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Biomonitoring of the atmospheric pollution using lichens in the metropolitan area of São Paulo city, Brazil

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The atmospheric pollution of São Paulo city is a serious problem due to the expansion of industrial area, increasing number of vehicles and population density. This work presents results obtained in the analysis of lichens collected in different sites of São Paulo city and in non-polluted areas of Atlantic Forest. Concentrations of twenty elements were determined in *Canoparmelia texana* species and comparisons were made between the results obtained in lichens from different sites. High concentrations of the elements As, Ba, Cd, Co, Cr, Fe, La, Mn, Sb and Zn were found for samples collected in sites located near industries and petrochemical plant. Br and Sb concentrations were also high in lichens from sites affected by vehicular emissions.

Introduction

In Brazil the use of lichens as biomonitors of trace elements present in the environment is not very widespread. Most analytical data on atmospheric pollution are obtained by conventional methods, requiring great efforts as to investments in infrastructure and manpower. Besides, it is not possible to install equipments in all locations needed due to the great extension of the Brazilian territory. Thus, air pollution studies using biomonitors represent an important contribution and an interesting and economic alternative to those performed by direct measurements of the contaminant elements.

The city of São Paulo, Capital of São Paulo State, is located at an altitude of 715–900 meters, with annual precipitation of about 1,300 mm and temperature ranging from 15 to 23 °C. Today this city presents a serious pollution problem due to the expansion of the industrial area, increasing number of vehicles and large population density. It covers an area of 5,000 km^2 with a population of about 18 million and about 5.5 million vehicles.

This work presents concentrations of As, Br, Ba, Ca, Cd, Cl, Co, Cr, Cs, Fe, K, La, Mn, Na, Rb, Sb, Sc, Se, U, and Zn found in *Canoparmelia texana* species collected in sites of São Paulo city where the governmental air quality control agency – CETESB – operates an automatic network with monitoring stations. Comparisons were made between the results obtained in these sites and in unpolluted areas.

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

Experimental

Sampling area

C. texana species were collected in the following areas:

In non-polluted areas, from one site in Ibiuna county, a part of the green ring (horticultural and touristic region) located about 100 km far from São Paulo city; in two sites in Itapetiniga region located in the Atlantic Forest about 300 km far from São Paulo city, and in one site of Manuel Botelho Park, also located in the Atlantic Forest.

In the metropolitan area of São Paulo city, in the sites Mauá, Santo André, and Santana, located close to industries; sites São Caetano do Sul, Ibirapuera Park, São Miguel Paulista, Santana, Cerqueira César, and Pinheiros, located in areas mainly influenced by vehicular emissions. In these sites the governmental air quality control agency – CETESB – has an automatic network for monitoring air quality of the area. Figure 1 shows the study area and the area with location of sampling sites.

Sampling and sample preparation

The species selected for sampling is an epiphytic foliose lichen called *Canoparmelia texana* (Tuck.) Elix & Hale of the *Parmeliaceae* family. It was chosen due to the wide distribution in the Brazilian territory, although it is not found in the coast. *C. texana* samples were collected from the bark of trees (mainly palm trees) at about 1.5 m from the soil, 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.

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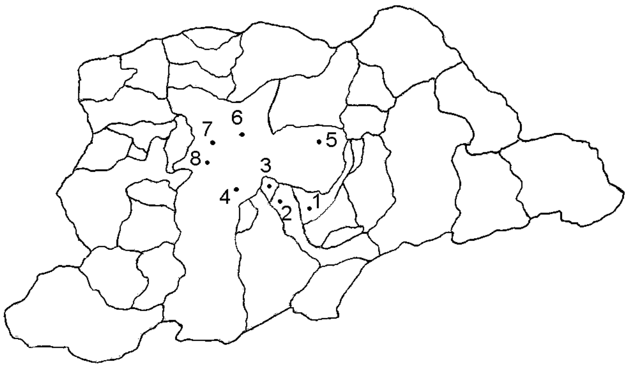

Fig. 1. Study area with location of sampling sites: 1. Mauá, 2. Santo André, 3. São Caetano do Sul, 4. Ibirapuera Park, 5. São Miguel Paulista, 6. Santana, 7. Cerqueira César, 8. Pinheiros

In the laboratory, the samples were analyzed by an Olympus zoom stereomicroscopy 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 adhering materials (dust and sand). During the washing procedure, the lichen samples were immersed in purified water for about 3–5 minutes. Within the experimental errors the results obtained for washed and unwashed lichens show no significant difference with the exception of the elements Al, K, Na, Se and Ti.[1] Then the samples were placed into plastic vials to be dried by freeze-drying for 16 hours under a pressure of about $4 \cdot 10^{-2}$ mbar. The fine powder of the lichen was obtained by grinding using a vibratory micro mill "pulverisette 0", Fritsch.

