DETERMINATION OF NATURAL RADIONUCLIDES 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 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 natural radionuclides of the U and Th decay series in air in the vicinity of Instituto de Pesquisas Energéticas e Nucleares (IPEN) installations. IPEN has as major activity to perform research in the field of the nuclear fuel cycle, and therefore deals with natural radionuclides of the U and Th series. The content of ^{238}U, ^{234}U, ^{230}Th, ^{210}Po and ^{232}Th in lichen samples were determined by alpha spectrometry after a radiochemical separation. Ra isotopes and ^{210}Pb were determined by gross alpha and beta counting after a radiochemical separation and measurement on a low background gas flow proportional detector. The results obtained for ^{238}U varied from 2.4 ± 0.4 Bq kg^{-1} to 6.6 ± 0.1 Bq kg^{-1} and from 4.4 ± 0.3 Bq kg^{-1} to 12.1 ± 2.6 Bq kg^{-1}, for ^{232}Th. For ^{226}Ra varied from 13 ± 1 Bq kg^{-1} to 38 ± 2 Bq kg^{-1} and from 200 ± 13 Bq kg^{-1} to 351 ± 12 Bqkg^{-1} for ^{228}Ra. The results obtained were compared with data obtained for the same radionuclides in lichen samples in an area affected by TENORM industry and can be considered as background for this lichen species. It can be concluded that the control of atmospheric discharges of IPEN facilities has been effective along the years, giving no evidence of radiological environmental impact.

1. 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 bio-indicators of air pollution.

The use of lichens as bio-indicator 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. The fungus absorbs water and minerals from the environment and provides an environment with light and humidity favorable to the algae photosynthesis [1]. 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 bio-indicators of air pollution.

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 [2]. 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 [3-7]. The objective of this work is to determine the U (^{238}U and ^{234}U), Th (^{232}Th and ^{230}Th) and Ra (^{226}Ra and ^{228}Ra) isotopes, ^{210}Pb and ^{210}Po in *Canoparmelia texana* lichen and to study the possibility of using this species as bio-indicator 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, located in Cubatão, is responsible for the production and storage of about 5.5×10^6 tons per year of a residue called phosphogypsum. This waste is stockpiled in the surrounding environment of the facilities and concentrates radionuclides of the U and Th natural series, originally present in the phosphate rock used as raw material [8-9].

2. MATERIALS AND METHODS

2.1 Sampling

The lichens samples were collected in five points in the campus of IPEN (Figure 1) and in seven points close to the phosphate industry in Cubatão (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. Lichen samples collected at IPEN were analyzed for the determination of natural radionuclides of the U (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po) and Th (^{232}Th and ^{228}Ra) decay series. Lichen samples collected in Cubatão were analyzed for the determination of U and Th isotopes.

