Lichen specie *Canoparmelia texana* as bioindicator of environmental impact from the phosphate fertilizer industry of São Paulo, Brazil

L. Leonardo · S. R. Damatto · B. R. Gios · B. P. Mazzilli

Received: 7 November 2013/Published online: 17 December 2013 © Akadémiai Kiadó, Budapest, Hungary 2013

Abstract The Brazilian phosphate industry is the sixth worldwide producer of phosphate rock concentrate generating phosphoric acid, fertilizers, intermediates for fertilizers and other products. Two of the most important of these industries are both located in the city of Cubatão-São Paulo, Brazil, and they are responsible for the production of P₂O₅, generating a residue known as phosphogypsum. The raw material, phosphate rock and products are commonly transported to the industrial complex by a railroad line and present in their composition natural radionuclides from the U and Th series and rare earth elements. Lichens have been used for monitoring atmospheric pollution and radiological contamination for a long time and have proven to be an important tool. This paper aims to highlight the use of the lichen specie Canoparmelia texana (family Parmeliacea) as a bioindicator of atmospheric pollution by the natural radionuclides from the U and Th series and RREs due to the operation of these industries and the storage of their residue in the open air. Samples of these lichen specie were collected in the vicinity of the industries and the railroad. The radionuclides ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb were measured by alpha and beta counting, after radiochemical separation, and ²³⁸U, ²³²Th as well as REEs were determined by instrumental neutron activation analysis. The results showed that the lichens present the same

L. Leonardo e-mail: lucioleo@ipen.br fingerprint as the phosphate rock and phosphogypsum, furthermore the cluster analysis of the results showed that the lichen samples collected near to the railroad line presented the highest values for all the elements studied.

Keywords Lichen · Bioindicator · REEs · INAA · Natural radionuclides

Introduction

The Brazilian phosphate industry is the sixth largest among the world's producers of phosphate rock concentrate producing phosphoric acid, fertilizers, intermediates for fertilizers and other products [1]. All national production of phosphate is controlled by four major companies that together represent 95 % of the total production. Among these, two industries are located in the city of Cubatão, state of São Paulo, Brazil, and are responsible for generating a residue of calcium sulphate, called phosphogypsum, which is stored in open air piles in the vicinity of the premises [2]. The phosphate fertilizer industries produce 269 Mton y^{-1} of P₂O₅, generating 1,076 Mton y^{-1} of phosphogypsum waste that concentrates rare earth elements (REEs) and radionuclides of the natural series of U and Th that are present in the phosphate rock used as raw material [3]. For these industries, the usual means of transportation of the rock concentrate and products is via railroad line.

The raw material used by the industries of phosphate fertilizers is the phosphate rock, which has low solubility in water; therefore, a physical-chemical treatment is necessary in order to increase the availability of phosphorus in the fertilizer. During the chemical attack of the rock concentrate, all the chemical species present in the reaction,

L. Leonardo · S. R. Damatto (⊠) · B. R. Gios · B. P. Mazzilli Laboratório de Radiometria Ambiental, Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes, 2242, São Paulo CEP 05508 000, Brazil e-mail: damatto@ipen.br

both stable and radioactive, are redistributed between phosphoric acid and the phosphogypsum produced. The distribution of the radionuclides and the stable elements is given by their solubility and chemical characteristics. The most common method to obtain phosphoric acid is the wet attack of phosphate rock with sulphuric acid, producing phosphoric acid and the residue of calcium sulphate, phosphogypsum.

The residues from the Brazilian phosphate fertilizer industry were very well characterized about the contents of the radionuclides from ²³⁸U and ²³²Th series, and these studies showed that the radionuclides (²³²Th, ²²⁸Ra, ²²⁶Ra, ²¹⁰Pb and ²¹⁰Po) migrate to the phosphogypsum while the uranium migrates to the phosphoric acid [3, 4].

The environmental impact of the phosphate industry can be studied by using bioindicators, such as lichens. These bioindicators have been used for monitoring atmospheric pollution and radiological contamination for a long time [5–11]. Previous studies using lichen from family *Parmeliacea*, specie *Canoparmelia texana*, confirm its use as a bioindicator of contamination by radionuclides [12, 13] and REEs [10, 14] in the surroundings of a tin industry that processes cassiterite, in Pirapora do Bom Jesus, state of São Paulo [11].

