



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



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## ABSTRACT

This paper describes the natural radioactivity due to  $^{238}\text{U}$  and  $^{234}\text{U}$  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 ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , 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  $\mu\text{g/L}$ , respectively. Significant relationships were found among the  $^{234}\text{U}/^{238}\text{U}$  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  $\mu\text{g/L}$ ) was well below the maximum allowed by WHO.

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## 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 radio-toxicity of U and some of its progeny nuclides. Worldwide soluble U concentrations generally range from 0.1 to 10  $\mu\text{g/L}^{-1}$  in rivers, lakes and groundwaters (Fritz and Fontes, 1980; Ivanovich and Harmon, 1992), but values up to 16  $\mu\text{g/L}^{-1}$  were obtained in the U survey of bottled (908 samples) and tap (164 samples) water in Germany (Birke et al., 2010).

$^{238}\text{U}$  is the principal isotope of natural U (99.72% abundance) and progenitor of the (4n + 2) series of radioelements ( $^{238}\text{U}$  decay chain), in which  $^{234}\text{U}$  is radiogenic.  $^{238}\text{U}$  and  $^{234}\text{U}$  reach secular equilibrium circa 1 Ma in all minerals and rocks remaining closed systems for U. The  $^{234}\text{U}/^{238}\text{U}$  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  $^{234}\text{U}$  due to radiation damage to crystal lattices or to autoxidation from  $\text{U}^{4+}$  to  $\text{U}^{6+}$  resulting from the decay of the parent  $^{238}\text{U}$ . Kigoshi (1971) showed that alpha-particle recoil ejection of the  $^{234}\text{U}$  precursor ( $^{234}\text{Th}$ ) 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  $^{234}\text{Th}$  nucleus from  $^{238}\text{U}$  decay, thereby enriching the solution and depleting the solid in  $^{234}\text{U}$ .

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  $^{234}\text{U}$  dissolution caused by the  $^{234}\text{Th}$  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 ( $^{222}\text{Rn}$ ) and thoron ( $^{220}\text{Rn}$ ) 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  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  (Bonotto, 2014).

Potential health hazards from natural radionuclides in drinking water have been considered worldwide, with many countries adopting the provisional guideline concentrations of  $30\text{ }\mu\text{g U/L}$  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 ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) and dissolved gases ( $^{222}\text{Rn}$ ,  $^{220}\text{Rn}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{S}^{2-}$ ). 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), Kimmelman 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  $W = D \times \text{TDS}$  where  $W$  [ $\text{MT}^{-1}$ ] is

the dissolution rate,  $D$  [ $\text{L}^3\text{T}^{-1}$ ] is the water source discharge and TDS [ $\text{ML}^{-3}$ ] 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  $\text{FeCl}_3$  plus 56.5 mBq (or 73.3 mBq) of  $^{232}\text{U}$  spike were added. U was co-precipitated on  $\text{Fe}(\text{OH})_3$  by increasing the pH to 7–8 through addition of concentrated  $\text{NH}_4\text{OH}$  solution; the precipitated was recovered, dissolved in 8 M HCl and  $\text{Fe}^{3+}$  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  $\text{Cl}^-$  and then on a  $\text{NO}_3^-$  column of 100–200 mesh Dowex 1-X8 resin. Uranium as finally eluted from the  $\text{NO}_3^-$  column with 0.1 M HCl and after evaporation to dryness was dissolved in 10 mL of 2 M  $(\text{NH}_4)_2\text{SO}_4$  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  $1\text{ Acm}^{-2}$  (Kameli, 1980).

The  $^{238}\text{U}$  and  $^{234}\text{U}$  activity concentrations were measured by alpha spectrometry. The  $\alpha$ -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,  $450\text{ mm}^2$  active area, and alpha resolution of 20 keV FWHM at 5.486 MeV. The spectra for natural U and  $^{232}\text{U}$  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  $^{238}\text{U}$  and  $^{232}\text{U}$  peaks, whereas the AR data were computed from the counting rates of  $^{238}\text{U}$  and  $^{234}\text{U}$  peaks. The Decision Level ( $L_c$ ) as proposed by Currie (1968) was adopted for accepting a positive measurement in the  $^{238}\text{U}$  and  $^{232}\text{U}$  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  $0.001\text{--}4.82\text{ }\mu\text{g L}^{-1}$ , not exceeding the typical maximum worldwide

**Table 1**

Parameters of the groundwaters analyzed in this study as reported by Bonotto (2015b).

Parameter	Unit	Minimum	Lower quartile	Median	Upper quartile	Maximum
Temp.	°C	20.4	23.4	24.6	25.8	35.7
pH	—	4.16	5.86	6.41	7.94	9.60
Eh	mV	−159	−72	−52	−28	112
EC	μS/cm	20	170	360	1235	6390
DO	mg/L	0.78	1.78	3.13	4.77	9.05
CO <sub>2</sub>	mg/L	0	110	236	1056	1840
H <sub>2</sub> S	μg/L	<1	2	4	13	3064
ALK	mg/L	1	32	93	261	2212
TDS	mg/L	11	135	229	459	2898
IS	×10 <sup>−4</sup>	3.1	8.5	19.9	67.5	793.6
SiO <sub>2</sub>	mg/L	6.7	17.8	28.3	34.5	63.5
Fe <sub>tot</sub>	mg/L	<0.006	0.01	0.04	0.14	5.18
Na <sup>+</sup>	mg/L	0.4	4.4	12.8	86.8	1510.0
K <sup>+</sup>	mg/L	0.29	2.08	4.95	11.78	25.25
Ca <sup>2+</sup>	mg/L	0.02	0.76	3.18	3.42	25.50
Mg <sup>2+</sup>	mg/L	<0.006	1.00	0.12	0.45	0.64
Cl <sup>−</sup>	mg/L	<0.3	48.0	3.1	5.6	7.8
F <sup>−</sup>	mg/L	0.02	0.10	0.40	1.73	32.27
NO <sub>3</sub> <sup>−</sup>	mg/L	<0.8	1.3	1.9	3.6	18.1
SO <sub>4</sub> <sup>2−</sup>	mg/L	<0.5	1	1	24	225
PO <sub>4</sub> <sup>3−</sup>	mg/L	<0.02	0.07	0.12	0.18	1.36

EC = electrical conductivity; DO = dissolved oxygen; TDS = total dissolved solids; ALK = total alkalinity; IS = ionic strength.

value of 10 μg/L<sup>−1</sup> in rivers, lakes and groundwaters (Osmond and Cowart, 1976; Fritz and Fontes, 1980; Ivanovich and Harmon, 1992). The AR's values found in the water sources are between 1

and 11.7 (Table 2), corresponding to the range of 1–12 reported by Ivanovich et al. (1991) in groundwater samples from the Milk River aquifer. Such ratios greater than unity in the liquid phase are typical

**Table 2**The dissolved uranium concentrations, <sup>234</sup>U/<sup>238</sup>U activity ratios (AR), and total committed effective doses (CED) from <sup>238</sup>U and <sup>234</sup>U of the waters analyzed in this study.

