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Exploring Al, Mn and Fe phytoextraction in 27 ferruginous rocky outcrops plant species

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ABSTRACT

Worldwide, substrates naturally rich in Al, Fe and Mn are the subject of mining, generating degradation of large areas and producing wastes with high pollution potential for water resources, soil and atmosphere, causing harm to human health and ecosystems. The present study investigated the total and phytoavailable concentration of these elements in soils and leaves of 27 native plant species from ferruginous rocky outcrops, finding values above the toxic limits described in literature and environmental legislation. Foliar levels of metals varied widely among species, demonstrating different phytoextraction or exclusion potentials, which were not explained by the total concentration of elements or available soil fractions. Although most species are not considered hyperaccumulators, the results indicate the existence of species related to sites of greater availability of certain metals or that can modify soil quality through their different phytoextraction skills, with potential future uses in decontamination, stabilization, phytomining and ecological restoration projects.

1. Introduction

Studies on accumulative plant species have been mostly focused on the hyperaccumulation capacity of toxic elements such as Cd, Cr, Ni, Zn, Cu and Pb in an attempt to find suitable species for decontamination or stabilization processes in post-mined areas or those contaminated by agricultural or municipal waste (Agarwal, 2009; Sarma, 2011). Usually considered less hazardous, Fe, Al and Mn are the focus of significantly fewer phytoremediation studies. However, the exposure of materials rich in these metals to the action of rain and wind can lead to contamination of water resources and atmosphere, causing harmful effects to environment and human health (Beyersmann and Hartwig, 2008; Duruibe et al., 2007; Murray and Finkelstein, 2007; Silva et al., 2015). In such situations, Fe, Al and Mn could be classified as hazardous elements.

In Brazil, currently world's third largest Fe and Al producer and sixth manganese producer (IBRAM, 2015), large areas originally covered by native metalliferous vegetation give way to mined landscapes each year. Contrary to national law, which advocates the use of native plant species in the recovery of degraded areas, most mined areas suffer introduction of exotic species or remain devoid of effective revegetation and ecological restoration action for decades, resulting in significant environmental liabilities. This reality reflects the lack of studies on the biology of native species of ecosystems naturally evolved on iron and aluminous formations, known as ferruginous rocky outcrops or *canga* vegetation (Carmo and Kamino, 2015; Jacobi et al., 2007; Skirycz et al., 2014). Floristic surveys in key areas of occurrence of *canga* vegetation in Brazil reveal the presence of a diverse flora with high degree of endemism. In southeastern Brazil, 616 species have been cataloged to date, but only two studies containing information on the potential for accumulation of metals in 13 native species of these ecosystems and others on soils rich in metals have been published (Porto and Silva, 1989; Silva, 1992). None of the species was considered hyperaccumulator of potentially toxic metals (Co, Cu, Cr, Pb and Ni >1000 ppm, and Mn and Zn >10,000 ppm) according to Baker and Brooks (1989).

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However, in recent years, in parallel to the search for species that are hyperaccumulator of toxic elements and associated methodologies aimed at increasing soil and water decontamination efficiency, there is a growing demand for studies to facilitate the ecological restoration of areas degraded by mining. In this case, the diversity of species and their ecological features are factors more important than just their hyperaccumulation potential (Benayas et al., 2009). Recent studies in selenium mines, for example, have shown that hyperaccumulator species affect soil quality, preventing the establishment of other species (Mehdawi et al., 2011). In this case, this species would be undesirable for use in ecosystem restoration projects, or its presence should follow relative phytosociological proportions to other species of lower accumulative or exclusion potential found in pristine natural areas. The coexistence of different ecophysiological strategies regarding the magnitude of uptake and distribution of potentially toxic elements in different plant parts brings diversity to the environment and creates different possibilities of interactions between soil and plant and between plants and other organisms, expanding the functional complexity of ecosystems.

The present study explored some relationships between Al, Fe and Mn concentrations in soil and leaves of 27 native species (belonging to 17 families) of a ferruginous rocky outcrop fragment in the Iron Quadrangle, Brazil. In agreement with findings in other environments evolved on tropical acid soils, we expected to detect few metal-hyperaccumulating species (Kramer, 2010), but still, a wide range of foliar Al, Fe, and Mn concentrations. Variations in metal phytoextraction ability, as a reflex of plant species and ecophysiological strategies diversities, should be high even under narrow ranges of soil metal availability, and thus, significant and linear relationships between soil and foliar Al, Fe and Mn concentrations will not be found. Some species, however, may be more related to certain soil levels of these metals, expressing different sensitivities or capabilities of soil alteration.

2. Material and methods

2.1. Study area

The study was conducted in a ferruginous rocky outcrop area located at the "Cachoeira das Andorinhas" State Environmental Protection Area, Ouro Preto, Minas Gerais, Brazil (20° 21′S, 43° 30′W). The area consists of herbaceous and shrubby strata associated with rocky outcrops of itabirites or cangas and shallow soils (Valim et al., 2013). The average altitude is 1492 m. The average annual temperature is 27.9 °C and annual rainfall of about 1204.8 mm, 95.5% concentrated in the months from October to April.

