# DERMAL EXPOSURE OF WORKERS AT RESIDUES OF DELTAMETRIN IN TREATED PLANTS, IN THE REENTRY COTTON CROP AFTER SPRAYING

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## Abstract

The objective of this work was to study the dermal exposure of workers to residues of the deltamethrin, applied in cotton. After 3 minutes of application four people dressed a group with cotton clothes (pants, shirt and gloves), entered and stayed in the treated area by 30 minutes, simulating a sampling. The procedure was repeated after 60 and 300 minutes and 1, 3, and 7 days after the application. The clothes were cut and put in plastic bags, and stored cold at -18ºC (-0.4ºF) until analyses was performed. The analytical method consisted on the extraction of deltamethrin residues with ethyl acetate and the quantitative determination was done by gas chromatography. Exposure was extrapolated to a workday of 8 hours. To evaluate safety's conditions at work was estimated the Working Condition Unsafe (margin of safety – MOS <1), Poisonous Dose (%PD/day), Dermal Dose Tolerable and the estimate of Safe Work Duration (SWD). The corresponding group for the forearms/arms/hands concentrated 61.27% of present residues in the clothes. The residues found on the clothes, chest, legs, thighs and back, were 13.40, 9.33, 9.32, and 6.65%, respectively. Results of deltamethrin amounts trapped on cotton clothes showed that 24h as a re-entry interval for Decis 25 EC is overestimated in Brazil.

## Introduction

The exposure assessment is part of the assessment process of health risk for the regulation of pesticides in many countries. In Brazil, the legislation of the pesticides and derivates requires only a revision of its hazards through a toxicological evaluation and not its risk assessment. The tools and information for the execution of the process are available and it would be desirable that were discussed towards its realization and capabilities (Trevisan, 2002). The assessment of exposure, can be accomplished by mathematical models, but it will always be closer of the reality when it be based on the collect of data and in the quantification of the found residues (Kotaka, 2005). Primary sceneries of exposure, as opening of the pesticides pack's, pre-mixture, loading and application always received more attention of the researches. Secondary sceneries as the risk of dislodgeable residues offer always presented few research works in all the world (Ramwell et al., 2006). Kissel & Fenske (2000) affirmed that agricultural workers that re-enter in crops after application of pesticides and that will pawn manuals activities are potential subject of dermal exposure through the foliar residues and of the soil residues. Crops that demand constants re-entries are worthy of studies in relation to dislodgeable residues. In the case of cotton crop, that receives a big load of pesticides in your production cycle, the activity of more intimate contact with the plants is the sampling. Cock (1995) affirmed that although the dermal exposure is considered very low compared the others activities like the manipulation of pesticides, that involve directly re-entered in the crop are much more frequent, almost always involving a lot of hours in contact with the crop.

The objective of this work was to study the dermal exposure of workers/scouts in the re-entry of cotton crop after spraying with deltamethrin insecticide (Decis 25 EC), quantifying the transfer of residues in the plants for the clothes (dosimeters) of the scout and to compare the results with the re-entry interval established by Brazilian legislation.

## Materials and Methods

The experiment was carried out in Experimental Farm of Unesp, located in Selvíria/MS/Brazil, in January 2007. The variety used was DeltaOpal, with 105 days after seeding (1,6 m/height,~5.2 feet). For the application a bars-sprayer was used, equipped with nozzles TVVK-8 (conic nozzles) and volume of 250 L/ha, in the area of 360m$^2$. The largest label dose of insecticide Decis 25 EC in cotton crop in Brazil was used (400 ml c.p ha$^{-1}$) (0.032 gal c.p/ac). The method used for exposure assessment was Whole Body Method, described by Kotaka (2005). Shirts and pants were made of raw cotton (unbleached). The raw cotton material was chosen since its texture permits a good trapping efficiency and it is necessary because the shirts and pants worked as dosimeters. The exposure of hands, was quantified, by the method of absorbent gloves, also made in raw cotton. After 3 minutes of application four people dressed a group of cotton clothes (pants, shirt and gloves), entered and stayed in the treated area by 30 minutes, simulating a sampling. The procedure was repeated after 60 and 300 minutes and 1, 3, and 7 days of the application. The clothes were cut and put in plastic bags, and stored cold at -18ºC (-0.4ºF) until analyses was performed. The data of laboratory coming the average of each clothes part taked in field (4 repetitions), were used for the correlation (extrapolation) of the dermal exposure of scout, considering a workday as 8 hours.

