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Potential Dermal Exposure in greenhouses for manual sprayers: Analysis of the mix/load, application and re-entry stages

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ABSTRACT

An evaluation of the Potential Dermal Exposure for the mix/load, application and re-entry stages, associated with procymidone and deltamethrin usage, was carried out for tomatoes grown in greenhouses of small production units in Argentina. Eight experiments were done with four different operators, under typical field conditions with a lever operated backpack sprayer. The methodology applied was based on the Whole Body Dosimetry technique, evaluating a set of different data for the mix and load, application and re-entry operations. These results indicated that the Potential Dermal Exposure of the application step was (38 ± 17) mL h^{-1} with the highest proportion on torso, head and arms. When the three stages were compared, re-entry was found to contribute least towards the total Potential Dermal Exposure; meanwhile in all cases, except one, the mix/load operation was the stage with highest exposure. The Margin of Safety for each different operation was also calculated and the proportion of pesticide drift from the greenhouse to the environment is presented.

These results emphasize the importance of improving the personal protection measures in the mix and load stage, an operation that is not usually associated with high-risk in small production units.

1. Introduction

Safe pesticide handling is a major concern during mix/load, application or re-entry operations in agricultural practices (Fenske and Day, 2005). This subject is particularly important in small scale production units surrounding Buenos Aires city, where all the aforementioned operations are usually performed by the same laborer (Hughes et al., 2004, 2006). The problem is usually magnified by poor working conditions, associated to lack of education, low technology and manpower dependence, a very different situation compared with extensive agriculture, the prevalent mainstream production in Argentina.

In these working scenarios, it is quite well established that transdermal absorption through the skin can be the most important pathway for pesticides uptake, under typical field working conditions (Drexler, 2003). For this purpose the measurement of the Potential Dermal Exposure (PDE) provides relevant information on the quantity of a chemical substance that contaminates uncovered body regions and clothing, worn by pesticide handlers (Glass et al., 2001, 2000; OECD, 1997). But PDE data by itself cannot be used as a risk indicator because it must be related to acceptable exposure limits. For this purpose, the Margin of Safety (MOS) has been proposed as a useful risk indicator (Machado-Neto, 2001) that relates the acceptable exposure to a product with the mass absorbed by the body, which can be estimated from PDE; MOS values lower than one are considered as an indication of unsafe procedures.

Special attention has been directed to the laborer's PDE under greenhouse working conditions, as consequence of the persistence of the pesticide mist generated during the application. It has been demonstrated that in greenhouses, handheld spraying equipment with the use of a spray lance whilst walking forwards is the worst scenario of application, causing the highest exposure risk for the operator, (Nuyttens et al., 2009). It has also been remarked that operator PDE and potential inhalation exposure were significantly increased when the pressure of the application devices was raised (Machera et al., 2003). For the particular case of handheld applications in tomato greenhouses, reported PDE contaminating the body of the operators ranges from 25.4 to 35.8 mL h^{-1} (Machera et al., 2003), and mean values of 48.1 mL h^{-1} for spray lance (Nuyttens et al., 2009) were also reported. In relation to the pesticide distribution on the laborer's body when pesticide application was performed in greenhouses by manual spraying, it has been observed that when a spray lance was used walking forward or backwards the main proportion of pesticide was found on lower legs and feet (Nuyttens et al., 2004, 2009). In the same sense, when exposure was studied in tomato

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greenhouses applying malathion, the left arm, chest and legs were identified as the most exposed body parts (Machera et al., 2003); lower legs, arms and chest were the most contaminated sections also in flower greenhouses when applying procymidone (Capri et al., 1999).

When the potential exposure was measured for the mix and load stage, very different situations were found. Using procymidone in greenhouses, an exposure during the preparation operation of 6–8% of the total PDE was found (Capri et al., 1999). During amateur applications in domestic orchards, the greatest risk of potential operator exposure was associated with the handling of the concentrate (Harrington et al., 2004). In a different context, Lebailly et al. (2009) measured the exposure in mechanized open field farms, finding that the mix and load operation accounted for two-thirds of the total daily exposure.

This paper reports the PDE and the corresponding risk estimate in workers spraying deltamethrin and procymidone in small scale, low-technology tomato greenhouses in Argentina. The mix/load stage is analyzed separately, in order to study its relative contribution to the total exposure, as well as its associated risk. Preliminary results of pesticide drift from the greenhouse to the surrounding area are also presented.

2. Experimental methods

2.1. Study sites and conditions

All field experiments were carried out at the “Estación Experimental INTA San Pedro”, in San Pedro district (Buenos Aires, Argentina), during autumn 2009 (14th–15th April). The greenhouse was 22 m long × 18 m wide, with a window in each long side, 20 m × 0.9 m, 0.5 m from the ground; two doorways, 2.0 × 1.0 m (on the front side) remained open throughout the experiences. Rows were 20 m long, separated by 2.0 m with 0.25 m between plants. Tomato plants were of the Superman and Beverly cultivars, ready for harvesting, the average height was 2.0–2.6 m. Fruit were not harvested after these experiments.