The soil of the study area showed the following average values: pH (4.63), P (5.6 mg kg^{-1}), N (5.3 g kg^{-1}), base saturation (V = 9.7%), aluminum saturation index (m = 32), Fe (458.3 g kg^{-1}), Mn (0.9 g kg^{-1}) and remaining phosphorus (P-rem = 41.3 mg L^{-1}). Other values are expressed in $cmol_c\ dm^{-3}$: Sum of bases (SB = 2.0), Ca (1.5), Mg (0.4), K (0.1), Al^{3+} (0.98).

2.2. Plant and soil samples

A total of 27 species belonging to 17 families commonly found in ferruginous fields in Minas Gerais were selected (Jacobi et al., 2007; Messias et al., 2012) (Appendix A, Supplementary material).

A 350-m transect was traced along the highest quota of the slope and every five meters, in a straight line, individuals of 27 species that were at a distance of three meters to the left and right of the transect axis were marked. Then, three individuals of each species were drawn for the chemical analysis of leaves. For eight species, however, only one or two individuals in the surveyed area were found, and in this case, the concentrations of elements shown in Table 1 are not accompanied by standard deviation. Species with n = 1 were *Achyrocline albicans*, *Bulbostylis fimbriata*, *Centrosema coriaceum*, *Nematanthus strigillosus*, *Pleopeltis hirsutissima* and *Doryopteris ornithopus*. Species with n = 2 were *Paliavana sericiflora* and *Psyllocarpus laricoides*. Healthy and mature leaves in the middle third of each woody individual and of all aerial parts of herbs were collected during the rainy season (February–March 2013).

In these ecosystems, soil only accumulates in small and shallow depressions in the relief, which generally do not exceed 5 cm in depth. Therefore, soil samples at 0–5 cm in depth were collected in the projection of the crown of each individual selected for leaf analyses.

2.3. Plant and soil analysis

Leaves were washed in deionized water and after drying in an oven at 40 °C for 72 h, were ground in a knife mill. Then, 250 mg samples underwent acid digestion (7.0 ml of nitric acid 2 mol/l and 1.0 ml of oxygen peroxide 30% v/v) in a microwave (Milestone/Ethos one) (Gonzalez et al., 2009). The reference material used was Apple leaves, NIST – 1515. Al, Fe and Mn were quantified in inductively coupled plasma atomic emission spectrometer (ICP – OES, Agilent 725).

After drying in an oven at 40 °C for 72 h, the soil collected was ground and sieved into 0.0625 mm mesh. pH was determined for 10 g sub-samples of sieved soil in 25 ml of distilled water. Another soil fraction underwent sequential digestion according to Standard, Measurements and Testing Program (Rauret et al., 2001) for extracting elements linked to readily available, oxidizable and reducible soil fractions. The values obtained in three steps were summed and the result was used for Enrichment Coefficient analysis (EC), as it represents the truly phytoavailable element pool (Podlesáková et al., 2001). Al, Fe and Mn were determined by inductively coupled plasma atomic emission spectrometry (ICP-OES – Agilent 725.). The reference material was BCR 701.

Soil fertility was also analyzed. The following parameters were determined: active acidity (pH), total nitrogen (N), available and remaining phosphorus (P, P-rem), available potassium (K), exchangeable calcium (Ca^{2+}), exchangeable magnesium (Mg^{2+}), exchangeable aluminum (Al^{3+}), potential acidity (H + Al), sum of bases (SB), effective CTC (t), CTC pH7 (t), base saturation (V) and aluminum saturation (m) using standard methods adopted by the Brazilian Research Center for Agriculture (EMBRAPA, 1997). The N determination was done by semi-micro Kjeldahl method. The available P and P-rem concentration were determined by molecular absorption spectroscopy at 725 nm after the formation of the molybdenite-P complex via reduction by ascorbic acid. The available phosphorus was extracted with Mehlich-1 and to estimate the remaining P (P-rem) it was used a solution of soil samples (5 g) with a 0.01 mol L^{-1} $CaCl_2$ and 60 mg kg^{-1} P (EMBRAPA, 1997).

2.4. Biological absorption coefficients

The biological absorption coefficient (BAC), which expresses the ratio between shoot (leaf) element concentration and soil concentration (see Baker, 1981), was calculated for the 19 species with a sample number equal to three with both the total concentration values as plant-available metals in soil. BAC values greater and lower than 1 classify plants, respectively, as accumulators and excluder.

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Table 1
Average (and standard deviation) Al, Fe and Mn concentration in soil sampled under the canopy of species in the ferruginous rocky outcrops located in the Serra da Brigida, MG, Brazil.

