ANALYSIS OF U-ISOTOPES IN GROUNDWATERS FROM AQUIFER SYSTEMS AT SÃO PAULO STATE, BRAZIL

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Abstract - This paper describes the characterization of the natural radioactivity due to dissolved U-isotopes ^{238}U and ^{234}U ingroundwaters occurring in sedimentary (Bauru, Guarani, and Tubarão) and fractured rock (Serra Geral) aquifer systems in the Paraná sedimentary basin (PSB), Brazil.Based on the isotope dilution analysis, U concentration and $^{234}U/^{238}U$ activity ratio (AR) data have been utilized to deduce the proportions of groundwater masses in a mixture. Thus, this study reported a novel dataset focusing the presence of these radionuclides in selected different aquifer systems that will be used in further investigations aiming to perform approaches evaluating how mixing processes are taking place in such very important Brazilian hydrological resources.

Keywords - dissolved U-238 and U-234, groundwaters, Paraná sedimentary basin, Brazilian state of São Paulo

I. INTRODUCTION

Primeval radionuclides have survived in detectable amounts since the time of nucleosynthesis and contribute to the natural terrestrial radioactivity. The major contribution comes from ^{40}K and from radionuclides generated through the sequence of decay transformations of the three alpha emitting radionuclides: ^{232}Th, ^{238}U, and ^{235}U. Each radioactive series ends by a stable Pb isotope after passing through several unstable members having half-lives much shorter than that of the respective precursors. The members in each decay chain have atomic numbers between 81 and 92.

Most of the alpha-emitting radionuclides can be grouped into four decay series genetically independent. Because the atomic mass modifies approximately in 4 units in the alpha-decay, remaining practically unaltered in the beta-decay, the several mass numbers in the series members differ by multiples of 4. Thus, the general formulas of the series are expressed by 4n (thorium series), 4n+1 (neptunium series), 4n+2 (uranium series) and 4n+3 (actinium series), where n is an integer whose range is 52-58 (4n series), 52-59 (4n+1 series), 51-59 (4n +2 series) and 51-58 (4n+ 3 series).

The natural radioelements uranium and thorium are lithophile elements widely distributed in crustal rocks, being concentrated preferentially in acid igneous rocks compared with intermediate, basic, and ultrabasic varities. There are three natural isotopes of uranium: ^{238}U, ^{235}U, and ^{234}U. ^{238}U is the principal isotope of natural U in a mixture (about 99.3% abundance) and is the parent nuclide in the mass number (4n+2) decay series of radionuclides, the longest known series (Fig. 1). ^{235}U is the primary nuclide in the mass number (4n+3) decay series of radioelements, and its proportion in a mixture of natural U can often be considered as 0.72% if exceptional cases like the ^{235}U fission reactor site at Oklo, Gabon are disregarded [1].

