

Original Research Article

Analysis of Lead-210 In Surface Water nearby a Phosphate Mining at Semi-Arid region In Santa Quitéria, Ceará State, Brazil

ABSTRACT

Aims: To report the activity concentrations of ^{210}Pb in surface waters in a semi-arid region, aiming to record these concentrations before the beginning of a NORM mining operation, facilitating subsequent comparisons with the operational phase besides verifying the radioecological characteristics of this radionuclide and the potability of the water used for human consumption by the local population.

Study design: The water samples were collected in a grid six points associated to places of human consumption, aiming to verify their radioecological characteristics and radiological potability.

Place and Duration of Study: The study site was a semi-arid region associated to a NORM phosphate deposit, between October 2009 and December 2011. No collection occurred in January and February 2010, accounting for 25 collections and 50 analyzes (soluble and particulate) per point.

Methodology: 1 l of water, per point, was collected acidulated and filtered. The filtered water was considered soluble fraction and the retained, particulate fraction. The ^{210}Pb was separated by coprecipitation and analyzed by total beta counts. Data were analyzed by uni and multivariate statistical methods and the values found were compared with international potability standards.

Results: The values found were within the international recommendations of ingestion of ^{210}Pb in water (mean value of $0.05 \text{ Bq}\cdot\text{l}^{-1}$ < recommended of $0.1 \text{ Bq}\cdot\text{l}^{-1}$). Radionuclide radioecology proved to be complex. The total AC of ^{210}Pb (sum of the soluble and particulate fractions) showed no difference between points, ranging from $0.05 \text{ Bq}\cdot\text{l}^{-1}$ at point 01SQ to $0.10 \text{ Bq}\cdot\text{l}^{-1}$ at point 04Sq. But when we analyze the AC of the fractions, we can systematically verify the AC of the particulate fraction higher than that of the soluble fraction.

Conclusion: The analyzed water, in relation to the activity concentration of ^{210}Pb , is considered potable and the particulate fraction has higher AC than the soluble fraction. The characterization of the water must be complemented when entering the operation of the phosphate mine to verify the radiological environmental impact assessment of the enterprise.

Keywords: *Pb-210, Santa Quitéria, NORM, phosphate mining, individual dose criterion, water potability.*

1. INTRODUCTION

Mining of minerals associated uranium, known as Naturally Occurring Radioactive Material (NORM), exposes the local population and biota to increased radiation exposure. Mining of phosphate [1], titanium [2], rare earths and thorium [3], zirconium and zirconia [4], and cassiterite [5] among others are recognized as causing increased exposure.

Brazil has the world's sixth largest uranium reserves [6]. From the mid-1980s until the mid-1990s, these reserves were mined at the "Osamu Utsami" mine in the city of Caldas, state of Minas Gerais. From the beginning of the 2000s the exploration is being carried out in the waterfall mine known as "Cachoeira", in the city of Caetité, state of Bahia. Aiming at the continuation of uranium exploration, the next deposit in conditions of economic, technical and environmental feasibility is "Jazida Itataia", a phosphate deposit with associated uranium, in the City of Santa Quitéria, state of Ceará [7].

The latter mine, in phase of implantation, possesses phosphate reserves estimated at nine million tons of P_2O_5 with associated uranium estimated in 79,500 tons of U_3O_8 [8]. It is located in a rather particular ecotone, an ecological transition zone between savanna and cerrado, two Brazilian ecosystems threatened with extinction [9].

One of the possible impacts of phosphate extraction may be the contamination of surface waters with phosphate, heavy metals and radionuclides. In semi-arid regions water management in quantity and quality (potability) is a vital variable for the local population that uses this resource without any treatment. This area has previously been studied, by Pereira et al. [9] focusing the radioecology of radium (both ^{226}Ra and ^{228}Ra isotopes) in surface waters.

