DETERMINATION OF U AND Th ISOTOPES IN LICHEN SAMPLES OF *CANOPARMELIA TEXANA*

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Abstract

Lichen plays an important role in studies of environmental pollution. It can be used for the evaluation of various air contaminants, including heavy metals and radionuclides. The main objective of this study is to verify the possibility of using the lichen species *Canoparmelia Texana* for the assessment of U and Th concentrations in air in the vicinity of installations which deal with these radionuclides. Two regions were chosen: a phosphate fertilizer industry and the Instituto de Pesquisas Energéticas e Nucleares (IPEN), both located in the state of São Paulo, Brazil. The content of U and Th in lichen samples were determined by alpha spectrometry after a radiochemical separation by ionic exchange resins.

Introduction

The conventional methods for air pollution evaluation, such as air filters and deposition collectors require high costs of implementation, operation and maintenance. An alternative method used in literature is the application of live organisms, such as lichens, as bioindicators of air pollution.

The use of lichens as bioindicator of atmospheric pollution presents advantages compared with conventional methods, such as easy and

economic sampling, less expensive equipments, and high degree of elemental accumulation that allows a continuous and retrospective monitoring. The air filters and deposition collectors, on the other hand, give information only about contaminations occurred in a small period of time that corresponds to the sampling time.

Lichens are formed from the symbioses between a fungus and one or more algae that result in a thallus with a stable structure[1].

The fungus absorbs water and minerals from the environment and provides an environment with light and humidity favorable to the algae photosynthesis[2]. They live over a substrate without interaction with it and absorb substances present in the air; therefore they can accumulate radioactive elements and metallic ions. With these characteristics the lichens are used as bioindicators of air pollution[1].

The lichen species used in this work was *Canoparmelia texana*, which is a foliose lichen, from the family Parmeliaceae, with large thallus (5 to 20 cm in diameter), and radial growth found on tree trunks or even on rocks, in several regions in Brazil[3]. The central part of the lichen is the oldest and it is the part that was exposed to the pollutant for a long period of time.

There are few studies concerning the use of *Canoparmelia texana* lichen for the assessment of air quality in urban regions of Brazil[4-8].

The objective of this work is to determine the U (^{238}U and ^{234}U) and Th (^{232}Th and ^{230}Th) isotopes concentration in *Canoparmelia texana* lichen and to study the possibility of using this species as bioindicator of air pollution by radionuclides.

Two regions were chosen for this study: a phosphate fertilizer industry and the Instituto de Pesquisas Energéticas e Nucleares (IPEN), both located in the state of São Paulo, Brazil. IPEN has as major activity to perform research in the field of the nuclear fuel cycle, and therefore deals with considerable amounts of natural radionuclides of the U and Th series. In particular, a plant of purification of U and Th was in operation in its campus for more than 10 years. The phosphate fertilizer industry is responsible for the production and storage of about $5.5x10^6$ tons per year of a residue called phosphogypsum. This waste is stockpiled in the surrounding environment of the facilities and concentrate radionuclides of the U and Th natural series, originally present in the phosphate rock used as raw material[9-10]

Materials and methods

The lichens samples were collected in six points in the campus of IPEN (Figure 1) and in seven points close to the phosphate industry (Figure 2); in the trees' barks at about 1.5 m above the ground level. They were extracted using a plastic knife and stored in paper bags. In the laboratory the lichens samples were washed with distilled water to remove dust and cleaned by a manual process. After this the samples were dried at 60˚C and pulverized in a glass mortar.

Alpha spectrometry was used for the determination of the U (^{238}U and ^{234}U) and Th (^{232}Th and ^{230}Th) isotopes concentration. Approximately 0,5g of lichen (duplicate samples) was weighed, spiked with ^{232}U and ^{229}Th and dissolved with concentrated HNO_3 and 30% H_2O_2. The solution was

neutralized with NH_4OH till the iron-hidroxide precipitation. The precipitate was dissolved with 9 mol L^{-1} HCl, evaporated almost to dryness and re-dissolved in 9 mol L^{-1} HCl. The obtained solution was passed through a pre-conditioned anionic exchange resin column in 9 mol L^{-1} HCl media. The eluate was evaporated to dryness and re-dissolved with 8 mol L^{-1} HNO_3, and passed through a pre-conditioned anionic exchange resin column in 8 mol L^{-} HNO_3 media. Both, U and Th were eluted with 0.1 mol L^{-1} HCl, evaporated and electroplated in a steel disk during one hour, using NH_4Cl as electrolyte[11] (Silva, 1998). The detection of alpha particles was done with a silicon barrier detector, samples were counted from 150.000 to 400.000 seconds.

Results and discussion

The results obtained for the U and Th isotopes concentration in lichens samples collected at IPEN are presented in Table 1. The activity concentrations obtained for the ^{238}U varied from 2.4 ± 0.4 to 8.7 ± 0.5 Bq kg^{-1} and for the ^{234}U from 2.7 ± 0.6 to 9.0 ± 0.2 Bq kg^{-1}.