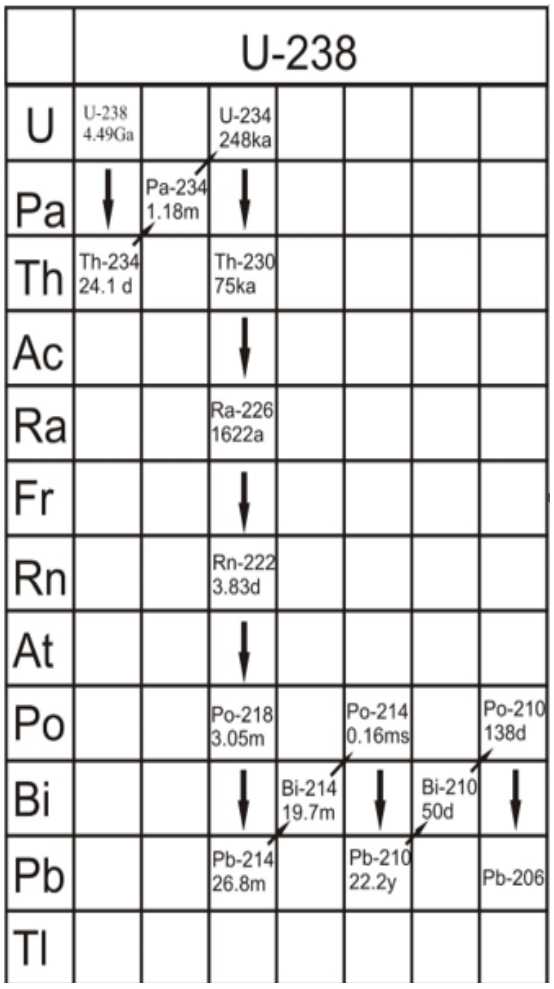

Figure 1: The natural uraniumdecay series (4n+2). Modifiedfrom[2].

The uranium and actinium decay series finish at stable lead isotopes. Disregarding the main complexities on the decay modes in the ^{238}U decay series, the stable ^{206}Pb is attained after 14 disintegrations, 8 alpha-type and 6 beta-type (Fig. 1).

Because the ^{235}U natural isotopic ratio relative to ^{238}U is often 0.72 and, consequently, the disintegration rate of ^{235}U in natural U occurring in minerals, soils and rocks is only 4.6% of that of ^{238}U, the presence of ^{235}U and descendants in the liquid phase during water/rock-soil interactions has been generally disregarded in guidelines for drinking water quality due to natural radioactivity [3].

^{234}U is radiogenic, being the fourth member of the ^{238}U radioactive decay chain (Fig. 1); its abundance in a mixture of natural U is 0.0054%, whereas its average crustal abundance corresponds to $2\text{-}3\times10^{-8}$%. It was firstly identified in 1907 by McCoy and Ross, who named it of U(II) [4]. ^{234}U may also be produced from ^{238}Pu alpha decay rather than the ^{234}Pa beta decay in the uranium series.

Since ^{234}U is a heavy radiogenic isotope, it is essentially immune to mass-fractionation effects. Despite this, studies on secondary minerals and groundwaters have found radioactive disequilibrium between ^{238}U and ^{234}U [4]. The isotopes ^{238}U and ^{234}U are in secular equilibrium only in minerals and rocks which are closed systems for U over a time-scale greater than 10^6 years. Considering that the $^{234}U/^{238}U$ activity ratio (AR) is defined as the ratio of the ^{234}U daughter activity to the ^{238}U parent activity, a unit value for this parameter is achieved in the bulk of rock/mineral matrices under these conditions. However, water/rock-soil interactions frequently result in AR values for dissolved uranium which are greater than unity [5, 6].

Various mechanisms have been suggested to interpret the generation of the elevated AR's in solution. For instance, Rosholt et al. [7] 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[8] 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.

Uranium concentration in solution may be depleted or enriched, depending on oxidation-reduction conditions [5].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 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 [5]. Based on the isotope dilution analysis, AR and U concentration data have been utilized to deduce the proportions of groundwater masses in a mixture, among other applications[5, 9-11].

Thus, the natural U-isotopes ^{238}U and ^{234}U have been utilized with success as an environmental tracer on the study of different aquifer systems worldwide, constituting another relevant tool to increase the knowledge of the underground resources. This paper reports a novel dataset of the seradionuclides in different aquifer systems inserted within the geological context of the Paraná SedimentaryBasin (PSB), Brazil.



Figure 2: The Paraná sedimentary basin in South America.

II. STUDY AREA

The area studied here is geologically situated within the PSBin Brazil, between parallels 10°-20° southern latitude and meridians 47°-64° western longitude (Fig. 2).The whole surface area of the PSB is ~1.6 million km^2 distributed along Brazil (62.5%), Paraguay (6.25%), Uruguay (6.25%), and Argentina (25%) [12]. It is an intercratonic basin, exhibiting sedimentary sequences that coversince the Silurian-Devonian and possessing gentle dips towards the center of the basin.

