

Soil-leaf transfer of chemical elements for the Atlantic Forest

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Soil analysis could improve environmental studies since soil is the main source of chemical elements for plants. In this study, soil samples collected at 0–10 cm depth under tree crown projection were analyzed by INAA. Using the chemical composition of the leaf previously determined, the leaf-soil transfer factors of chemical elements could be estimated for the Atlantic Forest. Despite the variability of the intra-species, the transfer factors were specific for some plant species due to their element accumulation in the leaves. Similar Br-Zn combined transfer factors were obtained for the species grouped according to habitats in relation to their position (understory or dominant species) in the forest canopy.

Introduction

The Parque Estadual Carlos Botelho (PECB) is one of the most representative conservation units of the Atlantic Forest in São Paulo State, Brazil. A long-term plot study supported by the Research Program BIOTA/FAPESP – The Virtual Institute of Biodiversity – was implemented in the PECB and three other conservation units of São Paulo State, Brazil, which is aimed at characterizing the biodiversity and at maintaining and sustaining it.^{1,2}

There is little information on the distribution of chemical elements in Brazilian ecosystems. The understanding the distribution of the chemical element in soils has uncountable environmental benefits attributed to the knowledge of their transfer and availability to plants.³ Soil is the main source of chemical elements for plants, but in some situations it can be a potential source of pollution. Plants can accumulate hazardous chemical elements available in soil solution that will affect the biodiversity maintenance in tropical forests.

Soil analysis becomes very promising for biomonitoring programs when the measurement of chemical elements in biomonitors and the study of the biochemical cycling of the ecosystem is combined. The transfer of trace elements within soil-plant compartments is a part of the biochemical cycle, in which an element flows from the abiotic to the biotic compartments of the ecosystem.⁴ The transfer factor (concentration ratio) concept, firstly applied to radioactive nuclides, was adapted to stable nuclides to assess how the concentrations in plants are connected to soil concentrations.⁵

Plant responses to chemical elements in soil and ambient air can vary and should always be investigated for a particular soil-plant system. The prediction of the uptake of trace elements by plants from a given growth medium should be based on several biotic and abiotic

parameters that control their behavior in soil.⁴ The prediction of the phytoavailability of trace elements is of crucial importance to the assessment of environmental quality.^{4,6}

In this study, soil was investigated by instrumental neutron activation analysis (INAA), which is used to improve environmental studies and is aimed at (1) the evaluation of total concentrations of diverse chemical elements of interest, and (2) the estimation and comparison of transfer factors in diverse species in the Atlantic Forest.

Experimental

The BIOTA's plot of 102,400 m² implanted in the Parque Estadual Carlos Botelho (PECB) is divided into 256 subplots of 400 m² each (Fig. 1). All trees with a diameter greater than 5 cm (measured in 2000) were identified, mapped and labeled, thus totaling 10,852 trees and 200 species. The most abundant tree species were selected for biomonitoring studies by determining the chemical elements in leaves (Table 1).^{1,2} Simultaneously soil under crown projection at 0–10 cm depth was collected. The samples were oven-dried at 100 °C, ground and directed to INAA together with certified reference materials (SRM 2711 Montana Soil and IAEA Soil 7).

Test portions of about 300 mg of soils and certified reference materials were inserted into polyethylene vials (Vrije Universiteit, Amsterdam). Ni-Cr wires were used as neutron flux monitors.⁷ The irradiation was carried out for 4 hours at a thermal neutron flux of 10¹³ n·cm⁻²·s⁻¹ in the nuclear research reactor IEA-R1m at the Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN), São Paulo. The induced radioactivity was measured in germanium detectors (45% and 50% relative efficiency at 1332 keV ⁶⁰Co) at the Laboratório de Radioisótopos (CENA/USP). Chemical elements were determined using INAA *k*₀-method and in-house

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software package Quantu⁸ for spectrum evaluation and the calculation of concentrations and individual uncertainties.

