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FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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DISCUSSION PAPER ON THE EVALUATION OF DISTRIBUTION OF PESTICIDE RESIDUES AFTER PRIMARY PROCESS IN CITRUS FRUIT, POME FRUIT, OILSEEDS AND WINE GRAPES

Prepared by the European Community

INTRODUCTION

Primary processed food (PPF) are those products resulting from the application of physical, chemical or biological processes or combination of them to raw agricultural commodities (RAC) intended for direct sale to the consumer or for direct use as an ingredient of secondary processed commodities.

So far and with the exception of some specific commodities such as spices, there is no international agreement on the setting of maximum residue levels (MRLs) for primary processed commodities; although in some countries (e.g. the EU countries) the common practice is to derive them from the MRL set in the RAC, applying the correspondent processing factors.

With the increased international trade in processed products, there is a need for guidance on when a processing study should be required, how to derive and apply the processing factor and in which situations it should be applied.

Many PPF are circulating in international trade in big volumes and in many cases they constitute a mayor component in the diet of certain groups such as children. These two characteristics make them important enough to be considered as candidates for MRL setting.

The present study is focused on the distribution of pesticide residues in the PPF compared with pesticide residues from the RAC. The processing studies are performed on three main PPFs:

(i) Fruit juice: apples and oranges

(ii) Alcoholic beverages: wine from grapes

(iii) Oils: olive oil.

GENERAL CONSIDERATIONS

1. Processing factors are very much affected and depend on the processing yield. For primary processed fruits its value varies usually between 15 to 60 % depending on the industrial or domestic process applied on the RAC and nature of the commodity. In general for fruits with non-edible peel (e.g.: oranges) or stone fruits (e.g.: olives) the yield is lower. Therefore, the processing factor should be considered as a combination of the process and the commodity.

2. The destiny of the processed fraction is also important and related to point 1. Juice, oil and syrups are the relevant fractions for human consumption while pulp and waste products for feed. These different fractions have important physico-chemical properties (hydrophilic/lipophilic) with respect to the pesticide residue distribution. These properties may help in setting default processing values.
3. Other pesticide characteristics such as the distribution of the pesticide on the commodity depending on the use pattern e.g. surface or systemic pesticide, or its application in pre or post-harvest treatments are also relevant.
4. All these reasons and the complexity of some pesticides make it very difficult in many cases to consider a single or combined theoretical value.

EXPERIMENTAL STUDIES

I.- Juice processing studies on apples and oranges.

Twenty pre-harvest and three post-harvest pesticides were studied. The distribution rates on the juice were around 20%. In some cases the pesticide residues concentration was below the detection levels of the analytical method. As the processing yields evaluated were in the range of 40 to 65%, the final concentration of the residues per liter of juice was lower or much lower than in the RAC in the majority of the cases. A good mass balance was obtained considering all the processed fractions. In the case of post-harvest pesticides on oranges, they were concentrated on the peel around 5-10 times higher than in the fresh pulp.

II. Wine processing studies

Fourteen residues of most common pesticides applied in wine grapes, were studied.

The distribution rates on the wine were variable depending on the pesticide. The variation was from 40% in some cases to 10% in the majority of the cases. Furthermore, the levels found of some residues were below the limit of detection of the analytical method. Considering processing yield from 50% to 30%, the final value per liter of the residues studied was from 1.30 the RAC MRLs to a lower or much lower concentration. The most important process that affect to the residue distribution is the obtaining process of grape juice must, that is the previous stage before fermentation process.

III. Oil processing studies in olives

Three of the main Spanish olives varieties called; Hojiblanca, Arbequina and Picual were evaluated with 16 pesticides commonly applied on olives for oil production. The processing yields of the different olive varieties may vary from 12 to 21% depending on the variety, mature status, time of the harvest, etc. These facts produce different pre-concentration factors of the residues in the oil produced. The final concentration of the residues studies per liter goes from 6 times higher in some insecticides with very high Kow to lower or much lower values, in some herbicides.

