

## DEMETON-S-METHYLSULPHON (164)

### EXPLANATION

Demeton-S-methylsulphon has been evaluated several times by the JMPR, the first in 1973 when an ADI of 0.005 mg/kg bw was allocated. In 1982 the ADI was withdrawn. Taking into account new toxicological data the 1989 JMPR estimated a new ADI of 0.0003 mg/kg bw for demeton-S-methyl and related compounds.

Residues from supervised trials were evaluated in 1968, 1973, 1979, 1984 and 1989 for the "demeton compounds".

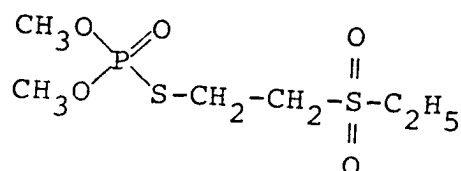
The present evaluation is in the CCPR periodic review programme. Together with the other demeton compounds (demeton-S-methyl and oxydemetonmethyl) demeton-S-methylsulphon has been proposed for review largely because of toxicological concerns and potential dietary exposure. As most of the proposed MRLs of the group date from 1973 it was considered appropriate to re-evaluate residue information in view of probable changes in GAP.

Residue data from supervised trials on pome and stone fruit, together with other information on use patterns, fate of residues, methods of analysis and national MRLs were provided by the manufacturer to the Meeting. Data on GAP from The Netherlands were also made available.

Further information on the effects of processing on crop residues, the fate in animals, photodegradation and the stability of stored analytical samples is given in the oxydemeton-methyl evaluation.

### IDENTITY

ISO common name:	Demeton-S-methylsulphon
Chemical name:	
IUPAC:	S-2-ethylsulphonylethyl 0,0-dimethyl phosphorothioate
CA:	S-[2-(Ethylsulfonyl)ethyl] 0,0-dimethyl phosphorothioate
CAS Registry No.:	17040-19-6
Synonyms:	Bayer 20 315; E 158; M3 158
Structural formula:	



Molecular formula:  $\text{C}_6\text{H}_{15}\text{O}_5\text{PS}_2$

Physical and chemical –properties

Molecular weight:	262.3 g/mol		
Appearance:	solid (crystals)		
Colour:	colourless		
Odour..	characteristic weak odour		
Melting point:	51.6°C		
Boiling point:	115°C at 0.01 hPa		
Vapour pressure:	5.6 x 10 <sup>-7</sup> hPa at 20°C		
Specific gravity:	1.416		
Solubility: (g substance in 1000 ml solvent at 20°C)			
	water:	>200	
in organic solvents	n-hexane:	0.1	- 1
in accordance with the DAPA resolution	dichloromethane:	>200	
	2-propanol:	50 -	100
	toluene:	50 -	100
Octanol/Water partition coefficient:	log P <sub>ow</sub> = 1.52 at 20°C		
Hydrolytic stability: (degradation in buffer systems)	pH4, 22°C:	half-life	147 days
	pH7, 22°C:	half-life	235 hours
	pH9, 22°C:	half-life	14 hours

**USE PATTERN**

Demeton-S-methylsulphon is a systemic organophosphorus insecticide. It is effective as a contact and stomach poison against sucking insects such as aphids (Aphidae), thrips (Thysanoptera), leaf hoppers (Cicadidae) and non-organophosphorus-resistant strains of mites (Tetranychidae).

Demeton-S-methylsulphon is one of two active ingredients in the product Gusathion MS. The second is azinphos-methyl (Bayer code: R 1582). Guathion MS is a WP formulation for application in water as a spray. Although the azinphos-methyl component can vary in quantity, demeton-S-methylsulphon is always present at 75 g ai/kg product. Gusathion MS has a broad range of activity including activity against sucking insects (demeton-S-methylsulphon component) and chewing insects (azinphos-methyl). It is used on pome and stone fruits in some European countries and Tunisia as well as on sugar beet in Italy.

Table 1 lists the registered uses of demeton-S-methylsulphon.

