https://doi.org/10.1590/S1413-415220200044

Technical Article

Naturally-Occurring Radioactive Materials at water treatment plant on the Poços de Caldas Plateau Region, Brazil

Materiais Radioativos de Ocorrência Natural em estações de tratamento de água no Planalto de Poços de Caldas, Brasil

Adriano Mota Ferreira[1]*, Henrique Takuji Fukuma[2], Rafael Brito de Moura[1], Alexandre Silveira[1], Rafael Oliveira Tiezzi[1], Raul Alberto Sodré Villegas[2]

ABSTRACT

Oil and gas, mining, among others, are examples of facilities where naturally occurring radioactive materials can be found. This study aims to evaluate the presence of natural radioactive series, especially those of ^{238}U and ^{232}Th, in the water treatment plants of Poços de Caldas City, Minas Gerais. The presence of these series was investigated in samples of raw water, treated water, sludge from decanters, and scale from Parshall gutters. The sludge, input, and scale samples were submitted to the gamma spectrometry technique to determine the ^{226}Ra, ^{228}Ra, and ^{210}Pb radionuclides. For U and Th, ultraviolet visible spectrophotometry was performed, and for the alpha and beta total values, radiochemical separation and subsequent alpha and beta total counts were performed. The results indicate that water samples are within the Ministry of Health Ordinance n° 5 (2017). Due to the different concentrations of radionuclide activity in the sludge, it was not possible to affirm the same order of magnitude with the sediment from the catchments. However, the values are in accordance with those established by the European Union Council for Naturally-Occurring Radioactive Materials. In the scale, the contents of 1192, 1704, and 301 Bq kg^{-1} were identified for ^{226}Ra, ^{228}Ra, and ^{210}Pb, respectively. In the inputs of aluminum sulfate and calcium hydroxide, no relevant activities were identified. The results obtained in the study can serve as an indicative regarding the need for a more detailed evaluation of the radiological issue in question concerning public water supplies.

Keywords: *norm*; uranium; radium; water treatment; sludge.

RESUMO

Petróleo e gás, mineração, estações de tratamento de água, entre outros, são exemplos de instalações que podem apresentar Materiais Radioativos de Ocorrência Natural. Neste estudo, objetivou-se avaliar a presença de séries radioativas naturais, especialmente as de ^{238}U e ^{232}Th nas estações de tratamento de água da cidade de Poços de Caldas/MG. Foram investigadas as presenças dessas séries em amostras de água bruta, de água tratada, no lodo dos decantadores e nas incrustações das calhas Parshall, além dos principais insumos utilizados. As amostras de lodo, insumos e incrustações foram submetidas à técnica de espectrometria gama para a determinação dos radionuclídeos ^{226}Ra, ^{228}Ra e ^{210}Pb. Para U e Th, realizou-se espectrofotometria ultravioleta-visível, e para os valores de Alfa e Beta totais foram realizadas separação radioquímica e posterior contagem Alfa e Beta total. Os resultados indicaram que as amostras de águas estão em conformidade com a Portaria de Consolidação nº 5 de 2017 do Ministério da Saúde. Dadas as diferentes concentrações de atividade dos radionuclídeos no lodo, não foi possível afirmar a mesma ordem de magnitude com o sedimento das captações. Entretanto, os valores estão consonantes com o estabelecido pelo conselho da União Europeia para Materiais Radioativos de Ocorrência Natural. Nas incrustações foram identificados teores de 1.192 $Bq.kg^{-1}$, 1.704 $Bq.kg^{-1}$ e 301 $Bq.kg^{-1}$ para ^{226}Ra, ^{228}Ra e ^{210}Pb, respetivamente. Já para os insumos Sulfato de Alumínio ($Al_4(SO_4)_3$) e Hidróxido de Cálcio $Ca(OH)_2$ não foram identificadas atividades relevantes. Os resultados obtidos no estudo podem servir como indicativos da necessidade de uma avaliação mais detalhada sobre a questão radiológica em foco, em relação ao abastecimento público de águas.

Palavras chave: *norm*; urânio; rádio; tratamento de águas; lodo.

[1]Universidade Federal de Alfenas – Alfenas (MG), Brazil.
[2]Comissão Nacional de Energia Nuclear – Poços de Caldas (MG), Brazil.
***Corresponding author:** adrianomotaferreira@gmail.com
Conflicts of interest: the authors declare no conflicts of interest.
Funding: Minas Gerais Research Foundation (FAPEMIG).
Received: 03/19/2019 – **Accepted:** 02/16/2021 – **Reg. ABES:** 20200044

INTRODUCTION

NORM stands for naturally occurring radioactive materials (O'BRIEN *et al.*, 1998). These materials are found in the earth's crust and are part of or can be used in various industrial processes. Examples are mining of various metals, which are usually associated with radioactive elements in the oil and gas industry, among others (HARIDASAN *et al.,* 2015). Once they have been used in the processes mentioned above, the radioactive materials found in a given raw material or input may undergo changes in concentration and thus may be concentrated in products, by-products, or waste (LAURIA *et al.*, 2007).

According to the International Atomic Energy Agency (IAEA, 2014), the most abundant radioisotopes in nature are ^{226}Ra, an alpha emitter with a half-life of 1622 years, and ^{228}Ra, a beta emitter with a half-life of 5.8 years. Both are decay products of the ^{238}U and ^{232}Th natural series, respectively, and are the radioisotopes of greatest radiological toxicity due to their relatively long half-lives. In addition, the chemical behavior of radium is similar to that of calcium; therefore, radium is deposited in the human body, mainly in the bones (AL-JASEEM *et al.,* 2016).

Another important point regarding the presence of NORM concerns the water supply. Recently, researchers in Brazil have shown an increased interest in radioactivity, such as Fianco (2011) and Corrêa *et al.* (2015), both associated with ^{222}Rn in well water. Radioactivity may be present in water sources as a result of natural processes or from disposing of radioactive materials (LAURIA *et al.*, 2007). Considering that the water distributed in the supply goes through a water treatment plant (WTP), these environments are suitable for monitoring the presence of NORM.

WTPs have been considered by several authors as NORM industries, because the water that is treated may contain certain radionuclides due to the geological means in which their catchments are found (GÄFVERT *et al.,* 2002; FONOLLOSA *et al.,* 2015; CERNY *et al.,* 2017). Another important factor to be mentioned regarding NORM in water treatment is the type of treatment applied during the whole process (e.g., coagulation, flocculation, decantation, and filtration) (FONOLLOSA *et al.,* 2015; LYTLE *et al.,* 2014).