Ratios between the total concentration in 0–10 cm of soil and leaves (Table 2) were used to estimate the transfer factors. To facilitate the interpretation, transfer factors were grouped according to the plant species. Statistical analysis was performed on the basis of the differences between the transfer factors of Br, Co, K, Na, Sr and Zn (the most representative elements in the covariance matrix) for all species except *Gomidesia spectabilis* and *Marlierea tomentosa* due to the

insufficient degrees of freedom (DF=2). The transfer factors were combined two by two thus totaling 15 possible combinations in order to take into account the correlation among the different transfer factors. It is known that the mean from normal distribution is distributed according to the *t*-probability density function using the Bayesian procedure described elsewhere.⁹ Therefore, the mean and its respective highest probability density interval at the 95% confidence level can easily be calculated for each combination and, consequently, compared with each other to assess the differences.

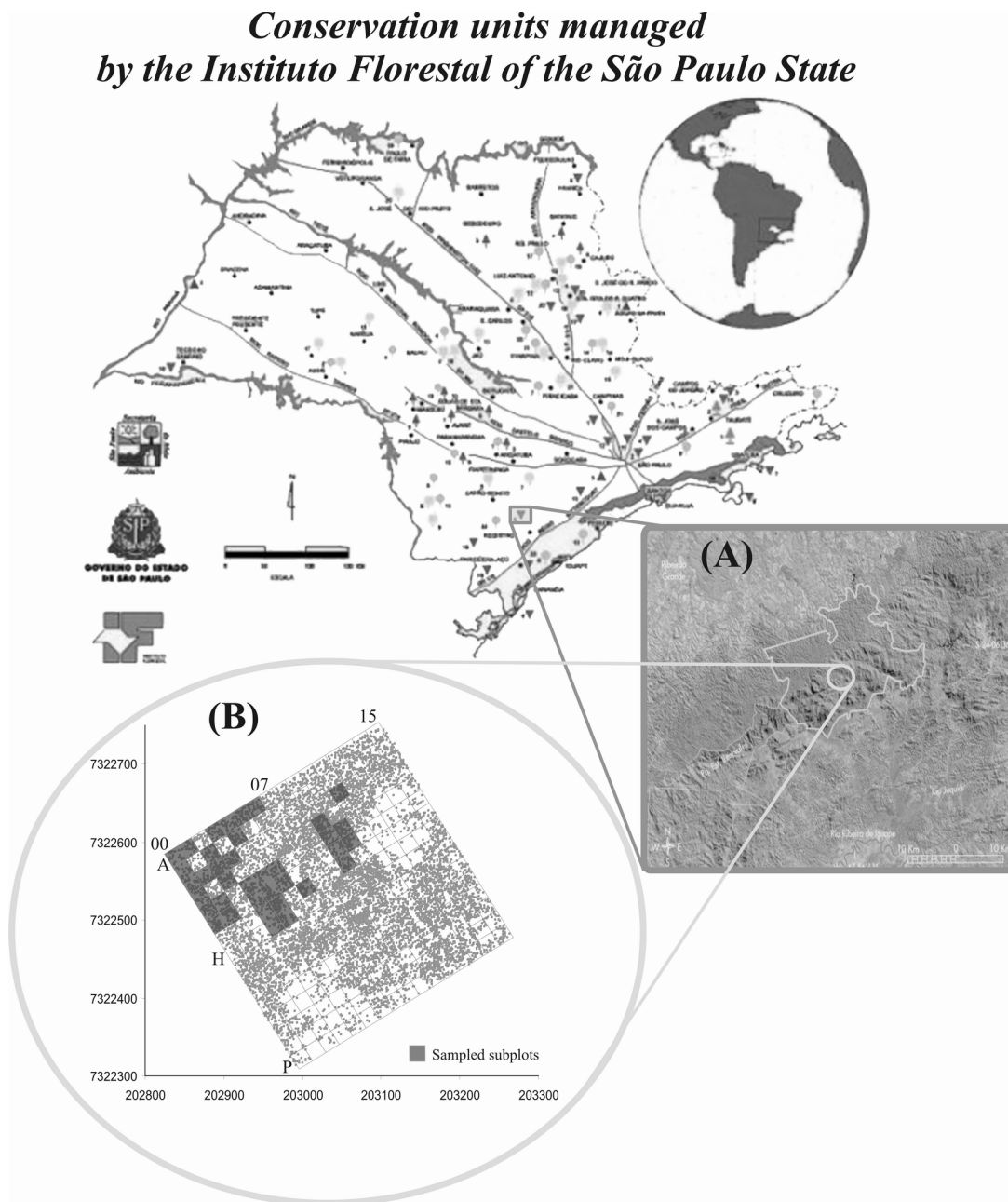


Fig. 1. Conservation units of the São Paulo State; (A) Landsat image of the Parque Estadual Carlos Botelho (PECB); (B) long-term plot with the sampled subplots. Points (gray) in the background refer to the mapped trees

Table 1. Tree species sampled in the long-term PECB plot. Sampling comprised leaves and soils under crown projection

Species*	Identification	Family	Total number of trees in the long-term plot	Number of sampled trees	Habitat
<i>Bathysa australis</i>	BA	Rubiaceae	209	14	C/U
<i>Chrysophyllum innornatum</i>	CI	Sapotaceae	86	8	C/U
<i>Eugenia cuprea</i>	EC	Myrtaceae	135	10	U
<i>Euterpe edulis</i>	EE	Arecaceae	2041	14	C/U
<i>Garcinia gardneriana</i>	GG	Clusiaceae	263	10	U
<i>Gomidesia flagellaris</i>	GF	Myrtaceae	122	14	U
