

Analysis of lichen species for atmospheric pollution biomonitoring in the Santo André municipality, São Paulo, Brazil

M. Saiki,^{1*} E. R. Alves,¹ M. P. Marcelli²

¹ Neutron Activation Analysis Laboratory, Av. Prof. Lineu Prestes 2242, CEP 05508-000, São Paulo, SP, Brazil

² Instituto de Botânica, Av. Miguel Stefano, CEP 01061-970, São Paulo, SP, Brazil

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Instrumental neutron activation analysis was applied for the determination of trace elements in *Canoparmelia texana* species collected in non-polluted areas of Atlantic Forest and in six sites of Santo André Municipality, SP, Brazil. Concentrations of As, Ba, Br, Ca, Cd, Cl, Cr, Cs, Co, Fe, K, La, Mn, Na, Rb, Sb, Sc, Se, U, and Zn were determined and comparisons were made between the results obtained in lichens from different sites.

Introduction

The use of lichens as atmospheric pollution biomonitors is well known.^{1–3} Lichens present several advantages since their sample collections are not expensive and can be used at several sites so that a comparative data can be achieved. Moreover, lichens are perennial and can accumulate elements originating from natural and anthropogenic sources over long periods of time. Their high degree of trace element accumulation enables the determination of several elements with high precision and accuracy.

The aim of this study was to evaluate the levels of trace element pollutants in the Santo André Municipality by analyzing lichen species. Santo André is part of the São Paulo Metropolitan Area, with a population of 625,000 and total area of 174.4 km². This municipality has a serious environmental pollution problem from industrial and vehicular origins.

This work presents concentrations of As, Br, Ba, Ca, Co, Cr, Cs, Fe, La, Na, Sb, Sc, Se, U, and Zn found in *Canoparmelia texana* species. Comparisons were made between the results obtained in different sites, as well as, in unpolluted areas.

Instrumental neutron activation analysis was applied because it is adequate to analyze several interesting elements from the environmental point of view in solid samples without the need of digesting the samples and also due to the high accuracy and precision.

Experimental

Sampling area

C. texana species were collected in the following sampling areas.

(1) In non-polluted areas, samples were collected in a site in Ibiuna county, part of the green ring (horticultural and tourist region) located about 100 km

from São Paulo city; in two Atlantic Forest sites in the Itapetininga region located about 300 km from São Paulo city, and in a site of Manuel Botelho Park, also located in the Atlantic Forest.

(2) In the Santo André Municipality, samples were collected in the sites of Parque Pedroso, Aterro Sanitário, Centro, Parque Celso Daniel, Estação Capuava and Escola Estadual José H. de Paula e Silva. Figure 1 shows the study area and the sampling sites.

As can be seen in Fig. 1, Santo André municipality is composed of two different areas: an urban area and a protected watershed area. There is a petrochemical industrial complex located in a neighboring county, which is the main source of pollution in Santo André area.

Sampling and sample preparation

The selected species for biomonitoring is epiphytic foliose lichen called *Canoparmelia texana* (Tuck.) Elix & Hale of the Parmeliaceae family. It was chosen because its wide distribution in the Brazilian territory, although it is not found in the coast. *C. texana* samples were collected from the bark of trees at about 1.5 m from the ground, using a titanium knife and stored in paper bags. Plastic bags were not adequate to store lichen samples because of their humidity and mould formation.

In the laboratory, the samples were analyzed by an Olympus zoom stereomicroscope Model SZ4045 to remove extraneous materials or pieces of the bark collected with the thallus during the field sampling, being afterwards washed in purified Milli-Q water to remove dust and sand. During the washing procedure, the lichen samples were immersed in purified water for about 3–5 minutes and then placed on filter papers to be dried by freeze-drying for 16 hours under a pressure of about 4·10⁻² mbar. The fine powder of the lichen was obtained by grinding using a vibratory micro mill “pulverisette 0”, Fritsch.