Hill *et al.* (2017) monitored the concentrations of iron, manganese, ^{226}Ra, and ^{228}Ra at different stages of the treatment process for later comparison in terms of removal efficiency and interaction between these elements. Leier *et al.* (2019) studied 18 treatment plants in Estonia and found high concentrations of ^{226}Ra and ^{228}Ra, of which they accumulate in the filter material, at a level where the material can be classified as radioactive material. Of the WTPs studied, 16 exceeded the levels allowed in the adopted legislation. Although there have been several studies, Shin *et al.* (2016) pointed out the shortage of studies on mineral water treatment processes associated with filtration processes in numerous countries. Torres *et al.* (2017) studied the risk perception in certain groups in relation to the management of NORM and water in the oil and gas industry. The authors affirmed the lack of study on the risk perception and impacts in North Dakota (USA).

In addition to natural radionuclides, studies show the presence of artificial radionuclides in WTP and sewage treatment plant (COSENZA *et al.*, 2015; MULAS *et al.*, 2017; MARTÍNEZ *et al.*, 2018).

The Poços de Caldas Plateau presents "radioactive anomalies," in which there are regions with levels of natural radioactivity above those usually observed on the earth's surface (ROSA, 2012). It also has a large hydrographic system distributed in anomalous areas, where the uranium mining industry was started in Brazil between 1970 and 1980 (OLIVEIRA, 1993; WILLIAMS *et al.*, 2001).

In the study area of Poços de Caldas where the WTP is located, radioactive residues can be produced in the sludge samples found in decanters or in washing water from filters, where radionuclides can accumulate, as suggested in the studies by Palomo *et al.* (2010) and Montaña *et al.* (2013).

Thus, the radiological analysis of sludge samples is extremely useful as it can provide valuable information about the presence of radionuclides in the water samples received from these plants without often analyzing them directly. Therefore, the sludge samples can be used as a sensitive indicator of the radiological content of the water entering the treatment plants (SUNDELL-BERGMAN *et al.,* 2008; MARTÍNEZ *et al.,* 2018).

Waste generated in WTPs has been discarded directly into water bodies without any type of treatment for a long time in Brazil (LIBÂNIO, 2010). According to Di Bernardo *et al.* (2005), from the qualitative and quantitative points of view, the waste generated in WTPs is a major problem for institutions that are responsible for this, including sludge from WTPs, according to the NBR 10004 (ABNT, 2004a) (Brazilian standard), considered as solid waste.

Another concern is the presence of iron and manganese in this sludge, which is often associated with a WTP. According to Moruzzi *et al.* (2012), iron and manganese ions cause deposits and scales in the treatment plants. In parallel, according to Moore *et al.* (1973), the formation of iron and manganese hydroxides produces an important mechanism concerning the removal of radium from the water, and radium coprecipitation with barium, calcium, magnesium, iron, and manganese salts can occur.

Due to a lack of research in the literature, mainly in Brazil, a study focusing on the water quality for public supplies is urgently needed, as well as a control of the waste generated in the treatment process. This work aimed to evaluate the presence and concentration of radioactive species activity in the water (raw and treated), sludge from decanters, scale from Parshall gutters, and inputs used in WTPs.

METHOD

Study area

The municipality of Poços de Caldas is located in the south-southwest mesoregion of the State of Minas Gerais (MG). In the geological context, the area called the Alkaline Massif in Poços de Caldas, from the Cretaceous period, was formed from a complex of effusive rocks, and mainly intrusive, originating from a volcanic process. The intrusion occurred in domains of the crystalline basement, and the mass surrounded by granites, gneisses, and precambrian migmatites is of high-degree metamorphic, polycyclic, and polydeformed, belonging to the Guaxupé Massif (CHRISTOFOLETTI, 1973; TINÓS *et al.*, 2014). Oliveira (1993), adds that after this event of intrusion, several rocky manifestations occurred, causing numerous rich mineral deposits, mainly in Zr, Mo, U, Th, V, K, Mn, and Fe, while intense hydrothermal actions were processed through eruptive rocks.

According to Ellert (1959), four types of lithology occurred in the interior of the Alkaline Massif:

i. effusive and hypabyssal rocks (tinguaite and phonolite);
ii. plutonic rocks (nepheline syenites, lujaurites, and chibinites);
iii. breaches, tufts, and conglomerates; and
iv. potassic rocks (associated with metasomatic processes).

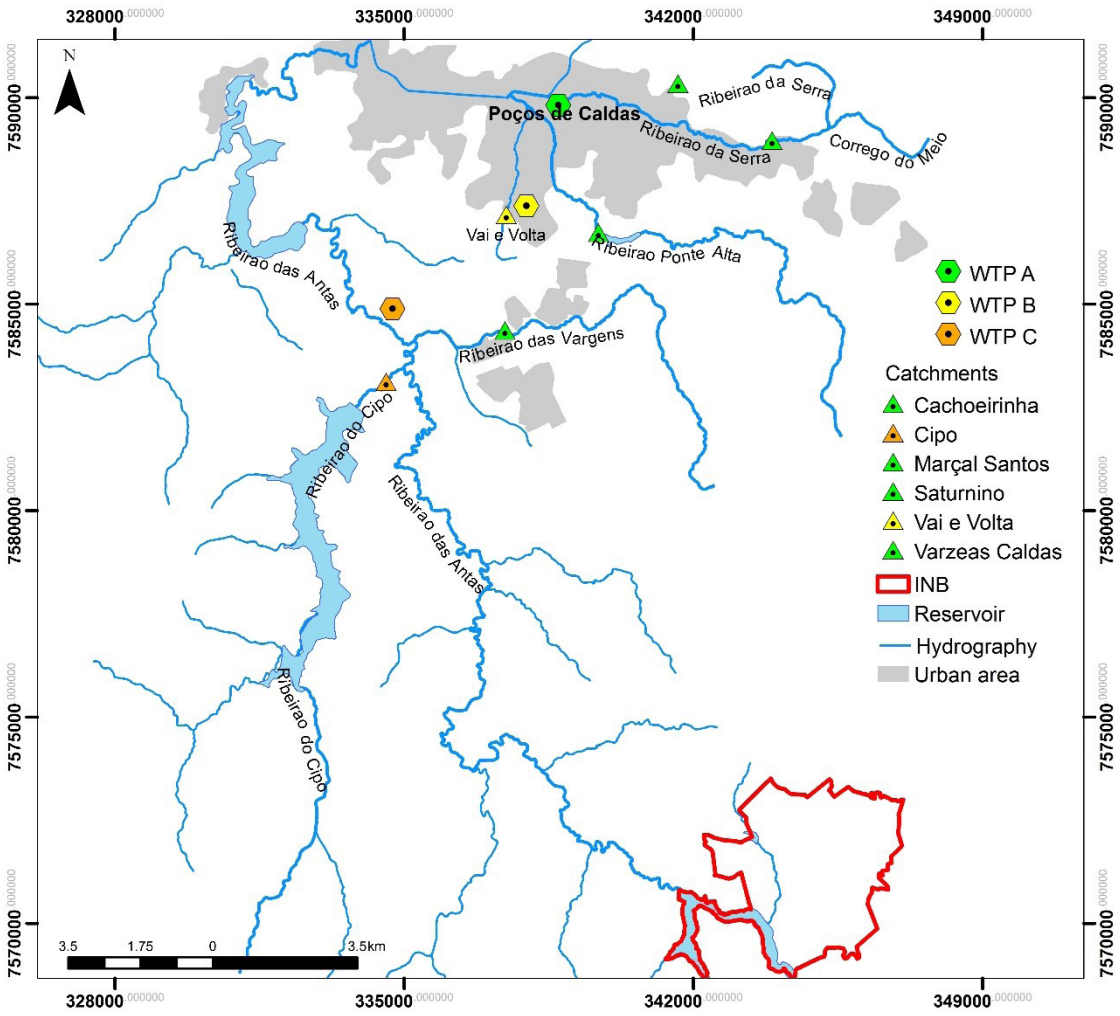
The massif stands out for the intense fracturing and hydrography strongly controlled by lithology and the fracture system (Tinós *et al.*, 2014).

