Native plant bioaccumulation strategies: a baseline study for biomonitoring the Atlantic Forest

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Abstract: The atmosphere may act as an important source of chemical elements for the Atlantic Forest, one of the hottest world biodiversity hotspots. However, chemical responses for chemical element availability are not expected to be equal for each plant species. In this sense, the present work encompasses a baseline study for biomonitoring purposes based on the identification of different strategies of native tree species in accumulating chemical elements. Instrumental neutron activation analysis was employed for chemical characterisation of leaf and soil compartments. Results indicated a low level of pollution because the major part of the studied species has shown chemical mass fractions within the expected range in leaf compartment. By estimating leaf–soil bioaccumulation factor, some species were found to accumulate the nutrients Co, Na, Se and Zn, some trace elements Br, Ba, Cs, Hg, Rb, Sc and Sr and the lanthanides Ce, La and Sm despite the environmental variability.

Keywords: environment; chemical element composition; hotspot; tree species; fern; Myrtaceae; distribution; spatial variability; transfer.

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Biographical notes: Elvis J. França, Doctor in Applied Ecology, is a Post-Doctorate Researcher at the University of São Paulo, São Paulo, Brazil. He started biomonitoring studies in the Atlantic Forest about ten years ago. In this ecosystem, chemical elements were investigated in soils and leaves of native tree species. This work is the first baseline information on chemical composition of Atlantic Forest species.

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1 Introduction

The Atlantic Forest is one of the most complex and diversified tropical forests. Owing to the high level of species endemism and the constant habitat reduction, this biome has been defined as one of the hottest hotspots for the world biodiversity conservation (Myers et al., 2000). The State Park Carlos Botelho (PECB) is one of the most representative conservation units in the São Paulo state, Brazil. A long-term plot of 0.1 km^2 was installed at the PECB through the thematic project 'Diversity, dynamics and conservation of São Paulo state forests: 40 ha of permanent plots', supported by the state of São Paulo Research Foundation (FAPESP). This long-term plot has been selected for the assessment of the chemical element distribution in the most diverse ecosystem compartments.

Chemical elements are essential for the ecosystem due to their functionality in essential physiological processes. Nutrients may also cause significant changes in the ecosystems if mass fractions were considerably high in tissues. Otherwise, other chemical elements even in trace amounts might affect the ecosystem (Markert et al., 2000), that is mass fractions lower than 100 mg/kg (Mcnaught and Wilkinson, 1997), which is the case of arsenic and mercury, for example.

Within forest ecosystem sustainability processes, plants, particularly tree species, are quite relevant because of their role as biological reservoirs of chemical elements (Golley et al., 1978; França et al., 2008a). Therefore, trees are also responsible for the movement and maintaining of chemical elements in the system (Hamilton, 1995). Compared to other vegetational parts, leaves are the most studied due to their high mass fractions of chemical elements and constant production during the life cycle, besides the facility of sampling and analysis (Markert, 1993).

According to Markert (1993), the advantages of using vascular plants as biomonitors encompass the well-known morphology, physiology and ecology, the relatively easy identification, cultivation and reproduction, high ecological relevance, acting as the main interceptors of chemical elements in forest ecosystems, and relative tolerance to the toxicity of chemical elements. Leaf, stem, bark, root and fruit of plants have been used in the biomonitoring studies (Markert, 1993). Additional potentialities of this practice are related to the evaluation of soil quality, since the chemical element accumulation in plants generally reflect its availability in soil, allowing inferences on prejudicial potential effects of such availability (Madejón et al., 2004; Madejón et al., 2006).

However, one of the main problems of using plants as environmental monitors is the existence of numerous processes affecting the plant chemical composition (Reimann et al., 2001; Mertens et al., 2005). First of all, the biomonitor can be dependent on the phytoavailability and uptake of chemical elements, which are dependent on species and plant variety. Second, only one plant may not attend diverse chemical elements simultaneously. Moreover, leaf mass fractions are also related to sampling period, development state and other environmental factors and, finally, the difficulty of sampling due to the height of trees and the roots can actively avoid hotspots of chemical element present in soil (Mertens et al., 2005). These limitations are especially relevant for biomonitoring studies based on the pathway of chemical elements within soil–plant system. Mertens et al. (2006) also consider that a biomonitor should not only reproduce the information already present in the soil analyses, but it should also provide additional knowledge about environmental quality. This occurs when plants are evaluated considering its functionality in the ecosystem, improving the interpretation of such results. Therefore, the chemical composition of plant or of their parts should be related to the ecophysiology such as the biological productivity and the plant functionality (Mertens et al., 2006).

To assess the anthropogenic influence on the ecosystems and establish the reference standards for the environmental impacts, the use of bioindicators has become more common in Brazilian ecosystems (Coccaro et al., 2000; Maria et al., 2000; França et al., 2004; França et al., 2005; Elias et al., 2006; Elias et al., 2008; França et al., 2008a; França et al., 2009). However, the major part of the studies involving biomonitors has been conducted in urban and industrialised areas, having a lack of studies in natural remote areas. As a result, the information of background chemical element composition is sparse (Bergamaschi et al., 2004). Here, this knowledge is considered essential for the assessment of environmental quality and any type of pollution as well as for the ecosystem biodiversity conservation (Liu et al., 1997).

