http://dx.doi.org/10.21577/0103-5053.20180174

J. Braz. Chem. Soc., Vol. 30, No. 2, 256-264, 2019
Printed in Brazil - ©2019 Sociedade Brasileira de Química

Article

Biomonitoring of Toxic Elements in Plants Collected Near Leather Tanning Industry

Alex R. H. De La Cruz,[a] Lorreine D. S. C. Ferreira,[a] Vinicius P. Andrade[a] and Adriana Gioda *,[a]*

[a]*Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225, 22451-900 Gávea, Rio de Janeiro-RJ, Brazil*

The present work aimed the study of atmospheric deposition of toxic elements near to a tannery industry by collecting black material deposited on leaf surfaces of cinnamon trees (*Cinnamomum zeylanicum*). Elements such as As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). For comparison purpose, black particles deposited on the leaf surface of lemon trees (*Citrus lemon*) collected away from the tannery industry were also analyzed. Results showed that the amount of toxic elements found in the black particles collected near tannery area was significantly higher than the amount of those measured in the comparison site. Enrichment factors (EF) of As and Cr were markedly impacted by anthropogenic emissions, whereas the other elements were moderately/slightly enriched. Cluster analysis (CA) identified the leather industry as the anthropogenic source, while As possibly comes from the wide use of pesticides and herbicides in agricultural practices. The results indicated that emissions from the leather industry and agricultural activities are the main source of pollution in this area.

Keywords: leather industry, ICP-MS, toxic elements, atmospheric particles

Introduction

Leather industry, an age-old activity, covers the manufacture of diverse consumer products (e.g. footwear, clothes, and leather goods), industrial processes, and has significant economic influence. However, this industry is considered of great concern because to turn the skin into leather (leather tanning) requires several stages and involves the use of large amounts of fresh water and several chemicals such as lime, sodium carbonate, sodium bicarbonate, common salt, sodium sulfite, chrome sulfate, oils, resins, biocides, among other reagents.[1,2] Increased levels of chromium in the environment result from the improper discharge of solids, wastewater, and gaseous emission from anthropogenic activities such as leather tanning, steel alloys and stainless steel manufacture, chrome plating, fabrication of paint pigments, wood preserving, textile, ceramic glazes, electroplating, and other activities.[3,4]

Atmospheric deposition of toxic elements in form of particulate matter (PM) can attain soils and plants by either dry or wet deposition. Plants are essential organisms (biomonitors) of the ecosystem because they may improve the air quality by filtering, absorbing and accumulating significant quantities of toxic elements.[5] Biomonitoring studies using tree leaves as passive sampler are particularly useful because they have the advantage of high spatial and temporal distribution, low-cost, high distribution density and trapping of atmospheric particles, mostly on the entire leaf surface.[6] The accumulation and distributions of contaminants in plants depend on the plant species, bioavailability and level of contaminants in the soil and air, and environmental conditions, such as rainfall, wind speed and direction and other factors.[7]

In the last years, several plant species have been used as bioindicators of elemental deposition from the atmosphere.[8-10] For instance, pine tree leaves have been used as biological indicators for assessing toxic metal pollution by Cd, Pb, As, and Hg in an industrial ecosystem in Turkey.[11] Leaves of five plants: *Padus serotina*, *Acer campestre*, *A. negundo*, *Quercus robur* and *Celtis occidentalis* were used as bioindicators to assess the amount and concentration of contaminants in deposited dust in and around the urban city of Debrecen, Hungary,[10] while in Beijing, China, fourteen plant species have been used as bioindicators to evaluate the air pollution in the urban area.[12]

The determination of Cr in environmental samples is of great importance due to its toxicity. Chromium is

*e-mail: agioda@puc-rio.br

a hard steel-grey toxic metal element and may occur naturally as chromite ($FeCr_2O_4$) in the environment. This element is usually found in two oxidation states: trivalent chromium (Cr^{III}) and hexavalent chromium (Cr^{VI}). Other valence states (less stable or short-lived) can also occur in biological materials. The trivalent form is more abundant and much less toxic and less mobile than Cr^{VI}. It acts as an essential dietary nutrient to the maintenance of normal glucose tolerance for human and animals in low doses, while Cr^{VI} compounds are considered 1,000 times more toxic than Cr^{III}.[13] Its toxicity is related to its high redox potential, mobility, and ability to penetrate biological membranes. Chromium(VI) is also known as carcinogenic and mutagenic agent and can cause several diseases.[14]

Nova Esperança do Sul, a small city in the south of Brazil, is named capital of the boot and has a big tannery, whose main articles are semi-finished and finished full-grain leather and their use is divided between furniture and automotive industries.[15,16] These goods are mainly sold to the foreign market. In general, leather industries eliminate leftover materials and leather shaving wastes through burning. As the industry is located in the center of the city, there are complaints from the population due to the constant atmospheric emissions.[17] The particles generated during the burning spread throughout the city, leaving the houses dirty, causing bad smell and health problems, although there is no official record. For this reason, the objective of this study was to verify if the black particles deposited in the soil and on the surfaces of plants are from the natural origin or are related to tanning activities. The specific goals of this study were (*i*) to investigate the levels of toxic elements (As, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn) present in the deposited material on the surface of the leaves of *Cinnamomum zeylanicum*, (*ii*) to assess contamination levels, and (*iii*) to identify the possible sources of toxic elements in an industrialized region (Nova Esperança do Sul, RS, Brazil).

