



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

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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 ²²⁶Ra and ²²⁸Ra. 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 ²²⁶Ra, ²²⁸Ra, and parent isotopes ²³⁸U and ²³²Th. Additionally, the elemental composition of aquifer solids is determined as a function of depth. Within solid phases, ²³⁸U and ²³²Th 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 ²²⁶Ra and ²²⁸Ra (U.S. EPA, 2000).

One source of radium to groundwater is the radioactive decay of parent elements uranium (U) and thorium (Th) (Fig. S1-1) (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 (BaSO₄). 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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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; Gonnee 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 BaSO₄ 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 ²²⁶Ra, ²²⁸Ra, ²³⁸U, ²³²Th, 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 (²³⁸U) and thorium (²³²Th) was conducted on samples

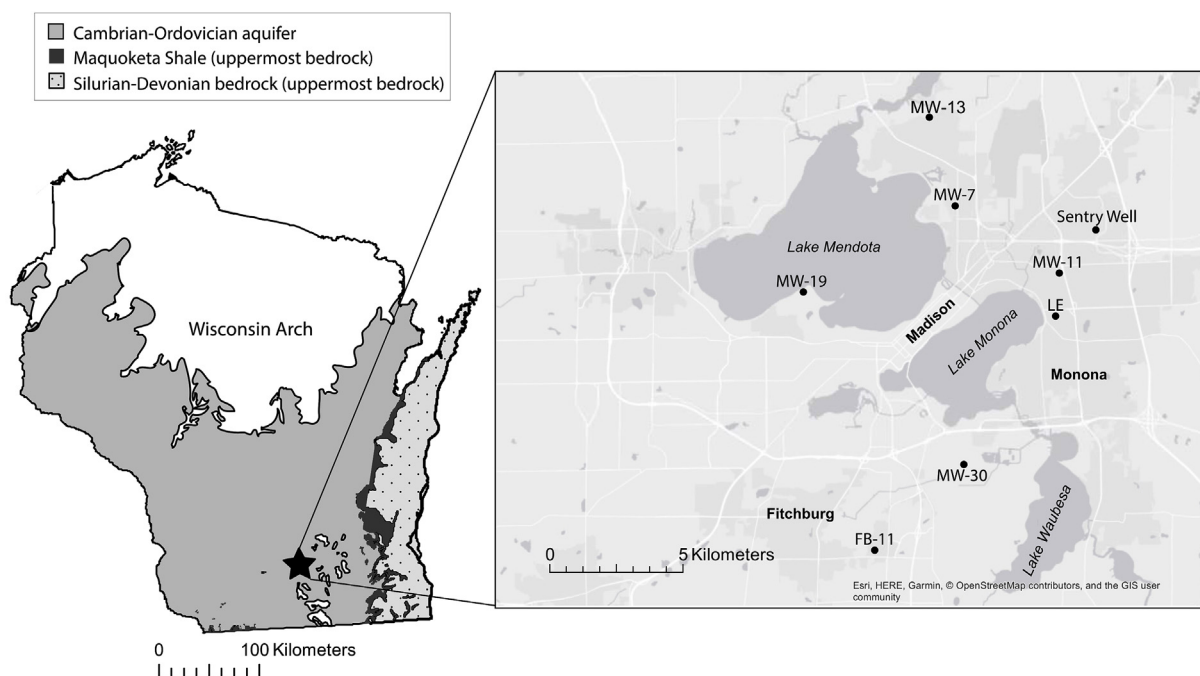


Fig. 1. Extent of the Cambrian-Ordovician aquifer in Wisconsin. The Maquoketa Shale underlies the Silurian-Devonian bedrock to the East, but forms the uppermost bedrock over a narrow area West of the Silurian. The inset map shows distribution of study sites; each site hosts multiple wells at various depths.

