

EVALUATING THE OCCURRENCE AND SPATIAL DISTRIBUTION OF THE RADIOACTIVE ISOTOPES ^{226}Ra , ^{228}Ra , ^{222}Rn AND ^{238}U IN THE GROUNDWATERS OF REGIÃO DOS LAGOS - RJ – BRAZIL

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Abstract

A survey of radionuclide concentrations in ground waters of Região dos Lagos, the Lake's Region - Rio de Janeiro State-Brazil, was performed in order to verify the natural levels of radionuclides in the groundwater, to identify main factors influencing the radioisotope concentration and in a first approach to estimate natural radionuclide ingestion levels by the adult inhabitants. The concentration values of the major ion concentrations varied widely, showing the seawater influence over the groundwaters. Unusual low pH values were found in a specific region and the statistical analysis stressed its strong influence on the high radium concentrations. Probably the high Ra concentrations in the waters are due to Ra leaching from rock matrix, which is incited by the low pH. Generally low concentrations of radon found even in samples with high radium concentrations were a consequence of radon de-gassing. The concentrations of uranium were lower than maximum allowable limit for all samples. Seventeen of the eighty-eight water samples collected in the region had levels of naturally occurring radium that exceeded the maximum allowable values recommended by Brazilian Health Minister for drinking water, being necessary to assess the potential risks for the population from the exposure to these radionuclides in the waters.

Keywords: radioactivity, coastal aquifer, radium, radon, uranium, statistical analysis, spatial analysis.

Resumo

Um levantamento da concentração de isótopos radioativos naturais nas águas subterrâneas da Região dos Lagos, estado do Rio de Janeiro-Brasil, foi realizado com a finalidade de verificar os níveis naturais de radioisótopos nas águas subterrâneas, identificar os principais fatores que influenciam as suas concentrações e, numa avaliação preliminar, estimar os níveis de ingestão destes isótopos pela população adulta da região. Os valores de concentração dos íons maiores nas águas variaram substancialmente, mostrando a influência da água do mar na composição das águas subterrâneas. Valores muito baixos de pH foram encontrados em uma específica área da região de estudo e a análise estatística enfatizou a forte influência das altas concentrações de íon hidrogênio nas altas concentrações de rádio encontradas. Baixas concentrações de radônio foram verificadas e são imputadas ao escape do gás diretamente dos poços de abastecimento. As concentrações de urânio em todas as amostras analisadas foram inferiores aos valores permissíveis. Das setenta e cinco amostras de água coletadas na região, dezessete tinham níveis de isótopos de rádio (Ra-226 e Ra-228) superiores aos níveis de radioatividade estabelecidos pelo Ministério Brasileiro de Saúde para água potável (0,1 Bq/l para alfa e 1 Bq/l para beta), sendo necessário avaliar o risco potencial para a saúde da população em decorrência da exposição a estes radioisótopos nas águas de abastecimento.

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INTRODUCTION

Radioactive isotopes behavior

The main naturally occurring radioactive isotopes that are found in ground water are the radium isotopes, radon and uranium. The main isotopes of radium, ^{226}Ra and ^{228}Ra , are generated in the natural radioactive series of uranium and thorium. The ^{226}Ra is an alpha emitter, whose half-life is relatively long (1602 years), it is produced from the sequential decay of five radioactive isotopes: $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{Pa} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra}$. The ^{228}Ra is a beta emitter, half-life 5.75 years, produced directly from the ^{232}Th decay. As an earth-alkaline metal, its chemical is basically characterized by sorption reactions. Radium concentration in surface waters normally ranges from 0.01 to 0.1 Bq.L⁻¹ (IYENGAR, 1990); the highest values have been found in waters close to uranium mining and milling (PASCHOA *et al.*, 1979). Nevertheless, in groundwater the concentration can reach values up to 38 Bq/L, that will be depend on factors such as kind of aquifer rock and chemical and physical water characteristics (GASCOYNE, 1989). A very important factor affecting the radium concentration in waters is the salinity. Based on groundwater data, a positive correlation between salinity and radium has been observed (KRAEMER & REID, 1984; LANGMUIR, 1985; BAEZA *et al.*, 1995). This increasing of radium concentrations in saline groundwater has been explained by the competition among Ra and cations for site adsorption on solids, resulting in the release of Ra to the aqueous phase (MOORE & SHAW, 1998).

