

**AN EVALUATION OF THE DISTRIBUTION AND
SOURCES OF DISSOLVED STRONTIUM IN THE
GROUNDWATER OF EASTERN WISCONSIN, WITH A
FOCUS ON BROWN AND OUTAGAMIE COUNTIES**

**John Luczaj
Michael Zorn
Joseph Baeten**

2013

**AN EVALUATION OF THE DISTRIBUTION AND SOURCES OF DISSOLVED
STRONTIUM IN THE GROUNDWATER OF EASTERN WISCONSIN, WITH A
FOCUS ON BROWN AND OUTAGAMIE COUNTIES**

John Luczaj, Ph.D.
Department of Natural and Applied Sciences
University of Wisconsin-Green Bay

Michael Zorn, Ph.D.
Department of Natural and Applied Sciences
University of Wisconsin-Green Bay

Joseph Baeten
Department of Natural and Applied Sciences
University of Wisconsin-Green Bay

Administered by:
University of Wisconsin Water Resources Institute

Funded by:
State of Wisconsin Groundwater Research and Monitoring Program

2013

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

**An Evaluation of the Distribution and Sources of Dissolved Strontium in the Groundwater
of Eastern Wisconsin, with a Focus on Brown and Outagamie Counties.**

A final report prepared for the University of Wisconsin Water Resources Institute

John A. Luczaj
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay

Michael Zorn
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay

Joseph Baeten (Graduate Student)
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay

November 15, 2013

TABLE OF CONTENTS

| | |
|--|-----------|
| List of Tables and Figures..... | 1 |
| Project Summary..... | 2 |
| Introduction..... | 4 |
| Procedures and Methods..... | 6 |
| Results and Discussion..... | 7 |
| Conclusions and Recommendations..... | 14 |
| Acknowledgements..... | 14 |
| References Cited..... | 15 |
| Appendix A – Awards, Publications, Reports, Patents, and Presentations..... | 16 |

LIST OF FIGURES AND TABLES

- Figure 1. Generalized bedrock geologic map of eastern Wisconsin and the ancestral Michigan basin.
- Figure 2. Stratigraphic column for northeastern Wisconsin.
- Figure 3. Statewide distribution of dissolved strontium in Wisconsin’s aquifers.
- Figure 4. Regional distribution of dissolved strontium in the Cambrian-Ordovician aquifers in northeastern Wisconsin.
- Figure 5. Bedrock geologic map of Brown County, Wisconsin with fault-delineated aquifer zones.
- Figure 6. Piper plots of groundwater chemistry for different aquifer compartments.
- Figure 7. SEM image showing bladed SrSO_4 and other minerals related to hydrothermal brine migration.
- Figure 8. Celestine saturation index versus dissolved strontium concentration in northeastern Wisconsin.
- Figure 9. Box plot showing Sr-isotopic composition for groundwater and minerals in the region.

Table 1. Wisconsin Groundwater Samples with Dissolved Strontium Values

PROJECT SUMMARY (2 pages)

Title: An Evaluation of the Distribution and Sources of Dissolved Strontium in the Groundwater of Eastern Wisconsin, with a Focus on Brown and Outagamie Counties.

Project I.D.: University of Wisconsin System (UWS) Project Number WR12R0004

Investigators:

Principal Investigators:

Dr. John Luczaj, Associate Professor and Dr. Michael Zorn, Associate Professor
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay, 2420 Nicolet Drive, Green Bay, WI 54311

Research Assistants:

Joseph Baeten, M.S. Candidate, Environmental Science & Policy Graduate Program
University of Wisconsin – Green Bay, 2420 Nicolet Drive, Green Bay, WI 54311

Mick Kiehl, Undergraduate Assistant, Geoscience Major
University of Wisconsin – Green Bay, 2420 Nicolet Drive, Green Bay, WI 54311

Period of Contract: 7/1/2012 – 6/30/2013

Background/Need:

Groundwater in parts of eastern Wisconsin contains dissolved strontium (Sr) levels that exceed lifetime and short-term EPA Health Advisories of 4 mg/L and 25 mg/L, respectively. Hundreds of wells are impacted throughout this region, including an area of anomalously high dissolved Sr in parts of Brown, Outagamie, and Calumet counties, which could potentially lead to health effects such as tooth enamel mottling or strontium rickets. Prior to this project, limited information was known about spatial distribution of dissolved strontium and how this relates to the aquifer chemistry, and very little was known about the source of the dissolved strontium.

Objectives:

This study had two principal objectives. The first objective was to determine the regional and stratigraphic distribution of dissolved strontium (Sr) in the groundwater of eastern Wisconsin, with a focus on Brown and Outagamie counties. The second objective was to evaluate potential sources of Sr in bedrock aquifers present in the region using various petrographic, geochemical, and isotopic methods.

Methods:

The study used several strategies, including detailed analysis of existing water quality and well construction data, collection of new water quality data, analysis of whole-rock samples, and isotopic “fingerprinting” of potential strontium sources. Water quality analytes included Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Cl^- , SO_4^{2-} , F^- , total hardness, and total alkalinity. Additional analytes in selected wells included Ba^{2+} , Mn^{2+} , Li^+ , B^+ , and heavy metals. The isotopic composition of dissolved Sr ($^{87}\text{Sr}/^{86}\text{Sr}$), as well as δD and $\delta^{18}\text{O}$ was performed on a large subset of the samples. Solid samples were characterized by 51-element analysis, with selected samples analyzed for strontium isotopic composition.

Results and Discussion:

Regionally, the distribution of dissolved Sr in the Cambrian-Ordovician aquifers varies dramatically from well below 1 mg/L to as high as 30 mg/L or more. Over 60% of the samples collected had dissolved strontium values over the lifetime Health Advisory Limit. For this study, the highest strontium value

recorded was 29.4 mg/L, although an earlier unpublished dataset shows dissolved strontium as high as 41.2 mg/L in the region.

Elevated dissolved strontium occurred in wells open to all Paleozoic stratigraphic units below the Maquoketa Shale. The likelihood that any particular stratigraphic unit would yield water with high dissolved strontium varied regionally in a complex way. Although some wells located west of the Maquoketa Shale subcrop have lower dissolved Sr-concentrations, as might be expected, this is not always the case.

One of the most surprising results of the study is the conclusion that the groundwater chemistry of the Cambrian-Ordovician aquifers in the region is surprisingly variable. This project provides the first known regional correlation between the deep aquifer groundwater chemistry and spatial distribution of regionally mapped fault zones in northeastern Wisconsin.

Strontium isotopic analysis of mineral, whole-rock, and groundwater has revealed the source of dissolved strontium in northeastern Wisconsin. The primary source originates from the dissolution of heterogeneously distributed celestine (SrSO_4) and possibly strontianite (SrCO_3) that occurs as mineral cement in vugs and fractures in carbonate rocks, and in intergranular porosity in sandstone aquifers.

Conclusions/Implications/Recommendations:

This study was successful in fulfilling our proposed objectives. A much clearer picture of the regional distribution of dissolved strontium is available, and the source of the problem has been identified. The area of concern for strontium has also been expanded to include parts of Door County and other areas, which were not identified by previous research. The stratigraphic distribution is better known, but the heterogeneous distribution of Sr sources in the aquifer, along with regional faults and variable flow histories due to aquifer compartmentalization requires a subregional focus to make accurate predictions.

