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Metals associated with airborne particulate matter in road dust and tree bark collected in a megacity (Buenos Aires, Argentina)

Fabián G. Fujiwara[a,b,c], Darío R. Gómez[a,b,d], Laura Dawidowski[a,b,d], Patricia Perelman[e], Ana Faggi[e,f,*]

[a] Gerencia Química, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, B1650KNA, San Martín, Prov. Buenos Aires, Argentina
[b] Instituto de Investigación e Ingeniería Ambiental, Universidad de San Martín, Peatonal Belgrano 3563, 1650, San Martín, Prov. Buenos Aires, Argentina
[c] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, C1033AAJ, Buenos Aires, Argentina
[d] Departamento de Ingeniería Química, Facultad de Ingeniería; Universidad de Buenos Aires, Pabellón de Industrias, Ciudad Universitaria, 1428, Buenos Aires, Argentina
[e] Museo Argentino de Ciencias Naturales, Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Angel Gallardo 470, DJR1405, Buenos Aires, Argentina
[f] Universidad de Flores, Av. Nazca 274, 1406, Buenos Aires, Argentina

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ABSTRACT

Multielemental profiles in bark suber of green ash trees and road dust collected in three representative areas of Buenos Aires, Argentina were assessed as potential air pollution indicators. Ten elements: Al, Ba, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, were measured by inductively coupled plasma optical emissions spectrometry and their concentrations in the Buenos Aires road dust are reported for the first time. Measured concentrations and enrichment factors were used to characterize the environmental signatures of air pollution sources with impact in the studied areas. The analysis based on enrichment factors provided a common framework for the comparison of our results on tree bark and road dust with PM10 concentrations measured in previous studies. This unified analysis proved to be a valuable tool showing the consistency of our findings. The analysis based on either concentration profiles or enrichment factors showed that bark clearly differentiated sampling areas, resulting to be a better air pollution indicator than road dust. Road dust did not provide a clear differentiation between areas; this might be indicative of a certain degree of spatial mixture on street surfaces.

1. Introduction

Levels of air pollution associated with airborne particulate matter can be assessed directly through passive, active or automatic monitoring (Chow, 1995) or indirectly by using biomonitors (Burger, 2006) or other accumulators such as road dust (Keller and Lamprecht, 1995) as atmospheric particles are deposited by dry and wet deposition both on vegetal (e.g., lichens, mosses, leaves and bark) and soil surfaces. Since the introduction in the last century of biomonitors as an alternative to direct detection of pollutants in air quality control, a number of studies worldwide reported on the effectiveness of tree bark as an environmental indicator (Nimis, 1990). More recently street or road dust has been used to analyze trends in pollution associated with particulate matter (de Miguel et al., 1997).

The levels of different metals and metalloids contained in tree bark constitute an ecological indicator that has the power to summarize and represent a larger body of statistics and to serve as proxy measures for lacking information (Cole et al., 1998). Bark is made of different compartments with their own biological role and their element content (Catinon et al., 2009). The analysis of suber, which as the outer layer of bark is a tissue exposed to the air for years, can give precise information about changes that occur in the air conditions of specific areas (Spangenberg et al., 2002; Bellis et al., 2003). Road dust constitutes also a primary receptor for urban pollutants being in general the material that firstly gets into contact with traffic emissions (Dongarrà et al., 2003). However, its residence time is much shorter than that of bark because it is easily removed under natural conditions (wind, rain) and by human activities.

Multiple sources contribute to metal pollution in road dust (Sutherland and Tolosa, 2000) and tree bark (Nimis, 1990). Air pollution related sources include automotive exhaust emission, vehicle wear, construction, and particulate emissions from diverse stationary sources (Abdul-Wahab and Yaghi, 2004).

In general, tree bark and road dust may be considered as complementary but not interchangeable indicators on a timescale basis. In spite of inherent differences, it is likely that assessing metal levels in both matrices would be useful for screening environmental conditions in areas of concern.

Many studies have shown that tree bark can be successfully used in atmospheric monitoring. Some authors have comparatively

* Corresponding author at: Universidad de Flores, Av. Nazca 274, 1406, Buenos Aires, Argentina. Tel.: +54 11 4982 6670x236; fax: +54 11 4982 6670x172.
E-mail addresses: afaggi@macn.gov.ar, afaggi2003@yahoo.com.ar (A. Faggi).

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assessed levels of metals accumulated in bark vs. those present in lichen samples (Pacheco et al., 2002, 2008; Rusu et al., 2006), vs. higher epiphyten (*Tillandsia usneoides*) or vs. airborne particulate matter (Ballach et al., 2002; Walkenhorst et al., 1993). For the particular case of Buenos Aires, Perelman et al. (2006) discussed the presence of Al, Ba, Cr, Cu, Fe, Ni and Pb in bark of green ash tree (*Fraxinus pennsylvanica*) along an urban to periurban gradient.

