Chemosphere 144 (2016) 1459–1466

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Massive airborne Endosulfan inputs related to intensive agriculture in Argentina's Pampa

Malena J. Astoviza [a, b, *], Natalia Cappelletti [a, b], Claudio Bilos [a], Maria C. Migoya [a, b], Juan C. Colombo [a, c]

[a] Laboratorio de Química Ambiental y Biogeoquímica (LAQAB), Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Av. Calchaquí y Av. del Trabajo (CP 1888) Florencio Varela, Buenos Aires, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina
[c] Comisión de Investigaciones Científicas, Provincia de Buenos Aires (CIC), Argentina

HIGHLIGHTS

- Extensive passive air sampling at Argentina's Pampa revealed worldwide Endosulfan maxima.
- Intensive soybean cultivation in the Rural area and horticulture in peri urban sites were main sources.
- Temporal pattern showed peaks during warm periods associated with seasonal application on soybean crops.
- A marked declining trend over time in Rural sites is related to incipient control policies.

ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form
6 October 2015
Accepted 8 October 2015
Available online xxx

Keywords:
Endosulfan
Passive air samplers (PAS)
Argentina's Pampa

ABSTRACT

In order to evaluate the impact of intensive agriculture on air quality in the most productive and populated Argentina's Pampas, a comprehensive assessment of airborne Endosulfan (∑Endo) was performed using polyurethane passive samplers deployed from 2010 to 2013 covering the critical period of Endosulfan restrictions at twenty nine sites in the Rural Pampa and Great Buenos Aires Metropolitan Area (GBA: Horticultural and Urban subareas). ∑Endo concentrations were very high and variable (0.01 −63 ng m^{-3}), exceeding worldwide reported maxima at Horticultural GBA and Rural Pampa with lowest values at Urban GBA (geometric means: 3.1, 1.1 and 0.53 ng m^{-3}, respectively). The composition was relatively fresh with strong predominance of Endo I (72 ± 18%) over Endo II (23 ± 15%) and Endo SO_4 (5 ± 10%). Airborne ∑Endo was significantly correlated to annual soybean crop in Rural Pampa. ∑Endo concentrations showed a temporal pattern defined by consistent peaks enriched in Endo I during summer application periods, cold temperature minima with higher proportions of Endo SO_4 and a general exponentially declining trend over time related to incipient control policies.

1. Introduction

The organochlorine pesticide Endosulfan is widely used as a pest control agent for a variety of crops (i.e. soybean, sunflower, cotton, corn, vegetables). Its global production has been estimated in 12,800 tonnes per year (Li and Macdonald, 2005) with a declining use over the last 15 years in the northern hemisphere and an increasing trend in the southern hemisphere (Weber et al., 2010). In Argentina, Endosulfan is the most used pesticide along with Cypermethrin (300% increment or 1500 t y^{-1}) principally related to intensive soybean culture (Bejarano Gonzalez, 2008).

In parallel to its broad utilization, during the last decade international concern has arisen due to the negative effects of Endosulfan on human health caused by acute and chronic exposure (hyperactivity, breathing difficulty, tremors, hunching, convulsions, birth defects and epilepsy; ATSDR, 2013). In the environment, it can undergo long range atmospheric transport (LRAT) to remote regions, bioaccumulate in organisms and biomagnify through food chains (van Pul et al., 1997; Jones and de Voogt, 1999; Goerke et al., 2004). The technical mixture, composed of >95% of two isomers,

* Corresponding author. Laboratorio de Química Ambiental y Biogeoquímica (LAQAB), Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Av. Calchaquí y Av. del Trabajo (CP 1888) Florencio Varela, Buenos Aires, Argentina.
E-mail address: m.j.astoviza@gmail.com (M.J. Astoviza).

http://dx.doi.org/10.1016/j.chemosphere.2015.10.033
0045-6535/

Endosulfan I and II (in ratios from 2:1 to 7:3), breaks down to Endosulfan sulphate (Endo SO_4) which is more persistent than and as toxic as parent compounds (US EPA, 2007). Consequently, in 2011 Endosulfan was listed under the Stockholm Convention (SC) as a Persistent Organic Pollutant (POP) in order to reduce/eliminate its release into the environment (UNEP, 2011). Argentina, as party of this Convention, has banned the import of the active ingredient from July 2012 and its use from July 2013 (SENASA, 2011).

To evaluate the efficiency of SC and to assess air concentration of POPs around the globe, a Global Monitoring Plan (GMP) has been deployed since 2009 (Klánová and Harner, 2013). For this purpose, high volume active samplers (HiVol) and two types of passive air samplers (PAS) are employed: XAD-based resin and polyurethane foam (PUFs) disks. Principal PAS advantages over HiVol are that they are more simple, low-cost devices, easy to handle and independent from any energy source so they can be used to assess temporal and spatial trends over long periods simultaneously at different geographic scales (local, regional and global; Harner et al., 2004; Pozo et al., 2006, 2009; Gouin et al., 2008; Wannaz et al., 2013).

Previous studies in Argentina have documented high levels of Endosulfan in a range of environmental matrices like sediment (Miglioranza et al., 2013), soil (Gonzalez et al., 2010), runoff (Jergentz et al., 2005) and biota (Ondarza et al., 2012). However, information on atmospheric concentrations is scarce and limited, both spatially and temporally, i.e. Santa Fe City (Lorenzatti et al., 2008) and Bahia Blanca, in southern region of Buenos Aires Province (Pozo et al., 2009; Tombesi et al., 2014) that were sampled for one and two periods.

In the present study we perform a comprehensive assessment of atmospheric concentrations of Endosulfan in the most productive and populated region of Argentina (Pampa) during 2.5 sampling years, covering the critical period of Endosulfan import restrictions in order to discriminate spatial and temporal patterns and assess the efficacy of incipient control policies.

1.1. Study area

The Pampa region is a flat area of 60 million ha below 200 m a. l. with warm (mean temperature 15–20 °C) and humid weather without a dry season (mean rainfall, 600–1000 mm per year; Grossi Gallego and Lopardo, 1988). It is characterized by its well-drained soils, with optimum pH, inorganic nutrient contents and rich in organic matter, constituting the prime agricultural land in Argentina (Merini et al., 2007). Intensive agricultural practices in this region produce 40–70% of cereal and legume crops of the country (≈100 millions of tonnes; NMACF, 2014). Floricultural and horticultural production is also an important economic activity of this area, especially on the peri-urban horticultural "ring" at Great Buenos Aires Metropolitan Area (GBA) where 135,300 tonnes of vegetables are produced annually (BAME, 2014a). GBA is also the most populated region of Argentina with more than 12 million people representing 32% of Argentina's population (INDEC, 2010).

