Assessment of atmospheric pollution in the vicinity of a tin and lead industry using lichen species *Canoparmelia texana*

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ARTICLE INFO

ABSTRACT

This paper examines the viability of using *Canoparmelia texana* lichen species as a bioindicator of air pollution by radionuclides and rare earth elements (REEs) in the vicinity of a tin and lead industry. The lichen and soil samples were analyzed for uranium, thorium and REEs by instrumental neutron activation analysis. The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were determined either by Gamma-ray spectrometry (GRS) (soils) or by radiochemical separation followed by gross alpha and beta counting using a gas flow proportional counter (lichens). The lichens samples concentrate radionuclides (on the average 25-fold higher than the background for this species) and REEs (on the average 10-fold higher), therefore they can be used as a fingerprint of contamination by the operation of the tin industry.

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1. Introduction

1.1. TENORM industries

It is well known that the operation of industries that create TENORM (technologically enhanced naturally occurring radioactive materials) 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. 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 7500 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). It comes from a mine located in Pitinga, Amazon, where the rock is concentrated to 55%. It is estimated that the amount of waste stored is about 54 000 tons annually. 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. Another source of pollution is the release from the smokestacks to the atmosphere during the combustion process.

1.2. Use of lichens as bioindicator of atmospheric pollution

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 equipment, and high-degree of elemental accumulation that allows a continuous and retrospective monitoring. The air filters and deposition collectors,

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on the other hand, give information only about contaminations that occurred in a small period of time corresponding to the sampling time. For many air pollutants, the use of air filters is more appropriate, since they are critical on a short time scale event; but for the radionuclides it is important to monitor long-term concentrations and deposition.

Several papers are found in the literature on the use of lichens as biomonitors of atmospheric contamination by metals; a comprehensive review was performed by Conti and Cecchetti (2001). Lichens were also widely used to indicate radioactive pollution by natural radionuclides (Jeran et al., 1995; Loppi et al., 2003; Golubev et al., 2005; Purvis et al., 2006).

The lichen species used in this work was *Canoparmelia texana* (Tuck.) Elix & Hale, which is a foliose lichen, from the family Parmeliaceae, with large thallus (5–20 cm in diameter), and radial growth found on tree trunks or even on rocks, in several regions in Brazil (Saiki et al., 2001). There are few studies concerning the use of *C. texana* lichen species for the assessment of air quality in urban regions of Brazil (Saiki et al., 2007a, b; Fuga et al., 2008).

This study aimed to evaluate the possibility of using lichen *C. texana* as bioindicator of air pollution by radionuclides and rare earth elements (REEs), in the vicinity of the tin and lead industry. To achieve this task, it is important to know the composition of the piles disposed at open air, comprising major, trace elements and radionuclides, to get the fingerprint of the pollutant; as well as the composition of the raw material used in the industry. Since the

lichen mechanism to obtain nutrients for growth and metabolism is mainly from wet- and dry- precipitates, the re-suspension of the soil–dust particles and the emissions from the smokestacks can accumulate in the lichen. The elemental and activity concentrations of the raw material, the residue, soil and lichens were determined by different methodologies. The lichen, soil, raw material and residue samples were analyzed for uranium, thorium and REEs determination by instrumental neutron activation analysis. The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in soil, raw material and residue samples were determined by GRS; and in the lichen samples, by radiochemical separation followed by gross alpha and beta counting in a gas flow proportional counter. The major elements in soil samples were determined by X-ray Fluorescence technique.

2. Materials and methods

2.1. Description of study area and sampling

The facility is located in the municipality of Pirapora do Bom Jesus, 38 km from São Paulo city in the northwest direction, at an altitude of 760 m. The prevailing wind directions in this area (Garcia, 2009) are South Southeast (34%) and Southeast (20%). The facility has four chimneys with height varying from 6 to 12 m.

Nine soil and lichen samples were collected randomly in the sites depicted in Fig. 1, at distances from 470 m to 2000 m from the main stack at an altitudes ranging from 700 m to 756 m.

