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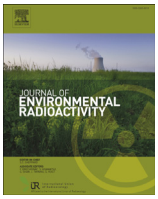

The dissolved uranium concentration and $^{234}U/^{238}U$ activity ratio in groundwaters from spas of southeastern Brazil

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ABSTRACT

This paper describes the natural radioactivity due to ^{238}U and ^{234}U in 75 water sources from spas located in 14 municipalities in São Paulo and Minas Gerais states, Brazil. These waters are extensively utilized for drinking in public places, bottling and bathing purposes, among other uses. The water samples were taken from springs and pumped tubular wells drilled into different aquifer systems in the Paraná and Southeastern Shield hydrogeological provinces. The measurements of alpha-emitting radionuclides were also accompanied by the monitoring of temperature, pH, Eh, electrical conductivity, dissolved gases (O_2, CO_2, H_2S, radon, thoron) and major constituents. The dissolved U concentration data were lognormally distributed. The median and mean values corresponded to 0.02 and 0.09 μg/L, respectively. Significant relationships were found among the $^{234}U/^{238}U$ activity ratio (AR) of dissolved uranium, the total dissolved solids (TDS) and dissolved bicarbonate contents, and also between the AR and dissolution rate in the monitored sites. The logU *versus* AR diagram used for the hydrogeochemical prospecting of concealed U deposits indicated that the water sources were mainly from reduced environments. The possibility of using the reciprocal of the dissolved U concentration and AR data to determine mixing volumes of different groundwater masses was demonstrated. The highest dissolved U concentration (4.82 μg/L) was well below the maximum allowed by WHO.

1. Introduction

Uranium (U) is widely distributed in crustal rocks, and under conditions present at the earth's surface, it tends to be a mobile element. In the hydrologic environment is of special interest because of its economic importance and the chemical and radiotoxicity of U and some of its progeny nuclides. Worldwide soluble U concentrations generally range from 0.1 to 10 μgL^{-1} in rivers, lakes and groundwaters (Fritz and Fontes, 1980; Ivanovich and Harmon, 1992), but values up to 16 μgL^{-1} were obtained in the U survey of bottled (908 samples) and tap (164 samples) water in Germany (Birke et al., 2010).

^{238}U is the principal isotope of natural U (99.72% abundance) and progenitor of the $(4n + 2)$ series of radioelements (^{238}U decay chain), in which ^{234}U is radiogenic. ^{238}U and ^{234}U reach secular equilibrium circa 1 Ma in all minerals and rocks remaining closed systems for U. The $^{234}U/^{238}U$ activity ratio (AR) is therefore one in the bulk of such systems, however, rock-water interaction frequently results in AR values greater than unity for dissolved U (Osmond and Cowart, 1976; Ivanovich and Harmon, 1992; Baskaran, 2011).

Various mechanisms have been suggested to interpret the generation of the elevated AR's in solution. For instance, Rosholt et al. (1963) proposed the occurrence of enhanced chemical solution of ^{234}U due to radiation damage to crystal lattices or to autoxidation from U^{4+} to U^{6+} resulting from the decay of the parent ^{238}U. Kigoshi (1971) showed that alpha-particle recoil ejection of the ^{234}U precursor (^{234}Th) into solution may also generate elevated AR's in the liquid phase. According to Kigoshi (1971), if the interstices of a rock or assemblage of mineral grains are filled with water, the water will act to bring to rest the recoiling ^{234}Th nucleus from ^{238}U decay, thereby enriching the solution and depleting the solid in ^{234}U.

Uranium AR in solution may be depleted or enriched, depending on oxidation-reduction conditions (Osmond and Cowart, 1976; Krauskopf and Bird, 1995). If oxidizing conditions prevail (positive Eh values), then U tends to remain in solution, migrating over long distances. If reducing conditions are dominant (negative Eh values), then U precipitation tends to occur, decreasing its concentration in

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the liquid phase. Enhanced AR's for dissolved U at more reducing conditions are favored due to ^{234}U dissolution caused by the ^{234}Th recoil process, and, therefore, lower U concentrations and higher AR's in the liquid phase are generally expected under such conditions (Osmond and Cowart, 1976). Based on the isotope dilution analysis, AR and U concentration data have been utilized to deduce the proportions of groundwater masses in a mixture (Osmond et al., 1968, 1974; Osmond and Cowart, 1976, 2000; Elliot et al., 2014).

In the last years, in-situ methods for measuring/monitoring radioactivity and radioactive gases radon (^{222}Rn) and thoron (^{220}Rn) in waters have been developed (Povinec et al., 2006; Tsabaris et al., 2012; etc.). The consumption of natural drinking water, either spring or mineral water (bottled or not), has also increased in several countries. Despite that potable tap water is accessible in households, many people believe that the naturally occurring waters are healthy and/or can be utilized for health cures, thus exhibiting better quality than the tap water. The commercialization of mineral waters has widely increased, including in Brazil where about 20 million consumers are involved (SEBRAE, 2012).

The thermal and mineral waters use in Brazil is not only recent, where the construction of thermal spas for therapeutic and leisure purposes reached a maximum number in the 1930s and 1950s (Mourão, 1992). The Brazilian Code of Mineral Waters (BCMW) classifies the mineral waters for spas and bottling uses, as well the potable waters for bottling (DFPM, 1966; Serra, 2009). It includes several parameters, among them the radioactivity due to dissolved ^{222}Rn and ^{220}Rn (Bonotto, 2014).

