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Persistent Organic Pollutants (POPs) in the atmosphere of agricultural and urban areas in the Province of Buenos Aires in Argentina using PUF disk passive air samplers

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ABSTRACT

Passive air samplers consisting of polyurethane foam (PUF) disks were deployed in a network of eight sites across agricultural and urban areas in the Province of Buenos Aires in Argentina to assess levels of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) during two sampling periods in 2006 and 2007. Concentrations (pg m^{-3}) of PCBs in air ranged from BDL to 360, with an average at urban sites of Bahia Blanca (200±130) about one order of magnitude higher than at agricultural sites in the Province of Buenos Aires (20±20). Endosulfan exhibited the highest concentrations of all the chemicals investigated with a maximum of 16 000 pg m^{-3} in the agricultural area. The remaining OCPs had lower levels (pg m^{-3}) in the following ranges: ΣHCH (*α*– + *γ*– hexachlorocyclohexane) from 1 to 50, HEPT (heptachlor) and HEPX (heptachlor epoxide) from BDL to 20, chlordanes (∑trans–chlordane, cis–chlordane and trans–nonachlor) from 1 to 40, dieldrin from BDL to 30, and *p,p´*–DDE (the only isomer of DDT that was detected) from BDL to 20. Concentrations of OCPs in air were highest at Bahia Blanca city and generally higher during the warmer sampling period. This study is one of the first investigations of the POPs composition in ambient air in the Province Buenos Aires of Argentina. The results support the Global Monitoring Plan of the Stockholm Convention on POPs and specifically, the need for air data to contribute to the regional report of the GRULAC (GRoUp of Latin American and Caribbean countries) region.

Keywords: *Passive air samplers, POPs, agriculture, endosulfan, Argentina*

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1. Introduction

Persistent organic pollutants (POPs) are chemicals of global concern due to their potential for long–range transport, persistence in the environment, ability to bio–magnify and bio–accumulate in ecosystems, as well as their significant negative effects on human health and the environment (WHO, 2011). International efforts to manage POPs include the global treaty of the Stockholm Convention (SC) on POPs that was signed in 2001 and came into force in 2004 with the aim to eliminate and reduce the release of POPs into the environment (UNEP, 2010). Under the SC, the Global Monitoring Program (GMP) was implemented to facilitate the evaluation of the effectiveness of the convention through monitoring of POPs in core media of air and human tissues. A guidance document for the GMP was also prepared by UNEP and recommends the use of passive air samplers for addressing data gaps on POPs. The first report of the GMP in 2009 identified significant data gaps for POPs in air in the GRoUp and Latin American and Caribbean countries (GRULAC) region (UNEP, 2009). POPs covered by the SC include the so–called "legacy POPs". These include a wide range of substances such as organochlorine pesticides and their metabolites; industrial chemicals [e.g., polychlorinated biphenyls (PCBs)]; and anthropogenic and natural combustion products such as chlorinated dioxins/furans. The Convention also defines criteria for adding new chemicals based on their persistence, bioaccumulation, potential for long–range transport, and adverse effects.

Several countries in South America are Parties to the Convention; Argentina ratified the Convention on January 2005 and became a Party in April of that year (SAyDS, 2005). Reporting to the GMP is coordinated through the five UN regions and Argentina is a member of the GRULAC region. Although there have been several initiatives in Argentina to address the reporting needs of the Stockholm Convention, studies on POPs are scarce and most of the studies on pollutants in Bahia Blanca and the surrounding regions have focused on the coastal system.

There is very limited information on air concentrations of POPs in Argentina. Air quality monitoring, typically conducted by municipal agencies have been carried out since 1997 for pollutants such as CO, NO_X, SO_2, O_3, NH_3, VOCs and particulate matter, in the industrial harbor area, and since 2002, for some organic contaminants (benzene, toluene, o–xylene ethylbenzene and vinyl chloride monomer) (MBB, 2012a). Moreover atmospheric pollution information, in other regions of Argentina, is limited to a few studies (e.g. Wannaz et al., 2013).

Passive air samplers (polyurethane foam (PUF) disk), have become increasingly popular over the past 10 years to address

data needs for assessing the regional and global distribution of POPs (Harner et al., 2004; Jaward et al., 2004; Pozo et al., 2004; Jaward et al., 2005; Harner et al., 2006; Pozo et al., 2006; Estellano et al., 2008; Klanova et al., 2008; Klanova et al., 2009; Pozo et al., 2009; Halse et al., 2011; Pozo et al., 2011; Estellano et al., 2012; Pozo et al., 2012). In 2005, under the Global Atmospheric Passive Sampling (GAPS) network, high levels of endosulfan were reported at an agricultural site in Bahia Blanca, Argentina (in the range of ng m^{-3}) during one sampling period (3 months) (Pozo et al., 2006). The preliminary findings from the GAPS network were the motivation for the current study that explores in further detail the concentrations in air of endosulfan and other POPs at eight agricultural and urban sites in the province of Buenos Aires using PUF disk samplers. These results will provide useful insight on the sources and occurrence of endosulfan and new information on POPs levels in the South eastern part of the GRULAC region to address national, regional and global data needs.