2. Materials and methods

2.1. Sampling

Twenty nine sites covering an area >400,000 km^2 between 30°43′ – 38°43′ S and 57°13′ – 62°33′ W were sampled in 2–7 periods (Table 1) of ≈4 months each (mean: 134 days) from August 2010 to January 2013 (a few months after import restrictions, on July 2012). Each sampling site was grouped into two geographic regions (Fig. 1), i.e. Rural Pampa (RP, 19 sites; 76 samples) and Great Buenos Aires Metropolitan Area (GBA, 10 sites; 37 samples). Annual agricultural and vegetable production data (tonnes of soybean + sunflower + corn and horticultural crops harvested in 2010–2011; BAME, 2014b; Bolsacer, 2014) were used to evaluate the incidence of economic activity. At Rural Pampa, agriculture production is very important at every site (27,950–1,027,740 t y^{-1}) with the exception of Punta Indio where stockbreeding is the prevailing activity (Stratta Fernandez et al., 2013). In GBA, Florencio Varela and Olmos were separated as horticultural sites (6806 and 45,802 t y^{-1} harvest, respectively) relative to the Urban sensu stricto subarea.

In general, samplers were placed 3–4 m above the ground on street lights or trees in public or private lands (yacht clubs, fishing/sport clubs, private houses/farms). At rural sites PAS were placed at variable distances (200–1000 m) from farmlands. Details of geographic location, population, agricultural production and sampling periods per site are described in Supplementary Material Table S1.

2.2. Passive air samplers

PUF-PAS were designed and constructed at the Environmental Chemistry and Biogeochemistry Laboratory (LAQAB, National University of La Plata) based on prototypes kindly provided by RECETOX (Research Centre for Toxic Compounds in the Environment, Masaryk University, Czech Republic) and Environment Canada (EC). Briefly, they consist on a polyurethane foam disk (14 cm diameter; 1.5 cm thick; 385 cm^2 surface area; 0.03 g cm^{-3} density) housed in a two stainless steel dome chamber (external diameters: 24.5 and 22.5 cm) separated by a 2 cm gap. The performance of this design was compared with the devices employed by RECETOX and EC (Astoviza, 2014). Briefly, regression analysis performed between the total mass captured by LAQAB device compared with the other samplers (LAQAB vs. RECETOX-LAQAB vs. EC) showed very significant correlations with slopes no different from 1 for several compounds indicating no significant differences between samplers (details in Supplementary Material).

Prior to exposure, PUF disks were pre-cleaned (distilled water wash and 1:1 v/v acetone:petroleum ether Soxhlet extraction for 24 h) and fortified with 10 ng of Depuration Compounds (PCB 30, 119 and 207) to calculate sampling rates (R) as described by Pozo et al. (2006). PUF disks were stored wrapped in foil and placed into ziplock polyethylene bags at −10 °C. Sampler chambers were rinsed with acetone and petroleum ether and stored in polyethylene bags until deployment.

2.3. Chemical analysis

Exposed disks were wrapped in aluminium foil, labelled, placed into ziplock polyethylene bags and transported in a cooler to the laboratory where they were stored frozen until analysis. Field blanks (n = 11) were obtained by transporting, installing and immediately removing PUF disks during each deployment.

Exposed PUF disks were spiked with internal standards (d_6-αHCH and d_8-DDT; C/N/D Isotopes Inc.) and Soxhlet extracted 24 h with petroleum ether. The extracts were concentrated under nitrogen and fractionated by chromatography on silica gel column (1000 mg SamplingQ, Agilent) to separate Endosulfan I (petroleum ether-dichloromethane) and Endosulfan II and sulfate (dichloromethane-methanol).

Target compounds were analysed by HRGC-ECD equipped with a DB5 capillary column (30 m × 320 μm i. d. × 0.25 μm film thickness). The initial oven temperature was programmed from 65 °C (2 min), to 130 °C (1 min) at 10 °C min^{-1} and then to 300 °C (10 min) at 5 °C min^{-1}. Injector and detector temperatures were maintained at 250 °C and 330 °C, respectively. Nitrogen (purity >99.99%) was employed as the carrier gas at a flow rate of

Table 1
Sampling information and Endosulfan concentrations.

Sampling sites, acronyms	Sampling periods	ΣEndos range (ng m^{-3})	Geometric mean (ng m^{-3})
Rural Pampa (RP)			
La Paz, LPZ	5	0.14–34	2.0
Concordia, CON	5	0.10–11	0.87
Paraná, PAR	5	0.09–18	1.6
Villaguay, VGY	4	0.45–26	2.7
Victoria, VIC	5	0.18–22	2.1
Gualeguaychú, GUA	7	0.12–37	1.0
San Nicolás, SN	6	0.12–11	1.7
Pergamino, PER	4	0.30–51	4.0
Zárate, ZAR	5	0.11–6.4	0.85
San Antonio de Areco, SAA	6	0.10–27	2.0
Ines Indart, INI	2	0.39–18	2.7
Magdalena, MGD	5	0.03–0.77	0.17
Punta Indio, PI	5	0.06–1.6	0.34
Saladillo, SAL	2	0.07–34	1.5
Trenquelauquen1, TR1	2	0.44–10	2.1
Trenquelauquen2, TR2	2	0.26–8.4	1.5
Bolivar, BOL	2	0.21–4.2	0.95
Rauch, RAU	2	0.01–0.07	0.03
Copetonas, COP	2	0.04–1.1	0.21
Great Buenos Aires metropolitan area (GBA)			
Urban sensu stricto			
Buenos Aires City1, CABA1	4	0.09–3.2	0.46
Buenos Aires City2, CABA2	6	0.09–6.9	0.99
Quilmes, QUI	7	0.02–15	0.41
Punta Lara, PTL	3	0.18–1.1	0.45
Ensenada, ENS	3	0.33–1.3	0.54
La Plata, LPT	4	0.16–2.2	0.76
La Balandra, BLD	5	0.04–0.91	0.34
Horticultural			
Florencio Varela, VAR	2	0.46–1.0	0.68
Olmos1, OL1	2	2.5–3.2	2.8
Olmos2, OL2	2	3.8–63	15