In all experiments ambient temperature was between 20 and 26 °C, relative humidity between 34 and 41% and air pressure 1019 mbar with no measurable inside wind current. Outside conditions were 15–16 °C with wind gusts up to 15 km h^{-1}. The greenhouse side openings were closed during the first day (normally, these windows are open in warm weather), and completely opened for the drift estimation.

2.2. Reagents, materials and chromatographic conditions

The deltamethrin commercial formulation used for application was Decis Forte® (EC, 10% w/v) (Bayer CropScience Argentina). For the preparation of reference material, deltamethrin ((*S*)-α-cyano-3-phenoxybenzyl-(1*R*,3*R*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate, CASRN [52918-63-5]) technical grade, was recrystallized (95% pure by GC-FID), and confirmed by ^{1}H- and ^{13}C-NMR; a primary solution of 128.8 ppm w/w was prepared in cyclohexane, and all other working solutions were made by dilution as needed. The procymidone commercial formulation used for application was Sumilex® (CS, 50% w/v) (Summit Agro Argentina). For the preparation of reference material, procymidone (3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]hexane-2,4-dione, CASRN [32809-16-8]) of technical grade, was recrystallized (95% pure by GC-FID), and confirmed by ^{1}H- and ^{13}C-NMR; a primary solution of 291.8 ppm w/w was prepared in cyclohexane, and all other working solutions were made by dilution as needed. Cyclohexane (Aberkon pa grade) was used for all solutions and extracts, distilled prior to use and chromatographically checked as suitable for use under GC-ECD conditions.

All chromatographic analyses were performed on a Perkin-Elmer (Norwalk CT, USA) AutoSystem XL Gas Chromatograph with Auto-sampler automatic injector, equipped with an electron capture detector (ECD), and a fused silica capillary column (PE-5, 100% methylpolisiloxane stationary phase, 30 m length, 0.25 mm i.d. and 0.25 µm film thickness). The GC-ECD operating conditions for PDE determinations 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: N_2, 30 psi; ECD auxiliary flow 30 mL min^{-1}.

2.3. Method validation

Experiments were performed in order to investigate if deltamethrin and procymidone were stable or suffered decomposition or were otherwise lost on the cotton cloth used for sampling. No loss was observed for storage periods of up to 24 h.

Chromatographic linear ranges were studied for deltamethrin and procymidone finding linear responses between 0.05 and 1 mg L^{-1} (R^2>0.998); and between 0.015 and 0.15 mg L^{-1} (R^2>0.998) respectively. The lowest points of each calibration curve were considered as the limit of quantitation. The precision was studied by injection of a complete calibration curve for deltamethrin and procymidone by duplicate on six consecutive days and calculating the percentual standard deviation of the slope of the calibration curves. A variation of 26% was found for deltamethrin and 10% for procymidone.

2.4. Sampling method and field procedure

For these experiences, the greenhouse was divided into two subplots of 140 lm of tomato plants, separated by two rows of plants which were left unsprayed as a neutral buffer zone. One of the subplots had a slightly higher presence of weeds between rows, as well as more trailers/runners and leaves extending into the aisle. One of the operators prepared and applied the first product (Decis) on subplot No 1, and repeated the whole procedure (mix/load, application) on subplot No 2. Another operator later repeated this routine but using the second product (Sumilex). Thus, each subplot was sprayed once with each product, with an interval of approximately 80 min between them. In this way re-entry PDE could be evaluated twice by measuring how much of the first active product (deltamethrin) was found on the overall used for the second spray. The set of four experiences was repeated on the second day, with different operators, for a total of eight spray PDEs with four operators and four re-entry PDE results. Experiences M_1, M_2, M_5 and M_6 were done with deltamethrin; M_3, M_4, M_7 and M_8 with procymidone. With respect to location, M_1, M_3, M_5 and M_7 were carried out in the first subplot, whilst M_2, M_4, M_6 and M_8 in the second.

As the spraying operations were carried out by four different operators with a similar degree of experience, they may be considered representative of typical behavior and procedures. For the same reason, all results were considered valid, including those where the tank or hoses leaked, the nozzle was cleaned, or any other similar operation was carried out.

PDE was measured using the whole body dosimetry technique (Hughes et al., 2006) as previously reported. The operator was dressed with protective equipment (30 cm high rubber boots, a Tyvek coverall, and latex gloves) over which the absorbent media were worn: cotton coverall with hood, cotton gloves and a half-face respiratory mask (for worker's protection) with two pads of 1.1 g of cotton-wool as filter material; goggles were also used as eye protection.

