J Radioanal Nucl Chem (2012) 291:71–76
DOI 10.1007/s10967-011-1237-1

Elemental composition evaluation in lichens collected in the industrial city of São Mateus Sul, Paraná, Brazil

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Received: 27 May 2011 / Published online: 17 June 2011

Abstract In this study, *Canoparmelia texana* lichenized fungi species was used as a passive biomonitor of the atmospheric pollution from the industrial city of São Mateus do Sul, PR, Brazil. Lichen samples collected from tree barks were cleaned, freeze-dried and analyzed by neutron activation analysis. Comparisons were made between the element concentrations obtained in lichens from this city and that from a clean area of Atlantic Forest in Intervales Park, SP. The high concentrations of elements As, Ca, Co, Cr, Fe, Hf, Sb, and Th found in lichens could be attributed to the emissions from a ceramic and an oil shale plants.

Keywords Atmospheric pollution · Lichen · Biomonitoring · Neutron activation analysis

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Introduction

Risks to human health caused by air pollution has been increasing due to industrial development, expanding agricultural production and growing global population. Thus the growing concern about current and future levels of environmental pollution has led to an increased demand for experimental methods to study the environment.

The control of atmospheric pollution is normally based on determinations of principal pollutants with conventional automatic recording equipment. However, the high cost of this automatic recording apparatus and its maintenance limit the number of sampling sites, even in relatively small urban areas. On the other hand, biomonitoring is known as an easy, inexpensive and indirect method of determining pollutants and their distributions over large areas.

Among several organisms that have been studied for air pollution monitoring, lichens are useful bioindicators since they accumulate heavy metals, pollutant gases and radionuclides to a greater degree than higher plants. Literature related to biomonitoring shows that lichens can be applied to monitor local depositions around various points and areas of different emission sources in several countries [1–11]. However, in Brazil, lichen analysis data for biomonitoring pollutant emissions are very scarce.

Within this context, the aim of this study was to investigate the use of lichen as biomonitor of emissions in São Mateus do Sul city where an oil shale and ceramic plants are operating. This study is of the great interest since it can assist decision makers in aerial pollution control of this city.

São Mateus do Sul is a municipality located at latitude 25° 52′26″ South and longitude 50° 22′58″ West, with an altitude of 835 m located in the state of Paraná in the Southern region of Brazil and occupies an area of

1,343 km^2 [12]. Its climate is subtropical humid mesothermic and its population in 2009 was 41,257 inhabitants [13]. The two most serious pollutant emission sources in the urban area are the oil shale plant of Brazilian Oil Company (PETROBRAS) where 7,800 tons of shale are processed daily and an INCEPA industry of ceramic material [14].

The extent of element deposition due to local sources in São Mateus do Sul was evaluated using *Canoparmelia texana* lichenized fungi (Tuck.) Elix & Hale. This species is one of the most widely spread in the Brazilian territory except in coastal cities. It is foliose lichen from the Parmeliaceae family with large thallus and considered to be tolerant to pollution found in urban areas. In polluted or urban areas, where its competitors can not be present, this species occurs frequently covering practically the entire tree trunk.

The elemental composition of an oil shale sample was also determined in order to associate with the elements found in the lichens.

Experimental

Study area

The study area included four sampling sites coded F1, F2, F3, and F4 in São Mateus do Sul, Paraná state and a reference site at the Intervales Park located in clean area of the Atlantic Forest in São Paulo state about 60 km from the São Paulo Metropolitan region. The sampling sites of São Mateus do Sul are show in Fig. 1.

Lichen sample collection and preparation

In April 2006, lichen samples were carefully collected from tree barks at a height of about 1.5 m from the ground and stored in paper bags. In each site, lichens collected from several trees were considered as one sample. In this process a titanium knife was used. For the analyses, lichen samples were first cleaned by examining them under a stereomicroscope to remove foreign materials, and then immersed in purified water for about 3–5 min. The cleaned samples were freeze-dried and then ground to a powder using a vibratory micro mill.

