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Biomonitoring levels and trends of PAHs and synthetic musks associated with land use in urban environments

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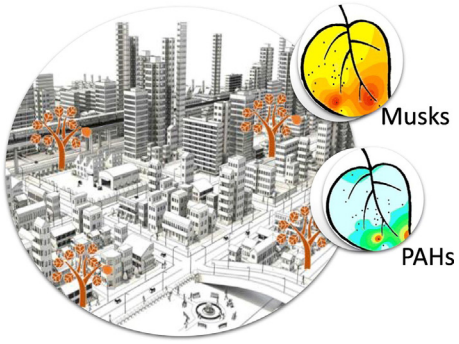
HIGHLIGHTS

- Higher PAH levels were found in industrial and urban areas.
- The PAH profile was dominated by the 4-ring PAHs.
- The highest level of total musks were found in the industrial sampling sites.
- Polycyclic musks were the most contributing compounds (90%), in all land use areas.
- The most frequently detected musk was HHCB, followed by AHMI and DPMI.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are some of the most studied organic compounds in urban environments, due to their known adverse effects on human health and persistence in environmental matrices. During the last decade, new groups of organic compounds with an intensive use worldwide such as synthetic musks have been raising the interest of the scientific community given their toxicity and health effects. However, literature is still scarce in studies dealing with their concentration in the environment, especially in developing countries, where they are even more rare or non-existing at all. We employed leaves of *Ligustrum lucidum* to assess the concentrations of PAHs and synthetic musks in different land use areas in Cordoba city, therefore contributing with environmental information in Argentina. We found higher levels of PAHs in urban and industrial areas than in the peri-urban sampling sites, naphthalene being one of the dominant PAHs in all sampling areas. Regarding synthetic musk fragrances, polycyclic musks were the most contributing compounds and the highest levels found in industrial areas as well. A high environmental risk could be expected due to the frequent occurrence of galaxolide in addition to the high hazardous potential of phantolide, which was present in 50% of the samples. The results of the present study indicate that leaves of an urban ubiquitous tree can be used to assess the spatial behavior of both "classic" and "emerging" organic pollutants, allowing an assessment of urban air quality in areas where common air sampling devices are unavailable.

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1. Introduction

Historically, environmental monitoring programs have tended to focus on organic chemicals, particularly those that are known to resist degradation, bioaccumulate in the fatty tissues of living organisms, and have an adverse toxicological effect. Some of the most studied organic compounds in urban environments are polycyclic aromatic hydrocarbons (PAHs), characterized by the presence of at least two fused aromatic rings in their molecules and released mainly by anthropogenic sources such as traffic, domestic heating, oil refining and other industrial processes (Ravindra et al., 2008). They have been classified as priority pollutants due to their detrimental effects on human health, persistence in environmental matrices, reactivity, and ability to transform into more reactive compounds (Ramírez et al., 2011). In fact, most anthropogenic PAHs are carcinogenic, and benzo[*a*]pyrene (BaP) is the usual marker for carcinogenic levels of PAHs in environmental studies (Ratola and Jiménez-Guerrero, 2016).

Previous studies in the city of Cordoba (Argentina), proved that the mean levels of particle-bound PAHs were high enough to pose a threat to human health, particularly during wintertime (Amarillo et al., 2014). Despite the fact that the levels of total PAHs were similar to those reported in other urban areas, a seasonal health risk, calculated as a sum of the partial risks of the individual pollutants, was several orders of magnitude higher than the values obtained elsewhere (Bartoš et al., 2009). Although this is valuable information, it cannot be used to assess the individual risk of exposure since the concentration of PAHs in the atmosphere is highly dependent on the presence of local emission sources. Therefore, their distribution all over the city is heterogeneous.

Biomonitoring has been used as a valid tool to assess the concentration levels of PAHs in the environment since the late 1980s (Eriksson et al., 1989). The lipid-rich cuticle of plant materials is likely to accumulate such persistent contaminants mainly by atmospheric deposition onto the leaf surface (Simonich and Hites, 1995). Since then, several plants and trees (evergreen species preferred over deciduous ones) have been used as bioindicators for PAHs and other pollutants (Murakami et al., 2012; De Nicola et al., 2008, 2013; Prajapati and Tripathi, 2008; Ratola et al., 2011; Wannaz et al., 2013).

In order to improve our previous estimations of PAHs levels within the urban area of Cordoba city, it was decided to use a tree species frequently employed in urban gardening (*Ligustrum lucidum* Ait), as a passive biomonitor (Carreras et al., 1996; Cañas et al., 1997). The leaves of this genus are covered by a cuticular waxy layer, which provides excellent properties for the uptake of air pollutants. Other species from the same genus have been reported as some of the most efficient in trapping particulate matter and the pollutants contained therein (Fellet et al., 2016). Considering that PAH concentrations on the leaves indicate the integrated incidence of these pollutants in the air over time, they can be useful to detect temporal and spatial pollution trends (Simonich and Hites, 1995).

