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Pesticide risk assessment in flower greenhouses in Argentina: The importance of manipulating concentrated products

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ABSTRACT

An evaluation of the Potential Dermal Exposure of workers to endosulfan and procymidone at the mix/load and application stages was done in small floricultural production units in Argentina. Seven experiments were performed with different operators under typical greenhouse conditions, based on the whole body dosimetry methodology. These results indicate that the mean Potential Dermal Exposure of the application step was $45.0 \pm 55.0\,mL\,h^{-1}$ with the highest proportion on torso, head, arms and hands. When the mix/load and application stages were compared, the first was found to contribute the most to the total exposure. Also, the Margin of Safety for the different operations was calculated, and a pesticide surrogate was developed and used to make comparative evaluations of hand exposure for different groups of operators.

These results emphasize the importance of the mix/load stage in the exposure process.

1. Introduction

Worker's exposure during pesticide manipulation is a major concern in agricultural activities [1]. In this sense, the development of predictive exposure scenarios would contribute to guarantee safe pesticide use practices [2]. With the aim to improve the quality of exposure information and develop better predictive scenarios, observational studies of occupational pesticide exposure that incorporate repeated measures are needed [3]. Although experimental exposure data have been widely produced in relation to the manipulation of agrochemical substances in the horticultural context [4], studying the impact of pesticide manipulation on floriculture industry workers is a less developed issue.

Floriculture, considered as ornamental horticulture, is an increasingly important agricultural activity worldwide: 190,000 people are employed in developing countries like Colombia, Ecuador, México, India, Kenya or Zimbabwe [5]; in U.S.A. floriculture sales represent a third of the total horticulture activity; in Argentina, considering Buenos Aires province only, the crop area dedicated to floriculture in 2005 was of 1242 ha.

In relation to the production methodology it has been recognized that pesticide use, especially in greenhouses, can have adverse effects on workers health. For example, an exploratory analysis suggested a potential correlation between employment in the Ecuadorian cut-flower industry and the risk of spontaneous abortion [6]. Paz-y-Miño et al. [7] analyzed the incidence of structural and numerical chromosomal aberrations in workers of a flower plantation in Quito, Ecuador, finding that workers exposed to pesticides showed an increased frequency of chromosomal aberrations compared to control groups. In these working scenarios, Tuomainen et al. [8,9] reported that the potential inhalation and hand and dermal exposure to malathion, deltamethrin, and iprodione applied to rose crops in Finnish greenhouses was between 70.9 and 935.5 mg of pesticide per kg of active ingredient (a.i.) for the mix-loader, and between 345.5 and 6718.9 mg/kg a.i. for the applicator. Capri et al. [10] measured the Potential Dermal Exposure (PDE) for floriculture workers at Albenga (Italy) greenhouses with hydrangeas and daisies, finding values between 15.4 and $37.1\,mL\,h^{-1}$. In these last experiments the PDE during the mixing and loading phase accounted for 6–8% of the exposure of the whole process.

It is important to note that 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 [11] that relates the acceptable exposure to a product with the mass absorbed by the body, which

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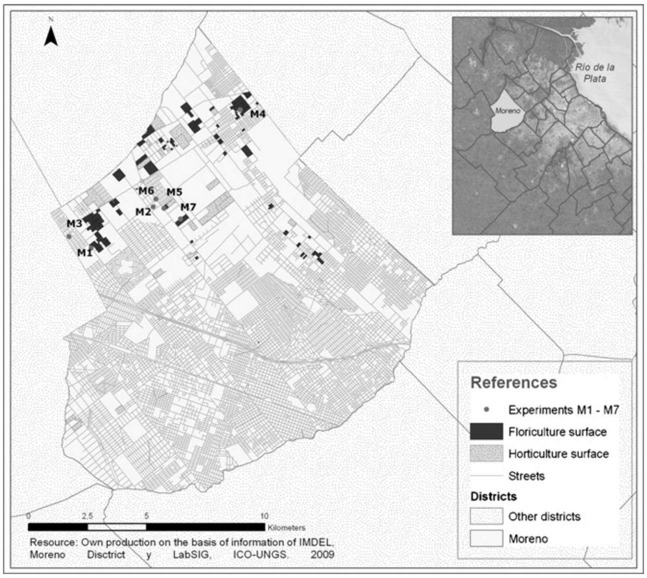

Fig. 1. Location of floricultural production units at Moreno district in Argentina.

can be estimated from PDE, considering MOS values lower than one an indication of unsafe procedures.