* E-mail: mitiko@ipen.br

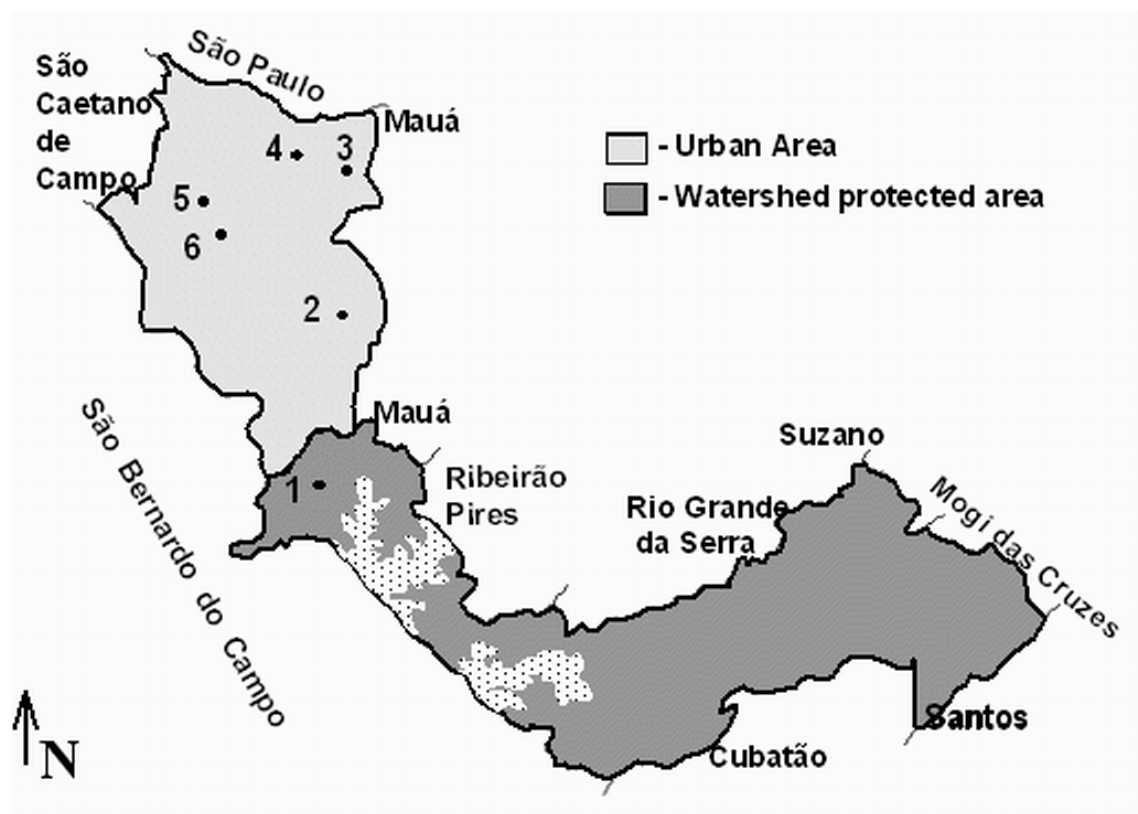


Fig. 1. Santo André Municipality area with location of sampling sites: 1 – Parque de Pedrosos; 2 – Aterro Sanitário; 3 – Estação Capuava; 4 – Escola Estadual José H. de Paula e Silva; 5 – Parque Celso Daniel and 6 – Centro

Procedure used for INAA of *C. texana* samples

For INAA about 150 mg of the sample weighed in clean polyethylene bags were irradiated at the IEA-R1 research nuclear reactor with synthetic standards of elements. Five-minute irradiations under a thermal neutron flux of $1.4 \cdot 10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ were carried out for Cl, K, Mn, Na, Sr and V determinations. Sixteen-hour irradiations under a thermal neutron flux of about $5 \cdot 10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ were performed for As, Ba, Br, Ca, Cd, Cr, Cs, Co, Fe, K, La, Mn, Na, Rb, Sb, Sc, Se, U, and Zn determinations. After adequate decay times, the samples and standards irradiated were measured by a hyperpure Ge detector Model GX2020 coupled to Model 1510 Integrated Signal Processor, being both from Canberra. Each sample and the standards were measured at least twice for different decay times. Counting times from 200 to 50,000 seconds were used, depending on the half-lives or activities of the radioisotopes considered. The radioisotopes measured were identified according to their half-lives and γ -ray energies. The concentration of elements was calculated by the comparative method.

