

^{226}Ra , ^{228}Ra and ^{210}Pb DETERMINATION IN SURFACE WATER AND GROUNDWATER BY LIQUID SCINTILLATION COUNTING

Lígia S. Faria¹ and Rubens M. Moreira²

Centro de Desenvolvimento da Tecnologia Nuclear (CDTN / CNEN – MG)
Av. Presidente Antônio Carlos 6.627
31270-901 Belo Horizonte, MG
¹ligsfaria@gmail.com
²rubens@cdtn.br

ABSTRACT

The municipalities of Brumadinho and Nova Lima are located in the metropolitan region of Belo Horizonte city, in the State of Minas Gerais. These two sites are important due to being located inside an Environmental Protection Area inserted in the Iron Quadrangle. In addition to the mineral wealth, the region has geological features that include quartz conglomerates associated with uranium and a significant groundwater potential exhibiting quite peculiar and complex hydrogeological features, such as the quartzite aquifer itself. Nuclear techniques applied to hydrology, such as Liquid Scintillation Counting technique (LSC), make possible the evaluation of natural radioactivity in surface water and groundwater. The objectives of this study were the determination of the activities of the long half-life radionuclides of the uranium and thorium series, such as ^{226}Ra , ^{228}Ra and ^{210}Pb , and provide an effective methodology to define if the direct consumption of these waters can cause risk to health due to its radioactivity. The results were compared with the recommendations of the Ministry of Health.

1. INTRODUCTION

Most countries in the world that use groundwater to meet their needs have exhibited accelerated growth in its use. [5] However, aquifers become elements of extreme importance because they represent valuable water supplies with potential use for human consumption [6].

Studies conducted in high natural radioactivity areas have been assessed for biological damage to humans due to prolonged exposure to low doses of ionizing radiation, basically due to natural radionuclides of uranium 238 (^{238}U) and thorium 232 (^{232}Th) series having relatively long half-lives [7]. Almost all isotopes of uranium and thorium series which have long half-lives decay by alpha particle emission. The alpha particle has a short range, its main radiation hazard comes when it is inhaled or ingested, because of the exposure pathway, particularly alpha particles emitted by uranium that due to their solubility can be present in food or water. [4].

The municipalities of Brumadinho and Nova Lima, areas chosen for the development of this work, are located in the metropolitan region of Belo Horizonte. They are important municipalities because of their significant hydro potential, which the local population using groundwater and surface water as a supply for both domestic and industrial consumption. In the 70's and 80 decades various uranium prospecting initiatives were conducted in the Iron

Quadrangle, specifically targeting the location of radioactive metaconglomerates, and found several occurrences of uranium and thorium ores. So the assessment of radioactivity in the water became important [6]. According to the Ministry of Health [9], every region that presents an occurrence of radioactive elements should characterize its groundwater for radiochemicals.

Precise and accurate measurements of radionuclides in low concentrations are required in monitoring activities and research in environmental areas. The importance of obtaining knowledge of the radionuclide concentrations in water is very valuable, as these appear as one of the main driveway of natural radionuclides into the human body [6].

2. MATERIALS AND METHODS

2.1. Sampling points

The Nova Lima and Brumadinho municipalities are located in the Environmental Protection Area to the southeast of the Metropolitan Region of Belo Horizonte city and are inserted in the Iron Quadrangle (Fig. 1) [5].

