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## **Extended Abstracts**

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at Paraná sedimentary basin, Brazil**

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## INTRODUCTION

The use of isotopic methods in Earth Sciences investigations gained widespread acceptance among several professionals. Well-established techniques such as using stable isotopes of hydrogen and oxygen as markers of water source have been applied in water resource investigations for several decades. Isotope methods became an integral part of geochemical studies in groundwater projects as constituted powerful tools when applied to the intractable problems of source attribution for the most common groundwater contaminants, including nitrate, VOCs, and perchlorate. The co-interpretation of geochemical and environmental isotope data within the hydrogeological context provided hydrogeologists with a powerful problem-solving tool not only restricted to research programs. Thus, non-conventional environmental radionuclides have been utilized for dating meteoric waters and groundwaters under time scales from 2.5 years up to more than 1 million years like  $^{22}\text{Na}$ ,  $^{32}\text{Si}$ ,  $^{39}\text{Ar}$ ,  $^{36}\text{Cl}$ ,  $^4\text{He}$  radiogenic and the natural uranium isotopes  $^{234}\text{U}$  and  $^{238}\text{U}$  (Ivanovich, Harmon, 1982). This study was held in São Paulo State, Brazil, and involved the sampling of different aquifer systems for evaluating the hydro-chemistry and radioactivity due to the nuclides  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{222}\text{Rn}$  and  $^{226}\text{Ra}$  in order to investigate their potential use as natural tracers of the water provenance in the area.

## STUDY AREA

Multi-aquifer systems mainly comprising sandstones and basalts plus sediments from Passa Dois Group (PDG) behaving as aquitards have been proposed to represent the hydrostratigraphy of the Paraná sedimentary basin in Brazil (Araújo et al., 1999), where the study area is located. Groundwater occurs within the interflow zones and along cooling joints in basalts and diabases from Serra Geral Formation (SGF), where interbedded sediments greatly increase the average porosity of large volumes of rocks. The sandstones of Cretaceous age (Bauru Group) are moderately cemented, and exhibit adequate properties to storage water. The Paleozoic sediments (Devonian-Permian age) also provide water that is relatively mineralized in the central parts of the basin and contains  $\text{H}_2\text{S}$  in some wells. The Guarani aquifer of Triassic-Jurassic age has continental dimensions and is composed of silty and shaly sandstones of fluvial-lacustrine origin, as well variegated quartzitic sandstones that were accumulated by eolian processes under desert conditions. Several investigations have focused the Guarani aquifer system, under different approaches (Araújo et al., 1999; Sracek and Hirata, 2002; Bonotto, 2006; etc.). This study was held in São Paulo State, Brazil, and involved the groundwater sampling in 20 municipalities situated along the sections AB, CD and EF in Fig. 1. Only Três Lagoas city was located in Mato Grosso do Sul State, close to the border of São Paulo State (Fig. 1). The groundwater samples (79) were collected from free-flowing and pumped tubular wells for physical and chemical analyses, including radionuclides.

Beyond cutting the superficial weathering mantle, the wells intercepted most of the stratigraphic units of the Paraná basin (Paleozoic-Cenozoic) (IPT, 1981): the Paraná Group, represented by coarse to mean grained whitish sandstones in a kaolinitic matrix, locally intercalated by micaceous/silty/clayey or fine sandstone layers, where about 1 m-thick conglomerates often occur in the base; the Tubarão Group, comprising the Itararé Subgroup (sandstones, conglomerates, diamictites, tillites, siltstones, shales and rythmites) and Tatuí Formation (siltstones, shales, silex and sandstones with local concretions); the Passa Dois Group, comprising the Irati Formation (siltstones, mudstones, black betuminous shales and limestones) and Corumbataí Forma-

tion (mudstones, shales and siltstones); the São Bento Group, comprising the Pirambóia Formation (sandstones, shales and muddy sandstones), Botucatu Formation (sandstones and muddy sandstones), Serra Geral Formation (basalts and diabases) and related basic intrusives; the Bauru Group, characterized by mean to fine sandstones with local occurrence of cement and carbonate nodules, arkoseous mean to very fine massif sandstones, fine to very fine sandstones exhibiting cementation and carbonate nodules with sandy siltstone lenses and massif mudstone layers, sandstones with clayey cement and elongated shales lenses, conglomerates, siltstones and limonitized sandstones.



