

Assessment of atmospheric metallic pollution in the metropolitan region of São Paulo, Brazil, employing *Tillandsia usneoides* L. as biomonitor

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This paper is the first work on the use of biomonitors to assess metal pollution in São Paulo, Brazil, the biggest city in Latin America.

Abstract

Tillandsia usneoides L. is an epiphytic bromeliad plant able to absorb water and nutrients directly from the air. For this reason this species was selected to carry out a monitoring study of air pollution in the metropolitan region of São Paulo, Brazil. Five consecutive transplantation experiments (8 weeks each) were performed in 10 sites of the city, submitted to different sources of air pollution (industrial, vehicular), using plants collected from an unpolluted area. After exposure, trace metals were analyzed in the plant by instrumental neutron activation analysis. Traffic-related elements such as Zn and Ba presented high concentrations in exposure sites near to heavy traffic avenues (cars, buses and trucks) and may be associated to vehicular sources. For Zn and Co the highest contents were related to industrial zones and can be associated to the presence of anthropogenic emission sources. The rare earth elements, Fe and Rb, probably have soil particles as main source.

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1. Introduction

Bioindicators can be defined as organisms (a part of an organism or a population of organisms) which are able to give informations on the quality (of a part) of its environment. Biomonitoring is the continuous observation of an area with the help of bioindicators, which may also be called biomonitors (Kettrup and Marth, 1998; De Temmerman et al., 2004).

Bioindicators may be very useful due to their high sensitivity towards a broad spectrum of substances or because of their

tolerance to high levels of a substance, accumulated in their tissues over an extended period of time or to integrate its influence in an area of known and relevant size. They are an alternative to conventional instrumentation of environmental pollution control, due to advantages such as allowing the monitoring of large areas, and to the low plant cultivation and maintenance cost (De Temmerman et al., 2004).

Several biological specimens species can be used as bioindicators of atmospheric pollutants. Plants as biomonitors have been used since the 19th century when Nylander (1886, apud De Temmerman et al., 2004) used the abundance of lichens as a measure of air pollution effects (De Temmerman et al., 2004). In the beginning of 1920s, alterations in the composition in some species provided information about the pollution in areas submitted to fumes originated from coal burn (Ruston,

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1921). The use of biological materials for monitoring heavy metal air pollution was introduced 30 years ago. Since then, a variety of organisms and materials have been proposed for biomonitoring purposes. These include mosses, lichens, tree barks, tree rings, pine needles, grass, leaves and ferns (De Bruin, 1990). Some plant species of these groups have the ability of accumulating high levels of metals and other toxic elements, without showing any visible injury, such as leaf necroses and discolorations. These are then denominated accumulator or biomonitor plants (De Temmerman et al., 2004).

The effect of atmospheric pollutants on the plants may occur in different levels from specific organs of single organisms to whole ecosystems. Macroscopically, necroses and discoloration of the leaves or other parts of the plant may be observed, as well as a decrease in its growth. Studies performed in the city of São Paulo (Batalha et al., 1999; Guimarães et al., 2000) showed that urban pollution can affect bioindicators species in a consistent and reproducible way.

The elemental concentration in the tissues of epiphytic air pollution bioindicators reflects largely the concentration of atmospheric pollutants in the monitored environment, as far as these organisms have no contact with soil, taking out nutrients and water from the atmosphere. In general, they are excellent biomonitors.

Tillandsia usneoides L. is an aerial epiphytic bromeliad that lives on trees or other kinds of inert substratum, absorbing water and nutrients directly from the environment. Due to its morphological and physiological characteristics this species accumulates the pollutants present in the atmosphere.

Different species of *Tillandsias* have been used as biomonitors in different countries (Brighigna et al., 1997; Pignata et al., 2002). In Brazil, *T. usneoides* has proved to be a suitable biomonitor for atmospheric mercury contamination, in a chlor-alkali plant (Calasans and Malm, 1997). However, its suitability for biomonitoring purposes in great metropolitan regions like São Paulo has rarely been tested.

The metropolitan region of São Paulo (MRSP) is composed of 39 municipalities, with a population of 18 million people, with about 8000 km² and a strong industrial activity. The city of São Paulo is the biggest city in South America. The urban area is polluted by industrial emissions but, according to the Environmental Protection Agency of the State of São Paulo (CETESB, 2005), the governmental agency of air quality control, emissions from about 7.8 million motor vehicles daily are the main sources of air pollution. Serious environmental and health problems have specially been observed in the region due to particulate material (PM₁₀) with varied composition (Molina and Molina, 2004). Additionally, Batalha et al. (1999) and Guimarães et al. (2004) showed experimentally that PM₁₀ sampled next to an avenue with intense traffic is potentially genotoxic to biosensor plants, effect that may be at least partially attributed to heavy metals adsorbed in the PM₁₀ surface. Therefore the use of a biomonitor complementary to conventional instrumentation becomes very interesting.

In a previous work (Figueiredo et al., 2004), samples of *T. usneoides*, taken from an unpolluted area, were exposed in different sites of the city of São Paulo and in a control area,

out of the city, for 8 weeks, in order to evaluate the potentiality of this species as a biomonitor of atmospheric pollution in São Paulo. Instrumental neutron activation analysis (INAA) was used to analyze trace elements in the plants. The preliminary results obtained showed a tendency of this species to accumulating elements such as Al, As, Cr, Fe, Mo, Sb, Ti, V and Zn in samples exposed in polluted sites. These results encouraged the authors to continue the study aiming to evaluate the metal pollution in the atmosphere of São Paulo, by using active biomonitoring with *T. usneoides*.

2. Sampling and exposure sites

The active biomonitoring method, which consists of transferring plants collected from unpolluted sites to the area to be monitored, was employed. This methodological approach was adopted because *T. usneoides* does not occur naturally in the polluted and urbanized sites of the MRSP. *T. usneoides* samples were sampled in a small farm, where natural vegetation still remains, located in the city of Mogi das Cruzes, about 70 km far from São Paulo city. This area has low industrialization and traffic influence and consequently low impact of PM₁₀ and metal pollution, making it adequate as the local of origin of plants for transplantation experiments. All samples were collected at the same area in order to guarantee that the exposed samples had the same origin.

In this study, 10 sites next to automatic monitoring stations operated by the government agency of air quality control (CETESB) were chosen in MRSP to transplant the samples of *T. usneoides* (Fig. 1). Seven sites were situated in the city of São Paulo and three in the extended city (Santo André, São Caetano and Mauá), having different levels of PM₁₀ and metal pollution. Four exposure sites were in downtown area, where there is a car shift, which consists of avoiding 20% of the total number of vehicles to run one day of the week (PI, DP, CC and IB; Fig. 1) by the number of the license plate. Besides, the transplantation of plants was also performed in Mogi das Cruzes, taking it as the control site. Each sample for exposure was composed of 5 g of plants, tied by Teflon strings to a gy-rator apparatus (six samples per apparatus), which turned with the wind so that homogenous contact with air contaminants was guaranteed. The samples of *T. usneoides* were submitted to exposure for 8 weeks and, after the exposure time, were sent to analysis and were substituted by new samples, allowing to performing five transplantation experiments (A = April–May/2002; B = June–July/2002; C = Nov/2002–Jan/2003; D = Feb–Apr/2003; E = April–May/2003). In the laboratory, they were separately frozen without washing and stored at –20 °C until analyses.

3. Analytical procedure

T. usneoides samples were freeze-dried without washing. According to the conclusions of the Workshop – Improvements of Trace Element Determinations in Plant Matrices (Quevauviller, 1995), washing is a critical step for plant analysis. Washing may result in a distinction between the physical

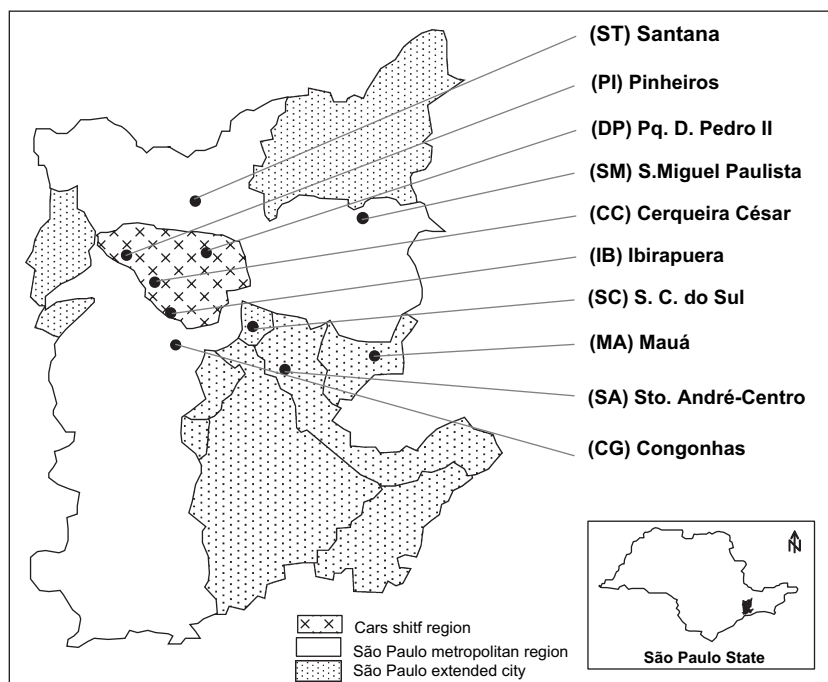


Fig. 1. Exposure sites of *T. usneoides* plants in the metropolitan region of São Paulo. Car shift region: area where 20% of the total number of vehicles are not allowed to run one day of the week by the number of the license plate.