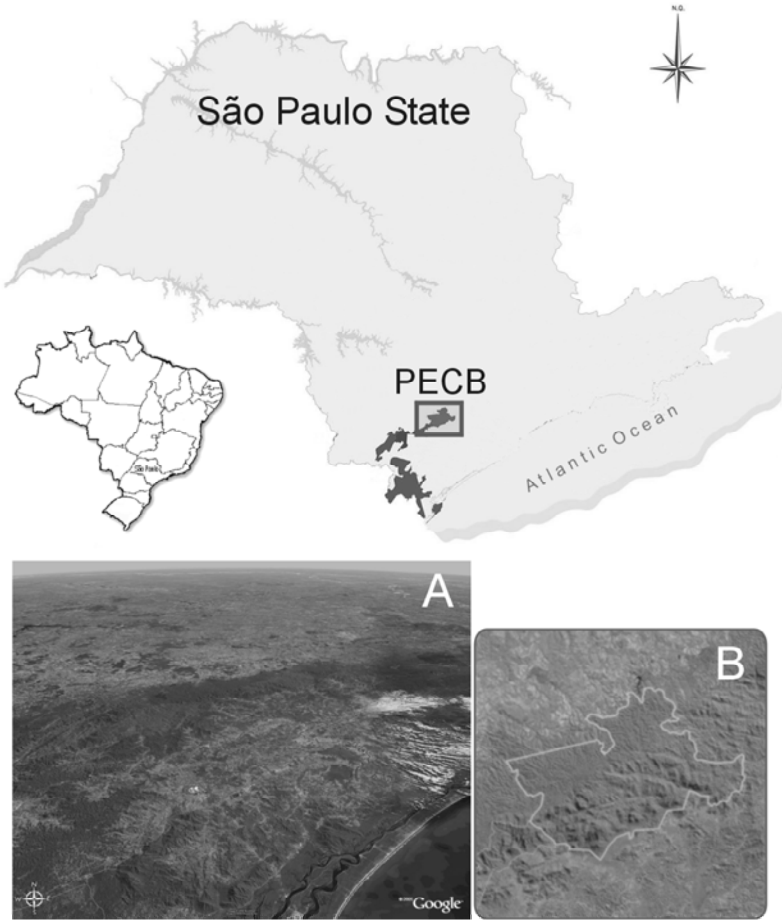
Considering that tree species can provide high sensitiveness in detecting impacts when based on the knowledge of the bioaccumulation process, this work consists of a baseline study involving the knowledge of the main strategies for plant accumulation of chemical elements in the Atlantic Forest. This approach will facilitate the monitoring of the Atlantic Forest unit conservations related to the flux of chemical elements because periodic chemical determinations can be successively done in these sensitive plants.

2 Experimental

The PECB is located at the southern region of the São Paulo state (coordinates 24°00’00” to 24°15’00”S; 47°45’00” to 48°10’00”W). PECB is part of the municipalities of São Miguel Arcanjo, Capão Bonito and Sete Barras, achieving a total area of 380 km^2 and altitudes varying from 30 to 1000 m (Domingues and Silva, 1988). The long-term plot was installed in 2000 facing at the Atlantic Ocean (Figure 1).

Table 1 summarises the tree species analysed, in which information on the diameter at breast height and tree height were also presented. Standardisation was adopted in the long-term plot, that is only trees of DBH higher than 5 cm were considered, avoiding taking into account very young trees. Leaf sampling was carried out in March 2003, January 2004 and July 2004. Branches were sampled from the middle- and top-crown of trees for collecting approximately 500 g of mature leaves (fresh mass). During the leaf sampling, about 100 g of soil were collected at the 0–10 cm layer under the tree crown projection.

Figure 1 Localisation of State Park Carlos Botelho (PECB) in São Paulo state, Brazil. A – PECB landscape (middle) (source: Google Earth); B – satellite image indicating PECB



Samples of leaves and soils were oven-dried at the temperatures of 60ºC and 100ºC, respectively. Particle size was reduced in rotor mill in the case of leaf samples, while orbital mill was employed for soils.

Following the Instrumental Neutron Activation Analysis (INAA) procedure of the Radioisotopes Laboratory, test portions of 200 mg were transferred to polyethylene vials. For neutron flux monitoring, test portions of 10 mg of Ni-Cr alloys were sandwiched among vials containing samples and certified reference materials (França et al., 2003a). All samples and monitors were irradiated at the Research Nuclear Reactor IEA-R1 of the Instituto de Pesquisas Energéticas e Nucleares – IPEN/SP in a thermal neutron flux of 10^{13} cm^{-2} s^{-1} by 4 and 8 hours in the case of leaves and soils, respectively. The measurement of the induced radioactivity was carried out in hyperpure germanium detectors from Ortec. After analysing gamma-ray spectra, chemical element mass fractions were calculated through the computer package Quantu for k_0-INAA (Bacchi and Fernandes, 2003), which also estimated the expanded analytical uncertainties at the 95% confidence level.

Table 1 Main characteristics of the tree species selected for leaf and soil sampling in the PECB long-term plot

Species	*Family*	*Sampled trees*	*IVI**	*Height (m)***		*PBH (cm)***		*Exposition****
				Mean	*STD*	*Mean*	*STD*	
Alsophila sternbergii	Cyatheaceae	9	6.7	3.4	1.7	30	4	regular
Bathysa australis	Rubiaceae	10	5.7	9	3	58	18	good
Calycorectes australis	Myrtaceae	9	3.2	7	4	31	19	regular
Chrysophyllum innornatum	Sapotaceae	8	3.4	6	3	29	10	regular
Chrysophyllum viride	Sapotaceae	10	6.5	12	4	108	62	good
Coussarea contracta	Rubiaceae	4	3	4.8	1.0	27	1.3	regular
Endlicheria paniculata	Lauraceae	11	2.8	7	3	28	15	regular
Eugenia cuprea	Myrtaceae	10	3.2	4.3	1.3	21	5	regular
Eugenia melanogyna	Myrtaceae	10	3.4	9	3	52	25	regular
Eugenia mosenii	Myrtaceae	9	3.2	8	2	52	21	regular
Eugenia xiriricana	Myrtaceae	1	2.2	15		37		regular
Euterpe edulis	Arecaceae	18	36	5	3	32	9	regular
Garcinia gardneriana	Clusiaceae	10	5.9	6.0	1.2	29	10	regular
Gomidesia flagellaris	Myrtaceae	9	3.0	4.6	1.2	27	6	regular
Guapira opposita	Nyctaginaceae	9	8.2	4	3	30	23	bad
Hyeronima alchorneoides	Euphorbiaceae	10	10	12	4	155	116	good
Marlierea suaveolens	Myrtaceae	10	3.7	7	2	28	13	regular
Marlierea tomentosa	Myrtaceae	7	3.0	8	6	22	5	regular
Myrceugenia myrcioides	Myrtaceae	1	0.9	6		25		regular

Table 1 Main characteristics of the tree species selected for leaf and soil sampling in the PECB long-term plot (continued)

Species	*Family*	*Sampled trees*	*IVI**	*Height (m)***		*PBH (cm)***		*Exposition****
				Mean	*STD*	*Mean*	*STD*	
Nectandra membranacea	Lauraceae	1	1.7	8		75		regular
Neomitranthes glomerata	Myrtaceae	10	2.8	7	2	36	13	regular
Rudgea jasminoides	Rubiaceae	16	3.7	5.5	1.3	32	8	regular
Tetrastylidium grandifolium	Olacaceae	9	7.5	10	3	51	20	good
Virola bicuhyba	Myristicaceae	11	7.7	10	6	70	46	good

Notes: PBH = perimeter at breast height.
STD = standard deviation.
IVI = importance index value.
* based on phytosociological parameters such as relative and absolute frequencies and relative and absolute abundances.
** measured in 2004.
*** relative to the sunlight exposition.

