Journal of Radioanalytical and Nuclear Chemistry, Vol. 249, No. 2 (2001) 317–320

Survey of elemental concentrations in lichen samples collected from São Paulo State

M. Saiki,[1]* L. K. Horimoto,[1] M. B. A. Vasconcellos,[1] M. P. Marcelli,[2] D. M. B. Coccaro[1]

[1]*Instituto de Pesquisas Energéticas e Nucleares, Caixa Postal 11049, CEP 05422-970, São Paulo, SP, Brazil*
[2] *Instituto de Botânica, Seção de Micologia e Liquenologia, Caixa Postal 4005, CEP 01061-970, São Paulo, SP, Brazil*

(Received December 13, 2000)

Samples of the lichen *Canoparmelia texana* collected in seven different sites of São Paulo State and one site of the Paraná State were analysed by neutron activation analysis in order to obtain information on the air quality in these regions and also to select a region of interest for the evaluation of baseline level of elements in lichen species. Concentrations of the elements Al, As, Br, Ca, Cd, Cl, Co, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sb, Sc, Se, Ti, Th, U, V, Zn and lanthanides were determined and a preliminary comparisons was made between the results obtained for samples collected in different sites.

Introduction

During the last decades, lichen analyses have played an important role in studies on environmental pollution monitoring. The accumulation of various air pollutants, including heavy metals by lichens is well documented and they are considered as useful monitors for air quality.[1–3]

The advantages of using lichens as biomonitors, instead of direct measurement of pollutants in several materials of the environment such as water and air, are their ease of sampling and their wide geographical distribution, they tend to concentrate air-borne contaminants, allowing comparison of metal concentrations from several regions and also permitting to draw more reliable pollution maps of a large area. Also the morphology of lichens does not vary with the seasons and this fact enables the accumulation of metals along the year.

The occurrence of about 2,800 lichen species in the Brazilian territory has been published,[4] however data concerning their use in monitoring studies and their elemental composition are very scarce. Among these several species, *Canoparmelia texana* is one of the most widely spread lichenized fungi species in the open places of the natural primary and secondary vegetable formations as well inside cities all over the Brazilian territory except on the coastal cities. This is a foliose lichen with large thallus (5 to 20 cm in diameter) and radial growth found on tree trunks or, more rarely, on rocks.

In a previous paper,[5] *C. texana* specimens were analyzed in order to establish adequate conditions for treatment of the sample and for neutron activation analysis to obtain reliable results.

The objective of this work was to analyze specimens growing naturally in several sites of São Paulo State (SP) and one site of Paraná State (PR), Brazil, to obtain preliminary information on the quality of the air in these regions based on lichen analysis data. Samples from sites considered as clean was also analyzed, in order to establish baseline levels of atmospheric pollutants and further identification of polluted areas.

This study is relevant due to the great extension of the country and to the serious problems of pollution encountered, especially in big cities like São Paulo or in industrialized areas.

Experimental

Location of sampling points

C. texana (Tuck) Elix & Hale is an epiphytic lichen species of the family Parmeliaceae and their samples were collected at the following sampling points:

Site Nr. 1: Ibiúna city, SP, that is part of the green ring (horticultural and tourist region) of São Paulo city, and located in the country in a region considered non polluted, about 100 km from São Paulo city, 850 meters above sea level and originally covered by a Mesophyllous Forest however not far from Serra do Mar.

Site Nr. 2: Paranapiacaba, Alto da Serra, São Bernardo do Campo city, SP is a region supposed to be clean, located in a high place near the top of the Serra do Mar, about 720 meters above sea level, surrounded by Tropical Rain Forest.

Site Nr. 3. Jardim Casqueiro, Praça Independência, Cubatão, SP is a town situated in a coastal region, in a place originally covered by mangroves, about two meters above sea level. This city is well known as one of the most polluted cities of the world, however, this sample from this site was collected in a clean place located before the south winds cross the industrial part of the city.

* E-mail:mitiko@curiango.ipen.br

0236–5731/2001/USD 17.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Site Nr. 4: Campo Limpo Paulista, SP, located about 100 km from São Paulo city, 750 meters above sea level. The sample was taken along a non paved road and it was particularly impacted by heavy dust from the soil. This region was originally covered by Cerrado vegetation.

Site Nr. 5: Instituto de Botânica, SP, inside the Botanical Garden, that is situated 15 km far from downtown São Paulo city, inside the urbane zone, 680 meters above sea level.

Site Nr. 6: Instituto de Pesquisas Energéticas e Nucleares (IPEN), located at the Campus of the University of São Paulo, in the urbane zone of São Paulo city and impacted by vehicular emissions.

Site Nr. 7: Campus of São Paulo University (USP), São Paulo, 650 meters above sea level, with heavy vehicular traffic and several building constructions.