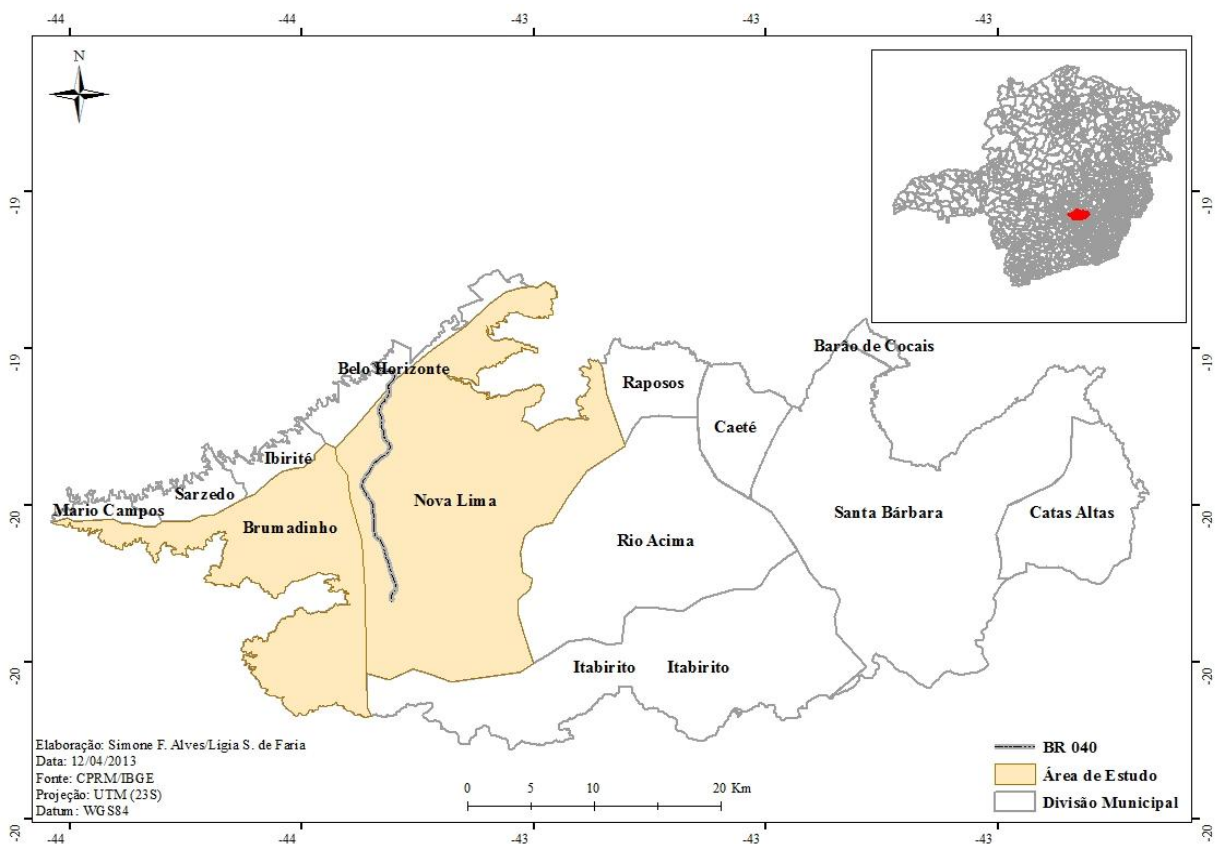


Figure 1: Location of the participating municipalities of APA South RMBH and their areas of study [6].

The ^{226}Ra , ^{228}Ra and ^{210}Pb levels were determined in four sampling stations, three of which (surface water) are sited in Brumadinho and a fourth station (groundwater) is sited in Nova Lima. In all the stations the same aquifer was sampled (Quartzito Aquifer System). The sampling stations are shown in Fig. 2.

