DELTAMETHRIN RESIDUES IN PRODUCTS OBTAINED FROM STORED TREATED CEREALS

Gian Pietro Molinari

Istituto di Chimica - Facoltà di Agraria - Università Cattolica del Sacro Cuore - Piacenza - Italy.

Summary

After cereals have been treated before storage for protection from the attack of insect, the active ingredients can remain unaltered in the cereal itself: then they can migrate to the cereals processing products (e.g. flour, bran, bread, pasta, grits, meal, starch, oil, etc.). In order to determine the levels of deltamethrin residues in food, studies were conducted to obtain information on the behaviour of this a.i. during the milling of wheat and corn.
Treated wheat and corn were stored in silos and warehouse and after different time one tonne of cereals were blended with two commercial milling: one with dry cleaning process and other with wet cleaning. In this process the cereals make flour and bran. The residue levels were measured by gaschromatography in cereals before milling, in foreign materials, in cleaned grains, in bran and flour.

The results obtained shown that the higher deltamethrin residues is mesured in foreign materials (30 - 60 time the level of blended wheat). In flour the deltamethrin residue is low (lower of 10% of blended cereals), detectable only in cereals treated with higher dose (1 g/ton).

INTRODUCTION

The protection of stored cereals from the insect damages by means of chemicals is not free from one of the major problems related the use of these products in agriculture: the presence of residues of not-natural substance in foodstuffs. After cereals treatment the insecticides can remain unaltered or can be degraded to more simple compounds in cereal istself and they can get to the cereals processing products (e.g. flour, bran, bread and pasta from wheat; grits, meal, starch, syrups and oil from corn).

The purposes of our studies were to obtain information on the behaviour of insecticide deltamethrin during the processing phase of wheat and corn milling and in bread and pasta prepared with contamined flours (table 1).

Two experimentations were set up: the one with hard and soft wheat and the other with corn. The flowsheets of wheat and corn experiment are show in fig. 1 and 2 respectively.

Table 1 - Research targets

- Study the deltamethrin fate in wheat and corn processing products under different practical operating conditions (e.g. dry and wet milling after different time of storage of treated cereals).

- Study the residue distribution in the cereal caryopsis as function of:
  - treatment dose;
  - type of cereals: hard or soft wheat or corn;
  - type of the used formulation: water emulsionable or oil solution;
  - time of cereal storage after treatment.

- Evaluate the residue level in the wholemeal, white flour and bran obtained by milling of treated wheat after storage and cleaning with dry and wet process.

- Evaluate the residue level in bread and pastas prepared with contaminated flours obtained fron the milling of treated wheat.

- Evaluate the residue level in the meal and germ obtained by dry and wet milling of treated and stored corn.

- Study the distribution and the trend of deltamethrin residues during the milling phase.

- Study the influence on deltamethrin residues in flour, bran, meal and germ of:
  - type of cleaning process: dry or wet;
  - type of milling process: dry and wet;
  - storage time between cereal treatment and milling.