**Figure 1.** The three sections in São Paulo State, Brazil, that were utilized for selecting tubular wells drilled in Bauru, Serra Geral and Guarani aquifers.

### ANALYTICAL METHODS

The groundwater samples (45–50 kg) were stored in polyethylene bottles, with the temperature, pH and Eh (redox potential) readings being performed in the field. The pH measurement was performed by a digital portable meter coupled to a combination glass electrode; buffer solutions equilibrated with the sample temperature were utilized to calibrate the equipment before the analyses. The Eh measurement was realized with the same pH digital portable meter after disconnecting the pH electrode, selecting the “mV” position, and connecting a combination platinum electrode — Ag/AgCl reference element. Such electrode was previously calibrated on using a prepared Zobell I reference solution (Zobell, 1946). A bench digital meter provided conductivity readings obtained through a 1 cm<sup>2</sup> area platinum electrode calibrated with KCl standards. The total alkalinity of the samples was determined by titration using a titrator with sulfuric acid standard solution to an end point evidenced by the color change of a standard indicator solution (APHA, 1989). The obtained values corresponded to bicarbonate, carbonate and hydroxide concentrations.

Aliquots were divided for evaluating the major/trace elements/compounds, and radionuclides. The suspended solids were separated on filtering each sample through a 47 (90)-mm diameter Millipore membrane of 0.45- $\mu$ m porosity. The dry residue (DR) (~ total dissolved solids, TDS) content was evaluated on evaporating the filtrate to dryness in a weighed flask that was dried to constant weight at 180°C, with the increase in flask weight representing DR (APHA, 1989). Filtered aliquots preserved with HCl or HNO<sub>3</sub> were used for obtaining the chemical composition in waters. The analyses of dissolved sodium were done using an atomic absorption spectropho-

tometer, whereas standard procedures were utilized for characterizing dissolved potassium, calcium, magnesium, silica, nitrate, sulfate and chloride by colorimetry (Hach, 1992), after adding reagents to the samples that are able to produce colored complexes read by a program stored in Hach DR/2000 spectrophotometer previously calibrated in variable concentrations at different wavelengths. Fluoride was potentiometrically measured, after adding a known amount of ionic strength adjustor to each sample; then, an Orion ion-selective electrode coupled into a digital meter was used, where standards containing variable concentrations of fluoride were utilized for preparing the calibration curve consisting on a logarithmic straight line involving the potential and concentration readings.

The  $^{222}\text{Rn}$  activity concentration in water was measured using an Alpha Guard PQ2000PRO (Genitron GmbH) equipped with an appropriate unit (Aquakit), following a protocol proposed by the manufacturer (Genitron, 2000). Alpha Guard is an ionizing chamber which measures radon via alpha spectrometric techniques. For measurement with Aquakit, the water samples were forced to degas their radon content within a radon tight assembly, which consists of two glass vessels and the Alpha Guard unit.  $^{226}\text{Ra}$  was evaluated from  $^{222}\text{Rn}$  data obtained in 1-L aliquots that were inserted in glass bottles fitted with inlet and outlet stopcocks, as well out-gassed with  $^{222}\text{Rn}$ -free  $\text{N}_2$  to remove the  $^{222}\text{Rn}$  originally present in the sample. The radon removal was performed only after waiting a time of about 25 days for  $^{222}\text{Rn}$  to reach radioactive equilibrium with  $^{226}\text{Ra}$ . The aliquots (20–25 kg) for U analysis were acidified to pH less than 2 on using HCl, about 500 mg of  $\text{FeCl}_3$  plus 3.39 dpm of  $^{232}\text{U}$  were added, and 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 8M HCl and  $\text{Fe}^{3+}$  was extracted into an equal volume of isopropyl ether. The acid U-bearing solution was purified by anion exchange, first on a  $\text{Cl}^-$  and then on a  $\text{NO}_3^-$  column of 100–200 mesh AG1-X8 resin. U was finally eluted from the  $\text{NO}_3^-$  column with 0.1 M HCl and after evaporation to dryness was dissolved in 10 mL of 2M  $(\text{NH}_4)_2\text{SO}_4$  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 hours at a current density of 1  $\text{Acm}^{-2}$ . The U content was measured by alpha spectrometry. The  $\alpha$ -activities were determined with four 0.1 mm depletion depth, 200/450  $\text{mm}^2$  area silicon surface barrier detectors. The spectra for natural U and  $^{232}\text{U}$  tracer extracted were recorded on an EG&G ORTEC 919 Spectrum Master Multichannel Buffer. The Decision Level  $L_c$  (Currie, 1968) for acceptance of a positive measurement in the  $^{238}\text{U}$  and  $^{232}\text{U}$  energy regions was 0.00082 and 0.00225 cpm, respectively. The concentration data were calculated by isotope dilution from the counting rates of  $^{238}\text{U}$  and  $^{232}\text{U}$  peaks, where the analytical details for these measurements were reported elsewhere (Ivanovich, Harmon, 1982).