Neutron activation analysis procedure

About 180 mg of the sample weighed in clean polyethylene bags were irradiated at the IEA-R1 nuclear research reactor with synthetic element standards. 16 h irradiations under a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} were performed for As, Br, Ca, Co Cr, Cs, Fe, Hf, K, La, Rb, Sb, Sc, Th, U, and Zn determinations. After adequate decay times, the irradiated samples and standards were measured by a hyperpure Ge detector Model GX2020 coupled to an Integrated Signal Processor Model 1510, both from Canberra. All samples and standards were measured at least twice for different decay times. Counting times from 5,400 to 50,000 s were used, based on the

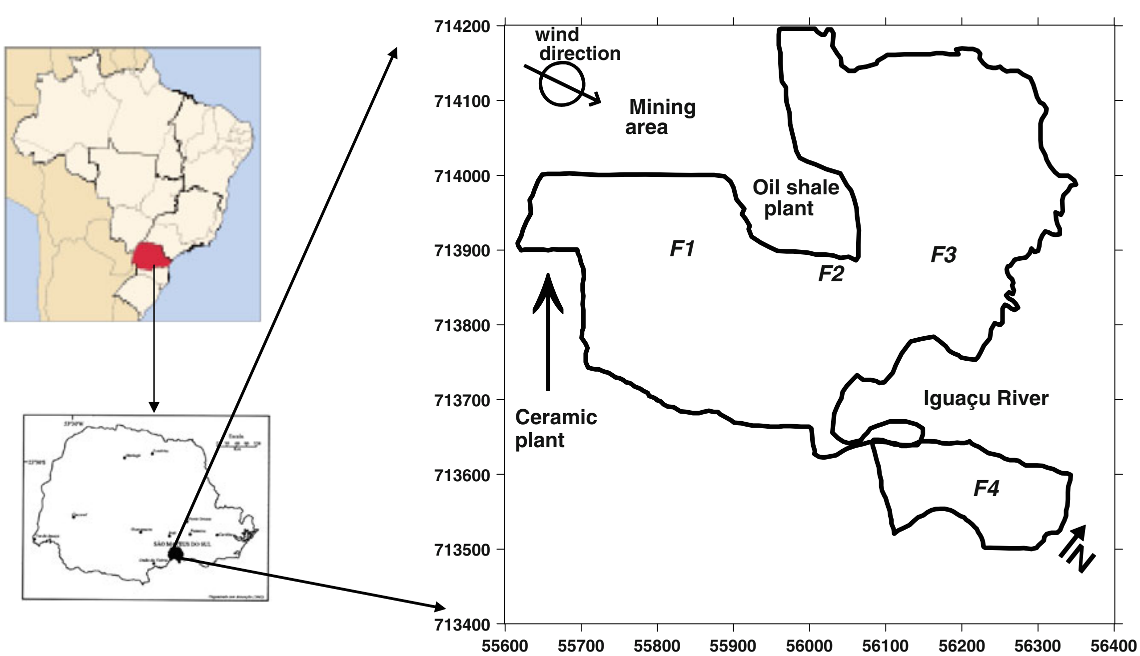

Fig. 1 Map of the study area of São Mateus do Sul, Paraná State, BR. The codes *F1*, *F2*, *F3* and *F4* are the sampling sites

half-lives or activities of the radioisotopes considered. The radioisotopes measured were identified according to their half-lives and gamma-ray energies. The concentrations of elements were calculated by a comparative method. The uncertainties of the results were evaluated using statistical counting errors of sample and standard.

A oil shale sample was ground and analyzed by applying the same experimental conditions adopted in the analyses of lichens excepting the time of irradiation that was of 8 h.

The quality of the analytical results was evaluated by analyzing certified reference material, IAEA 336 lichen provided by the International Atomic Energy Agency (IAEA) and CTA-VTL-2 Virginia Tobacco Leaves from the Institute of Nuclear Chemistry and Technology, Poland.