Table 1. Registered uses of demeton-S-methylsulphon

Type of formulation: wettable powder

75 g ai/kg, mixture with azinphos-methyl

Application: overall, broadcast, high-volume spraying

Crop, Country	Application			PHI, days
	No	Rate per applic. kg ai/ha from - to	Spray conc. kg ai/hl from - to	
<b>Apple</b>				
Italy	1 - 3	0.26 - 0.39	0.017 - 0.026	35
Portugal	4 - 5	0.15	0.015	28
Switzerland	1 - 3	0.3		42
Netherlands	1 - 2	0.15 - 0.22	0.015	21
<b>Peach</b>				
Italy	1 - 2	0.26 - 0.39	0.017 - 0.026	35
<b>Pear</b>				
Italy	1 - 2	0.26 - 0.39	0.017 - 0.026	35
Portugal	4 - 5	0.15	0.015	28
Netherlands	1 - 2	0.15 - 0.22	0.015	21
<b>Pome fruits</b>				
Belgium	1 - 2	0.21	0.014	21
France	1 - 2	0.17 - 0.2	0.011 - 0.013	21
Spain	2 - 3	0.23 - 0.28	0.015 - 0.019	28
Tunisia	2	0.15 - 0.23		42
<b>Stone fruits</b>				
Belgium	1 - 2	0.21	0.014	21
France	1 - 2	0.17 - 0.2	0.011 - 0.013	21
Spain	2 - 3	0.23 - 0.28	0.015 - 0.019	28
Tunisia	2	0.15 - 0.23		42
<b>Sugar beet</b>				
Italy	1 - 2	0.12 - 0.21	0.015 - 0.026	35

**RESIDUES RESULTING FROM SUPERVISED TRIALS**

Pome fruit. Table 2 summarizes the residue studies available to support the registered uses of demeton-S-methylsulphon, which is both an active ingredient in Gusathion MS and a known metabolite of oxydemeton-methyl. Analytical methods used in the residue studies in Table 4 determine demeton-S-methylsulphon. In some studies this residue has been calculated and reported as demeton-S-methyl.

Registered uses are current for Gusathion MS in Italy, Portugal, Switzerland, Belgium, France, Tunisia and Spain. Use patterns are reported in Table 1 and summarized below.

Country	Demeton-S-methylsulphon rate, kg ai/ha	No. of applications	PHI, days	Crop
Italy	0.26 - 0.39	1 - 3	35	apple, pear
Netherlands	0.15 - 0.22	1 - 2	21	apple, pear
Portugal	0.15	4 - 5	28	apple, pear
Switzerland	0.30	1 - 3	42	apple
Belgium	0.21	1 - 2	21	pome fruit
France	0.17 - 0.20	1 - 2	21	pome fruit
Tunisia	0.15 - 0.23	2	42	pome fruit
Spain	0.23 - 0.28	2 - 3	28	pome fruit

Four supervised residue trials were conducted on apples in Germany (1966) where rates between 0.27 and 0.315 kg ai/ha of demeton-S-methylsulphon were applied three times to apples. 21 days after the 3rd application (GAP in France, The Netherlands and Belgium) residues were between 0.1 and 0.3 mg/kg. At 28 days (GAP in Spain) residues were between 0.15 and 0.25 mg/kg. At 35 and 42 days (GAP in Italy and Switzerland respectively) residues were between 0.1 and 0.15 mg/kg.

Two supervised residue trials were conducted on apples in Portugal, where rates averaging 0.18 and 0.20 kg ai/ha were applied on each of 5 occasions. Residues at 28 days after the 5th application (GAP in Portugal) were either <0.01 or 0.02 mg/kg. At 42 days after the 5th application (nearest equivalent to use in Tunisia) residues were at or below the limit of determination (0.01 mg/kg).

Eleven supervised residue trials (9 on apples and 2 on pears) were conducted in Germany at rates between 0.225 and 0.3 kg ai/ha demeton-S-methylsulphon. 5 or 6 applications were made. These trials were used to support previous registrations of Gusathion MS, particularly in Germany. Although the number of applications exceeds current use patterns, with the exception of trial 4201/78 residues after 21, 28 and 35 days were of a similar order to those given above.

