AZINPHOS-METHYL (002)

EXPLANATION

Azinphos-methyl was originally evaluated in 1965 and has been reviewed on several occasions since. In 1991 the JMPR required additional data by 1993 to support the CXL for grapes. These data were not available to the 1993 Meeting, which was informed that data from trials on grapes in Germany and Italy, including processing studies, would be available for the 1995 Meeting. In 1993 the CCPR recommended deletion of the CXL and it was subsequently deleted by the CAC.

At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis for almonds and wheat (ALINORM 95/24, para 68). Several delegations observed that the database was not sufficient to establish MRLs for wheat. The proposed MRLs for almond and wheat were held at step 7B pending the review of written comments by the JMPR.

METHODS OF RESIDUE ANALYSIS

Plant material. Samples of plant material are extracted with acetone and after filtration the extract is evaporated to an aqueous remainder. Following the addition of distilled water the extract is added to a solid phase extraction column and the column eluted with ethyl acetate. The ethyl acetate eluate is concentrated, dissolved in cyclohexane and cleaned up on a silica gel column. After transfer of the relevant solvent fractions into ethyl acetate determination is by GLC with an FPD. This method was also suitable for the determination of demeton-S-methylsulphon. Recovery data were provided for apples, pears, peaches, grapes, must, wine, sugar beet, nectarines and potatoes as given in Table 1. (Seym, 1992a,b).

Table 1. Analytical recoveries of azinphos-methyl.

Substrate	Recovery, %	RSD[1]	LOD (mg/kg)	Reference
Apple	83-104	not specified	0.04	(Seym, 1992a)
Pear	74-90	not specified	0.04	(Seym, 1992a)
Peach	84-100	not specified	0.04	(Seym, 1992a)
Grapes - bunch segment	73-103	RSD 13.2	0.04	(Seym, 1992b)
Grape - must	72-85	RSD 8.7[2]	0.04	(Seym, 1992b)
Grape - wine	100-106	RSD 11.9[2]	0.04	(Seym, 1992b)
Sugar beat - root	81-88	not specified	0.04	(Seym, 1992b)
Sugar beat - leaf	89-98	not specified	0.04	(Seym, 1992b)
Nectarine	87-105	not specified	0.04	(Seym, 1992b)
Potato	81-93	not specified	0.04	(Seym, 1992b)

[1] Relative standard deviation
[2] These values were taken from the Italian residue trials report. (Seym, 1993)

USE PATTERN

Extensive information on GAP for the use of azinphos-methyl was given in the 1991 monograph. Information provided to the present Meeting on additional or amended GAP is shown in Tables 2 and 3.

Table 2. Registered uses of azinphos-methyl for grapes. WP formulation.

Country	Application				PHI, days	Reference
	Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.		
Germany	spray	0.26-0.82	0.016-0.051	1	49	Germany, 1994
Italy	spray	0.3-0.7[1]	0.0375-0.05	2	20	Thomas, 1995
New Zealand	HV spray to run-off	up to 1.0	0.0375-0.05	6-9	14	Lunn, 1995

[1] Calculated on the basis of a stated water volume of 800-1400 l/ha

Table 3. Registered uses of azinphos-methyl for commodities other than grapes.

Crop	Country	Form	Application				PHI,	Ref.
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	days	
Apple	Peru	EC	spray	0.4-1.5[1]	0.2-0.25	unspecified		Pastor Talledo, 1994
Apple and pear	Netherlands	WP	spray	0.375-0.56	0.0375	1-3[2]	21	Olthof, 1995
Apple and pear	Netherlands	WP[3]	spray	0.3-0.45	0.03	1-3[2]	21	Olthof, 1995
Apple and pear	New Zealand	WP	HV spray to run-off	up to 1.5	0.0375- 0.05	7-10	14	Lunn, 1995.
Potato	Netherlands	WP	spray	0.25	0.042-0.125[1]	1-2[2]	28	Olthof, 1995
Potato	Peru	EC	spray	0.375-1.2	0.25-0.4	unspecified		Pastor Talledo, 1994
Rice	Peru	EC	spray	1	0.4	unspecified		Pastor Talledo, 1994
Stone fruit - apricots, cherries, nectarines, Peaches & plums	New Zealand	WP	HV spray to run-off	up to 1.5	0.0375- 0.05	5-8	21 (Peach & apricot) 14 (other stone fruit)	Lunn, 1995.
Tomato	Peru	EC	spray	0.5	0.25	unspecified		Pastor Talledo, 1994