After donning the coverall, with no further instructions, the operator prepared an initial emulsion/suspension of pesticide in water, then poured it into the tank and diluted it up to the total volume of the sprayer (Jasco Heavy-Duty HD300, 3 gal. lever operated backpack, 60 cm lance with single nozzle) as usual; concentrations were as recommended by the manufacturers (average values were 53.9 mg L^{-1} for deltamethrin and 406.6 mg L^{-1} for procymidone). Both the measuring cylinder and sprayer were weighed before and after loading (pesticide formulations were weighed with 0.1 g resolution, the backpack with 20 g resolution). When the mix/load procedure was completed, the operator's cotton gloves were exchanged for a clean set, and placed in polyethylene bags for later analysis as "mix/load PDE". The operator started spraying following his usual technique, until the selected subplot was completed. They all walked forwards while spraying, but with their body half-turned to face the plants. Due to the geometry of the greenhouse all the operators chose to walk the first section spraying the plants on their right side, whilst the second section was sprayed towards the left (that is, crossing their right arm over their body). Application time was typical for small plots (140 lm): between 8 and 14 min, at an application rate of 30–42 L h^{-1}. Once finished the cotton coverall was taken off and placed in a polyethylene bag. Gloves, masks and goggles were also placed in individual polyethylene bags for later processing. The backpack was weighed again to determine how much mixture was actually sprayed.

Drift was estimated during the last four application experiences, as described previously (on the second day), with the greenhouse windows and doors opened. Twelve samplers (cotton cloth, 20 cm square) were nailed to the ground, evenly distributed in three rows, parallel to the downwind window, at 0.75 m, 2.0 m and 3.7 m distance (Fig. 3), each placed on a piece of polyethylene to minimize casual contamination from the ground. The samplers were left in place for 3 h after the last experience was finished, and then they were collected in individual polyethylene bags for later analysis.

2.5. Analysis

In the laboratory, the cotton coverall was cut into different sections as indicated in Fig. 1; each of these was extracted separately with cyclohexane (20 min, rotary shaker with solvent volume depending on the section size e.g. 100 mL for gloves, 800 mL for chest) not later than 8 h after the field trial. Drift samplers were similarly treated. Goggles and face mask were swabbed with cyclohexane moistened tissues and rinsed with the same solvent; all extracts were analyzed by GC-ECD, following the procedure previously reported (Hughes et al., 2006).

2.6. Calculation of PDE

The concentration of the sprayed mixture was calculated using the weight, concentration and density of pesticide and water loaded into the tank. The concentration of pesticide in each extract, and its volume, were used to calculate the amount extracted from each

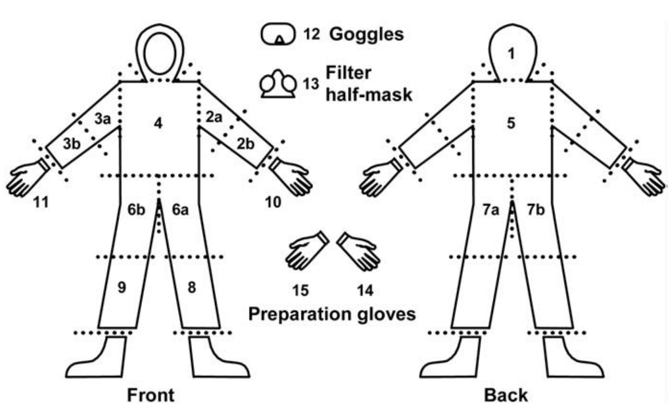


Fig. 1. Coverall sections for PDE.

coverall part. This value combined with the duration of each experience gives a time-rate value for the Potential Dermal Exposure. Results are expressed as volume of spray mix to which the operator would be exposed if he continued spraying for 1 h (in mL h^{-1}), or in an equivalent form, as the amount of pesticide (in mg) found on each body section.

2.7. MOS calculation

The MOS is defined as follows:

$$MOS = \mathrm{AE} / (DE \times AF \times SF)$$

where AE = acceptable exposure; DE = dermal exposure; AF = absorption factor and SF = safety factor.

AE values are calculated on the basis of appropriate toxicological end-points according to the following expression: AE = AOEL × average body weight (deltamethrine AOEL = 0.0075 mg kg^{-1} d^{-1}; procymidone AOEL = 0.035 mg kg^{-1} d^{-1}; UK-CRD — TEA, 2009a,b); and average body weight of 70 kg.

DE = PDE (as mg of deltamethrin or procymidone) resulting from the present study; this means that all body parts are considered, including goggles, mask and preparation gloves. As explained in Section 3.3, the MOS was evaluated on the basis of a complete greenhouse (360 lm), not just the subplot directly measured.

AF = 0.11, which considers an effective dermal absorption of 10%, with an additional 1% added to include the inhaled fraction (Machado-Neto, 2001). Additional protection due to clothing is not considered, because the normal workwear varies from a simple sweatshirt and shorts to long-sleeved shirts, sweaters, trousers and boots, so the worst case was considered.

SF = 1 as by definition the AOEL includes a safety factor.

Thus, the actual formula used was:

$$MOS = AOEL \times 70 / (PDE \times 0.11 \times 1)$$

3. Results

3.1. PDE results

The PDE results for tomato greenhouse deltamethrin and procymidone applications are presented in Table 1, expressed as volume of sprayed liquid per unit of time (mL h^{-1}) for each body section (Fig. 1). A set of eight experiments were done, four corresponding to deltamethrin (Table 1, M_1, M_2, M_5, M_6) and four to procymidone (Table 1, M_3, M_4, M_7, M_8). Data for face mask, goggles and gloves used during the preparation of the spray mix were not included in the "total PDE value" (Table 1) for easy comparison with other published data. The mean PDE total value was (38 ± 17) mL h^{-1} with a range from 6.3 to 188.2 mL h^{-1}. M_8, which gave values much higher than all others, was done by the same operator and with the same technique as in M_7; as no obvious procedural differences were noted by the observers, both results were considered equally valid.

