

DITHIANON (180)

EXPLANATION

Dithianon was first evaluated in 1992. At the 1994 CCPR the delegation of Germany questioned the underlying database for the maximum residue level of 1 mg/kg on cherries proposed by the 1992 JMPR. The present Meeting received updated information on GAP, summaries of residue data for cherries and detailed comments by Germany (Anon., 1994a). The manufacturer provided data on two supervised residue trials in Germany (Weeren *et al.*, 1994) and two in France (Carlton, 1992). A short summary giving information on GAP and on residues from supervised trials on apples was made available by Finland (Anon., 1994b). Information on GAP for pome fruits was provided by the UK (Anon., 1994c).

METHODS OF RESIDUE ANALYSIS

The cherry samples from the two new German trials were analysed for dithianon by the method of Specht (1994). A 50 g sample is homogenized with 30 ml water, 30 ml hydrochloric acid and 200 ml acetone. An aliquot of the extract is partitioned between water and acetone-hexane-dichloromethane. After the addition of 0.1 ml acetic acid the organic phase is brought to dryness and redissolved in 20 ml ethyl acetate/cyclohexane (1:1). A 5 ml-aliquot is cleaned up by gel permeation chromatography on Bio Beads S-X3 with cyclohexane/ethyl acetate (1:1) as eluent (eluate volume range 135-165 ml). After the addition of 0.1 ml acetic acid the eluate is evaporated to dryness and the residue is dissolved in dichloromethane/acetic acid (99.9:0.1) and cleaned up by silica gel column chromatography using the same solvent as eluent. The first 100 ml is discarded and chromatography is continued with a further 80 ml of the same eluent. The eluate containing 0.5 ml acetic acid is brought to dryness and the residue dissolved in 5 ml acetonitrile/acetic acid/methanol/water (46.8:0.2:8.0:45) for determination by HPLC with a UV detector (LOD 0.05 mg/kg).

In the trials on cherries conducted between 1967 and 1972 a colorimetric method (LOD between 0.03 and 0.06 mg/kg) was used (Sieper and Pies, 1968).

USE PATTERN

GAP for the world-wide use of dithianon was reported in the 1992 evaluation. The information on GAP provided to the present Meeting by Germany and the UK is basically the same as in 1992 but contains more details, e.g. in application rates (see Table 1). New information was provided only by Finland. German GAP for uses on cereals was requested in 1992. At present there is no authorization for uses on cereals in Germany; GAP for wheat is still pending.

dithianon

Table 1. Registered uses of dithianon in Germany, Finland and the UK.

Crop	Country	Form.	Application			PHI, days
			Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Apple	UK	750 SC	1.3	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
	Finland	750 SC		0.045	5	21
		500 SC				
Crab-apple	UK	750 SC	0.83	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
Pear	UK	750 SC	1.3	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
Quince	UK	750 SC	0.83	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
Pome fruits	Germany	750 SC	0.56	0.038	12	21
Cherries	Australia			0.075-0.11	2-4	21
	Germany	750 SC	0.56	0.038	3	28
	Netherlands		0.49-0.78	0.049-0.052	4	28
	Switzerland			0.05-0.075	multiple	21
Strawberry	Finland	750 SC			0.045	21
		250 SC				
Wine grapes	Germany	750 SC	0.23-0.9	0.038-0.056	3-8	42
		250 WP	0.19-0.5	0.03	3-8	42
		333 SC	0.1-0.27	0.017-0.033	3-8	42
Hops	Germany	750 SC	0.38-1.5	0.038	10	14
		250 WP	0.25-1.0	0.025	12	14
		333 SC	0.17-0.67	0.017	10	14

dithianon

RESIDUES RESULTING FROM SUPERVISED TRIALS

Cherries. In addition to the six German trials carried out in 1985/86 and evaluated in 1992, the Meeting received residue data from 1967 to 1972 on sour (7 trials) and sweet cherries (5 trials) in Germany. Two further trials on sour cherries which included residues in processed products were conducted in Germany in 1993. Two new trials on sweet cherries (1992) were also carried out in France. Details of the new and previously reported trials are given in Tables 2 and 3. The underlined residues are from treatments according to GAP.