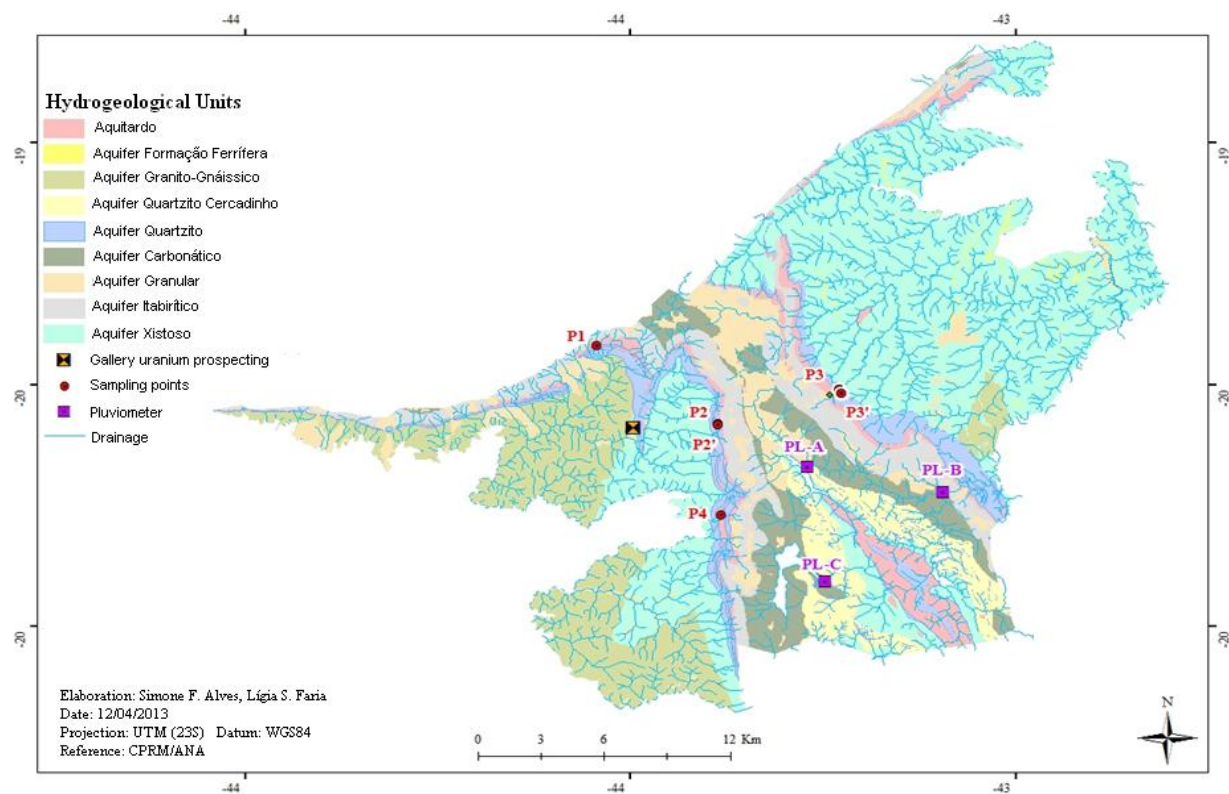


Figure 2: Representation of the location of collection points [6].

Point P2 has a different characteristics compared to the other points; in periods of drought the water emerges in places of lower altitudes, but sharing the same flow, so some samples were taken at the point P2'. Point P3 is the only in which groundwater was sampled. Water samples were collected at different wells, however, they share the same aquifer and flow in the hydrological system.

2.2. Sample preparation

The samples were collected in plastic bottles of 1 liter and acidified with nitric acid (HNO_3) 70%, to a $\text{pH} < 2$ to prevent the loss by adsorption of the radionuclides to be determined. When necessary they were filtered prior to acidification to prevent the release of radioactive material adsorbed on particulate matter [2,6].

The samples were pre-concentrated with barium and lead carriers. Precipitated $\text{Ba}(\text{Ra})\text{SO}_4$ and PbSO_4 were transferred to polyethylene counting vials. The scintillator cocktails used to determine radium were Instagel and Ultima Gold AB. The lead precipitate was solubilized

with EDTA and NH₄OH, its concentration was determined by Čerenkov counting [8]. The activity of the radium and lead were determined using equations (1), (2) and (3) [6].

$$A_{226} = f_{226} \cdot \frac{I_{2\alpha corr}}{60 \cdot E_{2\alpha}^{226} \cdot \delta \cdot Q \cdot Y} \quad (1)$$

where:

A_{226} = ²²⁶Ra activity in the sample (Bq L⁻¹).

$f_{226} = e^{-\lambda t}$ is correction factor in radium activity due to decay.

$I_{2\alpha corr}$ = sample corrected counting rate in high energy α window (count min⁻¹).

δ = is growth fraction.

$E_{2\alpha}^{226}$ = counting α efficiency for ²²⁶Ra standard solution.

Q = quantity of sample (L).

Y = m_{exp}/m_{theor} is chemical yield of BaSO₄. m_{exp} is Ba(Ra)SO₄ mass obtained and m_{theor} is Ba(Ra)SO₄ mass calculated by quantity of Ba carrier added.

$$A_{228} = f_{228} \cdot \frac{I_{1\beta corr}}{60 \cdot E_{1\beta}^{228} \cdot \delta \cdot Q \cdot Y} \quad (2)$$

where:

A_{228} = ²²⁸Ra activity in the sample (Bq L⁻¹).