Sample code <sup>a</sup>	U (μg/L) <sup>b</sup>	AR <sup>b</sup>	CED <sup>b</sup> (μSv/yr)	Sample code <sup>a</sup>	U (μg/L) <sup>b</sup>	AR <sup>b</sup>	CED <sup>b</sup> (μSv/yr)
ALS	0.02 ± 0.003	3.58 ± 0.64	0.04 ± 0.008	LA6	0.14 ± 0.02	1.13 ± 0.16	0.13 ± 0.02
GIO	0.34 ± 0.05	4.80 ± 0.85	0.86 ± 0.17	SL7	0.06 ± 0.006	2.96 ± 0.30	0.10 ± 0.01
JUV	0.14 ± 0.02	2.37 ± 0.42	0.20 ± 0.04	SL5	0.04 ± 0.004	1.35 ± 0.17	0.04 ± 0.004
PLA	0.24 ± 0.04	8.28 ± 1.47	0.98 ± 0.21	SL6	0.11 ± 0.01	1.55 ± 0.16	0.12 ± 0.01
POL	0.60 ± 0.09	11.68 ± 2.08	3.35 ± 0.74	SL3	0.08 ± 0.01	1.31 ± 0.18	0.08 ± 0.009
VIT	1.04 ± 0.16	4.04 ± 0.72	2.29 ± 0.44	SL4	0.04 ± 0.006	2.79 ± 0.42	0.06 ± 0.01
BOI	0.08 ± 0.01	4.04 ± 0.72	0.18 ± 0.03	SL1	0.03 ± 0.006	1.90 ± 0.43	0.04 ± 0.008
PTA	0.03 ± 0.005	6.05 ± 1.08	0.09 ± 0.02	SL10	0.02 ± 0.003	2.05 ± 0.31	0.03 ± 0.004
VIL	0.53 ± 0.08	3.66 ± 0.65	1.08 ± 0.21	SL9	0.15 ± 0.03	0.98 ± 0.20	0.13 ± 0.02
PDE	0.01 ± 0.002	1.81 ± 0.48	0.01 ± 0.003	ROR	0.02 ± 0.002	1.50 ± 0.22	0.02 ± 0.003
SIL	0.07 ± 0.01	2.12 ± 0.38	0.09 ± 0.02	REW	0.008 ± 0.002	1.58 ± 0.49	0.009 ± 0.002
FIL	0.13 ± 0.02	2.08 ± 0.37	0.17 ± 0.03	CAF	0.004 ± 0.0003	1.30 ± 0.13	0.004 ± 0.0003
BEL	0.21 ± 0.03	1.62 ± 0.29	0.24 ± 0.04	FEP	0.01 ± 0.001	3.07 ± 0.34	0.02 ± 0.002
SRE	0.13 ± 0.02	3.04 ± 0.54	0.23 ± 0.04	MAR	0.008 ± 0.0008	1.69 ± 0.21	0.009 ± 0.001
COM	0.16 ± 0.02	2.28 ± 0.40	0.23 ± 0.04	SLI	0.01 ± 0.0007	1.02 ± 0.10	0.008 ± 0.0006
LIN	0.06 ± 0.009	3.76 ± 0.67	0.12 ± 0.02	GFL	0.05 ± 0.01	1.85 ± 0.55	0.06 ± 0.02
CUR	0.02 ± 0.003	1.50 ± 0.24	0.02 ± 0.003	VEN	0.004 ± 0.0009	6.27 ± 1.47	0.01 ± 0.004
SJO	0.004 ± 0.0007	1.58 ± 0.35	0.004 ± 0.0008	MAY	0.007 ± 0.001	4.68 ± 1.07	0.02 ± 0.004
SCA	0.01 ± 0.002	1.95 ± 0.36	0.01 ± 0.002	EGU	0.06 ± 0.004	1.92 ± 0.12	0.08 ± 0.004
ITA	0.02 ± 0.002	2.22 ± 0.30	0.03 ± 0.004	VIO	0.02 ± 0.005	1.06 ± 0.36	0.02 ± 0.005
SLU	0.004 ± 0.0009	2.49 ± 0.63	0.006 ± 0.002	DPE	0.04 ± 0.004	1.97 ± 0.22	0.05 ± 0.005
SAT	0.006 ± 0.002	1.01 ± 0.41	0.005 ± 0.002	BZA	0.06 ± 0.008	4.46 ± 0.59	0.14 ± 0.02
BRU	0.01 ± 0.003	3.54 ± 1.32	0.02 ± 0.008	DXE	0.05 ± 0.02	1.36 ± 0.49	0.05 ± 0.02
LAN	0.002 ± 0.0004	2.00 ± 0.44	0.002 ± 0.0006	LEO	0.59 ± 0.03	1.34 ± 0.05	0.59 ± 0.03
SAA	0.01 ± 0.002	2.58 ± 0.51	0.02 ± 0.003	ISA	0.02 ± 0.004	6.14 ± 1.44	0.06 ± 0.02
SBE	0.09 ± 0.007	1.27 ± 0.11	0.09 ± 0.006	QUI	0.18 ± 0.03	1.26 ± 0.22	0.17 ± 0.03
BIO	0.006 ± 0.0005	1.90 ± 0.20	0.007 ± 0.0007	NOV	0.03 ± 0.005	3.52 ± 0.62	0.06 ± 0.01
JOR	0.02 ± 0.001	1.58 ± 0.10	0.02 ± 0.001	MAC	0.02 ± 0.003	2.83 ± 0.50	0.03 ± 0.006
ADB	0.34 ± 0.06	1.42 ± 0.21	0.35 ± 0.05	SIN	0.06 ± 0.009	1.77 ± 0.31	0.07 ± 0.01
CGO	0.94 ± 0.13	1.01 ± 0.10	0.80 ± 0.09	FRA	0.20 ± 0.03	1.57 ± 0.28	0.22 ± 0.04
SRC	0.12 ± 0.02	1.05 ± 0.17	0.10 ± 0.01	PEB	0.02 ± 0.003	2.26 ± 0.40	0.03 ± 0.005
SEI	0.02 ± 0.001	1.48 ± 0.11	0.02 ± 0.001	RIV	0.01 ± 0.001	1.85 ± 0.29	0.01 ± 0.002
BMU	4.82 ± 0.75	2.19 ± 0.39	6.64 ± 1.15	SMA	0.004 ± 0.0009	4.30 ± 1.11	0.009 ± 0.018
LA1	0.02 ± 0.004	3.47 ± 0.88	0.04 ± 0.01	SAJ	0.06 ± 0.01	1.82 ± 0.33	0.07 ± 0.01
LA2	0.10 ± 0.009	1.15 ± 0.12	0.09 ± 0.008	AMO	0.001 ± 0.0002	1.32 ± 0.35	0.001 ± 0.0002
LA3	0.02 ± 0.002	1.67 ± 0.23	0.02 ± 0.003	DBJ	0.16 ± 0.02	1.72 ± 0.23	0.19 ± 0.02
LA4	0.008 ± 0.002	2.64 ± 0.59	0.01 ± 0.003	AJU	0.06 ± 0.007	2.98 ± 0.38	0.10 ± 0.01
LA5	0.02 ± 0.003	3.10 ± 0.47	0.04 ± 0.006				

<sup>a</sup> The sample code is the same as adopted by Bonotto (2014).<sup>b</sup> Uncertainty calculated considering the Poisson counting statistics at 1σ standard deviation and the errors propagation theory (Young, 1962).

after water-soil/rock interactions as a consequence of the preferential chemical dissolution of  $^{234}\text{U}$  (Rosholt et al., 1963) and alpha-recoil release of  $^{234}\text{Th}$  at the rock-water interface (Kigoshi, 1971). The climate, lithology, stratigraphy, hydrogeology, geochemical conditions (Bonotto, 2014), and extent of water-soil/rock interactions are among the factors responsible by the distinct dissolved U concentration and AR values in the area studied.

