SCIENCE OF THE TOTAL ENVIRONMENT XX (2007) XXX–XXX

available at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/scitotenv

Potential dermal exposure to deltamethrin and risk assessment for manual sprayers: Influence of crop type

Enrique A. Hughes[a], Andrea P. Flores[a], Laura M. Ramos[a], Anita Zalts[a], C. Richard Glass[b], Javier M. Montserrat[a,c,*]

[a]Instituto de Ciencias, Universidad Nacional de General Sarmiento (UNGS), J. M. Gutiérrez 1150, B1613GSX Los Polvorines, Prov. de Buenos Aires, Argentina
[b]Department for Environment, Food and Rural Affairs, Central Science Laboratory, Sand Hutton, York Y041 1LZ, UK
[c]Instituto de Investigaciones en Ingeniería Genética y Biología Molecular (CONICET), Vuelta de Obligado 2490, 2° piso, Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 28 May 2007
Received in revised form
20 September 2007
Accepted 21 September 2007

Keywords:
Deltamethrin
Potential dermal exposure
Periurban agriculture
GC-ECD
MOS

ABSTRACT

A comparison of the Potential Dermal Exposure (PDE) of workers to the insecticide deltamethrin was made as a function of crop type, in small agricultural production units in Argentina. Seven experiments were done with two different crops (maize and broccoli, treated area between 600 and 1000 m^2) with three different operators under typical field conditions using a lever operated knapsack. The methodology is based on the whole body dosimetry technique, presenting separately the data for mixing/loading and application activities. These results indicate a higher concentration of pesticide in lower body sections for broccoli and a wider distribution for maize. The risk inherent in these agricultural procedures is estimated through Margin of Safety (MOS) values and was found to be generally safe.
Preliminary results of a mass balance distribution of the pesticide between crop, soil and operator are also presented.

1. Introduction

In Argentina, although improvements to the phytosanitary product registration process have occurred in the last ten years, no occupational exposure data are required to obtain a commercial license for a pesticide product; consequently very little research has been done to establish exposure levels with typical use scenarios for Argentina. The labourer's exposure situation is particularly delicate in the small scale periurban production units (Paquette and Domon, 1999) surrounding Buenos Aires city (poor working conditions, lack of education, low technology and manpower dependent). The working conditions of this community are very different from those in extensive agriculture, the prevalent mainstream production in Argentina. As a consequence of the social and economic vulnerability of this group, it is important to have realistic estimates of the exposure of these workers to the pesticides they handle, in order to evaluate the potential risk posed by their use of these substances.

There are three exposure pathways that need be considered: oral uptake, inhalation uptake and dermal absorption. It is quite well established that transdermal absorption through the skin can be the most important pathway for pesticides under typical field working conditions (Grandjean, 1990; Brand et al, 2007); oral uptake is not common under these conditions, and the same applies to the inhalation pathway (Machado-Neto, 2001; Juraske et al, 2007), and thus they were not considered in this study. In this sense, it is well accepted that the measurement of Potential Dermal Exposure (PDE) provides vital information on the quantity of a chemical substance that contaminates uncovered body regions and clothing worn by pesticide handlers (Glass et al., 2000;

* *Corresponding author.* Instituto de Ciencias, Universidad Nacional de General Sarmiento (UNGS), J. M. Gutiérrez 1150, B1613GSX Los Polvorines, Prov. de Buenos Aires, Argentina. Tel./fax: +54 11 4469 7501.
E-mail address: jmontser@ungs.edu.ar (J.M. Montserrat).

0048-9697/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2007.09.034

Glass et al., 2001; OECD, 1997); furthermore, it can be used as a base for estimating the risk involved in these activities. For this, the Margin of Safety (MOS) has been proposed as a useful risk indicator (Machado-Neto, 2001); it is simply a ratio of the acceptable exposure to a product and the mass absorbed by the body which has to be estimated from values for potential exposure.

Previous studies with these production units have shown how important factors like crop density (Glass et al., 2002; Hughes et al., 2004) and operator experience (Glass et al., 2002; Hughes et al., 2006) are, in terms of total PDE. In this study we present the results of the PDE to deltamethrin (oral LD_{50}: 139 mg/kg, rats; dermal LD_{50}: 2490 mg/kg, rats; inhalation LD_{50}: 0.72 g/m^3 air, 6 h, rats, IPCS-INCHEM), and the corresponding risk estimate, in workers of small scale, low-technology vegetable production units, as well as analysing its relation to crop type, namely maize (*Zea mays*) and broccoli (*Brassica oleracea*, Italica Group). Additionally preliminary results of a mass balance study are presented, showing the distribution of deltamethrin between crop, soil and operator.