On the other hand, new groups of organic compounds are continuously being released into the environment and some of them are raising interest and concern among scientific and regulatory organizations due to the increased understanding of their toxicological impact and health effects associated with an intensive use worldwide (Schiavone et al., 2010). These are commonly called emerging organic pollutants (EOPs) and currently include antimicrobial agents, pharmaceuticals, surfactants, industrial additives, plasticizers, insect repellents, preservatives, UV filters and fragrances (Liu and Wong, 2013). Therefore, in order to broaden the focus of this study to include these "new" chemicals, the presence of synthetic musks was also measured (Lu et al., 2011). Musks are used in perfumes, personal care products and household products (Roosens et al., 2007), hence being scented products the primary source of exposure to these chemicals. Nitro and polycyclic musks are the most frequently mentioned in literature (Wang et al., 2014): while the use of polycyclic musks doubled from 1987 to 2000 (Peck and Hornbuckle, 2006), nitro musks showed a strong decrease and have been largely replaced by polycyclic musks (Taylor et al., 2014). Indeed, the United states Environmental Protection Agency (USEPA) has listed galaxolide, a polycyclic musk, as one of the chemicals with the highest production volume (Wang et al., 2014). Some of these compounds are classified as carcinogenic, photoallergenic (Slanina, 2004), neurotoxic (Spencer and Bischoff-Fenton, 1984), mutagenic and with estrogenic activity (Bitsch et al., 2002; Homem et al., 2015b; Taylor et al., 2014). Other studies indicate that synthetic musks might induce asthma, as well as act as endocrine disruptors (Brunn et al., 2004; Witorsch and Thomas, 2010). Moreover, nitro musks and two polycyclic musks (tonalide and galaxolide) were filed in the Hazardous Substances Data Bank on the National Library of Medicine's Toxicology Data Network in the United States (Wang et al., 2014). Apart from their toxicity, synthetic musks have a good bioaccumulation capacity, volatility and resistance to natural breakdown, which make them prone to long-range atmospheric transport and to cause an environmental impact on areas far from their emission sources (Silva et al., 2015). Currently, there are still no certainties about the real impact of these compounds on the environment, due to the lack of information (Homem et al., 2015a). The most frequent form of human exposure is through skin contact since the musk-containing products are usually in liquid forms, but inhalation might be also critical given that airborne synthetic musks are ubiquitous over a wide variety of public places, occupational buildings, and homes (Mercier et al., 2012). However, due to the absence of widespread and effective sampling and analysis methodologies, very little research has focused on the distribution of these airborne contaminants (Wang et al., 2014). Although there have been several initiatives in Argentina to address the requirements of the Stockholm Convention regarding persistent organic pollutants (POPs), studies are still very scarce and most of them are focused in coastal areas (Pozo et al., 2012). Therefore, the present work has two main objectives: to employ a low cost methodology to assess PAHs atmospheric concentrations in many different urban sampling sites simultaneously, considering different land uses, and, at the same time, be a contribution to enhance the datasets on airborne EOPs that might be present in those areas. In addition, it is expected to identify the individual compounds that are the most environmentally relevant, considering not only their concentration but also their toxicity.

2. Material and methods

2.1. Study area

Cordoba is the second largest city in Argentina, located in the central part of the country, 400 m above sea level. It has a population of 1.5 million and an irregular topography. Its general structure is funnel-shaped, with an increasing positive slope from the center towards the surrounding area. This somewhat concave formation reduces the air circulation and causes frequent thermal inversions both in autumn and winter (Olcese and Toselli, 2002). The climate is sub-humid, with an average annual rainfall of 790 mm, concentrated mainly in the summer. The mean annual temperature is 17.4 °C and the prevailing winds come from the NE, S and SE.

The main source of air pollution in Cordoba city is traffic, which has a strong relationship with the emission of primary pollutants (CO, NO_x and PM_{10}). The city also has an important industrial development of mainly metallurgical and mechanical industries (Amarillo and Carreras, 2012).

2.2. Sampling

Twenty-eight different locations within the urban area of Cordoba were selected to include different land uses (Fig. 1). Sampling sites located in the downtown area were considered as urban, where the main pollutant emission source is vehicular traffic (n = 11). The sites located near two large industrial areas to the south and southwest of the

