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Indoor Persistent Organic Pollutants in agricultural areas from Argentina

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Running tittle: Presence of POPs and chlorpyrifos in household airborne particles

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Abstract

Persistent Organic Pollutants (POPs) are anthropogenic chemicals extensively used in the past for industrial and agricultural purposes, characterized by their lipophilicity, ubiquity, volatility and environmental persistence. By other hand, chlorpyrifos is the most widely used current pesticide (CUPs) being the main insecticide used for crops in Argentina. The aim of this work was to assess levels of POPs and CUPs in different fractions of airborne particles collected indoor in agricultural areas from Argentina. Particles higher than 2.5 μm were trapped in polyurethane foams (PUF) while particles smaller than 1 μm and volatile compounds were adsorbed on activated charcoal. Compounds were analyzed by gas chromatograph with electron capture detector (GC-ECD). Endosulfans, chlordanes, PCBs, and HCHs were detected in all PUF samples, while endosulfans, chlorpyrifos, PCBs and HCHs were the most abundant in smaller particles. Majority of pesticides showed higher concentrations during the summer season (1397,7 vs 832,5 pg m^{-3}). Even adding up all measured organic compounds no sample reach the threshold limit value for indoor pesticides levels (0.1 pg m^{-3}), neither in the large or small particle fraction. However, the fact that chronic exposure to POPs has been linked to several diseases, raises concern for human health.

Keywords

airborne particles, POPs, CUPs, Argentina, $PM_{2.5}$, agricultural fields

Practical Implications: Agricultural and non-agricultural POPs have been detected in airborne particles collected indoor in households from an agricultural area, suggesting a significant exposure of humans to these organic compounds. Overall compounds concentrations tend to increase during summertime, probably due to their volatilization with higher ambient temperatures. According to our results, home ventilation and cleaning activities fail to reduce chemicals concentrations at indoor environments.

1. Introduction

Persistent Organic Pollutants (POPs) are mainly anthropogenic chemicals extensively used for industrial and agricultural purposes around the globe. Among them, organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) are the most frequently found environmental pollutants. They are characterized by their lipophilicity,

ubiquity, with high to medium volatility and environmental persistence, leading to high bioaccumulation in organisms and biomagnification through the food chain[1]. They are forbidden at worldwide level and regulated by the Stockholm Convention due to their demonstrated adverse effects on human health[2, 3, 4]. However, they are still found in the environment due to their recalcitrant chemical and physical properties[6, 7].

Recently, as a result of the ban of most OCPs, the employment of current use pesticides (CUPs), has increased worldwide[8]. For instance, in Argentina, chlorpyrifos and cypermethrin, are the most widely used CUPs[9]. These compounds are less persistent and more water soluble, than the OCPs, therefore, they are not expected to be present in the environment to the same extent than OCPs [10]. However, the fact that CUPs have demonstrated a long-range atmospheric transport under certain conditions[8, 11] and that they are used extensively, representing more than 30 % of the total consumption of insecticides[12], points towards a possible exposure risk.

Urban and industrial activities could be also important emission sources of organic pollutants to the environment, such as, polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs). In Argentina, PCBs were widely used in electrical transformers until they were forbidden in 2010, however, levels of PCBs are still detected in different environments[5, 6, 13]. On the other hand, PBDEs are still employed as additive flame retardants in many household products and might leach out throughout their entire lifetimes[14, 15]. Additionally, their proved persistence, toxicity, and carcinogenic/mutagenic health effects have attracted scientific attention throughout the world[16, 17].

To date, there is still limited information about human exposure to POPs in Latin American countries[18, 19], and most of these studies have been done in outdoor environments. However, humans spend most of their time indoors where organic pollutants may be higher than outdoors [20]. In indoor environments, semivolatile organic compounds can be either adsorbed to a particle surface or absorbed to one or more of the particle phases, depending on the nature of the particle, the compound vapor pressure as well as ambient temperature [21].

Hence, analysis of organic contaminants in household dust should be performed in an effort to characterize human exposure in the indoor environment. Despite the fact Argentina experienced a rapid growth in agricultural production and a massive increase of pesticide use in the past two decades, there is no information about the presence of pesticides into households [21].

The main aim of this work was to study the levels and distribution of several POPs and chlorpyrifos associated to different fractions of airborne particles collected at indoor households

environments in agricultural areas. Thus, the study fills a gap related to actual POPs profiles in developing countries, assessing the potential drift from agricultural fields to indoor environments.

2. Material and methods

2.1. Study area

Las Higueras (33°5'32 S, 64°17'20 W) is a small city with 8000 inhabitants, located to the south of Cordoba Province (Argentina), in the center of a vast agricultural region in central Argentina. The main economic activities in the area are extensive agriculture and livestock, in addition to few industries related to agricultural activities.

The climate is sub-humid, with warm and humid summers and short, cold and dry winters. Annual mean temperature is 16.8 °C, prevailing winds come from the north and west direction and occur through August to December. Mean annual rainfall is 809 mm concentrated in the summer months.