A region of high dissolved Sr occurs in an arc-shaped band throughout eastern Wisconsin from suburban Milwaukee up through Brown, Outagamie, Calumet, Door, Oconto, and Marinette counties. This study confirms that there is a significant problem in northeastern Wisconsin, in which dissolved Sr levels exceed the EPA Lifetime Health Advisory level of 4 mg/L, and in many cases, exceed the 1 and 10 day Health Advisory levels for children of 25 mg/L. Analysis of Sr is easily conducted, and treatment systems (standard water softeners or reverse osmosis systems) are often available, but the public is generally unaware of the problem. We recommend establishing a Strontium Advisory Area or similar region of concern for Sr, and possibly for lithium (Li) and boron (B), throughout parts of eastern Wisconsin for wells located in the Cambrian-Ordovician aquifer system.

Related Publications:

Baeten, J.B., Luczaj, J., Zorn, M., and Johnson, D., 2013, Spatial Distribution of Dissolved Strontium in Eastern Wisconsin's Aquifers. American Association of Water Resources Wisconsin Section Meeting in Brookfield, Wisconsin on March 7-8, 2013. (Poster Presentation).

Key Words: Strontium, groundwater, isotopic, celestine, Cambrian, Ordovician, St. Peter, aquifer, Sinipee Group, health advisory, Brown County, Outagamie County, Calumet County

Funding:

University of Wisconsin System (UWS) Project Number WR12R0004 (majority)
University of Wisconsin – Green Bay Research Council (Grants-In-Aid-Of-Research) (supplemental)

INTRODUCTION

Eastern Wisconsin lies on the western flank of the ancestral Michigan basin and is bordered by the Wisconsin arch to the west, the Canadian Shield to the north, and the Illinois basin to the south (Figure 1). Here a sequence of several hundred feet of Paleozoic sedimentary rocks and Pleistocene glacial sediments overlies Precambrian igneous and metamorphic “basement” rocks (Figure 2). The thickness of the Paleozoic section ranges from near zero in eastern Waupaca County to as much as 1,600 feet (490 meters) in eastern Brown County. The relatively thin sequence of Paleozoic rocks in northeastern Wisconsin dips gently to the east into the ancestral Michigan basin, where the sedimentary section thickens substantially to over 15,700 feet (4,800 meters).

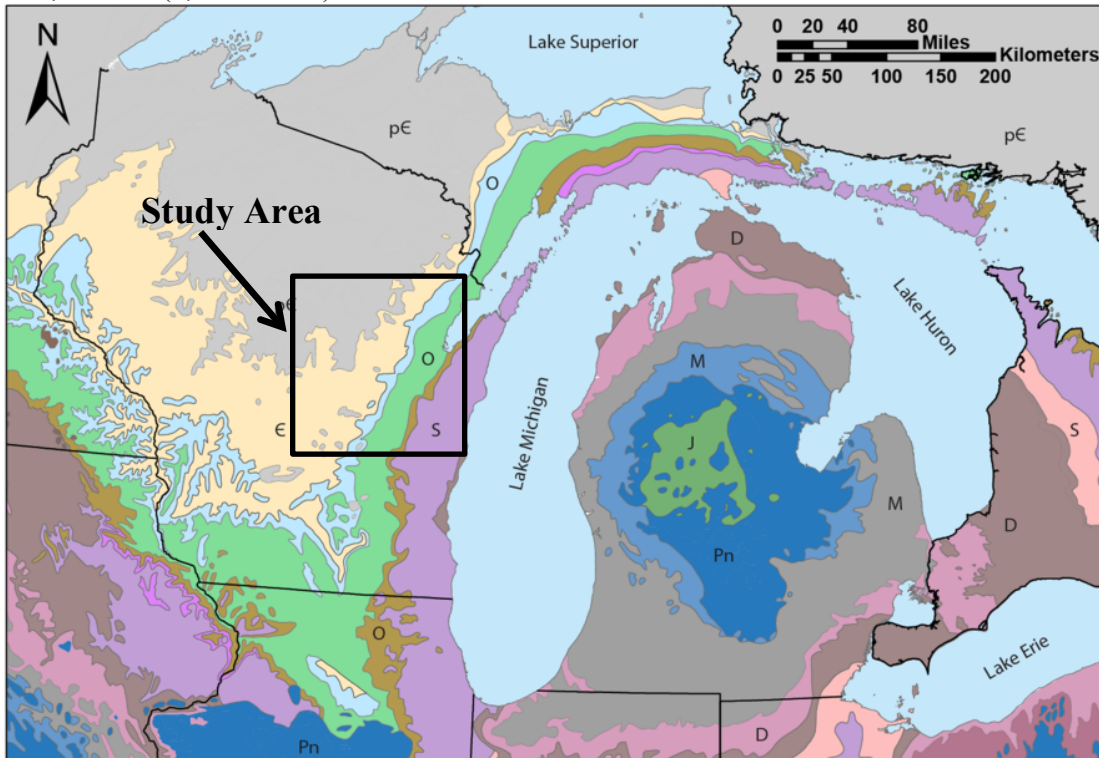


Figure 1: Generalized bedrock geologic map showing eastern Wisconsin and the ancestral Michigan basin. The study area for this project is located on the western flank of the Michigan basin as indicated by the boxed area. Sedimentary rocks range in age from Cambrian through Silurian and include mainly sandstone, shale, and dolostone. These units in this study area dip eastward towards the center of the Michigan basin. Base map from Luczaj (2013).

Groundwater in parts of eastern Wisconsin contains dissolved strontium (Sr) levels that exceed lifetime and short-term EPA Health Advisories of 4 mg/L and 25 mg/L, respectively. Hundreds of wells are impacted throughout this region, including an area of anomalously high dissolved Sr in parts of Brown, Outagamie, and Calumet counties. Although the full spectrum of adverse health effects from Sr ingestion is unclear, two health effects are well documented. One of these is known as “strontium rickets”, which is a musculoskeletal disease in which bones are thicker and shorter than normal and can be deformed (Özgür et al., 1996). Another health effect linked to the ingestion of groundwater-derived strontium, which has been documented in eastern Wisconsin, is tooth enamel mottling (Curzon and Spector, 1977).

Until recently, data regarding dissolved Sr in Wisconsin groundwater were limited, and it is now clear that a widespread problem exists in the aquifers in parts of eastern Wisconsin. Limited evidence for high Sr in the region’s groundwater had been available for over 50 years, yet little attention was given to this problem. Affected wells include many municipal wells from the suburban Milwaukee metropolitan area

north to Green Bay, with concentrations of strontium in groundwater drinking supplies reaching as high as 52 mg/L (White et al., 1963). In addition, an anomaly of very high Sr in domestic wells was recently identified in western Brown County in and near the Town of Lawrence (Dennis Rohr, Personal Communication). In 2009 a sampling event of 128 domestic wells in the Town of Lawrence was done showing 110 (86%) of these wells were above the lifetime EPA Health Advisory, and 39 (30%) of these wells tested above the short-term EPA Health Advisory. Overall, about 11,000 groundwater samples statewide have been analyzed for strontium (Table 1). In addition, very few of these groundwater samples were tested for complete suites of cation and anion chemistry, so limited information was known about the types of groundwater in the study area before this project began.