The dry season occurs from mid-April to the beginning of September. The maximum drought is normally in July. The rainfall index varies between 1100 and 1700 mm, with the driest month oscillating between January and February (MORAES, 2007).

Currently, the municipality's water treatment system has three WTPs which are presented in this work as follows: WTP A responsible for 200 L s^{-1} with a catchment area including the *Ribeirão da Serra*, *Córrego Marçal Santos*, and *Represa Saturnino de Brito*; WTP B responsible for 80 L s^{-1} with a catchment area including the *Córrego Várzea de Caldas* and *Córrego Vai e Volta*; and WTP C accounting for 280 L s^{-1} with a catchment area including the *Ribeirão do Cipó*. The location is shown in Figure 1.

Sampling

In the water treatment system for local public supplies, samples were collected from raw water, treated water, inputs used in the treatment process (i.e., aluminum sulfate [$Al_2(SO_4)_3$] and calcium hydroxide [$Ca(OH)_2$]), inlay present in the three WTPs, Parshall flumes, and sludge from the decanters. The raw water samples were collected at the WTP catchment and the treated water sample was collected at the WTP output, after the treatment processes. The sludge samples were collected directly in the decanters when they were emptied for cleaning. The flasks used for collecting both raw and treated water samples had a capacity of 5 L. The buckets to collect the sludge from the decanters had a capacity of 20 L. Moreover, spatulas were used for scraping the Parshall gutters. The input and scale samples were collected at their sources, which were inputs obtained prior to mixing in the treatment and the scraped scale from the Parshall gutter



Source: Author.

Figure 1 – Location of the study area.

walls. The samplings were carried out according to the Brandão *et al.* (2011) and the NBR 10007 (ABNT, 2004b).

Four sampling campaigns were conducted for both raw and treated water at the three WTPs. For the sludge generated in the decanters, three sampling campaigns were carried out. For the scale samples, four campaigns were conducted. In the latter, it was only possible to diagnose and scrape the scale from WTP C. Finally, for the chemicals used, only one sampling campaign was carried out. The established analytical methodology is described below.

Analytical Methodology

The gamma spectrometry technique was used to determine radionuclides ^{226}Ra, ^{228}Ra, and ^{210}Pb in the sludge, input, and scale samples previously treated in the Canberra GX4510 range detector.

In the method used for the determination of thorium, it is extracted from the aqueous solution using tri-n-octylphosphine oxide (TOPO) in cyclohexane medium, followed by re-extraction in aqueous solution. This reagent does not extract these interferers, except for zirconium, whose interference is eliminated using oxalic acid and ascorbic acid. After fluoride, sulfate, phosphate, and other ions have interfered in forming precipitates or complexes with the thorium ion, the determination is carried out in a strong acidic medium.

In the determination of uranium, the method is based on the separation by tri-n-butyl-phosphate (TBP) of a solution containing $Al(NO_3)_3$, EDTA, and tartaric acid. This is followed by a re-extraction of uranium with arsenazo (III) solution in pH 3 buffer containing sodium fluoride. The reaction with arsenazo (III) generates a stable red-violet complex whose absorption is measured at 650 nm for uranium and 665 nm for thorium. Both were read on the Varian spectrophotometer (Cary 50), using the ultraviolet (UV)-visible spectrophotometry technique. The Tennelec Canberra Model S5-XLB Low Gaseous Flow Proportional Counter was used for radiochemical separation and alpha and beta total counting.

Finally, after the triplicate analyses were carried out, the results were plotted with the uncertainty values, which express the degree of variability of the measure, in this case, the true value with 95% uncertainty, compared with each other and with results available in the literature.

RESULTS AND DISCUSSION

The analytical results obtained[1] for both raw and treated water are shown in Table 1. To compare the results of alpha and beta activities, Ordinance n° 5 from the Brazilian Ministry of Health), September 28, 2017, was considered, which follows the procedures for controlling and monitoring drinking water quality standards for human consumption (BRASIL, 2017). Guidelines for Drinking Water Quality from the World Health Organization (WHO, 2011) were also used. The organization recommends screening methods, i.e., measurements of total alpha and beta activities including values defined as 0.5 and 1 Bq L^{-1} for alpha and beta, respectively.

It was observed that the counts in the four sampling campaigns did not exceed the limits established by the WHO (2011) and the Ministry of Health Ordinance n° 5 (BRASIL, 2017), which were 0.5 and 1.0 Bq L^{-1} for alpha and beta total values, respectively. It is further defined in Ordinance n. 5 (BRASIL, 2017)that if the screening levels are exceeded, a specific analysis must be performed for the radionuclides present and the result should be compared with the reference levels established in Annex IX of the same Ordinance. It can be seen that considering the reference levels cited for ^{226}Ra (1 Bq L^{-1}) and ^{228}Ra (0.1 Bq L^{-1}), the results obtained for water samples are in accordance with the established parameters, as the detected activities are < 0.02 Bq L^{-1}. Similar values were found by Manu *et al.* (2014). The results found for ^{210}Pb are also less than 0.02 Bq L^{-1} in all the treatment plants. It is worth noting that although ^{210}Pb is not in the current ordinance, it is important from a radiological protection point of view because, according to the study by Smoak (1999), it may contribute significantly to the dose in an internal contamination scenario. Regarding the low concentration values of U and Th, the values are expected, since the alpha and beta total counts are within the established parameters. The results found are below the detection limit of the equipment and, although there is variation, this may be associated with factors such as sample rate or the presence of dissolved solids.

