

## PERSISTENCE OF DELTAMETHRIN RESIDUES IN STORED CEREALS

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### ABSTRACT

The purpose of this study was to evaluate the distribution and fate of deltamethrin and piperonyl butoxide residues in stored cereals wheat and corn. Cereals were treated with three formulations: i) emulsion K-OTHRINE GRAINS CE, containing 2.66% of deltamethrin and 23.9% of piperonyl butoxide, ii) oil solution K-OTHRINE GRAINS ULV containing 0.67% of deltamethrin and 6.0 % of piperonyl butoxide and iii) dust containing 0.2% of deltamethrin. The treatment rates for deltamethrin were in the around of 0.25, 0.5 and 1.0 mg/kg. Cereals samples were collected during the storage and analysed by gas-chromatography for the determination of deltamethrin residues. The results obtained from the wheat and corn experiments confirmed that in the 12 months period the loss, due to the degradation processes, does not affect significantly the quantities of deltamethrin in stored cereals.

The results also confirmed the high variability among the samples collected from the same bulk of treated cereals. The treatment and storage kinds affects the average residues of deltamethrin; the residue distribution in the vertical silos is function of height in the insiled mass. None of the wheat and corn samples examined in this study showed residue levels of deltamethrin higher than the FAO/WHO limits (1 mg/kg) when the treatment doses were the recommended ones: 0.25 and 0.5 g/tons for liquid formulations and 0.5- 1.0 g/tons for dust.

### INTRODUCTION

Deltamethrin [(S)- $\alpha$ -cyano-3-phenoxybenzyl-cis-(1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate] is a synthetic pyrethroid and it is widely used against insects infesting stored foodstuffs, especially cereals, such as *Sithophilus granarius*, *Rhizoperta dominica*, *Tribolium castaneum* and *T. confusum*, *Oryzaephilus surinamensis* and *O. mercator*, *Sitotroga cerealella* and *Plodia interpunctella* (Roussel Uclaf, 1982).

The determination of deltamethrin in stored foodstuffs, in

particular corn and wheat, is very important to assess the toxicological risk for man consuming the treated crops (Bengston et al., 1983; Molinari, 1986).

The purposes of this research (summarized in table I) requested to set up two experimentations: the one with hard and soft wheat and the other with corn. The wheat was treated with 3 different products containing deltamethrin; the corn with 2 (table II). The treated cereals were stored in vertical silos or horizontal warehouses for periods varying from 3 to 12 months (table III).

Table I - Research targets

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- Study the deltamethrin fate under different practical operating conditions, and to determine the significance of the values obtained as regards safety to humans.
  - Set up the application technique by measuring the levels of the a.i. immediately after the treatment.
  - Study the trend of residue levels during the cereals storage period.
  - Study the influence on residues of:
    - treatment dose;
    - type of cereal: hard and soft wheat or corn;
    - type of silo or warehouse;
    - type of the used formulation: emulsion (CE), oil solution (ULV) and dust (PP).
  - Study of residues distribution in vertical silo.
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## EXPERIMENTAL SECTION

### Treatment and storage of cereals

#### Wheat

Seven experiments were carried out in 6 Italian localities; each one was dedicated to a specific kind of storage structure, of treatment method and type of formulation used (table III).

For liquid formulations the used active ingredient doses were those normally prescribed in the label for 6 and 12 months protection (respectively 0.25 and 0.5 g/tons) and two times as much this dose (1.0 g/tons) in order to simulate possible dosage mistakes. For the dust the doses were 1.0 and 2.0 g/tons.

Wheats treated with different doses were stored in separated warehouses (horizontal) or silos (vertical).

Table II - Used formulations, their compositions and treated cereals with that product.