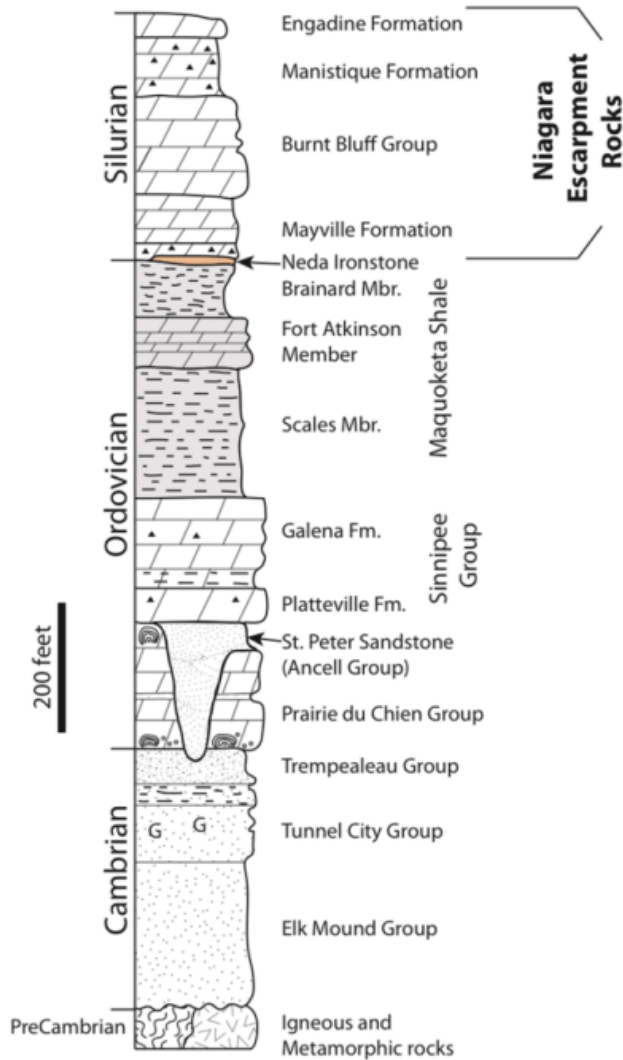


Figure 2: Stratigraphic column for northeastern Wisconsin (from Luczaj, 2013). The focus of this study includes the following units: Sinnipee Group, St. Peter Sandstone, Prairie du Chien Group and the Cambrian sandstones. Where present, the Maquoketa shale and the Sinnipee Group, along with Pleistocene sediments, generally act as confining units. In the eastern part of the study area, the Silurian dolomites are the primary aquifer with very few wells into the Cambrian-Ordovician aquifers.

Recognition that dissolved Sr might be a more significant problem than initially anticipated has prompted the recent addition of Sr to the State Lab of Hygiene water quality metals scan. As these new data become available, an analysis of how these groundwater values relate to the host rock aquifers is

necessary to understand the sources and mechanisms of release of Sr into the region’s groundwater. A better understanding of the regional and stratigraphic distribution of dissolved Sr was needed so that the full scope of the problem could be better understood.

| Table 1: Wisconsin Groundwater Samples with Dissolved Strontium Values | | | |
|---|--------------------------|-----------------------------|------------------------------|
| Source | Number of Samples | Samples above 4 mg/L | Samples above 25 mg/L |
| UWGB Sr Project* | 114 | 73 | 6 |
| USGS (Wilson, 2012) | 216 | 19 | 3 |
| NURE Data (U. S. Geological Survey, 2004)** | 4,417 | 5 | 0 |
| Wisconsin State Lab of Hygiene | 6,000 | 138 | 28 |
| Tim Grundl (UWM) (Personal Communication) | 33 | 13 | 7 |
| Dennis Rohr, Seymour High School, WI | 298 | 131 | 42 |
| Total | 11,078 | 379 | 86 |

**The number of samples for this project in this table does not include samples collected after water treatment. The effectiveness of strontium removal by treatment equipment will be discussed in a future publication.*

*** Many sample points from the NURE dataset were not sampled for strontium. Sampling occurred from 1975 to 1980. Not all samples in the NURE dataset are from groundwater; some samples taken from surface water sources.*

This study had two principal objectives. The first objective was to determine the regional and stratigraphic distribution of dissolved strontium (Sr) in the groundwater of eastern Wisconsin, with a focus on Brown and Outagamie counties. The Cambrian-Ordovician portion of the stratigraphic section in these two counties received the most attention, but additional sampling was conducted in adjacent counties and in some other stratigraphic units, which was helpful in expanding the regional distribution of high dissolved Sr. The second objective was to evaluate potential sources of Sr in bedrock aquifers present in the region using various petrographic, geochemical, and isotopic methods.

PROCEDURES AND METHODS

The study used several strategies, including detailed analysis of existing water quality and well construction data, collection of new water quality data, analysis of whole-rock samples, and isotopic “fingerprinting” of potential strontium sources. Several field and laboratory analytical methodologies were employed to investigate the chemical and isotopic composition of the groundwater and bedrock in the region. Geospatial mapping of various data were performed using ArcMap10.

Groundwater Sampling and Analysis

Groundwater sampling was conducted on available bedrock wells (domestic, municipal, farm, etc.) throughout the study area. Specific wells were identified using available well construction reports, where available, to maximize the regional and stratigraphic coverage in the study area. Groundwater sampling was conducted on 115 raw water samples (before treatment systems) and a few selected samples after certain treatment systems to assess the effectiveness of Sr removal. Wells were run for at least 3-5 minutes before sampling to gain a representative sample. Conductivity, temperature, and pH were recorded, and samples were collected for general inorganic chemistry, and in some cases, samples were collected for isotopic analysis of dissolved Sr, oxygen, and hydrogen.

The water quality analytes included dissolved Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Cl^- , SO_4^{2-} , F^- , total hardness, and total alkalinity (to calculate HCO_3^-). Some samples also included Ba^{2+} , Mn^{2+} , Li^+ , B, and various heavy metals. All general chemistry samples were run by Pace Analytical Services of Green Bay, WI using standard methods. Selected samples were also analyzed for isotopic composition. The isotopic composition of dissolved Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) was measured on 36 samples through a partnership established with the University of Illinois at Urbana-Champaign. Isotopic analysis of δD and $\delta^{18}\text{O}$ was performed on 63 samples at the W. M. Keck Paleoenvironmental and Environmental Stable Isotope Laboratory at the University of Kansas.

Additional data analysis included calculation of total dissolved solids as well as the saturation indices of several minerals, including celestine (SrSO_4), strontianite (SrCO_3), and others, and data evaluation is ongoing as part of a Master's Thesis project at UW-Green Bay.

Rock Sampling and Analysis

Solid samples were obtained from existing drill cores, well cuttings, and outcrop specimens at the University of Wisconsin-Green Bay. Over 100 samples were analyzed that represented rock units of northeast Wisconsin. Because of the limitations of using available sample sets, additional material was obtained in the form of well cuttings through a local well driller for key areas.

Solid samples were submitted to ALS Minerals of Vancouver, BC Canada for 51-element analysis using methods ME-MS41 and ME-MS41L, where necessary. In addition, selected samples of calcite, dolomite, celestine, and strontianite were submitted to the University of Illinois at Urbana-Champaign for $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic analysis.

RESULTS AND DISCUSSION

Several important results were obtained throughout the course of this research, some of which were unexpected. While the main objectives of the study were successfully completed, new information regarding aquifer compartmentalization, potential aquifer recharge anomalies, and additional emerging contaminants was also identified.