Different rock types exhibit variable U concentrations due to their mineral constituents, and this is certainly the case for the investigated sources where there is leaching of sandstones, siltstones, limestones, basalts, diabbases, migmatites, milonites, quartzites, phonolites, nepheline syenites, volcanic tuffs, gneisses, granites, schists and carbonatites, among other rock types. The mean U concentration values in rocks for the five major geological domains studied here are: Paraná basin (SP) (Kimmelmann et al., 1995) = 0.8  $\mu\text{g/g}$ ; Poços de Caldas intrusive complex (SP/MG) (Schorscher and Shea, 1992) = 1.2  $\mu\text{g/g}$ ; crystalline basement (SP) (Pascholati, 1990; Tassinari and Barretto, 1993) = 13.8  $\mu\text{g/g}$ ; southeastern shield (MG) (Fernandes, 1982) = 1.5  $\mu\text{g/g}$ ; Alto Paranaíba igneous Province (MG) (Traversa et al., 2001) = 12.9  $\mu\text{g/g}$ .

The ratio between the concentration of a minor element in the crystal of a mineral and the concentration of that element in the fluid from which the crystal formed has been named as distribution coefficient (Richardson and McSweeney, 1989; Krauskopf and Bird,

1995; Faure, 1998), or an enrichment factor (Szalay, 1964; Langmuir, 1978), expressed in  $\text{m}^3\text{kg}^{-1}$ . A reciprocal ratio named “mobility coefficient” and represented by  $m_{238}$  (for  $^{238}\text{U}$ ) allowed Bonotto (1998) to calculate  $4.8 \times 10^{-3} \text{ kgm}^{-3}$  at Morro do Ferro area, Poços de Caldas alkaline massif, Brazil. Such value is within the range of  $0.1 \times 10^{-3} \text{ kgm}^{-3}$  to  $5670 \times 10^{-3} \text{ kgm}^{-3}$  measured in this paper (Table 3).

The  $m_{238}$  values are highly variable (Table 3), reflecting the preferential solubility of  $^{238}\text{U}$  according to the different rock types. For instance,  $m_{238}$  is very low in the geological domain associated to the crystalline basement (Precambrian) at eastern of SP State (cities of Águas de Lindóia, Serra Negra and Lindóia), indicating that U is not easily leached from the U-host minerals occurring in the rock matrices (granites, gneisses, migmatites, schists, quartzites). An opposite situation was found in the geological domains comprising the Paraná sedimentary basin and Poços de Caldas alkaline massif as the non-silicified sandstones, nepheline syenites, phonolites, among other rock types, have demonstrated favorable conditions to weather, transferring more U to the liquid phase and implying higher  $m_{238}$  values. The highest W values were 145–217 ton/yr (Table 3) in the Paraná basin (samples coded GIO and JUV) and Poços de Caldas alkaline massif (sample coded POL).

The dissolved U concentration data were lognormally distributed, as illustrated in Fig. 1. The median and mean values were 0.02

**Table 3**  
 $^{238}\text{U}$  “mobility coefficient” ( $m_{238}$ ) and dissolution rate (W) in the water sources investigated in this paper.

Sample code <sup>a</sup>	$m_{238}^b$ ( $\times 10^{-3} \text{ kg/m}^3$ )	$D^c$ ( $\times 10^{-6} \text{ m}^2/\text{s}$ )	TDS <sup>d</sup> (mg/L)	W <sup>e</sup> (ton/yr)	Sample code <sup>a</sup>	$m_{238}^b$ ( $\times 10^{-3} \text{ kg/m}^3$ )	$D^c$ ( $\times 10^{-6} \text{ m}^2/\text{s}$ )	TDS <sup>d</sup> (mg/L)	W <sup>e</sup> (ton/yr)
ALS	24	694	1880	41.1	LA6	93	n.a.	139	n.c.
GIO	400	4051	1700	217.2	SL7	40	n.a.	198	n.c.
JUV	165	3472	1960	214.6	SL5	27	55	185	0.3
PLA	200	236	936	7.0	SL6	73	192	323	2.0
POL	500	1756	2625	145.4	SL3	53	39	214	0.3
VIT	867	22	1042	0.7	SL4	27	117	305	1.1
BOI	67	33	54	0.06	SL1	20	2778	296	25.9
PTA	25	42	2215	2.9	SL10	13	5	176	0.03
VIL	442	250	43	0.4	SL9	100	419	295	3.9
PDE	8	n.a.	240	n.c.	ROR	13	358	126	1.4
SIL	5	1889	59	3.5	REW	5	67	73	0.2
FIL	9	2056	38	2.5	CAF	3	69	40	0.09
BEL	15	500	89	1.4	FEP	7	200	257	1.6
SRE	9	7778	74	18.2	MAR	5	102	249	0.8
COM	12	1111	11	0.4	SLI	7	36	82	0.09
LIN	4	3889	86	10.6	GFL	33	n.a.	1241	n.c.
CUR	1	3611	154	17.5	VEN	3	532	757	12.7
SJO	0.3	n.a.	172	n.c.	MAY	5	n.a.	221	n.c.
SCA	0.7	142	233	1.0	EGU	40	n.a.	516	n.c.
ITA	1	n.a.	193	n.c.	VIO	13	276	179	1.6
SLU	0.3	211	225	1.5	DPE	27	220	170	1.2
SAT	0.4	278	167	1.5	BZA	40	21	757	0.5
BRU	0.7	n.a.	144	n.c.	DXE	33	28	820	0.7
LAN	0.1	n.a.	106	n.c.	LEO	393	88	315	0.9
SAA	0.7	n.a.	185	n.c.	ISA	13	14	700	0.3
SBE	6	369	286	3.3	QUI	150	n.a.	38	n.c.
BIO	0.4	n.a.	134	n.c.	NOV	25	118	398	1.5
JOR	24	n.a.	410	n.c.	MAC	17	n.a.	579	n.c.
ADB	400	n.a.	420	n.c.	SIN	50	6	574	0.1
CGO	1106	1389	380	16.6	FRA	167	83	70	0.2
SRC	141	n.a.	460	n.c.	PEB	17	694	600	13.1
SEI	24	n.a.	455	n.c.	RIV	8	67	567	1.2
BMU	5670	6522	200	41.1	SMA	3	67	773	1.6
LA1	13	1069	121	4.1	SAJ	50	75	424	1.0
LA2	67	126	212	0.8	AMO	0.8	n.a.	48	n.c.
LA3	13	81	198	0.5	DBJ	12	12537	70	27.7
LA4	5	43	256	0.3	AJU	5	1111	2898	101.5
LA5	13	n.a.	446	n.c.					

