

## METHAMIDOPHOS (100)

### EXPLANATION

Methamidophos was first evaluated in 1976 with further reviews of residue aspects in 1979, 1981, 1984, 1989, 1990, 1994, and 1996. The 1994 JMPR recommended an MRL of 0.5 mg/kg for pome fruits, based on a 21-day PHI.

At the 28th (1996) Session of the CCPR the delegations of The Netherlands, the UK and the EU expressed concern about the intake. At its 29th Session the CCPR retained the MRL for pome fruits at Step 7 pending the evaluation of new data on residues (ALINORM 97/24A, para 61).

Data on supervised trials and information on GAP were submitted to the Meeting to support the estimation of a maximum residue level for pome fruits.

### METHODS OF RESIDUES ANALYSIS

#### Analytical methods

The analytical methods used in supervised trials were the same as those reported in earlier evaluations. Methamidophos can be extracted with ethyl acetate, acetone/water, or acetonitrile. The extract is cleaned up by silica gel or gel permeation chromatography. The residues are quantified by GLC with NP or FP detection.

The analytical method used in most trials submitted to the present Meeting was described by Specht and Thier (1992) and modified by Thier and Kirchhoff (1992). Extraction is with ethyl acetate in the presence of anhydrous granulated sodium sulfate and the final extract is analysed by GLC with an NP detector. The limit of determination (LOD) for methamidophos was 0.01 mg/kg and recoveries were >80%.

#### Stability of pesticide residues in stored analytical samples

Studies of the stability of residues in frozen samples of several commodities (Lai, 1988a,b) were evaluated by the 1996 JMPR, but the stability of methamidophos was not established because most of the samples were of crops which had been treated with acephate and contained substantially higher levels of acephate than of methamidophos, and acephate could well be degraded to methamidophos during storage. The studies did not include apples and no studies of the stability methamidophos on apples have been submitted to the present Meeting.

### USE PATTERN

Methamidophos is an organophosphorus insecticide registered for use on many commodities to control a broad spectrum of insects. Information on registered uses of methamidophos on pome fruits in France, Greece and Italy was provided to the Meeting. Since residues of methamidophos can arise from the use of acephate, the uses of both pesticides have to be taken into account.

Table 1. Registered uses of methamidophos on pome fruits.

Crop	Country	Form.	Application			PHI, days
			kg ai/ha	kg ai/hl	No.	
Apples and pears	France	SL	0.5	0.05	1-2	21
Apples and pears	Greece	SL	0.9-1.2	0.045-0.06	1-2	21
Pome fruit	Italy	EC	0.5-0.75	0.025-0.0375	1	21
Pome fruit	Morocco	SL	0.9			28
Pome fruit	Spain	SL	0.68			28

Table 2. Registered uses of acephate on pome fruits.

Crop	Country	Form.	Application			PHI, days
			kg ai/ha	kg ai/hl	No.	
Pome fruit	Germany	50 WP	0.75		3	42
Pome fruit	South Africa			0.05	1-2	

## RESIDUES RESULTING FROM SUPERVISED TRIALS

### Residues arising from the use of methamidophos

**Pome fruits.** Three supervised trials on apples and two on pears in France in 1992 were evaluated in 1994 and reviewed again by the present Meeting. Methamidophos SL was applied twice with a 21-day interval to apples on plots of 32-96 m<sup>2</sup>. Samples were analysed after gel permeation clean-up by GLC with FP detection. The SAIs were 210-245 days. Residues 21 days after the second application were between 0.01 and 0.1 mg/kg and similar to those immediately before it. The data lacked both control and sample chromatograms.

Three trials at different locations in Italy on different varieties of apples were evaluated in 1994. Methamidophos was sprayed twice on to plots of 22.5 m<sup>2</sup> (2 trees) to 48 m<sup>2</sup> (4 trees), with a 15-day interval. The SAIs were 180-210 days. The residues were 0.02-0.33 mg/kg at a 21-day PHI.

Field trials on apples were carried out in 1995 and 1996 at six test sites in Greece and Spain. In Greece methamidophos 600 g/l was applied according to Greek GAP, with 13-16 days between applications, using a motorised knapsack sprayer. The plot sizes were 3-8 trees. The residues of methamidophos were 0.31-0.49 mg/kg. Residues in untreated samples were always below the LOD. The SAIs were 16-88 days.