For the sludge samples, the results are presented in Figure 2. To compare the results obtained for the sludge from the WTPs, the concentrations found in the sediments of catchments A and C were raised in the Water Commission Technical Report (COMISSÃO DAS ÁGUAS, 2012). The objective of the report was to evaluate the water and sediment quality of the microbasins of the *Antas* stream and the *Caldas* stream on the Poços de Caldas Plateau. Based on the concentration values of the elements studied in the catchments, values were compared, since it is known that the characterization of the sludge produced during the water treatment process depends on the physicochemical nature of the raw water and the type and dosage of the product chemicals used during treatment (CORDEIRO, 1993).

In ^{226}Ra samples, the average of five campaigns of the Water Commission Technical Report (COMISSÃO DAS ÁGUAS, 2012) presented values of 113 and 214 Bq kg^{-1} for the catchments A and C, respectively. In the first campaign carried out, higher values were found in the three WTPs for ^{226}Ra, and in WTP C, the concentrations are within the proposed range of significance, being able to affirm the same magnitude of concentration of ^{226}Ra in sludge and catchment from the WTP. The same was observed for the second and third campaigns of WTP A, with concentration values within the range proposed for ^{226}Ra, as well as for the first and third campaigns carried out for the ^{210}Pb and the first campaign of Th.

No concentrations were found within the proposed range for ^{228}Ra, where the values available for the two WTPs show activity concentrations of 226 and 245 Bq kg^{-1} for WTP A and WTP C, respectively, which are above the values found in the sludge, except for the second campaign of WTP C, where the concentration is 287 ± 17 Bq kg^{-1}.

According to the study by Peñalver *et al.* (2020), possible factors that might influence the radioactive content included the geology, river flow rate, suspended particulate matter, turbidity, water treatment processes, and industrial activities in the area of the river basin.

The values of U consulted for a concentration of activity in the catchment sediment were 259 and 525 Bq kg^{-1}, respectively, for WTP A and WTP C.

[1]Preliminary results of this research were presented at the 2014 International Joint Conference RADIO by Ferreira *et al.* (2014).

Table 1 – Results of concentration levels for both raw and treated water.

WTP	Sample	^{226}Ra (Bq L^{-1})	^{228}Ra (Bq L^{-1})	^{210}Pb (Bq L^{-1})	U (Bq L^{-1})	Th (Bq L^{-1})	Alpha total (Bq L^{-1})	Beta total (Bq L^{-1})
First campaign								
A	Raw	< 0.02	< 0.02	< 0.02	< 0.18	< 0.01	< 0.06	< 0.06
	Treated	< 0.02	< 0.02	< 0.02	< 0.18	< 0.01	< 0.06	< 0.06
B	Raw	< 0.02	< 0.02	< 0.02	< 0.18	< 0.01	< 0.06	< 0.06
	Treated	< 0.02	< 0.02	< 0.02	< 0.18	< 0.01	< 0.06	< 0.06
C	Raw	< 0.02	< 0.02	< 0.02	< 0.18	< 0.01	< 0.09	< 0.09
	Treated	< 0.02	< 0.02	< 0.02	< 0.18	< 0.01	< 0.06	< 0.06
Second campaign								
A	Raw	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.48	< 0.65
	Treated	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.48	< 0.65
B	Raw	< 0.02	< 0.02	< 0.02	< 0.10	< 0.01	< 0.48	< 0.65
	Treated	< 0.02	< 0.02	< 0.02	< 0.05	< 0.01	< 0.48	< 0.65
C	Raw	< 0.02	< 0.02	< 0.02	< 0.20	< 0.01	< 0.48	< 0.65
	Treated	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.48	< 0.65
Third campaign								
A	Raw	< 0.02	< 0.02	< 0.02	< 0.061	< 0.102	< 0.47	< 0.84
	Treated	< 0.02	< 0.02	< 0.02	< 0.061	< 0.102	< 0.47	< 0.84
B	Raw	< 0.02	< 0.02	< 0.02	< 0.061	< 0.102	< 0.47	< 0.84
	Treated	< 0.02	< 0.02	< 0.02	< 0.061	< 0.102	< 0.47	< 0.84
C	Raw	< 0.02	< 0.02	< 0.02	< 0.061	< 0.102	< 0.47	< 0.84
	Treated	< 0.02	< 0.02	< 0.02	< 0.061	< 0.102	< 0.47	< 0.84
Fourth campaign								
A	Raw	< 0.02	< 0.02	< 0.02	< 0.02	< 0.10	< 0.47	< 0.84
	Treated	< 0.02	< 0.02	< 0.02	< 0.02	< 0.10	< 0.47	< 0.84
B	Raw	< 0.02	< 0.02	< 0.02	< 0.02	< 0.10	< 0.47	< 0.84
	Treated	< 0.02	< 0.02	< 0.02	< 0.02	< 0.10	< 0.47	< 0.84
C	Raw	< 0.02	< 0.02	< 0.02	< 0.02	< 0.10	< 0.47	< 0.84
	Treated	< 0.02	< 0.02	<0.02	< 0.02	< 0.10	< 0.47	< 0.84