Preparation of synthetic standards of elements

The standards for comparative neutron activation analysis were obtained by pipetting known aliquots of multielemental or single standard solutions onto sheets of Whatman No. 40 filter paper. The standard solutions provided from SpexCertiprep Chemical were used to obtain the diluted solutions containing one or more elements. The quantities of each element, in μg (in parentheses) were the followings: As (1.5), Ba (200.2), Br (5.0), Ca (1000), Cd (10.0), Cl (200), Cr (1.5), Cs (530.0), Co (0.10), Fe (271), K (1000), La (0.50), Mn (1.5), Na (130), Rb (4.0), Sb (0.6), Sc (0.060), Se (40), U (5.0) and Zn (35.0). After drying at room temperature in a desiccator, these paper sheets were placed in clean polyethylene bags and irradiated with the samples.

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-minutes irradiations under a thermal neutron flux of $1.4 \cdot 10^{12}$ 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 $5 \cdot 10^{12}$ n·cm^{-2}·s^{-1} were performed for As, Ba, Br, Ca, Cr, Co, K, La, Mn, Na, Rb, Sb, Sc, U, and Zn determinations. After adequate cooling times, the irradiated samples and standards were measured by a hyper-pure Ge detector Model GX2020 coupled to Integrated Signal Processor Model 1510, being both from Canberra. Every samples and standards were measured at least twice for different decay times. Counting times from 200 to 50,000 seconds 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 elements were calculated by a comparative method. The uncertainties of the results were evaluated using statistical counting errors of sample and standard.

The quality assurance 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[2,3] for most elements. Precise results with relative standard deviations lower than 12% were obtained. The relative errors ranged from 0.1 to 12%, indicating the accuracy of the results obtained. The standardized difference or *Z*-score values[4] obtained for the elements analyzed are presented in Figs 2 and 3 and they were $|Z|<1$, indicating that the results obtained are satisfactory and in agreement with the certified values.

Concentrations of elements obtained in lichen samples collected in different sampling times are presented in Table 1. At Ibirapuera Park, samples were collected in April and October 2002 and in São Miguel Paulista, in February and April 2002. These chosen sampling times were before rainy and dry seasons since in São Paulo State, the rainy season is usually from October to April and the dry season, from May to September.[5] Table 1 shows that the concentrations of most elements obtained in lichens collected in these two sampling times were almost the same. For Zn and Br (being the latter related the sample from São Miguel Paulista) there was a slight increase in the concentrations with the time. For K, we have also found higher concentrations in lichens collected in the end of the rainy season (April). According to GARTY et al.,[6] rainwater facilitates the release of additional K amounts from dust particles, which subsequently accumulate in lichen species.

Table 2 summarizes the mean values of the element concentrations obtained in *C. texana* collected in unpolluted areas and in sites of the metropolitan area of São Paulo. The analysis of variance test applied to the results indicated that lichens from clean sites present lower concentrations of As, Br, Ba, Ca, Co, Cr, Cs, Fe, La, Na, Sb, Se, U, and Zn, when compared with those from polluted sites. Concentrations of As, Ba, Cd, Co, Cr, Fe, La, Mn, Sb, and Zn, obtained in lichens from Mauá, Santo André and Santana were higher than those from other sites. The high concentrations of these elements may be partially derived from several industries located very close to these sites. Due to traffic pollution, high concentrations of Br were found in lichens from Cerqueira Cesar and of Sb in lichens from Pinheiros. Sb is used as a tire additive[7] and Br is used in gasoline as an antiknock additive.[8]

The data of the Table 2 were also submitted for sampling sites classification by cluster analysis and the result is presented in Fig. 4. Three main groups of sites were revealed: (a) a non-polluted site; (b) Mauá, Santo André and Santana sites; (c) São Caetano do Sul, Ibirapuera Park, São Miguel Paulista, Cerqueira César and Pinheiros sites. These clusters substantially confirmed the three site groups of different levels of pollution considered in this work. Groups (b) and (c) reflects larger pollution due to industry pollution to traffic, respectively.