Site Nr. 8: Parque da Vila Velha, Ponta Grossa city, State of Paraná, is an open field with great rock formations, in a not polluted area of countryside, 950 meters above sea level.

These sampling sites were chosen based on their lichen abundance and also because they are located within or near the places known as polluted. Samples were also collected in regions considered clean in order to evaluate baseline level of elements in *C. texana*.

Collection of the sample

Lichen samples were collected from tree barks. They were carefully removed using a titanium knife and placed in paper bags. Plastic bags were not adequate for storing lichen samples because of the their humidity and the mould formation.

Treatment of the samples

In the laboratory the thalli were examined under an Olympus stereoscopic microscope model SZ4045 and they were cleaned in order to remove substrates or other adhered material. Then the samples were washed in distilled water where the samples remained immersed for about 5 minutes to remove dust and sand. Next the samples were freeze-dried for 16 hours under a pressure of about $4 \cdot 10^{-2}$ mbar. The fine powder of lichen sample was obtained by manual grinding in an agate mortar. The ground samples were stored in polyethylene vials in a desiccator.

Preparation of standards

Multielement standards were used for the INAA determinations. Stock solutions of elements were prepared by dissolving high purity metals, oxides or salts in high purity reagents or distilled water. In the case of Sb and Cd, certified standard solutions of these elements provided from Spex Chemical were used. Single or multielement solutions were prepared by using appropriate amounts of these stock solutions. The single and multielement standard solutions were then pipetted onto a sheet of Whatman 42 filter paper that were placed in a desiccator to dry. For irradiation these sheets of filter paper were folded and placed in polyethylene bags that were heat sealed for irradiation together with the samples.

Instrumental neutron activation analysis

The samples, ranging in mass from 100–180 mg, were weighed in polyethylene envelopes. Short irradiations of 5 minutes for the determination of Al, Cl, Mg, Mn, Na, Ti and V were carried out using a pneumatic transfer system of the IEA-R1m nuclear reactor and under a thermal neutron flux of $4 \cdot 10^{11}$ n·cm^{-2}·s^{-1}. Longer irradiations of 16 h under thermal neutron flux of about 10^{12} n·cm^{-2}·s^{-1} were carried out for As, Br, Ca, Cd, Co, Cs, Fe, Hf, K, lanthanides, Rb, Sb, Sc, Se, Th, U and Zn determinations.

After adequate decay times, gamma-ray measurements were performed using a Canberra GX2020 hyperpure Ge detector which was coupled to Model 1510 Integrated Signal Processor and System 100MCA Card, both from Canberra. The detector used had a resolution (FWHM) of 0.9 keV for 122 keV gamma-rays of ^{57}Co and 1.78 keV for 1332 keV gamma-rays of ^{60}Co. Samples and standards were measured at least twice and the sample-to-detector distances of 3.0 and 0.5 cm were used for first and second measurements, respectively. The gamma-ray spectra were processed using VISPECT software[6] that evaluates peak areas (counting rates) and gamma-ray energies. The standard comparative method was used for calculating the elemental concentrations.

Standard reference materials IAEA 336 Lichen and NIST 1570 Peach Leaves were irradiated with the samples and analyzed to control the quality of the results. The accuracy and the precision for most of elements were, generally, found to be within 11%.

Results and discussion

Tables 1 and 2 present results obtained in the samples of *C. texana* collected in seven sites of São Paulo State and one site of Paraná State. In all these samples, Ca was found in higher concentrations at levels of percentages. The elements Al, Br, Cl, Fe, K, Mg, Mn, La, Ce, Nd, Na, Rb, Ti, V and Zn are present at the levels of μg·g^{-1} and the elements As, Cd, Co, Cs, Hf, Sm, Eu, Tb, Lu, Sb, Sc, Se, Th and U at the levels of μg·kg^{-1}.

Table 1. Analyses of lichen samples collected in seven different sites from São Paulo State and one site of Paraná State

