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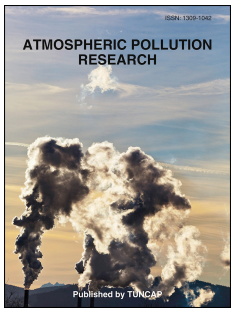

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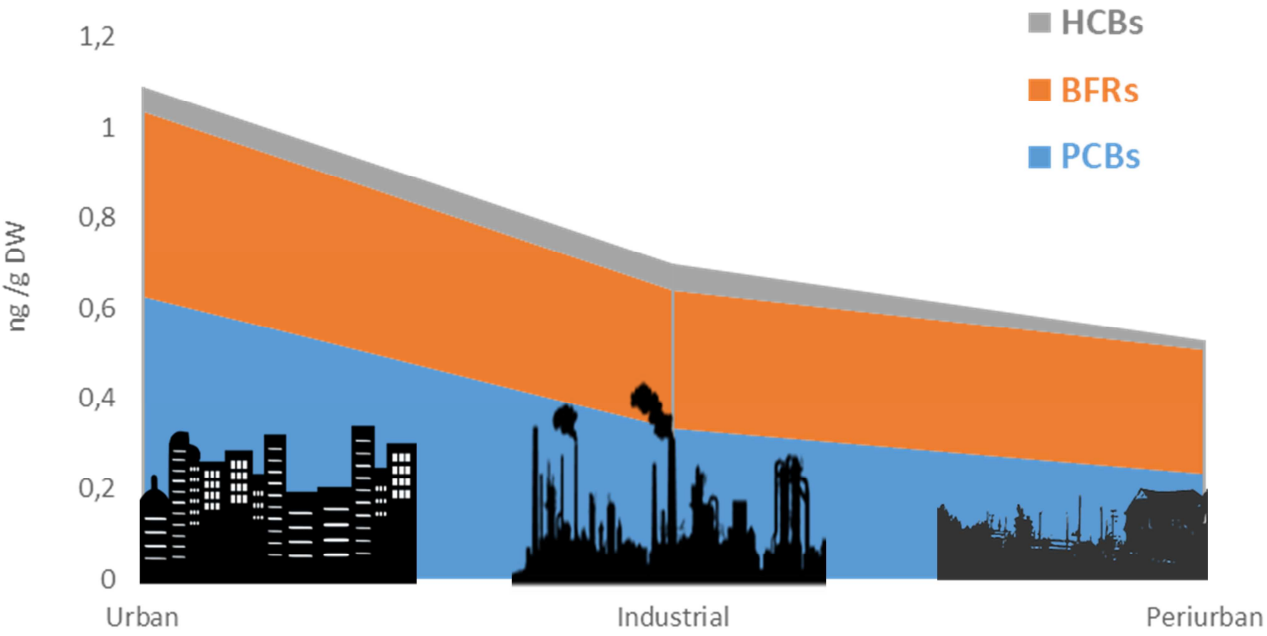

Estimation of urban POP and emerging SVOC levels employing *Ligustrum lucidum* leaves

Natalia Soledad Graziani [a], Ana Carolina Mateos [a], José Avelino Silva [b], Sara Ramos [b], Vera Homem [b], Nuno Ratola [b], Hebe Carreras [a,*]

[a]Instituto Multidisciplinario de Biología Vegetal, CONICET and Chemistry Department, FCEFyN, Universidad Nacional de Córdoba, Av. Velez Sarsfield, 1611, X5016 GCA Córdoba, Argentina.

[b]LEPABE. Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

*Corresponding author. E-mail address: hebe.carreras@unc.edu.ar (H. Carreras). Tel.: +54 351 5353800 int. 29771.

Abstract

Many persistent organic pollutants (POPs) have been banned in many countries including Argentina after enforcing the Stockholm Convention in 2014, while other emerging semi-volatile organic contaminants (SVOCs) are considered to enter the list due to their known environmental persistence and toxicity. However, there is still very little information regarding the distribution of these chemicals in the environment in developing countries. To address this issue, we employed leaves of *Ligustrum lucidum* Ait. as a passive monitor to estimate urban levels of polychlorinated biphenyls, brominated flame retardants and hexachlorobenzene (PCBs, BFRs, and HCB, respectively) considering three different land use areas in Córdoba city (Argentina). We found higher PCB values in urban and industrial areas, which could be attributed to local emission sources as well as a long-range transport of lightweight compound. BFRs were more abundant in the urban areas indicating that their main emission source is the volatilization from polymeric materials. HCB, on the other hand, was equally distributed at the three sampling areas. Overall, POP and SVOC levels were similar or even lower than some other urban environments and even comparable with remote places elsewhere.