[1] Calculated from the water volume given
[2] Interval of 10 days between applications
[3] Formulation combined with propoxur

RESIDUES RESULTING FROM SUPERVISED TRIALS

Grapes. The 1991 monograph reported six US trials in which residues following treatment at 0.84 kg ai/ha were 0.22-3.37 mg/kg in samples taken 14 days after the last treatment. US GAP involves a maximum application rate of 1.1-1.2 kg ai/ha with a PHI of 10 days (WP) or 7 days (EC). The 1991 Meeting concluded that the additional residues data were insufficient to propose an amendment to the CXL which existed at that time.

Four new Italian supervised trials conducted according to Italian GAP (0.3-0.7 kg ai/ha) were available from the manufacturer. Residues were <0.04-0.61 mg/kg at the GAP PHI of 20 days as shown in Table 4.

Table 4. Residues in grapes from Italian supervised trials (1992).

Region	Application	Sample	Residues, mg/kg, after PHI,	Ref.

						days				
	Form	No.	kg ai/ha	kg ai/hl		0	7	15	20	
Ravenna	WP	2	0.5	0.05	grape[1]	0.41	0.35	0.10	<u><0.04</u>	Seym, 1993
					must	-	-	-	0.06	
					wine	-	-	-	<0.04	
Ravenna	WP	2	0.5	0.05	grape[1]	0.47	0.24	0.21	<u>0.07</u>	Seym, 1993
					must	-	-	-	0.09	
					wine	-	-	-	<0.04	
Bisceglie	WP	2	0.5	0.05	grape[1]	-	-	-	<u>0.61</u>	Seym, 1993
Andria	WP	2	0.5	0.05	grape[1]	-	-	-	<u>0.25</u>	Seym, 1993

Underlined results are from treatments according to GAP
[1] The laboratory samples consisted of "segments of bunches of grapes"

Data from residue trials on Brussels sprouts were submitted but have not been evaluated as part of this review (Olthof, 1995).

The new Italian trials indicate that the residues resulting from Italian GAP are likely to be lower than those resulting from US GAP.

<u>Wheat</u>. The 1991 JMPR recommended an MRL of 0.2 mg/kg for wheat, based on trials conducted in the USA. At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis for wheat and almonds. Information was supplied indicating that in older azinphos-methyl studies residue analyses of many crops, among them almonds and wheat, were carried out by a colorimetric method in which the hydrolysis product anthranilic acid was determined. The method was quite unspecific and other hydrolysis products were capable of interfering with the quantification of azinphos-methyl. The manufacturer has stated that "newer studies on both crops have been performed using more specific analytical methods. The results of these studies show that the residues detected are considerably lower then previously assumed." (Thomas, 1994).

Analyses in the US residue trials reported in the 1991 monograph with references M80093-80094, M80110-80113 and M80161 were by the older colorimetric method. The seven remaining residue trials with references M69585-69589 and M80955-80956 were with the new specific method of analysis.

In addition to the question about the method of analysis several delegations at the 1994 CCPR observed that the database was not sufficient to establish an MRL for wheat. Of the seven trials with the new specific method of analysis, samples were taken 34-38 days (1 trial), 48-52 days (2 trials), 59 days (1 trial) and 71-75 days (3 trials) after the final application. GAP has been reported for Canada and Mexico in which the recommended PHI is 30 days. Only one trial included a PHI (34-38 days) close to that of GAP, with residues of <0.02 and 0.2 mg/kg in the grain and straw respectively.

<u>Almonds</u>. The 1991 JMPR recommended an MRL of 0.3 mg/kg for almonds, based on trials conducted in the USA. At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis. Information supplied confirmed that the results obtained with the colorimetric method were unreliable (see wheat above).