^{222}Rn is an inert radioactive gas also daughter product of the ^{238}U chain ($^{226}\text{Ra} \rightarrow ^{222}\text{Rn}$). So, the source of ^{222}Rn in groundwater is ^{226}Ra incorporated in aquifer matrix. As the ^{226}Ra decays, its daughter ^{222}Rn diffuses into the pore waters of rock formations and becomes concentrated in the aqueous phase. Provided that there is no escape of ^{222}Rn from groundwater system, the radionuclide remains in solution in the aquifer until the groundwater is discharged or until it decays through a series of chemically reactive daughter products to stable ^{206}Pb . A worldwide survey of groundwater indicated a ^{222}Rn mean concentration of about 183 Bq/L (NCRP, 1984).

Uranium concentrations in ground waters range from 0.1 and 10 mg/L (Osmond, 1980). The uranium migration in water-rock system is largely controlled by uranium solution-mineral equilibrium and sorption reactions. Complexing of uranyl carbonate inhibits uranyl adsorption especially in alkaline solutions (His and Langmuir, 1985) and uranyl complexes with hydroxide, carbonate, fluoride, sulfate or

phosphate can predominate in oxidized waters (LANGMUIR, 1978).

Basis for risk assessment

The risks to health from radioactive isotopes in water have been matter of concern worldwide. The protection agencies have established maximum contaminant levels (MCLs), a level of a contaminant that ensures the safety of the water over a lifetime of consumption. The MCL for combined ^{226}Ra and ^{228}Ra is 0.185 Bq/L and for total alpha is 0.555 Bq/L. It is estimated that the additional lifetime risks associated with drinking water containing 0.185 Bq/L is about 1 in 10000. This means that if 10000 people were to consume two liters of this water per day for 50 years, one additional fatal cancer would be estimated among the 10000 exposed individuals (USEPA, 1996). The Brazilian legislation proposed a maximum allowable value of 0.1 Bq/L for total alpha and 1 Bq/L for total beta, above which the Brazilian Nuclear Energy Commission should be consulted. For ^{222}Rn the MCL is not yet established, the proposed limit is 150 Bq/L. Natural U is classified as both a radiological and a chemo-toxicological agent and it is the only radioactive substance for which chemical toxicity is the limiting factor in risk assessments. The MCLs for U is 20 mg/L (USEPA, 1996).

Survey region

The Região dos Lagos is located 150 km east far from Rio de Janeiro City, between W 42° 42', S 23° 00' and W 41° 50', S 22° 31' geographic coordinates. The total area investigated was 1900 km², and 257 km² of that are formed by well known tourist lakes and lagoons. According to least census conducted by *Fundação Instituto Brasileiro de Geografia e Estatística* (IBGE, 2000) there are 340000 inhabitants, 10% of that are living in the rural area. The inhabitants of villages and rural areas are totally supplied by water from homeowner's wells without any previous treatment.

The objective of this study were to verify the natural levels of radionuclides in the groundwater, to identify the main factors influencing the radioisotope concentrations and in a first approach to estimate the natural radionuclide intake levels by the adult inhabitants of this region.

MATERIAL AND METHODS

Main characteristics of study area

The Região dos Lagos has a semi-arid climate with the mean annual temperature around 22.5 °C, the mean air moisture is 80% and the main wind direction is from NE. The

mean annual precipitation is between 900 e 1000 mm and the mean annual potential evaporation is 1600 mm, resulting in a net negative water balance of 600 a 700 mm per year. The shape of the costal line, the main wind direction (NE) (responsible for deposit marine aerosols) and the negative water balance are the main factors influencing the large occurrence of ground water with medium and high salinity, ALMEIDA & LIMA (2000).