Figure 1 -Wheat experimental planning

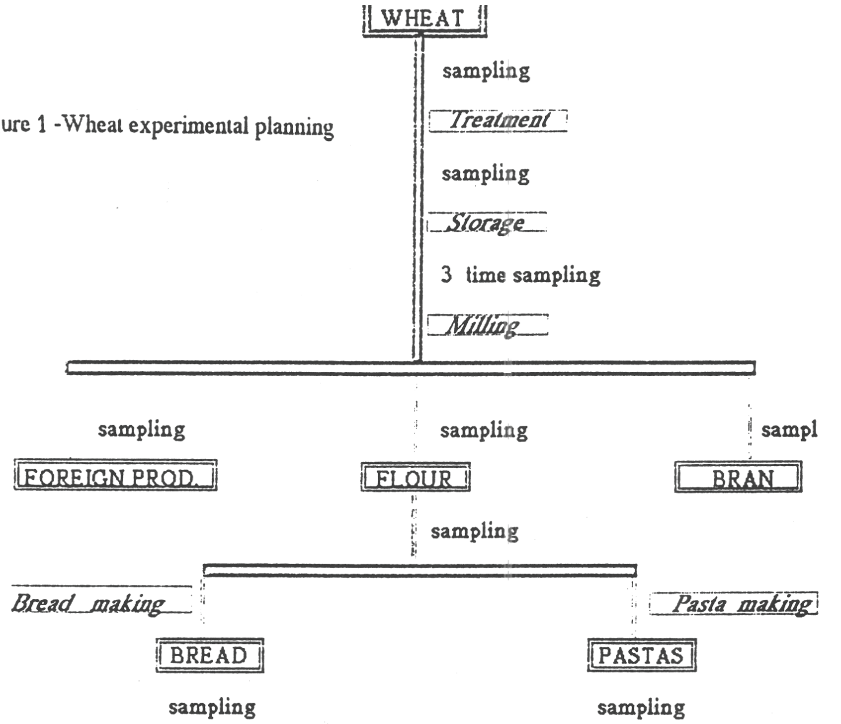
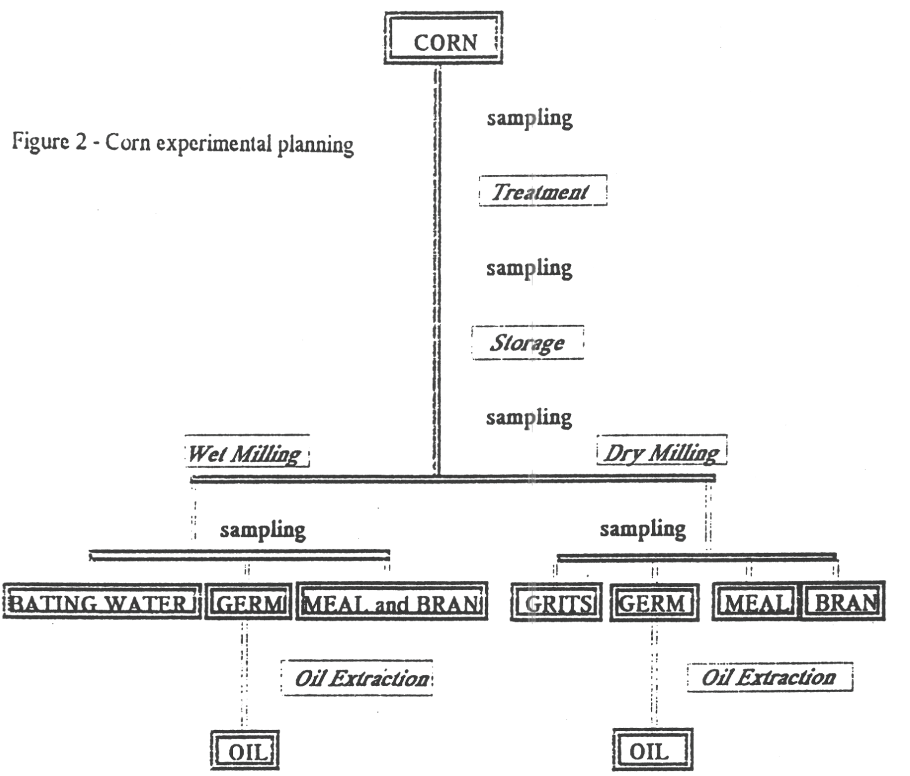


Figure 2 - Corn experimental planning



EXPERIMENTAL SECTION

The treatment and storage waies of wheat and corn used in milling experiments are described in the poster: G. P. MOLINARI "Persistence of deltamethrin residues in stored cereals." (1). The formulations and the rate of active ingredient used for the cereals treatment and the storage days before milling, are summarized in table 2.

Milling and sampling

After the storage days show in table 3, a stock (one tonne) of the cereals was taked from every experiment (table 2) and separately milled.

Sampling of cereals, before the milling and after the cleaning, and of milling products were carried out (table 4). For each sampling five samples were collected and stored at -25 °C until the analysis took place.

Wheat

One tonne of hard and soft wheat was milled by two small and modern plant: one with dry-cleaner of wheat (fig. 3) and an other with a wet-cleaner using a large amount of running water instead of aspirator, disc separator and scourer. The grinding of cleaned wheat was in seven steps for bran and flour production.

Corn

In the dry process one tonne of corn was milled by means of a dry corn degerming system to produce germ, grits and meal.

The wet milling process was laboratory simulated. The corn cleaned by industrial system was soaked with water slurry, coming from industrial plant, in 5L flask. After the corn was separated and degermined.