presence of soil particles and the soil-derived elements due to plant uptake (Wolterbeek and Bode, 1995). Washing efficiency will also depend on the surface structure of the plant, i.e., differences occur between smooth and hairy or rough surfaces (Quevauviller, 1995). In the case of *T. usneoides*, the stem and leaves are completely covered by scales, being responsible for the majority of water and aerosols absorption (Brighigna et al., 1997). The plants were not washed before analysis, following the procedure generally applied for biomonitoring (Quevauviller, 1995) and particularly for biomonitoring studies using *Tillandsia* genus as biomonitor (Calasans and Malm, 1997; Brighigna et al., 1997; Amado Filho et al., 2002; Husk et al., 2004). This procedure ensured that elements from dry deposition were also measured (Calasans and Malm, 1997). Samples were then grinded using an agate vibratory micromill in order to obtain a fine and homogeneous powder. Agate mills may contaminate the material being ground (Markert, 1995) mainly by SiO_2 (99.91% of the agate composition), aluminum and sodium oxides (0.02% of the agate composition) and iron, potassium, manganese, calcium and magnesium oxides (0.01% of the agate composition). Sample contamination from the agate mill could be considered negligible for the elements analyzed in this work. Two hundred milligram of the samples were accurately weighed in polyethylene envelopes, previously cleaned with diluted nitric acid solution. Samples were analyzed in duplicates and the results were given in $\mu\text{g g}^{-1}$ dry weight.

Standards of the elements of interest were prepared by mixing appropriate aliquots of solutions of these elements made from spectroscopically pure reagents or from SPEX Certiprep standard solutions. Aliquots of these solutions were pipetted

onto 1 cm^2 pieces of Whatman No. 40 filter paper, evaporated to dryness under an infrared lamp, and sealed in polyethylene envelopes, similar to those used in the preparation of the samples. About 200 mg of the biological standard reference materials Orchard Leaves (NIST SRM 1571), Apple Leaves (NIST SRM 1515) and of the geological reference material Soil-7 (IAEA) were also weighed and prepared similarly to the sample.

Samples and standards were irradiated for 16 h at a thermal neutron flux of $1 \times 10^{13}\text{ n cm}^{-2}\text{ s}^{-1}$ at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out using a GX20190 hyperpure Ge detector. The multichannel analyzer was an 8192 channel Canberra S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co . Two series of measurements were performed after the 16 h irradiation; the first was done from 5th to 7th day after irradiation and the second one after 15–20 days of decay. Counting times ranged from 3 to 10 h. The gamma-ray spectra were processed by using an in-house gamma-ray software, VISPECT.

4. Quality assurance

To evaluate the accuracy and precision of the data, three biological reference materials were analyzed: Orchard Leaves (NIST SRM 1571), Apple Leaves (NIST SRM 1515) and Soil-7 (IAEA). The results showed good accuracy (relative errors to certified values < 5% for most of elements) and good precision (relative standard deviations < 15%).

Table 1
Results obtained in *Tillandsia usneoides* in São Paulo ($\mu\text{g g}^{-1}$) — exposition period: April–May 2002 (A)

Element	CT (Control)	ST (Santana)	IB (Ibirapuera)	CG (Congonhas)	AS (Santo André)	SC (São Caetano)	MA (Mauá)	CC (Cerqueira César)	PI (Pinheiros)	DP (Parque D. Pedro)	SM (São Miguel)
Al	900 ± 11	1135 ± 14	1118 ± 12	1160 ± 15	1326 ± 14	1103 ± 14	981 ± 13	1403 ± 19	1232 ± 13	706 ± 8	955 ± 14
As	0.10 ± 0.05	0.13 ± 0.01	0.16 ± 0.01	0.11 ± 0.01	0.18 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.28 ± 0.02	0.12 ± 0.04	0.21 ± 0.01	0.12 ± 0.01
Ba	16 ± 1	16 ± 2	23 ± 1	32 ± 2	24 ± 2	25 ± 1	21 ± 2	32 ± 2	22 ± 1	32 ± 2	18 ± 1
Br	10.1 ± 0.1	6.8 ± 0.1	8.9 ± 0.1	7.7 ± 0.1	8.8 ± 0.1	8.8 ± 0.1	9.5 ± 0.1	10.2 ± 0.1	10.4 ± 0.1	7.5 ± 0.1	7.2 ± 0.1
Ca	3303 ± 40	2241 ± 47	3548 ± 75	3808 ± 70	3783 ± 90	3612 ± 41	3738 ± 69	3589 ± 85	3111 ± 50	3724 ± 75	4332 ± 76
Ce	1.4 ± 0.1	1.4 ± 0.1	1.9 ± 0.2	1.5 ± 0.1	2.1 ± 0.2	1.4 ± 0.1	1.8 ± 0.2	2.5 ± 0.3	2.0 ± 0.1	1.3 ± 0.1	1.4 ± 0.1
Cl	1484 ± 68	1130 ± 52	1179 ± 61	958 ± 42	1309 ± 53	1104 ± 45	1679 ± 71	1068 ± 46	1102 ± 51	1576 ± 65	1307 ± 57
Co	0.61 ± 0.03	1.3 ± 0.1	1.3 ± 0.1	2.1 ± 0.2	1.3 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	0.75 ± 0.03	2.1 ± 0.2	7.6 ± 0.9
Cr	1.3 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	2.9 ± 0.1	2.0 ± 0.1	2.1 ± 0.1	2.0 ± 0.1	3.7 ± 0.2	1.3 ± 0.1
Cu	2.7 ± 0.3	7.1 ± 0.9	18.2 ± 0.5	4.3 ± 0.5	56 ± 7	6.4 ± 0.7	31 ± 6	26 ± 7	12 ± 4	17 ± 4	15 ± 3
Eu (ng g^{-1})	160 ± 11	190 ± 12	211 ± 15	205 ± 15	232 ± 24	242 ± 65	232 ± 18	282 ± 16	252 ± 17	192 ± 10	150 ± 12
Fe	650 ± 12	820 ± 30	979 ± 42	782 ± 28	1073 ± 46	1058 ± 19	1025 ± 43	1189 ± 50	925 ± 17	804 ± 29	683 ± 25
K (%)	0.59 ± 0.01	0.26 ± 0.07	0.50 ± 0.02	0.56 ± 0.01	0.57 ± 0.03	0.43 ± 0.09	0.56 ± 0.03	0.41 ± 0.03	0.38 ± 0.06	0.52 ± 0.02	0.56 ± 0.01
La	0.90 ± 0.04	0.89 ± 0.06	1.2 ± 0.1	0.92 ± 0.01	1.36 ± 0.01	1.44 ± 0.01	1.20 ± 0.01	1.51 ± 0.01	1.32 ± 0.07	0.86 ± 0.08	0.98 ± 0.08
Mg	2324 ± 103	1640 ± 72	1855 ± 148	2214 ± 89	1915 ± 173	1877 ± 88	2286 ± 166	2386 ± 193	1885 ± 194	1886 ± 75	2304 ± 176
Mn	244 ± 8	137 ± 5	171 ± 5	187 ± 6	142 ± 4	135 ± 5	233 ± 7	161 ± 5	153 ± 5	234 ± 8	187 ± 6
Na	421 ± 15	222 ± 34	326 ± 10	277 ± 14	355 ± 11	285 ± 13	380 ± 11	240 ± 7	295 ± 13	334 ± 42	226 ± 9
Nd	0.66 ± 0.04	0.54 ± 0.05	0.94 ± 0.08	0.79 ± 0.01	1.2 ± 0.1	0.85 ± 0.02	1.0 ± 0.1	1.1 ± 0.1	0.95 ± 0.06	0.68 ± 0.05	0.68 ± 0.08
Rb	37 ± 2	14 ± 1	29 ± 2	30 ± 1	31 ± 2	24 ± 1	36 ± 2	24 ± 1	21 ± 1	29 ± 1	24 ± 1
Sb	0.26 ± 0.02	0.36 ± 0.02	0.43 ± 0.05	0.48 ± 0.05	0.54 ± 0.06	0.59 ± 0.02	0.41 ± 0.04	0.81 ± 0.07	0.44 ± 0.02	0.54 ± 0.04	0.20 ± 0.02
Sc	0.13 ± 0.01	0.12 ± 0.01	0.17 ± 0.01	0.10 ± 0.01	0.17 ± 0.01	0.19 ± 0.01	0.14 ± 0.01	0.18 ± 0.01	0.18 ± 0.01	0.09 ± 0.01	0.11 ± 0.01
Se	0.25 ± 0.02	0.30 ± 0.03	0.50 ± 0.05	0.28 ± 0.02	0.53 ± 0.04	0.46 ± 0.01	0.39 ± 0.02	0.67 ± 0.02	0.36 ± 0.01	0.44 ± 0.04	0.38 ± 0.03
Sm (ng g^{-1})	83 ± 20	83 ± 20	110 ± 37	85 ± 14	126 ± 10	115 ± 30	101 ± 35	147 ± 19	127 ± 23	77 ± 10	84 ± 14
V	1.6 ± 0.1	2.8 ± 0.1	2.0 ± 0.1	2.9 ± 0.2	3.6 ± 0.1	2.5 ± 0.1	2.5 ± 0.2	3.0 ± 0.2	2.6 ± 0.1	1.8 ± 0.1	2.9 ± 0.2
Yb (ng g^{-1})	30 ± 12	23 ± 2	39 ± 5	20 ± 5	31 ± 5	38 ± 6	24 ± 3	32 ± 8	34 ± 7	25 ± 2	27 ± 2
Zn	41 ± 1	58 ± 1	63 ± 2	69 ± 2	134 ± 4	91 ± 1	76 ± 2	67 ± 2	54 ± 1	102 ± 3	58 ± 2