Leonardo et al (2007)[12] analyzed lichens samples of *Canoparmelia texana* in six points located in the campus of IPEN and obtained concentrations of 1.21 Bq kg^{-1} to 34.2 Bq kg^{-1}, for ^{238}U. The results obtained in the present work are in the same range of concentration.

Saiki et al (2007)[8] analyzed lichens samples from the species *Canoparmelia texana* in the metropolitan area of São Paulo city and obtained concentration values varying from 0.93 ± 0.02 to 5.87 ± 0.05 Bq kg^{-1}, for the ^{238}U.

Saiki et al (1997)[4] also analyzed a lichen sample from the species *Canoparmelia texana* in a point located in IPEN and obtained value of concentration of 4.03 ± 0.02 Bq kg^{-1}, result in the range obtained in this work. However, in another paper, Saiki et al (2001)[6] analyzing the same species of lichen in the IPEN surroundings obtained 0.79 ± 0.02 Bq kg^{-1}, for the ^{238}U.

For thorium isotopes, the concentration varied from 4.4 ± 0.3 to 12.1 ± 2.6 Bq kg^{-1} for ^{232}Th and from 4.6 ± 0.6 to 8.9 ± 0.6 Bq kg^{-1} for ^{230}Th. Saiki et al (2001)[6] analyzed lichen sample from the species *Canoparmelia texana* in IPEN, and the concentration obtained was 1.13 ± 0.01 Bq kg^{-1} for the ^{232}Th in the same point where lower ^{238}U concentration was also found. Both radionuclides present very low concentrations in this point compared with the results obtained in the present work. In other work, Saiki et al (1997)[4] obtained a concentration from 3.69 ± 0.02 Bq kg^{-1} for the ^{232}Th.

The major concentration of ^{232}Th was found in the point IPLI02B.

The results obtained in the present work are within the range observed in the literature. Therefore, it can be concluded that no contamination of U and Th was observed in the surrounding of IPEN facilities.

The results obtained for the U and Th isotopes concentration in lichens samples collected in the phosphate industry region are presented in Table 2. The activity concentrations obtained for the U isotopes varied from 13.2 ± 3.8 a 68.4 ± 7.4 Bq kg^{-1}, for the ^{238}U and from 16.5 ± 4.3 to 56.8 ± 6.4 Bq kg^{-1}, for the ^{234}U. The point CULI07 presented the major concentrations.

The concentrations of ^{238}U and ^{234}U in all the samples analyzed are very close, indicating that these radionuclides are in almost equilibrium and no differences were observed in the adsorption process by lichens.

The concentrations of thorium varied from 7.2 ± 2.1 Bq kg^{-1} to 28.8 ± 6.0 Bq kg^{-1}, for the ^{232}Th and from 7.4 ± 2.1 Bq kg^{-1} a 30.7 ± 6.1 Bq kg^{-1}, for the ^{230}Th. These radionuclides belong to different natural decay series and therefore will behave in a different way in the absorption by the lichens.

The point CULI06 presented higher concentrations for all the studied isotopes, indicating a possible influence from the phosphate industries.

Conclusion

The results obtained for the U and Th isotopes show that the phosphate industry region is more impacted than IPEN, giving evidence of an environmental contamination by these elements. The phosphate fertilizer industry may be responsible for an increase of these elements concentration in the air. The results obtained suggest that the lichen *Canoparmelia Texana* can be used as bioindicator of atmospheric contamination by radionuclides.

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TABLE 1 - Concentration of U and Th ($Bq.kg^{-1}$) in lichens samples in the IPEN region

Sampling point	Collecting data	^{238}U	^{234}U	^{232}Th	^{230}Th
IPLI01A	06/07/06	2,4 ± 0,4	2,7 ± 0,6	7,0 ± 1,1	7,1 ± 0,2
IPLI01B	03/11/06	3,9 ± 0,4	4,0 ± 0,2	4,5 ± 0,1	4,6 ± 0,6
IPLI01C	20/03/07	5,2 ± 0,3	5,4 ± 0,1	6,1 ± 0,1	6,6 ± 0,1
IPLI02A	06/07/06	5,7 ± 0,1	6,0 ± 1,0	6,4 ± 0,4	6,1 ± 0,2
IPLI02B	03/11/06	6,0 ± 0,5	6,1 ± 0,6	12,1 ± 2,6	7,6 ± 0,4
IPLI03A	28/03/06	6,0 ± 0,1	6,4 ± 0,1	6,7 ± 0,2	6,9 ± 0,6
IPLI04A	12/02/08	6,6 ± 0,1	6,6 ± 0,1	8,6 ± 1,0	8,9 ± 0,6
IPLI05A	12/02/08	8,7 ± 0,5	9,0 ± 0,2	7,8 ± 0,6	6,0 ± 0,5
IPLI06A	12/02/08	4,3 ± 0,1	4,3 ± 0,1	4,4 ± 0,3	4,8 ± 0,5