We present in this work the PDE and MOS evaluation of floriculture workers spraying endosulfan and procymidone in floral crops in Moreno district, Buenos Aires, Argentina. The exposure originating from the mix/load stage was considered and analyzed separately. Additional exposure data was obtained using pesticide surrogates with different groups of operators, in order to evaluate the possibility of relating hand contamination to the manipulation of pesticide concentrates.

2. Materials and methods

2.1. Study sites and conditions

All field experiments were carried out during normal pest-control activities in commercial greenhouses in Cuartel V, Moreno district (Buenos Aires, Argentina, Fig. 1), during April–November of 2009. The greenhouse area, pesticide name, weather conditions, crop type and application system for each experiment are indicated in Table 1.

2.2. Reagents, materials and chromatographic conditions

The commercial formulations used for application were Thionex® (EC, 35% w/v, Magan) for endosulfan and Sumilex® (CS, 50% w/v, Summit Agro Argentina) for procymidone. For the preparation of reference materials 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]) technical grade, and procymidone (3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]hexane-2,4-dione, CASRN [32809-16-8]) technical grade, were recrystallized (95% pure by GC-FID), and confirmed by ^{1}H and ^{13}C NMR. Primary solutions of 491 ppm (w/w) endosulfan and 292 ppm (w/w) procymidone were prepared in cyclohexane, and all other working solutions were made by dilution as needed. Cyclohexane (Aberkon p.a. grade) used for all solutions and extracts, was distilled and chromatographically checked as suitable for use under GC-ECD conditions.

For the preparation of pesticide surrogates Brilliant Blue #1, CI N° 42090 (Sensient, Ardennes S.A.) and glicerine pharmaceutical grade (Qca. Wisconsin, Argentina) were used as provided.

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% diphenylpolisiloxane – 95% dimethylpolisiloxane 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 N_2, 30 mL min^{-1}.

A Lambda 20 spectrophotometer (Perkin–Elmer, Norwalk, NJ) with a 10 mm cell was used to measure the absorption of the dye extracts at 629 nm.

2.3. Method validation

Experiments were performed in order to investigate if endosulfan and procymidone were stable or suffered decomposition or were otherwise lost on the cotton cloth used for sampling [12]. No loss was observed for storage periods of up to 24 h.

Chromatographic linear ranges were studied for endosulfan and procymidone finding linear responses between 0.015 and 0.84 mg L^{-1} ($R^2 > 0.9919$); and between 0.027 and 0.7 mg L^{-1} ($R^2 > 0.9931$), respectively, for cloth extracts. In case of cotton gloves responses were 0.056 and 0.73 mg L^{-1} ($R^2 > 0.9793$) for endosulfan and 0.064 and 1.1 mg L^{-1} ($R^2 > 0.9931$) for procymidone. In cotton-wool extracts, linear ranges were 0.013–0.44 mg L^{-1} ($R^2 > 0.9888$) and 0.025–0.53 mg L^{-1} ($R^2 > 0.9854$), respectively. The lowest points of each calibration curve were considered as the limit of quantitation. The precision was studied on the cotton coverall by injection of a complete calibration curve for endosulfan and procymidone by duplicate on six consecutive days and calculating the percentual standard deviation of the slope of the calibration curves. A variation of 13.4% was found for endosulfan and 13.0% for procymidone.

2.4. Sampling method and field procedure

As the spraying operations were carried out by seven 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 [12] 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 for 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 (for experiences M_1–M_3 and M_5–M_6 a lever operated backpack, 60 cm lance with single nozzle; for M_4 and M_7 a motorized knapsack STIHL SR 400 and STIHL SR 420 were used) as usual; concentrations were as recommended by the manufacturers (average values were 100–150 mL hL^{-1} for endosulfan and 100 mL hL^{-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

Table 1
Experimental conditions.