<i>Gomidesia spectabilis</i>	GS	Myrtaceae	56	3	U
<i>Guapira opposita</i>	GO	Nyctaginaceae	343	10	U
<i>Hyeronima alchorneoides</i>	HA	Euphorbiaceae	120	14	C
<i>Marlierea tomentosa</i>	MT	Myrtaceae	115	3	U
<i>Tetrastylidium grandifolium</i>	TG	Olacaceae	216	10	C/U
<i>Virola bicuhyba</i>	VB	Myristicaceae	150	10	C

C: Canopy tree.

U: Understory tree.

* Details of plant sampling and leaf concentrations can be obtained from earlier publications.^{1,2}Table 2. Summary of the chemical concentrations of leaves (in mg·kg⁻¹) of tree species growing in the long-term PECB plot^{1,2}

Element	BM		CI		EC		EE		GF		GG	
	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Br	3.5	2.2	20.1	10.2	21.3	6.4	6.3	1.9	16.7	5.7	5.8	1.7
Ca*	7.1	2.0	12.0	4.6	10.6	2.4	3.6	1.0	7.5	1.0	7.9	2.3
Co	0.17	0.14	0.08	0.03	0.17	0.12	0.1	0.3	0.20	0.05	3	2
Cs	0.20	0.10	0.14	0.08	0.09	0.03	0.27	0.11	0.21	0.08	0.13	0.04
Fe	168	130	112	61	137	27	120	51	106	38	62	22
K*	21	5	12	4	7	2	9	2	8	2	7.0	1.5
Na*	1.1	0.3	0.7	1.3	0.7	0.5	1.2	1.0	1.1	0.5	1.1	0.4
Rb	68	26	31	13	18	5	33	10	24	6	19	5
Sc	0.041	0.040	0.016	0.009	0.035	0.008	0.021	0.012	0.022	0.008	0.011	0.004
Sr	131	37	293	123	200	66	29	12	135	39	183	73
Zn	37	7	13	2	19	5	43	13	12	3	51	20

Element	GO		GS		HA		MT		TG		VB	
	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Br	33.0	18.3	25	12	6.5	1.8	11	3	19.5	4.9	2.6	1.6
Ca*	13.0	4.7	6.1	2.4	6.5	2.3	5.1	1.2	4.0	1.5	7.0	2.1
Co	0.14	0.05	0.29	0.03	11	31	0.65	0.15	0.04	0.02	2	6
Cs	0.22	0.07	0.24	0.06	0.12	0.05	0.20	0.04	0.18	0.08	0.12	0.06
Fe	93	23	111	32	67	20	115	23	114	38	78	28
K*	25	7	9.0	1.0	14	3	8.4	0.4	11.2	1.3	12	3
Na*	7.4	1.3	2.1	0.5	0.6	0.2	0.5	0.2	2.3	0.4	0.5	0.4
Rb	73	21	29	6.6	42	12	27.4	3.4	27	7	39	10
Sc	0.019	0.007	0.021	0.009	0.007	0.002	0.024	0.005	0.024	0.012	0.011	0.008
Sr	291	87	135	24	109	28	92	26	93	35	108	39
Zn	27	13	15	4	24	4	16	2	17	3	25	6

* Values in g·kg⁻¹.

