline dolomite. Rare surface contamination.
213-218	Dolomite	Variegated	Medium-Fine	Very fine-medium variegated light brown-gray to dark gray crystalline dolomite. Some crinoids, few iron sulfides in vugs, rare pyrite in matrix.
218-223	Dolomite	Variegated	Medium-Fine	Very fine-medium variegated light brown-gray to dark gray crystalline dolomite. Few white chalky material, rare pyrite in matrix.
223-228	Dolomite	Variegated	Medium-Very Fine	Very fine-medium variegated light brown-gray to dark gray crystalline dolomite. Some dolomite has granular texture. Some patchy pyrite in matrix.
228-233	Dolomite	Variegated	Medium-Very Fine	Variegated mix light brown medium grained to light gray fine crystalline dolomite. Some pyrite in matrix, some welding related fragments.
233-238	Dolomite	Variegated	Coarse-Fine	Very variegated mix medium-coarse light yellow-brown to gray crystalline dolomite, some fine white crystalline dolomite, few pyrites in patches and matrix, possible small white chert.
238-243	Dolomite	Variegated	Coarse-Fine	Very variegated mix medium-coarse light yellow-brown to fine gray dolomite, few pyrites in patches and matrix, possible small white chert.
243-248	Dolomite	Light Yellow Brown	Medium	Medium light yellow-brown crystalline dolomite, minor gray crystalline dolomite, few fine pyrite in matrix.
248-253	Dolomite	Variegated	Medium-Fine	Variegated mix medium-coarse light yellow-brown to fine gray dolomite, rare pyrites in patches and matrix, some white chert.
253-258	Dolomite	Light Yellow Brown	Medium	Medium crystalline dolomite, minor gray dolomite, abundant chert, few pyrite in vugs and matrix, few calcite crystals.
258-263	Dolomite	Light Yellow Brown	Medium	Medium crystalline dolomite, light brown dolomite, abundant chert, few pyrite in matrix some copper grease contamination.
263-268	Dolomite	Light Yellow Brown	Medium-Coarse	Medium to coarse light yellow-brown crystalline dolomite, few chert, few sulfides with post drilling oxidation, few vugs with possible fluorite
268-273	Dolomite	Variegated	Medium-Fine	Medium to coarse yellow-brown crystalline dolomite with green-gray fine crystalline dolomite. Bryozoan fossils, few fine-medium pyrites in matrix.
273-278	Dolomite	Variegated	Medium-Fine	Medium gray crystalline shaley dolomite, some green-gray fine and coarse-very coarse dolomite. Few calcite some pyrite in dolomite matrix. Some crinoids and graptolite fragments.
278-283	Dolomite	Variegated	Coarse-Fine	Medium to coarse yellow-brown crystalline dolomite with green-gray fine crystalline dolomite. Few white chert, some fine-coarse pyrites and marcasite euhedral in vugs and in matrix. Few bryozoans.
283-288	Dolomite	Variegated	Medium-Fine	Predominately medium-fine yellow-brown crystalline dolomite, some gray crystalline dolomite, few medium grained pyrite.