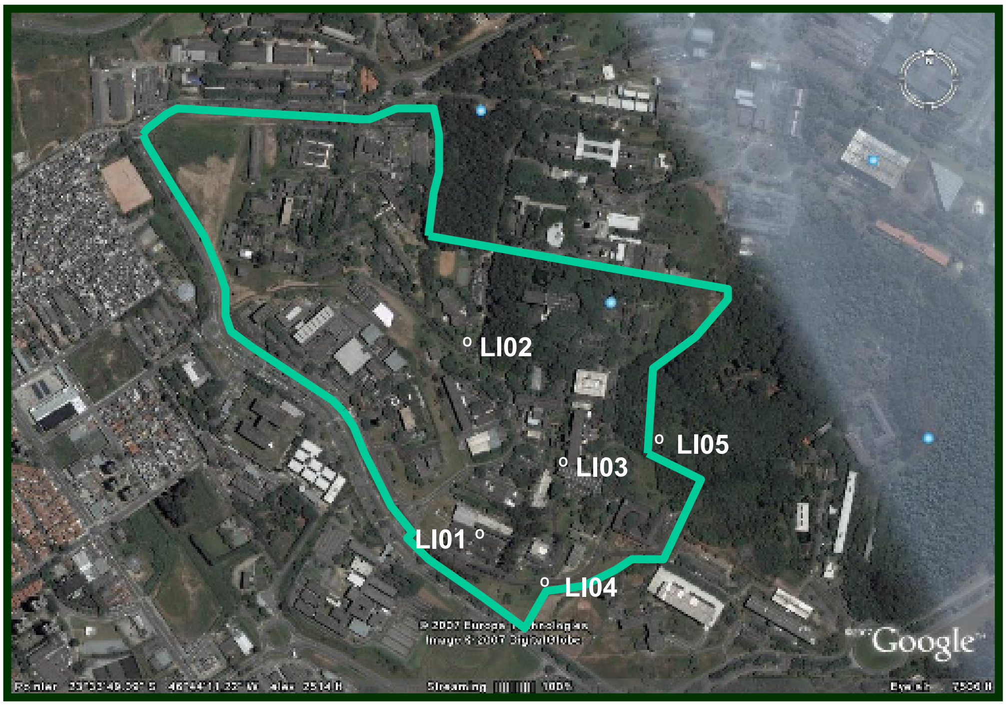

Figure 1. Sampling points in the campus of IPEN

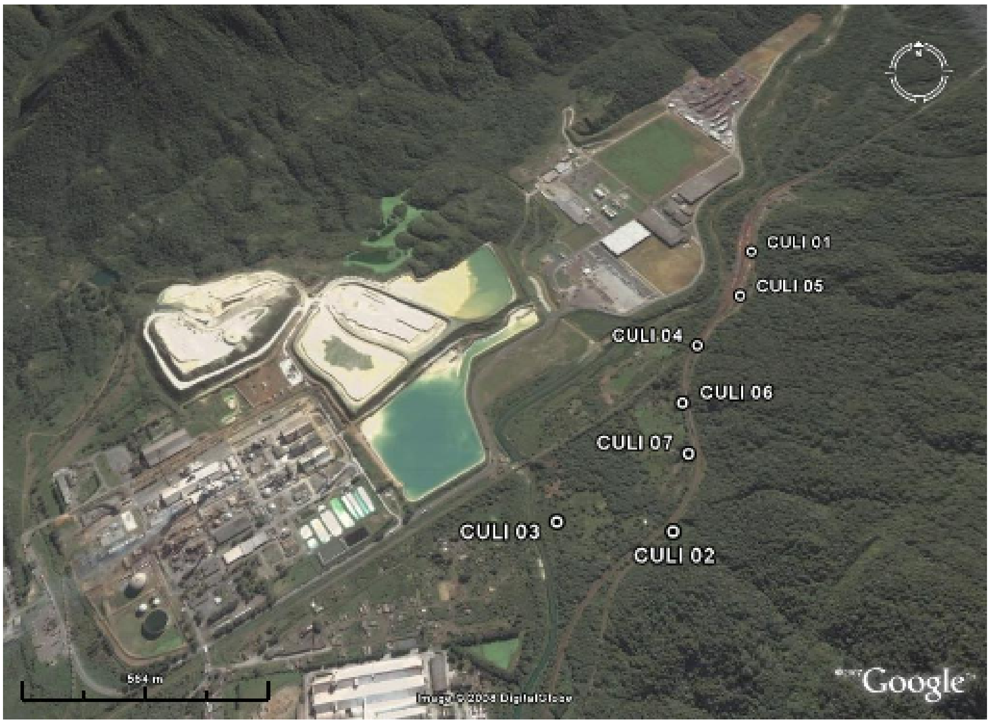

Figure 2. Sampling points in the phosphate fertilizer industry region

2.2 U (^{238}U and ^{234}U) and Th (^{232}Th and ^{230}Th) isotopes' determination

500 mg of lichen, in duplicate samples, was spiked with ^{232}U and ^{229}Th tracers and dissolved with concentrated HNO_3 and 30% H_2O_2. The solution was neutralized with NH_4OH till the iron-hydroxide 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^{-1} 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 [10]. The detection of alpha particles was done with a silicon barrier detector; samples were counted from 150.000 to 400.000 seconds.

2.3 ^{228}Ra, ^{226}Ra and ^{210}Pb determination

500 mg of lichen, in duplicate samples, were dissolved in mineral acids in a microwave digestor and submitted to a radiochemical procedure for the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb. This procedure consists in an initial precipitation of Ra and Pb with 3 mol L^{-1} H_2SO_4, dissolution of the precipitate with nitrilo-tri-acetic acid at basic pH, precipitation of $Ba(Ra)SO_4$ with ammonium sulfate and precipitation of $PbCrO_4$ with 30% sodium chromate. The ^{226}Ra and ^{228}Ra concentration were determined by gross alpha and beta counting of the precipitate of $Ba(Ra)SO_4$ [11] and the ^{210}Pb concentration through its decay product ^{210}Bi, by measuring the gross beta activity of the precipitate $PbCrO_4$ [12] All the radionuclides were measured in a low background gas flow proportional detector for 200 minutes.