Two orientation trials have recently been completed in Belgium (0506 and 0507/91) which demonstrate that the reduced rate of 0.169 kg ai/ha applied 3 times to apples resulted in residues below the limit of determination (0.04 mg/kg) at PHI of 55-90 days.

Table 2. Residues of demeton-S-methylsulphon in pome fruit. Application of Gusathion MS. Residues from treatments according to GAP are underlined

(Formulation: WP, 75 g ai/kg + 250 g azinphos-methyl per kg)

CROP Country/Year	Application			PHI, days	Residues mg/kg	Refs.
	No	kg ai/ha	kg ai/hl			
APPLE						
Belgium/1991	3	0.169	0.056	62	<0.04	0506/91 1), 3), 7)
				76	<0.04	
				90	<0.04	
	3	0.169	0.056	55	<0.04	0507/91 1), 3), 7)
				69	<0.04	
				83	<0.04	

Table 2 (contd.)

CROP Country/Year	Application		PHI, days	Residues mg/kg	Refs	
	No	kg ai/ha				kg ai/hl
APPLE Germany/1966	3	0.27	0.015	0	0.3	165/66 1), 6)
				7	0.2	
				14	0.1	
				21	<u>0.1</u>	
		28	<u>0.15</u>	35	<u>0.1</u>	
				42	<u>0.1</u>	
				49	0.05	
	3	0.315	0.045	0	0.5	166/66 1), 6)
				7	0.35	
				14	0.2	
				21	<u>0.25</u>	
				28	<u>0.2</u>	
				35	<u>0.15</u>	
				42	<u>0.15</u>	
49	0.1					
3	0.315	0.045	0	0.75	224/66 1), 6)	
			7	0.4		
			14	0.3		
			21	0.3		
			28	<u>0.25</u>		
			35	<u>0.15</u>		
			42	<u>0.1</u>		
3	0.315	0.015	0	0.3	225/66 1), 6)	
			7	0.2		
			14	0.25		
			21	<u>0.25</u>		
			28	<u>0.2</u>		
			35	<u>0.15</u>		
			42	<u>0.1</u>		
Germany/1975	5	0.3	0.015	0	0.44	4206/75 2), 4), 8)
				7	0.37	
				14	0.28	
				21	0.19	
				28	0.18	
	5	0.3	0.015	0	0.51	4207/75 2), 4), 8)
				7	0.39	
				14	0.21	
				21	0.34	
				28	<0.01	
5	0.3	0.015	0	0.43	4208/75 2), 4), 8)	
			7	0.41		
			14	0.23		
			21	0.29		
			28	0.21		
Germany/1978	6	0.3	0.03	0	0.89	4201/78 2), 5), 8)
				14	0.36	
				21	0.33	
				28	0.47	
				35	0.37	

Table 2 (contd.)

CROP Country/Year	Application			PHI, days	Residues mg/kg	Refs .
	No	kg ai/ha	kg ai/hl			
APPLE						
Germany/1979	5	0.225	0.015	0	0.21	4200/79 2), 5), 8)
				14	0.1	
				21	0.07	
				28	0.04	
				35	0.03	
Germany/1979	6	0.225	0.015	0	0.21	4201/79 2), 5), 8)
				14	0.12	
				21	0.14	
				28	0.07	
				35	<0.01	
Germany/1979	6	0.225	0.015	0	0.45	4202/79 2), 5), 8)
				14	0.24	
				21	0.19	
				28	0.11	
				35	0.09	
Germany/1982	5	0.23	0.015	0	0.66	4200/82 2), 5), 8)
				10	0.33	
				21	0.19	
				28	0.1	
				35	0.1	
Germany/1982	5	0.23	0.015	0	0.25	4201/82 2), 5), 8)
				10	<0.01	
				21	<0.01	
				28	<0.01	
				35	<0.01	
Portugal/1982	5	0.15- 0.19	0.026	0	0.05	4206/82 2), 5), 8)
				14	0.04	
				28	<u>&lt;0.01</u>	
				35	<0.01	
				42	0.01	
Portugal/1982	5	0.17- 0.22	0.03	0	0.08	4207/82 2), 5), 8)
				14	0.04	
				28	<u>0.02</u>	
				35	0.01	
				42	<0.01	
PEAR						
Germany/1966	1		0.015	0*)	2.65	205B/66 1), 6) *) 1st of 2 appls.
				3	1.89	
				7	0.91	
				14	0.57	
				21	<u>0.23</u>	
			0.015	0**)	2.34	**)2nd appl. to same trees
				3	1.82	
				5	1.37	
				12	0.6	
				<u>22</u>	<u>0.22</u>	