Exp. no	Greenhouse area (m^2)	Pesticide	Weather conditions[a] (*T*, *P*, RH, wind)	Crops	Knapsack
M_1	67.23	Endosulfan	27 °C/1012 hPa/38%/no wind	*Petunia hybrida* *Impatiens walleriana* *Viola wittrockiana* *Gazania hybrida* *Bellis perennis* *Antirrhinum majus*	Manual
M_2	506.91	Endosulfan	11 °C/1013 hPa/37%/6.8 km h^{-1} SW intermittent	*Brassica oleracea* *Bougainvillea* spp *Gazania hybrida* *Ranunculus asiaticus* *Freesia hybrida* *Lotus berthelotii*	Manual
M_3	40	Endosulfan	10 °C/1011 hPa/37%/no wind	*Pelargonium zonale* *Dianthus deltoides*	Manual
M_4	81.16	Procymidone	19 °C/1005 hPa/50%/no wind	*Viola wittrockiana* *Viola tricolor*	Motorized
M_5	34.2	Endosulfan	24 °C/1011 hPa/55%/no wind	*Jasminum officinale* *Camellia japonica*	Manual
M_6	32.55	Endosulfan	26 °C/1007 hPa/60%/no wind	*Tagetes erect* *Zinnia elegans* *Antirrhinum majus* *Viola wittrockiana* *Petunia hybrida*	Manual
M_7	206.25	Endosulfan	28 °C/1012 hPa/30%/no wind	*Cosmos bipinnatus*	Motorized

[a] Air temperature/pressure/relative humidity/wind speed in km h^{-1}.

in polyethylene bags for later analysis as "mix/load PDE". The operator started spraying following his usual technique, until the selected area was completed. 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.

2.5. Analysis

In the laboratory, the cotton coverall was cut into different sections as indicated in Fig. 2; each of these was extracted separately with cyclohexane (1: 300 mL; 2a: 150 mL; 2b: 150 mL; 3a: 150 mL; 3b: 150 mL; 4: 800 mL; 5: 800 mL; 6a: 400 mL; 6b: 400 mL; 7a: 400 mL; 7b: 400 mL; 8: 400 mL; 9: 400 mL; 10: 150 mL; 11: 150 mL; 12: 100 mL; 12: 100 mL; 13: 100 mL; 14: 150 mL; 15: 150 mL), not later than 8 h after the field trial. 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 indicated in Section 2.2.

2.6. Calculation of PDE

The PDE is defined as the amount of pesticide that reaches the cloth or the skin of a worker (applicator or bystander). It is generally expressed as the volume of the sprayed mixture per time unit (usually 1 h). In consequence, the pesticide concentration in the sprayed mixture, the time expended in the product application and the pesticide concentration on each coverall section, are experimental values to be measured in order to calculate the 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 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 alternative form, as the amount of pesticide (in mg) found on each body section normalized for the application of a 20 L knapsack.

This last normalization allowed comparisons of the MOS of different experiences, where it is more correct to normalize by operation (one knapsack application or one knapsack preparation), than for time unit, as there are important personal speed variations between operators.

Data for facemask, goggles and gloves used during the preparation of the spray mix were not included in the "total PDE value" (Table 2), for easy comparison with other published data.

2.7. MOS calculation

The MOS [11] is defined as follows:

$$\mathrm{MOS} = \frac{\mathrm{AE}}{\mathrm{DE} \times \mathrm{AF} \times \mathrm{SF}}$$

where AE is acceptable exposure, DE is dermal exposure, AF is absorption factor and SF is safety factor.

AE values are calculated on the basis of available toxicological end-points: AOEL for procymidone (0.035 mg kg^{-1} d^{-1})[13]; ADI for endosulfan (0.006 mg kg^{-1} d^{-1}) [14]. For all calculations an average body weight of 70 kg was considered for all workers.

For all cases DE was taken as total PDE (as mg of endosulfan 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 3.2, the MOS was evaluated considering the preparation and application of a complete 20 L knapsack.

A generic dermal absorption of 10% was used, with an additional 1% representing the inhaled fraction, thus AE = 0.11 [11]. Additional protection due to clothing is not considered, because the normal work wear varies from a simple sweatshirt and shorts to long-sleeved shirts, sweaters, trousers and boots, so the worst case was considered. No specific Safety Factor was considered, as these are included in the definition of AOEL and ADI, so SF = 1.

Thus, the actual formula used was:

$$\mathrm{MOS} = \frac{\mathrm{AOEL(ADI)} \times 70}{\mathrm{PDE} \times 0.11 \times 1}$$

