Contents lists available at SciVerse ScienceDirect

Chemical Geology

ELSEVIER



journal homepage: www.elsevier.com/locate/chemgeo

Implications of carbonate-like geochemical signatures in a sandstone aquifer: Radium and strontium isotopes in the Cambrian Jordan aquifer (Minnesota, USA)

David S. Vinson ^{a,*}, James R. Lundy ^b, Gary S. Dwyer ^a, Avner Vengosh ^a

^a Duke University, Nicholas School of the Environment, Division of Earth & Ocean Sciences, Box 90227, Durham, NC 27708, USA
^b Minnesota Department of Health, Environmental Health Division, 625 North Robert Street, St. Paul, MN 55164, USA

ARTICLE INFO

Article history: Received 3 February 2012 Received in revised form 31 July 2012 Accepted 14 October 2012 Available online 23 October 2012

Keywords: Radium Strontium Isotopes Sandstone aquifer Carbonates Uranium-series radionuclides

ABSTRACT

Water-rock interaction in sandstone aquifers can potentially mobilize U-and Th-series radionuclides, resulting in elevated levels of radioactive constituents such as radium (Ra) in groundwater. Previous studies have delineated the sources of Ra in groundwater by assuming that ²²⁸Ra/²²⁶Ra of groundwater parallels the ²³²Th/²³⁸U activity ratio of aquifer solids. We present an integrated geochemical and isotopic study of groundwater and aquifer solids for major and trace elements, radium (²²⁴Ra, ²²⁶Ra, ²²⁸Ra), strontium isotopes (⁸⁷Sr/⁸⁶Sr), and tritium in the Cambrian Jordan quartz sandstone aquifer of southeastern Minnesota (USA). The Jordan aquifer, part of the Cambrian-Ordovician aquifer system of the upper midwestern USA, is characterized by a wide range of Ra activities in groundwater. Uniform Ca-Mg-HCO₃⁻⁻ major element composition and patterns in ⁸⁷Sr/⁸⁶Sr indicate that interaction with carbonate minerals controls water chemistry. At least one contributing Sr source is radiogenic, yielding 87 Sr/ 86 Sr ratios up to 0.71347. Radium-226 activities exhibit especially large variations (<1–418 mBq L⁻¹), and the highest radium activities occupy a 100-km-long north-south region. Consistent with the carbonate-like elemental and Sr isotope signatures, ²²⁶Ra activity (median 85 mBq L⁻¹) is higher than ²²⁸Ra (median 47 mBq L⁻¹), yielding low ²²⁸Ra/²²⁶Ra ratios (median 0.5) that would be expected from a lithology preferentially containing U relative to Th, such as carbonate rocks. Collectively, results indicate the primary source of radium to the aquifer is alpha recoil from aquifer solids rather than external inputs of high-Ra waters, indicated by (1) similar ²²⁸Ra/²²⁶Ra ratios in aquifer solids and groundwater, including low, carbonate-like values in the high-²²⁶Ra samples; (2) some association between whole-rock ²²⁶Ra levels and groundwater ²²⁶Ra activities; and (3) groundwater ²²⁴Ra/ ²²⁸Ra averaging near unity. Furthermore, hydrogeologic setting (e.g. presence or absence of overlying carbonate units) is inconsistent with systematic inputs of high-Ra waters from overlying carbonate aquifers. The most proximate source of carbonate material in the sandstone aquifer seems to be the calcite and dolomite cement that yields different geochemical and isotopic fingerprints than silicate minerals would impart. Wholerock 226 Ra/ 238 U \approx 1 implies that any U enrichment in the carbonate cement occurred at least 350,000 years ago. High groundwater Ra activities relative to solids are attributable to anoxic conditions that play a role in maintaining inefficient radium removal for a fresh groundwater system, indicated by the estimated dimensionless whole-rock Ra distribution coefficient of 150–920 (median 560). Coprecipitation of Ra into barite is a potential but unquantified Ra removal mechanism. Overall, radium in the Jordan aquifer provides an example of a naturally-occurring trace element of health significance that may be derived not mainly from the quartz sandstone matrix, but from carbonate material such as calcite and dolomite cement. Especially when combined with complementary tracers such as ⁸⁷Sr/⁸⁶Sr, this study demonstrates the usefulness of the ²²⁸Ra/²²⁶Ra ratio as an indicator of the key mineral phases (silicate vs. carbonate) involved in supplying radium to groundwater. © 2012 Elsevier B.V. All rights reserved.

1. Introduction

Naturally-occurring trace elements of the uranium (U) and thorium (Th) decay series, including uranium, radium, and radon, can contribute

excessive levels of radioactivity to some groundwater resources used for drinking water. Sandstone aquifers in particular can yield radium (Ra) isotope activities that exceed allowable drinking water levels, although the aquifer rocks themselves may exhibit unexceptional whole-rock concentrations of U- and Th-series radionuclides (Lively et al., 1992; Szabo et al., 1997; 2005; 2012; Vengosh et al., 2009). In particular, activities of three of the four naturally-occurring Ra isotopes, ²²⁶Ra (t_{1/2} = 1600 yr; daughter of ²³⁰Th in the ²³⁸U series), ²²⁸Ra (t_{1/2} = 5.8 yr; daughter of ²³²Th), and ²²⁴Ra (t_{1/2} = 3.6 d; great-granddaughter of

^{*} Corresponding author at: University of Arizona, Department of Hydrology & Water Resources, 1133 East James E. Rogers Way, Tucson, AZ 85721, USA. Tel.: +1 520 621 5082; fax: +1 520 621 1422.

E-mail address: dsvinson@email.arizona.edu (D.S. Vinson).

^{0009-2541/\$ –} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.chemgeo.2012.10.030

²²⁸Ra), can reach levels of concern. Radium levels in groundwater are not commonly attributed to Ra transport due to its highly surface-reactive nature; instead, local water-rock interaction is typically responsible. This is characterized by Ra release to groundwater by alpha recoil (physical ejection by the alpha decay of its thorium parents) and subsequent retention to the solids by adsorption and other geochemical processes (Krishnaswami et al., 1982; Dickson, 1990). In some instances, the recoil source has been attributed to surface coatings enriched in Ra precursors (Dickson et al., 1987; Sturchio et al., 2001). In acidic waters (pH<5), Ra is removed inefficiently (Szabo et al., 1997; 2012), and Ra removal also becomes less efficient with increasing salinity (Kraemer and Reid, 1984; Moise et al., 2000; Sturchio et al., 2001; Tomita et al., 2010). In fresh, near-neutral bicarbonate-dominated groundwater (total dissolved solids < 1000 mg L^{-1}), the effects of salinity and pH on Ra are negligible, but redox conditions may significantly affect radium adsorption due to the redox-sensitivity of Mn and Fe oxides, which adsorb radium if present (Szabo and Zapecza, 1987; Vinson et al., 2009; Szabo et al., 2012). In addition to removal by adsorption, radium may coprecipitate with barium into barite, BaSO₄ (Gilkeson et al., 1983; Martin and Akber, 1999; Martin et al., 2003; Zhu, 2004; Grundl and Cape, 2006).

Given that radium isotopes primarily record localized water-rock interaction, isotopes of strontium, which like Ra is an alkaline earth metal, may provide additional information on critical processes affecting the mobility and removal of radium. Applications of strontium isotopes in groundwater systems include: (1) mixing of waters of distinctive Sr content (Stueber and Walter, 1994; Katz and Bullen, 1996; Frost and Toner, 2004; Warner et al., 2012); (2) silicate weathering (Franklyn et al., 1991; Bullen et al., 1996; Harrington and Herczeg, 2003); (3) interaction with primary and/or diagenetic carbonate minerals (Bishop et al., 1994; Cander, 1995; Dogramaci and Herczeg, 2002; Musgrove and Banner, 2004; McIntosh and Walter, 2006); and (4) fingerprinting of sources of divalent cations such as cation exchange and evaporite dissolution (Armstrong et al., 1998; Vengosh et al., 1999; 2002; Jacobson and Wasserburg, 2005).

Radium activity in groundwater in excess of the U.S. Environmental Protection Agency maximum contaminant level of 185 mBg L^{-1} (5 pCi L^{-1}) combined ²²⁶Ra + ²²⁸Ra activity is a well-documented issue in the Cambrian-Ordovician aguifer system of the upper midwestern United States, exhibiting the highest exceedance rate among major regional aquifers in the United States (Szabo et al., 2012), yet is poorly understood within the individual sandstone and carbonate aquifers of this system. Numerous potential sources and controls on radium have been suggested in previous studies of fresh waters in these aguifers, including shale content of sandstone aguifers (Weaver and Bahr, 1991), uranium enrichment in carbonate bedrock (Jansen, 1994), and control by barite solubility (Grundl and Cape, 2006). This study evaluates the mechanisms that control the distribution of Ra in the Jordan sandstone aquifer, a ~30-m thick, upper Cambrian quartz sandstone aquifer, incorporating multi-isotopic analysis of groundwater and aquifer solids.

The Jordan aquifer in Minnesota is a calcite- and dolomitecemented quartz sandstone including scattered tongue-shaped bodies of fine clastic material containing K-feldspar (Thomas, 1991; Runkel, 1994; Runkel et al., 2003). The Jordan also includes local carbonate rock units thought to yield relatively little water. The Jordan sandstone overlies the St. Lawrence confining unit, composed of shaly and dolomitic rocks, and is overlain by the Ordovician Prairie du Chien Group, which contains crystalline and sandy dolomite (Table 1). In subcrop areas, the Jordan aquifer is overlain by up to 100 m of Pleistocene glacial clay, sand, and/or gravel deposits that locally form areas of favorable recharge or, especially in the western portion of the study area where silt- and clay-rich tills dominate (Fig. 1), are an effective confining unit (Runkel et al., 2003). Variation of radium activities, especially radium-226, has been documented within the Jordan aquifer in Minnesota (Lively et al., 1992). However, the geographic extent of elevated radium levels in this aquifer was not fully documented prior to this study.

This objective of this research is to improve understanding of radium sources and removal mechanisms in this mostly anoxic, near-neutral pH, quartz sandstone aquifer. The isotopic data obtained in this study (²²⁴Ra, ²²⁶Ra, ²²⁸Ra, ⁸⁷Sr/⁸⁶Sr) are combined with additional data sets collected by the Minnesota Department of Health, Environmental Health Division, including stratigraphic and well depth information, radium-226 and radium-228 activities, and tritium activities. Using this broad combination of groundwater data and analysis of the radionuclide content of selected aquifer solids from wells, this study provides new insights on the identification of radium sources and its removal mechanisms.

2. Methods

Water samples were collected from wells after a period of pumping to ensure that the internal volume was flushed. Construction details and geologic information were obtained from the Minnesota Department of Health County Well Index (Table 2).

2.1. Major and trace element concentrations

Analysis of Ca, Mg, Na, Si, Sr, Ba, Fe, and Mn on filtered (<0.45 μ m), acidified water samples was performed by direct current plasma optical emission spectrometry on an ARL-Fisions Spectrascan 7 at Duke University, calibrated by a multi-element solution prepared from plasma-grade single element standards (precision $\pm 2\%$). Potassium was analyzed by flame atomic absorption spectrometry (expected precision $\pm 12\%$; Eaton et al., 2005). Selected filtered, acid-ified water samples were analyzed for U concentrations by inductively coupled plasma mass spectrometry (ICP-MS) on a VG Plasmaquad 3 at Duke University, calibrated using a plasma-grade U standard in a multi-element matrix solution (precision $\pm 3\%$). Anion concentrations (Cl⁻, NO₃⁻, and SO₄²⁻) were analyzed on a Dionex DX-500 ion chromatograph (precision $\pm 4\%$). Alkalinity concentrations were measured by titration of unfiltered samples to pH 4.5 with standardized HCl (precision $\pm 1\%$).

2.2. Strontium isotopes and tritium activity

Samples were prepared for strontium isotope analysis by drying filtered water samples containing ~3 µg Sr in Teflon vials in a laminar flow hood. After digestion in Optima HNO₃, Sr was separated with Eichrom SR-B50-S resin (procedural blank<80 pg Sr), loaded onto degassed Re filaments in a Ta solution, and analyzed for ⁸⁷Sr/⁸⁶Sr using a ThermoFisher TRITON thermal ionization mass spectrometer at Duke University. The long-term average ⁸⁷Sr/⁸⁶Sr value of NIST SRM 987 during the study was 0.710245 ± 0.000020 (2σ , n = 109) and sample ratios are reported without normalization to SRM 987. Tritium analysis of selected unfiltered water samples was performed at the University of Waterloo Environmental Isotope Laboratory by liquid scintillation counting subsequent to enrichment by electrolysis (precision~0.8 tritium units (TU)).