In relation to the pesticide body distribution, Fig. 2A shows the relative percentage distribution considering three main ranges: less than 5%, between 5 and 10% and more than 10%. There is a tendency for higher exposure in the forearms than arms, and also higher in the lower legs than thighs, although no lateral differentiation was seen between the left and right sides. The head was always affected (considering hood, goggles and face mask), though usually with less than 5% of the total PDE; only M_6 had a higher relative head exposure. In Fig. 2B, the PDE in mL h^{-1} is indicated considering four different body parts: hands; torso, head and arms; thighs; legs. It is interesting to note that the back section of the coverall had very low pesticide

Table 1
PDE expressed in mL h^{-1} for application of deltamethrin and procymidone to greenhouse tomato plants.

Coverall section	Potential Dermal Exposure (mL h^{-1}) [a]									
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	Mean	SD [b]
1	0.39	0.46	0.24	0.060	0.64	4.04	0.63	4.45	1.4	±1.7
2a	1.02	0.77	0.37	0.16	0.42	2.76	0.88	16.9	2.9	±5.3
2b	0.90	1.77	0.97	0.29	0.64	4.61	0.88	13.9	3.0	±4.3
3a	0.59	0.97	0.16	0.12	1.53	0.97	1.29	4.24	0.8	±0.5
3b	1.76	1.50	0.04	1.12	3.22	1.78	2.39	9.48	2.7	±2.8
4	0.85	1.09	0.30	0.30	1.69	15.7	1.81	31.7	3.1	±5.2
5	3.90	2.62	0.06	0.06	1.46	2.01	1.13	6.41	1.6	±1.3
6a	0.60	0.64	ND[c]	0.06	0.36	1.47	1.77	16.4	0.7	±0.4
6b	1.88	0.87	0.81	0.16	0.94	0.97	1.86	12.7	2.5	±3.9
7a	19.0	0.30	ND	ND	0.21	0.44	0.59	2.64	2.9	±6.1
7b	1.31	0.64	ND	0.12	0.30	0.65	0.73	2.97	0.8	±0.9
8	11.3	1.72	1.07	1.12	2.31	3.41	3.58	26.2	6.3	±8.1
9	3.21	1.91	0.93	1.46	2.31	3.91	6.12	17.0	4.6	±4.9
10	0.61	0.84	0.41	0.64	0.23	0.91	0.91	11.9	2.1	±3.7
11	0.81	0.60	0.93	1.78	0.56	0.55	2.42	9.23	2.1	±2.8
Total [d]	*48.1*	*16.7*	*6.3*	*7.5*	*16.8*	*44.2*	*27.0*	*188.2*	*38*	*±17*
12	0.07	ND	0.04	0.01	ND	0.09	0.06	0.67	0.1	±0.2
13	0.15	ND	0.07	0.02	0.22	0.32	0.05	1.49	0.3	±0.5
14 [e]	6.32	7.17	5.13	19.91	5.34	10.66	6.19	77.91	17.33	±24.96
15 [e]	4.36	10.56	17.13	14.78	4.52	8.75	100.8	43.76	25.58	±32.91
14+15	10.68	17.74	22.26	34.69	9.85	19.41	107.0	121.7	42.91	±44.91

Application mix data: time; amount; concentration.
M_1: deltamethrin, 11.2 min; 6.54 L; 58.2 mg L^{-1}.
M_2: deltamethrin, 14.6 min; 7.38 L; 58.7 mg L^{-1}.
M_3: procymidone, 7.7 min; 5.34 L; 363.5 mg L^{-1}.
M_4: procymidone, 8.6 min; 5.60 L; 413.4 mg L^{-1}.
M_5: deltamethrin, 11.6 min; 7.82 L; 50.4 mg L^{-1}.
M_6: deltamethrin, 10.08 min; 6.58 L; 48.4 mg L^{-1}.
M_7: procymidone, 12.95 min; 7.34 L; 401.3 mg L^{-1}.
M_8: procymidone, 11.6 min; 6.50 L; 448.3 mg L^{-1}.
[a] M_i denotes field experiment number i.
[b] Av = Average.
[c] ND = Not detected.
[d] For comparison with other published results, this Total does not include sections 12–15, i.e. facial protection and preparation gloves.
[e] Preparation gloves, EDP given in equivalent mL of sprayed mix.

exposure, which is in accordance with the forward-spraying technique used.

3.2. Relative operator exposure during the mix/load, application and re-entry operations

The total amounts of pesticide found for mix/load (on the gloves), application and re-entry (coveralls) operations, expressed as mg of the active ingredient, are presented in Table 2 adjusted so as to represent the exposure resulting from the application of each pesticide to a complete warehouse (both sides of nine 20 m rows, 360 lm). As more than one backpack would be necessary for this, the values for preparation gloves were multiplied by two. The re-entry stage considered was similar, in time and distance walked, to the application stage.

