Use of tree bark for comparing environmental pollution in different sites from Buenos Aires and Montevideo

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Abstract Multi-elemental profiles in bark of green ash trees collected in three representative areas of Buenos Aires, Argentina and Montevideo, Uruguay, were assessed as potential air pollution indicators. Ten elements: Al, Ba, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn, were measured using inductively coupled plasma optical emissions spectrometry from 70 samples collected in different environments: central, residential and rural (reference site), in order to compare spatial patterns of metal concentration. The samples used

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as a control were collected from a nature reserve situated far away from any significant influences, not even a nearby road. The reference site (RF) exhibited the lowest concentrations of Al, Cr, Fe, Ni, Pb, and Zn. However, Ba and Mn showed similar concentrations in all measured sites. Magnesium is the only element that had a greater concentration in RF than at the other sites. Copper did not show any clear pattern. The Centre of Montevideo (MVD) showed higher concentrations of Al, Ba, Cr, Fe, Pb and Zn than the Centre of Buenos Aires (BA). In the A sectors, Montevideo (SAMVD) showed higher concentrations of Al, Cu, Mg, Ni, and Zn and lower concentrations of Ba, Cr, Fe, Mn, and Pb than Buenos Aires (SABA). In the B sectors, Montevideo (SBMVD) showed higher concentrations of Al, Ba, Cu, Fe, Pb, and Zn and lower concentrations of Cr and Mg than Buenos Aires (SBBA), but similar concentrations of Mn and Ni. The use of bark for biomonitoring metals allowed us to detect concentration differences related to the urban fabric and the different kinds of vehicles and their fuels. In the cities, the differences in metal concentrations detected in bark were more striking between the sectors than between centers, despite CBA being much larger than CMVD in population, extension and vehicular traffic.

Keywords Metal pollution · Urban · Residential · City · Biomonitoring

Introduction

Pollution is one of the main environmental problems in cities. Urban air monitoring is very important because high concentrations of contaminants in close proximity to humans can significantly amplify their exposure to metals, which are known to have detrimental effects on health (Dion et al. 1993; Wong et al. 2006). Exposure to air polluted with particulate matter containing diverse chemicals and heavy metals can trigger heart disease and many respiratory illnesses, especially in children and the elderly (Heinrich et al. 2000; Rodriguez et al. 2007). Metals such as Co, Cr, and Sb are reportedly found in the lungs as a result of the accumulation of air contaminants (Yaghi and Abdul-Wahab 2003).

More than half of the population of both Uruguay and Argentina lives or works in metropolitan areas. In Montevideo (MVD) and Buenos Aires (BA) vehicular traffic has become one of the major sources of airborne particles. The gaseous and particulate pollution found in access roads is mainly derived from the flow of transport to and from these densely populated cities, since MVD and BA are also transit cities for trucks plying the transnational route to Mercosur countries. In both MVD and BA studies of air quality are fragmentary and scarce (Smichowski et al. 2004; DINAMA 2005) and the air quality monitoring networks are either too small or rudimentary, as they are costly to set up and run, especially because of the technical expertise required for their operation (Suzuki 2006).

Buenos Aires (34°35′S, 58°26′W), the capital and largest city of Argentina, is located on the southern shore of the La Plata river. It lies on a vast plain belonging to the Pampa region and covers a surface of about 200 km². It has a population of about 3 million people, which implies the highest average population density of the country (14,947 inhabitants per km²). The city is the financial, commercial and cultural center of Argentina. It is the hub of the metropolitan area of Buenos Aires (MABA) that is composed of the city itself and 24 neighboring districts, which, with about 14 million people, is the tenth largest 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 of about 1 million passenger cars, 40,000 taxis, 200,000 trucks, and 150 city bus lines comprising \sim 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 used exclusively by trucks and buses. Leaded gasoline was banned in 1995 in Argentina.