Experimental

Study area

This study was conducted in the city of Nova Esperança do Sul (S1, 29°24'24" S, 54°49'50" W), state of Rio Grande do Sul (RS), Brazil (Figure 1). The city (S1) is located in the southernmost part of the country with 5,087 inhabitants,[18] and covers an area of about 190,85 km^2 of which 0.72% is related to the urban area, 27.15% is used for agricultural activities and 72% is field. The climate is subtropical and the average temperature varies between a maximum of 38 °C and a minimum of –3 °C, with 17.8 °C as medium temperature.[15] The average annual precipitation is of 1795 mm and the relative humidity varies from 30 to 95%. The predominant wind direction is from the southwest (called "minuano") and north.[15] In this region, two sites were chosen: S1A (center), located about 300 m far from the tannery, and S1B (Planalto), located about 5 km from the tannery.

As the presence of sooty mold, a fungus spread by insects, may cause deposits of black particles on leaves of various plants, an erroneous affirmation may be stated if only the study area was evaluated. In order to identify if black particles deposited on leaf surface in S1 are from natural or anthropogenic origin, an area located about 100 km from Rio de Janeiro (RJ) without pollution of industries or traffic influence, but with tree leaves containing black particles on the leaf surfaces, was considered. Lumiar (S2, 22°22'0.12" S, 42°12'0" W), district of Nova Friburgo, Brazil (Figure 1), is a mountainous region in the Atlantic Forest covering an area of 7 km^2 with 5,000 inhabitants.[18] Climate is warm and temperate with average annual precipitation and temperature of 1437 mm and 19.5 °C, respectively.

Sampling

Sampling of cinnamon tree (*Cinnamon zeylanicum*) leaves was carried out in three periods: May 2016 (P1), September 2016 (P2) and October 2017 (P3) at Nova Esperança do Sul (S1). Cinnamon trees grow in tropical areas, have leaves of medium size and are elongated, slender, and oval to lanceolate in shape. About 300 g of both leaves without black particles on its surface (termed clean leaves (CL)) at S1A (CLS1A) and S1B (CLS1B) and leaves with particles at S1A were collected in the three periods (Figure 1a). Leaves containing black particles were not found at site S1B. Additional dry leaves (DL) were also collected at S1A (DLS1A). Soil samples (about 500 g) were also collected at the surface and at 10 cm depth in places adjacent to the trees from which leaf samples were collected (SS1A and SS1B).

For comparison purpose, clean leaves (CLS2) and leaves of lemon tree (*Citrus lemon*) covered by black particles (PS2) (Figure 1b) were collected at Lumiar (S2) on February 2017. Sampling collection was at a height of 1.5-2 m above the ground, using latex gloves, stored in self-sealing plastic bags and subsequently transported to the laboratory.

Sample preparation and chemical analysis

In the laboratory, the material (black particles) deposited on leaf surface was carefully removed using a plastic knife

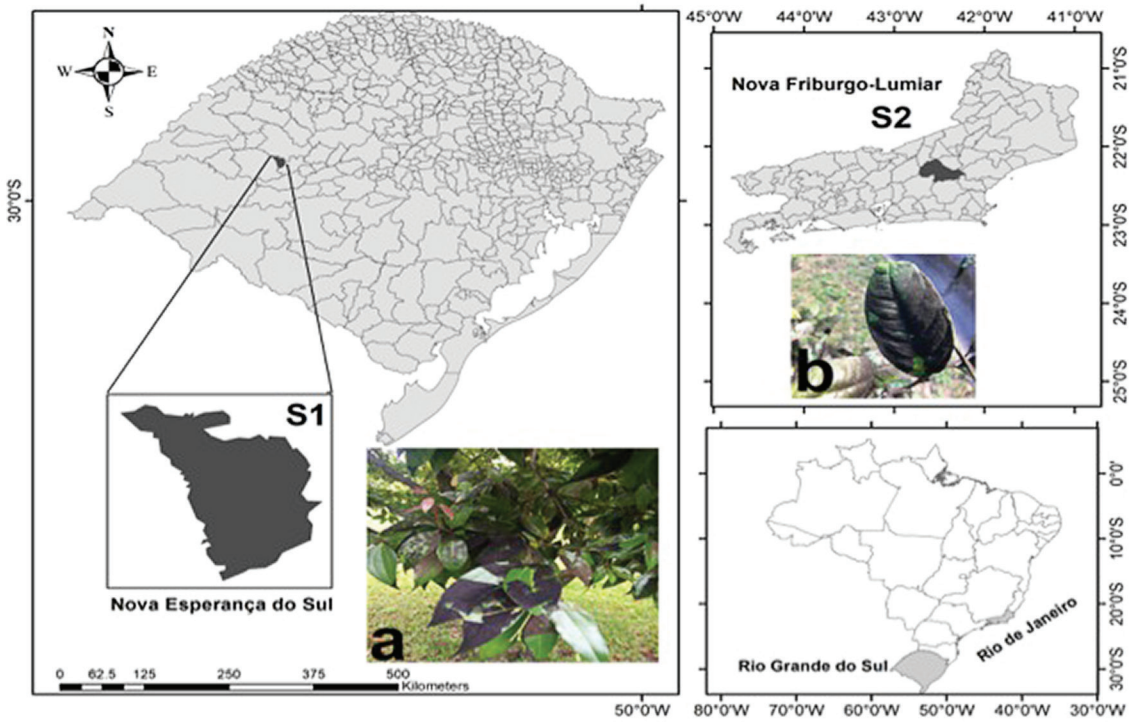

Figure 1. Location of the study area and samples collected in (S1) Nova Esperança do Sul, RS and (S2) Nova Friburgo-Lumiar, RJ. (a) Leaves of cinnamon tree covered by black particles at S1 and (b) leaves of citrus lemon tree covered by black particles at S2.