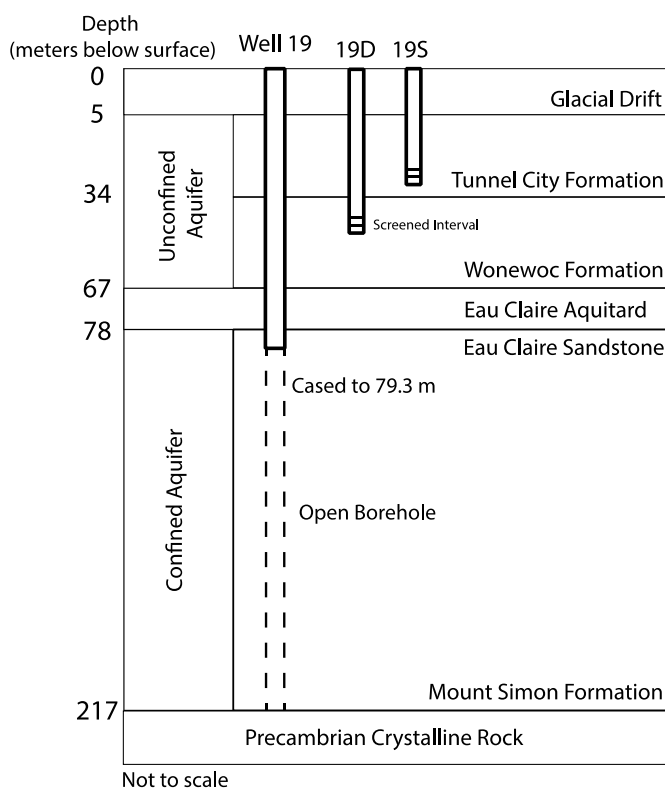


Fig. 2. Representative hydrostratigraphy and well construction at the municipal Well 19 field site. Municipal wells, such as Well 19, are open boreholes below the casing, while monitoring wells, like MW-19D and MW-19S, are screened across short intervals within hydrostratigraphic units. Figure not to scale.

collected during the second round of sampling.

²²⁶Ra and ²²⁸Ra analyses were conducted by Eurofins Eaton Analytical, Inc., in a manner consistent with the Georgia Tech method

(Georgia Institute of Technology, 2004). Radium values at or below the instrumental detection level were designated as Minimum Detectable Activity (MDA) or < MDA and have a value of 0 pCi/L on figures; the MDA is the concentration that can be measured with ± 100% certainty at the 95% confidence level. Analysis of ²³⁸U and ²³²Th was conducted, using a ThermoScientific ELEMENT2 High Resolution inductively coupled plasma mass spectrometer (Tables SI-1). A Dionex ICS-2100 ion chromatography system was used to determine the concentration of nitrate (NO₃⁻), sulfate (SO₄²⁻), and chloride (Cl⁻) in water samples (Tables SI-1). A PerkinElmer Optima 4300 DV inductively-coupled plasma optical emission spectrometer was used to quantify dissolved barium (Ba²⁺), calcium (Ca²⁺), iron (Fe²⁺), magnesium (Mg²⁺), manganese (Mn²⁺), and sodium (Na⁺) in aqueous samples (Tables SI-1). Tritium (³H) concentrations were compiled from previous studies conducted at these wells by the Wisconsin Geological and Natural History Survey (WGNHS) (Tables SI-2) (Gotkowitz, 2015).

A quality control sample was collected during each sampling round to evaluate the potential contribution of Ra(II) from field equipment. Control samples were collected by flushing the submersible pump and tubing with 40 L of ultrapure water, followed by collection of 4 L of ultrapure water for analysis. Sample MW-PL1 was collected through the entire length of the tubing in 2016, while MW-PL2 was collected through a short length (5 m) of tubing.

2.4. Solid-phase characterization

Aquifer solids were selected from well cuttings archived at the WGNHS. Cuttings collected during the construction of municipal well 19 in 1969 were available at 1.5 m intervals from the surficial glacial drift to the Precambrian crystalline bedrock at 219 m below ground surface (Fig. 2). Cuttings were prepared by placing in a medical grade polyethylene sample container, with a piece of 4.0 μm polypropylene thin film secured across the vial top by a rubber band. Elemental composition was determined using a Thermo Fisher Niton XL3t GOLDD + hand-held X-ray fluorescence (XRF) analyzer. The vial was turned to allow cuttings to rest on the film across the XRF stage (Rowe et al., 2012; Zambito et al., 2016).

Table 1

Sample field measurements and radium activity results from various sampling seasons. The Minimum Detectable Activity at a 95% confidence interval is represented by MDA 95. Ports sampled from the Sentry Well are represented as SW.