2.4 ^{210}Po determination

300 mg of lichen, in duplicate samples, spiked with ^{209}Po tracer were dissolved with concentrated HNO_3 under heating at 80°C on a hot plate. 30% H_2O_2 was added to destroy organic matter. Concentrated HCl was added to change the solution medium and evaporated to dryness three times. The final residue was dissolved with 6.25 mol L^{-1} HCl, filtered through a 0.1μ Millipore filter paper; and 20% hydroxylamine hydrochloride, 25% sodium citrate and Bi^{+3} carrier were added to the solution. The pH was adjusted to 1.5 with 1.5 mol L^{-1} HCl and 20% ammonia solution. Polonium was spontaneously plated on a silver disc at 80°C for 4 hours, under agitation on a hot plate with magnetic stirring [13-14]. The alpha measurement was performed on a surface barrier detector, EG&G Ortec, for 100 minutes.

3. RESULTS AND DISCUSSION

The results obtained for the U, Th and Ra isotopes, ^{210}Pb and ^{210}Po concentration in lichens samples collected at IPEN are presented in Table 1 and Figures 3 and 4; for comparison, data available in the literature for natural radionuclides in the lichen species *Canoparmelia texana* are presented in Table 2. The activity concentrations obtained for the U isotopes varied from 2.4 ± 0.4 to 6.6 ± 0.1 Bq kg^{-1} and for the Th isotopes from 4.4 ± 0.3 to 12.1 ± 2.6 Bq kg^{-1}. These results can be considered as background when compared with the concentrations of the same radionuclides in the vicinity of the phosphate industry (Table 3): from 13.2 ± 3.8 to 68.4 ± 7.4 Bq kg^{-1} for the U isotopes and from 7.2 ± 2.1 Bq kg^{-1} to 30.7 ± 6.1 Bq kg^{-1}, for the Th isotopes. The results obtained in the present work for the radionuclides concentration in the lichen samples collected at IPEN 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 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/desorption process by lichens. The isotopes ^{230}Th and ^{232}Th, belong to different natural decay series and therefore will behave in a different way in the absorption/desorption process.

Table 1. Concentration of U, Th and Ra isotopes, ^{210}Pb and ^{210}Po (Bq.kg^{-1}) in lichens samples in the IPEN region

Sampling point*	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th	^{228}Ra
LI01A	2.4 ± 0.4	2.7 ± 0.6	7.1 ± 0.2	30 ± 4	369 ± 23	349 ± 25	7.0 ± 1.1	200 ± 13
LI01B	3.9 ± 0.4	4.0 ± 0.2	4.6 ± 0.6	32 ± 2	375 ± 6	273 ± 23	4.5 ± 0.1	215 ± 20
LI01C	5.2 ± 0.3	5.4 ± 0.1	6.6 ± 0.1	13 ± 1	315 ± 22	211 ± 16	6.1 ± 0.1	341 ± 5
LI02A	5.7 ± 0.1	6.0 ± 1.0	6.1 ± 0.2	30 ± 4	449 ± 8	534 ± 36	6.4 ± 0.4	237 ± 24
LI02B	6.0 ± 0.5	6.1 ± 0.6	7.6 ± 0.4	35 ± 3	793 ± 68	761 ± 95	12.1 ± 2.6	253 ± 16
LI03A	6.0 ± 0.1	6.4 ± 0.1	6.9 ± 0.6	13 ± 2	392 ± 10	182 ± 12	6.7 ± 0.2	351 ± 12
LI04A	6.6 ± 0.1	6.6 ± 0.1	8.9 ± 0.6	38 ± 2	436 ± 16	322 ± 15	8.6 ± 1.0	247 ± 12
LI05A	4.3 ± 0.1	4.3 ± 0.1	4.8 ± 0.5	20 ± 5	678 ± 30	480 ± 26	4.4 ± 0.3	241 ± 65

* each sample was measured in duplicate

Table 2. Data from literature for natural radionuclides in lichen samples *Canoparmelia texana* (Bq kg^{-1})