2. Experimental methods

2.1. Study sites

All field experiments were done in a small production unit in Moreno district (Fig. 1) between February and November 2006. The selected maize field was 90 m long and 12 m wide. Rows were separated by 0.8 m with 0.4 m between plants; average height was between 1.9 and 2.1 m. Two broccoli fields were used: 12.8 m × 75 m, and 6.4 m × 95 m (the operator's walking pace determined the area sprayed in each case); rows were separated by 0.8 m and 0.4 m between plants of 0.4–0.7 m height, with similar height of weeds between plants.

In all experiments ambient temperature was between 25 and 30 °C, relative humidity 50–70% and the wind velocity did not exceed 10 km h^{-1}.

2.2. Reagents, materials and chromatographic conditions

For application the deltamethrin commercial formulation used 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 162 mg L^{-1} was prepared in hexane, and all other working solutions were made by dilution as needed. Hexane (Aberkon pesticide grade) was used for all solutions and extracts, and it was distilled prior to use and chromatographically checked as suitable for use under GC-ECD conditions.

All chromatographic analysis were performed on a Perkin–Elmer (Norwalk CT, USA) AutoSystem XL Gas Chromatograph with Autosampler automatic injector, equipped with an electron capture detector (ECD), and a fused silica capillary column (PE-5, 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 as follows; injector temperature: 350 °C; ECD temperature: 375 °C; oven temperature: 200 °C, then

Fig. 1 – Location of agricultural production at Moreno district in Argentina.

15 °C min^{-1} to 260 °C, hold 3.2 min, then 40 °C min^{-1} to 320 °C and hold 3 min; injection volume 1 μL, splitless; carrier gas: N_2, initial pressure 70 psi for 1 min then 10 psig min^{-1} to 30 psig, then constant; ECD auxiliary flow 30 mL min^{-1}.

2.3. *Method validation*

2.3.1. *Stability of deltamethrin on the cotton cloth matrix*

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

2.3.2. *Selectivity*

Chromatographic conditions were optimized so as to separate deltamethrin from thiophanate methyl, hexythiazox, captan and zineb. These were the agrochemical products most commonly used in combination (tank mix) with deltamethrin and thus might be expected to be co-extracted from the sampling coverall.

2.3.3. *Limits of detection (LD) and quantification (LQ)*

The LD was calculated as the standard deviation of a 0.012 mg L^{-1} sample analyzed ten times, and multiplied by the corresponding *t* factor. The LQ was determined as three times the LD. In this way the LD for deltamethrin was 0.0031 mg L^{-1} and the LQ was 0.010 mg L^{-1}.

2.3.4. *Linear range*

The deltamethrin response was linear between 0.05 and 1 mg L^{-1} with $R^2 > 0.998$.

2.3.5. *Precision*

The precision was studied following two different operators injecting ten times each day during four different days. The variation of precision versus deltamethrin concentration was: 15% (at 1 mg L^{-1} level) expressed as percent variation, and calculated as the standard deviation of all injections at each level.

2.4. *Sampling method and field procedure*

The potential dermal exposure was measured using the whole body dosimetry technique (Glass et al., 2002) 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 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 of Decis in water, then poured it into the tank and diluted it up to the total volume of the sprayer (Jasco 20 L lever operated knapsack, 60 cm lance with single nozzle, with working pressures typically between 45 and 70 psi) as usual. Both the measuring cup and sprayer were weighed before and after loading (at least 10 g of formulated deltamethrin were measured with a balance of 0.1 g resolution, and the full backpack with at least 25×10^3 g of final deltamethrin dilution, was weighed with a balance of 20 g resolution); concentrations actually employed varied between 20 and 100 mg L^{-1} (each operator's individual practices were respected).