Regional and Stratigraphic Distribution of Dissolved Strontium

Available groundwater quality data from numerous sources (Table 1) were used to generate spatial maps, a few of which are included in this report. The region of high dissolved Sr occurs in an arc-shaped band throughout eastern Wisconsin from suburban Milwaukee up through Brown, Outagamie, Calumet, Door, and Marinette counties. For the purposes of this report, high dissolved Sr concentrations are considered to be those that exceed the EPA lifetime health advisory of 4 mg/L (4,000 $\mu\text{g}/\text{L}$). Figure 3 shows the statewide distribution of Sr in Wisconsin aquifers.

This study focused on groundwater in Brown, Outagamie, Calumet, Oconto, and Door Counties. The distribution of high dissolved Sr is heterogeneous, both in a regional, as well as a stratigraphic sense. Elevated dissolved strontium was observed in wells open to the Sinnipee Group dolostones through the Cambrian Sandstones (see Figure 2), but not in higher stratigraphic units. However, some areas of Silurian dolostone in Manitowoc County also show evidence of high dissolved Sr (e.g., McLaughlin, 2013; SLOH data set), but these were not the focus of this study.

Regionally, the distribution of dissolved Sr in the Cambrian-Ordovician aquifers varies dramatically from well below 1 mg/L to as high as 30 mg/L or more (Figure 4). Over 60% of the samples collected had dissolved Sr values over the lifetime Health Advisory Limit. For this study, the highest strontium value recorded was 29.4 mg/L, although an earlier unpublished dataset shows dissolved strontium as high as 41.2 mg/L in the region.

Generally, wells located west of the Maquoketa subcrop have lower dissolved Sr-concentrations, as might be expected, but this is not always the case. Some areas, such as the Town of Lawrence and parts of west-central Brown County, had dissolved Sr concentrations that far exceeded some areas confined by the Maquoketa Shale. In central Brown County and northward, the highest dissolved strontium concentrations occurred mainly east of the Fox River, increasing in areas confined by the Maquoketa Shale. Elevated dissolved Sr in the study area was observed in wells as far north as Door County, which was not previously reported by Wilson (2012).

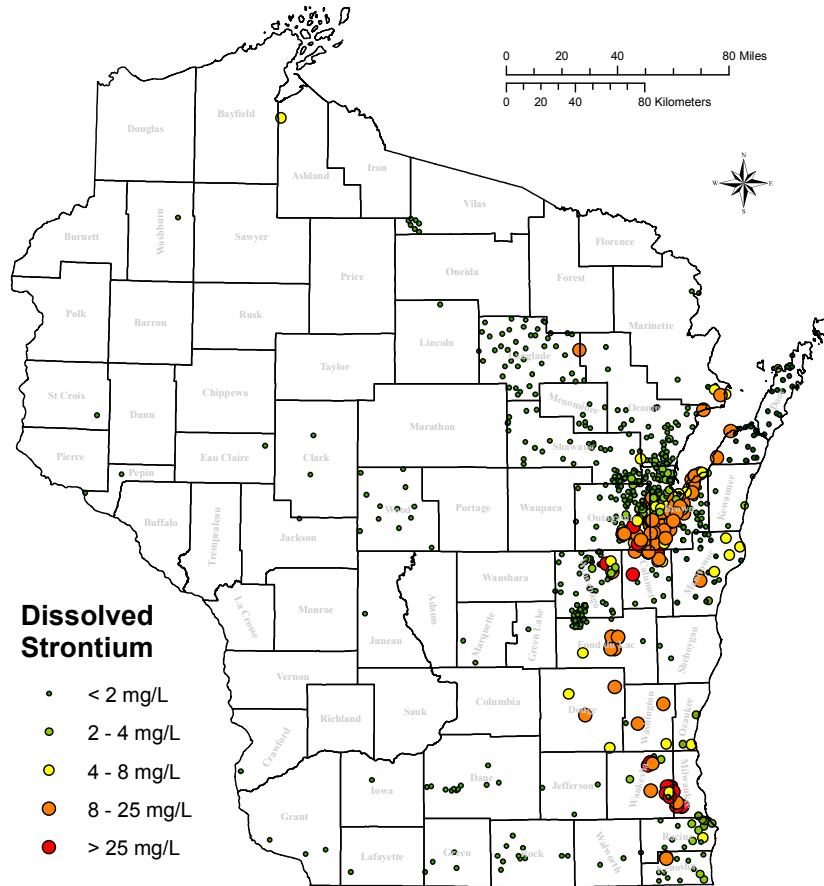


Figure 3: Statewide distribution of dissolved strontium in Wisconsin's aquifers. Samples are not separated to represent any specific aquifer system. Datasets included in this figure come from Wilson 2012, Wisconsin State Lab of Hygiene, Tim Grundl (personal communication), and Dennis Rohr (Table 1). NURE data were not included. Some data were not plotted due to time constraints and the inability to locate certain wells. A large focus was on the eastern part of the state because this is where most of the elevated samples exist. Results were mapped using ArcMap 10 by Joe Baeten and Mick Kiehl.

A different pattern is apparent for areas in southern Brown County, southeastern Outagamie County, and northwestern Calumet County. In these areas, high dissolved Sr concentrations do not appear to relate directly to the presence or absence of the Maquoketa Shale confining layer. High strontium occurs throughout this area.

Because of regional variability, it is difficult to generalize which Cambrian-Ordovician stratigraphic units in particular will yield water with the highest dissolved Sr concentrations. However, the average dissolved Sr for wells open to all units below the Maquoketa Shale exceeded the lifetime health advisory of 4 mg/L. The highest average dissolved Sr concentrations occurred in wells open to Sinnipee & St. Peter, Sinnipee through Prairie du Chien, and Sinnipee through Cambrian units. Stratigraphic analysis is complicated in some cases by thinning or pinch-out of the St. Peter Sandstone, which may not always

have been reported on well construction reports where the unit is ≤ 5 feet thick. Some wells only open to the Cambrian, such as one at Wrightstown and two at Freedom, also had very high dissolved Sr values.