Diabase gravels belonging to the Serra Geral Formation were also subjected to experimental etch/leach on a laboratory time-scale. Their specific surface area  $S$  ( $\text{cm}^2\cdot\text{g}^{-1}$ ) was determined on counting a large number of particles randomly selected and on measuring their maximum and minimum lengths. Then, after evaluating the average length, the assumption of a spherical geometry allowed estimate  $S$  by the equation  $S = 3/\rho r$ , where  $\rho$  is the rock density ( $2.91 \text{ g}\cdot\text{cm}^{-3}$ ). The mean diameter and  $S$  values were, respectively, 1.54 cm and  $1.34 \text{ cm}^2\cdot\text{g}^{-1}$ . The freshly crushed and sized diabase sample was submitted to chemical dissolution in the laboratory under controlled conditions, where the gravels were initially washed with distilled water to remove any finely divided material. After drying, 16 kg of diabase gravels were weighed into a 20 L glass

bottle and subjected to chemical etch/leach at room temperature ( $\sim 20^\circ\text{C}$ ) with distilled water equilibrated with the atmosphere ( $p_{\text{CO}_2} \sim 10^{-3.5}$  atm). The solution was daily circulated through the rock aggregates, periodically removed for analysis and replaced by a fresh one, where etching/leaching was continued in this sequential manner for up to 306 days. The etch/leach solutions were filtered through a  $0.45 \mu\text{m}$  Millipore membrane and acidified to  $\text{pH} < 2$  for the U content and  $^{238}\text{U}/^{234}\text{U}$  activity ratio determinations. These parameters were also evaluated in the diabase itself, as well in others selected rock samples from Paraná sedimentary basin, after their complete solution with HF,  $\text{HNO}_3$  and HCl.

## RESULTS AND DISCUSSION

The chemical data obtained for the studied groundwaters were plotted in an Eh-pH diagram (Krauskopf, Bird, 1995), which showed the following trends: Section AB — reducing (Bauru and Serra Geral aquifers), transitional + reducing (Guarani aquifer); Section CD — reducing (Bauru, Serra Geral and Guarani aquifers); Section EF — reducing (Bauru and Serra Geral aquifers), transitional + reducing + oxidizing (Guarani aquifer). Thus, most of the data fell into the reducing field, even under the more acidic and basic conditions. The software *Aquachem 4.0* of *Waterloo Hydrogeologic* allowed determine the ionic strength (ranged from  $0.61 \times 10^{-3}$  to  $10.14 \times 10^{-3}$ ) and define the dominant hydrogeochemical facies from the acquired data, i.e. the anion bicarbonate was dominant in practically all wells along the three sections, whereas sodium was the dominant cation in most of them.