Many studies of concentrations of heavy metals in street dust in large cities have been conducted in the Northern Hemisphere (Charlesworth et al., 2003; Shi et al., 2008 and references therein), but little has been done in Latin America, the most urbanized region of the world.

Recent studies in Italy have assessed air pollution levels through the combined analysis of road dust and either leaves (Dongarrà et al., 2003) or needles (Bosco et al., 2005). To the best of our knowledge, no studies address thus far the relationship between elements accumulated in bark and the particles of road dust deposited on the adjacent street floor. The aim of the present study is to face this existing gap by (i) addressing the comparison of the multielemental concentration profiles in bark and road dust, focusing on those metals exhibiting enrichment or depletion with respect to the corresponding environmental matrix selected as reference, and (ii) assessing the relative performance of bark and road dust to reveal the air pollution signatures in the environment. In addition, we report for the first time the content of ten elements in samples of road dust collected in Buenos Aires city.

We hypothesize that: (i) there is a recognizable concentration profile in bark and road dust collected from the same areas and that this distinctive characteristic allows differentiating areas and (ii) bark is a better indicator of pollution than road dust.

2. Materials and methods

2.1. Studied area

Buenos Aires (34°38′S, 58°28′W), the capital and largest city of Argentina, is located on the southern shore of the La Plata river. It lies over a vast plain that belongs to the pampa region covering a surface of about 200 km^2. It has a population of about 3 million people, which implies the highest average population density of the country (14,947 inhabitant km^{-2}). The city is the financial, commercial and cultural center of Argentina and the hub of the metropolitan area of Buenos Aires (MABA) that is composed by the city itself and 24 neighboring districts, which with about 14 million people is the 10th megalopolis in the world and the third in Latin America. Road traffic is the largest source of air pollutants in Buenos Aires, which has a fleet composed by about 1 million passenger cars, 40,000 taxis, 200,000 trucks and 150 city bus lines comprising ~15,000 buses (D'Angiola et al., 2010). Light-duty vehicles use unleaded gasoline, diesel oil or compressed natural gas while diesel oil is the fuel exclusively used by trucks and buses. Leaded gasoline was banned in 1995 in Argentina.

2.2. Sample collection

Nine bark samples of *Fraxinus pennsylvanica* (green ash) were collected in 2006 in three areas in Buenos Aires city (although we have collected samples of bark suber, we have opted to use the generic denomination of bark as this has been frequently used in the biomonitoring literature). These areas are located following a transect covering a 7.5 km length on the ENE-WSW direction (Fig. 1) and