Sample ID	Sampling Date	Screen Midpoint (meters below surface)	Screen Length (meters)	Hydrostratigraphic Unit	pH	Temperature (°C)	Specific conductance (µS/cm)	DO (mg/L)	Radium-228 (pCi/L)	Radium-226 (pCi/L)	Combined Radium (pCi/L)
MW-PL1	10/27/16	a	a	Control	a	a	a	a	0.7 ± 0.4	0.5 ± 0.3	1.1 ± 0.5
MW-PL2	5/31/17	a	a	Control	a	a	a	a	< MDA 95	< MDA 95	< MDA 95
MW-7S	10/24/16	12	5	Tunnel City	7.1	12.2	3030	b	0.7 ± 0.4	0.4 ± 0.2	1.1 ± 0.4
MW-7S	5/30/17	12	5	Tunnel City	6.8	13.4	2390	9.1	< MDA 95	0.5 ± 0.3	0.9 ± 0.7
MW-11S	10/21/16	13	3	Tunnel City	7.0	11.2	2240	b	1.4 ± 0.5	0.7 ± 0.3	2.1 ± 0.6
MW-11S	5/25/17	13	3	Tunnel City	6.9	12.4	2300	7.3	< MDA 95	0.5 ± 0.3	< MDA 95
MW-19S	10/14/16	16	5	Tunnel City	7.3	12.2	1390	b	< MDA 95	0.3 ± 0.2	0.6 ± 0.4
MW-19S	12/11/17	16	5	Tunnel City	6.3	12.8	1250	8.8	b	b	b
MW-30S	10/14/16	19	5	Tunnel City	7.3	10.6	920	b	< MDA 95	0.2 ± 0.1	< MDA 95
MW-30S	12/11/17	19	5	Tunnel City	6.8	11.3	800	8.5	b	b	b
MW-13S	10/24/16	16	3	Tunnel City	7.2	11.3	1630	b	1.0 ± 0.4	0.10 ± 0.07	1.1 ± 0.4
MW-13S	12/11/17	16	3	Tunnel City	6.3	11.9	1030	9.9	b	b	b
SW – port 1	10/17/16	27	1.5	Tunnel City	7.3	13.0	1400	b	< MDA 95	0.5 ± 0.2	0.7 ± 0.5
SW – port 1	5/25/17	27	1.5	Tunnel City	7.0	11.3	1770	7.8	b	b	b
FB-11S	10/14/16	31	1.5	Tunnel City	7.5	10.0	830	b	0.4 ± 0.4	0.2 ± 0.1	0.6 ± 0.4
FB-11S	5/22/17	31	1.5	Tunnel City	7.2	11.1	1010	9.5	< MDA 95	< MDA 95	< MDA 95
MW-13D	10/24/16	34	1.5	Tunnel City	7.2	11.2	870	b	< MDA 95	0.4 ± 0.2	0.5 ± 0.4
MW-13D	12/11/17	34	1.5	Tunnel City	6.3	11.5	810	9.1	b	b	b
MW-30D	10/14/16	41	1.5	Tunnel City	7.4	10.5	850	b	< MDA 95	0.2 ± 0.1	1.23 ± 0.52
MW-30D	5/25/17	41	1.5	Tunnel City	6.9	11.2	1040	8.9	0.8 ± 0.5	0.4 ± 0.3	0.5 ± 0.5
FB-11D	10/14/16	52	1.5	Tunnel City	7.5	10.4	570	b	0.7 ± 0.5	0.4 ± 0.2	1.1 ± 0.5
FB-11D	12/11/17	52	1.5	Tunnel City	7.1	10.7	510	10.6	b	b	b
MW-11D	10/21/16	23.5	1.5	Wonewoc	7.1	11.4	1290	b	1.7 ± 0.6	0.6 ± 0.3	2.3 ± 0.7
MW-11D	5/22/17	23.5	1.5	Wonewoc	7.1	12.2	1460	5.8	< MDA 95	< MDA 95	< MDA 95
MW-7D	10/24/16	29	3	Wonewoc	7.1	11.8	2650	b	1.3 ± 0.5	0.8 ± 0.3	2.1 ± 0.6
MW-7D	5/30/17	29	3	Wonewoc	6.6	13.0	2810	10.4	1.1 ± 0.6	1.0 ± 0.4	2.1 ± 0.7
MW-19D	10/14/16	42	1.5	Wonewoc	7.2	11.7	2410	b	3.6 ± 0.6	1.6 ± 0.3	5.2 ± 0.6
MW-19D	5/22/17	42	1.5	Wonewoc	7.0	12.3	2110	10.6	3.4 ± 0.6	1.8 ± 0.4	5.2 ± 0.8
MW-19D	12/11/17	42	1.5	Wonewoc	6.3	12.0	1520	10.1	b	b	b
SW – port 2	10/17/16	63	1.5	Wonewoc	7.3	12.6	590	b	0.5 ± 0.4	0.09 ± 0.08	0.6 ± 0.5
SW – port 2	5/25/17	63	1.5	Wonewoc	7.2	11.3	710	8.2	b	b	b
MW-7VD	10/24/16	64	3	Wonewoc	7.3	11.0	820	b	1.2 ± 0.5	0.6 ± 0.3	1.8 ± 0.6
MW-7VD	5/30/17	64	3	Wonewoc	6.9	12.1	980	2.1	< MDA 95	0.3 ± 0.2	< MDA 95
LE-D	10/21/16	71	1.5	Wonewoc	7.3	10.9	620	b	< MDA 95	MDA 95	< MDA 95
LE-D	5/30/17	71	1.5	Wonewoc	6.7	11.9	760	2.8	< MDA 95	0.3 ± 0.2	< MDA 95
SW – port 3	5/12/16	81.5	1.5	Eau Claire aquitard	7.3	13.5	590	b	< MDA 95	< MDA 95	< MDA 95
SW – port 3	5/25/17	81.5	1.5	Eau Claire aquitard	7.2	11.4	720	6.3	b	b	b
SW – port 4	10/17/16	91	1.5	Mount Simon	7.4	12.3	640	b	< MDA 95	0.4 ± 0.2	0.8 ± 0.6
SW – port 4	5/25/17	91	1.5	Mount Simon	7.3	12	760	5.5	< MDA 95	0.3 ± 0.2	< MDA 95
LE-VD	10/21/16	81	1.5	Mount Simon	7.2	10.8	700	b	1.0 ± 0.4	0.8 ± 0.2	1.8 ± 0.5
LE-VD	5/30/17	81	1.5	Mount Simon	6.6	11.9	860	0.1	0.8 ± 0.5	0.4 ± 0.2	1.2 ± 0.5
SW – port 5	10/17/16	124	6	Mount Simon	7.4	12.0	570	b	1.1 ± 0.4	1.0 ± 0.3	2.1 ± 0.5
SW – port 5	5/25/17	124	6	Mount Simon	7.4	11.6	770	0.2	1.0 ± 0.5	0.9 ± 0.3	1.9 ± 0.6
SW – port 6	10/21/16	139	6	Mount Simon	7.7	12.0	630	b	2.0 ± 0.5	1.8 ± 0.4	3.8 ± 0.6
SW – port 6	5/25/17	139	6	Mount Simon	7.2	12.8	760	0.0	2.1 ± 0.5	2.5 ± 0.5	4.6 ± 0.7

^a Not applicable.