Reference	Sampling location	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra
Coccaro *et al (*2000)	São Paulo - Botanic Institute	NA	NA	NA	0.34 - 1.09	NA
Saiki *et al* (2001)	São Paulo - Metropolitan area	0.34 - 2.36	NA	NA	0.34 - 7.85	NA
Saiki *et al (*2007a)	São Paulo - Metropolitan area	0.83 - 4.76	NA	NA	NA	NA
Saiki *et al (*2007b)	São Paulo - Metropolitan area	0.93 - 5.87	NA	NA	NA	NA
Leonardo *et al* in press	Pirapora do Bom Jesus (NORM industry)	18.6 - 473	21.4 - 265	401 - 1083	15.9 - 574	176 - 389

NA – not available

Table 3. Concentration of U and Th isotopes ($Bq.kg^{-1}$) in lichen samples in the phosphate fertilizer industry region

Sampling point*	^{238}U	^{234}U	^{230}Th	^{232}Th
CULI01	39.0 ± 7.0	41.2 ± 7.2	28.7 ± 5.4	28.4 ± 4.7
CULI02	27.0 ± 3.5	23.8 ± 3.2	20.7 ± 4.0	14.3 ± 3.4
CULI03	26.8 ± 5.4	29.4 ± 5.7	7.4 ± 2.1	7.2 ± 2.1
CULI04	35.2 ± 4.2	36.4 ± 4.2	18.9 ± 4.5	17.6 ± 4.4
CULI05	22.2 ± 2.7	23.5 ± 2.8	22.2 ± 5.4	20.1 ± 5.2
CULI06	68.4 ± 7.4	56.8 ± 6.4	30.7 ± 6.1	28.8 ± 6.0
CULI07	13.2 ± 3.8	16.5 ± 4.3	24.6 ± 7.3	21.3 ± 6.8

* each sample was measured in duplicate

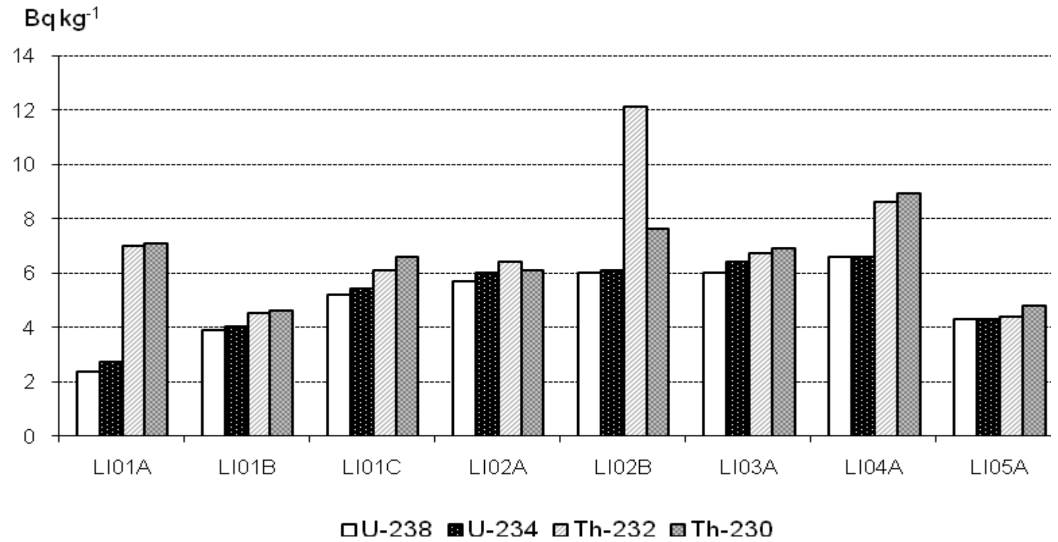

Figure 3. Representation of the concentration of U and Th isotopes ($Bq\ kg^{-1}$) in lichens samples in the IPEN region