Samples analysis

Normally, for the determination of deltamethrin residues three of the five collected samples were extracted with n-exane, the organic extract was dried on sodium sulphate, concentred and gaschromatography analyzed.

The gaschromatography condition and recovery are in the previous named poster.

Table 2 - Formulations and deltamethrin doses used for treatments of stored and milled cereals.

Cereals code	type	Formulation name	A.i. rate (g/ton)	Storage time (gg)
DVC2	Hard whe.	K-OTHRINE GRAINS CE	0,5 **	45 190 358
DVC3	Hard whe.	K-OTHRINE GRAINS CE	1,1 ***	44 190 358
DVU1	Hard whe.	K-OTHRINE GRAINS ULV	0,19 *	44 183
DVU3	Hard whe.	K-OTHRINE GRAINS ULV	1,03***	42 181
TOC1	Soft whe.	K-OTHRINE GRAINS CE	0,25 *	43 180 365
TOC3	Soft whe.	K-OTHRINE GRAINS CE	1,0 ***	43 180 365
TVU1	Soft whe.	K-OTHRINE GRAINS ULV	0,15 *	42 98
TVU2	Soft whe.	K-OTHRINE GRAINS ULV	0,31 **	98
TVU3	Soft whe.	K-OTHRINE GRAINS ULV	0,96***	42 98
MOC1	Corn	K-OTHRINE GRAINS CE	0,27 *	42 182
MOC3	Corn	K-OTHRINE GRAINS CE	1,24***	42 182

Note: * = normal dose for 6 months protection;
** = normal dose for 12 months protection;
*** = dose simulating possible treatment mistakes (2 - 4 times highter than normal doses).

