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Assessment of Atmospheric Metal Pollution in the Urban Area of Mexico City, Using *Ficus benjamina* as Biomonitor

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Abstract Concentrations of vanadium, chromium, cobalt, nickel, copper, zinc, antimony, and lead were measured in *Ficus benjamina* leaves from the Mexico City urban area in order to assess their enrichment against background values. The instrumental analysis was performed using inductively coupled plasma mass spectrometry and the analytical method was tested using two certified reference materials from the National Institute of Standards and Technology (1547 Peach Leaves and 1573a Tomato Leaves). Enrichment factors were calculated, i.e., total to background concentration ratio, for each metal. Low enrichments of vanadium, cobalt, nickel, and copper (≈ 2), and mild enrichments of chromium and zinc (4.4, 4.5 respectively) were found in the entire area; oppositely, high enrichments were assessed for antimony (28.6) and lead (17.2). However, results indicate that metal concentrations strongly depend on the specific urban sub-area. Increments of metals were attributed to natural, vehicular, and industrial sources.

Keywords *Ficus benjamina* · Metals · Mexico City · Biomonitors · ICP-MS

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High population density and the anthropogenic activities imply the presence of environmental pressure. The fast increase of urbanization and industrialization in Mexico City Metropolitan Area (MCMA) have made it into one of the most densely populated regions on Earth, with more than 20 million inhabitants over an area of approximately 4,700 km^2. The high degree of environmental pollution, originated mainly from the exhaust emission of more than 4 million automobiles, have made this urban zone a vital study area. Additionally, this area is subject to unfavorable conditions of atmospheric ventilation due to the mountainous scenery that surrounds the basin, which constitutes a natural barrier that hampers wind circulation and pollutants dispersion. Chow et al. (2002) have found that approximately 70%–80% of PM_{10} in Mexico City are constituted of metals, being 13% toxic metals; hence, the increment assessment of metals in this particular urban environment is of great concern.

Pollution gives rise to anomalously high concentrations of metals relative to the normal background levels (Alloway and Ayres 1993). The environmental characteristics of inorganic trace pollutants in air are the following, wide dispersion, long-distance transport, bioaccumulation, reaction in living tissues by disturbing the metabolic processes, and resistance to metabolic detoxification; entering the food chain (Kabata-Pendias 2001).