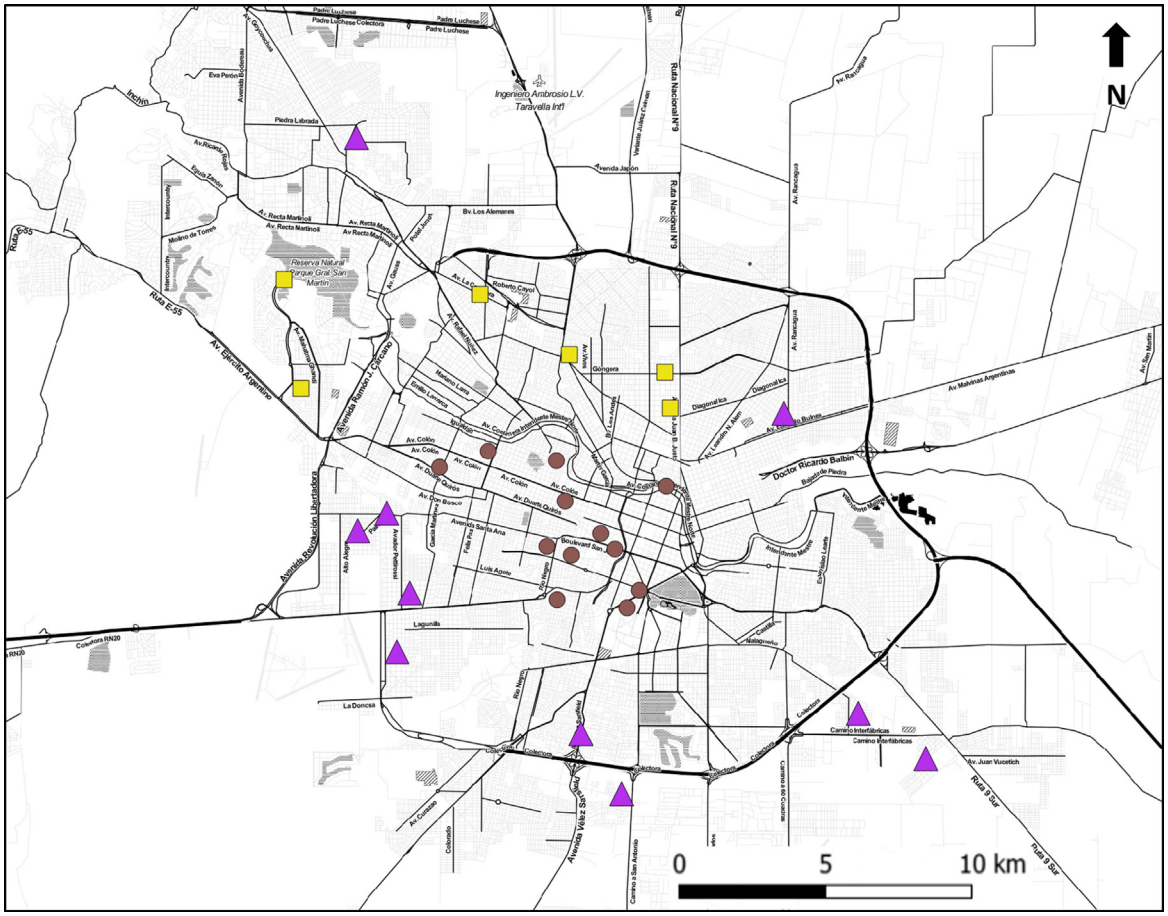

Fig. 1. Sampling sites in the urban area of Cordoba city (• urban; ▲ industrial; ■, peri-urban).

city, or near medium-sized metallurgical and mechanical factories, were categorized as industrial (n = 10). Finally, the sampling spots located far away from any main industries or heavy-traffic roads were named peri-urban (n = 7).

Ligustrum lucidum Ait. is an evergreen tree species widely occurring in the Cordoba urban area. It has a dense canopy of shiny, dark green, waxy leaves that favor the scavenging and retention of airborne particle-phase pollutants, as well as the absorption of lipophilic gas-phase organic pollutants. During the dry season, leaves (4–5 cm length) from two different trees at each sampling site were collected from the outer part of the canopy (2 m above ground), packed in polypropylene freezing bags and stored at −20 °C until extraction.

2.3. Extraction and quantification of PAHs and synthetic musks

A total of 16 PAHs—naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene and benzo(*k*)fluoranthene (BbF + BkF), benzo(*a*)pyrene (BaP), indeno(1,2,3-*cd*)pyrene (IcdP), dibenzo(*a*,*h*)anthracene (DahA), benzo(*g*,*h*,*i*)perylene (BghiP), 6 polycyclic musks - cashmeran (DPMI), celestolide (ADBI), traseolide (ATII), phantolide (AHMI), tonalide (AHTN), galaxolide (HHCB) and 5 nitro musks - musk moskene (MM), musk tibetene (MT), musk ketone (MK), musk ambrette (MA), musk xylene (MX) were analyzed. The analytical protocol used is adapted from a multi-residue method developed by Silva et al. (2015) for pine needles. In short, 2.5 g of *L. lucidum* leaves were cut into very small pieces and 25 ng g^{-1} of surrogate standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) were added to all samples. These deuterated standards were added to allow the quantification of the target analytes by the internal standard method. Then, samples were extracted for 30 min with 100 mL of hexane/dichloromethane (Hex/DCM 1:1) in an ultrasonic bath. After solvent reduction in a rotary evaporator, a clean-up in two steps was performed. First, the extract underwent solid phase extraction (SPE) in glass columns packed with 5 g of aluminum oxide and topped with sodium sulfate. Elution was performed with 50 mL Hex/DCM (1:1) before evaporation to almost dryness in a rotary evaporator. Then, gel permeation chromatography (GPC), with glass columns prepared using 6 g of S-X3 Bio-Beads from BioRad (Hercules, CA, USA) in Hex/DCM (1:1) was used. Samples were eluted with 40 mL of Hex/DCM (1:1), of which the first 15 mL were discarded. After nitrogen blow down, the extract was reconstituted in 100 μL of Hex for chromatographic analysis.