2.3. Radium isotopes

Radium isotopes were preconcentrated from unfiltered, 40 L samples on the same day as collection by slowly pumping these generally anoxic samples through two sequential columns each containing 10 g (dry weight) of Mn oxide-coated acrylic fibers. Radium-224 of the two columns was analyzed using a delayed coincidence alpha counter (Moore and Arnold, 1996; Garcia-Solsona et al., 2008), calibrated at an efficiency matching firmly hand-squeezed fibers and decay-corrected to the time of collection. Radium-226 was determined using a Durridge RAD7 radon monitor on samples incubated for three weeks (Kim et al.,

Simplified list of hydrostratigraphic units discussed in this paper (Mossler, 1990; Runkel et al., 2003) and median values of ²²⁶Ra activity and ²²⁸Ra/²²⁶Ra ratio for major Proterozoic to Ordovician and Quaternary aquifers in Minnesota within the area shown on Fig. 1 (data from this study plus additional data sources (Section 2.5)).

	Aquifer	Confining unit	Rock types	Thickness (m)	Abbreviation	Median ²²⁶ Ra (mBq L ⁻¹) (n) ^a	Median ²²⁸ Ra/ ²²⁶ Ra (n) ^b
Quaternary	Glacial sand and gravel		Sand, gravel	0-100	Q	<37 (80)	
		Clay-rich till	Silt, clay				
Ordovician	Galena		Limestone, dolomite, shale	55-65	GAL	104 (14)	0.3 (3)
		Decorah-Platteville-Glenwood	Shale, carbonate	10-35	DPG		
	St. Peter		Sandstone	40-50	STP	68 (6)	1.0 (5)
	Prairie du Chien		Dolomite and sandy dolomite	45-95	PDC	48 (29)	0.7 (20)
Cambrian	Jordan		Sandstone	20-40	JDN	45 (268)	0.6 (140)
		St. Lawrence	Siltstone and silty dolomite	15	STL		
	Tunnel City-Wonewoc		Sandstone	60-65	TCW	<37 (68)	1.2 (26)
		Eau Claire	Shale	25-35	ECR		
	Mt. Simon-		Sandstone	45-85	MHF	118 (137)	1.2 (125) ^c
Proterozoic	Hinckley-Fond du Lac		Sandstone	Variable			

^a Median reported from wells with ²²⁶Ra activity above detection in this study plus additional data.

^b Ratio calculated only from wells with both ²²⁶Ra and ²²⁸Ra activities above detection in this study plus additional data.

^c Values are for combined Mt. Simon-Hinckley-Fond du Lac aquifers.

2001), calibrated using a 226 Ra solution (National Institute for Standards and Technology) transferred onto Mn oxide fibers. Radium-228 was quantified by gamma spectrometry using the 911 keV peak of 228 Ac analyzed on the upper column's Mn fibers compressed into a disc (5 mm thick x 65 mm diameter), calibrated using DL-1a ore

(Canadian Certified Reference Materials Project), GSP-2 rock standard (USGS), and an aged ²³²Th solution on compressed fibers in matching geometry. Radium-224 error calculations follow the methods of Garcia-Solsona et al. (2008); for ²²⁶Ra and ²²⁸Ra, standard methods of counting statistics and propagation of error were used (Eaton et al.,



Fig. 1. Map showing geographic groups of wells sampled in this study, radium-226 activities in Jordan Aquifer groundwater from this study and additional data sources, and locations of wells from which solids were analyzed. Purple line represents extent of Prairie du Chien–Jordan aquifer system derived from maps (Mossler and Book, 1984; Mossler and Bloomgren, 1990; Runkel, 1998; Mossler and Tipping, 2000; Mossler, 2001) or inferred from well logs. Decorah confining unit extent is from Morey and Meints (2000), clay-rich till extent is from Hobbs and Goebel (1982), and northwestern edge of the Prairie du Chien Group, which otherwise overlies the Jordan aquifer, is from Olsen and Bloomgren (1989). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Major element chemistry and well construction information. Six-digit well identifiers are unique numbers in the Minnesota Department of Health County Well Index. Samples with dates not listed are unfiltered, unpreserved supplemental water samples analyzed for anions and ⁸⁷Sr/⁸⁶Sr only.

Unique ID	Sampling Date	Depth to bedrock (m)	Over- lying unit	Open interval (m)	рН	02	T (°C)	Ca	Mg	Na	Fe	Mn	К	Si	Cl	NO_3^- as $NO_3^{-(a)}$	SO_4^{2-}	HCO ₃
Unational	C	()		()														
207993 509053	16 May 2008	17 18	PDC PDC	96–122 63–87	7.65	3.3	11.4	76.5	26.6	17.4	0.02	0.01	1.2	7.4	32.8	13.36 21.81	41.3 31.4	278
Shakonee Groun																		
415975	04 Sep 2008	2	PDC	44-67	7.30	3.8	11.3	91.1	34.7	45.0	0.01	0.01	4.3	8.2	92.6	22.08	13.6	333
674456	04 Sep 2008	32	PDC	78–103	7.23	1.4	10.0	89.2	36.4	9.4	0.01	0.07	4.0	8.3	16.3	4.75	17.7	428
Northeast	ern Group																	
182655	05 May 2009	36	Q	52-61	7.43	1.3	9.8	48.8	18.2	4.2	0.02	0.00	1.3	8.1	3.8	1.51	7.5	223
208548 687180	05 May 2009	49 52	PDC O	62–105 53–67	7 98	0.8	11.8	29.6	113	46	123	0.03	18	53	10	7.44 0.41	4.0 0.1	168
		52	×.	55 67	1.00	0.0	1110	2010	1115	110	1120	0.005	110	010	110	0111	011	100
Southern 132254	Group 13 Ian 2009	73	PDC	94–122														
147951	29 Jul 2009	33	PDC	153-176	7.02	0.2	9.6	117.4	33.5	27.7	0.80	0.05	3.4	5.3	0.8	1.77	60.7	520
161402	12 May 2008	15	PDC	79-109	7.41		9.7	56.3	22.7	2.9	0.28	0.04	1.3	5.1	0.9	0.04	21.6	259
171005	12 May 2008	1	PDC	86-108	7.33		10.1	92.5	28.4	6.1	1.09	0.06	2.3	5.3	1.3	0.06	17.8	424
213638	16 Jul 2009	66	PDC	128-155	7.12	0.1	12.2	109.2	35.1	13.5	2.60	0.05	3.1	6.4	1.0	0.25	51.3	503
216520	06 Apr 2010	20	PDC	114-130	7.06	0.2	9.5	87.7	30.9	10.5	1.05	0.05	3.6	6.9	1.5	0.06	10.3	466
21/330	04 May 2010	20	PDC	204-229	7.19	0.4	10.4	08.2 78.8	23.9	3.4 4.5	0.29	0.01	1.0	4.0	0.8	0.07	27.8	322
228324	05 Sep 2008	14	PDC	177-201	7.30	< 0.1	11.3	68.9	21.2	4.0	0.23	0.03	3.2	3.3	4.1	1.29	58.0	270
228331	14 May 2008	6	PDC	139-150	7.77	0.7	8.3	76.3	25.7	3.7	0.35	0.08	1.1	5.2	0.8	0.11	30.0	338
433273	05 Sep 2008	2	PDC	91-120	7.56	0.0	10.5	49.4	18.5	2.9	0.24	0.03	1.2	4.9	4.5	1.29	25.7	227
463537	15 May 2008	35	PDC	124-149	7.21	1.6	9.9	105.1	30.7	22.8	1.09	0.06	3.2	5.8	1.4	< 0.01	43.3	475
466198	06 Apr 2010	4	PDC	136–147	7.68	1.9	10.6	80.8	26.0	3.9	0.05	0.07	1.4	6.2	1.6	0.04	15.3	357
516045	29 Jul 2009	37	PDC	159-185	7.26	0.2	9.8	92.5	28.5	21.2	0.61	0.04	2.8	6.1	1.1	0.08	46.0	422
541549 541775	29 Jul 2009 29 Jul 2009	16	PDC	100-123 78-144	7.07	0.7	10.2	119.5 111 1	34.4	14.1 20.5	0.86	0.05	2.7	5.5 5.2	5.2	0.10	54.6 24.1	433 521
559422	12 May 2008	13	PDC	87-112	7.12	0.5	9.5	82.5	31.0	36	0.07	0.03	13	5.9	5.8	0.10	35.6	360
601336	12 may 2000	24	PDC	121-146			010	0210	5110	5.0	0107	0.00	115	0.0	0.0	0.02	18.6	500
642018	29 Jul 2009	6	PDC	73-103	7.42	9.3	11.0	63.0	24.9	2.7	0.03	< 0.01	0.8	7.1	3.4	7.81	8.6	318
697770	14 May 2008	4	PDC	109-116	7.89	0.5	10.4	44.0	17.1	2.4	1.22	0.05	0.7	5.3	0.7	< 0.01	16.2	207
698933		17	PDC	114-143												0.02	29.3	
716426	16 Jul 2009	10	PDC	95-127	7.15	0.2	10.9	96.6	29.0	17.7	0.79	0.05	2.7	5.6	13.6	0.15	48.0	405
742062	12 May 2009	15	PDC	111-140	7.24		0.5	71 5	245	24	0.02	0.04	1 2	5.0	1.0	0.86	33.2 21.5	247
spring ^b	02 Aug 2009	0	rDC	150-158	7.24	11.2	9.2	60.0	24.J 27.1	4.0	0.92	< 0.04	0.7	6.8	7.6	18.69	6.4	301
Twin Citie	es Group																	
112234	16 May 2008	71	PDC	124-153	7.45	0.4	10.0	73.8	28.5	3.5	0.08	0.10	1.1	6.3	5.9	0.06	22.1	359
112235	04 Sep 2008	47	PDC	99-124	7.32	<0.1	10.1	80.3	29.1	5.3	0.31	0.06	2.0	5.8	15.0	1.30	21.6	369
127259	13 May 2008	26	PDC	91-118	7.01		10.2	70.3	25.2	3.5	0.26	0.08	2.2	5.3	5.0	< 0.01	18.7	346
127263	15 Jul 2009	15	PDC	130–155	7.33	0.4	10.1	73.4	24.2	6.7	0.41	0.07	1.8	6.3	13.4	0.05	20.7	323
133389	29 Apr 2010	86	PDC	86-115	7.26	0.1	9.9	80.4	31.9	6.4	2.36	0.07	2.8	9.3	17.7	0.05	9.4	406
151561	02 Sep 2008	24	PDC	131-15/	7.33	<0.1	10.2	85.9	30.1	9.8	0.53	0.07	l./	6.6 4 0	28.5	< 0.01	37.5	345
165640	12 May 2009	54	PDC	109_138	7.02	0.1	12.8	30.8 81.7	29.3	4.2	2.58	0.18	1.5	4.0 6.3	1.5	1.68	4.2 21.1	354
171018	29 Jul 2009	32	PDC	109-140	7.52	0.1	9.2	62.1	21.7	3.2	0.53	0.06	1.7	5.9	0.9	0.09	8.9	304
200160	01 May 2009	49	PDC	157-183	7.36	0.1	10.5	51.3	18.3	5.6	0.29	0.05	1.9	6.7	2.1	0.45	1.9	282
200664	15 May 2008	15	PDC	122-148	7.62	1.3	10.2	61.4	22.6	4.1	0.29	0.04	1.6	5.3	1.0	< 0.01	8.9	323
200665	15 May 2008	10	PDC	74-104	7.53	1.2	10.6	64.2	25.6	4.7	0.27	0.05	2.9	4.9	2.1	0.11	11.8	300
200674	16 May 2008	12	PDC	98-123	7.61	0.4	10.5	72.2	25.9	5.6	0.35	0.06	2.1	5.9	6.8	0.07	16.0	335
203613	30 Apr 2009	32	PDC	131-151	7.17	0.2	10.1	82.8	30.7	15.5	0.71	0.05	2.1	7.7	37.6	0.27	19.2	361
204470	14 May 2009	30 43	PDC	135-154	7.30	0.2	9.7	65.6	27.2	41	0.29	0.18	2.4	8.0 8.9	2.5	0.32	3.2	352
205627	09 Jul 2009	80	STP	96-118	7.45	0.2	9.7	88.0	41.4	23.2	0.54	0.20	4.2	7.7	1.4	0.05	21.9	509
205789	01 May 2009	40	PDC	141-157	7.61		10.6	45.1	16.0	5.2	1.29	0.05	2.0	5.8	1.7	0.39	1.5	254
205812	02 Sep 2008	37	PDC	146-179	7.44	< 0.1	10.1	66.1	25.9	3.3	0.28	0.07	1.1	5.8	5.7	< 0.01	23.3	320
205825	02 Sep 2008	22	PDC	132-162	7.42	< 0.1	11.0	71.3	23.7	4.9	0.33	0.05	1.7	6.5	3.9	1.36	5.8	344
206172	30 Mar 2010	34	PDC	83-109	7.14	0.1	9.9	77.5	30.3	5.6	0.51	0.07	2.2	6.4	16.1	0.16	23.5	373
206183	30 Apr 2009	55	PDC	98-123	7.19	0.1	10.2	83.4	32.0	15.3	0.59	0.06	2.0	7.6	51.4	0.76	26.9	358
206353	30 Apr 2009	01 48	PDC	105-134	1.24	0.1	10.4	80.2	30.0	15.9	0.41	0.08	2.3	7.9	54.2	0.28	27.1	344
200933	05 Sep 2008	-10 37	PDC	112-15/	7 4 5	<01	10.9	68.4	23.2	32	0 58	0.08	13	67	48	133	11.6	313
215447	23 Jul 2009	31	PDC	122-154	7.25	0.3	10.0	93.7	31.7	11.2	0.81	0.10	2.0	7.1	25.1	0.08	33.5	387
235373	16 May 2008	89	PDC	103-127	7.71	0.9	10.0	78.6	27.8	4.4	0.28	0.25	1.5	8.5	6.6	0.10	18.6	375
235586	-	24	PDC	114-146												0.02	20.6	
414034	21 Jul 2009	87	Q	89-102	7.30	0.3	9.7	83.2	39.3	11.7	0.45	0.03	3.6	5.5	1.3	0.18	14.4	478
420992	13 May 2008	45	PDC	142-173	7.24		9.9	/9.9	29.9	5.8	0.36	0.15	1.6	6.3	19.3	<0.01	20.1	356