^b Samples were not collected for analysis.

XRF analysis was conducted in “Test All Geo” mode, using the 8 mm aperture opening and a 50 kV beam, following established procedures (Zambito et al., 2016). A 105-s total filter duration time (main filter 30 s, light filter 30 s, low filter 30 s, and high filter 15 s) was applied to

each sample. XRF analysis was monitored using standards from the United States Geological Survey (USGS) for shale, carbonate, and quartz sandstone. Minimum detection limits for Ra parent isotopes were 1.24 mg/L for thorium and 2 mg/L for uranium (Haas et al., 2017).

Table 2
Redox category designation (McMahon and Chapelle, 2008; Stackelberg et al., 2018).

Redox Process	DO (mg/L)	Mn(II) (mg/L)	Number of Wells
Oxic	≥ 0.5	< 0.05	18
Suboxic	< 0.5	< 0.05	1
Anoxic	≤ 0.5	≥ 0.05	2

Geologic and geophysical logs available from the WGNHS were compared with the XRF results to identify the depth and thickness of hydrostratigraphic intervals.

3. Results

The pH of the samples ranged from 6.3 to 7.7, while the specific conductance values ranged from 510 to 3030 μS/cm (Table 1). Tritium, an indicator of groundwater age, ranged from < 0.8 to 11 ± 2 TU in the unconfined aquifer and from < 0.8 to 5.3 ± 0.6 TU in the confined system (Fig. SI-2, Tables SI-2).

The DO concentration in groundwater varied between the upper aquifer and the underlying confined aquifer (Table 2). Based upon these measurements, 18 wells were oxic (DO ≥ 0.5 mg/L, Mn(II) < 0.05 mg/L); 1 well suboxic (DO < 0.5 mg/L, Mn(II) < 0.05 mg/L); and 2 wells anoxic (DO < 0.5 mg/L, Mn(II) ≥ 0.05 mg/L). In the confined aquifer, DO ranged from 0.04 to 5.46 mg/L, and Ra(II) ranged from < MDA 95 to 4.6 pCi/L. In the unconfined aquifer, DO concentrations ranged from 2.13 to 10.64 mg/L, and Ra(II) ranged from < MDA 95 to 5.2 pCi/L (Fig. 3).

Overall, concentrations of parent isotopes ²³⁸U and ²³²Th were low in groundwater. Aqueous ²³⁸U concentrations ranged from 0.0004 ± 0.00001 to 5.3 ± 0.1 μg/L, while ²³²Th ranged from non-detectable to 0.005 ± 0.002 μg/L (Fig. 4). The sample with the highest ²³⁸U concentration, 5.3 ± 0.1 μg/L, was collected from the Mount Simon, just below the Eau Claire.

In this study, combined Ra(II) concentrations less than

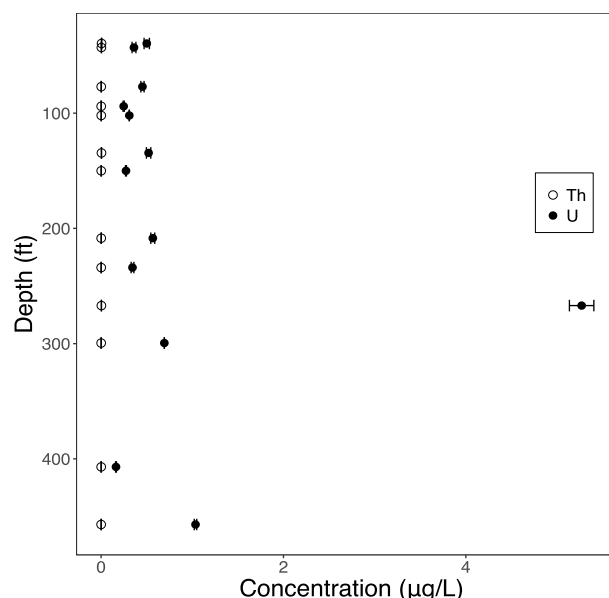


Fig. 4. Aqueous concentrations of Ra parent isotopes, ²³⁸U and ²³²Th, as a function of depth below ground surface.