This analysis was performed using a Varian 4000 GC/MS (Palo Alto, CA, USA) with a capillary column Agilent J&W DB-5 (30 m × 0.25 mm, 0.25 mm film thickness) and helium as carrier gas (1 mL min^{-1}). The oven temperature program began at 60 °C for 1 min and was then increased to 175 °C at 6 °C min^{-1} and held for 11.11 min, then raised to 300 °C at 5.5 °C min^{-1} and finally held for 10 min. The injection volume was 1 μL in splitless mode. The identification of the target compounds was based on the retention times and the relative abundance of the monitored ions. Quantification was done using the deuterated PAHs as surrogate standards.

2.4. Quality assurance/quality control (QA/QC)

The details about some validation parameters of the analytical method (linearity ranges, coefficients of determination and limits of detection (LODs)) can be found in Silva et al. (2015). In brief, the linearity

range was from 10 to 1500 μg L^{-1} with R^2 between 0.995 and 0.999 and LODs (calculated by a signal-to-noise (S/N) ratio of 3) were in the pg g^{-1} range for both PAHs (10 to 498 pg g^{-1}, fresh weight (FW)) and musks (0.4 to 129 pg g^{-1}, FW). The values for average recoveries of the adaptation of the method to *L. lucidum* leaves were 99 ± 10% for PAHs and 91 ± 14% for musks, and the repeatability was mostly below 10% for both classes of chemicals.

In this kind of analysis, there is always a possibility for external contaminations. In particular, musks may be introduced in the lab by the use of personal care products and cleaning agents. This practice was avoided in the days of analysis. Non-calibrated glassware was baked at 400 °C overnight before use, to eliminate possible residues of the target compounds. In order to keep a tight control on these possible interferences in the analysis, laboratory blanks were performed periodically and if the values were above the LODs, the results were corrected accordingly.

2.5. Dry weight/fresh weight ratio

The dry weight/fresh weight (DW/FW) ratio of the samples was determined by drying 1 g of fresh material at 60 ± 2 °C until constant weight. The mass differences correspond to the amount of water. The results were expressed in g DW·g^{-1} FW.

2.6. Statistical methods

A mapping procedure was used to evaluate the distribution of PAHs and musks in the area. The maps were calculated using Surfer 9.0 (Golden Software Inc.) with krigging as the gridding method; the intervals between the minimum and maximum concentrations were divided into 10 classes of equal extent.

3. Results and discussion

To help the interpretation of the results, PAHs and musks will be presented and discussed separately.

3.1. PAHs

The levels of individual PAHs, as well as the sum of total PAHs measured at the different land use areas in the city of Cordoba, are shown in Table 1.

Atmospheric individual PAH concentrations ranged between <LOD and 153.2 ng g^{-1} DW (Table 1) and showed a strong gradient of industrial > urban > peri-urban sampling sites (Fig. 2). These values as well as the levels of total PAHs were somewhat lower than those reported in other biomonitoring studies performed across European cities, bearing in mind that these studies were performed using different tree species. In Galicia (Spain) PAHs measured in oak leaves ranged from 132 to 363 ng g^{-1} DW (De Nicola et al., 2016) and in Naples (Italy) from 92 to 1454 ng g^{-1} DW (Alfani et al., 2001). Previous biomonitoring studies performed with *Tillandsia capillaris* (Wannaz et al., 2013) and *Lolium multiflorum* (Rodriguez et al., 2015), which include one sampling site in downtown Cordoba and another in the industrial area located to the SE, reported similar total PAH values (range: 362–464 ng g^{-1} DW and 347.9–463.9 ng g^{-1} DW, respectively). Despite the fact that the washing effect of rain was not considered, since the sampling was carried out during the dry season, this comparison may still be problematic due to the different species' accumulation rates (Blasco et al., 2011), which mostly depend on their surface/weight ratio (Adamo et al., 2007; Bertuzzi and Tretiach, 2013). In fact, substantial variability between several plant species collected in the same site have already been reported in regards to PAH bioaccumulation (Migaszewski et al., 2002; Ratola et al., 2011). In general, the atmospheric compounds in the gas phase can be adsorbed by vegetation, especially if a waxy layer is present. This would be the case of the lower molecular weight PAHs (2, 3 and even 4 aromatic rings) and of most fragrances. On the other hand, particulate-bound compounds may be deposited into the surface of the leaves, but not penetrate the leave itself, being more prone to suffer the effect of heavy rain, for instance, that would cause their removal into the soil. Naturally, the congener patterns could suffer some alterations regarding the ones found in the air due to these conditions. In this work, it was not possible to access data from traditional air monitoring systems for a thorough comparison. Nevertheless, our results evidenced a good performance from *L. lucidum* leaves in PAHs accumulation, in line with the patterns found in other studies in literature (e.g. Alfani et al., 2001; Augusto et al., 2009; Ratola et al., 2011; De Nicola et al., 2016).