(continued on next page)

Unique ID	Sampling Date	Depth to bedrock (m)	Over- lying unit	Open interval (m)	pН	02	T (°C)	Ca	Mg	Na	Fe	Mn	K	Si	Cl	NO ₃ ⁻ as NO ₃ ^{-(a)}	SO_4^{2-}	HCO ₃
433296	13 May 2008	76	PDC	160-188	7.53		9.8	73.8	24.0	5.6	0.36	0.07	1.6	5.4	1.6	0.36	7.9	369
453886	21 Jul 2009	64	PDC	94-102	7.17	0.3	12.9	91.4	36.4	14.6	0.20	1.71	4.9	6.1	1.5	0.13	12.7	492
463527	06 May 2009	49	PDC	128-157	7.23	< 0.1	10.0	69.8	24.7	4.0	0.11	0.25	1.8	7.9	1.7	0.03	11.0	338
468118		31	PDC	76-98														
519954	16 May 2008	1	PDC	102-125	7.69	2.3	12.0	65.3	24.6	4.3	0.28	0.10	1.6	6.0	5.0	0.05	19.1	325
583308	21 Jul 2009	72	Q	73-74	7.33	0.2	12.9	93.2	34.8	15.4	0.72	0.07	2.8	8.6	1.4	0.02	10.8	488
603079	15 Jul 2009	87	PDC	94-124	7.42	0.3	10.7	76.6	29.6	5.1	0.76	0.08	2.2	8.4	14.6	1.51	20.0	338
626784	04 Sep 2008	103	PDC	117-153	7.50	< 0.1	10.1	67.3	24.1	3.7	0.17	0.08	1.4	8.0	4.1	1.28	11.6	327
677176	04 May 2009	61	PDC	69-102	6.95	0.1	9.2	81.1	33.9	20.8	0.11	0.71	4.1	7.6	1.5	0.27	20.1	481
705735	12 May 2009	14	PDC	74-92	7.37	0.1	10.7	57.0	21.1	4.8	0.32	0.11	2.0	6.8	4.7	0.34	17.8	299
725107	16 Jul 2009	70	PDC	105-131	7.26	0.1	9.9	100.5	41.1	25.8	2.45	0.15	2.0	6.9	1.1	0.10	32.1	551
747666	14 May 2009	70	STP	95-116	7.30	0.2	9.0	81.4	30.0	5.9	0.48	0.31	2.6	10.5	1.3	0.27	5.0	452
753663	15 Jul 2009	44	PDC	119-149	7.30	0.4	9.8	73.8	26.9	3.8	0.09	0.08	1.8	5.5	5.6	4.02	24.4	307
759809	09 Jul 2009	57	STP	95-124	7.24	0.1	10.3	90.4	31.6	6.9	1.21	0.27	1.9	8.1	1.1	0.02	1.4	455

^a 1 mg L⁻¹ NO₃⁻ as NO₃⁻ \approx 0.23 mg L⁻¹ NO₃⁻ -N. The US EPA maximum contaminant level is 10 mg L NO₃⁻ -N (\approx 44 mg L⁻¹ NO₃⁻ as NO₃⁻).

^b Located outside extent of maps: 43.689°N, 91.543°W.

2005) including background count rate subtraction and correction for the fraction of Ra on the second column of fibers. Reported 2σ errors represent counting statistics but not potential uncertainties associated with factors such as varied counting geometry (²²⁸Ra) or moisture variation (²²⁴Ra).

2.4. Analysis of aquifer solids

Air-dried cuttings from wells constructed using cable tool methods were obtained from the Minnesota Geological Survey, crushed, and underwent three procedures. (1) Samples were extracted in 1 N HCl for 16 h (Hedley et al., 1982; Shang and Zelazny, 2008) to dissolve calcite, dolomite, and other HCl-soluble phases, then centrifuged and analyzed for U and Th by ICP-MS; four extracts were also prepared for Sr isotope analysis. (2) Samples were dissolved in a HF-HNO3 solution (modified from Stewart et al., 2002) for whole-rock analysis by ICP-MS, calibrated using nine rock standards. (3) Samples were sealed into polyethylene containers and analyzed by gamma spectrometry for ²³⁸U using the 63 keV peak of ²³⁴Th corrected for self-adsorption effects (Gilmore, 2008), ²²⁶Ra (weighted average of the 352 keV peak of ²¹⁴Pb and the 609 keV peak of ²¹⁴Bi), and ²²⁸Ra (583 keV peak of ²⁰⁸Tl) after 3 weeks of incubation, calibrated with DL-1a in matching geometry, and corrected for the background count rate.

2.5. Additional data sources

In addition to the samples collected for this study, unpublished radium and tritium data from the Minnesota Department of Health (MDH) are included in maps of Ra distribution and in Table 1. Radium-226 and radium-228 data are averages of available results for each well. These additional data also include Ra activities from the U.S. Geological Survey (http://water.usgs.gov; accessed June 2009) and Lively et al. (1992). For tritium activities presented in this study, the most recent available MDH result was used if not collected specifically for this study.

3. Results

3.1. Major element chemistry, tritium, and redox conditions

The major element composition of the groundwater in the Jordan aquifer is uniformly a Ca–Mg–HCO₃⁻ type. Throughout the aquifer but especially in non-subcrop areas, sodium concentrations are uniformly much lower than Ca and Mg (Table 2). In most of the aquifer, conditions are essentially anoxic, indicated by low dissolved oxygen concentrations and often by elevated concentrations of dissolved Fe and

Mn (Table 2). Some exceptions to this pattern of redox conditions are seen in subcropping areas of the Jordan aquifer. Samples were divided into five geographic groups based on hydrogeologic setting and variations in major element chemistry and tritium activity: (1) the Twin Cities Group, roughly corresponding to the Twin Cities Basin structural feature, and in which the highest radium activities were observed; (2) the Southern Group, in which the aquifer generally deepens to the south; and (3) the peripheral Hastings, (4) Shakopee, and (5) Northeastern groups (Fig. 1), providing examples of a relatively shallow hydrogeologic setting exhibiting indicators of rapid recharge such as detectable tritium activity (Table 3), elevated nitrate concentrations, and higher proportion of Na (Table 2). Other examples of the shallow setting were documented where the Jordan aquifer outcrops along the eastern edge of the Southern Group (e.g. well 642018 and the spring sample). The relationship between hydrogeologic setting and groundwater residence time is illustrated along the cross-section from east to west across the Jordan aquifer (Fig. 2). Areas where the aquifer subcrops below sandy glacial sediments and some portions of the Twin Cities metropolitan area (central and eastern parts of Fig. 2) exhibit measurable tritium. However, the Jordan aquifer in the western part of the study area generally exhibits activities<0.8 TU due to thick clay-rich tills in this area (e.g. the western one-third of Fig. 2). Also, beneath the Decorah shale confining unit in the Southern Group (Fig. 1), tritium activities are generally<0.8 TU (Table 3), which indicates that little or no recharge later than ~ 1950 has entered the aquifer in these areas.

3.2. Strontium

Strontium concentrations (mean 0.17 mg L⁻¹, median 0.14 mg L⁻¹, range 0.05–0.45 mg L⁻¹) and ⁸⁷Sr/⁸⁶Sr isotope ratios (mean 0.71124, median 0.71135, range 0.70861–0.71347) exhibit large variations within the study area (Table 3, Fig. 3a). The lowest concentrations of Sr were observed in areas in which the aquifer subcrops, increasing in deeper and in southern and western portions of the aquifer. In the Twin Cities Group, strontium concentration is well correlated with Mg (Spearman rank coefficient $\rho = 0.74$), Ca ($\rho = 0.78$), and HCO₃⁻ ($\rho = 0.81$) concentrations, but far less so with Ba ($\rho = 0.37$) or ²²⁶Ra ($\rho = 0.29$). In general, more radiogenic ⁸⁷Sr/⁸⁶Sr ratios (mean 0.71192, median 0.71200) were observed in the Twin Cities Group than the Southern Group (mean 0.70996, median 0.70995; Fig. 3b).

3.3. Radium, uranium, and barium

3.3.1. Water samples

Radium-226 activities occur over a large range (median 85 mBq L^{-1} , range below detection to 418 mBq L^{-1}) whereas ²²⁴Ra and ²²⁸Ra

Trace metal concentrations, Sr isotope ratios, and tritium and radium activities of Jordan aquifer groundwater. Italized tritium activities are from samples collected by the Minnesota Department of Health on different dates than indicated in Table 2. Errors are $\pm 2\sigma$.

