Monitoring anthropogenic airborne ^{210}Pb and ^{210}Po in the vicinity of a TENORM industry using lichen as bio-indicator

S. R. Damatto*, L. Leonardo, B. P. Mazzilli

Laboratório de Radiometria Ambiental, Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes, 2242, São Paulo, CEP 05508 000, Brazil

Introduction

It is well known that the operation of TENORM industries may affect the surrounding environment. The amount of natural radionuclides discharged to the atmosphere from a TENORM industry depends on a number of factors such as the composition of the raw material and final residue formed and the chemical process involved. The tin industry is a typical example of a TENORM industry, since the high temperatures used in the smelting and refining processes may lead to concentrations of natural radionuclides, mainly in the precipitated dust and in slag, which are stored in piles in open air. Lead-210 can also be released to the atmosphere during the combustion, depending on the efficiency of the emission control devices. All the process can increase the doses to such an extent that radiation measures may be needed to protect workers and members of the public.

The most important Brazilian company that produces tin and metallic lead is located in the city of Pirapora do Bom Jesus, in the state of São Paulo. This industry is responsible for the production of about 7,500 ton year^{-1} of tin and 120 ton year^{-1} of lead. The raw material used in this facility is the cassiterite (SnO_2), which is found together with other ores such as cryolite (Na_3AlF_6), niobium (Nb_2O_5) and tantalum (Ta_2O_5) (Minuzzi et al, 2008; Weber et al, 2007). It comes from a mine located in Pitinga, Amazon, where the rock is concentrated (55%). The concentrate presents in its composition concentrations of U and Th up to 42 kBq kg^{-1} and 60 kBq kg^{-1}, respectively (Garcia, 2009).

Although in the raw material the radionuclides from the uranium and thorium series are almost in equilibrium, during the processing this equilibrium is disrupted and the radionuclides migrate according to their chemical properties. Since this facility has been in operation for more than 20 years, it is expected an environmental impact due to re-suspension of the residue, atmospheric dispersion and deposition in the soil; and due to the emission of gaseous and particulate effluents from the stacks. The approximate height of the stacks is 10m. The residue of the process presents average ^{210}Pb concentration of 2.5 kBq kg^{-1} (Leonardo et al., in press).

The environmental impact of such facilities can be monitored by using lichen as bio-indicator. Lichens represent a symbiosis of algae (cyano-bacteria and/or green algae) and fungi (asco and basidio-mycetes), where the fungal partner is mainly responsible for the uptake of necessary nutrients or harmful substances, such as heavy metals or radionuclides. There are few data in the literature concerning the concentration of ^{210}Pb and ^{210}Po in lichens. Ugur et al. (2003) using lichens and mosses for biomonitoring coal-fired power plants found concentrations ranging from 600±19 to 1228±36 and from 446±15 to 650±21 Bq kg^{-1} for

*Corresponding author, E-mail: damatto@ipen.br

^{210}Po and ^{210}Pb, respectively. Skuterud et al. (2005) obtained lower concentrations, from 70±2 to 119±3 Bq kg^{-1} for ^{210}Po, in lichens in Norway.

This main objective of this paper is to study the viability of using *Canoparmelia texana* lichen species as bio-indicator of air pollution by ^{210}Pb and ^{210}Po. ^{210}Pb was determined by radiochemical separation followed by gross beta counting using a gas flow proportional counter. Po-210 was spontaneously plated on a silver disc and measured by alpha spectrometry.

Materials and Methods

Sampling

The lichen samples were collected in the tree barks, at about 1.5 m from the ground level. The samples were removed using a plastic knife and stored in paper bags. In the laboratory the lichens were cleaned using distilled water to remove dust and the unwanted materials such as barks and insects were separated manually. The samples were then dried at 60^{o}C and pulverized in a glass mortar. Seven lichen samples were collected in the sites depicted in Figure 2, at distances from 480 m to 1 830 m from the facility, at altitudes ranging from 700m to 760m. The installation is located at an altitude of 760m.The prevailing wind directions in this area are South Southeast (34%) and Southeast (20%).

^{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 ^{210}Pb determination. This procedure consists in an initial precipitation of Pb with H_2SO_4 3M, dissolution of the precipitate with nitrilo-tri-acetic acid at basic pH and precipitation of $PbCrO_4$ with 30% sodium chromate. The ^{210}Pb concentration was determined through its decay product ^{210}Bi, by measuring the gross beta activity of the precipitate of $PbCrO_4$ The ^{210}Pb radionuclide was measured in a low background gas flow proportional detector for 200 minutes.