Table 2

Results obtained in *Tillandsia usneoides* in São Paulo ($\mu\text{g g}^{-1}$) – exposition period: June–July 2002 (B)

Element	CT (Control)	ST (Santana)	IB (Ibirapuera)	CG (Congonhas)	SA (Santo André)	SC (São Caetano)	MA (Mauá)	CC (Cerqueira César)	PI (Pinheiros)	DP (Parque D. Pedro)
As	0.10 ± 0.01	0.26 ± 0.03	0.42 ± 0.04	0.35 ± 0.01	0.33 ± 0.03	0.22 ± 0.03	0.22 ± 0.03	0.44 ± 0.08	0.38 ± 0.02	0.43 ± 0.01
Ba	6.7 ± 0.7	16 ± 2	16 ± 1	32 ± 1	12 ± 4	14 ± 2	16 ± 3	22 ± 2	20 ± 1	23 ± 1
Br	7.2 ± 0.1	7.7 ± 0.1	8.1 ± 0.2	10.4 ± 0.4	8.9 ± 0.1	9.5 ± 0.1	7.4 ± 0.2	10.2 ± 0.3	8.1 ± 0.2	6.9 ± 0.1
Ca	1810 ± 70	2900 ± 35	2380 ± 47	4430 ± 30	1930 ± 65	1620 ± 61	2530 ± 45	3935 ± 75	2950 ± 82	2540 ± 80
Ce	0.66 ± 0.04	1.15 ± 0.02	2.23 ± 0.05	2.4 ± 0.1	1.73 ± 0.04	1.64 ± 0.03	1.3 ± 0.2	1.52 ± 0.04	1.3 ± 0.2	1.46 ± 0.08
Co	0.23 ± 0.01	0.48 ± 0.01	0.79 ± 0.02	0.78 ± 0.01	0.58 ± 0.01	0.48 ± 0.01	0.68 ± 0.01	0.53 ± 0.01	0.60 ± 0.05	1.24 ± 0.05
Cr	0.48 ± 0.02	0.99 ± 0.06	2.05 ± 0.09	1.76 ± 0.03	1.81 ± 0.07	1.55 ± 0.05	1.62 ± 0.03	1.40 ± 0.07	1.31 ± 0.05	1.36 ± 0.04
Eu (ng g^{-1})	50 ± 10	100 ± 30	350 ± 50	300 ± 30	250 ± 20	230 ± 30	280 ± 20	240 ± 30	200 ± 30	250 ± 20
Fe	440 ± 17	612 ± 20	1071 ± 42	918 ± 42	964 ± 36	930 ± 27	630 ± 20	809 ± 30	730 ± 30	769 ± 41
K (%)	0.40 ± 0.03	0.36 ± 0.01	0.12 ± 0.02	0.15 ± 0.01	0.30 ± 0.01	0.13 ± 0.01	0.38 ± 0.02	0.20 ± 0.01	0.30 ± 0.03	0.15 ± 0.02
La	0.40 ± 0.01	0.73 ± 0.02	1.07 ± 0.03	1.36 ± 0.03	1.09 ± 0.02	1.04 ± 0.02	0.85 ± 0.02	0.83 ± 0.02	1.10 ± 0.04	1.36 ± 0.03
Na	1235 ± 85	1632 ± 94	3200 ± 50	1735 ± 46	1435 ± 63	1525 ± 39	1350 ± 46	2950 ± 67	2250 ± 41	1230 ± 45
Nd	1.1 ± 0.1	2.9 ± 0.3	0.5 ± 0.1	0.66 ± 0.04	3.5 ± 0.4	3.6 ± 0.4	0.70 ± 0.03	1.3 ± 0.2	0.90 ± 0.05	0.6 ± 0.1
Rb	5.5 ± 0.3	5.6 ± 0.3	5.0 ± 0.3	6.5 ± 0.3	7.0 ± 0.3	3.03 ± 0.3	4.8 ± 0.2	7.6 ± 0.3	5.2 ± 0.1	5.1 ± 0.4
Sb	0.07 ± 0.01	0.40 ± 0.08	0.35 ± 0.02	0.53 ± 0.02	0.35 ± 0.02	0.62 ± 0.08	0.49 ± 0.02	0.99 ± 0.08	0.50 ± 0.08	0.43 ± 0.04
Sc	0.30 ± 0.02	0.71 ± 0.05	0.27 ± 0.02	1.10 ± 0.04	1.41 ± 0.06	1.04 ± 0.09	0.64 ± 0.05	0.97 ± 0.04	0.35 ± 0.02	0.80 ± 0.05
Sm (ng g^{-1})	40 ± 8	70 ± 8	105 ± 19	140 ± 29	112 ± 19	115 ± 28	81 ± 5	84 ± 9	92 ± 9	77 ± 8
Th	0.04 ± 0.01	0.09 ± 0.01	0.32 ± 0.01	0.18 ± 0.03	0.20 ± 0.01	0.15 ± 0.02	0.25 ± 0.02	0.12 ± 0.01	0.13 ± 0.02	0.12 ± 0.03
U (ng g^{-1})	20 ± 5	23 ± 2	40 ± 1	95 ± 4	72 ± 4	61 ± 3	31 ± 3	134 ± 9	35 ± 3	57 ± 5
Yb (ng g^{-1})	10 ± 2	20 ± 1	70 ± 2	35 ± 4	42 ± 1	30 ± 1	63 ± 2	22 ± 3	52 ± 2	35 ± 5
Zn	21.4 ± 0.6	41 ± 1	54 ± 1	60 ± 1	107 ± 2	64 ± 2	65 ± 4	44 ± 1	60 ± 1	60 ± 1

Table 3

Results obtained in *Tillandsia usneoides* in São Paulo ($\mu\text{g g}^{-1}$) – exposition period: Nov–Dec 2002/Jan 2003 (C)

Element	CT (Control)	ST (Santana)	IB (Ibirapuera)	CG (Congonhas)	AS (Santo André)	SC (São Caetano)	MA (Mauá)	CC (Cerqueira César)	PI (Pinheiros)	DP (Parque D. Pedro)	SM (São Miguel)
As	0.22 ± 0.03	0.35 ± 0.02	0.32 ± 0.04	0.40 ± 0.09	0.33 ± 0.02	0.29 ± 0.03	0.28 ± 0.02	0.35 ± 0.02	0.31 ± 0.03	0.39 ± 0.05	0.36 ± 0.04
Ba	22 ± 3	34 ± 3	30 ± 1	51 ± 2	36 ± 3	28 ± 2	32 ± 2	42 ± 3	31 ± 2	52 ± 2	32 ± 3
Br	4.2 ± 0.3	6.9 ± 0.2	5.5 ± 0.5	4.0 ± 0.4	5.6 ± 0.6	6.3 ± 0.2	5.4 ± 0.1	7.1 ± 0.4	6.4 ± 0.1	5.5 ± 0.4	5.2 ± 0.2
Ca	3728 ± 28	2632 ± 48	3280 ± 59	3230 ± 90	2430 ± 38	2980 ± 32	3872 ± 40	3482 ± 38	3258 ± 98	3428 ± 95	4530 ± 53
Ce	1.7 ± 0.2	2.1 ± 0.2	2.1 ± 0.2	1.8 ± 0.2	2.1 ± 0.2	2.2 ± 0.2	2.1 ± 0.2	2.5 ± 0.3	2.1 ± 0.1	1.8 ± 0.1	2.3 ± 0.2
Co	0.91 ± 0.03	1.2 ± 0.1	1.5 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	1.8 ± 0.1	1.6 ± 0.1	1.4 ± 0.1	1.9 ± 0.2	2.1 ± 0.2	2.3 ± 0.2
Cr	1.3 ± 0.1	1.7 ± 0.1	1.9 ± 0.1	2.3 ± 0.3	2.2 ± 0.8	2.3 ± 0.1	1.6 ± 0.1	2.4 ± 0.2	1.6 ± 0.1	2.7 ± 0.2	2.0 ± 0.2
Eu (ng g^{-1})	10 ± 1	30 ± 1	40 ± 1	22 ± 1	23 ± 2	32 ± 3	22 ± 2	32 ± 2	25 ± 3	26 ± 3	10 ± 1
Fe	1070 ± 32	1124 ± 24	1169 ± 34	1212 ± 40	1079 ± 28	1120 ± 20	935 ± 28	1227 ± 30	1080 ± 40	1173 ± 67	1324 ± 40
K (%)	0.97 ± 0.02	0.57 ± 0.05	0.54 ± 0.05	0.56 ± 0.03	0.60 ± 0.05	0.48 ± 0.06	0.79 ± 0.09	0.41 ± 0.06	0.70 ± 0.05	0.58 ± 0.04	0.66 ± 0.04
La	0.88 ± 0.08	1.24 ± 0.04	1.21 ± 0.02	1.46 ± 0.01	1.24 ± 0.01	1.29 ± 0.02	1.29 ± 0.02	1.47 ± 0.04	1.11 ± 0.04	1.26 ± 0.03	1.13 ± 0.05
Na	111 ± 10	89 ± 3	90 ± 8	139 ± 4	112 ± 8	98 ± 5	140 ± 3	84 ± 2	156 ± 10	140 ± 5	116 ± 9
Nd	0.35 ± 0.02	1.0 ± 0.1	1.2 ± 0.1	1.40 ± 0.06	1.20 ± 0.05	1.30 ± 0.08	1.1 ± 0.1	1.5 ± 0.2	1.3 ± 0.1	1.4 ± 0.1	1.1 ± 0.2
Rb	18 ± 1	25 ± 1	37 ± 2	30 ± 1	37 ± 2	23 ± 1	38 ± 2	20 ± 1	34 ± 3	27 ± 1	28 ± 1
Sb	0.11 ± 0.03	0.56 ± 0.05	0.33 ± 0.04	0.60 ± 0.08	0.38 ± 0.02	0.43 ± 0.01	0.42 ± 0.02	0.52 ± 0.01	0.30 ± 0.05	0.98 ± 0.05	0.38 ± 0.01
Sc	0.13 ± 0.01	0.16 ± 0.01	0.24 ± 0.02	0.16 ± 0.01	0.17 ± 0.01	0.15 ± 0.01	0.13 ± 0.01	0.19 ± 0.01	0.18 ± 0.01	0.17 ± 0.01	0.20 ± 0.01
Sm (ng g^{-1})	82 ± 2	120 ± 12	130 ± 10	150 ± 10	132 ± 12	125 ± 13	111 ± 18	142 ± 10	117 ± 16	112 ± 15	140 ± 21
Th	0.20 ± 0.01	0.22 ± 0.02	0.35 ± 0.01	0.25 ± 0.03	0.29 ± 0.08	0.22 ± 0.02	0.20 ± 0.02	0.27 ± 0.02	0.24 ± 0.01	0.23 ± 0.02	0.36 ± 0.09
U (ng g^{-1})	40 ± 13	70 ± 10	63 ± 12	75 ± 13	39 ± 10	70 ± 11	62 ± 12	53 ± 11	21 ± 9	28 ± 9	19 ± 8
Yb (ng g^{-1})	30 ± 6	41 ± 5	79 ± 6	27 ± 3	52 ± 4	42 ± 6	44 ± 6	63 ± 5	40 ± 3	32 ± 3	42 ± 10
Zn	41 ± 3	79 ± 6	79 ± 5	112 ± 9	145 ± 8	112 ± 10	72 ± 6	69 ± 3	58 ± 4	116 ± 6	57 ± 3