2.2. Sampling

Five different households within the town were selected according to their distance to the route and their distance to two grain-storage facilities (Figure 1). At each house and in the most frequently used room, weekly samples of large (higher than 2.5 μm in diameter) particles were collected during 4 weeks in winter and other 4 weeks in summer 2015, while fine particles (smaller than 1 μm in diameter) were collected only during the 4-week period in the summer.

All samples were collected using $PM_{2.5}$ sampler (Harvard Impactor) coupled to an air pump at a constant flow of 12.5 ± 2 L min^{-1}. Particles higher than 2.5 μm were trapped in polyurethane foams (PUF) located inside the impactor plate, *particles smaller than 2.5 um were collected on teflon filters with 1 um pore diameter (not used)*while particles smaller than 1 μm and volatile compounds were adsorbed as the air passes through a closed vessel containing activated charcoal.

3. Chemical analyses

3.1. Extraction

PUF samples were cut in small pieces and sonicated during 20 min with 50 mL mixture hexane:dichloromethane (50:50) + 10 μL PCB 103 as internal standard. Despite PCB 103 is not found in the environment, it has a common behavior with the rest of compounds in the

chromatography run. This procedure was repeated three times. All the extracts were then concentrated with a rotavapor, at 35-40 °C, until 2 mL final volume and stored in freezer.

Activated charcoal samples were homogenized using a blender jar. From each original sample, subsamples of 3 g were ground in a mortar with anhydrous sodium sulfate and extracted with a 50:50 mixture of hexane:dichloromethane in a Soxhlet apparatus (Melville, NJ, USA) for 6 h. Extracts were concentrated under nitrogen to approximately 3 mL and stored in freezer (-20 °C)[22].

3.2. Purification and contaminant determination

Lipids were removed from both extracts (PUF and activate charcoal samples) by gel permeation chromatography in Bio Beads S-X3 (200–400 mesh; Bio-Rads Laboratory, Hercules, CA, USA), and further purified by using column chromatography with activated silica (200 °C for 24 h). The final eluate was concentrated to 1 mL and kept in vials at -20 °C prior to gas chromatography analysis[22, 23].

Compounds were analyzed according to Miglioranza et al. [22]. Briefly, samples were screened for OCPs (α-, β-, γ- and δ-HCH, α- and β-endosulfan, endosulfan sulfate, p,p′-DDT, p,p′-DDE, p,p′-DDD, α- and γ-chlordane, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide), chlorpyrifos, PCBs (#8, #18, #31+28, #33, #52, #49, #44, #70+95, #66, #56+60, #101, #99, #97, #87, #110, #118, #105, #123+149, #153+132, #141, #138, #158, #128, #156, #187, #183, #174, #177, #180, and #170), and PBDEs (#28, 47, 99, 100, 153, 154, and 138). All compounds were analyzed on a Shimadzu gas chromatograph GC-17A with electron capture detector (ECD), equipped with a fused-silica SPB-5 capillary column (30 m, 0.25 mm i. d.,0.25 μm film thickness, Supelco, Bellefonte, PA, USA). The ECD was kept at 310 °C. The oven temperature program started at 100 °C, held for 1 min, followed by an increase of 5 °C min^{-1} up to 150 °C, held for 1 min, increase 1.5 °C min^{-1} up to 240 °C, and then 10 °C min^{-1} up to 300 °C, held for 10 min.

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

Laboratory and instrumental blanks were analyzed throughout the procedure and results indicated that there were no contaminants or interferences of the samples during laboratory handling. Recoveries, calculated by a spiking matrix and surrogate recovery (PCB #103), were greater than 90%. POPs detection limits, calculated according to Keith et al[24] ranged between 30 to 50 pg ml^{-1} for HCHs, 190 pg ml^{-1} for chlorpyrifos, and between 80 to 330 pg ml^{-1} for the

remaining compounds. Thus, method detection limits (MDLs) were calculated as the mean blank mass plus three standard deviations and they ranged from 120 to400 pg. g^{-1} dry weight. Only compounds with occurrences above LODs in at least one of the samples were analyzed.

4. Results and discussion

In the present study, twenty-eight different organic compounds were detected in particles > 2.5 μm and only 21 in smaller particles or gaseous phase (Table 1). Majority of compounds were more concentrated in $PM_{2.5}$, in agreement with Garcia-Jares et al. [25] who suggested that concentrations on dust particles far exceed those in the gaseous portion of indoor air. However, other authors advised that organic compounds in settled dust, airborne particles and in the gas phase are highly correlated [26]. Regarding abundance, HCHs, endosulfans and DDT showed the higher levels in larger particles while chlorpyrifos, HCHs and heptachlor were the most abundant in smaller ones.

