Toxic chemicals in the environment: from understanding pollution and its impact to removal and verification techniques

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A compendium of articlesfrom research projects supportedby the OPCW

OPCW – 2020

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The Technical Secretariat of the Organisation for the Prohibition of Chemical Weapons (OPCW) is pleased to announce its first compilation of original research papers summarizing the work of scientists who have received support from the Organisation between 2012 and 2017.

Support for research on the peaceful applications of chemistry in various fields were supported based on the Organisation's mandate to promote the technological and economic development of Member States under the provisions of Article XI of the Chemical Weapons Convention.

This publication highlights projects focused on chemical analysis and environmental safeguards, projects that are connected to the development of methods to monitor and mitigate the environmental impact of toxic chemicals. Toxic chemicals are an issue of global concern, regardless of whether they are released as remnants of war or through exposure to humans and the environment. Mitigating these concerns is a complex multidisciplinary task, requiring the participation of stakeholders with wide-ranging expertise. Toxic chemicals, including their environmental impact, are a central theme of the Organisation's programmes to build capacity and support scientific research.

A general objective of the international community, including international organisations, is a paradigm away from the exploitation of resources and to prevent and solve the problems that this has caused in the past. By supporting the development of chemistry for peaceful purposes, the OPCW prioritizes the principles of safety and security in the concept of sustainable chemistry practices, which is a key provision of the Organisation's mandate. From this perspective, it is essential to support relevant research activities because science and technology form the foundation of economic development through industrialization.

This publication aims to raise awareness of the efforts of the OPCW to support the research community in using the science of chemistry to make the world safer and more secure. The articles presented in this book contribute to the constantly growing body of scientific knowledge and informs potential new partners and beneficiaries about the expanding role of the OPCW in supporting scientific research. The OPCW provides an international forum for cooperation among scientists, industry and policymakers on issues that include chemical safety and security, and chemistry education. The Convention is underpinned by science and technology, with scientists playing a critical role in the implementation of the Convention. In the support of science, the OPCW runs a multitude of programmes, which are described on our website (www.opcw.org) in the International Cooperation section.

We hope you find the scientific content presented in this document interesting and informative, and we welcome you to our community of practitioners of peaceful and responsible chemistry.

Pesticide Exposure in Horticultural and Floricultural Periurban Production Units in Argentina

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Abstract

This study summarizes the results of the OPCW project titled “Persistent pesticide contamination in horticultural periurban production units” performed at Universidad Nacional de General Sarmiento, Argentina. This project highlighted the impact of pesticide use on three different nontargets: workers, soil, and horticultural plastics. Therefore, an exposure study among horticultural and floricultural workers was conducted, revealing the correlation between the pesticide formulation and the exposure level. Further, the exposure during the mixing and loading stage for manual applications was almost as important as that arising from the application step. The degradation of selected pesticides was faster in the horticultural soil than in the control soils, probably due to the modification of the autochthonous microbial community. Finally, the relative pesticide amounts that reached the agricultural plastics (mulching and greenhouse polyethylene films) after pesticide application were determined. The chemical and photochemical degradation of deltamethrin absorbed on the polyethylene film were studied.

Keywords: horticulture, floriculture, periurban agriculture, pesticide, potential dermal exposure, plastic film.

1. Introduction

The use of pesticides in modern agriculture has contributed to a consistent increase in crop yields in the past decades [1]. However, there are several negative impacts such as pesticide environmental persistence [2]. Periurban agricultural activities are primarily focused on small horticultural and floricultural production units located in green belts around large cities. The impact of pesticides on the nontarget systems in periurban production units can be investigated based on three different components: the workers, the soil, and the agricultural plastics (Figure 1).

Figure 1. Potential interactions of pesticides with crops, workers, soil, and plastics.

Safe pesticide handling is a major concern regarding worker exposure during the mix/load, application, and re-entry operations in agricultural practices [2], [3]. This issue is particularly important in small-scale production units, like those surrounding Buenos Aires, where all the aforementioned operations are usually performed by the same laborer [4]. Under typical working conditions in fields, dermal absorption is potentially the most important pathway for the uptake of pesticides [5]. Thus, measurement of the potential dermal exposure (PDE) provides relevant information on the quantity of a chemical substance that contaminates the uncovered body regions and clothing worn by pesticide handlers [6]. However, PDE data cannot be exclusively used as a risk indicator because they must be related to acceptable exposure limits. Consequently, the margin of safety (MOS) [7] has been proposed as a useful risk indicator linking the acceptable exposure to a product with the mass deposited on the worker’s cloth and skin. This mass can be estimated from the PDE.