The lichen samples were collected from tree bark, at about 1.5 m above ground level. The samples were removed using a plastic knife and stored in paper bags. In
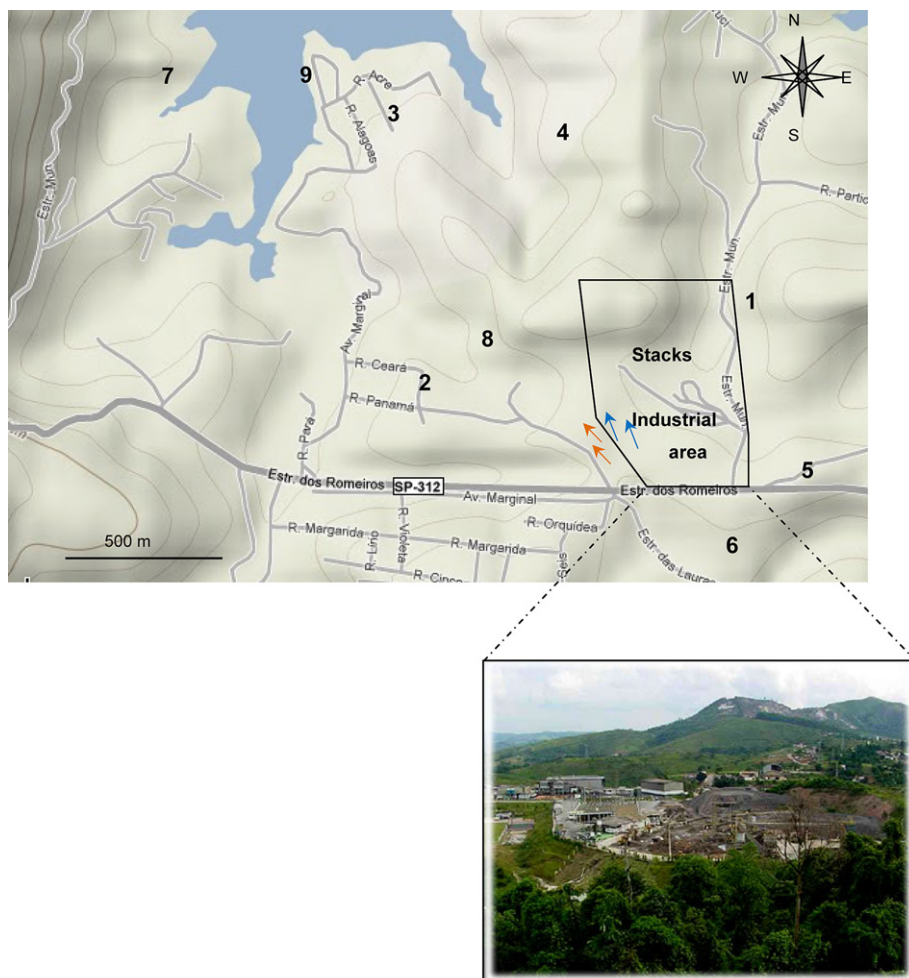

Fig. 1. Map of industrial area with sampling sites, stacks and wind prevailing direction.

the laboratory the lichens were cleaned using distilled water to remove dust and the unwanted materials such as bark and insects were separated manually using stereoscopic microscope. The samples were then dried at 60 °C and pulverized in a glass mortar. Samples of soils were collected, at a depth of 5 cm, were dried at room temperature and powdered until 0.125 mm of grain size.

2.2. ^{228}Ra, ^{226}Ra and ^{210}Pb determination by radiochemical separation

For the determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in lichen samples the procedure described in Alencar et al. (2009) was followed. Aliquots of 500 mg from each lichen sample, in duplicate, 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. After radiochemical separation, the ^{226}Ra and ^{228}Ra concentrations were determined by gross alpha and beta counting of the $Ba(Ra)SO_4$ precipitate and the ^{210}Pb concentration through its decay product, ^{210}Bi, by measuring the gross beta activity of the $PbCrO_4$ precipitate. Both radionuclides were determined in a low background gas flow proportional detector.