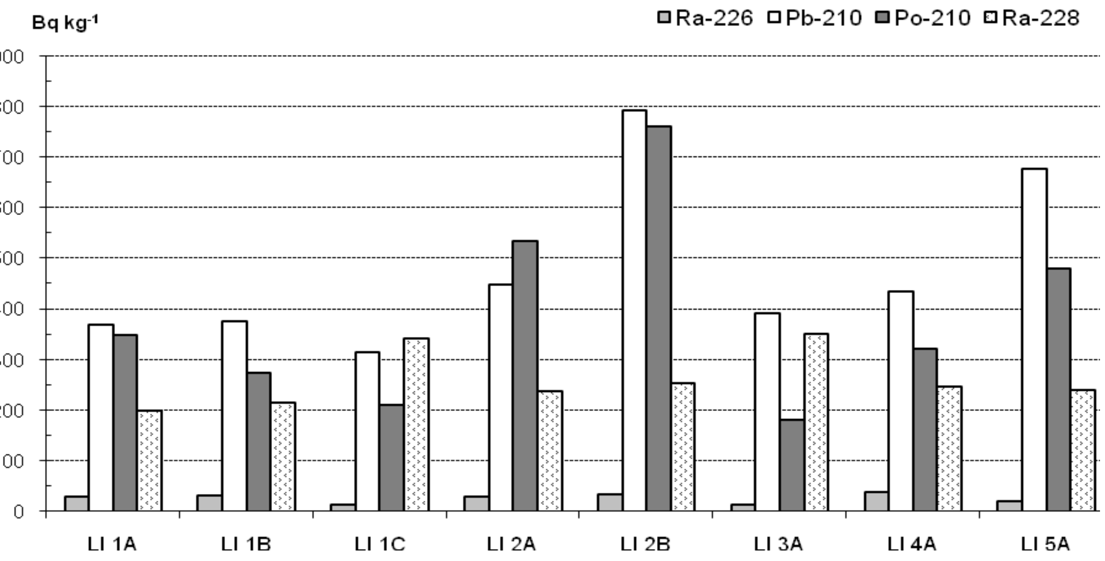

Figure 4. Representation of the concentration of ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po (Bq kg^{-1}) in lichens samples in the IPEN region

Activity concentrations for ^{226}Ra varied from 13 ± 1 to 38 ± 2 Bq kg^{-1} and for ^{228}Ra from 200 ± 13 to 351 ± 12 Bq kg^{-1}. ^{210}Pb and ^{210}Po presented higher concentrations at IPEN facilities, giving evidence of atmospheric deposition of ^{210}Pb from other sources than the nuclear installations available at IPEN. These two radionuclides reached equilibrium in the lichen samples (correlation coefficient of 0.865, see Figure 5).

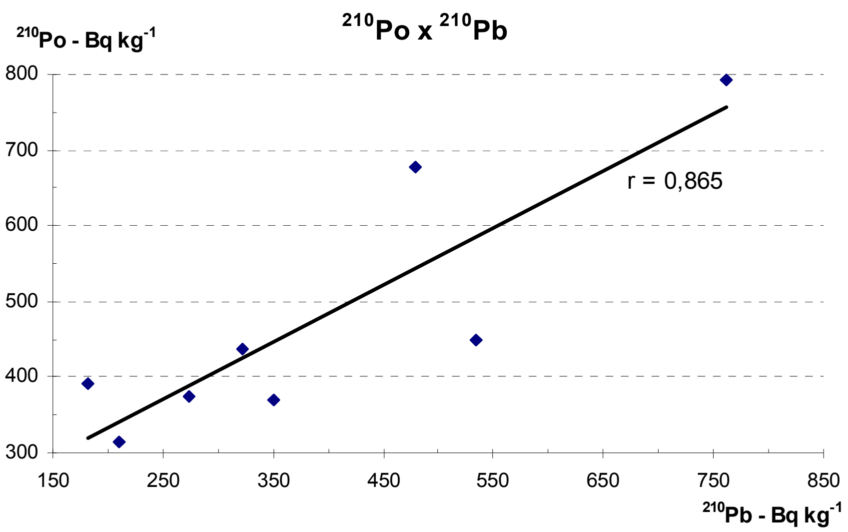

Figure 5. ^{210}Po and ^{210}Pb concentrations in Bq kg^{-1}in lichens samples

The results obtained for U and Th isotopes in the lichen samples collected in Cubatão, in the surrounding of the phosphate fertilizer industry ranged from 13.2 ± 3.8 to 68.4 ± 7.4 $Bqkg^{-1}$, and from 7.2 ± 2.1 to 30.7 ± 6.1 for ^{232}Th; 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. Leonardo *et al*. [7] also observed enrichment of all radionuclides studied in the vicinity of a NORM industry, which processes tin and lead from cassiterite (Table 2).

4. 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 bio-indicator of atmospheric contamination by radionuclides.

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