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Atmospheric pollutants monitoring by analysis of epiphytic lichens

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Canoparmelia texana lichenized fungi is a valuable biomonitor for atmospheric pollution.

Abstract

The *Canoparmelia texana* epiphytic lichenized fungi was used to monitor atmospheric pollution in the São Paulo metropolitan region, SP, Brazil. The cluster analysis applied to the element concentration values confirmed the site groups of different levels of pollution due to industrial and vehicular emissions. In the distribution maps of element concentrations, higher concentrations of Ba and Mn were observed in the vicinity of industries and of a petrochemical complex. The highest concentration of Co found in lichens from the São Miguel Paulista site is due to the emissions from a metallurgical processing plant that produces this element. For Br and Zn, the highest concentrations could be associated both to vehicular and industrial emissions. Exploratory analyses revealed that the accumulation of toxic elements in *C. texana* may be of use in evaluating the human risk of cardiopulmonary mortality due to prolonged exposure to ambient levels of air pollution.

Keywords: Air pollution; Lichen; Biomonitoring; *Canoparmelia texana*; Trace elements

1. Introduction

Lichens have long been considered one of the most valuable air pollution biomonitors. As such, they have been widely used to assess trace element atmospheric contaminants. The advantages of using lichens over conventional air sampling techniques are that lichens are perennial and can be found in most terrestrial habitats. They also present easy sampling, low cost and the possibility of monitoring wide areas. Besides that lichens do not have root systems and thus they are able to uptake elements and accumulate them in their tissues. The high degree of trace element accumulation enables the determination of several elements with high precision and accuracy.

Consequently, several papers have been published on monitoring trace elements using lichens in different geographic areas (Loppi and Bonini, 2000; Garty, 2001; Carreras and Pignata, 2002; Yenisoy-Karakas and Tuncel, 2004; Conti and Cecchetti, 2001; Bergamaschi et al., 2004). However, in Brazil studies on the use of lichens as biomonitors are very scarce and environmental pollution is an ever growing concern and problem. Biomonitoring is of great interest due to the extension of the country as well as to the serious problems of pollution encountered, especially in large cities such São Paulo.

The city of São Paulo is one of the largest and most populous cities in the world. The São Paulo Metropolitan Region (SPMR) has a population of about 20 million people, with an area about 8051 km^2 (IBGE, 2007). The area suffers of severe environmental problems due to the atmospheric emissions of about 2000 highly pollutant industries and emissions from about 7.84 million motor vehicles (CETESB, 2006).

Canoparmelia texana (Tuck.) Elix & Hale lichenized fungi chosen in the present study is one of the most widely spread species in the Brazilian territory except coastal cities. This species is foliose lichen from the Parmeliaceae family with large thallus. It is considered to be tolerant to pollution and can be found in urban areas. In polluted or urban areas, where

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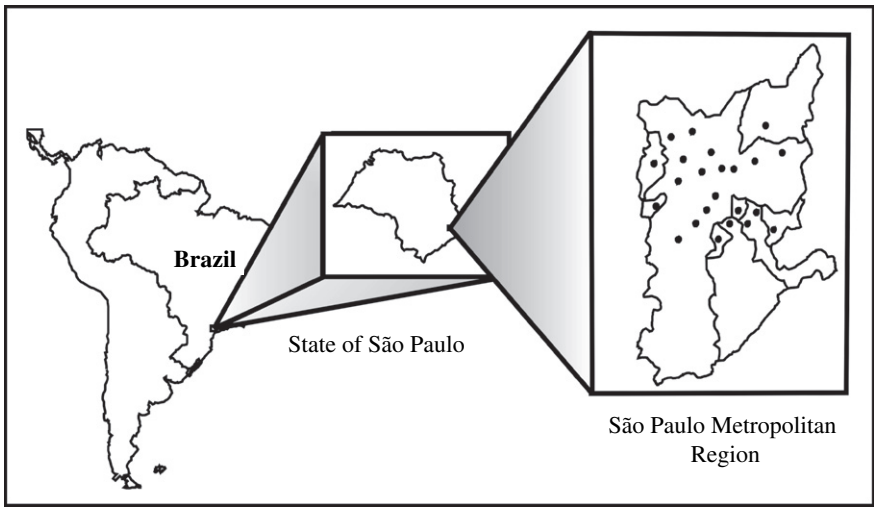

Fig. 1. Location of the studied sites in the São Paulo Metropolitan Region (SPMR). The dots indicate the sampling sites.

its competitors can not be present, this species occurs frequently covering practically the whole tree trunk.

In a preliminary study, results obtained in the analyses of this species collected in eight sampling sites of the SPMR were presented (Saiki et al., 2007). The present study aimed at increasing the number of sampling sites to 23. The samples were collected in an extended geographical area of the SPMR and in unpolluted areas of the Parque Estadual Carlos Botelho (PECB) and the Parque Estadual Intervales (PEI), Atlantic Forest, SP.

The analyses have been carried out by neutron activation analysis (NAA). Quality control of the analytical results was performed by analyzing, in the same way of the lichen samples, selected certified reference materials (CRMs).

2. Materials and methods

2.1. Sample collection and treatment

Fig. 1 shows the location of the SPMR. These sites are expected to be polluted by industrial and vehicular emissions. Downtown urban regions are considered polluted by dense car traffic.