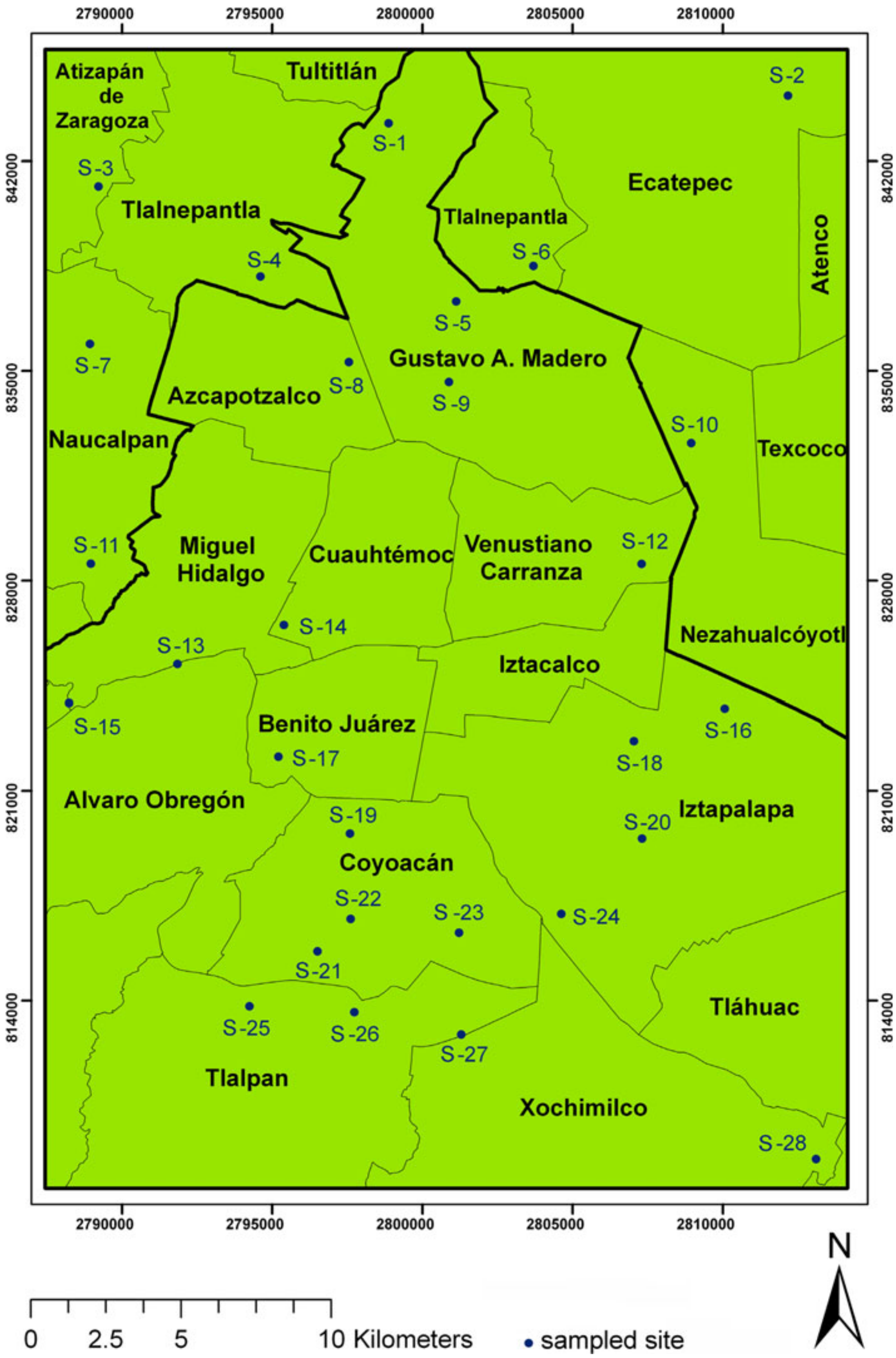

Fig. 1 Map of the studied area and sampling points

The leaded gasoline combustion during the past years generated considerable amounts of lead particles, mainly PbBrCl. It is widely recognized that the combustion of fuel with tetraethyllead has been the main anthropogenic source of Pb found in urban soils (Wong and Li 2004; Komárek et al. 2008). In Mexico the reduction of lead in fuels began in 1986, until the official banning in April 1996. Beside lead other metals such Ba, Cu, Fe, Mn and Zn have been also associated with wearing and corrosion of vehicular parts (Monaci et al. 2000).

Biomonitoring is the continuous observation of an area by repeated measuring of living organism responses to spatial and temporal changes, that provide valuable quantitative information about the environment; being an easy, economic, and practical method when compared with traditional monitoring methods (Zurayk et al. 2001). It is well known that mosses and lichens are the most sensitive indicators of atmospheric pollution, however in urban and industrial areas the lack of these organisms is common; therefore, major plants are suitable for monitoring metals pollution (Al-Alawi and Mandiwana 2007; Rossini and Fernández 2007). Plants can accumulate metals in or on their tissues; their ability to absorb trace elements directly by dry or wet depositions has been frequently reported, where leaf surface morphology is an important factor governing foliar uptake of trace elements (Kabata-Pendias 2001). Hence, for atmospheric purposes it is necessary to assess that aerial deposition is the main source of metals in the biomonitor. The present study is considered as a useful guide for more exhaustive pollution research in terms of metals increment in this urban zone.