This paper aims to highlight the use of the lichen specie *C. texana* as a bioindicator of air pollution caused by the operation of two fertilizer industries and the storage of their residue in the open air. Using the techniques instrumental neutron activation analysis (INAA) and gross alpha and beta counting, after radiochemical procedure, the rare earth elements (REEs) and the radionuclides ²³⁸U, ²²⁶Ra, ²¹⁰Pb and ²³²Th, ²²⁸Ra, from the ²³⁸U and ²³²Th series, respectively, were determined.

Materials and methods

Study area

The study area is located in the city of Cubatão, state of São Paulo, Brazil, where the most important industrial complex of Latin America is situated, with many industries operating there since the end of the nineteenth century. Among these industries, are the two most important fertilizer industries in Brazil [15]. The climate in the area is warm and wet with temperatures that can reach up to 40 °C in summer and with annual rainfall of 2,500 mm [16].

Sampling

Lichen samples were collected in ten sampling points distributed in the vicinity of phosphate fertilizer industries and the railroad line used for the transportation of the raw material and products (Fig. 1). The samples with a minimum 10 cm of diameter were irrigated with high pure water and extracted from tree barks, about 1.5 m from the ground. The lichen samples were removed with the aid of a plastic knife, to avoid metal contamination, and stored in paper bags. In the laboratory, the samples were separated from other materials such as soil, insects and small pieces of tree trunks with the help of a Coleman stereomicroscope with a maximum increase of $40 \times$. Afterwards, the samples were dried at 60 °C, ground and homogenized manually.

Instrumental neutron activation analysis (INAA)

The instrumental neutron activation analysis (INAA) was used for the determination of 238 U, 232 Th and REEs





Table 1 Activity concentration and range $(Bq kg^{-1})$ in lichen samples

| | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²³² Th | ²²⁸ Ra |
|------------|------------------|-------------------|-------------------------------------|-------------------|-------------------|
| LIC 01 | 34 ± 6 | nd | nd | 27 ± 2 | nd |
| LIC 02 | 32 ± 6 | 36 ± 4 | 920 ± 70 | 12 ± 1 | 310 ± 10 |
| LIC 03 | nd | nd | nd | 2.1 ± 0.2 | nd |
| LIC 04 | 53 ± 9 | 34 ± 3 | $1,540 \pm 160$ | 23 ± 2 | 500 ± 40 |
| LIC 05 | 42 ± 7 | 36 ± 6 | $1,410 \pm 170$ | 18 ± 2 | 390 ± 20 |
| LIC 06 | 94 ± 17 | 65 ± 9 | $2,780 \pm 260$ | 20 ± 2 | 470 ± 20 |
| LIC 07 | 9.8 ± 3.4 | nd | nd | 12 ± 1 | nd |
| LIC 08 | 1.9 ± 0.7 | 17 ± 3 | 920 ± 140 | 1.1 ± 0.1 | 520 ± 60 |
| LIC 09 | 1.8 ± 0.9 | 26 ± 3 | $1,890 \pm 190$ | 2.1 ± 0.2 | 820 ± 80 |
| LIC 10 | 5.1 ± 1.3 | 21 ± 3 | $1,310 \pm 220$ | 3.7 ± 0.3 | 440 ± 20 |
| Range | 1.8–94 | 17–65 | 920–2,780 | 1.1–27 | 310-820 |
| - <u>-</u> | | 228 | 226 210 | 222 | 228 |
| Area | | 23°U | ²²⁰ Ra ²¹⁰ Pb | ²³² Th | ²²⁸ Ra |

nd not determined

| Table 2 Activity concentration | |
|----------------------------------|--|
| range (Bq kg^{-1}) in lichen | |
| samples in different regions | |