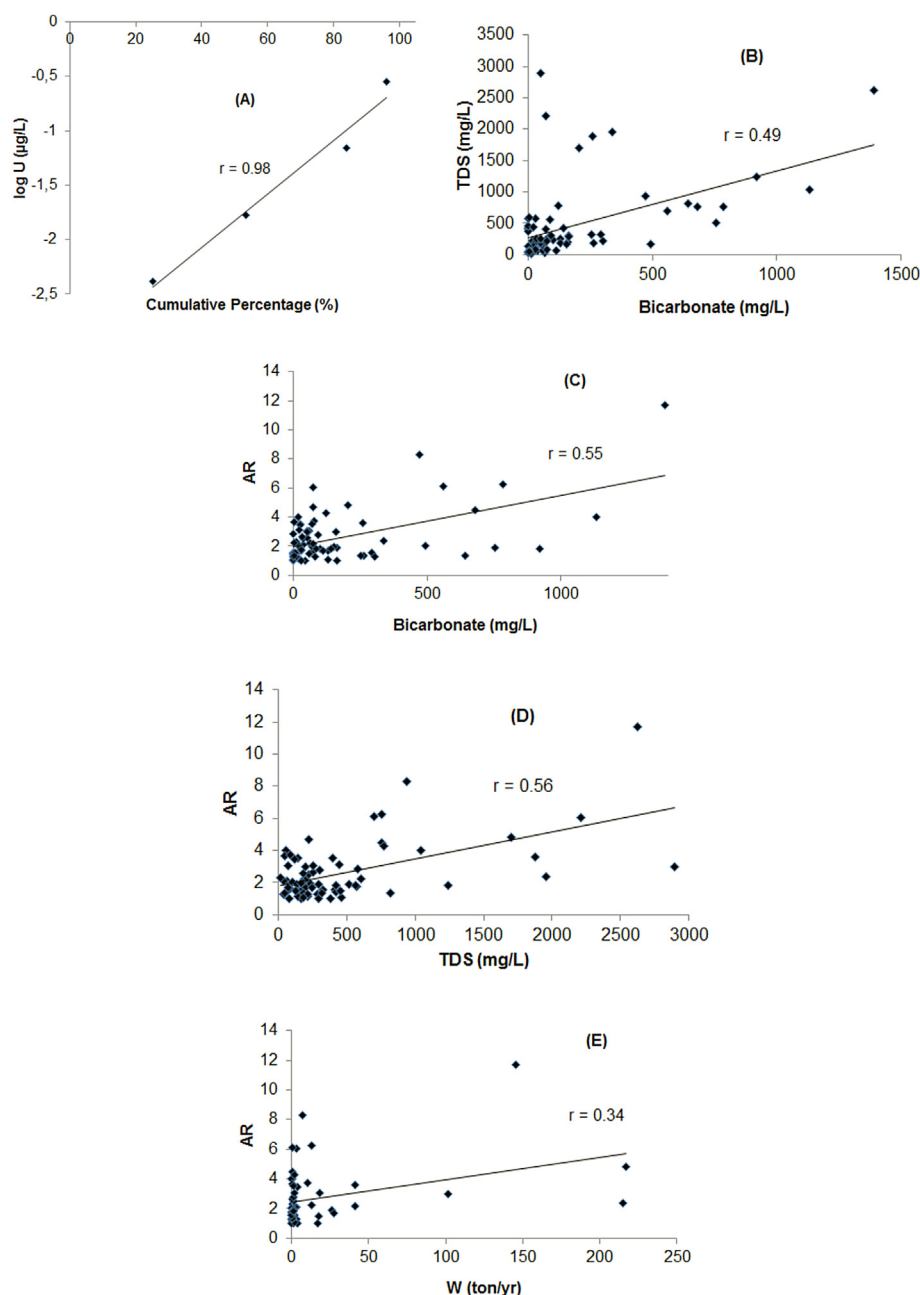
<sup>a</sup> The sample code is the same as adopted by Bonotto (2014).

<sup>b</sup>  $m_{238} = (^{238}\text{U})_{\text{water}} / (^{238}\text{U})_{\text{rock}}$ .

<sup>c</sup> D = discharge.

<sup>d</sup> TDS = total dissolved solids.

<sup>e</sup> W = dissolution rate; n.a. = not available; n.c. = not calculated.



**Fig. 1.** Diagrams showing (A) the logarithm distribution of the dissolved U concentrations and the relationships in the groundwaters between the (B) TDS and dissolved bicarbonate, (C) AR and dissolved bicarbonate, (D) AR and TDS, and (E) AR and W. AR =  $^{234}\text{U}/^{238}\text{U}$  activity ratio; TDS = total dissolved solids; W = dissolution rate.

and 0.09 µg/L, respectively. The two-tailed P value estimated by GraphPad software from the Pearson correlation coefficient between TDS and  $\text{HCO}_3^-$  ( $r = 0.49$ ,  $n = 75$ ), AR and  $\text{HCO}_3^-$  ( $r = 0.55$ ,  $n = 75$ ), and AR and TDS ( $r = 0.56$ ,  $n = 75$ ) equals 0.0001 by conventional criteria, suggesting this difference is extremely statistically significant among these parameters (Fig. 1). The same statistical test yielded a value of 0.0111 between AR and W ( $r = 0.34$ ,  $n = 55$ ; Fig. 1), indicating this difference is statistically significant.

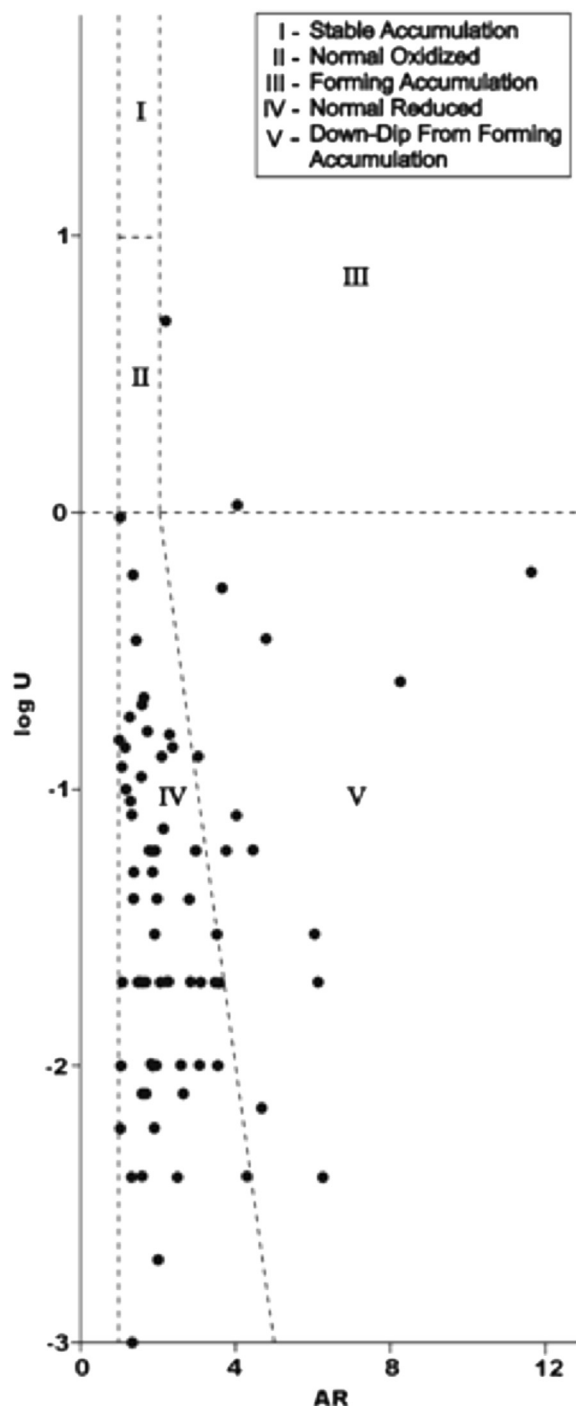
Bonotto and Andrews (1993, 2000) reported experimental data obtained in the laboratory with limestone and dolomite samples etched/leached by nitrogen-saturated water, air-saturated water, and  $\text{CO}_2$ -saturated water, within a time-scale of up to 190 days. The AR of dissolved U in leach/etch solutions generally increased as leach/etch proceeded. For each leachant/etchant, the results of the

successive leach/etch reactions with the same rock sample were plotted together with the calculated values for the cumulative amount of  $\text{Ca}^{2+}$  dissolved (depth of etch/leach). In general, for the sequential leach/etch solutions, the AR increased with each successive leach/etch. Such findings were compatible with the AR trends shown in Fig. 1.