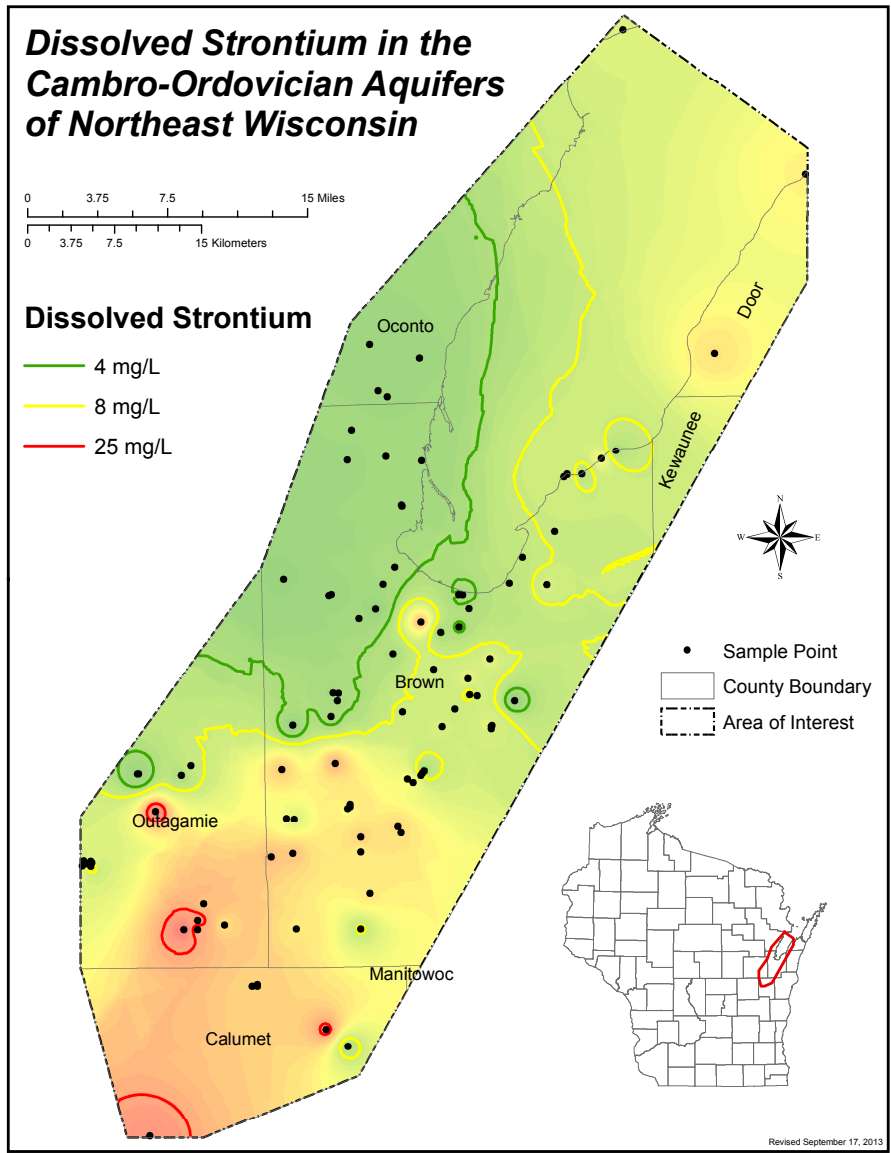


Figure 4: Regional distribution of dissolved strontium in the Cambrian-Ordovician aquifers of northeastern Wisconsin. Data are from samples collected during this project only. Map created by Joe Baeten using ArcMap 10.

General Chemistry and the Compartmentalization of Aquifers

The groundwater chemistry of the Cambrian-Ordovician aquifers in the region is surprisingly variable. Variation exists along easterly flow paths in some cases, as previously reported and modeled by Weaver and Bahr (1991a, 1991b), Conlon (1998), and Grundl et al. (2013). Weaver and Bahr (1991a, b) reported that as the Ordovician and Cambrian Sandstone aquifers trend beneath the Maquoketa Shale and become confined, the sulfate and chloride concentrations increase. Sodium and potassium concentrations also increase in the confined portion of the sandstone aquifers. Weaver and Bahr concluded that the elevated concentrations of sulfate, chloride, sodium, and potassium in the confined portion of the sandstone aquifers were most likely due to chloride-bearing minerals and trace evaporites and not remnants of Michigan Basin brines. Grundl et al. (2013) concluded that groundwater in the study area is up to 5,000 to 20,000 years old and contains an isotopic signature consistent with recharge by subglacial meltwater.

This project provides the first known regional correlation between the deep aquifer groundwater chemistry and spatial distribution of regional fault zones mapped by Luczaj (2011). The locations of these regional faults and the aquifer zones, or “compartments”, between them are shown in Figure 5. Compartments are designated as Zones 1 through 3, from north to south.

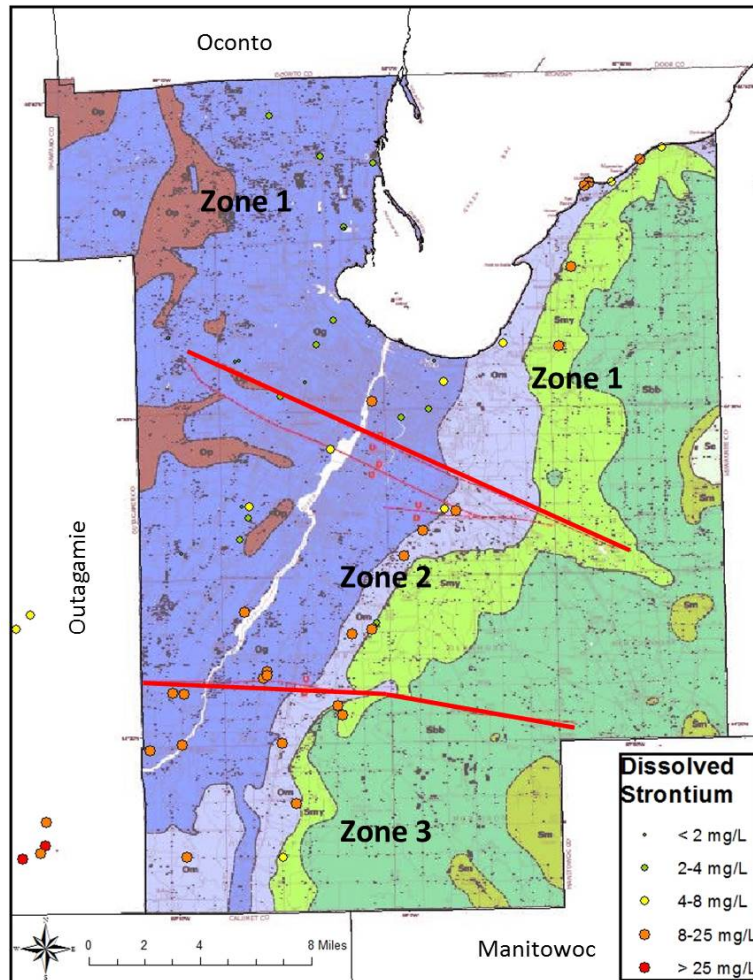


Figure 5: Bedrock Geologic Map for Brown County, Wisconsin (Luczaj, 2011) with aquifer “zones” (or compartments) delineated by regionally extensive faults. Dark blue and brown areas in western Brown County are the Sinnipee Group (Og and Op). Light blue (Om) represents the Maquoketa Shale. Green colors indicate Silurian dolostone units. Red lines indicate major faults along reactivated basement tectonic features that cut across the Paleozoic rocks in the region.

Major ion chemistry for deep aquifer samples collected from each of these aquifer zones in Brown County is presented on Piper Plots in Figure 6. The plots illustrate that even for Brown County, the major ion chemistry of the deep aquifer is surprisingly variable, and has to some extent, been controlled by aquifer compartmentalization. Zones 1 and 2 have typical Ca-Mg-HCO₃-type waters to the west, as expected, closer to the aquifer recharge areas. Groundwater in both zones trends along an apparent mixing line toward Na-SO₄-Cl-type waters. Zone 3 water is somewhat different, starting as a Ca-Na-SO₄-type water that also trends toward a Na-SO₄-Cl-type water. Groundwater from all three zones shows somewhat different chemistry than groundwater from southeastern Wisconsin (Grundl and Cape, 2006).