The Região dos Lagos has a rich geologic environment with pre-Cambrian rocks and recent Quaternary sediments, REIS & MANSUR (1985). Among the pre-Cambrian units, the Região dos Lagos unit is the most important, covering about 85% of the study region. The Região dos Lagos unit is composed of granitic gneisses and heterogeneous migmatites. The mineralogy of granitic gneisses includes quartz, microcline, plagioclase, biotite and some accessories as magnetite, ilmenite, apatite and zircon. BRANCO (1979) related a strong relationship between some Pre-Cambrian rocks like granitic and gnaisses and the presence of monazite. CASTRO (1979) studying the geochemistry of some breccias in the region found some opening associated to faults system, largely with a

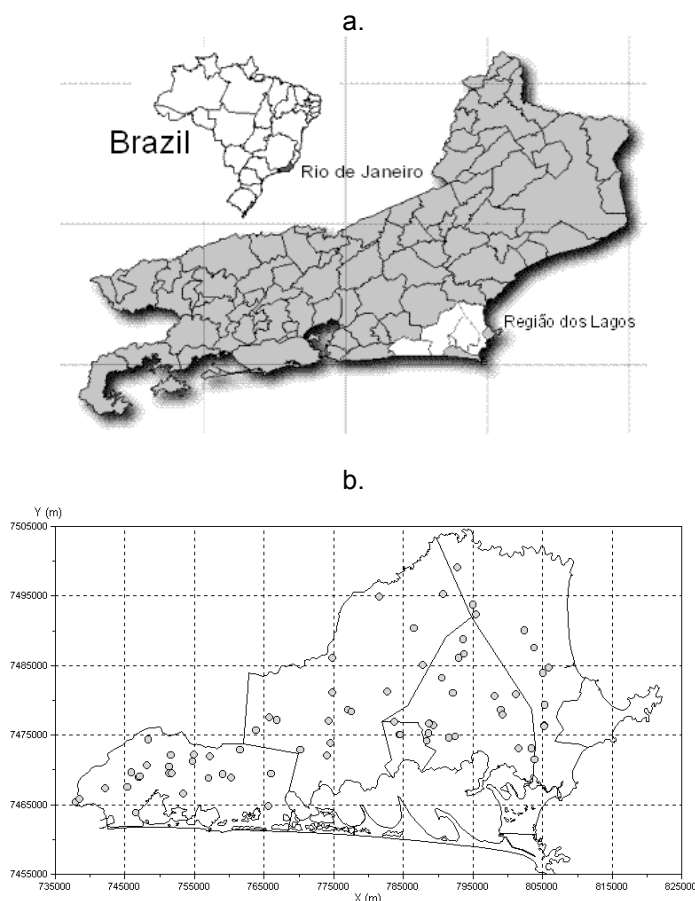
chalkcedonic matrix, exhibit important anomalous grades of Ba, which probably indicates the existence of significant Ba minerals.

The hydrogeology features are defined by the geologic, lithologic structural and geomorphologic characteristics. Partially eroded metamorphic fractured rocks are covered by altered material in the slopes and hills and by sandy and clayed Quaternary sediments in the valleys. The main aquifers are unconfined, their recharge is local, and water table levels are shallow, between 5 and 10 meters below ground surface. In the rural area the groundwaters are pumped from homeowner's dug wells with diameter of about 1 meter.

Sampling and Analysis of the samples

Groundwater samples from springs, domestic wells, hole wells and deep wells were collected during the months of October and September of 2000. Eighty-eight water samples spread across 1900 km² area resulting in about 22 km²/well were sampled, encompassing 5 municipal districts of the region (Saquarema, Araruama, Iguaba Grande, São Pedro da Aldeia and Cabo Frio), the sampling location are shown on Figure 1.

Figure 1: a. Map of Brazil with location of Rio de Janeiro State and study area Região dos Lagos; b. Location of the sampling points in the study area.



The well owner pumps were used for the sampling the waters. On the other hand, for sampling of wells without a pump a submerged portable 12V electric pump was used. Sampled water was discharged until the stabilization of some physical chemistry parameters like pH, temperature, and CE (electric conductivity) was reached. A 20 ml capacity syringe was connected to the pump rubber hose, and 10 mL of the water was sampled. Then this sample was immediately shaken with 10 mL of toluene containing scintillators in a scintillator vial. These samples were taken to the laboratory as soon as possible for the ^{222}Rn determination by a low background liquid scintillation spectrometer. (Manjon et al, 1997).