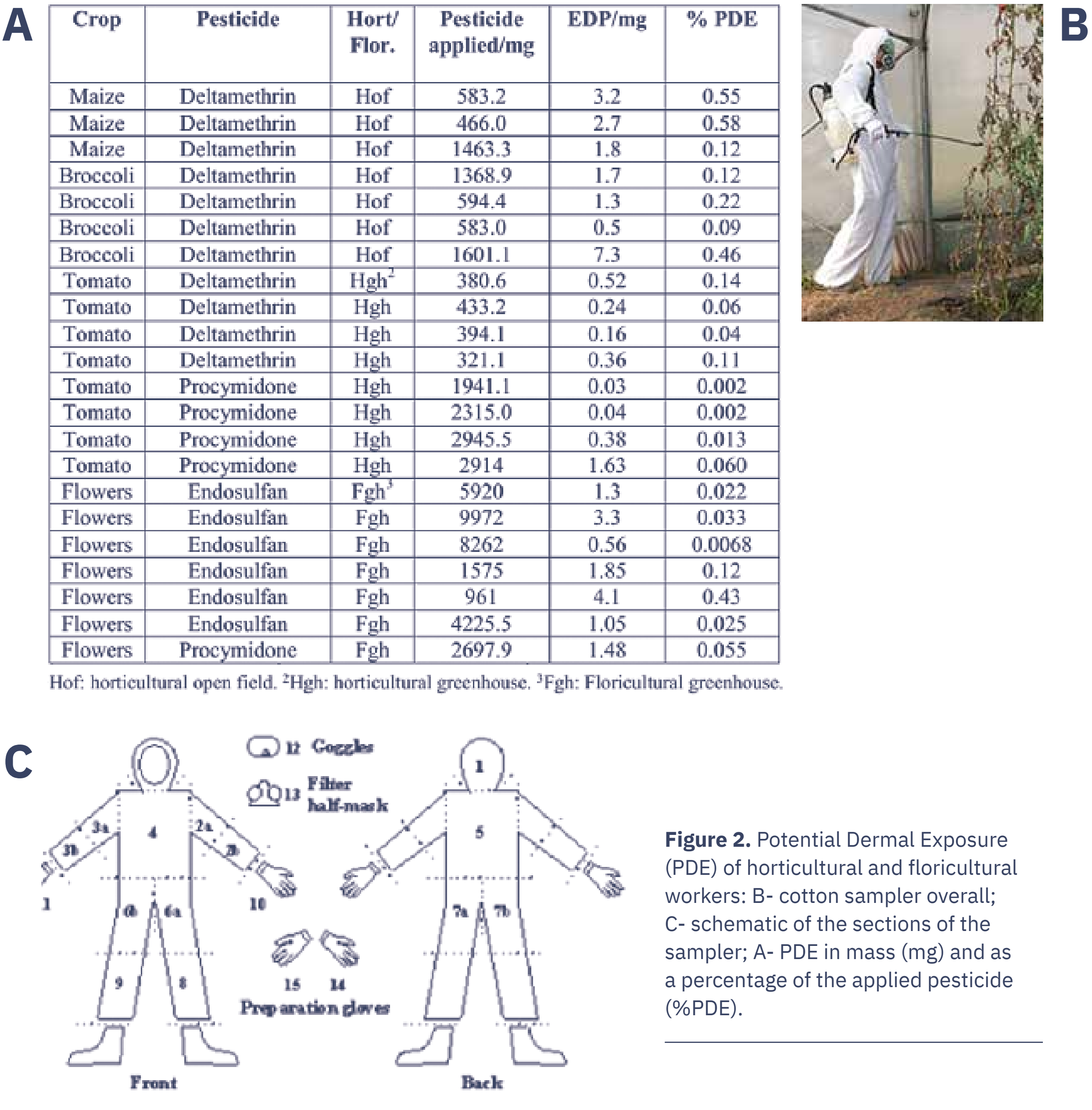
The quantitative estimation of pesticide exposure levels in soils is essential for investigating their fate in horticultural and nonlabored soils. Although there are detailed studies on different soils devoted to extensive agriculture [9] and pesticide drift outside the crop fields [8], to our best knowledge, there is no systematic study on pesticide distribution in soils during the application stage using manual knapsacks at small-scale horticultural production units. The pesticides that reach the soil during application not only have profound effects on its biological state, but the molecules can also migrate to water resources, thus spreading the contamination.

Another important matrix reached by pesticides in horticultural and floricultural production units is the plastic sheeting used for greenhouse construction or mulching purposes [10]. Hence, most research has focused on investigating the absorption of pesticides, primarily on low-density polyethylene (LDPE), and the recyclability of the LDPE used in mulching practices [10]. Conversely, the quantitative estimation of pesticides that reach the plastic surfaces and their chemical transformations have not been comprehensively investigated.

In brief, this project aims to assess the pesticide exposure of nontarget systems (workers, soil, and agricultural plastics) and the distribution in horticultural and floricultural periurban production units. Further, the findings of this study will be used for proposing possible measures to minimize the potentially negative effects of pesticides under the aforementioned production conditions.

2. Evaluation of pesticide exposure among horticultural workers

The PDE results of a set of horticultural and floricultural workers of small production units located in Moreno district (Provincia de Buenos Aires, Argentina) are shown in Figure 2A. This PDE data correspond to different crops at the application stage, and is expressed as the total mass of pesticide on the cotton sampler coverall (in mg), and as the percentage of PDE (%PDE: ratio of pesticide on the worker's coverall and the total applied mass). The PDE was obtained by analyzing the cotton sampler coverall (Figure 2B), which were cut in predetermined sections (Figure 2C), extracted with solvents, and quantified by gas chromatography-electron capture detector (GC-ECD) according to a previously described methodology [11], [12]. The absolute mass of pesticide detected on the work coveralls ranges from 0.03–3.2 mg, whereas the %PDE ranged from 0.06–0.58% of the total manipulated pesticide. The exposure values of the application stage were similar to those found in the European Community in equivalent application scenarios [13]. Notably, these values were obtained for a unique application of a 20 L knapsack and did not include the exposure of the mix and load stage.



Crop	Pesticide	Hort/ Flor.	Pesticide applied/mg	EDP/mg	% PDE
Maize	Deltamethrin	Hof	583.2	3.2	0.55
Maize	Deltamethrin	Hof	466.0	2.7	0.58
Maize	Deltamethrin	Hof	1463.3	1.8	0.12
Broccoli	Deltamethrin	Hof	1368.9	1.7	0.12
Broccoli	Deltamethrin	Hof	594.4	1.3	0.22
Broccoli	Deltamethrin	Hof	583.0	0.5	0.09
Broccoli	Deltamethrin	Hof	1601.1	7.3	0.46
Tomato	Deltamethrin	Hgh[2]	380.6	0.52	0.14
Tomato	Deltamethrin	Hgh	433.2	0.24	0.06
Tomato	Deltamethrin	Hgh	394.1	0.16	0.04
Tomato	Deltamethrin	Hgh	321.1	0.36	0.11
Tomato	Procymidone	Hgh	1941.1	0.03	0.002
Tomato	Procymidone	Hgh	2315.0	0.04	0.002
Tomato	Procymidone	Hgh	2945.5	0.38	0.013
Tomato	Procymidone	Hgh	2914	1.63	0.060
Flowers	Endosulfan	Fgh[3]	5920	1.3	0.022
Flowers	Endosulfan	Fgh	9972	3.3	0.033
Flowers	Endosulfan	Fgh	8262	0.56	0.0068
Flowers	Endosulfan	Fgh	1575	1.85	0.12
Flowers	Endosulfan	Fgh	961	4.1	0.43
Flowers	Endosulfan	Fgh	4225.5	1.05	0.025
Flowers	Procymidone	Fgh	2697.9	1.48	0.055

Hof: horticultural open field. [2]Hgh: horticultural greenhouse. [3]Fgh: Floricultural greenhouse.