Pesticides

HCHs concentrations ranged from non-detectable (nd) to 533.7 pg m^{-3} in larger particles; the most abundant was the γ-isomer which represented a 60% of total HCHs and was detected in all samples, while β-isomer and α- isomer were detected in 18 and 7 samples, respectively. In smaller particles, HCHs ranged from nd to 141 pg m^{-3}, the most abundant was the γ- isomer and then α- and β-isomers with similar concentrations, although they were detected in 3 and 10 samples, out of 22, respectively (Figure 2). The γ-HCH, also known as lindane, has been used as an agricultural insecticide but also as a pharmaceutical human treatment. In 2009, the production and agricultural use of lindane was banned under the Stockholm Convention. Argentina banned the use of technical grade HCHs in 1998, but lindane (99% γ-isomer) was still in use until 2011 for the treatment of scabies and lice infestations[27]. The fact that in this study lindane levels were twice the ones registered outdoor in southern Buenos Aires province, Argentina (50 - 62 [28]) suggests that this pesticide would be still in use. Similarly, Jaward et al.[29] reported the lindane use in some areas of Europe. Other study by Bohlin et al.[20] reported indoors lindane levels in Mexico City from 1.8 to 310 pg m^{-3} and larger variations in indoor homes from Lancaster, UK (from 47 to 1300 pg m^{-3}). Salquèbre et al.[30] and Schummer et al.[31] detected γ-HCH in hair samples and attributed this occurrence, partially, to its presence in the air. In the present work, higher mean and median HCHs values were detected in samples collected during the summer season (Σ HCHs mean 206.51 vs

107.49 pg m^{-3}; median 124.52 vs 111.59 pg m^{-3}) probably related to its intensive use to fight pest infestations during warm temperature periods.

Endosulfan has been shown to be one of the most abundant organochlorine pesticides in the global atmosphere, due to its massive use, persistence and low volatility in the environment[5]. Large particles showed total endosulfan concentrations, in a range from 18.56 to 196.7 pg m^{-3} while smaller ones showed concentrations ranging from nd to 23.09 pg m^{-3}. In $PM_{>2.5}$ more than 85 % of total endosulfan corresponded to α- isomer which is the most thermodynamically stable, while in $PM_{<1}$ only the α- isomer was detected (Figure 3). Isomers ratio may be affected also by degradation processes since both α- and β-endosulfan are converted to endosulfan sulfate, but the α-isomer is degraded faster than the β-endosulfan[32] modifying the original isomer composition. However, the higher proportion of the α-isomer over the β-form in our results, would suggest this degradation process is negligible or there is a prevalence of the atmospheric conversion of β to α-form. Previous studies in Argentina reported outdoor endosulfan levels in the range of 57 to 19000 pg m^{-3} in Bahía Blanca city, Buenos Aires province[33], between 190 and 16000 pg m^{-3} in the southwestern region of Buenos Aires province[7] and 10 to 63000 pg m^{-3} in a horticultural area in Buenos Aires[5]. Despite the use of endosulfan in Argentina has been banned since 2013, other authors already recorded high outdoor endosulfan levels during summer season, suggesting a possible current use[28]. In agreement, the highest content of both isomers was found during summer season (Σ Endosulfans mean 69.57 vs 47.36 pg m^{-3}; median 57.40 vs 39.38 pg m^{-3}), which could be attributed to fresh endosulfan application in spring/summer rather to the contribution of volatilization from soil due to high temperatures. Similar mean endosulfan values were measured at all studied households, except for the #3 that doubled the levels registered at the other homes during summer (Figure 4). Overall, the concentrations measured indoor are much lower than the ones previously mentioned for other outdoor agricultural environments. However, the values are still detectable indicating that inhalation of airborne particles is a significant exposure pathway for this pesticide, in addition to dermal uptake or ingestion which could be a relevant pathway for children [34].

Despite DDT was banned in Argentina in 1998, its residues can still be present in the environment. DDT was mainly detected associated to larger particles with concentrations ranging from 13.4 to 66.12 pg m^{-3}. Similar levels have been measured in outdoor samples at Bahia Blanca (< 0.1 - 20 pg m^{-3} [7]), Chile (<5 - 30 pg m^{-3} [34]) and Colombia (2 - 97 pg m^{-3} [33]). In this work, the relatively high indoor levels detected in 4 homes, suggest a probably recent use of this pesticide.

Since it was forbidden many years ago, a possible fresh DDT input could be due through the domestic use of the acaricide Dicofol, in agreement with other studies [35]. It is known that during Dicofol manufacturing, DDTs is generated as an impurity of this acaricide [36]. Moreover, DDT has been detected in antifouling paints [37, 38] which could also explain the high values detected indoor.

Cyclodienes are another group of OCPs already banned in Argentina. However, small quantities of these pesticides were still found in larger particles collected at all households. The α- and γ-chlordane were the most abundant (mean 14.82 and 16.18 pg m^{-3}; median 4.44 and 8.33 pg m^{-3}) while dieldrin was less concentrated (7.89 pg m^{-3}). Surprisingly, in one home chlordane values were seven times higher than those informed for outdoor environments in Bahía Blanca, Argentina (< d.l. - 5 pg m^{-3} [7]) and similar to levels observed in Colombia (< d.l. - 140 pg m^{-3} [33]) and Chile (5 - 190 pg m^{-3} [39]), which suggest a possible "fresh" input of this pesticide. This would be the case if obsoletes containers with chlordane were used as domestic insecticides for ant control. At the other homes (Figure 5), concentrations registered were within the range found in Bahia Blanca and Bolivia (< d.l. - 2 pg m^{-3} [18]). Comparing seasonal measurements we found similar values in all sampled homes, except in one where winter concentrations doubled those reported during the summer season (34.35 vs 18.61 pg m^{-3}), suggesting a possible indoor origin of these compounds. In smaller particles, α- chlordane and dieldrin were the most abundant cyclodienes, with concentrations that double the ones found for γ-chlordane (mean 11.31 and 13.78 vs 6.18 pg m^{-3}; median 7.71 and 6.87 vs 3.61 pg m^{-3}). These compounds were detected only in 3 $PM_{<1}$ homes.