From July 2003 to February 2004, lichens were collected from the bark of trees in 23 sites, near automatic monitoring stations belonging to the Environmental Protection Agency of the State of São Paulo (CETESB). For the analyses, lichen samples were first cleaned by examining them under a stereomicroscope to remove extraneous 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 an agate vibratory micro mill "pulverisette 0", Fritsch. Sample contamination from the agate mill could be considered negligible for the elements determined in this work.

Table 1
Element concentrations (mg kg^{-1}) in lichens from unpolluted areas of Parque Estadual Carlos Botelho (PECB) and Parque Estadual Intervales (PEI)

Elements	PECBX ± s_x[b]	PEI1[a]X ± s_x	PEI2X ± s_x	PEI3X ± s_x	PEI4X ± s_x
As	0.686 ± 0.009	0.282 ± 0.003	0.283 ± 0.006	0.209 ± 0.007	0.336 ± 0.014
Ba	55 ± 23	20 ± 9	7 ± 1	33 ± 1	10 ± 1
Br	44.05 ± 1.60	6.56 ± 0.14	2.34 ± 0.05	5.57 ± 0.15	9.75 ± 0.01
Ca	1218 ± 51	4530 ± 195	2694 ± 123	10404 ± 840	974 ± 91
Cl	1205 ± 58	492 ± 22	115 ± 13	359 ± 24	921 ± 50
Co	0.142 ± 0.003	0.289 ± 0.011	0.196 ± 0.019	0.137 ± 0.011	0.166 ± 0.002
Cr	1.92 ± 0.08	1.61 ± 0.12	1.04 ± 0.08	0.93 ± 0.01	1.31 ± 0.03
Cs	0.211 ± 0.023	0.141 ± 0.003	0.087 ± 0.006	0.355 ± 0.017	0.417 ± 0.001
Fe	848 ± 14	911 ± 39	629 ± 4	614 ± 47	736 ± 11
K	2738 ± 305	3333 ± 81	4701 ± 9	2023 ± 7	2355 ± 7
La	1.044 ± 0.104	0.814 ± 0.071	0.491 ± 0.048	0.575 ± 0.005	0.715 ± 0.007
Mn	90 ± 7	66 ± 5	33 ± 1	76 ± 4	19 ± 1
Mo	0.735 ± 0.040	0.370 ± 0.0 41	0.465 ± 0.052	0.143 ± 0.021	0.276 ± 0.009
Na	139 ± 10	70 ± 4	90 ± 7	52 ± 1	84 ± 1
Rb	8.3 ± 0.3	12.6 ± 0.6	12.6 ± 0.9	10.6 ± 0.7	10.1 ± 0.1
Sb	0.064 ± 0.007	0.069 ± 0.002	0.093 ± 0.012	0.060 ± 0.001	0.092 ± 0.003
Sc	0.301 ± 0.005	0.290 ± 0.016	0.191 ± 0.014	0.185 ± 0.010	0.237 ± 0.001
Se	0.244 ± 0.019	0.196 ± 0.018	0.203 ± 0.016	0.106 ± 0.010	0.242 ± 0.014
U	0.0686 ± 0.0002	0.0764 ± 0.004	0.0578 ± 0.0055	0.0568 ± 0.0006	0.00502 ± 0.0006
Zn	25.4 ± 0.5	29.5 ± 1.0	17.0 ± 0.7	26.2 ± 0.1	39.5 ± 1.0

[a] Four samples were colleted in the PEI.
[b] Uncertainty calculated using statistical counting errors of standard and sample.

Table 2
Element concentrations in lichens from Santana, Congonhas, Parque Ibirapuera, Cerqueira César, Pinheiros, São Caetano do Sul, Santo André (Centro) and Mauá sites of the SPMR