Figure 2. Potential Dermal Exposure (PDE) of horticultural and floricultural workers: B- cotton sampler overall; C- schematic of the sections of the sampler; A- PDE in mass (mg) and as a percentage of the applied pesticide (%PDE).

We previously determined that the mix and load stage could contribute to as much exposure as the application stage for manual pesticide applications in small horticultural production units [14], [15]. Therefore, we investigated the main factors that could modulate the exposure during the mix and load stage; these factors included the formulation type (solid or liquid, Figure 3A), the bottle size and seal (Figure 3B, C), the measuring devices (Figure 3D), and the formulation color (Figure 3E) [16]. Hence, we measured the potential manual exposure (PME), which is defined as the total amount of pesticide that reached the workers hands in a specific operation (measuring, transferring, rinsing, filling, Figure 3) [16]. To compare exposures when different pesticide amounts were used, the % PME was calculated as the ratio of the total amount of pesticides on the worker's hands during a specific operation and the total amount of pesticide used, expressed as a percentage.

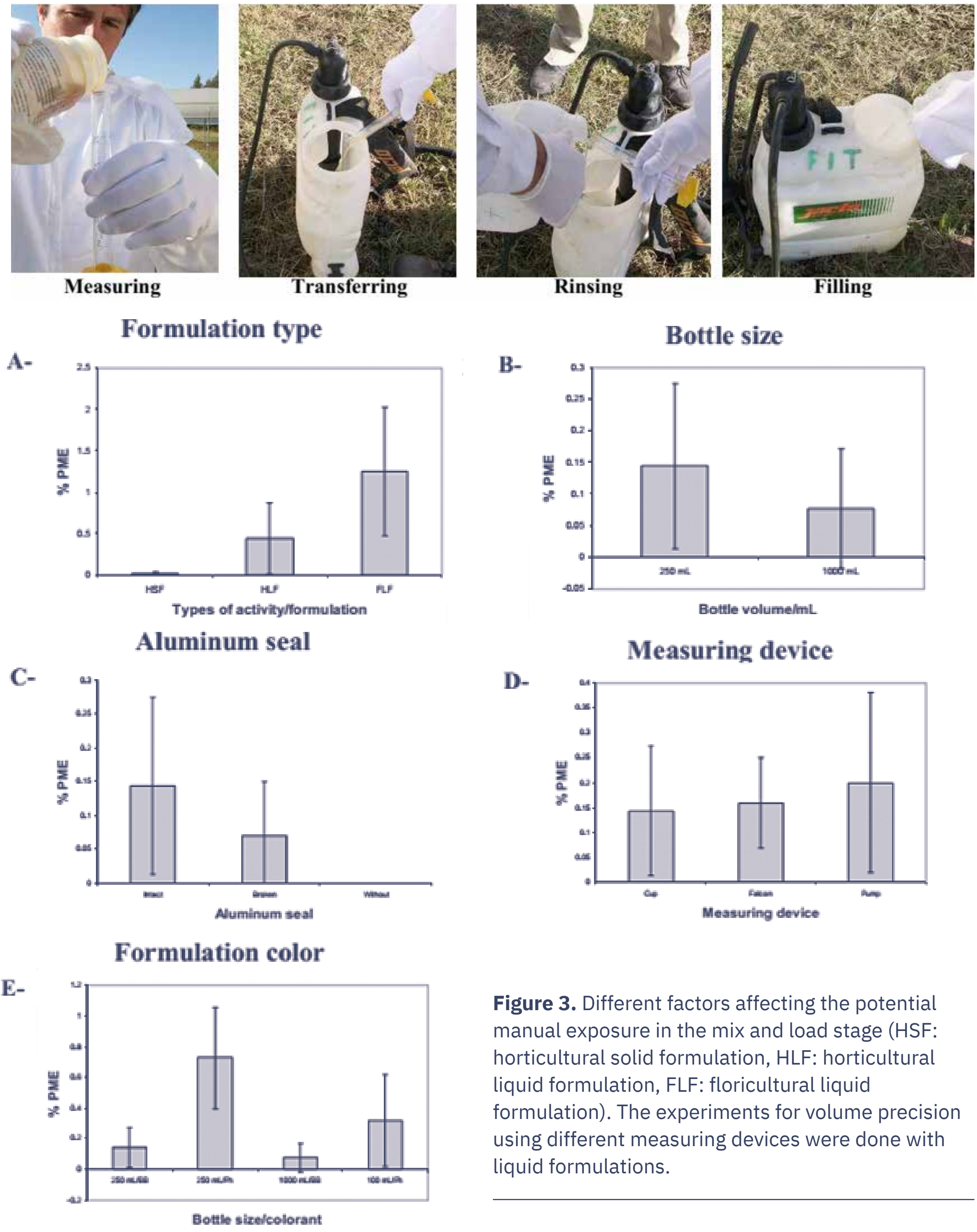


Figure 3. Different factors affecting the potential manual exposure in the mix and load stage (HSF: horticultural solid formulation, HLF: horticultural liquid formulation, FLF: floricultural liquid formulation). The experiments for volume precision using different measuring devices were done with liquid formulations.

The formulation type (solid or liquid) strongly influences the workers % PME (Figure 3A). The relative exposure was lower for solid formulations than for liquid formulations, both in the horticultural and floricultural scenarios. This behavior could be explained by the possibility of droplet splashing during the different steps of the mix and load stage (measuring, transferring, rinsing, filling). Based on the comparison of the % PME between powdered and granulated formulations, the granulated formulations were safer than the powdered products [16].

The size of the bottle containing the formulated liquid products was also studied, observing no difference in the PME when vessels of 250 mL or 1000 mL were used (Figure 3B) [16]. The presence or absence of an aluminum seal in the neck of the container was also assessed as another factor potentially contributing to PME. Breaking the seal or the presence of broken pieces of the seal in the bottle's neck, significantly increased the exposure compared to the case were no seal was present (Figure 3C, [16]).

The effect of the measuring device used to quantify the amount of formulated product () on the PME was analyzed (Figure 3D) [16], yielding no significant disparities between using a small cup, a Falcon tube, or a manual pump.

Surprisingly, when the variable was the formulation color (blue or uncolored) (Figure 3E) [16], an important difference in the PME was observed. The exposure levels were higher for the uncolored formulations, even when different bottle sizes were assayed (Figure 3E), suggesting that the addition of an inert dye to the formula could be a simple way to improve the exposure safety, at least when small bottle sizes (250–1000 mL) were handled.