and stored in Falcon tubes (50.0 mL). From each site and period, approximately 5 g of black particles were removed from leaves surfaces to guarantee the homogeneity during analysis. The black particles, clean leaves, and soil samples were dried in an oven at 50 °C until completely dried. Dried samples were ground in agate ceramic mortar, homogenized, sieved (passed through a 100 mesh nylon sieve) and stored in Falcon tubes. The elements were extracted from 250 ± 3 mg samples using mixed-acid digestion HNO_3 (3.0 mL) + H_2O_2 (0.5 mL) and HF (0.1 mL) method into a Teflon bottle (Savillex, Minnesota, USA) on a hotplate for 4 h at 250 °C.[19] After digestion, the samples were cooled, opened and evaporated at 175 °C to begin the drying. In order to remove remnant HF, 3.0 mL of HNO_3 was added and evaporated two to three times[20] and then transferred into a Falcon tube (15.0 mL) and diluted with deionized water. The concentration of As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn in the final solutions were measured by inductively coupled plasma mass spectrometry (ICP-MS) Elan DRC II mass spectrometer (PerkinElmer, USA). Prior analysis of ICP-MS, the instrumental parameters were adjusted to provide minimal oxide formation rates of Ce (< 3%) and double charged species ratio of Ba (< 2%), respectively. Operating conditions for sample analysis by ICP-MS are presented in Table 1. ^{103}Rh was used as internal standard (IS) to correct and/or compensate non-spectral interferences and matrix effects. The elements were quantified through a six-point external calibration. Blank and triplicate samples were analyzed to provide quality control. The sample digestion and analysis procedure were checked using three certified reference material (CRMs): SRM 1648a (urban particulate matter), SRM 1515 (apple leaves), and SRM 8704 (Buffalo River sediment), which were published by National Institute of Standards and Technology (NIST, Gaithersburg, USA).

The limits of detection (LOD) and quantification (LOQ) were calculated as three and ten times the standard

Table 1. Instrumental conditions for the ICP-MS measurements

ICP-MS condition	Value
RF power / W	1150
Frequency / MHz	27.2
Plasma gas flow rate / (L min^{-1})	11.5
Auxiliary gas flow rate / (L min^{-1})	0.55
Nebulizer gas flow rate / (L min^{-1})	0.97
Sample uptake rate / (mL min^{-1})	0.6
Measurement mode	dual (PC/analog)
Acquisition time / s	1
Dwell time / ms	200
Replicate	6

The oxide ratio of CeO^+/Ce^+ and double charged species ratio of BaO^+/Ba^+ were maintained below 0.03 and 0.02, respectively. ICP-MS: inductively coupled plasma mass spectrometry; RF: radio frequency.

deviation of 10 blank measurements divided by the slope of the analytical curve. Table 2 shows the LOD, LOQ, and the extraction efficiencies of the CRMs used. As it can be seen, extraction efficiencies higher than 80% were obtained for most elements in both CRMs.

Statistical analysis

Differences between concentrations of toxic elements among clean leaves (CL), black particles collected at each period (P1, P2, and P3), and soil samples were analyzed by one-way analysis of variance (ANOVA), and subsequent *post-hoc* comparison was made using least significant difference (LSD) Tukey's test (value of $p < 0.05$ was considered to be significant).

The enrichment factor (EF) using the concentration of each toxic element was calculated by equation 1 with the aim to evaluate the source contribution:

$$EF_X = \frac{(C_X/C_n)_{sample}}{(C_X/C_n)_{background}} \quad (1)$$

where C_X and C_n are the concentrations of the element X and n in the sample and in the background. "Sample" refers to the concentrations of the elements present in the black particles removed from the leaves at Nova Esperança do Sul (S1) and Lumiar (S2), while "background" for S1 consists in the average soil composition value of both soils (superficial and deep) collected in the surroundings,[21,22] while the crustal composition given by Taylor and McLennan[23] was considered for S2. Fe was used as the reference. If EF < 1, the element is depleted in the environment and natural sources are predominant; if EF > 1, it means that the element is relatively enriched in the environment; while EF > 5 suggests that a large fraction of the element may be ascribed to anthropogenic sources.[24,25]

Cluster analysis (CA) was used to identify and characterize the association of the group of elements as well as to have an idea of the probable source. Statistical analyses were performed using CRAN R[26] free software through the following packages: ggplot2,[27] dplyr,[28] and ClusterOfVar.[29]

Results

Descriptive statistics

Mean concentration ± standard deviation (S.D.) and ANOVA results for As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn from each collection site measured in clean leaves of cinnamon at Nova Esperanca do Sul (S1) and of lemon at Lumiar (S2) collected *in situ* are shown in Table 3. Results show that there is a statistically significant difference among sampling sites ($p < 0.05$) for most of the elements measured, except for Sb (all sites) and Ba (S1A and S1B). Dried leaves (DLS1A) collected show higher content of Cr, Cu, Ni, and V than samples collected at the same site (CLS1A). However, it is very immature to attribute the death of the leaves to these elements. Differences ($p < 0.05$) found among elements measured from S2 and S1 may be ascribed to that the leaves were collected in different areas and from different tree species (cinnamon at S1 and lemon at S2). Plants, even being of the same species, accumulate different levels of pollutants if they grow in different