Distribution maps for the case of Cd and Zn were drawn using Surfer 8 software[9] and presented in Figs 5 and 6. The contour lines show different concentrations of elements. In the maps, higher concentrations of elements can be seen in the areas Santo André, and Santana, and lower concentrations are observed in the vicinity from Ibirapuera Park, Cerqueira César and Pinheiros. Cd and Zn showed a very similar pattern because they have probably the same origin. The high concentrations of Cd and Zn found in lichens from Santo André may be associated to the emissions from with industries and petrochemical plant located in this region. The highest concentration of Co (Table 2) found in lichens from São Miguel Paulista is probably due to the emission from a metallurgical processing plant that produces this element.

Table 1. Concentrations of elements in *C. texana* collected in different periods

Element	Site 4. Ibirapuera Park		Site 5. São Miguel Paulista	
	April 4, 2002	Oct 22, 2002	Feb 4, 2002	Apr 4, 2002
As, $\mu g \cdot kg^{-1}$	1079 ± 10*	926 ± 4	1643 ± 16	1561 ± 10
Ba, $mg \cdot kg^{-1}$	23 ± 6	16 ± 5	60 ± 10	89 ± 8
Br, $\mu g \cdot kg^{-1}$	7384 ± 27	6272 ± 14	5684 ± 28	8460 ± 24
Ca, %	3.31 ± 0.09	4.54 ± 0.08	4.36 ± 0.11	2.86 ± 0.08
Cd, $\mu g \cdot kg^{-1}$	2015 ± 109	2479 ± 80	1599 ± 141	1023 ± 68
Cl, $mg \cdot kg^{-1}$	414 ± 18	435 ± 14	683 ± 25	404 ± 14
Co, $\mu g \cdot kg^{-1}$	731 ± 8	491 ± 4	1642 ± 34	1992 ± 21
Cr, $mg \cdot kg^{-1}$	6.67 ± 0.04	6.08 ± 0.03	11.4 ± 0.1	11.03 ± 0.06
Cs, $\mu g \cdot kg^{-1}$	277 ± 4	210 ± 3	726 ± 13	632 ± 6
Fe, $mg \cdot kg^{-1}$	2445 ± 11	2029 ± 6	4619 ± 38	4274 ± 18
K, $mg \cdot kg^{-1}$	7385 ± 27	2926 ± 12	3732 ± 32	8461 ± 24
La, $\mu g \cdot kg^{-1}$	3322 ± 12	3065 ± 7	6129 ± 33	6453 ± 20
Mn, $mg \cdot kg^{-1}$	41.1 ± 0.9	38.0 ± 2.2	61.2 ± 1.5	51.7 ± 1.0
Na, $mg \cdot kg^{-1}$	202 ± 9	143 ± 6	420 ± 16	525 ± 15
Rb, $mg \cdot kg^{-1}$	12.0 ± 0.1	11.56 ± 0.07	19.4 ± 0.4	17.3 ± 0.2
Sb, $\mu g \cdot kg^{-1}$	771 ± 4	650 ± 2	935 ± 7	928 ± 3
Sc, $\mu g \cdot kg^{-1}$	715 ± 2	573 ± 1	1224 ± 7	1123 ± 4
Se, $\mu g \cdot kg^{-1}$	564 ± 20	442 ± 15	625 ± 44	665 ± 21
U, $\mu g \cdot kg^{-1}$	216 ± 4	227 ± 4	402 ± 5	323 ± 3
Zn, $mg \cdot kg^{-1}$	136.7 ± 0.4	148.0 ± 0.5	114.4 ± 0.8	141.0 ± 0.4

* Results of one determination and the uncertainties of the results were evaluated using statistical counting errors of standards and of samples.