Figure 3 - Wheat milling process

Semplified flow diagram

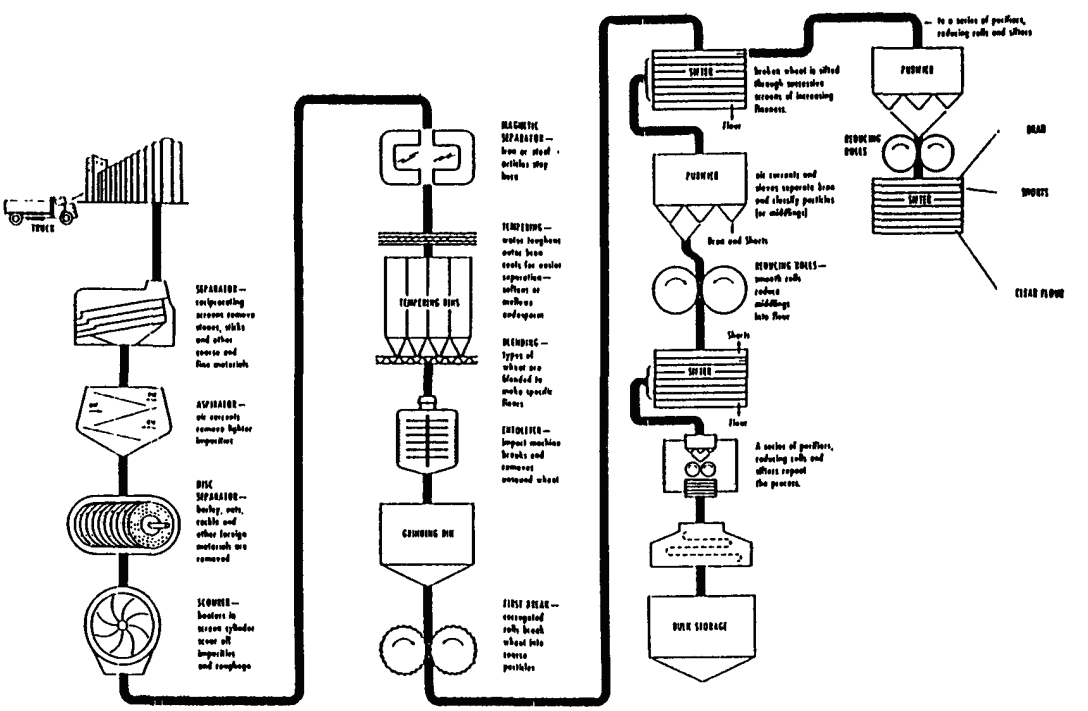


Table 3 - List of milling trials carried out

N.	Cereals code	Type of process	Storage days
WHEAT			
1	DVC2	dry cleaning	45
2	DVC3	dry cleaning	45
3	TVU1	dry cleaning	42
4	TVU3	dry cleaning	42
5	DVU1	dry cleaning	44
6	TOC1	dry cleaning	43
7	TOC3	dry cleaning	43
8	DVU3	dry cleaning	42
9	TVU1	dry cleaning	89
10	TVU2	dry cleaning	89
11	TVU3	dry cleaning	89
12	DVC2	dry cleaning	190
13	DVC3	dry cleaning	190
14	DVC2	wet cleaning	190
15	DVC3	wet cleaning	190
16	TOC1	dry cleaning	180
17	TOC3	dry cleaning	180
18	DVU1	dry cleaning	183
19	DVU3	dry cleaning	181
20	TOC1	dry cleaning	365
21	TOC3	dry cleaning	365
CORN			
23	MOC1	wet milling	42
24	MOC3	wet milling	42
25	MOC1	wet milling	182
26	MOC3	wet milling	182
27	MOC1	dry milling	182
28	MOC3	dry milling	182

Table 4 - List of samples collected in the milling process.

Code	Materials and milling phase
Wheat milling with dry cleaning	
G	wheat at the entry
P	cleaned wheat sampled after dedusting, sifting and tempering
D	wheat after the last cleaning phase with scourer (decorticated wheat)
I	impurity deriving from the first cleaning (fine materials, dust, etc.)
R	decortication residues of last cleaning phase
C	bran
S or F	grits or flour
Wheat milling with wet cleaning	
GW	wheat at the entry
PW	cleaned wheat sampled after dedusting, sifting and cleaning with water and before grinding
CW	bran
SW	grits
Corn dry milling	
MDE	corn at the entry
MDP	corn after cleaning
MDI	impurity - fine materials
MDD	degerminated corn
MDM	grinded degermined corn (grits)
MDG	germ
Corn wet milling	
MWE	corn at the entry
MWP	corn after cleaning
MWI	impurity - fine materials
MWW	bating water (slurry)
MWM	corn grinded after soaking
MWD	degermined corn
MWG	germ

RESULTS AND DISCUSSION

The statistical evaluation of the numerous data was carried out by means of factorial analysis of the variance after data division into homogeneous groups in order to obtain, for some factors more significant and specific relationships.

Wheat Milling

The overall data evaluation pointed out a significant dependence of the average residues, observed in milling products, on treatment doses: 1 g/ton dose is higher than others doses (fig. 4).

The dose effect is strongly observed on impurities I and on the decortication residues R; the effect on other milling products is not significant.

The emulsifiable formulation CE leads to average residues in products higher than those of oil formulation ULV at the significancy limit; this aspect is more evident at the lower dose.

Among the materials sampled during the milling it is worth noting:

- there are significant difference between the wheat on entering (G) and the wheat after the first (P) and second (D) cleaning (fig. 4 and 5);

- the highest deltamethrin residues were in the impurity (dust and fine materials)(I) and in decortication residues (R); the difference between the average residue levels of these fractions is significantly higher for the grains treated with CE formulation (from 5.025 to 1.588 mg/kg) than for the ULV formulation (from 3.068 to 3.125 mg/kg);

- for milling products, overall evaluated, no significant difference was observed between the hard and soft wheat;

- the evaluation of data on the milling of wheat TOC1 and TOC3 only, show that the average residue level significantly increase in the storage time; an increase in bran and flour is in particular observed;