The mix/load stage included opening the container, measuring the desired quantity of concentrated product in a measuring cylinder and transferring it to the backpack. In experiences M_1 through M_4, the product was first mixed with water in a bucket; in M_5–M_8 the measured product was poured directly into the backpack. In all cases the cylinder was rinsed, and the liquid added to the rest of the mix. It is interesting to remark that in all the measurements, except one (Table 2, M_1), PDE values of the mix/load stage were considerably higher compared to the application and re-entry stages. With deltamethrin, average PDE for the mix/load operation was 1.9 times higher than for the application stage and for procymidone this ratio was approximately 4.9.

The re-entry operation was measured for the application of deltamethrin, finding exposures between 0.073 and 0.244 mg of pesticide (mean value of 0.13 ± 0.07 mg, Table 2) that were in all cases lower than the corresponding application stage. In relation to the pesticide body distribution in the re-entry operations, the most exposed sections were the torso, left arm and legs, with very small amounts found on the back of the coverall.

When the mean values of deltamethrin in the application stage (0.83 mg, Table 2) are compared to procymidone data in the same step (12.3 mg, Table 2) a significant difference is observed that cannot be explained by the working pesticide concentrations alone (see Section 2.4). If the procymidone application data set is observed (Table 2), there is an experiment with an unusually high exposure level (M_8); if this data point is not considered the mean value would be 2.6 mg of procymidone, which is more in accordance to the deltamethrin value. In the mix/load stage, the difference found between both products is even greater (1.55 mg for deltamethrin, 60.0 mg for procymidone, Table 2) and consequently, the equivalent volumes of concentrated pesticides found in the preparation gloves (0.016 ± 0.0004 mL for Decis, 0.12 ± 0.07 mL for Sumilex) are very different.

3.3. Margin of Safety

In order to estimate the safety of what is a normal everyday operation, the spraying of one complete greenhouse with one product at a time was considered. The MOS was calculated separately for deltamethrin and procymidone, distinguishing between the mix/load and application stages, and adjusting the experimental results so as to consider the whole greenhouse (nine rows with a total length of 360 m). The MOS values are presented in Table 3 subdivided in three groups: A—for the mix/load stage only, B—for the application itself, and C—for the complete procedure.

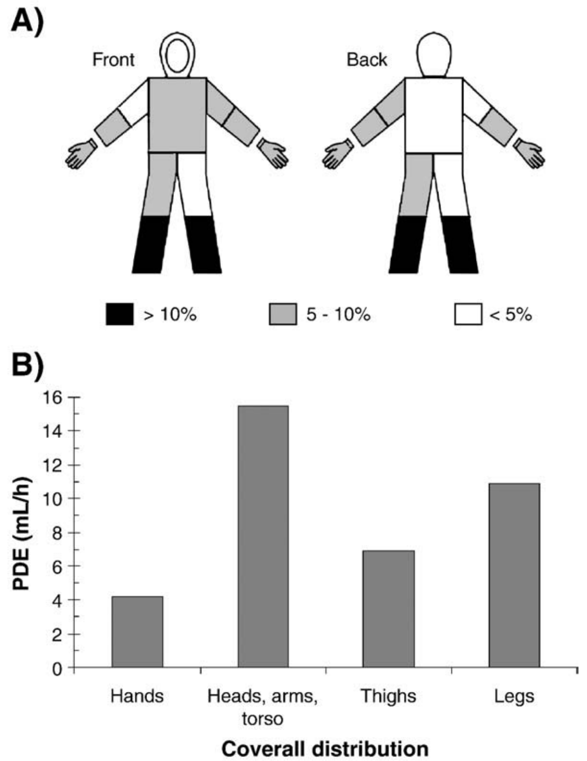


Fig. 2. Pesticide distribution for coverall sections at application and re-entry stages.

These results show that the application operation by itself is quite safe for deltamethrin and procymidone application (Table 3), with only one unsafe experience (M_8). It is interesting to remark that the difference between the mean MOS for the deltamethrin (6.9 ± 2.9) and procymidone (13 ± 11) at the application stage is modulated by the AOEL for each product, considering that the mean PDE values for both pesticides were in the same order.

On the other hand, the mix/load stage was riskier for both products, with MOS values lower than the corresponding application stage in all cases except one (M_1, Table 3) and three unsafe experiences (M_6, M_7 and M_8). The mean MOS for deltamethrin mix/load stage was half that of its application stage, but still a safe procedure. The procymidone mix/load mean MOS value was below one (Table 3), indicating that this sole operation was responsible for an unsafe pesticide handling procedure. It is important to note the difference found in the mean MOS values of the mix and load operations for deltamethrin and procymidone, which were carried out by the same operators using the same equipment under the same conditions.

Table 2
PDE in mg of pesticide for backpack application for the mix and load, application and re-entry stages.