#### 4.3. Uranium isotopes as prospecting tool

$^{238}\text{U}$  and  $^{234}\text{U}$  have been considered useful isotopes for hydro-geochemical prospecting of concealed U deposits, where dissolved U concentration and AR in groundwaters are plotted on a two-dimensional diagram containing several areas of associative significance (Coward and Osmond, 1980; Osmond and Cowart, 1981).





**Fig. 2.** Groundwaters log dissolved U concentrations versus the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) as utilized by Cowart and Osmond (1980).

In terms of dissolved U concentrations, the main categories defined are: oxidized aquifer containing “normal” U concentration (values of  $1\text{--}10\ \mu\text{g/L}$ ); oxidized aquifer containing “enhanced” U concentration (values higher than  $10\ \mu\text{g/L}$ ); and reduced aquifer or strata with low U concentration (values lower than  $1\ \mu\text{g/L}$ ). In terms of AR data, values between 1 and 2 define a “normal” worldwide situation, values higher than 2 suggest the formation of a U-accumulation, and values lower than 1 indicate the remobilization of a U-accumulation.

The U concentration and AR values measured in the water

sources were variable, as shown in the fence diagram plotted in Fig. 2. Their comparison with most of the data reported by Osmond and Cowart (1976) does not indicate a good agreement of the AR values as they exceeded in many cases the range of 1–2. Additionally, the dissolved U concentration was frequently lower than the range  $0.4\text{--}2.0\ \mu\text{g/L}$  as reported by Osmond and Cowart (1976). The water sources analyzed were mainly in fields IV and V, characterizing reduced environments. This classification is supported by the pH and Eh data of these waters (Table 1) (Bonotto, 2015b). The sample coded BMU was an exception to this pattern as it tended to fit the oxidized field (Fig. 2) that is more favorable for the U leaching from the rock matrices. Despite the Eh-pH diagram does not clearly indicate such trend in this case, it points out transitional redox conditions rather than the dominant reducing character.

#### 4.4. U-isotopes and mixing evaluation

The possibility of using the reciprocal of the dissolved U concentration ( $S = U^{-1}$ , in  $\text{L}/\mu\text{g}$ ) and the AR of dissolved U data to determine mixing volumes (V) of different groundwater masses has been demonstrated by Osmond et al. (1974). For two water sources, the resulting mixture (T) will have S and AR values falling on a straight line joining the corresponding plots of the two components, whose proportions can be calculated. For three source waters, characterized by their different S and AR, the resulting mixture produces water that plots within a triangle formed by the three components. For more than three sources, the resulting mixtures plot within polygons formed by the sources, but the mixing proportions are indeterminate without additional assumptions (Osmond et al., 1974).

The AR and reciprocal of the dissolved U concentrations reported in Table 2 allow the recognition of such systems for most of the geological contexts investigated (Table 4 and Fig. 3). The results are compatible with the field evidences in each area. For instance, Bonotto (2005) recognized that the ternary plot in Fig. 3 at the city of Poços de Caldas (MG) comprised the following components: mean of the colder waters (coded FRA and QUI), mean of the hotter waters (coded PEB and MAC), and water exhibiting intermediate temperature value (coded NOV). In the modeling, the groundwater coded SIN resulted from the admixture of three source waters possessing different temperature, AR and S values. The unique solution to their relative volumes in the mixture indicated that the hottest waters were the dominant phase (68%).

The largest number of possible scenarios of mixing processes was at the city of Águas de Lindóia (SP) (Fig. 3). The Monte Sião fault is an important structural element to understand the geological evolution of this site (del Rey, 1989). It begins at the north border of Morungaba granitic massif, has N10–20E direction, and involves a group of well deformed rocks, the majority represented by specimens enriched in quartz. The lineaments of the faults are disposed in the directions of the Monte Sião fault and control the drainage system southeastwards and northwestwards. Aerial photos in this zone have also shown many groups of small faults northwestwards whose genesis is linked to strains causing them that exhibit an original shear character (del Rey, 1989). The geologic-structural map of Águas de Lindóia area indicates that the springs are aligned to Monte Sião fault, where fractures and cracks are responsible for the water circulation and the flow occurs from the high to low topographic levels (del Rey, 1989). Such extremely fractured system favors the occurrence of many mixing processes affecting the different water sources and some of them have been identified by the natural U-isotopes modeling as reported in Table 4 and Fig. 3.

**Table 4**

Estimation of the relative volumes of the mixing source waters studied in the admixture, based on the natural U-isotopes modeling.

City (State)	No.	Sample code <sup>a</sup>	Scenario 1	Scenario 2	Scenario 3
Termas de Ibirá (SP)	1	SEI			
	2	JOR			
	1 and 2 (Mean)		88%	89%	
	3	CGO	10%	11%	
	4	ADB	2%	0%	
Serra Negra (SP)	5 (Mixed)	SRC	100%	100%	
	1	SAT	36.9%		
	2	LAN	36.9%		
	3	SLU	26.2%		
	4 (Mixed)	SJO	100%		
	1	SAT	37.3%	61.8%	
	5	BRU	47.8%	13.5%	
	6	ITA	14.9%	24.7%	
Águas de Lindóia (SP)	7 (Mixed)	SAA	100%		
	8 (Mixed)	SCA		100%	
	2	BEL	37.4%		
	4	SRE	62.6%		
	7 (Mixed)	COM	100%		
	2	BEL	46.7%		
	3	LIN	53.3%		
	6 (Mixed)	FIL	100%		
	1	CUR	51.4%		
	2	BEL	20.4%		
	3	LIN	28.2%		
	5 (Mixed)	SIL	100%		
	2	BEL	32.5%		
	4	SRE	24.2%		
	5	SIL	43.3%		
	6 (Mixed)	FIL	100%		
	2	BEL	15.4%		
	7	COM	42.8%		
	5	SIL	41.8%		
	6 (Mixed)	FIL	100%		
	1	CUR	65.3%	28.2%	
	2	BEL	14.8%	38.9%	
	4	SRE	19.8%	32.8%	
	5 (Mixed)	SIL	100%		
	6 (Mixed)	FIL		100%	
Águas da Prata (SP)	3	VIL			
	4	VIT			
	3 and 4 (Mean)		9.5%	1.4%	13.7%
	1	PDE	89.8%	96.7%	63.4%
	2	POL	0.7%	1.9%	22.9%
	5 (Mixed)	BOI	100%		
	6 (Mixed)	PTA		100%	
	7 (Mixed)	PLA			100%
Poços de Caldas (MG)	1	PEB and MAC (mean)	68%		
	2	FRA and QUI (mean)	23%		
	3	NOV	9%		
	4 (Mixed)	SIN	100%		
Pocinhos do Rio Verde (MG)	1	AMO	78%		
	2	SMA	1%		
	3	SAJ	21%		
	4 (Mixed)	RIV	100%		
São Lourenço (MG)	9	SL9	15.4%		
	10	SL10	84.6%		
	5 (Mixed)	SL5	100%		
	9	SL9	55.6%		
	7	SL7	44.4%		
	6 (Mixed)	SL6	100%		
	7	SL7	50%		
	10	SL10	50%		
	4 (Mixed)	SL4	100%		
	10	SL10	87%	43.9%	
	9	SL9	5.4%	41.8%	
	7	SL7	7.6%	14.3%	
	1 (Mixed)	SL1	100%		
	3 (Mixed)	SL3		100%	
Caxambu (MG)	1	VIO	94.8%		
	6	LEO	5.2%		
	8 (Mixed)	DXE	100%		
	1	VIO	10.5%		
	2	ISA	8.3%		
	3	VEN	81.4%		

