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Effect of geochemical conditions on radium mobility in discrete intervals within the Midwestern Cambrian-Ordovician aquifer system

Madeleine Mathews[a], Madeline Gotkowitz[b], Matthew Ginder-Vogel[a,*]

[a] Environmental Chemistry and Technology, Department of Civil and Environmental Engineering, University of Wisconsin – Madison, Madison, WI, United States
[b] Wisconsin Geological and Natural History Survey, Madison, WI, United States

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ABSTRACT

Radium (Ra) commonly occurs in groundwater obtained from the Midwestern Cambrian-Ordovician aquifer system (C-O-AS) at activities approaching and exceeding the United States Environmental Protection Agency's Maximum Contaminant Level (MCL) of 5 pCi/L for combined ^{226}Ra and ^{228}Ra. The occurrence of Ra(II) in groundwater is dependent on a number of factors, including the prevalence of parent radionuclides within hydrogeological strata, as well as aquifer geochemical conditions. Interbedded aquifer and aquitard sequences within the Midwestern C-O-AS are stratified with respect to Ra(II) activity and geochemical conditions, and thus the formations that serve as Ra(II) sources to groundwater remain poorly constrained. This study analyzes aqueous samples collected from short-screened wells at various depths within the Midwestern C-O-AS near Madison, WI, USA, to determine geochemical parameters including dissolved oxygen; pH; major and minor ions; and metals, including ^{226}Ra, ^{228}Ra, and parent isotopes ^{238}U and ^{232}Th. Additionally, the elemental composition of aquifer solids is determined as a function of depth. Within solid phases, ^{238}U and ^{232}Th occur in both fine-grained facies and as coatings on sandstone minerals. Most groundwater samples contain dissolved combined Ra (II) lower than 2.5 pCi/L; however, one well completed in the unconfined and one well completed in the confined portion of the groundwater system exceed 3.5 pCi/L. In the confined system, anoxic conditions are associated with elevated Ra(II) concentrations, while in the upper, oxic aquifer, elevated total dissolved solids are positively related to Ra(II). These results demonstrate that multiple factors impact Ra(II) sources and mobility in the regionally unconfined portion of the Midwestern C-O-AS.

1. Introduction

Radium (Ra) is a naturally occurring, radioactive contaminant, present in many groundwater systems. Ingestion of Ra is a human health concern, as it accumulates in bone tissue, where it continues to undergo radioactive decay. Long-term exposure may damage cell tissue and is related to various types of bone disease (Canu et al., 2011; Evans, 1933; Guse et al., 2002; International Atomic Energy Agency, 2014; Mays et al., 1985; Moss et al., 1995; Rowland et al., 1978). The United States Environmental Protection Agency (EPA) regulates Ra in drinking water at a maximum contaminant level (MCL) for Ra in drinking water of 5 pCi/L for the combined total of isotopes ^{226}Ra and ^{228}Ra (U.S. EPA, 2000).

One source of radium to groundwater is the radioactive decay of parent elements uranium (U) and thorium (Th) (Fig. SI-1) (Copenhaver et al., 1993; Gilkeson, 1984; International Atomic Energy Agency, 2014; Reynolds et al., 2003; Szabo et al., 2012; Tricca et al., 2001, 2000). These parent isotopes are common to fine-grained sedimentary deposits, such as shale and siltstone, and/or transition metal (e.g., Fe and Mn) (hydr)oxide coatings on mineral grains (Gilkeson et al., 1978; Grundl and Cape, 2006; International Atomic Energy Agency, 2014). Elevated concentrations of U and Th have also been observed in Precambrian crystalline bedrock (Mursky et al., 1989). Saline brines are also a possible source of dissolved U and Ra(II) to groundwater systems. During Pleistocene glaciation, increased pore pressure in the Lake Michigan basin, resulting from the overlying Laurentide ice sheet, may have driven saline groundwater West, providing a potential source of elevated Ra(II) concentrations in the Eastern portion of the Midwestern C-O-AS (Siegel, 1990; Weaver and Bahr, 1991a; Winter et al., 1996).