Family	Species	Soil-total ($mg\,kg^{-1}$)			Soil-available ($mg\,kg^{-1}$)			total/available (%)		
		Al	Fe	Mn	Al	Fe	Mn	Al	Fe	Mn
Asteraceae	*Baccharis reticularia*	6285.4 (1203.3)[a]	563212.2 (56447.7)[b]	999.5 (35.0)[b]	64.0 (22.0)[ab]	141.8 (56.5)[a]	73.5 (24.4)[a]	1.0	0.03	7.4
	Eremanthus erythropappus	8217.9 (597.1)[a]	416132.2 (106886.5)[ab]	784.5 (119.9)[ab]	123.6 (44.7)[ab]	327.7 (36.8)[a]	40.6 (11.7)[a]	1.5	0.08	5.2
	Eremanthus incanus	5348.4 (855.8)[a]	507384.8 (60941.4)[b]	1023.2 (104.5)[b]	44.7 (15.6)[ab]	110.2 (36.8)[a]	114.9 (109.2)[a]	0.8	0.02	11.2
Bromeliaceae	*Dyckia rariflora*	12751.4 (9474.4)[a]	440265.5 (74597.3)[ab]	851.5 (166.5)[ab]	98.8 (32.3)[ab]	303.0 (56.5)[a]	78.9 (35.5)[a]	0.9	0.07	9.0
Erythroxylaceae	*Erythroxylum gonocladum*	7201.8 (2322.2)[a]	420047.6 (125137.0)[ab]	803.6 (106.5)[ab]	55.3 (6.0)[ab]	225.0 (85.2)[a]	94.1 (44.7)[a]	0.8	0.05	11.7
Fabaceae	*Dalbergia villosa*	7082.6 (621.3)[a]	341532.0 (183468.5)[ab]	683.6 (254.5)[ab]	68.3 (5.7)[ab]	264.8 (15.7)[a]	97.3 (39.8)[a]	1.0	0.08	14.2
	Periandra mediterranea	7083.5 (5387.4)[a]	558038.0 (47726.4)[b]	1092.3 (149.1)[b]	61.0 (51.2)[ab]	113.0 (68.3)[a]	88.8 (92.1)[a]	0.9	0.02	8.1
	Senna reniformis	7604.5 (3322.4)[a]	512313.6 (9513.7)[ab]	916.3 (72.2)[ab]	55.0 (11.9)[ab]	284.3 (71.1)[a]	46.4 (29.6)[a]	1.2	0.06	5.1
Lythraceae	*Diplusodon buxifolius*	13036.5 (9201.4)[a]	454268.6 (94321.1)[ab]	842.9 (162.2)[ab]	104.8 (26.5)[ab]	292.4 (66.3)[a]	62.4 (50.4)[a]	1.0	0.07	7.2
Malpighiaceae	*Byrsonima variabilis*	9225.8 (2447.1)[a]	459082.7 (6243.2)[ab]	880.0 (151.0)[ab]	112.0 (26.0)[ab]	311.6 (54.9)[a]	62.8 (34.7)[a]	1.2	0.07	7.1
	Heteropterys campestris	11525.8 (10672.2)[a]	510117.1 (47820.0)[ab]	956.7 (60.1)[ab]	82.2 (56.0)[ab]	196.4 (101.4)[a]	61.0 (51.1)[a]	0.7	0.04	6.4
Melastomataceae	*Leandra australis*	8996.6 (3437.5)[a]	438917.3 (36390.3)[b]	1019.5 (134.3)[b]	106.9 (53.8)[ab]	292.3 (96.9)[a]	120.5 (111.1)[a]	1.2	0.07	11.8
	Miconia corallina	6680.2 (3296.2)[a]	512213.3 (37728.7)[ab]	939.3 (60.9)[ab]	87.5 (33.3)[ab]	305.1 (114.6)[a]	54.6 (30.0)[a]	1.3	0.06	5.8
	Tibouchina heteromalla	4493.1 (1307.0)[a]	545136.2 (30249.4)[ab]	944.0 (158.9)[ab]	61.6 (30.3)[ab]	128.5 (76.2)[a]	40.6 (38.0)[a]	1.4	0.02	4.3
Myrtaceae	*Myrcia splendens*	8624.0 (2144.1)[a]	331760.3 (155576.5)[ab]	886.1 (419.8)[ab]	124.5 (54.9)[ab]	215.1 (202.9)[a]	226.7 (220.1)[a]	1.4	0.06	25.6
Ochnaceae	*Ouratea semiserrata*	7901.3 (1798.6)[a]	496348.3 (32505.6)[ab]	952.0 (121.9)[ab]	63.8 (17.8)[ab]	208.6 (77.1)[a]	116.9 (70.5)[a]	0.8	0.04	12.3
Poaceae	*Sporobolus metallicolus*	12751.4 (9474.4)[a]	440265.5 (74597.3)[ab]	851.5 (166.5)[ab]	98.8 (32.3)[ab]	303.0 (56.5)[a]	78.9 (35.5)[a]	0.9	0.07	9.0
Sapindaceae	*Matayba marginata*	15278.4 (8760.1)[a]	224707.4 (157606.6)[a]	488.8 (188.9)[a]	170.3 (90.3)[b]	418.8 (328.5)[a]	58.2 (22.3)[a]	1.1	0.19	11.9
Verbenaceae	*Lantana fucata*	4301.5 (789.9)[a]	495869.3 (54482.7)[b]	1078.7 (77.4)[b]	38.3 ± 12.0[a]	84.3 (34.9)[a]	141.5 (73.3)[a]	0.9	0.02	13.1

Different letters within the same column indicate significant differences in average element concentration among species (Tukey 0.05).

2.5. Statistical analysis

Data distribution was tested for normality using the Kolmogorov-Smirnoff test with 5% significance. The comparison between mean Al, Fe and Mn concentrations in leaves and in total and available soil fractions was performed using ANOVA followed by Tukey test at 5%. The significance of linear regressions was tested among the concentrations of elements present in the soil (in the total and available fractions), among fractions and between leaf concentrations and soil fractions. The principal component analysis (PCA) was used for the spatial ordering of species by the standard concentration of soil elements. The Minitab 16 was used for the statistical tests.