Table 1 summarizes some major stratigraphic units occurring at PSB that are relevant for this study, highlighting sandstones, conglomerates, diamictites, siltstones, shales, mudstones, limestones, basalts and diabases, among other rock types. Local faults may

have served as channels for the extruding basalt flows of Jurassic-Cretaceous age (Serra Geral Formation), which cover about 1×10^6 km^2 of the basin. Renne et al. [13] utilized the ^{40}Ar-^{39}Ar technique to estimate volcanism ages between 127 and 137 Ma, and Turner et al. [14] suggested that the duration of the volcanism corresponded to 10 Ma, occurring at a rate of 0.1 km^3/yr.

Like other sedimentary sequences, the PSB has also been extensively investigated due to its economic potential for supplying water, petroleum, coal, clays, and metals like uranium, among other resources. Because about 55 million inhabitants live in the area of the basin occurring in Brazil and despite the abundance of surface water resources in this region, creeping pollution problems created by rapid industrialization have called for an increasing use of uncontaminated underground water resources.

PERIOD	GROUP	FORMATION	LITHOLOGY
Cretaceous	Bauru	Marília +	sandstones
To		Adamantina	siltstones
Jurassic			mudstones
		Caiuá	sandstones
			carbonatic nodules
	São Bento	Serra Geral	basalts
			diabase sills
		Botucatu	sandstones
Triassic		Pirambóia	sandstones
			shales
Upper	Passa	Corumbataí	mudstones
Permian	Dois		shales
			siltstones
		Irati	mudstones
			siltstones
			shales
			limestones
Mean	Tubarão	Tatuí	siltstones
Permian to			sandstones
Upper Carboniferous			limestone concretions
		Itararé	sandstones
			conglomerates
			diamictites
			tillites
			siltstones
			shales

Table 1: Simplified stratigraphic column of the PSB since Upper Carboniferous up to Cretaceous. According to [15].

The enormous groundwater potential in Paraná basin provided abundant resources for a region lacking heavy concentrations of population about 50 years ago [16]. However, the steady increase in industrialization, urbanization, and population size has caused problems on the very attractive groundwater exploitation, including the excessive over-pumping responsible by the groundwater table rapid sinking over the last decades as values corresponding to 100-120 m have been recorded[12].

In inland aquifers at the PSB, leaky multiaquifer systems composed of several aquifers separated by aquitards may occur [17, 18], and more saline groundwater is overlain by fresh water accumulated as a result of recharge from precipitation, irrigation systems and natural streams. Exploitation and mining of fresh waterresources in these aquifers take place regularly for recreation, irrigation, industrial and drinkingpurposes, and to mitigate droughts, especially in dry season. However, over-exploitation in these aquifers may be inducing low piezometric head that results in upward movement of more saline water through natural boundaries.Thus, multiaquifer systems mainly comprising sandstones and basalts plus sediments from PassaDois Group behaving as aquitards have been proposed to represent the hydrostratigraphy of the PSB, chiefly comprising the giantGuarani Aquifer System (GAS), Serra Geral Aquifer, Bauru Aquifer, and Tubarão Aquifer, among others[18].

III. EXPERIMENTAL

In this study, 19 municipalities located at São Paulo State, Brazil, have been selected for the collection of 85 groundwater samples providing from different aquifer systems as shown in Table 2. For U-isotopes analysis, the groundwater samples (20-25 L) were taken from taps installed in pumped tubular wells

drilled for exploiting theaquifers. The samples were stored in polyethylene vessels andacidified to pH≤2 (withHCl).