288-293	Dolomite	Variegated	Medium-Fine	Light yellow-brown to mottled gray-brown fine to medium crystalline dolomite, some white chert, vugs with euhedral dolomite, marcasite, pyrite, and possible chalcopyrite, minor surface contamination and steel fragments.
293-298	Dolomite	Light Brown Gray	Medium-Fine	Mottled light brown-gray crystalline dolomite few vugs with pyrite and dolomite crystals, minor matrix pyrite, rare surface contamination.
298-303	Dolomite	Light Brown	Medium-Fine	Light brown medium crystalline dolomite, few white chert, few fine to medium pyrite and marcasite crystals in matrix, abundant <i>stylocumulates</i> (brown clay).
303-308	Dolomite	Light Brown & Gray	Medium-Fine	Light brown medium to gray mottled crystalline dolomite, rare white chert, rare fine pyrite in matrix.
308-313	Dolomite	Light Brown & Gray	Medium-Fine	Light brown medium to gray mottled crystalline dolomite, rare white chert, rare fine pyrite in matrix and in vugs, some saddle dolomite.
313-318	Dolomite	Light Yellow Brown	Fine	Light yellow-brown to gray mottled medium crystalline dolomite, rare pyrite and sphalerite, few vugs with sulfides.
318-323	Dolomite	Light Yellow Brown	Fine	Burrow mottled gray to light yellow-brown medium crystalline dolomite, few pyrite, few dolomite crystals in vugs.
323-328	Dolomite	Light Yellow Brown	Fine	Burrow mottled gray to light yellow-brown medium crystalline dolomite, few pyrite, few dolomite crystals in vugs.
328-333	Dolomite & Sandstone	Light Yellow Brown	Medium-Fine	Abundant gray to yellow-gray fine to medium crystalline dolomite, some green shale, some well cemented medium-coarse grained quartz sandstone with sulfide cement horizon features, few white chert, pyrite in matrix.
333-338	Dolomite & Sandstone	Light Yellow Brown	Medium-Fine	Abundant gray to yellow-gray fine to medium crystalline dolomite, few green shale, some white/gray/green well cemented coarse-medium grained quartz sandstone with some sulfide cement, some iron sulfides, rare oolitic chert, rare sulfate with internal sulfide. Some welding contamination.
338-343	Dolomite & Sandstone	Light Yellow Brown	Fine	Abundant light yellow-brown fine crystalline dolomite, few green shale, abundant well cemented fine-medium grained quartz sandstone with dolomite cement, some pyrite octahedrons (>100 µm), rare sulfides in matrix of shale, rare white chert.
343-348	Dolomite & Sandstone	Light Gray	Fine	Abundant light gray to light yellow-brown fine crystalline dolomite, few green shale, some well cemented fine-medium grained quartz sandstone with dolomite and pyrite cement, some pyrite (>100 µm) crystals, some coarse pyrite. Welding contamination with oxidation related to contamination, few argillaceous sandstone.
348-353	Dolomite & Sandstone	Light Gray	Fine	Moderately abundant light gray to light yellow-brown fine crystalline dolomite, rare green shale, abundant quartz fine-medium grained well cemented sandstone, few pink orange sand grains.
353-358	Sandstone	White	Fine-Medium	Abundant white fine-medium grained quartz sandstone, some well cemented, few green shale, few light gray fine grained crystalline dolomite, rare coarse pyrite in dolomite, few (>100 µm) pyrite crystals, rare biotite.

358-363	Dolomite & Sandstone	Gray - Light Yellow Brown	Fine	Abundant gray to light yellow-brown fine crystalline dolomite, some well cemented quartz sandstone, some oolite, few pyrite crystal grains, some euhedral, few in matrix of dolomite.
363-368	Sandstone	White-Gray	Very Fine-Coarse	Very fine to coarse white-gray grained quartz sandstone, some gray fine crystalline dolomite, rare green shale, possible galena, rare sphalerite, euhedral dolomite in vugs, rare glauconite, few (>100 µm) pyrite crystals, few white chert.
368-373	Dolomite & Sandstone	Light Yellow-Gray	Fine-Medium	Light yellow-gray fine grained crystalline dolomite, some white-light gray medium to coarse grained quartz sandstone, rare green shale, few iron sulfides, some silicified oolite.
373-378	Dolomite & Sandstone	Light Gray-Gray Brown	Fine-Medium	Abundant light gray to gray-brown fine to medium crystalline dolomite, some fine to medium grained quartz sandstone, few (>100µm) pyrite crystals, some green shale, few oolite
378-383	Dolomite & Sandstone	Light Brown	Fine	Light brown fine crystalline dolomite with abundant white medium grained quartz sandstone. Some green shale. Rare oolite and rare iron sulfides.
383-388	Dolomite & Sandstone	Light Brown	Fine	Light brown-gray fine crystalline dolomite with abundant white-gray medium grained well-cemented sandstone. Rare clear coarse dolomite crystals, some green shale no sulfides present.
388-393	Dolomite	Light Brown	Fine-Medium	Light brown-gray medium-fine grained crystalline dolomite, rare medium-coarse grained, few green shale, rare maroon dolomite, rare iron sulfides present in fine fraction.
393-398	Dolomite	Light Brown	Fine-Medium	Light brown-gray medium-fine grained crystalline dolomite, rare medium-coarse grained, few green shale, rare maroon dolomite, rare oolite.

## Appendix D: Water Chemistry for Sampled Wells

**Table D 1.** Ions and metals concentrations for groundwater samples collected in this study. Red text indicates measured value higher than one standard deviation greater than the average for all wells sampled.