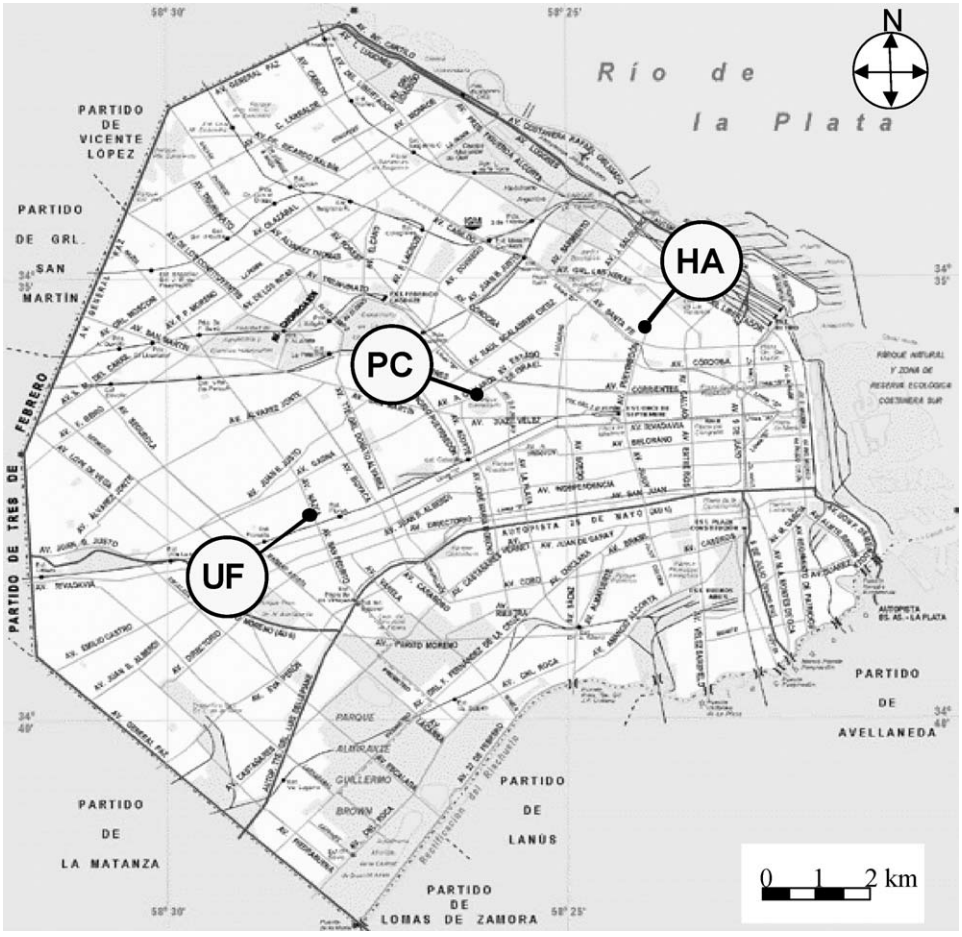

Fig. 1. Buenos Aires City with the sample collection areas.

Table 1
Characteristics of the sampling areas.

Sampling area	Name	Surrounding conditions
HA	Hospital Alemán	Located at ~3.6 km from the La Plata River on a densely populated area (28,049 inhabitants km^{-2}) with multistory buildings forming street canyons. Exposed to emissions from heavy traffic (~2700 vehicles h^{-1}), composed by cars and buses, that gets usually congested at rush hours of the morning and afternoon. Bark was collected from four trees that are planted along the streetscape of an arterial street and two side streets. Road dust was collected at the intersection of the arterial street and one side street.
PC	Parque Centenario	Located near the geographical center of the city close to a large park almost circular in shape with a diameter of ~500 m surrounded by a two-way street. The area is less densely populated than the area surrounding HA (25,045 inhabitants km^{-2}). Exposed to emissions from heavy traffic (~1600 vehicles h^{-1}), composed by cars and buses. The park was under rehabilitation and restoration processes. The park and its immediate vicinity offer better ventilation conditions and favor dust resuspension. Bark was collected from three trees that are planted along the sidewalk that surrounds the park. Road dust was collected at a place that is close to the trees at the surrounding street.
UF	Universidad de Flores	Located on a commercial neighborhood (19,294 inhabitants km^{-2}) at one of the heavy-weight traffic arterial roads of the city. Exposed to emissions from heavy traffic (~1600 vehicles h^{-1}), composed predominantly by large trucks. The area is characterized by a stop-and-go traffic pattern caused by the presence of railroad truck located at ~50 m of the sampling site. The circulation of the train provokes also an important resuspension of dust. Bark was collected from two trees that are planted along the sidewalk of this arterial street. Road dust was collected at the intersection of the arterial street and a side street.

were chosen because they represent different conditions regarding land use and traffic pattern (Table 1). Mature trees (~30–40 years old) with trunk about 30 cm in diameter were chosen growing along the thoroughfares in each area. The bark samples of ~10 cm × 10 cm in size were taken at 1.50 m height (starting from the base of the tree) and from the face of trunk exposed to vehicular traffic. Each tree was sampled twice and the samples were mixed to obtain one bulk sample. To have a reference tree bark from a cleaner area with negligible traffic influence, we collected bark from four trees growing in the natural reserve 'Los Robles' (Moreno district) which is located in the MABA, 45 km from the city core, covering ~1000 ha.

Roadside dust samples were collected from within two meters of the road curb, in the three areas described in Table 1, using a clean plastic dustpan and brush. An area of ~2 m^2 was swept to obtain a sufficiently large sample providing good spatial coverage. The collected samples were placed in a clean polyethylene bag for transfer to the laboratory and storage.

2.3. Sample preparation

For the determination of the elemental composition in tree bark, 2 g of suber sample was digested in 15 ml concentrated nitric acid (HNO_3, J.T. Baker, 69–70%) in a PTFE beaker (Schulz et al., 1999; Odukoya et al., 2000; Suzuki, 2006). The digest was left at room temperature over 24 h and subsequently heated at 100 °C to almost dryness. The residue was dissolved in 10 ml of deionized water and the resulting solution was centrifuged at 5000 rpm for ~4 min, no visible residual solid particles were detected. The solution was filtered and transferred to a 100 ml volumetric flask and diluted to the mark. Since to the best of our knowledge no standard reference material is available for tree bark and because of the lack of alternative reference materials in our laboratory, accuracy of measurements was estimated through a recovery test performed by adding aliquots of the analytes to the sample solutions, as appropriate. Road dust samples were dried at 100 °C for 2 h and sieved. After sieving four fractions were obtained with the following particle diameter: $A < 37$ μm, $B = 37–50$ μm, $C = 50–100$ μm and $D > 100$ μm. For one sample taken in area HA (HA-RD-2), only negligible amount of particles were present in fraction A. For this work, we selected fractions A and B since they are composed by the smaller size particles that are capable of being re-suspended. For each of these fractions, a 0.5 g portion was weighed into a PTFE beaker and an acid mixture containing 6 ml HCl, 2 ml HNO_3 and 1 ml HF was added and was allowed to undergo digestion at room temperature for 24 h (Imperato et al., 2003). The mixture of sample + acid was subsequently heated at 100 °C to almost dryness. After digestion, 10 ml of deionized water was added and the resulting mixture was centrifuged at 5000 rpm for four minutes. The solution was filtered and the resulting solution was transferred to a 25 ml volumetric flask and diluted to the mark. Aliquots of the standard reference materials SRM 2711 Montana soil (NIST, USA) and SRM 2709 San Joaquin soil (NIST, USA) were subject to the same treatment and included in the overall analytical process to assess the digestion procedure and check the accuracy of the determination. Deionized distilled water (DDW) was produced by a commercial mixed-bed ion exchange system Barnstead (Dubuque, IA, USA) fed with distilled water. All reagents were of analytical grade, HCl, HNO_3 and HF were used for sample treatment and preparation of the standards. Commercially available 1000 mg l^{-1} standard solutions (Merck) of the elements analyzed were used. Diluted working solutions were prepared daily by serial dilutions of those stock solutions. All glassware and plastic bottles were treated in a solution 10% (v/v) nitric acid for 24 h and then washed with deionized water.