Elements	Santana $X \pm s_x$[a]	Congonhas $X \pm s_x$	Parque Ibirapuera $X \pm s_x$	Cerqueira César $X \pm s_x$	Pinheiros $X \pm s_x$	São Caetano do Sul $X \pm s_x$	Santo André (Centro) $X \pm s_x$	Mauá $X \pm s_x$
As, mg kg^{-1}	1.359 ± 0.032	0.736 ± 0.021	1.528 ± 0.026	4.161 ± 0.032	0.542 ± 0.004	0.677 ± 0.004	1.539 ± 0.017	1.331 ± 0.011
Ba, mg kg^{-1}	67 ± 2	45 ± 2	22 ± 3	71 ± 4	19 ± 3	696 ± 6	85 ± 6	87 ± 3
Br, mg kg^{-1}	6.85 ± 0.04	21.09 ± 0.08	3.25 ± 0.01	23.82 ± 0.09	7.71 ± 0.02	5.39 ± 0.01	46.82 ± 0.11	13.56 ± 0.04
Ca, %	4.78 ± 0.23	4.26 ± 0.20	4.57 ± 0.29	0.196 ± 0.019	4.39 ± 0.22	1.81 ± 0.09	1.83 ± 0.09	3.29 ± 0.17
Cl, mg kg^{-1}	467 ± 7	414 ± 7	442 ± 8	503 ± 10	647 ± 12	271 ± 8	774 ± 20	476 ± 19
Co, mg kg^{-1}	0.834 ± 0.011	0.440 ± 0.006	0.394 ± 0.013	0.900 ± 0.016	0.391 ± 0.009	1.329 ± 0.026	0.835 ± 0.017	1.338 ± 0.024
Cr, mg kg^{-1}	11.05 ± 0.07	6.12 ± 0.04	3.69 ± 0.04	18.1 ± 0.15	6.56 ± 0.09	37.96 ± 0.42	17.26 ± 0.20	19.48 ± 0.23
Cs, mg kg^{-1}	0.340 ± 0.006	0.316 ± 0.006	0.176 ± 0.015	0.467 ± 0.012	0.272 ± 0.008	0.402 ± 0.009	537 ± 10	813 ± 13
Fe, mg kg^{-1}	3339 ± 18	1894 ± 10	1313 ± 10	7774 ± 55	2177 ± 19	3651 ± 30	5498 ± 45	8096 ± 59
K, mg kg^{-1}	4945 ± 160	4485 ± 229	1049 ± 3	6199 ± 83	3593 ± 5	550 ± 2	3996 ± 20	5243 ± 26
La, mg kg^{-1}	4.79 ± 0.026	2.871 ± 0.017	1.226 ± 0.006	7.412 ± 0.033	2.049 ± 0.005	2.494 ± 0.006	7.728 ± 0.017	9445 ± 30
Mn, mg kg^{-1}	66.7 ± 1.3	45.5 ± 0.2	43.9 ± 0.2	64.2 ± 0.3	40.2 ± 0.2	55.4 ± 0.2	55.3 ± 0.3	103.9 ± 0.6
Mo, mg kg^{-1}	2.12 ± 0.09	1.53 ± 0.08	0.65 ± 0.04	4.33 ± 0.14	0.89 ± 0.08	1.79 ± 0.08	4.06 ± 0.20	1.92 ± 0.10
Na, mg kg^{-1}	383 ± 4	237 ± 3	122 ± 3	484 ± 6	239 ± 4	325 ± 5	602 ± 9	829 ± 12
Rb, mg kg^{-1}	16.1 ± 0.2	8.7 ± 0.1	6.3 ± 0.1	10.6 ± 0.2	12.5 ± 0.2	10.3 ± 0.6	14,3 ± 0,2	18.8 ± 0.3
Sb, mg kg^{-1}	1.509 ± 0.010	1.058 ± 0.012	0.413 ± 0.009	2.513 ± 0.027	0.921 ± 0.005	1.181 ± 0.007	1.846 ± 0.010	1.618 ± 0.020
Sc, mg kg^{-1}	0.652 ± 0.003	0.392 ± 0.002	0.390 ± 0.002	1.777 ± 0.009	0.418 ± 0.002	0.601 ± 0.003	1.011 ± 0.005	1.731 ± 0.009
Se, mg kg^{-1}	0.675 ± 0.023	0.36 ± 0.02	0.40 ± 0.07	1.24 ± 0.04	0.45 ± 0.04	0.47 ± 0.05	0.71 ± 0.05	0.77 ± 0.05
U, mg kg^{-1}	0.300 ± 0.019	0.131 ± 0.018	0.109 ± 0,008	0.533 ± 0.029	0.062 ± 0.006	0.075 ± 0.005	0.194 ± 0.014	0.647 ± 0.019
Zn, mg kg^{-1}	149.5 ± 0.7	599.9 ± 2.5	113.1 ± 1.1	148.2 ± 0.8	93.3 ± 0.7	147.8 ± 1.1	142.4 ± 1.1	223.4 ± 2.1

[a] Uncertainty calculated using statistical counting errors of standard and sample.

Table 3
Element concentrations in lichens from Centro, São Miguel Paulista, Santo André (Capuava), Moóca, Parque Dom Pedro II, Diadema, Cambuci and Penha sites of the SPMR