3. Estimation of pesticide distribution between nontarget systems (soil, plastic, drift)

Having determined that 0.06–0.58% of the pesticide could reach the worker's cloths (section 1), we investigated the extent to which other nontarget subsystems, like soil (in the production unit or outside it by drift) or plastics could be exposed to pesticides. Therefore, we studied the pesticide distribution in small horticultural and floricultural production units between crop, soil, agricultural plastics (greenhouse and mulching sheeting), and drift. Figure 4 shows the percentage pesticide distribution referring to the total applied pesticide in horticultural open fields and horticultural and floricultural greenhouses. This parameter enabled comparison of the various situations in which different concentrations and volumes of pesticides were applied to various crops. The experiments were performed by applying different pesticides with manual knapsacks, in independent trials on different production units and under real working conditions with different workers [17].

We observed that besides the crop that is naturally the target, the relative amounts of pesticide found on soil or on soil plus plastic mulching were significant (Figure 4). In the case of broccoli and cauliflower, the amount of pesticide detected on the soil of open fields was higher than that found on the crop itself (Figure 4) [17]. In the case of strawberry open fields, the amount found on soil plus plastic mulching was similar to that found on the crop. Another interesting feature was that the pesticide distribution between the different nontarget systems differed between greenhouses (horticultural and floricultural) and open fields. In greenhouses (Figure 4) [17], a general pesticide distribution pattern was observed as fractions of the total amount applied, i.e., 2/3 crop, 1/4 soil, and 1/20 plastic. In all cases, when manual knapsack pesticide applications were performed, the pesticide drift into neighboring fields was < 5% of the total pesticide applied, and it declined to nondetectable values for distances longer than 7 m from the crop border.

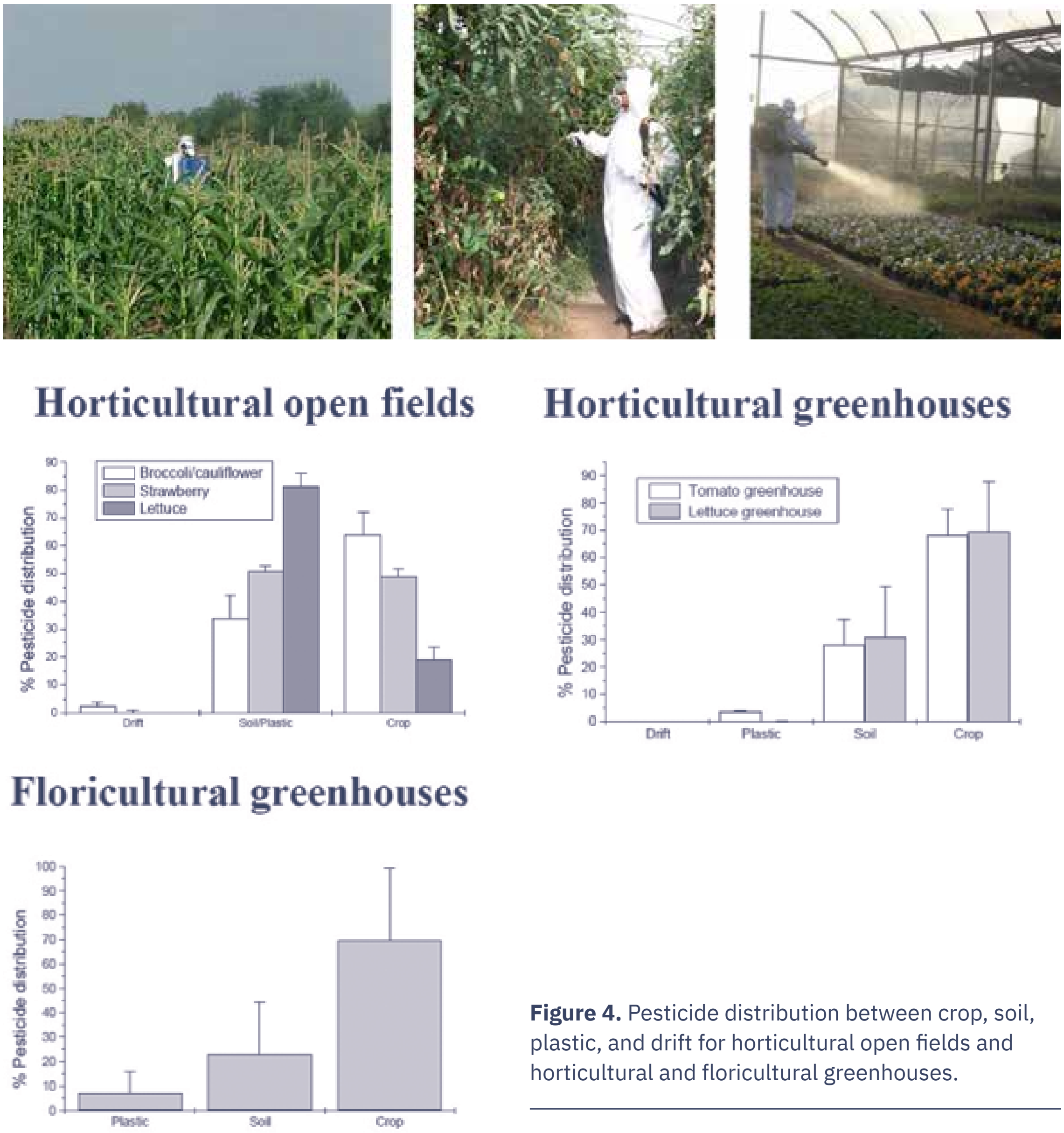


Figure 4. Pesticide distribution between crop, soil, plastic, and drift for horticultural open fields and horticultural and floricultural greenhouses.

An interesting conclusion of the previous measurements is that the amount of pesticide on the plastic surface of greenhouses was not negligible (Figure 4) [17]. Approximately 2% of the total pesticide applied was detected on the surface of horticultural greenhouses pesticide applied, whereas higher values were detected on the surface of floricultural greenhouses [17]. Considering this, we investigated the pesticide distribution in plastic greenhouses. To achieve this, we placed cotton sampling patches on the walls at three different heights and on the ceiling (Figure 5, center) [17]. Figure 5 shows the % relative pesticide distribution on the greenhouse plastics after application on four main sectors: lateral walls, front/back walls, crop roof, and aisle roof. In horticultural greenhouses, no specific distribution pattern was observed for two different crops: lettuce and tomato, whereas a higher exposure was detected on the lateral walls of floricultural greenhouses [17].