In Spain Methamidophos SL 600 g/l was applied twice with a hand-gun sprayer to three different varieties of apples at intervals of 13-16 days. The SAIs were 38-83 days. Residues of methamidophos at 21-day PHI were between 0.08 and 0.24 mg/kg.

Summary data from two trials on apples in 1970 in Israel were submitted to the Meeting. The residues of methamidophos at 19 days PHI were 0.14 and 0.23 mg/kg.

Two field trials on pears were conducted in France in 1992 according to French GAP. Residues 21 days after the last application were 0.15 and 0.21 mg/kg, similar to those in apples.

The results of the trials are shown in Table 3.

Table 3. Residues of methamidophos in pome fruit. All SL formulations. The underlined residues are from treatments according to GAP and were used to estimate maximum residue levels.

Crop, Country, Year	Application			PHI, days	Residues, mg/kg	Ref
	No.	kg ai/ha	kg ai/hl			
APPLES						
France 1992 Montfavert	2	0.675-0.688	0.05		0.04 <sup>1</sup>	Bayer 1992a
				0	0.24	
				7	0.08	
				21	<u>0.1</u>	
				28	0.05	
France 1992 Montfavert	2	0.49	0.05		<0.01 <sup>1</sup>	
				0	0.09	
				7	0.04	
				14	0.02	
				21	<u>0.01</u>	
				28	0.01	
France 1992, Pers les Fortaines	2	0.442	0.05		0.04 <sup>1</sup>	
				0	0.5	
				7	11	
				14	0.04	
				21	0.04	
				28	<u>0.06</u>	
Greece 1995	2	1.2	0.06	20	<u>0.4</u>	Tomen 1996
Greece Pipera 1996	2	1.2	0.06	21	<u>0.49</u>	
Greece 1996 Agras	2	1.2	0.06	0	1.53	
				3	0.42	
				6	0.38	
				13	0.24	
				21	<u>0.31</u>	
Israel 1970	1	1.416	0.0885	3	0.17	Bayer, 1970
				7	0.15	
				14	0.1	
				19	0.04	
				27	0.06	
Israel 1970	2	1.416	0.0885	6	0.25	
				11	0.22	
				19	0.23	
Italy, 1992 Ravenna	2	0.731	0.049		0.19 <sup>1</sup>	Bayer 1992b
				0	0.66	
				7	0.24	
				14	0.39	
				21	<u>0.29</u>	
				28	0.18	
Italy, 1992 S. Romaldo	2	0.731	0.049	0	1.3	
				7	0.59	
				14	0.64	
				21	<u>0.33</u>	
				28	0.17	
Italy, 1992 Fondi	2	0.731	0.049		0.03 <sup>1</sup>	
				0	0.51	
				7	0.07	
				14	0.05	
				21	<u>0.02</u>	
				28	0.02	
Spain, 1995	2	1.2	0.08	23	<u>0.24</u>	Tomen 1995b
Spain, 1995	2	1.2	0.08	0	1.32	
				3	0.35	

Crop, Country, Year	Application			PHI, days	Residues, mg/kg	Ref
	No.	kg ai/ha	kg ai/hl			
				7	0.17	
				14	0.09	
				21	<u>0.08</u>	
Spain, 1995	2	1.2	0.08	0	0.37	
				3	0.11	
				7	0.17	
				14	0.06	
				21	<u>0.14</u>	
<b>PEARS</b>						
France 1992	2	0.545	0.05		0.13 <sup>1</sup>	Bayer 1992c
				0	1.02	
				7	0.43	
				14	0.34	
				21	<u>0.21</u>	
				28	0.12	
France 1992	2	0.416-0.452	0.05		0.16 <sup>1</sup>	
				0	0.55	
				7	0.36	
				14	0.3	
				21	<u>0.15</u>	
				28	0.11	

<sup>1</sup>Before last application

### Residues arising from the use of acephate

One field trial in Greece in 1995 in which apple trees were treated with acephate was reported to the Meeting. Acephate (75% SP) was applied three times at 11- and 30-day intervals. Samples harvested at a 15-day PHI showed residues of 0.38 and 0.24 mg/kg acephate and 0.03 mg/kg methamidophos. Samples were stored frozen at -20°C until analysis. Residues in control samples were below the LOD.