Argentina has banned the production, marketing and employment of heptachlor for all uses since 1998 [40]. This pesticide was heavily used for potatoes crops and in some technical chlordanes mixtures for termites' treatments. The parental compound is rapidly metabolized to heptachlor epoxide which is commonly found in the environment [41, 42]. In $PM_{>2.5}$ heptachlor levels were detected in 3 homes (mean 11.21 pg m^{-3}; median 13.76 pg m^{-3}) and heptachlor epoxide in only one (2.64 pg m^{-3}), while in $PM_{<1}$ heptachlor was found in 4 homes (mean 18.74 pg m^{-3}; median 19.94 pg m^{-3}) and no sample had traces of heptachlor epoxide. Heptachlor values were much higher than the ones registered outdoor in agricultural sites from Buenos Aires province (0.9 to 2 pg m^{-3}) and more similar to the values measured outdoor in the urban area of Bahia Blanca city (10 pg m^{-3} [7]), which would indicate a more recent use of this insecticide in the study area, despite its prohibition. On the other hand, indoor levels of heptachlor epoxide were much lower than the values measured in agricultural areas (nd to 10 pg m^{-3} [7]).

Chlorpyrifos is one of the most sold and used CUPs in the world and is used for both agricultural and urban purposes. In the present study, chlorpyrifos levels in larger particles ranged between 2.04 to 173.1 pg.m^{-3}, which is far lower than the levels detected in dwelling facilities from South Korea, with active monitoring (2 μg m^{-3} [43]) or in agricultural sites in Ontario, Canada (110 – 770 pg m^{-3} [44]). To our knowledge, there are no records of chlorpyrifos concentrations in indoor air from Argentina, and only a few have been reported for other Latin American countries. For instance, Pozo et al. [45] reported outdoor chlorpyrifos values up to 14600 pg m^{-3} during sowing season in the Araucania Region, Chile. A clear seasonal trend was also noticeable: three times higher chlorpyrifos concentrations were observed during the summer than winter period (mean 35.21 vs 11.33 pg m^{-3}; median 13.07 vs 7.76 pg m^{-3}), which is probably consequence of its current outdoor use before and during the sowing season in the summer. On the other hand, chlorpyrifos levels in particles < 1 μm were much more concentrated, ranging between 249.9 to 6193.7 pg m^{-3}, which are more similar to the levels detected in outdoor air in South Argentina (from < 2 to 2300 pg.m-3 [28]) although the mentioned study was done with an artificial passive atmospheric sampler (resin XAD-2). The notably higher concentration of chlorpyrifos in smaller than larger particles could be associated with the relatively small octanol–gas-phase partition coefficient (Kog) that influence its distribution mainly in the gas phase. In agreement, Weschler et al. [46] informed that organic compounds with a log (Kog) value of nine or less are expected to be primarily gaseous.

Earlier researchers have reported that indoor places in rural districts contained higher levels of pesticide contamination than those in urban districts[47, 48]. This is because during application, up to 99.9 % of the pesticides are lost and move to into the environment [49] and more than 30-50 % can reach the air [50]. In addition, pesticides can also enter the atmosphere by volatilization and resuspension of historically contaminated soil particles [51]. As a result, the indoor environment has become one of the most common places where people are exposed to pesticides [52, 53]. Our results confirm this fact and provide evidence of a significant indoor exposition to pesticides through ingestion, inhalation or dermal absorption of compounds adsorbed to household dust, in a rural area in Cordoba Argentina.

Even considering the sum of pesticides from each sample, none of them reach the threshold limit value suggested by US Environmental Protection Agency for indoor pesticides levels (0.1 mg m^{-3}), neither in the large or small particle fraction. However, the fact that chronic exposure to OCPs has been linked to diabetes and liver, pancreas and breast cancer [54, 55, 56], raises concern for

human health. Moreover, recent studies have demonstrated that pesticides can act as neurotoxic substances [57] and that exposure to pesticides can even lead to death [58].