Table 2 (contd.)

CROP Country/Year	Application			PHI, days	Residues mg/kg	Refs
	No	kg ai/ha	kg ai/hl			
PEAR						
Germany/1982	5	0.23	0.015	0	0.49	4203/82 2), 5), 8)
				10	0.25	
				21	0.09	
				28	0.07	
				35	0.04	
	5	0.23	0.015	0	0.01	4204/82 2), 5), 8)
				10	<0.01	
				21	<0.01	
				28	<0.01	
				35	<0.01	
35						

1) Residues calculated as demeton-S-methylsulphon 2) Residues calculated as demeton-S-methyl 3) Analytical method 00260 4) Analytical method 1 47 5) Analytical method 00009 6) Limit of determination 0.05 mg/kg 7) Limit of determination 0.04 mg/kg 8) Limit of determination 0.01 mg/kg

Table 3. Residues of demeton-S-methylsulphon in stone fruit. Application of Gusathion MS. (Formulation WP, 75 g ai/kg + 250 g azinphos-methyl/kg)

CROP Country/Year	Application			PHI, days	Residues mg/kg	Refs
	No	kg ai/ha	kg ai/hl			
PEACH						
Spain/1991	2	0.225	0.015	0	0.34	0498/91 1), 3), 5)
				14	0.17	
				28	<u>0.05</u>	
	2	0.225	0.015	0	0.34	0500/91 1), 3), 5)
				14	0.08	
				28	<u>&lt;0.04</u>	
PLUM						
Germany/1975	3	0.225	0.015	0	0.1	4200/75 2), 4), 7)
				7	0.09	
				14	0.05	
				21	<u>0.15</u>	
				28	<u>0.08</u>	
	3	0.225	0.015	0	0.14	4201/75 2), 4), 7)
				7	0.16	
				14	0.02	
				21	<u>0.15</u>	
				28	<u>0.1</u>	
	3	0.225	0.015	0	0.03	4202/75 2), 4), 7)
				7	0.02	
				14	<0.01	
				21	<u>&lt;0.01</u>	
				28	<u>&lt;0.01</u>	

Table 2 (contd.)

CROP Country/Year	Application		PHI, days	Residues mg/kg	Refs .	
	No	kg ai/ha				kg ai/hl
PLUM						
Germany/1978	5	0.3	0.015	0	1.1	4202/78 2), 4), 8)
				14	1.6	
				21	0.57	
				28	0.56	
				35	0.54	
Germany/1978	5	0.3	0.03	0	1.1	4203/78 2), 4), 8)
				14	0.34	
				21	0.32	
				28	0.27	
				35	0.22	
Germany/1979	5	0.3	0.015	0	0.04	4203/79 2), 4), 8)
				14	0.05	
				21	0.07	
				28	0.05	
				35	0.04	
Germany/1979	5	0.225	0.015	0	0.23	4204/79 2), 4), 8)
				14	0.1	
				21	0.14	
				28	0.22	
				35	0.19	
Germany/1979	5	0.225	0.015	0	0.23	4205/79 2), 4), 8)
				14	0.1	
				21	0.15	
				28	0.14	
				35	0.1	
Germany/1984	4	0.225	0.015	0	0.5	4200/84 1), 4), 6)
				14	0.2	
				28	0.15	
				35	0.05	
				Germany/1984	4	
14	0.4					
28	0.14					
35	0.05					
Germany/1984	4	0.225	0.015			0
				14	0.04	
				28	0.2	
				35	0.08	
				Germany/1984	4	0.225
14	0.38					
28	0.03					
35	0.18					
SOUR CHERRY						
Germany/1978	3	0.3	0.015	0	1.58	4204/78 2), 4), 8)
				14	1.06	
				21	0.43	
				28	0.2	
				35	0.17	



Table 3 (contd.)