Element	Samples from the sites							
	Nr. 1 Ibiuna	Nr. 2 Paranapiacaba	Nr. 3 Jardim Casqueiro	Nr. 4 Campo Limpo	Nr. 5 Int. Botanica	Nr. 6 IPEN	Nr. 7 Campus USP	Nr. 8 Parque V. Velha
Al, $\mu g \cdot g^{-1}$	2747 ± 44	1164 ± 33	930 ± 20	306 ± 9	426 ± 17	789 ± 24	7129 ± 137	733 ± 22
As, $\mu g \cdot kg^{-1}$	411 ± 14	315 ± 4	450 ± 6	786 ± 9	274 ± 7	469 ± 11	1057 ± 14	343 ± 6
Br, $\mu g \cdot g^{-1}$	39.40 ± 0.07	11.00 ± 0.05	6.59 ± 0.01	5.70 ± 0.03	1.3 ± 0.4	23.8 ± 3.8	24.80 ± 0.05	3.30 ± 0.01
Ca, %	4.67 ± 0.08	4.79 ± 0.08	1.90 ± 0.02	1.68 ± 0.03	1.96 ± 0.06	2.67 ± 0.02	4.13 ± 0.07	5.74 ± 0.03
Cd, $\mu g \cdot kg^{-1}$	459 ± 59	139 ± 5	266 ± 36	600 ± 15	799 ± 43	640 ± 105	3917 ± 209	1140 ± 122
Cl, $\mu g \cdot g^{-1}$	639 ± 14	308 ± 17	946 ± 43	601 ± 24	449 ± 11	529 ± 21	284 ± 39	665 ± 15
Co, $\mu g \cdot kg^{-1}$	219 ± 4	358 ± 6	353 ± 5	584 ± 8	*	295 ± 4	1063 ± 14	110 ± 2
Cs, $\mu g \cdot kg^{-1}$	117 ± 4	356 ± 7	185 ± 12	276 ± 5	213 ± 1	155 ± 4	1016 ± 9	95 ± 3
Fe, $\mu g \cdot g^{-1}$	1033 ± 6	4276 ± 19	1351 ± 12	1637 ± 7	366 ± 3	540 ± 3	4135 ± 21	540 ± 3
Hf, $\mu g \cdot kg^{-1}$	378 ± 3	182 ± 4	103 ± 7	639 ± 4	–	120 ± 2	1464 ± 5	100 ± 2
K, $\mu g \cdot g^{-1}$	1892 ± 116	1957 ± 468	1262 ± 4	682 ± 249	1491 ± 72	2516 ± 87	3849 ± 233	96 ± 42
Mg, $\mu g \cdot g^{-1}$	251 ± 13	865 ± 96	855 ± 151	122 ± 18	570 ± 54	781 ± 76	3540 ± 437	699 ± 77
Mn, $\mu g \cdot g^{-1}$	37.8 ± 0.9	73.2 ± 1.3	366 ± 9	115 ± 2	11.4 ± 0.2	138 ± 2	164 ± 1	62.7 ± 0.6
Na, $\mu g \cdot g^{-1}$	77.2 ± 0.1	132.8 ± 11.2	81.8 ± 0.1	96.0 ± 7.1	33.9 ± 0.8	53.0 ± 0.5	422.9 ± 0.5	20.6 ± 0.3
Rb, $\mu g \cdot g^{-1}$	6.0 ± 0.1	9.1 ± 0.2	7.7 ± 0.3	13.8 ± 0.2	9.1 ± 0.1	12.9 ± 0.2	20.2 ± 0.2	1.1 ± 0.1
Sb, $\mu g \cdot kg^{-1}$	280 ± 6	192 ± 2	250 ± 6	177 ± 2	191 ± 1	200 ± 2	2000 ± 10	57.7 ± 0.8
Se, $\mu g \cdot kg^{-1}$	201 ± 18	873 ± 29	283 ± 11	278 ± 22	104 ± 9	141 ± 17	665 ± 24	98 ± 15
Th, $\mu g \cdot kg^{-1}$	327 ± 2	412 ± 4	198 ± 1	802 ± 4	83 ± 1	278 ± 2	1933 ± 5	133 ± 2
Ti, $\mu g \cdot g^{-1}$	195 ± 39	64 ± 11	37 ± 7	171 ± 25	47 ± 7	342 ± 77	510 ± 89	114 ± 32
U, $\mu g \cdot kg^{-1}$	55 ± 6	128 ± 4	45 ± 5	152 ± 4	–	64 ± 2	190 ± 9	27 ± 3
V, $\mu g \cdot g^{-1}$	1.5 ± 0.3	3.9 ± 0.2	3.5 ± 0.2	0.40 ± 0.03	1.26 ± 0.08	2.7 ± 0.2	14.0 ± 0.9	1.9 ± 0.1
Zn, $\mu g \cdot g^{-1}$	137.0 ± 0.5	72.8 ± 0.4	58.0 ± 0.2	73.0 ± 0.3	66.1 ± 0.2	97.8 ± 0.4	145.7 ± 0.5	31.9 ± 0.2

The uncertainties of the results were calculated using statistical counting errors of the samples and standards.
* The element was not analysed.