No data were available from earlier evaluations on residues of methamidophos resulting from the use of acephate on pome fruits.

Table 4. Residues of acephate and methamidophos in apples after applications of acephate in Greece, 1995 (Tomen 1995a).

Application				PHI, days	Residues, mg/kg	
Form	No.	kg ai/ha	kg ai/hl		Acephate	Methamidophos
SP, 750 g/kg	3	1.55-1.60	0.0075	15	0.38, 0.24	0.03, 0.03

### FATE OF RESIDUES IN STORAGE AND PROCESSING

No information on the effects of processing pome fruit was provided.

## RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No data were submitted to the Meeting. A market basket study conducted in Australia in 1992, in which pears were included, was reported at the 1994 Meeting.

## NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs for pome fruits were reported to the Meeting.

Country	Commodity	MRL, mg/kg
Argentina	Pome fruit	0.1
Denmark	Pome fruit	0.01* T
France	Apple	0.3
	Pear	0.3
Germany	Pome fruit	0.2
Italy	Pome fruit	0.15
Spain	Pome fruit	0.2
Sweden	Fruit	0.2

T: temporary

## APPRAISAL

Methamidophos is a widely used organophosphorus insecticide with systemic properties; its residues may also occur as a metabolite of acephate. It was first evaluated in 1976 with further reviews of residue aspects in 1979, 1981, 1984, 1989, 1990, 1994 and 1996. The 1994 JMPR recommended an MRL of 0.5 mg/kg for pome fruit, based on a 21-day PHI. It was held at step 7B by the 29th (1997) Session of the CCPR. The manufacturer has submitted new residue data to support the estimation of a maximum residue level for pome fruit.

The analytical methods employed in supervised trials were based on GLC. Recoveries were >70% and the LOD in all the methods was 0.01 mg/kg.

Studies of the storage stability of residues in several commodities were included in the studies of the stability of acephate residues evaluated in 1996 but no studies of the stability of methamidophos on apples were submitted.

Trials conducted in France and Italy in 1992 on apples and pears were evaluated by the 1994 JMPR and again reviewed by the present Meeting. In three trials on apples according to French GAP (1-2 applications at 0.5 kg ai/ha, 21-day PHI) the residues were 0.01, 0.06 and 0.1 mg/kg. The residue of 0.06 mg/kg was at 28 days; the residue at day 21 was 0.04 mg/kg. Three Italian trials on apples carried out with two applications of methamidophos (Italian GAP allows one) at 0.049 kg ai/hl were evaluated against Greek GAP (1 or 2 applications at 0.045-0.06 kg ai/hl, 21-day PHI). The residues were 0.02, 0.29 and 0.33 mg/kg.

The residues in three trials on apples according to GAP in Greece in 1995/96 were 0.31, 0.4 and 0.49 mg/kg. In similar trials in Spain in 1995 the residues were somewhat lower: 0.08, 0.14 and 0.24 mg/kg at a 21-day PHI. As the application rates were higher than in Spanish GAP the results were evaluated against Greek GAP.

Several of these trials were designed to produce residue decline curves. They showed that when methamidophos was applied twice with an interval of 3 weeks most of the residues resulted from the second application.

Two trials on apples in Israel in 1970 gave residues of 0.04 and 0.23 mg/kg at a 19-day PHI. Since no relevant GAP was reported these results were not considered for the estimation of a maximum residue level.

In a trial in which apples were treated with acephate at an application rate of 1.55-1.6 kg ai/ha the residue of methamidophos at a 15-day PHI was 0.03 mg/kg.

The residues of methamidophos in apples in rank order from the 12 trials according to GAP were 0.01, 0.02, 0.06, 0.08, 0.1, 0.14, 0.24, 0.29, 0.31, 0.33, 0.4 and 0.49 mg/kg.

Pears treated with methamidophos in France in 1992 according to GAP showed residues of 0.15 and 0.21 mg/kg after 21 days.

In view of the identical use patterns on apples and pears the Meeting agreed to evaluate the combined data as applying to pome fruit.

The residues of methamidophos in apples and pears in rank order (median underlined) were 0.01, 0.02, 0.06, 0.08, 0.1, 0.14, 0.15, 0.21, 0.24, 0.29, 0.31, 0.33, 0.4 and 0.49 mg/kg.