| Area | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²³² Th | ²²⁸ Ra |
|----------------------------|------------------|-------------------|-------------------|-------------------|-------------------|
| Cubatão-present study | 2–94 | 17–65 | 920-2,780 | 1–27 | 310-820 |
| Pirapora do Bom Jesus [11] | 17-472 | 21-265 | 401-1,461 | 15-574 | 175–535 |
| Cidade Universitária [13] | 2–7 | 13–38 | 315-793 | 4-12 | 200-351 |
| São Paulo State [14] | 0.3–2.4 | nd | nd | 0.3–7.9 | nd |

nd not determined

concentrations. The lichen samples and reference materials 336 Lichen and Soil 7, both from IAEA and BEN (IWG-GIT) were irradiated for 8 h, under a thermal neutron flux of 10^{12} cm⁻² s⁻¹ at the IEA-R1 nuclear reactor in IPEN— Instituto de Pesquisas Energéticas e Nucleares. Two sets of gamma counting were performed: the first after 1 week of decay and the second after 15 days of decay due to the different half lives of the interest radionuclides. The counting time was 90 min for each sample and standards. Gamma spectrometry was performed with an HPGe detector GMX 25190-ORTEC with 23 % of relative efficiency, resolution of 2.09 keV for 60Co 1,332.49 keV and associated electronics. The spectra were obtained by multichannel SpectrumMaster and analyzed with the Inter-Winner-Gamma 6.0 software from Ortec [17]. More details of the analytical methodology are described by Leonardo et al. [11]. The uncertainties of the results were calculated by error propagation, and the methodology validation was done by analyzing reference materials BEN (Basalt-IWG-GIT) and Soil 7 (IAEA). The relative standard deviations ranged from 0.1 to 14 % and relative errors, from 0.8 to 15 % for the elements analyzed by INAA. The obtained results for the concentrations of lichen samples were above of detection limit [18], except for terbium in two samples.

Determination of ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb

For the determination of the radionuclides ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb lichen samples aliquots of 500 mg, in duplicate, were dissolved in mineral acids in a microwave digestor and submitted to a radiochemical method. After the radiochemical separation, the ²²⁶Ra and ²²⁸Ra concentrations were respectively determined by gross alpha and beta counting of the Ba(Ra)SO₄ precipitate, and the ²¹⁰Pb concentration through its decay product, ²¹⁰Bi, by measuring the gross beta activity of the PbCrO₄ precipitate. Both radionuclides were determined in a low background gas flow proportional detector Berthold, model LB770-2 [13]. For the methodology validation, the reference materials Pacific Ocean Sediment 367 and Irish Sea Sediment 385, both from IAEA were analyzed yielding results in agreement with the certified values [18]. The detection limits for gross alpha and beta methodology were 2.2 mBq kg⁻¹ for ²²⁶Ra, 3.7 mBq kg⁻¹ for ²²⁸Ra and 4.9 mBq kg⁻¹ for ²¹⁰Pb.

Results and discussion

The activity concentrations (Bq kg⁻¹) for the radionuclides 238 U, 226 Ra, 210 Pb, 232 Th and 228 Ra in the lichen samples analyzed are shown in Table 1.

The range activity concentrations obtained in the present study of the natural radionuclides were compared with the range activity concentrations found in lichen samples of the same species collected in the city of Pirapora do Bom Jesus—São Paulo, the University of São Paulo campus (USP-SP), and in the state of São Paulo (Table 2).

The highest concentration determined was for ²¹⁰Pb in the lichen samples collected in Cubatão; these high concentrations can be explained due to the dry and wet fallout of ²¹⁰Pb formed by the decay of ²²²Rn emanating not only from phosphogypsum stacks but also from various industries