$f_{228} = e^{-\lambda t}$ correction factor in radium activity due to decay.

$I_{1\beta corr}$ = sample corrected counting rate in low energy β window (count min⁻¹).

δ = growth fraction.

$E_{1\beta}^{228}$ = counting efficiency for ²²⁸Ra standard solution in low energy β window.

Q = quantity of sample (L).

Y = m_{exp}/m_{theor} is chemical yield of BaSO₄. m_{exp} is Ba(Ra)SO₄ mass obtained and m_{theor} is Ba(Ra)SO₄ mass calculated by quantity of Ba carrier added.

$$A_{Pb} = \frac{cpm_a - cpm_b}{60 \cdot CCE \cdot R \cdot V [1 - \exp(-\lambda t)]} \quad (3)$$

where:

A_{Pb} = ²¹⁰Pb activity in the sample (Bq L⁻¹).

cpm_a = counting rate of sample (count min⁻¹).

cpm_b = counting rate of blank (count min⁻¹).

CCE = counting efficiency for Čerenkov radiation.

R = m_e/m_t chemical yield of lead. m_e is PbSO₄ mass obtained and m_t is PbSO₄ mass theoretical.

V = quantity of sample (L).

λ = the decay constant of ²¹⁰Pb (0,138 days⁻¹).

t = time passed between the precipitation of PbSO₄ and the count time (days).

The chemical yields of Ra/Pb were not satisfactory, but there was a low variance between samples, which indicates stability in the methodology applied.

The liquid scintillation counting technique (LSC) has advantages such as reducing the background and measurement of ultra low activities. It is ideal for various areas of monitoring and control of environmental radioactivity of vital importance for nuclear installations including the Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) which has a liquid scintillation spectrometer (Quantulus 1220TM - Perkin Elmer/Wallac) for analysis of low activity radionuclides.

3. RESULTS AND DISCUSSION

The reference values for radioactivity in water for consumption an aim to provide criteria for assessing the safety of consumption of drinking water taking into account the content of radionuclides present. The indicative values of radioactivity in drinking water recommended by the World Health Organization (WHO) have been based in the relation of exposure risks and consequences to health [10].

According to WHO, the values of the activities of the long long-lived of radionuclides (²²⁶Ra, ²²⁸Ra and ²¹⁰Pb) shall comply with the reference values (Maximum Allowable Values–MAV's) [10]. In 2011, the Ministry of Health [9] amended the level of screening to ²²⁶Ra and ²²⁸Ra that define the potability of water from the radiological point of view, the limit are set in table 1.

Table 1: Reference values for radionuclides of series ²³⁸U and ²³²Th.

Radionuclides	Reference values (Bq L ⁻¹)
²²⁶ Ra	1,0
²²⁸ Ra	0,1
²¹⁰ Pb ^a	0,1

a.Value defined by WHO.

The groundwater and surface water samples were collected once a month during thirteen months. The detection limit was determined for each nuclide, the data are presented in table 2 [6].

Table 2: Detection limit values ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb.

Radionuclides	Detection limit (Bq L ⁻¹)
²²⁶ Ra	0,002
²²⁸ Ra	0,036
²¹⁰ Pb	0,111

The concentrations of ²²⁸Ra, ²¹⁰Pb, and ²²⁶Ra found in the water samples collected in the point P1 are shown in Fig. 3.

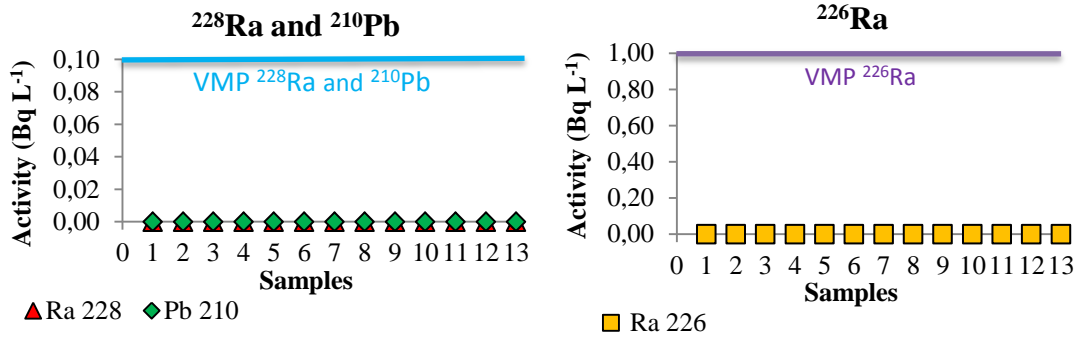


Figure 3: Sampling results in point P1.