1.1 ± 0.5 pCi/L were considered below the limit of quantification, due to the presence of combined Ra(II) at this concentration in control sample MW-PL1. The combined Ra(II) concentration in most groundwater samples ranged from non-detectable to 2.2 pCi/L, with two wells, MW-19D and SW – port 6, exceeding this range (Fig. 5). Wells with Ra (II) exceeding detection levels in Spring (2017) were at concentrations within the error bounds reported from the Fall 2016 samples, and other samples exhibited little variation. Both samples collected from well MW-19D, screened in the Wonewoc sandstone, contained 5.2 pCi/L Ra (II); all other samples completed in the unconfined aquifer had Ra(II) concentrations less than the MCL. Dissolved Ra(II) in well SW – port 3, the only well associated with the Eau Claire aquitard, was below the

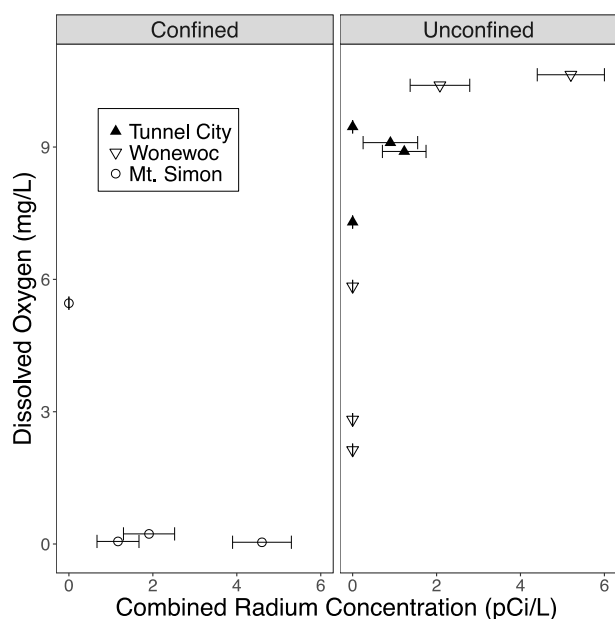


Fig. 3. The relationship between combined radium concentration (²²⁶Ra + ²²⁸Ra) and DO from Spring (2017) sampling, distinguished by hydrostratigraphic unit and aquifer designation. Error estimates are shown for combined Ra(II) concentrations above minimum detectable activity at the 95% confidence level (MDA 95); values at or below MDA 95 are represented as 0 pCi/L aquitard, in well LE-VD.

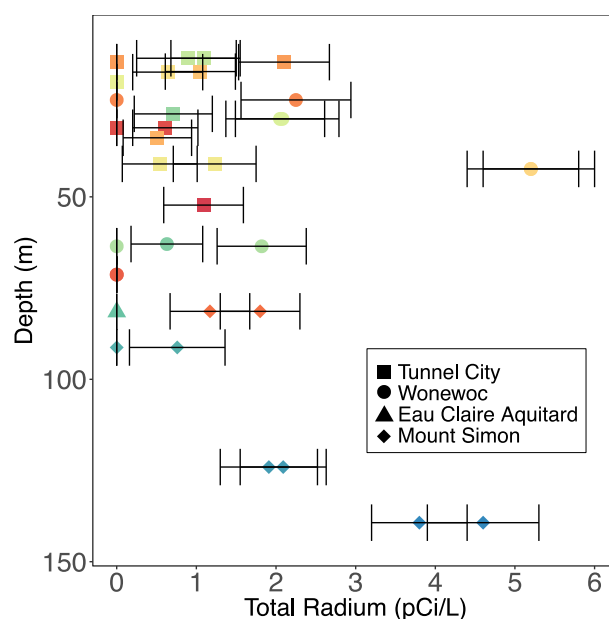


Fig. 5. Combined radium concentration (²²⁶Ra + ²²⁸Ra) by well depth from both sampling periods. Results from wells sampled twice to examine replicability are shown with the same color. Dissolved Ra(II) values at or below minimum detectable activity at the 95% confidence interval (MDA 95) are plotted at 0 pCi/L. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

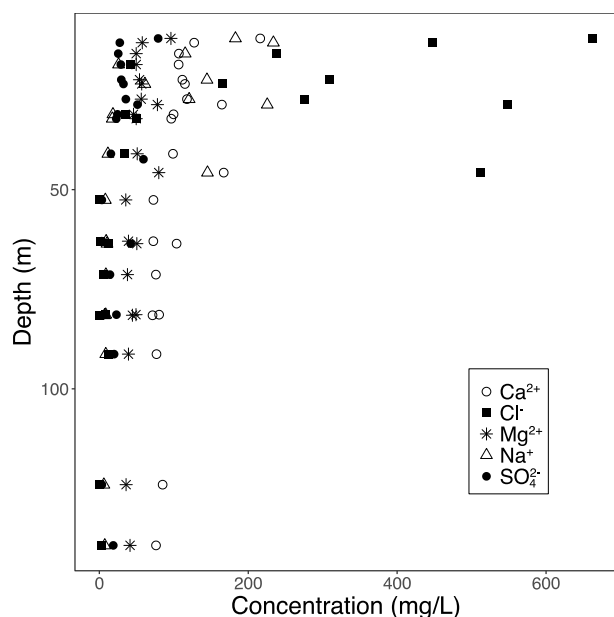


Fig. 6. Concentration of major ions versus depth from surface, from monitoring wells in Madison, WI, from 2016 samples.