Results and discussion

The results of the analysis of certified reference materials (CRM) correspond with the reference values (Table 3). As a consequence, En scores, which take into account the uncertainties of the obtained, and the reference values, were inferior to 1 (Table 3). Therefore, the analytical procedure was considered adequate for determining 25 elements in soils from the PECB long-term plot.

Soil results were grouped according to the plant species (Table 4) to facilitate the discussion. Concentrations of As, Cr and Zn in soils correspond with the normal values proposed elsewhere.¹⁰ The comparison with similar data from Amazon soils reveals higher concentrations of As, Ba, Cr, Rb, Sr and Zn in the Atlantic Forest.¹¹ However, the concentrations of these elements in the leaf lie in the normal range, corroborating the low status of pollution of the Atlantic Forest.¹

The biomonitoring of tropical forests must take into account the biogeochemical cycling, because several factors contribute to the uptake, accumulation and recycling of chemical elements by plants. The calculated transfer factors in the Atlantic Forest are presented in Table 5. The transfer factors were not consistent for trees of the same species due to the high standard deviation obtained. The variability of transfer factors in the Atlantic Forest was similar to the transfer factors of grass-pasture.¹² Depending on the species, transfer factors close to 1 were found for the nutrients Ca, Co, K, Na and Zn, and the trace elements Br, Rb and Sr (Table 5). This fact reveals the great capability of each specific plant to accumulate some of these chemical elements. Cesium showed an average transfer factor of 0.04 ± 0.02 , which is ten times higher than the transfer factors obtained in needles growing on soil with similar total Cs concentrations.⁵ The palm tree *Euterpe edulis* presented

a consistent Zn transfer factor of 1.17 (STD=27%; $n=14$). The high transfer factors found for Br can be indicative of oceanic influence since species with high transfer factors of this element (*Chrysophyllum innormatum*, *Eugenia cuprea*, *Guapira opposita*, *Gomidesia spectabilis* and *Tetrastylidium grandifolium*) also presented high transfer factors of Na.¹³ With a transfer factor of 4.52 (STD=15%, $n=10$), *Guapira opposita* seems to be an accumulator of Na.

Despite the distinct differences at the 95% confidence level for the combined transfer factor for *Euterpe edulis* (Br-Zn), *Garcinia gardneriana* (Co-K), *Gomidesia flagellaris* (Br-Co), *Guapira opposita* (Br-Na; Co-Na) and *Tetrastylidium grandifolium* (Co-Na), the other species presented similar combined transfer factors (Fig. 2). As a result, the transfer of chemical elements from soil to leaves can be considered proportional for these Atlantic Forest species.

Table 3. Chemical concentrations (in $\text{mg}\cdot\text{kg}^{-1}$) of the certified reference materials analyzed