Currently, in BA, there are only three air monitoring stations and unfortunately records only are available from two of them; these record carbon monoxide (CO), nitrogen oxides (NO₂), and particulate matter (PTS, PM10, and PM2.5). There is evidence showing that Buenos Aires is less polluted than other Latin American cities, such as Mexico D.F., Santiago de Chile or São Paulo, due to lower concentrations of Fe, Mn, Pb, and Zn, however higher concentrations of sulfur were found in BA air in the winter of 2001 (Smichowski et al. 2004).

The city of Montevideo $(34^{\circ}53' \text{ S}, 56^{\circ}10' \text{ W})$ has a population of 1,325,968 people spread over an area of 525.54 km². This area together with the adjacent departments of San José and Canelones make up the Montevideo metropolitan area— 1,668,335 inhabitants—the most urbanized place in Uruguay. In 2005, eight air monitoring stations were set up to measure black smoke, CO, SO₂, NO₂, O₃, total particulate matter (PTS) and PM10 in the city of Montevideo; however, not all those variables have been recorded since then (DINAMA 2005).

Besides traffic, thermal power plants are the other sources of pollution in both cities. These power plants mostly run on natural gas, except in winter when they may burn liquid fossil fuels (Smichowski et al. 2004). Very few industrial activities take place in the immediate surroundings of the city. There always is a need to gather data for assessing pollutant deposition trends in areas located far from monitoring stations, irrespective of the completeness of air quality measurements in a monitoring network. In this case, the use of biomonitors is the approach of choice, because of its comparative methodological simplicity and the reliability of its results. In view of this and the lack of data from a monitoring network, the measurement of airborne metal deposition on tree bark can be used to construct a useful pollution profile for a city. The aim of this study was to obtain those profiles for BA and MVD; we hypothesize that: the sampled areas in distinctive urban sectors can be differentiated according to the concentrations found in the metal profiles in tree bark and linked to city structure and traffic flow.

Biomonitoring using bark

Many European authors have used different plant taxa in diverse indirect methods for assessing pollution trends. In recent years tree bark has been used for the biomonitoring of diverse airborne pollutants, including metals, since the concentration of a pollutant in bark is associated with the concentration in the air surrounding the tree (Spangenberg et al. 2002; Ballach et al. 2002; Bohm et al. 1998; Walkenhorst et al. 1993). Some authors found that metals deposited on bark better reflected the levels of surrounding air pollution than metals detected in leaves of either trees or grasses (Panichev and Mc Crindle 2004).

Tree bark is an ideal natural accumulator and/or adsorbent and also a reliable atmospheric probe because its long-term exposure to the air makes it a reliable 'legacy of deposition' (Rusu et al. 2006) of accurate information about changes that occur in the surrounding gaseous environment (Bellis et al. 2003). Also bark-sampling is an interesting, easy and economic alternative for the monitoring of pollutants, because of tree availability, non-specialist species recognition and easy sampling (Wolterbeek and Bode 1995), particularly in the case of large areas where instrumental air monitoring is occasional or absent (Böhm et al. 1998). It has been successfully employed as a monitor of airborne lead and many other trace elements (Ward et al. 1974; Laaksovirta et al. 1976; Huhn et al. 1995; Böhm et al. 1998; Walkenhorst et al. 1993). Some Argentine biomonitoring studies have used lichens, bryophytes and epiphytes in order to overcome the lack of suitable instrumental resources for the direct measurement of air quality (Graciano et al. 2003; Jasan et al. 2004; Pignata et al. 2002; Carreras et al. 2005), whereas bark has been used less frequently. Platanus acerifolia and Fraxinus pennsylvanica barks were employed to compare pollution levels in the city of Buenos Aires and nearby rural or periurban locations (Plá et al. 2000; Perelman et al. 2006). On the other hand no data is available on the use of tree bark for assessing pollution in Uruguay.