2.4. Sample elemental analysis

Ten elements namely, Al, Ba, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, were measured by inductively coupled plasma optical emissions spectrometry (ICP OES). A PerkinElmer (Norwalk, CT, USA) ICP Optima 3100 XL (axial view) simultaneous inductively coupled Ar plasma optical emission spectrometer provided with a Model AS 90 autosampler was used for trace elements determination. Welding Ar from Indura (Buenos Aires, Argentina) was used for ICP OES determinations.

2.5. Data analysis

Correlation and cluster analysis were carried out using the STATISTICA software (StatSoft Inc.). Correlations between element concentrations per area and per each type of particulate sample (road dust or bark) were analyzed through correlation matrices and scatter plots of all possible pairs.

The two sets of measured concentrations were independently classified by cluster analysis using hierarchical tree plots in the 10-dimensional concentration space to elucidate the potential of the measured set of concentrations to differentiate areas. Several combinations of linkage rules and distances were explored.

For each element (X), enrichment factors as defined in Eq. (1), were used to obtain a common basis to compare two different types of concentrations as road dust concentration is referred to the total mass of dust in the sample and tree bark concentration is referred

to the total mass of the bark.

$$EF_X = \frac{(X/E)_{sample}}{(X/E)_{reference\ soil}} \quad (1)$$

where *sample* refers to either road dust or tree bark; *reference soil* corresponds to the elemental profile of the local soil as measured by Custo et al. (2005) for Cr, Cu, Fe, Mn, Pb and Zn. For the three remaining elements, Al, Ba and Mg, the values reported by Taylor (1964) were adopted because these elements were not reported in the local reference. This selection is justified on the basis that the data by Custo et al. (2005) are in good agreement with the average composition of the crustal rock. EFs for both matrices were calculated using Eq. (1) using the geological component Fe as normalizing element. Aluminum was not considered because of the relatively low recovery obtained for the reference materials (Section 3.1.1)

We have used EF as defined in Eq. (1) also for suber because this tree bark component is the exterior part of the substrate on which the trace elements are deposited as a consequence of the dispersion and distribution of the airborne particles containing them. Furthermore, the use of this normalizing index has provided a common ground for the comparison of tree bark and road dust levels with those of airborne PM10 measured in the city of Buenos Aires by Smichowski et al. (2004). This study collected PM10 samples in nine areas of the city and reported concentrations of 13 elements, seven of which (Al, Cu, Fe, Mn, Ni, Pb and Zn) were also considered in our study.

3. Results

3.1. Results

3.1.1. Concentration profiles in tree bark and road dust

Recovery data of the tree bark samples spiked with 40 ng l^{-1} of Cr and Ni, 1 μg l^{-1} of Mn and Pb, 2 μg l^{-1} of Ba, Cu and Zn, 10 μg l^{-1} of Al and 20 μg l^{-1} of Fe and Mg resulted to be in the range 96–102%. For road dust, the analysis of the two standard reference materials exhibits a general good agreement between the certified values for each element and the experimental data obtained in this study. For the SRM NIST 2711 (Montana soil), recovery values were between 78.9% for Cu and 126.7% for Mg while for SRM NIST 2709 (San Joaquin soil), the values were between 88.6% for Ni and 112% for Fe. Low recoveries were obtained only for Al for both SRM (~65%) and for Mg for SRM NIST 2709 (62.9%). It is plausible to attribute these values to the dilution necessary to obtain acceptable analytical signal levels. As these recovery values may be associated with a potential source of errors, Al and Mg concentrations measured in this study are considered cautiously.