2.3. ^{228}Ra, ^{226}Ra and ^{210}Pb determination by gamma spectrometry

The concentration of the natural radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in the soil samples were carried out by non-destructive GRS. Soil samples were packed in 100 ml PVC cylindrical containers and they were kept sealed for 21 days in order to reach radioactive equilibrium between ^{226}Ra and ^{222}Rn and their progenies. A coaxial Be-layer HPGe detector with 15% relative efficiency, 2.09 keV resolution at 1.33 MeV and associated electronic devices were used, with live counting time of 150 000 s. The activity concentration of ^{210}Pb in the samples was corrected for self-absorption (Cutshall et al., 1983). The detector was calibrated using the Standard Reference Material IAEA 300-Baltic Sea Sediment.

2.4. Multi elemental analysis

Lichens and soil samples were analyzed by neutron activation analysis to determine As, Ba, Br, Co, Cr, Cs, Fe, Hf, Rb, Sb, Sc, Se, Ta, Th, U, Zn, Zr and the rare earth elements La, Ce, Nd, Sm, Eu, Tb, Yb and Lu. Approximately 200 mg of lichen and 150 mg of soil (duplicate samples), and about 150 mg of reference materials were accurately weighed and sealed in pre-cleaned double polyethylene bags, for irradiation. The samples and reference materials were irradiated for 16 h, under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at IPEN. Two series of counting were carried out: the first, after one week decay and the second, after 15 days. The counting time was 1.5 h for each sample and reference material. Gamma spectrometry was performed using a coaxial Be-layer HPGe detector with 22% relative efficiency, resolution of 2.09 keV at 1.33 MeV and associated electronic devices. The accuracy and precision was performed by measuring the reference materials lichen IAEA-336, IAEA-Soil 7 and MAG from USGS.

2.5. X-ray fluorescence

Major elements (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and P) and selected trace elements (Cu, F, Ga, Nb, Ni, Pb, Sr, and V) were determined by conventional wavelength-dispersive X-ray fluorescence spectrometry (XRF), using a Philips PW2400 instrument on glass fusion beads (major elements) and pressed-powder briquettes (trace elements). Loss on ignition (LOI) was obtained by calcinations of dry samples at 1000 °C for 60 min. Analyses of standard reference material showed the accuracy and precision to be better than 5% RSD for chemical determinations (Mori et al., 1999). The XRF procedures were carried out at the Institute of Geo-sciences-University of São Paulo. The accuracy and precision of the results were evaluated by measuring JG-1a (granodiorite) and JB-1a (basalt) (Geological Survey of Japan) reference materials analysis.

3. Results and discussion

3.1. Soil samples

The results obtained for trace and major elements, REEs and radionuclide activity concentrations in soil samples and residue are presented in Table 1. For the sake of comparison, the average concentrations for the earth's crust (NASC: North American Shale Composite from Gromet et al., 1984; UCC: Upper Continental Crust from Wedepohl, 1995) are also presented.

The results show that Soil 4 differed from the others in content of Fe and in the Si/Al ratio, indicating that it is probably derived from basic rocks, while the remaining soils seems to be derived from acid rocks. It can be seen that, to some extent the soil samples are enriched in the elements present in the residue (REEs, Ta, Nb and radionuclides), which is the possible contaminant source, when compared with UCC and NASC.

The correlation matrix for all the results obtained in soil samples shows that all radionuclides (^{238}U, ^{226}Ra, ^{232}Th, ^{228}Ra and ^{210}Pb) correlate well between them and with Ta, Hf, Ce, Nb, CaO and MgO (correlation coefficient >0.7); the REEs correlate quite well between themselves. The correlation coefficient between REEs and radionuclides is variable, but generally higher than 0.6.

To better understand the inter-relationship between the major oxides, trace elements and radionuclides in soil samples, an R-mode factor analysis with varimax rotation was applied out. Five factors were extracted accounting for 90.2% of the total variance. Factor 1 (25.4% of the total variance) has high positive loadings from radionuclides (^{238}U ^{226}Ra, ^{232}Th, ^{228}Ra and ^{210}Pb), Ta, Hf, Nb, CaO and MgO. This group refers to the contribution of the residue. Factor 2 (26.3% of the total variance) has positive loadings from SiO_2 and Zr, and negative loadings from Mn, Fe, Ti, Co, Cr, Cu, Ni, Sc, V and Zn, reflecting the differences between soils derived from acid and basic

Table 1
Major element (%) and trace element concentrations (mg kg^{-1}), and activity concentration (Bq kg^{-1}) in soil samples, residues (Res. 1 and Res. 2), and UCC/NASC.