Following Brazilian law [10-13], areas with ore reserves associated with uranium and thorium needs to be accompanied by a radioecology evaluation and of a radiological environmental impact assessment (REIA) based on an environmental radiological monitoring program.

This study aims to evaluate the activity concentrations (AC) of ^{210}Pb in surface waters of the Santa Quitéria region, using statistical analytical tools with univariate and multivariate approaches and the potability of water from the radiological point of view

2. MATERIAL AND METHODS

2.1 Study Area.

The study area is situated in the municipality of Santa Quitéria, state of Ceará, Brazilian semi-arid northeast, in the surroundings of the phosphate deposit with associated uranium and thorium (Figure 1).

2.2 Sample collection and preparation.

The water samples were collected at six different points, (01SQ to 06SQ) see Table 1. One liter of surface water was collected at each point every month over a period of 25 months. They were acidified with 1 ml conc. HNO_3 , and then filtered on an acetate filter with porosity $0.45\text{ }\mu\text{m}$. The filtrate was considered the soluble fraction and the material retained onto the filter was considered the particulate fraction.

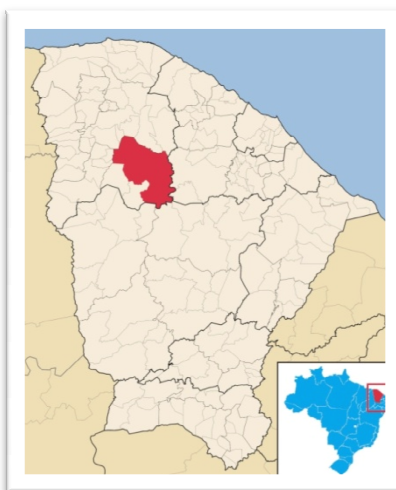


Figure 1. Location of Santa Quitéria municipality in the state of Ceará, Brazil (adapted from Wikipedia).

Table 1. Geographical locations of water collecting points in “UTM” coordinates.

POINTS	UTM E	UTM N
01SQ	0408575	9495305
02SQ	0409766	9496141
03SQ	0415241	9496141
04SQ	0413784	9493155
05SQ	0410362	9494800
06SQ	0411850	9494292

2.3 Determinations of ^{210}Pb .

^{210}Pb was concentrated from water by selective co-precipitation. The precipitate was collected on a filter and then submitted to gross beta counting in a proportional counter, following Godoy et al. [14].

2.4 Samples design and data organization.

Data were arranged in a matrix, where the columns represent the combination of collecting points and fractions, and the lines the collection dates, creating a data matrix of 12x25 containing the 300 values of ^{210}Pb activity concentration analyzed for the sampled area.

2.5 Univariate statistical analysis.

A descriptive statistics of data was performed that furnished the mean values, standard deviation, maximum value, and the number of samples. After that, a one-tailed Z test was carried out to compare the means of activity concentration between the soluble and particulate fractions [15]. Tested hypotheses were:

$$H_0 = \text{the means of the fractions are statistically identical}$$

$$H_1 = \text{the means of the fractions are statistically different}$$

Then two ANalysis Of VAriance (ANOVA) was performed in the data matrix to identify the relationship between the average per point in total fraction and per point in soluble and particulate fraction [15], following the hypotheses:

$$H_0 = \text{all the means are statistically identical}$$

$$H_1 = \text{there is at least one mean different}$$

Observing a difference, a Fisher's test was performed for classifying means [15-17].

2.6 Multivariate statistical analysis

2.6.1 Principal Component Analysis

The evaluation of multiple data is always difficult to perform for different reasons. One way to solve these problems is the use of multivariate analysis techniques. Among such techniques, the Principal Component Analysis (PCA) is most the used one. This technique employs a matrix arrangement of data and generates from this array a pair of orthogonal axes, where the data are organized in function of parameters (factors) related on the variance of the data [18-19].

2.6.2 Cluster Analysis

This analysis joins or separates multiple data in groups based on data similarities and differences [18-19].