About 500 mg of $FeCl_3$ plus 4.4dpm of theartificial uranium isotope ^{232}U were added. ^{232}U is a spike (tracer) that originates ^{228}Th bythe emission of α-particles, whose daughters correspond to those occurring in the ^{232}Th decay series, among them ^{224}Ra. The natural U-isotopes (^{238}U and ^{234}U) and artificial ^{232}Uwere co-precipitated on $Fe(OH)_3$ by increasing the pH to 7-8 through addition of concentrated NH_4OH solution.The precipitate was recovered, dissolved in 8M HCl and Fe^{3+} was extracted into an equal volume of isopropyl ether. The acid U-isotopes bearing solution was purified by anion exchange, first on a Cl^- and then on a NO_3^- column of 50-100 mesh Rexyn 201 resin. U was finally eluted from the NO_3^- column with 0.1 M HCl and after evaporation to dryness was dissolved in 10 mL of 2M $(NH_4)_2SO_4$ 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 hours at a current density of 1 Acm^{-2}.

Radionuclide	Channel	Energy (MeV)
U – 238	496	4.20
U – 234	573	4.77
U – 232	648	5.32
Th – 228	659	5.42
Ra – 224	697	5.68

Table 2: Channels and energy of major radionuclides identified in the alpha spectrum obtained for the radioactive source prepared at the Centre de FaiblesRadioactivités, France.

The ^{238}U content and AR data wereobtained by alpha spectrometry. The α-activities were determined with four 0.1 mm depletion depth, 200-450 mm^2 area silicon surface barrier detectors. The spectra for natural U-ísotopes and ^{232}U tracer extracted were recorded on an EG&G ORTEC 919 Spectrum Master Multichannel Buffer.The system was calibrated in energy on using a radioactive source prepared at the Centre de FaiblesRadioactivités, CNRS-CEA, Gif-sur-Yvette, France, that contains 0.91 Bq of ^{238}U, 0.91 Bq of ^{234}U and 0.17 Bqof ^{232}U, allowing to record the channels occurring in the alpha spectrum and the corresponding α-particles energy for the respective radionuclides (Table 2),as well to plot the energy calibration curve of the alpha spectrometer (Fig. 3).

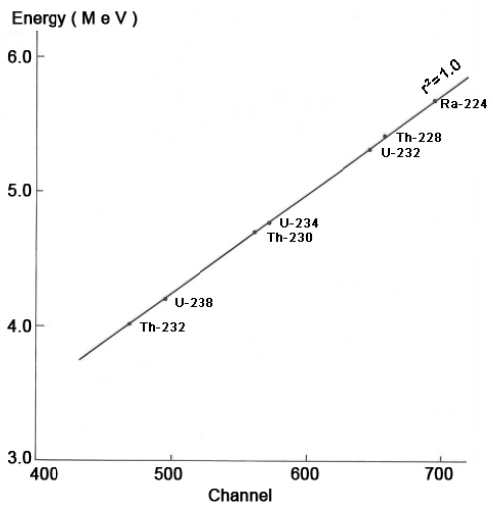

Figure 3: Calibration curve of the Si(Au) spectrometer for α-particles energy readings of groundwater samples from the study area.

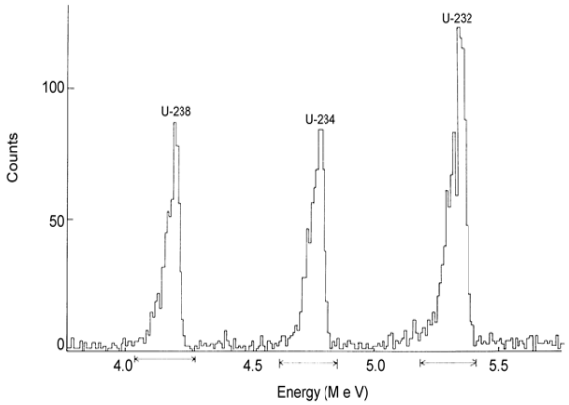

Figure 4: Alpha spectrum obtained for U-isotopes analysis of a groundwater sample from the study area. Volume = 20 L. Counting time = 21 hours.

The Decision Level L_c[19] for acceptance of a positive measurement in the ^{238}U and ^{232}U energy regions was 0.00082 and 0.00225 cpm, respectively. The concentration data were calculated by isotope dilution from the counting rates of ^{238}U and ^{232}U peaks, while the AR data were determined from the counting rates of ^{238}U and ^{234}U peaks. More analytical details for these measurements are reported elsewhere [6]. Fig. 4 shows a typical alpha spectrum obtained during the data acquisition.