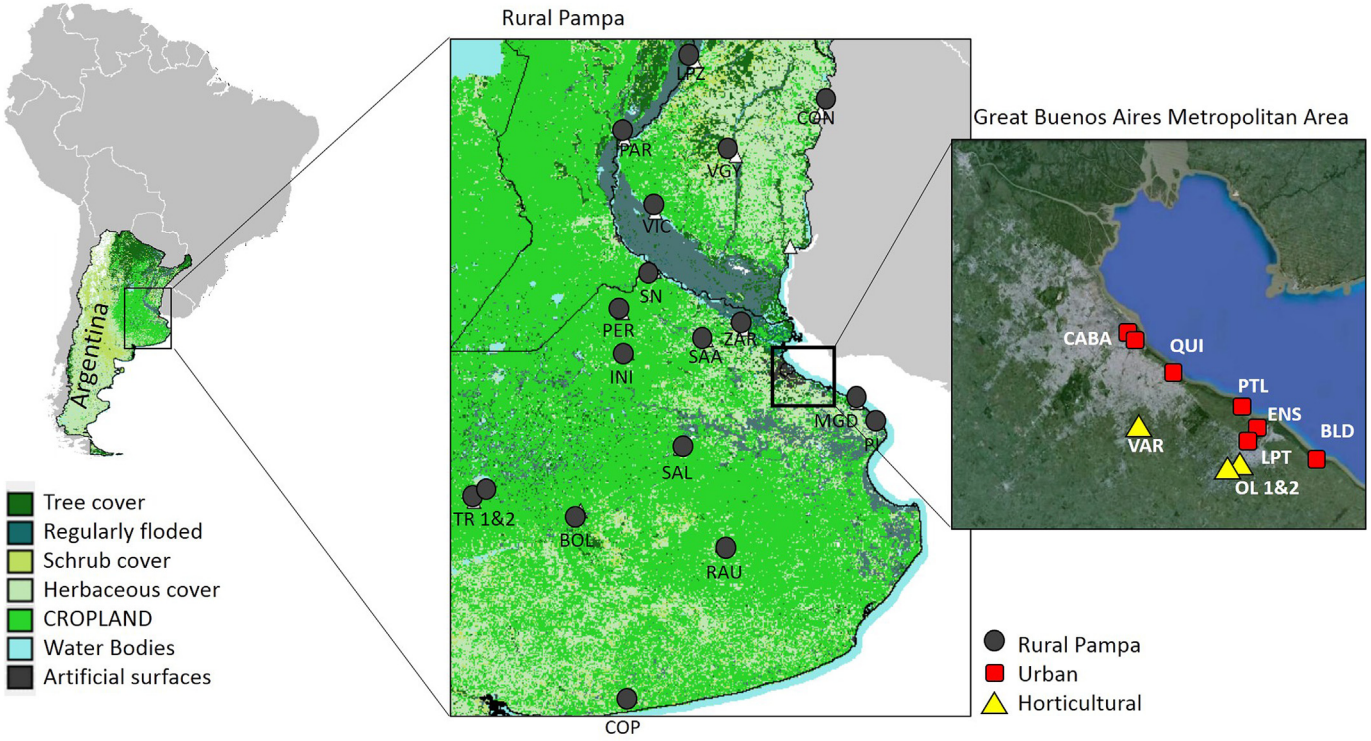

Fig. 1. Sampling sites at Argentina's Pampa showing land use (source: DIVA GIS, 2015) and a satellite image of Great Buenos Aires Metropolitan Area.

1.5 ml min^{-1}. Quantification was performed by a five-point calibration curve using external standard solutions (M-680P Pesticide Mix AccuStandar Inc.). Compounds were confirmed by gas chromatograph coupled to mass spectrometry (Agilent 6850-5973N MSD; EI 70 eV, 2.94 scans seg^{-1}, 50–550 amu).

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

Method detection limits (MDL) were defined as the average of blanks (field blanks; $n = 11$ and laboratory blanks; $n = 4$) plus three standard deviations. When target compounds were not detected in blanks, one half of the instrumental detection limit (IDL: equivalent amount of the signal–to–noise ratio ≥3) was used as MDL. For Endo I, Endo II and Endo SO_4, MDLs were 2.4, 0.2 and 0.2 ng $sample^{-1}$, respectively. Method recovery averaged 75 ± 16% for d_6-αHCH and 72 ± 26% for d_8-DDT; correction was applied when sample recovery was <85%.

2.5. Calculation of air concentrations from depuration compounds

Site–specific sampling rates (R) were calculated based on the loss of DCs according to previously described PUFs techniques (e.g. Shoeib and Harner, 2002a; Pozo et al., 2004; Moeckel et al., 2009). Briefly, average ambient temperature for each period and site were used to calculate DCs and target compound octanol-air (K_{OA}) and PUF-air partition coefficients ($K_{PUF\text{-}A}$ in with units of $m^3\ g^{-1}$) according to log $K_{OA} = A + B/T$ (Odabasi and Cetin, 2012) and log $K_{PUF\text{-}A} = 0.6366 \log K_{OA} - 3.1774$ (equation 9b from Shoeib and Harner, 2002a). R, the effective air volumes (V_{ef}), and ultimately air concentration (C_{air}) were calculated according to:

$$R = \frac{-ln\left(\frac{C_{CD}^{corr}}{C_{CD,0}}\right) * K'_{PUF-A} * \delta_{PUF} * V_{PUF}}{t} \quad \text{ec.1}$$

(Moeckel et al., 2009)

$$V_{ef} = K_{PUF-A} V_{PUF}\left(1 - exp - \left(\frac{R}{V_{PUF} K_{PUF-A}}\right)t\right) \quad \text{ec.2}$$

(Motelay-Massei et al., 2005)

$$C_{air} = \frac{M_{PUF}}{V_{ef}} \quad \text{ec.3}$$

where $C_{DC,0}$ and C_{DC} are the concentrations of the DC (ng $sample^{-1}$) at the beginning and the end of the deployment period, respectively (C_{DC} values are corrected based on recoveries of the stable DC [PCB 207] that does not volatilize from the PUF); δ_{PUF} is the PUF bulk density (g m^{-3}), V_{PUF} is the volume of the PUF (m^3), t is the deployment period in days and M_{PUF} is the amount of Endosulfan in the PUF (ng).

Only DCs with recoveries between 15 and 85% were used for calculations, either PCB-30 or PCB-119 or an average of both of them. In some samples lighter DCs were below detection limit due to enhanced volatilization during longer deployments. Therefore, it would be advisable to increase the spiking level of these more volatile compounds and/or use a larger DCs set with contrasting physical–chemical properties.