Leaf samples already encapsulated were again analysed in the Reactor Institute of Delft – RID, Delft University of Technology – TUDelft for the determination of Cl and Mn. In this case, for neutron flux monitoring, vials containing 2 mg of Zn were sandwiched between each sample. The irradiation was carried out in a neutron flux of 5×10^{16} cm^{-2} s^{-1} during 15 minutes. The induced radioactivity was measured by means of high-resolution gamma-ray spectrometry with well-type germanium detector from Ortec. After interpretation of the gamma-ray spectra, Cl and Mn mass fractions and their respective analytical uncertainties were also calculated using the in-house RID software on the k_0 method (Blaauw, 1993).

For the identification of bioaccumulator trees, the definition of Leaf–Soil Bioaccumulation Factor (LSBF) took into account the mass fraction of chemical elements in leaves and soil according to equation (1), adapted from Luoma and Rainbow (2005):

$$\mathrm{LSBF}_{\mathrm{soil}} = \frac{w_b}{w_{\mathrm{soil}}} \sim \frac{k_{a,\mathrm{soil}}}{k_e}, \tag{1}$$

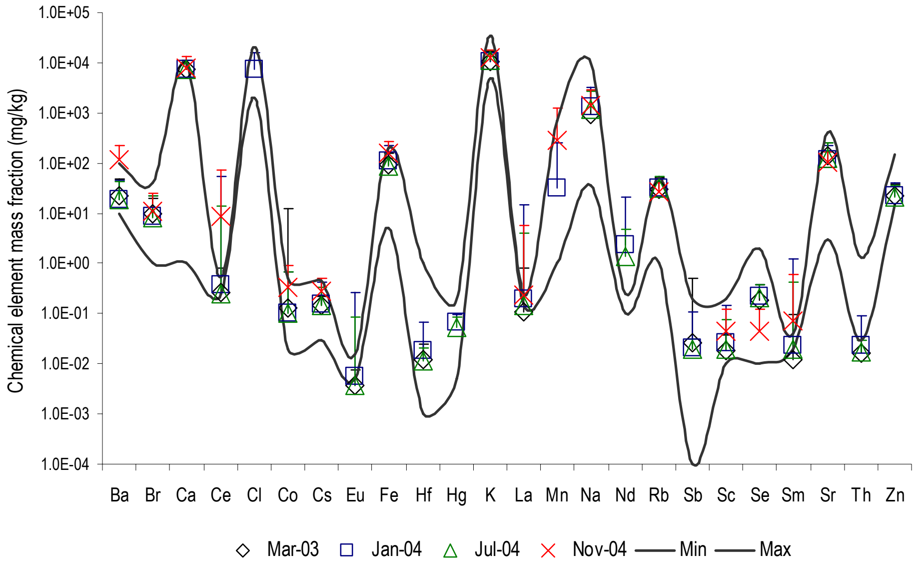
in which w_b is the leaf mass fraction (mg/kg), w_{soil} is soil mass fraction (mg/kg), $k_{a,\mathrm{soil}}$ is the uptake constant (kg/kg/day) and k_e is the elimination constant (day^{-1}).

Target transformation Monte Carlo factor analysis (TTMCFA) was utilised for identifying the principal sources of chemical elements for leaves (Kuik et al., 1993). This multivariate statistical analysis takes into account the analytical uncertainties for estimating errors of the factor loadings. The chemical elements considered in this analysis were Ba, Br, Ca, Co, Cs, Fe, Na, Rb, Sc, Sr and Zn, whose normal distribution was tested at the 95% confidence level. However, biomonitoring also included Cl, Ce, Hf, Hg, La, Mn, Sm and Th by obtaining maps through kriging interpolation.

3 Results and discussion

The chemical composition of leaves from tree species was compared to the reference values proposed by Schüürmann and Markert (1998). The leaf compartment presented mass fractions within the expected range in plants (Figure 2). However, the average values were superior for some chemical elements like Ce, La and Sm, for example. This phenomenon is related to high mass fractions found in some species, since at least one result exceeded the reference values for Ba, Ce, Co, Cs, Eu, Fe, La, Mn, Nd, Sb, Sm and Sr (Figure 2). Also, there was no evidence of seasonal fluctuation in the average leaf chemical composition (Figure 2). This evaluated portion of the Atlantic Forest was considered to have a low level of pollution because the major part of the studied species showed chemical element mass fractions within the expected range.

Figure 2 Average mass fractions determined in leaves according to the sampling period (see online version for colours)



Notes: Error bars are the standard deviation (values higher than the median). Lines indicate the expected range mass fraction in plants proposed by Schüürmann and Markert (1998).

3.1 *Bioaccumulation*

The averaged LSBF values were ordered according to the vegetal species in Table 2. Estimated standard deviation represented the contribution of spatial and temporal variability. This variability of chemical elements for the same species can be greatly associated to the increase of local availability and/or intrinsic characteristics of the individual (Vogt et al., 1995). According to França et al. (2008b), the first values of LSBF for some Atlantic Forest tree species, based on the analysis of some individuals (from 10 to 14), were similar to the update values found in this work, indicating that LSBF could be a consistent tool to study the bioaccumulation strategies of native species. Therefore, plant species of high LSBF values were presented in Table 3 as bioaccumulators, as well as the baseline mass fractions of chemical elements to be used in further biomonitoring studies.

Table 2 Updated mean Leaf–Soil Bioaccumulator Factor (LSBF) of chemical elements for the Atlantic Forest tree species