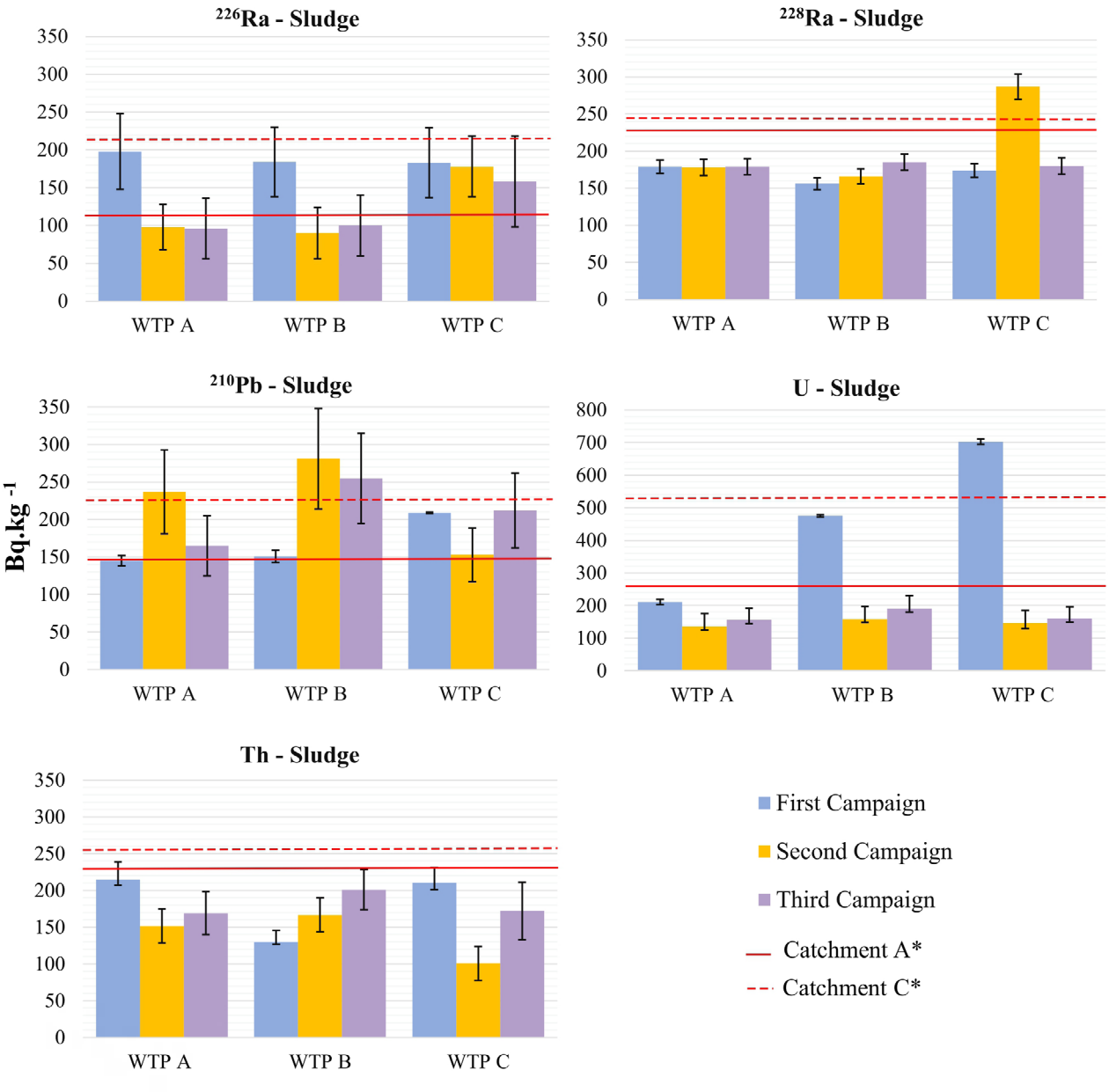
WTP: water treatment plants. Source: Author.

With the exception of the first campaign at stations B and C, the other results found are below 259 Bq kg^{-1}.

In the analytical results of the scale from WTP A, concentrations of practically negligible activities, as well as those from WTP B, are found. In the results from WTP C, higher levels were detected in the scale samples, as shown in Table 2. The determinations of ^{226}Ra, ^{228}Ra, and ^{210}Pb presented 1192, 1704, and 301 Bq kg^{-1}, respectively, and there was a decrease in the second campaign for the 619, 790, and 98 Bq kg^{-1} levels of ^{226}Ra, ^{228}Ra, and ^{210}Pb, respectively. In the third sample, the activity concentration levels of ^{226}Ra, ^{228}Ra, and ^{210}Pb increased. This was then followed by a decrease in the fourth sampling campaign. It is noteworthy that in this last sampling campaign, it was not possible to carry out scale sampling on the Parshall gutters of WTP A and WTP B because there was no precipitate on the walls of the gutters.

In addition to the disinfectant agent, the products used in the plants are $Al_2(SO_4)_3$ and $Ca(OH)_2$. Table 3 shows the results for the chemical samples used in the treatment. The activity concentrations of ^{226}Ra, ^{228}Ra, and ^{210}Pb are low and, in some cases, are below the detection levels of the analytical techniques used. A similar behavior was observed for U and Th concentrations. The low values found in the inputs indicate that there is no significant contribution in the total of radionuclides determined in other phases, i.e., the water source and the local environment.

The data collected in the literature for radionuclides in water treatment sludge are presented in Table 4.



Source: Author. *Adapted according Water Commission Technical Report (COMISSÃO DAS ÁGUAS, 2012).

Figure 2 – Results of concentration levels for sludge samples.

Table 4 shows very different values that are associated with the concentration of radionuclide activity in WTP residues. The values obtained in this study are in a smaller order of magnitude when compared with higher values in a study by Lytle *et al.* (2014). In most of the sampling campaigns, an increase in the levels of ^{228}Ra was observed. According to the literature, this increase in concentration is associated with the natural geochemical enrichment of ^{232}Th in relation to ^{238}U (IAEA, 2014). Although the results in the sludge showed concentrations that did not exceed the value of 1 Bq g^{-1} (1 kBq kg^{-1}) proposed by European Union (EU) member states to NORM, this situation was verified in the scale in two campaigns for ^{226}Ra and ^{228}Ra.

Although, in the water itself, no significant values of activity were detected, the concentration activities of ^{226}Ra, ^{228}Ra, and ^{210}Pb in the scale, especially of WTP C, deserve special attention. It was indicated that there is a possibility of concentration of these radionuclides by coprecipitation with manganese, an element found at a significant concentration in the water from the region (COMISSÃO DAS ÁGUAS, 2012). According to the study by Chałupnik *et al.* (2020) in situations where aeration processes are used to remove iron and manganese from water, iron hydroxide and manganese dioxide are produced, and radioisotopes are adsorbed on these materials (PATEL *et al.*, 1992).

Table 2 - Results of concentration levels for the scale samples.