At the point P1 the samples presented concentrations below the detection limit, therefore, below the MAV. This surface water is used to supply a housing complex, and taking into account the radioactivity limits for water quality, these samples demonstrated there is no risk of a dose that compromises human health.

Samples of point 2 (P2 and P2') also showed low activities for the three nuclides, except for the sample collected in July (sample 7) at the point P2' which showed a concentration of 0.052 ± 0.002 Bq L⁻¹ for ²²⁸Ra (Fig. 4).

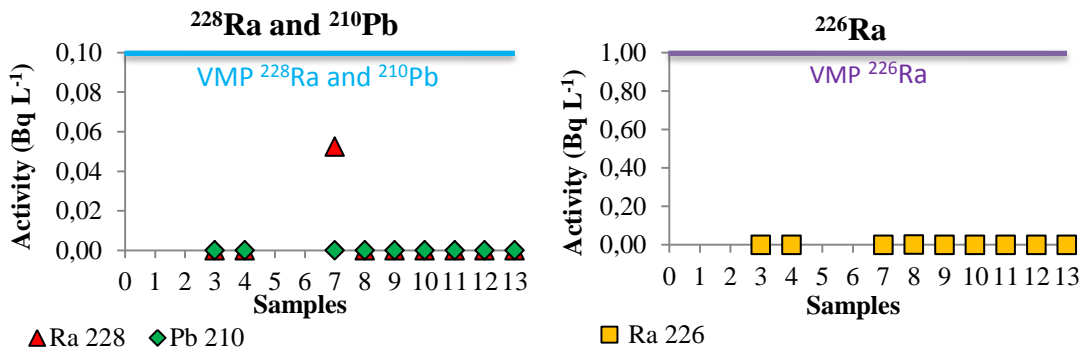


Figure 4: Sampling results in point P2.

Samples collected at the point P3 showed maximum concentrations of 0.130 ± 0.046 Bq L⁻¹ for ²²⁶Ra and 0.096 ± 0.005 Bq L⁻¹ for ²²⁸Ra. All the results on the activities of ²¹⁰Pb samples were below detection limit. The values obtained from samples collected at point P3 for ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb are graphically presented in Fig. 5.

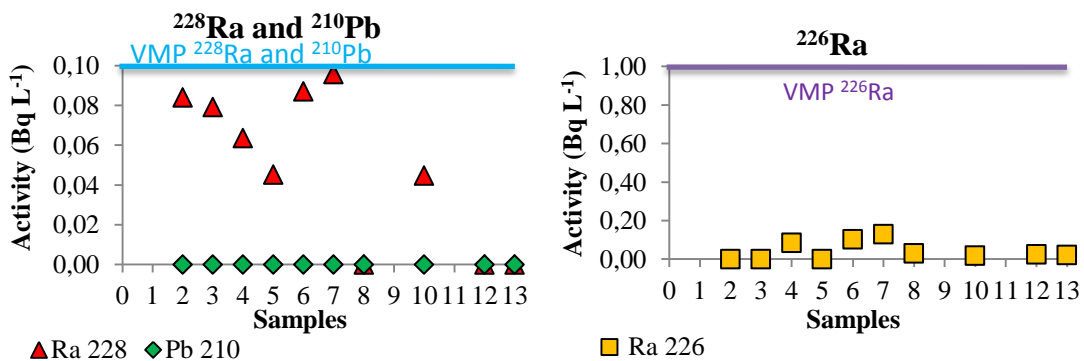


Figure 5: Sampling results in point P3.