* each point was determined in duplicate

TABLE 2 - Concentration of U and Th isotopes ($Bq.kg^{-1}$) in lichen samples in the phosphate fertilizer industry region

Sampling point	Collecting data	^{238}U	^{234}U	^{232}Th	^{230}Th
CULI01	30/01/08	39,0 ± 7.0	41.2 ± 7,2	28,4 ± 4,7	28,7 ± 5,4
CULI02	30/01/08	27,0 ± 3,5	23,8 ± 3,2	14,3 ± 3,4	20,7 ± 4,0
CULI03	30/01/08	26,8 ± 5,4	29,4 ± 5,7	7,2 ± 2,1	7,4 ± 2,1
CULI04	30/01/08	35,2 ± 4,2	36,4 ± 4,2	17,6 ± 4,4	18,9 ± 4,5
CULI05	30/01/08	22,2 ± 2,7	23,5 ± 2,8	20,1 ± 5,2	22,2 ± 5,4
CULI06	30/01/08	68,4 ± 7,4	56,8 ± 6,4	28,8 ± 6,0	30,7 ± 6,1
CULI07	30/01/08	13,2 ± 3,8	16,5 ± 4,3	21,3 ± 6,8	24,6 ± 7,3

* each point was determined in duplicate

Figure 1 – Sampling points in the campus of IPEN

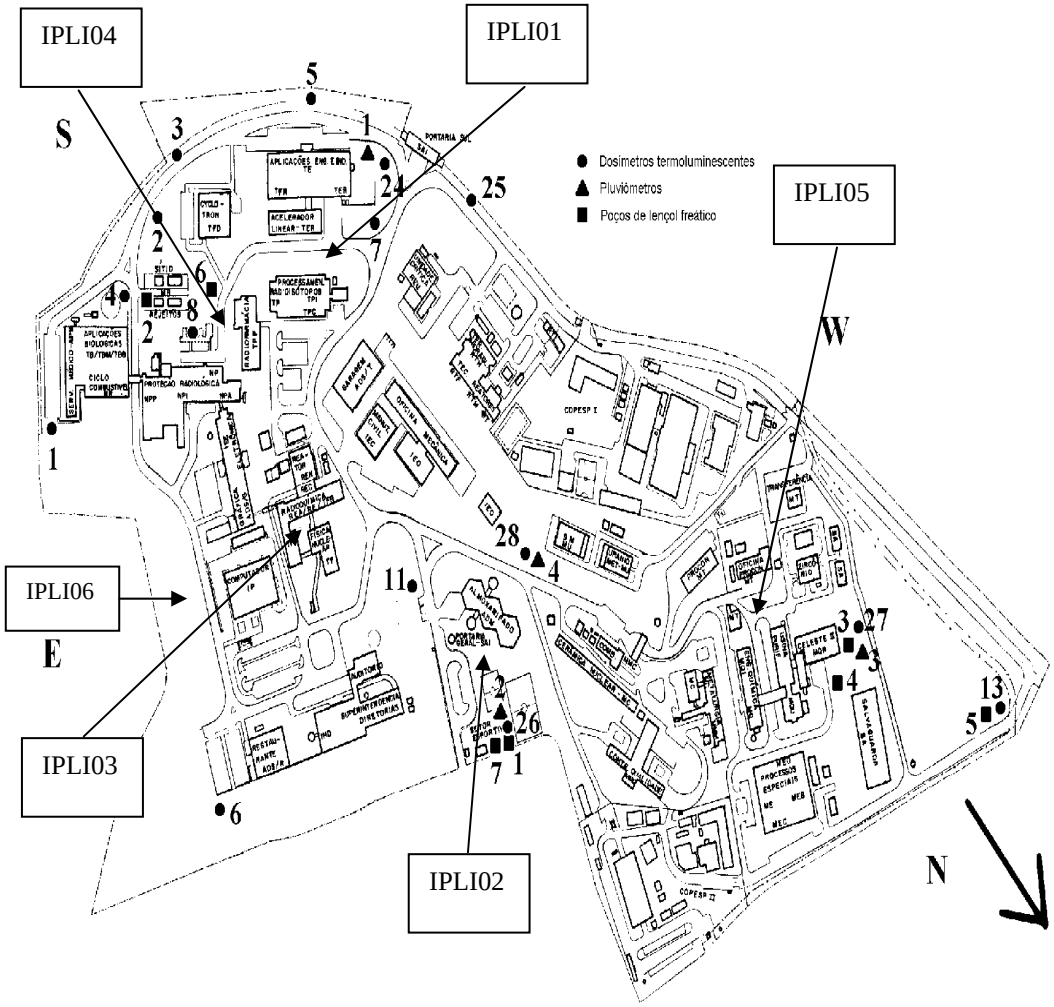

Figure 2 - Sampling points in the phosphate fertilizer industry region