Table 2 summarizes the average values of the measured concentrations of the collected samples in the three areas. It also reports the concentration profiles of reference tree bark and topsoil. In general, Al, Fe, Mg and Zn exhibit the highest concentrations in the two types of samples. However, element concentrations follow different order not only per sample type but also per area. Lowest concentrations correspond to Cr > Ni for all samples and all areas.

Concentrations of Al, Fe and Mg in tree bark in area PC are significantly different than in the two other areas. Aluminum and Fe levels in PC are ~twice higher than in HA and UF while Mg level is ~three times lower. Tree bark samples exhibit similar profiles for the rest of the elements. Concentrations of Al, Cr, Fe, Ni, Pb and Zn in the three studied areas are higher than those measured in the reference site, which is relatively isolated from traffic influence. Conversely, the plant essential element Mg in the reference area is higher than those measured in the three areas while concentration levels of Ba, Cu and Mn are in general similar in the four areas. The relatively higher concentrations of Al, Ba, Cr, Fe, Mn, Ni and Pb in the PC area are remarkable.

Inter-elemental relationships in all tree bark samples were assessed on the basis of the Pearson correlation coefficient (r). The following pairs exhibited significant correlations ($p < 0.05$) with $r \geq 0.8$ Al:Ba ($r = 0.85$), Al:Fe (0.93), Al:Mn (0.92), Ba:Fe (0.92) and Fe:Mn (0.80). Magnesium exhibits negative correlations with Al (−0.81) and Fe (−0.87).

Element concentrations for road dust in areas HA and UF are in the order: Fe > Al > Mg > Zn > Mn > Ba > Pb > Cu > Cr > Ni. Except for Al, element concentrations in area PC are lower than in the other two areas. The sequencing in the PC area is also different with noticeably lower Mg and Zn levels, being the corresponding ratios per area as follows for Mg, 7:1 (HA:PC) and 17:1 (UF:PC) and for Zn, 4:1 (HA:PC) and 6:1 (UF:PC). In addition, Pb and Cu levels in the PC area are about twice lower than in the UF area and about three times lower than in the HA area.

Concentration levels of Al, Fe, Mg and Mn (Table 2) are always higher in the reference topsoil than those in the road dust collected in the three areas under study. Conversely, concentrations of Cr, Cu, Ni and Pb are always higher in the three studied areas than in the reference topsoil. The PC area exhibits the lowest concentrations of Ba and Zn. The concentrations levels for Ba are in the order UF > reference topsoil > HA > PC while those for Zn are in the order UF > HA > reference topsoil > PC.

Table 2 reports average concentration of fractions *A* (<37 μm) and *B* (37–50 μm) from the samples collected. Levels of elements in fractions A and B are as follows: higher concentrations of Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are typically found in fraction *A*; Al concentration is always higher in fraction *B* while Mg concentrations are higher in fraction *A* in areas HA and UF and lower in area PC.

Significant correlations ($p < 0.05$) with $r \geq 0.8$ for the complete set of road dust samples were detected for the following pairs Ba:Mg ($r = 1$), Ba:Zn (0.95), Cu:Fe (0.81), Cu:Mn (0.88), Cu:Pb (0.98), Cr:Ni (0.86), Fe:Mn (0.83), Mg:Zn (0.93), Mn:Pb (0.89) and Ni:Pb (0.86).

The potential of these concentration profiles to characterize sampling areas was explored through cluster analysis. Fig. 2 shows hierarchical tree plots of the 10-dimensional element concentration. As consistent results were obtained with all linkage-distance combinations explored, we finally adopted single linkage (nearest neighbor) and geometrical (Euclidean) distance as the final criteria. Since these distances were computed from raw measured data, they reflect the difference in magnitude of the multielemental concentration profiles. The bark samples belonging to each urban area are grouped and neatly separated from the rest in Fig. 2a, indicating that the multielemental profiles possess distinctive characteristics that allow differentiating sampling areas. Unlike the clear trend showed by tree barks, road dust samples appear somehow merged by areas and by size fractions (Fig. 2b).

3.1.2. Enrichment factors

Fig. 3 provides an overall picture of the EF values for the tree bark and road dust samples analyzed. For comparative purposes we have included the results of EFs of Al, Cu, Mn, Ni, Pb and Zn reported by Smichowski et al. (2004) that are representative of average PM10 levels in the city. Copper, Pb and Zn show the highest EF values in the three types of samples with PM10 EFs exhibiting intermediate values between those of road dust and tree bark. For Cr, Mn and Ni the EF values for road dust were higher than those for tree bark.

The EFs for all elements and road dust and tree bark samples are displayed in Fig. 4. In general, EF values were in the order Cu > Pb > Zn, with Cu exhibiting always highest levels. Aluminum, with EF ≤ 1, exhibited a behavior typical of a geological element in both matrices. Magnesium EFs in road dust showed the lowest (or second lowest) values. The rest of the elements did not exhibit such clear patterns.