Materials and Methods

In the geographic context, the study site is the major part of Mexico City and some conurbated districts, located within the MCMA (Fig. 1), it has an average altitude of ca. 2,240 masl at latitude (19° 03′–19° 54′ N) and longitude (98° 38′–99° 31′ W).

An active biomonitoring, using *Ficus bejamina* leaves as quantitative indicator of the atmospheric state was carried out in April–May 2008, during a period of 15 days without rain. The study site was divided in three sub-areas: north, center and south; based on the intensity and type of anthropogenic activity. The north area is characterized by industrial activities with high population and vehicular density. The center area includes the most important historic district with the highest socio-economic activity and also high vehicular density; whereas, in the south area prevails residential and commercial activities, being the area with the largest extension of green areas and conservational soils.

At each sample site approximately 50 g of leaves were taken from the basal stratum surrounding the tree periphery. In order to avoid the removal of surface pollutants during manipulation leaves were cut off from the petioles using latex gloves, in total 28 samples were collected from the study area. Samples from S-1 to S-10 correspond to north; S-11 to S-20 to center; and S-21 to S-28 to south area Fig. 1 the locations of the sampling sites were recorded by means of GPS. As possible, for each sub-area the sampling included sites exposed to diverse sources and intensities of pollution: residential and industrial sites, gardens, parks, traffic roads and cropping soils. Independently a greenhouse plant (control plant) located at 65 km from de study area (Cuautla, Morelos) was sampled as background specimen.

In laboratory each sample was divided into two groups. The fist group was washed with deionized water, while the second group was left intact. Both groups were dried at 45°C in oven (Binder) for 48 h. The samples were labeled and stored in polyethylene bags. For analytical procedure 0.5 g (dry weight) of vegetal sample were weighed on analytic balance Ohaus Analytical Plus. A predigestion procedure was performed for 24 h at room temperature, adding 10 mL of nitric acid J. T. Baker Ultrex II. The mixture was finally digested by closed microwave system (CEM MarsX press). After cooling, the samples were filtered with Whatman® No. 46 paper, and brought to 100 mL volume with deionized water. Indium was added (In High Purity Standards) as internal standard to a final concentration of 10 μg L^{-1}. The control plant was processed for triplicate. The samples were analyzed by ICP-MS using a ThermoElemental XSeries instrument. The isotopes determined for analysis were: ^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{121}Sb, ^{208}Pb, and ^{115}In. Calibration curves were prepared from a multielement standard solution (QCS-19 High Purity Standards).

For quality purposes two certified standard materials, 1573a Tomato Leaves and 1547 Peach Leaves, from NIST were digested and analyzed as described above, at least for triplicate. Obtained results by the analytical procedure are shown in Table 1. For both CRMs, percentage recovery ranges from 63.6 to 107.7, while the replicates have % RSD ≤ 18.2. The method detection limits are 0.02, 0.22,

Table 1 Measured and certified metal concentrations (μg g^{-1}) in certified reference materials

Metal	1547 Peach leaves				1573a Tomato leaves			
	Certified	Measure	% Recovery	% RSD	Certified	Measure	% Recovery	% RSD
V	0.37	0.31	83.3	1.1	0.835	0.769	92.1	4.7
Cr	1[a]	0.87	86.8	2.1	1.99	1.88	94.6	1.6
Co	0.07[a]	0.08	107.7	1.2	0.57	0.61	107.1	1.5
Ni	0.69	0.61	88.8	5.0	1.59	1.59	100.2	2.4
Cu	3.7	3.4	90.7	6.7	4.7	4.4	94.3	2.1
Zn	17.9	15.5	86.7	1.6	30.9	25.2	81.5	3.2
Sb	0.02[a]	0.02	87.3	18.9	0.063	0.040	63.6	7.2
Pb	0.87[a]	0.75	86.4	9.8	nr	0.470		2.4

[a] Not certified values. Not reported value nr. (n = 3)

0.003, 0.002, 0.30, 1.69, 0.02, and 0.26 μg g^{-1} for V, Cr, Co, Ni, Cu, Zn, Sb, and Pb respectively, which are lower than the measured concentrations in samples and CRMs, excepting for Cr concentration determined in several washed samples, such data were not considered for the pair t-test analysis.