Once in groundwater, Ra(II) mobility is largely controlled by sorption to transition metal (e.g., Fe and Mn) (hydr)oxide minerals and/or co-precipitation with barite ($BaSO_4$). These processes are affected by local aquifer geochemical conditions (Gilkeson et al., 1978; Tricca et al., 2000; Vinson et al., 2012). For example, in the Midwestern C-O-

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[*] Corresponding author.
E-mail address: matt.ginder-vogel@wisc.edu (M. Ginder-Vogel).

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AS, elevated dissolved Ra(II) is generally correlated with low pH, low dissolved oxygen (DO), and high total dissolved solids (TDS) (Ayotte et al., 2011; Gilkeson, 1984; Grundl and Cape, 2006; Krishnaswami et al., 1991; Stackelberg et al., 2018; Szabo et al., 2012; Tomita et al., 2010; U.S. Department of the Interior and U.S. Geological Survey, 2012; Vinson et al., 2013, 2009). Reducing conditions are often associated with elevated dissolved Ra(II), because these conditions do not favor the presence of transition metal (hydr)oxides (Ayotte et al., 2011; Burghardt and Kassahun, 2005; Gonneea et al., 2008; Nathwani and Phillips, 1979; Reynolds et al., 2003; Stackelberg et al., 2018; Szabo et al., 2012; Tricca et al., 2001). Elevated ionic strength is also associated with elevated dissolved Ra(II), due to sorption-site competition (Szabo et al., 2012; Wilson, 2012). Within sulfate-rich, oxic aquifer systems, such as a regionally unconfined portion of the Midwestern C-O-AS in Southeast Wisconsin, co-precipitation with $BaSO_4$ may limit dissolved Ra(II) (Grundl and Cape, 2006; Szabo et al., 2012).

Elevated dissolved Ra(II) is common to the Midwestern C-O-AS, and is commonly associated with anoxic conditions and elevated ionic strength (Stackelberg et al., 2018; Szabo et al., 2012). Similar trends are observed throughout Wisconsin (Grundl and Cape, 2006; Stackelberg et al., 2018; Vinson et al., 2018). However, these studies rely on water samples collected from municipal wells open to hundreds of meters of aquifer, resulting in water produced from multiple hydrostratigraphic units (Grundl and Cape, 2006; Stackelberg et al., 2018; Szabo et al., 2012; Vinson et al., 2012, 2009; Weaver and Bahr, 1991a). This makes it difficult to attribute the geologic source of Ra to specific strata within the groundwater system.

This study investigates sources of dissolved Ra(II) within discrete hydrostratigraphic units in the Midwestern C-O-AS near Madison, Wisconsin, where the upper and lower sandstone aquifers are separated by a locally-confining shale aquitard (Weaver and Bahr, 1991a; Young and Siegel, 1992). Possible sources of Ra to groundwater include Ra-bearing aquifer solids, such as oxide rinds on silicate minerals; shales or other fine-grained, interbedded strata enriched in parent isotopes; and deep brines (Gilkeson et al., 1983; Grundl and Cape, 2006; Siegel, 1990; Sturchio et al., 2001; Vinson et al., 2009; Weaver and Bahr, 1991b). Here, water samples collected from a network of twenty-one short-screened monitoring wells, at depths ranging from 12 to 139 m, are analyzed to determine ^{226}Ra, ^{228}Ra, ^{238}U, ^{232}Th, ionic composition, pH, specific conductance, and DO (Fig. 1). The elemental composition of aquifer solids is also determined. These data provide insight into the geologic sources of Ra and the geochemical conditions that promote the mobility of Ra(II) within discrete hydrostratigraphic intervals.

2. Materials and methods

2.1. Regional hydrogeology

As discussed in Young and Siegel (1992), the Midwestern C-O-AS extends across much of the Midwestern United States, including parts of Minnesota, Wisconsin, Iowa, Missouri, and Illinois. It consists of a complexly layered sequence of sedimentary aquifers, with interbedded confining units, overlain by unconsolidated glacial drift. Crystalline Precambrian rock forms the base of the system and is overlain by marine-deposited Paleozoic sandstones, dolostones, and shales. These formations range from the Late Cambrian to Late Devonian age, with stratigraphic units increasing in thickness away from the arches and toward basins. In Wisconsin, these layered sedimentary sequences slope from the Wisconsin Arch toward the Michigan basin in the East, the Illinois basin in the South, and toward Iowa and Minnesota to the West. The Maquoketa Shale confines much of the Midwestern C-O-AS in Eastern Wisconsin, but it is absent in Central and Western Wisconsin (Fig. 1) (Young and Siegel, 1992).

