



Polyethylene film incorporation into the horticultural soil of small periurban production units in Argentina

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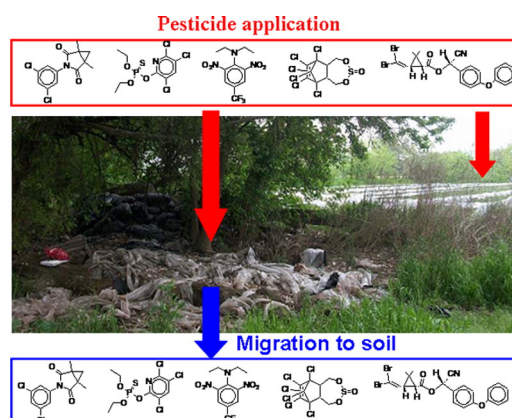
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HIGHLIGHTS

- PE plastic residue was found in horticultural soils (equals to 10% of the area).
- The predominant fragment size was ($28 \text{ cm}^2 \pm 13 \text{ cm}^2$).
- Pesticides can migrate to the inside of the PE film.
- Further bidirectional migrations between soil and plastic film can occur.

GRAPHICAL ABSTRACT



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ABSTRACT

Horticulture makes intensive use of soil and extensive use of polyethylene (PE) sheeting and pesticides, producing an environment where the dynamics between soil and plastics can affect pesticide fate. We have determined that the presence of plastic residues in the horticultural soil of small production units equals 10% of the soil area, being meso and macro-sections the predominant fragment sizes. All soil samples were taken from different plots located in Cuartel V, Moreno district, in the suburbs of Buenos Aires city, Argentina. Laboratory experiments were conducted to see the relations among pesticide, soil and PE film. Endosulfan recovery from LDPE films ($25 \mu\text{m}$ and $100 \mu\text{m}$) was studied, observing evidence that indicated migration to the inside of the plastic matrix. To further analyze the dynamics of pesticide migration to soil and atmosphere, experiments using chlorpyrifos, procymidone and trifluralin were performed in soil–plastic–atmosphere microenvironments, showing that up to 24 h significant amounts of pesticides moved away from the PE film. To determine whether PE residues could act as potential pesticide collector in soil, column elution experiments were done using chlorpyrifos, procymidone and trifluralin. Results showed an important pesticide accumulation in the mulch film ($584 \mu\text{g}$ – $2284 \mu\text{g}$ pesticide/g plastic) compared to soil ($13 \mu\text{g}$ – $32 \mu\text{g}$ pesticide/g soil). Finally, chemical and photochemical degradation of deltamethrin adsorbed in PE film was studied, finding a protective effect on hydrolysis but no protective effect on photodegradation.

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We believe that a deeper understanding of the dynamics among soil, plastic and pesticides in horticultural productive systems may contribute to alert for the implications of PE use for plastic sheeting.

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1. Introduction

Horticultural productivity has partially increased due to plastic sheeting (Espí et al., 2012) and pesticide application (Hillocks, 2012). PE sheeting is used in greenhouses, walk-in tunnels, low tunnel covers and mulching applications. More than 80% of the agricultural film sold worldwide is made of low density polyethylene (LDPE), mainly used in greenhouse 150 µm–200 µm films containing ethyl vinyl acetate (EVA) as a copolymer. The mean lifetime of greenhouse sheeting is 6–8 months. Mulch film is the second most common agricultural film application, usually as black monolayer LDPE 12 µm–80 µm film, with a mean lifetime of 2 to 4 months. China, Japan and South Korea represent about 80% of the worldwide mulched surface, employing 700,000 t LDPE/year for this purpose (Espí et al., 2012). Plastic residues of various sizes have been reported in the ocean and freshwaters (McCormick et al., 2014; Rochman et al., 2004); plastic particles are also common in soil, but are infrequently measured (Rilling, 2002).

Intensive pesticide use is another factor affecting horticultural productivity (Cooper and Dobson, 2007; Nakajima and Ortega, 2014). Studies show the negative environmental aspects related to the application of pesticides, including their presence on non-target systems such as water (Licciardello et al., 2011; Masiá et al., 2015a,b; Oliver et al., 2012), soil (Jacobsen and Hjelmsø, 2014) and non-target organisms (Damalas and Eleftherohorinos, 2011).

In horticulture, the concurrent combination of intensive pesticide use, plastic sheeting and soil exploitation sets an environmental scenario that requires further attention. Fragments of plastic sheeting may represent a novel vector of pesticides into soil, considering the significant amount of pesticides that reach these plastic covers during the application process (Querejeta et al., 2012).

It has been reported that plastic film can absorb pesticides in aqueous solutions (Nerín et al., 1996) and that these molecules can be desorbed from plastic surfaces to organic solvents (Nerín and Battle, 1999). The development of PE membrane passive pesticide samplers (Khairy et al., 2014) is based on this phenomenon. Pesticides migrate through the polyethylene pores in the non-crystalline areas of the film (Huckins et al., 1993). It has also been shown that volatile molecules like methylene bromide, propargyl bromide or chloropicrin can permeate polyethylene films in the gaseous phase (Papiernik et al., 2001). The migration of small organic stabilizers from plastic films has also been reported (Haider and Karlsson, 2001).