Stage	M_1	M_2	M_5	M_6	Mean	SD
Deltamethrin Potential Dermal Exposure (mg of Deltamethrin)						
Mix/load[a,b]	1.25	2.08	0.99	1.88	1.55	±0.44
	(0.012)	(0.021)	(0.010)	(0.019)	(0.016)	(±0.004)
Applic.[c]	1.34	0.61	0.42	0.93	0.83	±0.35
Re-entry [c]	0.073	0.134	0.056	0.244	0.13	±0.07
Procymidone Potential Dermal Exposure (mg of Procymidone)						
Stage	M_3	M_4	M_7	M_8	Mean	SD
Mix/load[a,b]	16.18	28.68	85.87	109.10	60.0	±38.7
	(0.032)	(0.057)	(0.17)	(0.22)	(0.12)	(±0.07)
Applic.[c]	0.75	1.13	6.01	41.46	12.3	±16.9

[a] Preparation gloves: Sections 14 + 15.
[b] In parenthesis the volume (mL) of the concentrated product (Decis, Sumilex).
[c] Coverall and gloves: Sections 1–11.

Table 3
MOS for deltamethrin and procymidone for mix/load, application and combination of both stages for a complete greenhouse application.

Exp.	M_1	M_2	M_5	M_6	Mean
Deltamethrin MOS					
A – Mix/load[a]	3.8	2.3	4.8	2.5	3.4 ± 1.0
B – Application[b]	3.5	7.8	11.2	5.1	6.9 ± 2.9
C – Mix/load + Applic.	1.8	1.8	3.4	1.7	2.2 ± 0.7
Procymidone MOS					
Exp.	M_3	M_4	M_7	M_8	Mean
A – Mix/load[a]	1.4	0.8	0.3	0.2	0.7 ± 0.5
B – Application[b]	29.3	19.6	3.7	0.5	13 ± 11
C – Mix/load + Applic.	1.3	0.7	0.2	0.1	0.6 ± 0.5

[a] Preparation gloves: Sections 14–15.
[b] Coverall, gloves, goggles and face mask: Sections 1–13.

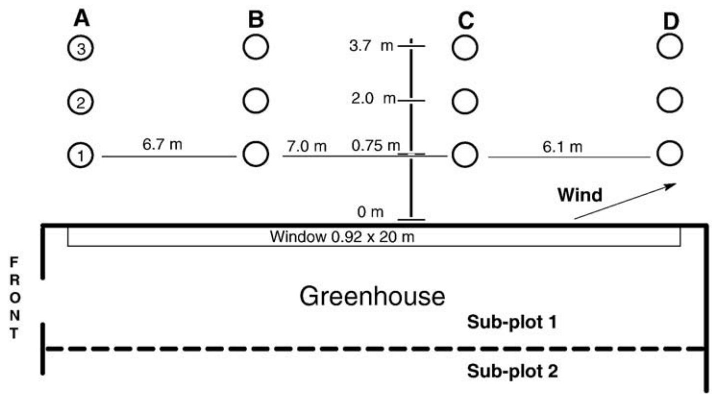
3.4. Pesticide drift estimation from the greenhouse

An interesting issue is the fraction of pesticide that drifts from the greenhouse to the surrounding land, contaminating the environment, and what would be a safe distance to maintain from a greenhouse in order to avoid contamination with pesticides. In order to evaluate this, a set of preliminary measurements was done by sampling procymidone and deltamethrin drifts from the greenhouse window to the adjacent ground. It must be emphasized that there was no measurable wind current within the greenhouse, even with the doors/windows open. Deltamethrin and procymidone drift values for the different sampling positions (20 cm × 20 cm) are presented in Fig. 3. From these data it can be concluded that even with no measurable wind, some of the sprayed products drifted outside. As expected, the amount of pesticide on the ground decreases with distance to the greenhouse, and compared with the total amounts sprayed (9.0 g deltamethrine from $M_5 + M_6$ and 23.4 g procymidone, $M_7 + M_8$), the total drift would seem to be negligible, in the order of tens of milligrams. This last can be very roughly estimated by considering the average found in the middle samplers as representative of a 4 m wide, 20 m long strip of terrain; this gives 6.2 mg for procymidone and 3.5 mg for deltamethrin.

4. Discussion

4.1. PDE discussion

Taking into account that three different stages (mix/load, application, re-entry) contribute to the total exposure, it is necessary to evaluate each separately. PDE results for the application stage in greenhouses of small production units in Argentina (38 ± 17 mL h^{-1}, Section 3.1), are in accordance with those previously reported for the case of the application of malathion on greenhouse tomatoes at low spraying pressures (22.2–33.5 mL h^{-1}; Machera et al., 2003). The pesticide exposure measurement in crops of similar geometry, like pepper in greenhouses showed also comparable values (Nuyttens et al., 2009), which indicates that the application stage was similar in terms of exposure to other reported situations. With respect to the wide PDE range found (6.3 to 188.2 mL h^{-1}) we have previously reported that this variability could be explained by the different operator techniques employed during the application (Hughes et al., 2004). The dispersion was high on both subplots assayed (subplot 1: 6.3 to 48.1 mL h^{-1}; subplot 2: 7.5 to 188.2 mL h^{-1}) when four different operators applied two different pesticides in the same