3. RESULTS AND DISCUSSION

3.1 Univariate statistical analysis.

In the particulate fraction, the ^{210}Pb activity concentrations ranged from 0.0442 Bq l⁻¹ at point 03SQ to 0.0292 Bq·l⁻¹ at point 05SQ in the soluble fraction, the highest activity concentration was observed for the same point (05SQ) with the same value 0.0292 Bq·l⁻¹. Instead, the lowest activity concentration of the soluble fraction appeared at point 04SQ (0.0099 Bq l⁻¹). For the total fraction, the value ranged from 0.05 to 0.10 Bq·l⁻¹ (respectively 01SQ and 04SQ point). Descriptive statistics can be seen in Table 2, and visualized in Figure 2 for soluble and particulate fraction and figure 3 for total fraction.

Table 2 – Estatística descritiva das AC, para ^{210}Pb em águas superficiais na região de Santa Quitéria ($\text{Bq}\cdot\text{l}^{-1}$)

point	Soluble fraction		Particulate fraction		Total fraction		N
	Mean $\pm$ st. dev.	Max.	Mean $\pm$ st. dev.	Max.	Mean $\pm$ st. dev.	Max.	
01SQ	0.013 $\pm$ 0.011	0.041	0.035 $\pm$ 0.031	0.118	0,051 $\pm$ 0,040	0,159	25
02SQ	0.012 $\pm$ 0.011	0.037	0.109 $\pm$ 0.313	1.318	0,093 $\pm$ 0,256	1,318	25
03SQ	0.020 $\pm$ 0.023	0.096	0.044 $\pm$ 0.040	0.167	0.080 $\pm$ 0.081	0.395	25
04SQ	0.010 $\pm$ 0.008	0.032	0.034 $\pm$ 0.033	0.114	0.097 $\pm$ 0.244	1.244	25
05SQ	0.029 $\pm$ 0.033	0.118	0.029 $\pm$ 0.028	0.104	0.076 $\pm$ 0.115	0.593	25
06SQ	0.019 $\pm$ 0.017	0.061	0.032 $\pm$ 0.031	0.107	0.067 $\pm$ 0.069	0.277	25

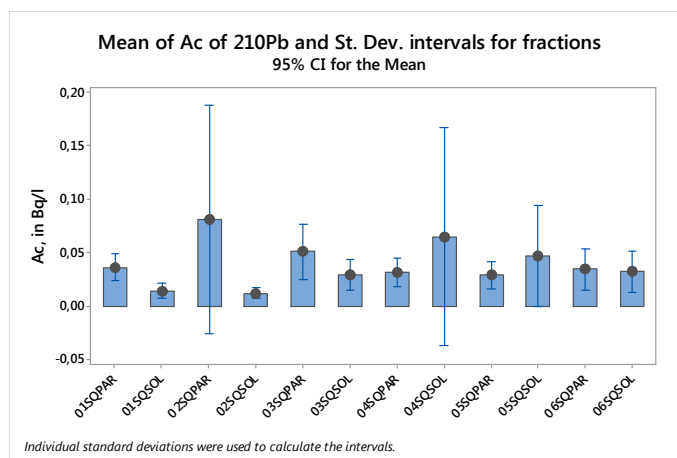


Figure 2 – Mean and intervals (st. dev.) for AC of ^{210}Pb in soluble and particulate fractions in surface water of Santa Quitéria region.