Table 2
Concentrations ($\mu g\, g^{-1}$) in bark and road dust in the three areas. Concentrations in reference soil (Custo et al., 2005; Taylor, 1964) and reference tree bark in 'Los Robles' natural reserve have been included.

Elements	Measured road dust concentrations (this study)				Reference soil	Measured tree bark concentrations (this study)			Reference tree bark
	Fraction size	Hospital Aleman (HA)	Parque Centenario (PC)	Universidad de Flores (UF)		Hospital Aleman (HA)	ParqueCentenario (PC)	Universidad de Flores	
Al	FA	10,786	12,832	4767	82,300	469	1130	498.2	210.7
	FB	16,132	22,721	8989					
Ba	FA	332.8	237.3	498.9	425	62.1	105	89.6	87.8
	FB	320.3	227.9	461.2					
Cr	FA	148.9	71.5	89.6	42	1.81	12.1	2.08	ND
	FB	110.3	58.9	66.7					
Cu	FA	360	92.9	195.3	29	99.3	69.7	31.9	72.2
	FB	236.7	70.7	183.1					
Fe	FA	17,803	9518	9707	32,579	454.5	1230	790	111.2
	FB	10,275	8851	9679					
Mg	FA	871.2	94.2	2407	23,300	1340	429.7	1099	1517
	FB	867.2	160.2	2139					
Mn	FA	681.6	542.4	593.2	853	20.6	31.3	21.4	24.28
	FB	559.3	462.8	575.1					
Ni	FA	70.6	32.9	62.7	29	1.79	2.84	0.94	ND
	FB	54.9	28.9	47.6					
Pb	FA	363.9	93.6	234.7	48	24.1	50.1	42.2	0.71
	FB	246.5	83.9	226.8					
Zn	FA	977.2	210.5	1267	325	110.2	126.7	212.4	22.67
	FB	667.9	175.8	1206					

Arithmetic mean concentration of each element is listed. Concentrations in bark referred to mass of analyzed bark. Concentrations in road dust referred to mass of dust.

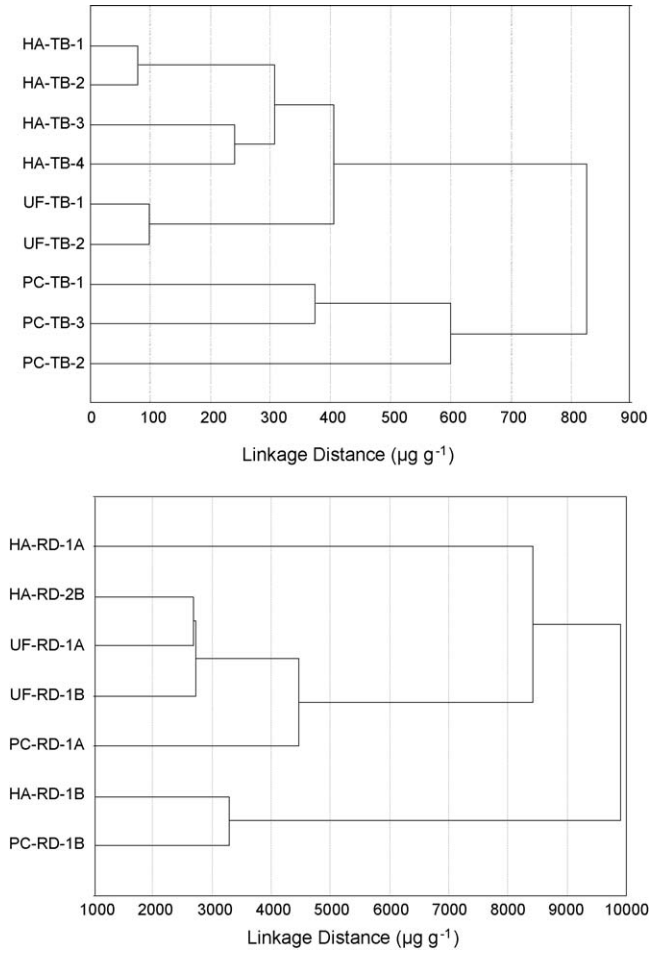

Fig. 2. Hierarchical tree plots. (a) Results of the clustering analysis performed on the tree bark concentration matrix (9 samples × 10 elements) using Euclidean distance and the nearest neighbor amalgamation rule. (The first two letters of the names on the *y*-axis indicate the sampling area.) (b) Results of the clustering analysis performed on the road dust concentration matrix (7 samples × 10 elements) using Euclidean distance and the nearest neighbor amalgamation rule. (The first two letters of the names on the *y*-axis indicate the sampling area. The last letter indicates the size fraction, with $A < 37$ μm and $B = 37–100$ μm.)