	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Res. 2	UCC	NASC
SiO_2	52.5 ± 2.6	58.5 ± 2.9	52.0 ± 2.6	32.5 ± 1.6	61.1 ± 3.1	66.6 ± 3.3	46.3 ± 2.3	51.6 ± 2.6	64.1 ± 3.2	33.2 ± 1.7	64.57	64.80
Al_2O_3	16.6 ± 0.8	18.9 ± 0.9	23.0 ± 1.1	17.8 ± 0.9	14.8 ± 0.7	13.8 ± 0.7	16.0 ± 0.8	17.1 ± 0.9	16.2 ± 0.8	3.1 ± 0.2	14.60	16.90
MgO	0.68 ± 0.03	1.25 ± 0.06	0.63 ± 0.03	0.22 ± 0.01	1.27 ± 0.06	0.55 ± 0.03	0.77 ± 0.04	2.66 ± 0.13	0.05 ± 0.01	0.94 ± 0.05	2.25	2.85
CaO	1.2 ± 0.1	0.48 ± 0.02	0.06 ± 0.01	0.35 ± 0.02	0.48 ± 0.02	0.45 ± 0.02	0.84 ± 0.04	2.71 ± 0.14	0.15 ± 0.01	12.8 ± 0.6	4.15	3.63
Fe_2O_3	6.4 ± 0.3	7.6 ± 0.4	9.2 ± 0.5	21.6 ± 1.1	6.6 ± 0.3	5.8 ± 0.3	7.7 ± 0.4	6.8 ± 0.3	5.5 ± 0.3	4.5 ± 0.2	4.41	6.33
La	63.3 ± 2.4	143 ± 5	9.8 ± 0.4	9.6 ± 0.5	38.5 ± 1.4	30.8 ± 1.1	44.7 ± 1.5	65.3 ± 2.4	13.1 ± 0.5	1672 ± 45	32.3	31.10
Ce	173 ± 9	102 ± 4	131 ± 6	19.2 ± 0.8	94 ± 4	80.5 ± 6.2	109 ± 8	125 ± 5	48.2 ± 2.7	11,631 ± 815	65.7	66.70
Nd	58.9 ± 7.9	160 ± 20	14.8 ± 2.0	13.9 ± 2.0	32.5 ± 4.5	29.1 ± 7.5	37.2 ± 9.9	44.2 ± 6.7	18.2 ± 6.3	1617 ± 576	25.9	27.40
Sm	8.3 ± 0.4	21.4 ± 1.1	2.1 ± 0.1	3.3 ± 0.2	6.0 ± 0.3	5.3 ± 0.3	6.1 ± 0.3	11.1 ± 0.6	2.1 ± 0.1	1383 ± 53	4.7	5.59
Eu	1.84 ± 0.09	4.68 ± 0.23	0.39 ± 0.02	1.04 ± 0.04	1.08 ± 0.04	1.05 ± 0.08	1.31 ± 0.1	1.97 ± 0.07	0.36 ± 0.02	436 ± 55	1.0	1.18
Yb	3.84 ± 0.26	7.43 ± 0.49	1.89 ± 0.15	2.4 ± 0.2	2.78 ± 0.20	5.6 ± 0.4	3.3 ± 0.3	5 66 ± 0.57	2.15 ± 0.25	2673 ± 166	1.5	3.06
Lu	0.45 ± 0.11	0.87 ± 0.20	0.34 ± 0.08	0.39 ± 0.09	0.50 ± 0.12	0.80 ± 0.14	0.55 ± 0.11	0.91 ± 0.21	0.35 ± 0.08	28 ± 7	0.27	0.46
REEs	310	440	160	49.8	175	154	203	254	84.5	19,440	131.3	135.5
Hf	21.5 ± 0.9	10.7 ± 0.4	10.4 ± 0.5	3.7 ± 0.2	8.8 ± 0.4	17.3 ± 0.9	13.2 ± 0.7	17.6 ± 1.1	13.9 ± 0.9	11,264 ± 459	5.8	6.3
Nb	77.3 ± 3.9	42.0 ± 2.1	33.5 ± 1.7	9.5 ± 0.5	40.5 ± 2.0	nd	95.3 ± 4.8	nd	34.3 ± 1.7	nd	26.0	13.0
Ta	14.7 ± 1.7	5.5 ± 0.7	3.2 ± 0.4	0.81 ± 0.14	5.3 ± 0.6	12.4 ± 1.3	7.0 ± 0.7	15.5 ± 0.7	4.6 ± 0.8	4960 ± 387	1.5	
^{238}U	90 ± 12	110 ± 15	55 ± 8	<16.1	48 ± 7	73 ± 12	49 ± 9	165 ± 16	48 ± 7	(63 ± 6) 10^3		
^{226}Ra	115 ± 2	63 ± 5	46 ± 4	8 ± 2	44 ± 2	75 ± 2	40 ± 1	152 ± 8	45.5 ± 3	(69 ± 4) 10^3		
^{210}Pb	206 ± 18	98 ± 21	55 ± 10	112 ± 13	80 ± 10	113 ± 6	117 ± 6	223 ± 19	66.4 ± 9	2500 ± 300		
^{232}Th	142 ± 7	93 ± 5	70 ± 3	7.5 ± 0.4	66 ± 3	136 ± 11	87 ± 7	167 ± 7	67 ± 4	(128 ± 7) 10^3		
^{228}Ra	175 ± 12	74 ± 5	65 ± 5	16 ± 2	63 ± 5	113 ± 4	61 ± 3	214 ± 8	68 ± 5	(120 ± 10) 10^3		