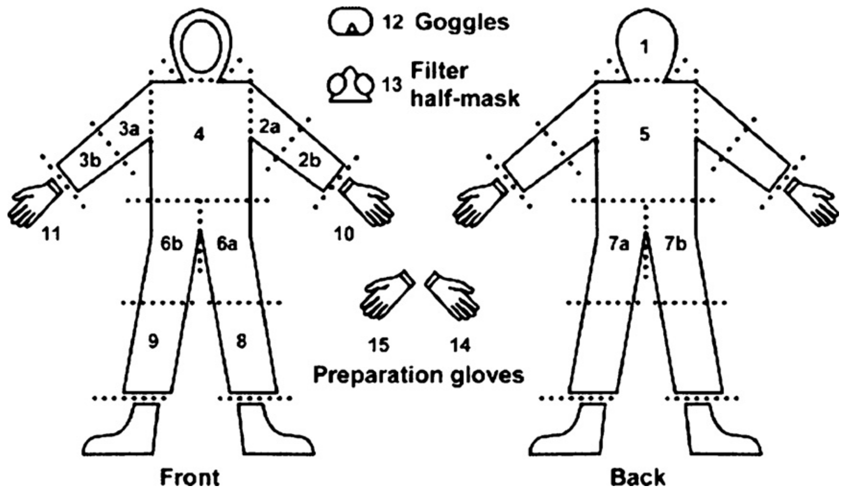

Fig. 2. Coverall sections for PDE.

2.8. Pesticide surrogates exposure

In order to investigate the mix/load procedure under controlled conditions, a colored non-toxic surrogate was developed, using a food-dye (Brilliant Blue) dissolved (1×10^{-2} M) in a glicerine–water mixture (92% w/w) of the same viscosity as the procymidone commercial formulation (Sumilex®). 50 mL of the pesticide surrogate were placed in 250 mL wide-mouth bottles with aluminum seal and plastic screw-top.

In the first experience, during a flower growers meeting, six volunteers from a hygiene/safety roundtable (M_8–M_{13}, Table 5) wearing white cotton gloves over latex ones, were given a surrogate bottle, a 15 mL plastic measuring cup, a plastic vessel similar to the backpack, and a bucket of water with plastic glasses for rinsing. They were instructed to load 15 mL of the mixture into the vessel, rinsing the measuring cup with water, with no indications whatsoever about breaking the seal, rinsing, etc.

The second experience was done with six first-year undergraduate student volunteers, wearing white cotton gloves over latex ones. Each participant was given a surrogate bottle, a measuring cup, a 250 mL beaker and a wash-bottle. They were instructed to measure 10 mL of the mix into the beaker, and rinse out the cup with water.

In all cases, after completing the task the gloves were taken off and bagged separately, then extracted individually with 100 mL of distilled water, and the dye content measured spectrophotometrically (linear range was between 1.0×10^{-6} and 2.5×10^{-5} M Brillant Blue, recovery from gloves fabric using water as solvent was between 75 and 110% in all cases).

Table 2
PDE during the application stage.

Coverall section	Application Potential Dermal Exposure (mL h^{-1})							
	M_1	M_2	M_3	M_5	M_6	M_4	M_7	Mean ± SD
1	0.14	0.06	0.03	1.05	9.90	0.51	0.31	1.7 ± 3.4
2a	0.18	0.05	0.67	NM	3.20	0.95	1.96	1.2 ± 1.2
2b	0.30	0.06	0.19	1.37	35.33	0.32	1.33	5.6 ± 13.1
3a	0.20	0.04	0.04	10.48	4.62	0.74	0.67	2.4 ± 3.9
3b	0.17	0.05	0.05	3.21	16.29	0.23	0.55	2.9 ± 6.0
4	1.81	0.28	1.64	8.73	22.27	2.08	3.29	5.7 ± 7.2
5	1.44	9.41	0.10	2.53	16.12	1.31	0.60	4.5 ± 5.6
6a	0.17	0.07	0.09	1.90	4.95	0.39	0.26	1.1 ± 1.8
6b	0.45	0.07	0.14	2.07	3.64	0.86	13.67	3.0 ± 4.9
7a	0.33	0.07	0.06	2.89	2.97	0.96	0.66	1.1 ± 1.3
7b	0.16	0.06	0.11	0.81	3.54	1.07	0.07	0.8 ± 1.2
8	0.50	1.03	0.18	0.97	1.46	1.54	1.09	1.0 ± 2.5
9	0.47	1.09	0.22	1.50	2.44	2.27	0.75	1.3 ± 2.9
10	3.67	3.85	0.08	2.46	15.34	2.04	12.29	5.7 ± 5.6
11	3.21	3.69	0.15	5.35	33.37	1.49	2.86	7.2 ± 10.9
Total	13.2	19.9	3.8	45.3	175.4	16.8	40.4	45.0 ± 55.4
Mean	51.5 ± 70.9					28.6 ± 16.7		
12	0.54	ND	0.02	ND	0.16	ND	0.02	0.11 ± 0.19
13	0.82	0.03	0.01	0.01	0.42	ND	0.10	0.20 ± 0.29