IV. RESULTS AND DISCUSSION

The results of the measurements are reported in Table 3.The dissolved U concentration in the groundwater samples analyzed ranged 0.001-0.83 μg/L,neither exceeding the typical maximum worldwide value of 10 μg/Lin rivers, lakes and groundwaters[5, 6] nor the maximumguideline reference value established by

the WHO [3] for ingestion of this radionuclide in drinking-water, i.e. 30 μg/L.

The AR's values found in the groundwater samples are between 0.91 and 12.1 (Table 3).The great majority of these ratios are greater than unity in the liquid phase as expected during water-soil/rock interactions due to preferential chemical dissolution of ^{234}U [7] and alpha-recoil release of ^{234}Th at the rock-water interface [8]. The climate, lithology, stratigraphy, hydrogeology, geochemical conditions, 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[5, 6].

^{238}U and ^{234}U have been considered useful isotopes for hydrogeochemical 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 [20]. In terms of dissolved U concentrations, the main categories defined are (Fig. 5): oxidized aquifer containing "normal" U concentration (values of 1-10 μg/L); oxidized aquifer containing "enhanced" U concentration (values higher than 10 μg/L); and reduced aquifer or strata with low U concentration (values lower than 1 μg/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 groundwater samples were variable, as shown in Fig. 5. All them are inserted in fields IV and V, characterizing reduced environments. Such classification is supported by their pH and Eh data, not reported in this paper.

Fig. 6compares the U concentration and AR data in groundwaters from this study with the values reported by [21-23] in different groundwater systems. The variability in Morro do Ferro area is notoriously less pronounced than in other aquifer due to the dissimilarity of lithologies. Morro do Ferro is a well-known thorium/rare-earth ore body located at the Poços de Caldas alkaline massif, Minas Gerais State, Brazil. A shallow aquifer system developed in the weathered profile of the Morro do Ferro area. The water-table there is a subdued replica of the topography, with recharge on the higher elevations from precipitation and discharge locally to streams. Such groundwater belongs to an oxidizing low-temperature aquifer system. The groundwater chemistry and rainwater at Morro do Ferro indicated an aquifer mineralogy enriched in K and strongly depleted in other cations due to intense conditions of weathering, with the groundwater reflecting the composition of rainwater, where small amounts of Ca, K, Fe and SiO_2 were added from contact with the aquifer. This scenario is very different of others related to the aquifers shown in Fig. 6, inclusive those focused in this paper, which are multiaquifer systems mainly comprising sandstones and basalts plus Paleozoic sediments whose waters are often mixed and subjected to be tracked by the U-isotopes ^{238}U and ^{234}U.

Sample No.	City[1]	Depth (m)	Aquifer[2]	^{238}U (μg/L)	AR[3]
1	ASB	258	BA+SG	0.04	1.42
2	ASB	299	BO+PI+SG	0.05	5.93
3	ASB	120	SG+BO	0.03	3.46
4	ASB	120	SG+BO	0.02	6.81
5	ASB	180	SG	0.01	1.96
6	ASB	100	BA+SG	0.03	2.36
7	BCS	509	SG+BO+PI	0.38	4.90
8	BCS	102	SG?	0.002	2.82
9	AVR	403	SG+BP	0.11	2.07
10	AVR	420	BO+PD	0.07	1.57
11	AVR	150	SG	0.02	2.89
12	BCS	99	SG	0.06	1.85
13	BCS	67	SG	0.06	1.94
14	AVR	101	BA+SG	0.01	3.20
15	AVR	120	BA+SG+BO	0.10	1.47
16	AVR	100	BA	0.02	1.0
17	AVR	150	BA+BP(?)	0.10	4.18
18	AVR	100	CR(?)	0.01	1.14
19	AVR	92	PI	0.007	1.83
20	SAM	100	BA	0.003	2.76
21	SAM	100	SG	0.004	2.39
22	SAM	100	BA+SG	0.01	1.30
23	ARE	120	SG	0.04	2.75
24	ARE	356	BO+PI+SG	0.05	1.49