Ba	Sp*	Eedu	Epan	Msua	Mtom	Nglom	Vbic	Emii	Gfla	Caus	Tgra	Baus	Aste	Gopp	Halc	Rjas	Ecup	Emna	Ggar	Cvir	Cinn	Ccon
	Mean	0.004	0.009	0.011	0.011	0.013	0.014	0.014	0.015	0.016	0.018	0.018	0.019	0.021	0.023	0.024	0.025	0.028	0.032	0.036	0.043	0.047
	STD	*0.003*	*0.007*	*0.004*	*0.004*	*0.009*	*0.006*	*0.005*	*0.006*	*0.007*	*0.009*	*0.014*	*0.006*	*0.008*	*0.018*	*0.018*	*0.011*	*0.017*	*0.018*	*0.017*	*0.037*	*0.025*
Br	Sp*	Ccon	Vbic	Nglom	Caus	Ggar	Msua	Baus	Epan	Mtom	Eedu	Halc	Cvir	Gfla	Tgra	Gopp	Emii	Aste	Ecup	Cinn	Rjas	Emna
	Mean	0.085	0.110	0.180	0.22	0.230	0.250	0.26	0.270	0.31	0.31	0.36	0.55	0.69	0.88	1.05	1.07	1.09	1.26	1.40	1.50	2.20
	STD	*0.024*	*0.082*	*0.088*	*0.17*	*0.098*	*0.077*	*0.15*	*0.081*	*0.10*	*0.11*	*0.14*	*0.15*	*0.22*	*0.32*	*0.34*	*0.61*	*0.47*	*0.48*	*1.00*	*1.10*	*0.74*
Ce	Sp*	Halc	Vbic	Ccon	Ggar	Tgra	Epan	Nglom	Gopp	Gfla	Mtom	Caus	Baus	Msua	Rjas	Eedu	Ecup	Cvir	Cinn	Emna	Emii	Aste
	Mean	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.005	0.006	0.007	0.008	0.011	0.012	0.051	0.120	0.85
	STD	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.002*	*0.001*	*0.002*	*0.003*	*0.002*	*0.004*	*0.003*	*0.005*	*0.004*	*0.009*	*0.006*	*0.009*	*0.010*	*0.030*	*0.061*	*0.45*
Co	Sp*	Tgra	Nglom	Emna	Cinn	Rjas	Emii	Cvir	Eedu	Gopp	Caus	Vbic	Epan	Msua	Baus	Ccon	Ecup	Aste	Gfla	Mtom	Halc	Ggar
	Mean	0.013	0.015	0.016	0.021	0.024	0.026	0.027	0.035	0.041	0.043	0.044	0.044	0.047	0.048	0.050	0.052	0.058	0.059	0.064	0.130	0.90
	STD	*0.008*	*0.004*	*0.007*	*0.021*	*0.022*	*0.024*	*0.013*	*0.092*	*0.021*	*0.018*	*0.026*	*0.037*	*0.014*	*0.035*	*0.015*	*0.049*	*0.041*	*0.023*	*0.018*	*0.079*	*0.40*
Cs	Sp*	Msua	Halc	Cvir	Vbic	Ecup	Ccon	Nglom	Cinn	Ggar	Baus	Mtom	Rjas	Caus	Tgra	Gfla	Epan	Gopp	Eedu	Emii	Emna	Aste
	Mean	0.018	0.021	0.022	0.023	0.026	0.029	0.031	0.031	0.031	0.033	0.035	0.037	0.038	0.038	0.042	0.043	0.045	0.051	0.067	0.081	0.20
	STD	*0.008*	*0.010*	*0.009*	*0.012*	*0.012*	*0.017*	*0.012*	*0.019*	*0.008*	*0.015*	*0.023*	*0.024*	*0.019*	*0.018*	*0.015*	*0.029*	*0.016*	*0.023*	*0.028*	*0.042*	*0.10*
Fe	Sp*	Ggar	Ccon	Mtom	Msua	Caus	Vbic	Emii	Gopp	Nglom	Emna	Halc	Epan	Gfla	Rjas	Tgra	Cvir	Cinn	Ecup	Eedu	Aste	Baus
	Mean	0.002	0.002	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.005	0.005	0.005	0.006
	STD	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.003*	*0.001*	*0.003*	*0.001*	*0.001*	*0.004*	*0.001*	*0.004*	*0.002*	*0.001*	*0.004*	*0.002*	*0.003*
K	Sp*	Mtom	Ecup	Cinn	Eedu	Gfla	Ccon	Msua	Nglom	Emna	Ggar	Emii	Rjas	Epan	Cvir	Tgra	Caus	Halc	Baus	Aste	Vbic	Gopp
	Mean	0.250	0.270	0.290	0.30	0.320	0.33	0.33	0.37	0.41	0.43	0.45	0.47	0.49	0.49	0.53	0.58	0.61	0.66	0.77	0.77	0.84
	STD	*0.097*	*0.091*	*0.083*	*0.14*	*0.093*	*0.12*	*0.24*	*0.13*	*0.12*	*0.29*	*0.16*	*0.12*	*0.24*	*0.17*	*0.24*	*0.18*	*0.54*	*0.37*	*0.27*	*0.47*	*0.19*
La	Sp*	Ccon	Vbic	Nglom	Ggar	Halc	Tgra	Gfla	Gopp	Baus	Mtom	Epan	Caus	Rjas	Msua	Ecup	Eedu	Cvir	Emna	Cinn	Emii	Aste
	Mean	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.004	0.004	0.005	0.005	0.009	0.026	0.031	0.085	0.47
	STD	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.002*	*0.002*	*0.004*	*0.004*	*0.006*	*0.003*	*0.008*	*0.008*	*0.017*	*0.052*	*0.072*	*0.28*

Table 2 Updated mean Leaf–Soil Bioaccumulator Factor (LSBF) of chemical elements for the Atlantic Forest tree species (continued)