CONCLUSIONS

1. The Factors affecting the concentration or dilution of pesticide residues in the PPF are various: the different industrial or domestic process applied to the RAC, the nature of the commodity (with edible or inedible peel), final use of the PPF (food or feed), the way on which the pesticide is applied and the interaction of the residues with the plant metabolism.
2. In the juice studied cases from citrus and pome fruits, a decrease of the residues present in the RAC (dilution) was the general processing trend. It means processing factors (PF) below 1. In general, the PF values for juices were in the range of 30 to 20% of the total residue in the RAC but lower values were also possible. It is mainly due to the favorable distribution/adsorption of the residues on the solid fase of the PPF obtained.
3. In the case of wine on which the production yield was around 70%, PF values are between 1 to 0.5. This is the case of those pesticides with low Kow and high water solubility. As an average, the PF values are around 20 % of the studied pesticide residues in the RAC. Fermentation process does not seem of great importance in pesticide residue degradation or elimination.

4. In the case of olive oil, where the production yield was around 20%, an important increase of residue levels occurred (concentration) from 2 to 5, related to the Kow value of the pesticides applied. The PF value can be even higher, up to 6, in specific pesticides with very high Kow values (fat soluble) and specific olive varieties.

5. For risk assessment purpose, a rough estimation of the pesticide distribution (mass balance between the different sub-products obtained after process) could be performed for the three different types of PPF studied in this experiments by the EU Community Reference Laboratory for Pesticide Residues in Fruit and Vegetables.

6. For further consideration by the CCPR:

   a. The topic of setting MRLs on processed commodities (e.g. milk powder). So, some processed commodities to be considered as "raw commodities".

   b. The risk of most frequent transformation products after industrial process from pesticide residues present on the RAC and the need to take them into account when setting MRLs in the RAC.

Annex: Log Kow and water solubility of pesticide used in the experiments

Olives		
Pesticide	**Log K_{OW}**	**S_w**
Chlorpyriphos	4.70	1.4
α-Endosulfan	4.74	0.32
β-Endosulfan	4.79	0.33
Oxyfluorfen	4.47	0.12
Diflufenican	4.9	0.05
β-Cyfluthrin	5.9	0.0012
Terbuthylazine	3.21	8.5
Malathion	2.75	145
Methidathion	2.2	200
Phosmet	2.95	25
α-Cypermethrin	6.6	0.004
Difenoconazole	4.2	15
Diuron	2.85	36.4
MCPA	-0.71	273,9

Grapes		
Pesticide	**Log K_{OW}**	**S_w**
Imidacloprid	0.57	610
Dimethoate	0.7	23800
Acetamiprid	0.8	4250
Carbendazim	1.51	29
Carbaril	1.85	120
Thiabendazol	2.39	30
Azoxystrobin	2.5	6
Dimethomorph	2.7	18
Procymidone	3.14	0,018
Kresoxim methyl	3.4	2
Penconazole	3.72	0,00017
Imazalil*	3.82	180
Cyprodinil*	4	0,00051

Apple and Orange		
Pesticide	**Log K_{OW}**	**S_w**
Acetamiprid	0.8	4250
Azoxystrobin	2.5	6
Carbaril	1.85	120
Carbendazim	1.5	29
Dimethoate	0.7	23800
Fenhexamid	3.51	20
Fenoxicarb	4.07	7.9
Fluquinconazole	3.24	1
Imazalil	4.6	180
Iprodione	3.0	13
Metalaxyl	1.75	8400
Myclobutanil	2.94	142
Omethoate	-0.74	10000
Pirimicarb	1.7	0,0004
Pyrimethanil	2.84	0,0022
Tebufenozide	4.25	0,83
Thiabendazole	2.4	30
Thiacloprid	1.26	185
Triadimefon	3.11	64
Triadimenol	3.08, 3.28	62, 33