25	BOT	228	SG+BO	0.006	3.94
26	BOT	76	BO	0.02	2.0
27	SAM	430	BO	0.003	6.65
28	SAM	386	BP	0.01	8.73
29	SAM	120	SG+BO	0.004	2.83
30	SAM	385	BA+SG+BP	0.009	7.08
31	BOT	236	BA+SG+BO	0.02	3.04
32	BOT	124	BO	0.01	1.43
33	BOT	150	BA+SG	0.05	1.67
34	BOT	140	PI	0.01	2.10
35	BOT	70	BO	0.08	1.51
36	AVR	60	BA+SG	0.004	2.49
37	PAR	150	SG+BO	0.002	3.72
38	PAR	78	PI	0.004	1.09
39	SPO	150	PI	0.09	2.09
40	SPO	80	PI	0.03	2.0
41	SPO	126	PI	0.004	2.17
42	SPO	70	PI	0.001	1.67
43	SPO	80	PI	0.06	1.06
44	SPO	64	TU	0.002	1.33
45	SPO	250	PI	0.008	1.12
46	SPO	174	IT	0.02	1.50
47	ASP	182	PI	0.02	4.02
48	ABI	183	PI	0.05	3.25
49	SMS	132	SG+PI	0.03	5.14
50	SMS	200	BA	0.06	1.28
51	SMS	225	PI	0.02	3.67
52	SMS	175	BO	0.03	2.47
53	SMS	120	SG+PI	0.01	12.12
54	CHA	455	IT	0.09	8.86
55	IPE	250	PD+TU	0.008	3.33
56	IPE	51	PI	0.06	2.64
57	IPE	50	PI	0.03	2.49
58	CDP	261	TU	0.008	3.09
59	CDP	228	CO+CO?	0.02	4.77
60	CDP	300	PD+SG+TU	0.009	4.0
61	CDP	300	CO	0.04	1.50
62	CDP	197	SG+CO+TA	0.01	1.20
63	SAM	400	BA+SG+BP	0.004	3.50
64	MOM	300	IT	0.007	6.61
65	SAL	200	PD	0.008	11.73
66	SGE	300	TU	0.002	3.80
67	SPO	320	PI+CO	0.03	2.64
68	RCL	198	SG+PD+TU	0.01	3.70
69	RCL	156	IT	0.04	3.20
70	RCL	282	IT	0.03	2.94
71	RCL	350	CO+IT	0.001	2.36
72	MOM	100	IT	0.006	5.12
73	MOM	262	TU+SG	0.02	2.06
74	RCL	60	PD	0.23	1.21
75	RCL	101	CO	0.83	2.56
76	RCL	120	CO	0.006	3.0
77	RCL	240	IT	0.006	2.83
78	RCL	239	PD+SG+TU	0.06	2.07
79	RCL	250	TU	0.02	2.90
80	RCL	201	PD+SG	0.04	0.91
81	RCL	275	SG+TU	0.37	1.36
82	LEE	384	TU	0.03	3.10
83	LEE	384	TU	0.04	4.15
84	RCL	306	IR+IT	0.16	4.09

85	RCL	183	SG+PD	0.23	3.22

Table 3: Analytical results of dissolved U-isotopes in groundwater samples from different aquifer systems at São Paulo State, Brazil. Analytical uncertainty ±10-15% at 1σ standard deviation.