FIGURE 4 - RESIDUES IN WHEAT PRODUCTS

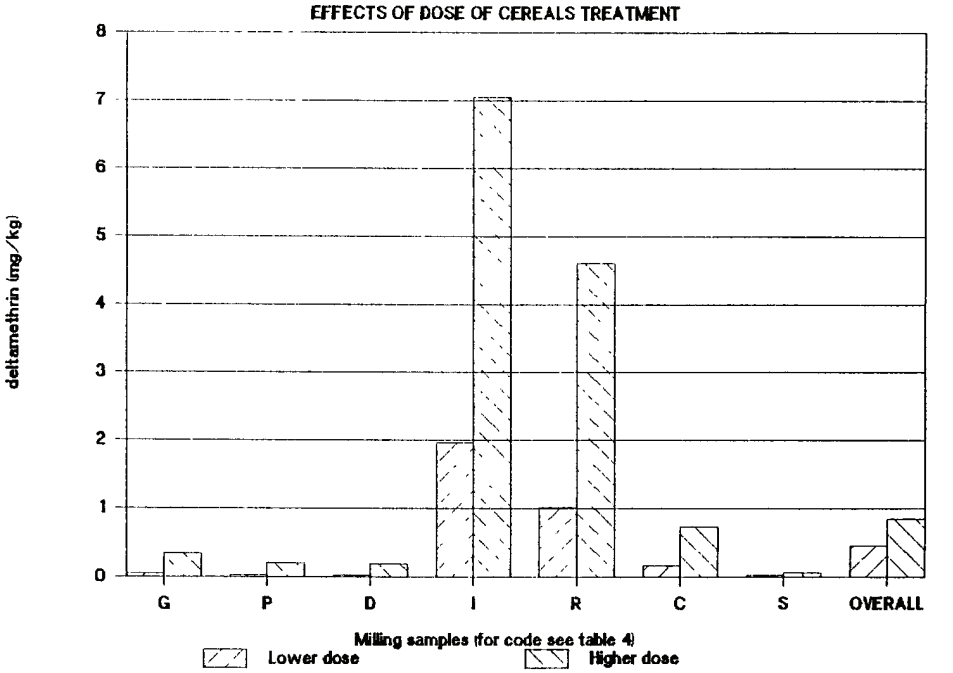
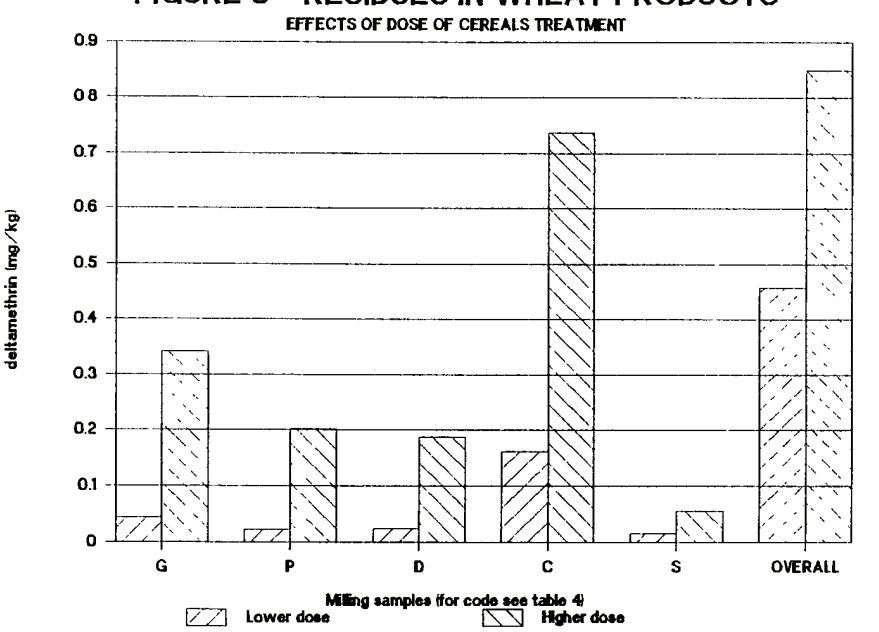


FIGURE 5 - RESIDUES IN WHEAT PRODUCTS



- in the bran the residues were lower than 1 mg/kg for all samples except for bran obtained by milling of soft wheat TOC3, treated with 1 mg/kg of a.i. and stored more than 180 days;

- the wet or dry cleaning do not affect significantly the residue levels in the bran and flour;

- the deltamethrin residues were 2 - 5 time higher on the bran than on the wheat (before every cleaning); the wheat type and storage time affect this ratio, but not significantly;

- among the 83 flour and grits analysed only in 5 samples, all coming from highest treatment rate, residues were higher than 0.100 mg/kg. Most (65%) flour samples produced from wheat treated with normally rates (0.25 and 0.5 g/ton), were with not detectable residues (lower than 0.01 mg/kg).