Two series of trials were reported in the 1991 JMPR monograph. Trials with references M46359-46364, M52654-52655 and M66738-66739 used the older colorimetric method. Residues from these trials were reported as <0.10-0.21 mg/kg in the kernels and 0.72-8.24 mg/kg in the hulls. It is these trials which appear to have been used to support the MRL of 0.3 mg/kg.

The 24 trials in the 1991 monograph with report references M69959-69982 were with the new

specific method of analysis. Residues were reported as <0.02-0.04 mg/kg in the kernels and 0.04-3.65 mg/kg in the hulls. (Thomas, 1995b).

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were submitted.

In processing

Data were provided on the residues following the processing of grapes into must and wine as part of two of the Italian residue trials (see Table 4). When grapes containing residues of <0.04-0.07 mg/kg were processed the residues in must and wine were 0.06-0.09 and <0.04 mg/kg, respectively. However the experimental details of the processing were submitted too late for full consideration by the Meeting and were in the form of a draft translation (Seym, 1993).

Residues in the edible portion of food commodities

No data were submitted, but none would be required for grapes.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Results of random monitoring analyses undertaken by the Australian Department of Primary Industries and Energy between 1 January 1989 and 30 June 1992 are shown in Table 5. Sampling of fruit and vegetables was of the whole item, excluding stones, stems, crowns etc. (Coleman, 1995).

Table 5. Australian monitoring data for azinphos-methyl.

Commodity	Residue, mg/kg	Number of samples
grapes	<0.1	228
	0.1-0.4	1
	TOTAL	229
broccoli	<0.1	4
Brussels sprouts	<0.1	12
cabbage	<0.1	67
capsicum (peppers), whole	<0.1	3
carrot	<0.1	84
cauliflower	<0.1	70
celery	<0.1	8
citrus fruit	<0.1	88
cucumber	<0.1	20
dried tree fruits	<0.1	52
dried vine fruits	<0.1	98
Grapes, fresh	<0.1	248
lettuce, whole	<0.1	69
melons, whole	<0.1	20
nectarines, whole	<0.1	4
papaws	<0.1	6
Peaches	<0.1	8
Pears	<0.1	355
	trace only	3
	<0.1 - 0.4	7
	TOTAL	366
plums	<0.1	2
Potatoes	<0.1	112
pumpkin	<0.1	31
raspberry	<0.1	3
strawberry	<0.1	14
tomato	<0.1	43
zucchini	<0.1	22
onion, whole	<0.1	442

NATIONAL MAXIMUM RESIDUE LIMITS

Table 6. National MRLs for azinphos-methyl in grapes (Thomas, 1995).

Country	MRL (mg/kg)
Australia	2
Belgium	1
Canada	5
Chile	4
France	1
Germany	1
Greece	1
Italy	1
Kenya	4 (temporary)
Luxembourg	1

Country	MRL (mg/kg)
Malaysia	4
Mexico	5
Netherlands	1
Portugal	1
South Korea	1
Spain	1
Taiwan	0.5
Turkey	0.5
UK	2
USA	5

Coleman (1995) and Olthof (1995) reported the Australian and Netherlands national MRLs, respectively, for other commodities. These were the same as reported in the 1991 JMPR monograph and are not reproduced here.

APPRAISAL

Azinphos-methyl was originally evaluated in 1965 and has been reviewed on several occasions since. In 1991, the JMPR carried out an extensive re-evaluation and required additional data by 1993 to support the Codex maximum residue limit (CXL) for grapes. These data were not available to the 1993 Joint Meeting, which was informed that data from trials on grapes in Germany and Italy, including processing studies, would be available for the 1995 Meeting. In 1993 the CCPR recommended deletion of the CXL and it was subsequently deleted by the CAC.

At the 1994 CCPR, the delegation of Germany questioned the accuracy of the method of analysis for almonds and wheat (ALINORM 95/24, para 68). Several delegations observed that the data were not sufficient to establish an MRL for wheat. The proposed MRLs for almonds and wheat were held at step 7B pending the review of written comments by the JMPR.