Table 2. Residues of dithianon in sour cherries.

Country, Year	Application				PHI, days	Residues, mg/kg	Reference or report
	Form	No	kg ai/ha	kg ai/hl			
Germany, 1967	253 SC	4	0.4	0.05	0	11	R 118-69/1
					3	9.8	
					9	7.9	
					16	6.3	
					23	<u>2.9</u> ¹	
					30	0.85	
					37	0.75	
Germany, 1968	253 SC	4	0.4	0.05	0	9.6	R 118-69/2
					4	10	
					11	1.9	
					18	0.6	
					22	<u>0.62</u> ¹	
Germany, 1969	253 SC	5	1.4	0.05	0	10	R 118-69/3
					2	6.9	
					7	7.7	
Germany, 1971	253 SC	3	1.4	0.05	0	12	R 123-72/1
					7	6.4	
					14	6.8	
					21	<u>4.3</u> ¹	
					28	4.3	
Germany, 1971	253 SC	3	0.75	0.05	0	13	R 123-72/2
					7	13	
					14	8.4	
					21	<u>3.7</u> ¹	
					28	1.6	
					35	0.89	
					42	1.0	
Germany, 1972	253 SC	3	0.75	0.05	0	3	R 123-72/3
					2	2.6	
					4	1.9	

dithianon

Country, Year	Application				PHI, days	Residues, mg/kg	Reference or report
	Form	No	kg ai/ha	kg ai/hl			
					7	1.4	
					14	0.62	
1972	253 SC	3	0.75	0.05	0	5.6	R 123-72/4
					2	5.2	
					4	3.7	
					8	2.9	
					14	1.5	
1985	750 SC	3	0.75	0.15	0	1.3	CME 02444
					13	0.66	
					20	0.17	
					27	0.2	
					34	0.14	
1985	750 SC	3	0.56	0.11	0	1.9	CME 02449
					14	1.3	
					21	0.8	
					28	<u>0.41</u> ²	
1985	253 SC	3	1.0	0.2	0	0.86	CME 02443
					13	0.53	
					20	0.16	
					27	0.14	
					34	0.13	
1985	253 SC	3	0.76	0.15	0	2.6	CME 02445
					14	0.81	
					21	0.84	
					28	0.76	
					35	0.57	
Germany,	253 SC	3	0.59	0.15	0	2.5	CME 02223
1986					14	0.92	
					21	0.49	
					28	<u>0.26</u> ²	
					35	0.2	
1986	750 SC	3	0.44	0.11	0	2.2	CME 02221
					14	0.86	
					21	0.28	
					28	0.22	
					35	0.12	

dithianon

1993	750 SC	3	0.54	0.075	0	fruit 2.5	SKG-9303-01
			0.57		27	fruit <u>0.48</u> ²	15079
			0.56			fruit, washed 0.24	
						preserved <0.05	
						jam <0.05	
						juice <0.05	
1993	750 SC	3	0.56	0.075	0	fruit 3	SKG 9303-02
					27	fruit <u>0.77</u> ²	15080
						fruit, washed 0.28	
						preserved <0.05	
						jam <0.05	
						juice <0.05	
Netherlands, 1976		3	0.245		19	0.18	JMPR 1992 Evaluation
		3	0.245		21	2.0	

dithianon

¹ according to Swiss GAP

² according to German GAP

Table 3. Residues of dithianon in sweet cherries.

Country, Year	Application				PHI, days	Residues, mg/kg	Reference or report
	Form	No	kg ai/ha	kg ai/hl			
Germany,	253 SC	10	0.4	0.05	0	4.5	R 118-69/4
1968					4	3.1	
					6	1.8	
					7	1.9	
1969	253 SC	6	0.4	0.05	0	6.9	R 118-69/5
					2	7.1	
					7	6.6	
1971	253 SC	3	1.6	0.05	0	7.4	R 123-72/5
					7	4.1	
					14	2.1	
					21	<u>2.3</u> ¹	
					28	1.4	
1971	253 SC	3	0.75	0.05	0	9.2	R 123-72/6
					7	7.6	
					14	3	
					21	<u>1.9</u> ¹	
					28	1.1	
Germany,	253 SC	3	0.75	0.05	0	6	R 123-72/7
1972					2	4.1	
					4	3.8	
					8	2.9	
					14	1.5	
France, 1992	750 SC	3	0.38	0.038	14	0.11	S/FR/R/92/072
1992	750 SC	3	0.38	0.038	28	0.05	S/FR/R/92/073

¹ According to Swiss GAP

Apples. Summary information on residues from supervised trials on apples was made available by Finland (Anon., 1994b). The trials (Table 4) do not reflect GAP in Finland: they may be considered only as supplementary to those reviewed in 1992 on which the maximum residue level estimated for pome fruit was based.

