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University of Minnesota
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SESSION IV: THE QUALITY OF AGRICULTURAL PRODUCTS AND HUMAN HEALTH

PAPER 7: QUALITY ASSURANCE OF AGRICULTURAL PRODUCTS AND HUMAN HEALTH: PESTICIDES RESIDUES IN GRAPES, WINES AND VEGETABLES

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QUALITY ASSURANCE OF AGRICULTURAL PRODUCTS AND HUMAN HEALTH: PESTICIDES RESIDUES IN GRAPES, WINES AND VEGETABLES

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INTRODUCTION

Quality Assurance is defined according to ISO 9000, i.e. rules, regulations and guidelines about Quality Systems, as "the whole of activities that management carry out for a periodical audit and improvement of the Company Quality System".

In order to achieve maximum quality in manufacturing field the attention of companies progressively shifted from *product quality*, that means control of the final products only, to *process quality*, stressing the importance of control at each critical step of production process, to *system quality* which needs the co-operation of everyone involved in production, from ones who are responsible of production means achievement to final consumer in order to find out inefficiencies and continuously improve consumer satisfaction.

Agriculture is in delay; to date in the agricultural sector the attention has been drawn on the quality of the product whereas the quality of process, or even better of the food system, has been neglected.

The sustainable farming approach is one step ahead in this direction because it does not take into account only the final products but mainly the agronomic techniques consequences on the productive process, on the environment and on the quality of the product.

In the Veneto Region the "Quality as a System" approach in the food sector has just started; one first step forward was the institution of a regional trademark, which is named "Paniere Veneto", as a guarantee of healthy and hygienic products.

The Agrochemical Centre laboratories of the Regional Organisation for Agricultural Development asked for and obtained the accreditation according with the ISO 9000 and the EN 45000 in order to be ready in working for farms or food companies which want to start applying the Quality System approach.

An investigation was carried out between September 1992 and December 1993 to check the pesticides residues content of grapes at harvest time ond of wines before bottling in some vineries that asked to use the regional trademark. Part of grapes samples came from one single farm while another part came from different farms delivering the harvest to the same vinery. All farms were applying the Integrated Pest Management and using only pesticides allowed by the protocol of regional trademark.

Another type of control activity were realized in 1993 collecting vegetables samples in a group of about 30 farms managing horticoltural crops with the same constraints pointed out for vine farms.
A series of analysis were performed on some grapes, wines and vegetables that came from farms of the Region of Veneto; here is a review of results in order to verify if application of process control, particularly through Integrated Pest Management, could give sufficient guarantees for hygienic quality of products.

METHODS

The enquiry involved 25 farms placed in various Veneto areas for two years (1992 and 1993) for grapes, for one year only (1992) for wines, whereas 30 farms for two years for vegetables, the last of which (1994) is still under way.
The samples have been collected from farms by few operators following methods previously agreed with the Agrochemical Centre in order to guarantee homogeneous results.
51 grapes and 46 wines samples in the first year, 71 grapes in the second year and 78 vegetables in 1993 were tested.
All pesticides residues have been analyzed by homogenizing, extracting and purifying the samples and by singling out the residues by means of gas chromatography, EC and NP Detectors.
In grapes and wines we looked for the pesticides residues showed in table1.
As for vegetables, different pesticides have been considered according to their species and phytopathological risks; we looked for the pesticides residues showed in table 2.:

RESULTS AND DISCUSSION

Grapes and wines

In the first year of enquiry grapes and corresponding wines have been tested in order to check the dynamics of residue degradation during the wine-making process.
The samples analyzed in the first year revealed no trace of the following pesticides: Benalaxyl, Chlozolinate, Cymoxanyl, Diclobutrazolo, Esaconazolo, Myclobutanil, Oxadixyl, Penconazolo, Triadimephon; in the following year no further search for these pesticides (with the exception of Chlozolinate) has been carried out.
No amount exceeding the law limit has been observed for any pesticide.
The pesticides for which residues have been observed are showed in table 3.
Some considerations comes up from results:
1) There is a great decreasing of residues level from grapes to wines; infact while 40 samples of grapes on 51 had residues greater than detectability limit, only 7 samples of wines on 46 had them;
2) Very few samples had residues greater than 20% of law limit; for grapes, excluding ditiocarbammates that easily and fastly decompose after harvesting, only 3 samples on 51 had it, while no sample of wine had it.

3) Most problematic pesticides seem to be dicarbossimides (iprodione, procymidone, vinclozolin) which residues are found in many samples (26 on 51 for grapes), and particularly the only found in wines (7 on 51).