For the other determinations, about 3.1 L were sampled: 2 L in a polyethylene bottle for radium; 1 L in a polyethylene bottle for alkalinity; 20 mL for major cations and 40 mL for anion determinations. For major cations 20 mL of the water were filtered with a filter, 0.45 mm, connected to a syringe, and stored in a polyethylene centrifuge tube. The solution was acidified with 0.1 mL 65% concentrated Suprapur HNO_3 . Another 40 mL were filtered and stored in a polyethylene centrifuge tube, for anion determination. The sample for alkalinity as well as the one for anion determination were stored in 4°C prior to analysis.

Analysis for anions determinations were performed on the anion unacidified aliquot for Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-} by ion chromatography. The acidified aliquot was analyzed for the major cations and metals by inductively coupled plasma atomic emission spectrograph (ICP-AES) and for ^{238}U by inductively coupled plasma-mass spectrometry, ICP-MS, Perkin-Elmer SCIEX ELAN 6000 (GODOY *et al.*, 2001).

The major ions, metals and alkalinity were analyzed by LAMIN, the Laboratory of Mineral Analysis of CPRM, the Brazilian Geological Survey.

Using 1-liter sample, ^{228}Ra and ^{226}Ra were analyzed by total alpha and beta counting, after radium co-precipitation as $\text{Ba}(\text{Ra,Pb})\text{SO}_4$, purification with nitrilotriacetic acid (NTA) followed by radium re-precipitation and filtration of the sulphate precipitate (GODOY *et al.*, 1994). Alpha and beta activities were counted in a low-background anticoincidence proportional detector (Bertold, model: LB770-1). As a method routinely used at IRD laboratories, its analytical performance is routinely tested through the participation in inter-laboratory exercises organized by different international organizations as the EML/U.S.DOE, New York, MAPEP/RESL/U.S. DOE, Idaho Falls, and the

PNI/IRD/ CNEN, Rio de Janeiro (VIANNA *et al.*, 1998).

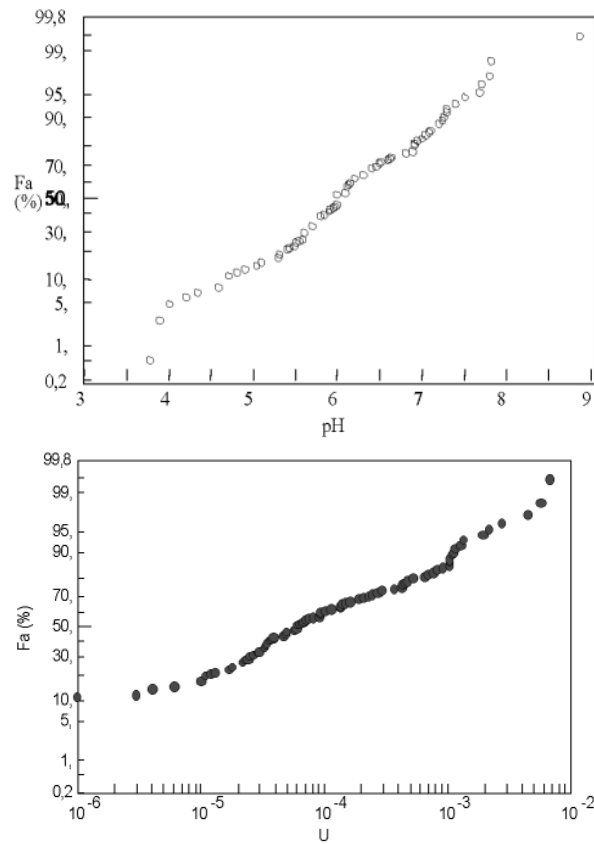
RESULTS AND DISCUSSION

For each variable, the distribution of the combined data was verified by the curve of accumulated frequency (MILLER and MILLER, 1989). The best correlation coefficients were found for a lognormal fit. Therefore, as usually observed in environmental samples, the concentrations of the variables are better represented by the log-normal distribution and the central tendency is then represented by the geometric average (median) (WAYNE, 1990). The major ion composition of the groundwaters and the ^{222}Rn , ^{226}Ra , ^{228}Ra and ^{238}U are given on Table 1 as medians, geometric standard deviations and minimum and maximum values.