Table 4 (continued)

City (State)	No.	Sample code <sup>a</sup>	Scenario 1	Scenario 2	Scenario 3
Lambari (MG)	4 (Mixed)	MAY	100%		
	1	VIO	79%		
	5	BZA	17.2%		
	6	LEO	3.8%		
	7, 9, 10 (Mean) – Mixed	EGU, GFL, DPE	100%		
	2	LA2			
	6	LA6			
	2 and 6 (Mean)		11.7%		
	4	LA4	88.3%		
	3 (Mixed)	LA3	100%		
Cambuquira (MG)	2 and 6 (Mean)		2.3%		
	1	LA1	79.4%		
	4	LA4	18.3%		
	5 (Mixed)	LA5	100%		
	1	ROR	21%		
	3	FEP	10.6%		
	4	CAF	68.4%		
	5 and 6 (Mean) – Mixed	REW, MAR	100%		
	2	SLI	44.3%		
	3	FEP	22.4%		
	4	CAF	33.7%		
	5 and 6 (Mean) – Mixed	REW, MAR	100%		

<sup>a</sup> The sample code is the same as adopted by Bonotto (2014); the resulting mixture from two, three or more than three components has been estimated according to the equations described by Osmond et al. (1974) which were applied to the data set plotted in Fig. 3.

#### 4.5. Implications on water quality

With exception of geyser “Floriano de Lemos” (code GFL), all waters analyzed in this research have been used for drinking purposes in thermal and non-thermal spas, whilst some are commercialized by private companies. The highest dissolved U

concentration was  $4.82 \mu\text{g L}^{-1}$  in sample coded BMU (Table 2) that also exhibited the highest dissolved  $\text{Ca}^{2+}$  concentration ( $25.5 \text{ mg L}^{-1}$ , Table 1). The temperature ( $24.6^\circ\text{C}$ ), pH (7.6) and Eh (+112 mV) of this water source favor the U and Ca release from its reservoir containing sandstones and carbonate cement in them. The highest values found for both U and Ca may be explained by the

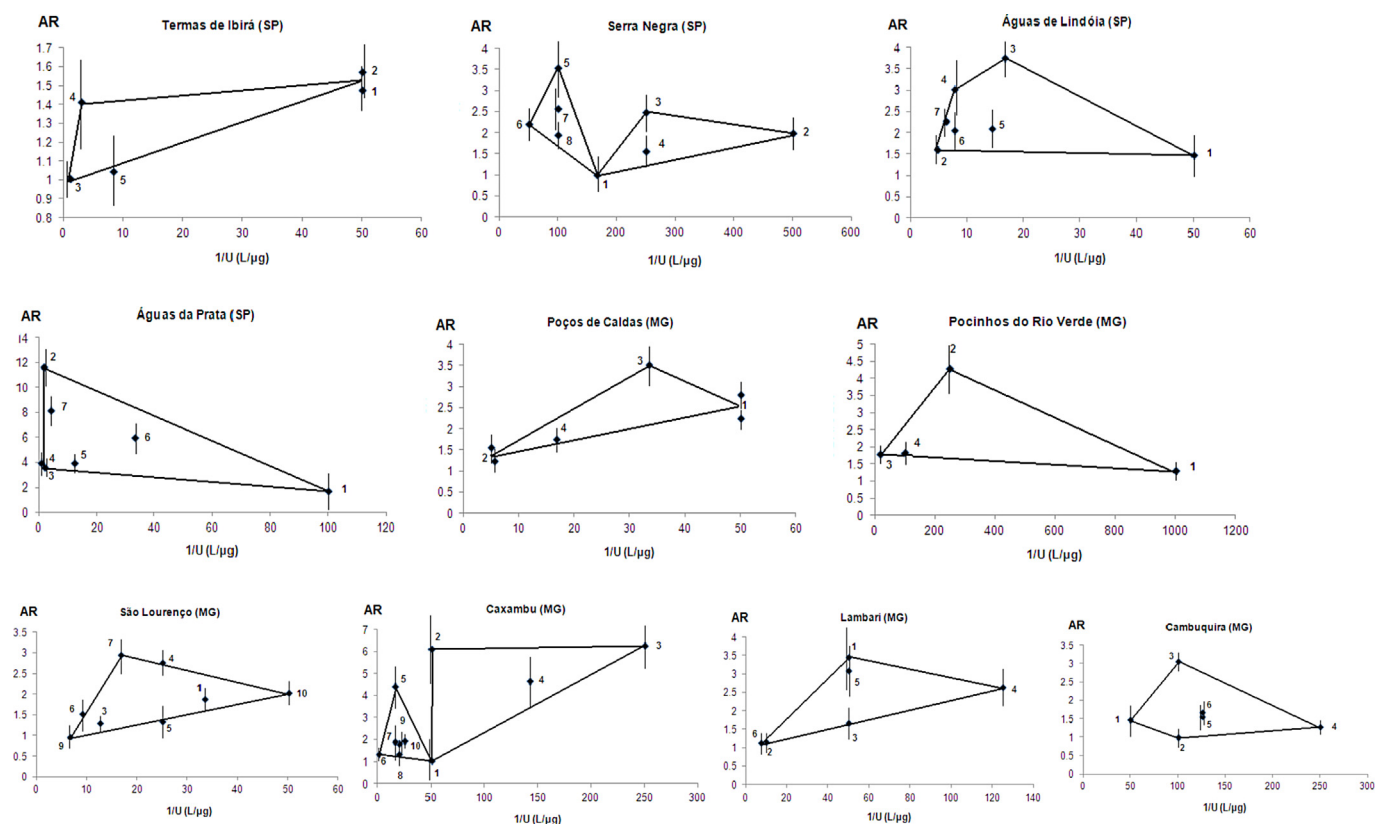


Fig. 3. The  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) and the reciprocal of the U concentrations (in  $\text{L}/\mu\text{g}$ ) in the groundwaters (numbers corresponding to the sample identification – Table 4).



findings of Bonotto and Andrews (1993, 2000) in their controlled laboratory experiments held with limestone and dolomite samples. They have indicated that the amount of dissolved U was strongly correlated with both Ca and Mg dissolution, where the uranyl ion ( $\text{UO}_2^{2+}$ ) was complexed in solution by bicarbonate and carbonate ions.

The highest U concentration value ( $4.82 \mu\text{g L}^{-1}$ ) is well below the maximum of  $30 \mu\text{g L}^{-1}$  allowed by WHO (2011). The corresponding activity concentrations of  $^{238}\text{U}$  and  $^{234}\text{U}$  were, respectively, 60 and  $131 \text{ mBq L}^{-1}$ . These are also much lower than the guidance levels for  $^{238}\text{U}$  and  $^{234}\text{U}$  proposed by WHO (2011) of  $10 \text{ Bq L}^{-1}$  and  $1 \text{ Bq L}^{-1}$ , respectively.