nd: not determined.

Table 2
Elemental concentration (mg kg^{-1}) and activity concentration (Bq kg^{-1}) in lichen samples.

	LS 1	LS 2	LS 3	LS 4	LS 5	LS 6	LS 7	LS 8	LS 9
La	8.9 ± 0.5	19.2 ± 1.5	8.6 ± 0.7	3.4 ± 0.3	31.8 ± 2.5	5.3 ± 0.3	3.0 ± 0.2	17.3 ± 1.3	9.2 ± 0.5
Ce	25.2 ± 1.9	45.3 ± 5.2	22.9 ± 2.7	4.3 ± 0.5	51.9 ± 5.9	22.1 ± 1.7	8.5 ± 0.6	30.8 ± 3.6	29.7 ± 2.3
Nd	11.3 ± 2.4	29.9 ± 4.5	3.9 ± 0.8	2.3 ± 0.6	28.6 ± 4.0	2.9 ± 1.5	<12	22.0 ± 3.1	26.2 ± 3.7
Sm	2.05 ± 0.12	4.44 ± 0.36	1.81 ± 0.15	0.35 ± 0.02	5.09 ± 0.41	1.86 ± 0.11	0.54 ± 0.03	2.94 ± 0.24	2.29 ± 0.13
Eu	0.18 ± 0.07	0.24 ± 0.16	0.12 ± 0.07	0.06 ± 0.02	0.30 ± 0.24	0.09 ± 0.03	0.06 ± 0.02	0.10 ± 0.06	0.15 ± 0.05
Tb	0.29 ± 0.06	0.61 ± 0.13	0.39 ± 0.09	<0.25	0.77 ± 0.14	0.34 ± 0.07	0.09 ± 0.02	0.41 ± 0.10	0.36 ± 0.07
Yb	2.94 ± 0.31	9.2 ± 0.9	3.8 ± 0.4	0.37 ± 0.05	12.8 ± 1.3	6.9 ± 0.5	1.44 ± 0.11	8.1 ± 0.8	6.6 ± 0.5
Lu	0.57 ± 0.14	1.33 ± 0.14	0.49 ± 0.05	0.05 ± 0.01	1.53 ± 0.16	0.81 ± 0.20	0.16 ± 0.04	1.19 ± 0.13	0.77 ± 0.18
REEs	51.4	110.2	41.9	10.9	132.9	40.3	<25.7	82.9	75.3
As	2.7 ± 0.2	4.7 ± 0.9	2.7 ± 0.5	<1.1	5.1 ± 0.9	2.5 ± 0.21	0.9 ± 0.1	2.3 ± 0.5	3.8 ± 0.3
Ba	145 ± 17	224 ± 35	122 ± 26	<72.4	291 ± 43	135 ± 16	46 ± 6	222 ± 39	165 ± 20
Br	5.1 ± 0.5	14.2 ± 0.7	10.1 ± 0.5	63.4 ± 2.2	7.9 ± 0.4	5.7 ± 0.6	7.0 ± 0.7	3.9 ± 0.2	6.1 ± 0.6
Co	1.02 ± 0.06	2.63 ± 0.24	0.84 ± 0.08	0.47 ± 0.04	1.66 ± 0.15	0.68 ± 0.04	0.44 ± 0.03	0.87 ± 0.08	1.04 ± 0.06
Cr	7.3 ± 0.7	13.3 ± 3.0	9.4 ± 2.2	6.3 ± 1.2	15.9 ± 3.6	5.0 ± 0.5	3.4 ± 0.3	6.4 ± 1.6	9.9 ± 0.9