### Analytical method validation

For the studies of fortification/recovery the samples (present residues in the cotton dosimeters) were fortified, joining 1 mL of the solutions of appropriate concentrations, obtained by successive dilutions in ethyl / acetate, starting from stock solution, where clothes parts were fortified in order to obtain concentrations of 1.6 and 16 µg/m$^2$ respectively with 5 and 4 repetitions.

The analytical method, adapted of Nilsson & Papantoni (1996) consisted on the extraction of deltamethrin residues with a ethyl acetate; the cleaning of the extract was made by Gel Permeation Chromatograph (GPC), being the elution proceeded with a mixture cyclehexane + ethyl acetate. For the quantitative determination was used chromatography technique in gaseous phase, being used gas chromatograph equipped with electron capture detector (GC/ECD).

### Estimate of Working Condition Safe

The conditions of safety work of scout with the deltamethrin were calculated with the formula of Margin of Safety (MOS), adapted of Machado Neto (1997):

$$MOS = \frac{NOEL \times 70}{AEQ \times 100}$$

In this formula the NOEL is the "No Observable Effect Level" (1 mg kg$^{-1}$ day$^{-1}$; FAO, 2006). The expressed value in mg kg$^{-1}$ day$^{-1}$, is obtained in tests of evaluation of the laboratory toxicity in animals. The number 70 is the corporal weight considered for the worker/scout (kg). The AEQ is the absorbed exposure quantity (dermal penetration or inhalation) in (mg day$^{-1}$). The dermal penetration was considered as 10%. The absorption for inhalation was considered as 1% of the dermal absorption, because it usually acts less than 1% of the total exposure (WHO, 1982). The number 100 multiplying AEQ is a factor of safety used to compensate the extrapolation of the toxicological data obtained in laboratory animals. The used criterion, if MOS $\geq$ 1, the condition is classified as safe. If MOS < 1, the condition is classified as unsafe.

### Estimative of Poisonous Dose

The estimative of risk of occupational intoxication was estimated through the formula proposed for WHO (1975):

$$\%PD = \frac{1.1 \times DE}{LD_{50} \times 70} \times 100$$

In this formula PD is the Poisonous Dose, estimated through of multiplying of $LD_{50}$ (mg/kg) for the exposed worker's corporal weight (70kg,~155pounds). DE is the dermal exposure, estimated in the workday (mg/day). $LD_{50}$: amount of pesticide that has killed 50% of the test animal population by dermal or oral exposure (mg/day). In this formula, the inhalation exposure was substituted by 10% of dermal exposure, in agreement with document of the WHO (1975).

**Estimative of Dermal Dose Tolerable**

The estimative of Dermal Dose Tolerable ($D^{tol}$), considered the formula described by Lundehn et al. (1992):

$$D^{tol} = \frac{NOEL_D \times 70}{25 \times AF} = mg/day$$

In this formula the $NOEL_D$ is the "No Observable Effect Level Dermal". The expressed value in mg $kg^{-1}$ $day^{-1}$, is obtained in tests of evaluation of the toxicity in laboratory animals, in this case 1000 mg/kg/day (FAO, 2006). The number 70 is the corporal weight considered for the worker (kg). The AF is the factor of absorption of the substance for the skin (10%) in percentage and the number 25 a factor of safety.

**Estimate the Safe Work Duration (SWD)**

Starting from the beginning of the exposure to the worker/scout to be exposed to the equivalent dosage to the limit of exposure tolerance there is an interval of time that can be denominated of Safe Work Duration (SWD).
The limitation of the time of work to SWD it is constituted in measure of collective safety that the can be applied any work condition (Machado Neto, 1997).
The SWD it is calculated in the following way:

SWD = MOS x TSW

Where:
- TSW it is the time of exposure in hours (workday: 8h);
- SWD is the time of safe work, expressed in hours of safe exposure (h).

## Results

According to the presented data (Tab. 1) in the experimental conditions, the analytical method showed satisfactory for the analysis of dislodgeable residues of deltamethrin (originating of dermal exposure in the cotton dosimeters) with limit of quantification (LOQ) of 1.6 $\mu g/m^2$. The recovery percentages are framed in the established criterion by the Brazilian legislation (Anvisa, 2007), where the interval of the recovery should be between 70 and 120% (average recovery).