MDA. Among samples from the Mount Simon sandstone, the highest combined Ra(II) concentration, 4.6 ± 0.7 pCi/L, was collected from the deepest well, SW-port 6, at 139 m at depth.

Specific conductance, used here as an indicator of total dissolved solids, varied widely in groundwater, from 510 to 3030 $\mu\text{S}/\text{cm}$. The highest concentrations of Ca^{2+} (max. 220 mg/L at 12-m depth), Cl^- (max. 660 mg/L at 12-m depth), Mg^{2+} (max. 120 mg/L at 29-m depth), Na^+ (max. 240 mg/L at 29-m depth), and SO_4^{2-} (max. 79 mg/L at 12-m depth) were observed in wells completed in the unconfined aquifer. Major ion concentrations decreased with depth, as did specific conductance, which ranged from 570 to 860 $\mu\text{S}/\text{cm}$ in wells completed in the confined system (Figs. 6 and 7).

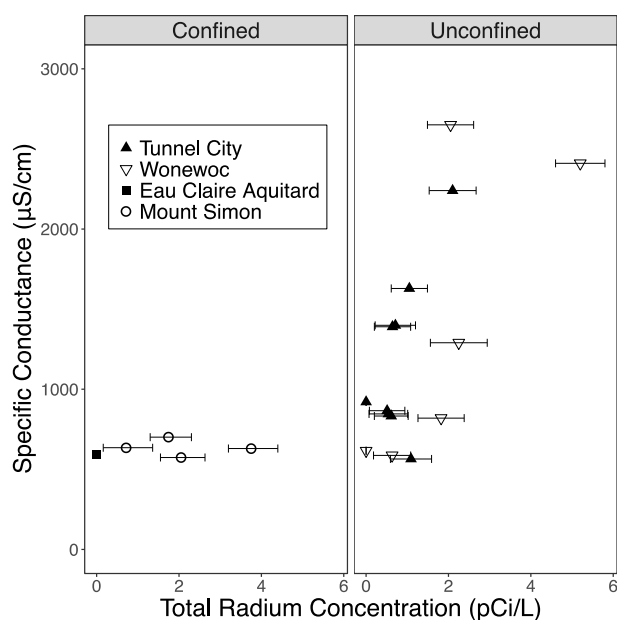


Fig. 7. The relationship between combined radium ($^{226}\text{Ra} + ^{228}\text{Ra}$) and specific conductance from Fall (2016) sampling, distinguished by hydrostratigraphic units and aquifer designation. Ra(II) concentrations at or below the minimum detectable activity at the 95% confidence interval (MDA 95) are represented as 0 pCi/L.

In general, there was a weak correlation between Ra(II) concentration and specific conductance in the Wonewoc sandstone ($r^2 = 0.54$) and the Tunnel City stratigraphic unit ($r^2 = 0.25$; Fig. 7). Estimated Ba^{2+} activities, calculated according to the method described in Brezonik and Arnold (2011), did not vary significantly (p -value = 0.34) as a function of aquifer formation (Tables SI-1). The calculated barite saturation index (SI) did not exceed a value of 1 for any of the samples collected in this study (Calculations S4, Fig. SI-3). While Ba^{2+} concentration increased as sulfate concentration increased within the Wonewoc, this trend was not observed in groundwater from the Tunnel City unit (Fig. SI-3).

XRF analyses of aquifer solids from municipal Well 19 demonstrated the heterogeneity of elemental composition within discrete stratigraphic horizons (Fig. 8). Primary elements at the study site included Si (median 30, ranging 8–45% by weight), Ca (median 4, ranging 0–20% by weight), and Mg (median 1, ranging 0–17% by weight). Samples with elevated K and Al indicated clay mineralogy (e.g., 67–78 m below the surface) and corresponded to the depth of the Eau Claire aquitard at well 19. Elevated Fe concentrations appear in the Wonewoc Formation (median 0.2, ranging 0–3.7% by weight), the Eau Claire Formation (median 1.1, ranging 0.2–2.7% by weight), and the Mount Simon Formation (median 0.1, ranging 0–6.3% by weight). Manganese concentrations in aquifer solids were more consistent, with a median of 0.02% by weight over the groundwater system, ranging 0–0.15% by weight. Solid-phase concentrations of U (median 8, ranging 0–10 mg/kg) and Th (median 5, ranging 0–8 mg/kg) were notable in the Eau Claire aquitard (Fig. 8). Elevated concentrations of U and Th were also observed at several depths in both the Wonewoc (U median 0, ranging 0–14 mg/kg; Th median 0, ranging 0–15 mg/kg) and Mount Simon sandstones (U median 0, ranging 0–30 mg/kg; Th median 0, ranging 0–28 mg/kg; Fig. 8).

