Determination and degradation study of endosulfan, captan and penconazole residues in strawberries

Silvia R. García, Maria R. Repetti, Jaquelina Vierling and Horacio R. Beldoménico.

Central Laboratory, School of Chemical Engineering, UNL, Santa Fe, Argentina

E-mail: srgarcia@fiq.unl.edu.ar

INTRODUCTION

The persistence of the insecticide and acaricide endosulfan (isomers α, β and sulfate) and two fungicides captan and penconazole in strawberry fruit was studied in real operating conditions.
Endosulfan is an organochlorine compound that has emerged as a highly controversial agrochemical due to its acute toxicity (class I-EPA), potential for bioacumulation, and role as an endocrine disruptor. Banned in more than 50 countries, including the European Union,it is still used extensively in many other countries including Argentina, principally in soya. Because of its threats to the environment, a global ban on the use and manufacture of endosulfan is being considered under the Stockholm Convention.
Captan belongs to the nonsystemic phthalimide class and Penconazole is a systemic triazole, both considered slightly toxic (class IV and III-EPA)
The objective of this work was to determine safe pre-harvest intervals that do not exceed national and international MRLs values, because these pesticides are widely used in strawberries farms to prevent various diseases.
The trial was carried out in strawberry orchard of 2,5 hectare, near Santa Fe city (Argentina). The variety under study was ***Camarosa***; the fruit size is medium to small and the yield is 1 kg/plant.
The fruits were in field sprayed once with backpack device at recommended doses, in September 2008. The products and doses were TOPAS (Penconazol 10g/100ml) – 100cm3/100 l/ha, ZEBRA (Endosulfan 25 g/100 ml) – 125 ml/100 l/ha and captan (Captan 80 g/100 g) – 125 g/100 l/ha.
The climatic conditions were registered during the whole experience. Temperature varied between 8 and 24 ºC, the humidity between 30 and 60%, rains did not get registered with sunny days and light winds.

EXPERIMENTAL PROCEDURE

ANALYTICAL METHOD

The pesticides were extracted with the QuEChERS method [1]. The final determination was by GC-ECD
In order to evaluate the efficiency of the analytical procedures, recovery assay was conducted with untreated blank samples of fruits. Fortification of fruits were prepared by spiking with standard solutions to 15 g of sample homogenized to give fortification levels of 0,05 and 0,5 mg/kg, five replicates of each sample and analysed according to the extraction procedure. Satisfactory recoveries between 72 and 118% and relative standard deviations lower than 15% in all cases were obtained. For all studied pesticides the limit of detection was estimated to be 0.02 mg/kg.

SAMPLING [2, 3]

Correct sampling is a difficult process that requires the necessity of obtaining a properly representative sample. We applied the procedure recommended by the FDA by adapting to the particular circumstances of this orchard and learning about the history of pesticides applied and any important information.
The farming has been treated with other pesticides, procedure that the farmer repeated every 7 to 10 days, and we started to take the samples after one programmed application.
The portions collected were representatives of the local harvesting practices (e.g. the damaged fruits were isolated).

The Codex recommends a minimum sample size of 1 kg minimum for small or light fruits of unit weights of 25 g or less (e.g. berries, peas, olives).

The field was divided in an imaginary grid and 18 of these areas were ramdomly selected to form a representative sample. Fruits samples were collected before the application and from 2 hours to 10 days after the application. Each portion was collected in plastic bags and identified with number and date and immediately transported to the laboratory where we made subsampling and stored in refrigerator until the analysis to determine the content and dissipation rate of these pesticides.

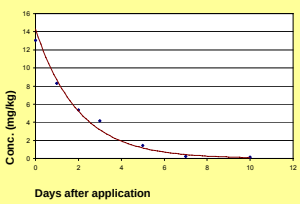
RESULTS

The **MRLs** and **PHI** (pre-harvest interval) are established by Codex Alimentarius Directives (Directive 06/135, **2006**), Official Journal of the European Union (Resolution 396/**2005**) and Boletín Oficial de la República Argentina (Res SAGPYA 507-08, ***2008***, *Nº 31.546).*

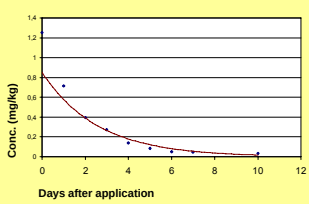
Pesticide	Res. 507/08 MRL (mg/kg)	Codex Alim. MRL(mg/kg)	European Union MRL(mg/kg)	PHI (days)
Captan	15	20	3	5
Penconazole	0.1	0.1	----	----
Endosulfan	1	2	0.05	4

We can observe that in the obtained graphs they obey an approximately exponential tendency with first-rate kinetics (each point represents three replicates with R^2 ranged 0.90 - 0.97) .
As from these data , the residual average life (RL_{50}) was calculated like half-life=(ln 0,5)/k.
Estimated half-lives found were 1.4 days for captan, 1.8 days endosulfan and 2.9 days for penconazole.
Residues of captan were high at the beginning, and ranged from 13 to 0.12 mg/kg; residues of endosulfan between 1.25 to 0.04 mg/kg and residues of penconazole were very low, between 0.12 to 0.04 mg/kg. The results indicated the formation of endosulfan sulfate as a residue component of the fruit and also slowly higher persistence of the β-isomer as compared to the α-isomer.

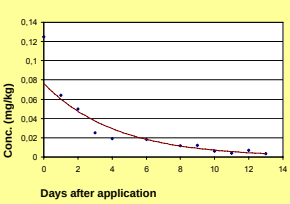
DEGRADATION OF CAPTAN



DEGRADATION OF PENCONAZOLE



DEGRADATION OF ENDOSULFAN (sum of isomers)



CONCLUSIONS

It is known the complexity of the dynamics of dissipation for the amount of variables that intervene. Nevertheless, as this work was accomplished in real conditions, it gives us an approximation to what happens with fruit predestined to internal consumption. We can see the differences in tolerances established by the legislations, but considering this, after the pre-harvest interval all pesticides residues were within the limits established by even the most rigurous laws (EU).

REFERENCES

[1] Lehotay, S.J. et. al., *J AOAC Intern* 88 (**2005**) 615-629.
[2] FAO - CODEX - ALINORM 99 - 23. Methods and sampling.
[3] ISO 874 - 1980 (E). Fresh fruits and vegetables sampling.

AKNOWLEDGEMENTS

UNL CAI+D: Nº 33-185 (2007-2008)