An analytical method suitable for plant material was submitted together with validation data for a number of crops. Determination was by GLC with an FPD with a reported limit of determination of 0.04 mg/kg.

Information on GAP was supplied by Germany, Australia, New Zealand and the manufacturer. Information from Australia on monitoring analyses of a large number of commodities showed that residues were all below the limit of determination (<0.1 mg/kg) except in one grape sample of 229 (reported within the range 0.1-0.4 mg/kg), and seven pear samples of 366 (<0.1-0.4 mg/kg).

Grapes. The 1991 monograph reported six US trials, carried out in one season, in which residues following treatment at 0.84 kg ai/ha were 0.22-3.37 mg/kg in samples taken 14 days after the last treatment. GAP in the USA requires a maximum application rate of 1.1-1.2 kg ai/ha with a PHI of 10 days for WP and 7 days for EC. The 1991 Meeting concluded that the additional residues data were insufficient to propose amendment to the CXL of 4 mg/kg for grapes and that residues data from countries other than the USA were desirable.

New Italian supervised trials conducted according to Italian GAP were available from the manufacturer. Residues were <0.04-0.61 mg/kg at a PHI of 20 days. However only four trials were available, conducted at three locations. The Meeting agreed that the six US trials could not support a

recommendation because a combination of the low application rate and the longer PHI used in these trials might lead to an underestimate of the maximum residue, and concluded that the data were insufficient to recommend an MRL for such an important commodity. The Meeting was informed that the manufacturer was considering carrying out further trials on grapes in Southern Europe.

The new Italian trials indicate that the residues resulting from Italian GAP are likely to be lower than those resulting from US GAP.

Wheat. At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis used and the MRL of 0.2 mg/kg recommended by the 1991 JMPR. In addition, several delegations observed that the data were not sufficient to establish an MRL for wheat. Information was brought to the attention of the Meeting that indicated that the accuracy of the old colorimetric method of analysis used in some of these trials was inadequate. Although a new specific method of analysis was used in seven of the US wheat trials only one of the trials included results at the PHI reported as Canadian and Mexican GAP (30 days). In the other six trials the PHIs were 48-75 days. The Meeting recommended that the MRL for wheat should be withdrawn.

The 1991 JMPR had recommended the MRL for wheat to replace the CXL for cereal grains, which it concluded was not adequately supported.

Almonds. At the 1994 CCPR the delegation of Germany questioned the MRL of 0.3 mg/kg for almonds recommended by the 1991 JMPR. The Meeting was informed that the accuracy of the old colorimetric method of analysis used in some of these trials was inadequate. Data from two series of trials were presented in the 1991 JMPR monograph. Samples from the trials which appear to have been used to support the MRL of 0.3 mg/kg were analysed by the colorimetric method. In a further 24 US trials in which a new specific method of analysis was used, residues were reported as <0.02-0.04 mg/kg in the kernels and 0.04-3.65 mg/kg in the hulls. On the basis of these trials the Meeting estimated maximum residue levels of 0.05 mg/kg for almonds and 5 mg/kg for almond hulls.

When grapes containing residues of <0.04-0.07 mg/kg were processed the residues in must and wine were 0.06-0.09 and <0.04 mg/kg, respectively. However the details of the processing were submitted too late for full consideration by the Meeting and were in the form of a draft translation. The Meeting understood that the manufacturer had agreed to submit the original study report and the final translation containing the full experimental details to the FAO for future consideration by the FAO Panel.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels shown below, which are recommended for use as MRLs.

Definition of the residue: azinphos-methyl

Commodity		Recommended MRL (mg/kg)		PHI on which based, days
CCN	Name	New[1]	Previous	
TN 0660	Almonds	0.05	0.3	28
AM 0660	Almond hulls	5	-	28
GC 0080	Cereal grain	W[2]	0.2	-
GC 0654	Wheat	W	0.2	-

[1] W: the previous recommendation is withdrawn
[2] This CXL had already been marked for deletion by the 1991 JMPR.

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