Non-agricultural POPs

Regarding other POPs that can be detected in household dust, it was found higher PCBs levels in large than in small particles (Table 2). The values measured were similar to those reported in outdoor urban areas from Bahia Blanca city, (40 - 360 pg m^{-3} [7]) an urban center with more than 100,000 inhabitants and Río de la Plata basin (< l.d. - 940 pg m^{-3} [5]) which is the largest steel making plant of Argentina. Since a PCB removal program was boosted by the Córdoba province government in 2003 and majority of sampled houses were built before this regulation, we hypothesized that indoor PCB concentrations are related to building age and came from building materials such as cable insulation, capacitors, paints and varnishes [2]. However, the influence of outdoor particles coming from polluted areas cannot be discarded. The fact that levels of PCBs in indoor air are similar to the ones registered in outdoor air, points to indoor pollutants being more persistent than outdoors, as fewer opportunities exist for losses through air flow and photolytic reactions [59, 60]. Despite there are no previous data about indoor PCBs levels in Argentina we hypothesized that levels of PCBs have remained relatively consistent over the last 15 years, with the differences being attributed to building age or building sealants rather than temporal changes caused by fate processes such as ventilation or degradation reactions. Information on use and levels of PCBs in ambient and indoor air in Latin American countries is very scarce [61]. Few reports from Mexico City indicated indoor levels of ΣPCB ranged from 100 to 840 pg m^{-3}, which are larger than the levels registered in the present study. Harrad et al. [19] reported indoor PCBs values from European cities much higher than the ones measured in Córdoba. For instance, 330 to 1600 pg m^{-3} were measured in Gothenburg, 150 to 2100 pg m^{-3} in Lancaster, and 2820 pg m^{-3} in Birmingham. These authors argued that the measurements could be not attributed to primary PCB sources since all values were much lower than those reported for buildings containing PCB-treated sealants, particularly those constructed before 1984 [62, 63, 64].

In our study, we found a higher proportion of tetra-CBs and fewer concentrations of tri- and penta- CBs in $PM_{>2.5}$ (Figure 6), while in $PM_{<1}$ we found a higher proportion of bi- tri- and tetra-CB. This trend is more similar to the uniform profile found for urban areas by Astoviza et al.[5], who reported penta-CBs followed by tri-, tetra-and hexa-CBs rather to the composition pattern found in outdoor rural areas in Buenos Aires, Argentina, that showed an enrichment in penta- plus

hexa-CBs and lower tetra-, tri- and hepta-CBs. Thus, the PCBs congener distribution pattern would be related to different facts, such as the old uses of PCB technical mixtures in indoor applications (paints, sealants, adhesives, varnishes), a possible atmospheric transport where the occurrence of light PCBs would be highlighted and, biotic and abiotic transformation processes of more chlorinated PCBs in the surrounding areas.

PBDEs compounds were exclusively found in smaller particles at all homes, which suggest their presence only in the smallest particle fraction or the gas phase. This is consistent with two hypothetical migration pathways: volatilization from the polymeric material due to physicochemical processes or migration into gaseous phase due to the abrasion of the polymer materials [65]. Several authors already mentioned that over time PBDEs diffuse out of the polymer matrix and become airborne and widely dispersed [66] due to their weak carbon-bromine bond [66]. The indoor levels registered in this study (mean 18.28 pg m^{-3}; median 17.52 pg m^{-3}) are lower than the measured in indoor air in Dilovasi, Turkey (94.7 ± 78.9 [67]), in Ottawa, Canada (100 pg m^{-3} [68]), Temuco, Chile (0.4 to 55 pg m^{-3} [45]) and Mexico City (0.68 to 620 pg m^{-3} [19]). However, majority of the mentioned studies reported sums of 7 to 9 different congeners while in the present one, we measured only the BDE-153 congener one of the most frequently found in the environment, with a recognized neurobehavioral developmental toxicity according to the United States Environmental Protection Agency [69].

Humans are rarely exposed to individual pollutants but rather to a complex mixture of potentially harmful compounds. Thus, in indoor environments it was demonstrated the presence of non- agricultural POPs, that could have joint effect with pesticides on human health.

5. Conclusions

Despite the fact that previous authors already documented the occurrence of POPs in indoor dust or airborne particles, none of these studies have been performed in developing countries from Latin America, where regulations regarding the use and storage of toxic compounds are less restricted. Moreover, to our knowledge this is the first study of this kind performed in a strictly agricultural area. PCBs, OCPs and PBDEs were consistently detected in indoor households environments, clearly denoting their environmental persistence decades after several compounds were already restricted. The agricultural fields that surround the study area behaved as an emission source of legacy OCPs and the current use pesticide, chlorpyrifos, which reinforce the role of airborne particles as vehicles of chemicals from outside to indoor environments. However, an

indoor source cannot be discarded, since old buildings by themselves are sources for persistent contaminants such as PCBs and PBDEs. Moreover, the high levels of HCHs, DDTs, chlordane, and heptachlor in indoor air compared to outdoor air strongly support the influence of fresh emission sources probably because of the employment of pesticides for domestic use. However, future studies are needed to confirm this hypothesis.

Overall, majority of pesticides showed higher concentrations during the summer season. This result could be related to the fact that samples were collected during the period where volatilization is enhanced due to the incidence of high temperatures.

Our results confirm the importance of indoor microenvironments in the total exposure to POPs decades after restrictions on use. Therefore, the present study adds insight into the importance of both primary and secondary POPs sources, and the challenges faced in managing chemicals after they have been used widely. The information provided could help local authorities to develop efficient methodologies to decrease indoor POPs levels for preserving resident's health.

Further studies are recommended in order to characterize the atmospheric burden of pesticides in other areas in Argentina, particularly those located near agricultural fields with intensive use of pesticides.

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Table 1. Descriptive statistics (pg m^{-3}) of pesticides measured in different particle size fractions collected indoor at households in Cordoba, Argentina.