Na	Sp*	Cinn	Cvir	Nglom	Ecup	Gfla	Baus	Halc	Vbic	Aste	Eedu	Ccon	Caus	Epan	Mtom	Ggar	Rjas	Msua	Emii	Emna	Tgra	Gopp
	Mean	0.088	0.150	0.29	0.41	0.56	0.60	0.63	0.65	0.66	0.69	0.86	0.90	0.96	1.00	1.20	1.20	1.20	1.30	1.6	1.8	4.40
	STD	*0.083*	*0.083*	*0.15*	*0.41*	*0.28*	*0.40*	*0.77*	*0.67*	*0.32*	*0.66*	*0.64*	*0.66*	*0.63*	*0.74*	*0.94*	*0.58*	*0.56*	*0.87*	*1.1*	*1.4*	*0.77*
Rb	*Sp**	*Msua*	*Mtom*	*Cinn*	*Ecup*	*Eedu*	*Gfla*	*Ccon*	*Ggar*	*Halc*	*Nglom*	*Tgra*	*Cvir*	*Emna*	*Rjas*	*Emii*	*Epan*	*Baus*	*Vbic*	*Caus*	*Gopp*	*Aste*
	Mean	0.19	0.200	0.220	0.220	0.240	0.280	0.31	0.32	0.32	0.340	0.340	0.36	0.38	0.40	0.41	0.42	0.48	0.52	0.55	0.77	0.82
	STD	*0.10*	*0.093*	*0.092*	*0.096*	*0.063*	*0.077*	*0.11*	*0.18*	*0.17*	*0.077*	*0.089*	*0.12*	*0.14*	*0.11*	*0.16*	*0.18*	*0.20*	*0.21*	*0.17*	*0.20*	*0.31*
Sc	Sp*	Ggar	Nglom	Vbic	Cvir	Halc	Msua	Caus	Cinn	Gopp	Gfla	Tgra	Mtom	Epan	Ecup	Eedu	Emii	Baus	Rjas	Ccon	Emna	Aste
	Mean	0.002	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.005	0.005	0.005	0.006	0.007	0.007	0.009	0.009	0.012	0.016	0.037	0.045
	STD	*0.001*	*0.001*	*0.002*	*0.001*	*0.002*	*0.001*	*0.002*	*0.002*	*0.002*	*0.001*	*0.002*	*0.004*	*0.002*	*0.002*	*0.006*	*0.005*	*0.006*	*0.007*	*0.008*	*0.027*	*0.028*
Sm	Sp*	Vbic	Nglom	Ggar	Gfla	Halc	Ccon	Tgra	Gopp	Epan	Mtom	Caus	Rjas	Baus	Msua	Cvir	Ecup	Eedu	Cinn	Emna	Emii	Aste
	Mean	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.004	0.005	0.006	0.006	0.007	0.008	0.008	0.008	0.008	0.038	0.13	0.13	0.36
	STD	*0.001*	*0.001*	*0.002*	*0.001*	*0.002*	*0.002*	*0.002*	*0.001*	*0.001*	*0.002*	*0.012*	*0.005*	*0.004*	*0.016*	*0.012*	*0.006*	*0.008*	*0.064*	*0.12*	*0.14*	*0.23*
Sr	Sp*	Eedu	Aste	Mtom	Emii	Epan	Tgra	Msua	Gfla	Halc	Baus	Nglom	Vbic	Caus	Cvir	Emna	Cinn	Ecup	Ggar	Gopp	Rjas	Ccon
	Mean	0.098	0.190	0.25	0.270	0.34	0.34	0.37	0.380	0.41	0.41	0.49	0.53	0.53	0.65	0.66	0.68	0.70	0.93	1.00	1.20	2.00
	STD	*0.055*	*0.063*	*0.17*	*0.097*	*0.19*	*0.16*	*0.11*	*0.097*	*0.24*	*0.18*	*0.25*	*0.28*	*0.19*	*0.21*	*0.23*	*0.31*	*0.30*	*0.63*	*0.20*	*0.66*	*0.76*
Zn	Sp*	Cinn	Gfla	Emna	Msua	Cvir	Nglom	Emii	Ecup	Tgra	Caus	Mtom	Halc	Vbic	Rjas	Gopp	Ccon	Baus	Aste	Ggar	Eedu	Epan
	Mean	0.260	0.35	0.360	0.36	0.400	0.41	0.460	0.56	0.58	0.64	0.64	0.67	0.70	0.74	0.82	0.98	1.00	1.00	1.50	1.51	1.54
	STD	*0.085*	*0.11*	*0.093*	*0.13*	*0.084*	*0.10*	*0.074*	*0.15*	*0.21*	*0.16*	*0.18*	*0.23*	*0.28*	*0.34*	*0.30*	*0.24*	*0.29*	*0.18*	*0.33*	*0.57*	*0.67*

Notes: STD = standard deviation, Aste = *Alsophilla sternbergii*, Baus = *Bathysa australis*, Caus = *Calycorectes australis*, Cinn = *Chrysophyllum innornatum*, Cvir = *Chrysophyllum viride*, Ccon = *Coussarea contracta*, Ecup = *Eugenia cuprea*, Eedu = *Euterpe edulis*, Emii = *Eugenia mosenii*, Emna = *Eugenia melanogyna*, Epan = *Endlicheria paniculata*, Gfla = *Gomidesia flagellaris*, Ggar = *Garcinia gardneriana*, Gopp = *Guapira opposita*, Halc = *Hyeronima alchorneoides*, Msua = *Marlierea suaveolens*, Mtom = *Marlierea tomentosa*, Nglo = *Neomitranthes glomerata*, Rjas = *Rudgea jasminoides*, Tgra = *Tetrastylidium grandifolium*, Vbic = *Virola bicuhyba*.

* Sp = tree species in ascending order according to LSBF values.

Table 3 Tree species from the Atlantic Forest identified as potentially bioaccumulators. Expected range of chemical element mass fraction (mg/kg) in leaves

Element	*Species*	*Range (mg/kg)*
Ba	*Coussarea contracta*	20–60
	Chrysophyllum innornaturm	10–170
Br	*Eugenia melanogyna*	20–90
	Guapira opposita	10–50
Ce	*Alsophila sternbergii*	20–500
	Eugenia mosenii	0.4–20
Co	*Garcinia gardneriana*	0.5–8.0
	Hyeronima alchorneoides	0.1–1.0
Cs	*Alsophila sternbergii*	0.3–2.0
La	*Alsophila sternbergii*	6.0–100
Na	*Guapira opposita*	4000–9000
Rb	*Guapira opposita*	40–100
	Alsophila sternbergii	20–120
Sc	*Alsophila sternbergii*	0.05–1.0
	Eugenia melanogyna	0.03–0.40
Sm	*Coussarea contracta*	0.3–9.0
Sr	*Coussarea contracta*	350–950
Zn	*Garcinia gardneriana*	30–100
	Euterpe edulis	30–80
	Endlicheria paniculata	10–100

Considering the high degree of preservation of the studied area and the distance of pollution sources, the bioaccumulation potential of these species might be more expressive in modified regions in the São Paulo state or a depletion could occur depending on the plant species and environmental conditions (Araújo et al., 2008). In fact, results of tree species from other regions in São Paulo state were quite different, although there was a tendency of decreasing of mass fractions depending on chemical element (nutrients, for example) from very impacted areas like Cubatão (Araújo et al., 2008) and São Paulo city (Vives et al., 2006) and natural preserved areas like PECB. Besides, some chemical elements of environmental interest such as As and Sb were detected in leaves of same species growing in Cubatão (Araújo et al., 2008). By analysing litter chemical element mass fractions, Fostier et al. (2003) also observed enrichment of some chemical elements according to environmental conditions.