After preparing the knapsack for spraying, the cotton gloves were exchanged for a clean set. The operator started spraying following his usual technique, with no other instructions. Application time was typical for small plot treatments, usually between 15 and 20 min, at an application rate of 60–80 L h^{-1}. At the end of each row the operator was inspected for overexposure (if media saturation was observed the experiment was discarded) and/or runoff of the spray-mix. Then when all the knapsack product was applied, the cotton coverall was taken off and hung up to dry in the shade. The Tyvek coverall was checked for stains that could indicate penetration of the cotton outer suit. All gloves, mask, cotton-wool, etc. were placed in individual polyethylene bags for later processing.

2.5. *Analysis*

In the laboratory the cotton coverall was cut into different sections as indicated in Fig. 2; each of these, as well as all other sampling material, was extracted separately with hexane (20 min., rotary shaker with solvent volume depending on section size, e.g. 150 mL for gloves, 800 mL for chest) not later than 5 h after the field trial and 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 Decis and water loaded into the tank. The concentration of pesticide in each extract, and its volume, were used to calculate the amount deposited on each coverall part. This value combined with the duration of each experience gives a time-rate value for the potential dermal exposure.

2.7. *MOS calculation*

The MOS is defined as follows:

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

where AE = acceptable exposure; DE = dermal exposure; AF = absorption factor and SF = safety factor. Thus, a value of MOS ≥ 1 would indicate safe working conditions, whereas a MOS < 1 would mean unsafe conditions. AE values are calculated on the basis of appropriate toxicological end-points: AOEL (Acceptable Operator Exposure Level) if available, if not then

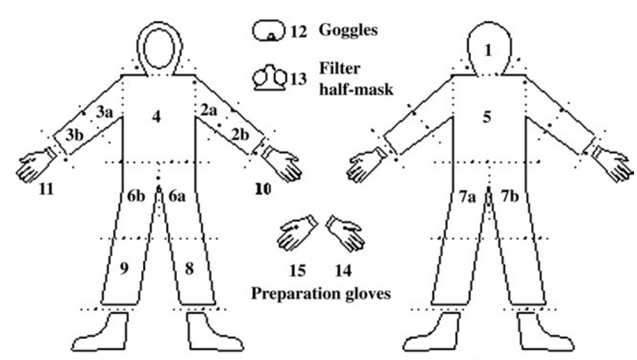

Fig. 2 – Coverall cutting scheme for PDE determination.

Please cite this article as: Hughes EA, et al, Potential dermal exposure to deltamethrin and risk assessment for manual sprayers: Influence of crop type, Sci Total Environ (2007), doi:10.1016/j.scitotenv.2007.09.034

NOAEL (No Observed Adverse Effect Level) or others can be used.The values considered in the cases reported here were:

AE = AOEL × average body weight; for which the following were used: AOEL = 0.0075 mg kg^{-1} d^{-1} (UK-PSD, 2002); and average body weight 70 kg.

AF = 0.11, this considers a dermal absorption of 10% (UK-PSD, 2006), with an additional 1% added to consider 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 and trousers, so the worst case was considered.

DE = PDE (as mg of deltamethrin) resulting from the present study for one complete procedure with a 20 L tank (mixing/loading/application), including body and preparation gloves.

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

Thus, the actual formula used was:

$$\mathrm{MOS} = 0.0075 \times 70/(\mathrm{PDE} \times 0.11 \times 1)$$

2.8. Mass balance

For the mass balance, four randomly selected plants were wrapped in cloth, 0.75 m square (plant-samplers), before spraying the field. Another set of four strips of cloth, 0.2 m × 0.8 m (ground-samplers), were placed in random sites covering the ground entirely between rows, even under the broccoli plants (any weeds around the selected plant were manually removed in order to have a more regular area). For spray-drift, four strips of the same cloth, 0.15 m wide (drift-samplers), were placed vertically on wooden supports from ground level to 1.2 m height, along two sides of the field where drift was expected. The cloth used was the same cotton material used for the sampling coverall. After spraying, all samplers were placed in individual bags for later extraction at the laboratory.

The concentration of pesticide in each extract, and its volume, were used to calculate the amount deposited on each piece of cloth. The amount found on the plant-samplers was averaged and multiplied by the total number of plants to give the total of deltamethrin deposited on the crop. The amount found on the ground-samplers was divided by their surface, averaged and multiplied by the total area of the field to give the total deposited on the ground. Drift-samplers results were divided by their width, averaged and multiplied by the length of the corresponding side, to obtain the total for the field. PDE results (with facemask and goggles included) were taken as the total amount of deltamethrin on the operator.