Table 4
Results obtained in *Tillandsia usneoides* in São Paulo ($\mu\text{g g}^{-1}$) – exposition period: Feb/April 2003 (D)

Element	CT (Control)	ST (Santana)	IB (Ibirapuera)	CG (Congonhas)	SA (Santo André)	SC (São Caetano)	MA (Mauá)	CC (Cerqueira César)	PI (Pinheiros)	DP (Parque D. Pedro)	SM (São Miguel)
As	0.22 ± 0.03	0.31 ± 0.03	0.33 ± 0.03	0.42 ± 0.08	0.34 ± 0.01	0.33 ± 0.01	0.24 ± 0.01	0.24 ± 0.02	0.22 ± 0.04	0.53 ± 0.09	0.33 ± 0.03
Ba	22 ± 2	26 ± 3	30 ± 2	39 ± 2	28 ± 3	28 ± 3	26 ± 2	31 ± 1	27 ± 3	44 ± 5	27 ± 1
Br	5.0 ± 0.3	5.0 ± 0.5	6.2 ± 0.5	5.6 ± 0.4	6.7 ± 0.8	7.2 ± 0.2	5.0 ± 0.6	6.3 ± 0.5	4.0 ± 0.2	5.7 ± 0.6	5.3 ± 0.4
Ca	3242 ± 32	3132 ± 27	3920 ± 35	3820 ± 35	3235 ± 23	4442 ± 38	3700 ± 19	3723 ± 35	3820 ± 30	4135 ± 25	4130 ± 30
Ce	1.1 ± 0.1	1.2 ± 0.2	1.7 ± 0.2	2.1 ± 0.2	1.6 ± 0.1	1.5 ± 0.2	1.9 ± 0.3	1.4 ± 0.1	1.2 ± 0.1	2.0 ± 0.1	1.3 ± 0.4
Co	0.6 ± 0.1	1.1 ± 0.2	1.4 ± 0.1	1.8 ± 0.1	0.9 ± 0.1	1.2 ± 0.1	1.0 ± 0.1	0.9 ± 0.1	0.6 ± 0.1	1.1 ± 0.2	2.9 ± 0.3
Cr	0.8 ± 0.1	1.0 ± 0.1	1.5 ± 0.1	1.8 ± 0.1	2.0 ± 0.1	1.8 ± 0.1	1.6 ± 0.1	1.6 ± 0.1	1.1 ± 0.1	2.0 ± 0.2	1.5 ± 0.1
Eu (ng g^{-1})	10 ± 1	12 ± 1	20 ± 1	20 ± 2	23 ± 2	22 ± 2	24 ± 1	22 ± 1	12 ± 2	31 ± 2	42 ± 1
Fe	926 ± 18	768 ± 20	990 ± 23	1095 ± 35	992 ± 16	975 ± 20	1031 ± 42	775 ± 14	1155 ± 35	770 ± 19	783 ± 14
K (%)	0.90 ± 0.05	0.46 ± 0.07	0.73 ± 0.04	0.67 ± 0.09	0.80 ± 0.06	0.74 ± 0.06	0.81 ± 0.05	0.82 ± 0.03	0.75 ± 0.05	0.78 ± 0.02	0.72 ± 0.03
La	0.62 ± 0.02	0.69 ± 0.03	1.00 ± 0.05	1.21 ± 0.01	1.05 ± 0.02	0.99 ± 0.02	1.44 ± 0.02	0.82 ± 0.03	0.66 ± 0.02	1.21 ± 0.01	0.87 ± 0.03
Na	109 ± 20	121 ± 12	408 ± 32	217 ± 25	259 ± 21	416 ± 32	137 ± 30	265 ± 34	122 ± 30	380 ± 40	148 ± 20
Nd	0.80 ± 0.06	0.90 ± 0.05	1.22 ± 0.06	1.53 ± 0.07	1.15 ± 0.06	1.69 ± 0.08	1.35 ± 0.09	1.18 ± 0.07	0.94 ± 0.09	1.81 ± 0.08	1.14 ± 0.07
Rb	32 ± 5	32 ± 3	38 ± 1	32 ± 1	44 ± 4	37 ± 4	38 ± 4	39 ± 1	48 ± 5	50 ± 3	35 ± 1
Sb	0.29 ± 0.02	0.34 ± 0.02	0.36 ± 0.03	0.63 ± 0.05	0.56 ± 0.04	0.57 ± 0.04	0.26 ± 0.03	0.56 ± 0.04	0.39 ± 0.06	1.05 ± 0.08	0.25 ± 0.04
Sc	0.10 ± 0.01	0.10 ± 0.01	0.17 ± 0.01	0.14 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	0.12 ± 0.01	0.11 ± 0.01
Sm (ng g^{-1})	53 ± 6	58 ± 8	110 ± 9	140 ± 10	138 ± 22	110 ± 15	115 ± 21	98 ± 11	77 ± 11	122 ± 16	105 ± 12
Th	0.14 ± 0.01	0.12 ± 0.01	0.26 ± 0.01	0.22 ± 0.03	0.21 ± 0.03	0.17 ± 0.03	0.26 ± 0.04	0.15 ± 0.02	0.15 ± 0.02	0.22 ± 0.04	0.19 ± 0.02
U (ng g^{-1})	30 ± 5	80 ± 10	93 ± 7	105 ± 13	75 ± 6	84 ± 5	72 ± 9	84 ± 12	63 ± 7	92 ± 10	52 ± 9
Yb (ng g^{-1})	30 ± 3	25 ± 2	50 ± 4	42 ± 5	51 ± 4	39 ± 2	41 ± 2	42 ± 3	23 ± 3	45 ± 3	31 ± 2
Zn	52 ± 3	175 ± 12	73 ± 8	99 ± 12	189 ± 12	151 ± 22	86 ± 8	72 ± 12	70 ± 10	128 ± 25	65 ± 6

Table 5
Results obtained in *Tillandsia usneoides* in São Paulo ($\mu\text{g g}^{-1}$) – exposition period: April/May 2003 (E)