CROP Country/Year	Application			PHI, days	Residues mg/kg	Reference .Remarks
	No	kg ai/ha	kg ai/hl			
<b>SOUR CHERRY</b>						
Germany/1978	3	0.3	0.015	0	2.33	4205/78 2), 4), 8)
				14	0.69	
				21	<u>0.55</u>	
				28	<u>0.19</u>	
				35	0.27	
Germany/1984	3	0.3	0.03	0	2.1	4206/78 2), 4), 8)
				14	0.58	
				21	<u>0.37</u>	
				28	<u>0.22</u>	
				35	0.14	
Germany/1984	4	0.225	0.0151	0	2.5	4204/84 1), 4), 6)
				14	0.22	
				28	0.92	
				35	0.37	
				42	<u>0.09</u>	
Germany/1984	4	0.225	0.015	0	0.98	4205/84 1), 4), 6)
				14	0.33	
				28	0.17	
				35	0.1	

Residues from treatments according to GAP are underlined

- 1) Residues calculated as demeton-S-methylsulphon
- 2) Residues calculated as demeton-S-methyl
- 3) Limit of determination 0.04 mg/kg
- 4) Limit of determination 0.01 mg/kg
- 5) Analytical method 00260
- 6) Analytical method 00012
- 7) Analytical method 1 47
- 8) Analytical method 00009

Stone fruit (Table 3). Registered uses are current for Gusathion MS in Belgium, France, Tunisia, Spain and Italy. Use patterns are reported in Table 1 and summarized below

Country	Demeton-S-methylsulphon rate, kg ai/ha	No. of application	PHI, days	Crop
Belgium	0.21	1 - 2	21	stone fruit
France	0.17 - 0.2	1 - 2	21	stone fruit
Tunisia	0.15 - 0.23	2	42	stone fruit
Spain	0.23 - 0.28	2 - 3	28	stone fruit
Italy	0.26 - 0.39	1 - 2	35	peaches

Eight supervised residue trials (3 on sour cherry, 3 on plums and 2 on peaches) were conducted in Germany and Spain, in which rates between 0.225 and 0.3kg ai/ha demeton-S-methylsulphon were applied 2-3 times per crop season. Residues at 21 days after the last application (GAP in Belgium and France) were between 0.37 and 0.55mg/kg in sour cherries and between <0.01 and 0.15 mg/kg in plums. At 28 days after the last application (GAP in Spain) residues were between 0.19 and 0.22 mg/kg in sour cherries, <0.01-0.1 mg/kg in plums and <0.04-0.05 mg/kg in peaches. In one supervised residue trial (4204/84) conducted in Germany, samples were taken at 42 days (GAP in Tunisia). Four applications, double the Tunisian use pattern, were made on sour cherries at

0.225 kg ai/ha. Residues of 0.09 mg/kg were found 42 days after the 4th application.

Twelve supervised residue trials are also tabulated (1 on sour cherries and 11 on plums) to provide extra residue data at relevant rates of application, although the number of applications (4-5) exceeded current use patterns.

## FATE OF RESIDUES

Studies are summarized which have not been previously submitted to the JMPR. The last submission of metabolism studies was in 1989. Figure 1 provides a complete overview of the metabolic and degradation pathways for demeton-S-methylsulphon in plants and soil. See also the oxydemeton-methyl evaluation.