Results and discussion

Results obtained in the analyses of Certified Reference Materials IAEA 336 lichen and CTA-VTL-2 Virginia Tobacco Leaves are presented in Tables 1 and 2, respectively, together with the values of their certificates. These results indicated good accuracy and precision with relative standard deviations and relative errors lower than 13.5%. The standardized difference or *Z*-score values [17] obtained for certified elements in these references materials were |*Z*-score| < 2, indicating that our results are satisfactory and are within the ranges of certified data at the 95% confidence level.

Results obtained in the analyses of lichens from sites of São Mateus do Sul, Intervales Park as well as of an oil shale sample are presented in Table 3. A preliminary comparison made between the results obtained in different sampling sites indicated that lichens collected in the São Mateus do Sul city presented the highest concentrations for the elements As, Ca, Co, Cr, Fe, Hf, Sb, and Th when compared with those obtained for ones collected in clean area of the Intervales Park (IP). For Br, Cs, Rb, Sc, U, and Zn their concentrations were of the same order of magnitude. Potassium is an essential element for lichens and it was an exception. Lower concentrations of K found in lichens from São Mateus do Sul may be due to the stress caused by pollutants affecting its uptake. According Garty et al. [18], a decrease of K is expected in lichen exposed to heavy pollutions.

The data presented in Table 3 were submitted for sampling site classification by cluster analysis. The resulting dendrogram from this treatment revealed two main groups of samples, as can be seen in Fig. 2. The first group 1 was formed by the sample of oil shale that presented higher concentrations of elements than those found for lichen samples. The second group 2 was formed by two subgroups: 2A formed by the samples from the sites F1 and F3 located around oil shale processing and ceramic plants. The subgroup 2B was formed by sampling sites considered clean (reference site) of Intervales Park and the sites F2 and F4 located in less polluted urban area. F2 located very close to the oil shale plant presented lower concentrations than those from the F1 and F3 sites for most of the elements (see Table 3). The F2 site is a region of depression (shallow valley) in this city. The lower altitude and wind factor can be a hypothesis to explain the reduced deposition at the site. According Král et al. [19] and Kwapulin et al. [20], element concentrations in Fig. 2 lichens depend on altitude. As such, accumulation rises with increasing altitude. Lichens from F4 site also presented low element concentrations since it is farther from the oil shale plant.

Table 1 Element concentrations (in mg kg^{-1}) in the IAEA-336 trace and minor elements in lichen

Elements	This study				Values of the certificate [15]
	M ± SD	RSD, %	RE, %	*Z*-score	
As	0.661 ± 0.076	11.5	4.9	0.18	0.63 (0.55–0.71)*
Br	12.6 ± 0.8	6.2	2.4	−0.09	12.9 (11.2–14.6)*
Ca	2488 ± 111	5.3	–	–	–
Co	0.292 ± 0.019	6.6	0.7	0.015	0.29 (0.24–0.34)*
Cr	1.13 ± 0.06	5.3	–	–	[1.06 (0.89–1.23)*]
Fe	436 ± 17	3.9	1.4	0.04	430 (380–480)*
K	1879 ± 97	5.2	2.1	0.08	1840 (1640–2040)*
La	0.61 ± 0.03	5.2	7.7	0.32	0.66 (0.56–0.76)*
Rb	1.72 ± 0.09	5.1	–	–	[1.76 (1.54–1.98)*]
Sb	0.079 ± 0,01	12.6	8.5	0.33	0.073(0.063–0.083)*
Sc	0.173 ± 0.004	2.3	–	–	[0.17 (0.15-0.19)*]
Se	0.245 ± 0.024	9.7	11.2	0.37	0.22 (0.18–0.26)*
Th	0.148 ± 0.002	1.5	5.6	0.21	0.14 (0.12–0.16)*
Zn	32.6 ± 0.5	1.5	7.3	0.21	30.4 (27.0–33.8)*

M ± SD = Arithmetic mean and standard deviation of at least three determinations; *RSD* relative standard deviation, *RE* relative error; * Recommended value and 95% confidence interval. Numbers between *brackets* are informative values