In previous pesticide degradation studies in horticultural soils (Querejeta et al., 2014), we noticed the ubiquitous presence of plastic residues. Taking into account that pesticide mobility and degradation in soil may be affected by the presence of plastic fragments, we aimed at quantifying the presence of plastic residues in horticultural soil and studying the interactions among plastic films, pesticides and soil.

2. Materials and methods

2.1. Chemicals and solvents

Chemicals and solvents were of the best analytical grade. To prepare each reference material, technical grade pesticides were purified by recrystallization (>95% pure by GC-FID). The identity and purity of the active principles were confirmed by ¹H- and ¹³C-NMR. A primary solution of 300–1000 ppm w/w was prepared in acetone or cyclohexane,

and the working solutions were obtained by dilution as needed. Acetone and cyclohexane (Aberkon p.a. grade) used for all solutions and extracts were previously distilled and chromatographically checked as suitable for GC-ECD use.

2.2. Pesticides

Endosulfan, chlorpyrifos, procymidone, trifluralin and deltamethrin were chosen for this study due to their extensive use in horticultural and floricultural production units in Argentina (Berenstetín et al., 2014; Flores et al., 2011; Hughes et al., 2008; Querejeta et al., 2012; Querejeta et al., 2014; Ramos et al., 2010). Additionally, endosulfan was selected for swabbing and immersion experiments due to its high stability. Chlorpyrifos, procymidone and trifluralin were used for migration trials in microenvironments and columns, as three different examples of hydrophobic pesticides with different volatility. Finally, deltamethrin was adopted for chemical and photochemical degradation studies because of its fast reaction kinetics under the described experimental conditions.

Commercial products used in the laboratory experiments were as follows:

- Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide), CASRN [115-29-7]: Thionex® (EC, 35% w/v, Magan).
- Procymidone (3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo [3.1.0]hexane-2,4-dione, CASRN [32809-16-8]) liquid: Sumilex® (CS, 50% w/v) (Summit Agro Argentina); and solid: Sumilex® (WP, 50% w/w) (S. Ando Argentina).
- Chlorpyrifos (0,0-diethyl-0-(3,5,6-trichloro-2-pyridinyl)-phosphorothioate, CASRN [2921-88-2]), Lorsban® (EC, 48% w/v, Dow AgroSciences)
- Trifluralin (α,α,α trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine), CASRN [1582-09-8], Trigermin® (CS, 48% w/v, Cheminova)
- Deltamethrin ((S)-α-cyano-3-phenoxybenzyl-(1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate, CASRN [52918-63-5]): Decis Forte® (EC, 10% w/v) (Bayer CropScienceArgentina).

2.3. Plastics used in the assays

Two types of plastic PE film were used: LDPE black 25 µm mulch film and LDPE crystal 100 µm film with EVA (used for tunnels and greenhouses). The specific kinds of plastic used are defined in each experiment.

2.4. Chromatographic conditions

All chromatographic analysis were performed on a Perkin-Elmer (Norwalk CT, USA) AutoSystem XL Gas Chromatograph with Autosampler automatic injector, equipped with an electron capture detector (ECD), and a fused silica capillary column (PE-5, 5% diphenylpolysiloxane – 95% dimethylpolysiloxane stationary phase, 30 m length, 0.25 mm i.d. and 0.25 µm film thickness). The GC-ECD operating conditions were injector temperature: 280 °C; ECD temperature: 375 °C; oven temperature: 190 °C for 1.5 min, 45 °C min⁻¹ to 300 °C then 10 °C min⁻¹ to 320 °C and hold 2 min; injection volume 1 µL, splitless; carrier gas: N₂, 30 psi; and ECD auxiliary flow 30 mL min⁻¹.

2.5. Field trials

All soil samples were taken from seven different plots located in Cuartel V, Moreno district, Provincia de Buenos Aires, Argentina (Figure I-Supplementary Material). A predefined field sampling scheme for PE determination in soil was applied. Twelve sampling points were selected for each studied plot, according to its width and length (Figure II-Supplementary Material). At each point, 1 m² × 10 cm deep soil sample was taken, and PE presence was quantified by manual collection, separation and washing of plastic residues followed by a gravimetric determination. Average PE mass and its standard deviation were obtained for each plot (Table 1). PE mass was converted to mulch PE area using a calibration curve (Figure III-Supplementary Material). Complete data for all sampling points are provided in the Supplementary Material (Table I-Supplementary Material). The minimum size of PE plastic that could be reliably recovered from soil was circa 0.50 cm². The surface range for the PE film found in all experiments was 0.60 cm²–2850 cm² which could be considered as meso and macroplastics (Rilling, 2012). The maximum and minimum plastic size found was determined for each sampling experiment (sampling 1–7, Figure IV-Supplementary Material). This range was divided in percentiles, the number of pieces for each percentile was counted and the surface of each fragment was gravimetrically determined (Figure IV-Supplementary Material).