2. Material and Methods

2.1. Sampling sites characteristics

The study area is within the Pampas region of Argentina (located between 31° and 39° South latitude). The Argentina Pampas is a wide plain with more than 52 million ha of lands dedicated mainly to cattle and crop production (Viglizzo et al., 2004). Although this region has a relatively short farming history, the expansion of no–till practice and the increasing adoption of genetically modified crops in recent years have resulted in a continuous increase in pesticide, herbicide and fertilizer inputs (Zabaloy et al., 2008). More details about sampling site descriptions are given in the Supporting Material (SM, S1).

Bahia Blanca city (latitude 38° 43´S and longitude 62° 16´W, population 302 000) is the most important urban centre of the region (INDEC, 2012) and is a centre of agricultural export via its harbor (MBB, 2012b). Its petrochemical complex is one of the largest in South America and represents 60% of the productive capacity in Argentina (CREEBBA, 2011).

2.2. Air masses characterization

This study region in the Province of Buenos Aires is under the influence of semi–permanent anticyclone centers located in the Atlantic and Pacific Oceans. These two major systems generate typical air masses and determine the dominant synoptic conditions of the area (Piccolo, 2008). Further information is provided in the SM (S2). The synoptic conditions of these systems and wind prevalence are illustrated in Figures S1 and S2 (see the SM).

2.3. Sampling sites

PUF disk samplers were deployed at 3 urban sites located in different neighborhoods of Bahia Blanca city (B1: Nueva Belgrano, B2: Universitario and B3: Villa Delfina) and at 5 agricultural sites (A1: Chasico Lake, A2: Argerich, A3: Ascasubi, A4: CONICET and A5: Paso de las Piedras Lake) of southwest of Buenos Aires Province (Figure 1) to assess POPs in different land–use categories (Table 1). Air sampling in Bahia Blanca city was conducted in two consecutive periods of six months each, during the autumn and winter of 2006 (Period 1), and the spring 2006 to mid–autumn of 2007 (Period 2). At the agricultural sites, sampling was conducted during two, non–consecutive periods. Period 1 was for ~4 months, from the early summer to mid–autumn 2006 and period 2 was for ~5 months, spanning late winter 2006 to early summer. Additional details are presented in Figure S3 (see the SM).

2.4. Passive air sampler

PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}; Tisch Environmental, Cleaves Ohio, USA) were housed inside a stainless steel chamber. The chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm, the same as the ones used under the GAPS Network (Pozo et al., 2006). Description of PUF disk clean up is presented in the SM (S3). PUF disks were fortified with 1 mL depuration compounds (DCs) (d_6–γ–HCH and labelled ^{13}C PCB–9 and –15, and native PCB–30, –107 and –198) that were spiked onto the surface of the PUF disk in order to assess sampling rate variability from site to site (Pozo et al., 2006). The depuration compounds do not typically exist in air and cover a range of volatility. Sample preparation and chemical analyses were carried out at the Hazardous Air Pollutants Laboratory, Thomson Labs, Environment Canada, in Toronto.

2.5. Extraction

Just prior to extraction, PUF disk samples were spiked with a recovery standard consisting of ^{13}C12 PCB–105 (240 ng, 99%, Cambridge Isotope Laboratory) to assess the integrity of the samples (Pozo et al., 2004). Method recoveries were assessed previously for the target compounds (Pozo et al., 2004) and shown to be satisfactory so no recovery corrections were applied to the data.

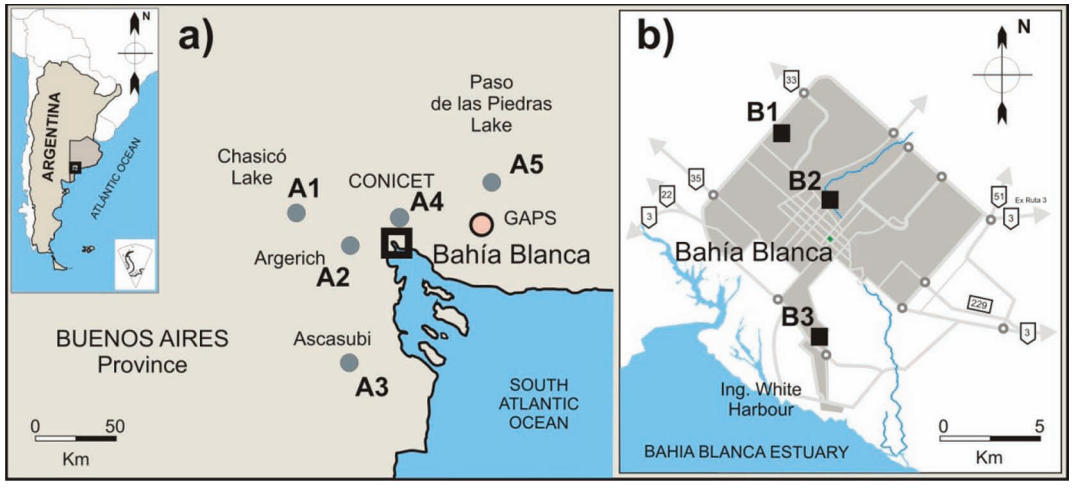

Figure 1. *Location of sampling sites:* ***(a)*** *agricultural sites (A1–A5 and GAPS site) located in southwest region of Buenos Aires Province, and* ***(b)*** *urban sites (B1–B3) in Bahia Blanca City.*

PUF disk samples were extracted in a Soxhlet apparatus for 24 h using petroleum ether. Extracts were concentrated by rotary evaporation and Mirex (10 µL) was added as internal standard to correct for volume difference. The extract was transferred to isooctane to a final volume of 1 mL and then blown down under a gentle stream of nitrogen to about 0.5 mL. Details for the extraction procedure have been presented by Pozo et al. (2004).