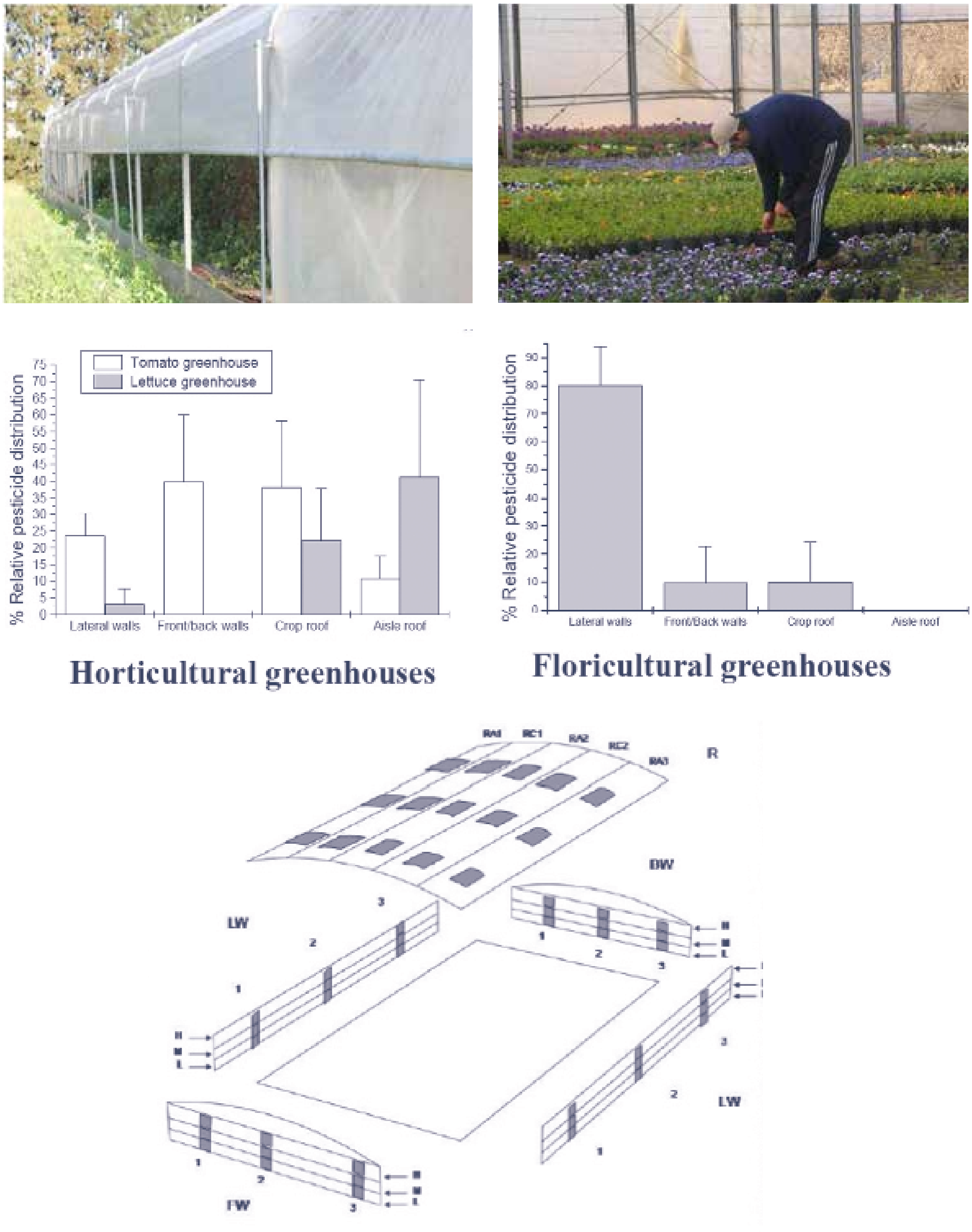


Figure 5. Pesticide relative distribution on greenhouse plastics.

The measurement of pesticides that could reach agricultural plastic films (mainly PE for greenhouses and mulching) is important because significant amounts of discarded plastic sheeting were usually found next to cultivated fields (Figure 6). Plastics could act as the source or sink for pesticides, impacting their environmental fate. Similarly, we recently reported that small pieces of the plastic film were found in horticultural soils, in up to 10% of the soil area. Evidently, plastic fragments have become a significant component in productive soils; hence, they must be considered to understand the pesticide fate in this environment. [18].

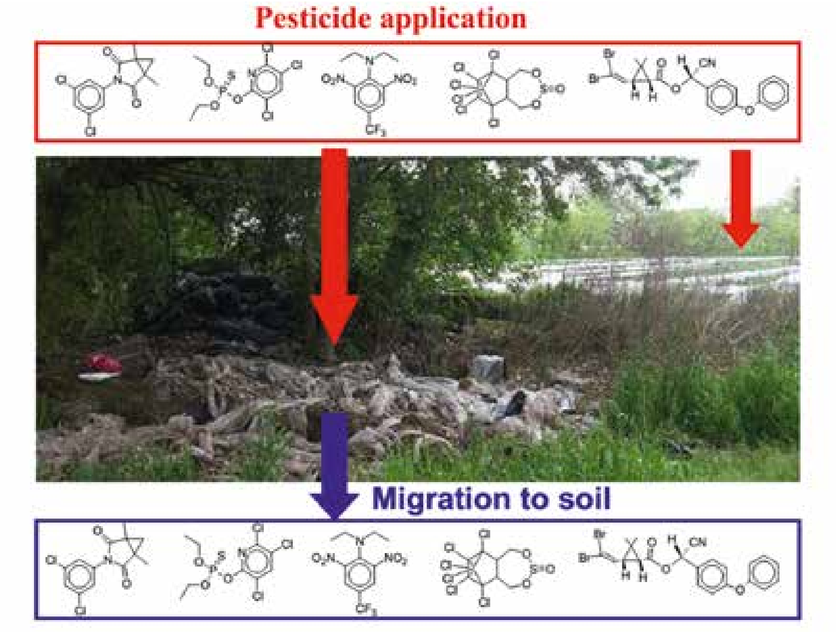


Figure 6. Used PE sheeting next to a horticultural production.