4. Discussion

This study focuses on determining dissolved Ra(II) concentrations in discrete hydrostratigraphic intervals, within a locally-confined region of the Midwestern C-O-AS, in order to build upon studies that rely on data from wells with long open intervals (Grundl and Cape, 2006; Stackelberg et al., 2018; Szabo et al., 2012; Vinson et al., 2012, 2009; Weaver and Bahr, 1991a). In this study, a majority of monitored depths have dissolved Ra(II) concentrations below background levels, but differences in geochemical conditions appear to result in locally elevated Ra(II).

Low DO, low pH, and/or high specific conductance in groundwater systems are often correlated with Ra(II) concentrations above the MCL, both in general and within the Midwestern C-O-AS (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). Groundwater in the study area is relatively neutral in pH (e.g., 6.3 to 7.7), and Ra(II) mobilization due to acidic conditions is unlikely (Table 1). The two wells with elevated dissolved Ra(II) are dissimilar (Fig. 5, Table 1). MW-19D, completed in the unconfined aquifer, is oxic with elevated specific conductance; SW - port 6 is completed in the confined aquifer, and is anoxic with low dissolved solids. This suggests that multiple factors contribute to elevated Ra(II) in this setting.

Radium parent radionuclides (^{238}U and ^{232}Th) are found in association with fine-grained sedimentary layers, including shale aquitards, or oxide coatings on mineral grains (Gilkeson et al., 1983; Grundl and Cape, 2006; Senior and Vogel, 1995; Sturchio et al., 2001; Weaver and Bahr, 1991a). Aqueous and solid-phase parent radionuclide concentrations are relatively low throughout most of the stratigraphic section in the study area (Figs. 5 and 8). The solid-phase composition varies with depth; higher concentrations of U and Th occur in the Eau Claire aquitard, and the Wonewoc and Mount Simon Formations

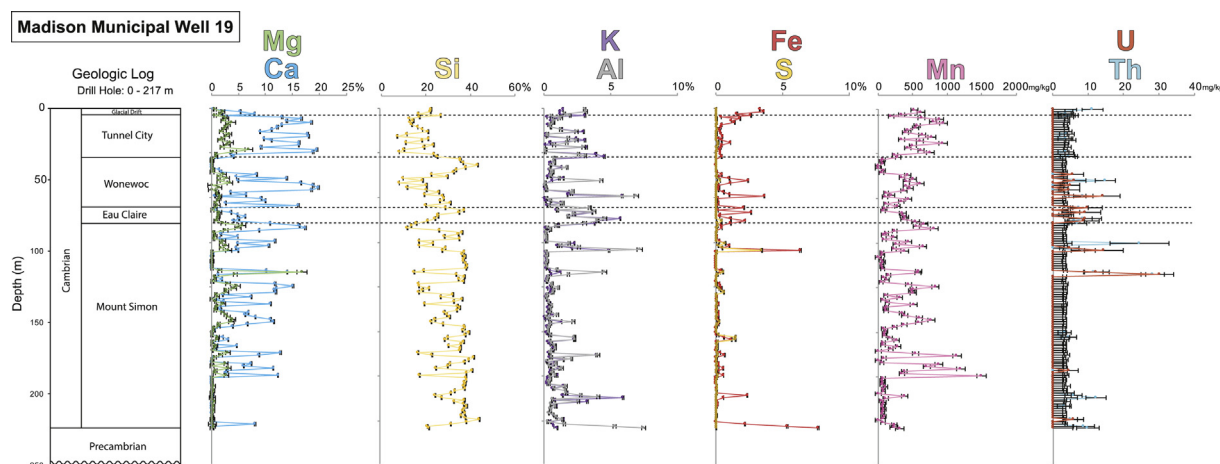


Fig. 8. Solid-phase elemental composition from X-ray fluorescence analysis of municipal well 19. Concentration scales differ for each element grouping. Elemental weight abundance is either presented as parts per million (mg/kg) or weight percent (%), defining 1% = 10,000 mg/kg.

contain elevated U and Th (Fig. 8). Since U and Th are present in the unconfined and confined aquifers and in the Eau Claire aquitard, production of Ra(II) via radioactive decay from U and Th can occur in any of these hydrostratigraphic units. However, shale layers, although enriched in parent nuclides, tend to have relatively low dissolved Ra(II), due to their high sorption capacity (Gilkeson, 1984; Gilkeson et al., 1978; Szabo et al., 2012). This is consistent with the less than detectable level of combined dissolved Ra(II) from SW – port 3, completed within the Eau Claire aquitard (Fig. 5).

The ^3H content of water is a general indicator of groundwater age. Eight wells produced water with low tritium (< 0.8 TU), suggesting that these wells produce old (pre-1950) water (Tables SI–2). Thirteen wells produced water with tritium > 4 TU, indicating more recent recharge, since 1950 (Stackelberg et al., 2018). The two wells with dissolved Ra(II) above 3 pCi/L differ with respect to tritium. Tritium at MW-19D, 10 ± 2 TU, indicates recently recharged groundwater, whereas tritium levels are below detection in SW – port 6.