^{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^{o}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 6.25M 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 1,5M HCl and 20% ammonia solution. Polonium was spontaneously plated on a silver disc at 80^{o}C for 4 hours, under agitation on a hot plate magnetic stirring. The alpha measurement was performed on a surface barrier detector, EG&G Ortec for 100 minutes.

Results and conclusion

Table 1 presents the distances from the sampling points to the installation, the altitudes and the results obtained for ^{210}Pb and ^{210}Po in lichen samples. Concentration values varied from 401 ± 8 Bq kg^{-1} to 1083 ± 92 Bq kg^{-1} for ^{210}Pb and from 115 ± 4 Bq kg^{-1} to 1318 ± 30 Bq kg^{-1} for ^{210}Po. A good correlation is observed if ^{210}Pb concentrations in lichen samples are plotted versus ^{210}Po activities in the same samples (correlation coefficient of 0.93), indicating that these radionuclides reached equilibrium (Figure1).

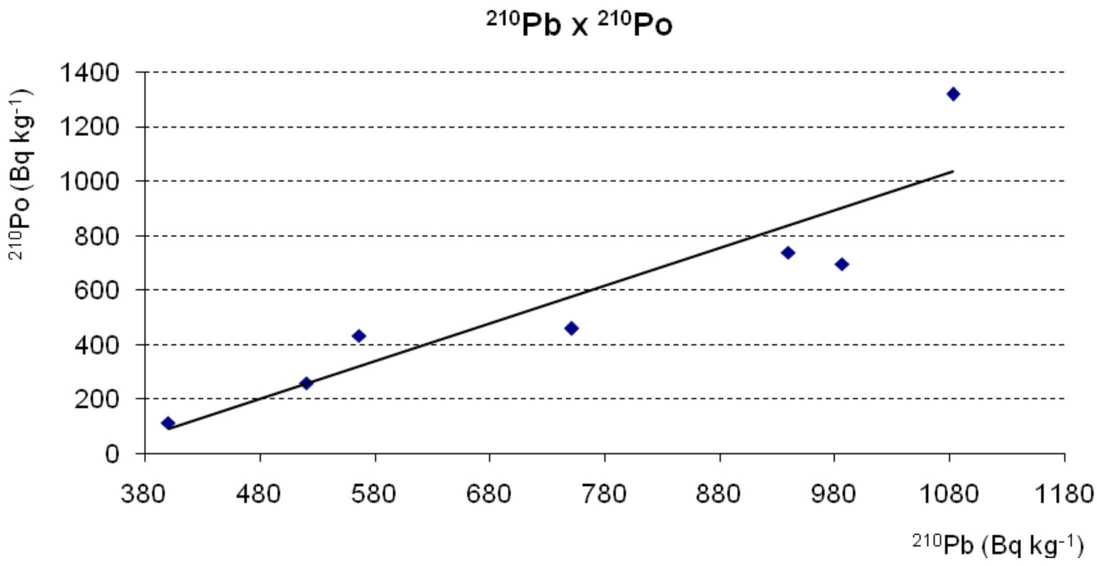

Figure 1.- *^{210}Po and ^{210}Pb concentrations in Bq kg^{-1}in lichens samples*

There are just a few data in the literature concerning the use of the lichen species *Canoparmelia texana* as bio-indicator of air pollution by metals (Coccaro et al, 2000; Saiki et al, 2001, 2007a, 2007b; Fuga et al, 2008) and by natural radionuclides (Alencar et al, 2009). Alencar et al. (2009) observed concentrations varying from 315 ± 22 to 793 ± 68 for ^{210}Pb and from 182 ± 12 Bq kg^{-1} to 761 ± 95 Bq kg^{-1} for ^{210}Po, in lichen samples of the same species in the vicinity of the Instituto de Pesquisas Energéticas e Nucleares (IPEN), located in the state of São Paulo, Brazil. The results obtained in the present work are higher than the range observed in the literature, giving evidence of local environmental contamination by the tin and lead production.