Table 2 Element concentrations (in mg kg^{-1}) in CTA-VTL-2 Virginia tobacco leaves

Elements	This study				Values of the certificate [16]
	M ± SD	RSD (%)	RE (%)	Z-score	
As	0.980 ± 0.066	6.7	1.2	0.12	0.969 ± 0.072
Br	14.2 ± 1.3	9.1	0.7	−0.04	14.3 ± 1.4
Ca	36131 ± 1078	3.0	0.4	0.07	36000 ± 1500
Co	0.459 ± 0.049	10.7	7.0	0.55	0.429 ± 0.026
Cr	2.044 ± 0.118	5.8	9.1	0.87	1.87 ± 0.16
Cs	0.513 ± 0.020	3.9	0.4	−0.03	0.515 ± 0.046
Fe	1129 ± 21	1.9	4.2	1.17	1083 ± 33
Hf	0.102 ± 0.010	9.8	13.5	−0.65	0.118 ± 0.022
K	10089 ± 308	3.1	2.1	−0.42	10300 ± 400
La	0.898 ± 0.068	7.5	11.1	−0.93	1.01 ± 0.10
Rb	47.5 ± 1.0	2.1	2.2	0.43	48.6 ± 2.3
Sc	0.307 ± 0.010	3.3	–	–	(0.268)
Th	0.350 ± 0.040	11.4	7.5	−0.56	0.378 ± 0.031
Zn	45.9 ± 1.0	2.1	6.0	1.1	43.3 ± 2.1

M ± SD Arithmetic mean and standard deviation of at least three determinations; *RSD* relative standard deviation, *RE* relative error; Numbers between *parenthesis* are informative values

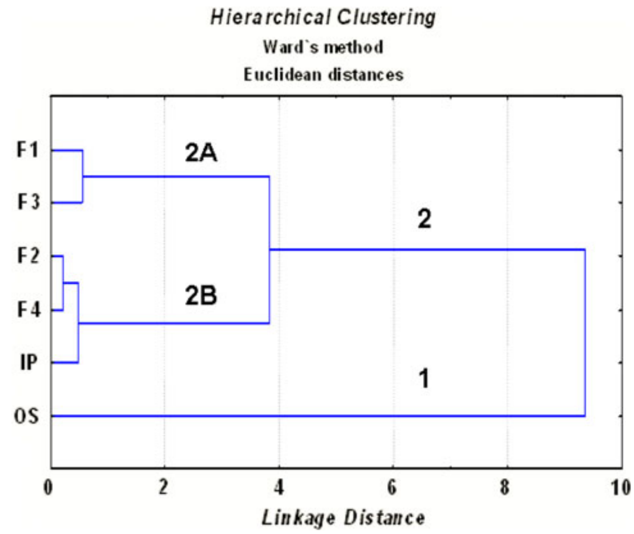

Fig. 2 Dendrogram obtained in cluster analysis using data of lichens and a sample of oil shale. *F1*, *F2*, *F3* and *F4* are samples from the sites in São Mateus do Sul city, *IP* is a sample from Intervales Park and *OS* is of oil shale sample

The cluster analysis substantially confirmed coherent groups of pollution levels.

Distribution maps of element concentrations found in lichen analyses were also drawn using Surfer 8 program [21]. For the elements As, Ca, Cr and Fe these maps are presented in Fig. 3. The highest as concentrations found mainly in lichens in São Mateus do Sul can be attributed mostly to the emissions from oil shale processing plant and to lesser extend from the soil derived from the deposition on lichen of solid particles stirred up by the wind. Elements Ca, Cr and Fe presented the highest concentrations in the sites F1 and F3 Fig. 3 located around the oil shale

Table 3 Element concentrations (mg kg^{-1}) obtained in lichens from São Mateus do Sul city, Intervales Park and in an oil shale sample