Radiation dose calculations also confirm this scenario. WHO (2011) reported the following dose coefficient values:  $4.5 \times 10^{-8} \text{ Sv/Bq}$  and  $4.9 \times 10^{-8} \text{ Sv/Bq}$  for  $^{238}\text{U}$  and  $^{234}\text{U}$ , respectively. Table 2 reports the results of the total Committed Effective Dose (CED) arising from  $^{238}\text{U}$  and  $^{234}\text{U}$  in the waters analyzed and taking into account a consumption of 2 L of water per day for 1 year (WHO, 2011). The highest dose ( $6.6 \mu\text{Sv/yr}$ ) was in sample coded BMU, as expected, that is significantly lower than the WHO (2011) guidance level of  $0.1 \text{ mSv/yr}$ .

## 5. Conclusion

Groundwaters from spas located at São Paulo (SP) and Minas Gerais (MG) states, Brazil, are an important resource that has been extensively utilized for drinking in public places, bottling and bathing purposes, among other uses. This investigation involved the sampling 75 groundwaters from springs and tube wells occurring in 14 municipalities. The dissolved U concentrations ranged  $0.001\text{--}4.82 \mu\text{g L}^{-1}$ , whereas the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) of dissolved U ranged  $1\text{--}11.7$ . The dissolved U concentrations were lognormally distributed and the AR values were correlated with the dissolution rate. The “mobility coefficient” estimated for  $^{238}\text{U}$  that is greatly variable reflects the solubility of  $^{238}\text{U}$  according to the different rock types. It was very low associated to the crystalline basement (Precambrian) at eastern SP State (cities of Águas de Lindóia, Serra Negra and Lindóia), and high in the Paraná sedimentary basin and Poços de Caldas alkaline massif. The dissolved U concentration versus AR diagram for the hydrogeochemical prospecting of concealed U-deposits allowed verify that the groundwaters are in reduced environments. The AR and reciprocal of the dissolved U concentrations allowed determine mixing volumes of most of the sampled groundwaters. The results obtained were compatible with the field evidences of each site. The maximum value of the radiation dose due to the natural dissolved U-isotopes  $^{238}\text{U}$  and  $^{234}\text{U}$  in the waters corresponded to  $6.6 \mu\text{Sv/yr}$ . The WHO guideline values were not exceeded and so these radionuclides are not a health threat in the area studied.

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## References

- Almeida, F.F.M., Hasui, Y., 1984. O Pré-cambriano do Brasil. Edgard Blücher, São Paulo, p. 378.
- Baskaran, M., 2011. Handbook of Environmental Isotope Geochemistry. Springer, New York.
- Beato, D.A.C., Viana, H.S., Davis, E.G., 2000. Avaliação e diagnóstico hidrogeológico dos aquíferos de águas minerais do Barreiro do Araxá, MG, Brasil. In: Proc. I

- Joint World Congress on Groundwater, Fortaleza, pp. 1–20.
- Birke, M., Rauch, U., Lorenz, H., Kringel, R., 2010. Distribution of uranium in German bottled and tap water. J. Geochem. Explor. 107, 272–282.
- Bonotto, D.M., 1998. Implications of groundwater weathered profile interactions to the mobilization of radionuclides. J. S. Am. Earth Sci. 11, 389–405.
- Bonotto, D.M., 2005. The U-isotopes modeling in aquífers from Poços de Caldas plateau, Brazil. Environ. Geol. 48, 507–523.
- Bonotto, D.M., 2014.  $^{222}\text{Rn}$ ,  $^{220}\text{Rn}$  and other dissolved gases in mineral waters of southeast Brazil. J. Environ. Radioact. 132, 21–30.
- Bonotto, D.M., 2015a.  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in mineral waters of southeast Brazil. Environ. Earth Sci. 74, 839–853.
- Bonotto, D.M., 2015b. Hydrochemical composition of natural mineral waters in Southern Brazil. In: Proc. 42nd IAH Congress, Rome, p. 1.
- Bonotto, D.M., Andrews, J.N., 1993. The mechanism of  $^{234}\text{U}/^{238}\text{U}$  activity ratio enhancement in karstic limestone groundwater. Isot. Geosci. 103, 193–206.
- Bonotto, D.M., Andrews, J.N., 2000. The transfer of uranium isotopes  $^{234}\text{U}$  and  $^{238}\text{U}$  to the waters interacting with carbonates from Mendip Hills area (England). Appl. Radiat. Isot. 52, 965–983.
- Borges, G.B.C., 2006. Avaliação de tecnologias para o monitoramento de recursos hidrominerais: o caso do sistema aquífero São Lourenço em Minas Gerais (Ms. Dissertation). Universidade Federal de Itajubá, Itajubá, p. 250.
- Cowart, J.B., Osmond, J.K., 1980. Uranium Isotopes in Groundwater: Their Use in Prospecting for Sandstone-type Uranium Deposits, p. 112. US DOE, Rep. GJBX-119(80).
- CPRM (Brazilian Geological Survey), 1999. Projeto Circuito das Águas do Estado de Minas Gerais – Estudos Geoambientais das Fontes Hidrominerais de Águas de Contendas, Cambuquira, Caxambu, Lambari e São Lourenço. Serviço Geológico do Brasil, Belo Horizonte, p. 142.
- Cruz, W.B., Peixoto, C.A.M., 1989. Thermal waters from Poços de Caldas, MG: experimental study of water-rock interactions. Rev. Bras. Geoc. 19, 76–86.
- Currie, L.A., 1968. Limits for qualitative and quantitative determination. Anal. Chem. 40, 586–593.
- del Rey, A.C., 1989. Estudo hidrogeotérmico da região de Águas de Lindóia, Amparo e Socorro-nordeste do Estado de São Paulo (Ms. Dissertation). USP-Universidade de São Paulo, São Paulo, p. 124.
- DFPM (Division for Supporting the Mineral Production), 1966. The Mining Code, the Mineral Waters Code and How Applying Research in a Mineral Deposit, eighth ed. DFPM, Rio de Janeiro.
- Ebert, H., 1955. Sedimentos metamórficos de origem clástica e sua significação para o esclarecimento da estrutura geológica do Escudo Cristalino Brasileiro. Eng. Mineração Metal. 22, 39–40.
- Elliot, T., Bonotto, D.M., Andrews, J.N., 2014. Dissolved uranium, radium and radon evolution in the continental intercalaire aquifer, Algeria and Tunisia. J. Environ. Radioact. 137, 150–162.
- Faure, G., 1998. Principles and Applications of Geochemistry, second ed. Prentice-Hall, Upper Saddle River, NJ, p. 600.
- Fernandes, J.F., 1982. Geoquímica do U, Th e outros elementos litófilos em rochas de alto grau de metamorfismo do “Maciço de Guaxupé”, sul de Minas Gerais (Ms. Dissertation). IPEN-Instituto de Pesquisas Energéticas e Nucleares, São Paulo, p. 69.
- Fritz, P., Fontes, J.C., 1980. Handbook of Environmental Isotope Geochemistry. Elsevier, Amsterdam.
- Hurter, S.J., Eston, S.M., Hamza, V.M., 1983. Brazilian Collection of Geothermal Data – Series 2: Thermal Springs. IPT (Technological Research Institute of São Paulo State), São Paulo, p. 111.
- IPT (Technological Research Institute of São Paulo State), 1981. Geological Map from São Paulo State: Scale 1:500,000. Monographs. IPT, São Paulo, p. 94.
- Ivanovich, M., Harmon, R.S., 1992. Uranium Series Disequilibrium: Applications to Environmental Problems, second ed. Clarendon Press, Oxford.
- Ivanovich, M., Fröhlich, K., Hendry, M.J., 1991. Uranium-series radionuclides in fluids and solids, Milk River aquifer, Alberta, Canada. Appl. Geochem. 6, 405–418.
- Kamel, M., 1980.  $^{230}\text{Th}/^{238}\text{U}$  Dating of Speleothems (MSc. Dissertation). University of Bath, Bath.
- Kigoshi, K., 1971. Alpha-recoil  $^{234}\text{Th}$ : dissolution into water and the  $^{234}\text{U}/^{238}\text{U}$  disequilibrium in nature. Science 173, 47–48.
- Kimmelman, A.A., Yoshinaga, S., Murakami, H., Mattos, J.A., 1987. Novos aspectos hidrogeológicos, hidroquímicos e isotópicos das águas termominerais de Águas de São Pedro no Estado de São Paulo. In: Proc. VII Simp. Bras. de Hidrologia e Rec. Hídricos, Salvador, pp. 26–41.
- Kimmelman, A.A., Forster, M., Coelho, R., 1995. Environmental isotope and hydrogeochemical investigation of Bauru and Botucatu aquífers, Paraná basin, Brazil. In: IAEA (International Atomic Energy Agency) (Ed.), Isotope Hydrology Investigations in Latin America 1994. IAEA-TECDOC-835. IAEA, Vienna, pp. 57–74.
- Krauskopf, K.B., Bird, D.K., 1995. Introduction to Geochemistry, third ed. McGraw-Hill, New York.
- Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta 42, 547–569.
- Lazzerini, F.T., 2013. Fontes hidrominerais do Brasil: componentes biologicamente ativos (BAC) naturais (PhD Thesis). UNESP, Rio Claro, p. 388.
- Mente, A., 2008. Mapa Hidrogeológico do Brasil. In: Feitosa, F.A.C., Manoel Filho, J., Feitosa, E.C., Demetrio, J.G. (Eds.), Hidrogeologia – conceitos e aplicações. CPRM-LABHID, Rio de Janeiro, pp. 31–48.
- Mourão, B.M., 1992. Medicina hidrológica – moderna terapêutica das águas