2.6. Chemical analysis

A detailed description of target compounds and the instrumental method is reported elsewhere (Pozo et al., 2004). Briefly, air samples were screened for 20 OCPs and 48 PCB congeners (Supelco INC, USA) (Table 1). PCBs and OCPs were analyzed by gas chromatography–mass spectrometry (GC–MS) on a Hewlett–Packard 6890 GC–5973 MS. PCBs were monitored using electron impact–selected ion monitoring (EI–SIM) and OCPs were determined in negative chemical ionization (NCI) mode. Conditions for EI and NCI analysis and selection of target/qualifier ions are described elsewhere (Pozo et al., 2004).

2.7. Quality assurance/Quality control (QA/QC)

The procedures described above were checked for recoveries and reproducibility (Pozo et al., 2004). Individual sample integrities (recoveries) were assessed using the surrogate ^{13}C PCB–105 that was added to all the samples prior to extraction as described earlier. Surrogate recoveries for ^{13}C PCB–105 ranged from 75–85%. This result coupled with previous external recovery checks for target compounds indicated that the analysis method was satisfactory. Results were not corrected for recoveries.

Blank levels were assessed from the field blanks (n=2) and laboratory solvent blanks (n=2). The instrumental detection limits (IDL) were determined by assessing the injection amount that corresponded to a signal–to–noise value ≥3. Method detection limits (MDL) in air samples were defined as the average blank (by combining field and laboratory blanks, n=4) plus three standard deviations (SD). When target compounds were not detected in blanks, 1/2 of IDL value was substituted for the MDL. The MDL values for each target compound are reported in Table 1.

3. Results and Discussion

3.1. Air concentration calculations

Air concentrations for the target chemicals were derived from the amount accumulated in the PUF disk (ng sampler^{-1}) divided for the effective air volume (V_{AIR}, m^3). Details on how air volumes are calculated are reported elsewhere (Shoeib and Harner, 2002; Pozo et al., 2004; Gouin et al., 2005). For the estimation of the effective air volume (V_{AIR}) the equation proposed by Shoeib and Harner (2002) was used; this equation considers the full uptake profile that includes the linear phase and the plateau phase. The V_{AIR} calculations are based on site–specific linear phase sampling rates (R=m^3 d^{-1} see the SM, Table S1) that were derived from depuration compounds added to each PUF disk prior to deployment according to previous methods (Pozo et al., 2006), the duration of exposure, and the PUF–air partition coefficient (of each compound), for estimating the plateaus phase of the uptake profile. The plateau phase is only relevant for chemicals with low K_{OA} values that may approach equilibrium between the air and the PUF disk during the deployment period. Information regarding the uptake behavior of low versus high octanol–air partition coefficient (K_{OA}) chemicals and the role of the PUF–air partition coefficient ($K_{PUF–A}$) has been reported in previous investigations (e.g. Estellano et al., 2012). Calculations of V_{AIR} were performed using a template provided by the GAPS Network (GAPS.Network@ec.gc.ca). Resulting V_{AIR} and R–values are summarized in Tables S1 (see the SM) for PCBs and OCPs using the average values calculated for individual OCPs and PCBs.

R–values are derived from the loss of depuration compounds (DCs) (Pozo et al., 2004; Gouin et al., 2005). R (m^3 d^{-1}) are presented in Table S1 (see the SM) and ranged from 2 to 7 (4±2). This variability in R–values between sites is consistent with results from previous studies (e.g. Pozo et al., 2009). The resulting air concentrations for PCBs, and OCPs, are summarized in Table 1 and discussed below.

3.2. Organochlorine pesticides (OCPs)

Historical information on the periods of use in Argentina of the pesticides targeted in this study, is provided in Figure S4 (see the SM).

Endosulfans (ΣEndosulfan I, II and SO_4). Endosulfan is a current–use pesticide that is used globally and recently listed under the Stockholm Convention on POPs (UNEP, 2011). Endosulfan was introduced as a broad spectrum insecticide in 1954 by Farbwerke Hoechst, Germany (Maier–Bode, 1968), and become an important agrochemical and pest control agent resulting in its global use to control a range of insect pests for a number of diverse applications (Weber et al., 2010). Technical grade endosulfan is commercially available as a mixture, typically containing >95% of two diastereoisomers, known as α–endosulfan (or Endo I) and β–endosulfan (or Endo II) in ratios from 2:1 to 7:3 along with impurities and degradation products (GFEA, 2007). Both isomers break down in the environment to produce endosulfan sulfate (SO_4) and endosulfan diol, both of which have structures similar to the parent compound and are also of toxicological concern. Large quantities of endosulfan have been imported into Argentina with 1.8 million kg in 2006 (Casadinho, 2008). A ban on imports of endosulfan was put in place on July 2012 (SENASA, 2011) and production was prohibited in July 2013, in accordance with its listing under the Stockholm Convention (SENASA, 2011).