Table 2. Limits of detection and quantification by ICP-MS and concentration of certified reference materials of leaves (NIST SRM 151 - apple leaves), PM (NIST SRM 1648 - urban particulate matter) and sediment (NIST 8704 - Buffalo River sediment) used to evaluate the extraction efficiencies

Element	LOQ / (μg g^{-1})	LOD / (μg g^{-1})	SRM - apple leaves			SRM - urban particulate matter			SRM - Buffalo River sediment		
			Certified value / (μg g^{-1})	Found value / (μg g^{-1})	Extracted / %	Certified value / (μg g^{-1})	Found value / (μg g^{-1})	Extracted / %	Certified value / (μg g^{-1})	Found value / (μg g^{-1})	Extracted / %
As	0.004	0.013	0.038 ± 0.007	0.041 ± 0.011	108	115.5 ± 3.9	94.1 ± 4.2	81.5	17	16 ± 2	94
Ba	0.11	0.36	49 ± 2	45.13 ± 1.22	77.9	–	–	–	413 ± 13	409 ± 21	99
Cr	0.02	0.07	0.30	0.34 ± 0.03	113	402 ± 13	347 ± 10	86.3	121.9 ± 3.8	122.4 ± 3.0	100
Cu	0.01	0.04	5.64 ± 0.24	4.94 ± 0.51	87.6	610 ± 70	616 ± 21	101	5.64 ± 0.24	5.04 ± 0.34	89
Fe	4.16	13.73	83 ± 5	76 ± 7	91.0	3.92 ± 0.21	3.53 ± 0.03	90.0	3.97 ± 0.10	3.86 ± 0.20	97
Ni	0.02	0.06	0.91 ± 0.12	1.02 ± 0.05	112	81.1 ± 6.8	80.3 ± 5.2	99.0	42.9 ± 3.7	41.5 ± 2.12	96
Pb	0.09	0.30	0.47 ± 0.02	0.44 ± 0.03	93.3	6550 ± 33	6573 ± 21	94.2	150 ± 17	138 ± 12	92
Sb	0.002	0.006	0.013	0.012 ± 0.004	90.9	45.4 ± 1.4	29.4 ± 3.1	65	3.07 ± 0.32	2.85 ± 0.42	93
V	0.02	0.08	0.26 ± 0.03	0.30 ± 0.04	115	127 ± 11	138 ± 8	109	94.6 ± 4.0	91.2 ± 3.2	96
Zn	0.15	0.49	12.50 ± 0.30	13.40 ± 1.30	107	4800 ± 270	4286 ± 167	89.2	408 ± 15	419 ± 7	103

LOQ: limit of quantification; LOD: limit of detection; SRM: standard reference material; –: non reported.

Table 3. Mean values ± standard deviation (S.D.) and results of analysis of variance (ANOVA) of the elements measured in clean (CL) and dry leaves (DL) (without material deposited on the surface) collected at Nova Esperança do Sul (S1A and S1B) and Lumiar (S2)

Element	Mean ± S.D. / (μg g^{-1})				ANOVA *p*-value
	S1			S2	
	CLS1A 300 m	DLS1A 300 m	CLS1B 5 km	CLS2	
As	0.37 ± 0.06^{B}	0.44 ± 0.05^{AB}	0.49 ± 0.04^{A}	0.15 ± 0.04^{C}	[a]
Ba	65 ± 5^{A}	63 ± 3^{A}	69 ± 3^{A}	27 ± 3^{B}	[a]
Cr	0.28 ± 0.04^{C}	3.82 ± 0.88^{A}	0.78 ± 0.08^{C}	2.58 ± 0.20^{B}	[a]
Cu	3.96 ± 0.30^{C}	6.57 ± 0.39^{B}	8.40 ± 0.68^{A}	2.59 ± 0.29^{D}	[a]
Fe	113 ± 8^{C}	135 ± 19^{C}	180 ± 35^{B}	573 ± 18^{A}	[a]
Ni	1.27 ± 0.11^{C}	2.40 ± 0.53^{B}	5.65 ± 0.58^{A}	1.51 ± 0.27^{C}	[a]
Pb	0.12 ± 0.03^{B}	0.15 ± 0.02^{B}	0.26 ± 0.03^{A}	0.29 ± 0.04^{A}	[a]
Sb	0.05 ± 0.01	0.03 ± 0.02	0.02 ± 0.01	0.03 ± 0.01	n.d
V	0.12 ± 0.03^{B}	0.51 ± 0.14^{A}	0.42 ± 0.07^{A}	0.42 ± 0.04^{A}	[b]
Zn	23 ± 2^{A}	21 ± 3^{A}	18 ± 2^{B}	24 ± 2^{A}	[b]

Values on each horizontal line followed by the same capitalized letter do not differ significantly ($p = 0.05$). [a]Significant at 0.001 probability level; [b]significant at 0.01 probability level; n.d: no difference.

environments.[30] Similar to our results, Simon *et al*.[31] found significant differences in concentrations of Al, Ba, Cr, Fe, Mn, Si, Sr, and Zn among leaf tissues of three different trees and studied areas.

Table 4 shows the elemental concentrations of As, Ba, Cr, Cu, Fe, Ni, Pb, Sb, V, and Zn analyzed and ANOVA results from black particles removed from the leaves collected at S1 (three periods, P1, P2, and P3) and S2 (PS2). All elements present higher concentration values at S1 than S2. Statistically significant differences were observed between the three periods at S1 and PS2 for most of the elements, suggesting that black particles do not have the same origin. A similar tendency was observed for all elements over the three periods.