Keywords: Biomonitoring, *Ligustrum lucidum*, PCBs, BFRs, HCB.

1. Introduction

During the last decade, persistent organic pollutants (POPs) have received increasing attention due to their persistence, ubiquity, biomagnification ability and presence in different environmental matrices worldwide (Darnerud et al., 2001; Schecter et al., 2005; Law et al., 2006; Turk et al., 2007). Among them, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs) are the compounds most frequently studied because of their toxicity and bioaccumulative properties (UNEP, 2011). PCBs were used as fire retardants, heat transfer fluids, organic diluents, plasticizers, lubricant inks, paint additives, adhesives, as well as dielectric fluids for capacitors and transformers (Safe, 1990), while PBDEs were employed as flame retardants since the 1970s in a variety of products such as textiles, carpets, polyurethane foams used in furniture and cars, electronic cables, television sets and computers (Costa and Giordano, 2007, Wang et al., 2007, Ratola et al. 2011). Both PCBs and PBDEs were recognized as industrial pollutants (Borghesi et al., 2008), released by volatilization during their manufacture or by incineration when the products were disposed (Rahman et al., 2001, Harrad, 2009). OCPs on the other hand, comprise a wide range of currently-banned pesticides almost everywhere, but that are still found in the environment due to the incineration of chlorinated compounds at open landfills and in some metallurgist processes (Swackhamer et al., 2004; Harrad, 2009). Among them, hexachlorobenzene (HCB) was the first used fungicide to treat seeds and the most common OCP found in the environment (Estellano et al., 2012). This chemical can also arise as an unintended sub-product of some industrial processes (Barber et al., 2005).

Many studies suggested that the occurrence of POPs in the environment is associated with reproductive and developmental anomalies, biochemical, histological or carcinogenic effects, endocrine disruption, and neurotoxicity, described in biota and humans (Muñoz-de-Toro et al., 2006; Costa and Giordano, 2007; Ridolfi et al., 2008; El-Shahawi et al., 2010; Ballesteros et al., 2014). With the restriction or ban of many of these contaminants, other chemicals emerge as alternatives and are under recent concern by the scientific community. For instance, brominated flame retardants (BFRs) like hexabromobenzene (HBB), pentabromoethylbenzene (PBEB) or pentabromotoluene (PBT) are being used to replace PBDEs and already detected in the environment (Li et al., 2015; McGrath et al., 2017).

Pesticides are the main POP source to the environment in Latin American countries (Harrad, 2009). In Argentina, they are extensively employed in agricultural activities (Pegoraro et al., 2015) and vast regions in the country evidenced long prolonged environmental exposition as high levels of POPs were found in blood samples (Lucero et al., 2008). Despite this fact, only a few studies have been carried out in the country, mainly in the province of Buenos Aires and with a special focus on

endosulfan, the most employed OCP for soybean cultivation. Higher levels detected in the air were related to aerial spraying of crops (Tombesi et al., 2014). PCBs were found in coastal sediments of Rio de la Plata in concentrations ranging from <0.1 to 100 ng g^{-1}, the highest being in the industrialized area close to Buenos Aires. Also, in a lagoon located to the northeast of Córdoba province, PCBs and OCPs were detected in sediments and associated crabs (Menone et al., 2001). Regarding PBDEs, there is no local information on their environmental levels except for an emission inventory performed in Mendoza province, which suggests that open burning processes are the main sources (Allende et al., 2014).

In Argentina, the use of most OCPs and PCBs have been banned since 1998 and 2005 respectively, after the country addressed the Stockholm Convention in 2004. In addition, restrictions for PBDEs were recently implemented (UNEP, 2011). Despite this fact, their residues are still found in the environment mainly due to the incorrect disposal of containers (Ballesteros et al., 2014). Still, the information on their environmental levels is scarce and most studies are focused on coastal areas and aquatic pollution (Pozo et al., 2012) or urban and agricultural lands from Buenos Aires (Miglioranza et al., 2013).

Either active or passive air samplers are commonly employed to measure atmospheric POP levels (Harner et al., 2004; Turk et al., 2007; Pozo et al., 2012). However, some studies have promoted the use of vegetation instead of instrumental monitors due to low cost, easy collection and the possibility of extensive sampling, even in remote areas (Calamari et al., 1991; Simonich and Hites, 1995). Indeed, over the last years, biomonitoring has become a useful tool to study the environmental fate, trends, emission sources and human exposure to airborne organic pollutants (Schuhmacher et al., 2004) employing particularly evergreen species (Moreno et al., 2003; De Nicola et al., 2008, 2013; Ratola et al., 2011). One of these perennial species, *Ligustrum lucidum*, has already been employed as a passive biomonitor because of its abundance in urban streets and parks, and its excellent ability to uptake air pollutants (Carreras et al., 1996; Cañas et al., 1997, Fellet et al., 2016). The waxy layer covering their leaves allows the retention of pollutants adsorbed to particles as well as the uptake of lipophilic gas-phase pollutants.