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Code	Name	Deltamethrin %	Piperonyl butoxide %	Treated cereals
Liquid formulations				
CE	K-OTHRINE GRAINS CE	2.66	23.9	wheat, corn
ULV	K-OTHRINE GRAINS ULV	0.67	6.0	wheat
Dust formulation				
PP	K-OTHRINE GRAINS PP	0.2	0.0	wheat, corn

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Five grain samples (500 g) for deltamethrin residues determination during storage were taken at the times of table III. In consequence of the structural difference of the plants, which allowed the access to the treated wheat mass only in specific points, the sampling was carried out with different techniques in the various localities.

### Corn

The kind of storage structure, the treatment methods and the type of used formulation were summarized in table III.

For liquid formulation the used active ingredient doses were the normally prescribed in the label for 6 months protection (0.25 g/tons) and four times as much this dose (1.0 g/tons) in order to simulate possible dosage mistakes. For the dust the dose was 1.0 g/tons.

Corn treated with different dose was stored in separated warehouses.

Five corn samples (500 g at least) for deltamethrin residues determination during storage were taken at the times of table III.

### Sample analysis

Only 3 out of the 5 repeated samples were normally analysed. Only when there was a high result variability (on average a standard deviation higher than 50%) the other two samples were analysed.

Samples were extracted with n-hexane. The organic phase was dried on sodium sulphate, concentrated and analyzed by gaschromatography (table IV) for deltamethrin residues.

Table III - General characteristics of storage, wheat-handling, treatments and sampling plan (storage days after treatment and before sampling).

Code	Structure kind	Cereals type	Cereals tons	Formul. type	Treatm. methods	Sampling (days)					
						1	2	3	4	5	6
<b>WHEAT</b>											
TVU	Vertical	soft	80	ULV	BE	0	42	89			
TOC	Horizontal	soft	30	CE	TS	0	43	90			
TOC	Vertical *	soft	400	CE	BE	0	43	90	155	180	365
DVU	Vertical	hard	3900	ULV	BE	0	43	92			182
DVC	Vertical	hard	900	CE	BE	0	45	91		190	358
DVC	Vertical	hard	540	CE	TS	0	43	95		193	365
DOP	Horizontal	hard	3	PP	MT	0	41	90			
<b>CORN</b>											
MOC	Horizontal		25	CE	BE	0	42	91	182		
MOP	Horizontal		2	PP	MT	0	42	91	182		

### Legend:

Formul.type: see table II; treatm. methods: BE = treatment at the base of the elevator; TS = treatment at the top of the sciew feeder MT = treatment in the mixing truck. \*

Note: \* Wheat was considered as stored in horizontal warehouse because wheat heap (130 tons) was low (<2m) and wide (≈15m radius).

Table IV - Gaschromatography conditions

Column:	glass (100 cm x 2 mm i.d.) filled with OV-1, 3% on Cromosorb W, AW-DMCS, 80-100 mesh;
Column temp.:	255 °C
Injector temp.:	270 °C
Detector:	<sup>63</sup> Ni Electron Capture
Detector temp.:	280 °C
Carrier gas:	nitrogen, 35 mL/min
Injection volume:	2 µL
Deltamethrin retention time:	10.7 min
Minimum amount detected:	0.1 ng

## RESULTS AND DISCUSSION

Average recoveries of deltamethrin from wheat and corn are  $90.2 \pm 5.5$  and  $81.5 \pm 6.5\%$  respectively in the range 0.2 - 1.0 mg/kg sample concentration.

The average amounts of deltamethrin residues determined at each sampling time are summarized in figures 1 and 2 for wheat and in figure 4 for corn.

### Wheat

The statistical evaluation of the data points out that:

- there is a high variability of the residual determinations within the same group;
- there is a significant difference among the average residues in the 6 experiments;
- the treatment dose does not influence significantly the average deltamethrin residues of all experiments for all sampling, while in the single experiment becomes significant;
- the time elapsed from the treatment exerts a significant effect on the residues level. The average level of deltamethrin residues in the six experiments significantly increases as sampling proceeds from the 1st to the 2nd one and to the 3rd one (fig. 1);
- the increase of average residues as sampling proceeds, especially when the wheat is carried out from the bottom of silos, could be apparent, linked to non-homogeneous residues distribution in the silo and samples collected at different points of wheat mass. Samples collected during the silo emptying showed a concentration gradient growing from the bottom to the top (fig 3), which is probably due to the different dust distribution in the cereal-loading phase.