Considering each PAH individually, significantly higher values were observed for Chry and Flt at all sampling sites. In the urban and industrial areas, Pyr and Naph were largely represented, while in the peri-urban area the levels of Phen were also high. Similar PAH profiles, dominated by Flt and Chry, were detected in oak leaves collected in a biomonitoring study across Galicia, Spain (De Nicola et al., 2016). Odabasi et al. (2006) also mentioned that the most dominant PAHs in an urban area close to the center of Izmir, Turkey, were Phen, followed by Flt and Pyr. Fluo levels were also high in urban sampling sites, in perfect accordance with previous reports where a higher contribution of Fluo was observed in urban rather than industrial environments (Rehwagen et al., 2005). The PAH profile was dominated by the 4-ring PAHs, accounting for

Table 1
Concentration of individual and total PAHs (ng g^{-1} DW) measured in *L. lucidum* leaves collected in different land use areas in Cordoba city.

	Urban (n = 11)				Industrial (n = 10)				Peri-urban (n = 7)			
	Mean	SE	Min	Max	Mean	SE	Min	Max	Mean	SE	Min	Max
Naph	16.36	5.24	0.98	63.5	21.5	9.15	0.3	99.05	8.37	2.79	1.82	17.55
Acy	1.06	0.25	0.19	3.6	1.84	0.51	0.03	4.49	0.79	0.56	0.03	3.57
Ace	0.58	0.19	0.12	2.07	0.44	0.1	0.13	1.01	0.41	0.3	0.04	1.88
Fluo	1.95	0.89	0.03	11.4	1.15	0.44	0.06	4.62	1.34	0.56	0.2	3.62
Phen	8.24	1.3	2.65	16.1	13.12	2.74	4.65	33.71	10.07	1.71	2.59	13.99
Ant	0.37	0.08	0.11	1.01	0.45	0.09	0.07	1.01	1.26	0.89	0.27	5.69
Flt	20.41	4.18	4.61	47.72	35.71	4.9	11.24	60.19	29.64	9.48	7.37	69.01
Pyr	14.49	2.84	1.74	31.23	20.99	4.05	4.91	47.88	13.78	2.91	5.53	26.59
BaA	3.29	0.81	0.49	8.4	5.08	1.1	0.41	10.05	1.89	0.86	0.42	4.99
Chry	34.88	10.4	6.05	120.5	57.42	17.88	5.23	153.2	19.23	5.07	5.41	38.12
BbF + BkF	5.07	0.99	1.39	10.28	4.33	1.31	0.79	13.46	3.79	1.05	1.24	8.67
BaP	3.2	0.46	0.98	5.92	3.34	0.63	0.66	6.66	3.01	0.82	1.76	7.06
IcdP	0.45	0.24	n.d.	2.15	0.49	0.28	n.d.	2.59	0.19	0.19	n.d.	1.13
DBahA	0.78	0.26	n.d.	2.14	0.99	0.78	n.d.	7.89	0	n.d.	n.d.	n.d.
BghiP	1.49	0.26	0.46	3.8	1.19	0.22	0.46	2.72	1.09	0.16	0.5	1.58
Total PAHs	112.62	17.1	41.81	229.4	168.04	30.43	59.12	368.9	94.87	16.43	37.78	144.5

n.d.: not detected.