The grand mean R average for the entire study (6.3 ± 3.9 $m^3\ day^{-1}$) is comparable to previous PAS-PUF reports, i.e. 4.8 ± 2.3 $m^3\ day^{-1}$ (Pozo et al., 2004), 5.9 ± 0.9 $m^3\ day^{-1}$ (Gouin et al., 2008) and 6.1 ± 1.8 $m^3\ day^{-1}$ (Persoon and Hornbuckle, 2009).

In general, PAS exposed to free air currents in rural sites (e g Ines Indart, Saladillo, Rauch) presented higher R values (up to 9 $m^3\ day^{-1}$) compared to PAS deployed in more protected and constructed urban areas (lower than 4 $m^3\ day^{-1}$ for CABA, La Plata and Ensenada). However, no significant correlations were observed between R values and site-specific relevant meteorological parameters like wind speed (Tuduri et al., 2006) or ambient temperature (Kennedy et al., 2010). Individual meteorological conditions and R values are summarized in Supplementary Material, Table S1.

2.6. Statistical analysis

Air concentrations of ∑Endo (isomers I and II + Endosulfan SO_4) are presented as Geometric Mean (GM) values rather than arithmetic means to prevent the skew introduced by outliers. ANOVA test were used to compare differences between sampling areas (significance level set at $p < 0.05$) and regression analysis was used to evaluate covariation of agriculture activity and ∑Endo air concentrations. All statistical analysis were executed using Xlstat 2014 (Addinsoft).

3. Results and discussion

Air concentration of ∑Endo (Table 1) showed large variability (0.01–63 ng m^{-3}) with highest values at Horticultural GBA (0.46–63 ng m^{-3}) followed by Rural Pampa (0.01–51 ng m^{-3}) and lowest at Urban GBA (0.02–15 ng m^{-3}), with an overall relatively fresh composition (Endo I: 72 ± 18%; Endo II: 23 ± 15%; Endo SO4: 5 ± 10%). These concentrations are globally very high; at some sites from Rural Pampa and Horticultural GBA exceeded other reported PAS-PUF maxima (India: ≈26 ng m^{-3}, Pozo et al., 2011; Mexico: ≈27 ng m^{-3}, Wong et al., 2009). The remarkable range of airborne ∑Endo concentrations reflects marked spatial as well as temporal variability as described below (Sections 3.2 and 3.3). Details of sampling locations and ∑Endo concentrations at each site are shown in Supplementary Material (Table S1).

3.1. Global comparison

Fig. 2 shows air concentration of ∑Endo (GM + one standard deviation, sd) at each sampling subarea compared with other monitoring programmes. Our grand GM value (0.93 ng m^{-3}) corresponds to high/very high range compared to the first-year results of the Global Atmospheric Passive Sampling Programme (0.08 ng m^{-3}; Pozo et al., 2009).

The highest concentrations from Horticultural stations (3.1 ng m^{-3}), are similar to values described for a rural site of Ghana (3.0 ng m^{-3}; Pozo et al., 2009). Both regions are characterized by an intensive horticulture activity where Endosulfan is sprayed to control pests of several crops (tomato, pepper, lettuce) and is usually overused (Cieza, 2004; Ntow, 2008). These results reflect the intensive use of agrochemicals per unit area characteristic of horticultural activity (Cieza, 2004).

At Rural Pampa, ∑Endo concentrations (1.1 ng m^{-3}) are comparable to those reported for global largest producers and major consumers of this pesticide, i.e. India and South Korea (2.3 and 1.8 ng m^{-3}, respectively; Pozo et al., 2009) and are equivalent to concentrations reported for Southern Buenos Aires province (1.5 ng m^{-3}; Tombesi et al., 2014), revealing the importance of farming as the principal Endosulfan source in Argentina.

Finally, levels at Urban GBA (0.53 ng m^{-3}) are similar to those reported for bordering countries such as Bolivia and Brazil (0.44 and 0.65 ng m^{-3}, respectively) which is the major Endosulfan consumer in Latin America (4400–7200 t y^{-1}, UNECE, 2010). Our urban GBA ∑Endo concentrations are also comparable to those

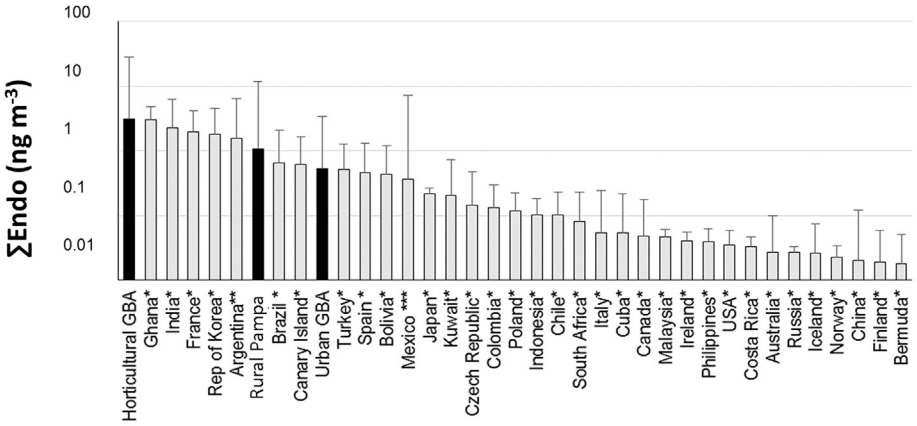

Fig. 2. Endosulfan concentrations in air (geometric means, ng m^{-3} + sd) from this study (in black) compared with other PAS-PUF monitoring programmes (* Pozo et al., 2009; ** Tombesi et al., 2014; *** Wong et al., 2009).

reported for some European countries such as Turkey and Spain (0.51 and 0.46 ng m^{-3}, respectively) which consume about 50% of the European Union total volume (Endosulfan Preliminary Dossier, 2003). Since direct application of Endosulfan at Urban GBA has not been reported, the intermediate concentrations found suggest atmospheric transport from agricultural sites.

3.2. Spatial distribution

Air concentration of ∑Endo (GM; ng m^{-3}) at each sampling site is mapped in Fig. 3. Briefly, the most remarkable spatial pattern is that at Rural Pampa concentrations vary in a wide range (0.03–4.0 ng m^{-3}) and almost everywhere (70% of sites) exceed 1 ng m^{-3}, whereas at GBA, strictly urban stations present more homogeneous and significantly (p-value: 0.05) lower concentrations (0.33–0.98 ng m^{-3}) compared to Horticultural sites (0.68–15 ng m^{-3}).