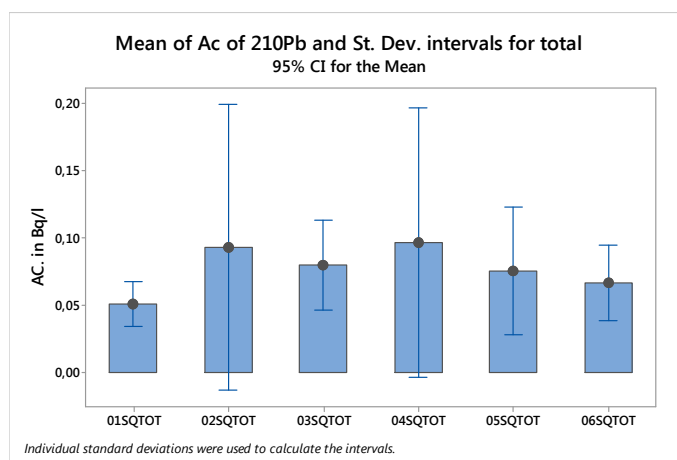


Figure 3 – Mean and intervals (st. dev.) for AC of ^{210}Pb in total fractions in surface water of Santa Quitéria region.

The Z test ($Z_{cal} = 2.01$) associated with a P value of 0.02, indicated H_0 as the accepted hypothesis, suggesting similarity between the fractions. Thus, the mean activity concentration of the particulate fraction ($0.0334 \text{ Bq}\cdot\text{l}^{-1}$) was considered the same as that of the soluble fraction ($0.0191 \text{ Bq}\cdot\text{l}^{-1}$).

The same conclusion occurred when to made analysis of variance for the total fractions. Whith Fcal igual to 0.29 ($P = 0.92$) accepted H_0 , suggesting equality between the AC of points. In this case, there are no point with diferentes AC.

However, the analysis of variance (ANOVA) resulted in a different frame. In this case the calculated value of F (F_{cal}) was 1.33, with an associated P value of 0.21. Thus, H_0 was rejected, accepting H_1 , and at least one mean was considered different. A Fisher test was thus carried out.

Fisher's test identified different groups (Table 3) which were ranked according to the activity concentrations. The highest activity concentrations belong to group G1 that includes the particulate fractions of points 03SQ, 01SQ and 04SQ. The intermediate group, G2, includes the particulate fractions of points 06SQ and 05SQ and the soluble fractions of points 05SQ, 03SQ and 06SQ. The group associated with de lowest AC, G3, includes the soluble fractions of point 01SQ, 02SQ and 04SQ. In summary, groups can be organized in function of decreasing activity concentrations as follows:

Table 3 - Fisher Test for mean ordination

Point and fraction under same line are considered same AC												
Fraction	Particulate						SOLUBLE					
Point	03SQ	01SQ	04SQ	02SQ	06SQ	05SQ	05SQ	03SQ	06SQ	01SQ	02SQ	04SQ
Mean (Bq·l ⁻¹)	0.044	0.035	0.033	0.032	0.030	0.029	0.029	0.020	0.018	0.012	0.011	0.009
Tukey test												
	G1						G2			G3		
Grouping G1> G2> G3												

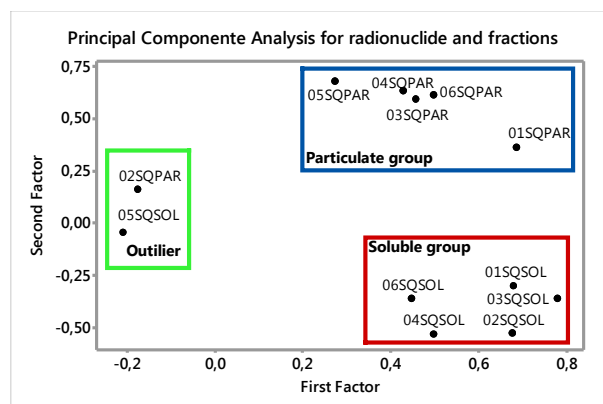


Figure 4 – Principal component analysis of data organized by point and fraction, demonstrating the separation between the soluble and particulate fraction

3.2.2. Cluster analysis.

Cluster analysis reinforced the assessment made by PCA and Fisher's tests, refuting once more the Z test conclusion. Thus, different behaviors are observed between the soluble and particulate fractions (PCA and Cluster) with the particulate fractions showing higher activity concentrations than the soluble fractions (Fisher).