### In plants

Metabolism was investigated after the application of [ ethylene- 1-  $^{14}\text{C}$  ]demeton-S-methyl sulphon to apples (variety James Grieve). Wagner et al. (1985) applied approximately 10 mg active ingredient per apple. One apple was harvested at 0, 6, 13, 20 and 27 days following the application. The amount of unchanged parent compound as a percentage of the applied radioactivity decreased relatively quickly in the beginning and then more slowly over the time of the study (day 0: 100%, day 7: 60%, day 13: 51%, day 20: 50% and day 27: 48%). On day 27, 24.4% and 23.6% of the applied radioactivity was identified as parent compound in the pulp and peel respectively while 7% was unextractable with solvents of different polarity such as dichloromethane, acetone, methanol and water. The following metabolites were formed by hydrolysis and oxidation reactions (% of applied radioactivity in fruit/peel on day 27).

0-methyl S-2-ethylsulphonylethyl thiophosphate (2.6/2.9)

S-2-ethylsulphonylethyl thiophosphate (1.2/3.4)

bis(2-ethylsulphonylethyl) disulphide (0.9/0.9)

2-(ethylsulphonyl)ethylsulphonic acid (3.2/2.2)

1-(ethylsulphonyl)-2-(methylsulphinyl)ethane (1.6/1.3)

1-(ethylsulphonyl)-2-(methylsulphonyl)ethane (0.7/0.6)

2-(ethylsulphonyl)ethanol (2.9/2.2)

### In soil

Degradation. Wagner et al. (1980) investigated the degradation of demeton-S-methylsulphon in soil after the application of [ethylene- $^{14}\text{C}$ ] demeton-S-methylsulphon to a sandy loam. 31 days after the application 30.5% of the applied radioactivity was eliminated as  $^{14}\text{CO}_2$ . This percentage increased only slightly after 50 days to 31.8%. To identify the degradation products, 1000 mg/kg was applied. After 31 days 92.1% of the applied radioactivity was extracted from the soil with methanol and water. 7.9% remained in the soil. After 73 days 21.7% was unextractable, and the amount of parent compound in the soil had decreased to 56.9% of the applied radioactivity. The degradation products were formed by oxidation and hydrolysis reactions. The identified compounds were:

0-methyl S-(2-ethylsulphonyl)ethyl thiophosphate (demethyl- demeton-S-methylsulphon),

S-(2-ethylsulphonyl)ethyl thiophosphate (bisdemethyl demeton-S-methylsulphon),

2-(ethylsulphonyl)ethanethiol,

bis[(2-ethylsulphonyl)ethyl] disulphide and

2-(ethylsulphonyl)ethanesulphonic acid.

The main product was the sulphonic acid, which increased during the course of the experiment to 10.8% of the applied radioactivity on day 73, while levels of the other compounds were disulphide 2.2%; ethanethiol 3.2%; bisdemethyl-demeton-S-methylsulphon 0.7%; demethyl-demeton-S-methylsulphon 2.8% .

The quantitative and qualitative distribution of products was also investigated by Wagner (1983) in a sandy loam after a lower application rate of [ ethylene-1-<sup>14</sup>C ]demeton-S-methylsulphon (0.78 mg/kg instead of 1000 mg/kg) . In this study, 25.1% of the applied radioactivity was extracted with methanol and water on day 45 (24.1% on day 18). The unextractable radioactivity on day 45 was 67.5% (69.5% on day 18), and the <sup>14</sup>C<sub>2</sub>O was 8.7% (6.2% on day 18). Owing to the lower application rate, the radioactivity balance and the quantitative distribution of the products were different from the earlier study. The qualitative pattern in both studies was the same. On day 18, the main product, constituting 12.2% of the applied radioactivity, was the sulphonic acid, with the disulphide 0.3%, the ethanethiol 1.6%, bis demethyl-demeton-S-methyl sulphon 0.1%, and demethyl-demeton-S-methylsulphon 0.8% of the applied radioactivity. The parent compound was detected at 5.4% on day 18. On day 73, the main product, 2-(ethylsulphonyl)ethanesulphonic acid, had increased to 14.9%.