Materials and methods

Study area

The cities of Montevideo $(34^{\circ} 53' \text{ S}, 56^{\circ}10' \text{ W})$ and Buenos Aires $(34^{\circ} 35' \text{ S}, 58^{\circ} 26' \text{ W})$ are located on opposite margins of the Rio de la Plata river at a distance of about 210 km (orthodromic distance). In both cities the climate is mild and characteristic of mid-latitudes (Cfa in the Köppen–Geiger scale) with no dry-season and a hot summer. The mean annual temperature is ~16°C. Mean annual precipitation is about 1,200 mm, evenly distributed throughout the year.

BA and MVD are under the influence of sealand winds which facilitate the dilution of air pollutants because they are located in the fairly flat relief of the Pampas plains. Therefore, air pollution is not as severe as in industrialized countries/megacities and other Latin American ones like Mexico City (Mexico), Santiago de Chile (Chile), or Sao Paulo (Brazil; USEPA 2002).

In the two cities under study, bark from trees was collected in three different sectors (Table 1), one situated at the city center and the other two located in districts in the neighborhood, one characterized by the presence of large parks (Sector A) and the other by dense traffic (Sector B). Bark was also collected from a reference area (RF) situated far away from Buenos Aires city (\sim 45 km) with minimal traffic influence. This area, Los Robles, is a municipal reserve (1,000 ha) located in Moreno, Gran Buenos Aires.

Sampling and analysis

In each one of the city sectors defined, ten samples of *F. pennsylvanica* bark were collected from the curbside zone of the streets (40 cm from the road) in May 2006. This species is the most common tree (48%) in Buenos Aires (Perelman et al. 2006). In Los Robles reserve samples were taken from trees adjacent to the administration building. In

Table 1 Description of	Montevideo (MVD)	Buenos Aires (BA)						
the sampling sites in the	Center							
Montevideo and of the	Densely built-up area used for residential or commercial activities or both.							
reference for the comparison of chemical	Area name: "Intendencia" (CMV) Avenue: 18 de Iulio	Area name: "Hospital Alemán" (CBA) Avenue: Puevrredón						
element pollution	I S 34°54′48″–I W 56° 11′ 34″	L \$ 34°35′92″–L W 58° 24′ 30″						
	Population density: 650 inhab/ha	Population density: 958 inhab/ha						
	Traffic flow: 900 vehicles /h	Traffic flow: 2.674 vehicles/h						
	Sector A							
	Residential and service area with tree-lined streets and avenues and large public parks.							
	Area name: "Tres Cruces" (SAMV)	Area name: "Parque Centenario" (SABA)						
	Avenue: Bv. Gral. Artigas	Street: Patricias Argentinas						
	LS 34°53′63″–LW 56° 09′ 85″	LS 34°36′48″–LW 58° 26′ 98″						
	Located at about 2 km from downtown	Located at about 5 km from downtown						
	Population density: 350 inhab/ha	Population density: 772 inhab/ha Traffic flow: 1,628 vehicles/h						
	Traffic flow: 1,100 vehicles/h							
	Sector B							
	Residential area with dense traffic flow of buses and lorries along the main street.							
	Area name: "Prado" (SBMV)	Area name: "Flores" (SBBA)						
	Avenue: Av. Millán	Avenue: Nazca						
	LS 34°51′58″–LW 56° 12′ 07″	LS 34°37′81″–LW 58° 28′ 21″						
	Located at about 6 km from downtown	Located at about 7 km from downtown						
	Population density: 350 inhab/ha	Population density: 313 inhab/ha						
	Traffic flow: 800 vehicles/h	Traffic flow: 1,524 vehicles/h						
	Private gardens and urban trees	Lack of private gardens and few urban trees						
	Reference							
	The "Los Robles" (RF) reserve (1,000 ha, 45 km from downtown) located on the outskirts							
	of La Reja village, Moreno district, Buenos Aires province. It is made up of woody and							
	wetland patches interspersed with meadows. The surrounding area consists of a							
	patchwork of residential (mostly weekend homes) and agricultural (mostly vegetable							
	farms) properties. The population density is 2.33 inhabitants/ha. Vehicular traffic is very							
	infrequent within this area. LS 34°39′62″–LW 58° 51′ 11″							

this study mature trees (\sim 30–40 years old) were chosen with a stem diameter of about 30 cm at breast height.