Thus, in the present work, we aimed to estimate the atmospheric levels of PCBs, legacy and novel BFRs and HCB in an urban environment employing *L. lucidum* as biomonitor and to assess their emission sources considering different land uses. In addition, we aim to contribute with information on the environmental distribution of POPs and emerging SVOCs in Argentina.

2. Materials and Methods

2.1. Study area

Córdoba is a medium-sized city in Argentina, located in a depression with a positive slope towards the surrounding area which reduces the air circulation and causes frequent thermal inversions (Olcese and Toselli, 2002). Mean temperature is 17.4 °C, the average annual rainfall is 790 mm and the prevailing winds come from the NE, S, and SE.

2.2. Vegetation sampling

Twenty-eight sampling sites were selected considering they were located at different land use areas: urban (n=12), industrial (n=10) and periurban (n=6) (figure S1, Supplementary data). *Ligustrum lucidum* Ait. leaves (4-5 cm length) from two different trees at each sampling site were collected during August-September 2013, from the outer part of the canopy and stored in polypropylene freezing bags at −20 °C.

2.3. Extraction and quantification of PCBs, BFRs, and HCB

A total of 19 PCB congeners [tri-(PCB 28), tetra-(PCB 52, 77, 81), penta-(PCB 101, 105, 114, 118+123, 126), hexa-(PCB 138, 153, 156, 157, 167, 169), hepta-(PCB 180, 189), deca-CB(PCB 209)], 11 BFRs [tri-(BDE 28), tetra-(BDE 47), penta-(BDE 85, 99, 100), hexa-(BDE 153, 154), hepta-(BDE 183), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT)] and one OCP (HCB-hexachlorobenzene) were targeted in this study. A mix of $^{13}C_{12}$ mass-labelled PCBs (28L, 52L, 101L, 118L, 138L, 153L, 180L) were used as surrogate standards for quantification purposes by the internal standard method. PBDE and PCB congeners are represented by their IUPAC numbers throughout the text.

The analytical protocol used is explained in detail in Busso et al (2018). Briefly, 2.5 g of unwashed *L. lucidum* leaves were cut into small pieces (1*3 cm) using Teflon scissors and 10 ng g^{-1} of the surrogate standards were added. Samples were extracted with 100 mL of hexane/dichloromethane (Hex/DCM 1:1) for 30 min in an ultrasonic bath. After solvent reduction, a two-step clean-up using alumina SPE glass columns and gel-permeation chromatography (GPC) was employed and the final extract was dried under a gentle nitrogen stream and re-suspended in 100 μL of Hex for chromatographic analysis by GC/MS. This analysis was performed using a Varian 450 GC/MS (Palo Alto, CA, USA) equipped with a CP-Sil 8 CB column (50 m x 0.25 mm I.D., 0.2 μm film thickness) and a fused silica deactivated retention gap (5 m × 0.25 mm I.D.) from Agilent (Santa Clara, CA, USA) and helium as carrier gas (1 mL min^{-1}). The oven temperature program began at 110 °C (held 1.5 min) then was raised to 150 °C at 20 °C min^{-1}, and then to 220 °C at 5 °C min^{-1} (held 17.5 min) and finally to 300 °C at the same rate and kept constant for 9 min. Total runtime was 60 min. The injection volume was 1 μL in splitless mode and the temperatures of

the injector, transfer line, manifold, and ion trap were 300 ºC, 250 °C, 50 °C and 250 °C, respectively. The identification and quantification of the target compounds was based on the retention times and the relative abundance of the monitored ions (for more details, see Silva et al., 2015) using the selected ion storage (SIS) system of Varian MS workstation v. 6.9.3 software.

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

Calibration was performed at a range between 4 and 400 µg L^{-1} with correlation coefficients above 0.9904. The recoveries were determined with triplicate assays of spiked leaves samples, at a level of 2 ng/g (dw). The values for the mean recoveries were: PCBs, 87 ± 14%; BRFs, 84 ± 15%; HCB, 74% (final results not recovery-corrected). Regarding the method limits of detection (LODs, calculated by the signal-to-noise ratio of 3), a range from 2.3 to 22.6 pg g^{-1} (dry weight) was obtained for PCBs, while for BFRs they varied from 9.2 to 162.6 pg g^{-1} (dw) and for HCB the LOD was 0.1 pg g^{-1} (dw).