Element	SRM 2711 Montana Soil				IAEA Soil 7				En score
	Reference value		Obtained value ($n=11$)		Reference value		Obtained value ($n=11$)		
	Mean	Unc.	Mean	STD	Mean	Conf. interval	Mean	STD	
As	105	8	99	3	13.4	12.5–14.2	13.5	0.6	0.4
Ba	726	38	740	20	159	131–196	210	30	0.6
Br	5		5.1	1.0	7	3–10	8.7	0.3	0.3
Ca	28800	800	29100	3200	163000	157000–174000	151000	6200	0.6
Ce	69		78.8	0.8	61	50–63	62.8	0.7	0.4
Co	10		9.41	0.14	8.9	8.4–10.1	8.38	0.10	0.4
Cr	47		48.8	1.0	60	49–74	73.4	1.3	0.7
Cs	6.1		6.35	0.10	5.4	4.9–6.4	5.21	0.06	0.2
Eu	1.1		0.878	0.016	1	0.9–1.3	0.813	0.017	0.8
Fe	28900	600	27900	300	25700	25200–26300	25100	230	1.0
Hf	7.3		8.17	0.12	5.1	4.8–5.5	5.05	0.09	0.3
K	24500	800	25150	1150	12100	11300–12700	12150	770	0.2
La	40		37.2	0.7	28	27–29	27.7	0.2	0.3
Na	11400	300	11800	250	2400	2300–2500	2350	34	0.6
Nd	31		38	4	30	22–34	33	4	0.5
Rb	110		118	2	51	47–56	56	2	0.6
Sc	9		9.25	0.13	8.3	6.9–9	8.41	0.07	0.1
Sm	5.9		5.74	0.13	5.1	4.8–5.5	4.80	0.08	0.6
Sr	245.3	0.7	273	17	108	103–114	130	18	0.7
Ta	np*		1.28	0.04	0.8	0.6–1	0.71	0.02	0.4
Tb	np*		0.76	0.05	0.6	0.5–0.9	0.64	0.02	0.2
Th	14		13.87	0.17	8.2	6.5–8.7	8.20	0.14	0.0
Yb	2.7		3.21	0.13	2.4	1.9–2.6	2.37	0.09	0.4
Zn	350.4	4.8	342	6	104	101–113	98	3	0.7

Unc.: Uncertainty.

Conf. interval: 95% confidence interval.

* Uncertainties not provided for information values.

Table 4. Concentrations (in $\text{mg}\cdot\text{kg}^{-1}$) of chemical elements in 0–10 cm soil taken under crown projections. Samples were grouped by species to facilitate discussion

	As	Ba*	Br	Ce	Co	Cr	Cs	Fe*	Hf	K*	La	Nd*	Nd	Rb	Sc	Sm	Sr	Ta	Tb	Th	Yb	Zn	
BA	Mean	3.8	1.5	19	73	3.0	22	4.1	22	11	33	41	3	31	108	4.1	3.8	336	1.4	0.32	15	0.94	34