[1]ASB=Águas de Santa Bárbara; [1]BCS=Bernardino de Campos; AVR=Avaré; SAM=São Manuel; ARE=Areiópolis; BOT=Botucatu; PAR=Pardinho; SPO=São Pedro; ASP=Águas de São Pedro; ABI=Anhembi; SMS=Santa Maria da Serra; CHA=Charqueada; IPE=Ipeúna; CDP=Cordeirópolis; MOM=Mombuca; SAL=Saltinho; SGE=Santa Gertrudes; RCL=Rio Claro; LEE=Leme
[2]BO=BotucatuFm; PI=PirambóiaFm; BP=undif.BO/PI; SG=Serra GeralFm; BA=Bauru Gp; PD=PassaDoisGp; TU=Tubarão GP; CR=Crystalline; IT=ItararéFm; CO=CorumbataíFm; IR=IratiFm; IT=ItararéFm; TA=TatuíFm
[3]AR = $^{234}U/^{238}U$ activity ratio

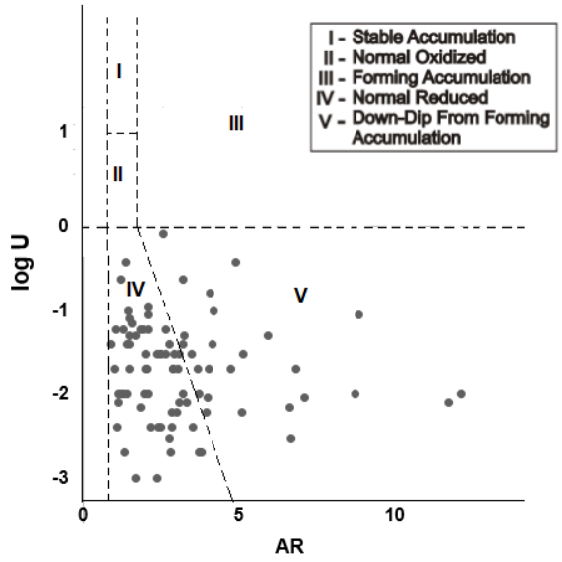

Figure 5: Plotting of the dissolved U concentration (in log scale) versus the $^{234}U/^{238}U$ activity ratio (AR) of the groundwaters analyzed here as utilized by [20].

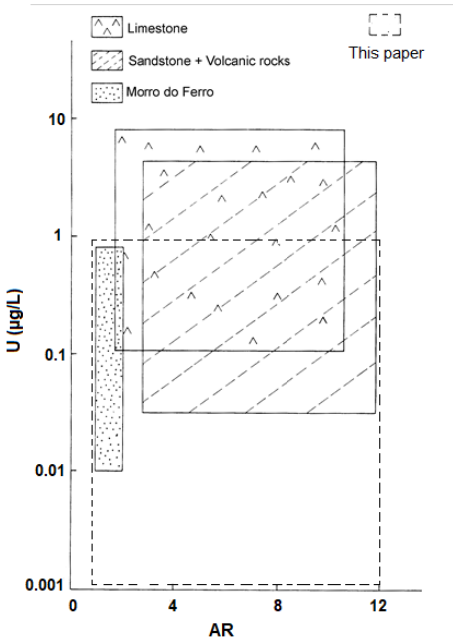

Figure 6: Comparison of the dissolved U concentration and ARdatareported here with values in other aquifer systemsinvestigated by Gomes(1978),Bonotto and Fujimori (1984), and Bonotto (1998).

V. CONCLUSION

Ground waters from different aquifer systems located at São Paulo State, Brazil, are an important resource that has been extensively utilized for drinking purposes in several cities. This investigation involved the sampling 85 ground waters from tube wellsoccurringin 19 municipalities. The dissolved U concentration ranged 0.001-0.83µg/L, whereas the $^{234}U/^{238}U$ activity ratio (AR) of dissolved U ranged

0.91-12.1.None groundwater sample surpassed the limiting value of 30 µg/L for ingestion of ^{238}Uin drinking-water as proposed by the WHO. The obtained dataset is relevant for further investigation to be held in the study area aiming to determine mixing volumes of groundwaters providing from different aquifer systems as reported in the literature taking into account the reciprocal of the U concentration and AR data.

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