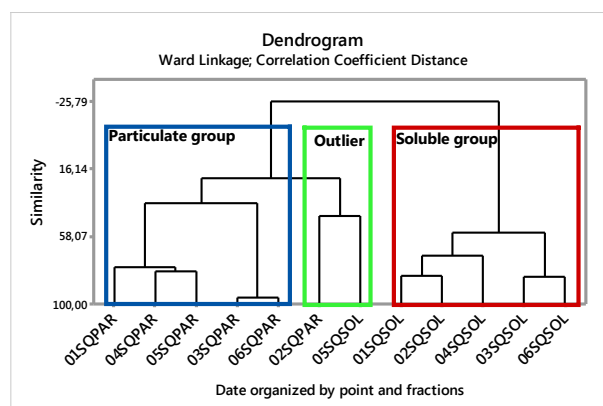


Figure 5 – Dendrogram of the data organized by point and fraction, demonstrating the separation between the soluble and particulate fraction

The approach used in this study showed the importance of mixing univariate and multivariate analyses for a better understanding of the behavior of radionuclides in the fractions. Indeed, a general assessment of the data carried out with Z test (univariate) showed similar behavior. Refining the assessment introducing the component "collection point" and use ANOVA approach, the conclusion is similar: There are no different AC by points. However, and using the ANOVA and divided the dates by point and fractions, a different conclusion appeared: there are differences between points and fractions, but without pointing which are different and which are equal.

This difficulty was remedied by Fisher's exact test (univariate), that ordered the data from highest to lowest activity concentration, grouping the data according to their concentrations. At this stage, the analysis showed that the particulate fraction displayed higher levels of activity.

In his turn, the multivariate analysis confirmed the assessment of the Fisher's test, and with stood the Z test conclusion. In both analyzes (PCA and cluster) soluble fractions of collecting points were grouped and the particulate fractions put together in another group

4. CONCLUSION

The assessment has shown that there are differences in the activity concentrations of ^{210}Pb between the soluble and particulate phases of water samples collected in the region of the Santa Quitéria phosphate deposit. From all this, it can be stated that the radioecology of ^{210}Pb in sampled area is complex, with spatial difference between the points and distribution difference between the fractions, with the particulate fraction showing higher AC than the soluble one.

An increase of sampling must be considered as a tool to increase the reliability both of the statistics and conclusions. A next step to be assessed is the analysis of the differences between the fractions at the collecting points. Another important aspect to be looked at is the geographic variation, comparing the same fractions (soluble or particulate) between the points.

In terms of public health, the WHO uses an 'individual dose criterion' (IDC) of 0.1 mSv for one year's consumption of drinking water [1] as the recommended limit of ingestion of radionuclides from water. This organization develops dosimetric models that estimate the concentration of activity that generates this dose for different radionuclides. In the case of ^{210}Pb this value is $0.1 \text{ Bq}\cdot\text{l}^{-1}$ [20]. Considering a linear relationship between ingestion of water and received dose and that the sum of the means of the soluble and particulate fractions is $0.05 \text{ Bq}\cdot\text{l}^{-1}$, it results that the average dose rate resulting from the intake of ^{210}Pb in water is half of the IDC value indicated by WHO.

In specific cases, this value may be higher than the IDC, as observed for point 02SQ, where the sum of the maximum values of AC in the soluble and particulate fractions returns an estimated value of AC of $1.35 \text{ Bq}\cdot\text{l}^{-1}$, that is 13 times the limit derived of 0.1. But on the whole, the values are considered within the values indicated by the WHO, and the waters may thus be considered as potable from a radiological point of view.