From all OCPs analyzed in this study, endosulfans showed the highest levels detected (Table 1). Concentrations (pg m^{-3}) in air of endosulfan I ranged from ~150 (site A3, during period 2) to ~15 500 (A2, period 2), endosulfan II from 2 (A5, period 1) to ~1 800 (A4 period 1), and endosulfan SO_4 from BDL (A3 period 1) to 80 (A4, period 1). The maximum level of ∑endosulfans was observed at A2 (16 000 pg m^{-3}) (Figure 2). These results confirm the previous GAPS data in 2005 where high levels of endosulfan were reported at an agricultural site in Bahia Blanca, Argentina (in the range of ng m^{-3}) during one sampling period of 3 months (Pozo et al., 2006). High concentrations of endosulfans in air have also been reported at agricultural sites in other parts of the world e.g. Mexico (~27 000 pg m^{-3}) (Wong et al., 2009), and Mudhol, India (~26 000 pg m^{-3}) (Pozo et al., 2011) (see the SM, Table S2).

The endosulfan I/endosulfan II ratio varies widely across sites; however, in general it fluctuates from about 3 to 8 with the exception of sites A2, A3, A5 and B3 during period 1. These results could be related to fresh isolated use of endosulfan. For instance, the maximum value of ΣEndosulfans was found at A2 (16 000 pg m^{-3}), close to a traditional garlic producing area (Iurman, 2009). Otherwise in the vicinity of A4 (~7 800 pg m^{-3}) there are some sectors of high agricultural production (Lorda and Gaido, 2002). However, these results might also be influenced by the north and northwest winds that pass through the areas of soybean production enhancing the drift of endosulfan to the southern areas of this region. Although this crop is not typical of the region, soybean fields extend from the northern areas in the Province of Buenos Aires to the study area, as shown in Figure S5 (see the SM) (Stadler et al., 2006). Soybean cultivation in Argentina has increased exponentially in the last two decades coupled with extensive use of endosulfan (Stadler et al., 2006), and is now one of the main agricultural exports. Aerial spraying in Argentina is a frequent practice of application of agrochemicals. In this regard, adverse effects have been recorded amongst the population in the application area of endosulfan in some locations inside the country (Bejarano, 2008).

Table 1. *Air concentrations (pg m^{-3}) of OCPs and PCBs at study sites*

Location	Period	α–HCH	γ–HCH	∑HCH	HEPT	HEPTX	Dieldrin	TC	CC	TN	∑Chlor	Endo I	Endo II	Endo SO_4	∑Endo	pp´–DDE	∑PCBs
Southwestern Region of Buenos Aires Province																	
A1	1	0.5	3	3	<0.1	<0.1	2	0.5	<0.4	0.9	2	3 500	590	10	4 100	3	10
	2	<0.1	3	3	<0.1	2	3	0.6	0.7	0.4	2	160	30	10	200	3	<0.1
A2	1	1	1	2	<0.1	2	4	0.6	<0.4	0.8	2	2 800	280	20	3 100	2	10
	2	<0.1	1	1	<0.1	3	5	1	0.5	0.6	2	15 500	30	10	16 000	<0.1	10
A3	1	2	2	4	2	10	4	3	<0.4	0.5	4	1 800	20	<0.5	1 800	10	10
	2	<0.1	9	9	<0.1	10	<0.1	2	0.7	0.9	4	150	30	5	190	5	<0.1
A4	1	2	3	5	<0.1	10	10	2	<0.4	2	4	6 000	1 800	80	7 900	<0.1	60
	2	<0.1	3	3	<0.1	2	3	1	0.7	2	4	410	50	10	470	<0.1	20
A5	1	3	2	5	0.9	5	7	0.3	<0.4	0.6	1	3 100	2	30	3 100	10	20
	2	4	5	9	<0.1	2	2	0.7	0.4	0.6	2	420	50	10	480	4	10
Average		1	3	4	0.4	4	4	1	0.5	0.9	3	3 400	290	20	3 680	5	20
SD		1	2	3	0.6	4	3	0.9	0.1	0.6	1	4 700	560	20	4 800	3	20
Bahia Blanca City																	
B1	1	20	20	40	10	<0.1	3	20	3	2	25	400	90	20	500	7	40
	2	20	30	50	15	20	25	20	6	10	40	5 500	800	50	6 300	20	50
B2	1	15	10	25	7	<0.1	5	2	2	2	6	570	170	35	780	10	190
	2	20	30	50	20	20	30	20	6	10	40	5 700	840	50	6 600	20	360
B3	1	3	2	5	<0.1	<0.1	<0.1	3	<0.4	0.4	4	3 000	4	2	3 000	<0.1	230
	2	20	20	40	10	10	10	7	3	4	10	2 600	380	20	3 000	10	310
Average		16	19	35	10	8	12	11	3	5	20	3 000	380	30	3 400	11	200
SD		7	11	17	7	10	12	9	2	4	15	2 300	360	20	2 600	8	130
MDL (pg m^{-3})		0.1	0.3		0.1	0.1	0.1	0.1	0.4	0.1		0.7	0.8	0.5		0.1	0.1