The peak concentration at Olmos 2 is 1–2 orders of magnitude higher than at the other horticultural sites, Olmos 1 and F. Varela, reflecting the differences in labour at both stations. Olmos 2 is a conventional farm, i.e. several vegetables are co-cultivated and pesticides are applied all over the year, whereas Olmos 1 is an organic farm emphasizing management practices (i.e. probably affected by Endosulfan transport from nearby conventional farms) and F. Varela is a monoculture farm (floriculture) where Endosulfan is used irregularly.

At Rural Pampa the highest Endo concentrations were detected in NW/W of Buenos Aires province (PER, INI, TR1, and SAA, GM: 4.0, 2.6, 2.1 and 2.0 ng m^{-3}, respectively) and in Entre Rios province (VGY, VIC and LPZ; GM: 2.7, 2.1 and 2.0 ng m^{-3}, respectively). These locations comprise the most fertile land of the region, where agriculture is the main economic activity. To evaluate the significance of this activity as key factor determining airborne Endosulfan patterns, a regression analysis was performed between ∑Endo and main crop annual production for each site (soybean, corn and sunflower in thousands of tonnes). Only soybean production was significantly correlated (p-level< 0.05) with ∑Endo concentration (Fig. 4) indicating that this is the principal source of residues collected by our PUF-PAS. This explanation is consistent with the intensification of soybean culture in Argentina (~400% acreage increase from 1995 to 2005; see SM Fig. S2; Conte et al., 2007), which placed the country as the third largest exporter of this leguminous

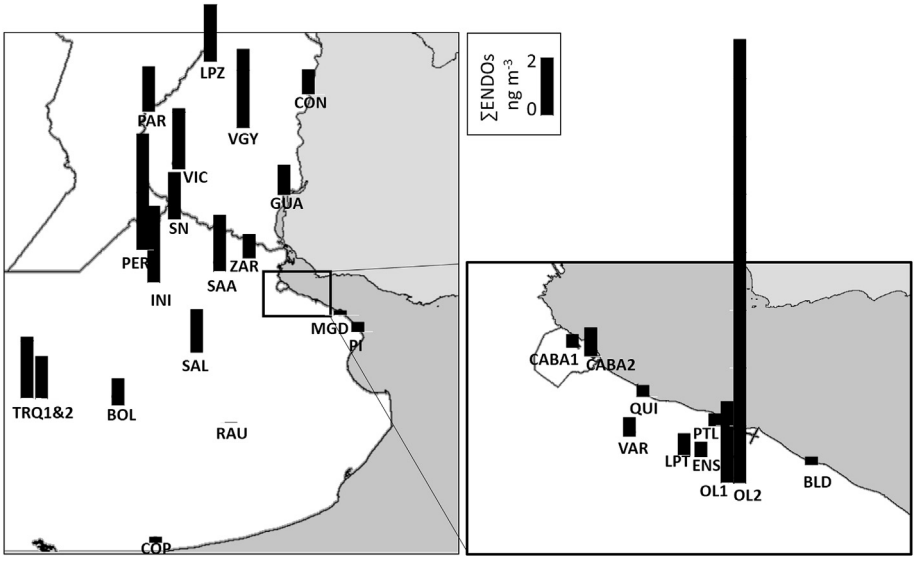

Fig. 3. Spatial variation of Endosulfan concentrations (geometric means, ng m^{-3}) in air.

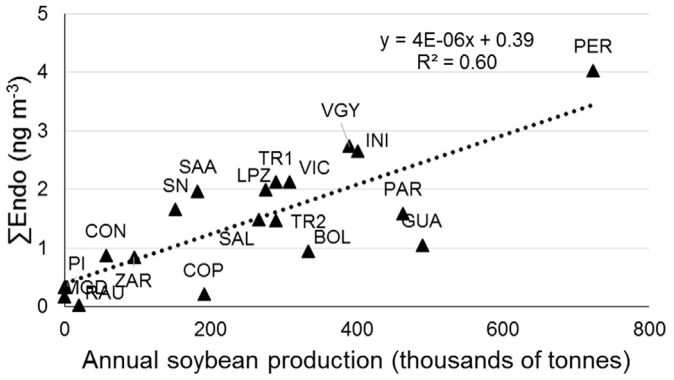

Fig. 4. Linear regression between annual soybean production (thousands of tonnes) and Endosulfan concentrations (geometric mean, ng m^{-3}) in air at Rural Pampa sites.

(Cuniberti et al., 2011). This crop is characterized by its high performance due to the new labour technologies, glyphosate resistant transgenic seeds, and intensive pesticide use, namely Endosulfans, Cypermethrin and Chlorpyrifos which comprise ~75% of the total agrochemicals applied (Jergentz et al., 2005).

3.3. Temporal variations

In order to assess temporal variations in a context of heterogeneous sampling times (2–7 sampling periods of 63–298 days each; Table 1), sampling periods were classified according to average temperature as warm (>20 °C), temperate (15–20 °C) or cool (<15 °C).

Generally, a strong variability of airborne ∑Endo concentration (0.01–0.1 to 1 – >10 ng m^{-3}) is observed at each sampling site. There is a marked temporal pattern, basically defined by consistent peaks enriched in Endo I (81 ± 12%) during warm periods, ∑Endo minima with higher proportions of Endo SO_4 (7.9 ± 13% vs. 1.6 ± 2.4%) in cool periods, and a generally declining trend over time (SM Table S1 and Fig. 5).

This pattern is more evident at Rural Pampa where highest concentrations at each site correspond to the first warm period (2010–2011), principally at 5 sites which exceed reported ∑Endo global maxima (PER, LPZ, GUA, SAA and VGY: 35 ± 9.9 ng m^{-3} Vs. India: ≈26 ng m^{-3}, Pozo et al., 2011; Mexico: ≈27 ng m^{-3}, Wong et al., 2009). These peak concentrations are basically composed of Endo I with little Endo II and only trace amounts of Endo SO_4 (85 ± 14; 11 ± 13 and 0.7 ± 1.4%, respectively). A similar Endo I predominance is observed in the following lower warm peaks suggesting pulse signals associated to the seasonal application of Endosulfan on soybean crops from November to April.