The analyses of soil samples collected at 300 m and 5 km far from the tannery area (S1) are shown in Table 5. Results show minimal variation (not significant difference, $p > 0.05$) between soils collected at 300 m for most elements, except Sb. In contrast, higher concentration values for all elements collected were observed at 300 m than 5 km. These results may indicate the influence of anthropogenic sources.

Table 4. Mean values ± standard deviation (S.D.) and results of the analysis of variance (ANOVA) of the elements measured in black particles collected at Nova Esperança do Sul (S1) during the three periods (P1, P2, and P3) and Lumiar (PS2)

Element	Mean ± S.D. / (μg g^{-1})				ANOVA *p*-value
	S1			S2	
	P1	P2	P3	PS2	
As	3.75 ± 0.20^{AB}	4.12 ± 0.38^{A}	3.13 ± 0.62^{B}	0.34 ± 0.05^{C}	[a]
Ba	87 ± 3^{AB}	91 ± 3^{A}	83 ± 6^{B}	61 ± 2^{C}	[a]
Cr	69 ± 3^{A}	44 ± 2^{B}	52 ± 12^{B}	11 ± 2^{C}	[a]
Cu	18 ± 2^{B}	25 ± 3^{A}	26 ± 2^{A}	4.14 ± 0.46^{C}	[a]
Fe	7484 ± 189^{A}	7083 ± 259^{A}	7107 ± 825^{A}	4745 ± 123^{B}	[a]
Ni	4.01 ± 0.19^{A}	5.21 ± 0.19^{B}	5.31 ± 1.11^{B}	3.05 ± 0.32^{B}	[a]
Pb	5.10 ± 0.41^{AB}	7.40 ± 0.40^{A}	7.17 ± 2.43^{A}	2.97 ± 0.30^{B}	[b]
Sb	0.37 ± 0.04^{A}	0.54 ± 0.05^{B}	0.29 ± 0.02^{C}	0.05 ± 0.02^{D}	[a]
V	24 ± 3^{B}	32 ± 3^{A}	25 ± 2^{B}	6.2 ± 0.3^{C}	[a]
Zn	76 ± 2^{B}	84 ± 5^{A}	80 ± 2^{AB}	30 ± 4^{C}	[a]

Values on each horizontal line followed by the same capitalized letter do not differ significantly ($p = 0.05$). [a]Significant at 0.001 probability level; [b]significant at 0.01 probability level.

Table 5. Mean values ± standard deviation (S.D.) and results of the analysis of variance (ANOVA) of the trace elements measured in soil samples collected at 300 m and 5 km of distance from the tannery area (all samples collected in October 2017)

Element	Mean ± S.D. / (μg g^{-1})			ANOVA *p*-value
	Deep soil	Superficial soil	Deep soil	
	300 m	300 m	5 km	
As	5.79 ± 1.20^{A}	5.92 ± 1.19^{A}	1.54 ± 0.34^{B}	[b]
Ba	421 ± 22^{A}	358 ± 86^{A}	47.6 ± 1.4^{B}	[a]
Cr	47.78 ± 2.24^{B}	60.93 ± 3.82^{A}	5.43 ± 0.14^{C}	[a]
Cu	83.01 ± 2.15^{A}	70.81 ± 6.13^{B}	5.35 ± 0.18^{C}	[a]
Fe	54496 ± 1427^{A}	54940 ± 1486^{A}	4582 ± 249^{B}	[a]
Ni	13.68 ± 1.50^{A}	9.93 ± 0.83^{B}	2.10 ± 0.03^{C}	[a]
Pb	35.87 ± 2.77^{A}	34.03 ± 1.48^{A}	4.93 ± 0.67^{B}	[a]
Sb	1.24 ± 0.79^{A}	0.45 ± 0.07^{AB}	0.09 ± 0.02^{B}	n.d
V	167 ± 27^{A}	183 ± 29^{A}	18.97 ± 1.11^{B}	[a]
Zn	197 ± 5^{A}	209 ± 9^{B}	14.73 ± 2.14^{C}	[a]

Values on each horizontal line followed by the same capitalized letter do not differ significantly ($p = 0.05$). [a]Significant at 0.001 probability level; [b]significant at 0.01 probability level; n.d: no difference.

Enrichment factor (EF)

The EF of each element was calculated according to equation 1 only for black particles collected at site S1A (three periods independently, P1, P2, and P3) and S2 and are shown in Figure 2. EF > 5 suggests anthropogenic influence, as it is seen here for Cr (all periods) and As (P1 and P2) in site SA1, while Ni, Pb, Ba, Zn, Sb, V, and Cu present 1 < EF < 4, indicating a slight enrichment of these elements in the environment. In contrast, EF ≤ 1 were observed for As, Pb, Ba, Zn, Sb, V, and Cu at site S2 suggesting depletion of these elements in this area (except Cr and Ni). This is not surprising because S2 is a rural area. In general, EF values were in the order: Cr > As > Zn > Ni > Cu > Sb > Ba > V > Pb, with Cr exhibiting always the highest levels during the three periods at S1A.

Cluster analysis (CA)

CA was applied to the concentration data of soils (superficial and deep) and black particles removed from leaves (three periods) collected at site S1A (black particles collected at S2 were not considered). The resulting dendrogram (Figure 3) revealed two main groups: Cr constitutes the group 1, cluster 1, while Ni, V, Zn, Fe, Ba, Cu, and Pb (subgroup 2A) and As and Sb (subgroup 2B) constitute the group 2. These results suggest that group 1 has an anthropogenic origin, while group 2 may have a mixture of both natural and anthropogenic sources.