Location	Well Type	Identifier	SO <sub>4</sub> <sup>2-</sup> mg/L	Cl <sup>-</sup> mg/L	Total Alkalinity mg/L as CaCO <sub>3</sub>	F <sup>-</sup> mg/L	Al µg/L	As µg/L	B µg/L	Ca mg/L	Fe mg/L	Zn µg/L	Mg mg/L	Mn µg/L	K mg/L	Na mg/L	Sr µg/L
Kimberly	Municipal	BG581	170	5.2	258	1.08	nd	nd	87.9	79.5	0.44	8.65	32.2	10.8	3.22	8.51	16800
Kimberly	Municipal	BG579	134	5.65	261	1.23	10.8	1.4	91.4	70.2	0.45	4.71	33.4	11.3	3.44	8.65	40500
Kaukauna	Municipal	HJ196	725	7.4	170	2.1	16.7	nd	109	193	0.53	6.44	21.1	22.1	3.94	11	21400
Kaukauna	Municipal	AY326	581	5.85	198	2.03	nd	nd	104	210	0.54	5.76	25	15.6	3.99	9.47	25000
Kaukauna	Municipal	BG576	555	9.28	191	1.85	nd	nd	128	175	0.56	6.91	23.6	18.3	4.28	14	25500
Kaukauna	Municipal	BG575	995	11.7	169	2.09	nd	2.3	125	268	0.73	18.7	21.6	24.1	4.46	16.1	19400
Kaukauna	Municipal	BG574	995	8.63	173	2.35	nd	3.3	123	265	0.57	8.37	19.5	21.9	4.37	13	23800
Kimberly	Municipal	BG580	793	8.28	164	1.68	nd	nd	85.4	188	0.56	22.7	34.6	11.4	3.68	11.2	27900
Little Chute	Municipal	NQ265	760	5.52	176	2.15	nd	nd	88.8	178	0.29	3.69	22.9	13.4	3.33	9.3	27300
Little Chute	Municipal	BG582	312	6.69	232	1.57	12	nd	101	108	0.44	12.3	28.5	8.61	3.71	10.1	33300
Little Chute	Municipal	BG584	171	4.63	243	1.46	20	1.1	92.8	83.3	0.4	4.08	28.8	9.05	3.39	8.22	40100
Green Bay	Monitoring	BN435* - 75	471	27.2	261	1.88	14.9	nd	666	149	4.94	nd	73.7	nd	16	54.1	12400
Green Bay	Monitoring	BN435* - 177	1740	107	270	1.71	16.2	1.4	399	312	13.1	74.9	188	200	13.5	47.5	11300
Green Bay	Monitoring	BN435* - 219	1470	95.8	265	1.71	13.4	2.3	403	315	13	38.4	193	211	13.7	53.6	13000
Green Bay	Monitoring	BN435* - 269	1620	104	272	1.75	14.7	2.5	371	305	12.6	26.1	187	208	13.3	51.8	12900
Kaukauna	Monitoring	ABQ564 - 160	779	61.2	46	0.61	20.4	1.5	373	134	1.28	112	45	22.1	3.86	128	9310
Kaukauna	Monitoring	ABQ564 - 185	767	61.2	26	0.62	22.8	nd	381	137	1.63	11.6	44.7	19.9	3.68	124	8250
Kaukauna	Monitoring	ABQ564 - 325	903	61.3	50	0.61	27.3	nd	375	135	1.1	34.6	47.2	25.5	3.94	124	8450
Kaukauna	Monitoring	ABQ564 - 340	776	61.3	46	0.59	50.2	nd	335	125	1.82	15	57.5	36.5	3.96	125	11100
Kaukauna	Monitoring	ABQ564 - 355	784	61.3	50	0.59	51.3	nd	385	139	1.72	48.5	47.5	39.6	4.25	121	8070
Kaukauna	Monitoring	ABQ564 - 380	787	61.2	38	0.59	62.8	nd	390	139	2.24	17.5	50.3	37	4.63	124	7700
Green Bay	Industrial	RG481	62.5	4.12	188	1.73	14.1	nd	122	49.8	0.32	6.91	20.8	16.8	4.6	14.5	3440
Darboy	Municipal	DG402	53.5	12.7	216	2.25	12.9	nd	123	229	0.58	17.6	26.8	21.2	4.18	11.3	22500
Darboy	Municipal	HW895	474	61.5	230	0.6	18.2	nd	105	198	0.54	17.8	30	14.1	4.09	9.32	26100
De Pere	Irrigation	YK934	97.8	13.3	162	2.51	15.9	nd	172	49.7	0.18	26.4	20.2	13.8	5.44	19.4	7250
De Pere	Irrigation	NC422	206	13	130	0.71	11.1	nd	409	42.4	0.37	6230	20.2	7.8	2.98	59.4	2050
Kaukauna	Monitoring	AAJ872 - 283	176	11.4	34	2.29	10.8	nd	171	41.6	3.11	16.1	14.9	86.5	6.43	26.6	6340
Kaukauna	Monitoring	AAJ872 - 296	218	14.9	102	2.47	33.7	nd	208	72	4.92	10.6	19.8	45.3	7.2	31.1	8560
Kaukauna	Monitoring	AAJ872 - 306	217	13.7	140	2.38	31.3	nd	202	87.3	4.31	18.2	20.3	36.4	6.49	25.1	14000
Average			613.5	31.9	164.2	1.6	22.8	2.0	231.9	154.4	2.5	243.7	48.2	43.1	5.7	43.8	17024.8
Std. Dev.			459.2	33.1	83.0	0.7	14.6	0.7	152.5	83.1	3.8	1173.4	50.6	59.7	3.6	44.7	10504.7