Pasta- making

Grits and flours with average deltamethrin residues of 0.103 mg/kg were used for the pasta made in a pilot plant. In the produced doughs, in the fresh, dried and cooked pastas and in the cooking water, the residues were not detected (lower than detection limit).

Bread-making

Soft wheat flour with 0.103 mg/kg of deltamethrin average residue was baked in a artisan industry using water, sal and yeast. In the produced bread the residues were not detected.

Corn Milling

In all the samples of meals, grits and germ produced by milling the residue levels greatly vary but were never higher than 0.410 mg/kg (for grits coming from corn treated with the higher dose). In the germ the residues always were lower than 0.1 mg/kg.

Statistical analysis of overall data show:

- no significant difference between the residues at the two different storage time (0.214 and 0.118 mg/kg respectively for 42 and 182 days);

- the significant effect of teatment dose on residue levels in different milling products: 0.218+/-0.170 and 0.082+/-0.088 mg/kg average residues for higher and lower doses respectively;
- the two different milling process (wet and dry) influences not significantly the global deltamethrin residues in collected samples (0.118 and 0.117 mg/kg). The effect was different in the various products considered: the residues were lower on germ and degermined corn in wet than in dry milling; higher on cleaned corn.(fig 6-7)

CONCLUSIONS

The following conclusions may be drawn from the result of this trial:

- deltamethrin is not degradated when treated cereals is milled to produce bran, flour (for wheat), grits and germ (for corn). In the milling process deltamethrin is distributed in the bran, flour, grits and germ fractions;

- the effect of teatment doses of cereals before the storage is strongly on foreign materials, separated in cleaning phase of milling, and decrease from the outer superficial layers (bran) to inner (flour);

- the cleaning step of milling process is very important in the residues reduction: after the cleaning the residue on cereal is reducted to about 50 to 60 %. The deltamethrin residue levels in cleaned cereals are about 10 to 30 % of the applied rate;

- in the production of white flour from deltamethrin teated wheat, there is a reduction in the deltamethrin level to about 10 % of the level applied to the wheat, so detectable only in flour made from wheat treated with higher dose (1 mg/kg);

- in the germ production from treated corn the reduction in deltamethrin level is to 5 % of the level applied to the corn;

- when deltamethrin contaminated flour, made from deltamethrin treated wheat, is transformed in the pasta and bread, there is a reduction of residue lower than analytical detection limit.