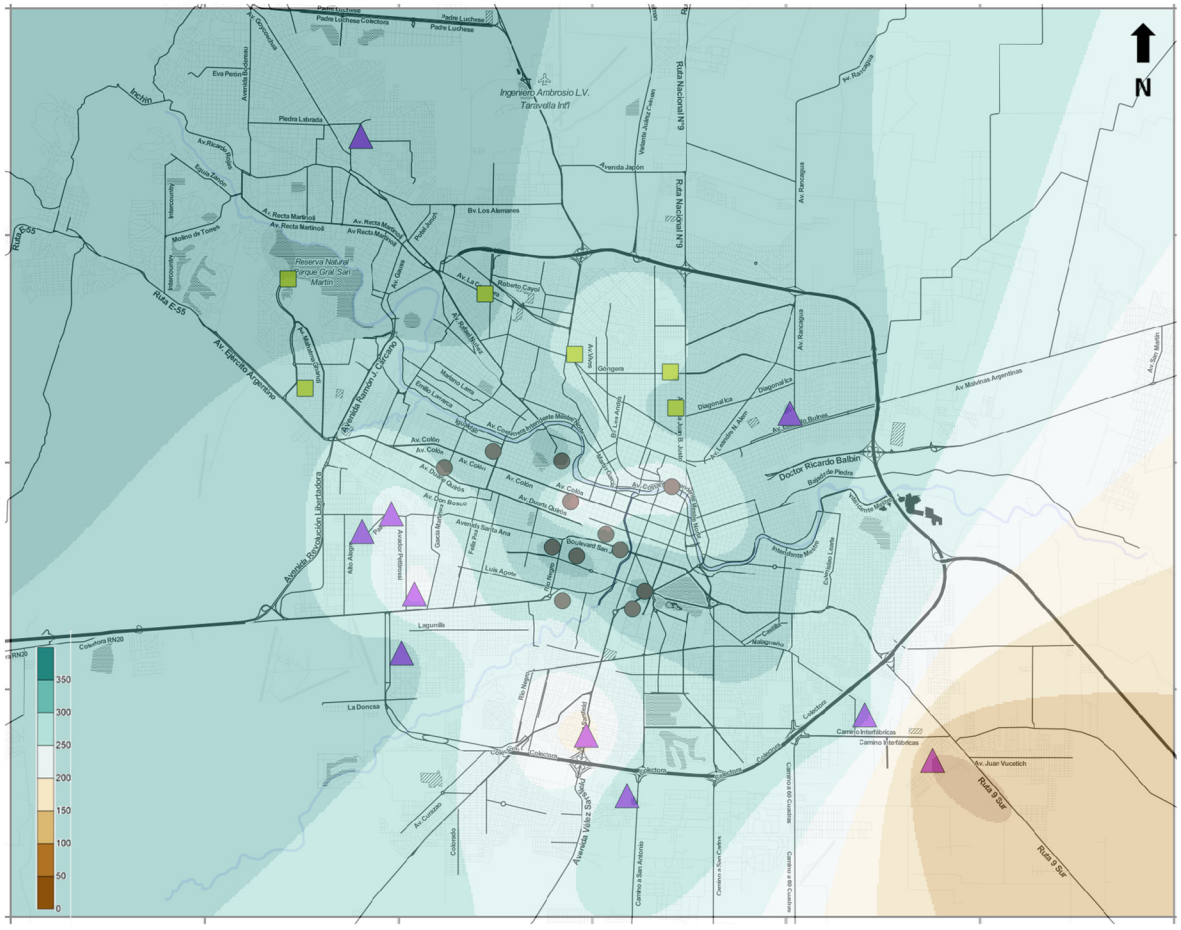

Fig. 2. Spatial distribution of total PAHs (ng g^{-1} DW) in the urban area of Cordoba city (• urban; ▲ industrial; ■, peri-urban).

more than 60% of the PAHs content in all sampling areas (Fig. 3). This is probably related to the temperature dependence of the gas/particle partitioning process in these intermediate vapor pressure compounds, which can easily undergo wet and dry deposition (Ohkouchi et al., 1999; Lane, 1988). 4-ring PAHs are also usually associated to urban sampling sites (Augusto et al., 2009). In addition, the incomplete fuel combustion of vehicular traffic has been mentioned as one of their possible emission sources (Kodnik et al., 2015), which reinforces previous studies that found traffic to be the main emission source of atmospheric pollutants in Cordoba (Mateos and González, 2016). The higher levels of BghiP in the urban area support this conclusion, since it is a compound that is commonly related to traffic emissions (Nielsen et al., 1996).

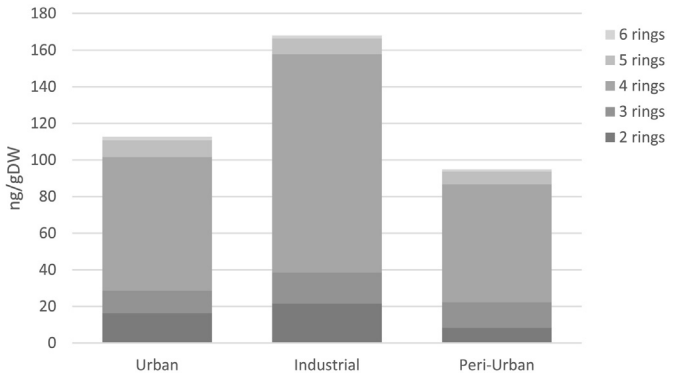

Fig. 3. Contribution of individual PAHs on different land use areas in Cordoba, Argentina.

The concentrations of the more volatile 2-ring and 3-ring PAHs were not as high, probably due to the higher vapor pressures of these low molecular weight PAHs, which tend to be associated with the gas phase rather than the particulate material. In addition, they are more affected by small increments in ambient temperature. Low molecular weight PAHs have been reported as abundant in diesel vehicle exhaust particles (Boonyatumanond et al., 2007), which is consistent with the fact they showed a stronger incidence in the industrial areas, where diesel trucks are more frequent. Contrastingly, the less volatile 5-ring and 6-ring PAHs, which are more likely deposited on the plant surface bound to particles in wet and dry deposition (Jouraeva et al., 2002), were prevalent in both urban and industrial areas, probably as a result of combined emissions coming from vehicular traffic and industrial sources. The large amounts of PAHs found in leaves from urban sampling sites agree with the high atmospheric PAH concentrations collected in Cordoba urban area employing medium-volume sampler filters (Amarillo et al., 2014). A different proportion of low and heavy molecular weight PAHs was observed in these daily samples, maybe due to the fact that leaves convey a time-integrated concentration, whereas the active sampling provides a more "on the spot" measurement, with materials of different constitution that vegetation. Wannaz et al. (2013) and Rodriguez et al. (2015) already demonstrated high total PAHs content and a higher proportion of low molecular weight compounds, but only in one industrial site in Cordoba. This agrees with the high total PAHs concentrations measured in *L. lucidum* leaves at all industrial sites covered in the current study.

Table 2
Mean + SE and range of individual, polycyclic, nitro, and total musks (ng g^{-1} DW) measured in *L. lucidum* leaves collected in different land use areas in Cordoba city.