| Table 3 C | oncentration and ra | unge of rare earth e | elements in mg kg | -1 in lichen samples | | | | | |
|------------------------|---------------------|----------------------|-------------------|----------------------|-----------------|--------------------|-------------------|-----------------|-----------------|
| | La | Ce | PN | Sm | Eu | Tb | Lu | Yb | Sc |
| LIC 01 | 35 ± 1.3 | 74 ± 6 | 27 ± 3 | 4.5 ± 0.2 | 1.00 ± 0.08 | 0.18 ± 0.06 | 0.15 ± 0.03 | 1.23 ± 0.13 | 3.59 ± 0.11 |
| LIC 02 | 23 ± 0.8 | 42 ± 3 | 16 ± 2 | 3.7 ± 0.2 | 0.70 ± 0.06 | 0.37 ± 0.09 | 0.12 ± 0.03 | 0.92 ± 0.10 | 2.49 ± 0.08 |
| LIC 03 | 6.4 ± 0.2 | 10 ± 1 | 2.9 ± 0.6 | 0.74 ± 0.04 | 0.18 ± 0.02 | <0.07 ^a | 0.009 ± 0.003 | 0.06 ± 0.01 | 0.26 ± 0.01 |
| LIC 04 | 38 ± 1.4 | 69 ± 5 | 27 ± 3 | 5.6 ± 0.3 | 1.05 ± 0.08 | 0.48 ± 0.12 | 0.17 ± 0.04 | 1.17 ± 0.13 | 3.49 ± 0.11 |
| LIC 05 | 28 ± 1.0 | 53 ± 4 | 22 ± 2 | 4.5 ± 0.2 | 0.44 ± 0.05 | 0.72 ± 0.17 | 0.12 ± 0.03 | 0.92 ± 0.10 | 3.10 ± 0.10 |
| LIC 06 | 35 ± 1.3 | 71 ± 5 | 25 ± 3 | 4.8 ± 0.2 | 1.04 ± 0.08 | 1.00 ± 0.23 | 0.14 ± 0.03 | 1.12 ± 0.12 | 3.41 ± 0.11 |
| LIC 07 | 23 ± 0.8 | 45 ± 3 | 12 ± 2 | 3.0 ± 0.2 | 0.57 ± 0.05 | 0.27 ± 0.07 | 0.018 ± 0.006 | 0.17 ± 0.03 | 1.60 ± 0.05 |
| LIC 08 | 4.2 ± 0.2 | 7.5 ± 0.5 | 3.5 ± 0.4 | 0.46 ± 0.02 | 0.13 ± 0.06 | <0.07 ^a | 0.004 ± 0.001 | 0.05 ± 0.01 | 0.11 ± 0.01 |
| LIC 09 | 5.4 ± 0.2 | 8.4 ± 0.5 | 3.5 ± 0.4 | 0.55 ± 0.03 | 0.14 ± 0.06 | 0.07 ± 0.01 | 0.010 ± 0.003 | 0.08 ± 0.01 | 0.31 ± 0.01 |
| LIC 10 | 10 ± 0.5 | 18 ± 1 | 4.3 ± 0.9 | 1.2 ± 0.1 | 0.27 ± 0.12 | 0.11 ± 0.02 | 0.018 ± 0.006 | 0.14 ± 0.02 | 0.41 ± 0.02 |
| Range | 4.2–38 | 7.5–74.0 | 3.5–27 | 0.5-5.6 | 0.13-1.05 | < 0.07 - 1.00 | 0.01-0.17 | 0.05-1.2 | 0.11–3.59 |
| ^a Detection | n limit for Th | | | | | | | | |

chimneys, present in the area, that release ²¹⁰Pb to the atmosphere. The values obtained from the lichens samples collected in the campus of the University of São Paulo indicate concentration ranges related to the background radiation, considering the absence of pollution sources in the area. It was observed that the lowest concentrations found in the present work are comparable to the results obtained in the campus of the University of São Paulo, and these values can be considered as background for this specie.

The results for the concentrations of REEs (mg kg⁻¹) obtained in lichen samples are shown in Table 3.

Saueia and Mazzilli [4] characterized the phosphate rock and the residue phosphogypsum of the two most significant Brazilian phosphate fertilizer industries by the content of natural radionuclides. The authors concluded that the radionuclides 226 Ra, 228 Ra, 232 Th, and 210 Pb migrate to the phosphogypsum while the uranium migrates to the phosphoric acid. The results (mg kg⁻¹) for these radionuclides cited in phosphate rock, and phosphogypsium samples are shown in Table 4. For both industries, the 238 U concentration is lower in phosphogypsium than in phosphate rock and for the other radionuclides the values are in the same order of magnitude.