FIGURE 6 - RESIDUES IN CORN PRODUCTS

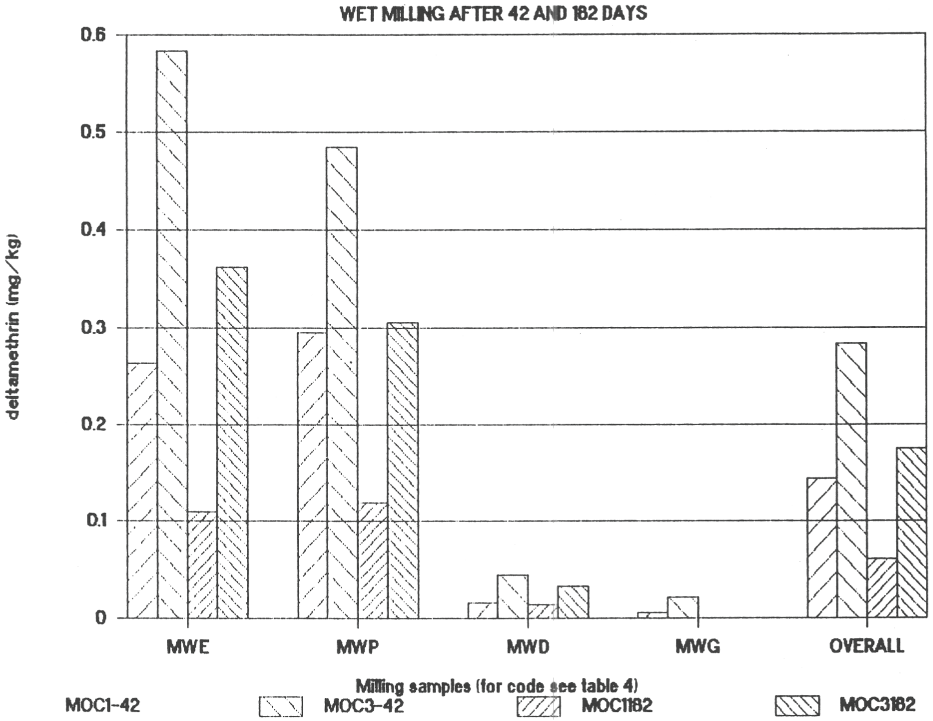
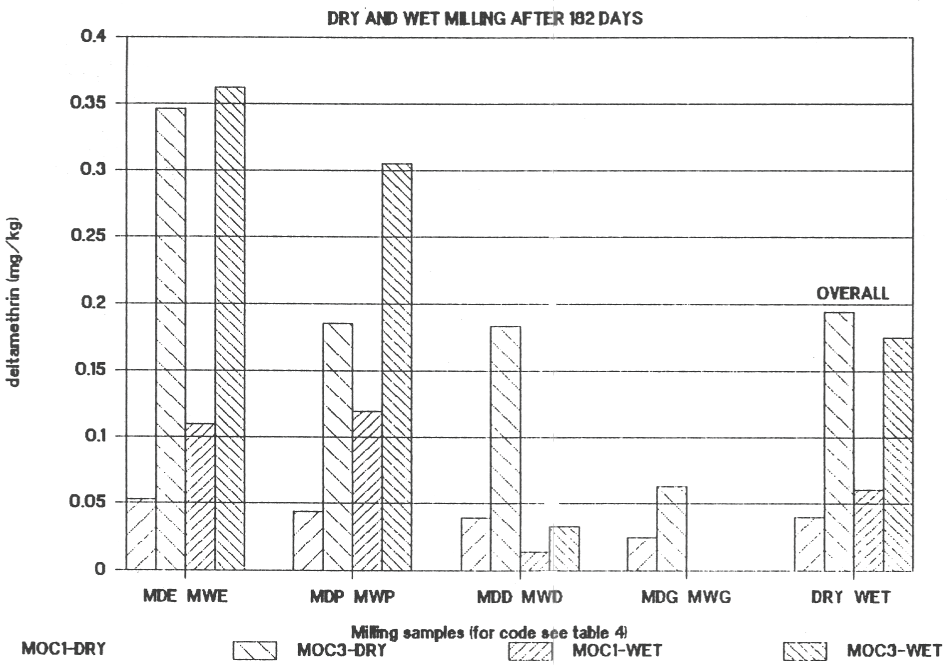


FIGURE 7 - RESIDUES IN CORN PRODUCTS



LES RESIDUS DE DELTAMETHRINE DANS LES PRODUITS PROVENANT DES STOCKS DE CEREALES

Gian Pietro MOLINARI

Istituto di Chimica, Facoltà di Agraria
Università Cattolica di Sacro Cuore, Piacenza, Italia

Résumé

Après le traitement insecticide et avant le stockage des céréales, certains principes actifs restent intacts dans le grain. Ils peuvent alors se retrouver dans les produits dérivés (par ex. : farine, son, pain, pâte, gruau, tourteaux, amidon, huile, etc.). Afin d'évaluer le taux de résidus de deltaméthrine dans l'alimentation, des études ont été entreprises pour connaître le comportement de ces principes actifs (a.i.) au cours de la mouture du blé ou du maïs.

Du blé et du maïs traités ont été stockés en silos et en magasin et, après différentes durées, une tonne de ces céréales a été mélangées à deux moutures du commerce : l'une nettoyée à sec et l'autre en milieu humide. par ce procédé, on obtient de la farine et du son. Les taux de pesticides résiduels ont été mesurés par chromatographie en phase gazeuse dans les céréales avant mouture, dans le produit du commerce, dans les grains nettoyés, dans le son et dans la farine.

Les rèsultats obtenus montrent que le taux de résidus de deltaméthrine le plus élevé se trouvait dans les issues (30 à 60 fois le taux du mélange de blé). Dans la farine, le taux de deltaméthrine était bas (inférieur à 10 % par rapport aux mélanges de céréales) et n'était détectable que dans les céréales traitées à des doses élevées (1 g/ T).