	Urban (n = 11)				Industrial (n = 10)				Peri-urban (n = 7)			
	Mean	SE	Min	Max	Mean	SE	Min	Max	Mean	SE	Min	Max
DPMI	5.69	5.63	n.d.	67.66	0.18	0.08	n.d.	0.64	0.27	0.18	n.d.	1.16
ADBI	0.01	0.01	n.d.	0.07	0.01	0.01	n.d.	0.09	0.86	0.86	n.d.	5.16
AHMI	1.39	0.92	n.d.	10.23	3.09	1.51	n.d.	13.63	3.35	1.63	n.d.	10.05
ATII	0.01	0.01	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	0.04	0.04	n.d.	0.27
HHCB	10.38	4.78	n.d.	41.85	81.36	32.97	n.d.	279.5	4.49	1.9	n.d.	9.97
MX	0.57	0.27	n.d.	3.19	n.d.	n.d.	n.d.	n.d.	0.03	0.03	n.d.	0.19
AHTN	0.3	0.28	n.d.	3.36	0.18	0.07	n.d.	0.55	0.24	0.15	n.d.	0.73
Polycyclic	17.78	8.03	n.d.	86.31	84.82	33.11	0.23	280.6	9.25	3.44	n.d.	23.17
Nitro	0.57	0.27	n.d.	3.19	n.d.	n.d.	n.d.	n.d.	0.03	0.03	n.d.	0.19
Total musks	18.35	8.01	n.d.	87.18	84.82	33.11	0.23	280.6	9.28	3.44	n.d.	23.17

n.d.: not detected. Polycyclic: DPMI, ADBI, AHMI, ATII, HHCB, AHTN; Nitro: MX.

3.2. Musks

Regarding synthetic musk fragrances, only seven out of eleven compounds were detectable in *L. lucidum* leaves. The highest levels of total musks were found at the industrial sites, with concentrations four times higher than in the urban areas and eight times higher than in the peri-urban sampling sites (see Table 2 and Fig. 4). The mean values of individual musks varied from 0.01 (ADBI and ATII) to 81.36 ng g^{-1} DW (HHCB). The most frequently detected musk in *L. lucidum* leaves was HHCB, found in 61% of the samples analyzed, followed by AHMI and DPMI in 50 and 43% of the samples, respectively (Table 2).

While the occurrence of PAHs in vegetation is frequently reported in different studies, the use of plants as bio-samplers of synthetic musks has been poorly investigated. Exceptions include naturally contaminated pine needles (Silva et al., 2015), some vegetables (Aguirre et al., 2014), alfalfa, and apple tree leaves (Calderón-Preciado et al., 2011). Silva et al. (2015) assessed the presence of the same synthetic musks targeted in this work in pine needles from Portugal and reported concentrations ranging from 0.09 to 72.6 ng g^{-1} DW, in line with the current study. HHCB and AHTN were the predominant compounds. Calderón-Preciado et al. (2011) reported the presence of HHCB and AHTN in alfalfa and apple tree leaves collected in Spain, and found also similar mean concentrations (from 0.024 to 67.6 ng g^{-1} DW). On the other hand, Aguirre et al. (2014) found synthetic musks in three vegetables (carrot, pepper and lettuce) in lower levels (0.03–3.7 ng g^{-1}) and with only AHTN, HHCB and MK detected. The difference