Element	CT (Control)	ST (Santana)	IB (Ibirapuera)	CG (Congonhas)	SA (Santo André)	SC (São Caetano)	MA (Mauá)	CC (Cerqueira César)	PI (Pinheiros)	DP (Parque D. Pedro)	SM (São Miguel)
As	0.13 ± 0.02	0.30 ± 0.03	0.21 ± 0.02	0.31 ± 0.01	0.43 ± 0.02	0.53 ± 0.01	0.33 ± 0.01	0.48 ± 0.04	0.22 ± 0.02	0.67 ± 0.09	0.31 ± 0.02
Ba	21 ± 1	24 ± 2	23 ± 1	31 ± 2	29 ± 2	26 ± 1	21 ± 2	38 ± 2	22 ± 1	40 ± 3	25 ± 1
Br	5.2 ± 0.3	6.0 ± 0.4	4.7 ± 0.7	5.7 ± 0.9	7.1 ± 0.3	6.0 ± 0.6	5.3 ± 0.3	8.7 ± 0.8	5.5 ± 0.3	9.4 ± 0.2	6.7 ± 0.1
Ca	3110 ± 24	3740 ± 35	3420 ± 32	3425 ± 35	3642 ± 22	3532 ± 28	3732 ± 41	3432 ± 35	2825 ± 30	3835 ± 34	3320 ± 25
Ce	1.4 ± 0.1	1.4 ± 0.1	1.9 ± 0.2	1.5 ± 0.1	2.1 ± 0.2	1.4 ± 0.1	1.8 ± 0.2	2.5 ± 0.3	2.0 ± 0.1	1.4 ± 0.1	1.4 ± 0.1
Co	0.49 ± 0.03	0.80 ± 0.09	0.76 ± 0.03	0.66 ± 0.02	1.00 ± 0.04	0.79 ± 0.04	0.86 ± 0.04	0.63 ± 0.03	0.63 ± 0.03	0.91 ± 0.02	1.33 ± 0.06
Cr	1.46 ± 0.05	1.70 ± 0.08	1.90 ± 0.09	1.72 ± 0.07	1.75 ± 0.05	2.2 ± 0.1	1.38 ± 0.05	1.9 ± 0.1	1.3 ± 0.1	2.8 ± 0.2	2.3 ± 0.2
Eu (ng g^{-1})	18 ± 1	23 ± 1	22 ± 1	22 ± 1	23 ± 2	24 ± 3	19 ± 1	18 ± 1	21 ± 3	19 ± 2	19 ± 2
Fe	1222 ± 35	912 ± 12	860 ± 28	775 ± 20	984 ± 26	1042 ± 21	745 ± 12	935 ± 20	771 ± 27	1210 ± 20	1140 ± 30
K (%)	0.87 ± 0.04	0.59 ± 0.07	0.72 ± 0.02	0.76 ± 0.03	0.72 ± 0.04	0.60 ± 0.03	0.75 ± 0.03	0.69 ± 0.03	0.76 ± 0.04	0.55 ± 0.02	0.67 ± 0.03
La	0.97 ± 0.04	0.89 ± 0.02	0.68 ± 0.02	0.94 ± 0.03	0.98 ± 0.01	1.13 ± 0.02	0.90 ± 0.02	0.92 ± 0.01	0.88 ± 0.02	1.42 ± 0.01	1.22 ± 0.02
Na	95 ± 19	347 ± 18	105 ± 12	125 ± 20	308 ± 20	300 ± 17	550 ± 30	212 ± 33	138 ± 23	483 ± 26	236 ± 36
Nd	1.00 ± 0.03	1.03 ± 0.08	1.31 ± 0.08	1.27 ± 0.06	1.10 ± 0.01	1.07 ± 0.09	1.29 ± 0.08	1.20 ± 0.04	0.84 ± 0.04	1.25 ± 0.05	1.70 ± 0.08
Rb	33 ± 1	36 ± 2	37 ± 1	38 ± 1	38 ± 1	39 ± 2	37 ± 2	40 ± 1	33 ± 2	37 ± 2	32 ± 2
Sb	0.17 ± 0.02	0.43 ± 0.04	0.26 ± 0.01	0.43 ± 0.02	0.52 ± 0.04	0.82 ± 0.08	0.35 ± 0.04	0.39 ± 0.07	0.39 ± 0.04	0.65 ± 0.01	0.27 ± 0.02
Sc	0.13 ± 0.01	0.20 ± 0.01	0.18 ± 0.01	0.13 ± 0.01	0.13 ± 0.01	0.19 ± 0.01	0.14 ± 0.01	0.14 ± 0.01	0.13 ± 0.01	0.22 ± 0.01	0.22 ± 0.01
Sm (ng g^{-1})	9 ± 1	14 ± 2	10 ± 1	11 ± 2	10 ± 1	15 ± 2	10 ± 2	10 ± 1	12 ± 2	17 ± 3	13 ± 2
Th	0.27 ± 0.02	0.19 ± 0.01	0.28 ± 0.03	0.21 ± 0.02	0.19 ± 0.02	0.25 ± 0.02	0.15 ± 0.01	0.24 ± 0.03	0.18 ± 0.02	0.36 ± 0.03	0.31 ± 0.02
U (ng g^{-1})	38 ± 7	67 ± 3	71 ± 8	52 ± 4	53 ± 6	72 ± 11	83 ± 9	54 ± 8	43 ± 8	132 ± 25	92 ± 8
Yb (ng g^{-1})	30 ± 5	53 ± 4	63 ± 3	42 ± 2	41 ± 3	53 ± 5	34 ± 3	42 ± 4	34 ± 2	53 ± 2	57 ± 4
Zn	62 ± 3	72 ± 4	74 ± 8	75 ± 6	118 ± 9	110 ± 10	90 ± 10	70 ± 6	56 ± 3	103 ± 3	65 ± 6

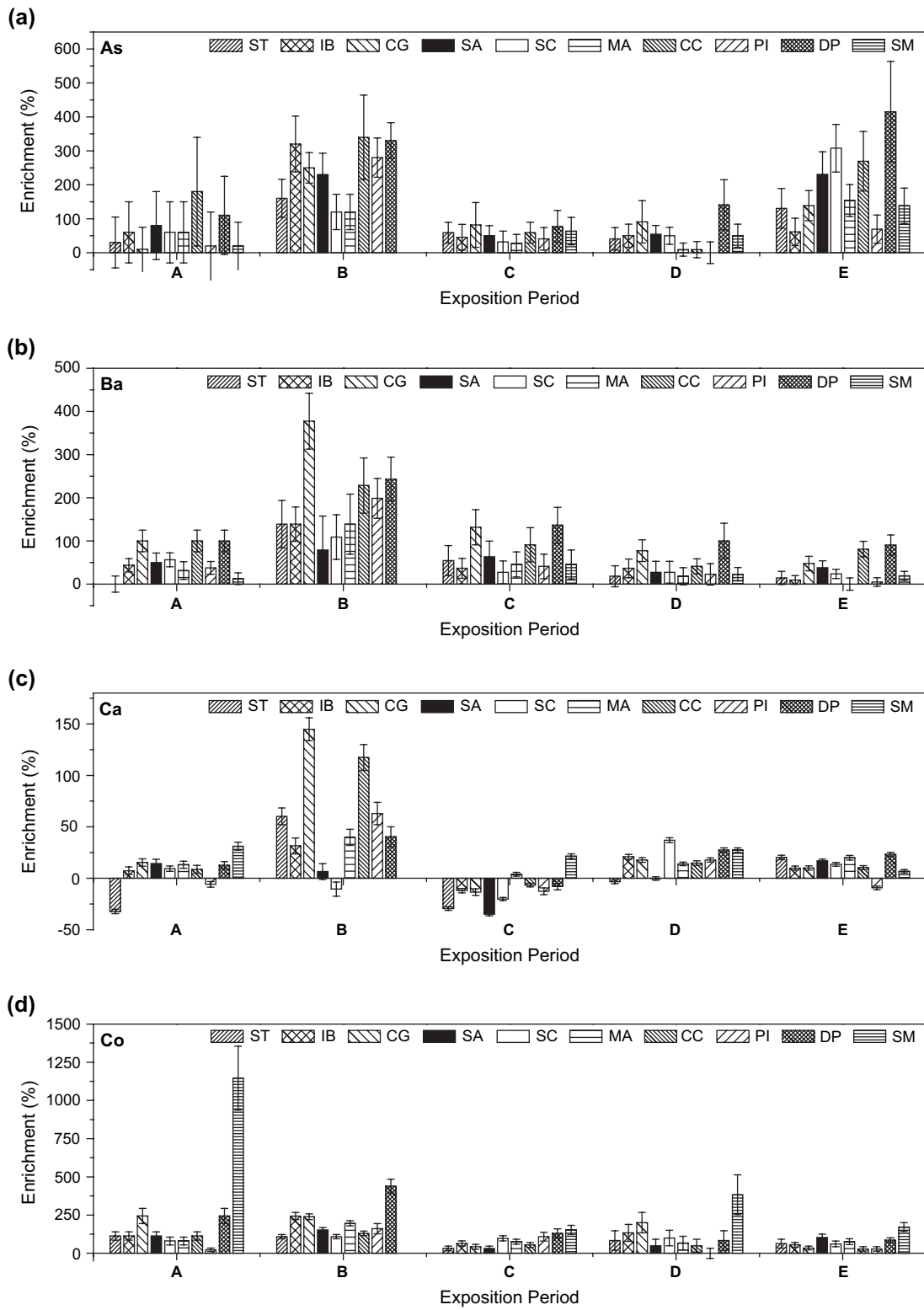


Fig. 2. Enrichment in concentration of the element (%) in *T. usneoides* relation to the exposure site and exposure period. (a) As; (b) Ba; (c) Ca; (d) Co; (e) Cr; (f) Fe; (g) Sb; (h) Zn. Exposure Period: A = April–May/2002; B = June–July/2002; C = Nov/2002–Jan/2003; D = Feb–Apr/2003; E = April–May/2003. Stations: ST = Santana; IB = Ibirapuera; CG = Congonhas; SA = Santo André; SC = São Caetano; MA = Mauá; CC = Cerqueira César; PI = Pinheiros; DP = Parque D. Pedro; SM = São Miguel.