It is important to underline that out of a total of 64 cases of pesticides residues present in grapes, only 10 were exceeding one fifth of the law limit and therefore can be easily eliminated during the transformation process; this is proved by the fact that in wines only one case of pesticides residues presence was detected and only in an amount 200 times lower than the law limit.

Considering the presence of fungicides and insecticides in grapes and wines the situation showed in figure 1 ensues.

During the wine-making process there is a considerable drop in pesticides residues present in grapes (from 40 to 8 positive samples) - an event often reported in bibliography - thereby allowing a sufficient degree of safety in the hygienic quality of wine when grapes are produced following the principles of integrated pest management (IPM) requested by the Paniere Veneto Consortium for the use of trademark. The very low number of samples with insecticides residues demonstrates that farmers use spring insectides only if there is a rela damage risk, as suggested by IPM.

A similar analysis was carried out on the content of some heavy metals (copper and lead) in grapes and wines; the results - an average of tested samples - are shown in figure 2.

It is clear that there is a strong decrease in copper and lead contents during grape-wine transformation; they probably are captured by organic compounds and through away with refuse substances. Infact copper drop down from 6.69 to 0.136 ppm and lead from 0.256 to 0.006 ppm that is fifty times lower for both elements.

In order to confirm these results an enquiry campaign was carried out also in 1993 only on 71 grapes samples; the results are shown in table.

There is a percentage reduction from 1992 to 1993 in samples with pesticides residues, even if some pesticides, DTC and Folpet, have been detected in large amounts given by the scarce spring-summer rainfall that did not exert a sufficient cleansing action over the crops.

Vegetables

The following pesticides were not detected on vegetables: Azinphos Methyl, Benalaxyl, Carbaryl, Cyflutrin, Dicloran, Fenarimol, Fluvalinate, Heptenophos, Iprodione, MBC, Parathion Methyl, Permetrina, Pirimicarb, Procymidone. The vegetables samples results are shown in table 5.

Out of a total of 807 tests carried out, only 40 cases (5%) have been detected to have residues of the searched pesticide and among these, amounts greater than 20% of law limit have been detected only for Dithiocarbammates (DTC); considering that DTC is easily degraded (for example by photodegradation) it is possible that in the time period between sampling and selling the content can be considerably reduced, furthermore a simple washing can remove it from the products.

Such results were achieved because the farms taken into consideration are associated and included in an organization that provide qualified services (such as qualified production means supply, assistance in integrated pest management and in use of pesticides, assistance in farm management and product

sale and marketing, etc.) to farmers; the organization, appropriately supported with documentary evidence may become a Quality System as intended by ISO 9000.

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Pesticides	*1992 (wines also)*	*1993 (grapes only)*	*Law limit (ppm)*	*Detectability limit (ppm)*
Benalaxyl	yes	no	0.5	0.05
Chlozolinate	yes	yes	5	0.02
Cymoxanyl	yes	no	0.1	0.01
Diclobutrazole	yes	no	0.3	0.05
Diclofluanide	no	yes	10	0.05
DTC	yes	yes	4	0.4
Fenitrothion	yes	no	0.5	0.02
Folpet	yes	yes	3	0.025
Hesaconazole	yes	no	0.1	0.03
Iprodione	yes	yes	5	0.05
MBC	no	yes	not allowed	0.001
Metalaxyl	yes	no	1	0.05
Myclobutanil	yes	no	0.2	0.03
Oxadixyl	yes	no	1	0.1
Parathion Methyl	yes	no	0.5	0.02
Penconazole	yes	no	0.1	0.025
Procymidone	yes	yes	1.5	0.02
Triadimephon	yes	no	0.5	0.1
Vinclozolin	yes	yes	3	0.01

Table 1 - Pesticides residues searched in grapes and wines, italian law limit and detectability limit.

Pesticides	*Crops*	*Detectability limit (ppm)*
Azinphos Methyl	String beans, Chicory	0.015
Benalaxyl	Lettuce, Pepper	0.05
Carbaryl	Eggplant	0.1
Chlortalonil	Tomato, String beans, Pepper, Chicory	0.05
Cyflutrin	Eggplant, String beans	0.1
Deltametrina	Lettuce, Eggplant, String beans, Pepper, Chicory	0.1
Dicloran	Lettuce, String beans, Chicory	0.05
DTC	Lettuce, Eggplant, String beans, Pepper	0.4
Fenarimol	Chicory	0.01
Fluvalinate	Lettuce, Eggplant, String beans, Pepper, Chicory	0.1
Heptenophos	Lettuce, Pepper	0.01
Iprodione	Lettuce, Tomato, Eggplant, Pepper, Chicory	0.05
MBC	Lettuce, Chicory	0.001
Metalaxyl	Lettuce, Tomato, Pepper	0.05
Parathion Methyl	String beans, Chicory	0.02
Permetrina	Lettuce, Eggplant, String beans, Pepper, Chicory	0.1
Pirimicarb	Lettuce, String beans, Pepper	0.1
Procymidone	Chicory	0.02
Vinclozolin	Lettuce, Tomato, Eggplant, String beans, Pepper, Chicory	0.01

Table 2 - Pesticides residues searched in vegetables, and detectability limit.