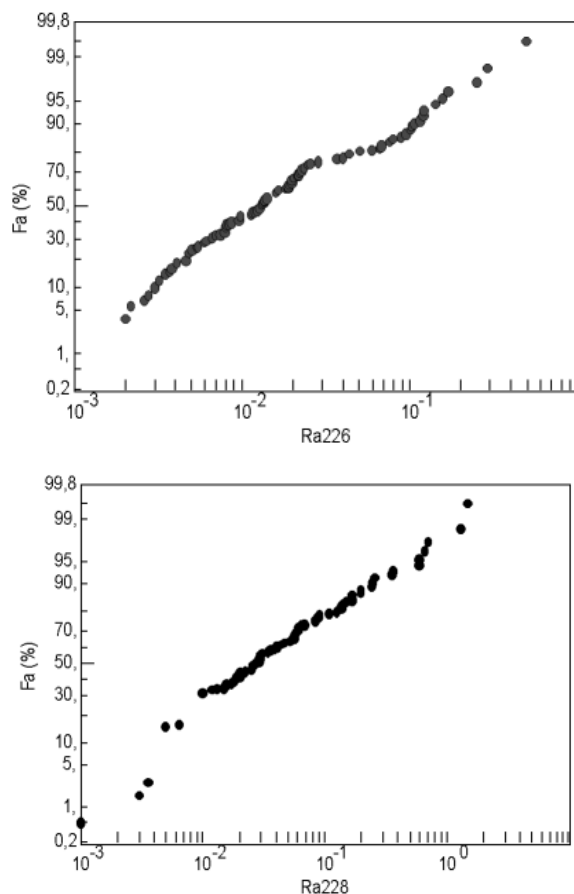
The ranges of concentrations were from $<2.0 \cdot 10^{-3}$ to 0.49 Bq/L for ^{226}Ra , from $<8.0 \cdot 10^{-3}$ to 1.50 Bq/L for ^{228}Ra and from $<1.0 \cdot 10^{-4}$ to $8.0 \cdot 10^{-2}$ Bq/L for ^{238}U . Detectable ^{222}Rn concentrations (>3 Bq/L) were found in only two samples. All the determined variables showed a wide range of values. The conductivity varied from 63 to 19100 μS and pH values varied from 3.77 to 8.87. On Figure 2 and 3 is shown the cumulative frequency distribution plot of pH values and ^{238}U , ^{226}Ra and ^{228}Ra concentration values.

Table 1: Median, geometric standard deviation and minimum and maximum values of pH, Eh, conductivity and the concentration of the major ions, radium isotopes, ^{222}Rn and ^{238}U in ground waters from Lake's Region.

Variable	Median (geo std. dev.)	Minimum-maximum
pH	6.04 (1.19)	3.77-8.87
Eh (mV)	345 (1.67)	48-565
Conductivity ($\mu\text{S}/\text{cm}$)	494 (2.96)	63-19110
^{226}Ra (Bq/L)	0.022 (4.12)	<0.002 -0.492
^{228}Ra (Bq/L)	0.256 (7.67)	<0.01 -1.50
^{238}U (mg/L)	$8.35 \cdot 10^{-5}$ (7.52)	$<2 \cdot 10^{-4}$ -6.67 10^{-1}
Rn (Bq/L)		<3 -75
HCO_3^- (mg/L)	36 (4.84)	<0.5 -742
CO_3^{2-} (mg/L)	0.05 (2.14)	<0.05 -47
SO_4^{2-} (mg/L)	27 (5.64)	0.1-3984
NO_3^- (mg/L)	3.0 (8.46)	<0.1 -145
Cl^- (mg/L)	78 (5.45)	9-30517
Ca^{2+} (mg/L)	8.5 (5.07)	0.8-565
Mg^{2+} (mg/L)	7.0 (5.16)	0.9-1858
Na^+ (mg/L)	65 (4.95)	5.4-17750
K^+ (mg/L)	5.2 (3.89)	1.7-810

Figure 2: Cumulative frequency distribution plots showing the distribution of pH and ^{238}U concentration values.**Table 2:** Speciation of ground water samples with highest Uranium concentration.