Discussion

Concentration levels of Cr obtained near tannery area (300 m) for both soils and black particles were always higher than samples collected at 5 km and in the Lumiar site (S2). In terms of EF, Cr (EF > 5) and As (EF > 5, two first periods) were clearly enriched in the sampling periods in the center of Nova Esperança do Sul (S1A) and are likely associated with anthropogenic sources. In the literature,[2,32-34] several researchers related high concentrations levels of Cr and other toxic metals found in groundwater, effluents, and soils due to poor waste management of leather industries. In the study area, chromium-tanned leather has been used for many decades in the manufacture of a large variety of leather-based products by several companies installed here; therefore, the enrichment of this element may be attributed to the tannery industry.

Arsenic is a metalloid that belongs to group 15 of the periodic table and occurs naturally in the environment.[35] However, this element is related to cancer risk.[36,37] Arsenic is used in the manufacture of several products such as glass, ceramics, electronics, cosmetics, in pesticides and herbicides formulations[38] and biocides that usually are used to wastewater treatment.[39] The land in the study area is used to produce a variety of products, such as corn, soy, tobacco, cassava, sugar cane and rice, and agrochemicals are usually employed by farmers. As there are no other industries in this area, we may affirm that most of found

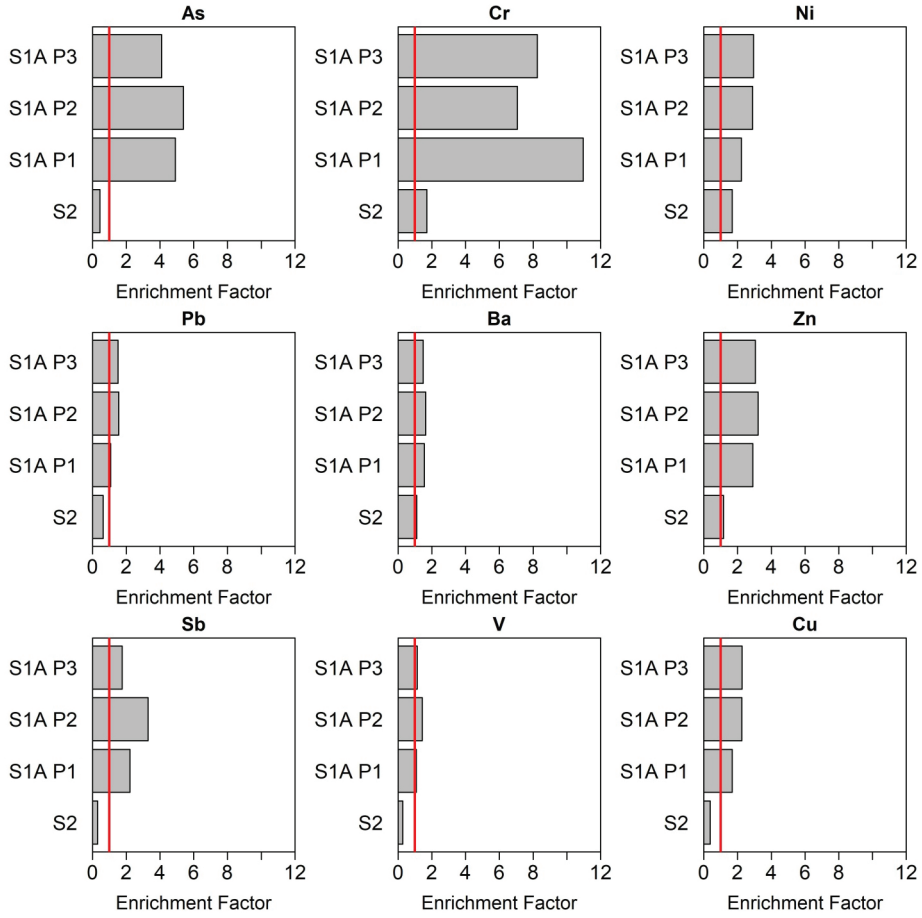

Figure 2. Comparison among EFs of the elements measured in black particles removed from leaves in Nova Esperança do Sul, RS (S1) (three periods: P1, P2, and P3) and Lumiar, RJ (S2). Fe is used as the reference element (red vertical line).

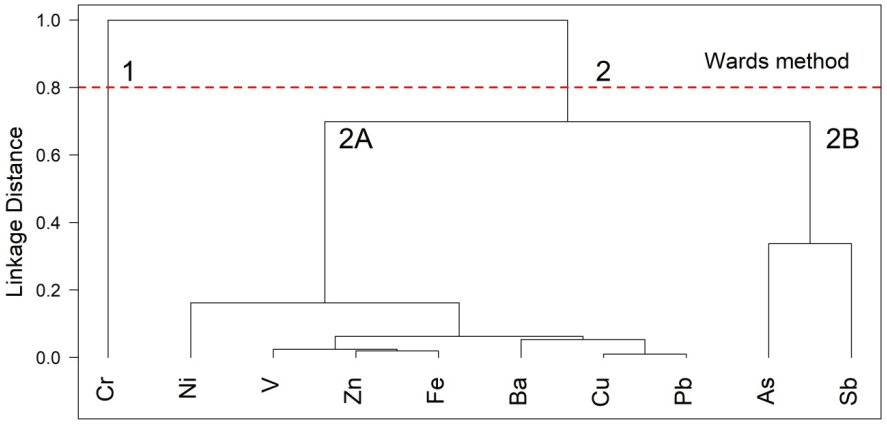

Figure 3. Dendrogram representing the grouping of elements based on analysis of black particles removed from leaves of the three sampling periods and soil samples collected at Nova Esperança do Sul, RS (S1A).