### Corn

Average data ranged from 0.113 to 0.282 and to 0.325 mg/kg in corn treated respectively with 0.27 and 1.24 mg/kg of deltamethrin emulsion and with 1.0 mg/kg deltamethrin in dust formulation. However the statistical evaluation of the data by means of factorial analysis of variance showed:

- the high variability makes not significant the differences between the average levels of residues in the 3 experiments;
- the average levels of deltamethrin residues did not signific

FIGURE 1 - RESIDUES IN WHEAT AFTER STORAGE TIMES IN DIFFERENT STRUCTURES  
(For codes see table III)

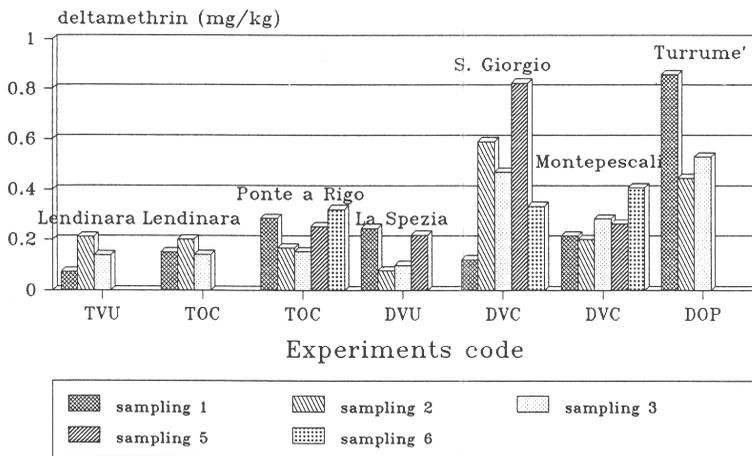


FIGURE 2 - RESIDUES IN WHEAT AFTER STORAGE TIMES IN WAREHOUSES (CODE TOC)  
(For codes see table III)