Wagner (1974) conducted two laboratory studies to determine the half-life of demeton-S-methylsulphon in two standard, BBA classified soils. From the data it was possible to calculate disappearance times in accordance with new guidelines. In standard soil 1 (a loamy sand with high organic matter: organically bound carbon 2.5% ± 15%, suspensible soil particles 10% ± 15%, pH 5.5-7.5) the DT<sub>50</sub> and DT<sub>90</sub> values were 6 and 24 hours respectively. In standard soil 2 (a loamy sand with medium organic matter: organically bound carbon 1.0% ± 15%. suspensible soil particles 20% ± 15%, pH 5.5-7.5) the DT<sub>50</sub>, and DT<sub>90</sub> values were 22 and 74 hours respectively. The data are indicative of the rapid breakdown of demeton-S-methylsulphon in soil.

Adsorption/Desorption. Arzur (1988) conducted a study to determine the a d a o r p t i o n / d e s o r p t i o n p r o f i l e b y a p p l y i n g [ethylene-1-<sup>14</sup>C]demeton-S-methylsulphon to four different types of soil (silt loam, sand, silty clay loam and sandy loam; air-dried and passed through a 2 mm mesh sieve) . The parent compound demonstrated an extremely low level (less than 0.02%) of adsorption to soil, which is probably due to the hydrophilic nature of this compound. The adsorption values were too low to generate adsorption/desorption isotherms under the experimental conditions.

Leaching. Scholz et al. (1985) investigated the leaching characteristics of [ ethylene-1-<sup>14</sup>C ]demeton-S-methylsulphon in a loamy sand. The soil samples were aged for 0, 30 and 90 days. The application rate was in accordance with the maximum commercial use rate of 0.5 kg/ha, corresponding to 0.1 mg parent compound per leaching column. On day 0, 65.5% of the recovered radioactivity was found in the leach water. After aging 30 and 90 days, this decreased to 18.5 and 14% <sup>14</sup>C. During aging, a high proportion of the parent compound was degraded to <sup>14</sup>C<sub>2</sub>O (27%, by day 30; 35.5% by day 90). The degradation, as investigated in the leachate, proceeded by hydrolytic and oxidative steps. On day 0, the main product was demethyl-demeton-S-methylsulphon, which decreased rapidly from 23.5% to 3.5% on day 30 and 1.5% on day 90. The bisdemethyl-demeton-S-methylsulphon was detected on day 0 at 6% and constituted less than 1% on days 30 and 90. The ethanethiol increased from 1.5% on day 0 to 12% on day 30 then decreased to 9% on day 90. The disulphide was detected at less than 1% on all three sampling days. 2-(ethyl sulphonyl) ethanesulphonic acid was detected on day 0 at 1.5% and constituted less than 1% on days 30 and 90. The parent compound decreased from 32.5% on day 0 to 2.5% on day 30 and 2% on day 90. On the evidence of these results, demeton-S-methylsulphon is to be

classified as moderately mobile in non-aged loamy sand and of slight mobility in aged soil.

In water/sediment systems. Spiteller (1990) investigated the degradation of demeton-S-methylsulphon in two aquatic micro-ecosystems which included sediment. The samples originated from a recultivated gravel pit at Lienden and from a drainage ditch at Izendoorn, both locations in The Netherlands. The samples from Lienden represented an oligotrophic type of water, whereas those from Izendoorn were eutrophic. The [ethylene-1-<sup>14</sup>C]-demeton-S-methylsulphon was added at 0.5 mg/l of water. The maximum incubation period was 89 days. The parent compound was degraded very rapidly. After 7 days less than 0.1% (Lienden) and 0.2% (Izendoorn) of the applied radioactivity was detected in the waters. In the sediment extracts, 0.2 to 1.2% of parent compound was found after 7 days and less than 0.1% after 89 days. In both test systems, the first half-life for the degradation of the parent compound was only a few hours. The main compound in the water layer at a maximum concentration of 51.5% (Lienden, day 0) and 47.5% (Izendoorn, day 0) was the disulphide. 2-(ethylsulphonyl)ethanesulphonic acid accounted for 26.3% (Lienden, day 37) and 15.4% (Izendoorn, day 7). 1-(ethylsulphonyl) -2 -(methylsulphonyl) ethane reached maximum levels of 4.2% (Lienden, day 89) and 6.1% (Izendoorn, day 7). After an incubation period of 89 days, 21.5% (Lienden) and 13.6% (Izendoorn) of the applied radioactivity was detected as <sup>14</sup>C<sub>2</sub>.