2.6. Laboratory experiments

All experiments were conducted on PE film sections spiked with set amounts of pesticides.

2.6.1. Swabbing PE surfaces exposed to endosulfan

A commercial formulation of endosulfan dispersed in water (3.5 µg of endosulfan, 100 µL of dispersion), in a concentration similar to manufacturer's recommendation were deposited on the surface of a piece (6 cm × 3 cm) of LDPE 100 µm PE film. The sample was left to dry at room temperature. Each plastic film was extracted by swabbing with three different pieces of cotton cloth (6 cm × 3 cm) soaked in cyclohexane (1 mL). These cotton cloths were later extracted separately with cyclohexane (5 mL) in an ultrasound bath (15 min). Finally, the plastic piece was thoroughly extracted using cyclohexane (10 mL) in an ultrasound bath (15 min). The endosulfan content of each cyclohexane extract was chromatographically determined (GC-ECD).

A control experiment was carried out with glass coverslips instead of the PE film.

2.6.2. Rapid immersion of PE surfaces exposed to endosulfan

LDPE 25 µm and 100 µm sections were spiked with endosulfan as described in Section 2.6.1. Each plastic section was sequentially immersed in three Hach tubes containing cyclohexane (6 mL) for 2 s in each tube. The plastic was thoroughly extracted with cyclohexane (20 mL) with

sonication assistance (15 min). The endosulfan content in the cyclohexane extracts was determined by GC-ECD.

2.6.3. Pesticide migration in soil–plastic microenvironments

To study pesticide migration from PE film to soil and atmosphere, small portions of soil were covered with PE mulch film and spiked with pesticide. Each set was covered with a clean PE film leaving small air volume between the films (Figure VA-Supplementary Material). Specifically, 3 g of horticultural soil was placed on a clean glass surface (3 cm × 7 cm). The soil was covered with a small mulch film section (5 cm × 10 cm) fixing the plastic edges of the PE film to the glass surface with adhesive tape. Then 10 µL of a pesticide (chlorpyrifos 2880 ppm, procymidone 3000 ppm, trifluralin 2880 ppm, in different experiments) emulsion (water)/solution (ethanol) was spiked on the PE film and left to dry at room temperature. All this was covered with a clean PE film (top PE film) section of 7 cm × 12 cm, fixing again the plastic edges to the glass surface with adhesive tape. The spiked and top PE films were prevented to be in contact using a small glass pole. We called this “microenvironmental cell”.

Triplicates were prepared for each sampling time (in the range of 0 h to 144 h). The spiked film, top film and soil were extracted separately at each sampling time as described in the Supplementary Material, and the pesticide content in these extracts was chromatographically (GC-ECD) analyzed.

2.6.4. Pesticide migration in soil–plastic columns

A classical column assay for studying pesticide migration in soil was adapted to evaluate the collector effect of small PE film sections present in the soil (Figure VB-Supplementary Material). With this purpose, a 50 cm long and 4 cm width glass column with a Teflon stopper and a cotton top was filled with 20 g of horticultural soil. Then, 8 pieces of mulch LDPE (25 µm, total area 1.8 cm²) were introduced in the column and covered with additional soil (10 g). The plastic to soil rate followed the relation found in the field trials. Next, 10 mL of pesticide solution prepared from commercial products (960 µg procymidone, 960 µg chlorpyrifos, 960 µg trifluralin, each in separate experiments) was poured on top of the column. Additional 100 mL of a CaCl₂ aqueous solution (0.01 M) was used to elute the column. When liquid stopped dropping from the column, it was unpacked. The plastic pieces and the soil were manually separated. The plastic film was washed with distilled water and air dried at room temperature. Then, corresponding extraction methods were applied to each matrix (see Supplementary Material) and the pesticide content in the extracts was determined by GC-ECD. All the experiments were done in triplicate.

2.6.5. Deltamethrin degradation assay with NaOH

A deltamethrin solution in ethanol (25 µL, 600 ppm m/v) was deposited on PE 100 µm pieces (3 cm × 3 cm) and left to dry at room temperature. The same procedure was repeated with glass coverslips (used as control). All samples were immersed separately in water or NaOH solution (1 M) for various times (between 0 h and 72 h). The plastic and glass samples were removed, left to dry at room temperature and extracted with 10 mL of cyclohexane using an ultrasound bath. The deltamethrin content of these extracts was then chromatographically (GC-ECD) determined.

The “protective” effect of the plastic matrix was tested by studying the remaining concentration of insecticide versus immersion time.

2.6.6. Deltamethrin photodegradation assay

LDPE sections of 3 cm × 3 cm of mulch (25 µm) and greenhouse (100 µm) films were spiked with 10 µL of a deltamethrin solution in cyclohexane (1502 ppm, m/v). A set of six PE film pieces was located under a Hg arc lamp (250 W, Hg vapor street lighting lamp, type HPLN, Osram HQI E E40, with the outer glass sleeve removed) at a distance of 40 cm. The temperature on the irradiated section was measured

Table 1
Mulching PE film incorporation into the horticultural soil, quantitative characterization.