(n=10)	STD	1.6	0.5	6	14	0.9	6	0.8	6	2	11	6	3	4	27	1.0	0.5	137	0.3	0.06	3	0.18	8
CI	Mean	2.0	2.0	17	111	5.1	21	4.5	23	10.1	43	62	4	48	146	4.1	6.2	461	1.38	0.48	16	1.09	48
(n=8)	STD	1.4	0.3	8	29	1.4	2	0.7	3	1.0	6	15	2	15	30	0.5	1.8	93	0.11	0.12	3	0.18	11
EC	Mean	2.8	1.4	18	75	3.2	21	4.0	21	10.1	33	44	2.0	32	108	3.9	3.9	311	1.4	0.31	14	0.95	34
(n=10)	STD	1.6	0.3	5	21	1.0	4	0.6	4	1.7	6	11	0.7	7	17	0.6	0.7	60	0.2	0.05	2	0.18	9
EE	Mean	2.9	1.5	22	79	3.2	21	4.1	22.4	9.8	33	46	2.9	33	110	4.0	4.0	349	1.38	0.30	13.9	0.90	34
(n=10)	STD	1.0	0.2	4	18	0.8	2	0.6	1.9	1.5	5	10	1.0	7	13	0.4	0.9	48	0.14	0.05	1.2	0.14	7
GF	Mean	3.4	1.4	25	83	3.1	22	4.3	17	10.2	30	49	1.5	34	102	4.1	4.3	328	1.5	0.34	15	1.0	32
(n=10)	STD	1.2	0.2	5	32	1.1	4	0.6	12	1.2	5	15	1.3	10	13	0.9	1.3	48	0.2	0.10	3	0.2	12
GG	Mean	4	1.1	25	76	2.5	25	4.4	25	11.4	24	48	1.6	34	82	4.3	4.3	254	1.6	0.33	16	1.1	29
(n=10)	STD	2	0.5	8	18	0.8	6	0.9	6	1.5	12	10	1.7	6	32	1.0	0.7	108	0.3	0.06	3	0.2	8
GO	Mean	4.0	1.3	29	87	3.0	24	4.6	25	11.1	29	49	1.6	34	95	4.4	4.5	295	1.58	0.36	16	1.03	31
(n=10)	STD	0.5	0.1	4	25	0.8	3	0.4	3	0.7	2	10	0.3	7	9	0.7	0.9	21	0.09	0.06	3	0.10	9
HA	Mean	4	1.3	22	83	3.1	23	4.5	24	10.2	29	48	2.5	35	104	4.2	4.4	325	1.5	0.35	15	1.03	37
(n=10)	STD	2	0.5	7	29	1.5	6	0.8	6	1.9	12	16	1.8	14	35	1.0	1.8	115	0.3	0.11	4	0.25	18
TG	Mean	4.4	1.1	23	69	3.4	24	4.6	24	11.6	25	41	1.8	30	86	4.3	3.7	269	1.62	0.32	14	1.01	28
(n=10)	STD	1.3	0.3	5	19	3.4	4	0.4	4	1.3	8	7	1.3	6	21	0.6	0.6	74	0.12	0.05	3	0.10	7
VB	Mean	5.1	0.8	27	79	2.4	26	4.8	26	11.2	18	49	1.3	35	73	4.4	4.3	224	1.7	0.37	16	1.08	31
(n=10)	STD	1.6	0.4	6	20	1.1	3	0.5	4	1.1	10	6	1.0	5	31	0.5	0.5	92	0.2	0.03	2	0.12	9