Concerning to the data processing a pair t-test was performed to evaluate the airborne metal contribution to unwashed leaves concentrations, and a Pearson correlation matrix was calculated in order to assess anthropogenic or natural sources to the resulting metal groups. Both statistical tests were performed using a statistical software package (Statistica, Statsoft, USA).

Results and Discussion

The metal concentrations found in the 28 unwashed leaves samples, as well as the background values are shown in Table 2. The concentration range of the eight metals analyzed in the control sample varies from 1 to 2 magnitude orders, which indicates the natural relative abundance of the metals.

The enrichment factor of plant (EF_{plant}) is a specific approach to assess pollution using vegetal biomonitors and has been defined by Mingorance et al. (2007) as:

$$EF_{\mathrm{plant}} = \frac{M_{\mathrm{plant}}}{M_{\mathrm{control}}}$$

where M_{plant} is the metal concentration in the vegetal sample and $M_{control}$ is the metal concentration in the background sample. In agreement with the division criteria of the study area, Table 3 shows the average concentration, and enrichment factors of the north, center, and south sub-areas, as well as for the entire area. The total enrichment factors show a general metal increment; nevertheless, the magnitude increment is fundamental to assess the pollution degree. In the present study for practical purposes the environment impact assessment is restricted to EF $\geq$ 3. Based on the latest the enrichment factors of V, Co, Ni, and Cu are in general moderated at the urban zone and specially low in the south samples (1 $\leq$ EF $\leq$ 1.6). Although some significant exceptions are found at S-18 with EF values of 8.1, 8.9, and 5.4 for V, Co, and Ni respectively, and at S-6 with an EF value of 9.5 for Cu, indicating for all these metals a significant anthropogenic source at the proximities of the mentioned sites. The EF values for Cr and Zn are of medium impact at two sub-areas (north and center), whereas the highest EF values were determined for Sb and Pb at the three sub-areas.

Figure 2 displays comparative and decreasing graphics of the calculated enrichment factors. In the three sub-areas the highest EF values correspond to Sb, Pb, Zn, and Cr, noticing that the center and south areas hold an identical enrichment order among the mentioned metals, while the concentrations found in the north exhibits a similar trend.