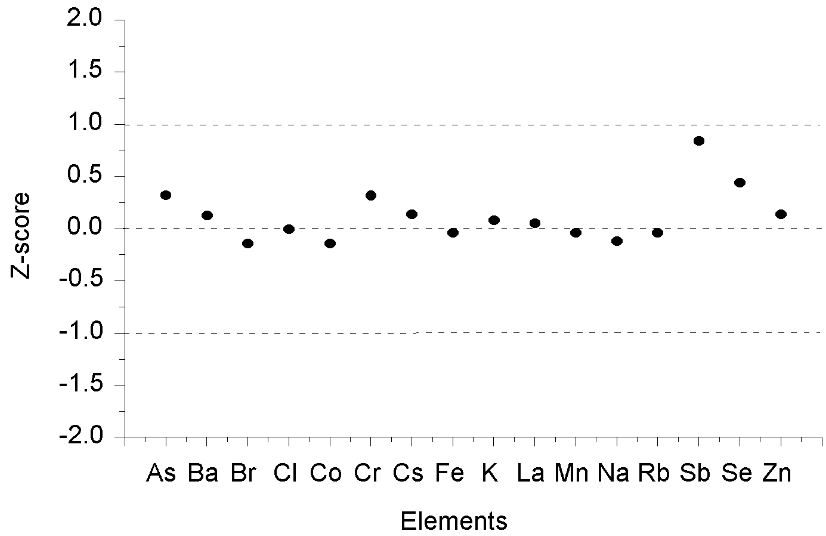

Fig. 2. Values of standardized differences (*Z*-score values) for elements analyzed in IAEA 336 Lichen

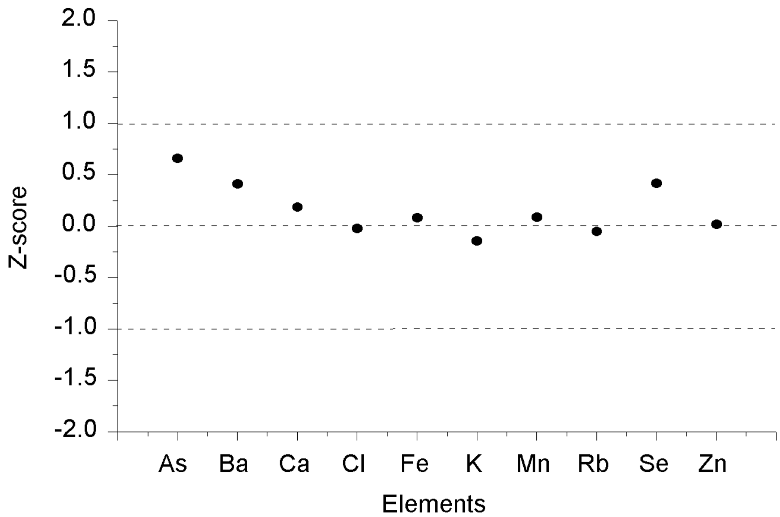

Fig. 3. Values of standardized differences (*Z*-score values) for elements analyzed in NIST 1547 Peach Leaves

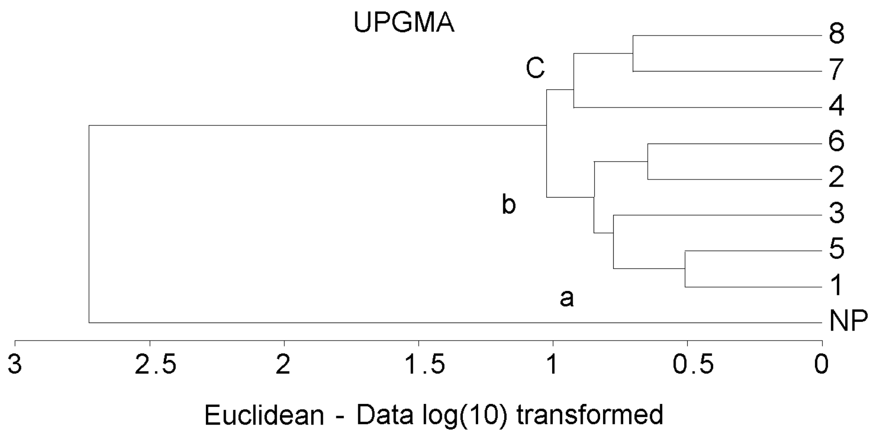

Fig. 4. Dendrogram of the discriminant analysis using all element results obtained in lichen from the sites: NP = Non-Polluted sites; 1 = Mauá; 2 = Santo André; 3 = São Caetano do Sul; 4 = Ibirapuera Park; 5 = São Miguel Paulista; 6 = Santana; 7 = Cerqueira César; and 8 = Pinheiros

Table 2. Concentrations of elements in ***C. texana*** collected in different sites