3. Results

3.1. Total and available Al, Fe and Mn soil concentration

The lowest total Fe and Mn concentrations (224,707.4 mg Fe kg^{-1} and 488.8 mg Mn kg^{-1}) were found around *Matayba marginata* (Table 1), which were at least two times and significantly lower than those found in soil under the canopy of *B. reticularia*, *E. incanus*, *P. mediterranea*, *H. campestris*, *T. heteromalla*, *M. corallina* and *S. reniformis* (considering only Fe), and *L. australis* and *Lantana fucata* (considering only Mn). Mean concentrations of total Al, and available Fe and Mn in the soil did not differ among species. Regarding available Al, significant differences were only observed in soil under the canopy of *Lantana fucata* (38. mg kg^{-1}) and *M. marginata* (170.3 mg kg^{-1}).

Total Fe and Mn concentrations were positively correlated ($F = 84.759$, $p < 0.001$). No other significant relationship between total or available concentrations of elements was found. Available Fe, Al and Mn fractions represent, respectively, only 0.1%, 1.1% and 9.9% of the total fraction (Table 1).

3.2. Foliar Al, Fe and Mn concentration

Average foliar Al concentrations ranged from 46.6 mg kg^{-1} (*P. mediterranea*) to 5794.6 mg kg^{-1} (*L. australis*) (Table 2). The three Melastomataceae species showed values significant higher than those found in other species. The average Fe concentrations showed lower amplitude among species (from 90.6 mg kg^{-1} in *O. semiserrata* to 696.5 mg kg^{-1} in *S. metallicolus*). Only this grassy species differed significantly from other species. In contrast, this species showed the lowest average foliar Mn concentration (331.9 mg kg^{-1}). Significantly higher Mn levels were found in only three species, *B. reticulata*, *D. rariflora* and *L. fucata*, whose mean values were higher than 1606.4 mg kg^{-1}. In the analysis of species whose leaf concentrations were determined in a single individual, the lowest Mn concentration was 100.5 (*P. sericiflora*) and the highest was 3935.1 mg kg^{-1} (*A. albicans*).

A positive linear relationship was found in Al and Fe concentrations in leaves by excluding the three Melastomataceae species from the analysis ($R^2 = 0.77$, $F = 154.4$, $p < 0.001$). With the exception of Melastomataceae and *C. coriaceum*, which accumulated respectively from 15.3 to 1.2 times more Al than Fe, all the other species have accumulated on average twice as much Fe than Al in their leaves. No other significant relationship among leaf elements was found.

3.3. Soil-plant relationship

Regressions revealed no significant relationship between total and available concentrations of elements in soil and leaves of the species under study. The concentrations of elements in soil, however, segregated species or species groups, as can be seen by the spatial ordinations obtained by the Principal Component Analyses (PCA) (Fig. 1).

PCA using, respectively, total and available Al, Fe and Mn contents in soil under the canopy of species indicated that the first two axes explained, respectively, 95% and 96% of the total variance. The first axis of PCA using the total content of elements explained more than 78% of the variance found and was strongly and positively correlated to Al and Fe contents and negatively correlated to Mn content. *Matayba marginata* occurs preferentially in sites with lower total Mn concentrations, while the opposite is observed for *B. reticularia*, *E. incanus*, *P. mediterranea*, *H. campestris*, *T. heteromalla*, *M. corallina* and *S. reniformis* (Fig. 1A). In relation to the available concentration of these elements, PCA indicated that Mn and Fe are positively correlated with the first axis (Fig. 1B). The available Al content is negatively correlated with the first axis and strongly and positively related to the second axis, segregating *M. marginata* from the remaining species (Fig. 1B). *M. marginata* occurs at sites with higher available Al concentrations, in contrast *to L. fucata* and *E. incanus*, which occur in locations of lower concentration of this element. *D. villosa* is associated with sites with lower available Fe and Mn concentrations (Fig. 1B).

Table 2
Foliar concentration of Al, Fe and Mn (mean and standard deviation) for the 27 species of ferruginous rocky outcrops located in the Serra da Brigida, Ouro Preto, MG, Brazil. (−) denotes lack of standard deviation due to n < 3.