These fresh Endosulfan pulses are also indicated by the Endo I/(I+II) isomeric ratio which is typically around 0.70 in the formulation (Weber et al., 2010; Hapeman et al., 2013) and average 0.83 ± 0.12 during warm periods (0.68 ± 0.17 in cool periods). This higher enrichment of Endo I could be explained by the contrasting physical properties of both Endosulfan isomers: higher Henry's Law constant for Endo I (0.70 vs 0.045 Pa m^3 mol^{-1}; Shen and Wania, 2005) and higher octanol-air partition coefficient of Endo II (log K_{OA}: 9.28 vs 8.64; Shoeib and Harner, 2002b; Odabasi and Cetin, 2012) promoting a stronger volatilization from soils and plants of

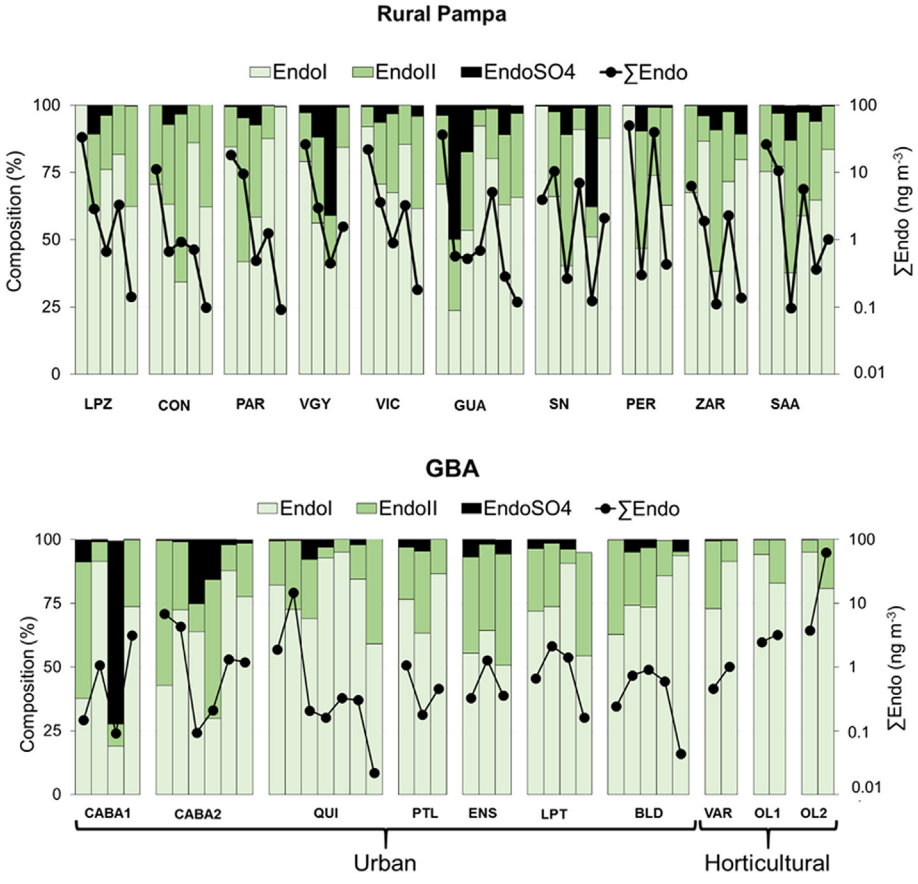

Fig. 5. Variability of Endosulfan concentrations and composition at representatives sites from Rural Pampa (top) and GBA (sampling periods arranged in chronologycal sequence).

Endo I (Ruedel, 1997; Rice et al., 2002) and stronger adsorption to soil and to airborne particles of Endo II (Shoeib and Harner, 2002a). In addition, isomerization of Endo II to Endo I could also contribute to Endo I enrichment during warm periods. This process is positively correlated with temperature (Rice et al., 1997) and has been observed in the solid-water and the air–water interphases (Walse et al., 2002).

On the other hand, in soils the less volatile Endo SO_4 (Weber et al., 2010) is formed through biologically catalyzed oxidation of both isomers with a faster rate for Endo I (Ghadiri and Rose, 2001). This would explain the 10 times relative increase of Endo SO_4 (0.7 ± 1.4 to 6.9 ± 9.0%) during no application-cooler periods.

The long-term declining trend of ∑Endo concentrations over time (5 to more than 300 times reduction) follow an exponential decrease at all sites of Rural Pampa and is especially marked at LPZ, CON, PAR, VIC and GUA implying a 92 ± 2.4% loss during the first year. This pattern contrast with the slight increment of soybean harvest from 2010 to 2013 (19–21 millions of tonnes, BASM, 2014) reflecting a change in the agrochemicals applied related to incipient control policies, i.e. banning of Endosulfan imports in July 2012 (SENASA, 2011) and probable substitution with less persistent pesticides such as pyrethroids and organophosphates (Gonzalez et al., 2010). This type of exponentially decreasing temporal patterns are a common feature observed in longer-time series after control measures of persistent pollutants; both in biotic (Bignert et al., 1998; de Boer et al., 2010) and abiotic environmental compartments (Olson et al., 2000; Marvin et al., 2004) with steepest slopes reported for air (Jones and de Voogt, 1999; Schuster et al., 2010).

At GBA there is no homogeneous pattern and temporal variations differ between subareas. Horticultural sites show a prominent warm peak at all sites (including the highest value ever reported: Olmos 2: ≈63 ng m^{-3}) with strong Endo I predominance and only traces of Endo SO_4 (85 ± 5.6% and 0.15 ± 0.18%, respectively). In addition, the high I/(I+II) ratio (0.85 ± 0.06) indicates recent application as observed in Rural Pampa peaks. On the other hand, at Urban sites there is no uniform temporal pattern: some stations insinuate warm peaks and a slight declining trend, while others show an opposite increasing pattern or irregular airborne ∑Endo concentrations. In general, there is a predominance of Endo I (70 ± 19%), followed by Endo II (24 ± 15%) and Endo SO_4 (7.1 ± 14%) suggesting prevailing atmospheric transport from agricultural areas.

4. Conclusions

The comprehensive study of airborne Endosulfan in the most productive and populated Argentina's Pampas revealed high to very high concentrations (GM: 0.93 ng m^{-3}; range: 0.01–63 ng m^{-3}) doubling previous worldwide reported maxima. The strong variability reflect spatial differences related to intensive use of agrochemicals in horticultural activities in the peri urban area of Buenos Aires and agriculture in the rural area as indicated the significant correlation between airborne Endosulfan and annual soybean crop. A marked temporal pattern, basically defined by consistent peaks enriched in Endo I during warm periods, ∑Endo minima with higher proportions of Endo SO_4 during no application/cooler periods and a generally declining trend over time related to incipient control policies, is also detected, especially at Rural Pampa.