Sampling plot	PE amount		PE size (first percentile)		
	PE mass (g)/soil area (m ²)	PE area (m ²)/soil area (m ²)	No. pieces/m ²	Mean PE area (cm ²)	% Mass
1	2.6 ± 4.1	0.09 ± 0.014	15	18 ± 23	30.6
2	6.1 ± 14.9	0.23 ± 0.56	31	35 ± 50	47.6
3	3.9 ± 4.5	0.14 ± 0.16	11	20 ± 20	16.5
4	3.7 ± 3.7	0.13 ± 0.13	10	27 ± 28	21.3
5	0.89 ± 0.89	0.03 ± 0.03	3	14 ± 10	15.4
6	0.6 ± 1.5	0.02 ± 0.05	3	23 ± 28	36.5
7	3.2 ± 4.6	0.11 ± 0.16	1	57 ± 46	4.7
Mean	3.0 ± 1.9	0.11 ± 0.07	11 ± 10	28 ± 13	24.7 ± 13.4

along the experiment and kept below 25 °C with the assistance of a small fan. PE pieces were sampled at fixed times and extracted with 5 mL of cyclohexane using sonication (15 min). The deltamethrin content in the cyclohexane solution was then chromatographically (GC-ECD) determined.

3. Results

3.1. Quantitative estimation of PE film residues in horticultural soils

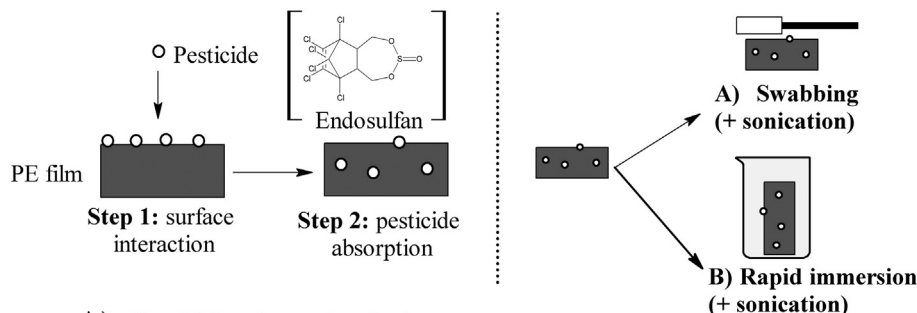
A sampling scheme was applied in seven different horticultural plots, located in Moreno district, Buenos Aires, Argentina (Figure I-Supplementary Material), in order to quantitatively characterize the PE film residues in soil. In all cases the fragments were LDPE 25 µm black mulch film. PE presence in soil is shown in Table 1 as averaged film mass (g) and area (m²) for one square meter of sampled soil for the seven plots (the amount for each individual sampling point is shown in Table I-Supplementary Material). The mean PE film area found in the horticultural soil was $0.11 \text{ m}^2 \pm 0.07 \text{ m}^2$ plastic/m² of soil, that equals the 10% of the total sampled surface.

Size distribution is another significant aspect of the presence of plastic film fragments in soil. For this purpose, plastic pieces found on each sampling plot were divided into ten groups (percentiles) according to their area range (percentiles, Figure IV-Supplementary Material). Table 1 shows the results (the number of plastic film pieces per square meter, the mean area of these pieces, and the mass percentage with respect to the total PE found) for the first percentile, which is the smallest one. This percentile represents one fourth ($24.7\% \pm 13.4\%$) of all the found film, being the average area for this percentile of $28 \text{ cm}^2 \pm 13 \text{ cm}^2$, and the mean number of pieces per square meter 11 ± 10 .

3.2. Swabbing and immersion of PE surfaces exposed to endosulfan and deltamethrin

Considering the high amounts of LDPE film found in soil and that pesticides can reach the plastic film during the application process (Querejeta et al., 2012), we studied the interactions between the plastic residue and a set of pesticides usually employed in horticulture. We investigated the adsorption process under application conditions. To determine whether the pesticide remains on the PE film surface or it migrate in the absence of solvent into the interior of the plastic matrix, after the application, we spiked 100 µm PE film pieces with a commercial water emulsion of endosulfan and with a cyclohexane solution of the active ingredient (Fig. 1A). Film of 100 µm width was chosen for these studies because its thickness was between that used for mulching and greenhouse construction. Endosulfan was selected as a model pesticide because it had been detected in plastic films (data not shown), and additionally is a very stable molecule. The endosulfan commercial formulation and a cyclohexane solution were deposited on the plastic surface in similar concentration to real application conditions. Once the solvent evaporated, the surface was swabbed three times with three pieces of cotton cloth soaked in cyclohexane. Finally, the plastic piece was thoroughly extracted with cyclohexane in an ultrasound bath. The endosulfan recovery for each step was determined and is shown in Fig. 1A (five replicates). In the case of endosulfan in the LDPE film, most of the pesticide was removed in the last extraction (sonication, $73 \pm 12\%$ recovery, $92 \pm 5\%$ recovery, Fig. 1A). A control experiment was made replacing the plastic with glass. In this case most of the endosulfan was removed in the first cotton swab ($74 \pm 9\%$ recovery, Fig. 1A).