Deltamethrin (Dt) and procymidone (Pr) drifted from greenhouse (mg)								
Position	A		B		C		D	
	Dt	Pr	Dt	Pr	Dt	Pr	Dt	Pr
3	0.0014	ND	0.0008	ND	0.0006	ND	0.0009	ND
2	0.0038	0.0002	0.0010	0.0057	0.0011	0.0011	0.0010	0.0054
1	0.0033	0.0022	0.0020	0.0288	0.0079	0.0036	0.0007	ND

Fig. 3. Procymidone and deltamethrin drifts from the greenhouse to the adjacent soil.

weather conditions. It is interesting to remark that the amount of pesticide detected in the "face" sections was low (coverall sections 12 and 13, Table 1) in comparison to the total PDE, being comparable to the PDE found in mask of operators working in open field conditions (Hughes et al., 2008).

In relation to the pesticide body distribution during the application stage, the relative pattern found is consistent with the application in high plants when the operator is walking forwards, where the torso is the main exposed section, followed by the legs (Hughes et al., 2008).

These results reinforce the hypothesis that the exposure during the application stage in these small production units is not substantially different to values found in developed countries.

4.2. Relative operator exposure during the mix/load, application and re-entry operations discussion

When the PDE mean values, expressed as mg of pesticide, are compared for the different stages on both pesticides (Table 2), the importance of the mix/load operation in the total dermal exposure can be concluded. While for the application stage the mean exposure was 0.83 ± 0.35 mg for deltamethrin and 60.0 ± 38.7 mg for procymidone, the corresponding mean values for the mix and load operations were 1.55 ± 0.84 mg and 12.3 ± 16.9 mg. This is particularly important considering that most local rural workers do not like to wear gloves, and frequently wipe sweat of their faces with the back of their hands. When the pesticide found in the preparation gloves was expressed as equivalent volume of concentrated product, very different values were found for deltamethrin (0.016 ± 0.0004 mL of Decis) than for procymidone (0.12 ± 0.07 mL of Sumilex), and in both cases higher than the values found previously (Glass et al., 2002). Taking into account that all preparations were made by the same set of operators using the same equipment, a possible explanation could be that particular formulation properties (such as viscosity and concentration) have an important effect on hand exposure, especially when using small volumetric cylinders for measuring.

In a comparative context, the re-entry operation was analyzed for a complete greenhouse application of deltamethrin, finding a mean value of 0.13 ± 0.07 mg, which compared to 0.83 ± 0.35 mg for the application and 1.55 ± 0.44 mg for mix/load stages, emphasizes the idea that in this pesticide use scenario the mix/load step produced the highest exposure of the three stages considered. These results contrasted with the exposure levels of mixer/loaders in greenhouse trials during preparation and application of penconazole on tomatoes (Machera et al., 2001).

4.3. Margin of Safety discussion

In terms of risk evaluation, the MOS is a better indicator than the PDE because it establishes a comparative frame, generating an indicator that allows comparisons under very different field situations (different pesticides, different concentrations, different application techniques, etc). It is interesting to note that when the MOS of the application stage of deltamethrin (6.9 ± 2.9, Table 2) and procymidone (13 ± 11, Table 2) are compared, both mean values can be considered as in the same range. Meanwhile, if the MOS of the mix and load stage are compared a very different situation is found. In the deltamethrin case the value was 3.4 ± 1.0, while for procymidone it was 0.7 ± 0.5. This difference might be related to two concurring factors: first and obvious is that AOEL values are different for both products. The second is that the formulations are of different viscosities (Decis is very fluid, and Sumilex is a thick, viscous suspension) and concentrations (Decis 10%, Sumilex 50%); so, although the total volumes measured out were not so different (approximately 5 and 8 ml, respectively), manipulating the thicker product left more residues on the operator's hands (0.016 mL Decis and 0.12 mL Sumilex). Further investigation into the influence of formulation viscosity during the exposure of the mix/load stage is in progress in our laboratory.

4.4. Pesticide drift estimation from the greenhouse discussion

Drift is one of the pesticides mobilization mechanisms that contribute to the deposition of this kind of molecules beyond the boundaries of a treated area. This problem has been mainly studied for air and terrestrial motorized applications. For example, when using boom sprayers in conditions where the maximum wind speed was 5 m s^{-1}, a mean drift of 1.4% of the total pesticide applied was found in a neighboring field (Huber et al, 2000). When manual pesticide application was performed, we have shown that drift originated by spraying at open field plantations of broccoli produced drift values between 1.5 and 5.0% of the total pesticide applied (Hughes et al., 2008; Ramos, 2010). In the present case (Section 3.4) showed that the fraction of pesticide that moves away from the greenhouse by ventilation is negligible in relative terms and corresponds to 0.04% and 0.03% of the total deltamethrin and procymidone applied. The lower drift levels found in comparison to open field situations could be explained by the closed nature of the greenhouse and the practically null wind conditions during application.