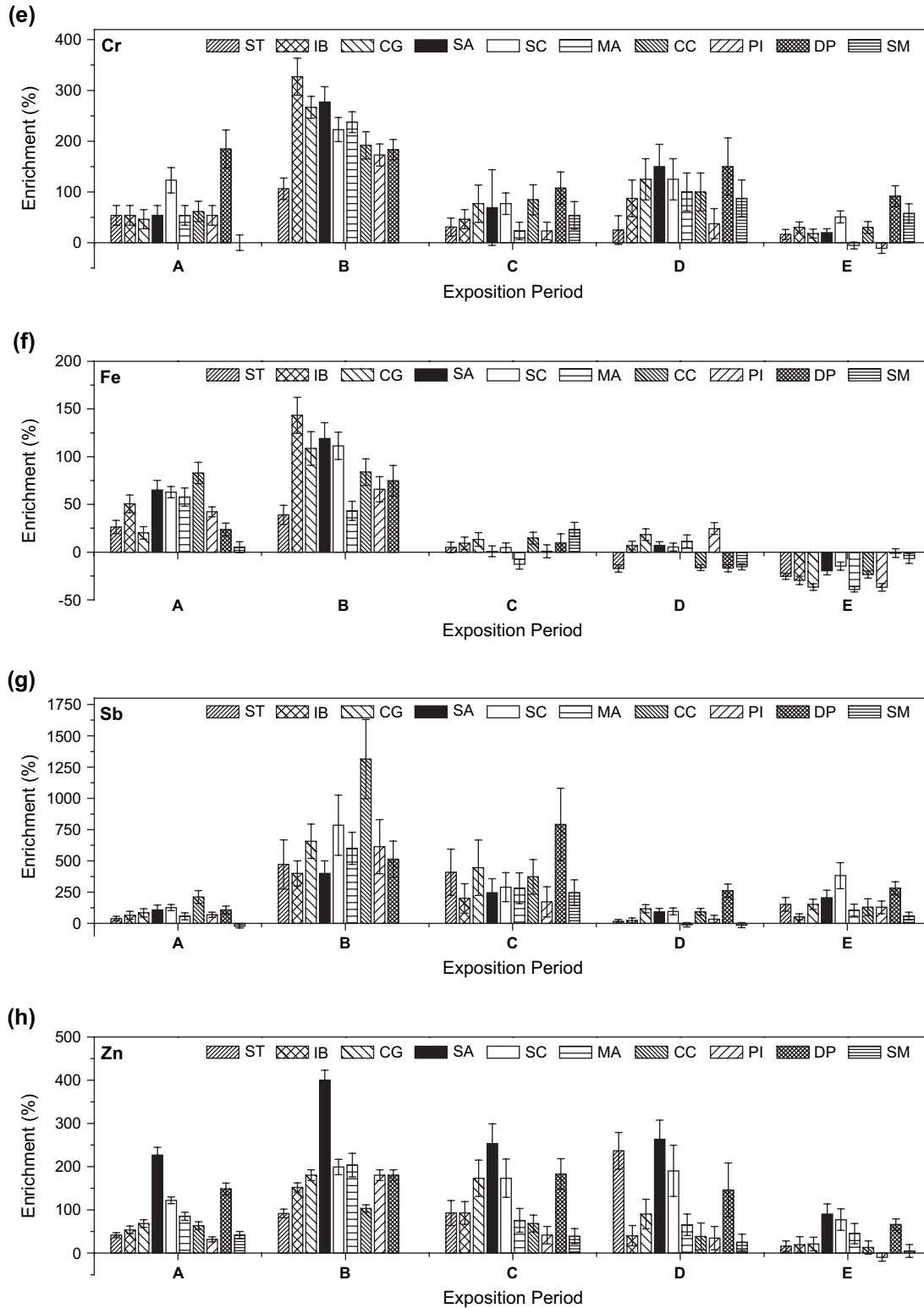


Fig. 2 (continued).

5. Results and discussion

The concentration values for the analyzed elements are presented in Tables 1–5. The associated errors are the standard deviation of two replicates. The *T. usneoides* plants in the polluted and reference sites remained green

during the monitoring period, even showing some growth. This indicates that the plants were physiological and metabolically able to accumulate toxic elements from the atmosphere. Regarding it, the species showed to be suitable for active monitoring studies in urban environments, such as the MRSP.

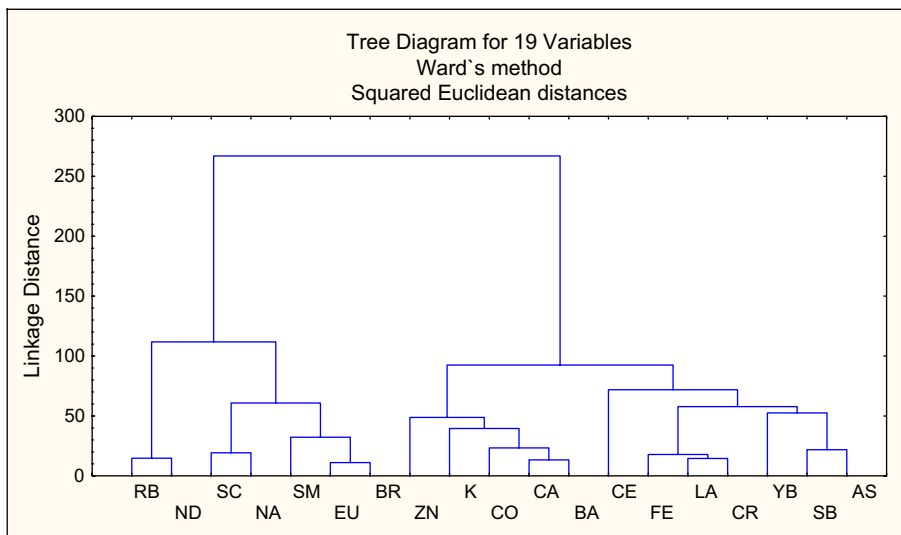


Fig. 3. Dendrogram obtained from the data.

Fig. 2(a–h) show the enrichment in concentration of some of the analyzed elements in plants of *T. usneoides* exposed in the monitoring sites in relation to the concentrations measured in plants from the control site during the monitoring period. This relation, in percentage, was calculated by:

$$RC_E = (CE_A - CE_C / CE_C) 100 \quad (1)$$

where:

- RC_E = enrichment (%) of the concentration of the element E;
- CE_A = concentration of the element E in the sample;
- CE_C = concentration of the element E in the control sample.

In many cases, the highest increase in concentration occurred in winter time (Exposure B: June–July/2002), in opposition of a period of lower enrichment in relation to the control sample observed in summer (Exposure C: Nov/2002–Jan/2003). In fact, the concentrations of pollutants in São Paulo, especially PM₁₀, are higher in winter than in summer (Orsini et al., 1984, 1986; Artaxo and Orsini, 1987).

For a better understanding of the behavior of the elements analyzed in the plants exposed in the polluted sites, a cluster analysis was applied by using Statistica software and the dendrogram obtained from the data is presented in Fig. 3. The dendrogram shows that there are two main groups of elements: Zn, K, Co, Ca, Ba, Ce, Fe, Cr, As and Sb in one group and Rb, Sc, Na, Sm, Nd, Eu and Br in another group. The elements Zn, Ba, Ca, K and Co form a sub-group. Zn, Ba and Ca are traffic-related elements and may be associated to vehicular sources (Zn is used in lubricant oils and Ba and Ca in diesel). Monaci et al. (2000) emphasized that Ba and Zn are new tracers of vehicle emission, instead of Pb. In fact, the highest concentrations of Ba were observed in Cerqueira César, Parque Dom Pedro II and Congonhas (Fig. 2b), where the exposure sites were near to heavy traffic avenues

(cars, buses and trucks). Organometallic compounds containing barium and calcium have been used to reduce diesel smoke and 85–95% of the metal is emitted as particulates in the vehicle exhausts. According to CETESB, diesel engine exhausts are responsible for 80% of NO_x emissions (CETESB, 2005). Fig. 4 presents the similar distribution patterns of the normalized average levels of Ba, Ca and of the NO_x emissions (data provided by CETESB) during the studied period, indicating that they may have the same source, the diesel engines.

For Co, there was a huge enrichment in São Miguel Paulista (SM), much higher than in the other sites (Fig. 2d), mainly in the exposition periods A and D (Co was not analyzed in SM in exposition period B). In this area, there is a metal processing plant, which produces about 16 000 tons/year of Ni and 600 tons/year of Co, which indicates that Co may be related to industrial activities.

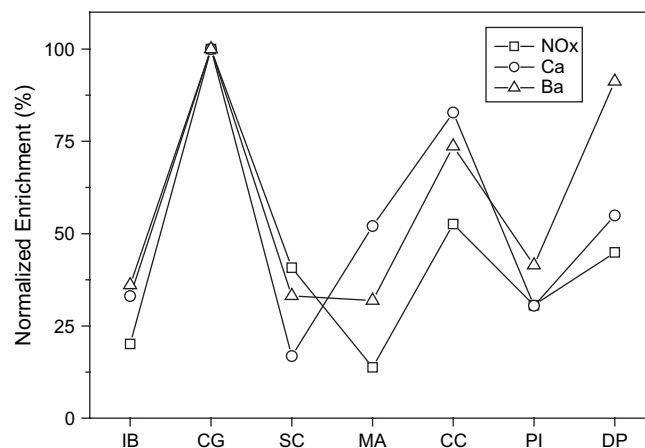


Fig. 4. Normalized enrichment of Ba and Ca (%) in *T. usneoides* and NO_x normalized concentration (%) in the exposure sites IB = Ibirapuera; CG = Congonhas; SC = São Caetano; MA = Mauá; CC = Cerqueira César; PI = Pinheiros; DP = Parque D. Pedro.