4. Degradation of different pesticides in horticultural soils

Since horticultural and floricultural soils are directly exposed to significant pesticide amounts, it is important to investigate the pesticide fate in this environment. However, this requires considering whether horticultural soils, in which different crops are cultivated and rotated in different sections of the same production unit, are homogenous (Figure 7).

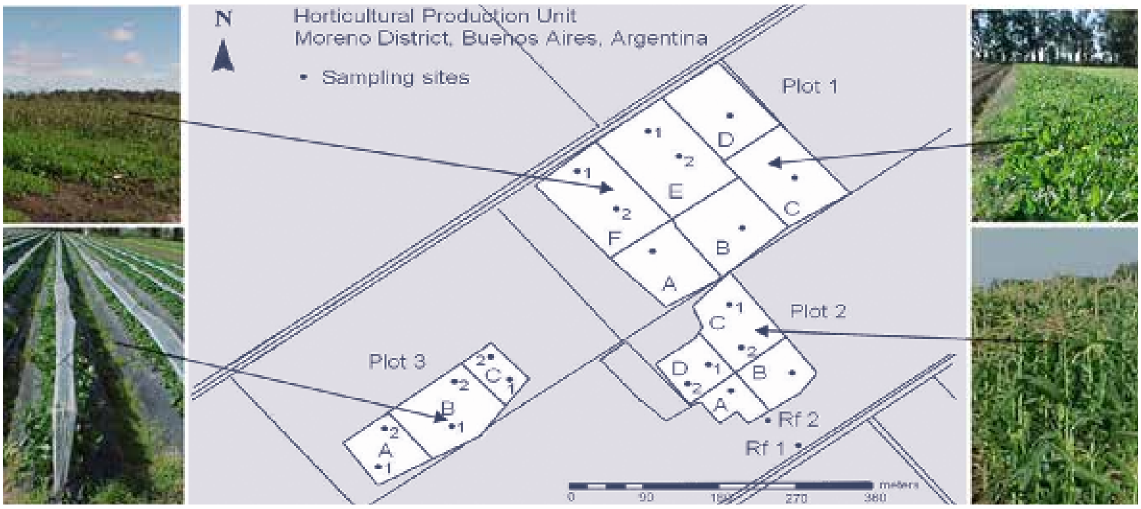


Figure 7. Different crops and sections of a small periurban horticultural production unit in Buenos Aires.

To achieve the aforementioned, we selected several physicochemical soil properties as indicators of soil conditions: microbial respiration, humidity, organic matter, conductivity, pH, and total phosphorous content. All measurements were done in selected sampling points (Figure 7) of three different subsections of a horticultural production unit located at the Moreno district in Buenos Aires, Argentina [19]. According to these selected properties, the mean values for each of the three subsections did not exhibit relevant heterogeneity within the production unit [19]

Table 5. Soil properties for the different sampling points of plots P1, P2, and P3.

Sample	Soil Properties							
	MR[1] (mg CO_2/g soil)	**Hum.**[2] (%)	**O.M.**[3] (%)	**Cond.**[4] (mS/cm)	**pH**	**R.V.**[5] (mL/g)	**Density** (g/mL)	**P**[6] (mg/g soil)
P1-A1	0.42	15.5	4.79	0.114	6.45	1.44	NM[7]	0.277
P1-B1	0.29	17.8	4.40	0.067	5.99	1.28	1.10	0.226
P1-C1	0.39	14.5	4.36	0.051	6.45	1.12	1.80	0.258
P1-D1	0.42	16.9	4.41	0.045	6.55	0.99	2.01	0.248
P1-E1	0.32	20.3	4.75	0.032	6.09	0.94	1.66	0.214
P1-E2	0.46	19.6	4.39	0.144	7.04	1.29	1.52	0.194
P1-F1	0.45	20.4	4.82	0.058	6.35	1.10	NM	0.185
P1-F2	2.41	21.3	4.61	0.133	6.15	1.34	0.29	0.202
P2-A	1.16	12.7	6.05	0.083	5.95	0.94	1.52	0.066
P2-B	0.60	22.3	6.42	0.031	5.39	0.76	1.91	0.088
P2-C1	0.68	22.4	4.01	0.143	5.17	1.02	1.82	0.104
P2-C2	0.46	14.1	6.31	0.050	6.09	0.94	1.63	0.204
P2-D1	0.84	17.5	4.27	0.027	5.19	0.81	1.90	0.149
P2-D2	0.38	13.6	4.28	0.046	6.03	0.70	1.62	0.290
P3-A1	0.25	16.3	4.35	0.268	7.05	1.20	1.62	0.160
P3-A2	0.55	21.6	4.42	0.061	5.65	0.73	1.70	0.164
P3-B1	0.57	19.6	5.71	0.056	5.75	1.05	1.57	0.155
P3-B2	0.51	19.4	4.70	0.063	6.21	0.77	2.50	0.147
P3-C1	0.44	14.9	2.78	0.027	5.21	1.12	1.52	0.186
P3-C2	0.37	17.1	6.23	0.054	5.65	0.83	NM	0.168

[1]MR: Microbial respiration (mg CO_2/g dry soil). [2]Hum: Humidity (% referred to dry soil). [3]O.M.: Organic matter content (% referred to dry soil). [4]Cond.: Conductivity. [5]R.V.: Retention volume (mL of water/g dry soil). [6]Total phosphorus (mg of P/g dry soil).[7]Not Measured.

When the homogeneity within the production unit was confirmed, we investigated the pertubation of the horticultural soil relative to a reference soil of the same edaphological kind, but not used for at least 20 years. This was achieved by determining the same set of physicochemical properties in the reference soil, which confirmed significant differences in the phosphorous and organic matter content. The phosphorus content in the horticultural system was twice that of the reference soil, whereas the organic matter in the horticultural soil was half that in the reference soil [19].