REFERENCES

1. International Atomic Energy Agency. 1st ed. Radiation protection and management of norm residues in the phosphate industry. Vienna: IAEA; 2013.
2. International Atomic Energy Agency. 1st ed. Radiation protection and norm residue management in the titanium dioxide and related industries . Vienna: IAEA, 2012.
3. International Atomic Energy Agency. 1st ed. Radiation protection and norm residue management in the production of rare earths from thorium containing minerals. Vienna: IAEA, 2011.
4. International Atomic Energy Agency. 1st ed. Radiation protection and norm residue management in the zircon and zirconia industries. Vienna: IAEA, 2007.
5. Garcia, M. A. Caracterização radioquímica e impacto radiológico Ambiental no processamento da casiterita para a produção de estanho e chumbo metálico. M. Sc Dissertation, São Paulo, SP, Br: IPEN/USP, 2009.
6. Cipriani, M Mitigação dos impactos sociais e ambientais decorrentes do fechamento definitivo de minas de urânio, Ph. D. Thess, Campinas, SP, BR: Unicamp, 2002.
7. Pereira, W. S., Kelecom, A., Espindola, C. B. and Silva, A. X. Urânio em material biológico i: urânio na bahia, brasil, in: *X Congreso Regional Latinoamericano IRPA de Protección y Seguridad Radiológica, Buenos Aires, AR, 2015*
8. Silva, J. R. "Caracterização Hidrogeológica da Jazida de. *Master degree's dissertation* . Ceará: Universidade Federal do Ceará, 2003.
9. Pereira, W. d., Kelecom, A., & Pereira, J. R. Analysis of Radium Isotopes in Surface Waters nearby a Phosphate Mining with NORM at Santa Quitéria, Brazil. *Journal of Environmental Protection* , pp. 193 – 199, 2014.

- 252 10. National Comission for Nuclear Energy - CNEN. Requisitos de segurança e proteção radiológica para
253 instalações mineros-industriais. Rio de Janeiro, RJ, Brasil: CNEN, 2016.
- 254 11. National Comission for Nuclear Energy - CNEN. Standart CNEN -NN-3.01 - Diretrizes básicas de
255 proteção radiologica. Rio de Janeiro, RJ, Brasil: CNEN, 2014
- 256 12. National Comission for Nuclear Energy - CNEN. Standart Posição Regulatória CNEN -NN-
257 3.01/008:2011 Programa de Monitoração radiológico ambiental . Rio de Janeiro, RJ, Brasil: CNEN,
258 2011.
- 259 13. National Comission for Nuclear Energy. Standart Posição RegulatoriaCNEN-NN-3,01/009:2011
260 Modelo para elaboração de relatórios de programa de monitoração radiológica ambiental. Rio de
261 Janeiro, RJ, Brasil: CNEN, 2011.
- 262 14. Godoy, J. M., Lauria, C. D., Godoy, M. L., & Cunha, R. P. Development of a sequential method for
263 determination of ²³⁸U, ²³⁴U, ²³²Th, ²³⁰Th, ²²⁸Th, ²²⁸Ra, ²²⁶Ra and ²¹⁰Pb in environmental
264 samples. *Journal of Radioanalytical Nuclear Chemistry*, 182 (No.1), pp. 165-169, 1994.
- 265 15. Gotelli, N. J., & Ellison, A. M. *A primer of ecological statistic*. 1st ed. Sunderland: Sinauer Associates,
266 2004.
- 267 16. Rosner, B. *Fundamentals of biostatistic*. Stanford: Duxbury Thonson Learning. 1st ed., 2000.
- 268 17. Schork, M. A., & Remington, R. D. *Statistic with applications to the biological and Health*
269 *science*.Prentice: Upper Saddle River, 1st ed., 2000.
- 270 18. Valentin, J. L. *Ecologia numérica. Uma introdução a análise multivariada de dados ecológicos*.Rio de
271 janeiro: Interciência, 1st ed., 2000.
- 272 19. Ferreira, D. F. *Estatística Multivariada*. Lavras: UFLA, 1st ed., 2008.
- 273 20. World Health Organization, Guidelines for Drinking-water Quality — 4th Ed., WHO, Geneva, 1st ed.,
274 2011.