BDL: below detection limit; MDL: method detection limit; SD: standard deviation

A1: *Chasico Lake,* ***A2:*** *Argerich,* ***A3:*** *Ascasubi,* ***A4:*** *CONICET (Technological Scientific Center of Bahia Blanca), and* ***A5:*** *Paso de las Piedras Lake.*

B1*: Nueva Belgrano,* ***B2****: Universitario and* ***B3****: Villa Delfina*

HCH: Hexachlorocyclohexane; ***∑HCH:*** *sum of a-HCH and g-HCH; HEPT: Heptaclor; HEPTX: Heptaclor epoxide; TC: trans-chlordane; CC: cis-chlordane; TN: trans-nonachlor;* ***∑Chlor:*** *sum of TC, CC and TN; Endo I: Endosulfan ; Endo II: Endosulfan II; Endo SO_4: Endosulfan sulfate;* ***∑Endo****: sum of Endo I, Endo II and Endo SO_4;* ***∑PCB:*** *sum of PCB-8, -18, -17, -15, -16+32, -28, -33, -37, -52, -49, -44, -42, -74, -70, -66, -56+60, -95, -101, -99, -87, -110, -118, -114, -105, -123,-126, -128, -157, -149, -153, -137, -138, -156, -187, -183, -185, -174, -177, -171, -180, -170, -199, -200, -203, -194, -205.*

Aldrin and pp´-DDT were BDL

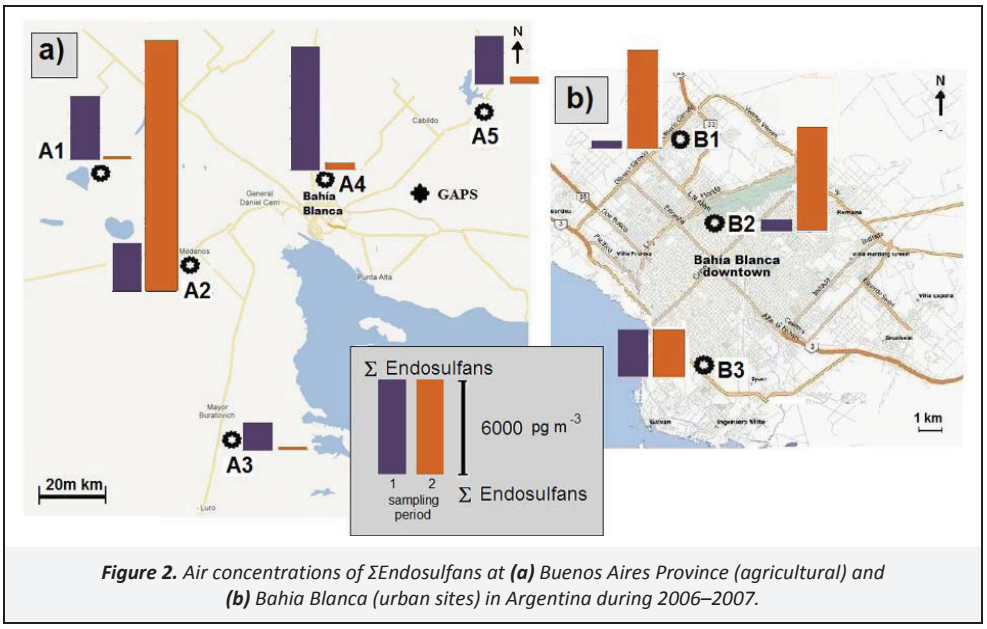

Figure 2. *Air concentrations of ΣEndosulfans at* ***(a)*** *Buenos Aires Province (agricultural) and* ***(b)*** *Bahia Blanca (urban sites) in Argentina during 2006–2007.*

Hexachlorocyclohexanes. Hexachlorocyclohexane (HCH) is a commercial organochlorine insecticide available in two technical formulations: technical HCH and lindane. Technical HCH is a mixture of several isomers of which *α*–HCH comprises 60–70% and *γ*–HCH comprises 10–12% (Li et al., 2000), while lindane consists almost entirely of *γ*–HCH (Shen et al., 2004). Technical HCH was banned in Argentina from 1980 and 1998 for agricultural use, while the first restriction of lindane occurred in 1968 for use in livestock (SENASA, 1968); however, it was still permitted for human medical treatment of pediculosis and scabicides until 2011 (ANMAT, 2011).

In general, concentrations (pg m^{-3}) in air of HCHs (α– + γ–) ranged from 1 (A2) to 50 (B1 and B2) during period 2 (Table 1). The highest concentrations in air were detected at Bahia Blanca city (4±20, max. of 50) excluding one low concentration value at site B3 (period 1) (3 pg m^{-3}). These levels are about one order of magnitude higher than those observed at the agricultural sites (4±3) (Table 1). Concentrations (pg m^{-3}) in air of *α*–HCH at agricultural sites ranged from BDL to 4 (A5, period 2), and at urban sites from 3 (B3, period 1) to 20 (B1, B2, B3 during period 2) (Table 1). These results are comparable to those reported by Pozo et al. (2004) at remote sites of Chile (~4 to 7 pg m^{-3}), and to those found at rural sites (California, USA: ~10 pg m^{-3}) (Pozo et al., 2006), and background sites (Darwin, Australia: BDL–1 pg m^{-3}), and urban sites (Downsview, Canada: ~10–20 pg m^{-3}; Kuwait City: ~1–20 pg m^{-3}) under the GAPS network (Pozo et al., 2009) (se the SM, Table S2).