Family	Species	Elements (mg kg^{-1})		
		Al	Fe	Mn
Asteraceae	*A. albicans*	477.7 (−)	983.4 (−)	3935.1 (−)
	B. reticularia	143.3 (39.2)^{a}	255.1 (51.8)^{ab}	1606.4 (589.3)^{bcd}
	E. erythropappus	212.1 (41.0)^{a}	352.8 (55.6)^{ab}	835.9 (87.4)^{abcd}
	E. incanus	73.6 (7.1)^{a}	195.3 (41.1)^{a}	1240.7 (401.6)^{abcd}
Bromeliaceae	*D. rariflora*	113.0 (26.8)^{a}	434.3 (191.2)^{ab}	1929.4 (377.6)^{d}
Cyperaceae	*B. fimbriata*	161.3 (−)	376.2 (−)	560.1 (−)
Erythroxylaceae	*E. gonocladum*	80.2 (29.3)^{a}	176.3 (49.3)^{a}	428.4 (78.4)^{ab}
Fabaceae	*C. coriaceum*	466.8 (−)	382.7 (−)	164.5 (−)
	D. villosa	148.9 (62.1)^{a}	214.9 (24.1)^{a}	1438.3 (399.7)^{abcd}
	P. mediterranea	46.6 (11.2)^{a}	174.9 (70.6)^{a}	570.6 (345.5)^{abc}
	S. reniformis	58.4 (9.4)^{a}	172.1 (6.4)^{a}	854.2 (135.0)^{abcd}
Gesnenaceae	*N. strigillosus*	246.5 (−)	498.8 (−)	249.2 (−)
	P. sericiflora	519.8 (−)	861.7 (−)	100.5 (−)
Lythraceae	*D. microphyllus*	146.0 (25.1)^{a}	154.7 (23.7)^{a}	385.2 (113.3)^{ab}
Malpighiaceae	*B. variabilis*	87.9 (16.7)^{a}	201.3 (32.1)^{a}	360.6 (183.6)^{a}
	H. campestris	244.3 (1.5)^{a}	424.7 (1.5)^{ab}	1250.7 (1.5)^{abcd}
Melastomataceae	*L. australis*	5794.6 (1913.1)^{c}	379.6 (206.8)^{ab}	1475.6 (537.1)^{abcd}
	M. corallina	2154.3 (521.5)^{b}	401.1 (90.6)^{ab}	661.3 (175.2)^{abc}
	T. heteromalla	892.9 (90.4)^{b}	321.0 (51.1)^{ab}	1017.9 (322.2)^{abcd}
Myrtaceae	*M. splendens*	144.0 (96.1)^{a}	203.6 (102.7)^{a}	352.7 (55.0)^{a}
Ochnaceae	*O. semiserrata*	55.7 (12.6)^{a}	90.6 (14.8)^{a}	1378.7 (753.0)^{abcd}
Poaceae	*S. metallicolus*	340.7 (313.9)^{a}	696.5 (500.1)^{b}	331.9 (63.24)^{a}
Polypodiaceae	*P. hirsutissima*	284.4 (−)	576.0 (−)	325.0 (−)
Pteridaceae	*D. ornithopus*	280.5 (−)	487.6 (−)	194.0 (−)
Rubiaceae	*P. laricoides*	241.7 (−)	300.7 (−)	297.3 (−)
Sapindaceae	*M. marginata*	375.0 (103.5)^{a}	519.0 (112.6)^{ab}	435.9 (372.6)^{ab}
Verbenaceae	*L. fucata*	214.4 (92.1)^{a}	438.2 (113.6)^{ab}	1758.5 (966.4)^{cd}

Different letters within the same column indicate significant differences in average element concentration among species (Tukey 0.05).

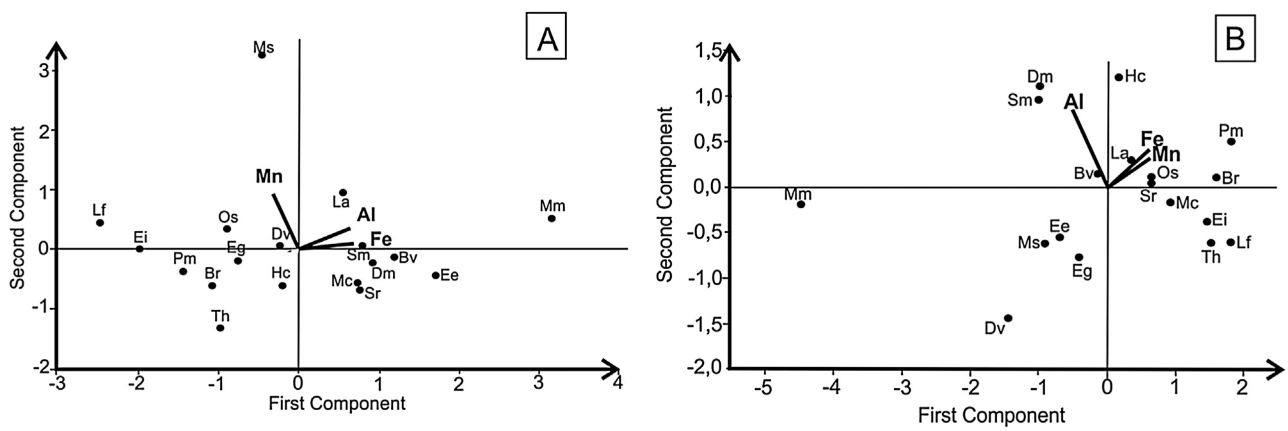

Fig. 1. Spatial ordering diagram of the two axes of the Principal Component Analysis showing the spatial ordering of species in relation to (A) total and (B) available Fe, Al and Mn soil concentration. Code of species (see Appendix A, Supplementary material).

3.4. Biological absorption coefficient

When considering the total Al and Fe concentrations in soil, all species showed enrichment ratios lower than 1, being classified as excluding species for these elements (Figs. 2 and 3). Values greater than 1 were estimated for Mn in 10 out of 19 species (Fig. 4), which were considered Mn accumulators. However, using the available fraction of elements to calculate the coefficient, most species would be classified as Al (15 species, Fig. 2) and Fe accumulators (13 species, Fig. 3), and all of them Mn accumulators (Fig. 4). CAB values >1 (Al available) ranged from 54.1 to 1.1, and from 5.2 to 1.1 (CAB Fe available) and 24.5 and 3.0 (CAB Mn available). While CAB values obtained with total and available Al contents seem to follow a positive linear relationship, the same is not true for Fe and Mn.