Table 1 – PDE expressed in mL h^{-1} for application of deltamethrin to maize and broccoli crops

Cover-all section	Potential dermal exposure (mL h^{-1})[a]								
	Maize				Broccoli				
	M1	M2	M3	Av.[b]	M4	M5	M6	M7	Av.[b]
1	0.33	0.30	0.18	0.27 ± 0.06	0.035	0.54	0.053	2.53	0.8 ± 1.0
2a	15.0	0.93	3.29	6.4 ± 6.2	0.052	0.96	0.43	2.84	1.1 ± 1.1
2b	34.2	12.3	12.4	19.6 ± 10.3	0.095	2.25	0.227	3.67	1.6 ± 1.5
3a	54.8	73.7	2.22	43.6 ± 30.2	0.374	0.63	1.36	1.09	0.86 ± 0.38
3b	80.7	54.6	3.14	46.1 ± 32.2	0.125	1.36	10.38	2.13	3.5 ± 4.0
4	54.6	9.26	0.344	21.4 ± 23.8	NM[c]	5.9	2.76	6.42	5.0 ± 1.6
5	3.80	0.51	2.11	2.1 ± 1.3	NM	11.5	NM	2.42	7.0 ± 4.5
6a	15.9	21.5	2.99	13.5 ± 7.8	14.96	4.10	6.11	1.85	6.8 ± 5.0
6b	35.2	72.1	1.44	36.2 ± 28.9	15.46	5.70	2.98	40.7	16.2 ± 14.9
7a	2.01	3.62	6.70	4.1 ± 1.9	0.88	1.15	0.139	21.6	5.9 ± 9.0
7b	2.78	5.34	8.54	5.6 ± 2.4	2.08	6.50	0.501	4.78	3.5 ± 2.3
8	17.6	27.1	4.69	16.5 ± 9.2	22.91	30.90	8.15	107.4	42.3 ± 38.4
9	36.0	34.5	6.69	25.7 ± 13.5	28.33	28.35	9.03	101.2	41.7 ± 35.2
10	11.9	7.53	4.00	7.8 ± 3.2	0.285	7.65	0.912	7.09	4.0 ± 3.4
11	12.6	11.6	4.22	6.3 ± 4.5	0.430	2.95	1.36	11.4	4.0 ± 4.3
Total[d,e]	377 (3.18)	335 (2.73)	63.0 (1.76)	258 ± 139 (2.6 ± 0.6)	85.6 (1.65)	110 (1.30)	44.4 (0.48)	317.1 (7.34)	140 ± 105 (2.7 ± 2.6)
12[e]	8.87 (0.09)	0.095 (0.001)	0.043 (0.001)	3.0 ± 4.1	NM	0.50 (0.006)	0.292 (0.003)	0.190 (0.004)	0.33 ± 0.13
13[e]	NM	NM	NM	NM	0.082 (0.002)	0.25 (0.003)	0.171 (0.002)	1.140 (0.026)	0.41 ± 0.43
14[e]	0.50 (0.005)	152 (1.24)	0.297 (0.009)	50.9 ± 71.5 (0.42 ± 0.58)	9.56 (0.18)	20.0 (0.24)	0.362 (0.004)	449 (10.38)	120 ± 190 (2.7 ± 4.4)
15[e]	0.537 (0.005)	5.00 (0.04)	0.397 (0.012)	2.0 ± 2.1 (0.02 ± 0.01)	29.3 (0.56)	156.2 (1.84)	4.90 (0.05)	458 (10.60)	162 ± 180 (3.3 ± 4.3)

Application data: time; total volume; concentration: M1: 21 min; 20.18 L; 28.9 mg L^{-1}; M2: 21 min; 20.00 L; 23.3 mg L^{-1}; M3: 20 min; 17.40 L; 84.1 mg L^{-1}; M4: 17 min; 20.16; 67.9 mg L^{-1}; M5: 23 min; 19.30 L; 30.8 mg L^{-1}; M6: 23 min; 20.82 L; 28.0 mg L^{-1}; M7: 14 min; 16.14 L; 99.2 mg L^{-1}.

[a] Mi denotes field experiment number i.