Elements	Centro $X \pm s_x$	São Miguel Paulista $X \pm s_x$	Santo André (Capuava) $X \pm s_x$	Móoca $X \pm s_x$	Pq. D. Pedro II $X \pm s_x$	Diadema $X \pm s_x$	Cambuci $X \pm s_x$	Penha $X \pm s_x$
As, mg kg^{-1}	1.473 ± 0.015	1.717 ± 0.020	2.258 ± 0.017	1.488 ± 0.012	2.202 ± 0.022	0.700 ± 0.007	0.2321 ± 0.015	2.022 ± 0.037
Ba, mg kg^{-1}	66 ± 1	57 ± 7	96 ± 15	52 ± 2	81 ± 2	50 ± 2	70 ± 2	105 ± 2
Br, mg kg^{-1}	13.62 ± 0.04	10.99 ± 0.04	10.75 ± 0.03	6.36 ± 0.02	9.34 ± 0.03	3.62 ± 0.01	3.25 ± 0.01	7.19 ± 0.02
Ca, %	4.45 ± 0.14	2.67 ± 0.08	3.57 ± 0.17	2.68 ± 0.13	4.87 ± 0.23	6.76 ± 0.32	4.01 ± 0.19	6.74 ± 032
Cl, mg kg^{-1}	489 ± 46	459 ± 56	636 ± 78	554 ± 68	402 ± 25	469 ± 25	283 ± 36	258 ± 25
Co, mg kg^{-1}	0.741 ± 0.008	2.127 ± 0.040	2.084 ± 0.039	0.986 ± 0.013	1.202 ± 0.016	0.661 ± 0.009	1.465 ± 0.020	2.760 ± 0.037
Cr, mg kg^{-1}	10.51 ± 0.06	16.4 ± 0.21	14.68 ± 0.20	39.96 ± 0.29	16.58 ± 0.13	9.88 ± 0.08	18.31 ± 0.14	16.92 ± 0.13
Cs, mg kg^{-1}	0.351 ± 0.005	0.899 ± 0.016	0.497 ± 0.014	0.292 ± 0.006	0.495 ± 0.007	0.355 ± 0.006	0.858 ± 0.010	0.601 ± 0.010
Fe, mg kg^{-1}	2998 ± 12	6296 ± 52	3826 ± 29	3106 ± 17	4694 ± 24	2411 ± 13	4060 ± 21	6339 ± 32
K, mg kg^{-1}	3089 ± 11	4499 ± 16	3245 ± 18	4716 ± 63	4472 ± 116	4696 ± 51	4798 ± 49	3713 ± 142
La, mg kg^{-1}	5.170 ± 0.016	7.159 ± 0.048	11.258 ± 0.036	4.511 ± 0.014	5.564 ± 0.018	3.189 ± 0.010	6.083 ± 0.025	9926 ± 41
Mn, mg kg^{-1}	61.8 ± 0.4	73.9 ± 0.5	180.5 ± 1.0	73.5 ± 0.5	83.1 ± 0.4	66.0 ± 0.3	85.0 ± 0.4	70.0 ± 0.3
Mo, mg kg^{-1}	1.40 ± 0.09	3.80 ± 0.19	3.94 ± 0.16	7.84 ± 0.11	2.08 ± 0.09	9.36 ± 0.11	4.49 ± 0.31	1.74 ± 0.12
Na, mg kg^{-1}	580 ± 9	1033 ± 13	396 ± 6	469 ± 7	703 ± 8	431 ± 6	448 ± 6	692 ± 8
Rb, mg kg^{-1}	9.5 ± 0.1	15.6 ± 0.3	10.3 ± 0.2	8.0 ± 0.1	14.4 ± 0.1	10.3 ± 0.1	23.3 ± 0.2	14.4 ± 0.2
Sb, mg kg^{-1}	2.101 ± 0.009	1.586 ± 0.025	3.515 ± 0.016	1.224 ± 0.008	1.981 ± 0.011	0.969 ± 0.006	1.980 ± 0.011	1.926 ± 0.014
Sc, mg kg^{-1}	0.825 ± 0.003	1.544 ± 0.008	0.714 ± 0.004	0.631 ± 0.002	0.983 ± 0.003	0.571 ± 0.002	0.836 ± 0.003	1.495 ± 0.006
Se, mg kg^{-1}	1.58 ± 0.03	0.91 ± 0.07	0.40 ± 0.06	0.69 ± 0.04	1.34 ± 0.04	0.37 ± 0.03	1.11 ± 0.04	1.07 ± 0.05
U, mg kg^{-1}	0.248 ± 0.013	0.370 ± 0.046	0.447 ± 0.043	0.195 ± 0.012	0.511 ± 0.019	0.162 ± 0.011	0.109 ± 0.008	1.742 ± 0.026
Zn, mg kg^{-1}	104.2 ± 0.4	109.3 ± 0.8	440.4 ± 2.8	140.6 ± 0.6	159.6 ± 0.7	164.4 ± 0.7	168.3 ± 0.8	158.2 ± 0.7

Table 4
Element concentrations in lichens from Lapa, Nossa Sra do Ó, Osasco, São Bernardo do Campo, Instituto de Botânica, Taboão da Serra and Santo Amaro sites of the SPMR