Considering the possibility for external contaminations, the non-calibrated material was baked overnight at 400°C after proper washing to remove any residues from potential adsorption upon the glassware. Also, blanks were performed periodically to control possible interferences. The blank levels detected were residual, but all results were blank-corrected.

In order to have the results referred to dry weight, the water content of the leaves was measured by drying 1 g of fresh material in triplicate at 60 ± 2 °C until constant weight.

2.5. Statistical analysis

An exploratory analysis of the results was carried out using the multivariate principal component analysis (PCA). We used parametric analysis of variance and Tukey's test when possible (comparison of HCB concentrations) and non-parametric analysis of variance with the Kruskal-Wallis test to compare PCBs and BFRs concentrations. Significance level was set to 0.05. Data were processed with statistical software Infostat version 2008 (Di Rienzo et al., 2008). Only compounds with occurrences above LODs in at least one of the samples were included in the statistical analysis while half of LOD value was assigned to the sites where concentrations were under the LODs. BFRs and PCBs were analyzed per congener and by degree of bromination/chlorination (number of bromine-chlorine substitutes atoms) in homologue groups.

3. Results and discussion

3.6. PCBs

The mean concentration of total PCBs found in the 28 sampling sites was 0.90 ± 0.37 ng g^{-1} dw, which could, at first sight, be considered a low range, considering that Córdoba is the second largest

city in Argentina. In fact, the levels measured are like those reported for small cities located in the Italian Alps (1.1 ± 0.50 ng g^{-1} dw, Tato et al., 2011) and in other Italian rural areas (range 1.2 ± 0.46 to 1.7 ± 0.50 ng g^{-1} dw) in different tree species such as white ash, beech, spruce, chestnut, etc. (Nizzetto et al., 2008), but much lower than in pine needles collected in several Chinese cities: Beijing (93.1 ng g^{-1} dw), Shanghai (88 ng g^{-1} dw) and Fujian Province (19 ng g^{-1} dw) (Xu et al., 2004). Naturally, the uptake rate of *L. lucidum* leaves may be different from the species sampled in these studies, so the comparisons must be addressed with care.

Among the individual congeners, there was a predominance of PCB 101 (median 0.099 ng g^{-1} dw) followed by 28 (median 0.068 ng g^{-1} dw) and 153 (median 0.053 ng g^{-1} dw), while PCBs 52, 81 and 209 had the lowest concentrations (medians 4.8 10^{-4}, 0.003 and 0.001 ng g^{-1} dw) and were found only in one sampling site. PCBs 77, 105, 114, 126, 156, 167, 169, 189, which belong to the 12 dioxin-like PCBs (Alcock et al., 1998; Hong et al., 2009) were not detected in any sampling site, suggesting that the impact of the most toxic PCBs may not be high in the Córdoba region.

Regarding the homologues, the highest levels were found for penta-CBs (median 0.182 ng g^{-1} dw) followed by hexa-CBs (median 0.087 ng g^{-1} dw) and tri-CBs (median 0.068 ng g^{-1} dw). However, the comparison with previous studies that also used biomonitors is complicated since differences could arise on the species employed, as suggested by Ockenden et al. (1998). These authors already observed that the PCB accumulation profile was related to the biomonitor, e.g. pine needles were dominated by low chlorinated PCBs while lichen species were dominated by penta and hexa-CBs.

The total PCB content according to land use as well as the congener distribution is summarized in Table 1. The highest content was measured in urban sampling sites, followed by industrial and periurban areas (Figure 1), although differences were not significant (Kruskal-Wallis test, $p>0.05$). In agreement, Schuhmacher et al. (2004) reported values in chard leaves from urban, unpolluted and industrial places with no significant differences among them. The PCB levels these authors found even in unpolluted sites of Tarragona (Spain), were higher than the ones reported here. In a recent study performed with *Piptatherum L.* leaves in the same area, Domínguez-Morueco et al. (2018) found PCBs from 0.52 to 4.41 ng g^{-1} dw and predominant in a chemical industry. Instead, Astoviza (2014) found a decreasing trend of PCBs from urban/periurban sites to more remote sites in the Rio de la Plata watershed.