To explore the relationship between the plastic film thickness and the pesticide absorption, mulch (25 µm) and greenhouse (100 µm)



A)- Swabbing (+ sonication):

Operation	% Recovery		
	Endosulfan in water on PE	Endosulfan in cyclohexane on PE	Endosulfan on glass (control)
Swab 1	3.6 ± 0.5	5.8 ± 3.2	74 ± 9
Swab 2	2.7 ± 0.8	0.5 ± 0.3	9.0 ± 1.9
Swab 3	2.4 ± 1.1	0.5 ± 0.4	14.9 ± 0.2
Sonication	73 ± 12	92 ± 5	-
Total	82 ± 12	99 ± 3	98 ± 8

B)- Rapid immersion (+ sonication):

Operation	% Pesticide recovery	
	25 µm LDPE	100 µm LDPE
Immersion 1	64 ± 2	32 ± 4
Immersion 2	16 ± 6	6 ± 1
Immersion 3	9.5 ± 0.4	5 ± 1
Sonication	11 ± 2	58 ± 4

¹Plastics were saturated in a 200 ppm endosulfan solution 80:20 methanol:water.

Fig. 1. Swabbing and immersion of PE and glass surfaces exposed to endosulfan.

films were spiked with a 200 ppm solution of endosulfan. The plastics were extracted by a rapid immersion in cyclohexane, repeating the immersion twice (immersions 1, 2 and 3, Fig. 1B, five replicates). The plastic pieces were finally fully extracted with this solvent by sonication (Fig. 1B, five replicates). In the case of the 25 μm film, most of the pesticide was recovered in the first extraction ($64 \pm 2\%$ recovery, Fig. 1B), while for the 100 μm film most of the endosulfan was removed in the final sonication ($58 \pm 4\%$ recovery, Fig. 1B).

To further study the absorption behavior, 25 μm and 100 μm thick PE pieces of fixed size were immersed in different deltamethrin solutions in cyclohexane (20 ppm to 1000 ppm, Figure VI-Supplementary Material) for 10 h. The plastic pieces were removed from the solution and the total amount of deltamethrin in the plastic was determined. A graphic of deltamethrin mass (μg) in the plastic versus the deltamethrin concentration in the spiking solution was made, finding that the plastic correlated with the film width (Figure VI-Supplementary Material).

3.3. Pesticide migration in soil–plastic microenvironments

After determining that pesticides can migrate from PE film surface to the inside of the matrix, we addressed two further questions: i) in the case of mulch film, can the pesticide deposited on it during application migrate to the soil (Figure VIIA-Supplementary Material)?; and ii) once the plastic residues are in the soil, can they concentrate pesticides from it (Figure VIIB-Supplementary Material)?

To study pesticide migration from PE film to soil and atmosphere, three different hydrophobic pesticides (chlorpyrifos, procymidone and trifluralin) were spiked onto the surface of a piece of mulching PE in microenvironmental cells (see Figure VA-Supplementary Material). Chlorpyrifos migration was studied under two different application conditions, spiking the pesticide as a pure compound dissolved in ethanol, and using the commercial formulated product suspended in water (Table 2). Chlorpyrifos content in mulch film, PE covering and soil was measured chromatographically, 24 h and 96 h after spiking. The results showed (Table 2) that as soon as after 24 h, chlorpyrifos was equally distributed between mulching and soil, with a negligible fraction on the cover PE, and after 96 h of contact, most of it has reached the soil. The experiment was repeated with the formulated product dispersed in water with similar results (Table 2): after 24 h, chlorpyrifos was equally distributed between soil and PE mulch, but with a higher fraction on the PE cover. When microenvironmental cells were left for 168 h contact,

Table 2
Pesticide migration in soil–plastic microenvironments.

Conditions	% Recovery top plastic	% Recovery mulching ^b	% Recovery soil	% Total Recovery
<i>Chlorpyrifos (pure product,^c ethanol)</i>				
24 h ^a	5.7 ± 0.3	58 ± 10	56 ± 12	120 ± 8
96 h	3 ± 1	19 ± 10	63 ± 12	85 ± 4
<i>Chlorpyrifos (formulated product,^d water)</i>				
24 h	11 ± 2	39 ± 4	34 ± 6	84.8 ± 0.2
168 h	26 ± 12	27 ± 7	46 ± 13	99 ± 9
<i>Procymidone (formulated product,^e water)</i>				
96 h	13 ± 9	61 ± 3	7.0 ± 0.5	81 ± 6
216 h	6 ± 1	61 ± 7	7 ± 1	73 ± 7
<i>Trifluralin (formulated product,^f water)</i>				
24 h	34 ± 11	57 ± 13	25 ± 9	116 ± 20
72 h	66 ± 15	20 ± 4	39 ± 14	124 ± 20
144 h	69 ± 11	11 ± 4	45 ± 7	126 ± 5

^a Contact time before extraction.

^b Mulching PE surface: 10 cm \times 7 cm.