γ–HCH concentrations (pg m^{-3}) in air ranged from 1 to 30 and were detected at all sampling sites and during both sampling periods. Similar to *α*–HCH, the highest γ–HCH concentrations in air were detected at Bahia Blanca City (20±10, max. of 30) (again excluding B3 in period 1 with 2 pg m^{-3}) compared with much lower concentrations at agricultural sites (3±2) (Table 1). The specific source of elevated *γ*–HCH at the urban sites is unknown, although it may be associated with continued use of lindane in the population. Previous studies have also reported high levels in other urban areas of the world. For instance, a previous study in Toronto reported episodes of high *γ*–HCH that occurred years after the lindane ban; however, the emission sources in that study were also not determined (Yao et al., 2010). High levels of *γ*–HCH, from unknown sources have also been detected in other urban sites in central Italy (Estellano et al., 2012) and in Concepcion in Chile (Pozo et al., 2012) (see the SM, Table S2).

At agricultural sites, the low levels of γ–HCHs are similar to those reported at remote and background sites i.e., sites in Chile (~6 to 10 pg m^{-3}) (Pozo et al., 2004), Alaska, USA (5–10 pg m^{-3}), Australia (Darwin: BDL –3 pg m^{-3}) (Pozo et al., 2009) and in Europe (2±7) (Halse et al., 2011) (see the SM, Table S2).

The relative abundance of the two main HCH isomers is often expressed by the *α*/*γ*–HCH ratio to distinguish fresh use of the technical mixture (*α*/*γ*–HCH=4 to 7) from an aged signature of technical HCH and/or use of lindane (mainly γ–HCH) that would result in much lower ratios (Shen et al., 2004). In this study the *α*/*γ* ratio at agricultural sites ranged from 0.2–1.7 and at urban sites from 0.7–1.5 reflecting the international restrictions on the use of technical HCH.

Dieldrin. Dieldrin and aldrin are organochlorine pesticides that have been banned in Argentina since 1980 and 1990, respectively (Garcia et al., 2003). The occurrence of dieldrin in the atmosphere arises from volatilization of dieldrin applied to soil and also from the use of aldrin, which can be converted to dieldrin in the environment. Concentrations (pg m^{-3}) in air of dieldrin at Bahia Blanca City were generally low, ranging from BDL (B3, period 1) to 30 (B2, period 2), and at agricultural areas from BDL (A3, period 2) to 10 (A4, period 1) (Table 1). These levels are low and similar to other studies at background sites (Storhofdi, Iceland: ~3–30 pg m^{-3}; Barrow, Alaska (USA): ~2 to 10 pg m^{-3}) (Pozo et al., 2009), and also similar to those found at other urban sites of the world (i.e., Izmir, Turkey: BDL to 20 pg m^{-3}; Barcelona, Spain: BDL to 40 pg m^{-3}) (see the SM, Table S2).

Heptachlor (HEPT) and heptachlor epoxide (HEPX). Heptachlor is an insecticide used primarily against soil insects and termites but also against cotton insects, grasshoppers, and malaria–carrying mosquitoes. Argentina has banned the production, marketing and use of heptachlor for use on animals and plants since 1993 and since 1998 for sanitation uses of public and private environments (Garcia et al., 2003). Heptachlor is metabolized in soils, plants and animals to heptachlor epoxide, which is more stable in air and biological systems (Bidleman et al., 1998).

Concentrations (pg m^{-3}) in air of HEPX at agricultural sites ranged from BDL (A1, period 1) to 10 (A3), while at Bahia Blanca city ranged from BDL (all sites, period 1) to 20 (B1 and B2). However, its precursor HEPT was detected at 83% of urban sites (Bahia Blanca) and ranged from BDL (B3) during period 1 to 20 (B2) during period 2, while at agricultural sites HEPT was only detected at two sites (A3 and A5 at levels of 2 and 0.9 pg m^{-3}, respectively) during period 1. The results observed at agricultural sites are in the

range of those found at other sites around the globe (see the SM, Table S2). However, the results from Bahia Blanca city (HEPT: 10±7 pg m^{-3}, HEPTX: 8±10 pg m^{-3}) suggest a more recent, post–prohibition use of HEPT.

DDTs. Widely applied as an insecticide in the past, DDT has been totally banned in Argentina since 1998. In the environment, *p,p´*–DDT (the main component of DDT) is converted to *p,p´*–DDE, and the relative abundance of parent and metabolite is often used to distinguish recent use (DDT/DDE >1) from an aged signature (DDT/DDE <1) (Pozo et al., 2009).

Of all DDT isomers analyzed in samples, *p,p'*–DDE was the only compound detected. Concentrations of *p,p´*–DDE in air ranged from BDL to 20 pg m^{-3}, with the highest levels detected during the warmer summer sampling period (period 2) at the urban sites (B1 and B2). These levels were low and comparable to those reported at remote/background sites in the world, at Cape Grim, Australia (BDL to ~10 pg m^{-3}) and Storhofdi, Iceland (BDL to 30 pg m^{-3}), and in Barrow, Alaska (BDL to ~20 pg m^{-3}) (Pozo et al., 2009).