As are related to agricultural activities. In the literature, for instance, Zhou *et al.*[38] determined As concentrations in arable soils and found an increasing accumulation trend over past decades, which is related to the long-term application of phosphate fertilizers in agricultural practice, while Bolan *et al.*[40] related this element to the production of rice grain and complementary medicines.

For the other elements (Ni, Pb, Ba, Zn, Sb, V, and Cu) low enrichment was observed in this area. These elements usually are related to vehicular sources,[41-44] and its low enrichment may be explained because this region is a rural area with reduced vehicular fleet.

The group 1 of CA shows clearly Cr as a separate variable, which is consistent with the fact that chromium is

a key element in the tanning process to obtain leather. From subgroup 2B, it can be noted the presence of Sb, which is a metalloid occurring naturally in the environment as trace elements.[35] However, in the last decades, Sb was associated with traffic because several parts of the vehicle contain Sb alloys and other Sb compounds.[45-47] As can be seen in the subgroup 2B from CA, arsenic is a little separated of the other elements, which may indicate that it is released from anthropogenic sources, but not necessarily from the same source as Ni, Cu, and Zn. Arsenic also occurs naturally and it is noted for its relation with Sb. Both elements were related to anthropogenic activities that can produce adverse effects on humans and the environment.[48]

Conclusions

This study evaluated the content of toxic elements in a region surrounded by a tannery area, located at Nova Esperança do Sul, RS, Brazil. The results of the analysis of black particles collected near leather industry show a higher concentration of all elements analyzed, especially Cr in the three sampling periods compared to a rural area (Lumiar, RJ, Brazil). This result confirmed that the presence of black particles mostly is related to the leather industry than the presence of sooty mold spread by insects. In the same way, soil samples (both deep soil and surface soil) collected around tannery area showed higher concentration for all elements than deep soil collected at 5 km of distance. Enrichment factor higher than 5 were obtained for Cr (three periods) and As (two periods) suggesting the anthropogenic influence of both elements. Cluster analysis isolated Cr in the first group demonstrating clearly the influence of this element in the study area, whereas As was related to the use of agrochemicals (pesticides or herbicides) by farmers. On the other hand, EF > 4 for Ni, Pb, Ba, Zn, Sb, and Cu were found, which is in agreement because the study area has rural characteristics.

Acknowledgments

The authors are grateful to CAPES, FAPERJ, and CNPq for financial support. A. G. thanks CNPq for the Bolsa de Produtividade and to FAPERJ for the Auxilio Cientista do Nosso Estado.

References

1. Mwinyihija, M.; *Ecotoxicological Diagnosis in the Tanning Industry*; Springer Science: Aberdeen, 2010.
2. Mondal, N. C.; Saxena, V. K.; Singh, V. S.; *Environ. Geol.* **2005**, *48*, 149.
3. Langård, S.; Costa, M. In *Handbook on the Toxicology of Metals*, vol. 3, 3rd ed.; Nordberg, G. F.; Fowler, B. A.; Nordberg, M.; Friberg, L. T., eds.; Academic Press: New York, 2007, ch. 24.
4. Monteiro, M. I. C.; Fraga, I. C. S.; Yallouz, A. V.; de Oliveira, N. M. M.; Ribeiro, S. H.; *Talanta* **2002**, *58*, 629.
5. Liang, J.; Fang, H. L.; Zhang, T. L.; Wang, X. X.; Liu, Y. D.; *Urban For. Urban Greening* **2017**, *27*, 390.
6. Tarricone, K.; Wagner, G.; Klein, R.; *Ecol. Indic.* **2015**, *57*, 341.
7. Filipović-Trajković, R.; Ilić, Z. S.; Šunić, L.; Andjelković, S.; *J. Food Agric. Environ.* **2012**, *10*, 959.
8. Deljanin, I. V.; Tomašević, M. N.; Urošević, M. P. A.; Antanasijević, D. Z.; Perić-Grujić, A.; Ristić, M.; *Ecol. Indic.* **2014**, *45*, 640.
9. Bhattacharya, T.; Chakraborty, S.; Tuteja, D.; Patel, M.; *Open J. Met.* **2013**, *3*, 42.
10. Simon, E.; Baranyai, E.; Braun, M.; Cserháti, C.; Fábián, I.; Tóthmérész, B.; *Sci. Total Environ.* **2014**, *490*, 514.
11. Matin, G.; Kargar, N.; Buyukisik, H. B.; *Ecol. Eng.* **2016**, *90*, 331.
12. Shi, J.; Zhang, G.; An, H.; Yin, W.; Xia, X.; *Atmos. Pollut. Res.* **2017**, *8*, 836.
13. Kimbrough, D. E.; Cohen, Y.; Winer, A. M.; Creelman, L.; Mabuni, C.; *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 1.
14. World Health Organization (WHO); *WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide*; WHO Press: Geneva, 2006. Available at http://apps.who.int/iris/bitstream/10665/69477/1/WHO_SDE_PHE_OEH_06.02_eng.pdf, accessed in September 2018.
15. Paraginski, A. L.; *Rev. Adm. Innov.* **2014**, *11*, 55.
16. Giannetti, B. F.; Bonilla, S. H.; Almeida, C. M. V. B.; *J. Cleaner Prod.* **2004**, *12*, 361.
17. Joseph, K.; Nithya, N.; *J. Cleaner Prod.* **2009**, *17*, 676.
18. ftp://ftp.ibge.gov.br/Estimativas_de_Populacao/Estimativas_2016/estimativa_dou_2016_20160913.pdf, accessed in August 2018.
19. Bing, H.; Wu, Y.; Zhou, J.; Sun, H.; *Chemosphere* **2016**, *165*, 388.
20. Ardini, F.; Soggia, F.; Rugi, F.; Udisti, R.; Grotti, M.; *J. Anal. At. Spectrom.* **2010**, *25*, 1588.
21. Liu, E.; Yan, T.; Birch, G.; Zhu, Y.; *Sci. Total Environ.* **2014**, *476-477*, 522.
22. Kara, M.; Dumanoglu, Y.; Altiok, H.; Elbir, T.; Odabasi, M.; Bayram, A.; *Atmos. Res.* **2014**, *149*, 204.
23. Taylor, S. R.; McLennan, S. M.; *The Continental Crust: Its Composition and Evolution: An Examination of the Geochemical Record Preserved in Sedimentary Rocks*; Blackwell Scientific Publications: Oxford, Melbourne, 1985.
24. Enamorado-Báez, S. M.; Gómez-Guzmán, J. M.; Chamizo, E.; Abril, J. M.; *Atmos. Res.* **2015**, *155*, 118.
25. Wu, Y. S.; Fang, G. C.; Lee, W. J.; Lee, J. F.; Chang, C. C.; Lee, C. Z.; *J. Hazard. Mater.* **2007**, *143*, 511.