Elements	Lapa $X \pm s_x$	Nossa Sra. do Ó $X \pm s_x$	Osasco $X \pm s_x$	São Bernardo do Campo $X \pm s_x$	Instituto de Botânica $X \pm s_x$	Taboão da Serra $X \pm s_x$	Santo Amaro $X \pm s_x$
As, mg kg^{-1}	1.298 ± 0.019	0.750 ± 0.009	0.791 ± 0.011	0.783 ± 0.008	0.605 ± 0.012	0.538 ± 0.013	0.774 ± 0.010
Ba, mg kg^{-1}	79 ± 2	84 ± 2	57 ± 2	65 ± 2	22 ± 1	205 ± 3	108 ± 3
Br, mg kg^{-1}	21.49 ± 0.05	5.66 ± 0.02	1.811 ± 0.02	8.37 ± 0.02	8.64 ± 0.02	14.66 ± 0.60	56.0 ± 4.2
Ca, %	4.67 ± 0.19	8.08 ± 0.32	5.70 ± 0.23	6.28 ± 0.25	8.39 ± 0.34	1.47 ± 598	5.60 ± 0.42
Cl, mg kg^{-1}	707 ± 15	658 ± 18	838 ± 16	6176 ± 116	5446 ± 112	6378 ± 148	4635 ± 138
Co, mg kg^{-1}	1.212 ± 0.015	1.048 ± 0.014	0.654 ± 0.009	1.286 ± 0.015	0.441 ± 0.006	1.606 ± 0.018	1.172 ± 0.013
Cr, mg kg^{-1}	15.56 ± 0.12	13.12 ± 0.10	9.97 ± 0.08	14.06 ± 0.09	5.89 ± 0.05	13.64 ± 0.10	12.01 ± 0.09
Cs, mg kg^{-1}	0.619 ± 0.008	0.644 ± 0.008	0.473 ± 0.007	0.649 ± 0.007	0.184 ± 0.004	1.336 ± 0.011	0.571 ± 0.007
Fe, mg kg^{-1}	4331 ± 22	4288 ± 22	2907 ± 16	3984 ± 16	1871 ± 8	5568 ± 23	4404 ± 18
K, mg kg^{-1}	5356 ± 110	5075 ± 32	4279 ± 44	5141 ± 33	2596 ± 69	10200 ± 80	6478 ± 90
La, mg kg^{-1}	6.01 ± 0.02	5.79 ± 0.02	5.29 ± 0.02	10.89 ± 0.03	2.49 ± 0.01	8.05 ± 0.03	9.10 ± 0.03
Mn, mg kg^{-1}	79.8 ± 0.3	103.9 ± 0.4	79.2 ± 0.3	66.2 ± 0.3	48.1 ± 0.2	92.7 ± 0.5	74.1 ± 0.4
Mo, mg kg^{-1}	1.47 ± 0.09	0.87 ± 0.07	1.37 ± 0.07	1.58 ± 0.07	1.46 ± 0.07	1.44 ± 0.08	1.33 ± 0.09
Na, mg kg^{-1}	702 ± 6	859 ± 7	487 ± 5	462 ± 5	226 ± 3	976 ± 9	838 ± 8
Rb, mg kg^{-1}	17.8 ± 0.2	18.3 ± 0.2	14.8 ± 0.2	16.3 ± 0.2	7.8 ± 0.1	46.9 ± 0.3	16.1 ± 0.2
Sb, mg kg^{-1}	1.502 ± 0.008	1.606 ± 0.010	1.079 ± 0.009	1.159 ± 0.007	0.726 ± 0.005	1.538 ± 0.008	1.582 ± 0.030
Sc, mg kg^{-1}	0.909 ± 0.003	0.943 ± 0.003	0.624 ± 0.002	0.845 ± 0.003	0.349 ± 0.001	1.422 ± 0.004	1.156 ± 0.004
Se, mg kg^{-1}	1.90 ± 0.04	0.80 ± 0.04	0.57 ± 0.03	0.69 ± 0.03	0.42 ± 0.03	0.62 ± 0.04	0.64 ± 0.03
U, mg kg^{-1}	0.69 ± 0.02	0.53 ± 0.02	0.43 ± 0.02	0.73 ± 0.02	0.08 ± 0.01	0.73 ± 0.02	0.64 ± 0.02
Zn, mg g^{-1}	160.9 ± 0.7	141.9 ± 0.6	430.9 ± 1.8	156.8 ± 0.7	76.1 ± 0.4	157.9 ± 0.7	181.9 ± 0.7

2.2. Neutron activation analysis (NAA)

About 150 mg of the sample weighed in clean polyethylene bags were irradiated at the IEA-R1 nuclear research reactor together with aliquots of synthetic primary standards of the elements to be determined. Five-minute irradiations under a thermal neutron flux of 1.4×10^{12} n cm^{-2} s^{-1} were carried out for Cl, K, Mn and Na determinations. Sixteen-hours irradiations under a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} were performed for As, Ba, Br, Ca, Cr, Co, K, Fe, La, Mn, Mo, Na, Rb, Sb, Sc, Se, U, and Zn determinations. After adequate cooling times, the irradiated samples and standards were measured by a hyperpure Ge detector model GX2020 coupled to integrated signal processor model 1510, being both Canberra, (USA). Samples and standards were measured at least twice for different decay times. Counting times from 200 to 50,000 s were used, based on the 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

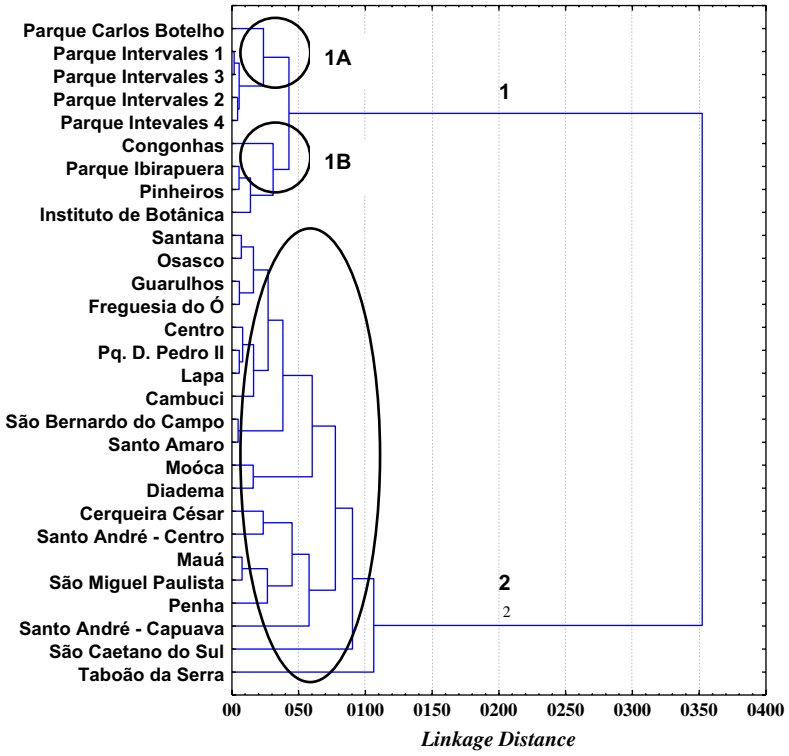

Fig. 2. Dendrogram of element concentrations in *C. texana*.

elements were calculated by a comparative method. The uncertainties of the results were evaluated using statistical counting errors of sample and standard.