Element	Unpolluted sites	Sites of metropolitan area of São Paulo city							
		1. Mauá	2. Sto. André	3. São Caetano do Sul	4. Ibirapuera Park	5. São Miguel Paulista	6. Santana	7. Cequeira César	8. Pinheiros
As, μg·kg^{-1}	550 ± 4*	1437 ± 12	1571 ± 8	1314 ± 6	1002 ± 5	1602 ± 9	1949 ± 13	1380 ± 7	927 ± 5
Ba, mg·kg^{-1}	n.d.	67 ± 5	92 ± 5	57 ± 8	20 ± 4	74 ± 6	88 ± 8	58 ± 6	45 ± 6
Br, μg·kg^{-1}	3050 ± 900	16094 ± 32	5674 ± 16	5196 ± 15	6828 ± 15	7072 ± 18	10991 ± 31	17177 ± 24	4107 ± 8
Ca, %	0.50 ± 0.01	2.69 ± 0.06	5.10 ± 0.09	3.77 ± 0.10	3.42 ± 0.06	3.61 ± 0.07	4.59 ± 0.04	4.69 ± 0.09	6.12 ± 0.06
Cd, μg·kg^{-1}	n.d.	1051 ± 137	9003 ± 101	1472 ± 53	2247 ± 68	1311 ± 78	5155 ± 78	2711 ± 109	1492 ± 43
Cl, mg·kg^{-1}	607 ± 8	517 ± 15	629 ± 24	339 ± 15	424 ± 11	543 ± 14	445 ± 16	465 ± 17	508 ± 20
Co, μg·kg^{-1}	142 ± 3	1047 ± 12	1035 ± 13	1441 ± 15	611 ± 5	1817 ± 20	1366 ± 11	690 ± 10	526 ± 5
Cr, mg·kg^{-1}	1.08 ± 0.02	16.12 ± 0.07	16.0 ± 0.1	41.7 ± 0.2	6.37 ± 0.03	11.20 ± 0.06	18.45 ± 0.09	9.27 ± 0.07	5.85 ± 0.03
Cs, μg·kg^{-1}	82 ± 2	599 ± 7	534 ± 8	320 ± 5	243 ± 2	679 ± 7	547 ± 4	288 ± 5	377 ± 4
Fe, mg·kg^{-1}	709 ± 4	6027 ± 26	4598 ± 23	3651 ± 15	2237 ± 6	4446 ± 21	5742 ± 18	2694 ± 14	2851 ± 8
K, mg·kg^{-1}	3202 ± 10	4762 ± 24	5588 ± 19	5197 ± 15	5150 ± 15	6096 ± 20	2399 ± 9	2399 ± 9	3723 ± 17
La, μg·kg^{-1}	1076 ± 6	9583 ± 25	7557 ± 25	4781 ± 15	3193 ± 12	6291 ± 19	8526 ± 19	4246 ± 13	4267 ± 10
Mn, mg·kg^{-1}	74 ± 9	69 ± 1	65 ± 1	50.7 ± 1.1	39.6 ± 1.2	56.4 ± 0.9	102 ± 6	51.0 ± 1.1	60.8 ± 1.0
Na, mg·kg^{-1}	64.4 ± 0.1	566 ± 11	458 ± 15	311 ± 11	173 ± 5	472 ± 11	725 ± 18	378 ± 11	470 ± 11
Rb, mg·kg^{-1}	6.30 ± 0.07	19.0 ± 0.2	14.9 ± 0.2	13.2 ± 0.1	11.78 ± 0.06	18.4 ± 0.2	20.0 ± 0.1	9.26 ± 0.09	12.25 ± 0.09
Sb, μg·kg^{-1}	94 ± 10	1581 ± 6	1157 ± 4	1216 ± 3	710 ± 2	931 ± 4	2205 ± 5	1722 ± 5	1625 ± 3
Sc, μg·kg^{-1}	309 ± 1	1190 ± 4	1099 ± 4	686 ± 2	644 ± 1	1173 ± 3	1157 ± 3	593 ± 2	744 ± 2
Se, μg·kg^{-1}	231 ± 11	907 ± 29	712 ± 29	688 ± 22	503 ± 13	645 ± 24	762 ± 19	915 ± 24	471 ± 14
U, μg·kg^{-1}	75 ± 2	472 ± 4	408 ± 5	214 ± 3	222 ± 4	362 ± 3	375 ± 3	149 ± 5	261 ± 12
Zn, mg·kg^{-1}	37.0 ± 0.2	119.5 ± 0.5	235 ± 1	180.0 ± 0.6	142.0 ± 0.3	128.0 ± 0.4	199.8 ± 0.6	145.6 ± 0.6	115.3 ± 0.4

* Number of replicates varied from to 2 to 4 and the uncertainties were evaluated using statistical counting errors of standards and of samples.
n.d.: Not detected.