NM: not measured; ND: not detected.
Application mix data: time; applied amount; concentration of the active ingredient; method of application. M_1: endosulfan, 10 min; 10 L; 592 mg L^{-1}; manual knapsack. M_2: endosulfan, 42 min; 18 L; 554 mg L^{-1}; manual knapsack. M_3: endosulfan, 19.3 min; 18 L; 459 mg L^{-1}; manual knapsack. M_4: procymidone, 3.7 min; 5.1 L; 529 mg L^{-1}; motorized knapsack. M_5: endosulfan, 7 min; 4.5 L; 350 mg L^{-1}; manual knapsack. M_6: endosulfan, 4.5 min; 3.1 L; 310 mg L^{-1}; manual knapsack. M_7: endosulfan, 5 min; 13.5 L; 313 mg L^{-1}; motorized knapsack.

3. Results

3.1. Potential Dermal Exposure in floricultural greenhouses

Table 2 shows the results of seven pesticide application experiments done at floricultural greenhouses of Moreno district, where the PDE values were expressed as volume of sprayed liquid per unit of time (mL h^{-1}). M_1, M_2, M_3, M_5, M_6 and M_7 applications were done with endosulfan, meanwhile in experiment M_4, procymidone was used. Taking into account the application technique, experiments M_4 and M_7 were performed using a motorized knapsack meanwhile in the other experiments a manual lever operated knapsack was used.

If all pesticide application experiments were considered (M_1–M_7), a total PDE of 45.0 ± 55.4 mL h^{-1} was found (Table 2). Discriminating between experiments done with a lever operated knapsack (M_1–M_3 + M_5–M_6) and a motorized one (M_4 and M_7), mean values of 51.5 ± 70.9 mL h^{-1} and 28.6 ± 16.7 mL h^{-1} were found (Table 2), showing that the motorized application does not have higher exposure levels as might be pre-supposed. Another interesting issue was the wide dispersion of PDE values (3.8–175.4 mL h^{-1}, Table 2), even considering the same application technique, which could be explained by the fact that the measurements were done with different operators, with various degrees of experience and in different production units.

Fig. 3A shows the pesticide body distribution considering a 100% body mass balance. Three ranges were defined less than 5%, between 5 and 10% and more than 10% (Fig. 3A). As can be appreciated, the higher exposure was on the torso, back and hands. There is a higher tendency of exposure on forearms than arms, finding less significant pesticide amounts on thighs and legs. Fig. 3B shows the coverall pesticide distribution, expressed in mL of pesticide applied per hour for four different body parts: hands; torso, head and arms; thighs; and legs.

3.2. Comparison of the PDE and MOS of the mix/load and application operations

With the aim of comparing the exposure of the mix/load and application stages, the PDE of both operations were expressed as mg of pesticide (Table 3), assuming for each experiment a complete preparation and spraying of a 20 L knapsack. PDE expressed as pesticide mass was preferred to the volume per time units, because the mix/load stage is a discrete operation not time-dependent, but directly proportional to the number of tanks loaded. For this reason one mix/load operation was assumed to correspond to the spraying of a complete knapsack content, after which, the mix/load stage should be repeated. For the mixer/loader, only the PDE on hands was evaluated because studies done to generate data for the U.K. Predictive Operator Exposure Model database had shown that coverall contamination rarely occurred during the mixing and loading process.

Results of Table 3 show that while the mean PDE value for the application stage was 7.2 ± 9.0 mg, the mean PDE for the mix/load operation was 66.7 ± 73.2 mg, indicating that there was between 1.4 and 75.0 times (23.0 times mean, Table 3) more exposure during the mix/load stage than during the application. When the mix/load and application MOS for the endosulfan and procymidone experiments were calculated, four of seven application operations were safe (with MOS > 1, Table 4), while only one of the seven mix/load operations resulted safe (with MOS > 1). If the combination of mix/load and one application is considered to be done by the same operator, which is the common practice in small production units, six of the seven experiments resulted unsafe for the combined process (Table 4). It is interesting to remark, that in floriculture working scenarios the execution of more than one mix/load and application cycle per day is a common practice.

3.3. Hands dermal exposure to pesticide and pesticide surrogates in the mix/load stage

With the intention to evaluate if the high exposure levels found during the mix/load stage could be consistent with spills and splashes during the manipulation of the concentrated formulation, hands exposure was also calculated as the volume of this formulation which contained the same amount of active product (Table 5).