Radium partitioning to Fe and/or Mn (hydr)oxides can decrease aqueous Ra(II) concentrations (Reynolds et al., 2003; Szabo et al., 2012; Tricca et al., 2000). However, anoxic conditions contribute to Ra(II) mobility and an increase in concentrations, due to the absence or dissolution of these minerals (International Atomic Energy Agency, 2014; Szabo et al., 2012). In groundwater samples from the confined system, elevated Ra(II) is associated with low DO (Fig. 3). In several samples obtained from the unconfined system, the DO content ranges from 2.1 to 7.3 mg/L, while Ra(II) remains undetectable. However, in five samples from the unconfined system with $\text{DO} \geq 8.9$ mg/L, dissolved Ra(II) ranges from non-detectable to 5.2 pCi/L (Fig. 3). Due to the oxic nature of the unconfined aquifer, the occurrence of elevated dissolved Ra(II) in the unconfined aquifer is not likely due to the absence of Fe and Mn (hydr)oxides (Szabo et al., 2012). Additionally, there is no evidence of elevated ^{238}U or ^{232}Th in the unconfined aquifer (Tables SI–1). This suggests that elevated dissolved Ra(II) in the unconfined aquifer is likely due to other geochemical conditions, discussed below.

Elevated dissolved Ra(II) is commonly correlated with elevated ionic strength (Nathwani and Phillips, 1979; Oden and Szabo, 2016; Sajih et al., 2014; Tomita et al., 2010). In this study, concentrations of Ca^{2+} , Cl^- , Mg^{2+} , Na^+ , and SO_4^{2-} are elevated in groundwater in the Tunnel City and Wonewoc hydrostratigraphic units (Fig. 6). Increased specific conductance is also observed with elevated combined Ra(II) concentration in the unconfined aquifer (Fig. 7). Despite the large range in TDS, water in all wells remains undersaturated with respect to BaSO_4 (Fig. SI-3). This indicates that BaSO_4 formation is likely not an important factor in controlling Ra(II) concentration in this setting (Grundl and Cape, 2006; Stackelberg et al., 2018; Szabo et al., 2012).

Geochemistry in the well pair, MW-19S and MW-19D, differ from each other. These wells, installed within 10 m of each other, are completed in the unconfined aquifer at depths of 16 and 42 m, respectively. Water from the deeper well, MW-19D, contains 5.2 pCi/L combined Ra(II), the highest concentration amongst the study wells, while Ra(II) is below the detection limit at MW-19S (Table 1). Consistent with greater Ra(II) mobility associated with elevated ionic strength, MW-19D had higher Cl^- , and TDS, than MW-19S. This, in addition to higher tritium at MW-19D, suggests good connectivity from the water table to MW-19D (Gellasch et al., 2013; Gotkowitz, 2015). Elevated TDS and relatively young groundwater age at the deeper of the paired wells suggest the presence of a preferential flow pathway, such as a fracture, connecting MW-19D to the surface. Such fractures in the Tunnel City and Wonewoc Formations are well documented in the study area (Gellasch et al., 2013; Parsen et al., 2016). These results indicate that groundwater quality in the upper aquifer is affected by chloride-rich urban storm water impacted by sanitary sewers and/or road salt. Although the direct contribution of dissolved Ra(II) from infiltration of storm water cannot be ruled out, the elevated TDS correlated with greater dissolved Ra(II) in the unconfined aquifer supports increased Ra mobility due to sorption site competition. In contrast, absence of redox-sensitive transition metal (hydr)oxides likely contributes to mobility of dissolved Ra(II) in the confined aquifer.

5. Conclusions

This study utilizes short-screened monitoring wells to characterize variability in the distribution of Ra(II) and identify potential Ra sources and sinks within specific hydrostratigraphic strata within the Midwestern C-O-AS. Overall, ^{238}U and ^{232}Th concentrations were relatively low in both the aqueous and solid-phase samples analyzed as part of this study. Background concentrations of dissolved Ra(II) in this region of the Midwestern C-O-AS ranged from non-detectable to 2.4 pCi/L; however, elevated Ra(II) was observed at discrete depths in both the upper, unconfined surface aquifer and the underlying confined aquifer. Anoxic conditions in the confined system likely result in the absence of Fe and Mn (hydr)oxides, resulting in limited Ra(II) sorption sites (Gilkeson et al., 1978; Tricca et al., 2000; Vinson et al., 2012). In wells in the unconfined aquifer that reflect the impact of surface processes (e.g., elevated specific conductance), elevated dissolved Ra(II) is attributed to sorption site competition.

Multiple mechanisms, including absence or dissolution of Fe and Mn (hydr)oxide coatings and elevated dissolved ion content, result in elevated Ra(II) within these discrete aquifer intervals. This study expands knowledge of the contribution of dissolved Ra(II) from distinct

hydrostratigraphic units within the Midwestern C-O-AS. While low levels of Ra are observed throughout the system, local changes in hydrostratigraphic geochemistry can result in elevated Ra(II) in the groundwater.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.apgeochem.2018.08.025>.

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