The most abundant PCBs in all sampling areas were penta-CBs, representing 48, 41 and 31 % of the total PCBs at the urban, industrial and periurban areas, respectively. In urban and periurban areas the second most abundant PCBs were tri-CBs (22 and 24 % respectively), which could be due

to local emission sources as well as to the atmospheric transport from distant sources since these light-weight compounds are easily transported due to their high volatility (Astoviza et al., 2016). In agreement, Allende et al. (2014) made an inventory of PCB emissions in another province from Argentina, Mendoza, and reported that almost 70% of PCBs were due to open burning of solid urban waste. Therefore, low weight PCBs could have been emitted from open landfills that favor waste dumping and incineration. At industrial areas, the heavier PCBs congeners were noticeable. Hexa-CBs were the second most abundant compounds (28%) while hepta-CBs had the highest contribution (14 %) in this sampling area thereby reflecting the potential presence of primary emission sources.

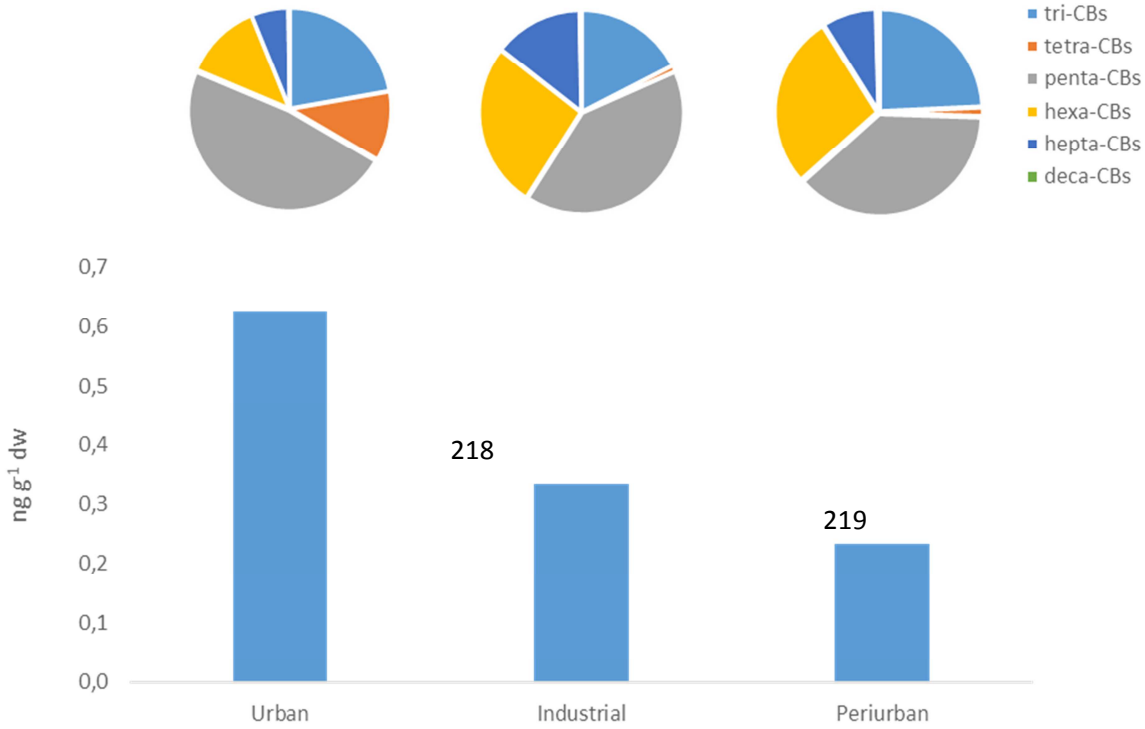

Figure 1. Median values of total PCB and congener levels measured in leaves of *L. lucidum* from different land use areas in Córdoba city.

Table 1. Median values of individual PCB congeners and total PCBs collected in urban, industrial and periurban sampling sites in Córdoba, Argentina.

Compound	**Urban**	**Industrial**	**Periurban**
	(ng g^{-1} dw)	(ng g^{-1} dw)	(ng g^{-1} dw)
PCB 28	0.101	0.058	0.057
PCB 52	0.048	0.00048	nd
PCB 101	0.175	0.098	0.071
PCB 118+123	0.047	0.028	0.005
PCB 138	0.001	0.001	0.001
PCB 153	0.033	0.074	0.06
PCB 157	0.001	0.001	0.001
PCB 180	0.026	0.046	0.019
PCB 209	0.001	nd	nd
∑PCBs	0.626	0.333	0.234