	$PM_{>2.5}$					$PM_{<1}$				
	Mean	Median	S.E.	Min	Max	Mean	Median	S.E.	Min	Max
Σ HCH (α-, β- and γ-)	158,5	117	22,7	0	533,7	40,2	32,4	8,7	0	141
Σ Chlordanes (α and γ)	26	10,9	7,3	0	208,5	11,3	6,9	3,5	0,4	34,8
Σ Endosulfans (α,β- and sulfate)	58,8	46,2	7,3	18,6	196,7	8,1	8,7	1	0	23,1
p,p´ DDT	36,3	28,2	5,9	13,4	66,1	12,8	12,8	5,6	7,2	18,4
Heptachlor	11,2	13,8	3,3	4,7	15,2	18,7	19,9	4,2	7,7	27,4
Heptachlor epoxide	1,3	1,3	0,04	1,3	1,4	sd	sd	sd	sd	sd
Dieldrin	7,9	3,6	2,3	1,2	22	13,8	7,2	7	6	34,7
Chlorpyrifos	24,5	9,4	9	2	173,1	2063,3	1513	396,3	169,6	6193,7

(S.E: standard error)

Table 2. Descriptive statistics (pg m^{-3}) of non-agricultural organic compounds measured at different particle size fractions collected indoor at households in Cordoba, Argentina.

	$PM_{>2.5}$					$PM_{<1}$				
	Mean	Median	S.E.	Min	Max	Mean	Median	S.E.	Min	Max
Σ PCBs	316,4	243,5	44,4	39,8	1097,4	113,3	98,5	22,2	0	488
PBDEs (# 153)	sd	sd	sd	sd	sd	18,3	17,5	2	9,4	28,2

(S.E: standard error)

Figure 1. Location of sampling sites (●) and storage-grain facilities (★) in Las Higueras, Cordoba, Argentina.

Figure 2. Mean HCHs isomers in $PM_{>2.5}$ and $PM_{<1}$ collected in indoor household environments from Córdoba, Argentina.

Figure 3. Mean endosulfan isomers and endosulfan sulfate in $PM_{>2.5}$ and $PM_{<1}$ collected in indoor household environments from Córdoba, Argentina.

Figure 4. Mean levels of α-endosulfan, β-endosulfan and endosulfan sulfate measured in $PM_{>2.5}$ collected at five households in Córdoba, Argentina, during different sampling periods.

Figure 5. Mean levels of α-, γ-chlordane and Dieldrin measured in $PM_{>2.5}$ collected at the five individual households in Córdoba, Argentina, during different sampling periods.

Figure 6. PBDEs and individual PCBs concentrations in $PM_{>2.5}$ and $PM_{<1}$ collected in indoor household environments from Córdoba, Argentina.

Figure 1.