The Meeting agreed to confirm the previously estimated maximum residue level of 0.5 mg/kg, and estimated an STMR of 0.18 mg/kg for methamidophos in pome fruit. The Meeting expressed its concern at the long period of storage of many of the samples and the lack of data on the stability of residues during storage, but noted that methamidophos was scheduled for periodic review in 2002.

## RECOMMENDATIONS

On the basis of data from supervised trials the Meeting concluded that the residue level shown below is suitable for establishing a Maximum Residue Limit and the supervised trials median residue is suitable for use in dietary intake estimations.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: methamidophos.

Commodity		MRL, mg/kg		PHI, days	STMR, mg/kg
CCN	Name	new	previous		
FP 0009	Pome Fruit	0.5	0.5	21	0.18

## FURTHER WORK OR INFORMATION

### Desirable

1. Information on methamidophos residues in processed apples.
2. Data on the storage stability of residues of methamidophos for the full duration of studies to be submitted for periodic review in 2002.

## REFERENCES

- Bayer. 1970. Residue Report for Methamidophos on Apple in Israel. Residue Data Summary from Supervised Trials. Study Nos. 212-70, 214-70. Unpublished.
- Bayer. 1992a. Residue Report for Methamidophos on Apple in France. Determination of Residue of Taramon 400 SL in/on Apple and Pear Under Actual Use conditions in France. Report No. RA-2102/92, 0599-92, 0600-92. Unpublished.
- Bayer. 1992b. Residue Report for Methamidophos on Apple in Italy. Determination of Residue of Taramon 19.5 SL in/on Apple Under Actual Use Conditions in Italy. Report No. RA-2103/92, 0595-92, 0596-92, 0597-92. Unpublished.
- Bayer. 1992c. Residue Report for Methamidophos on Pear in France. Determination of Residue of Taramon 400 SL in/on Apple and Pear Under Actual Use Conditions in France. Report No. RA-2102/92: 0601-92, 0602-92. Unpublished.
- Lai, J.C. 1988a. Storage Stability of Acephate in Frozen Celery Macerates. Project No. R12-T7037SS. Chevron Chemical Company. Richmond, CA, USA. Unpublished.
- Lai, J.C. 1988b. Storage Stability of Acephate in Frozen Macerated Beans. Project No. R12-T7017SS. Chevron Chemical Company. Richmond, CA, USA. Unpublished.
- Rhône-Poulenc. Multiresidue Method 5-Part I-54, SDU Publishers. Taken from Rhone-Poulenc Secteur Agro. Analytical Study Code: AR 35-96. Lyon, France.
- Specht, W. and Thier, H.P. 1992. Organochlorine, Organophosphate, Nitrogen-Containing and Other Pesticides S19 (Deutsch Forschungsgemeinschaft). Manual of Pesticide Residue Analysis I, pp. 383-400, 1987. Bayer Method No. 00086.
- Specht, W. and Partner. 1992. Az 97413/92. Validation of Method DFG-S19 for the Determination of Methamidophos in/on Apples and Pears. Bayer Method No. 00086/E042.
- Thier, H.P. and Kirchhoff 1992. Update of Method S19, Organochlorine, Organophosphate, Nitrogen-Containing and Other Pesticides S19 (Deutsch Forschungsgemeinschaft). Manual of Pesticide Residue Analysis II, pp. 317-322, 1992. Bayer Method No. 00086 (updated).
- Tomen. 1995a. Residue Report for Methamidophos on Apple in Greece. Acephate and Methamidophos (metabolite) Formulation Exp 05383A (SP) Trial Greece 1995 Residues in Apples. Study No. 95-709. Unpublished.
- Tomen. 1995b. Residue Report for Methamidophos on Apple in Spain. Magnitude of the Residue of Methamidophos in Apple Raw Agricultural Commodity, Greece and Spain- 1995 & 1996. Study Nos. EA950140-SP01, EA950141-SP01, SP02. Unpublished.
- Tomen. 1996. Residue Report for Methamidophos on Apple in Greece. Magnitude of the Residue of Methamidophos in Apple Raw Agricultural Commodity, Greece and Spain- 1995 & 1996. Study Nos. EA950140-GR01, GR02, EA950141-GR03. Unpublished.