Unique ID	Ba (mg L^{-1})	$Sr (mg L^{-1})$	⁸⁷ Sr/ ⁸⁶ Sr	Tritium (TU)	²²⁴ Ra (mBq L ⁻¹)	²²⁶ Ra (mBq L ⁻¹)	²²⁸ Ra (mBq L ⁻¹)	U (μ g L ⁻¹)
Hastings Group								
207993			0.710870	7.2				
509053	0.05	0.10	0.710985	10.2	7.3 ± 1.2	8.2 ± 2.7	<8.7	
Northeastern G	roup	0.00	0 740 407	6.0	0.0 + 0.0			0.7
182655	<0.01	0.06	0.712407	6.3	0.6 ± 0.3	<0.8	No peak	0.7
208548	0.04	0.07	0.712073	2.0	49+07	0.0 + 1.3	30+25	
087180	0.04	0.07	0.710355	2.3	4.5 ± 0.7	5.0±1.5	5.5 ± 2.5	
Shakopee Grou	D							
415975	0.11	0.18	0.711653	6.0	33.8 ± 2.0	10.0 ± 2.9	10.9 ± 2.4	
674456	0.17	0.29	0.710698	1.9	18.6 ± 1.5	6.6 ± 3.6	9.3 ± 2.3	
Southern Group)		0.700005					
132254	0.06	0.26	0.709965	<0.9	112 7	02 9 1 4 4	0/0 10/	<01
161402	0.00	0.00	0.709334	< 0.8	112 ± 7 23 3 ± 1.8	52.0 ± 4.4 597 + 38	34.0 ± 10.4 33 5 \pm 7 3	<0.1
171005	0.11	0.03	0.710026	<0.8	54.1 ± 2.9	94.5 ± 4.0	56.5 ± 10.5	0.3
213638	0.06	0.37	0.709732	<0.8	69.6 ± 3.1	61.0 ± 3.1	86.4 ± 15.8	0.8
216520	0.22	0.33	0.709933	<0.8	147 ± 6	214 ± 7	127 ± 20	
217550	0.06	0.12	0.710631	<0.8	54.7 ± 3.8	31.1 ± 1.9	47.4 ± 12.3	
228317	0.08	0.11	0.710465	2.3	43.5 ± 2.5	46.2 ± 2.6	43.8 ± 10.0	
228324	0.04	0.25	0.709802	<0.8	83.2 ± 5.6	79.1±3.9	63.0 ± 11.8	
228331	0.05	0.13	0.710362	<0.8	40.8 ± 2.5	48.1 ± 3.6	46.9 ± 9.2	
433273	0.03	0.09	0.710234	< 0.8	30.0 ± 3.0	57.3 ± 3.9	21.0 ± 5.2 577 + 12.8	
466198	0.06	0.20	0.709701	<0.8	59.0 ± 3.9	751 ± 34	57.7 ± 15.8 70.6 + 19.4	04
516045	0.06	0.25	0.710258	<0.8	88.5 ± 3.8	64.2 ± 2.9	108 ± 16	0.4
541549	0.17	0.27	0.709793	1.2	77.5 ± 3.7	64.4 ± 3.4	74.0 ± 12.0	
541775	0.09	0.45		<0.8	34.6 ± 2.5	140 ± 6	47.7 ± 13.5	
559422	0.03	0.10	0.710185	3.3	38.9 ± 2.6	22.1 ± 4.1	26.2 ± 7.0	1.4
601336			0.709943	1.2				
642018	0.04	0.06	0.709451	3.3	17.8 ± 1.7	4.7 ± 1.0	16.8 ± 5.5	
697770	0.02	0.05	0.709595	<0.8	13.4 ± 1.3	37.4 ± 3.1	11.3 ± 3.4	
098933 716426	0.22	0.26	0.710147	1.9	807 20	145 7	01 9 19 0	
733087	0.52	0.20	0.709827	<0.8 3.7	89.7 ± 3.9	145 ± 7	91.0±10.9	
743063	0.05	0.09	0.710660	<0.8	18.8 ± 1.4	21.2 + 3.0	34.5 + 7.7	< 0.1
spring	0.04	0.05	0.708610		10.6 ± 0.9	3.8 ± 0.5	8.5 ± 4.9	
Twin Cities Gro	ир							
112234	0.05	0.09	0.713091		47.0 ± 2.4	87.3±4.3 l	47.1±9.5	0.4
112235	0.22	0.14	0.712394	5.0	47.8 ± 3.0	119 ± 4	54.6 ± 13.4	0.5
127259	0.12	0.14	0.711415	2.7	38.2 ± 3.1	84.0 ± 4.3	39.3 ± 8.8	0.5
133389	0.18	0.14	0.711352	2.2	43.1 ± 3.2 55.9 ± 3.7	92.2 ± 4.0 94.6 ± 3.9	42.3 ± 10.9 43.4 ± 13.2	0.2
151561	0.15	0.13	0.712413	6.1	61.2 ± 5.7	137 + 6	47.7 ± 9.3	
151590	0.04	0.10	0.711970	<0.8	6.3 ± 1.3	30.8 ± 2.1	11.9 ± 2.5	
165640	0.27	0.12	0.712516	5.2	61.8 ± 8.0	233 ± 8	60.6 ± 21.2	
171018	0.12	0.09	0.711885	<0.8	26.9 ± 2.4	73.7 ± 3.8	29.0 ± 9.7	
200160	0.07	0.14	0.712201	<0.8	34.7 ± 2.1	82.3 ± 3.8	36.8 ± 5.3	
200664	0.09	0.12	0.712034	<0.8	56.4 ± 9.9	418 ± 12	58.3 ± 37.6	0.2
200665	0.10	0.18	0.710503	<0.8	23.1 ± 2.1	86.9 ± 5.9	39.7 ± 9.3	0.2
200674	0.11	0.14	0.711780	24	32.1 ± 2.1 78 4 \pm 5 1	61.7 ± 3.8 156 ± 6	39.8 ± 7.0 82.7 ± 0.2	0.2
203013	0.10	0.15	0.712005	<0.8	574 ± 3.1	130 ± 0 149 ± 5	41.7 ± 5.2	15
204617	0.14	0.12	0.712333	<0.8	205 ± 17	143 ± 3 107 ± 4	194 + 29	1.5
205627	0.10	0.29	0.711360	<0.8	145 ± 8	213 ± 7	130 ± 27	
205789	0.04	0.10	0.712467	<0.8	20.4 ± 0.9	49.6 ± 2.3	16.7 ± 3.1	<0.1
205812	0.09	0.09	0.713123	2.8	29.8 ± 2.1	51.8 ± 3.9	30.7 ± 5.7	
205825	0.23	0.14	0.711540	<0.8	69.5 ± 5.7	148 ± 6	61.8 ± 11.4	
206172	0.27	0.16	0.712159		40.6 ± 2.1	97.6 ± 4.1	44.1 ± 7.6	
206183	0.19	0.19	0.712253	6.1	81.7 ± 4.1	125 ± 5	68.6 ± 8.9	
206353	0.12	0.20	0.712093	5.8	100 ± 6	128 ± 5	75.9 ± 7.4	
206933	0.17	0.10	0.710852	16	612.157	120 - 6	55 1 1 1 2 1	0.5
207727 215447	0.17	0.10	0.712004	1.0	60.4 ± 4.9	129 ± 0 167 ± 5	33.4 ± 12.4 724 + 174	0.5
235373	0.19	0.12	0.712393	3.7	40.2 ± 2.8	110 ± 5	67.3 ± 15.7	0.5
235586	0.15	0,12	0.710743	2.9	10.2 ± 2.0	110 ± 5	07.5 ± 15.7	0.5
414034	< 0.01	0.28	0.711670		2.5 ± 0.6	1.9 ± 0.7	<2.8	
420992	0.21	0.13	0.712833		35.6 ± 2.2	63.5 ± 3.9	37.8 ± 9.1	
433296	0.17	0.14	0.711519	1.1	46.6 ± 2.7	117 ± 5	56.0 ± 14.7	
453886	0.19	0.41	0.710350		71.7 ± 4.9	21.9 ± 1.8	51.8±11.3	

(continued on next page)

286

Unique ID	Ba (mg L^{-1})	$Sr (mg L^{-1})$	⁸⁷ Sr/ ⁸⁶ Sr	Tritium (TU)	224 Ra (mBq L $^{-1}$)	226 Ra (mBq L $^{-1}$)	228 Ra (mBq L $^{-1}$)	U ($\mu g \ L^{-1}$)
463527	0.23	0.11	0.712545	<0.8	58.1 ± 4.8	250 ± 7	69.7 ± 9.2	
468118			0.712977					
519954	0.10	0.12	0.711983	1.6	52.1 ± 3.8	298 ± 7	48.8 ± 13.7	0.2
583308	0.15	0.26	0.711204	<0.8	55.4 ± 4.8	83.4 ± 3.5	40.5 ± 13.3	
603079	0.29	0.17	0.711923	3.8	36.2 ± 2.6	113 ± 5	37.3 ± 9.2	0.1
626784	0.15	0.11	0.712135	<0.8	45.9 ± 3.4	105 ± 5	37.2 ± 6.6	
677176	0.06	0.40	0.710786	<0.8	85.1 ± 3.4	30.4 ± 2.1	47.4 ± 7.0	
705735	0.11	0.12	0.712582	1.6	102 ± 6	136 ± 5	79.7 ± 9.9	0.5
725107	0.10	0.26	0.711361	<0.8	72.6 ± 4.4	116 ± 5	70.5 ± 15.4	0.9
747666	0.10	0.25	0.711160	<0.8	129 ± 6	188 ± 7	127 ± 26	
753663	0.06	0.09	0.713466	2.7	41.8 ± 3.6	63.5 ± 2.7	31.5 ± 9.2	6.3
759809	0.09	0.23	0.711239	<0.8	83.8 ± 5.9	211 ± 7	84.4 ± 20.0	1.3

activities are lower (²²⁴Ra median 47 mBq L⁻¹, range 0.6–147 mBq L⁻¹; ²²⁸Ra median 47 mBq L⁻¹, range below detection to 130 mBq L⁻¹). Elevated activities of ²²⁶Ra occur in a broad region that occupies the center of the Twin Cities Group and a narrow north–south belt south of the Minneapolis-St. Paul metropolitan area (Fig. 1). ²²⁸Ra/²²⁶Ra activity ratios are significantly below 1 (median 0.5; Fig. 4), and these ratios are lowest in the waters highest in Ra (Fig. 5). There is a significant correlation between ²²⁶Ra activity and ²²⁸Ra activity (ρ =0.70). Activities of ²²⁴Ra and its great-grandparent ²²⁸Ra are generally similar, yielding ²²⁴Ra/²²⁸Ra averaging approximately unity (median 1.0). In relationship to US Environmental Protection Agency drinking water standards, 27% of the wells sampled nonrandomly in the Jordan aquifer for this study exceed the Ra standard of 185 mBq L⁻¹ (5 pCi L⁻¹) combined ²²⁶Ra + ²²⁸Ra activity. In contrast to radium activities, uranium concentrations (median 0.4 µg L⁻¹, range<0.1–6.3 µg L⁻¹) are significantly below the levels of concern throughout the primarily anoxic waters analyzed for U (Table 3).

Concentrations of barium (Ba), a chemical analogue for Ra, exhibit large variations within the study area, approximately two orders of magnitude (median 0.10 mg L⁻¹, range<0.01–0.32 mg L⁻¹; Table 3). Barium concentration is generally lowest in the subcrop areas of the aquifer (e.g. well 182655), the western area (e.g. well 414034), and the more deep, confined portions of the aquifer (e.g. well 217550), and is generally higher in the Twin Cities metropolitan area (Table 3). Barium concentration is not well correlated with the other alkaline

earth metals Mg (ρ = 0.33), Ca (ρ = 0.38), or Sr (ρ = 0.38), but is better correlated with its chemical analogue ²²⁶Ra (ρ = 0.59).

3.3.2. Aquifer solids

Based on gamma spectrometric analysis of bulk rock samples, ²²⁶Ra and ²³⁸U activities of aquifer solids vary within approximately one order of magnitude (226 Ra 1.6–15.2 Bq kg⁻¹; 238 U 4.1–15.2 Bq kg⁻¹; Table 4). Solid-phase 228 Ra activities are consistently low throughout the samples analyzed (median 3.0 Bq kg⁻¹), yielding 228 Ra/ 226 Ra<1 (median 0.6; Fig. 6a; Table 4). Moreover, the whole-rock ²²⁶Ra/²³⁸U activity ratio is ~1 within counting error (Fig. 6b), which provides a rationale for using Th/U ratios to approximate ²²⁸Ra/²²⁶Ra because of the apparent solid-phase secular equilibrium between ²³⁸U and ²²⁶Ra. Equivalent isotope activities calculated from whole-rock ICP-MS analysis of U and Th are broadly consistent with gamma spectrometric analysis, also indicating Th/U<1 (Fig. 6c). Modestly lower levels of U and Th were extracted with 1 N HCl from the solids than whole-rock radionuclide activities, typically about one-half of the whole-rock values (Table 4). Limited Sr analysis of 1 N HCl extracts indicates a large range of Sr concentrations $(0.7-25.7 \text{ mg kg}^{-1})$ and ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios (0.70920-0.71279; Table 4). Whole-rock Ra isotope activities were also compared with groundwater Ra isotope activities. Although there is considerable vertical and geographic variability in whole-rock ²²⁶Ra activity, the three highest average values of whole-rock ²²⁶Ra are generally associated with the highest groundwater ²²⁶Ra in wells for which



Fig. 2. Cross-section along an east–west line (Fig. 1) indicating hydrogeologic setting, open intervals (box lengths), tritium activities (in tritium units, indicated by box colors), ${}^{87}Sr_{1}{}^{86}Sr$ (black numbers), and ${}^{226}Ra$ activity in mBq L⁻¹ (red numbers). Heavy green line represents land surface elevation. See Table 1 for hydrostratigraphic unit abbreviations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 3. ⁸⁷Sr/⁸⁶Sr ratios: (a) Comparison of ⁸⁷Sr/⁸⁶Sr between tritium-bearing and tritium-free waters. (b) Relationship between ⁸⁷Sr/⁸⁶Sr and inverse Sr concentration. (c) Relationship between ⁸⁷Sr/⁸⁶Sr and Ca/Sr ratios in groundwater and 0.1 N HCl extracts (large diamonds). Panels b and c show hypothetical two-component mixing fractions of the radiogenic Sr source for waters of the Twin Cities Group. Dashed line represents ⁸⁷Sr/⁸⁶Sr of late Cambrian marine carbonates (McArthur et al., 2001).

both groundwater and solids were analyzed (Fig. 6d). Also, the 228 Ra/ 226 Ra activity ratios of water samples are generally close to whole-rock 228 Ra/ 226 Ra ratios from the same six wells (Fig. 6e).

4. Discussion

4.1. Major element composition of groundwaters: relationship to water-rock interaction and groundwater flow

The essentially carbonate-controlled nature of the major element chemistry of waters is indicated by the $(Ca + Mg)/HCO_3^-$ molar ratio consistently ~0.5 (median 0.51, mean 0.51) and the overall dominance

of dissolved solids concentrations by Ca, Mg, and HCO₃⁻. Concentrations of Ca and Mg are highly correlated (ρ =0.88), and the Ca/Mg ratio exhibits minor variations. Waters of the generally deeper Southern Group exhibit the highest values of Ca/Mg (median 1.87), whereas lower values were observed in the generally shallower Twin Cities Group and the three outlying groups (median 1.65). This apparent increase of Ca/Mg ratios as the Jordan aquifer becomes deeper and of longer groundwater residence time is of unknown significance. Overall, this range of Ca/Mg ratios is consistent with fresh waters in other Paleozoic carbonate aquifers in the region and shows the effects of incongruent dissolution of carbonate minerals (McIntosh and Walter, 2006). Variations of Ca/Mg are smaller in the Jordan aquifer than in other



Fig. 4. Map showing ²²⁸Ra/²²⁶Ra activity ratios of Jordan aquifer groundwater. Data sources are as described in the caption to Fig. 1.