In experiences M_1–M_7, a mean volume of 191 ± 194 μL of formulation was found on the preparation gloves of floriculture workers. In the first surrogate experience for the six workers a mean volume of 39 ± 50 μL was found on the preparation gloves (Table 5); while in the second surrogate experience, a mean value of 16.6 ± 10.5 μL was found for the five experiments done.

4. Discussion

4.1. Discussion of the PDE found in floricultural greenhouses

The mean PDE found in the studied greenhouses (45.0 ± 55.4 mL h^{-1}, Table 2) is in good agreement with values measured in similar working scenarios. For example, when Capri et al. [10] determined the PDE of workers applying procymidone in greenhouses with daisies and hydrangeas in Italy, a range of 7.7–37.7 mL h^{-1} of PDE was found. For the application process, Tuomainen et al. reported PDE values of 6718.9; 345.5 and 1459.1 mg of malathion; deltamethrin and procymidone per kg of active ingredient [8]. If mean PDE values of Table 2 are converted to the aforementioned units 2058.1 and 200.4 mg of endosulfan and procymidone per kg of active ingredient were found.

With respect to the wide PDE range found in our study (3.8–175.5 mL h^{-1}), we have previously reported that this variability could be explained by the different operator techniques employed during the application [15]. The potential inhalation exposure (13, Table 2) was only relevant in M_1, indicating that it was not the main exposure route during the studied applications.

It is interesting to note, that when total PDE is analyzed considering the application technique: manual lever operated knapsack (M_1–M_3 + M_5–M_6, mean PDE of 51.5 ± 70.9 mL h^{-1}, Table 2) versus motorized equipment (M_4 and M_7, mean PDE of 28.6 ± 16.7 mL h^{-1}, Table 2), no significant difference was found, indicating that in the cases studied the application equipment seems not to have an important influence.

In relation to the pesticide body distribution, the most exposed sections were torso, head and arms, especially the chest, back and hands of the applicators (Fig. 3). This distribution pattern is different to previously reported cases in similar working scenarios. For example, Capri el al. [10], reported that for the application of daisies and hydrangeas in Italian greenhouses the most exposed sections were applicator's gloves and lower legs. Tuomainen et al. showed that for the application of malathion, deltamethrin and iprodione in Finish greenhouses with rose crops the most exposed sections were the lower limbs [8].

4.2. Discussion of the EDP and MOS of the mix/load and application operations

It has been generally recognized that pesticide application in greenhouses could represent a dangerous exposure situation for workers, especially as a consequence of the remaining product mist. In this sense, it would be interesting to analyze the relative exposure of the mix/load and application operations.

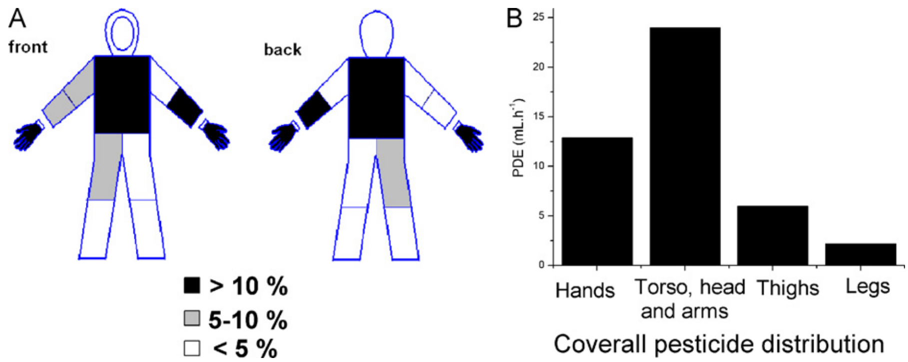

Fig. 3. Coverall pesticide distribution of the application stage.

Table 3
Comparison of application and mix/load exposures (PDE in mg of pesticide by 20 L of applied product).

	Potential Dermal Exposure (mg)							
	M_1	M_2	M_3	M_5	M_6	M_4	M_7	Mean ± SD
Application	2.86	8.59	0.62	8.23	26.3	2.12	1.57	7.2 ± 9.0
Mix/load								
14	50.8	207.6	28.2	0.94	46.9	2.03	24.8	51.6 ± 71.5
15	8.62	19.3	18.3	26.0	9.2	0.87	24.7	15.3 ± 9.3
14 + 15	59.4	226.9	46.5	26.9	56.1	2.90	49.5	66.7 ± 73.2
Mix/load:application ratio	20.8	26.4	75.0	3.3	2.3	1.4	31.5	23.0 ± 26.0

Table 4
MOS for endosulfan and procymidone for mix/load, application and combination of both stages for a complete 20 L knapsack application.