**Table 1**. Percentage (%) of recovery of deltamethrin residues in samples of cotton (vegetable fiber) fortified.

| Fortification levels ($\mu g/m^2$) | Repetitions (%) | | | | | a ± sd (%) |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | |
| 1.6 | 102 | 109 | 93 | 115 | 106 | 105 ± 8 |
| 16 | 86 | 97 | 89 | 81 | -- | 88 ± 6.6 |

In Table 2, a significant decline was verified from the dermal exposure to the present residues, in the second re-entry (60 minutes). Analyzing the data extrapolation (eight-hour workday), was verified that the dislodgeable residues in the plants for the dosimeters of scout presented a decline of 34%, of the first re-entry (3 minutes) for the second re-entry (1h). Of second re-entry (1h) for the third (5h), the decline was the 53%. Therefore, after 5 hours the application, the dermal exposure of scout for the deltamethrin decline 69%. Similar results are obtained by Rotundo et. al. (2006) that in similar experiment affirmed that the dislodgeable residues decreased 3 times of the first re-entry for the second re-entry.

**Table 2.** Residues of deltamethrin (µg/m$^2$) relative of dermal exposure (30 minutes) in parts in the dosimeters of raw cotton relative of different parts of human body. Selvíria/MS/Brazil, 2007.

| Areas of the body | 3 minutes | 1 h | 5 h | 1 d.a.a | 3 d.a.a | 7 d.a.a |
|---|---|---|---|---|---|---|
| | 0.05h | 1h | 5h | 24h | 72h | 168h |
| 1.Chest | 57.78 | 52.71 | 24.84 | 6.23 | 0.77 | 0.59 |
| 2.Back | 48.34 | 22.15 | 6.50 | 2.27 | 0.53 | 0.36 |
| 3.Thighs | 38.87 | 43.26 | 18.20 | 2.84 | 0.62 | 0.44 |
| 4.Legs | 45.02 | 18.38 | 22.29 | 1.28 | 0.71 | 0.76 |
| 5.Hands | 115.98 | 72.96 | 30.49 | 10.45 | 2.92 | 1.15 |
| 6.Forearms | 117.71 | 87.39 | 34.63 | 12.20 | 2.02 | 0.84 |
| 7.Arms | 81.76 | 37.58 | 21.46 | 3.37 | 1.05 | 0.59 |

d.a.a: days after application of deltamethrin

The decrease was significant in the first hours, and relatively stable in the others re-entries. After 1 day, the dermal exposure only resulted in the 8% of the closest dermal exposure of the application, decreasing to 2% to the 3 days after application (d.a.a) and 1% in the last re-entry to 7 d.a.a. The deltamethrin found in the dosimeters (originating from dislodgeable residues in the plants) along the time agree with Gunther (1969) that affirms that the disappearance of a pesticide in the nature, applied by pulverization, it can be separate in two phases: a degradation phase, in that there are the fast disappearance of the initial deposit and a persistence phase, where it happens a slow decrease in the level of the existent residues in the substratum, for the action of atmospheric factors and metabolic attack. Besides, the deltamethrin was still being absorbed by the plants in the first hours, that were evident for the significant decrease of the dermal exposure in the second and third re-entry. The data of the dislodgeable residues, coming of the dermal exposure (extrapolated for 8 hours), were well represented by the regression curve (Fig. 1).

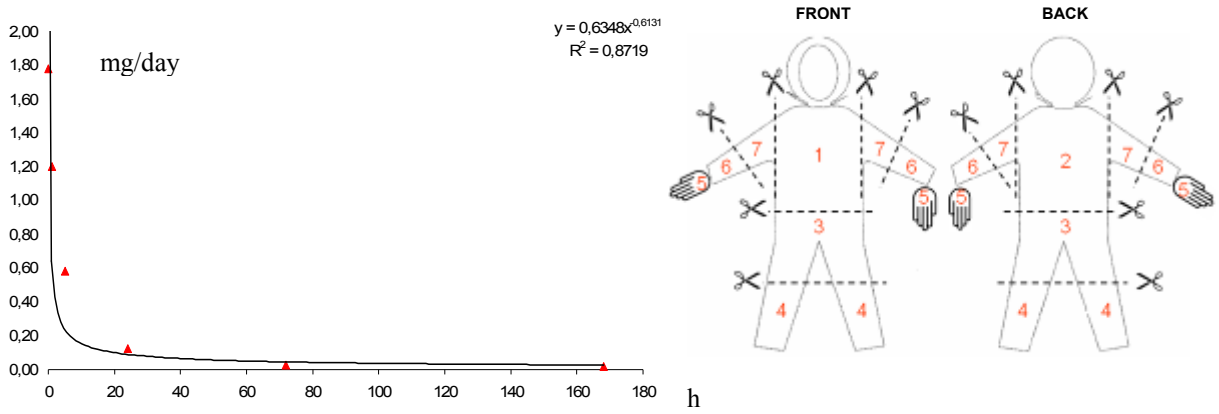


**Figure 1**. Regression curve of dermal exposure (mg/day) of deltamethrin in the body of scout, relative the dermal exposure in each time of re-entry (in hours) in the cotton crop after application (extrapolation for worday of 8 hours) (a) Place of the clothes that were split up and analyzed. 1-Chest; 2-Back; 3-Thighs front/back; 4-Legs front/back; 5-Gloves (hands); 6- Forearms front/back; 7- Arms front/back (b).