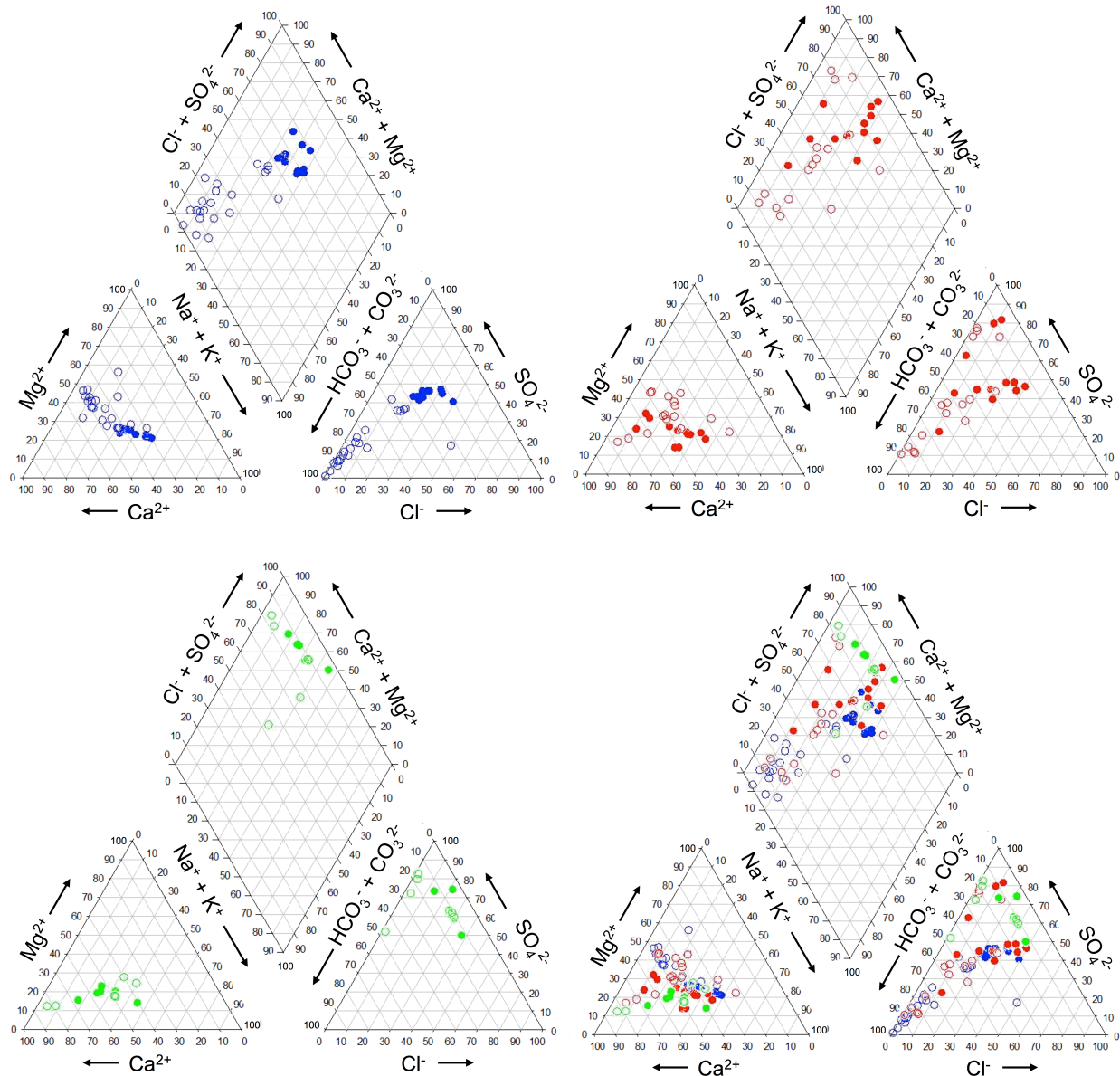


Figure 6. Piper plots showing selected data from different aquifer compartments in Brown County, where fault locations are well documented. Open circles in each plot represent samples that occur west of the Maquoketa subcrop (i.e., “unconfined”), whereas solid circles represent samples from parts of the deep aquifer that are confined, at least in part, by the Maquoketa Shale. Blue circles (upper left) represent Zone 1 in the northern portion of Brown County, Red circles (upper right) represent Zone 2 in central Brown County, and Green circles (lower left) represent Zone 3 (southern Brown County). All data for Brown County are shown on the plot on the lower right.

To our knowledge, this study presents the first evidence for aquifer compartmentalization by faults in Wisconsin. This has important implications for understanding groundwater chemistry throughout the region, as well as a better understanding of groundwater flow systems through the development of more accurate numerical flow models.

Source Evaluation of Strontium in Bedrock Units

Stratigraphically, the highest whole-rock strontium concentrations exist in the Sinnipee and Prairie du Chien Group dolostones as well as localized areas of the St. Peter and Cambrian sandstones, especially in areas further eastward. However, none of the whole-rock dolomite or sandstone samples analyzed appear sufficiently enriched in strontium to explain the high levels of dissolved strontium in the aquifers, in comparison to other dissolved ions, suggesting heterogeneous source for strontium in the bedrock. Strontium minerals such as celestine (SrSO_4) and strontianite (SrCO_3) have been reported as vug and fracture fills, as well as intergranular cements at several locations in Ordovician units of eastern Wisconsin (Tyler, 1936; Cordua, 2011; Luczaj and McIntire, 2008). Intergranular celestine cement was reported in the St. Peter Sandstone in well cuttings from De Pere, Cedarburg, Two Rivers, and Milwaukee (Tyler, 1936). All these cities are located along the eastern part of the state. The region with the most reported surface examples of Sr-minerals occurs in eastern Outagamie County at the Mackville Quarry and in west-central Brown County at the Northeast Asphalt Lawrence Quarry and in well cuttings from the City of De Pere (Figure 7). Together, the rock units that host these minerals include the Ordovician Sinnipee Group, St. Peter Sandstone, and the Prairie du Chien Group.

No regional trends were observed in whole-rock data for two reasons: limited regional sample availability and strongly heterogeneous distribution of Sr-rich minerals. To illustrate this heterogeneity, we analyzed different parts of dolostone samples with large celestine (SrSO_4) crystals. The areas with no visible SrSO_4 crystals had whole-rock Sr concentrations less than or equal to other samples analyzed throughout the region ($< 100 \text{ mg/kg}$), despite being only centimeters from the celestine in the same sample.

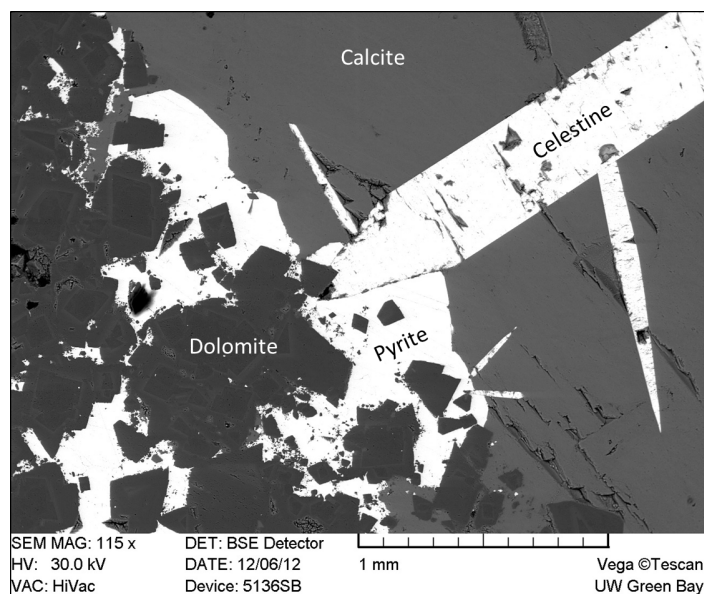


Figure 7. SEM image showing bladed SrSO_4 (Celestine) and associated vug-filling minerals from the Lawrence Quarry near De Pere, Wisconsin. Mineralization sequence shows dolomite first, followed by celestine, pyrite, and late calcite. The fact that celestine is enveloped by later coarse calcite crystals indicates that the rocks have contained abundant Sr-mineralization for extended periods of geologic time, likely due to hydrothermal brine migration from the ancestral Michigan basin during the mid-late Paleozoic Era.