The same behaviour can be observed in the lichen samples analyzed in the present work. The samples collected near the stacks, LIC 3, LIC 8 and LIC 10, presented lower values for ²³⁸U while the other samples collected near the railroad presented higher values, as well as for the other radionuclides, showing, therefore, the influence of the transportation of the raw material.

Bourlegat et al. [19] and Saueia et al. [20] determined REEs in phosphate rock and phosphogypsium from the same industries, Table 5. The phosphate rock, for both industries, presents higher values of REEs than the phosphogypsium. This behaviour can be observed again in the lichen samples collected near the stacks, LIC 3, LIC 8 and LIC 10, where the concentrations of these elements are lower when compared with the railroad samples, which received the influence of the raw material transported by train. The same fingerprint observed in phosphogypsium was also verified by Silva et al. [21] and Oliveira et al. [22] who analyzed sediment samples collected near the stacks of the same industries in Cubatão.

To recognize the similarity among the lichens samples and verify if the phosphogypsium stacks stored in the open air, and the transportation of the phosphate rock could affect the natural radionuclides and REEs content in lichens samples, cluster analysis (dendrogram) was performed with the normalized values of the REEs and radionuclides ³⁸U, ²²⁶Ra, ²¹⁰Pb, ²³²Th and ²²⁸Ra concentrations as a function of the sampling points (Fig. 2).

Two groups were formed: group A, made by the lichen samples LIC 03, LIC 08, LIC 09 and LIC 10 and group B,

1939

Table 4 Activity concentration, mean \pm standard deviation (M \pm SD) and range in Bq kg⁻¹ for the radionuclides in phosphate rock and phosphogypsium from the Brazilian industries [4]

| | Copebrás | | | | Ultrafertil | | | | | |
|-------------------|-----------------|-------------|-----------------|-----------|--------------|---------|--------------|---------|--|--|
| | Phosphate rock | | Phosphogypsiur | n | Phosphate ro | ock | Phosphogyps | sium | | |
| | $M \pm SD$ | Range | $M \pm SD$ | Range | $M \pm SD$ | Range | $M \pm SD$ | Range | | |
| ²³⁸ U | $1,179 \pm 48$ | 841-1,868 | 48 ± 5 | 42–53 | 527 ± 36 | 498–672 | 49 ± 13 | 40–58 | | |
| ²²⁶ Ra | $1,114 \pm 31$ | 948-1,581 | 744 ± 160 | 550-940 | 261 ± 10 | 222-296 | 344 ± 65 | 280-434 | | |
| ²¹⁰ Pb | $1,310 \pm 223$ | 1,085-1,698 | $1,061 \pm 132$ | 834-1,163 | 543 ± 94 | 463-666 | 347 ± 44 | 316-378 | | |
| ²³² Th | 314 ± 11 | 250-462 | 226 ± 31 | 189–257 | 393 ± 14 | 372–457 | 204 ± 33 | 172-243 | | |
| ²²⁸ Ra | 346 ± 95 | 236–492 | 242 ± 43 | 210-273 | 320 ± 51 | 255–367 | 219 ± 40 | 191–247 | | |

| Table 5 Concentration (mean ± standard deviation) in | | Copebrás | | Ultrafertil | |
|--|----|-----------------|-----------------|-------------------|-----------------|
| mg kg ^{-1} for the REEs in | | Phosphate rock | Phosphogypsium | Phosphate rock | Phosphogypsium |
| phosphogypsum from the | La | $1,717 \pm 170$ | $1,136 \pm 330$ | 2,319 ± 718 | $1,485 \pm 282$ |
| Brazilian industries [20, 21] | Ce | $4,217 \pm 661$ | $2,\!579\pm756$ | $5,468 \pm 1,537$ | $3,015 \pm 54$ |
| | Nd | $1,752 \pm 543$ | $1,401 \pm 545$ | $1,720 \pm 560$ | 970 ± 358 |
| | Sm | 224 ± 23 | 137 ± 43 | 245 ± 61 | 150 ± 3 |
| | Eu | 58 ± 7 | 36 ± 10 | 67 ± 15 | 37 ± 1 |
| | Tb | 12 ± 7 | 6 ± 1 | 12 ± 6 | 6 ± 2 |
| | Yb | 13 ± 4 | 5 ± 2 | 13 ± 3 | 6 ± 1 |
| | Lu | 0.62 ± 0.11 | 0.23 ± 0.04 | 0.65 ± 0.19 | 0.17 ± 0.07 |