* Values in $\text{g}\cdot\text{kg}^{-1}$.Additional soil results not mentioned in this table can be obtained elsewhere.¹

Table 5. Transfer factors of the chemical elements for some studied species from the Atlantic Forest

Sp	N		Br	Ca	Co	Cs	Fe*	K	Na	Rb	Sc*	Sr	Zn
BA	(n=12)	Mean	0.15	0.63	0.04	0.042	6.08	0.65	0.49	0.61	6.92	0.38	1.04
		Min	0.06	0.43	0.01	0.024	2.27	0.29	0.12	0.26	1.80	0.20	0.75
		Max	0.38	0.83	0.14	0.079	15.8	1.64	2.91	2.03	24.2	0.97	1.59
		STD%	27	32	112	42	87	68	152	79	126	56	29
CI	(n=8)	Mean	1.14	0.50	0.02	0.027	4.38	0.28	0.09	0.20	3.55	0.59	0.27
		Min	0.50	0.28	0.01	0.016	2.429	0.16	0.02	0.11	1.86	0.31	0.19
		Max	3.27	0.90	0.07	0.066	9.396	0.38	1.77	0.34	10.3	1.05	0.48
		STD%	90	52	126	69	62	30	652	46	78	46	35
EC	(n=10)	Mean	1.18	0.71	0.05	0.022	6.33	0.20	0.26	0.16	8.73	0.63	0.58
		Min	0.80	0.63	0.02	0.010	4.53	0.10	0.09	0.08	5.53	0.40	0.36
		Max	1.81	0.86	0.27	0.036	10.2	0.39	1.13	0.32	12.3	1.11	0.82
		STD%	32	18	162	38	28	42	136	42	24	41	28
EE	(n=14)	Mean	0.24	0.29	0.013	0.058	4.59	0.31	0.42	0.33	4.28	0.08	1.17
		Min	0.14	0.22	0.004	0.026	2.03	0.16	0.06	0.14	1.37	0.03	0.75
		Max	0.40	0.46	0.50	0.113	11.2	0.80	2.50	0.88	12.8	0.13	1.64
		STD%	34	46	966	46	51	56	167	65	68	39	27
GF	(n=13)	Mean	0.59	–	0.07	0.045	4.27	0.30	0.54	0.25	4.80	0.41	0.36
		Min	0.42		0.03	0.017	2.24	0.13	0.30	0.13	2.26	0.20	0.16
		Max	0.90		0.10	0.090	8.66	0.63	1.77	0.50	9.80	0.65	0.68
		STD%	26	11	34	44	36	45	76	41	38	34	36
GG	(n=10)	Mean	0.23	0.62	0.86	0.027	2.47	0.33	0.92	0.24	2.43	0.73	1.70
		Min	0.14	0.60	0.45	0.016	1.51	0.18	0.10	0.12	1.57	0.18	1.16
		Max	0.42	0.64	2.56	0.042	11.2	0.78	2.83	0.50	4.15	1.92	3.60
		STD%	37	5	75	28	32	64	122	50	38	83	42
GO	(n=10)	Mean	1.02	–	0.046	0.046	3.62	0.83	4.52	0.75	3.93	0.94	0.81
		Min	0.40		0.03	0.027	2.12	0.55	3.60	0.50	1.58	0.50	0.47
		Max	2.20		0.86	0.084	5.36	1.28	5.73	1.12	6.69	1.49	1.89
		STD%	48		51	34	25	27	15	27	37	31	48
GS	(n=3)	Mean	0.68	–	0.076	0.051	3.99	0.30	0.95	0.29	4.08	0.34	0.32
		Min	0.51		0.06	0.037	3.18	0.21	0.49	0.20	3.03	0.23	0.24
		Max	1.17		0.11	0.060	4.85	0.44	2.53	0.39	5.10	0.59	0.50
		STD%	55	11	34	25	21	39	118	33	26	57	45
HA	(n=14)	Mean	0.27	0.94	0.21	0.024	2.47	0.56	0.32	0.44	1.35	0.36	0.60
		Min	0.17	0.77	0.06	0.009	0.93	0.29	0.08	0.16	0.27	0.16	0.18
		Max	0.70	1.14	33.7	0.053	5.10	2.09	1.44	1.15	3.68	0.96	1.19
		STD%	50	29	4260	45	47	96	129	61	61	68	48
MT	(n=3)	Mean	0.35	–	0.15	0.040	4.06	0.32	0.41	0.28	4.65	0.24	0.31
		Min	0.25		0.11	0.034	3.13	0.25	0.29	0.22	3.20	0.19	0.29
		Max	0.49		0.19	0.113	4.83	0.36	0.61	0.33	6.20	0.28	0.34
		STD%	33		27	24	22	19	41	22	33	19	11
TG	(n=10)	Mean	0.84	–	0.015	0.038	4.55	0.48	1.48	0.32	5.12	0.34	0.60
		Min	0.52		0.003	0.024	2.72	0.32	0.41	0.21	2.29	0.14	0.30
		Max	1.15		0.04	0.086	7.75	1.06	5.17	0.43	10.8	0.69	0.87
		STD%	30		73	49	38	45	92	23	51	54	34
VB	(n=10)	Mean	0.09	–	0.074	0.023	2.85	0.75	0.41	0.57	1.89	0.49	0.83
		Min	0.05		0.013	0.011	1.78	0.30	0.08	0.33	0.60	0.23	0.47
		Max	0.30		13.4	0.051	5.27	1.60	2.63	0.94	5.66	1.02	1.34
		STD%	92		5745	59	41	75	208	41	103	64	38

* Values multiplied by a factor of 1000.
STD%: Standard deviation in percentage.

Moreover, there is similar behavior in terms of the transfer factors for species occupying the same habitat according to their relative position (understory or dominant species) in the forest canopy. The species were separated into these two groups by Br–Co, Br–Zn and Br–Na combined transfer factors (Fig. 2). In fact, the environmental conditions can be quite unfavorable in

terms of photosynthesis for understory trees resulting in the higher absorption of some non-essential chemical elements (Br and Na). These elements substitute functionally essential elements¹⁴ and therefore, owing to their leaf-soil transfer factors can be higher in ecosystems.