4. Discussion

The soil of the study area is similar to those found in other ferruginous outcrops in southern Brazil and typically classified as dystrophic (Carmo and Jacobi, 2016; Messias et al., 2013; Vincent and Meguro, 2008. Factors such as high amount of iron oxides that have low CEC in addition to the land slope, contribute to the leaching of essential soil nutrients. Total Fe, Mn and Al concentrations were many times higher than the average values of soils worldwide (Kabata-Pendias, 2011). Although only 0.1%, 1.1% and 9.9%, respectively, of total Fe, Al and Mn are in the available soil fraction, these concentrations exceed the limit established by the Brazilian Agricultural Research Company (Ribeiro et al., 1999) for agricultural crops (>45 mg Fe kg^{-1}, >12 mg Mn kg^{-1} and exchangeable aluminum >1). This fact imposes restrictions on the establishment of some species in adjacent ecosystems under different chemical

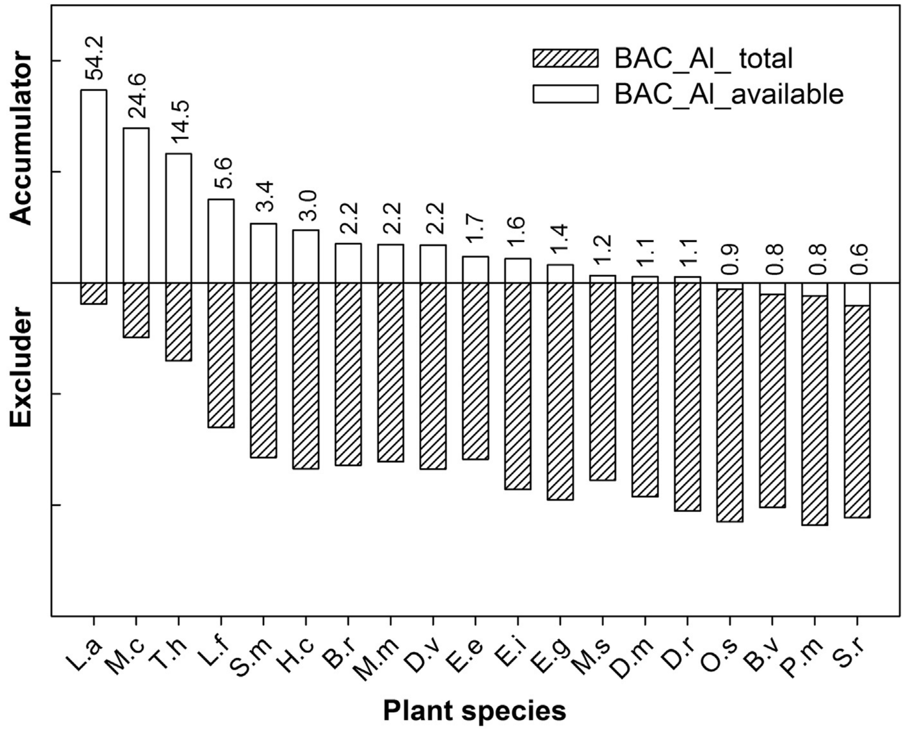

Fig. 2. Biological absorption coefficients of Al for species (n = 3) of the ferruginous field of Serra da Brigida, MG, Brazil. Values calculated with total and available Al concentration in soil are respectively represented by the black and white bars. Y-axis is in logarithmic scale. BAC values not log-transformed are displayed next to the bars. Names of species are abbreviated according to their initials (Appendix A, Supplementary material, Table 2).