Sampling point	Distances (m)	Altitudes (m)	^{210}Pb	^{210}Po
5	560	756	1083 ± 92	1318 ± 30
9	1430	701	940 ± 57	738 ± 14
3	1200	717	986 ± 73	697 ± 13
1	480	738	752 ± 29	459 ± 10
2	750	740	567 ± 20	434 ± 13
8	630	735	521 ± 57	259 ± 9
4	1000	736	401 ± 8	115 ± 4

Table 1.- *Concentration of ^{210}Pb and ^{210}Po in lichens samples (Bq.kg^{-1})*

The residue of the tin industry stored in open air and the emission from the stacks cause contamination of the surrounding environment by ^{210}Pb and ^{210}Po. The lichens collected more close to the installation in the wind prevailing directions (South Southeast and Southeast), point 2, point 8, point 9 and point 3, presented higher concentrations of the radionuclides studied. Sampling point 5, which was clearly more exposed to the stack emission, due to the local topography is the only one that presented ratio $^{210}Po/^{210}Pb$ above one, giving evidence of

Po not supported by ^{210}Pb already present in the lichen sample. Point 4, physically isolated from the installation (at a height of 760m) by a geographical barrier (at a height of 790m) presented the lower concentrations, and can be considered as the background of the region. It was also observed that the lichens more exposed to atmospheric deposition and for a longer period of time presented a higher accumulation of these elements. The results obtained suggest that the lichen *Canoparmelia texana* can be used as bio-indicator of atmospheric contamination by ^{210}Pb and ^{210}Po.