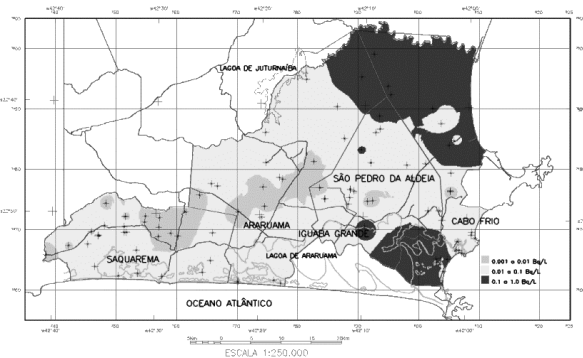
Sample ID	Field pH	U [mg/L]	$\text{UO}_2 \text{ OH}^+ [\%]$	$\text{UO}_2^{+2} [\%]$	$\text{UO}_2 \text{ CO}_3 [\%]$	$\text{UO}_2 \text{ H}_3\text{SiO} [\%]$	$\text{UO}_2 \text{ F}^+ [\%]$	$\text{UO}_2 \text{ (CO}_3)_2^{-2} [\%]$	$\text{UO}_2 \text{ SO}_4 [\%]$	Total [%]
SPA-095	5.7	8.2e-9	52.58	17.08	5.10	10.52	9.36	0.00	4.79	99.43
SPA-035	7	2.8e-8	61.86	1.14	23.28	8.01	2.08	0.89	0.34	97.59
CFR-075	7.08	1.2e-8	67.63	1.30	21.39	6.82	0.00	1.24	0.80	99.19
CFR-053	4	9.2e-9	5.99	90.63	0.01	0.16	1.24	0.00	1.60	99.62
CFR-072	6.9	1.9e-8	76.60	3.07	15.61	1.68	0.03	0.75	0.74	98.49

Figure 3: Cumulative frequency distribution plot of ^{226}Ra and ^{228}Ra concentration values.

The correlation analysis for uranium showed a significant correlation among its concentration and Conductivity, Ca, Mg, Na, K and Cl, at the 0.05 level (2-tailed). This result probably indicates a seawater influence because these ions are common in sea water. The highest concentration of uranium was found in samples with high concentrations of sulfate and bi-carbonate. However, all analyzed samples had U concentration value lower than the recommended uranium maximum allowable value for drinking water. The samples that presented the highest U concentrations were speciated using the geochemical model PHREEQC (PARKHURST, 1995). On Table 2 it is shown the results of speciation modeling for U. As observed by Langmuir (1978), the principal complexes in the samples with about neutral pH values are hydroxide and carbonate complexes, comprising of about 80% of the total dissolved uranium. For a sample with the lowest pH value, the uranyl ion UO_2^{2+} comprises about 90 % of the total dissolved U. On the other hand, the fluoride, sulfate and phosphate complexes do not play a significant role in the uranium migration in those waters.

On Figure 4 the spatial distribution of the ^{226}Ra activity concentration values is shown. It is

of interest to note that spatial distribution of Radium concentration delineate some large continuous areas, provably due to the homogeneous rock and soil distribution. The principal area with highest water Ra concentration corresponds to the area of low pH values (in some case <4.0) in the NE of the study area. The reason for such low pH values remain unclear, but it seems to be a combination of acidic precipitation concentrated by evapotranspiration, lack of carbonate buffers in soil, and equilibrium with ferric oxides and hydroxides.

Figure 4: Spatial distribution of ^{226}Ra concentration

The second anomaly is found in the region with EC values higher than $2000 \mu\text{S}\cdot\text{cm}^{-1}$, close to the lagoon Araruama.

The radium speciation is shown on Table 3. It is evident that besides of the free radium, Ra^{2+} , by far the most significant is RaSO_4^0 complex. In sample CFR-075 with high concentration of sulfate (almost 10 mmol/L), this complex accounts for about 40 % of total dissolved radium.