INLAY	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	U (Bq kg^{-1})	Th (Bq kg^{-1})
First campaign					
A	69 ± 17	71 ± 4	37 ± 2	< 505.63	< 202.20
B	164 ± 41	226 ± 11	30 ± 2	< 505.63	< 202.20
C	1192 ± 298	1704 ± 85	301 ± 15	< 505.63	< 202.20
Second campaign					
A	69 ± 23	105 ± 9	66 ± 20	< 244	134
B	164 ± 41	252 ± 18	74 ± 19	< 244	< 103
C	619 ± 110	790 ± 52	98 ± 24	< 244	170
Third campaign					
A	22 ± 11	30 ± 3	24 ± 8	53 ± 15	21 ± 7
B	93 ± 19	128 ± 8	28 ± 9	158 ± 37	20 ± 7
C	1055 ± 180	1443 ± 84	205 ± 48	155 ± 35	93 ± 22
Fourth campaign					
A	-	-	-	-	-
B	-	-	-	-	-
C	555 ± 150	769 ± 46	78 ± 20	161 ± 15	126 ± 26

Source: Author.

Table 3 - Results for the chemical samples used in the treatment.

INPUT	^{226}Ra (Bq kg^{-1})	^{228}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	U (Bq kg^{-1})	Th (Bq kg^{-1})
$Al_4(SO_4)_3$	19 ± 5.00	7 ± 1.00	10 ± 1	< 505.63	< 202.20
$Ca(OH)_2$	4 ± 0.40	< 10.00	< 6.30	< 505.63	< 202.20

Source: Author.

Table 4 - Data collected in the literature.

	^{226}Ra	^{228}Ra	^{232}Th	^{238}U	^{210}Pb
	Bq kg^{-1}				
USEPA, 1993	590	-	7.4	150	-
Gaefvert *et al.*, 2002	-	-	4.5	63	230 - 368
Kleinschmidt *et al.*, 2008	6 - 120	-	-	-	10 - 110
Palomo *et al.*, 2010	-	-	4 - 30	19 - 590	10 - 1050
Kleinschmidt *et al.*, 2008	37 - 74	-	46 - 77	130 - 200	-
Chmielewska *et al.*, 2014	48 - 437	80 - 3654	-	15 - 49	-
Mola *et al.*, 2014	-	-	-	-	38 - 64
Baeza *et al.*, 2014	23 - 7140	-	-	-	-
Lytle *et al.* (2014)	111 - 9250	148 - 12987	-	-	-

The study of these radionuclides is of fundamental importance in Brazil, where WTP sludge is released directly into the rivers, as well as the scale of the WTP gutters.

There is no Brazilian legislation with parameters for these elements in WTP waste, especially because the legislation classifies this as solid waste. Thus, they must be classified by NBR 10004 (ABNT, 2004a) and sent to an appropriate destination.

A major factor in determining the activity concentrations found is characterized by different geological characteristics. It can be concluded that the activity concentrations in the WTP residues should be evaluated locally to determine their disposition (IAEA, 2014; GÄFVERT,*et al.* 2002; KLEINSCHMIDT *et al.*, 2008; PALOMO *et al.*, 2010; USEPA, 1993).

CONCLUSIONS

The results presented here show that, mainly, no significant presence of radionuclides was detected in the water provided to the population by the catchment and treatment system of Poços de Caldas.

The main waste from the water treatment, the sludge, presented different concentrations of radionuclides in different campaigns and WTP, when compared to the average of those found in the sediments of the study region. Although some values appear within the significance range, there is a need for better investigation and analysis with the values found in the region's sediments. The values are within those consulted in the literature and below the standard established by EU member states to NORM.

Although water does not present high values of radionuclides, Ra and Pb are possibly concentrated in the fouling present in the treatment tanks, by coprecipitation of manganese, which is the matrix of the precipitate.

In the inputs used in the WTPs, no relevant concentrations of activity were found.

It is suggested the need for a dose-based study, as well as the continuation of continuous sampling at WTP in its different phases, mainly in filtration, which was not investigated here.

ACKNOWLEDGEMENT

The authors acknowledge all the support received from: Brazilian Commission for Nuclear Energy/CNEN; Poços de Caldas Laboratory – LAPOC; Minas Gerais Research Foundation (FAPEMIG); Federal University of Alfenas – UNIFAL/MG and Water & Sewerage Department (DMAE). A special thanks to Prof. Dr. Rodrigo Leandro Bonifácio for the discussions that increased the quality of the manuscript. Last but not least, we dedicate this work to co-author and great friend Raul Villegas.

AUTHORS'CONTRIBUTIONS

Ferreira, A.M.: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. Fukuma, H.T.: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Project administration, Validation, Visualization and Writing – review & editing. Moura, R.B.: Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. Silveira, A.: Data curation, Formal Analysis, Investigation and Writing – review & editing. Tiezzi, R.O.: Data curation, Formal Analysis, Investigation and Writing – review & editing. Villegas, R.A.S.: Data curation, Formal Analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing.

REFERENCES

AL-JASEEM, Q.; ALMASOUD; F.; ABABNEH, A.; AL-HOBAIB, A. Radiological assessment of water treatment processes in a water treatment plant in Saudi Arabia: Water and sludge radium content, radon air concentrations and dose rates. *Science of The Total Environment*, v. 563-564, p.1030-1036, 2016. https://doi.org/10.1016/j.scitotenv.2016.04.049

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (ABNT). *NBR 10004*: Resíduos sólidos: classificação. Rio de Janeiro, 2004a.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (ABNT). *NBR 10007*: Amostragem de Resíduos Sólidos. Rio de Janeiro, 2004b.

BAEZA, A.; SALAS, A.; GUILLEN, J.; MUNOZ-SERRANO, A. Association of Naturally occurring radionuclides in sludges from drinking water treatment plants previously optimized for their removal. *Chemosphere*, v.97, p.108-114, 2014.

BRANDÃO, C.J.; BOTELHO, M.J.C.; SATO, M.I.Z.; AGÊNCIA NACIONAL DAS ÁGUAS (ANA); COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL (CETESB). *Guia nacional de coleta e preservação de amostras:* Água, Sedimento, Comunidades aquáticas e efluentes líquidos. Brasília: ANA, 2011.

BRASIL. Portaria de Consolidação nº 5, de 28 de setembro de 2017. Ministério da Saúde. Consolidação das normas sobre as ações e os serviços de saúde do Sistema Único de Saúde. *Diário Oficial da União*. Brasília: Ministério da Saúde, 2017.