^c 25.6 μg chlorpyrifos.

^d 28.8 μg chlorpyrifos.

^e 30 μg procymidone.

^f 28.8 μg trifluralin.

the most contaminated matrix was soil, although 27% of the applied pesticide was found on the PE cover (Table 2). The same experiment repeated using procymidone showed that at 96 h and 216 h most of the pesticide remained in the film. The migration of this pesticide to the soil was significantly lower than in chlorpyrifos case. Finally, the migration experiment was repeated for the herbicide trifluralin after 24 h, 72 h and 144 h (Table 2) of contact, following a pattern similar to chlorpyrifos.

3.4. Pesticide migration in soil–plastic columns

As the plastic can also be present without pesticide in the horticultural soil, we have wondered whether this plastic residue could act as a potential pesticide collector. To test this hypothesis, small pieces of 25 μm mulching film were placed inside a soil column (Figure VB-Supplementary Material) reproducing the soil: plastic ratio found in field measurements. A pesticide (chlorpyrifos, trifluralin or procymidone)/water mixture was spiked in different experiments on the top of the column, which was then eluted using a CaCl_2 solution. The column was disassembled; the plastic film was manually separated from soil, and treated as indicated in Section 2 for quantifying the pesticide content. Results shown in Table 3 indicate that in all cases most of the pesticide was found in soil, with 0.23–0.90% of the total product found on the plastic pieces (Table 3, five replicates).

3.5. Deltamethrin chemical and photochemical degradation assays

Considering that LDPE film can absorb pesticides, we attempted to determine whether this absorption process could have a “protective effect” on pesticides regarding degradation conditions. A “chemical” degradation condition was selected for deltamethrin, an easily hydrolysable insecticide (Laskowski, 2002). Small sections of greenhouse film were spiked with deltamethrin and the stability of this product on PE was controlled for a long time (75 days) observing no degradation (Figure IX-Supplementary Material, five replicates). The saturated PE films were then exposed to hydrolysis by immersion in water or in a 1 M NaOH solution (Fig. 2, five replicates); deltamethrin on a glass surface was also used as control experiment. When deltamethrin was exposed to water (either in plastic or glass) it remained stable for at least 72 h, whereas upon exposure to a 1 M NaOH solution, fast degradation was observed on glass, while the pesticide remained stable in greenhouse PE up to 72 h.

In a complementary set of experiments, deltamethrin photodegradation was tested under UV forced conditions (Hg arc lamp) on PE mulching, greenhouse film and glass (Fig. 3, five replicates). Fast photodegradation was observed on both plastics, with residual deltamethrin percentages even lower than on the glass control.

4. Discussion

4.1. PE film residue in horticultural soils

The presence of plastic material in soil has been identified as environmentally relevant (Rilling, 2012). The large amount of LDPE 25 μm

Table 3
Pesticide distribution in soil–plastic columns.

Pesticide ^a	PE film		Soil		Total % recovery
	% Rec. ^b	$\mu\text{g}_{\text{pest}}/\text{g PE}$	% Rec.	$\mu\text{g}_{\text{pest}}/\text{g soil}$	
Chlorpyrifos	0.9 ± 0.6	2284	103 ± 9	32	104 ± 9
Procymidone	0.23 ± 0.03	584	74 ± 6	24	74 ± 9
Trifluralin	0.5 ± 0.1	1269	40 ± 5	13	40 ± 5

^a In all cases 960 μg of each pesticide was poured onto the column.

^b % Rec.: % Recovery.

Pesticide hydrolytic degradation in PE films:

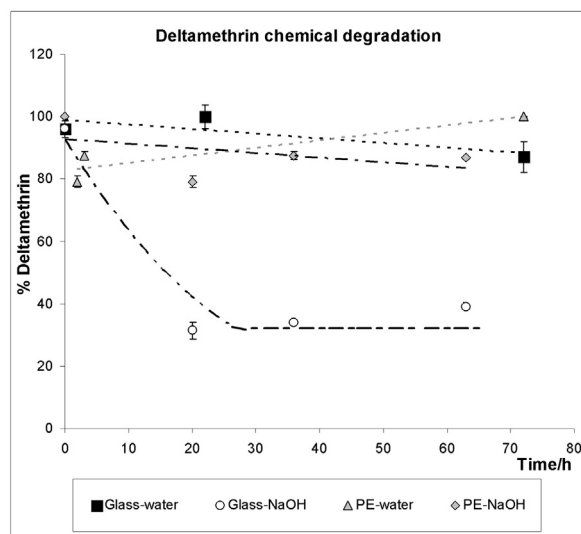


Fig. 2. Deltamethrin chemical degradation on glass/PE films in water and NaOH 1 M solution.

black film found (10% of the total surface) could be related to the use of the mulching technique in these horticultural production units. Additionally, in some sampling plots (1, 2 and 5, Table 1) several PE

accumulation focuses were observed nearby. These focuses were abandoned heaps of mainly old mulch film, sometimes partially incinerated and mixed with earth, crop residues and vegetation (Figure IB, C, Supplementary Material). At the other sites no evident plastic focuses were observed. In all cases, the plastic residues were probably originated from either the PE accumulation focuses or the plastic sheeting removal.