Potential health hazards from natural radionuclides in drinking water have been considered worldwide, with many countries adopting the provisional guideline concentrations of 30 μg U/L from WHO (2011). In general, the recommendations apply to routine operational conditions of water-supply systems, however, special attention must be also given to frequently ingested mineral waters.

In view of the actual increased use of groundwaters from spas in Brazil, mainly in São Paulo (SP) and Minas Gerais (MG) states, and due to the lack of a comprehensive U-isotopes database like that given by Birke et al. (2010), this paper reports the dissolved U concentration and AR data in them for evaluating a) the uranium mobility to the liquid phase, b) its applicability for prospecting concealed U-deposits, c) the proportions of mixing volumes of different groundwater masses and d) the radiological quality of the waters.

2. Sampling

The groundwater samples (75) were collected in 14 cities located at SP and MG states in Brazil as reported by Bonotto (2014, 2015a, 2015b). They corresponded to the same springs and pumped tubular wells analyzed in terms of physico–chemical parameters, major constituents, radium isotopes (^{226}Ra and ^{228}Ra) and dissolved gases (^{222}Rn, ^{220}Rn, O_2, CO_2, S^{2-}). The codes adopted by Bonotto (2014) for their identification will be also used in this paper.

The water sources were from different geological contexts and aquifer systems of the Paraná and Southeastern Shield hydrogeological provinces (Mente, 2008) as described by Bonotto (2014) from the reports of Ebert (1955), IPT (1981), Szikszay (1981), Almeida and Hasui (1984), Kimmelmann et al. (1987), del Rey (1989), Cruz and Peixoto (1989), Schorscher and Shea (1992), Renne et al. (1992), Turner et al. (1994), CPRM (1999), Beato et al. (2000) and Traversa et al. (2001), among others.

3. Methods

The rocks weatherability in the different geological domains has been estimated from the equation $W = D \times TDS$ where W [MT^{-1}] is the dissolution rate, D [L^{3}T^{-1}] is the water source discharge and TDS [ML^{-3}] is its total dissolved solids concentration. The discharge values adopted in the calculation provided from Hurter et al. (1983), del Rey (1989), Borges (2006) and Lazzerini (2013).

The aliquots (20–25 L) for U analysis were acidified to pH less than 2 using HCl, and about 500 mg of $FeCl_3$ plus 56.5 mBq (or 73.3 mBq) of ^{232}U spike were added. U was co-precipitated on $Fe(OH)_3$ by increasing the pH to 7–8 through addition of concentrated NH_4OH solution; the precipitated was recovered, dissolved in 8 M HCl and Fe^{3+} was extracted into an equal volume of isopropyl ether. The acid U-bearing solution was purified by a strong chloride anion exchanger, first on a Cl^- and then on a NO_3^- column of 100–200 mesh Dowex 1-X8 resin. Uranium as finally eluted from the NO_3^- column with 0.1 M HCl and after evaporation to dryness was dissolved in 10 mL of 2 M $(NH_4)_2SO_4$ electrolyte and transferred to an electrodeposition cell. The pH was adjusted to 2.4 and electrodeposition of U on a stainless steel planchet was complete after 3 h at a current density of 1 Acm^{-2} (Kameli, 1980).

The ^{238}U and ^{234}U activity concentrations were measured by alpha spectrometry. The α-activities were determined with four EG&G ORTEC Model BU-020-450-AS ULTRA-AS Ion-Implanted Detectors with B-Mount that have the following characteristics: 0.1 mm depletion depth, 450 mm^2 active area, and alpha resolution of 20 keV FWHM at 5.486 MeV. The spectra for natural U and ^{232}U tracer extracted were recorded on an EG&G ORTEC 919 Spectrum Master Multichannel Buffer. The dissolved U concentration was calculated by isotope dilution from the counting rates of ^{238}U and ^{232}U peaks, whereas the AR data were computed from the counting rates of ^{238}U and ^{234}U peaks. The Decision Level (L_c) as proposed by Currie (1968) was adopted for accepting a positive measurement in the ^{238}U and ^{232}U energy regions. More analytical details for these readings have been reported elsewhere (Osmond and Cowart, 1976; Ivanovich and Harmon, 1992).

4. Results and discussion

4.1. Major hydrochemical trends

Table 1 summarizes the hydrochemical data reported by Bonotto (2015b) for the water sources analyzed in this paper. A detailed discussion of them is beyond the scope of this paper, thus, only some general aspects will be highlighted. The redox conditions indicate that the sample coded BMU (Bonotto, 2014) exhibited transitional character, whereas all other waters analyzed were reducing as indicated by the Eh-pH diagram (Krauskopf and Bird, 1995). The total dissolved solids (TDS) was directly related to the electrical conductivity (EC) of the waters. The ionic strength (IS) evaluated by the Aquachem 4.0 software (Waterloo Hydrogeologic, 2003) correlated positively with TDS in the waters. The TDS-EC relationship implied on a direct correlation between the IS and EC in the water sources, despite the non-existence of a theoretical relationship between these parameters. The major ions justifying such trends were sodium, (bi)carbonate, chloride, sulfate and phosphate that also correlated positively with IS due to the mathematical relations among the variables, thus, reinforcing the reliability of the database and respective IS calculations. Additionally, the significant Pearson correlation coefficient found between pH and ions like sodium and sulfate justified the direct relationship between pH and IS (Bonotto, 2015b).

4.2. U-isotopes dissolution

The dissolved U concentration and AR values are shown in Table 2. The U concentration in the waters samples analyzed ranged 0.001–4.82 μgL^{-1}, not exceeding the typical maximum worldwide

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