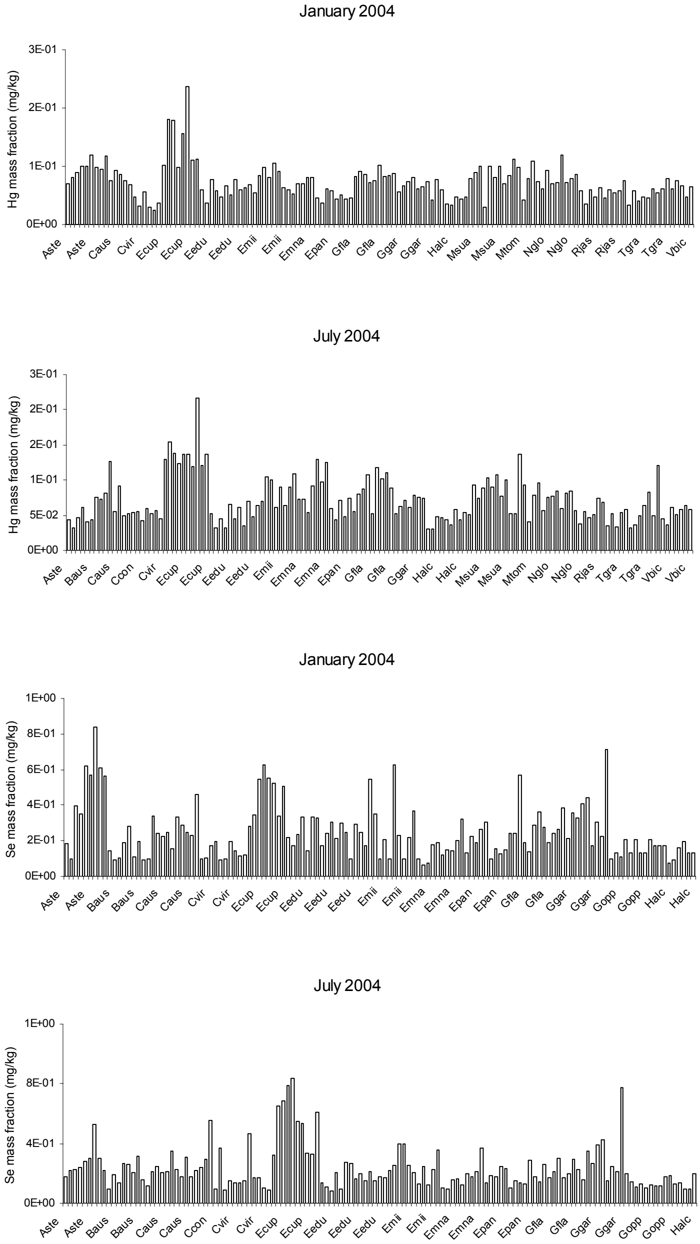
Nutrients such as Co, Fe, K, Na (animals) and Zn showed LSBF values approximately equal to 1 for, at least, one tree species (Table 2). In the case of Co, *Garcinia gardneriana* (Clusiaceae family) was considered as an accumulator because of the average LSBF value of 0.9 ± 0.4 (Table 2). For *Hyeronima alchorneoides*, from Euphorbiaceae family, recognised as an accumulator of Co (Koyama et al., 1987), the accumulation was relatively lower (0.13 ± 0.08); however, about twice higher than the other species (0.044). For Fe, the soluble fraction is surely quite low compared to the total mass fractions utilised in the LSBF calculation. Taking this into account, *Alsophila sternbergii*, *Bathysa australis* and *Euterpe edulis* could be Fe accumulators. In soils having low level of K like the semi-deciduous forest located in Campinas, São Paulo, Brazil, bioaccumulation factors of this element were approximately equal to 12 (França et al., 2003b). However, Atlantic Forest species showed LSBF approximately equal to 1 in the case of *Guapira opposita*, *Virola bicuhyba*, *Alsophila sternbergii*, *Bathysa australis* and *Hyeronima alchorneoides*. This divergence between the forest types was due to the higher mass fraction of K in Atlantic Forest soils compared to semi-deciduous forest. For Rb, from the same chemical family of K, the high LSBF were found for *Alsophila sternbergii* and *Guapira opposita*. The last species showed an average Na LSBF of 4.4 ± 0.8, demonstrating its high capability of accumulation of this element in leaves. Zinc was accumulated by *Endlicheria paniculata*, *Euterpe edulis* and *Garcinia gardneriana* species.

With ^{137}Cs and ^{134}Cs fallout, there is interest in the distribution of these radionuclides and its stable isotope in forest ecosystems for the evaluation of equilibrium among these chemical species (Wyttenbach et al., 1995; Yoshida et al., 2004). The Cs accumulation presented by *Alsophila sternbergii* was from 0.10 to 0.30, while the maximum LSBF for Cs found by Wyttenbach et al. (1995) was 0.24 in *Picea abies* needles. For ferns, the values obtained by Yoshida et al. (2004) were 1.17–0.66 in the region directly affected by the Chernobyl accident. In the case of semi-deciduous forest, the species *Pachystroma longifolium* showed an estimated bioaccumulation factor of 0.18 (França et al., 2003b). Therefore, the species *Alsophila sternbergii* has demonstrated an interesting capacity in accumulating Cs. This species also presented the accumulation of Rare-Earth Elements (REEs), whose association with actinides series has been already identified elsewhere (Koyama et al., 1987).

For Ce, La, Sc and Sm, the high LSBF values were found for *Alsophila sternbergii*, *Eugenia melanogyna* and *Eugenia mosenii*. The accumulation of lanthanides is common for ferns (Wyttenbach et al., 1998) like *Alsophila sternbergii*. However, *Eugenia melanogyna* (this work), *Eugenia mosenii* (this work), *Pachystroma longifolium* (França et al., 2002) and *Solanum lycocarpum* (Maria et al., 2000) also presented this characteristic. Otherwise, Sc accumulation was not commonly observed due to the low availability of this element for plants (Kabata-Pendias and Pendias, 1984). Nevertheless, a considerable uptake was noticed for *Alsophila sternbergii* and *Eugenia melanogyna* according to the LSBF values from Table 2. According to Shtangeeva et al. (2004), there is an active uptake of Sc in plants.

The total mass fractions of Hg and Se in the Atlantic Forest soils were not superior to 1.4 and 5.0 mg/kg, respectively. Considering the aspect of potential bioaccumulators also presented high contents when compared to the other plant species growing in the same habitat, *Eugenia cuprea* can be an Hg and Se accumulator (Figure 3). Mercury is a problematic element since it is easily transported through the atmosphere, being accumulated in the ecosystems. For Se, the narrow limit between toxicity and essentiality can intensify its environmental impacts. *Alsophila sternbergii* and *Tetrastylidium grandifolium* also presented appreciable Se quantities in their leaves (Figure 3).