Chlordanes [Σ: trans–chlordane (TC), cis–chlordane (CC) and trans–nonachlor (TN)]. Chlordane was used as a pesticide on agricultural crops, lawns, and gardens including vegetables, small grains, maize, other oilseeds, potatoes, sugarcane, sugar beets, fruits, nuts, cotton and jute. Chlordane has been banned completely in Argentina since 1998 (Garcia et al., 2003).

Concentrations (pg m^{-3}) in air of chlordanes were in the range of 4 (B3, period 1) to 40 (B1 and B2, period 2) at Bahia Blanca City, and from 1 (A5, period 1) to 4 (A3 and A4) at agricultural sites. These values are similar to the range of published results, including: remote sites in Chile (~5 to 10 pg m^{-3}) (Pozo et al., 2004), background sites of Europe (4±3 pg m^{-3}) (Halse et al., 2011), and different urban sites in the world such as Concepcion, Chile (35 pg m^{-3}) (Pozo et al., 2004), Kuwait City, Kuwait (5–20 pg m^{-3}) and Barcelona, Spain (5–20 pg m^{-3}) (Pozo et al., 2009), and Patna, India (2–10 pg m^{-3}) (Pozo et al., 2011) (see the SM, Table S2).

Concentrations in air at urban sites were dominated by TC, representing 58% of the total chlordanes air concentration, and followed by TN (26%) and CC (16%). Technical chlordane has a TC/CC value of 1.56 (Bidleman et al., 2002) and this ratio decreases for aged chlordane due to greater reactivity of TC. In this study the TC/CC ratio was 4±3 at urban sites suggesting its possible recent use in Bahia Blanca city.

3.3. Polychlorinated biphenyls (PCBs)

PCBs were widely used in Argentina, principally in electrical equipment (e.g. transformers). In 2002, Argentina banned the import of PCBs and the installation of machines containing them and created a register of possessors of PCBs. The law also established that owners of PCB–containing equipment should formulate a plan to achieve PCB elimination (or de–contamination) before 2010 (SAyDS, 2002).

Results of Σ_{48} PCB for each site are presented in Table 1 and Figure 3. In general, PCB concentrations (pg m^{-3}) in air were one order of magnitude higher at urban sites of Bahia Blanca (from 40 to 360, 200±130), than at agricultural sites in the Province of Buenos Aires (BDL to 60, 20±20). The highest PCB concentrations in air were detected at urban site B2 (360) during period 2. Results for Bahia Blanca City are in the range of values observed at other urban sites around the world. For instance, concentrations (pg m^{-3}) in air of PCBs were reported at Barcelona–Spain (~30 to 260), Downsview–Canada (~80 to 300), Kuwait City–Kuwait (~90 to 500) (Pozo et al., 2009), Patna in India (~130 to 400) (Pozo et al., 2011), Concepcion City (16) and at Libertad (industrial sector of Talcahuano) (350) in Chile (Pozo et al., 2012), and at Taichung (320), suburban site of Taiwan (Hogarh et al., 2012) (see the SM, Table S2).

For the agricultural areas, the site A4 (the closest site to the city) showed the highest PCB levels with 60 pg m^{-3} during period 1, also coinciding with the warmest sampling period (mean air temperature of 21 °C), followed by site A5 (20 pg m^{-3}) located ~55 km from Bahia Blanca City, and A3 (~10 pg m^{-3}) and A1 (~10 pg m^{-3}) situated approximately 80 and 65 km from the city boundary, respectively. These results are similar to PCB levels (pg m^{-3}) reported at GAPS sites in rural areas of similar latitude in the Southern Hemisphere: Laja Lake (~30) and Nahuelbuta National Park (20) in Chile (Pozo et al., 2004), and Cape Grim in Australia (from BDL to ~30) (Pozo et al., 2009). Klanova et al. (2009) reported similar PCB concentrations (pg m^{-3}) in air at background sites in South Africa in Barberspan (mean ~10), and Molopo Res. (mean ~20) (see the SM, Table S2).