Breivik et al. (2004) stated that congeners 28 (tri-CB) and 52 (tetra-CB) are the most common to find not only because they are more volatile but also because they are two of the most abundant PCBs produced historically. Moreover, another study suggests that out of all technical mixtures of PCBs, 27.7% were produced as tri-CBs, 25.3% as tetra-CBs, 19.5% as penta-CBs, 11.3% as hexa-CBs, 4.7% as hepta-CBs and 0.02% as deca-CB (Breivik et al., 2007). However, in Córdoba, the congener 101 (penta-CBs) dominated all the sampling sites, which could be related to the fact that higher chlorinated PCBs are more associated with the particle phase and they will be preferentially removed from the atmosphere through particle deposition over leaves. In agreement with the mentioned previous studies, the second most abundant PCB was the more volatile congener 28. Harner et al. (2004) observed there was a trend of depletion of the higher chlorinated PCBs and enrichment of the lower chlorinated congeners, with distance from the urban source. Therefore, it is probable that the less volatile and more chlorinated compounds tend to remain close to their emission source, while the more volatile ones tend to volatilize and be transported over long distances. This hypothesis is supported by the fact that the higher content of heavier PCBs (hexa and hepta-CBs) were found at industrial sampling sites. In agreement, Pozo et al. (2012) affirmed that PCBs derived from fresh emissions are enriched in the higher homologue groups, whereas a PCB profile that is enriched in lower molecular weight congeners indicates the contribution from secondary sources and a long-range transport. The results of the present study suggest that urban and industrial emission sources would be releasing PCBs to the atmosphere, therefore higher

chlorinated and heavier PCBs are found in these areas, while lightweight PCBs could be transported from distant areas.

The PCB levels measured in Córdoba city are lower than the levels measured in other countries probably because PCBs were never manufactured in Argentina. On the contrary, they were imported during the 1960s due to significant power supply requirements in urban centers. Later in the 1970s, the importation of equipments with PCBs as insulators or coolants was banned and in 2003, Córdoba encouraged a program for PCB removal, which resulted in a significant overall decrease of PCB levels in Córdoba province (Miglioranza et al., 2013).

The congeners 118 and 123 were individually included in the Group 1 of carcinogenic agents according to the International Agency for Research on Cancer (IARC) (Lauby-Secretan et al., 2013). There is consistent evidence showing that the individual congener 118 can induce cancer in experimental animals (Lauby-Secretan et al., 2013), while for the much less studied congener 123, some reports sustain that it can induce tumors (Strathmann et al., 2006; Glauert et al., 2008), induces DNA damages (Marabini et al., 2011) and reduces intelligence quotient (IQ) in exposed children (Hussain et al., 2000). In the present study we were not able to differentiate between PCB 123 and 118; however, the fact this sum value showed high levels in urban samples is worrisome, either if we measured the sum of both or just one of them.

3.7. BFRs

Out of the 11 BFRs studied, 9 were detected at least in one of the 28 sampling sites (BDE 28, 47, 99, 100, 153, 154, 183, PBEB, HBB) while BDE 85 and PBT were always below LOD, and therefore not considered in the analysis (Table 2).

The total BFR concentration (sum of the congeners mentioned) at each sampling area ranged from 0.17 to 1.81 ng g^{-1} dw, being the mean concentration of Σ9 BDE 0.417 ng g^{-1} dw (median 0.341 ng g^{-1} dw). This concentration range is comparable with that found by St. Amand et al. (2007) in spruce needles (0.156 to 1.873 ng g^{-1} dw), although the mean found in our study (0.417 ng g^{-1} dw) is half the one reported for the coniferous needles (0.994 ng g^{-1} dw). The most abundant congeners were BDEs 47 (median 0.133 ng g^{-1} dw), 99 (median 0.048 ng g^{-1} dw) and 100 (median 0.032 ng g^{-1} dw), representing up to 70% of the BFRs detected. In agreement, Deng et al. (2007) and Hoh and Hites (2005) also reported the highest levels of these congeners in the atmosphere of a town from China and east-central United States, respectively. According to Gouin and Harner (2003), BDEs 47 and 99 are the main components of the penta-PBDE products and most commonly detected in biotic and abiotic environmental samples (Palm et al., 2002). Yogui et al. (2011) also found BDE 47 and 99 as the most abundant ones in *Usnea* species and mosses growing in

Antarctica. In this study, they found a higher PBDE accumulation in mosses than in lichens and was attributed to the lipids present in mosses cuticle that may facilitate the accumulation of hydrophobic chemicals such as PBDEs. Indeed, PBDE levels registered in mosses (0.59 ± 0.08 ng g^{-1} dw) are similar to the levels we found in urban sampling sites (0.51 ± 0.13 ng g^{-1} dw).