In each sampled tree two pieces of bark of 10 cm^2 and 3 mm thick were cut with a steel knife. These samples were taken at a height of 1.30 m from the side of the trunk facing the traffic. This particular side of a trunk was chosen on the assumption that it is more exposed to air pollutants. We did not sample bark covered with either lichens or mosses. The samples were combined into one bulk sample.

We used the same sampling procedure on trees growing in the RF area to collect data for building a baseline for each metal in order to assess the urban effect on its concentration in the air. Samples preparation and elemental analysis

Individual bark samples were air-dried for the analysis. Two grams of each sample were digested in 20 ml of concentrated HNO₃ at 200°C during 12–24 h. The resulting solution was filtered and diluted to 100 ml with deionized water. The amount of the each element present was measured in each of three aliquots of that solution.

Ten elements, Al, Ba, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn were measured by inductively coupled plasma optical emissions spectrometry (ICP OES). We used a simultaneous inductively coupled Ar plasma optical emission spectrometer (Perkin-Elmer (Norwalk, CT, USA) ICP Optima 3100 XL (axial view)) together with a Model AS 90 autosampler. Welding Ar from Indura (Buenos Aires, Argentina) was used for ICP OES determinations. The wavelengths set for each metal (nm) and the limits of detection (mg/kg) were: Al, 308.215–1.6; Cr, 267.716–0.1; Cu, 324.742–0.3; Fe 238.204–0.4; Mn, 257.610–0.01; Ni, 232.003–0.08; Pb, 217.000–0.3; Zn, 206.200–0.02, Ba, 233.527–0.04; and Mg, 285.213–0.09.

Results

Table 2 summarizes the metal concentrations in each of the three selected urban areas and the reference site (RF). The means showed high variability, a feature mentioned in different components of urban ecosystems (Lopez et al. 2006; Madrid et al. 2002).

In general terms, all measured sites had similar concentrations of Ba and Mn (Table 2). RF exhibited the lowest concentrations of Al, Cr, Fe, Ni, Pb, and Zn; Magnesium was the only element that had a higher concentration in RF than in the other sites and no clear pattern was seen for copper.

When we compared the two center sectors, Montevideo (CMVD) showed higher concentrations of Al, Ba, Cr, Fe, Pb, and Zn and lower concentrations of Cu and Mg than Buenos Aires (CBA) and they had similar concentrations of Mn and Ni. When the same comparison was done for sectors A, Montevideo showed higher concentrations of Al, Cu, Mg, Ni, and Zn and lower concentrations of Ba, Cr, Fe, Mn, and Pb than Buenos Aires. And finally, when this comparison was done for sectors B, Montevideo showed higher concentrations of Al, Ba, Cu, Fe, Pb, and Zn, lower concentrations of Cr and Mg than Buenos Aires they had similar concentrations of Mn and Ni.

Similar concentration values to those measured by us were reported for Fe and Mn on *Tillandsia* species in central Argentina (Wannaz et al. 2006) and for Al, Cr, Fe, Zn, and Ni in the UK and Ireland (Suzuki 2006). These data further confirmed the plausibility of the results obtained in our study.