Elements	Samples					
	F1	F2	F3	F4	IP	OS
As	1.637 ± 0.009	0.863 ± 0.009	0.310 ± 0.001	1.190 ± 0.004	0.255 ± 0,058	32.9 ± 0.1
Br	7.33 ± 0.02	6.17 ± 0.02	5.92 ± 0.11	3.62 ± 0.01	5.4 ± 0.03	<1.0
Ca	22760 ± 331	3318 ± 92	19527 ± 235	3419 ± 69	5379 ± 485	21852 ± 699
Co	2.75 ± 0.04	1.45 ± 0.02	0.444 ± 0.005	0.444 ± 0.005	0.173 ± 0.033	17.5 ± 0.3
Cr	4.86 ± 0.05	1.02 ± 0.01	2.13 ± 0.03	2.13 ± 0.03	1.10 ± 0.13	42.2 ± 0.3
Cs	0.664 ± 0.008	0.204 ± 0.004	0.249 ± 0.003	0.249 ± 0.003	0.291 ± 0.020	6.62 ± 0.07
Fe	3212 ± 200	795 ± 5	3220 ± 16	1292 ± 7	669 ± 59	41500 ± 300
Hf	0.567 ± 0.004	0.128 ± 0.001	0.549 ± 0.003	0.176 ± 0.001	0.079 ± 0.011	4.39 ± 0.02
K	1952 ± 50	1280 ± 39	478 ± 3	1082 ± 3	2948 ± 181	17500 ± 200
La	2.93 ± 0.01	1.67 ± 0.01	2.80 ± 0.03	1.363 ± 0.005	0.67 ± 0.06	35.5 ± 0.2
Rb	10.6 ± 0.1	2.17 ± 0.04	20.1 ± 0.2	7.5 ± 0.1	11.5 ± 2.0	96.1 ± 1.1
Sb	0.227 ± 0.001	0.170 ± 0.002	0.236 ± 0.003	0.274 ± 0.001	0.073 ± 0.006	5.31 ± 0.16
Sc	0.920 ± 0.004	0.273 ± 0.001	0.850 ± 0.003	0.359 ± 0.001	0.174 ± 0.083	8.88 ± 0.04
Th	0.757 ± 0.004	0.157 ± 0.001	0.817 ± 0.003	0.266 ± 0.001	0.170 ± 0.031	12.14 ± 0.04
U	0.318 ± 0.004	0.147 ± 0.001	0.590 ± 0.021	0.120 ± 0.004	0.062 ± 0.005	7.98 ± 0.05
Zn	54.0 ± 0.3	41.0 ± 0.2	21.7 ± 0.2	28.4 ± 0.2	28.3 ± 2.2	93.7 ± 0.9

F1, F2, F3 and *F4* are samples from sites of São Mateus doSul, *IP* is from Intervales Park and *OS* is a sample of oil shale sample