\* BN435 an outdated identifier; it is located at the National Railroad Museum and also uses the identifiers USGS-442859088025801 or WGNHS Well ID: 5000435

**Table D 2.** Water quality field measurements for groundwater samples collected in this study.

Location	Well Type	Identifier	pH	DO*	Conductivity
			pH	% sat	µS/cm
Kimberly	Municipal	BG581	7.39		782
Kimberly	Municipal	BG579	7.48		744
Kaukauna	Municipal	HJ196	7.26	10.3	1152
Kaukauna	Municipal	AY326	7.18	4.2	1223
Kaukauna	Municipal	BG576	7.3	12.6	1115
Kaukauna	Municipal	BG575	7.20	11.2	1482
Kaukauna	Municipal	BG574	7.30	12.3	1418
Kimberly	Municipal	BG580	7.24		1256
Little Chute	Municipal	NQ265	7.36		1138
Little Chute	Municipal	BG582	7.3		890
Little Chute	Municipal	BG584	7.37		784
Green Bay	Monitoring	BN435 - 75FT	7.25	15.4	1152
Green Bay	Monitoring	BN435 - 177FT	6.86	8.1	2432
Green Bay	Monitoring	BN435 - 219FT	6.86	13.8	2490
Green Bay	Monitoring	BN435 - 269FT	6.86	7.6	2500
Kaukauna	Monitoring	ABQ564 - 160FT	6.85	85	1557
Kaukauna	Monitoring	ABQ564 - 185FT	7.78	88.7	1553
Kaukauna	Monitoring	ABQ564 - 325FT	7.68		1561
Kaukauna	Monitoring	ABQ564 - 340FT	7.68		1568
Kaukauna	Monitoring	ABQ564 - 355FT	7.73		1570
Kaukauna	Monitoring	ABQ564 - 380FT	7.8		1569
Green Bay	Industrial	RG481	7.61	3.1	493.6
Darboy	Municipal	DG402	7.12		1307
Darboy	Municipal	HW895	7.18		1238
De Pere	Irrigation	YK934			
De Pere	Irrigation	NC422	7.71	6.1	696
Kaukauna	Monitoring	AAJ872 - 283FT	7.66	11.3	510
Kaukauna	Monitoring	AAJ872 - 296FT	7.81	6.6	695
Kaukauna	Monitoring	AAJ872 - 306FT	7.71	5.3	744
Kaukauna	Monitoring	AAJ872 - 306FT	7.74	7.6	753