## **METHODS OF RESIDUE ANALYSIS**

For the determination of demeton-S-methylsulphon for enforcement purposes, the same analytical methods are used as for oxydemeton-methyl. They are described in the oxydemeton-methyl evaluation.

The same also applies to the main analytical methods 00009 (= I 191) and I 47 which were used in the residue studies. Two methods, 00012 and 00260, have also been used for the simultaneous determination of azinphos-methyl and demeton-S-methylsulphon. These methods use the same gas-chromatographic techniques with an FPD or alkali nitrogen detector. The lower limit of the practical working range of 00260 (the most recent method) was 0.04 mg/kg. The residue methods are described below.

### Summary of analytical methods

#### Method 00009

This method is the same as method 1 191 by Wagner and Thornton (1977) published in Pflanzenschutz-Nachrichten, Volume 30.

#### Method 147

This is a forerunner of method 00009, internally reported by Thornton and Olsen in Mobay Report No. 2100.

#### Method 00012

This method consists of DFG 63-A (1976) with an unpublished modification by Burger (1988) for the determination of the demeton-S-methylsulphon component.

#### Method 00260

This is an unpublished method by Seym (1992) allowing the simultaneous determination of the azinphos-methyl and demeton-S-methylsulphon components in Gusathion MS.

## **NATIONAL MAXIMUM RESIDUE LIMITS**

The national maximum residue limits are summarized in the oxydemeton-methyl evaluation.



## APPRAISAL

Demeton-S-methylsulphon, together with the other demeton-methyl compounds (demeton-S-methyl and oxydemeton-methyl) is included in the CCPR periodic review programme.

Residue data from supervised trials on pome and stone fruit, together with other information on use patterns, fate of residues, methods of analysis and national MRLs, were provided by the manufacturer. Information on GAP in The Netherlands was also made available.

Demeton-S-methylsulphon is a systemic organophosphorus insecticide. It is effective as a contact and stomach poison against sucking insects such as aphids (Aphidae), thrips (Thysanoptera), leaf hoppers (Cicadidae) and nonorganophosphorus-resistant strains of mites (Tetranychidae).

It is used on pome and stone fruits in some European countries and Tunisia as well as on sugar beet in Italy.

The new data on residues from supervised trials together with the information on GAP were evaluated.

Pome fruit. In four trials carried out in Germany 1966 on apples, residues up to 0.3 mg/kg were found 21-42 days after application (GAP in France, Belgium, The Netherlands, Italy, Switzerland and Spain). Other available results support the estimation that residues from applications according to GAP are unlikely to exceed 0.5 mg/kg. Results from Germany on pears were used to support GAP in The Netherlands.

Plums. In three trials carried out in Germany in 1975, residues up to 0.15 mg/kg were found 21-28 days after application (GAP in Belgium, France and Spain). These results support an MRL of 0.2 mg/kg.

Cherries. On the basis of three trials in Germany where residues were 0.19-0.55 mg/kg 21-28 days after application, and assuming that these results can be used to support GAP in Belgium, France and Spain, the Meeting estimated a maximum residue level of 1 mg/kg.

Peaches. Results of two trials from Spain were insufficient to estimate a maximum residue level.

The Meeting was not able to re-evaluate the temporary MRLs for Currants, Black, Red and White, Grapes, Plums (including Prunes), Potato, Strawberry or Sugar beet because no current GAP was reported and/or residue data were not made available.

Data were also received on the fate of residues in plants, soil and water/sediment systems, and on methods of residue analysis. Further information on the effects of processing on crop residues, fate in animals, photodegradation and storage stability are given in the oxydemeton-methyl evaluation.

The Meeting proposes to change the definition of the residue because the main uses are now of oxydemeton-methyl and the residue data are largely derived from such uses.

For estimations of maximum residue levels see the oxydemeton-methyl report.

**FURTHER WORK OR INFORMATION**Desirable

Additional residue data on apples, pears and peaches, which a producer stated were being developed.

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