To verify a possible presence of uranium and thorium dissolved in water, Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used. The values from point P3 relative to sample concentrations are below the detection limit for thorium. However, the concentration for uranium ranged from $0.053 \mu\text{g L}^{-1}$ to $0.068 \mu\text{g L}^{-1}$. The relationship obtained between the concentrations of uranium and ^{226}Ra activity is shown in Fig. 6 [6].

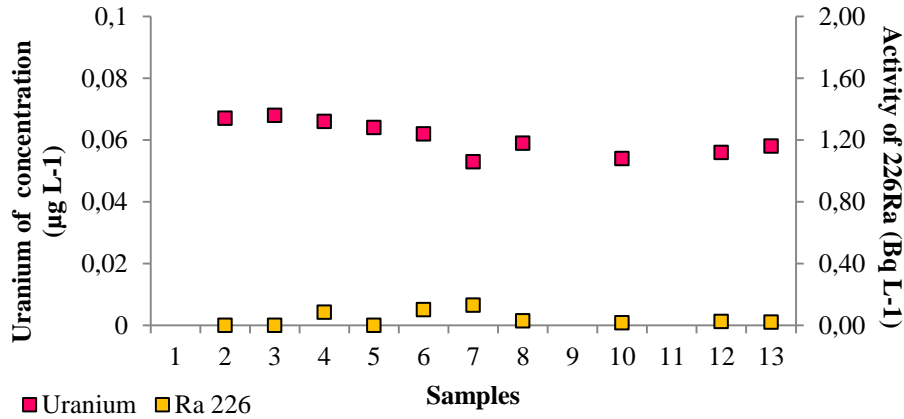


Figure 6: Uranium behavior and ^{226}Ra in water samples at point P3.

The results may indicate a relationship between the concentration of uranium and ^{226}Ra activities obtained in samples collected at P3. It is observed that in this case the uranium concentration decreased while the activity of ^{226}Ra tended to increase [6].

The uranium concentration was compared with the monthly rainfall index data obtained from the National Water Agency [1] to check the occurrence of possible seasonal variations. The pluviometric stations were chosen according to the proximity to collection points and the topography of the region. The location of these points can be seen in Fig. 2.

The relationship with rainfall was investigated. In Fig. 7 it may be noticed that the uranium concentration decreased with low rainfall and at the initial period of the rainy season the increase of uranium dissolved in water was more intense. According to Bonoto [3], this behavior occurs due to dissolution of uranium in the strata of aquifers during the infiltration of rainwater.

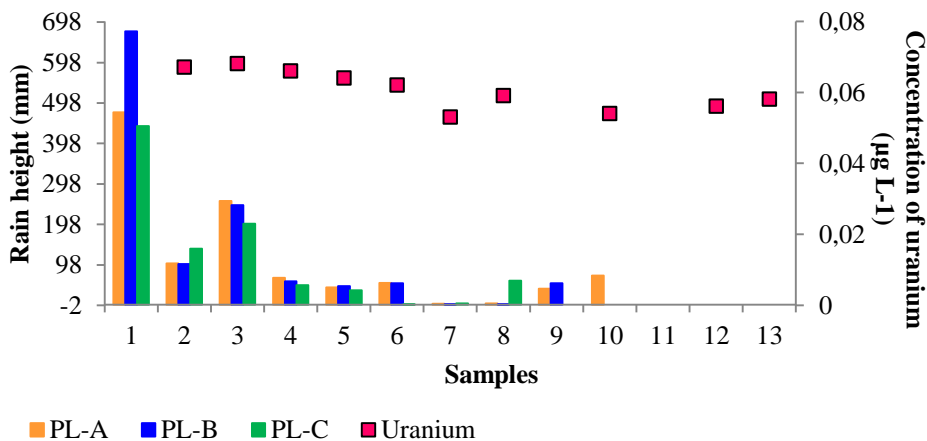


Figure 7: Relationship between rainfall and uranium concentrations at the point P3.

At the P4 collection station, the maximum concentration obtained was July (7) which showed an activity of $0.040 \pm 0.002 \text{ Bq L}^{-1}$ for ^{228}Ra , in the August (8) the concentration of ^{226}Ra was $0.012 \pm 0.005 \text{ Bq L}^{-1}$. The other samples present activities below the detection limit (Fig. 8).