 Table 2
 Concentrations of metals in tree bark in a mostly rural area—the natural reserve—and in urban settings: the centre and two residential areas in each of the cities of Montevideo and Buenos Aires

	Al	Ba	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn
Reference										
Los Robles (RF)	205.8	87,8	<ld< td=""><td>72.2</td><td>111.3</td><td>1,517.3</td><td>24.3</td><td>0.0</td><td>0.7</td><td>22.7</td></ld<>	72.2	111.3	1,517.3	24.3	0.0	0.7	22.7
S.D.	13.49	2.94	-	4.93	13.06	135.03	4.47	0.00	0.08	1.07
City of Buenos Aires										
Center (CBA)	443.1	60.5	1.7	94.4	440.1	1,304.9	20.5	1.8	24.3	118.6
S.D.	85.78	13.79	0.33	30.94	90.39	201.49	0.51	0.41	11.64	41.59
Sector A (SABA)	1,001.05	99.5	5.4	55.9	1,105.1	437.6	26.5	2.0	34.5	104.1
S.D.	238.63	16.14	6.6	16.62	193.60	122.71	6.67	0.82	13.34	34.58
Sector B (SBBA)	558.7	72,1	3.2	30.4	733.33	1,319.2	21.4	2.0	35.1	176.5
S.D.	54.93	11.76	1.16	1.67	46.12	199.58	1.02	0.94	10.40	54.81
City of Montevideo										
Center (CMVD)	567.9	94.00	2.1	39.2	801.0	1,191.6	19.3	1,6	38.9	176.7
S.D.	0.52	0.04	0.03	0.14	0.47	0.26	0.50	0.16	0.41	0.45
Sector A (SAMVD)	1,417.04	44.4	3.4	76	808.5	1,417.0	22.1	3.5	16.8	181.4
S.D.	157.94	11.09	0.85	30.58	11.82	157.94	0.39	0.40	10.12	60.76
Sector B (SBMVD)	567,4	96.1	2.1	36.9	793.3	1,215.9	19.2	1.3	43.0	189.1
S.D.	0.83	1.78	0.03	2.53	22.51	90.53	0.05	0.04	0.05	0.08

S.D. standard deviation, LD detection limit, N = 10

Chemical element analysis in bark (ppm)

Mean concentrations, standard deviations and numbers of sampled trees are shown for each sampling site and chemical element

Discussion

The kind and intensity of traffic generates trends in atmospheric pollution in urban environments that are more evident in urban centers than in residential areas. The high level of metal concentrations measured in tree bark from streets along highly transited avenues in the centers and urban districts B in both cities, might be associated with particulate emissions produced by fuel combustion, wear and tear of vehicular parts and leakage of motor oils (Plá et al. 2000). The comparatively larger concentration of Zn in the city of Montevideo is likely to be the consequence of the large number of vehicles propelled by twostroke engines, such as mopeds, scooters, and motorbikes (Alander et al. 2005). The residential and service areas (Sector A), e.g., a large bus station in Montevideo-with tree-lined streets and avenues and large public parks and hospitals in both cities exhibited higher concentrations of Al and Fe than those measured in Sector B, which might have been of crustal (soils blown from parks) and/or anthropogenic origin (vehicular traffic). Also, in general terms, in both cities Sector A showed higher concentrations of Cu and Ni than those measured in Sector B. Nickel is primarily used for making stainless steel and many other corrosion resistant alloys, which are common in public transport. This element is also used in vehicle batteries (WHO 2000).

The highest concentrations of Pb and Zn in Sector B samples showed the influence of the heavy traffic flow of buses and trucks along the streets where samples were taken.

In absolute terms, however, the mean Pb concentration in both cities (see Table 2) was comparatively low in comparison to other cities; for instance was lower than the mean Pb concentration found in the bark of *Fraxinus excelsior* trees in Frankfurt, Germany (422.7 ppm; Ballach et al. 2002) and in the bark of *Prunus sargentii* and *Acer saccharum* in Derbyshire, UK (1,070 ppm; Suzuki 2006), respectively. The comparatively small Pb contamination in BA and MVD is very likely due to the increased use of Pb-free fuels in Buenos Aires since 1995 and in Montevideo since 2002 (Perelman et al. 2006). In general terms, metals showed differences in concentrations between rural and urban sampling sites, except for Ba and Mn. The higher concentrations of Al, Cr, Fe, Ni, Pb, and Zn deposited on tree trunks in both metropolises in comparison to the nature reserve can be attributed to engine exhaust particles produced by the combustion of the particular formulations of fuels and lubricating oil currently in use.