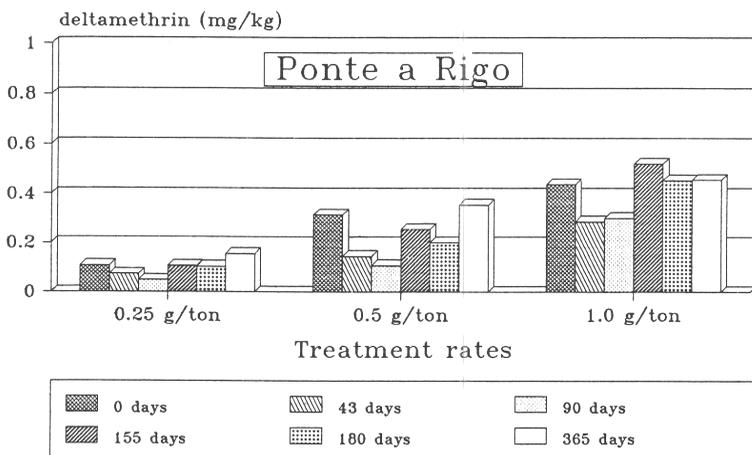


FIGURE 3 - DISTRIBUTION OF RESIDUE LEVELS (mg/kg) IN THE SILO MASS

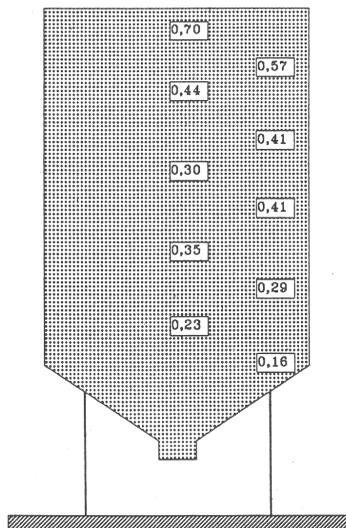
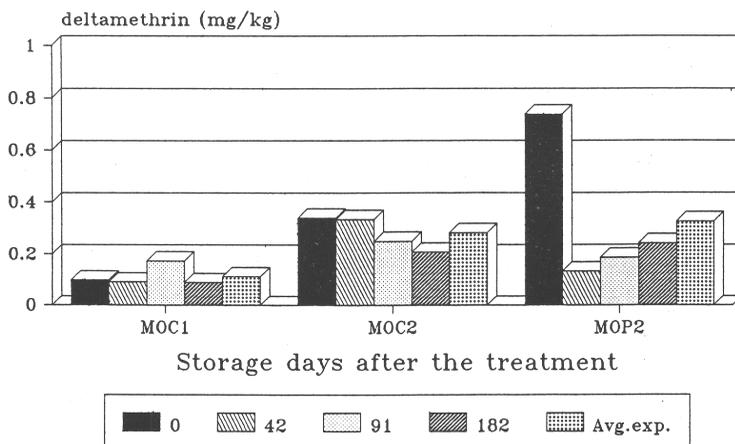


FIGURE 4 - RESIDUES IN CORN AFTER STORAGE TIMES  
(For the code see table III)



tively decrease during the corn storage (0.392; 0.186; 0.203; 0.179 mg/kg for 0, 41, 91, and 182 days respectively).

### CONCLUSIONS

Data obtained in this study confirm previous ones and allow to point out the fundamental features:

- 1- There is a high variability of residue levels among the samples collected from the same bulk of treated wheat and corn.
- 2- The degradation processes do not affect deltamethrin compounds in stored cereals.
- 3- The largest loss of deltamethrin occurs during the treatment phase.
- 4- In the treated cereals mass the highest residue concentration is in dust. Their distribution in the mass causes the observed variability of the residue levels.
- 5- Although we had to cope with the high variability of the residual amounts detected in samples, a problem encountered also by other investigators, none of the samples examined in this study showed a deltamethrin residue higher than maximum residue limit (1 mg/kg) recommended by FAO, when the dose of treatment was the recommended one.

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DANS LES STOCKS DE CEREALES**

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**RESUME**

Le but de cette étude était d'évaluer la distribution et l'allure de la dégradation des résidus de la deltaméthrine et du pipérolhyl butoxyde dans des stocks de maïs et de blé. Les céréales ont été traitées par trois formulations : i) émulsion K-OTHRINE GRAINS CE, contenant 2,66 % de deltaméthrine et 23,9 % de pypéronyl butoxyde. ii) solution huileuse K-OTHRINE GRAINS ULV contenant 0,67 % de deltaméthrine et 6,0 % de pypéronyl butoxyde. iii) poudre contenant 0,2 % de deltaméthrine. Les doses de traitement à la deltaméthrine ont été d'environ 0,25, 0,5 et 1,0 mg/kg. Les échantillons de céréales ont été récoltés pendant le stockage et analysés par chromatographie en phase gazeuse pour mesurer les résidus de deltaméthrine. Les résultats obtenus pour le blé et le maïs ont confirmé que la perte sur 12 mois, due aux processus de dégradation, n'affectait pas significativement les quantités de deltaméthrine dans le stock. Les résultats ont également confirmé la grande variabilité existant entre les divers échantillons d'un même stock. La manière de stocker et de traiter les céréales affecte la moyenne des résidus de deltaméthrine ; la distribution de ces résidus dans les silos verticaux est fonction de la hauteur de la masse ensilée.

Aucun des échantillons de blé ou de maïs examiné dans cette étude n'a présenté de résidu en deltaméthrine supérieur à celui imposé par la FAO/WHO (1 mg/kg) lorsque les doses étaient celles recommandées, à savoir : 0,25 et 0,5 g/t pour les formules liquides et 0,5 - 1,0 g/t pour la poudre.