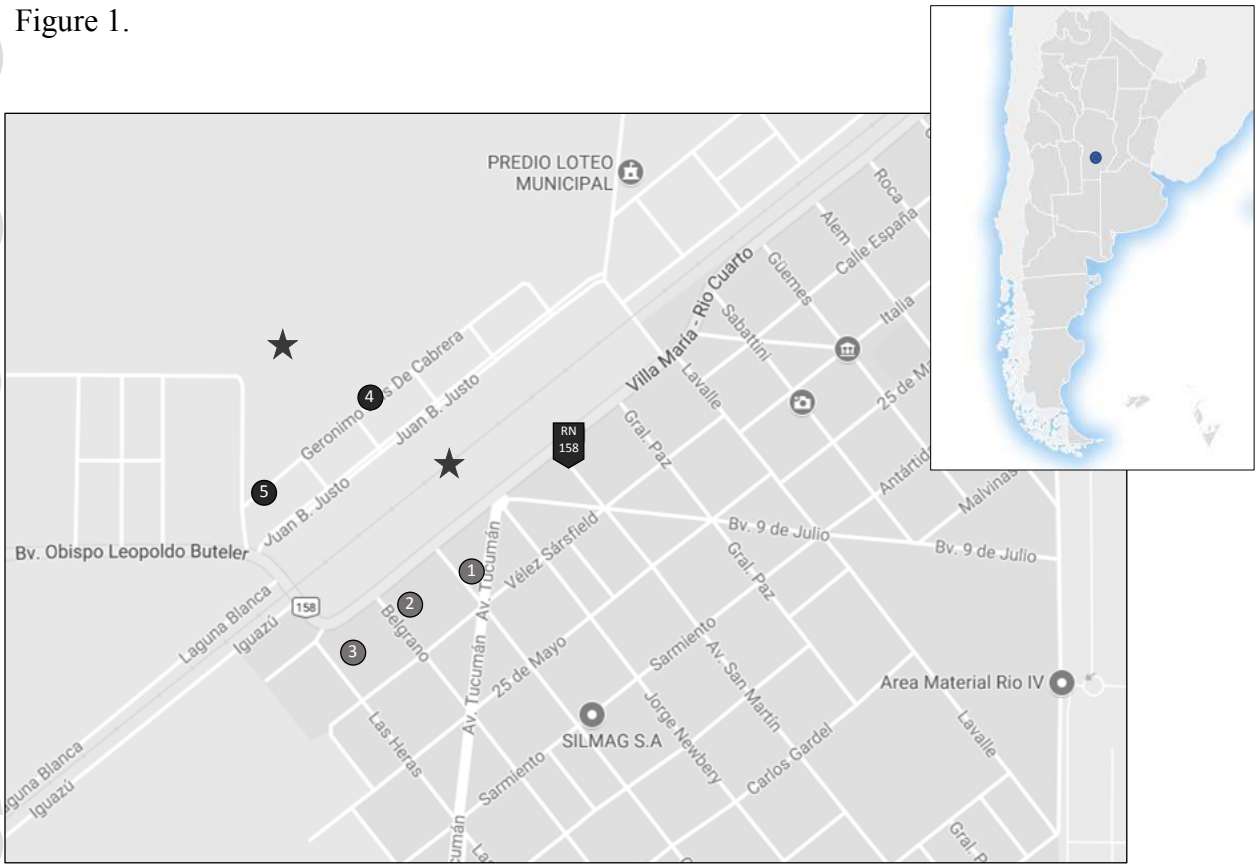

Figure 2.

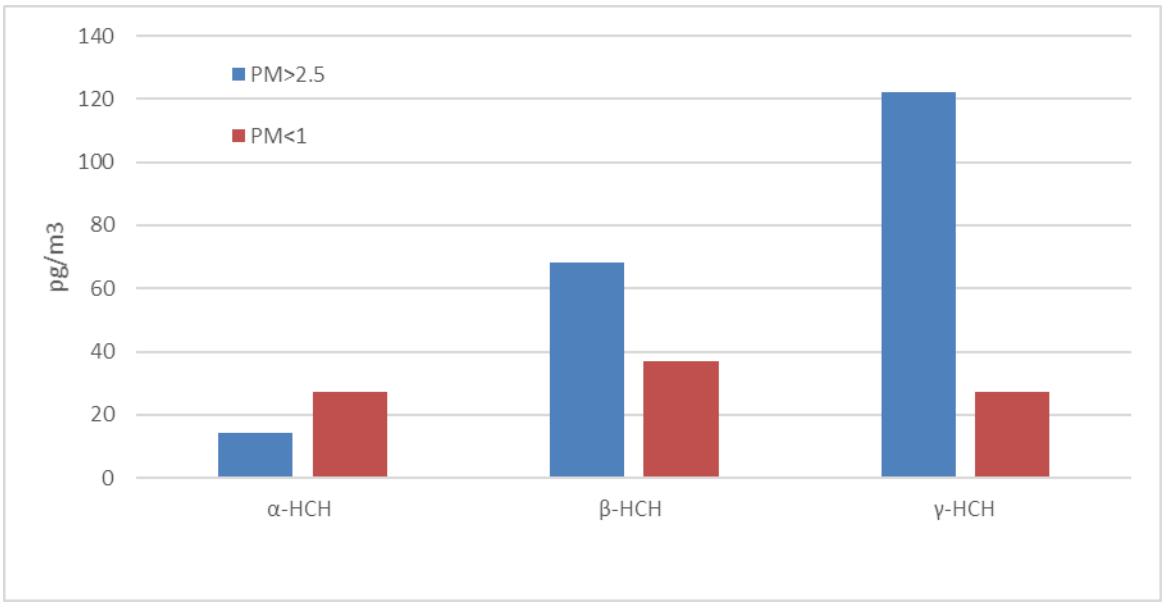

Figure 3.

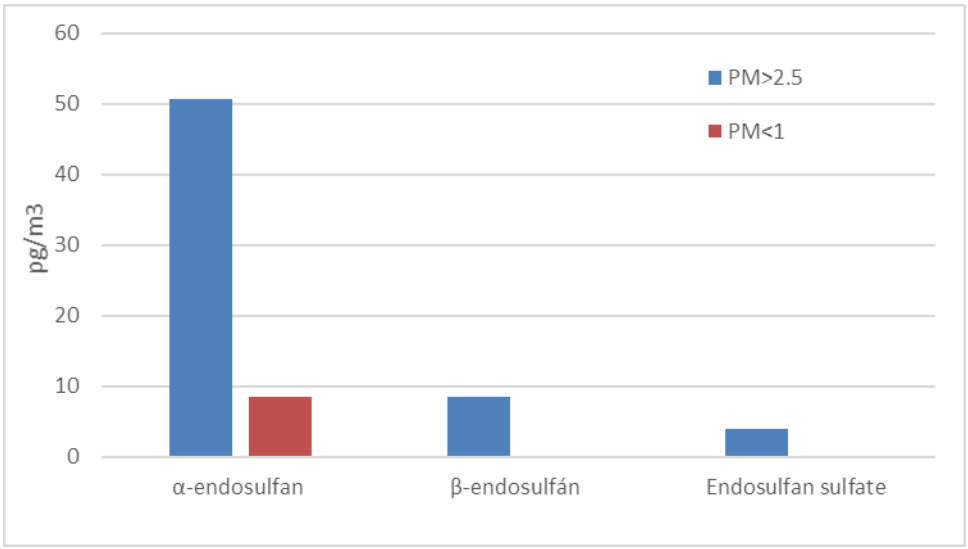

Figure 4.