Cs	0.86 ± 0.07	1.38 ± 0.21	0.46 ± 0.13	0.38 ± 0.08	0.88 ± 0.18	0.57 ± 0.05	0.34 ± 0.03	0.85 ± 0.17	0.48 ± 0.05
Hf	20.2 ± 1.6	38.0 ± 3.7	17.9 ± 1.8	1.7 ± 0.1	53.4 ± 5.2	25.7 ± 2.1	5.4 ± 0.4	37.2 ± 3.7	29.3 ± 2.4
Rb	18.5 ± 2.1	27.3 ± 5.3	15.6 ± 3.3	7.3 ± 1.5	9.2 ± 2.5	16.2 ± 1.8	17.0 ± 1.9	14.2 ± 3.3	12.8 ± 1.5
Sb	0.66 ± 0.12	1.08 ± 0.13	0.53 ± 0.07	0.29 ± 0.03	0.94 ± 0.12	0.57 ± 0.10	0.28 ± 0.05	0.46 ± 0.06	0.79 ± 0.14
Sc	1.18 ± 0.05	2.46 ± 0.16	1.07 ± 0.07	0.62 ± 0.03	1.88 ± 0.12	0.77 ± 0.04	0.42 ± 0.02	1.02 ± 0.07	1.19 ± 0.05
Se	34.5 ± 12.6	22.8 ± 10.1	9.01 ± 3.99	0.80 ± 0.27	29.6 ± 13.1	33.3 ± 12.1	8.72 ± 3.18	17.8 ± 7.9	45.7 ± 16.7
Ta	28.2 ± 3.7	63.0 ± 6.6	24.9 ± 2.6	2.52 ± 0.19	79.0 ± 8.3	27.7 ± 3.7	6.72 ± 0.89	52.0 ± 5.4	37.5 ± 5.0
Zn	129 ± 7	139 ± 11	109 ± 9	90 ± 6	192 ± 15	125 ± 6	73 ± 4	91 ± 7	131 ± 7
Zr	275 ± 35	326 ± 95	105 ± 36	<72	431 ± 123	283 ± 35	66 ± 9	251 ± 75	354 ± 42
^{238}U	262 ± 65	362 ± 54	164 ± 25	18.6 ± 2	473 ± 71	255 ± 63	64 ± 16	286 ± 43	335 ± 82
^{226}Ra	101 ± 7	105 ± 1	53 ± 3	21 ± 3	265 ± 8	151 ± 6	80 ± 40	123 ± 7	176 ± 38
^{210}Pb	778 ± 196	567 ± 20	986 ± 73	401 ± 8	1083 ± 92	998 ± 211	575 ± 55	521 ± 57	940 ± 57
^{232}Th	240 ± 18	373 ± 42	163 ± 18	15.9 ± 1	574 ± 65	320 ± 24	61 ± 5	330 ± 37	312 ± 23
^{228}Ra	379 ± 23	666 ± 98	243 ± 22	176 ± 8	306 ± 5	527 ± 60	410 ± 31	379 ± 15	250 ± 12

LS: Lichen sample.

rocks. Factor 3, with positive loadings from REEs and Y, accounts for 17.8% of the total variance. This group also refers to the contribution of the residue. Factors 4 and 5 account for less than 11% of the total variance each, being therefore of little interpretative use.