Considering the degree of bromination, tetra (0.20 ± 0.09 ng g^{-1} dw) and penta (0.16 ± 0.06 ng g^{-1} dw) were, on average, the most abundant compounds. It is already known that tetra and penta BFRs are the most persistent in the environment and can be transported long distances, whereas the higher brominated compounds with a higher octanol-air partition coefficient tend to deposit next to the emission sources (Palm et al., 2002). Therefore, we can expect high concentrations of low and medium brominated compounds in the atmosphere due to their high volatility.

Regarding PBDEs spatial distribution, a decreasing trend was seen from urban>industrial >periurban sampling areas although many compounds were only found at the urban sampling sites (Table 2). The highest total PBDE levels and also all the congeners were found at the urban sampling sites. In addition, the highest concentrations of penta-BDEs were found at urban and periurban areas, which is a worrisome result considering that penta- and octa-BDE have been reported as carcinogenic, neurotoxic and endocrine disruptors (Syed et al., 2013).

Table 2. Median values of individual BFR congeners (ng g^{-1} dw), homologue groups and total BFRs collected in urban, industrial and periurban sampling sites in Córdoba city.

	Urban	Industrial	Periurban
	(ng g^{-1} dw)	(ng g^{-1} dw)	(ng g^{-1} dw)
BDE 28	0.002	nd	nd
BDE 47	0.118	0.162	0.121
BDE 99	0.059	0.043	0.055
BDE 100	0.02	0.04	0.008
BDE 153	0.004	0.004	0.004
BDE 154	0.003	nd	0.003
BDE 183	0.022	0.026	0.01
PBEB	0.005	nd	nd
HBB	0.003	nd	nd
ΣBDE	0.411	0.308	0.272
tri-BDEs	0.002	nd	nd
tetra-BDEs	0.118	0.162	0.121

penta-BDEs	0.143	0.12	0.11
hexa-BDEs	0.007	0.007	0.007
hepta-BDEs	0.073	0.058	0.024

Regarding new BFRs, only HBB and PBEB were found in only one sampling site at the urban area (Table 2) and in levels well below the most used legacy congeners (0.017 ng g^{-1} dw). This means that they are already being used as alternative flame retardants, but still not with a very strong presence. Moreover, the three compounds targeted in this study (HBB, PBEB, PBT) are only examples of these new options, so others may have been chosen in Argentina to cope with the PBDE limitations. In a study performed in Norway with the same three new BFRs measured in pine needles, Arp et al. (2011) found that HBB was widely distributed with higher concentrations than in Córdoba (0.015 ng g^{-1} dw), while PBEB was detected only near a metal recycling factory, and PBT only in a few additional locations.

3.8. Hexachlorobenzene (HCB)

The mean concentration of HCB accumulated in *L. lucidum* leaves was 0.057 ± 0.010 ng g^{-1} dw, which is quite low compared to results reported for others cities like Beijing (2.3 ng g^{-1} dw in pine needles), a remote region from Slovenia (0.5 - 0.9 ng g^{-1} dw in pine needles), Germany (4.1 ng g^{-1} dw) Antarctica (0.30 - 2.2 ng g^{-1} dw in moss and lichens) and other European countries (1.4 - 30 ng g^{-1} dw in pine needles). The HCB levels measure in Córdoba city were more similar to those found in pine needles from Tenerife (0.01 - 0.59 ng g^{-1} dw) and other European locations (< 0.1 ng g^{-1} dw in mango leaves) (Bacci et al., 1986; Calamari et al., 1991; Calamari et al., 1994; Wenzel et al., 1997; Weiss, 2001; Villa et al., 2003; Xu et al., 2004). It has been mentioned that levels of HCBs in air vegetation have a strong seasonal trend, highly dependant on temperature (Barber et al., 2005 and references therein). Thus the present values can be considered as maximum values since our sampling was carried out during wintertime (Wenzel et al., 1997).

Even if OCPs are the most abundant organic pollutants in agricultural countries like Argentina, the concentrations measured in the present study are quite low. We could hypothesize that this is due to the fact they were banned for agricultural use (Barber et al., 2005). However, there is no information on previous atmospheric levels of HCB in Córdoba to confirm this fact. If the situation in Córdoba province was to be similar to the western region in Argentina where levels of HCB in vegetation ranged from 0.6 to 1.7 ng g^{-1} dw near downtown and 0.9 to 1.3 ng g^{-1} dw in remote sites (Wenzel et al., 1997), we might assume that HCB levels could have dropped substantially.

The levels of HCB did not show any significant difference between sampling areas, although slightly higher levels were observed in industrial areas (0.058 vs 0.055 and 0.022 ng g^{-1} dw in urban and periurban areas respectively).

