



Radium mobility and the age of groundwater in public-drinking-water supplies from the Cambrian-Ordovician aquifer system, north-central USA

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ABSTRACT

High radium (Ra) concentrations in potable portions of the Cambrian-Ordovician (C-O) aquifer system were investigated using water-quality data and environmental tracers (³H, ³He_{trit}, SF₆, ¹⁴C and ⁴He_{rad}) of groundwater age from 80 public-supply wells (PSWs). Groundwater ages were estimated by calibration of tracers to lumped parameter models and ranged from modern (< 50 yr) in upgradient, regionally unconfined areas to ancient (> 1 Myr) in the most downgradient, confined portions of the potable system. More than 80 and 40 percent of mean groundwater ages were older than 1000 and 50,000 yr, respectively. Anoxic, Fe-reducing conditions and increased mineralization develop with time in the aquifer system and mobilize Ra into solution resulting in the frequent occurrence of combined Ra (Ra_c = ²²⁶Ra + ²²⁸Ra) at concentrations exceeding the USEPA MCL of 185 mBq/L (5 pCi/L). The distribution of the three Ra isotopes comprising total Ra (Ra_t = ²²⁴Ra + ²²⁶Ra + ²²⁸Ra) differed across the aquifer system. The concentrations of ²²⁴Ra and ²²⁸Ra were strongly correlated and comprised a larger proportion of the Ra_t concentration in samples from the regionally unconfined area, where arkosic sandstones provide an enhanced source for progeny from the ²³²Th decay series. ²²⁶Ra comprised a larger proportion of the Ra_t concentration in samples from downgradient confined regions. Concentrations of Ra_t were significantly greater in samples from the regionally confined area of the aquifer system because of the increase in ²²⁶Ra concentrations there as compared to the regionally unconfined area. ²²⁶Ra distribution coefficients decreased substantially with anoxic conditions and increasing ionic strength of groundwater (mineralization), indicating that Ra is mobilized to solution from solid phases of the aquifer as adsorption capacity is diminished. The amount of ²²⁶Ra released from solid phases by alpha-recoil mechanisms and retained in solution increases relative to the amount of Ra sequestered by adsorption processes or co-precipitation with barite as adsorption capacity and the concentration of Ba decreases. Although ²²⁶Ra occurred at concentrations greater than ²²⁴Ra or ²²⁸Ra, the ingestion exposure risk was greater for ²²⁸Ra owing to its greater toxicity. In addition, ²²⁴Ra added substantial alpha-particle radioactivity to potable samples from the C-O aquifer system. Thus, monitoring for Ra isotopes and gross-alpha-activity (GAA) is important in upgradient, regionally unconfined areas as downgradient, and GAA measurements made within 72 h of sample collection would best capture alpha-particle radiation from the short-lived ²²⁴Ra.

1. Introduction

The local occurrence of ²²⁶Ra and ²²⁸Ra in water from the Cambrian-Ordovician (C-O) aquifer system at concentrations that frequently exceed the US Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for combined Ra (Ra_c = ²²⁶Ra + ²²⁸Ra) (185 mBq/L; 5 pCi/L) has been known for decades (Brown and Morris, 1959; Hess et al., 1985; Lucas and Ilcewicz, 1958; Lucas and Krause, 1960; Siegel, 1989; Stehney, 1955). More recent studies by Szabo et al. (2012) and Wilson (2012) expanded on the occurrence and

distribution of elevated Ra_c concentrations across the C-O aquifer system providing broad geochemical characterizations and estimates of groundwater age. These aquifer-wide investigations, however, did not include ²²⁴Ra and other radionuclides (isotopes that decay and release radiation and which are referred to as isotopes herein), such as ²¹⁰Po and ²¹⁰Pb, which have been shown to occur at concentrations of potential human-health concern in other aquifers (Rubaru et al., 2007; Seiler, 2011; Szabo et al., 2005). They also did not provide estimates of groundwater ages other than those that can be determined with ³H, which provides a relative measure of groundwater age. Other more

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localized studies, such as Grundl et al. (2013); Klump et al. (2008); Siegel (1989, 1991), have presented groundwater ages determined with ^{14}C , which are limited to about 25 kyr in the C-O aquifer system. In 2014, the U.S. Geological Survey's (USGS) National Water Quality Assessment (NAWQA) project measured radioactive isotopes and a wide variety of other constituents in samples of water collected from 80 public-supply wells (PSWs) across potable portions of the C-O aquifer system (Arnold et al., 2017; Burow and Belitz, 2014). This study provides the first aquifer-wide, systematic assessment of ^{224}Ra , ^{226}Ra and ^{228}Ra occurrence in potable portions of the C-O aquifer system and includes more comprehensive estimates of groundwater age.