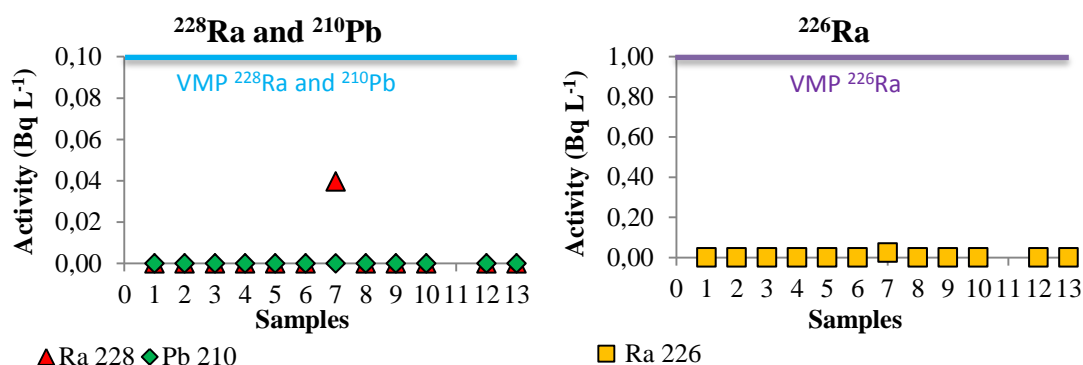


Figure 8: Sampling results at point P4.

4. CONCLUSIONS

The LSC technique used in the determination of ^{226}Ra , ^{228}Ra and ^{210}Pb was efficient for monitoring environmental samples with low activity. According to the standard specified by the Ministry of Health regarding the level of radioactivity of water used for human consumption, all samples analyzed for approximately one year of collection, had concentrations within the potable water standards, taking into account radioactivity levels.

ACKNOWLEDGMENTS

The authors are grateful to Raquel Maia Mingote by teachings of the technique applied in this work and Helena Eugênia L. Palmieri by analyzing the uranium and thorium samples. This research project is supported by the following Brazilian institutions: Nuclear Technology Development Center (CDTN), Brazilian Nuclear Energy Commission (CNEN), Research Support Foundation of the State of Minas Gerais (FAPEMIG), and Brazilian Council for Scientific and Technological Development (CNPq).

REFERENCES

1. “AGÊNCIA NACIONAL DAS ÁGUAS,” www.hidroweb.ana.gov.br (2013).
2. AGUDO, E. G. *et al. Guia de coleta e preservação de amostras de água*. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, Brazil (1988)
3. BONOTO, D. M. Utilização de modelo isotópico de urânio no estudo de aquíferos do morro do ferro, Poços de Caldas (MG). *Revista Brasileira de Geociências*, [S.l.], vol.24, n. 1, p.52–59, 1994.

4. CAMARGO, Iara Maria Carneiro. *Determinação da concentração dos isótopos naturais de urânio e tório em amostras de água*. 1994. 90 f. Dissertação (Mestrado em Ciências) – Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 1994.
5. DAVIS, E. G.; PINTO, E. J. A.; PINTO, M. C. F. *Projeto APA Sul estudos do meio físico: Hidrologia*. Belo Horizonte: CPRM/SEMAD/CEMIG, Brazil (2005).
6. FARIA, Lígia Santana de. *Determinação da radioatividade natural de águas subterrânea e superficial de Brumadinho e Nova Lima, Brasil*. Belo Horizonte, Brazil (2013).
7. MALANCA, A.; REPETTI, M.; MACÊDO, H. R. Gross alpha and beta activities in surface and ground water of Rio Grande do Norte, Brazil. *Appl. Radiat. Isot*, **v.49**, p.893-898, (1998).
8. MINGOTE, Raquel Maia. *Desenvolvimento de metodologia para determinação de ²¹⁰Pb em água usando o efeito Čerenkov*, Belo Horizonte, Brazil (2006).
9. “Vigilância da qualidade da água para consumo humano,” Ministério Da Saúde. Ms N° 2914/201, www.saude.gov.br/svs/pisast, (2011).
10. WORLD HEALTH ORGANIZATION, Guidelines for Drinking-water Quality (2011).