Fuel, especially diesel oil, contains Fe, Mg, Cr, Ni, Pb, Zn, Ba, and Cu and additives of lubricant oils also influence the chemical composition of exhaust gases (Barnes et al. 2001; Fujiwara et al. 2006). Lubricant oil is suspected of contributing up to 95% of the total exhausts particulate mass (Sugiura and Kagaya 1977; Pattschull and Roth 1994).

Wang and Huang (2003) reported various metal emission rates for a composite sample of several diesel vehicles. The most abundant metals in exhaust gases were Zn, Fe, Ca, P, Ba, and La. Sharma et al. (2005) found higher concentrations of crust elements like Fe, Mg, Ca in diesel soot than of Cr, Ni, Pb, Zn, Ba, and Cd (elements of anthropogenic origin from traffic, building, etc.).

Aluminum is linked to the wear and tear of construction materials, wood burning and coal combustion (Gómez et al. 2007). Iron is associated with highway infrastructure facilities, industrial activities and material corrosion. Nickel and Cr are metals related to industrial activities, auto repair shops and waste (Birke and Rauch 2000).

Unexpectedly, similar concentrations of Ba were recorded in both the urban settings and the nature reserve. This might be attributed to the exhaust of diesel engines and of small two-stroke engines, widely used in both rural and recreational applications (e.g., lawn mowers and hedge trimmers). Small engines used in gardens also appeared to be a significant contributor to the deterioration of the air quality in many residential areas (Christensen et al. 2001).

In addition to fuel exhaust, other sources that might contribute to the large deposition of Cu on tree bark in the nature reserve are products used for water purification in swimming pools, which are a common feature in the many weekend houses present in the area, as well as pesticides used in many vegetable farms in the area (Perelman et al. 2006).

Higher values of Cu and Mg at the urban centers compared to sectors A and B may also be associated with vehicular traffic, including exhaust gases, and the wear and tear of tires. On the contrary, larger concentrations of Al, Mg, and Fe in sectors A and B are likely to be of natural origin; i.e., from soil carried away from the green areas by the wind and deposited on tree trunks.

Cr and Zn can be related to vehicle repair shops and other industrial activities also located in the residential areas (Ward et al. 1977; Cameron 1992).

Conclusions

In our case, biomonitoring with bark allowed us to detect metals concentration differences related to the urban fabric and the kinds of vehicles and fuels used.

In some cases, e.g., sector A, differences in metal concentrations detected in bark between urban sectors in the cities were more striking than between city centers, despite CBA being much larger than CMVD in population, extension and vehicular traffic. Different concentrations of Al, Cu, Fe, Ni, Pb, and Zn allowed us to distinguish between city areas that have different traffic densities and urban activities.

Some characteristics of the urban fabric, such as the presence of parks within densely built-up areas, are reflected by the relatively large concentrations of chemical elements like Fe and Al which come from airborne soil particles deposited on bark.

It is interesting to note that our reference (RF) for testing urban chemical pollution—the nature reserve—was not a strong reference for some chemical elements, such as Ba and Cu as their concentrations in bark were comparatively high. This was very likely to have been caused by pollution derived from the use of pesticides and oil-derived fuels in farming activities in the neighborhood of the reserve. Therefore, the choice of a reference area for these kinds of studies must be made on basis of elements present. So, a natural reserve is a good reference for some chemical compounds but not for others, depending on the surrounding environment. Fortunately, in our case, the nature reserve chosen was useful as a reference for the elements related to traffic-derived pollution.

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