5. Conclusions

The mean PDE value for spraying a tomato greenhouse using a manual sprayer was (38 ± 17) mL h^{-1} which is consistent with previously reported data. During the application step the body distribution is asymmetrical with higher levels of exposure in the forearms and lower legs. If the relative exposures of the three main operations: mix/load, application and re-entry are compared, the mix and load operation can be identified with higher exposure levels and unsafe scenario, as reflected by the low MOS. This situation could be explained by the volumetric measuring step of the active ingredient, necessary to reach appropriate application concentrations. These results are of particular importance considering that these workers rarely use protective gloves.

Under these application conditions pesticide drift from the greenhouse to the surrounding soil seems not to be an important environmental risk.

Further experiments are in progress in our laboratory to explore the influence of the container and formulation properties on the exposure of the mix and load stage.

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References

Capri E, Alberici R, Glass CR, Minuto G, Trevisan M. Potential operator exposure to procymidone in greenhouses. J Agric Food Chem 1999;47:4443–9.

Drexler H. Skin protection and percutaneous absorption of chemical hazards. Int Arch Ocupp Environ Health 2003;76:359–71.

Fenske R, Day E. Assessment of exposure for pesticide handlers in agricultural. residential and institutional environments. In: Franklin C, Worgan J, editors. Occupational and residential exposure assesment for pesticides. J. Wiley and sons; 2005. p. 13–44.

Glass R, Gilbert A, Mathers J, Moreira J, Machera K, Kapetanakis K, Capri E. Worker exposure to pesticides — a pan European approach. Asp Appl Biol 2000;57:363–8.

Glass R, Mathers J, Vidal J, Egea González F, Delgado Cobos P, Moreira J, et al. Factores que influyen en la exposición de los trabajadores agrícolas a los plaguicidas en el área mediterránea. Phytoma 2001;129:91–3.

Glass R, Gilbert A, Mathers J, Lewis R, Harrington P, Perez Duran S. Potential for operator and environmental contamination during concentrate handling in UK agriculture. Asp Appl Biol 2002;55:379–87.

Harrington P, Mathers J, Lewis R, Perez Durán S, Glass R. Potential exposure to pesticides during amateur applications of home and garden products. In: Lichtfouse E, Schwerzbauer J, Robert D, editors. Environmental chemistry green chemistry and pollutants in ecosystem. Springer; 2004. p. 529–38.

Huber A, Bach M, Frede HG. Pollution of surface waters with pesticides in Germany: modeling non-point source inputs. Agric Ecosyst Environ 2000;80:191–204.

Hughes E, Zalts A, Ojeda J, Montserrat J, Glass R. Potential pesticide exposure of small scale vegetable growers in Moreno district. Asp Appl Biol 2004;71:399–404.

Hughes E, Zalts A, Ojeda J, Flores A, Glass R, Montserrat J. Analytical method for assessing potential dermal exposure to captan, using whole body dosimetry, in small vegetable production units in Argentina. Pest Manag Sci 2006;62:811–8.

Hughes E, Flores A, Ramos L, Zalts A, Glass C, Montserrat J. Potential dermal exposure to deltamethrin and risk assessment for manual sprayers: influence of crop type. Sci Total Environ 2008;391:34–40.

Lebailly P, Bouchart V, Baldi I, Lecluse Y, Heutte N, Gislard A, et al. Exposure to pesticides in open-field farming in France. Ann Occup Hyg 2009;53:69–81.

Machado-Neto J. Determination of safe work time and exposure control need for pesticide applicators. Bull Environ Contam Toxicol 2001;67:20–6.

Machera K, Goumenou M, Kapetanakis E, Kalamarakis A, Glass R. Determination of the potential dermal and inhalation exposure of operators, following spray applications of the fungicide penconazole in vineyards and greenhouses. Fresenius Environ Bull 2001;10:464–9.

Machera K, Goumenou M, Kapetanakis E, Kalamarakis A, Glass CR. Determination of potential dermal and inhalation operator exposure to malathion in greenhouses with the whole body dosimetry method. Ann Occup Hyg 2003;47:61–70.

Nuyttens D, Windey S, Sonck B. Comparison of operator exposure for five different greenhouse spraying applications. J Agric Saf Health 2004;10:187–95.

Nuyttens D, Braekman P, Windey S, Sonck B. Potential dermal pesticide exposure affected by greenhouse spray application technique. Pest Manag Sci 2009;65:781–90.

OECD. Guidance document for the conduct of studies of occupational exposure to pesticides during agricultural application. OECD environmental health and safety publications. Series on Testing and AssessmentParis: Environmental Directorate; 1997. OECD/GD(97).

Ramos L. Efectos del uso de productos fitosanitarios sobre el suelo productivo, en prácticas de horticultura periurbana bonaerense. Thesis in Urban Ecology, Univ. Nac. de Gral. Sarmiento, 2010.

UK-CRD Chemicals Regulation Directorate—Pesticides, Glossary. 2009. In http://www.pesticides.gov.uk/appendices.asp?id=744#AOEL. Accessed October 2009.

UK-CRD Chemicals Regulation Directorate—Pesticides, Toxicological Endpoints Database; 2009. In https://secure.pesticides.gov.uk/TEAWeb/intro.asp. Accessed October 2009.