made by the lichen samples LIC 01, LIC 02, LIC 04, LIC 05, LIC 06 and LIC 07. The samples of group B presented higher concentrations due to the proximity of the railroad line. The samples of group A collected far from the railroad exhibited behavior that suggest the influence of phosphogypsum stacks. The lichen sample LIC 10, collected closer to the stacks, showed the highest concentration in this group; the values obtained for the lichen sample LIC 09, collected far from the industries, were considered as a background value for all radionuclides and REEs analyzed.

In order to ascertain the re-suspension of the dust particles from the phosphogypsium stacks, soil samples were collected in the same lichen sampling points 08, 09 and 10 and analyzed for the radionuclides ²³⁸U, ²²⁶Ra, ²¹⁰Pb, ²³²Th and ²²⁸Ra and REEs contents. A coaxial Be-layer HPGe detector with 25 % relative efficiency, 2.09 keV resolution at 1.33 MeV and associated electronic devices were used, with live counting time of 150,000 s for ²²⁶Ra, ²¹⁰Pb, ²²⁸Ra determination. More details about the soil sample preparation and analysis can be obtained in

| Table 6 Activity concentration $(Bq kg^{-1})$ in soil samples and | | ²³⁸ U | ²²⁶ Ra | ²¹⁰ Pb | ²³² Th | ²²⁸ Ra |
|--|---------|------------------|-------------------|-------------------|-------------------|-------------------|
| reference values from | SLC 08 | 48 ± 9 | 40 ± 1 | 75 ± 4 | 69 ± 5 | 52 ± 2 |
| UNSCEAR [24] | SLC 09 | 49 ± 9 | 46 ± 1 | 34 ± 2 | 88 ± 6 | 70 ± 3 |
| | SLC 10 | 90 ± 10 | 65 ± 2 | 86 ± 4 | 71 ± 5 | 69 ± 3 |
| | UNSCEAR | 35 | 35 | | 30 | |

Table 7 Concentration of rare earth elements, in mg kg⁻¹, in soil samples and UCC values [26]

| | La | Ce | Nd | Sm | Eu | Tb | Lu | Yb | Sc |
|--------|------------|-------------|------------|---------------|-------------|---------------|---------------|-------------|----------------|
| SLC 08 | 50 ± 2 | 99 ± 6 | 61 ± 5 | 8.0 ± 0.4 | 1.5 ± 0.6 | 0.6 ± 0.1 | 0.4 ± 0.1 | 2.5 ± 0.3 | 12.6 ± 0.6 |
| SLC 09 | 52 ± 2 | 101 ± 6 | 39 ± 4 | 8.3 ± 0.4 | 0.6 ± 0.3 | 0.7 ± 0.1 | 0.3 ± 0.1 | 2.2 ± 0.2 | 5.2 ± 0.2 |
| SLC 10 | 91 ± 4 | 170 ± 10 | 72 ± 7 | 13 ± 1 | 2.2 ± 0.9 | 1.1 ± 0.2 | 0.4 ± 0.1 | 2.8 ± 0.3 | 6.0 ± 0.3 |
| UCC | 32.3 | 65.7 | 25.9 | 4.7 | 0.95 | 0.50 | 0.27 | 1.5 | 7.0 |

Leonardo [18]. The detection limits for gamma analysis were 1.90 Bq kg⁻¹ for ²¹⁰Pb, 0.30 Bq kg⁻¹ for ²²⁶Ra and 0.70 Bq kg⁻¹ for ²²⁸Ra and the methodology validation was performed using the reference materials IAEA 385 and IAEA 326. ²³⁸U and ²³²Th concentrations were determined by INAA, in the same way of the lichens samples. The results for the radionuclides concentrations and reference values (Bq kg⁻¹) for the radionuclides ²³⁸U, ²²⁶Ra and ²³²Th, from UNSCEAR [23] are shown in Table 6.