2.3. Quality control of the results

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- Vienna) and the National Institute of Standards and Technology (NIST- USA), respectively. Results obtained in these analyses showed good precision and good agreement with the certified values for most elements. Precise results with relative standard deviations lower than 12% were obtained. The relative error ranged from 0.1 to 12%, indicating the accuracy of the results obtained. The standardized difference or *Z*-score values (Bode, 1996) obtained for the elements analyzed were $\|Z\| < 1$, indicating that the results obtained are satisfactory and in agreement with the certified values.

3. Results and discussion

Results obtained in the analyses of lichens from unpolluted areas of the Parque Estadual Carlos Botelho (PECB) and Intervales (PEI) are presented in Table 1 and those from polluted sites of the SPMR are presented from Tables 2–4. These results showed that the elements As, Co, Cs, La, Sb, Sc, Se and U are present at the levels of μg kg^{-1} in lichens, Ba, Br, Cl, Cr, Fe, K, Mn, Mo, Na, Rb and Zn at mg kg^{-1} levels and Ca at percentage levels. The comparison made between the results obtained in different sampling sites indicated that lichens collected in clean areas of the parks present the lowest concentrations for the elements As, Co, Cr, Fe, La, Mo, Na, Sb, Sc, U and Zn in relation to those collected in the SPMR. The samples from clean regions of the PECB presented high concentrations of Br and Cl probably due to the marine influence since this park is located close to the coast of the State of São Paulo. Concentrations of Cs, K, Mn and Rb found in lichens from clean regions were of the same order of magnitude of those colleted in the SPMR.

The lichen analysis data were submitted for sampling site classification by cluster analysis. The resulting dendrogram from this treatment revealed two main groups of sites, as can be seen in Fig. 2. The first, group 1, was formed by sampling sites considered clean regions of PECB and PEI (Subgroup 1A) and Congonhas, Parque Ibirapuera, Pinheiros and Instituto de Botânica sites (Subgroup 1B). Subgroup 1B sites are located in less polluted urban areas. The second, group 2, was formed by the sites located near industrial and urban area with heavy traffic. The cluster analysis substantially confirmed coherent groups of pollution levels.

Distribution maps of element concentrations found in lichen analyses were drawn using Surfer 8 program (Golden Software, 2002). For the elements Ba, Br, Co, Mn and Zn these maps are presented from Figs. 3 to 7. In these maps the contours indicate the different concentrations of elements. High concentrations of Ba obtained in lichens from São Caetano do Sul and surrounding regions that make up an industrial area called ABC Paulista Region (Santo André, São Bernardo do Campo and São Caetano) can be seen in Fig. 3. These high concentrations of Ba can be attributed to several industries and petrochemical complex located in the region. The bromine

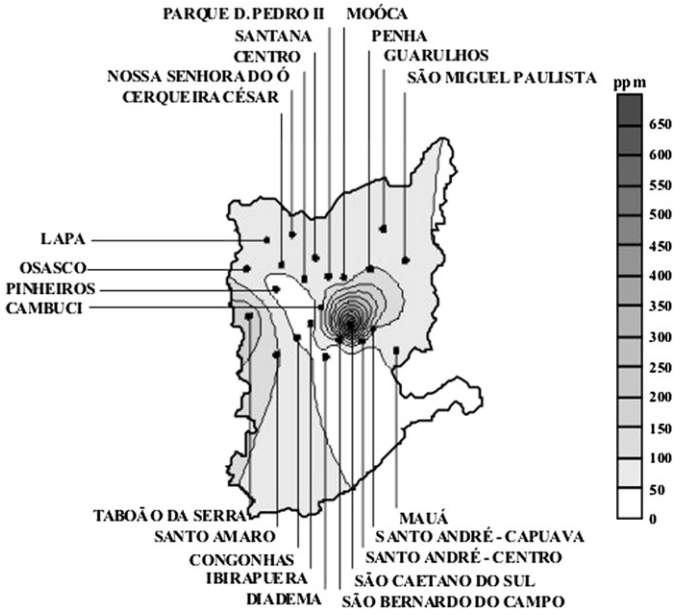

Fig. 3. Distribution map of Ba concentrations (mg kg^{-1}) in *C. texana*, for the areas covered by the dots.

was found concentrated in the sites of Lapa, Cerqueira César, Taboão da Serra, Congonhas, Mauá, Santo André-Capuava, Santo André-Centro, São Caetano do Sul and São Bernardo do Campo (Fig. 4). The Br distribution in the São Paulo Metropolitan Region indicates that its emission sources can either be from vehicular or industrial origins. Fig. 5 shows that lichens collected in sites located in the Eastern part of the SPMR (in the sites São Miguel Paulista, Penha and Santo André-Capuava) presented the highest concentration of Co. The high concentration of Co in the São Miguel Paulista site can be associated to the emission of a metallurgical industry. In