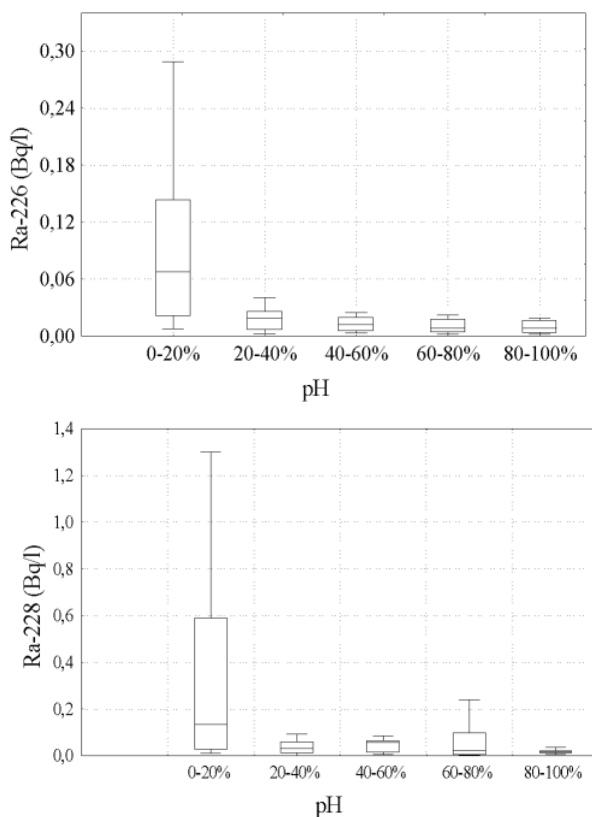
Table 3: Speciation of Ra for selected samples.

1	pH	Ra [mg/L]	Ra^{2+} [%]	RaSO_4^0 [%]	RaCl^+ [%]	Total [%]
SPA-095	5.7	6.48×10^{-10}	76.5	23.3	0.1	99.9
SPA-035	7.0	5.20×10^{-10}	74.9	24.8	0.3	100
CFR-010	3.8	1.36×10^{-9}	84.4	14.6	0.9	99.9
CFR-075	7.1	5.23×10^{-10}	59.7	39.9	0.4	100

The correlation analysis between Ra and other variables showed only a significant negative correlation between the radium isotope concentrations and the pH values. None of major ion concentrations showed significant statistical correlation with Ra isotope concentrations, and there was not found a significant correlation between the radium isotopes and the conductivity or salinity values.

Trying to improve the identification of factors influencing the observed Ra concentrations, the data-set was sorted according to increasing pH and conductivity values and divided into five 20-percentile groups. The distributions are presented as "box and whisker" plots, where the box contains the interquartile (25-75 percentile) range of data, with a horizontal line at median value (figure 5).

Figure 5: Distribution of the pH values and radium isotopes in 20 percentile categories: 0-20% (pH 3.77-5.33); 20-40% (pH 5.33-5.99); 40-60% (pH 5.99-6.18); 60-80% (pH 6.18-6.84); 80-100% (pH 6.84-8.87)