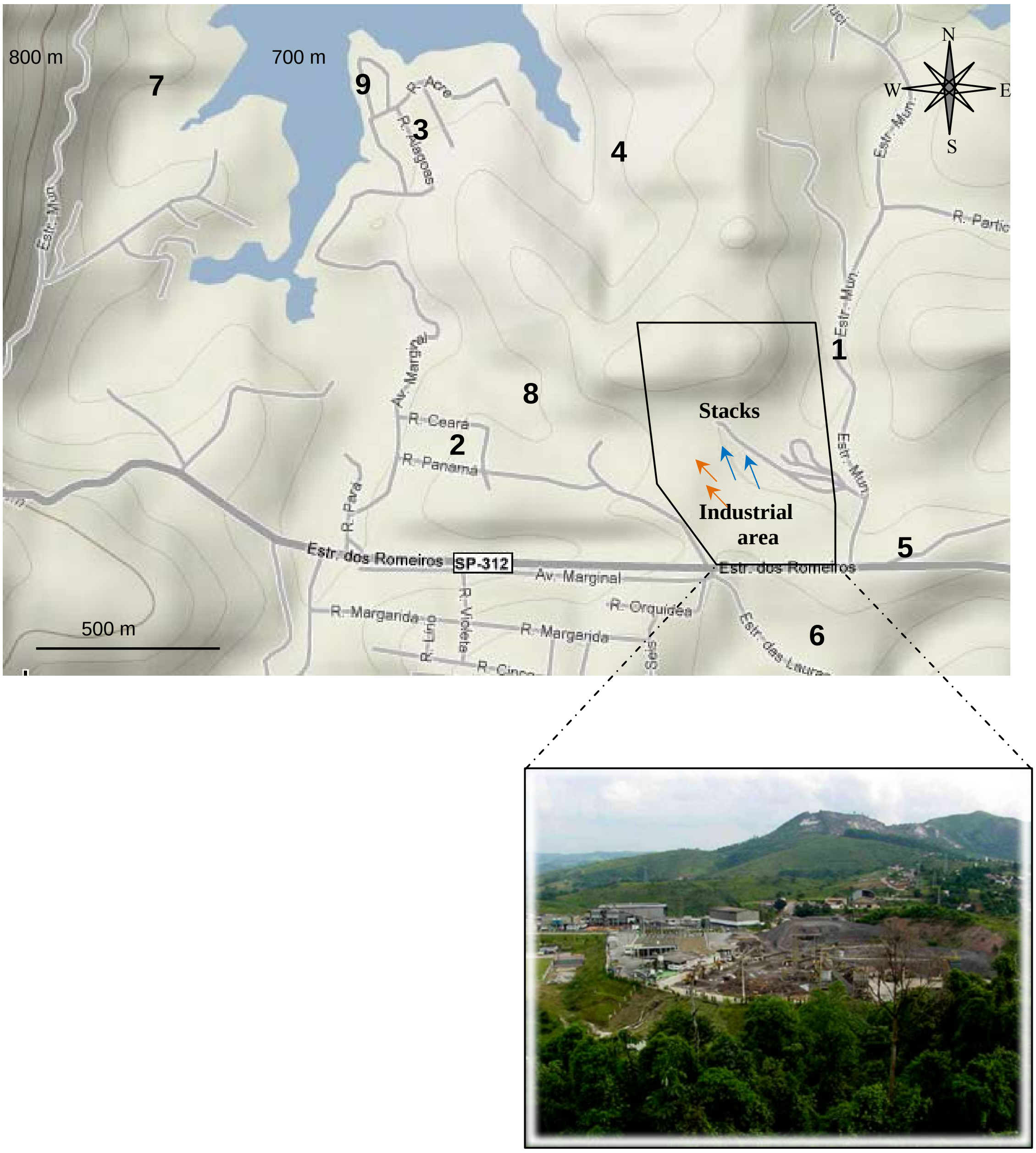

Figure 2.- *Map of industrial area with sampling sites, stacks and wind prevailing direction*

Acknowledgments

This project was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq, grant 300835/95-7; by Comissão Nacional de Energia Nuclear - CNEN, Ph.D. Grant 1312/06; and Fundação de Amparo à Pesquisa do Estado de São Paulo - FAPESP, Project 2007/07351-2.

References

M. M. Alencar, S. R. Damatto, B. P. Mazzilli. *"Determination of natural radionuclides in lichen samples of Canoparmelia texana"*. International Nuclear Atlantic Conference (2009).

D. M. B. Coccaro, M. Saiki, M. B. A. Vasconcellos, M. P. Marcelli. *"Evaluation of trace elements in different species of lichens by neutron activation analysis"*. Journal of Radionalytical and Nuclear Chemistry, 244 (2000) 141-145

A. Fuga, M. Saiki, M. P. Marcelli, P. H. N. Saldiva. *"Atmospheric pollutants monitoring by analysis of epiphytic lichens"*. Environmental Pollution 151 (2008) 334-340

M. A. A. Garcia. "*Caracterização radioquímica e impacto radiológico ambiental no processamento de cassiterita para a produção de estanho e chumbo metálicos"*. Dissertação de Mestrado, Instituto de Pesquisas Energéticas e Nucleares, IPEN, Brasil (2009).

O. R. R. Minuzzi, A. C. N. Bastos, M. L. L.Formoso, S. Andrade, V. A. Janasi, J. A. Flores, **"***Rare earth element and yttrium geochemistry applied to the genetic study of cryolite ore at the Pitinga Mine (Amazon, Brazil)"*. Anais da Academia Brasileira de Ciências 80(4)(2008) 719-733

M. Saiki, L. K. Hiromoto, M. B. A. Vasconcellos, M. P. Marcelli, D. M. B. Coccaro, *"Survey of elemental concentrations in lichen samples collected from São Paulo State"*. Journal of Radionalytical and Nuclear Chemistry 249 (2001) 317-320

M. Saiki, E. R. Alves, M. P. Marcelli. "*Analysis of lichen species for atmospheric pollution biomonitoring in the Santo André municipality, São Paulo, Brazil"*. Journal of Radionalytical and Nuclear Chemistry 273(3) (2007a) 543–547

M. Saiki, A. Fuga, E. R. Alves, M. B. A. Vasconcellos, M. P. Marcelli. *"Biomonitoring of the atmospheric pollution using lichens in the metropolitan area of São Paulo city, Brazil"*. Journal of Radionalytical and Nuclear Chemistry 271(1) (2007b) 213–219

L. Leonardo, S. R. Damatto, B. P. Mazzilli, *"Assessment of atmospheric pollution in the vicinity of a tin and lead industry using lichenized fungii Canoparmelia texana"*. Journal of Environmental Radioactivity, in press.

L. Skuterud, J. P. Gwynn, E. Gaare, E. Steinnes, K. Hove. *"^{90}Sr, ^{210}Po and ^{210}Pb in lichen and reindeer in Norway"*. Journal of Environmental Radioactivity 84 (2005) 441-456

A. Ugur, B. Özden, M. M. Saç, G. Yener. *"Biomonitoring of ^{210}Po and ^{210}Pb using lichens and mosses around a uraniferous coal-fired power plant in western"*. Turkey Atmospheric Environment 37(16) (2003) 2237-2245

M. L. Weber, S. C. Gedoz, F. Benetti, L. H. Ronchi, A. C. Bastos Neto, V. P. Pereira, F. J. Althoff.. "*Variações mineralógicas e petrográficas na porção central do albita-granito Madeira, Pitinga, AM"*. Gaea (Unisinos) 3 (2007) 9-17