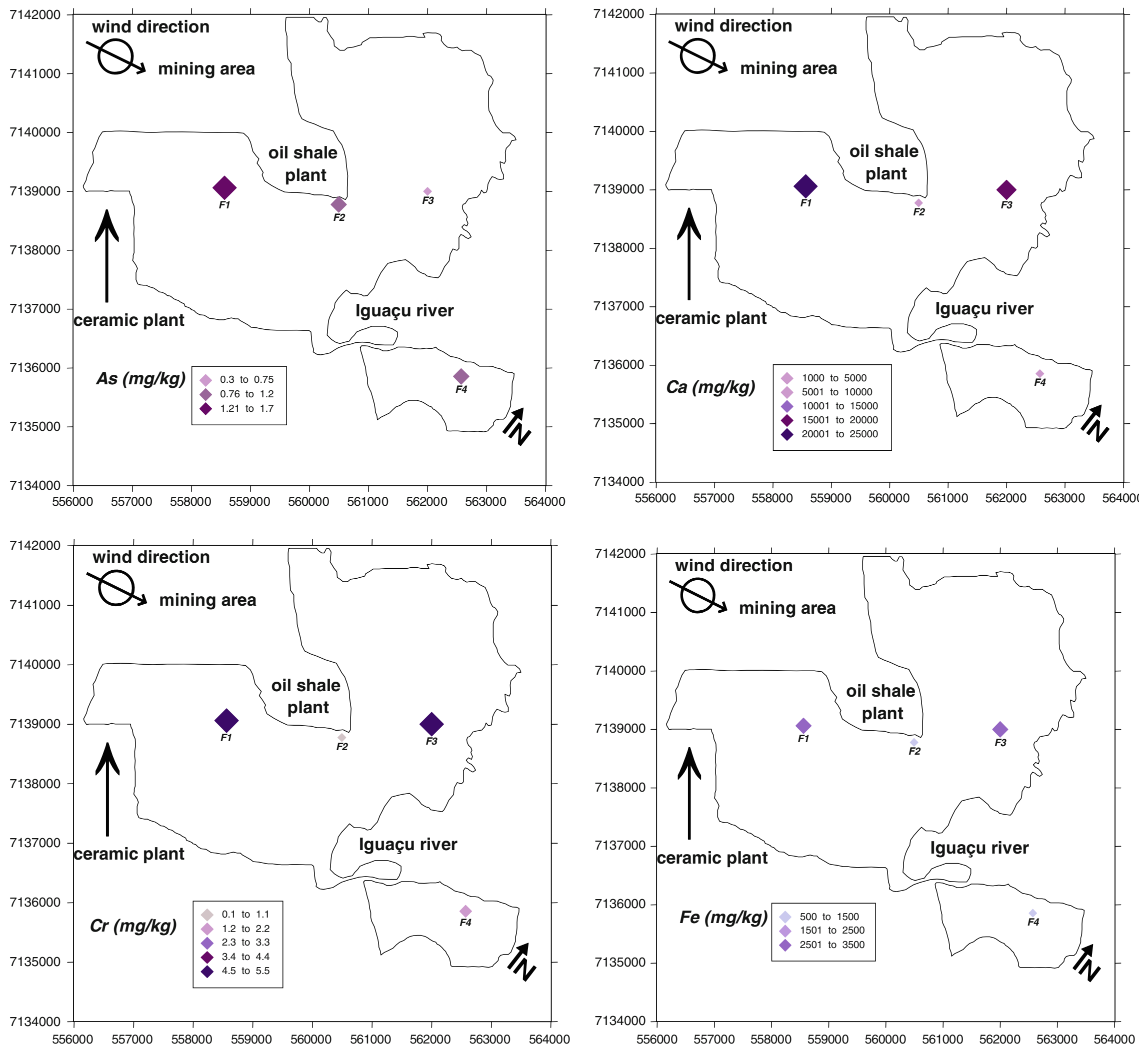

Fig. 3 Distribution maps of As, Ca Cr and Fe concentrations in lichen samples from the city of São Mateus do Sul

processing plant, as can be seen in Fig. 3. In previous study [22] concentrations of Ca, Fe and Si were determined in particulate matter and tree bark samples collected in several sites of São Mateus do Sul city, employing energy dispersive X-ray fluorescence spectrometry. The presence of high levels of these elements in the sites F1 and F3 was attributed as originating from shale oil and ceramic industries. The highest concentrations of Ca and Fe found in lichens in the sites F1 and F3 are similar to the results obtained for particulate matter and tree barks in previous study [22] and thus may be attributed to the emissions from the oil shale and ceramic plants.

Conclusion

From the results obtained we can conclude that higher element concentrations found in lichens from São Mateus do Sul than those from the control site of Intervales Park indicate that emissions from the oil shale and ceramic plants could be a health risk to the population. In addition, results obtained proved that biomonitoring is a simple, efficient and cost-effective method. The findings of this study indicate that the use of lichens as biomonitors is an adequate strategy in environmental impact studies in areas without conventional air pollution monitoring networks.

Acknowledgment Authors are indebted to the financial support from the São Paulo Research Foundation (FAPESP) and the Brazilian National Council for Scientific and Technological Development (CNPq).

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