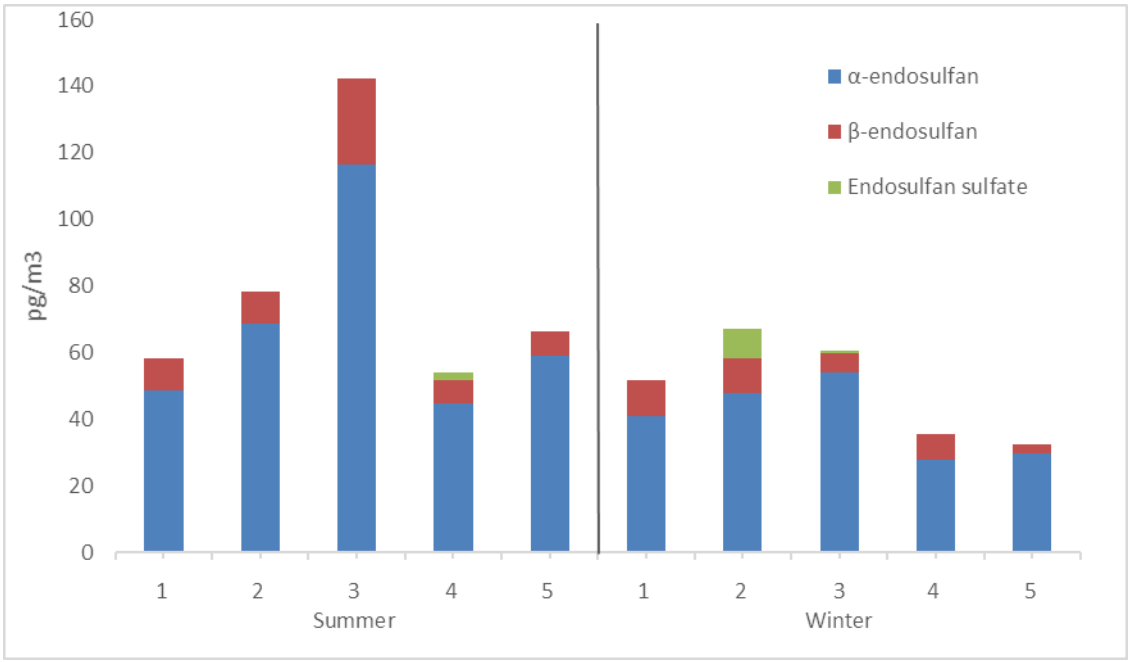

Figure 5.

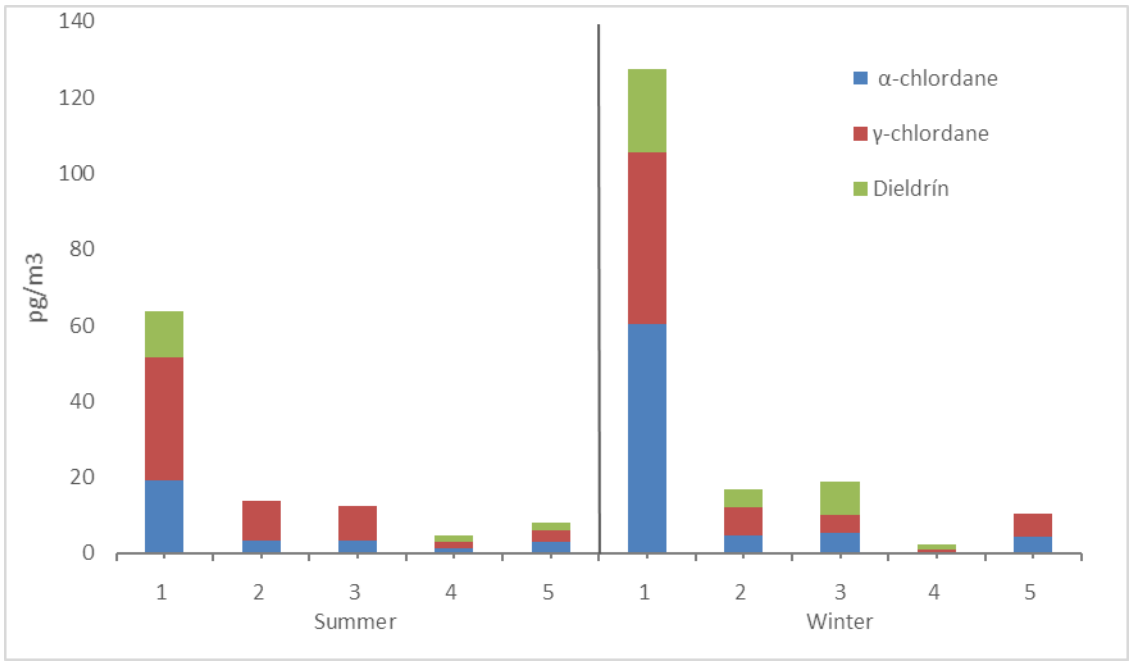

Figure 6.