[b] Av = average.

[c] NM = Not Measured.

[d] For comparison with other published results, this Total does not include Sections 12–15, i.e. facial protection and preparation gloves.

[e] Expressed as mL h^{-1} (mg).

Please cite this article as: Hughes EA, et al, Potential dermal exposure to deltamethrin and risk assessment for manual sprayers: Influence of crop type, Sci Total Environ (2007), doi:10.1016/j.scitotenv.2007.09.034

3. Results and discussion

3.1. PDE results

As previously mentioned PDE is a magnitude that depends greatly on a set of factors, one of the most relevant being the size and geometry of the crop. These variables critically affect the amount of product that comes into contact with the operator's clothing. Field experiment results are presented in Table 1 as volume of sprayed liquid per unit of time (i.e. mL h^{-1}), for each body part. Data for facemask, goggles and gloves used during the preparation of the spray mix were not included in the "total" PDE value for easy comparison with other published values. Data for gloves used during the preparation of the spray mix are given in two forms: as total exposure (in mg), as this step is not actually time-dependent, and for comparison purposes also as time-rate, considering the volume of spray-mix which would have deposited the same amount of product. For comparison purposes, "total", facemask and goggles are also expressed in mg.

During the field experiences for this study we worked on two different cases: broccoli and maize. Broccoli was planted in regular rows of knee-high plants, while maize had a mean height of 2.0 m, with the same separation between rows (0.8 m) for both crops. The spraying operations were carried out by different operators, with similar degrees of experience, so as to obtain a representative sample of typical behaviour and procedures. For the same reason, all results were considered valid, including those where the tank and/or hoses leaked considerably, or where the operator used too much of the concentrated product in the tank mix.

Table 1 shows the PDE for all experiences with both crops. As can be seen, the mean PDE value for maize was 258.4 mL h^{-1}, which is in accordance with our previously reported values of 25 to 170 mL h^{-1}, measured for application of captan to maize in similar situations (Hughes et al., 2006). Other researchers have reported average values for maize of 191 ± 82 mL h^{-1} (Machado-Neto et al., 1998) which are comparable to these. The PDE mean value for broccoli was 139.4 mL h^{-1}, also in agreement with our previously published data for lower crops — chard and lettuce — as discussed below.

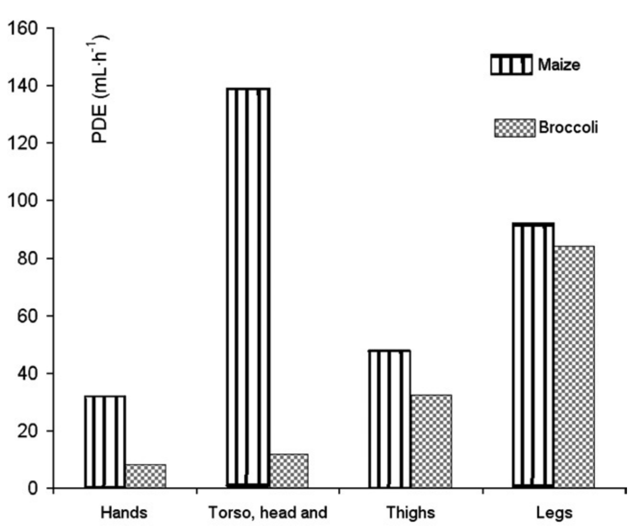

Fig. 3 – Deltamethrin PDE distribution in hands; torso, head and arms; thigh and leg sections.