CERNY, R.; OTAHAL, P.; MERTA, J.; BURIAN, I. Concentration of natural radionuclides in private drinking water wells. *Radiation Protection Dosimetry*, v. 177, n. 1-2, p. 190-193, 2017. https://doi.org/10.1093/rpd/ncx144

CHAŁUPNIK, S.; WYSOCKA, M.; CHMIELEWSKA, I.; SAMOLEJ, K. Modern technologies for radium removal from water – Polish mining industry case study. *Water Resources and Industry*, v. 23, p. 100125, 2020. https://doi.org/10.1016/j.wri.2020.100125

CHMIELEWSKA, I.; CHAŁUPNIK, S.; BONCZYK, M. Natural radioactivity in drinking underground waters in Upper Silesia and solid wastes produced during treatment. *Applied radiation and isotopes*: including data, instrumentation and methods for use in agriculture, industry and medicine, v. 93, p. 96-100, 2014. https://doi.org/10.1016/j.apradiso.2014.01.017

CHRISTOFOLETTI, A. *A unidade morfoestrutural do planalto de Poços de Caldas*. Notícias Geomorfológicas, v. 13, n. 26, p. 77-85, 1973.

COSENZA, A.; RIZZO, S.; SANTAMARIA, A.S.; VIVIANI, G. Radionuclides in wastewater treatment plants: monitoring of Sicilian plants. *Water Science and Technology*, v.71 n. 2, p.252-258, 2015. https://doi.org/10.2166/wst.2014.501

COMISSÃO DAS ÁGUAS. *Avaliação da qualidade das águas e sedimentos das microbacias do Ribeirão das Antas e do Ribeirão de Caldas no Planalto de Poços de Caldas*. Relatório técnico, 2012. Disponível em: https://www.pocosdecaldas.mg.leg.br/legislacao/gt_relatorio_tecnico_versao_cnen-inb_19-03-12.pdf. Acesso em: 3 jul. de 2018.

CORDEIRO, J.S. O problema dos lodos gerados nos decantadores em estações de tratamento de água. São Carlos: Escola de Engenharia de São Carlos, Universidade de São Paulo, 1993.

CORRÊA, J.N.; PASCHUK, S.A.; KAPPKE, J.; DENYAK, V.; SCHELIN, H.R.; DEL

CLARO, F.; PERNA, A.F.N.; REQUE, M.; ROCHA, Z.; SANTOS, T.O. Monitoramento da radioatividade alfa relacionada ao radônio-222 em águas de poços da Região Metropolitana de Curitiba-PR. *Engenharia Sanitária e Ambiental*, v. 20, n. 2, p. 243-249, 2015. https://doi.org/10.1590/S1413-41522015020000124599

DI BERNARDO, L.; DANTAS, A.D.B. *Métodos e técnicas de tratamento de água*. v. 2. São Carlos: RiMa, 2005.

ELLERT, R. Contribuição à Geologia do Maciço Alcalino de Poços de Caldas. *Boletim da Faculdade de Filosofia Ciências e Letras* – USP, v. 237, n. 18, p. 5-63, 1959. https://doi.org/10.11606/issn.2526-3862.bffcluspgeologia.1959.121851

FERREIRA, A.M.; FUKUMA, H.T.; VILLEGAS, R.A.S. Avaliação da presença de NORM no tratamento de água do município de Poços de Caldas – Resultados Preliminares. *In: International Joint Conference RADIO 2014*. Gramado: Brasilrad, 2014. Disponível em: https://inis.iaea.org/collection/NCLCollectionStore/_Public/46/034/46034398.pdf. Acesso em: 7 fev. 2019.

FIANCO, A.C.B. *Concentrações de radônio nas águas subterrâneas, rochas e solo de Porto Alegre, RS*. 99 f. Dissertação (Mestrado em Ciências) – Universidade Federal do Rio Grande do Sul, Porto Alegre, 2011.

FONOLLOSA, E.; NIETO, A.; PEÑALVER, A.; AGUILAR, C.; BORRULL, F. Presence of radionuclides in sludge from conventional drinking water treatment plants. A review. *Journal of environmental radioactivity*, v.141, 24-31, 2015. https://doi.org/10.1016/j.jenvrad.2014.11.017

GÄFVERT, T; ELLMARK, C.; HOLM, E. Removal of radionuclides at a waterworks. *Journal of environmental radioactivity*, v. 63, n. 2, p.105-115, 2002. https://doi.org/10.1016/s0265-931x(02)00020-6

HARIDASAN P.P, HARIKUMAR M, RAVI P.M, TRIPATHI R.M. Radiological protection against exposure to naturally occurring radioactive material. *Radiation Protection and Environment*, v.38, p.59-67, 2015.

HILL, L.; SUURSOO, S.; KIISK, M.; JANTSIKENE, A.; NILB, N.; MUNTER, R.; ISAKAR, K. Long-term monitoring of water treatment technology designed for radium removal–removal efficiencies and NORM formation. *Journal of Radiological Protection*, v. 38, n.1, p.1-24, 2017. https://doi.org/10.1088/1361-6498/aa97f2

INTERNATIONAL ATOMIC ENERGY AGENCY (IAEA). The Environmental Behaviour of Radium: Revised Edition. *Technical Report Series n. 476*, 2014.

KLEINSCHMIDT, R.; AKBER, R. Naturally occurring radionuclides in materials derived from urban water treatment plants in southeast Queensland, Australia. *Journal of environmental radioactivity*, v. 99, n.4, p. 607-620, 2008. https://doi.org/10.1016/j.jenvrad.2007.09.001

LAURIA, D. C.; MARTINS N. S. F.; ZENARO, R. Monitoração Ambiental. *Instituto de Radioproteção e Dosimetria*, v.01. p.166, 2007.

LEIER, M.; KIISK, M.; SUURSOO, S.; VAASMA, T.; PUTK, K. Formation of radioactive waste in Estonian water treatment plants. *Journal of Radiological Protection*, v. 39, n. 1, p. 1-10, 2019. https://doi.org/10.1088/1361-6498/aaed49

LIBÂNIO, M. *Fundamentos de qualidade e tratamento de água*. 3. ed. Campinas: Átomo, 2010. 496p.