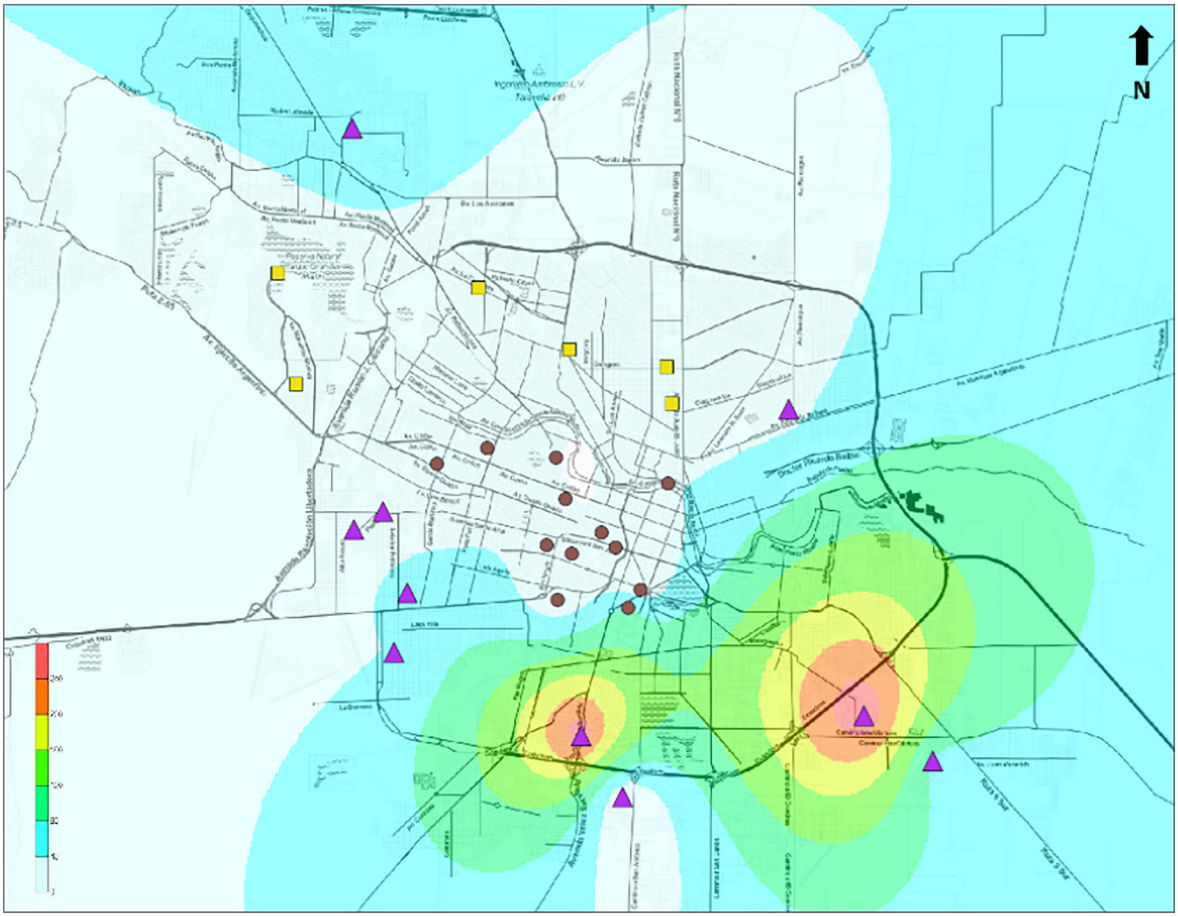

Fig. 4. Spatial distribution of total musks (ng g^{-1} DW) in the urban area of Cordoba city (• urban; ▲ industrial; ■, periurban).

in the type of vegetation matrices used in each case makes the attempt of a thorough comparison difficult.

Polycyclic musks were the most contributing compounds (90%) to the total musks, in all land use areas from Cordoba city, in line with the trend found by Silva et al. (2015) and Aguirre et al. (2014). Regarding nitro musks, only musk xylene was detected in the samples. The higher proportion (3%) was measured in urban samples, while its presence was almost negligible at the peri-urban sites and absent at the industrial sites. This compound is mostly used in personal care products, which may explain the previous result. Comparing the obtained results with those found by Peck and Hornbuckle (2006) for Iowa atmospheric air samples, a similar trend of the abundance of synthetic musks was found. In fact, a higher proportion of synthetic musks was detected in urban rather than in suburban and rural samples. HHCB and AHTN were more often detected and in higher concentrations. Although risk assessment studies for HHCB concluded that there is no risk within all scenarios (EC, 2008), a relatively strong effect might be expected due to its overwhelming occurrence in the environment. The second most frequent synthetic musk in the study area (AHMI) has a higher hazardous potential than HHCB, but as it is present in only 50% of the samples, that is, has a moderate occurrence, AHMI results in a medium environmental risk. In general, polycyclic musks were more frequently detected than nitro musks. Interestingly, there were detectable levels of polycyclic musks and musk xylene at almost all sampling sites, suggesting the ubiquitous nature of these chemicals. Nitro musks were widely used as fragrance ingredients in personal care products (Mersch-Sundermann et al., 1996), but they were banned in several countries and replaced by polycyclic musks. However, they are still being produced in some countries and used in non-cosmetic compounds (Taylor et al., 2014).

Unfortunately, data for the patterns of musks use in Argentina are not available, which would help a more clear interpretation of the potential local sources.

4. Conclusions

The higher amounts of PAHs detected in leaves of *L. lucidum* from the urban or industrial areas of Cordoba reflect strong gradients of pollution compared with the peri-urban sampling sites attributable to both emission sources and different degrees of air dispersion. One of the dominant compounds in all sampling areas is Naph, which is concerning particularly in urban and industrial areas due to its high levels, although it has a low carcinogenic potential. The determination of PAHs in the leaves of *L. lucidum* allows us to assess not only the air quality over a long-time period, since PAHs are accumulated over the whole leaf's lifetime, but also to identify zones within the urban area with a high concentration of total PAHs. Thus, biomonitors offer an additional source of information that could not be obtained by traditional instrumental methods.

Regarding synthetic musk fragrances, previous studies on environmental risk that assess both chemical toxicity and occurrence in the environment, showed that the levels of risk are quite varied, ranging from very low for MM and ATII to very high for AHTN (Homem et al., 2015a). Considering their extensive use, HHCB and AHTN have become the most popular worldwide. This trend is also true in the city of Cordoba where HHCB was also the most abundant synthetic musk. The spatial distribution of musks suggests a close relationship with industries, located to the south and south east, however more studies are needed to confirm their emission sources.

The present study opens the possibility that leaves of an urban ubiquitous tree can be used to assess the spatial behavior of PAHs and EOPs, allowing for a comprehensive understanding of urban air quality in areas where common air sampling devices are unavailable. Despite these promising results, further research on the levels of EOPs in the atmosphere is needed considering they are rather novel and therefore, still barely studied. Also, it is important to identify borderline compounds, for which it is vital to clarify the level of risk they effectively pose. Thus, monitoring efforts should focus on the needed information, avoiding non-targeted and, consequently, more expensive protocols.

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