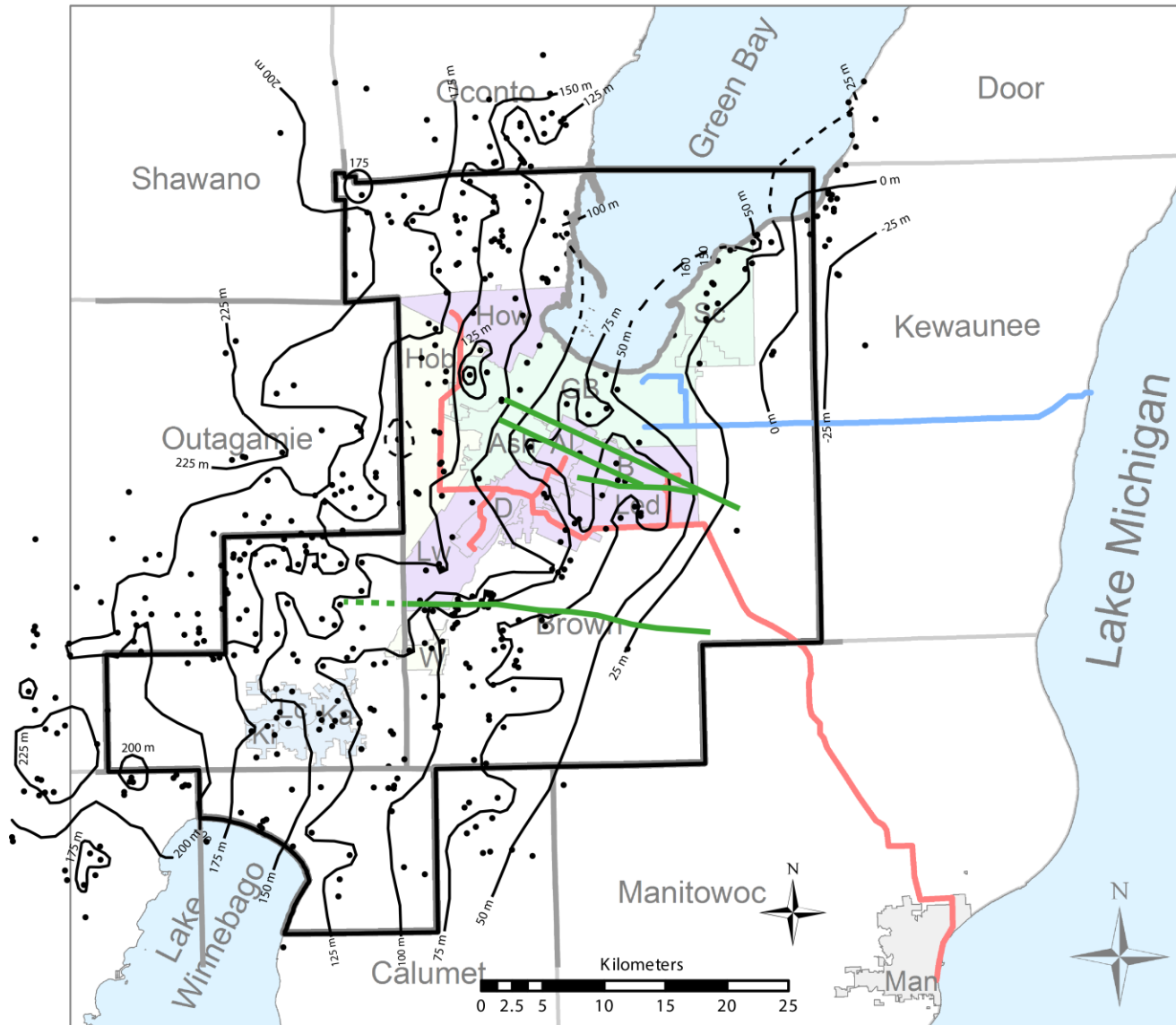
\* DO measured ex-situ after pumping; only represents an upper bound on dissolved oxygen

Grey shading represents data gaps

**Table D 3.** Water, sulfur, and carbon isotopes for wells sampled in this study. Carbon isotopes were used to approximate the groundwater age.