The quality of the analytical results was evaluated by analyzing two certified reference materials, IAEA 336 Lichen and NIST 1547 Peach Leaves provided by the International Atomic Energy Agency (IAEA) and the National Institute of Standards and Technology (NIST), respectively. These reference materials were analyzed by applying the same experimental conditions used in lichen analyses.

Results and discussion

Results obtained for certified reference materials IAEA 336 Lichen and NIST 1547 Peach Leaves showed a good precision and a good agreement with the certified values^{4,5} for the analyzed elements. The relative standard deviations that indicate reproducibility of the results were lower than 12%. The relative errors that indicate the accuracy of the results varied from 0.1 to 12.3%. The standardized difference or Z-score values⁶ obtained for the elements analyzed are presented in Figs 2 and 3 and they were $|Z| < 1$, indicating that our results are satisfactory and in agreement with the certified values.

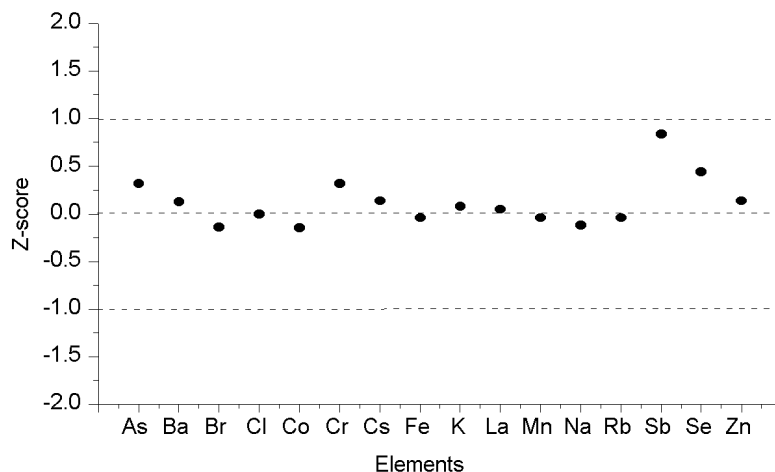


Fig. 2. Values of standardized differences (Z-values) for elements analyzed in IAEA 336 Lichen

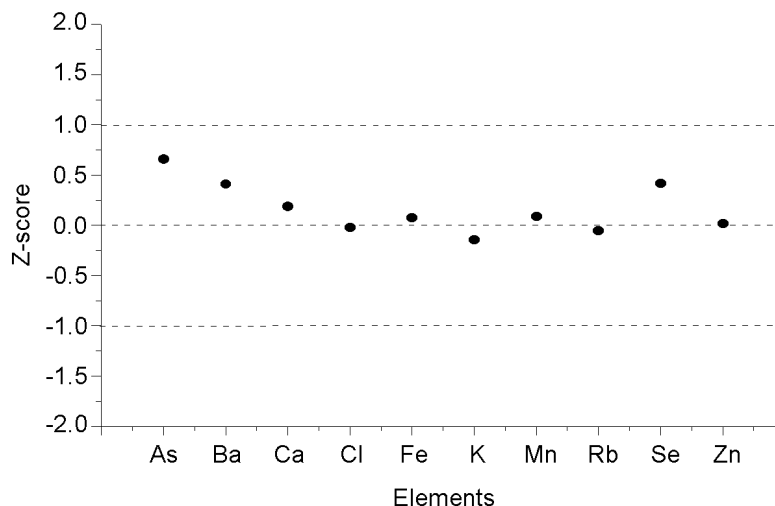


Fig. 3. Values of standardized differences (Z-values) for elements analyzed in Peach Leaves

Concentrations of elements obtained in lichen samples from different sites of the Santo André Municipality and those from unpolluted area are presented in Table 1. The analysis of variance test applied to the results indicated that lichens from unpolluted sites presented lower concentrations of As, Br, Ba, Cd, Co, Cr, Cs, Fe, La, Na, Sb, Sc, U, and Zn when compared with those from the Santo André sites. The highest concentrations of As, Ba, Cd, Co, Cr, La, Mn, Sb, and Zn were obtained in lichens from the sites Estação Capuava and Escola Estadual José H. de Paula e Silva, both located near the industrial areas. The high concentrations of elements obtained in lichens from the sites located near industrial areas could indicate that the

contribution of industrial pollution is higher than that from car pollution. For the elements Cl, Cs, Na, Rb, Sc, Se, and U, their elemental concentrations were the same magnitude for all Santo André sites.