26. R Core Team; *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing, Vienna, Austria, 2015.
27. Wickham, H.; Chang, W.; Henry, L.; *ggplot2: Elegant Graphics for Data Analysis*, R Package Version 3.3.3; Springer-Verlag: New York, 2009. Available at https://cran.r-project.org/web/packages/ggplot2/ggplot2.pdf, accessed in September 2018.
28. Wickham, H.; François, R.; Henry, L.; Müller, K.; *dplyr: A Grammar of Data Manipulation*, R Package Version 0.7.4.; 2017. Available at https://CRAN.R-project.org/package=dplyr, accessed in September 2018.
29. Chavent, M.; Kuentz, V.; Liquet, B.; Saracco, J.; *ClustOfVar: Clustering of variables*, R Package Version 0.8; 2013. Available at https://CRAN.R-project.org/package=ClustOfVar, accessed in September 2018.
30. Annan, K.; Dickson, R.; Nooni, I.; Amponsah, I.; *Pharmacogn. Res.* **2013**, *5*, 103.
31. Simon, E.; Harangi, S.; Baranyai, E.; Fábián, I.; Tóthmérész, B.; *Urban For. Urban Greening* **2016**, *20*, 12.
32. Srinivasa Gowd, S.; Ramakrishna Reddy, M.; Govil, P. K.; *J. Hazard. Mater.* **2010**, *174*, 113.
33. Febriana, S. A.; Jungbauer, F.; Soebono, H.; Coenraads, P. J.; *Int. Arch. Occup. Environ. Health* **2012**, *85*, 517.
34. Júnior, H. M.; da Silva, J.; Arenzon, A.; Portela, C. S.; Ferreira, I. C. F. S.; Henriques, J. A. P.; *Chemosphere* **2007**, *67*, 1211.
35. Wilson, S. C.; Lockwood, P. V.; Ashley, P. M.; Tighe, M.; *Environ. Pollut.* **2010**, *158*, 1169.
36. Morais, S.; Garcia e Costa, F.; Pereira, M. L. In *Environmental Health - Emerging Issues and Practice*, vol. 10; Oosthuizen, J., ed.; IntechOpen: Rijeka, 2012, p. 227-246.
37. Gamboa-Loira, B.; Cebrián, M. E.; Franco-Marina, F.; López-Carrillo, L.; *Environ. Res.* **2017**, *156*, 551.
38. Zhou, Y.; Niu, L.; Liu, K.; Yin, S.; Liu, W.; *Sci. Total Environ.* **2018**, *616-617*, 156.
39. Bollmann, U. E.; Tang, C.; Eriksson, E.; Jönsson, K.; Vollertsen, J.; Bester, K.; *Water Res.* **2014**, *60*, 64.
40. Bolan, S.; Kunhikrishnan, A.; Chowdhury, S.; Seshadri, B.; Naidu, R.; Ok, Y. S.; *Chemosphere* **2017**, *182*, 433.
41. Kertész, Z.; Szoboszlai, Z.; Angyal, A.; Dobos, E.; Borbély-Kiss, I.; *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 1924.
42. Akiyama, K.; *Talanta* **2006**, *70*, 178.
43. Matti Maricq, M.; *J. Aerosol Sci.* **2007**, *38*, 1079.
44. Amato, F.; Pandolfi, M.; Viana, M.; Querol, X.; Alastuey, A.; Moreno, T.; *Atmos. Environ.* **2009**, *43*, 1650.
45. Fujiwara, F.; Rebagliati, R. J.; Marrero, J.; Gómez, D.; Smichowski, P.; *Microchem. J.* **2011**, *97*, 62.
46. Sanchez-Rodas, D.; Alsioufi, L.; Sanchez de la Campa, A. M.; Gonzalez-Castanedo, Y.; *J. Hazard. Mater.* **2017**, *324*, 213.
47. Hu, X.; He, M.; Li, S.; *J. Environ. Sci. (China)* **2015**, *29*, 11.
48. Cooper, R. G.; Harrison, A. P.; *Indian J. Occup. Environ. Med.* **2009**, *13*, 3.

Submitted: May 23, 2018
Published onlline: September 4, 2018