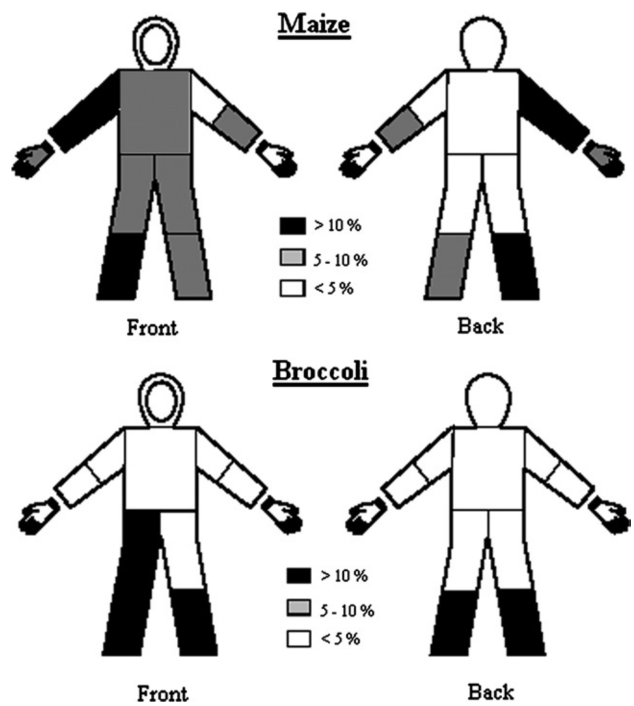

Fig. 4 – Deltamethrin relative PDE distribution in different body sections.

As shown in Table 1, the mean value of total maize PDE practically doubles that of broccoli; major differences are found to be in the values of Sections 1–4 (Fig. 2), while differences in the rest of the body are not so important. If all these sections are reordered into four main body groups (Fig. 3: hands; head, torso and arms; thighs; legs), the different distribution of PDE in both crops can be clearly appreciated: similar values are observed for thighs and legs, but there is far greater exposure in the upper body for maize than for broccoli. This effect can be explained simply by the operator's movements: in maize, to cover adequately all the plant the operator has to spray upwards and downwards, practically from shoulder height to knee height; instead broccoli only needs to be sprayed downwards.

Fig. 4 represents the total PDE for each crop expressed as a percentage of the total mean exposure, indicating the distribution on the coverall scheme at three levels: less than 5%, between 5 and 10%, and more than 10%. It must be noted that these percentages are relative for each crop and comparisons between maize and broccoli are only meaningful in relative terms. This figure shows that while there is no appreciable exposure with broccoli for the upper body sections, in maize there is a considerable amount on hands, arms and chest but not on the back. This could be due to the operators' movements: they all walked forward, moving into the spray cloud and also making contact with the recently sprayed leaves. The back of the operator would be shielded from these sources of exposure, in addition to the protective effect of the knapsack sprayer.

Table 2 – MOS for different pesticides

Crop	Maize			Broccoli			
Experiment N°	M1 [c]	M2	M3	M4	M5	M6	M7
Deltamethrin [a]	1.2	1.2	2.7	2.0	1.4	8.9	0.2
Chlorpyrifos [b]	0.005	0.004	0.03	0.02	0.006	0.04	0.002
Methamidophos [b]	0.004	0.003	0.03	0.02	0.005	0.03	0.002

[a] Based on measured PDE.
[b] Hypothetical MOS, assuming the same PDE as measured for deltamethrin.
[c] Mi denotes field experiment number *i*. In the case of chlorpyrifos and methamidophos data were extrapolated from PDE measured for deltamethrin.

Another effect (Table 1 and Fig. 4) is lateralization: there was more exposure on the right half of the body for both cases. This is considered to be due to the fact that the knapsack has the pump handle on the left side, with the operator holding the spray gun with his right hand; thus, all leaks from the lance, trigger handle and hose were concentrated on that side of the body.

Different crop height and density can also explain the differences between the mean PDE to broccoli and the previously published values for two other low crops: chard (78.2 mL h^{-1}) and lettuce (12.0 mL h^{-1}) (Hughes et al., 2004): broccoli plants were well developed, with leaves from adjacent rows in close contact, and weeds in between; chard were 40–50 cm high but widely separated, with fewer weeds, while lettuce were small plants (20 cm high) in neat rows with no weeds.

The mixing and loading stage merits separate consideration: it includes opening the container, measurement and transfer of the concentrated pesticide to a plastic container for preliminary dilution, and then to the 20 L knapsack. As can be seen in Table 1 for Sections 14 and 15 (preparation gloves), PDE values are very disperse but include very large values (M2, M5, M7) which is consistent with data for hand held application equipment of this type, illustrating the importance of the mixing and loading operation in the exposure assessment.

3.2. MOS of deltamethrin

PDE values by themselves do not define if pesticide applications result in levels of exposure which could be considered to be safe or unsafe. To evaluate quantitatively this issue the MOS can be used.