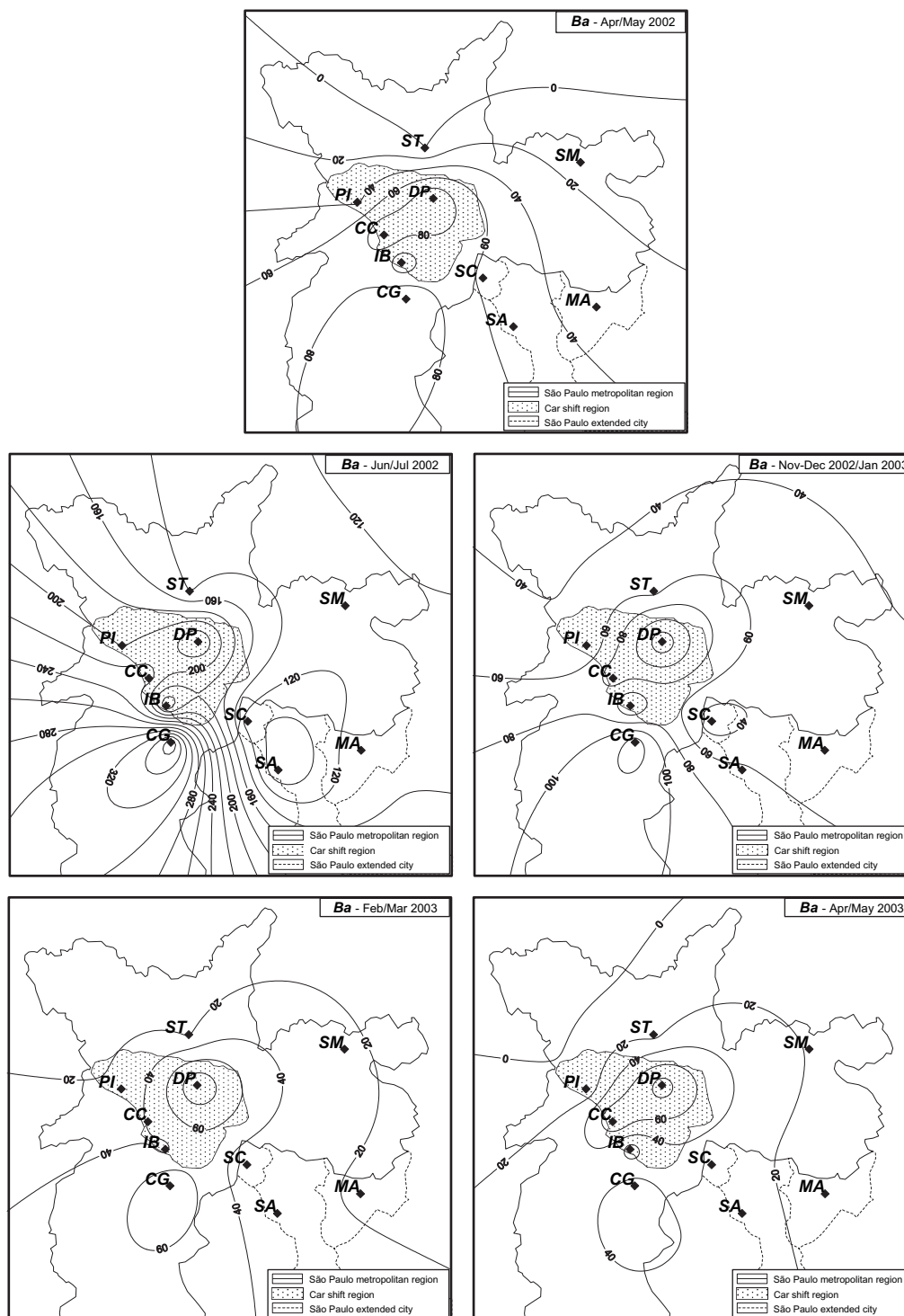


Fig. 5. Distribution maps of Ba in the metropolitan region of São Paulo (April/2002–April/2003).

As and Sb form another sub-group with Fe, Cr, La, Ce and Yb. The elements As, Sb and Cr did not show any particular tendency in their distribution pattern during the exposure time (Fig. 2a, g and e), and it is not possible to identify a specific source. On the other hand, the highest enrichment of Sb was observed in Cerqueira César (CC) and Congonhas (CG), regions with high traffic density, which may associate Sb to vehicular sources.

The rare earth elements, Fe and Rb probably have soil particles as main source.

Distribution maps for Ba, Co, Cr and Zn were drawn using Surfer 8 software and are presented in Figs. 5–8, respectively. The concentration range in the maps was also expressed in percentage of enrichment in relation to the concentration of the element in the control sample, calculated by Eq. (1). The contour lines show the different levels of enrichment of

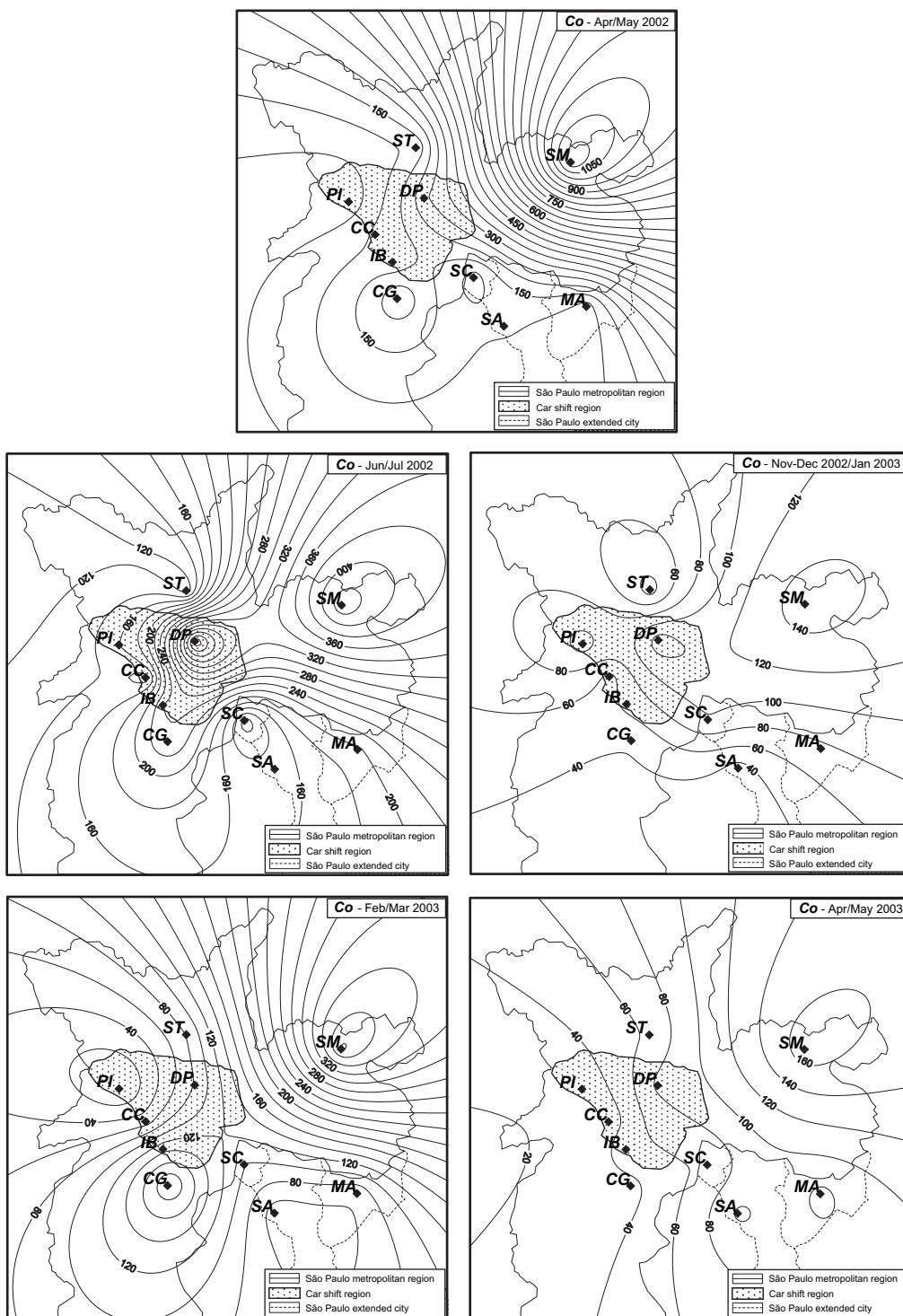


Fig. 6. Distribution maps of Co in the metropolitan region of São Paulo (April/2002–April/2003).

elements obtained during the period of the biomonitoring. The highest enrichment in concentration of all elements was observed in June/2002, in winter (dry period). The traffic-related element Ba is concentrated in Congonhas and Parque D. Pedro II (downtown area) and may be associated to vehicular sources.