Considering these parameters, we investigated the possible differences in pesticide degradation rates between horticultural and reference soils. Consolidated samples were made with equal amounts of soil from each sampling point for both horticultural soil and the reference soil. The influence of soil characteristics on pesticide degradation was investigated by applying a single pulse of a mixture of pesticides (commercial formulations of chlorpyrifos, procymidone, and trifluralin) to the composite samples of both soil types. We also assessed the simultaneous degradation of a group of pesticides because simultaneous application of different active ingredients is a common practice among the horticultural workers. The pesticides were selected as representatives of the herbicide, insecticide, and fungicide groups. A single dose of 0.015–0.035 mg of each pesticide per gram of dried soil (twice the manufacturer's recommended dose) was applied. The soil pesticide content was determined at different exposure times by solvent extraction and quantification by GC-ECD. Figure 8 depicts the chlorpyrifos, procymidone, and trifluralin degradation profiles for both soils. All pesticides experienced faster degradation in the horticultural soil than in the reference soil, exhibiting first order exponential kinetics for procymidone and trifluralin in the first case. To evaluate whether the pesticide application impacted the microbiota, microbial respiration was measured, using composite samples with and without pesticides. The results (not shown) of microbial respiration versus time for both experiments indicated negligible differences between them [19].

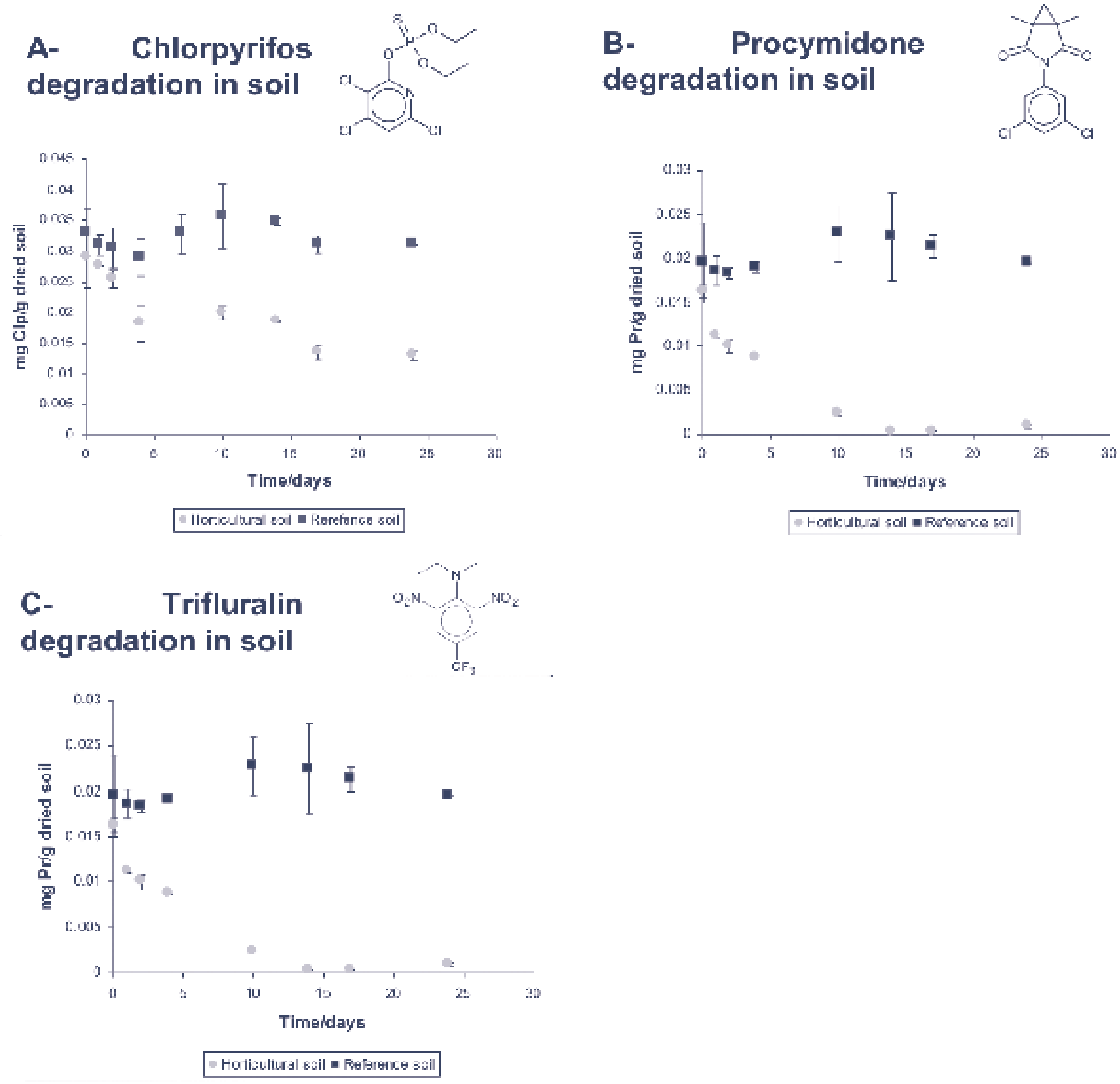
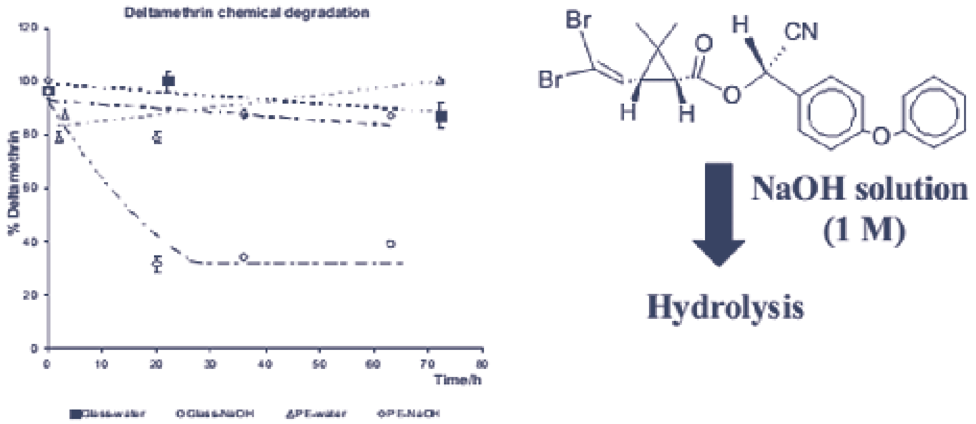


Figure 8. Chlorpyrifos, procymidone, and trifluralin degradation in microcosm assays of the horticultural and reference soils.