The radionuclides concentrations found in the three soil samples are in agreement with Silva [24] that analyzed bottom sediment samples collected in the Mogi River, which is located in the area of the fertilizer industries. It can also be observed that for the point SLC 09, that was considered as a background value for the lichen samples, the radionuclides are in equilibrium within their respective series, that is, ²³⁸U–²²⁶Ra–²¹⁰Pb and ²³²Th–²²⁸Ra, from ²³⁸U and ²³²Th series, respectively. For samples SLC 08 and SLC 10 the radionuclides ²³⁸U and ²³²Th presented higher concentrations than their daughters, ²²⁶Ra and ²²⁸Ra, respectively. The concentrations of ²¹⁰Pb are in excess, in both samples in relation to its indirect father ²²⁶Ra, probably due to its release from the industries chimneys of the industrial complex of Cubatão.

The concentrations of ²³⁸U, ²²⁶Ra and ²³²Th obtained for the three soil samples analyzed were compared with world mean concentrations values of soil from UNSCEAR [23], presented in Table 6. It can be verified that, for these three radionuclides, the values found in the present work are higher than the UNSCEAR values, in some samples more than twice, what could be attributed to the dust particles that come from of the huge phosphogypsium stacks.

Table 7 presents the results obtained for the REEs concentrations, mg kg⁻¹, and the reference values from Upper Continental Crust–UCC, from Wedepohl [25]. The



Fig. 3 Enrichment factor (EF), for the soil samples

majority of the REEs analyzed in the three samples presented values higher than the UCC.

To assess if these soil samples are enriched in REEs, the enrichment factor—EF—was calculated using the element Sc as a normalizer element [26]. The EF was calculated according to Eq. (1):

$$EF = (C_i/C_n)_{sample} / (C_i/C_n)_{reference}, \qquad (1)$$

where C_i element analyzed and C_n normalizer element.

The values from UCC were used as reference values. Sutherland [27] proposed a criterion to evaluate sediment samples with five enrichment categories. For the author, values of EF <2 indicate that an element is depleted or low enriched; for values between 2 and 5 the element is moderately enriched; and values between 5 and higher than 40, the sediment can be classified as significant, very high and extremely enriched.

Figure 3 presents the results of the REEs' EF for the three soil samples. The values obtained varied from 0.67 (Tb) to 1.30 (Nd) for soil sample SLC 08; 0.85 (Eu) to 2.38 (Sm) for soil sample SLC 09; and 1.57 (Lu) to 2.99 (La) for

soil sample SLC 10. With these EF values, the soil samples can be classified as depleted or low enriched (SLC 08) and moderately enriched (SLC 09 and SLC 10). The soil sample SLC 10, located near to the phosphogypsium stacks, was the sample that presented the higher values of EF for REEs indicating probably the re-suspension of the dust particles from the phosphogypsium stacks.

Conclusions

The concentrations of the natural radionuclides from the U and Th series, ²²⁶Ra, ²²⁸Ra and ²¹⁰Pb, as well as ²³⁸U and ²³²Th, and Rare Earth Elements, REEs, were determined in lichens samples, specie C. texana, family Parmeliacea, collected in the vicinity of the two largest Brazilian phosphate fertilizer industries and near the railroad that is used for the transportation of the raw material, that is, the phosphate rock. The results, for both, natural radionuclides and REEs, showed that the lichens present the same fingerprint as the phosphate rock and phosphogypsum; higher values for ²³⁸U and ²³²Th in lichens samples collected near to the phosphogypsium stacks and higher values for ²²⁶Ra and ²²⁸Ra in lichens samples collected near the railroad. The same behavior was obtained for the REEs concentrations, higher values in the lichen samples collected near the railroad and lower in the samples collected near the phosphogypsium stacks.

The highest concentrations obtained were for ²¹⁰Pb in all the lichens samples collected showing the direct impact of the phosphogypsium stacks, due to the ²²²Rn emanation and to the release of ²¹⁰Pb from chimneys of the industries present in the area. The cluster analysis of the data proved the results obtained, giving evidence and supporting, therefore, the use of this lichen specie studied as a good bioindicator of atmospheric pollution by radionuclides in areas impacted by TENORM and REEs.