Table 2 Metals concentrations (μg g^{-1}) from the urban area of Mexico City

Sample	V	Cr	Co	Ni	Cu	Zn	Sb	Pb
S-1	0.77	0.49	0.20	1.73	5.0	15.1	0.066	1.37
S-2	1.79	1.10	0.21	1.26	5.8	19.4	0.113	2.51
S-3	2.00	2.24	0.23	1.31	7.3	24.2	0.180	4.27
S-4	3.08	2.17	0.34	1.82	9.3	30.9	0.115	7.34
S-5	1.39	1.50	0.29	3.49	12.4	85.9	0.205	4.12
S-6	1.94	2.08	0.30	2.63	53.5	95.7	0.235	12.70
S-7	3.51	2.62	0.40	2.34	13.0	32.7	0.409	8.96
S-8	2.24	2.14	0.33	2.30	26.6	89.7	0.183	7.62
S-9	1.48	1.43	0.20	1.37	17.3	93.6	0.306	4.58
S-10	1.02	0.80	0.18	1.88	10.5	25.6	0.126	1.79
S-11	1.73	2.17	0.22	1.41	15.0	25.0	0.778	7.98
S-12	1.28	1.12	0.19	1.10	8.0	17.6	0.139	2.73
S-13	2.24	3.80	0.34	2.21	25.7	77.7	1.239	6.56
S-14	1.18	1.23	0.16	1.09	12.0	16.8	0.443	3.86
S-15	0.68	0.76	0.09	1.09	7.6	9.8	0.463	1.88
S-16	0.92	1.10	0.13	1.76	6.5	16.3	0.213	2.40
S-17	1.51	1.24	0.19	1.18	8.7	15.9	0.342	4.05
S-18	6.61	7.01	0.92	4.59	22.8	88.2	0.536	16.88
S-19	1.26	1.25	0.23	2.35	11.4	19.5	0.347	3.66
S-20	1.98	3.10	0.31	2.84	15.5	61.6	0.366	6.25
S-21	0.87	1.13	0.13	1.08	5.7	12.2	0.225	2.37
S-22	1.18	1.24	0.17	1.21	6.1	15.3	0.280	3.33
S-23	0.67	0.53	0.13	1.03	5.4	16.9	0.141	1.57
S-24	0.84	0.94	0.13	1.68	10.1	18.9	0.341	2.35
S-25	0.43	0.37	0.10	1.37	6.5	11.9	0.210	0.87
S-26	0.89	0.79	0.18	1.90	6.5	14.2	0.183	2.02
S-27	0.72	0.68	0.14	1.76	6.6	14.7	0.206	2.75
S-28	0.82	0.69	0.21	0.86	3.8	9.3	0.064	1.76
Background	0.81	0.37	0.10	0.84	5.6	7.7	0.011	0.27

Table 3 Concentration averages (μg g^{-1}), and enrichment factors for the study area and sub-areas

		V	Cr	Co	Ni	Cu	Zn	Sb	Pb
North	$\bar{x}_N$ (n = 10)	1.92	1.66	0.27	2.01	16.1	51.3	0.194	5.53
	EF_N	2.4	**4.4**	2.6	2.4	2.9	**6.7**	**18.3**	**20.7**
Centre	$\bar{x}_C$ (n = 10)	1.94	2.28	0.28	1.96	13.3	34.8	0.487	5.62
	EF_C	2.4	**6.1**	2.7	2.3	2.4	**4.5**	**46.0**	**21.0**
South	$\bar{x}_S$ (n = 8)	0.80	0.80	0.15	1.36	6.3	14.2	0.206	2.13
	EF_S	1.0	2.1	1.4	1.6	1.1	1.8	**19.5**	**8.0**
Total	$\bar{x}$ (n = 28)	1.61	1.63	0.24	1.81	12.3	34.8	0.302	4.59
	EF	2.0	4.4	2.3	2.1	2.2	**4.5**	**28.6**	**17.2**