Ra is an alkaline-earth cation with chemical properties similar to Ca, Sr and Ba which occurs as one of four isotopes (^{223}Ra , ^{224}Ra , ^{226}Ra and ^{228}Ra) (Langmuir and Riese, 1985). Although isotopes of Ra are chemically similar, their concentrations in groundwater differ because of differences in chemical properties of the parent isotopes at the head of the decay series, either ^{235}U , ^{238}U or ^{232}Th , and the $\frac{1}{2}$ -life of each isotope, which vary considerably. ^{226}Ra is the 5th decay product in the ^{238}U decay series (online Supplemental Figs. SI-1), has a $\frac{1}{2}$ -life of 1600 yr (IAEA, 2014) and decays by alpha-particle emission. ^{228}Ra and ^{224}Ra are the 1st and 4th decay products in the ^{232}Th decay series, respectively (online Supplemental Figs. SI-1). ^{228}Ra has a $\frac{1}{2}$ -life of 5.75 yr and decays by beta-particle emission whereas ^{224}Ra has a $\frac{1}{2}$ -life of 3.6 days (d) and decays by alpha-particle emission. The amount of alpha-particle radiation in a sample that is derived from the short-lived ^{224}Ra declines rapidly after about one half-life (Parsa, 1998). The Th isotopes ^{230}Th , ^{232}Th , and ^{228}Th – which are virtually insoluble in groundwater – are the immediate radioactive sources for ^{226}Ra , ^{228}Ra , and ^{224}Ra , respectively. The individual Th nuclides remain adsorbed or deposited on the solid mineral-grain matrix surfaces because they have distribution coefficients (K_d) orders of magnitudes greater than those for the Ra isotopes. The radioactive decay of these alpha-emitting Th isotopes originates the recoil-based emission of Ra isotopes to solution (Davidson and Dickson, 1986; Reynolds et al., 2003). The moderately soluble radioactive noble gas ^{222}Rn is the 6th decay product in the ^{238}U decay series (online Supplemental Figs. SI-1), has a $\frac{1}{2}$ -life of 3.8 d and also decays by alpha-particle emission. Because of its relatively high solubility, ^{222}Rn in solution can provide a proportional, quantitative estimate of the amount of ^{226}Ra in the solid matrix adsorbed or deposited on the surfaces producing the ^{222}Rn (Wanty et al., 1992; Weaver and Bahr, 1991). ^{223}Ra is a product of the ^{235}U decay series. ^{235}U comprises < 1% of natural U and, thus, ^{223}Ra occurs infrequently in the environment at high concentrations (Davidson and Dickson, 1986; Gilkeson et al., 1983). As a result, ^{223}Ra is not discussed further in this report.

U is more soluble than Th under typical groundwater conditions (Langmuir, 1978) and, therefore, ^{238}U and its decay products are generally more abundant in groundwater as compared to ^{232}Th and its decay products (Langmuir and Herman, 1980). U and its decay products are also, therefore, more abundant in pore-filling and grain-coating secondary minerals in aquifer solids. Under reducing conditions, U species precipitate from groundwater and can become enriched in solid material – especially in sandstone and carbonate rocks that have sharp redox gradients (Gilkeson et al., 1983; Langmuir, 1978) – providing a potential enhanced source of ^{226}Ra and other decay products in the ^{238}U decay series. Marine carbonates generally have primary depositional U:Th ratio values greater than unity because carbonate rocks precipitate from shallow oxic seawater that contains U in solution which can readily be incorporated in carbonate minerals (Banner et al., 1990; Kelly, 2003; Michel and Cothorn, 1986; Robinson et al., 2004; Sturchio et al., 2001). Conversely, Th is practically insoluble in water and is not readily incorporated in carbonate minerals. Th is associated with feldspars and accessory minerals that occur in granites (Langmuir and Herman, 1980). The physical accumulation of these minerals in arkosic sandstones provides a potential enhanced source of ^{224}Ra , ^{228}Ra and other decay products in the ^{232}Th decay