4. Discussion

Concentration levels of Cr, Ni and Pb were always higher in both tree bark and road dust than in the corresponding reference environmental matrices while Mg is the only element exhibiting the opposite behavior. In terms of EFs, Cu, Pb and Zn exhibited a similar pattern distribution with EFs in order: tree bark > PM10 > road dust, with Cu > Pb being clearly enriched in the three matrices. These

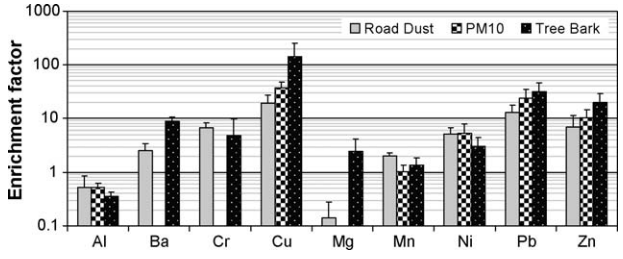

Fig. 3. Mean value and standard deviation of enrichment factors for each element and matrix. Values for bark and dust correspond to the average of the EFs belonging to the three areas HA, PC and UF. Values for PM10 correspond to the average of the EFs belonging to the nine areas considered in the study by Smichowski et al. (2004).

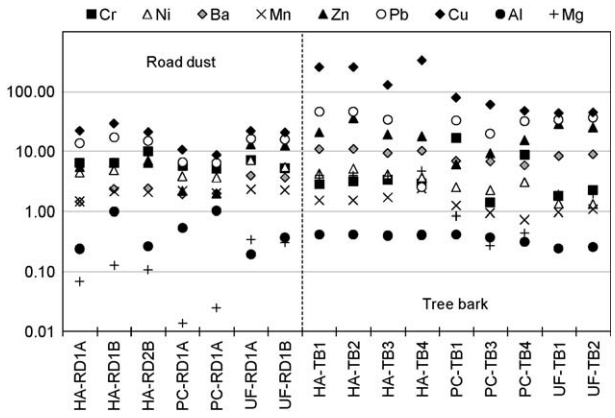

Fig. 4. Distribution of element enrichment factors for each sample of either analyzed matrix.

three elements are likely to be associated with vehicular traffic as discussed below.

Automobile emissions were the major source of urban exposure to Pb before alkyl-Pb compounds were banned as gasoline anti-knock additives. Although in Argentina Pb is no longer added to gasoline since 1995, it is nevertheless present at trace levels as a natural component in automotive fuels. However, it has been reported that after phasing out leaded gasoline, vehicular Pb emissions are now caused mainly from brake wear and loss of Pb wheel weights (Harrison et al., 2003; Lough et al., 2005). In similar way, transition metals (including Cu and Zn) are also emitted from traffic exhaust, tires and brake wear in the current urban atmospheres (Steiner et al., 2007). Copper is a common component of tissues but is also typically associated with traffic emissions, particularly with brake wear (Weckwerth, 2001). The highest EF levels of Cu are indicative of its anthropogenic nature while the highest levels of Pb in the tree bark samples of the UF and HA areas bear witness to the role of this environmental matrix as an accumulator of this heavy metal during the last three decades that registered the use of leaded gasoline until 1995. The higher EF values of Pb in the road dust samples of UF and HA also reflect the differences in traffic patterns and fleet composition. The UF area is impacted with emissions from heavy trucks, while the arterial street in the HA area is the route for several bus lines. Both types of vehicles, trucks and buses, burn diesel oil which typically has a Pb content one order of magnitude higher than gasoline (Harris and Davidson, 2005). To corroborate that Zn is also an appropriate marker of traffic emissions, we compare our results of Pb and Zn EFs in the three areas under study with those by Smichowski et al. (2004) of PM10 in nine sites of the city. Although only one area, namely Hospital Alemán (HA), has been considered in both studies, the unified results allow confirming our hypothesis. The overall picture in Fig. 5 indicates an expectable good correlation between road dust and tree bark samples but also between these matrices and PM10. In general, EF levels are in the order tree bark > PM10 > road dust, except for some cases where EF values for road dust are higher than those for tree bark. The samples belonging to the HA area are indicated in Fig. 5 by means of black triangles and show a remarkable correlation between the three sample types.

The findings about Cu, Pb and Zn discussed above are consistent with previously reported data for road dust for other cities (Shi et al., 2008; Charlesworth et al., 2003; Dongarrà et al., 2003). Although the strength and distribution of road dust sources depend on the diverse characteristics of each city (de Miguel et al., 1997), it was deemed valuable to compare the elemental composition of these three elements from the road dust collected in Buenos Aires with that reported for other cities. Values of measured Pb concentrations