Fig. 5. Radium-226 and radium-228 activities. Lines marked "MCL" indicate the EPA maximum contaminant level of 185 mBq L^{-1 226}Ra + ²²⁸Ra (5 pCi L⁻¹). Error bars are ± 2 σ .

carbonate aquifer systems exhibiting the progressive effects of incongruent dissolution yielding Mg-enriched groundwater (e.g. Dogramaci and Herczeg, 2002). Given that uncharacterized carbonate phases of calcite and dolomite composition control the major element composition chemistry of groundwater in the Jordan sandstone, a more detailed examination of groundwater residence time and water–rock interaction mechanisms may provide additional constraints on the sources of carbonate-derived material to groundwater and its potential relationship to radium activity.

4.2. Groundwater residence time: relationship to Sr and Ra isotope signatures

Residence time of Jordan aquifer groundwater was evaluated using tritium activities, defined at a threshold of 0.8 TU because of the decay of tritium since the mid-twentieth century (Clark and Fritz, 1997). Therefore, the tritium activities obtained in this study provide qualitative evidence of inputs of younger waters. Tritium detections were more widespread in the shallow, outlying Hastings, Shakopee, and Northeastern groups (present in all six wells analyzed) than in the Twin Cities Group (present in 42%) or the generally deeper Southern Group (present in 35%). The locations of younger waters are consistent with the hydrogeologic setting (Fig. 2). Potential hypotheses for evaluating Sr and Ra isotopes include (1) as fingerprints of mixing of distinct waters, or (2) progressive water-rock interaction effects that become more pronounced over time, either of which could be associated with tritium activity. Therefore, patterns of tritium activity were examined for any associations with ⁸⁷Sr/⁸⁶Sr, Ra activity, and ²²⁸Ra/²²⁶Ra.

Although ⁸⁷Sr/⁸⁶Sr ratios overlap among the geographic groups in the aquifer, mean ⁸⁷Sr/⁸⁶Sr within the Twin Cities Group is significantly higher in tritium-bearing waters as determined by Student's t-test (p < 0.05), which implies that inputs of radiogenic Sr are somewhat associated with more recent recharge and/or that interaction with confining units supplies less radiogenic Sr to the aquifer (Fig. 3a). Inputs of shallow waters may contribute distinctive ions that are otherwise found in low concentrations in Jordan aquifer groundwater, evidenced by the chloride and nitrate concentrations in the Northeastern, Hastings, and Shakopee groups. Consistent with evidence from tritium activities, there is a moderate positive correlation within the Twin Cities Group between ⁸⁷Sr/⁸⁶Sr and chloride concentration ($\rho = 0.48$) that was weaker in the overall data set ($\rho = 0.38$). Yet, where downward inputs are believed to be most significant (Northeastern, Hastings, and Shakopee Groups), these shallow, surfaceconnected waters do not exhibit distinctively high or low values of ⁸⁷Sr/⁸⁶Sr (Fig. 3b-c). Overall, the data indicate that external waters could influence ⁸⁷Sr/⁸⁶Sr, but that variations in groundwater residence time do not exhibit a consistent relationship with ⁸⁷Sr/⁸⁶Sr.

Examination of radium in relationship to tritium activities suggests that, although the lowest radium activities were observed in subcrop areas with tritium-bearing waters (e.g. Northeastern, Shakopee, and Hastings groups; Fig. 1; Fig. 7a), there is not a clear relationship between radium activity and groundwater residence time. This is in part because the oldest ³H-free waters, under the Decorah confining unit (thousands of years; Campion, 1997; 2002; Berg and Bradt, 2003), also exhibit relatively low radium. Furthermore, unlike Sr isotopes that exhibit some associations with groundwater residence time and chloride concentrations, indicating a possible role of inputs from shallow groundwater to the Jordan aquifer, In ²²⁶Ra and In ²²⁸Ra/ ²²⁶Ra (Ra activities and isotope ratios tend to be lognormally distributed; King et al., 1982) exhibit no systematic difference in means between tritium-free and tritium-bearing waters (Fig. 7a-b). Elevated radium occurs in some, but not all (Fig. 2), waters of intermediate or mixed groundwater residence time, which implies that radium does not significantly accumulate in groundwater and is thus unrelated to groundwater residence time. Overall, the distribution and relationship of Sr and Ra isotope signatures to inferred residence time is not identical; whereas Sr isotopes exhibit a limited relationship to near-surface inputs, Ra isotopes are apparently insensitive to groundwater residence time. This is consistent with previous studies showing that Ra in fresh, near-neutral groundwater is typically derived from local water-rock interaction and rapidly reaches a steady-state activity (Section 1). Therefore, detailed examination of water-rock interaction is required to understand the controls on ⁸⁷Sr/⁸⁶Sr and to address the cause of the observed ²²⁶Ra activities and ²²⁸Ra/²²⁶Ra ratios.

4.3. Strontium isotope constraints on the carbonate phase

In the Jordan aquifer, the ⁸⁷Sr/⁸⁶Sr ratio in groundwater and solids (up to 0.71347; Fig. 3b) is significantly more radiogenic than latest Cambrian (~490 Ma) seawater (~0.7090; McArthur et al., 2001), which indicates that either some or all of the Sr contributing to the present-day groundwater system may be from diagenetically modified carbonate containing radiogenic ⁸⁷Sr/⁸⁶Sr, rather than primary marine carbonate. Overall, the multiple trends of Sr concentrations and isotope ratios imply that more than two Sr sources affect groundwater composition (Fig. 3b). In the Twin Cities Group, the area of greatest interest for elevated Ra activities, a systematic relationship was observed between the inverse Sr concentration and ⁸⁷Sr/⁸⁶Sr (Fig. 3b), which suggests two or more principal Sr sources including a low-Sr source with more radiogenic ⁸⁷Sr/⁸⁶Sr and a high-Sr source with low 87Sr/86Sr. The 87Sr/86Sr ratio is associated with the Ca/Sr ratio (Fig. 3c), which could be consistent with carbonate dissolution or mixing of distinct waters (Dogramaci and Herczeg, 2002).

Given, however that ⁸⁷Sr/⁸⁶Sr is not simply explained by systematic mixing of *water* sources (Section 4.2), a simple mixing model is used to evaluate combinations of *strontium* sources derived from carbonate

Results of analysis of solids from Jordan aquifer wells. Locations of these wells (sites S1-S6) are shown on Fig. 1.

Unique	Depth	1 N-HCl extractable							Equivalent activities			Whole-rock Equivalent activities			Whole-rock gamma analysis (Bq kg^{-1})					
ID	(m)	(g kg ⁻¹)		$(mg kg^{-1})$		$(mg kg^{-1})$		(Bq kg	(Bd kg)			$(mg kg^{-1})$		(вц кд т)			2σ			
		Mg	Ca	Sr	⁸⁷ Sr/ ⁸⁶ Sr	U	Th	²³⁸ U	²³² Th	²³² Th/ ²³⁸ U	U	Th	²³⁸ U	²³² Th	²³² Th/ ²³⁸ U	²²⁶ Ra	²²⁸ Ra	²²⁸ Ra/ ²²⁶ Ra	²³⁸ U	К
151582	87-96	28.2	51.6	18.7	0.709330	0.6	0.5	7.1	2.1	0.3	1.1	0.7	13.4	2.7	0.2	15.2 ± 0.8	3.7 ± 1.4	0.2 ± 0.1	15.2 ± 3.3	350
S2	96-106	2.3	11.1	18.0	0.709490	0.7	0.5	8.1	2.1	0.3	0.9	0.9	11.6	3.5	0.3	6.2 ± 1.0	3.2 ± 1.8	0.5 ± 0.3		
	106-115			5.3		0.2	0.2	2.6	0.9	0.3	0.4	0.4	4.7	1.5	0.3	5.3 ± 0.5	2.1 ± 1.0	0.4 ± 0.2	8.1 ± 2.5	
	115-119			7.8		0.2	0.9	2.8	3.6	1.3	0.5	1.1	6.8	4.4	0.6	6.7 ± 0.7	3.8 ± 1.3	0.6 ± 0.2	4.3 ± 3.5	
161435	70-78			3.7		0.3	0.6	4.2	2.6	0.6						4.5 ± 1.1	3.3 ± 2.0	0.7 ± 0.5		920
S1	78-83			0.7		0.1	0.2	1.2	0.8	0.6						2.4 ± 0.7	2.8 ± 1.4	1.2 ± 0.7		
(^a)	83-92			0.9		0.1	0.2	1.1	0.7	0.7						3.1 ± 1.0	4.2 ± 1.6	1.4 ± 0.7		
	92-98			10.2		0.2	0.7	2.2	3.0	1.4						1.9 ± 1.1	3.5 ± 2.0	1.8 ± 1.5		
133389	81-90															1.6 ± 0.7	1.9 ± 1.4	1.2 ± 1.1		430
S3	92-96			3.8		0.1	0.2	1.7	0.9	0.5						3.2 ± 0.9	1.9 ± 1.8	<0.6		
	107-112			4.3		0.4	0.4	4.7	1.7	0.4	0.9	0.8	11.1	3.2	0.3	8.1 ± 0.8	4.5 ± 1.5	0.5 ± 0.2		
151561	138-141			2.6		0.4	0.7	4.5	2.7	0.6	0.8	1.1	10.1	4.3	0.4	12.4 ± 0.5	4.1 ± 0.9	0.3 ± 0.1	9.0 ± 1.9	760
S4	144-147	10.3	18.6	6.1	0.712794	0.4	0.6	4.4	2.6	0.6	0.9	1.4	10.9	5.8	0.5	9.7 ± 0.6	6.8 ± 1.3	0.7 ± 0.1	11.9 ± 2.6	
753663	116-118			10.9		0.3	0.4	3.9	1.6	0.4						5.9 ± 0.6	2.1 ± 1.1	0.4 ± 0.2	5.6 ± 1.8	680
S5	118-119			5.7		0.1	0.3	1.6	1.1	0.7						2.8 ± 0.6	2.1 ± 1.1	0.8 ± 0.4	4.1 ± 2.5	
	131-133			2.9		0.3	0.2	3.2	0.6	0.2						3.6 ± 0.6	1.4 ± 1.1	0.4 ± 0.3	6.6 ± 2.2	
	145-147			5.2		0.3	0.5	3.1	2.1	0.7						6.1 ± 0.5	3.5 ± 1.0	0.6 ± 0.2	7.2 ± 2.0	
200664	116-125	38.0	68.6	25.7	0.709196	0.6	0.4	5.8	1.3	0.2	1.0	0.5	12.4	2.1	0.2	9.1 ± 0.9	2.5 ± 1.5	0.3 ± 0.2		150
S6	125-135			2.6		0.5	0.2	6.1	1.0	0.2	0.8	0.7	10.0	2.6	0.3	7.1 ± 1.0	2.1 ± 1.7	0.3 ± 0.2		
	135–142			2.0		0.3	0.2	4.1	0.8	0.2	0.6	0.4	7.1	1.5	0.2	3.8 ± 0.9	<1.5	<0.4		

^a Well 161435 is adjacent to Jordan aquifer well 677176 sampled for water.



Fig. 6. Plots showing Ra and U isotope activities in aquifer solids (a–c; dashed lines represent ratios of 1) and relationship between radium in groundwater and solids (d–e). (a) Relationship between 226 Ra and 228 Ra of aquifer solids by gamma spectrometry. (b) Relationship between whole-rock 226 Ra and 238 U by gamma spectrometry. (c) Relationship between whole-rock U and Th of aquifer solids by ICP-MS. Note the similar trends in 228 Ra/ 226 Ra and 232 Th/ 238 U ratios. (d) Relationship between whole-rock 226 Ra and groundwater 226 Ra activity. (e) Relationship between 228 Ra/ 226 Ra activity ratio of solids and 228 Ra/ 226 Ra activity ratio of groundwater. Error bars are $\pm 2\sigma$.

components of the aquifer solids. The Ca, Mg, and Sr concentrations of waters in the Twin Cities Group can be explained by hypothetical two-component mixing between end members (1) containing approximately 0.001 mM Sr, 1.8 mM Ca, and ⁸⁷Sr/⁸⁷Sr of 0.7135; and (2) containing approximately 0.025 mM Sr, 2 mM Ca, and ⁸⁷Sr/⁸⁷Sr of 0.710 (Fig. 3b-c). It should be noted that these hypothetical end members exhibit 25-fold variation in Sr content but only 10% variation in Ca content. A potential mechanism for interactions with multiple carbonate-hosted Sr sources (Cander, 1995) is indicated by the importance of both intergranular and secondary porosity features for Jordan aquifer groundwater flow (Runkel et al., 2006). A different pattern was observed in the southern portion of the study area, where the relationship between ⁸⁷Sr/⁸⁶Sr and 1/[Sr] and Ca/Sr (Fig. 3b-c) diverges into two trends. One trend parallels the trend observed in the Twin Cities Group, although offset toward lower values of ⁸⁷Sr/⁸⁶Sr and/or lower Sr concentration. The significance of this apparent offset is unknown. A second, divergent trend suggests an unidentified end-member with low-Sr, high-Ca/Sr, waters and low ⁸⁷Sr/⁸⁶Sr~0.709 (Fig. 3b-c).