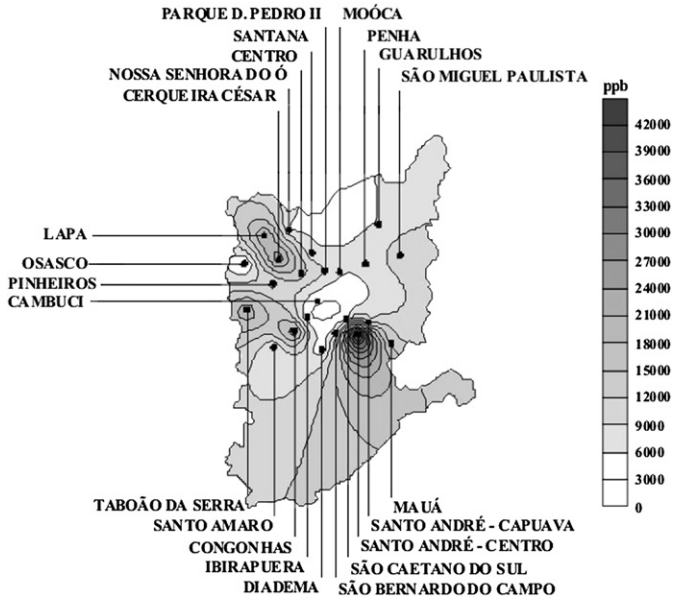

Fig. 4. Distribution map of Br concentrations (μg kg^{-1}) in *C. texana*, for the areas covered by the dots.

this area there is a metal processing plant that has a capacity of producing 960 tons of this element per year (Votorantim, 2007). The results of Mn concentrations in lichens are illustrated in Fig. 6. The emission of this element can be mainly related to the industrial emission particularly in the site of Santo André-Capuava. The distribution map of Zn presented in Fig. 7 shows three sites (Osasco, Congonhas and Santo Amaro) with high concentrations of this element. The origin of Zn in the air can also be attributed to industrial and vehicular sources. This element in the environment can be released to the environment from the wearing down of vehicle motors and from burning old vehicle tires (Carreras and Pignata, 2002). The elements Ca, Cs, K, La, Na, Rb, Se and U found in lichens reflect their soil origin.

The results obtained in the present study indicate that lichens are of use in determining the spatial distribution of pollutants across a metropolitan area. Such information characterizes patterns of pollution produced by different sources. Considering that millions of people are impacted by such emissions, it is tempting to think about the possibility of using the information provided by the accumulation of toxic elements in lichens to evaluate human health risk. The results obtained in long cohort studies conducted in the USA indicate that prolonged exposure to ambient levels of air pollution is a major risk for cardiopulmonary mortality (Dockery et al., 1993; Pope et al., 2002). In these studies, fine particulate is the pollutant most consistently associated with mortality, with no evidence of a safety threshold. In general terms, an increment of 10 μg m^{-3} of fine particles is associated with a 9% increase in cardiopulmonary mortality (Pope et al., 2002). In the municipality of São Paulo, it is possible to obtain mortality data disaggregated by sanitary district in a database maintained by the municipal government, in which causes of death

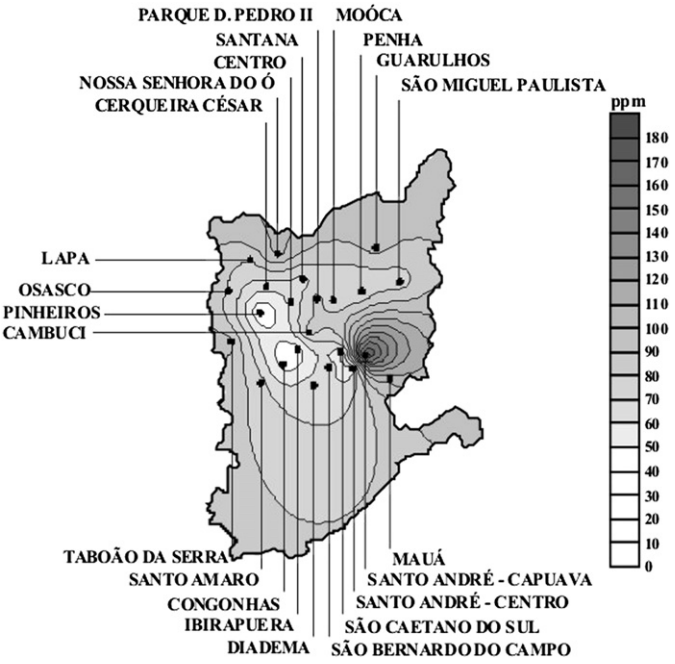

Fig. 6. Distribution map of Mn concentrations (mg kg^{-1}) in *C. texana*, for the areas covered by the dots.

were coded according to the International Code of Diseases (ICD10) Thus, we determined the proportion between cardiopulmonary mortality (ICD I00–I99 and J0–J99) in respect to all cause mortality (excluding violent deaths) in adults over 45 years of age for the sanitary districts of São Paulo. Only for exploratory purposes, we measured the association between cardiopulmonary proportion and the values of element accumulation in lichens in the corresponding sanitary districts