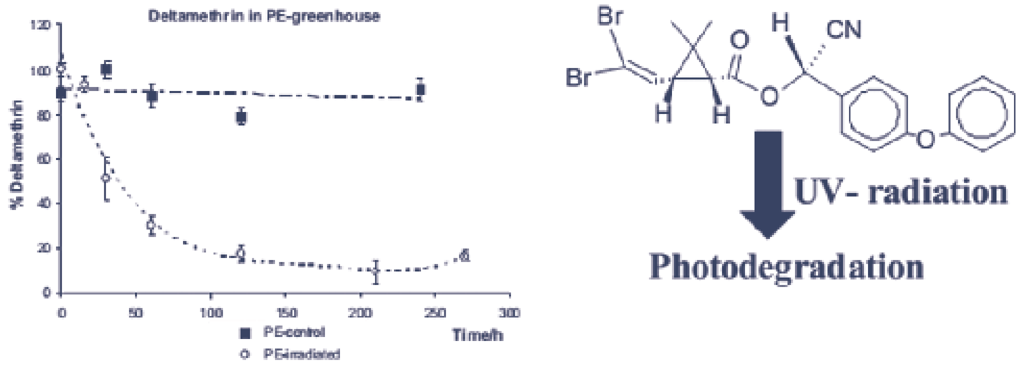
5. Stability and pesticide degradation processes on agricultural plastics

As previously discussed in section 2, horticultural plastic sheeting is significantly exposed to pesticides during the application stage. Therefore, significant amounts of these products are absorbed into the plastic film (Figure 4). Hence, it should be interesting to assess whether pesticides in the LDPE film could experience a protective effect against chemical or photochemical degradation [18]. To validate this hypothesis, we allowed deltamethrin to be absorbed in small LDPE sections (25 and 100 μm thick) and exposed them to a 1 M NaOH solution or to UV radiation (different experiments). In both cases, deltamethrin on a glass surface was also exposed as a positive control and deltamethrin absorbed on LDPE, but not exposed to NaOH or UV, was used as negative control. Figure 9 depicts the remaining deltamethrin content versus time. During the hydrolytic experiment, the deltamethrin that was absorbed into the LDPE and exposed to NaOH remained stable, whereas that on the glass surface (negative control) was significantly decomposed. These findings were attributed to a protective effect of the LDPE.

Conversely, when deltamethrin on both LDPE and glass was exposed to UV radiation, the photodegradation rate was higher on the LDPE than on the glass (Figure 9) [18]. These results could be explained by considering the amorphous polymer phase as a solvent with an infinite viscosity, where photodegradation can occur because of the mobility of the radical fragments, which is a phenomenon that is undesirable on glass [18].



Pesticide hydrolitic degradation in PE films:



Pesticide photodegradation in PE films:

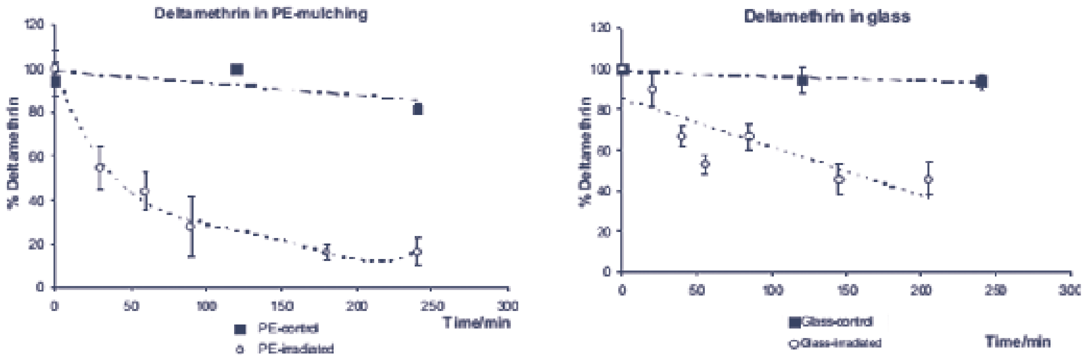


Figure 9. Hydrolytic and photolytic degradation of deltamethrin on PE films.

6. Educational training

Importantly, we conducted educational activities with the horticultural workers to raise awareness of the risk associated with pesticide manipulation. We observed that workers of small periurban horticultural production units are not typically cognizant of the risks associated with these substances. Hence, to contribute to their education in risk perception, conducted some awareness activities using Brilliant Blue—a harmless bromatological dye—as a pesticide surrogate. Workers were encouraged to perform their usual preparation and application activities using the pesticide surrogate and the cotton sampler overall described in section 1 (Figure 10). Once the preparation/application stages were complete, the blue dyes on the overall surface were used to show the workers the magnitude of the exposure.

Figure 10. Operator’s educational training with a pesticide surrogate.

7. Conclusions

Pesticide exposure during horticultural and floricultural practices such as preparing and applying these products was evaluated by determining the PDE. The critical aspects that could impact the exposure during the mix and load step were also investigated. Simple factors like colored formulations could help to diminish workers exposure during the mix and load stage.

A relative mass distribution of pesticide between the crop and the nontarget systems (soil, plastic, drift) was done in open fields and in horticultural and floricultural greenhouses, determining that the soil and plastic exposure could be significant.

Horticultural soil heterogeneity was considered for a small production unit with different subsections. Pesticide degradation in horticultural and reference soils was investigated, revealing that degradation was enhanced in horticultural soil, possibly due to microbiota adaptation.

The hydrolytic and photolytic degradation of pesticides absorbed on LDPE was also studied, confirming that photolytic degradation was faster in the LDPE than in the control system. In the case of hydrolytic degradation, a protective effect was observed on the LDPE.

Finally, educational training activities regarding workers safety during pesticide manipulation were conducted with horticultural laborers.

Acknowledgments

We would like to thank Universidad Nacional de General Sarmiento, CONICET, MinCyT, INTA and the OPCW for providing financial support. The OPCW grant was essential for the execution of this project. The OPCW's promotion of the safe use of chemistry is a fundamental ideology that we profoundly share.

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