Possible geologic sources of radiogenic Sr of to the secondary carbonate phase include: (1) near-surface radiogenic Sr related to the Precambrian crystalline source rock content of Quaternary glacial deposits (Franklyn et al., 1991; Vinson et al., 2010); (2) Sr derived from clay minerals interacting with the aquifer, which could exhibit significantly different ⁸⁷Sr/⁸⁶Sr than carbonates (Section 1); (3) radiogenic Sr from diagenetic dolomite (e.g. Michigan Basin; Winter et al., 1995); and/or (4) Sr derived from weathering of K-feldspar that is locally present in the Jordan sandstone (Odom, 1975; Thomas, 1991; Runkel, 1994), which with its high Rb/Sr ratio and Precambrian age of crystallization could contribute radiogenic Sr. Multiple Sr sources may be regionally significant, indicated by the multiple trends of ⁸⁷Sr/⁸⁶Sr and Sr concentration (Fig. 3b).

As was described for groundwater sampling, limited Sr analysis of 1 N HCl extracts of aquifer solids is consistent with a mixture of sources of low Sr concentration but high ⁸⁷Sr/⁸⁶Sr with high Sr concentration but low ⁸⁷Sr/⁸⁶Sr (Table 4). Although Sr extracted from Twin Cities Group aquifer solids exhibits a large range of ⁸⁷Sr/⁸⁶Sr



Fig. 7. Relationship between ²²⁶Ra and ²²⁸Ra/²²⁶Ra and tritium activity (a, b – note log scale); and between ²²⁸Ra/²²⁶Ra and ⁸⁷Sr/⁸⁶Sr (c) in Jordan aquifer groundwater. Dashed line represents late Cambrian marine carbonates (McArthur et al., 2001).

(0.70920–0.71279), the extracts do not match the exact range of 87 Sr/ ⁸⁶Sr in waters of the Twin Cities Group (0.71035–0.71347). As an additional discrepancy between groundwater and extracted Sr, two of the four extracts exhibit Ca/Sr vs. ⁸⁷Sr/⁸⁶Sr ratios that differ from groundwater of the Twin Cities Group (Fig. 3c). The Ca/Mg ratios of three of four 0.1 N HCl extracts are ~1.1, lower than groundwater ratio values (Section 4.1). Therefore, the 0.1 N HCl extractions did not simply dissolve the carbonate phases influencing groundwater, but may have incorporated less soluble phases. For example, ~1 N HCl can extract Sr from clays (Winter et al., 1995; Bullen et al., 1996; Katz and Bullen, 1996) or dissolve Fe and Mn oxides (Roden and Edmonds, 1997) in addition to dissolving calcite and dolomite. As a check on the specificity of 1 N HCl extraction, the ⁸⁷Rb/⁸⁶Sr ratio was monitored during TIMS analysis to be below 0.08, implying minimal contamination from clay-derived Sr (Winter et al., 1995). Overall, the data suggest that multiple Sr sources of varying ⁸⁷Sr/⁸⁶Sr ratios contribute to the aquifer rather than simple mixing between a radiogenic and a less radiogenic end member. Even within the more straightforward mixing trend observed in the Twin Cities Group, the carbonate-like signature of Sr contributions might contain localized radiogenic inputs derived from waters that have interacted with overlying aquifers.

4.4. Radium sources to groundwater

4.4.1. The significance of ²²⁸Ra/²²⁶Ra

The ratio between ²²⁸Ra and ²²⁶Ra is primarily considered to indicate Ra sources rather than Ra-mobilizing mechanisms, and thus should be close to the ²³²Th/²³⁸U activity ratio of the aquifer rocks (Dickson, 1990; Szabo et al., 1997). In sandstone aquifers, the ²²⁸Ra/²²⁶Ra activity ratio is typically \geq 1 (Dickson et al., 1987; Szabo et al., 1997, 2005, 2012; Vengosh et al., 2009) due to the tendency of ²³⁸U and ²³²Th to co-occur at similar activities in major silicate minerals. In contrast, carbonate aquifers are characterized by ²²⁸Ra/²²⁶Ra<1 (Moise et al., 2000; Sturchio et al., 2001; Szabo et al., 2012) due to the greater affinity for U than Th in carbonate minerals. In the Jordan aquifer, whole-rock ²²⁸Ra/²²⁶Ra ratios (Fig. 6a) and groundwater ²²⁸Ra/²²⁶Ra ratios (Fig. 5) exhibit a continuum between low Ra activity with ²²⁸Ra/ 226 Ra \approx 1 and high Ra activity with 228 Ra/ 226 Ra < 1. Similarity of 228 Ra/ ²²⁶Ra ratios in solids and coexisting groundwater (Fig. 6e), and to some degree an association between whole-rock ²²⁶Ra and groundwater ²²⁶Ra (Fig. 6d), imply that the U and Th content of the aquifer solids controls the distribution of Ra in the groundwater. The low, carbonate-like ²²⁸Ra/²²⁶Ra ratios in both groundwater and aquifer solids (Fig. 6e) are consistent with an additional U-series radionuclide source to the aquifer beyond the quartz sandstone matrix alone and imply that a carbonate-precipitating diagenetic event could have contributed uranium to the aquifer solids. Moreover, the apparent whole-rock ²²⁶Ra/²³⁸U activity ratio, generally within error of 1 (Fig. 6b), implies secular equilibrium between ²²⁶Ra and ²³⁸U, which suggests that the solids have been closed to additional U inputs for at least 350,000 yr (5 half-lives of ²³⁰Th; Ivanovich et al., 1992). The 1 N HCl-extractable U and Th concentrations indicate that approximately one-half of the radionuclide content of the entire rock was easily extractable using a method intended for calcite, dolomite, and other HCl-soluble minerals (Table 4). Although 1 N HCl-extractable U and Th cannot be specifically attributed to calcite or dolomite and may represent other soluble phases (Section 4.3), it is noteworthy that such a significant proportion of whole-rock radioactivity was dissolved in 1 N HCl, further implying that radionuclides of low ²²⁸Ra/²²⁶Ra ratio are not retained in silicates.

To the extent that ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ records the nature of water–rock interaction with the carbonate portion of the aquifer solids, it may be informative to correlate ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ with the sources and mechanisms of water–rock interaction affecting radium. The lowest values of ${}^{228}\text{Ra}/{}^{226}\text{Ra}$ and the most radiogenic values of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ are seen

in the Twin Cities Group (Fig. 7c). Although some negative correlation was observed between ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ${}^{228}\text{Ra}/{}^{226}\text{Ra}$ in the overall data set ($\rho = -0.52$), this correlation was insignificant in the Twin Cities Group, where the highest Ra activities occur ($\rho = -0.16$). The results do not specifically indicate a single shared mechanism for radiogenic ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and high radium activities to occur, and in particular, the most radiogenic values of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ (>0.713) are not associated with especially high Ra activity or low ${}^{228}\text{Ra}/{}^{226}\text{Ra}$. Nonetheless, both the Sr and Ra isotope systems exhibit carbonate-like isotope signatures suggesting that these elements are derived from the carbonate solids present in the sandstone aquifer.

4.4.2. Water-rock interaction vs. mixing as Ra sources

Although the relationships between solid-phase and groundwater ²²⁶Ra levels and ²²⁸Ra/²²⁶Ra ratios suggest that the Jordan aquifer solid phase is the main source of Ra in groundwater through waterrock interaction, low, carbonate-like ²²⁸Ra/²²⁶Ra ratios have also been documented in groundwater sampling of single-aquifer wells in overlying Cambrian–Ordovician carbonate aquifers in Minnesota (Table 1). Sufficient inputs of shallow waters to the Jordan aquifer could contribute elevated Ra (primarily as ²²⁶Ra given the carbonate-dominated nature of the overlying Prairie du Chien Group) or could perhaps dilute the Ra activity of Jordan aquifer groundwater. In contrast to the upper Cambrian–Ordovician carbonate aquifers exhibiting 228 Ra/ 226 Ra ≤ 1 , groundwater in the underlying Cambrian and Proterozoic sandstone aquifers generally exhibits ²²⁸Ra/²²⁶Ra>1 (Table 1; Gilkeson et al. 1983; Lively et al. 1992). These data, compiled from sampling of single-aquifer wells, suggest that Ra sources are distinct between the upper and lower portions of the Cambrian-Ordovician groundwater system. Although the Ordovician carbonate aquifers yield carbonatelike ²²⁸Ra/²²⁶Ra ratios, exceedingly high ²²⁶Ra has not been documented which, when hypothetically diluted into the Jordan aquifer, would be sufficient to yield high Ra in Jordan aquifer groundwater. Furthermore, although the ²²⁴Ra/²²⁸Ra ratio does not directly constrain inputs of ²²⁶Ra, activities of short-lived ²²⁴Ra activity are generally close to its longer-lived great-grandparent ²²⁸Ra (Section 3.3.1), suggesting local water-rock interaction as the Ra source.

The potential role of overlying carbonate bedrock units can be evaluated by comparing Jordan aquifer waters in areas where a downward flow component is known to be significant against areas in which the only bedrock unit overlying the aquifer is another sandstone. The first case can be seen in the peripheral Shakopee and Hastings groups, where the Jordan aquifer is overlain by the subcropping Prairie du Chien Group and truncated laterally by Quaternary erosional valleys that separate it from the main body of the Jordan aquifer. Significant nitrate concentrations (Table 2) and detectable tritium (Table 3) in the wells of these two groups imply the presence of downward inputs, likely in part through overlying carbonates. Yet these groups exhibit low radium activities (Fig. 1; Table 3). The second case is addressed near the northwestern edge of the Twin Cities Group (Fig. 1) where the carbonate Prairie du Chien Group thinned out prior to deposition of the overlying St. Peter Sandstone (Olsen and Bloomgren, 1989). In this area, the Jordan aquifer is directly overlain by the St. Peter, the Prairie du Chien Group is absent, and high levels of 226 Ra (188–213 mBq L⁻¹) and 228 Ra/ 226 Ra ratios of 0.4–0.7 were measured in three Jordan aquifer wells (wells 205627, 747666, and 759809; Table 2). Therefore, high Ra or 228 Ra/ 226 Ra<1 do not require the presence of overlying carbonate units. However, the lowest radium activities in the study were observed in subcrop areas (e.g. Northeastern Group; Fig. 1; Table 3). The presence of low Ra in some subcrop wells may be consistent with shallow waters locally diluting radium in Jordan aquifer groundwater, although the tracers utilized in this study do not specifically test the possibility of dilution. Finally, it should be noted that downward flow from overlying aquifers may introduce dissolved oxygen (Ayotte et al., 2011), which would promote Ra adsorption onto redox-sensitive Mn and

Fe oxides, rather than these inputs serving as an external source of radium to the aquifer or mobilizing Ra from aquifer solids.

Overall, the geochemical and isotopic tracers in this study cannot completely rule out inter-aquifer flows as an influence on radium levels in the Jordan aquifer because waters in the carbonatecemented Jordan aquifer and the overlying carbonate units exhibit similar, carbonate-like major ion chemistry and radium isotopic signatures (Table 1). It is simpler to infer that solids in the Jordan aquifer are the primary source of *radium* to waters in the aquifer even if inputs of shallow *waters* are locally present. Indeed, the similar, carbonate-like signatures between carbonate and sandstone units (Table 1) are consistent with a regional diagenetic carbonate source that affects multiple aquifers in similar ways.

4.5. Radium removal mechanisms

In fresh, near-neutral waters, where the effects of salinity and acidity in promoting high levels of radium in groundwater are negligible, the primary mechanisms removing Ra from groundwater to balance alpha recoil inputs from the aquifer solids are adsorption and coprecipitation in barium sulfate (barite).

4.5.1. Adsorption and redox conditions

The most effective adsorption sites for radium include Mn oxides. Therefore, Mn oxide-reducing conditions could increase observed levels of radium in groundwater (Szabo and Zapecza, 1987; Vinson et al., 2009; Szabo et al., 2012). Several wells exhibit measurable dissolved oxygen, and all of these exhibit low radium. However, the large majority of wells in this study are essentially anoxic (Table 2) and encompass a large range of radium activities. Overall, the anoxic, Fe- and Mn-oxide reducing conditions in the Jordan aquifer make radium adsorption less efficient than oxic conditions. It should be emphasized that large differences in Ra activities occur among anoxic waters with high Fe and Mn concentrations. Therefore, anoxic conditions *alone* do not ensure elevated Ra in groundwater, but rather a combination of source activities and inefficient removal is responsible.