Considered EF values are in bold

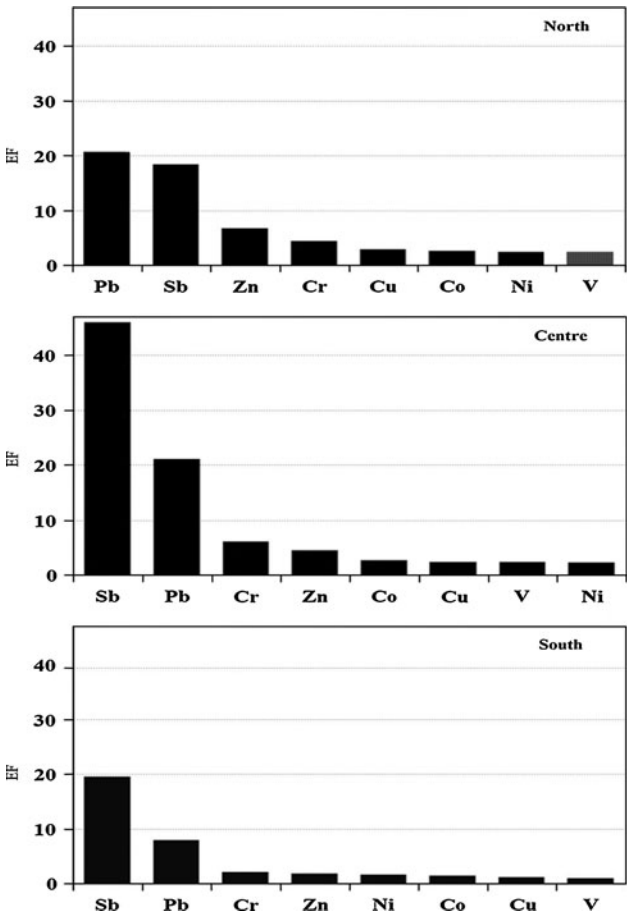

Fig. 2 Enrichment factors comparison between sub-areas

The lower enrichment factors (V, Co, Ni, and Cu) do not hold any relative identical position among the sub-areas. These observations allow establishing a metal enrichment order valid to the entire study area: Sb, Pb > Cr, Zn > Cu, V, Co, Ni.

Even enrichment factor order is very similar between sub-areas the enrichments magnitude are considerably different. Metals determined in the south show the lowest concentrations and so EF values, excepting for antimony, which behave uniquely between sub-areas ($EF_C > EF_S > EF_N$) Therefore the enrichment trend is directly related to intensity and type of the anthropogenic activities within a defined zone at the Mexico City urban area.

The significant positive correlations found between V, Co, and Ni (Table 4), are mainly ascribed to parental material of the study site in agreement to their poor enrichment factors. In the north and center, Cr enrichment (4.4 and 6.6 respectively) points out at anthropogenic sources; hence, the high correlation of Cr with V, Co, and Ni might result from the contribution of two common factors in these metals:1 the anomalous sample S-18 and 2 the poor enrichment in the south sub-area.

Table 4 Pearson correlation matrix (n = 28)

V		Co	Cr	Ni	Cu	Zn	Sb	Pb
V	1.00							
Co	**0.93**[a]	1.00						
Cr	**0.96**[a]	**0.93**[a]	1.00					
Ni	**0.71**[a]	**0.75**[a]	**0.81**[a]	1.00				
Cu	0.40	0.49	0.43	0.51	1.00			
Zn	0.53	**0.62**[b]	**0.60**[b]	**0.69**[b]	**0.79**[c]	1.00		
Sb	0.31	0.53	0.29	0.22	0.34	0.30	1.00	
Pb	**0.88**[b]	**0.87**[b]	**0.86**[b]	**0.72**[b]	**0.74**[c]	**0.69**[c]	0.38	1.00

Significant correlations ($\alpha < 0.001$ and $v = 26$ freedom grades) are in bold. [a] Correlation mainly attributed to natural sources. [b] Correlation attributed to stationary sources, probably industrial. [c] Correlation mainly attributed to vehicular sources

The extended enrichment of lead in the study area, especially uniform in the north and center sub-areas suggests a source present in the whole area. Lead contained in soils particles can be brought to air by wind or vehicular movement. Monaci et al. (2000) based on *Q. Ilex* leaves and PM_{10} analysis have determined that Pb, Cu, and Zn are metals related by (to) traffic. According to the authors tyre (ingles britanico es tyre, ingles Americano es tire) wear and vehicle component detachment are important sources of Zn; while brakes release Cu particles. In this context and given the Pb/Cu (0.74), Pb/Zn (0.69) and Cu/Zn (0.79) correlations, these metals can be associated to vehicular sources. Nevertheless, zinc shows the largest area of high concentration located in the urban districts Gustavo A. Madero, Azcapotzalco, and Tlalnepantla, at the north area characterized by a high industrial development. The high enrichment factors and the absence of significant positive correlations for Sb indicate anthropogenic sources related, at a minor extent, to the emission of the others studied metals. The rest of significant positive correlation (Cr/Pb, Ni/Pb, Pb/V, Pb/Co, Zn/Co, Zn/Cr, Zn/Ni) and specifically the correlations of metals attributed to anthropogenic activities with those attributed to natural sources; are associated to the incidence of high concentrations at S-18 that may be explained by a distinctive stationary source.