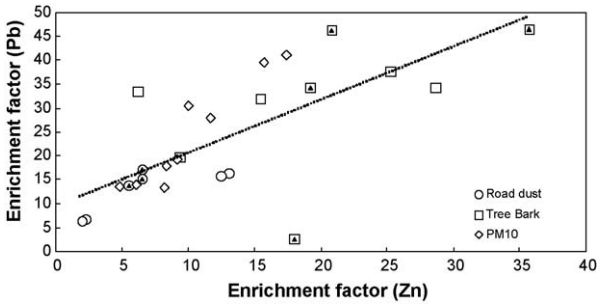

Fig. 5. Enrichment factors for Pb and Zn, which show significant correlation in both tree bark and road dust. Results for PM10 samples analyzed by Smichowski et al. (2004) are also plotted. The monitoring areas of PM10 do not generally coincide with those selected in this study, except for area HA that is represented with black triangles. Trend line is also shown in the figure.

in road dust (83.9–363.9 $\mu g\,g^{-1}$) were in the order of those recently reported (Shi et al., 2008 and references therein) for several cities worldwide where the phase-out of lead in all grades of gasoline had been enforced for several years before road dust sampling had taken place. These concentrations as reported by Shi et al. (2008) spanned from 33.5 $\mu g\,g^{-1}$ (in Ottawa, >300,000 people) to 295 $\mu g\,g^{-1}$ (in Shangai, ~1,700,000 people). These levels are well below the concentrations of Pb in road dust reported for cities for which Pb additives were used for all grades of gasoline (Charlesworth et al., 2003 and references therein; Shi et al., 2008), which were in the range 527 $\mu g\,g^{-1}$ (Birminghan, 2,300,000 people, 1987) to 3,030 $\mu g\,g^{-1}$ (London, >9,000,000 people, 1984). Copper concentrations in Buenos Aires road dust (70.7–360 $\mu g\,g^{-1}$) were within the range of concentrations reported by Charlesworth et al. (2003) and Shi et al. (2008) for ~30 cities worldwide (49–620 $\mu g\,g^{-1}$). A similar correlation between Cu and Pb observed for Buenos Aires data is present, although weaker, between the referenced cities when the data are disaggregated according to the different periods of use of Pb additives. Significant correlations ($p < 0.05$) were found when lead was use ($r = 0.73$) and during the transition period ($r = 0.69$); however no significant correlation was found after the phase-out Pb additives. Similar to Cu, the range of Zn concentrations measured in Buenos Aires road dust (175.8–1267 $\mu g\,g^{-1}$) was within the reported data of the reference cities mentioned above (152–3358 $\mu g\,g^{-1}$).

Regarding elements from natural sources, in addition to the well-known geological elements (Al and Fe), Mn is most likely from crustal origin in both types of samples (Pacheco et al., 2002). This is corroborated on the basis that (i) concentrations of Mn, together with those of Al, Fe and Mg are always lower in road dust than in the reference local soil and (ii) EFs are in the range 0.7–2.4 for both sample types. Magnesium is one of the main elements, which mostly accumulates by root uptake and translocation. The relatively uniform concentrations and low EF values (<4.7) in the three areas under study are also indicative of a natural origin.

The remaining elements (Ba, Cr and Ni) did not show a distinct pattern. However, they may arise from both natural and anthropogenic sources. Although Ba is hardly considered among elements of environmental concern, it has many applications in the automotive industries and is also present in gasoline and diesel oil (Monaci and Bargagli, 1997). A hint of the role as Ba as a traffic related element is given by its EFs in tree bark which are in general the fourth highest in value and closely follow the pattern of Zn EFs. Chromium is an essential nutrient in plants, most of the Cr uptake accumulates in the roots and only a small fraction is translocated to the aerial part of the plants (Kimbrough et al., 1999). Shewry and Peterson (1974) found that Cr uptake increases with rising Fe concentration, a fact that could explain the Cr values in the PC area. In general, Cr and Ni show a similar pattern in both matrices, they are possible from similar sources (e.g., oil combustion).

5. Conclusions

Tree bark and road dust constitute suitable environmental matrices that allow characterizing air pollution sources on the basis of their multielemental concentration profiles. Although we have considered a relatively small number of samples, our results showed that the concentration levels of the set of selected elements measured in tree barks provide a clear differentiation of areas impacted by distinct traffic patterns. Conversely, road dust is not sensitive enough to reflect these differences, probably because it is also composed by sources other than traffic and undergoes frequent resuspension which implies a short residence time for airborne particles as opposed to the long-life history recorded by tree bark (Schelle et al., 2008).

The EF-based analysis proved to be a useful tool for the combined analysis of both samples types. It allowed (i) obtaining an improved discrimination of urban areas with different traffic patterns, (ii) identifying three groups of elements with different underlying behavior, (iii) confirming the role of Pb, Zn, Ba as traffic markers, (iv) indicating the predominant crustal nature of Cr, Mn and Ni in the urban atmosphere of Buenos Aires even when these three elements are also emitted by anthropogenic source, and (v) providing a common framework for the comparison of enrichment and depletion of metals and metalloids not only in the two environmental matrices considered but also with PM10 measured in previous studies.

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