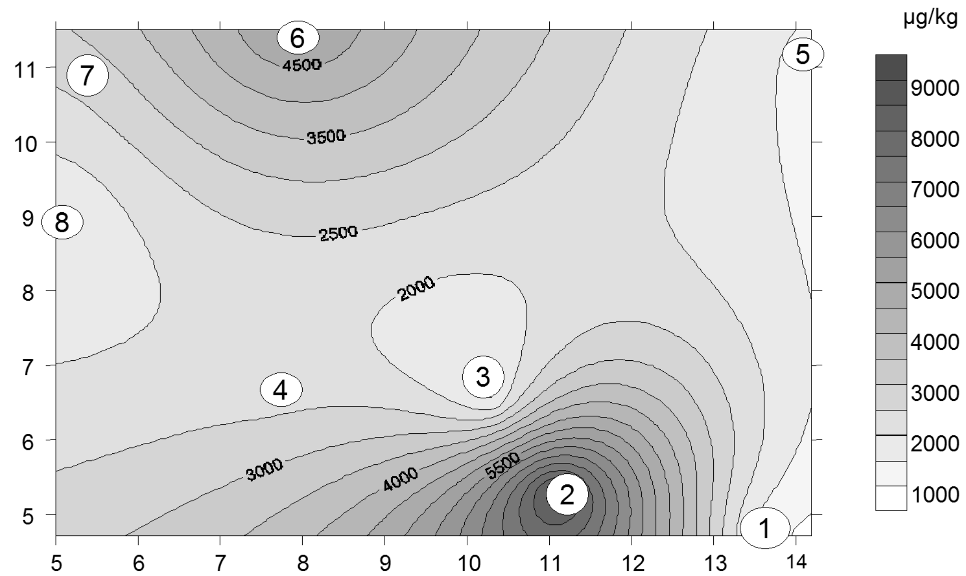

Fig. 5. Distribution map of Cd concentrations in *C. texana*

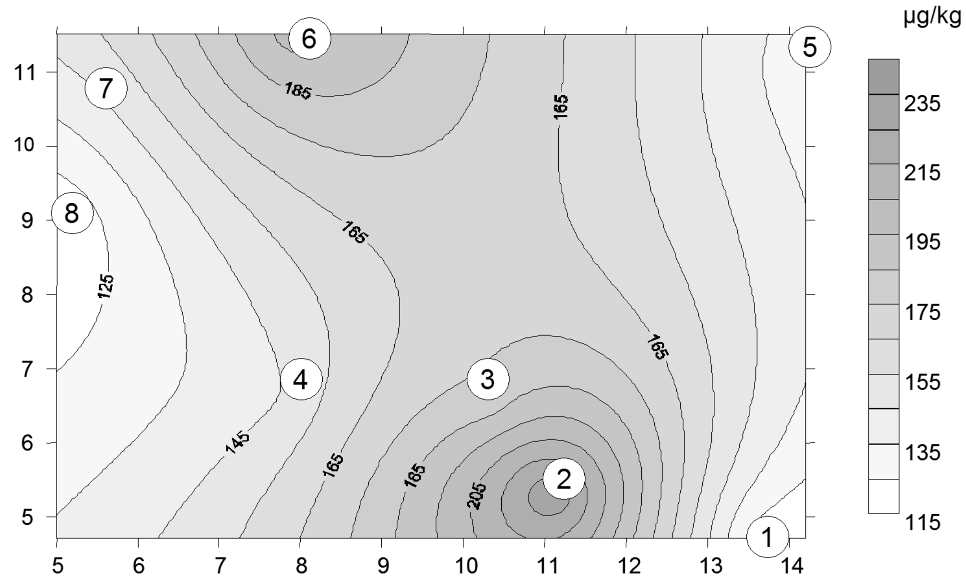

Fig. 6. Distribution map of Zn concentrations in *C. texana*

Conclusions

The obtained results indicated that the use of *C. texana* species is quite suited for passive environmental biomonitoring. The high concentrations of elements obtained in lichen from sites located near industrial areas indicated that the contribution of industrial pollution is higher than that from car pollution origin.

Further studies will be carried out by increasing number of sampling sites for lichen sample collection.

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