Acknowledgements

The authors want to thank to RECETOX (Masaryk University, Czech Republic) and Air Quality Processes Research Section, Environment Canada for providing passive air samplers. The assistance of Tom Harner for sampling rate calculations is greatly appreciated.

The first author thanks the Argentinean Research Council (CONICET) for her doctoral and postdoctoral fellowships. This study received financial support from National University of La Plata (11/N597).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.10.033.

References

Astoviza, M.J., 2014. Evaluación de la distribución de contaminantes orgánicos persistentes (COPs) en aire en la zona Sur de la cuenca del Plata mediante muestreadores pasivos artificiales. Doctoral Thesis. National University of La Plata, Argentina.

ATSDR (Agency for Toxic Substances and Disease Registry, Division of Toxicology and Human Health Sciences/Environmental Toxicology), 2013. Draft Toxicological Profile for Endosulfan. http://www.atsdr.cdc.gov/ (accessed in January 2015).

BAME (Buenos Aires Province Ministry of Economy), 2014a. Horticultural Census 2010. http://www.ec.gba.gov.ar/ (accessed in November 2014).

BAME (Buenos Aires Province Ministry of Economy), 2014b. Annuary 2010-2011. http://www.ec.gba.gov.ar/ (accessed in November 2014).

BASM, (Buenos Aires Stock Market), 2014. http://www.bolsadecereales.com.ar/ (accessed November 2014).

Bejarano Gonzalez, F., 2008. Endosulfan, a Threat to the Health and Environment. In: Bejarano, F. (Ed.), El endosulfan y sus alternativas en America Latina. RAP–AL (Latin American Pesticide Action Network), pp. 9–34.

Bignert, A., Olsson, M., Persson, W., Jensen, S., Zakrisson, S., Litzén, K., Eriksson, U., Häggberg, L., Alsberg, T., 1998. Temporal trends of organochlorines in northern Europe, 1967–1995, relation to global fractionation, leakage from sediments and international measures. Environ. Pollut. 99, 177–198.

Bolsacer (Bolsa de Cereales de Entre Ríos, Entre Ríos Cereal Stock Market), 2014. http://www.bolsacer.org.ar/ (accessed November 2014).

Cieza, R.I., 2004. Potencialidades y limitantes de la incorporación de tecnologías sustentables en la horticultura del Gran La Plata, Argentina. In: VII Congreso Latinoamericano de Sociología Rural. Quito, Ecuador. http://www.alasru.org/wp-content/uploads/2011/12/14-GT-Cieza-Ramon.doc.

Conte, A., Etchepareborda, M., Marino, M., Vazquez Rovere, A., 2007. Oleaginización de la agricultura argentina, p. 11. http://ffyl.uncu.edu.ar/ (accessed in March 2013).

Cuniberti, M., Herrero, R., Masiero, B., 2011. Evolución del contenido de proteína y de aceite en la región sojera argentina. In: Mercosoja 2011, V Congress of MERCOSUR Soybean, I Forum Asia-MERCOSUR Soybean. September 2011, Rosario-Santa Fe, Argentina.

de Boer, J., Dao, Q.T., van Leeuwen, S.P.J., Kotterman, M.J.J., Schobben, J.H.M., 2010. Thirty year monitoring of PCBs, organochlorine pesticides and tetrabromodiphenylether in eel from The Netherlands. Environ. Pollut 158, 1228–1236.

DIVA GIS, 2015. Land cover shape of Argentina. http://www.diva-gis.org/datadown/ (accessed in August 2015).

Endosulfan Preliminary Dossier, 2003. Umweltbundesamt, Berlin, p. 55.

Ghadiri, H., Rose, C.W., 2001. Degradation of endosulfan in a clay soil from cotton farms of western Queensland. J. Environ. Manag. 62, 155–169.

Goerke, H., Weber, K., Bornemann, H., Ramdohr, S., Plotz, J., 2004. Increasing levels and biomagnification of persistent organic pollutants (POPS) in Antarctic biota. Mar. Pollut. Bull. 48, 295–302.

Gonzalez, M., Miglioranza, K.S.B., Aizpún, J.E., Isla, F.I., Peña, A., 2010. Assessing pesticide leaching and desorption in soils with different agricultural activities from Argentina (Pampa and Patagonia). Chemosphere 81, 351–358.

Gouin, T., Wania, F., Ruepert, C., Castillo, L.E., 2008. Field testing passive air samplers for current use pesticides in a tropical environment. Environ. Sci. Technol. 42, 6625–6630.

Grossi Gallego, H., Lopardo, R., 1988. Spatial variability of the global solar radiation obtained by the solarimetric network in the Argentine Pampa Humeda. Sol. Energy 40, 397–404.

Hapeman, C., McConnell, L.L., Potter, T.L., Harman-Fetcho, J., Schmidt, W.F., Rice, C.P., Schaffer, B.A., Curry, R., 2013. Endosulfan in the atmosphere of south Florida: transport to everglades and Biscayne National Parks. Atmos. Environ. 66, 131–140.

Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B., 2004. Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. Environ. Sci. Technol. 38, 4474–4483.

INDEC (National Institute of Statistics and Census of Argentina), 2010. National Census. http://www.indec.mecon.ar/ (accessed in July 2014).

Jergentz, S., Mugni, H., Bonetto, C., Schulz, R., 2005. Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina. Chemosphere 61, 817–826.

Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): state of the

science. Environ. Pollut. 100, 209–221.
Kennedy, K., Hawker, D.W., Bartkow, M.E., Carter, S., Ishikawa, Y., Mueller, J.F., 2010. The potential effect of differential ambient and deployment chamber temperatures on PRC derived sampling rates with polyurethane foam (PUF) passive air samplers. Environ. Pollut. 158, 142–147.
Klánová, J., Harner, T., 2013. The challenge of producing reliable results under highly variable conditions and the role of passive air samplers in the global monitoring plan. Trends Anal. Chem. 46, 139–149.
Li, Y.F., Macdonald, R.E., 2005. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. Sci. Total Environ. 342, 87–106.
Lorenzatti, E., Negro, C.L., de la Sierra, P., Marino, F. y, Lenardón, A., 2008. Plaguicidas en el aire. Estudio preliminar en la Ciudad de Santa Fe. FABICIB 12, 129–135.
Marvin, C.H., Painter, S., Charlton, M.N., Fox, M.E., Thiessen, P.A.L., 2004. Trends in spatial and temporal levels of persistent organic pollutants in Lake Erie sediments. Chemosphere 54, 33–40.
Merini, L.J., Cuadrado, V., Flocco, C.G., Giuletti, A.M., 2007. Dissipation of 2,4-D in soils of the Humid Pampa region, Argentina: a microcosm study. Chemosphere 68, 259–265.
Miglioranza, K.S.B., Gonzalez, M., Ondarza, P.M., Shimabukuro, V.M., Isla, F.I., Fillmann, G., Aizpún, J.E., Moreno, V.J., 2013. Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Río Negro basin. Sci. Total Environ. 452–453, 275–285.
Moeckel, C., Harner, T., Nizzetto, L., Strandberg, B., Lindroth, A., Jones, K.C., 2009. Use of depuration compounds in passive air samplers: results from active sampling-supported field deployment, potential uses, and recommendations. Environ. Sci. Technol. 43, 3227–3232.
Motelay-Massei, A., Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B., 2005. Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs, and organochlorine pesticides. Environ. Sci. Technol. 39, 5763–5773.
NMACF, 2014. National Ministry of Agriculture, Cattle Farming and Fishing. http://www.siia.gov.ar/ (accessed in November 2014).
Ntow, W.J., 2008. The Use and Fate of Pesticides in Vegetable-based Agroecosystems in Ghana. PhD Thesis. Wageningen University, The Netherlands.
Odabasi, M., Cetin, B., 2012. Determination of octanol-air partition coefficients of organochlorine pesticides (OCPs) as a function of temperature: application to air-soil exchange. J. Environ. Manag. 113, 432–439.
Olson, M., Bignert, M., EckhÃ©ll, J., Jonsson, P., 2000. Comparison of temporal trends (1940s–1990â€™s) of DDT and PCB in Baltic sediment and biota in relation to eutrophication. Ambio 29, 195–201.
Ondarza, P.M., Gonzalez, M., Fillmann, G., Miglioranza, K.S.B., 2012. Increasing levels of persistent organic pollutants in rainbow trout (*Oncorhynchus mykiss*) following a mega-flooding episode in the Negro River basin. Argent. Patagon. Sci. Total Environ. 419, 233–239.
Persoon, C., Hornbuckle, K.C., 2009. Calculation of passive sampling rates from both native PCBs and depuration compounds in indoor and outdoor environments. Chemosphere 74, 917–923.
Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S., 2004. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. Environ. Sci. Technol. 38, 6529–6537.
Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. Environ. Sci. Technol. 40, 4867–4873.
Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. Environ. Sci. Technol. 43, 796–803.
Pozo, K., Harner, T., Lee, S.C., Sinha, R.K., Sengupta, B., Loewen, M., Geethalakshmi, V., Kannan, K., Volpi, V., 2011. Assessing seasonal and spatial trends of persistent organic pollutants (POPs) in Indian agricultural regions using PUF disk passive air samplers. Environ. Pollut. 159, 646–653.
Rice, C.P., Chernyak, S.M., Hapeman, C.J., Biboulian, S., 1997. Air-water distribution of the endosulfan isomers. J. Environ. Qual. 26, 1101–1106.
Ruedel, H., 1997. Volatilisation of pesticides from soil and plant surfaces. Chemosphere 35, 143–152.
Rice, C.P., Nochetto, C.B., Zara, P., 2002. Volatilization of trifluralin, atrazine, metolachlor, chlorpyrifos, α-endosulfan, and β-endosulfan from freshly tilled soil. J. Agric. Food Chem. 50, 4009–4017.
Schuster, J.K., Gioia, R., Sweetman, A.J., Jones, K.C., 2010. Temporal trends and controlling factors for polychlorinated biphenyls in the UK atmosphere. Environ. Sci. Technol. 44, 8068–8074.
SENASA (National Animal Health and Agrifood Quality Service of Argentina), 2011. Resolution 511/2011, Prohibiting Imports of the Active Ingredient Endosulfan and Its Formulated Products. http://www.senasa.gov.ar/ (accessed in March 2013).
Shen, L., Wania, F., 2005. Compilation, evaluation, and selection of physical - chemical property data for organochlorine pesticides. J. Chem. Eng. Data 50, 742–768.
Shoeib, M., Harner, T., 2002a. Characterization and comparison of three passive air samplers for persistent organic pollutants. Environ. Sci. Technol. 36, 4142–4151.
Shoeib, M., Harner, T., 2002b. Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. Environ. Toxicol. Chem. 21, 984–990.
Stratta Fernandez, R., Gomez Gajardo, F., Rodriguez Saez, P., 2013. Rural depopulation in the Pampean region of Argentina: intervention model. Cuad. Desarro. Rural 10, 201–218.
Tombesi, N., Pozo, K., Harner, T., 2014. 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. Atmos. Pollut. Res. 5, 170–178.
Tuduri, L., Harner, T., Hung, H., 2006. Polyurethane foam (PUF) disks passive air samplers: wind effect on sampling rates. Environ. Pollut. 144, 377–383.
UNECE, 2010. Risk Management Evaluation Endosulfan. May 2010 Germany.
UNEP (United Nations Environment Programme), 2011. The New POPs Under the Stockholm Convention. http://www.chm.pops.int/ (accessed in March 2014).
US EPA, 2007. Note to Reader. Endosulfan Readers Guide. Nov 16.EPA-HQ-OPP-2002-0262-0057.
van Pul, W., de Leeuw, F., van Jaarsveld, J., van der Gaag, M., Sliggers, C., 1997. The potential for long-range transboundary atmospheric transport. Chemosphere 37, 113–141.
Walse, S.S., Shimizu, K.D., Ferry, J.L., 2002. Surface-catalyzed transformations of aqueous endosulfan. Environ. Sci. Technol. 36, 4846–4853.
Wannaz, E.D., Abril, G.A., Rodriguez, J.H., Pignata, M.L., 2013. Assessment of polycyclic aromatic hydrocarbons in industrial and urban areas using passive air samplers and leaves of *Tillandsia capillaris*. J. Environ. Chem. Eng. 1, 1028–1035.
Weber, J., Halsall, C.J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T., 2010. Endosulfan, a global pesticide: a review of its fate in the environment and occurrence in the Arctic. Sci. Total Environ. 408, 2966–2984.
Wong, F., Alegria, H.A., Bidleman, T.F., Alvarado, F., Angeles, F., Vilagarza, A., Bandala, E.R., De la Cerda Hinojosa, I., Galindo Estrada, I., Galindo Reyes, G., Gold-Bouchot, G., Macías Zamora, J.V., Murguía Gonzalez, J., Ramirez Espinosa, E., 2009. Passive air sampling of organochlorine pesticides in Mexico. Environ. Sci. Technol. 43, 704–710.