In the particular situation of these operators working in small plots, they rarely apply more than one or two backpacks (20–40 L) per day, so the MOS formula was adapted to describe the situation for a single backpack. For those situations in which more than one knapsack would be necessary (e.g., bigger fields) the DE factor would be the total exposure, i.e. the single PDE data multiplied by the number of backpacks applied. In this sense the MOS is inversely proportional to the number of applied knapsacks.

The MOS values calculated for all experiences are shown in Table 2. Values are mainly between 1.2 and 2.7 with a high point of 8.9 and a very low point of 0.2, the latter value corresponding to an overly concentrated spray-mix made and applied by the least experienced operator (M7). This means that the application of deltamethrin under the working conditions studied should be classified as safe, in terms of acceptable daily exposure limits. Furthermore, the difference between M7 and the other determinations shows that the operator's experience is an important factor even in relatively simple tasks such as these. In this sense previous studies with maize (Hughes et al., 2006) have shown that operator experience, equipment maintenance and especially application technique (walking backwards) are key aspects for reducing exposure, and could transform an unsafe case into a safe situation. In this particular study, for example, if the operator had respected the manufacturer's recommended concentration (10–15 mg L^{-1}) the last case would have been safe (MOS = 1.7–1.1).

In order to estimate the influence of the pesticides used on the resulting risk, an interesting extrapolation exercise can be made: by supposing that two other locally used insecticides were applied, instead of deltamethrin, and assuming that they are sprayed with the same technique, the same PDE (in mL h^{-1}) would result. So, if methamidophos (dermal NOAEL = 0.75 mg kg^{-1} day^{-1}) (US-EPA, 2000a) or chlorpyrifos (oral NOAEL = 0.03 mg kg^{-1} day^{-1}, 3% dermal absorption) (US-EPA, 2000b) were applied in the locally recommended concentrations (900 and 768 mg L^{-1} respectively), the MOS for these seven experiences would be those shown in Table 2. Both products show very small MOS, and consequently this hypothetical activity, if carried out, would be classified as extremely risky. Consequently they shouldn't even be considered for eventual applications in these situations.

Another result of this exercise is that it demonstrates the difference between toxicity and risk: although deltamethrin has a level of mammalian toxicity similar to the organophosphates, it is actually less risky, due mainly to the concentrations applied in the field; the corresponding LD50 values are (rats, oral): deltamethrin 30–130 mg kg^{-1} (IPCS - INCHEM, 2000), chlorpyrifos 96 mg kg^{-1} (IPCS - INCHEM, 1999), methamidophos 13–23 mg kg^{-1} (IPCS - INCHEM, 2002).

3.3. Mass balance of deltamethrin after application

The distribution of the pesticide between soil, crop and the operator is an interesting issue; Table 3 presents the mass balance for deltamethrin on a broccoli field, for studies M6 and M7. These preliminary results indicate that the sampling method is acceptable, because all of the product found (on plants, ground, operator and drift) adds up to 113–118% of the deltamethrin initially loaded in the knapsack. As expected, the

Table 3 – Mass balance of deltamethrin after application to broccoli

Experiment	Soil %	Crop %	Operator %	Drift %
M6 [a]	29.5	70.5	<0.1	NM
M7 [b]	18.8	78.0	1.6	1.7

[a] Soil + crop + operator + drift = 118% of deltamethrin loaded in the knapsack.
[b] Soil + crop + operator + drift = 113% of deltamethrin loaded in the knapsack.

Please cite this article as: Hughes EA, et al, Potential dermal exposure to deltamethrin and risk assessment for manual sprayers: Influence of crop type, Sci Total Environ (2007), doi:10.1016/j.scitotenv.2007.09.034

main fraction (70.5–78.2% of the amount recovered) was deposited on the plants, with comparatively very little "lost" as drift and on the operator; nonetheless a considerable proportion ended directly on the soil. This fraction may have an important effect on the soil's biological and physical properties, as a consequence of which the sustainability of crop production may be compromised. Studies are currently being carried out in order to establish these effects, such as deltamethrin depth profiles and microfauna disappearance.

4. Conclusions

It can be concluded that PDE values strongly depend on crop type. PDE mean values for maize are practically double those of broccoli, which is in good agreement with previously reported data.

A characteristic distribution pattern on workers clothes was found for both crops. While exposure was mainly concentrated in lower sections for broccoli, in the case of maize, a much broader distribution was found. In both situations, exposure of hands during preparation is of particular importance.