2.2. Local hydrogeology and sampling sites

This study examines Ra(II) concentration and groundwater geochemistry in the Midwestern C-O-AS near Madison, Wisconsin, which is about 250 m thick in this region (Parsen et al., 2016). Relatively impermeable Precambrian crystalline rock forms the base of the Cambrian groundwater system and is overlain by the coarse-to medium-grained sandstone of the Mount Simon Formation. The Eau Claire Formation, which overlies the Mount Simon, consists of an upper sandstone facies underlain by interbedded siltstone and shale layers. These fine-grained deposits make up the locally extensive Eau Claire aquitard, which varies from 0 to 15 m in thickness across the greater Madison region. The aquitard restricts the exchange of water between the overlying formations and the underlying Mount Simon sandstone (Fig. 2). The dolomitic Eau Claire sandstone forms the base of the upper bedrock aquifer and is overlain by the quartz sandstone of the Wonewoc Formation and the glauconitic sandstone of the Tunnel City Formation. In upland areas, the water table lies within the upper-most bedrock formations. In low-lying areas near the lakes and streams, the water table is relatively shallow and lies within saturated fine-grained till and lacustrine sediment that overlie bedrock. Land use in the study area is principally urban; however, agricultural areas surround the area. Extensive pumping for regional water supplies has reversed pre-development conditions, resulting in downward hydraulic gradients from the upper, unconfined aquifer to the deep, confined aquifer, over much of the study area (Parsen et al., 2016).

A network of twenty-one monitoring wells, with screen lengths ranging from 1.5 to 6.0 m, were sampled during this study. The wells are distributed across eight field sites in the greater Madison area, with six of these sites associated with nearby municipal wells (Fig. 1). Each of the field sites hosts two monitoring wells at various depths, with the exception of MW-7, which has three monitoring wells, and the Sentry Well (Table 1, Fig. 2). The Sentry Well contains a FLUTe™ multi-level sampling device that consists of six sampling ports at a variety of depths, isolated from each other with hydraulic seals. The well network was installed for an unrelated study; construction details are described in Gotkowitz et al. (2016). The monitoring wells target specific hydrostratigraphic units and are completed in the Tunnel City Formation ($n = 10$), the Wonewoc Formation ($n = 6$), the Eau Claire aquitard ($n = 1$), and the Mount Simon Formation ($n = 4$). For the purposes of this study, wells completed above the aquitard are referred to as unconfined. Wells screened within or below the aquitard are described as confined. Dedicated gas displacement pumps were used to purge and collect samples from the ports of the Sentry Well. A submersible electric pump was used to sample all other wells.

2.3. Groundwater characterization

During the Fall of 2016, all twenty-one monitoring wells in the study were sampled. A subset of thirteen wells were sampled a second time, in the spring of 2017. These wells were selected to include wells above and below the aquitard. Prior to sample collection, monitoring wells were purged of approximately 10 well volumes, using a stainless-steel submersible pump. Sentry well (SW) ports were purged a minimum of five times over a two-day period, prior to sample collection.

During both sampling campaigns, pH, temperature, and specific conductance were measured in the field following purging. DO was also measured in a flow-through cell during the second round of sampling. Samples for Ra(II) analysis were not filtered, in order to remain consistent with compliance sampling methods required of municipal water supply systems, and preserved with concentrated nitric acid to pH ≤ 2. Samples for aqueous metals analysis were field-filtered (0.45 μm) and acid preserved (pH ≤ 2), while samples for inorganic ion were filtered. Both types of samples were stored at 4 °C until further analysis. Analysis for uranium (^{238}U) and thorium (^{232}Th) was conducted on samples