The primary source of dissolved strontium in the groundwater of northeastern Wisconsin seems to originate from the dissolution of heterogeneously distributed celestine (SrSO_4) (Figure 7) and possibly strontianite (SrCO_3). This conclusion is supported by three principal arguments. First, the typical concentration of Sr in bedrock in the region is $< 165 \text{ ppm}$, which is insufficient to explain the high dissolved concentrations in the aquifers if dissolution of dolomite alone were the source. Second, plots of groundwater in the region approach the saturation index of celestine as Sr concentrations increase (Figure

8). Third, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic signature of available celestine and strontianite mineral samples from eastern Wisconsin is nearly identical to the isotopic signature of dissolved Sr in Ordovician and Cambrian aquifers in northeastern Wisconsin (Figure 9), **but does not match the isotopic composition of the host dolostones**. Because of its isotopic similarity to hydrothermal fluids described for the St. Peter Sandstone in the Michigan basin (see Winter et al., 1995, “fluid type 3”), we believe that these minerals formed from fluids that invaded Wisconsin via flow along the main aquifer systems, precipitating celestine as the fluids moved updip. This is also consistent with Ordovician-hosted brines in the Michigan basin today (McNutt et al., 1987) and hydrothermal fluid flow interpretations by Luczaj (2006). While some limited influence from host dolomite and calcite may exist, it is clear that the strontium minerals are isotopically most similar to the dissolved Sr in the Cambrian-Ordovician aquifers.

The regional distribution of elevated dissolved Sr is likely controlled by two main factors. First, eastward flow in the Cambrian-Ordovician aquifer system from the recharge areas west of the study area takes relatively fresh water toward the ancestral Michigan basin. Eastward flow allows dissolved Sr concentrations to increase over time while in contact with celestine and other Sr-rich minerals in the aquifer. This is consistent with plots of the Celestine saturation index (SI) approaching zero as dissolved Sr increases (Figure 8).

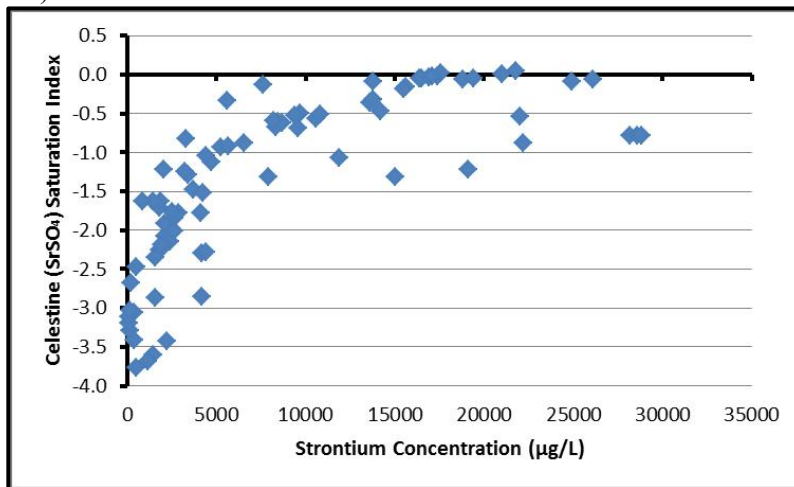


Figure 8. Celestine saturation index versus dissolved strontium concentration in the groundwater of northeastern Wisconsin. Dissolution of celestine is the primary control on dissolved Sr in the aquifers.

Additional Contaminants Identified

Analyses of dissolved boron (B) and lithium (Li) in selected samples has identified that these may also be important elements of concern in the deep aquifer system. Two of 49 samples analyzed for dissolved B exceeded the MCL of 1,000 µg/L. One sample was 3,300 µg/L, over three times the MCL established by the State of Wisconsin. Although Li does not have an established MCL, concentrations varied dramatically in parts of the region from 1.7 µg/L to 305 µg/L. High levels of dissolved Sr, Li, B, and F have been reported elsewhere in carbonate rock on marginal parts of high salinity basins (e.g., Klimas and Mališauskas, 2008). We recommend that sampling of all four ions be considered in deep aquifer wells in the eastern portion of Wisconsin.

Water Treatment Recommendations

A limited subset of water samples from 3 domestic and 2 municipal water treatment systems, such as water softeners and ion exchange systems, were also analyzed to assess their effectiveness in removing dissolved Sr. Water softeners at household locations were very effective at removing at least 97% of the dissolved Sr. Municipal systems, designed for removal of Radium, were somewhat less effective, with 56.6% and 73.7% Sr removal in two wells analyzed.

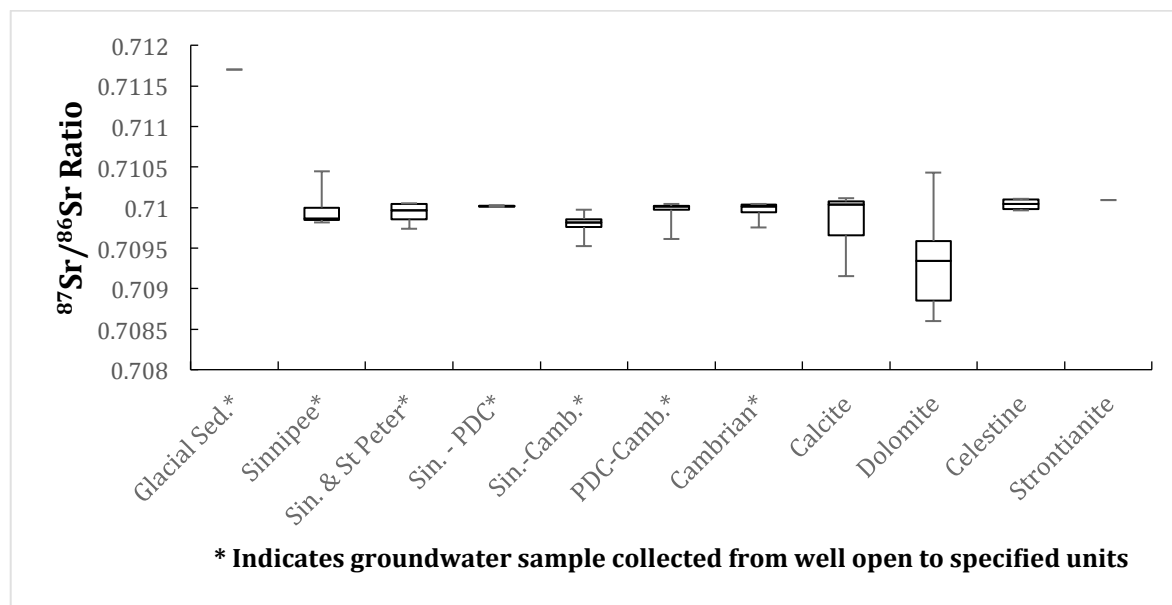


Figure 9. Box plot graph showing distribution of Sr-isotope values for groundwater and minerals in northeastern Wisconsin's aquifers. Groundwater samples were further subdivided into 7 categories. Top of line is the maximum, bottom of line is the minimum, top of box is the 75th percentile, bottom of box in the 25 percentile, and the central line in the box is the median.