Regarding the size of the film pieces in soil, small fragments were the most abundant (Table 1, Figure IV-Supplementary Material). When all percentiles were considered, in five of the seven plots the first or second percentile showed the most abundant range in terms of the total PE mass (Figure IV-Supplementary Material), which could be a potential indication of a fragmentation process of the film.

4.2. Swabbing and immersion of PE surfaces exposed to endosulfan and deltamethrin

Considering that the PE film could be an important component of the horticultural soil, we studied the potential pesticide absorption process, simulating application conditions (pesticides reach the plastic surface in small water droplets that rapidly evaporate). We studied whether a pesticide migration process could occur in the LDPE film, moving the pesticide molecules from the film surface to the interior of the plastic matrix. Swabbing experiments with LDPE film spiked with endosulfan showed that the highest recovery corresponded to the final extraction step. In the control glass experiment all the pesticides were on the surface. The first swab removed most of the endosulfan, being an indirect evidence of the pesticide migration to the plastic matrix. When the experiment was repeated using the same amount of endosulfan

Pesticide photodegradation in PE films:

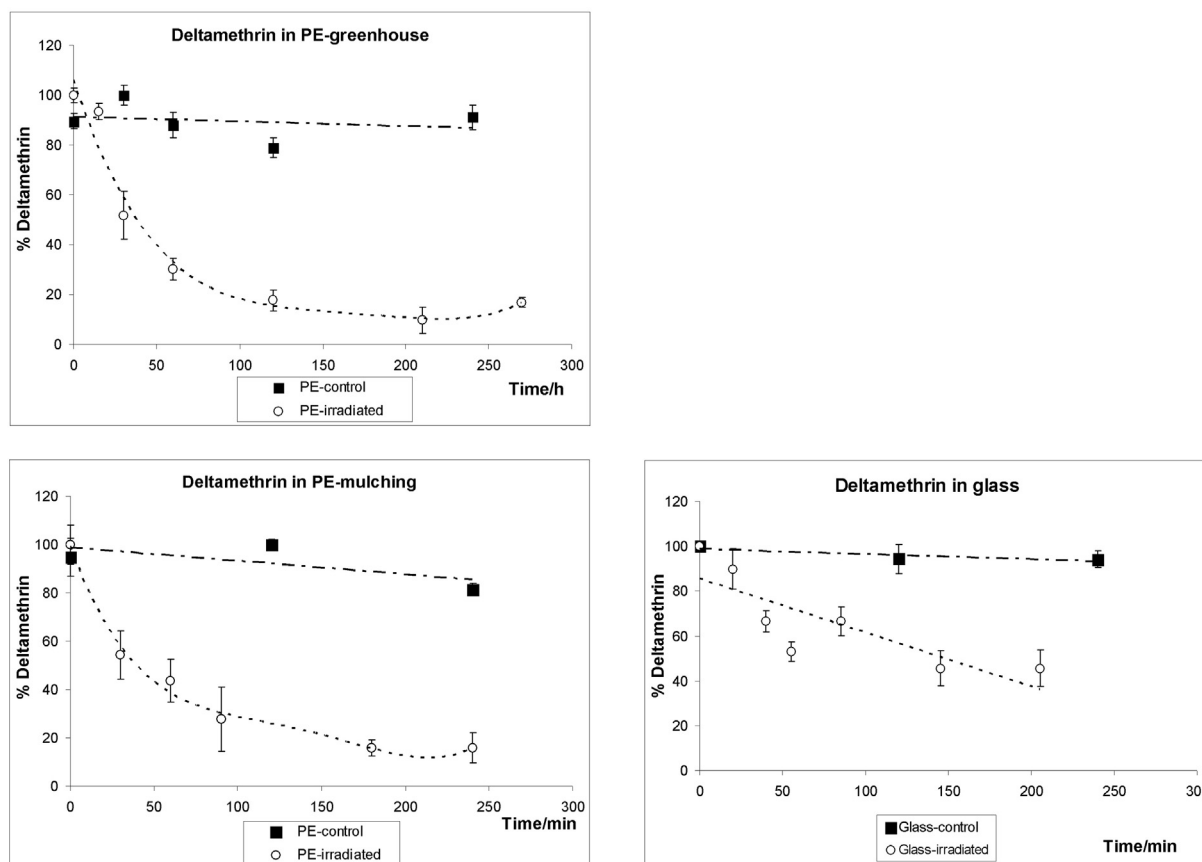


Fig. 3. Deltamethrin photodegradation in glass and PE films.

dissolved in cyclohexane instead of water (Fig. 1A, five replicates), similar results were obtained, indicating that endosulfan migration to the plastic is a fast process, which does not require the assistance of an organic solvent.

To further confirm the hypothesis that the pesticide can migrate from the surface to the plastic inside, we designed a rapid extraction experiment using 25 μm and 100 μm LDPE film (Fig. 1B). While in mulch PE (25 μm) most of the endosulfan migrated to the solvent in the first immersion, in the thicker greenhouse film (100 μm) most of the endosulfan remained inside, which is a further indication of endosulfan location inside the plastic.