In spite of it not being done to the quantification of the dislodgeable residues in the leaves of the cotton plant, the dermal exposure in the re-entry is due to the presence of those residues in the leaves of the plants. Giles & Blewet (1991) affirmed that the dislodgeable residues is correlated strongly with levels of residues foliate dislodgeable.

The dermal exposure of scout, originating from the dislodgeable residues of the cotton plants, went larger for the gloves and forearms, on average 24.87% and 24.00%, of dermal exposure, respectively. The group forearms/arms/hands concentrated 61.27% of present residues in the dosimeters. These three parts of the body, that concentrate 61.27% of the dermal exposure, represent only 23.4% of the area of the human body, according to CNA

(2006). The results agree with the study of Rotundo et al. (2006) that showed the parts corresponding of the dosimeters regarding the forearms, arms, hands and abdomen were the most exposure by dislodgeable residues, in the simulation of the sampling in cotton crop.

Besides representing a small portion of human body, the group of forearms/arms/hands it is hardly ever protected by gloves that would restrict the contamination of the skin. Even though of the use of long sleeve shirt for some scouts, the use of gloves in the sampling is an uncommon practice in Brazil. In agreement with safety's margin (MOS) (Tab. 3) all the re-entries of scouts, after the application with deltamethrin 25 EC in the dosage of 400 ml c.p.ha$^{-1}$ (10 g.a.i. ha$^{-1}$) (0.032 gal c.p/ac), showed working condition safe (MOS $\geq$ 1), resulting in Save Work Duration (SWD) proportionally superiors the workday considered (Tab. 3).

The intoxication risk (Poisonous dose/day) varied from 0.00139 to 0.00001%. The low risk, agrees with safety's margins obtained, whose values calculations were always very superiors of the workday established.

The Dermal Dose Tolerable, calculated in 280 mg/day, was a result always very superiors of the total values found at the end of the extrapolation of the workday of the scout in all the re-entries that varied the 1.77 a 0.01 mg day$^{-1}$ (Tab. 3). The IPCS - *International Programme on Chemical Safety* (2007) affirmed though deltamethrin is relatively persistent, low application rates ensure low residue levels. Unprotected persons may enter treated areas immediately after spraying without being exposed to hazardous amounts of deltamethrin.

**Table 3.** Margin of safety, Poisonous Dose (% PD/day), Dermal Dose Tolerable and Save Work Duration of scout in the cotton crop. Selvíria/MS/Brazil, 2007.

| Estimated of Safety | deltamethrin EC (Decis 25 EC) 400 ml c.p/ha (0.032 gal c.p/ac) | | | | | |
|---|---|---|---|---|---|---|
| | 3 minutes | 1 h | 5 h | 1 d.a.a | 3 d.a.a | 7 d.a.a |
| MOS (Margin of safety) | 3.59 | 5.30 | 10.95 | 51.51 | 240.06 | 377.64 |
| Poisonous Dose (% PD/day) | 0.0013927 | 0.0009425 | 0.0004566 | 0.0000971 | 0.0000208 | 0.0000132 |
| Dermal Dose Tolerable (mg/day) in comparison with the dermal dose found (mg/day) | 280 (1.77) | 280 (1.19) | 280 (0.58) | 280 (0.12) | 280 (0.02) | 280 (0.01) |
| Save Work Duration (SWD) | 28.72 | 42.40 | 87.60 | 412.08 | 1920.48 | 3021.12 |

d.a.a: days after application of deltamethrin

Nilsson & Papantoni (1996) affirmed that absorption on cotton fiber might be larger compared to bare skin since the cloth is more porous resulting in a larger surface. In the estimation was not considered the risk for overestimation depending on larger surface. The amount of deltamethrin which might have penetrated the cloth into the skin during the sampling period leading to an underestimation has not been taken into account.

## Conclusions

The analytical method used for the analyses of deltamethrin residues in dosimeters made with vegetable fiber (raw cotton) is adapted and feasible. The corresponding group of the forearms/arms/hands concentrated 61.27% of present residues in the clothes. Results of deltamethrin amounts trapped on cotton clothes showed that 24h as a re-entry for Decis 25 EC is overestimated by Brazilian legislation.

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