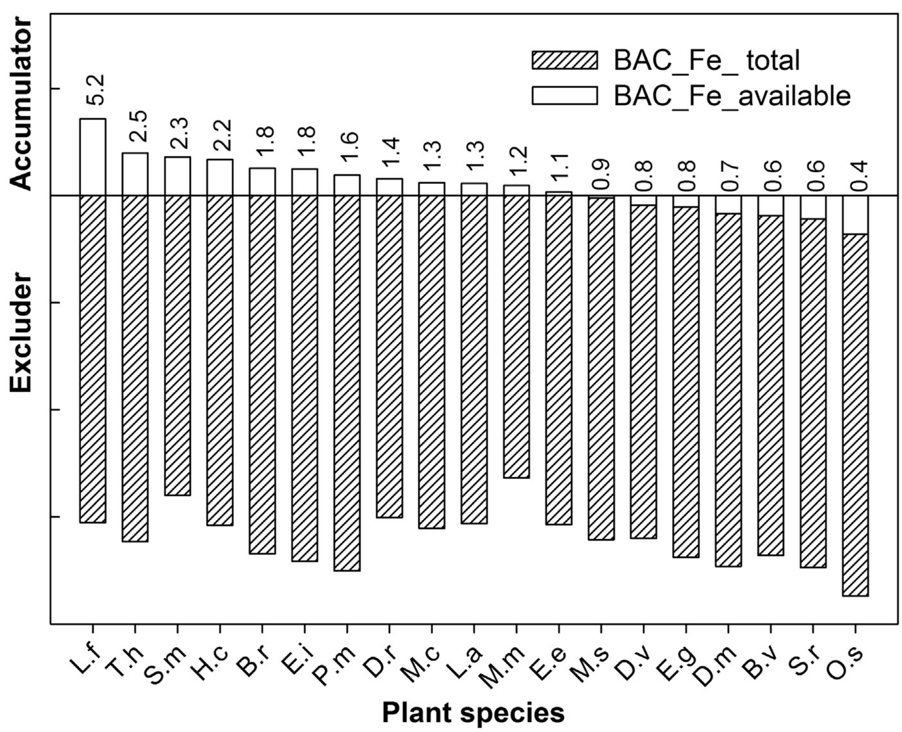

Fig. 3. Biological absorption coefficients (BAC) of Fe for species (n = 3) of the ferruginous field of Serra da Brigida, MG, Brazil. Values calculated with total and available Fe concentration in soil are respectively represented by the black and white bars. X-axis is in logarithmic scale. BAC values not log-transformed are displayed next to the bars and were below 0.01 for all species when considering total BAC. Names of species are abbreviated according to their initials (Appendix A, Supplementary material, Table 2).

soil conditions, as rocky outcrops on quartzite (Messias et al., 2013). Although these mean soil conditions are not restrictive for a high diverse flora of ferruginous rocky outcrops and probably to other plants adapted to Al-richer lateritic soils (but poorer in Fe and Mn, Haridasan and Araújo, 1988), the metal variation in microtopographic scale, as performed in this study, suggests segregation of species or groups of species. Fine-scale surveys on rocky outcrops

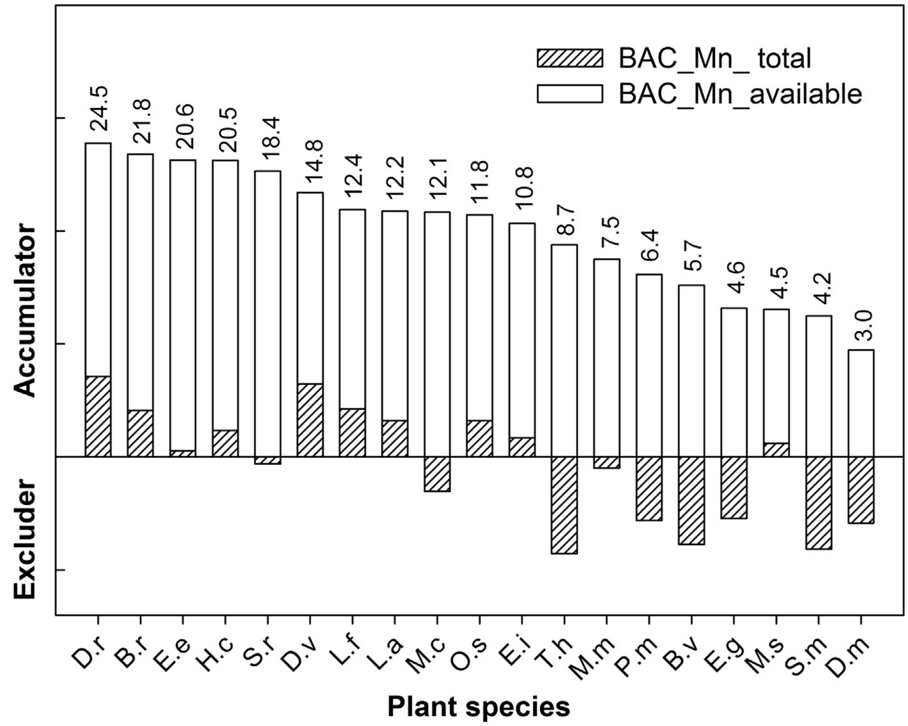

Fig. 4. Biological absorption coefficients of Mn for species (n = 3) of the ferruginous field of Serra da Brigida, MG, Brazil. Values calculated with total and available Mn soil concentration are respectively represented by the black and white bars. Y-axis is in logarithmic scale. BAC values not log-transformed are displayed next to the bars. Names of species are abbreviated according to their initials (Appendix A, Supplementary material, Table 2).

surfaces have proved to be a strong tool for identifying patterns of functional groups distribution (Carmo et al., 2016).

The study area presented great spatial heterogeneity regarding total and available concentrations of elements in the soil below the canopies of the different species, representing a mosaic of different landscape occupation opportunities for species with various degrees of sensitivity to abundant elements (Fe, Mn and Al). *Matayba marginata* seems to be the most sensitive species, as it occupied sites with lower Fe and Mn concentrations, and at the same time, with higher Al levels. The Al concentration varied 3.6 times between the upper and lower limits in the area, and about 2.5 and 2.2 times for Fe and Mn. To what extent this variation range works as a selection factor for the establishment of species or is the result of the action of these species on the physical and chemical soil properties is still controversial. Plants have mechanisms for selectively uptaking soil chemical elements, favoring the absorption of a certain group while avoiding others, thereby changing the relative proportions of soil elements. This species-specific effect might be especially relevant in rocky outcrops, where in general, soil volumes explored by plants are very small. In such type of environments, soil may only accumulate discontinuously in shallow (usually less than 5 cm in depth, Carmo et al., 2016) and small relief depressions. Each spot of reduced soil volume undergo continuous influence of roots and litter produced by initially established plant species. Our results indicate patterns of soil-plant species relationship, but do not allow mechanistic explanation concerning soil biogeochemistry dynamics. *Eremanthus incanus* and *L. fucata* are found on soil patches with lower Al but with higher Mn concentration. *Baccharis reticularia* occurs in soils with higher Fe and Mn and lower Al concentrations, while the opposite was observed for *M. marginata*. *Dalbergia villosa*. *E. erythropappus* and *E. gonocladum*, which occur in soils with lower Fe and Mn concentrations. In a natural seleniferous area, two hyperaccumulator species enhanced soil Se concentrations while preventing the establishment of Se-sensitive species (Mehdawi et al., 2011). On the contrary, the soil under the canopy of *T. heteromalla* and *M. corallina*, two Al accumulator species, exhibited lower Al but higher Fe concentration. The Melastomataceae has been recognized as having a large number of Al hyperaccumulator species worldwide (Haridasan, 2008; Jansen et al., 2002), however, there is no conclusive evidence about the ability of this family to significantly alter the Al concentration in soils. In certain ecosystems, litterfall may represent a major aboveground input of Al to the soil organic horizon (Rustad and Cronan, 1995). Most of the Al remains for long periods immobilized in decaying litter, adsorbed onto humic carboxyl group exchange sites, and thus, Al accumulates over time in the O-horizon. In the Cerrado, the soil Al availability did not vary over four studied years even in plots treated with twice the litter biomass found in the untreated area (Villalobos-Vega et al., 2011).