Distribution maps for the case of As and Cr were drawn using Surfer 8 software⁷ and presented in Fig. 4. The contour lines show different concentrations of elements. In the maps, high concentrations of elements can be seen in the areas of Estação Capuava and Escola Estadual Prof. José H. de Paula e Silva and lower concentrations, observed in vicinity from Parque Pedroso and Centro. Besides As, Co, Cr and, Zn showed a very similar pattern because they probably have the same origin.

Table 1. Elemental concentrations in lichens collected in six sites of Santo André Municipality and in unpolluted area (in $\mu\text{g}\cdot\text{g}^{-1}$)

Element	Sampling sites of Santo André Municipality						Unpolluted area mean value
	1	2	3	4	5	6	
As	0.720 ± 0.012	1.329 ± 0.007	3.309 ± 0.021	2.132 ± 0.022	1.578 ± 0.011	0.969 ± 0.007	0.388 ± 0.002
Ba	47.4 ± 2.5	75.9 ± 2.0	95.1 ± 4.2	112.9 ± 2.6	89.6 ± 3.9	33.3 ± 3.7	20.0 ± 4.0
Br	19.89 ± 0.04	7.82 ± 0.02	18.27 ± 0.05	14.78 ± 0.04	10.60 ± 0.03	11.32 ± 0.03	5.52 ± 0.24
Ca	5152 ± 196	16040 ± 569	28026 ± 769	42511 ± 1532	43937 ± 1193	20436 ± 561	7100 ± 100
Cd	≤0.04	≤0.04	1.337 ± 0.002	0.201 ± 0.013	0.728 ± 0.014	0.060 ± 0.009	≤0.04
Cl	929 ± 22	403 ± 10	775 ± 26	620 ± 19	479 ± 13	1052 ± 23	529 ± 5
Cr	6.33 ± 0.05	10.01 ± 0.07	20.44 ± 0.13	22.33 ± 0.14	10.78 ± 0.08	6.78 ± 0.05	1.20 ± 0.01
Cs	0.547 ± 0.005	0.400 ± 0.005	0.696 ± 0.009	0.550 ± 0.006	0.540 ± 0.008	0.622 ± 0.007	0.175 ± 0.002
Co	0.459 ± 0.006	0.979 ± 0.011	2.471 ± 0.030	1.431 ± 0.016	0.894 ± 0.011	0.443 ± 0.006	0.175 ± 0.002
Fe	3339 ± 17	3780 ± 19	4873 ± 25	6018 ± 31	3887 ± 20	2128 ± 12	714 ± 2
K	2873 ± 37	3539 ± 35	4521 ± 39	4255 ± 78	5563 ± 32	5712 ± 31	3195 ± 5
La	6.35 ± 0.03	4.8 ± 0.2	17.50 ± 0.06	10.38 ± 0.04	7.04 ± 0.02	2.90 ± 0.01	0.831 ± 0.003
Mn	65.0 ± 0.4	50.4 ± 0.3	190.7 ± 0.9	121.1 ± 0.6	63.0 ± 0.3	53.6 ± 0.3	60.1 ± 0.3
Na	258.5 ± 5.8	328.4 ± 4.9	360.4 ± 7.5	461.7 ± 8.5	387.7 ± 6.4	250.1 ± 5.2	69.1 ± 1.1
Rb	27.0 ± 0.3	11.0 ± 0.2	13.4 ± 0.2	14.3 ± 0.2	17.7 ± 0.2	12.5 ± 0.2	9.20 ± 0.05
Sb	2.890 ± 0.014	1.136 ± 0.006	5.565 ± 0.018	2.890 ± 0.014	0.794 ± 0.005	0.952 ± 0.005	0.079 ± 0.001
Sc	0.518 ± 0.002	0.970 ± 0.004	0.864 ± 0.004	1.117 ± 0.005	1.123 ± 0.004	0.622 ± 0.007	0.228 ± 0.001
Se	0.450 ± 0.016	0.404 ± 0.019	0.714 ± 0.033	0.897 ± 0.023	0.702 ± 0.029	0.475 ± 0.026	0.154 ± 0.006
U	0.211 ± 0.004	0.362 ± 0.003	0.334 ± 0.006	0.483 ± 0.007	0.383 ± 0.005	0.126 ± 0.005	0.067 ± 0.002
Zn	80.3 ± 0.4	112.5 ± 0.5	765.5 ± 3.2	297.2 ± 1.2	222.2 ± 0.9	108.7 ± 0.5	31.9 ± 0.2