For Co, the distribution maps show a notable concentration in São Miguel, instead of in downtown area. As it was already

mentioned, in this area, there is an Ni/Co metal processing plant, which indicates that Co may be related to industrial activities.

Chromium showed the same seasonal variation but it is spread along the region. The highest concentration observed was in Ibirapuera Park, the largest park in the city. On the other hand, high increments in concentrations were also obtained in Santo André and in Congonhas, an industrial region

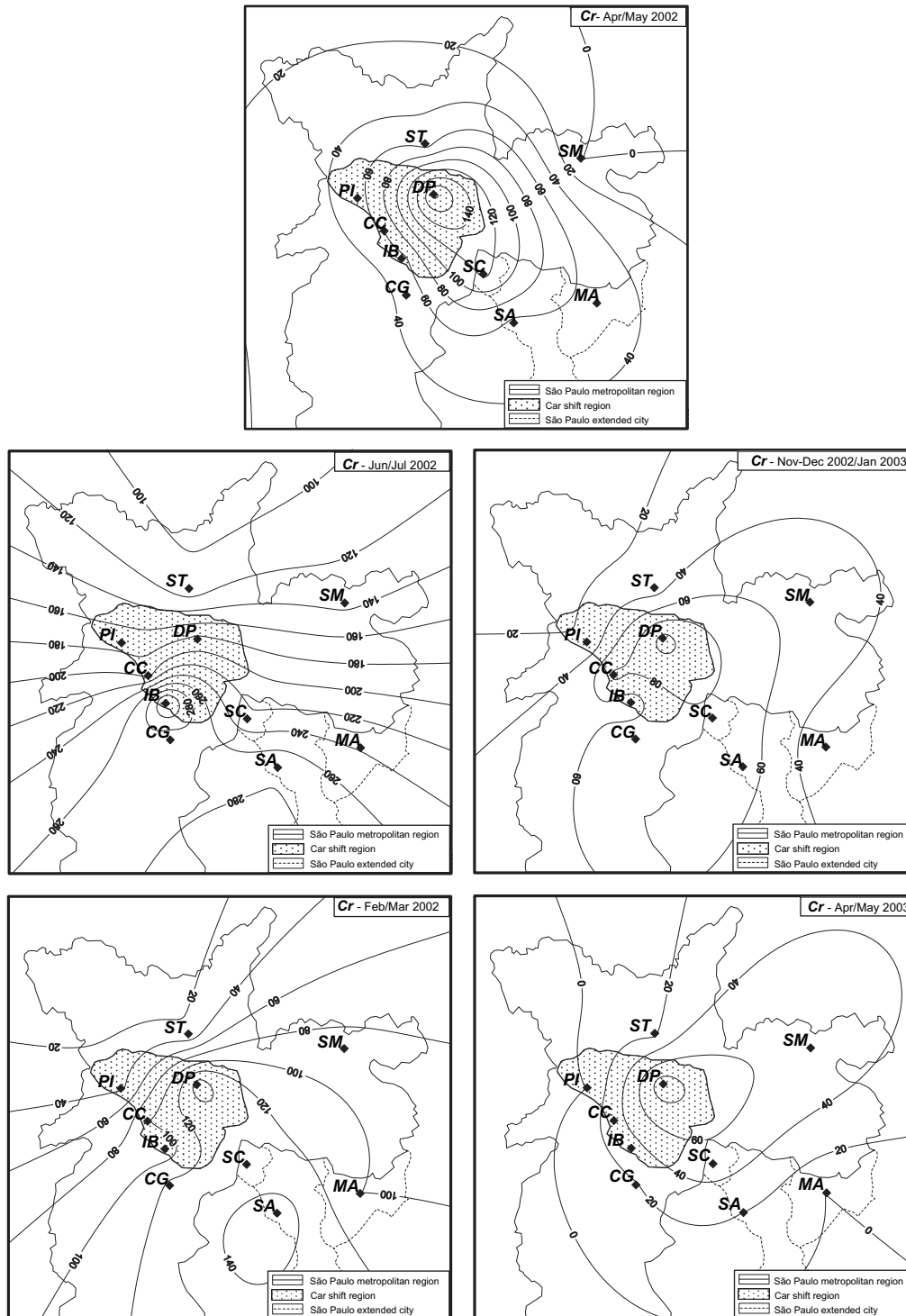


Fig. 7. Distribution maps of Cr in the metropolitan region of São Paulo (April/2002–April/2003).

and a site near heavy traffic avenues, respectively, showing that its source is not evident, and that Cr can be associated either to vehicular and industrial sources.

The highest concentration of Zn was observed in Santo André, an industrial region, but this element was also observed in downtown area, showing that Zn can be associated also to vehicular and industrial sources.

6. Conclusions

Traffic-related elements such as Zn and Ba presented high concentrations in exposure sites near to heavy traffic avenues (cars, buses and trucks) and may be associated to vehicular sources. For Zn and Co, the highest contents were related to industrial zones and can be associated to the presence of

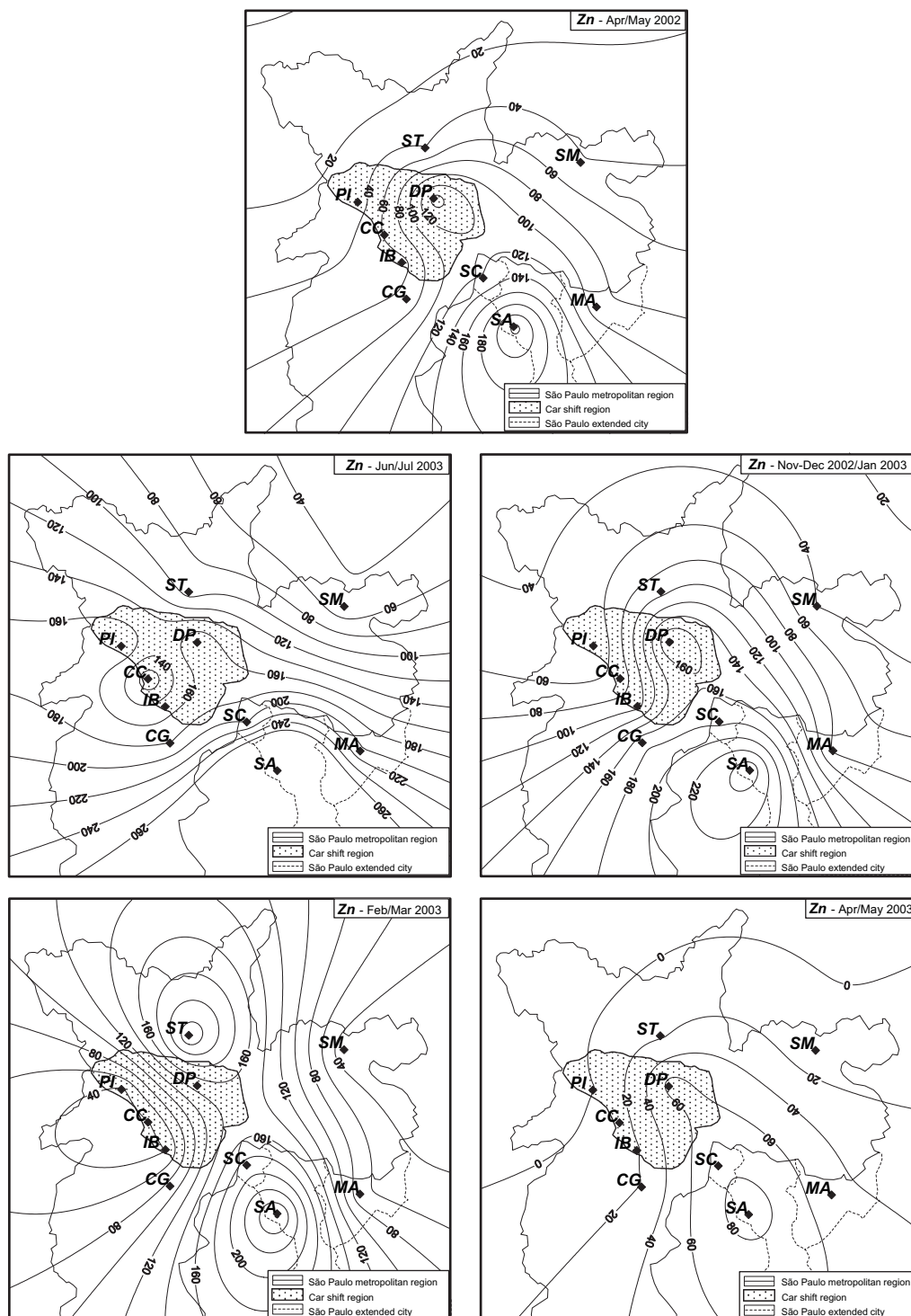


Fig. 8. Distribution maps of Zn in the metropolitan region of São Paulo (April/2002–April/2003).

anthropogenic emission sources. According to the results it can be inferred that rare earth elements, Fe and Rb, probably originated in the soil.

Biological monitors, combined with an analytical technique that provides information on concentrations of a broad pattern of elements, proved to be a powerful tool for detecting and identifying sources of metal pollution. Taking into account the metal enrichment properties of *T. usneoides*, it

could be proposed as a biomonitor of air quality in urbanized areas.

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