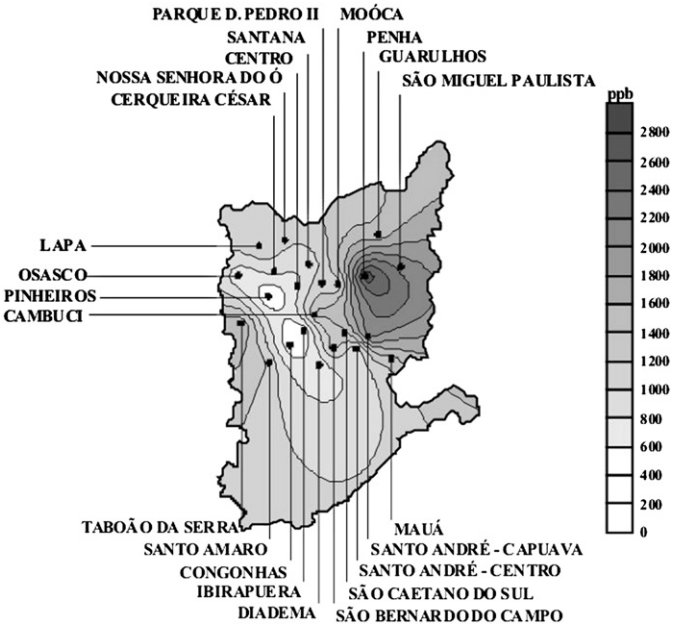

Fig. 5. Distribution map of Co concentrations (μg kg^{-1}) in *C. texana*, for the areas covered by the dots.

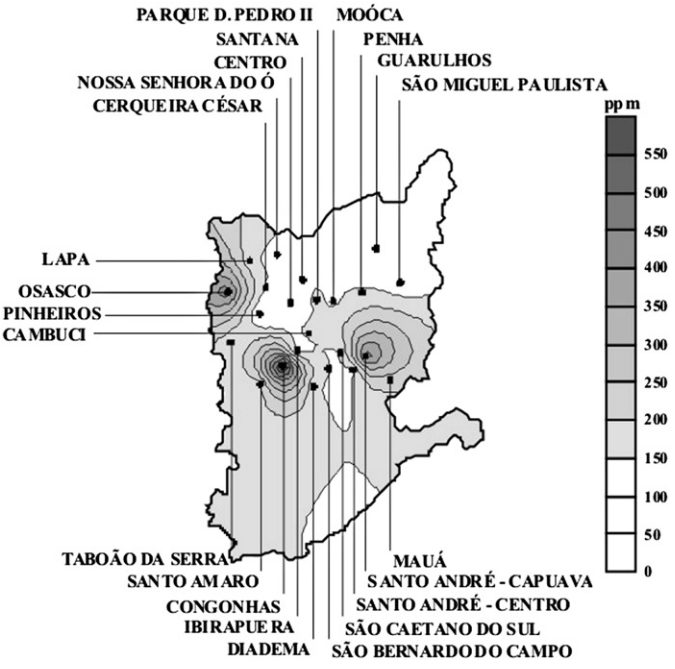

Fig. 7. Distribution map of Zn concentrations (mg kg^{-1}) in *C. texana*, for the areas covered by the dots.

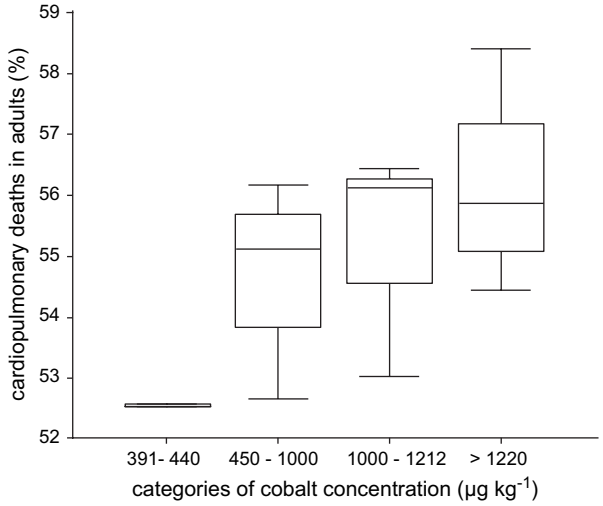

Fig. 8. Box plot representing the variation of the proportion of cardiopulmonary mortality in adults over 45 years of age as a function of quartiles of cobalt accumulation in lichens.

ICD S00–T98 and V01–Y88. For such procedure, we excluded the locations of Osasco, Diadema, São Bernardo do Campo, Santo André, Taboão da Serra e Mauá (out of the municipality of São Paulo and where mortality information was not available by sanitary district). Significant associations (Sperman's test) were obtained for Co ($p = 0.021$), Fe ($p = 0.019$), Mn ($p = 0.044$) and Na ($p = 0.012$). An example of the observed associations is depicted in Fig. 8. Results indicate the necessity of further studies designed specifically to investigate the role of element accumulation in *C. texana* as an instrument to evaluate the risk of cardiopulmonary diseases in humans chronically exposed to ambient levels of air pollution.

4. Conclusion

In this study, the element concentrations in *C. texana* lichenized fungi samples colleted in different levels of pollution were compared and the findings indicated this species can be used to monitor polluted urban areas. The lichen analysis results give, in relative terms, a general idea of the state of the pollution level of several elements in the area of São Paulo Metropolitan region. Although it is still difficult to point out the exact sources of elements that are accumulated by lichen, their distribution helps to elucidate their origin.

As expected, the distribution maps of element concentrations showed the highest values around the petrochemical complex, metallurgical industry and in urban areas affected by vehicular emissions. Exploratory analyses revealed that the accumulation of toxic elements in *C. texana* may be of use in determining the human risk of cardiopulmonary mortality due to prolonged exposure to ambient levels of air pollution.

Acknowledgments

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