1 – Parque de Pedroso, 2 – Aterro Sanitário, 3 – Estação Capuava, 4 – Escola Estadual José H. de Paula e Silva, 5 – Parque Celso Daniel, 6 – Centro.

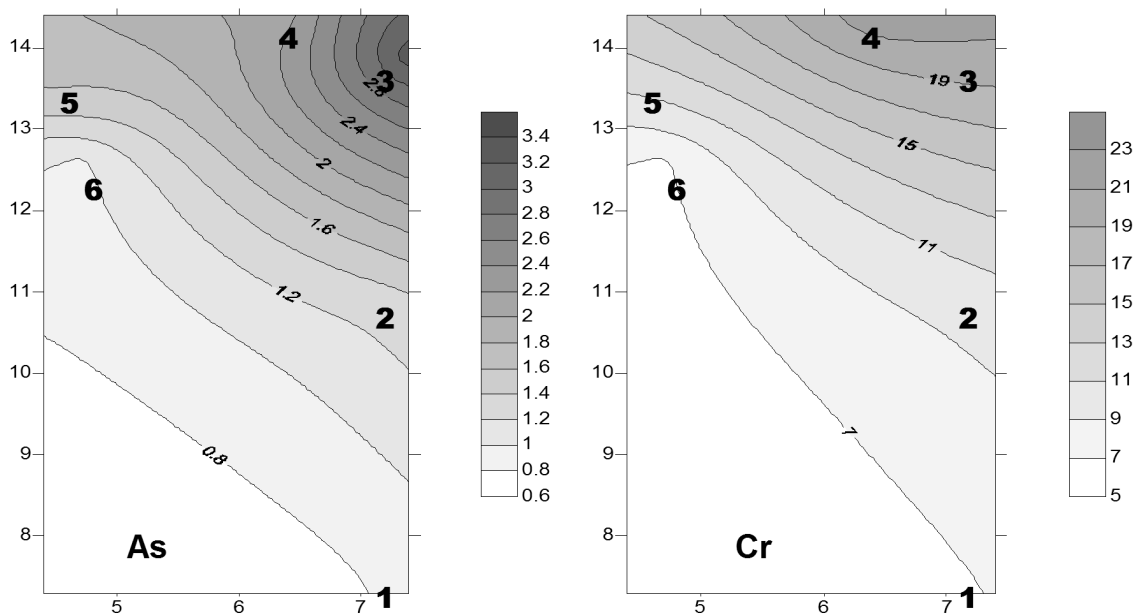


Fig. 4. Distribution maps of As and Cr concentrations (in $\mu\text{g}\cdot\text{g}^{-1}$) in different sites of Santo André Municipality. Sites: 1 – Parque de Pedroso; 2 – Aterro Sanitário; 3 – Estação Capuava; 4 – Escola Estadual José H. de Paula e Silva; 5 – Parque Celso Daniel and 6 – Centro

Conclusions

In conclusion, the results showed that the *C. texana* species might be used as indicators of air quality, as well as, a biomonitor of trace element pollution in complex urban environments.

In general, Santo André has earned the reputation of being highly polluted region. However, according to this study it depends on which area within the Municipality one is looking at.

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