CONCLUSIONS AND RECOMMENDATIONS

This study was successful in fulfilling our proposed objectives. The source of the Sr appears to be the dissolution of heterogeneously distributed crystals of celestine (SrSO_4), and possibly strontianite (SrCO_3), in the aquifers, that were associated with ancient hydrothermal brine migration. This conclusion is based upon mineral identification and Sr-isotopic fingerprinting that associates Sr minerals with dissolved Sr in groundwater. The regional distribution of dissolved Sr is better known, and the area of concern for Sr has been expanded to include parts of Door County and other areas, which were not identified by previous research (e.g., Wilson, 2012). The stratigraphic distribution is also better known, but the heterogeneous distribution of strontium sources in the aquifer, along with regional faults and variable flow histories due to aquifer compartmentalization requires a subregional focus to make accurate predictions.

This study confirms that there is a significant problem in northeastern Wisconsin, in which dissolved Sr exceeds the EPA Lifetime Health Advisory level of 4 mg/L, and in many cases, exceeds the 1 and 10 day Health Advisory levels for children of 25 mg/L. Analysis of dissolved Sr is possible at most water quality laboratories, and treatment systems (standard water softeners or reverse osmosis systems) are often available, but the public is generally unaware of the Sr problem. We recommend establishing a Strontium Advisory Area or similar region of concern, and possibly for Li and B, throughout parts of eastern Wisconsin for wells located in the Cambrian-Ordovician aquifer system.

ACKNOWLEDGEMENTS

We would like to thank Dave Johnson (Wisconsin DNR) for suggesting the idea of studying dissolved strontium. We also thank the numerous homeowners, municipalities, and businesses that allowed us to sample their wells, without which, this project would not have been possible. Groundsource, Inc. helped obtain well cuttings from some locations. The UW-Green Bay Research Council also supplied some funding that aided in chemical and isotopic analyses presented in this project. Alyssa Shiel (Univ. of Illinois) and Greg Cane (Univ. of Kansas) aided in the analysis of Sr, H, and O isotopes that were important to this study. Undergraduate student Mick Kiehl helped to plot some of the strontium data for counties south of the study area in Figure 3.

REFERENCES

- Conlon, T. D., 1998, Hydrogeology and simulation of ground-water flow in the Sandstone Aquifer, northeastern Wisconsin. Water-Resources Investigation – USGS Report Number WRI 97-4096.
- Cordua, W., 2011, Minerals of Wisconsin Online Database. Accessed on November 6, 2011. <<http://wisconsin Geological Survey.org/MinIndexIntro.htm>>.
- Curzon, M. E. J., and Spector, P. C., 1977, Enamel mottling in a high strontium area of the U.S.A. *Community Dentistry and Oral Epidemiology*, 5, p. 243-247.
- Grundl, T., and Cape, M., 2006, Geochemical factors controlling radium activity in a sandstone aquifer. *Ground Water*, 44, 518-527.
- Grundl, T., Magnusson, N., Brennwald, M.S., and Kipfer, R., 2013, Mechanisms of subglacial groundwater recharge as derived from noble gas, ¹⁴C, and stable isotope data. *Earth and Planetary Science Letters*, v. 369-370, p. 78-85.
- Klimas, A. and Mališauskas, A., 2008, Boron, fluoride, strontium, and lithium anomalies in fresh groundwater of Lithuania. *Geologija*, v. 50, no. 2, p. 114-124.
- Luczaj, J. A., 2006, Evidence against the Dorag (Mixing-Zone) model for dolomitization along the Wisconsin arch – A case for hydrothermal diagenesis. *AAPG Bulletin*, v. 90, p. 1719-1738.
- Luczaj, J.A., 2010, The Significance of Faulting to the Hydrogeology of the Cambro-Ordovician Aquifer System in Northeastern Wisconsin. *WGWA Newsletter*, v. 24, no. 4.
- Luczaj, J.A., 2011, Preliminary Geologic Map of the Buried Bedrock Surface, Brown County, Wisconsin. Wisconsin Geological and Natural History Survey, Open File Report 2011-2, 1:100,000 Scale Map Sht.
- Luczaj, J.A., 2013, Geology of the Niagara Escarpment in Wisconsin. *Geoscience Wisconsin*, v. 22, p. 1-34.
- Luczaj, J. A. and McIntire, M. J., 2008, Geochemical Characterization of Sulfide Mineralization in Eastern Wisconsin Carbonate Rocks. Final Project Report (#WR07R0004) submitted to the University of Wisconsin – Water Resources Institute on October 6, 2008, 13 pages.
- McLaughlin, P., Bradbury, K., Chase, P., and Emsbo, P., 2013, Brine Water Chemistry and Relationship to Bedrock Geology in the Deep Subsurface of Manitowoc County, WI. AWRA Wisconsin Section Meeting, March 7-8, 2013, Brookfield, Wisconsin, page 44.
- McNutt, R.H., Frape, S.K., and Dollar, P., 1987, A strontium, oxygen, and hydrogen isotopic composition of brines, Michigan and Appalachian Basins, Ontario and Michigan. *Applied Geochemistry*, v. 2, p. 495-505.
- Özgür, S., Sümer, H., and Koçoğlu, G., 1996, Rickets and soil strontium. *Archives of Disease in Childhood*, 75, p. 524-526.
- Rohr, Dennis. Personal Communication. April 9, 2012.
- Tyler, S. A. (1936). Heavy Minerals of the St. Peter Sandstone in Wisconsin. *Journal of Sedimentary Petrology*, v. 6, No. 2, pp. 55-84.
- U. S. Geological Survey, 2004, National Uranium Resource Evaluation (NURE) Hydrogeochemical and Stream Sediment Reconnaissance data: U. S. Geological Survey, Denver, CO. Online Database.
- Wilson, J. T., 2012, Water-Quality Assessment of the Cambrian-Ordovician Aquifer System in the Northern Midwest, United States. U.S. Geological Survey. Scientific Investigation Report 2011-5229, 154 pages.
- Wilson, T. P. and Long, D. T., 1992,. Geochemistry and isotope chemistry of Michigan Basin brines: Devonian formations. *Applied Geochemistry*, Vol. 8. pp. 81-100.
- Weaver, T. R., and Bahr, J. M., 1991a, Geochemical evolution in the Cambrian-Ordovician sandstone aquifer, eastern Wisconsin: 1. Major ion and radionuclide distribution. *Ground Water*, 29, 350-356.
- Weaver, T. R. and Bahr, J. M., 1991 b, Geochemical evolution in the Cambrian-Ordovician sandstone aquifer, eastern Wisconsin. 2. Correlation between flow paths and ground-water chemistry. *Ground Water*, 29, 510-515.
- Winter, B.L., Johnson, C.M, Simo, J.A., and Valley, J.W., 1995, Paleozoic fluid history of the Michigan Basin: Evidence from dolomite geochemistry in the Middle Ordovician St. Peter Sandstone. *Journal of Sedimentary Research*, v. A65, no. 2, p. 306-320.

APPENDIX A – Awards, Publications, Reports, Patents, and Presentations

Baeten, J.B., Luczaj, J., Zorn, M., and Johnson, D., 2013, Spatial Distribution of Dissolved Strontium in Eastern Wisconsin's Aquifers. American Association of Water Resources Wisconsin Section Meeting in Brookfield, Wisconsin on March 7-8, 2013. (Poster Presentation).

This project will also lead to a Master's Thesis (in draft stage at present), as well as 1 or 2 peer-reviewed publications.