Exp.	Mix/load[a]	Application[b]	Total
Endosulfan MOS			
M_1	0.06	1.33	0.06
M_2	0.02	0.44	0.02
M_3	0.08	6.14	0.08
M_5	0.14	0.46	0.11
M_6	0.07	0.14	0.05
M_7	0.08	2.40	0.07
Procymidone MOS			
M_4	7.66	10.49	4.4

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

Table 5
Comparison of pesticide concentrated volume during mix/load stage.

Hands	Volume of formulated pesticide in floricultural workers' hands (14 + 15, μL)						
	M_1	M_2	M_3	M_4	M_5	M_6	M_7
Left (14)	145.1	593.1	80.6	2.7	134.0	4.1	70.9
Right (15)	24.6	55.3	52.1	74.1	26.3	1.7	70.6
Total	169.7	648.4	132.7	76.8	160.3	5.8	141.5
Mean 14 + 15				191 ± 194			

Hands	Volume of formulated Brillant Blue in floricultural workers' hands (14 + 15, μL)					
	M_8	M_9	M_{10}	M_{11}	M_{12}	M_{13}
Left (14)	74.8	0.66	1.23	1.16	4.48	76.6
Right (15)	48.0	1.4	1.31	4.12	1.16	20.4
Total 14 + 15	123.6	2.06	2.54	5.28	5.64	94.0
Mean 14 + 15			39 ± 50			

Hands	Volume of formulated Brillant Blue in chemistry students' hands (14 + 15, μL)				
	M_{14}	M_{15}	M_{16}	M_{17}	M_{18}
Left (14)	6.3	3.8	4.8	1.7	2.3
Right (15)	23.3	5.9	24.3	6.7	3.7
Total 14 + 15	29.6	9.7	29.1	8.4	6.0
Mean 14 + 15			16.6 ± 10.5		

Surprisingly, the mix/load process was more risky than the application stage for the seven experiments performed (Table 3). These phenomena could be associated to the manipulation of concentrated formulations (35% w/w for endosulfan and 50% for procymidone). Spilling of small drops, or external contamination of the pesticide containers handled, could transfer to worker's hands pesticide quantities equivalent to or higher than those in the application step, where a comparatively very diluted solution was handled.

Some studies about floriculture greenhouses emphasize the application process as the fundamental cause of exposure. For example, Capri et al. found six to eight times more pesticide in the applicators than the mixer–loader [10]. Tuomainen reported higher applicator exposure for malathion and iprodione in roses greenhouses, but for the application of deltamethrin the exposure was three times higher for the mixer–loader than the applicator [8]. In the same sense, we have recently reported that for the application of deltamethrin and procymidone to tomato greenhouses, which could be supposed to be a similar scenario, the exposure was riskier for the mixer/loader than for the applicator [16].

As the exposure is not a direct indicator of the safety or risk associated to an operation, the MOS levels must be considered. In six of the seven experiments, the mix/load stage was unsafe (Table 4). Furthermore, considering that in these small production units the mixer/loader is usually also the applicator, the mix/load/application of one 20 L knapsack was an unsafe process in the same number of occasions (Table 3).

4.3. Hands exposure to pesticide and pesticide surrogates in the mix/load stage discussion

Although the volume of formulated procymidone or endosulfan found in the mix/load operators gloves could be compatible with spills and splashing occurring during the process ($191 \pm 194\,\mu L$, Table 5), the volumes observed when an equally viscous dye solution was used as pesticide surrogate ($39 \pm 50\,\mu L$, Table 5) were five times lower. When the experiment was repeated with first year chemistry students as operators, a twelve-fold decrease in the exposure was observed, compared with that resulting from real greenhouse conditions. The difference between surrogate volumes found for the floriculture workers versus the chemistry students could be attributed to better training of the last group, in addition to more controlled working conditions (University laboratory), which might induce a cleaner/tidier attitude.

A possible hypothesis to explain the difference in exposure between the manipulation of real pesticide containers under real working conditions and the experiments using surrogates, both carried out by equally experienced workers, could arise from the fact that under field conditions, the real pesticide bottles used were not new and noticeably soiled, presumably due to spills of the pesticide formula. The surrogate bottles, on the other hand, were completely new and externally clean. So, it could be that the difference in hand exposure was due to the external contamination of the pesticide bottles, with accumulated active ingredient in their external surface as a consequence of repeated use. Further experiments are in progress in our laboratory to try to verify this hypothesis.