series (Gilkeson et al., 1983; Hess et al., 1985; Michel and Cothorn, 1986; Wilson, 2012). The aqueous phase concentrations of ^{224}Ra and ^{228}Ra may also be elevated in quartzose sandstones with high total dissolved solids (TDS) due to competition for limited adsorption sites on the aquifer solids (Michel and Cothorn, 1986).

The occurrence of Ra and other radioactive isotopes in drinking-water supplies is a human-health concern because they are a source of ionizing radiation and are known human carcinogens (ATSDR, 1999; Weinhold, 2012). When ingested, Ra deposits primarily in bone (Finkelstein and Kreiger, 1996; Wrenn et al., 1985) where it can substitute for Ca. The occurrence of ^{226}Ra in drinking-water supplies has been associated with increased risk for bone cancers (Finkelstein, 1994; Finkelstein and Kreiger, 1996; Petersen et al., 1966) and has been linked with bladder, breast and lung cancer, leukemia and other adverse health effects (Bean et al., 1982; Canu et al., 2011; Fuortes et al., 1990; Lyman et al., 1985; Petersen et al., 1966; Weinhold, 2012).

This paper builds on previous research that described radioactive isotope occurrence and mobility in highly mineralized groundwater by using estimates of mean groundwater ages, ranging from modern to over 1 Myr, to describe the sequence of geochemical processes that mobilize high concentrations of Ra in potable parts of the C-O aquifer system. A general increase in net aqueous ^{226}Ra accumulation in the C-O aquifer system is illustrated by relating estimates of ^{226}Ra K_d to groundwater properties. The relative radiation dose provided by each Ra isotope was also estimated to provide a human-health context for each. Finally, we provide the first description of the occurrence and distribution of other radioactive isotopes not previously sampled for in the C-O aquifer system in a systematic manner, with concentrations of ^{224}Ra reported herein, and those for ^{222}Rn , ^{210}Pb and ^{210}Po and also gross measures of alpha- and beta-activities in the online supplemental materials.

1.1. Description of study area

The C-O aquifer system underlies an area of about 476,560 km² extending across parts of 7 midwestern States (Fig. 1) and is an important source for both domestic (187,299 m³/d) and public (2,682,193 m³/d) water supplies – except in Indiana, central Illinois (IL), northern Missouri (MO) and western Iowa (IA) where the aquifer system contains saline water (Maupin and Arnold, 2010; Maupin and Barber, 2005). Detailed descriptions of the hydrogeology and regional flow patterns in the C-O aquifer system are available in Feinstein et al. (2004); Mandel and Kontis (1992); Olcott (1992); Wilson (2012); and Young (1992a) and are briefly summarized here. The aquifer system consists mainly of sandstone and carbonate aquifers of marine origin that are separated by leaky confining units of shale and dolomite. The aquifer system outcrops or subcrops beneath glacial drift in southeastern Minnesota (MN), northeastern IA, southern Wisconsin (WI) and northern IL – an area referred to herein as being regionally unconfined (Fig. 1). In the remainder of IA and IL, eastern WI, and most of northern MO, the aquifer system is confined by the Ordovician Maquoketa Shale and rocks of progressively younger age – an area referred to herein as being regionally confined (Fig. 1). Rocks of the aquifer system dip and thicken away from structural highs in the underlying Precambrian bedrock surface in the regionally unconfined area towards structural lows in southwestern IA, central IL and the Michigan (MI) basin. Aquifers of Cambrian age are dominated by sandstones some of which transition to carbonates towards the south and east in MO and IL (Wilson, 2012; Young, 1992a). Aquifers of Ordovician age are dominated by carbonates with the notable exception of the St. Peter sandstone; however, upper Ordovician strata have been eroded away in portions of the regionally unconfined area (Wilson, 2012; Young, 1992a).

Much of the recharge in the regionally unconfined area discharges to streams through local flow systems that are no more than a few kilometers in length. The remaining recharge moves downward to

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