Sample Label	Date	<sup>18</sup> O		<sup>2</sup> H		d-excess	<sup>34</sup> S		Repeat	<sup>18</sup> O		Repeat	<sup>13</sup> C/ <sup>14</sup> C		RCAge		<sup>14</sup> C	
		AVG	STDEV	AVG	STDEV		SO <sub>4</sub>	Result		SO <sub>4</sub>	VSMOW ± 0.3‰		DIC/	Result	BP	±	pmC	±
BG579	7/29/2024	-10.63	0.16	-72.61	0.68	12.46	X	17.66		X	14.10		x	-12.058	11650	30	23.44	0.10
BG580	7/29/2024	-11.04	0.04	-75.52	0.20	12.78	X	20.21		X	14.84		x	-12.569	12570	30	20.9	0.09
BG581	7/29/2024	-10.42	0.04	-70.60	0.29	12.74	X	18.39	18.44	X	15.64	15.40	x	-12.405	11270	30	24.58	0.09
BG574	7/23/2024	-13.96	0.02	-98.52	0.16	13.13	X	20.99		X	13.84		x	-11.689	18630	40	9.83	0.06
BG575	7/23/2024	-14.15	0.01	-99.80	0.07	13.37	X	21.34	21.26	X	14.70		x	-10.59	19080	40	9.3	0.05
HJ196	7/23/2024	-13.79	0.04	-97.14	0.13	13.17	X	20.99		X	15.13		x	-11.861	18510	40	9.98	0.05
AY326	7/23/2024	-12.47	0.05	-87.26	0.05	12.52	X	20.97		X	15.05		x	-11.936	16320	40	13.11	0.06
BG576	7/23/2024	-13.15	0.02	-92.29	0.15	12.88	X	19.63		X	13.93	14.08	x	-11.98	17300	40	11.61	0.06
BG582	7/29/2024	-11.40	0.06	-78.29	0.15	12.87	X	19.61		X	14.42		x	-11.96	13840	35	17.86	0.07
BG584	7/29/2024	-11.00	0.04	-75.31	0.21	12.73	X	19.12		X	14.42		x	-12.435	13620	30	18.36	0.08
NQ265	7/29/2024	-12.85	0.04	-89.69	0.06	13.09	X	21.08		X	14.45		x	-10.69	16920	40	12.16	0.06
DG402	8/14/2024	-10.77	0.03	-72.60	0.10	13.59	X	20.03	19.98	X	13.74		x	-13.011	13090	35	19.61	0.08
HW895	8/14/2024	-9.98	0.03	-68.03	0.08	11.78	X	20.49		X	13.31		x	-11.741	11760	30	23.12	0.09
ABQ564-160ft	8/13/2024	-17.67	0.05	-127.77	0.08	13.58												
ABQ564-185ft	8/13/2024	-17.68	0.02	-127.91	0.06	13.53	x	26.45										
ABQ564-325ft	8/13/2024	-17.63	0.01	-127.87	0.10	13.19	x	26.47										
ABQ564-340ft	8/13/2024	-17.63	0.02	-127.84	0.02	13.22	x	26.45										
ABQ564-355ft	8/13/2024	-17.72	0.04	-128.04	0.18	13.68	x	26.48										
ABQ564-380ft	8/13/2024	-17.70	0.03	-127.91	0.05	13.72	x	26.33	26.48									
AAJ872-283ft	8/22/2024	-14.24	0.06	-99.77	0.25	14.15	x	25.87										
AAJ872-296ft	8/22/2024	-14.15	0.04	-100.36	0.15	12.82	x	22.57	22.44									
AAJ872-306ft	8/22/2024	-13.95	0.07	-98.95	0.19	12.67	x	21.12										
AAJ872-317ft	8/22/2024	-14.00	0.04	-98.97	0.15	13.01	x	21.15										
RG481	8/6/2024	-14.25	0.03	-100.45	0.09	13.52	X	8.13		X	3.71	3.58	x	-12.112	16090	40	13.49	0.07
NC422	8/30/2024	-11.37	0.02	-78.42	0.17	12.57	x	24.30	24.28	x	13.45	13.46	x	-13.55	7890	30	37.4	0.1
YK934	9/17/2024	-15.25	0.07	-108.65	0.14	13.35	X	14.83	14.76	X	6.37	6.05	x	-11.05	22740	55	5.90	0.04
BN-435-75ft	8/2/2024	-14.21	0.07	-100.99	0.25	12.70	x	9.87										
BN-435-177ft	8/2/2024	-13.44	0.09	-94.96	0.38	12.54	x	6.27										
BN-435-219ft	8/2/2024	-13.43	0.05	-94.90	0.23	12.52	x	6.25										
BN-435-269ft	8/2/2024	-13.42	0.04	-94.89	0.16	12.44	x	6.27										

## Appendix E: Base of the Sinnipee Structure Contour Map



Preliminary map of the Northeast GMA in Wisconsin showing structure contours for the base of the Sinnipee Group (black lines, meters above sea level). Selected municipalities are shown as abbreviations (Ki = Kimberly, Lc = Little Chute, Ka = Kaukauna, W = Wrightstown, GB = Green Bay, Sc = Town of Scott, B = Bellevue, Led = Ledgeview, Al = Allouez, D = De Pere, L = Lawrence, How = Howard, Hob = Hobart, Man = Manitowoc). Green lines show the location of faults mapped by Luczaj (2011). Blue and red lines show locations of regional water supply lines for the Green Bay Water Utility (blue) and CBCWA (red).