It is already known that HCB is mainly found in the gas phase which means that this compound can be transported over long distances in the atmosphere before removal, therefore it could be widely distributed (Barber, et al., 2005; Shen et al., 2005). This fact could explain why we did not found differences between the three land use areas at a local scale. Many other studies corroborate this HCB spatial distribution trend (Jensen, et al., 1992; Jaward et al., 2004; Chakraborty and Zhang, 2012). Moreover, Wenzel (1997) carried out a comparative study between two urban parks in Mendoza (Argentina) and the industrial district of Leipzig-Halle region (central Germany) and did not observe any difference between background and loaded sites in both countries. Recently, Domínguez-Morueco et al. (2018) also found lower levels of HCB than others in literature in *Piptatherum L.* leaves from a chemical/petrochemical industrial complex in Southern Europe. The levels varied from 0.13 ± 0.08 to 0.17 ± 0.10 ng g^{-1} dw, which are higher than in Córdoba, but there were no statistically significant differences recorded between petrochemical, chemical, urban and background areas.

Nowadays in Argentina, the HCB production, importation, fractionation, commercialization and use for agricultural application is completely banned. However, it can still be released as a byproduct of chemical processes such as incineration of chlorine-containing products and pesticides manufacturing (Bailey, 2001) or being re-suspended as legacy HCBs from soil (Barber et al., 2005). Even when there is no evidence of its direct use, there are records about some allowed pesticides that have traces of HCB (Wang et al., 2010). Indeed, the Institute of Agricultural Health and Quality from Mendoza reported that OCPs that contain low proportions of HCB are still used as fungicides in some crops like chickpeas and potatoes, which have been raising their production over the last years in Córdoba.

Nevertheless, the presence of HCB in the region is likely due to residues of its past use, reflecting the persistence of this compound in the environment. HCB was classified as “Extremely hazardous” by the World Health Organization (2010) and as a possible carcinogen for humans, so it is important that the ban is enforced and that levels continue to decrease as a result.

4. Conclusions

The present study gives a snapshot on the atmospheric levels and spatial distribution of POPs and some emerging SVOCs over the city of Córdoba (Argentina), employing vegetation as passive samplers. PCBs, PBDEs and HCB were consistently detected in *Ligustrum lucidum* Ait. Leaves,

demonstrating these compounds are present in an urban environment. To our knowledge, this is the first study in Argentina that employed biomonitors to assess POPs levels in the atmosphere.

Regarding the spatial distribution of PCBs, we found much higher levels at the urban areas due to the contribution of medium (penta-CBs) and light-weight (tri-CBs) compounds. This fact suggests the presence of local sources as well as a long-range PCB transport of the lightweight, hence more volatile compounds. Heavy weight PCBs, on the contrary were more abundant in industrial areas indicating these compounds are locally emitted.

BFRs were more abundant in the urban areas indicating that their main emission source is probably the volatilization from the polymeric material due to physicochemical processes or migration into gaseous phase due to the abrasion of the polymer materials. On the other hand, HCB was homogenously distributed at the urban, periurban and industrial areas, clearly demonstrating their environmental persistence decades after they were banned.

Overall POP and SVOC levels found in the present study, were similar or lower than those reported in other countries, even in remotes places. However, this comparison is difficult because just a few of them employed biomonitors, and none of them use the same species, which can lead to an underestimation of the actual presence of these chemicals in Córdoba city.

Beyond the current emission sources, a critical issue to keep in mind is that environmental levels may be strongly influenced by diffusive sources from past use of POPs in urban areas, and by secondary sources, both of which are difficult to quantify accurately. Indeed, in the province of Córdoba, there are 6 controlled dumps and almost 300 uncontrolled open-air dumps scattered throughout the province where waste burning is commonly practiced (Marconetti, 2017). Still, the presence of new BFRs used as alternatives to the PBDE banned in some of the target samples indicates that the Stockholm Convention guidelines are being followed in the region.

The present study opens the possibility that leaves of an urban ubiquitous tree as *L. lucidum* can be used to assess the spatial distribution of PCBs, or other OCPs allowing for a continuous and inexpensive monitoring program in the city. Despite these promising results, further research on the levels of POPs and especially of emerging contaminants in the atmosphere are needed to understand their spatial and temporal trends and effects to the environment and to human health.

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644

- Levels of PBCs, BFRs and HCB are similar or lower than those reported in other countries, even in remotes places.
- Higher PCBs levels were registered in urban and industrial areas, suggesting the presence of local emission sources as well as transport of lightweight compounds.
- *L. lucidum* trees can be used to assess the spatial distribution of OCPs allowing for a continuous and inexpensive monitoring program in urban areas.