Pesticide	*Number of samples with residues greater than Detectability limit*		*Number of samples with residues greater than 20 % of law limit*	
	Grapes	*Wines*	*Grapes*	*Wines*
Fenitrothion	1	0	1	0
Folpet	8	0	0	0
Iprodione	3	6	1	0
Metalaxyl	2	0	0	0
Parathion Methyl	3	0	0	0
Procymidone	8	0	1	0
Vinclozolin	15	1	0	0
DTC	24	n.d.	7	n.d.

Table 3 - Number of samples with pesticides residues greater than detectability limit or greater than 20% of law limit for listed pesticedes in grapes and wines analyzed in 1992.

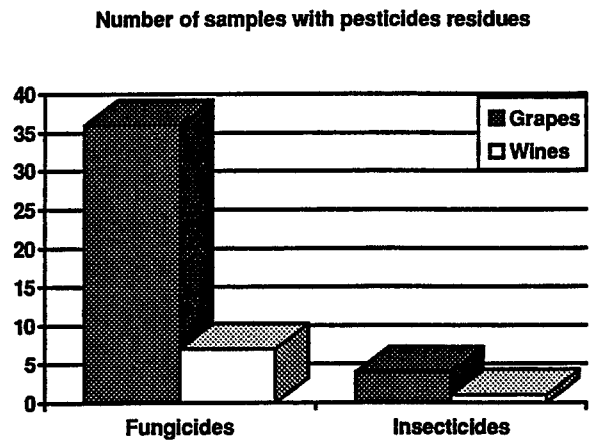

Figure 1 - Number of samples with pesticides residues classified by fungides or insecticides in grapes or wines analyzed in 1992.

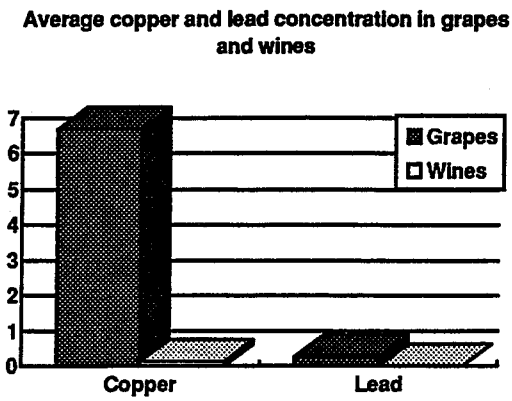

Figure 2 - Average concentration (ppm) of copper and lead in grapes and wines analyzed in 1992.

Pesticides	*Number of samples with residues greater than Detectability limit*		*Number of samples with residues greater than 20 % of law*	
	1993	*1992*	*1993*	*1992*
Folpet	11 (15%)	8 (17%)	3	0
Iprodione	9 (13%)	3 (6%)	1	1
Chlozolinate	1 (1%)	0	0	0
Procymidone	1 (1%)	8 (17%)	0	1
Vinclozolin	15 (21%)	15 (33%)	0	0
DTC	30 (42%)	24 (52%)	14	7

Table 4 - Number of samples with pesticides residues greater than detectability limit or greater than 20% of law limit for listed pesticedes in grapes and wines analyzed in 1992 and 1993.

Vegetable	*N. of samples*	*DTC*	*Vinclozolin*	*Deltametrina*	*Chlortalonil*	*Metalaxyl*
Lettuce	20	12 (7)	3 (0)	1 (0)	0	1 (0)
Tomato	9	0	2 (0)	0	4 (0)	0
Eggplant	12	6 (2)	0	0	0	0
Pepper	9	2 (2)	1 (0)	1 (0)	0	0
String bean	5	1 (0)	1 (0)	0	0	0
Chicory	23	0	5 (0)	0	0	0
TOTAL	*78*	*21 (11)*	*12 (0)*	*2 (0)*	*4 (0)*	*1 (0)*

Table 5 - Number of samples with pesticides residues greater than detectability limit or greater than 20% of law limit for listed pesticedes in vegetables analyzed in 1993; numbers of samples with pesticides residues greater than 20% of law limit are reported in parenthesis.