Working conditions using deltamethrin were found to be generally safe, as indicated by a MOS>1 in most cases.

A preliminary mass balance distribution of deltamethrin was established, confirming most of the product is deposited on the crop, but with an important fraction falling on the soil.

Acknowledgements

The authors wish to thank the "Instituto de Desarrollo Económico Local de la Municipalidad de Moreno" and the agricultural workers of Moreno district for their kind cooperation. The map in Fig. 1 has been elaborated on the basis of existing information, by LabSIG-ICO-UNGS. This work has been financially supported by the Universidad Nacional de General Sarmiento. J. M. M. is member of CONICET.

REFERENCES

Brand R, McMahon L, Jendrzejewski J, Charron A. Transdermal absorption of the herbicide 2,4-dichlorophenoxyacetic acid is enhanced by both ethanol consumption and sunscreen application. Food Chem Toxicol 2007;45:93–7.

Glass R, Gilbert A, Mathers J, Moreira J, Machera K, Kapetanakis K, et al. 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., Martínez Vidal, J., Egea González, F., González Pradas, E., et al. Assessment of operator, bystander and environmental exposure to pesticides. Report EUR 20489, European Commission, Brussels. 2002.

Grandjean P. Skin penetration — hazardous chemicals at work. London: Taylor and Francis; 1990. p. 171–3.

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.

IPCS–INCHEM. Pesticide residues in food—1999; CHLORPYRIFOS. In http://www.inchem.org/documents/jmpr/jmpmono/v99pr03.htm; accessed May 2007.

IPCS–INCHEM. Pesticide residues in food 2000 : DELTAMETHRIN. In http://www.inchem.org/documents/jmpr/jmpmono/v00pr04.htm#_00042210; accessed May 2007.

IPCS–INCHEM Data Sheet on Pesticides N° 50: DELTAMETHRIN: http://www.inchem.org/documents/pds/pds/pest50_e.htm; accessed May 2007.

IPCS–INCHEM. Pesticide residues in food — 2002 — Joint FAO/WHO Meeting on Pesticide Residues: METHAMIDOPHOS. In http://www.inchem.org/documents/jmpr/jmpmono/2002pr10.htm#3.0; accessed May 2007.

Juraske R, Antón A, Castells F, Huijbregts M. Human intake fractions of pesticides via greenhouse tomato consumption: comparing model estimates with measurements for captan. Chemosphere 2007;67:1102–7.

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

Machado-Neto JG, Matuo T, Matuo YK. Efficiency of safety measures applied to a manual knapsack sprayer for paraquat application to maize (*Zea mays* L.). Arch Environ Contam Toxicol 1998;35:698–701.

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 Assessment. OCDE/GD(97) Paris: Environmental Directorate; 1997.

Paquette S, Domon G. Agricultural trajectories (1961–1991), resulting agricultural profiles and current sociodemographic profiles of rural communities in Southern Quebec (Canada): A Typological Outline. J Rural Stud 1999;15:279–95.

UK-PSD Pesticides Safety Directorate. Toxicological endpoints database; deltamethrin endpoints; 2002. http://www.pesticides.gov.uk/psd_databases.asp; accessed February 2007.

UK-PSD Pesticides Safety Directorate, Glossary. 2006. In http://www.pesticides.gov.uk/appendices.asp?id=744; accessed April 2007.

US-EPA. Acephate: Revised Occupational and Non-Occupational Exposure and Risk Assessments for the Reregistration Eligibility Decision (RED) Document [Case # 819371, PC Code 103301, DP Barcode D262573] 2000a. In http://www.epa.gov/pesticides/op/acephate/rev_ore.pdf; accessed February 2007.

US-EPA. Occupational/Residential Handler and Postapplication Residential/Non-Occupational Risk Assessment for Chlorpyrifos. DP Barcode: D266562. Case No. 818975. PC Code: 059101. Submission: S568580. 2000b. In http://www.epa.gov/oppsrrd1/op/chlorpyrifos/rev_ore.pdf; accessed February 2007.

Please cite this article as: Hughes EA, et al, Potential dermal exposure to deltamethrin and risk assessment for manual sprayers: Influence of crop type, Sci Total Environ (2007), doi:10.1016/j.scitotenv.2007.09.034