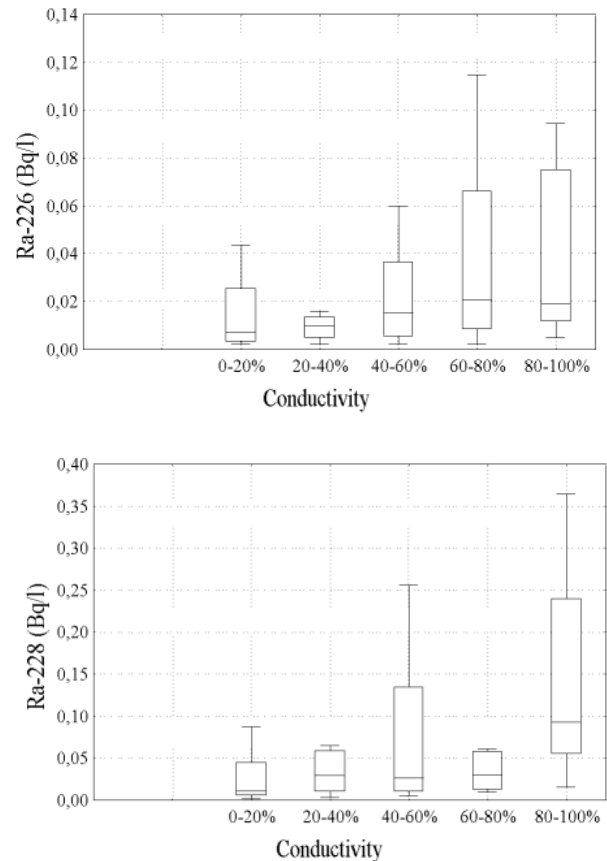


Parentheses above and below the median value show the 95% confidence interval for the median as can be seen on Figure 6. It can be noticed that only on percentile 0-20% (pH between 3.75-5.33) the radium concentration median value is higher than that one of the other percentiles, thus from 20 to 100% the median value is quite constant. Consequently, this result suggests no directly relationship between pH values and radium concentration, but stress the strong influence of low pH values on high radium concentrations.

On the other hand, the conductivity influence on the radium concentration was not so clear as for pH, Figure 6. For ^{226}Ra a small increase at the concentration median value could

be noticed from 60-80% percentile (from 936 μS), whereas for ^{228}Ra the influence can only be observed from 1714 μS (80-100% percentile).

Figure 6: Box-plots showing the distribution of radium isotope concentrations according to conductivity values in 20 percentile categories: 0-20% (CE 63-225); 20-40% (CE 225-430); 40-60% (CE 430-936); 60-80% (CE 936-1714); 80-100% (Cond. 1714-20100)



There is an abundance of ferric oxides and hydroxides in tropical soils of the region. These minerals act as adsorbents and they have a variable surface charge depending on pH range (LANGMUIR, 1997; APPELO and POSTMA, 1999). When pH is low, surface charge is highly positive with resulting repulsion of cations (DREVER, 1982). When pH value increases, there also is increasing adsorption of cations (so called adsorption edge). Thus, at low pH values radium present as Ra^{2+} remains mobile in ground water. A primary source of Ra is unknown, but it can be accessory uranium and thorium in monazite

Except by the samples SPA-095 (75 Bq/L) and SPA-100 (35 Bq/L), all the samples had ^{222}Rn concentrations lower than 3 Bq/L, the minimum activity concentration of the employed method. This is inconsistent with expected secular equilibrium with radium, especially taking

into account elevated dissolved radium concentrations in some areas. However, this may be related to de-gassing of radon into vadose zone followed by its escape through ground surface. Also, some wells had a large diameter and it can be assumed that at least a part of radon escaped from ground water during storage of ground water in wells.

Spatially, see Figure 4, it could be observed two very well defined regions of high radium concentrations, one in the area of low pH and the other one in the region whose conductivity value is higher than 2000 μS , whose values are higher than the recommended value for drinking water (Ministério da Saúde), being necessary to assess the potential risks from exposure to these radionuclides in the waters.

CONCLUSIONS

In a general way, this work brings a contribution to the knowledge of the behavior and distribution of radionuclides in groundwater of costal areas in tropical environment. High radium concentrations in the NE of the area of the Região dos Lagos are related to low pH values (in some cases <4.0). The low pH value have a direct impact on the adsorption behavior of Ra. Ferric oxides and hydroxides in soils have highly positive charge at the pH range and radium present in cationic form as Ra^{2+} is not adsorbed and remains in ground water. Contrary to a common opinion, the Ra concentration did not

show a good correlation with the salinity. The potential original source of radium is accessory thorium and uranium in monazite. Higher dissolved uranium concentrations in ground water close to the Araruama Lagoon were attributed to the formation of carbonate and hydroxide complexes. There was a significant correlation between uranium concentration and EC, Ca, Mg, Na, K and Cl. These results probably indicate sea water impact on the concentration of uranium in ground water. Finally, generally low concentrations of radon found even in samples with high radium concentrations were probably a consequence of radon de-gassing. It was found that 19% out of the eighty-eight samples had Ra concentrations exceeding the maximum allowable values recommended by the Brazilian Health Ministry for tap water, whereas the observed uranium and radon concentrations were lower than the maximum allowable values.

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