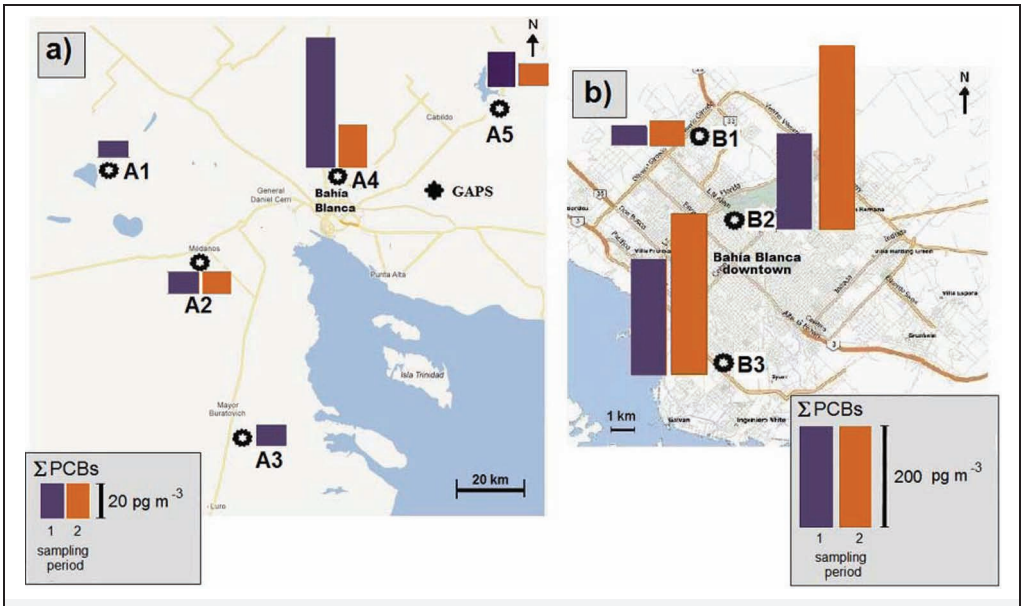

Figure 3. *Concentrations in air (pg m^{-3}) of of ΣPCBs at* ***(a)*** *Buenos Aires Province (agricultural) and* ***(b)*** *Bahia Blanca (urban sites) in Argentina during 2006–2007.*

The individual PCB congeners most frequently detected in this study were PCB–18, –31, –52, –101 and –110 (see the SM, Table S3). At agricultural sites more than 75% of the PCB congeners targeted were BDL and of the detected congeners >50% of the contribution was from the 4–Cl and 5–Cl congeners. The apparent different homolog pattern at the agricultural sites may be partly due to biases introduced by the much lower air concentrations, because many of the PCB congeners were near their detection levels.

Regarding PCB homolog composition at urban sites, PCBs were dominated by the 3–Cl (38±7%), 4–Cl (27±12%) and 5–Cl (25±10%) (Figure S5). Despite their low volatility, 6–Cl congeners were also easily detected in air at the urban sites (particularly during period 2) which is indicative of an urban, near–source signature (Harner et al., 2004; Estellano et al., 2012). Their contributions ranged from: BDL to 19% (B1), 9 to 15% (B2), and 3 to 8% (B3) (see the SM, Figure S6).

3.4 Seasonal variations

Variability in the concentrations in air of target analytes was observed at both sampling sites for all compound classes (Table 1). At the urban sites, the higher concentrations observed during period 2 (during the warmer period) are attributed to higher air temperatures that enhanced surface-air exchange of chemicals and their advection from agricultural sites (see Figure S3. At the agricultural sites, where sampling periods were not consecutive, there was negligible temperature difference between period 1 and period 2, with less variable concentrations of the target compounds.

4. Conclusions

This study represents the first investigation that reports concentrations of POPs in air at agricultural and urban sites in the south western area in the Province of Buenos Aires in Argentina using PUF disk passive air samplers. The study highlights the elevated concentrations in air for endosulfans (in the ng m^{-3} range) at all study sites that are attributed to on–going uses for agriculture. Although endosulfan restrictions have been implemented recently in the country, information regarding present stocks of this insecticide (active ingredient and its formulated products) in the Argentine territory is currently lacking.

Interestingly, levels of γ–HCHs were about one order of magnitude higher in air at urban sites versus agricultural sites. High levels of γ–HCHs have been detected in other urban areas but urban–specific sources have not been identified. PCB levels detected at Bahia Blanca city are in the same range of other urban sites around the world. Seasonal differences in air concentrations of target compounds were observed at both urban and agricultural sites. Further research is needed to explore the role of secondary sources of POPs to air, such as soil–air exchange.

Finally, this study demonstrates the feasibility of PUF disk passive air samplers as a simple tool for generating new information on legacy and new POPs in support of national, regional and global risk assessment and risk management efforts.

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Supporting Material Available

Characteristics of study area (S1), Air masses characterization (S2), PAS Chamber description and PUF disk clean up procedure (S3). Typical synoptic weather conditions in the Bahia Blanca estuary. (A) Pampero winds (name used to identify the winds of south and southwest), (B) southeast winds, and (C) north winds (Figure S1), Wind Rose representation for CONICET Station (at sampling site A4, next to Bahía Blanca city) for the 2006–2007 sampling period (Figure S2), (a) sampling site details, location and sample durations (total days) represented by Gantt chart, and (b) average monthly temperatures (°C) during the study period (January 2006 to May 2007) (Figure S3), Period of usage of chlorinated pesticides in Argentina (Figure S4), Main areas of soybeans cultivation [Glycine max (Fabaceae)] in the northern area of Argentina, during 2001–2005 (Figure S5), Homolog composition of ∑PCBs (pg m^{-3}) at sampling sites in Buenos Aires province and Bahia Blanca city during January 2006 to May 2007 (Figure S6), Sampling sites time of exposure (days), sampling rate (R) and air of volumes (V_{AIR}, m^3) during two period of sampling at Buenos Aires Province and Bahía Blanca city (Table S1), Comparison of results from the present study with other studies across the globe measuring OCPs and PCBs using PUF disk passive air samplers (Table S2), Average of air concentrations (pg m^{-3}) of selected dominant PCBs congeners at study sites (Table S3). This information is available free of charge via the Internet at http://www.atmospolres.com.

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