5. Conclusions

The mean PDE value for the application of procymidone and endosulfan in ornamental greenhouses was $45.0 \pm 55.0\,mL\,h^{-1}$, with no significant difference found due to the knapsack used (manual or motorized). The higher pesticide exposure was found on torso, head and arms, being particularly important in the application gloves. Comparing the mix/load and the application operations, the first stage was considerably riskier, which is important taking into account that in most cases it is the same worker who performs both stages. In six of the seven analyzed cases the combination of the mix/load plus the application should be considered unsafe.

Although the origin of the pesticide exposure in the mix/load stage can be attributed to spills and splashing, additional contamination sources should be considered to explain the exposure differences found during the manipulation of real pesticide containers or surrogates. This last issue is particularly important, specially considering that workers do not usually use the appropriate glove protection in the mix/load operation.

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References

[1] H. Drexler, Skin protection and percutaneous absorption of chemical hazards, Int. Arch. Occup. Environ. Health 76 (2003) 359–371.
[2] R. Glass, A. Gilbert, J. Mathers, J. Moreira, K. Machera, K. Kapetanakis, E. Capri, Worker exposure to pesticides – a pan European approach, Aspects Appl. Biol. 57 (2000) 363–368.
[3] R.A. Fenske, State-of-the-art measurement of agricultural pesticide exposures, Scand. J. Work Environ. Health 31 (2005) 67–72.
[4] E.A. Hughes, A.P. Flores, L.M. Ramos, A. Zalts, J.M. Montserrat, Potential Dermal Exposure to deltamethrin and risk assessment for manual sprayers: influence of crop type, Sci. Total Environ. 391 (2008) 34–40.
[5] D. Tenenbaum, Would a rose, Environ. Health Perspect. 110 (2002) A240–A247.
[6] J.H. Handal, S.D. Harlow, Employment in the Ecuadorian cut-flower industry and the risk of spontaneous abortion, BMC Int. Health Hum. Rights 9 (2009), doi:10.1186/1472-698x-9-25.
[7] C. Paz-y-Miño, G. Bustamante, M.E. Sánchez, P.E. Leone, Cytogenetic monitoring in a population occupationally exposed to pesticides in Ecuador, Environ. Health Perspect. 110 (2002) 1077–1080.
[8] A. Tuomainen, M. Mäkinen, R. Glass, J. Kangas, Potential exposure in nordic greenhouses, Bull. Environ. Contam. Toxicol. 69 (2002) 342–349.
[9] A. Toumainen, J.A. Kangas, W.J.A. Meuling, R.C. Glass, Monitoring of pesticide applicators for Potential Dermal Exposure to malathion and biomarkers in urine, Toxicol. Lett. 134 (2002) 125–132.
[10] E. Capri, R. Alberici, C.R. Glass, G. Minuto, M. Trevisan, Potential operator exposure to procymidone in greenhouses, J. Agric. Food Chem. 47 (1999) 4443–4449.
[11] J. Machado-Neto, Determination of safe work time and exposure control need for pesticide applicators, Bull. Environ. Contam. Toxicol. 67 (2001) 20–26.
[12] E. Hughes, A. Zalts, J. Ojeda, A. Flores, R. Glass, J. Montserrat, Analytical method for assessing Potential Dermal Exposure to captan, using whole body dosimetry, in small vegetable production units in Argentina, Pest Manag. Sci. 62 (2006) 811–818.
[13] Agriculture and Environment Research Unit, Pesticide Properties Database. http://sitem.herts.ac.uk/aeru/footprint/en/Reports/537.htm, 2010 (accessed September 2010).
[14] UK-CRD Chemicals Regulation Directorate – Pesticides, Toxicological Endpoints Database. https://secure.pesticides.gov.uk/TEAWeb/intro.asp, 2009 (accessed October 2009).
[15] E. Hughes, A. Zalts, J. Ojeda, J.M. Montserrat, R. Glass, Potential pesticide exposure of small scale vegetable growers in Moreno district, Aspects Appl. Biol. 71 (2004) 399–404.
[16] L.M. Ramos, G.A. Querejeta, A.P. Flores, E.A. Hughes, A. Zalts, J.M. Montserrat, Potential Dermal Exposure in greenhouses for manual sprayers: analysis of the mix/load, application and re-entry stages, Sci. Total Environ. 408 (2010) 4062–4068.