If our migration hypothesis was correct, the pesticide absorption amount must correlate then with the plastic thickness. To explore this relationship, mulch (25 μm) and greenhouse (100 μm) films were spiked by immersion with deltamethrin at different concentrations. The pesticide amounts found (Figure VI, Supplementary Material) correlated with the film thickness, which is an additional indication that the plastic film absorbs the pesticide.

Although we are aware that these results are an indirect evidence of the absorption process, we believe that this reinforces the hypothesis that under usual application conditions, pesticides can migrate from the surface to the interior of the plastic film without the assistance of an organic solvent, and that the retained fractions depend on the film thickness. Further experiments using surface spectroscopy techniques should be done to confirm these assumptions.

4.3. Pesticide migration in soil–plastic microenvironments

After determining that pesticides can migrate from the surface to the inside of LDPE film, we were interested in studying whether phytosanitary products could be naturally desorbed to soil and to atmosphere. With this aim, chlorpyrifos, procymidone and trifluralin migration was studied in microenvironmental cells. Results shown in Table 2 indicated that the pesticide migration was significant at 24 h in the three cases, and that it increased for chlorpyrifos and trifluralin at longer times. In the case of procymidone, the amount in the plastic film remained higher and constant compared to the relative percentages found in soil and atmosphere. No obvious molecular reason could be found to explain this behavior. In the case of trifluralin, a clear migration trend to the soil and to atmosphere was observed (Table 2, Figure VIII-Supplementary Material), that is consistent with its significant vapor pressure (4.58×10^{-5} mm Hg, 25 °C, Pubchem, 2014).

These results indicate that once the pesticide is deposited on the plastic film, it migrates both to the soil and the atmosphere. The molecule distribution among plastic, soil and air was different for pesticides with diverse structures, although migration mechanisms remain to be studied.

4.4. Pesticide migration in soil–plastic columns

We have shown in Section 4.3 that pesticides absorbed in LDPE film can migrate to soil and atmosphere. Also, film fragments, once in soil, could concentrate pesticides. To corroborate this, we have done a column distribution experiment with plastic film. Keeping in mind that soil mass was 750 times greater than PE film, these results, should be considered although the arbitrary experimental conditions of the test. When the pesticide amounts were normalized by the mass of soil or plastic, the relative quantities found in the film are higher than in soil (Table 3). For example, in the case of chlorpyrifos 2284 μg pesticides were found per gram of plastic film, while only 32 μg of chlorpyrifos was detected per gram of soil. Similar results were obtained in the case of procymidone (584 $\mu\text{g/g}$ PE, 24 $\mu\text{g/g}$ soil, Table 3) and trifluralin (1269 $\mu\text{g/g}$ PE, 13 $\mu\text{g/g}$ soil, Table 3), clearly indicating a collector behavior of the plastic residues.

4.5. Deltamethrin chemical and photochemical degradation assays

It is known that LDPE alternates crystalline and amorphous phases. The amorphous structure has transient cavities, due to the thermal motion of the polymer chains, with diameters up to 10 Å that allows the diffusion of small molecules (Huckins et al., 1993). Then, the amorphous LDPE phase could be considered as a hydrophobic solvent with infinite viscosity.

In the case of hydrolytic degradation of deltamethrin, there was a clear difference in the degradation rate in the spiked LDPE film and the control glass experiment (Fig. 2). In the first case, no degradation was observed while on glass 65% disappearance was observed in less than 30 min (Fig. 2). These results could be understood supposing that the deltamethrin was absorbed in the amorphous phase of the LDPE where the access of a NaOH water solution was more difficult due to the polymer hydrophobicity. In the case of the control experiment on glass, the insecticide was completely available to the NaOH solution, facilitating the reaction.

On the other hand, when accelerated UV photodegradation was assayed on 25 μm and 10 μm LDPE spiked with deltamethrin, the degradation rate was higher than in the control experiment (Fig. 3). These results could be interpreted considering the amorphous polymer phase as a solvent where the photodegradation mechanism can occur because of the mobility of the radical fragments. However, when the photodegradation was performed on glass, deltamethrin molecules had no mobility; hence the degradation was disfavored and the rate was slower.

5. Conclusions

The presence of PE mulch film in horticultural soil is significant, representing around 10% of the sampled surface. Small pieces were the most abundant. The plastic residue could be presumably originated from the PE accumulation focuses or from the plastic sheeting removal.

We have also shown that pesticides can migrate from the surface to the interior of the plastic film without the assistance of an organic solvent, and that the retained fractions depend on the film thickness. The pesticides accumulated in the plastic film can migrate from these plastics to other matrix like soil and atmosphere, being this process modulated by their structure. When plastic film residue is present in the horticultural soil it may act as a pesticide collector. Some absorbed pesticides may experience a “protective effect” against chemical degradation, otherwise in the case of photodegradation this “protective effect” was absent.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.03.142>.

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