4.5.2. Coprecipitation with barite

Precipitation of barite ($BaSO_4$) in groundwater systems may be a significant radium removal mechanism (Martin and Akber, 1999; Grundl and Cape, 2006; Szabo et al., 2012) unless prevented by sulfatereducing conditions (Martin et al., 2003). Specifically, coprecipitation has been suggested as a control on radium in the Cambrian-Ordovician aguifer system in Wisconsin (Grundl and Cape, 2006) and has been directly observed subsequent to mixing of distinct waters in multi-aquifer wells in Illinois (Gilkeson et al., 1983), whereas Sturchio et al. (2001) argued that barite saturation alone was not evidence of a significant Ra removal mechanism in Midwestern carbonate aquifers. In this study, saturation index values calculated using the PHREEQC geochemical code (Parkhurst and Appelo, 1999) indicate that groundwater in the Jordan aquifer is near saturation with respect to barite (median saturation index -0.06, range -2.7 to 0.8; Fig. 8). Despite calculated saturation, barite has not been observed directly in the studied aquifer; it has also been suggested that slow barite precipitation may allow persistent calculated supersaturation (Nordstrom and Ball, 1989). Also, sulfate reduction is not widespread in the studied aquifer to inhibit barite precipitation; the high iron concentrations in many anoxic waters (Table 2) imply that sulfate reduction is ineffective due to the strong affinity of Fe²⁺ for sulfide. In addition to calculated saturation index values, correlation between Ra and Ba concentrations (Section 3.3.1) implies that they may experience similar sources or removal mechanisms, in contrast to Ra being controlled solely by radioactive decay and Ba by chemical mechanisms. As with radium, geographic variation in barium and radium concentrations occurs, but geographic patterns of radium (Fig. 1) and barium (Section 3.3.1) do not exactly coincide. Overall, given the lack of direct evidence of barite



Fig. 8. Relationship between barite saturation index and ²²⁶Ra activity in Jordan aquifer groundwater (dashed line represents saturation). At top, histogram of barium saturation index values in the Twin Cities Group, where the highest Ra activities occur.

precipitation, this is a potential but unquantified Ra removal mechanism that, as with adsorption to metal oxides, would result in lower radium in groundwater where it occurs.

4.6. Relationship to alpha recoil model of Ra isotopes in groundwater

Models of Ra mobility in groundwater depict a balance between Ra sources (Section 4.4) and removal mechanisms (Section 4.5) for individual Ra isotopes of different half-lives (e.g. Krishnaswami et al., 1982). As used to develop retardation and distribution coefficients, the alpha recoil model uses the relationship between the Ra supply rate to first-order Ra removal kinetics to depict the effects of hydrochemical conditions on Ra mobility (Krishnaswami et al., 1982; Copenhaver et al., 1993; Sturchio et al., 2001). In the low-Ra areas of the aquifer, low solid-phase 226 Ra and 228 Ra activities and 228 Ra/ 226 Ra ≈ 1 (e.g. well 161435; Table 3) are consistent with quartz sands that exhibit low U and Th concentrations and inferred 232 Th/ 238 U activity ratios ≈ 1 (Murray and Adams, 1958; Rogers and Richardson, 1964). In the high-Ra samples, lower values of 228 Ra/ 226 Ra (Fig. 5) imply that precursors of 226 Ra are related to a secondary enrichment (e.g. diagenetic carbonate) and not the quartz sandstone.

Radionuclide analyses of aquifer solids and groundwater from the same wells allow calculation of the dimensionless Ra distribution coefficient *K* for either the whole rock or the carbonate cement as the Ra source, which is an expression of the removal effectiveness of radium relative to its supply rate. Petrographic analysis of Jordan sandstone samples (Thomas, 1991) indicates that, on average, 69% of the rock is primary or secondary quartz, 21% is open porosity (φ), and 10% is occupied by carbonate cement (χ_{cement}). *K* is described (Krishnaswami et al., 1982) by the expression:

$$K = \frac{C^d}{C} \left[\frac{\rho_s(1 - \varphi)}{\varphi} \right] \tag{1}$$

in which C_d is the radionuclide activity of the solids (activity/mass), C is the radionuclide activity of groundwater (activity/volume), ρ_s is the density of the solid (2.5 g cm⁻³), and φ is porosity (0.21; Thomas, 1991). Here, C_d was obtained by averaging the ²²⁶Ra activity of available rock samples from each well. Using Eq. 1 and the data for the Jordan aquifer in the six wells where both solids and groundwater were analyzed, K exhibits a median value of 550 (range 150–920) if the whole rock is treated as the source of radioactivity (Table 4). This is consistent with some anoxic aquifers (e.g. Copenhaver et al., 1993) but lower than oxic aquifers by up to one order of magnitude (e.g. Krishnaswami et al., 1982), possibly reflecting the relative inefficiency of Ra adsorption under reducing conditions. If the carbonate cement is treated as the sole radioactivity source and the quartz sand is treated as inert (here $\varphi_{cement} = \varphi/(\varphi + \chi_{cement}) = 0.68$), and recalculating C_d based on the radionuclides being concentrated in only 10% of the rock (χ_{cement}), median K would increase to 2200 (range 1200–4300), still consistent with estimated K values for fresh, anoxic carbonate aquifers in the midwestern USA (Sturchio et al., 2001). Although this second interpretation could require potentially unrealistic carbonate-phase U and Ra activities (up to 150 Bq kg^{-1}), these calculations illustrate that the inferred location and nature of the radionuclide source within the aquifer solids may affect estimated K values by about a factor of 5; however, both models produce reasonable estimates of Ra removal behavior for an anoxic aguifer in which the primary Ra source to the groundwater is the aguifer solids, not inputs from adjacent formations.

5. Conclusions

Radium levels in Jordan aquifer groundwater reflect a balance between geographically-variable Ra source and removal mechanisms. The results of this study demonstrate that the primary depositional minerals of the quartz sandstone matrix are not necessarily the main source of Ra in groundwater. Instead, carbonate-like geochemical and isotopic signatures in water samples and aquifer solids suggest that the carbonate cement phase can be a significant source of radium precursors. Moreover, evaluation of inter-aquifer flow suggests that this mechanism is probably not a regionally significant radium source to the Jordan aquifer. Although the data do not allow external inputs of high-²²⁶Ra waters from other carbonate aquifers to be ruled out completely, the documented levels of radioactivity in Jordan aquifer solids and estimated distribution coefficients are consistent with Ra being derived from local water-rock interaction. In the anoxic conditions of the Jordan aquifer, redox-sensitive Ra adsorption may be somewhat inefficient, facilitating high levels of groundwater radium relative to comparable oxic groundwater systems. Barite precipitation is an unquantified but potentially significant influence to mitigate groundwater Ra activities where waters reach barite saturation. The similarity of ²²⁸Ra/²²⁶Ra ratios between solids and water samples, some relationship between solid-phase and groundwater ²²⁶Ra activities, and ²²⁴Ra/²²⁸Ra of water samples averaging near unity imply that the solid-phase radionuclides near each well are the source of radium. No specific depositional or diagenetic control was identified to explain the vertical or geographic variation in radionuclide levels within the study area, except that any addition of U to the aquifer solids occurred > 350,000 years ago as indicated by apparent ²³⁸U-²²⁶Ra secular equilibrium. Although Sr in aquifer solids is not directly associated with Ra and the specific solid-phase sources of both elements were not identified, the carbonate-like Sr and Ra isotope signatures imply that Sr and the precursors of Ra are retained in carbonate phase(s) that interact with groundwater. This study provides an example of how Ra and Sr isotopes can provide complementary insights on water-rock interaction and Ra sources in a sandstone aquifer influenced by carbonate dissolution and geographic variations in solid-phase radionuclide content.

Acknowledgments

Sampling and analysis were supported by Duke University, Nicholas School of the Environment and the Minnesota Department of Health. Helpful discussions on the hydrogeology of Minnesota with Robert Tipping, Anthony Runkel (Minnesota Geological Survey); Bruce Olsen, Sheila Grow, Justin Blum, Richard Soule, Tom Alvarez, Steve Robertson (Minnesota Department of Health); and E. Calvin Alexander (University of Minnesota) improved the research. Alan Knaeble of the Minnesota Geological Survey provided access to cuttings from Jordan aquifer wells. Additional analytical assistance was provided by Paul Heine, Paul Baker, Emily Klein, Anton Tonchev, Nathaniel Warner, and Hadas Raanan of Duke University; and John Diemer of the University of North Carolina-Charlotte. We also thank two anonymous reviewers for their constructive comments and Joel Blum for editorial handling.

References

- Armstrong, S.C., Sturchio, N.C., Hendry, M.J., 1998. Strontium isotopic evidence on the chemical evolution of pore waters in the Milk River Aquifer, Alberta, Canada. Applied Geochemistry 13, 463–475.
- Ayotte, J.D., Szabo, Z., Focazio, M.J., Eberts, S.M., 2011. Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water-supply wells. Applied Geochemistry 26, 747–762.
- Berg, J.A., Bradt, R., 2003. Bedrock and water-table hydrogeology [scale 1:100,000], in: Goodhue County Geologic Atlas, County Atlas Series, Minnesota Department of Natural Resources, St. Paul, MN, plate 7.
- Bishop, P.K., Smalley, P.C., Emery, D., Dickson, J.A.D., 1994. Strontium isotopes as indicators of the dissolving phase in a carbonate aquifer: implications for ¹⁴C dating of groundwater. Journal of Hydrology 154, 301–321.
- Bullen, T.D., Krabbenhoft, D.P., Kendall, C., 1996. Kinetic and mineralogic controls on the evolution of groundwater chemistry and ⁸⁷Sr/⁸⁶Sr in a sandy silicate aquifer, northern Wisconsin, USA. Geochimica et Cosmochimica Acta 60, 1807–1821.
- Campion, M., 1997. Bedrock hydrogeology [scale 1:100,000], in: Rice County Geologic Atlas, County Atlas Series, Minnesota Department of Natural Resources, St. Paul, MN, plate 8.
- Campion, M., 2002. Bedrock hydrogeology [scale 1:100,000], in: Mower County Geologic Atlas, County Atlas Series, Minnesota Department of Natural Resources, St. Paul, MN, plate 7.
- Cander, H., 1995. Interplay of water-rock interaction efficiency, unconformities, and fluid flow in a carbonate aquifer: Floridan aquifer system. In: Budd, D.A., Saller, A.H., Harris, P.M. (Eds.), Unconformities and Porosity in Carbonate Strata: American Association of Petroleum Geologists Memoir, 63, pp. 103–124.
- Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, Boca Raton, FL.
- Copenhaver, S.A., Krishnaswami, S., Turekian, K.K., Epler, N., Cochran, J.K., 1993. Retardation of ²³⁸U and ²³²Th decay chain radionuclides in Long Island and Connecticut aquifers. Geochimica et Cosmochimica Acta 57, 597–603.
- Dickson, B.L., 1990. Radium in groundwater. The Environmental Behaviour of Radium, Vol. 1, International Atomic Energy Agency: Technical Reports Series, 310, pp. 335–372.
- Dickson, B.L., Giblin, A.M., Snelling, A.A., 1987. The source of radium in anomalous accumulations near sandstone escarpments, Australia. Applied Geochemistry 2, 385–398.
- Dogramaci, S.S., Herczeg, A.L., 2002. Strontium and carbon isotope constraints on carbonate-solution interactions and inter-aquifer mixing in groundwaters of the semi-arid Murray Basin, Australia. Journal of Hydrology 262, 50–67.
- Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E., 2005. Standard Methods for the Examination of Water & Wastewater, 21st ed. American Public Health Association, Washington, DC.
- Franklyn, M.T., McNutt, R.H., Kamineni, D.C., Gascoyne, M., Frape, S.K., 1991. Groundwater ⁸⁷Sr/⁸⁶Sr values in the Eye-Dashwa Lakes pluton, Canada: evidence for plagioclase–water reaction. Chemical Geology 86, 111–122.
- Frost, C.D., Toner, R.N., 2004. Strontium isotopic identification of water-rock interaction and ground water mixing. Ground Water 42, 418–432.
- Garcia-Solsona, E., Garcia-Orellana, J., Masqué, P., Dulaiova, H., 2008. Uncertainties associated with ²²³Ra and ²²⁴Ra measurements in water via a Delayed Coincidence Counter (RaDeCC). Marine Chemistry 109, 198–219.
- Gilkeson, R.H., Cartwright, K., Cowart, J.B., Holtzman, R.B., 1983. Hydrogeologic and geochemical studies of selected natural radioisotopes and barium in groundwater in Illinois. Final Technical Completion Report to U.S. Bureau of Reclamation, Project B-108-ILL.
- Gilmore, G.R., 2008. Practical Gamma-ray Spectrometry, 2nd ed. Wiley, Chichester.
- Grundl, T., Cape, M., 2006. Geochemical factors controlling radium activity in a sandstone aquifer. Ground Water 44, 518–527.
- Harrington, G.A., Herczeg, A.L., 2003. The importance of silicate weathering of a sedimentary aquifer in and Central Australia indicated by very high Sr-87/Sr-86 ratios. Chemical Geology 199, 281–292.
- Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorous fractions induced by cultivation practices and by laboratory incubations. Soil Science Society of America Journal 46, 970–976.
- Hobbs, H.C., Goebel, J.E., 1982. Geologic map of Minnesota, Quaternary geology [scale 1:500,000]. Minnesota Geological Survey, State Map Series S-01.
- Ivanovich, M., Latham, A.G., Ku, T.-L., 1992. Uranium-series disequilibrium applications in geochronology, In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences, 2nd ed. Clarendon Press, Oxford, pp. 62–94.
- Jacobson, A.D., Wasserburg, G.J., 2005. Anhydrite and the Sr isotope evolution of groundwater in a carbonate aquifer. Chemical Geology 214, 331–350.
- Jansen, J., 1994. Geophysical well logging and pumping water column sampling for radionuclide reduction studies in municipal wells. In: Bell, R.S., Lipper, C.M. (Eds.), Proceedings of the Symposium on the Application of Geophysics to Engineering

and Environmental Problems. Environmental and Engineering Geophysical Society, 1. Englewood, CO, pp. 177–193.