Figure 3 Hg and Se mass fractions determined in leaves sampled in January and July 2004



Notes: Aste = *Alsophilla sternbergii*, Baus = *Bathysa australis*, Caus = *Calycorectes australis*, Ccon = *Coussarea contracta*, Cinn = *Chrysophyllum innornatum*, Cvir = *Chrysophyllum viride*, Ecup = *Eugenia cuprea*, Eedu = *Euterpe edulis*, Emii = *Eugenia mosenii*, Emna = *Eugenia melanogyna*, Epan = *Endlicheria paniculata*, Gfla = *Gomidesia flagellaris*, Ggar = *Garcinia gardneriana*, Gopp = *Guapira opposita*, Halc = *Hyeronima alchorneoides*, Msua = *Marlierea suaveolens*, Mtom = *Marlierea tomentosa*, Nglo = *Neomitranthes glomerata*, Rjas = *Rudgea jasminoides*, Tgla = *Tetrastylidium grandifolium* and Vbic = *Virola bicuhyba*.

3.2 Biomonitoring

The study of leaves as biomonitors was carried out taking into account the functionality of plants in the ecosystem, because the analysed species represent the most abundant species in the long-term plot. This evaluation was directed according to the results obtained by TTMTFA (Table 4). Six main sources of chemical elements for plants were identified according to the pilot element, that is an element of major correlation in the factor loading profile, together with the other significantly correlated chemical elements. The elements from family IA and IIA, as well as Br and Sc, were distributed in Factors 1 and 2. The correlation between Fe and Sc with Factor 3 indicated the leaf surface contamination with soil (Ferrari et al., 2006). Cobalt was almost exclusively correlated to Factor 4 with small contribution of Ba, Br, K, Sc and Zn. Factor 5 showed positive correlation of Na, Br, Ca and Cs, probably associated to the marine aerosol contribution, since there is prevalence of oceanic winds in the long-term plot (Rodrigues, 2004). Factor 6 indicated a common source of Ca, Cs, Fe, Sr and Zn. Zinc in atmosphere is present in dust, rain and probably particulate from pollution (oil burning). Occasionally, Zn can be combined with Ca during wet precipitation (Wedepohl, 1970).

Table 4 Average contributions (%) for the total occurrence of chemical elements calculated by TTMTFA. Details can be found elsewhere (França, 2006)

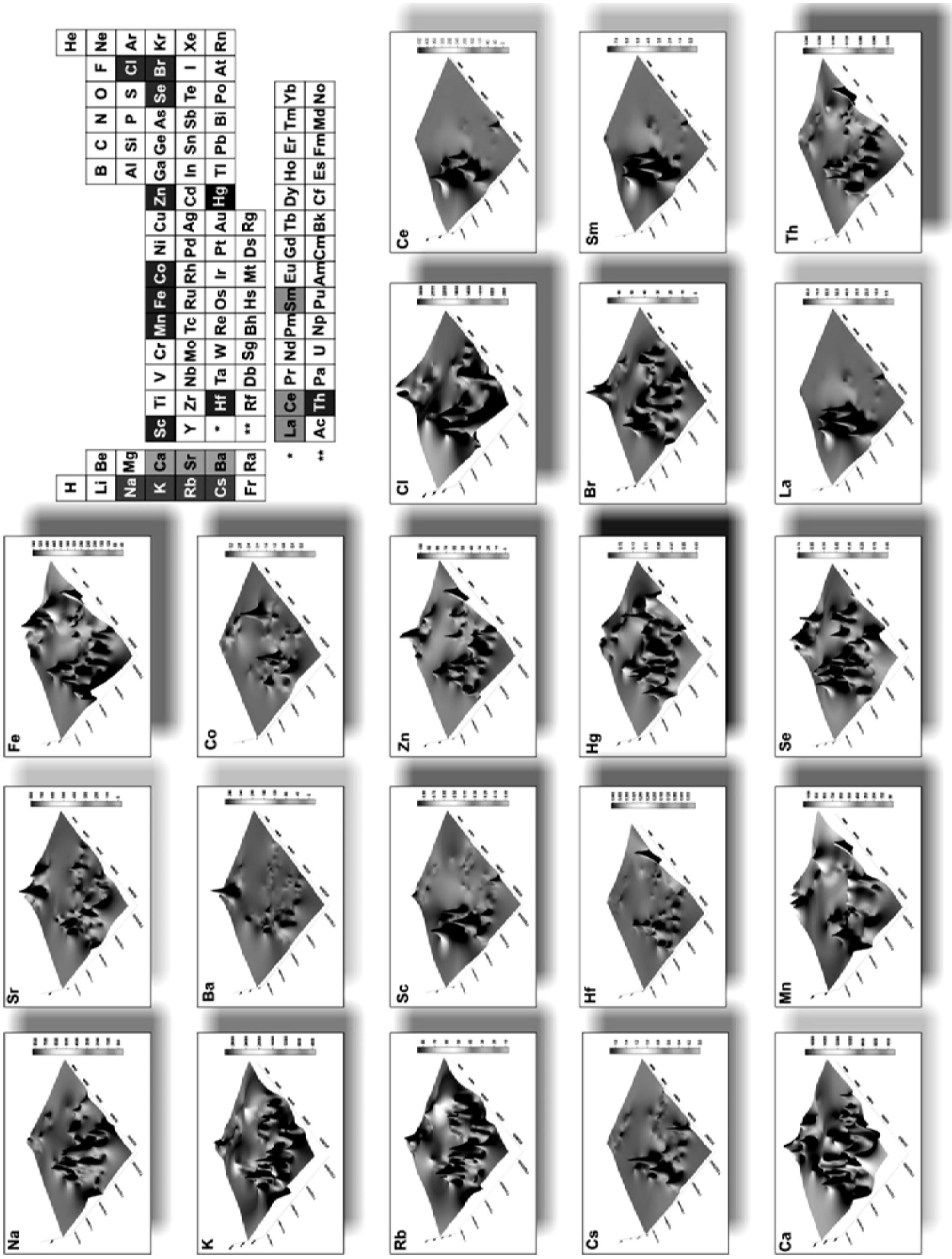
	Factor 1	*Factor 2*	*Factor 3*	*Factor 4*	*Factor 5*	*Factor 6*	*Total*
Ba	51.6*	0.45	2.66+	1.42+	0	0.22	56.4
Br	34.9*	22.8*	8.25*	1.66*	10.0*	0	77.7
Ca	32.7*	8.35*	0.11	0	0.5+	3.89+	45.6
Co	0	0.23	0.02	82.2P	0	0	82.4
Cs	0	19.7*	4.05+	0.04	4.98*	18.3*	47.1
Fe	0	1.57	24.1*	0	0	55.3*	81.0
K	3.14+	53.7P	0.81	0.31*	0.04	0.01	58.0
Na	10.3*	59.9*	0.01	0	11.4P	12.3*	93.8
Rb	1.51	56.9*	0.78	0.15	0.45	1.42	61.2
Sc	28.3*	0	49.9P	1.67*	5.61*	2.43	88.1
Sr	56.7P	9.94+	0.04	0.01	0.18	6.26*	73.1
Zn	0.06	0	0.05	5.31*	0.1	88.0P	93.5

Notes: P = pilot element (the most representative element in the correlation matrix)
+ = 5% error; * = 1% error.