LYTLE, D.A.; SORG, T.; WANG, L.; CHEN, A. The accumulation of radioactive contaminants in drinking water distribution systems. *Water Research*, v. 50, p. 396-407, 2014. https://doi.org/10.1016/j.watres.2013.10.050

MANU, A.; SANTHANAKRISHNAN, V.; RAJARAM, S.; RAVI, P.M. Concentration of Natural Radionuclides in Raw Water and Packaged Drinking Water and the Effect of Water Treatment. *Journal of Environmental Radioactivity*, v. 138, p. 456-59, 2014.https://doi.org/10.1016/j.jenvrad.2014.08.013

MARTÍNEZ, J.; PEÑALVER, A.; BACIU, T.; ARTIGUES, M.; DANÚS, M.; AGUILAR, C.; BORRULL, F. Presence of artificial radionuclides in samples from potable water and wastewater treatment plants. *Journal of Environmental Radioactivity*, v. 192, p. 187-193, 2018. https://doi.org/10.1016/j.jenvrad.2018.06.024

MOLA, M.; AVIVAR, J.; NIETO, A.; PEÑALVER, A.; AGUILAR, C.; FERRER, L.; CERDÀ, V.; BORRULL, F. Determination of ^{90}Sr and ^{210}Pb in sludge samples using a LOV-MSFIA system and liquid scintillation counting. *Applied radiation and isotopes*: including data, instrumentation and methods for use in agriculture, industry and medicine, v.86, p. 28-35, 2014. https://doi.org/10.1016/j.apradiso.2013.11.123

MONTAÑA, M.; CAMACHO, A.; SERRANO, I.; DEVESA, R.; MATIA, L.; VALLÉS, I. Removal of radionuclides in drinking water by membrane treatment using ultrafiltration, reverse osmosis and electrodialysis reversal. *Journal of Environmental Radioactivity*, v.125, p. 86-92, 2013. https://doi.org/10.1016/j.jenvrad.2013.01.010

MOORE, W.S.; REID, D.F. Extraction of radium from natural water using manganese impregnated acrylic fibers. *Journal of Geophysics Research*. v. 78, n. 36, p. 8880-8886, 1973. https://doi.org/10.1029/JC078i036p08880

MORAES, F.T. Zoneamento geomanbiental do Planalto de Poços de Caldas, MG/SP a partir de análise fisiográfica e pedoestratigráfica. 173f. Tese (Doutorado em Geociências e Meio Ambiente) – Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Rio Claro, 2007.

MORUZZI, R.B.; REALI, M.A.P. Oxidação e remoção de ferro e manganês em águas para fins de abastecimento público ou industrial – Uma abordagem geral. *Revista de Engenharia e Tecnologia*, v. 4, n. 1, p. 29, 2012.

MULAS, D.; CAMACHO, A.; SERRANO, I.; MONTES, S.; DEVESA, R.; DUCH, M. A. Natural and artificial radionuclides in sludge, sand, granular activated carbon and reverse osmosis brine from a metropolitan drinking water treatment plant. *Journal of Environmental Radioactivity*, v.177, p.233-240, 2017. https://doi.org/10.1016/j.jenvrad.2017.07.001

O'BRIEN, R.S.; COOPER, M.B. Technologically enhanced naturally occurring radioactive material (NORM): pathway analysis and radiological impact. *Applied radiation and isotopes*: including data, instrumentation and methods for use in agriculture, industry and medicine, v. 49, n. 3, p.227-239, 1998. https://doi.org/10.1016/s0969-8043(97)00244-3

OLIVEIRA, J. *Determinação de ^{226}Ra e ^{228}Ra em águas minerais da região de Águas da Prata*. 85 f. Dissertação (Mestrado em Ciências) – Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo, 1993.

PALOMO, M.; PEÑALVER, A.; AGUILAR, C.; BORRULL, F. Radioactivity evaluation of Ebro river water and sludge treated in a potable water treatment plant located in the South of Catalonia (Spain). *Applied Radiation and Isotopes*, v. 68, n.3, p. 474-480, 2010. https://doi.org/10.1016/j.apradiso.2009.11.071

PATEL, R.; CLIFFORD, D. *Radium removal from water by manganese dioxide adsorption and diatomaceous-earth filtration*. Final report (EPA/600/S2–91/063). EPA: Cincinnati, 1992.

PEÑALVER, A.; BACIU, T.; BORRULL, F.; AGUILAR, C. Possible factors influencing the accumulation of different radionuclides in sludge from a drinking water treatment plant located in southern catalonia between 2002 and 2018. *Water Air and Soil Pollution*, v.231, n. 121, 2020. https://doi.org/10.1007/s11270-020-04491-4

ROSA, M.M.L. *Avaliação dos teores de U, Th, ^{226}Ra,^{228}Ra, ^{210}Pb e outros elementos de interesse presentes em cogumelos em uma região de elevada radioatividade natural no Brasil*. Dissertação (Mestrado em Tecnologia Nuclear – Aplicações) – Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo, 2012. https://doi.org/10.11606/D.85.2012.tde-04062012-152126

SHIN, W.; OH, J.; CHOUNG, S.; CHO, B.W.; LEE, K.S.; YUN, U; KIM, H.K. Distribution and potential health risk of groundwater uranium in Korea. *Chemosphere*, v. 163, p.108-115, 2016. https://doi.org/10.1016/j.chemosphere.2016.08.021

SMOAK, J.M.; MOORE, W.S.; THUNELL, R.C.; SHAW, T.J. Comparison of 234Th, 228Th, and 210Pb fluxes of major sediment components in the Guaymas Basin, Gulf of California. *Marine Chemistry*, v. 65, 1999, p. 177-194. https://doi.org/10.1016/s0304-4203(98)00095-4

SUNDELL-BERGMAN, S.; DE LA CRUZ, I.; AVILA, R.; HASSELBLAD, S. A new approach to assessment and management of the impact from medical liquid radioactive waste. *Journal of environmental radioactivity*, v. 99, n. 10, p. 1572-1577, 2008. https://doi.org/10.1016/j.jenvrad.2007.12.005

TINÓS, T.M.; FERREIRA, M.V.; RIEDEL, P.S.; ZAINE, J.E. Aplicação e avaliação de metodologia de classificação automática de padrões de formas semelhantes do relevo. *Revista Brasileira de Geomorfologia*, v. 15, n. 3, p.353-370, 2014. https://doi.org/10.20502/rbg.v15i3.455

TORRES, L.; YADAV, O.P.; KHAN, E. Perceived risks of produced water management and naturally occurring radioactive material content in North Dakota. *Journal of Environmental Management*, v.196, p. 56-62, 2017. https://doi.org/10.1016/j.jenvman.2017.02.077

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA); Office of Radiation and Indoor Air. *Diffuse NORM Wastes* – Waste Characterization and Preliminary Risk Assessment. Washignton: USEPA, 1993.

WILLIAMS, D.D; PRADO, A. *Memorial da Companhia Geral de Minas (subisidiária da Alcoa Alumínio S/A)*: seus 65 anos (1935-2000) e apontamentos da história da mineração no planalto de Poços de Caldas. Alcoa Alumínio: Poços de Caldas, 2001.

WORLD HEALTH ORGANIZATION (WHO). *Guidelines for drinking-water quality*. 4. ed. Geneva: World Health Organization, 2011.