Most species have been considered excluders, when considering the BAC values calculated using the total concentrations of soil elements (Baker, 1981). However, when considering the phytoavailable concentration, the scenery changes. A gradient of foliar concentrations and BAC values is found, with BAC variations of about 8, 12 and 87 times between maximum and minimum Mn, Fe and Al values, indicating the coexistence of functional groups of high, medium and low accumulation or exclusion capacity. Even among the three Melastomataceae species under study, which had the highest Al phytoextraction values, being two of them (*L. australis and M. corallina*) classified as hyperaccumulators according to Jansen et al. (2002, foliar Al >1000 ppm), the $BAC_{available}$ values varied widely (14.5 in *T. heteromalla* and 54.2 in *L. australis*).

Regardless of not being classified as hyperaccumulator plants, foliar Al, Mn and Fe concentrations in several species under study are high, showing that they are not fully effective in excluding these elements from aerial tissues, even in the case of Al, which is not an essential element. Thus, these species are working like accumulator species, where Al usually accumulates on the leaf epidermis by transpiration stream (Leitenmaier and Küpper 2013; Malta et al., 2016). Curiously, although no specific metabolic role of Al in plants has been described so far, some common plant species of Cerrado only survive in the presence of exchangeable aluminum (Haridasan, 2008). Al^{+3} may reach about two times higher values than the mean value found in the study area (Haridasan and Araújo, 1988) and a considerable number of plants accumulating more than 1000 ppm of Al in leaves have been found in Cerrado biome (Haridasan, 1982, 2008; Haridasan and Araújo, 1988; Souza et al., 2015). According to Bressan et al. (2016) the pattern of Al accumulation in leaves in association with cell walls suggests that Al has structural rather than physiological roles in Cerrado woody species, and that Al is possibly isolated from metabolism. On the other hand, with very few exceptions, Cerrado plants accumulate much lower Fe and Mn concentration in leaves (Miatto and Batalha, 2016) than those recorded in ferruginous rocky outcrop species.

In the study area, manganese hyperaccumulation (foliar Mn >10,000 ppm, Baker and Brooks, 1989) was not identified, but values exceeding 400 mg/kg were found in the leaves of 18 of the 27 species under study in levels considered toxic for most cultivated plants (Kabata-Pendias, 2011; Millaleo et al., 2010). *Achyrocline albicans* showed average concentration of about 10 times this limit. There are evidences that some plant species benefit from Mn accumulation (Millaleo et al., 2010). High Mn concentrations have been found in species typical of dystrophic rocky fields and are associated with a strategy to enhance phosphor uptake (Lambers et al., 2015). In addition, manganese, as well as aluminum (Hajiboland et al., 2013), seems to have a negative effect on iron uptake in the soil due to competitive inhibition by the same absorption site (Foy et al., 1978). To date, no threshold has been set for Fe hyperaccumulation in plants and leaf concentrations higher than 500 ppm suggest Fe toxicity (Marschner, 2012). Among the 27 species studied, only five exceeded this concentration in leaves. Again, *A. albicans* presented the highest concentration, 983.4 mg kg^{-1}.

The understanding of biogeochemical interactions among soil elements, the physiological functions and ecological consequences of their accumulation at different levels and in different plant tissues remain a current target of scientific demand due to the potential use of this knowledge in the phytomining and phytoextraction areas and in the recovery of degraded areas.

The results found for the 27 species under study indicate the co-existence, in ferruginous ecosystems, of different exclusion and accumulation capabilities of abundant and potentially toxic elements in the soil, resulting in high complexity of ecological functions mediated by the metal-plant relationship. Insect-plant interactions (Behmer et al., 2005; Quinn et al., 2011; Ribeiro et al., 2017; Søvik et al., 2015) and interactions between plants and microorganisms can also be mutually affected by the functional skills of accumulating or excluding metals (Khan, 2005). Metal hyperaccumulation strategy does not appear to be dominant in the flora of ferruginous rock outcrops, similarly to that observed by Kramer (2010) in different ecosystems. Thus, efforts for the restoration of ferruginous field ecosystems should be based on facilitating the establishment of the greatest possible number of species and functional groups of plants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.flora.2017.05.004.

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