Acknowledgments This project was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico e CNPq, grant 300835/95-7, by Comissão Nacional de Energia Nuclear-CNEN, Ph.D. Grant 1312/2006 and Fundação de Amparo à Pesquisa do Estado de São Paulo- FAPESP, Project 2007/07351-2.

References

1. Departamento Nacional de Produção Mineral—DNPM (2006) Anuário Mineral Brasileiro 2006, Ministério de Minas e Energia

- Departamento Nacional de Produção Mineral—DNPM (2008) Sumário Mineral 2008, Ministério de Minas e Energia
- Mazzilli BP, Palmiro V, Saueia CHR, Nisti MB (2000) J Environ Radioact 49(1):113–122
- 4. Saueia CHR, Mazzilli BP (2006) J Environ Radioact 89:229-239
- 5. Garty J, Galun M, Kessel M (1979) New Phytol 82:159–168
- Chibowski S, Solecki J, Bystrek J (1998) J Radioanal Nucl Chem 230(1–2):319–322
- 7. Conti ME, Cecchetti G (2001) Environ Pollut 114:471-492
- Loppi S, Riccobono F, Zhang ZH, Savic S, Ivanov D, Piritsos SA (2003) Environ Pollut 125:277–280
- Golubev AV, Golubev VN, Krilov NG, Kuznetsova VF, Mavrin SV, Aleinikov AY, Hoppes WG, Surano KA (2005) J Environ Radioact 84:333–342
- Saiki M, Alves ER, Marcelli MP (2007) J Radional Nucl Chem 273(3):543–547
- Leonardo L, Mazzilli BP, Damatto SR, Saiki M, Oliveira SMB (2010) J Environ Radioact 102:906–910
- Leonardo L, Damatto SR, Mazzilli BP, Saiki M (2008) In: Paschoa AS, Steinhäusle F (eds) The natural radiation environmental. Melville, New York
- Alencar MM, Damatto SR, Mazzilli BP (2009) In: International Nuclear Atlantic Conference—INAC 2009, Rio de Janeiro, ISBN 978-85-99141-03-8
- Saiki M, Hiromoto LK, Vasconcellos MBA, Marcelli MP, Coccaro DMB (2001) J Radional Nucl Chem 249:317–320
- Afonso CM (2006) A paisagem da Baixada Santista—Urbanização. Transformação e Conservação, Edusp
- Armani G, Tavares R, Rocha BN (2006) XIV Congresso Brasileiro de Meteorologia, Florianóplis. http://www.cbmet.com/ index.php. Accessed 10 Sept 2013
- 17. ORTEC. INTERWINNERTM 6.0 MCA IW B-32 2004 (2004) Oak Ridge
- Leonardo L, (2010) Utilização de liquens como bioindicadores de contaminação atmosférica por radionuclídeos naturais e metais em região impactada por TENORM. PhD Thesis, IPEN-USP, p 83
- Bourlegat FML, Saueia CHR, Mazzilli BP, Fávaro DIT (2009) In: International Nuclear Atlantic Conference Rio de Janeiro ISBN: 978-85-99141-03-8
- Saueia CHR, Mazzilli BP, Fávaro DIT (2005) J Radioanal Nucl Chem 264(2):445–448
- Silva PSC, Mazzilli BP, Fávaro DIT (2002) Radioprot Colloq 37(C1):795–799
- Oliveira SMB, Silva PSC, Mazzilli BP, Fávaro DIT, Saueia CHR (2007) Appl Geochem 22:837–850
- 23. United Nations Scientific Committee on the effects of atomic radiation (UNSCEAR) (2000). Report Vol. I—Sources and effects of ionizing radiation. Report to the general assembly, with scientific annexes. United Nations, New York
- 24. Silva PSC (2004) Caracterização química e radiológica dos sedimentos do estuário de Santos, São Vicente e baía de Santos. PhD Thesis, IPEN-USP, p 254
- 25. Wedepohl KH (1995) Geochim Cosmochim Acta 59(7): 1217–1232
- 26. Dinescu LC, Duliu OG (2000) Appl Radiat Isot 54:853-859
- 27. Sutherland RA (2000) Environ Geo 39(6):611-627