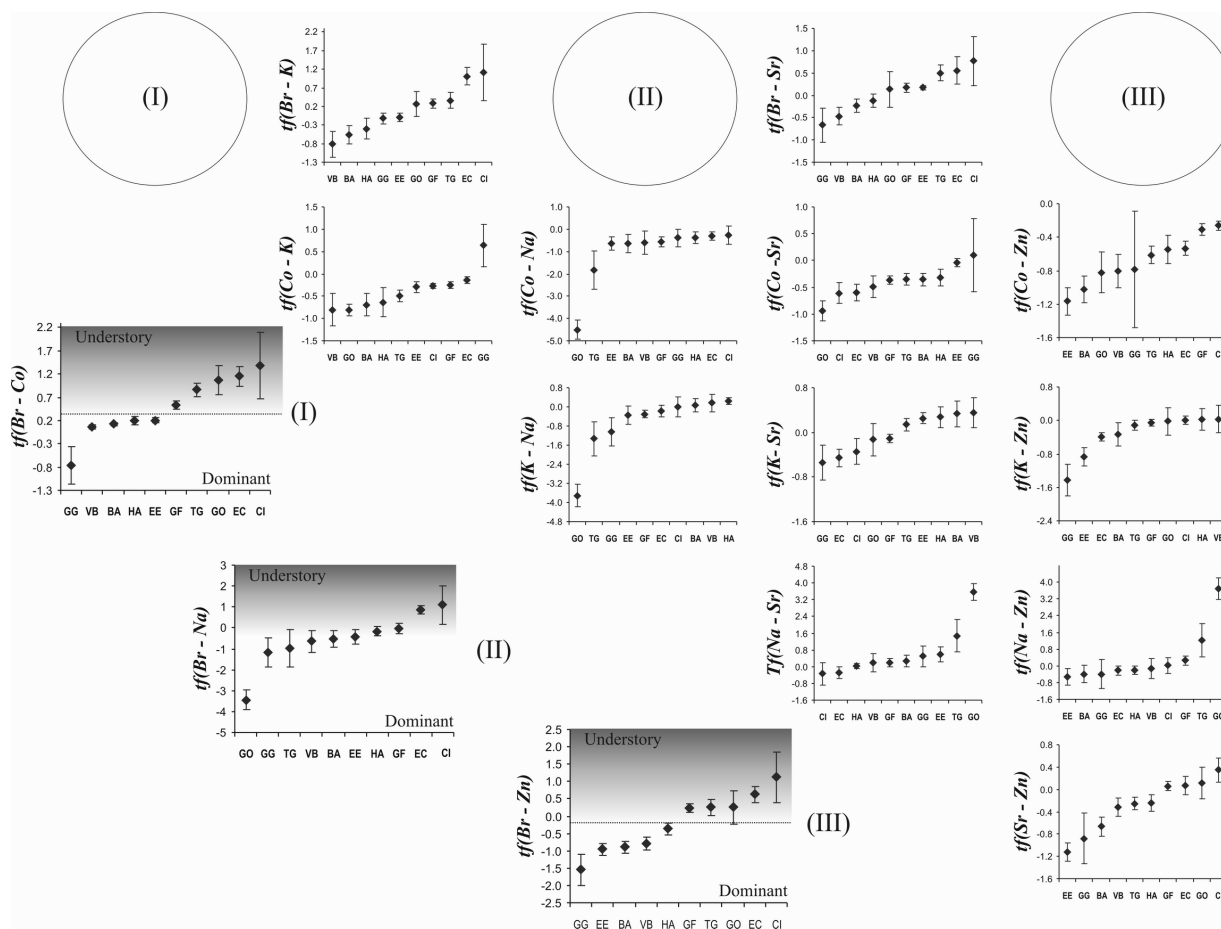


Fig. 2. Average combined transfer factors (tf) and their respective highest density intervals (95%) for tree species (BA = *Bathysa australis*, CI = *Chrysophyllum inornatum*, EC = *Eugenia cuprea*, EE = *Euterpe edulis*, GG = *Garcinia gardneriana*, GF = *Gomidesia flagellaris*, GO = *Guapira opposita*, HA = *Hyeronima alchorneoides*, TG = *Tetrastylidium grandifolium*, VB = *Virola bicuhyba*).

(I) and (II) show species separated according to their habits (understory and dominant species relative to the position at the forest canopy), while (III) indicates a slight differentiation

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