3.3 Ba, Ca and Sr (family IIA)

Differently from other tropical ecosystems (Breulmann et al., 2002; França et al., 2003b), Ba mean mass fraction in leaves of the Atlantic Forest was high. Information on Ba distribution in tropical ecosystem is considered to be sparse (Pichtel et al., 2000). In Figure 4, the chemical element distribution was mapped according to the results found in tree leaves. The peaks are referring to the accumulator individuals. The similarity between Ca, essential element, and Sr was constantly observed in the tree species, while between Ca and Ba the correlation was altered depending on the evaluated species.

Figure 4 Distribution maps of chemical elements (mass fractions in mg/kg) for leaves collected in January 2004



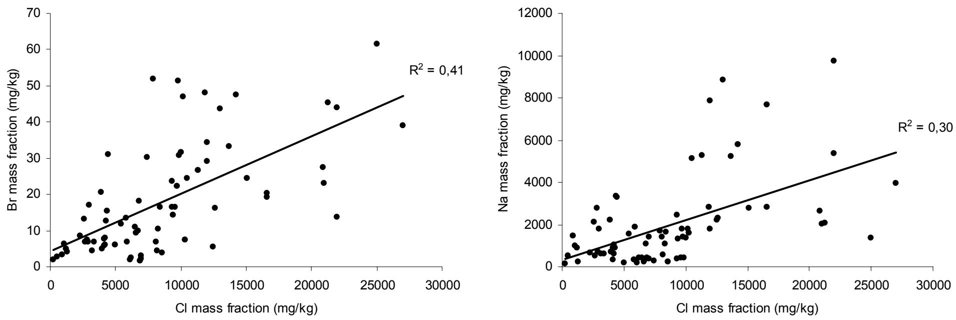
3.4 Cs, K and Rb (family IA)

Mass fractions of K up to 5.2% on dry weight in leaves were comparable to those obtained in epiphyte leaves (up to 4.5%) from the Atlantic Forest analysed elsewhere (Elias et al., 2006). The maps of K and Rb from Figure 4 indicated similarity in their distribution in the long-term plot, while Cs showed distinct behaviour.

3.5 Br, Cl and Na – oceanic influence

The oceanic source can be responsible for the high mass fractions of Br, Cl and Na in leaves. The distribution of Br, Cl and Na in the long-term plot is in Figure 4. Besides oceanic influence, Br can be related to coal, pesticides (García and Muñoz, 2002) and fire retardants. The correlation among Br, Na and Cl from Figure 5 corroborated preferentially oceanic source for explaining the mass fractions observed in leaves.

Figure 5 Correlation among Cl, Br and Na in tree leaves



3.6 Fe, Hf, Mn, Sc, Th and Zn

The correlation between Fe and Sc, observed in leaves, may be an indication of the contamination of vegetal material with soil particles adhered (Ferrari et al., 2006). Zinc was also partially correlated to these chemical elements, which corroborated the contribution of adhered particles for its mass fraction determined in leaves. The atmosphere can be considered as potential source of Zn for the ecosystem, because of increasing of this element in bromeliad leaves near to the highways that cross the PECB (Elias et al., 2006). Zn mass fractions were about 26 mg/kg (percent standard variation = 36%), whilst the median mass fractions in tree leaves were in the range of 21 to 23 mg/kg (percent standard deviation = 60%).

Figure 4 also shows the Mn distribution in the long-term plot. The presence of peaks refers the accumulator plants as well as the other chemical elements. This element can easily be uptaken by plants (Mills and Benton Jones, 1996); however, it can be related to anthropogenic activities mainly for aquatic ecosystems (Viers et al., 2009). Leaf mass fractions up to 1000 mg/kg were found in tree leaves.

3.7 Co – Garcinia

The distribution of Co, with the exception of accumulator peaks, is quite homogeneous in the long-term plot (Figure 4). Cobalt availability when associated to Ni (its mass fraction in leaves were below the detection limit of 4 mg/kg) is related to the metallurgic industry (Opydo, 2001). The distinct behaviour of Co was associated to the presence of *Garcinia gardneriana* species, whose mass fractions were high for Co and Zn. Otherwise, the correlation found between Co and Zn also can be an indication of anthropic influence by atmospheric emissions.

3.8 Ce, La and Sm – lanthanides

These elements together with the other lanthanides, Sc and Y comprise the group recognised as the REEs. Their use in industry and agriculture has increased the availability to the environment (Hedrick, 1995). As the other vegetational types in Brazil also showed REE high mass fractions (Maria et al., 2000; França et al., 2002), this knowledge of background composition is quite relevant in the establishment of natural composition of tropical ecosystems.

4 Conclusion

By calculating LSBF, native tree species were identified as accumulator of nutrients (Co, Na, Se and Zn), trace elements (Br, Ba, Cs, Hg, Rb and Sr) and REEs (Ce, La, Sc and Sm). For Hg and Se, one species was considered accumulator because of high mass fractions observed in leaves. The application of MCTTFA to the chemical element data set allowed the identification of chemical element sources for plants. Leaves of tree species could be used as biomonitors in Atlantic Forest conservation units for obtaining chemical element distribution maps. This knowledge was based on the biodiversity of the Atlantic Forest, being useful for the definition of reference standards for environmental impact studies related to the distribution of chemical elements in the São Paulo state. Moreover, the present study also corroborated the utilisation of native species in the evaluation of environmental quality despite of the complexity of relationship among chemical elements and biodiversity in the Atlantic Forest. The importance of the knowledge of chemical composition was demonstrated for the definition of conservation strategies, including the detection of impacts on the chemical composition of the vegetation.

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