- minerais e estâncias de cura. Secretaria Municipal de Educação, Poços de Caldas.
- Osmond, J.K., Cowart, J.B., 1976. The theory and uses of natural uranium isotopic variations in hydrology. *At. Energy Rev.* 14, 621–679.
- Osmond, J.K., Cowart, J.B., 1981. Uranium-series Disequilibrium in Groundwater and Core Composite Samples from the San Juan Basin and Copper Mountain Research Sites, p. 126. US DOE, Rep. GJBX-364(81).
- Osmond, J.K., Cowart, J.B., 2000. U-series nuclides as tracers in groundwater hydrology. In: Cook, P., Herczeg, A.L. (Eds.), *Environmental Tracers in Subsurface Hydrology*. Springer, New York, pp. 145–173.
- Osmond, J.K., Rydell, H.S., Kaufman, M.I., 1968. Uranium disequilibrium in groundwater: an isotope dilution approach in hydrologic investigations. *Science* 162, 997–999.
- Osmond, J.K., Kaufman, M.I., Cowart, J.B., 1974. Mixing volume calculations, sources and aging trends of Floridan aquifer water by uranium isotopic methods. *Geochim. Cosmochim. Acta* 38, 1083–1100.
- Pascholati, E.M., 1990. Caracterização geofísica da Suite Intrusiva de Itu (PhD Thesis). USP, São Paulo, p. 135.
- Povinec, P.P., Comanducci, J.-F., Levy-Palomo, I., Oregioni, B., 2006. Monitoring of submarine groundwater discharge along the Donnalucata coast in the south-eastern Sicily using underwater gamma-ray spectrometry. *Cont. Shelf Res.* 26 (7), 874–884.
- Renne, P.R., Ernesto, M., Pacca, I.G., Coe, R.S., Glen, J.M., Prévot, M., Perrin, M., 1992. The age of Paraná flood volcanism, rifting of Gondwanaland, and the Jurassic-Cretaceous boundary. *Science* 258, 975–979.
- Richardson, S.M., McSween Jr., H.Y., 1989. *Geochemistry: Pathways and Processes*. Prentice-Hall Inc., New Jersey, p. 487.
- Rosholt, J.N., Shields, W.R., Garner, E.L., 1963. Isotope fractionation of uranium in sandstone. *Science* 139, 224–226.
- Schorscher, J.H.D., Shea, M.E., 1992. The regional geology of the Poços de Caldas alkaline complex: mineralogy and geochemistry of selected nepheline syenites and phonolites. *J. Geochem. Explor.* 45, 25–51.
- SEBRAE (Service for Supporting the Small Businesses in São Paulo State), 2012. *Comércio de água mineral*. [www.sebrae-sc.com.br/ideais/default.asp?vcdtexto=31586&%5E%5E](http://www.sebrae-sc.com.br/ideais/default.asp?vcdtexto=31586&%5E%5E).
- Serra, S.H., 2009. Águas minerais do Brasil. Millenium Editora, Campinas, p. 272.
- Szalay, A., 1964. Cation exchange properties of humic acids and their importance in the geochemical enrichment of  $\text{UO}_2^{2+}$  and other cations. *Geochim. Cosmochim. Acta* 28, 1605–1614.
- Szikszy, M., 1981. Hidrogeoquímica das fontes de Águas da Prata, Estado de São Paulo (Post Ph.D. Thesis). USP-Universidade de São Paulo, São Paulo, p. 193.
- Tassinari, C.C., Barretto, P.M., 1993. Características geoquímicas e geocronológicas de granitóides enriquecidos em urânio no Brasil. In: *Proc. IX Semana de Geoquímica e II Congresso de Geoquímica dos Países de Língua Portuguesa*. Memórias No. 3. Universidade do Porto, Porto, pp. 423–427.
- Traversa, G., Gomes, C.B., Brotzu, P., Buraglini, N., Morbidelli, L., Principato, M.S., Ronca, S., Ruberti, E., 2001. Petrography and mineral chemistry of carbonatites and mica-rich rocks from the Araxá complex (Alto Paranaíba Province, Brazil). *An. Acad. Bras. Ciênc.* 73, 71–98.
- Tsabarlis, C., Patiris, D.L., Karageorgis, A.P., Eleftheriou, G., Papadopoulos, V.P., Georgopoulos, D., Papathanassiou, E., Povinec, P.P., 2012. In-situ radionuclide characterization of a submarine groundwater discharge site at Kalogria Bay, Stoupa, Greece. *J. Environ. Radioact.* 108, 50–59.
- Turner, S., Regelous, M., Kelley, S., Hawkesworth, C.J., Mantovani, M.S.M., 1994. Magmatism and continental break-up in the South Atlantic: high precision  $^{40}\text{Ar}$ – $^{39}\text{Ar}$  geochronology. *Earth Planet. Sc. Lett.* 121, 333–348.
- Waterloo Hydrogeologic, 2003. *AquaChem User's Manual: Water Quality Data Analysis, Plotting & Modeling*. Waterloo Hydrogeologic, Waterloo, p. 276.
- WHO (World Health Organization), 2011. *Guidelines for Drinking Water Quality*, fourth ed. WHO Press, Geneva.
- Young, H.D., 1962. *Statistical Treatment of Experimental Data*. McGraw Hill, New York.