- Katz, B.G., Bullen, T.D., 1996. The combined use of ⁸⁷Sr/⁸⁶Sr and carbon and water isotopes to study the hydrochemical interaction between groundwater and lakewater in mantled karst. Geochimica et Cosmochimica Acta 60, 5075–5087.
- Kim, G., Burnett, W.C., Dulaiova, H., Swarzenski, P.W., Moore, W.S., 2001. Measurement of ²²⁴Ra and ²²⁶Ra activities in natural waters using a radon-in-air monitor. Environmental Science and Technology 35, 4680–4683.
- King, P.T., Michel, J., Moore, W.S., 1982. Ground water geochemistry of ²²⁸Ra, ²²⁶Ra and ²²²Rn. Geochimica et Cosmochimica Acta 46, 1173–1182.
- Kraemer, T.F., Reid, D.F., 1984. The occurrence and behavior of radium in saline formation water of the U.S. Gulf Coast region. Isotope Geoscience 2, 153–174.
- Krishnaswami, S., Graustein, W.C., Turekian, K.K., Dowd, J.F., 1982. Radium, thorium, and radioactive lead isotopes in groundwaters: application to the in situ determination of adsorption-desorption rate constants and retardation factors. Water Resources Research 18, 1663–1675.
- Lively, R.S., Jameson, R., Alexander, E.C., Morey, G.B., 1992. Radium in the Mt. Simon-Hinckley aquifer, east-central and southeastern Minnesota. Minnesota Geological Survey, Information Circular 36.
- Martin, P., Akber, R.A., 1999. Radium isotopes as indicators of adsorption–desorption interactions and barite formation in groundwater. Journal of Environmental Radioactivity 46, 271–286.
- Martin, A.J., Crusius, J., McNee, J.J., Yanful, E.K., 2003. The mobility of radium-226 and trace metals in pre-oxidized subaqueous uranium mill tailings. Applied Geochemistry 18, 1095–1110.
- McArthur, J.M., Howarth, R.J., Bailey, T.R., 2001. Strontium isotope stratigraphy; LOWESS Version 3; best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. Journal of Geology 109, 155–170.
- McIntosh, J.C., Walter, L.M., 2006. Paleowaters in Silurian–Devonian carbonate aquifers; geochemical evolution of ground water in the Great Lakes region since the late Pleistocene. Geochimica et Cosmochimica Acta 70, 2454–2479.
- Moise, T., Starinsky, A., Katz, A., Kolodny, Y., 2000. Ra isotopes and Rn in brines and ground waters of the Jordan-Dead Sea Rift Valley: enrichment, retardation, and mixing. Geochimica et Cosmochimica Acta 64, 2371–2388.
 Moore, W.S., Arnold, R., 1996. Measurement of ²²³Ra and ²²⁴Ra in coastal waters using
- Moore, W.S., Arnold, R., 1996. Measurement of ²²³Ra and ²²⁴Ra in coastal waters using a delayed coincidence counter. Journal of Geophysical Research 101, 1321–1329.
- Morey, G.B., Meints, J., 2000. Geologic map of Minnesota, bedrock geology [1:1,000,000]. Minnesota Geological Survey, St. Paul, MN
- Mossler, J.H., 1990. Bedrock geology [scale 1:100,000], in: Dakota County Geologic Atlas. County Geologic Atlas, Minnesota Geological Survey, St. Paul, MN, plate 2. Mossler, J.H., 2001. Bedrock geology [scale 1:100,000], in: Wabasha County Geologic
- Atlas. County Atlas Series, Minnesota Geological Survey, St. Paul, MN, plate 2.
- Mossler, J.H., Bloomgren, B.A., 1990. Bedrock geology [scale 1:100,000], in: Washington County Geologic Atlas. County Atlas Series, Minnesota Geological Survey, St. Paul, MN, plate 2.
- Mossler, J.H., Book, P.R., 1984. Bedrock geology [scale 1:100,000], in: Winona County Geologic Atlas. County Atlas Series, Minnesota Geological Survey, St. Paul, MN, plate 2.
- Mossler, J.H., Tipping, R.G., 2000. Bedrock geology and structure of the seven-county Twin Cities metropolitan area, Minnesota [scale 1:125,000]. Minnesota Geological Survey, Miscellaneous Map M-104.
- Murray, E.G., Adams, J.A.S., 1958. Thorium, uranium and potassium in some sandstones. Geochimica et Cosmochimica Acta 13, 260–269.
- Musgrove, M., Banner, J.L., 2004. Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards aquifer, central Texas. Geochimica et Cosmochimica Acta 68, 1007–1020.
- Nordstrom, D.K., Ball, J.W., 1989. Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytic errors. Sciences Geologiques - Bulletin 42, 269–280.
- Odom, I.E., 1975. Feldspar-grain size relations in Cambrian arenites, upper Mississippi Valley. Journal of Sedimentary Petrology 45, 636–650.
- Olsen, B.M., Bloomgren, B.A., 1989. Bedrock geology [scale 1:100,000], in: Hennepin County Geologic Atlas. County Atlas Series, Minnesota Geological Survey, St. Paul, MN, plate 2.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2) a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Water-Resources Investigations Report 99–4259.
- Roden, E.E., Edmonds, J.W., 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction versus iron-sulfide formation. Archiv für Hydrobiologie 139, 347–378.
- Rogers, J.J.W., Richardson, K.A., 1964. Thorium and uranium contents of some sandstones. Geochimica et Cosmochimica Acta 28, 2005–2011.
- Runkel, A.C., 1994. Deposition of the uppermost Cambrian (Croixan) Jordan Sandstone, and the nature of the Cambrian–Ordovician boundary in the Upper Mississippi Valley. Geological Society of America Bulletin 106, 492–506.

- Runkel, A.C., 1998. Bedrock geology [scale 1:100,000], in: Goodhue County Geologic Atlas. County Atlas Series, Minnesota Geological Survey, St. Paul, MN, plate 2.
- Runkel, A.C., Alexander, E.C., Mossler, J.H., Tipping, R.G., Green, J.A., Alexander, S.C., 2003. Hydrogeology of the Paleozoic bedrock in southeastern Minnesota. Minnesota Geological Survey, Report of Investigations 61.
- Runkel, A.C., Tipping, R.G., Alexander, E.C., Alexander, S.C., 2006. Hydrostratigraphic characterization of intergranular and secondary porosity in part of the Cambrian sandstone aquifer system of the cratonic interior of North America: Improving predictability of hydrogeologic properties. Sedimentary Geology 184, 281–304.
- Shang, C., Zelazny, L.W., 2008. Selective dissolution techniques for mineral analysis of soils and sediments. (Madison, WI) Methods of Soil Analysis, Part 5, Mineralogical Methods: Soil Science Society of America, pp. 33–80.
- Stewart, M.A., Klein, E.M., Karson, J.A., 2002. Geochemistry of dikes and lavas from the north wall of the Hess Deep Rift: insights into the four-dimensional character of crustal construction at fast spreading mid-ocean ridges. Journal of Geophysical Research 107 (article 2238).
- Stueber, A.M., Walter, L.M., 1994. Glacial recharge and paleohydrologic flow systems in the Illinois Basin; evidence from chemistry of Ordovician carbonate (Galena) formation waters. Geological Society of America Bulletin 106, 1430–1439.
- Sturchio, N.C., Banner, J.L., Binz, C.M., Heraty, L.B., Musgrove, M., 2001. Radium geochemistry of ground waters in Paleozoic carbonate aquifers, midcontinent, USA. Applied Geochemistry 16, 109–122.
- Szabo, Z., Zapecza, O.S., 1987. Relation between natural radionuclide activities and chemical constituents in ground water in the Newark Basin, New Jersey. In: Graves, B. (Ed.), Radon, Radium, and Other Radioactivity in Ground Water. Lewis Publishers, Chelsea, MI, pp. 283–308.
- Szabo, Z., Rice, D.E., MacLeod, C.L., Barringer, T.H., 1997. Relation of distribution of radium, nitrate, and pesticides to agricultural land use and depth, Kirkwood-Cohansey Aquifer System, New Jersey Coastal Plain, 1990–1991. US Geological Survey Water-Resources Investigations Report 96–4165.
- Szabo, Z., dePaul, V.T., Kraemer, T.F., Parsa, B., 2005. Occurrence of radium-224, radium-226, and radium-228 in water of the unconfined Kirkwood-Cohansey aquifer system, southern New Jersey. US Geological Survey Scientific Investigations Report 2004–5224.
- Szabo, Z., dePaul, V.T., Fischer, J.M., Kraemer, T.F., Jacobsen, E., 2012. Occurrence and geochemistry of radium in water from principal drinking-water aquifer systems of the United States. Applied Geochemistry 27, 729–752.
- Thomas, D.A., 1991. Lithostratigraphy, Petrology, Diagenesis, and Environments of Deposition of the Upper Cambrian Jordan Sandstone, Southeastern Minnesota. MS thesis, University of Minnesota.
- Tomita, J., Satake, H., Fukuyama, T., Sasaki, K., Sakaguchi, A., Yamamoto, M., 2010. Radium geochemistry in Na–Cl type groundwater in Niigata Prefecture. Japan. Journal of Environmental Radioactivity 101, 201–210.
- Vengosh, A., Spivack, A.J., Artzi, Y., Ayalon, A., 1999. Geochemical and boron, strontium, and oxygen isotopic constraints on the origin of the salinity in groundwater from the Mediterranean coast of Israel. Water Resources Research 35, 1877–1894.
- Vengosh, A., Gill, J., Davisson, M.L., Hudson, G.B., 2002. A multi-isotope (B, Sr, O, H, and C) and age dating (³H-³He and ¹⁴C) study of groundwater from Salinas Valley, California: hydrochemistry, dynamics, and contamination processes. Water Resources Research 38. http://dx.doi.org/10.1029/2001WR000517.
- Vengosh, A., Hirschfeld, D., Vinson, D., Dwyer, G., Raanan, H., Rimawi, O., Al-Zoubi, A., Akkawi, E., Marie, A., Haquin, G., Zaarur, S., Ganor, J., 2009. High naturally occurring radioactivity in fossil groundwater from the Middle East. Environmental Science and Technology 43, 1769–1775.
- Vinson, D.S., Vengosh, A., Hirschfeld, D., Dwyer, G.S., 2009. Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina (USA). Chemical Geology 260, 159–171.
- Vinson, D.S., Lundy, J.R., Dwyer, G.S., Vengosh, A., 2010. Sr isotopes, hydrogeologic setting, and water-rock interaction in the Mt. Simon sandstone (Minnesota, USA). In: Birkle, P., Torres-Alvarado, I.S. (Eds.), Water Rock Interaction: Proceedings of the 13th International Conference on Water-Rock Interaction WRI-13, Guanajuato, Mexico, 16–20 August 2010. CRC Press, Boca Raton, FL, pp. 111–114.
- Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., Vengosh, A., 2012. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. Proceedings of the National Academy of Sciences 109, 11961–11966.
- Weaver, T.R., Bahr, J.M., 1991. Geochemical evolution in the Cambrian–Ordovician sandstone aquifer, eastern Wisconsin: 1. Major ion and radionuclide distribution. Ground Water 29, 350–356.
- Winter, B.L., Johnson, C.M., Simo, J.A., 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 65, 306–320.
- Zhu, C., 2004. Coprecipitation in the barite isostructural family: 1. Binary mixing properties. Geochimica et Cosmochimica Acta 68, 3327–3337.