These results provide an improved and more in depth analysis of soil contamination by the elements present in the stack, particularly the separation of the elements in two groups: one formed by radionuclides, Hf and Ta and the second one formed by the REEs.

From these results it can be stated that soils are in some extent influenced by the air pollution due to the operation of the installation.

3.2. Lichen samples

The results of measurements of radionuclides (Bq kg^{-1}) and elements (mg kg^{-1}) in lichen samples are presented in Table 2. The cluster analysis for the radionuclides concentration, REEs, Ba, Hf, Se Ta, Zn, Zr (Fig. 2) shows the separation of the lichen samples in two groups contaminated, group A (1, 3, 6 and 9) and group B (2, 5 and
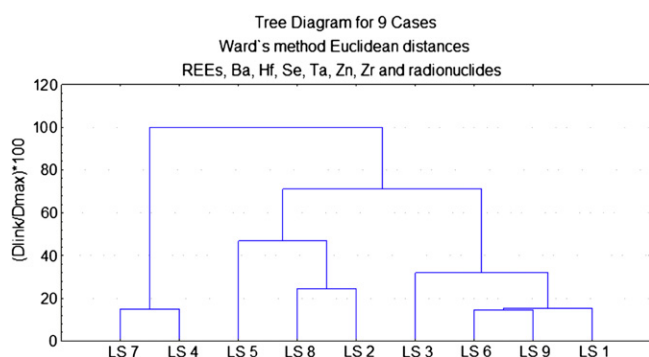

Fig. 2. Dendrogram for lichen samples considering the measurements of REEs, Ba, Hf, Se, Ta, Zn, Zr, ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{228}Ra.

8) and a third group formed by points 4 and 7 that can be considered as the background for the lichen samples. Point 4, physically isolated from the installation (at a height of 760 m) by a geographical barrier (at a height of 790 m) and point 7 more distant from the installation presented the lower concentrations and can be considered as the background of the region.

The lichens collected in the wind prevailing directions (South Southeast, Southeast and North–West) and closer to the installation, point 2, point 5 and point 8, presented higher concentrations of the radionuclides studied.

There are just a few data in the literature concerning the use of *C. texana* as bioindicator of air pollution by metals (Coccaro et al., 2000; Saiki et al., 2001, 2007a, b; Fuga et al., 2008) and by radionuclides (Alencar, 2008). Alencar (2008) observed concentrations in lichen samples ranging from 13.2 ± 3.8 Bq kg^{-1} to 68.4 ± 7.4 Bq kg^{-1} and from 7.2 ± 2.1 Bq kg^{-1} to 28.8 ± 6.0 Bq kg^{-1} for ^{238}U and ^{232}Th, respectively, in a location close to a phosphate fertilizer processing plant. This plant is also classified as a TENORM facility due to the huge amounts of phosphogypsum residue formed in the processing of the phosphate rock, which is stored in the nearby. The results obtained in the present study for the REEs and radionuclides in the contaminated area are considerably higher than those observed from these authors, showing an enhancement due to the stack influence.

4. Conclusions

The residue of the tin industry stored in open air and the emission from the smokestacks cause contamination of the surrounding environment by radionuclides and REEs. The lichens samples concentrate radionuclides (on the average 25-fold higher than the background for this species) and REEs (on the average 10-fold higher), therefore they can be used as a fingerprint of contamination by the operation of the tin industry. It was observed that in case of lichens the contribution of the anthropogenic source

for the studied elements is high in comparison with the background values expected in the area for the same matrix, while in the soils the anthropogenic contribution is only a minor fraction of their natural content (and for that reason in some cases quite difficult to distinguish). In conclusion, it can be stated that lichens are suitable as bioindicator of atmospheric contamination by a TENORM industries.

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