The study carried out by Sharma et al. (2008) shows that the wash technique is a useful tool to evaluate the input of metals by atmospheric depositions in vegetal material. One of the criteria to select a biomonitor is its capability to distinguish between airborne and soil borne metals. As a fist approximation Fig. 3 displays the percentage concentration translocated into the leaf and the percentage concentration deposited on the leaf surface. The total metal concentration determined for the unwashed leaves represents 100%. The washed leaves concentration is considered as the metal inside the leaf (black fraction). The content deposited superficially on the leave (gray fraction) is given

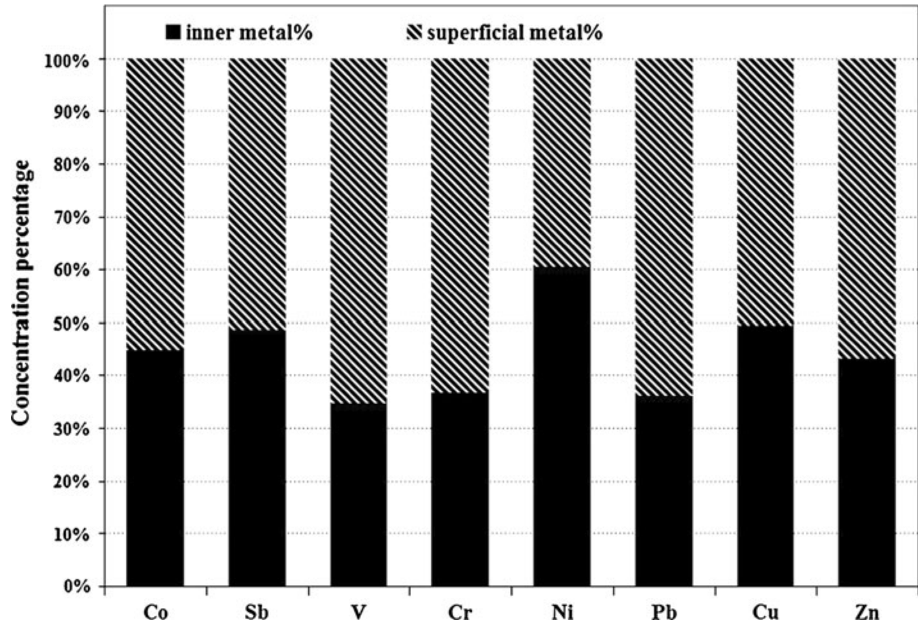

Fig. 3 Metal percentage reduction during wash procedure

Table 5 Results of paired t-test

Metal	UW concentration	W concentration	Calculated t	*p* value
V	1.61	0.73	4.50	0.000116
Cr	1.85	0.60	5.04	0.000055
Co	0.24	0.11	4.45	0.000134
Ni	1.81	1.09	5.38	0.000011
Cu	13.6	6.1	3.63	0.000403
Zn	35.5	15.0	4.13	0.000328
Sb	0.302	0.146	6.73	0.000000
Pb	4.59	1.66	4.55	0.000103

Significant values are in bold ($\alpha < 0.05$). *p* value is the probability that unwashed and washed concentrations are equal. *UW* unwashed leaves, *W* washed leaves. Concentrations are given in ($\mu g\ g^{-1}$) n = 22

by the difference of the unwashed leaves concentration and the washed leaves concentration. The graphic allow visualizing qualitatively a considerable metal content reduction (65%–40%) during the wash procedure. The concentrations for washed and unwashed leaves were compared using a paired t-test. The results of the statistical test demonstrate (Table 5) that content of all the studied metals are significantly higher in the unwashed leaves. Therefore the total metal concentration in *Ficus bejamina* leaves is due mainly to airborne metals, being the translocation and bioavailability of the metals via soil negligible.

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