Table 2. Rare earth elements in lichens collected in different sites

Elements	Samples from the sites							
	Nr. 1 Ibiuna	Nr. 6 IPEN	Nr. 3 Jardim Casqueiro	Nr. 8 Parque da V. Velha	Nr. 5 Int. Botânica	Nr. 7 Campus USP	Nr. 2 Paranapiacaba	Nr. 4 Campo Limpo P.
La, $\mu g \cdot g^{-1}$	1.454 ± 0.006	1.238 ± 0.005	2.096 ± 0.004	0.77 ± 0.04	0.936 ± 0.004	7.05 ± 0.05	8.31 ± 0.03	38.7 ± 0.1
Ce, $\mu g \cdot g^{-1}$	3.30 ± 0.02	2.89 ± 0.01	3.07 ± 0.01	1.85 ± 0.01	1.70 ± 0.01	16.58 ± 0.04	15.80 ± 0.04	11.82 ± 0.03
Nd, $\mu g \cdot g^{-1}$	1.62 ± 0.09	1.53 ± 0.07	1.47 ± 0.03	0.66 ± 0.02	0.65 ± 0.05	6.52 ± 0.21	6.87 ± 0.07	4.05 ± 0.05
Sm, $\mu g \cdot kg^{-1}$	180.7 ± 0.4	117.3 ± 0.3	203.0 ± 0.3	102.6 ± 0.3	113 ± 1	1055 ± 1	843 ± 1	523.2 ± 0.7
Eu, $\mu g \cdot kg^{-1}$	39.4 ± 2.4	26.9 ± 0.9	39.2 ± 0.7	21.9 ± 0.6	15.8 ± 0.4	181 ± 2	219 ± 3	108 ± 1
Tb, $\mu g \cdot kg^{-1}$	20.7 ± 1.9	11.1 ± 1.6	14.8 ± 1.2	14.6 ± 1.4	11.2 ± 0.7	203.6 ± 3.2	73.5 ± 3.5	60.7 ± 2.5
Yb, $\mu g \cdot kg^{-1}$	53.1 ± 4.1	44.7 ± 1.6	36.8 ± 3.3	53.3 ± 1.0	28.0 ± 3.0	346.6 ± 6.7	120.0 ± 7.6	134.2 ± 6.2
Lu, $\mu g \cdot kg^{-1}$	10.8 ± 0.4	9.9 ± 0.3	10.5 ± 0.7	10.7 ± 0.3	3.4 ± 0.2	60.1 ± 0.5	17.5 ± 0.4	23.3 ± 0.3
Sc, $\mu g \cdot kg^{-1}$	315 ± 1	125.7 ± 0.7	161 ± 1	163.1 ± 0.7	56.9 ± 0.2	1190 ± 3	306 ± 1	568 ± 2

A comparison between the results obtained for samples collected in different sites indicates that lichen samples from Ibiúna, Instituto de Botânica and Parque da Vila Velha present low concentrations for most elements analyzed. As expected, low concentrations of elements were obtained in samples collected in regions considered clean. These results indicate that samples from these regions could be analyzed to establish baseline levels of elements in *C. texana* for monitoring purposes. The concentrations of several elements in the lichens collected in the open places like Campus of São Paulo University were higher than those found in lichens from clean region of Parque da Vila Velha and Ibiuna, presumably due to accumulation of elements originating from heavy vehicular traffic and from soil (Table 1). The lichen sample from Jardim Casqueiro presented relatively high level of Mn and that from Paranapiacaba presented slightly high levels of Fe and Se. This high levels of elements collected in these samples may be explained due to the air contamination by the smoke from the industries and refineries of the highly polluted area of Cubatão city. The highest concentrations of Na and Cl were expected for lichen collected in Jardim Casqueiro since this city is situated at coastal region, however their concentrations were not so high.

Also samples from Campo Limpo, Paranapiacaba and Campus of São Paulo University presented high levels of rare earth elements probably due to the accumulation of the elements from soil dust (Table 2). Regarding the lanthanide elements, their biological effects of long exposure even at low concentrations are unknown and should be matter of concern.

Although the results reported here represent only samples collected only one sampling time, these data indicate the possibility of using *C. texana* as a bioindicator of atmospheric pollution.

*

The authors wish to acknowledge financial support from CNPq and FAPESP from Brazil and from International Atomic Energy Agency.

References

1. J. E. SLOF, Environmental lichenology: biomonitoring trace element air pollution. Thesis, Technische Universiteit, Delft, 1993.
2. J. GARTY, J. HAGEMEYER, Water, Air and Soil Pollution, 38 (1988) 311.
3. D. H. S. RICHARDSON, Pollution Monitoring with Lichens. Richarmond Publishing Co. Ltd., Slough, England, 1991, p. 25.
4. M. P. MARCELLI, History and current knowledge of Brazilian lichenology, in: M. P. MARCELLI & M. R. D. SEAWARD, Lichenology in Latin America: History, Current Knowledge and Applications: CETESB, São Paulo, 1998, p. 25.
5. M. SAIKI, C. G. CHAPARRO, M. B. A. VASCONCELLOS, M. P. MARCELLI, J. Radioanal. Nucl. Chem., 127 (1997) 111.
6. D. PICCOT, Laboratoire Pierre Sue, CEA-CNRS, Centre d'Études de Saclay, F-91191, Gif-sur Yvette, CEDX, France (personal communication), 1989.