

**Title: Maquoketa Shale as Radium Source for the Cambro-Ordovician Aquifer in Eastern Wisconsin**

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**Key Words:** Radium, Cambro-Ordovician aquifer, deep sandstone aquifer

**Background/Need:** The Cambro-Ordovician aquifer system in eastern Wisconsin is becoming ever more heavily relied upon as a source of drinking water by many of the rapidly growing urban centers of eastern Wisconsin. The water produced from this aquifer often contains combined radium activities in excess of the drinking water limit of 5 pCi/L, in some cases in excess of 30 pCi/L. Because the source of this radium is not fully understood, basic questions as to how best to manage this increasingly important source of drinking water are unanswerable. Previous studies have shown that radium concentrations in excess of approximately 5 pCi/L are not supportable by the presence of parent isotopes in the aquifer solids. It is possible that high radium concentrations in Cambro-Ordovician water originate from downward flow of recharge water through the Maquoketa Shale. The Maquoketa outcrop pattern forms the demarcation between unconfined conditions in the underlying Cambro-Ordovician aquifer to the west and confined conditions to the east. Strong downward gradients exist across the Maquoketa and flow across the unit should be maximal near the outcrop where total thickness is at a minimum. This strong downward gradient is very recent and is caused by heavy pumpage of the Cambro-Ordovician in urban areas.

**Objectives:**

- 1) Define the extent of the radium problem within the Cambro-Ordovician aquifer in both the spatial and temporal domains.
- 2) Determine if the Maquoketa Shale serves as the source for the high radium content observed in portions of the Cambro-Ordovician aquifer.

**Methods:** This study was performed by making extensive use of both water quality and well construction data contained in the WDNR Drinking Water Database. This was combined with a laboratory study of the parent radioisotope content ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{230}\text{Th}$ ) of Maquoketa Shale itself. Isotope analyses were performed on both the bulk solids and the surface coatings (using a 6 M HCl extraction).  $^{226}\text{Ra}$  content of the bulk solids was also performed. Major ion chemistry and radium ( $^{228}\text{Ra}$  and  $^{226}\text{Ra}$ ) content of Maquoketa water was also obtained from the WGNHS research well in Minooka Park, Waukesha.

**Results and Discussion:** A summary of the important results is given below.

- High radium activity occurs in the Cambro-Ordovician in a band roughly coincident with the Maquoketa subcrop pattern. This pattern extends across the entire eastern portion of the state from Brown County in the north to Racine County in the south. Maps are presented depicting this trend. Radium activities have remained relatively constant from the middle 1970s to the present.
- High gross alpha activity also occurs in a band roughly coincident with the Maquoketa subcrop pattern extending along the entire eastern portion of the state. Maps are presented depicting this trend. Gross alpha activity has been steadily rising from the middle 1970s to the present.

- Stable isotope and major ion chemistry indicate that water is moving through the Maquoketa Shale. Major ion chemistry indicates that water is moving through the dolomitic Fort Atkinson member of the Maquoketa Shale with little time for geochemical evolution. Water contained in the hydraulically resistive Brainard and Scales Shale members of the Maquoketa have evolved to a Na-CO<sub>3</sub> signature most likely from the microbial oxidation of organic carbon, dissolution of dolomite and the exchange of Ca and Mg for Na on aquifer solids. The mass balance for these reactions can be written:

$$m\text{CO}_2 = \Delta M_{\text{HCO}_3} - \Delta M_{\text{Ca}} - \Delta M_{\text{Mg}} - (\Delta M_{\text{Na}} + \Delta M_{\text{Cl}})/2$$

where  $m\text{CO}_2$  = moles CO<sub>2</sub> gas produced from organic carbon oxidation

$\Delta M_{\text{Na}}$  = change in molarity of Na along flowpath.

- The stable isotopic data suggests that Pleistocene water (ca. 12,000 years old) remains in portions of the Maquoketa. Weaver and Bahr (1991a, b) calculate a residence time of about 5600 years in the Maquoketa. These travel time estimates yield rates of 6E-4 to 1.3E-3 mMol/yr organic carbon oxidized. This oxidation rate matches literature values for carbon oxidation rates in deep aquifer systems which range from 1E-3 to 1E-6 mMol/L (Chapelle and Lovely, 1990).
- Radioisotope ratios within the solids of the Maquoketa Shale indicate that parent radioisotopes are being mobilized from their original position in the silicate minerals to surface coatings. This mobilization is most pronounced near the westernmost extent of the Maquoketa where water movement is at a maximum. <sup>234</sup>U/<sup>238</sup>U vs <sup>230</sup>Th/<sup>238</sup>U crossplots were to illustrate this trend.
- The presence of the Maquoketa Shale causes changes in the major ion chemistry of the underlying Cambro-Ordovician, in particular an increase in SO<sub>4</sub><sup>2-</sup> at the expense of HCO<sub>3</sub><sup>-</sup>. Limited data indicate that other subtle changes are occurring over time in the Cambro-Ordovician that could be the cause of high radioactivity near the subcrop pattern of the Maquoketa. There are indications that radium content to the west of the Maquoketa subcrop may be largely controlled by dissolution of barite. To the east of the subcrop other processes are likely in operation. These could include reductive dissolution of ferric hydroxides, cation exchange reactions, or mobilization of the parent isotopes of uranium. Specific wells can be found to indicate that one or more of these processes are occurring locally.

In any given aquifer system, the bulk of the radioactivity will reside on the solids, not in the aqueous phase. Determining which process(es) control the release of solid- phase radioactivity in the Cambro-Ordovician into the groundwater will require a more thorough understanding of the system. The actual cause for high radium and gross alpha activities in the Cambro-Ordovician is undoubtedly a combination of multiple, sometimes subtle, processes that may differ from location to location. The largest gap in our understanding of the Cambro-Ordovician is the lack of vertically discrete chemical information caused by the fact that deep sandstone wells are screened across large portions of the aquifer. There is essentially no information as to the spatial extent of high radioactivity in the vertical direction. The paucity of major ion chemistry over time represents another gap in our understanding. This limits our ability to model the underlying causes behind the trends in the radiometric content. Future research efforts should focus on developing vertically discrete information and the initiation of a long- term program to monitor changes in major ion chemistry.

## References

Chapelle, F. and Lovely, D. 1990. Rates of microbial metabolism in deep coastal plain aquifers. *Appl. Environmental Microbiol.* 56(6):1865-1874.

Weaver, T. and Bahr, J. 1991a. Geochemical evolution of the Cambro-Ordovician aquifer, eastern Wisconsin: 1. Major ion and radionuclide distribution. *Ground Water* 29:350-356.

Weaver, T. and Bahr, J. 1991b. Geochemical evolution of the Cambro-Ordovician aquifer, eastern Wisconsin: 2. Correlation between flow paths and ground water chemistry. *Ground Water* 29:510-515.

**Conclusions/Implications/Recommendations:** This study has furthered the understanding of the geochemical and radiometric conditions within the Maquoketa Shale and the underlying Cambro-Ordovician aquifer system. The extent of high radioactivity in the Cambro-Ordovician has been defined both spatially and temporally. Insights into the geochemical processes that are contributing to high radioactivity have been elucidated.