The analytical uncertainty for the radiometric data was often  $\pm 10\%$  ( $1\sigma$  standard deviation). The range of the values obtained for groundwater samples from Bauru aquifer ( $n = 35$ ) was:  $^{238}\text{U} = 0.007\text{--}0.20 \mu\text{g/L}$  (mean =  $0.04 \mu\text{g/L}$ );  $^{234}\text{U}/^{238}\text{U}$  activity ratio =  $0.90\text{--}4.84$  (mean =  $2.14$ );  $^{222}\text{Rn} = 0.78\text{--}11.76 \text{ Bq/L}$  (mean =  $3.80 \text{ Bq/L}$ );  $^{226}\text{Ra} = 0.07\text{--}1.44 \text{ Bq/L}$  (mean =  $0.33 \text{ Bq/L}$ );  $^{222}\text{Rn}/^{226}\text{Ra}$  activity ratio =  $1.57\text{--}73.50$  (mean =  $20.97$ ). The range of the values obtained for groundwater samples from Serra Geral aquifer ( $n = 16$ ) was:  $^{238}\text{U} = 0.002\text{--}0.09 \mu\text{g/L}$  (mean =  $0.02 \mu\text{g/L}$ );  $^{234}\text{U}/^{238}\text{U}$  activity ratio =  $0.96\text{--}3.44$  (mean =  $2.08$ );  $^{222}\text{Rn} = 0.93\text{--}21.18 \text{ Bq/L}$  (mean =  $6.70 \text{ Bq/L}$ );  $^{226}\text{Ra} = 0.001\text{--}0.32 \text{ Bq/L}$  (mean =  $0.14 \text{ Bq/L}$ );  $^{222}\text{Rn}/^{226}\text{Ra}$  activity ratio =  $13.55\text{--}8370.0$  (mean =  $757.79$ ). The range of the values obtained for ground water samples from Guarani aquifer ( $n = 28$ ) was:  $^{238}\text{U} = 0.02\text{--}7.47 \mu\text{g/L}$  (mean =  $1.19 \mu\text{g/L}$ );  $^{234}\text{U}/^{238}\text{U}$  activity ratio =  $1.33\text{--}5.56$  (mean =  $2.87$ );  $^{222}\text{Rn} = 0.23\text{--}50.46 \text{ Bq/L}$  (mean =  $13.71 \text{ Bq/L}$ );  $^{226}\text{Ra} = 0.03\text{--}1.17 \text{ Bq/L}$  (mean =  $0.20 \text{ Bq/L}$ );  $^{222}\text{Rn}/^{226}\text{Ra}$  activity ratio =  $1.66\text{--}624.33$  (mean =  $105.50$ ). The variability in radionuclides data suggests some influence of the underlying Paleozoic sediments in the composition of waters from Guarani aquifer, as already pointed out by Bonotto (2006). The  $^{234}\text{U}/^{238}\text{U}$  A.R. for dissolved uranium was generally greater than unity and related to the  $^{234}\text{U}$ -enhancement in the liquid phase as a consequence of the water-rock interactions. The  $^{222}\text{Rn}/^{226}\text{Ra}$  A.R. greatly exceeded unity in the three aquifer systems, as already pointed out in the literature (Andrews, 1983), due to the low  $^{226}\text{Ra}$  activity concentration generally found in groundwaters. The  $^{222}\text{Rn}/^{226}\text{Ra}$  ratios are significantly higher in waters coupled to fracture flow (Serra Geral aquifer) relatively to those associated to porous flow (Bauru and Guarani aquifers).

There were significant correlations among pH, conductivity, bicarbonate and dissolved uranium in groundwaters from Bauru and Serra Geral aquifers, as well verified in Guarani aquifer. The relationships suggest that U-migration may be occurring through the complexation of the uranyl ions ( $\text{UO}_2^{2+}$ ) with bicarbonate/carbonate anions. However, the U mobility coefficient associated

to groundwater dissolution is  $2 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$  for Bauru aquifer and  $7 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$  for Serra Geral aquifer, which are greatly lower than the estimate of  $1.7 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$  for Guarani aquifer. Thus, the U content and  $^{222}\text{Rn}/^{226}\text{Ra}$  A.R. are potentially useful parameters for indicating the water provenance. The amount of uranium etched/ leached in the laboratory experiments held with the diabase sample was 0.12–0.28  $\mu\text{g}/\text{kg}$  that is within the range of 0.07–1.09  $\mu\text{g}/\text{kg}$  obtained by Bonotto and Andrews (2000) for the etching/leaching of exposed areas of calcite/dolomite surfaces at the same conditions. Therefore, the volcanic rocks of the Paraná basin release bicarbonate, uranium and others compounds during the water-rock interactions occurring in the fractures flow, but the uranium transfer to the liquid phase is less accentuated if compared with that involving the flow through the porous media.

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