Table 4. Residues of dithianon in apples from supervised trials in Finland (Anon., 1994b).

dithianon

Year	Application				PHI, days	Residues, mg/kg
	Form	No	kg ai/ha	kg ai/hl		
1985	750 SC	4	2.0	0.045	34	0.03
		4	2.0	0.045	34	0.04
1986	750 SC	5	0.6	0.045	14	2.2 ¹
		5	0.6	0.045	21	0.5 ¹
		5	0.6	0.045	28	2.5 ¹
1987	750 SC	5	0.6	0.045	21	16 ¹
		5	0.6	0.045	28	12 ¹
		5	0.6	0.045	35	9 ¹
1988	750 SC	5	0.8	0.045	31	0.06
		5	0.8	0.045	32	0.2
		5	0.7	0.045	45	0.2
1989	750 SC	5	0.75	0.045	14	1.0 ¹
		5	0.75	0.045	21	0.8 ¹
		5	0.75	0.045	28	0.3 ¹
1993	500 SC	5	0.5	0.045	14	1.1 ¹
		5	0.5	0.045	21	1.1 ¹
		5	0.5	0.045	28	0.9 ¹

¹ Last spraying carried out about 30 days later than normal

APPRAISAL

Dithianon is a multi-site protective fungicide which inhibits spore germination. It was first reviewed by the 1992 JMPR. At the 1994 CCPR the delegation of Germany questioned the data on which the maximum residue level of 1 mg/kg on cherries estimated by the 1992 JMPR were based.

Items of further work or information listed as desirable by the 1992 JMPR were (1) additional studies on the fate of residues in farm animals (metabolism and transfer studies), and on plant metabolism and soil degradation, and (2) GAP and residue information for uses on cereals in Germany, The Netherlands and the UK.

The present Meeting received updated information on GAP, summaries of residue trials on cherries and explanatory notes by Germany. The manufacturer provided reports of two supervised residue trials from Germany and two from France. Summarized information on GAP was made available by Finland and the UK. A summary of residue trials on apples was also provided by Finland.

The determination of residues in cherries in older trials was by the formation of a coloured morpholine adduct. In the current procedure, cherries are homogenized with acetone, hydrochloric acid and water, the homogenate is partitioned with hexane and dichloromethane and the residue cleaned up by gel permeation chromatography with cyclohexane/ethyl acetate. After addition of 0.1 ml acetic acid the solvent is evaporated and the residue dissolved in acidified dichloromethane and cleaned up further by silica gel column chromatography. The determination is carried out by HPLC with UV detection. The LOD is 0.05 mg/kg.

dithianon

The information on GAP provided by Germany and the UK is basically the same as supplied in 1992. Therefore at present there is no approved use on cereals in Germany or the UK.

The present Meeting reviewed the new reports of residue trials on cherries and apples in the context of those previously reviewed.

Cherries. The 1992 JMPR estimated a maximum residue level of 1 mg/kg, based on six German and two Dutch trials (3 treatments, 0.15-0.75 kg ai/ha) with residues from 0.14 mg/kg to 0.8 mg/kg at 21-28 days after treatment. The critical GAP exists in Australia (2-4 treatments, 0.075-0.113 kg ai/hl, 21-day PHI), and Switzerland (multiple applications, 0.05-0.075 kg ai/hl, 21-day PHI), followed by The Netherlands (4 treatments, 0.049-0.052 kg ai/hl, 0.49-0.78 kg ai/ha, 28-day PHI) and Germany (3 treatments, 0.038 kg ai/hl, 0.56 kg ai/ha, 28-day PHI).

In addition to the six German trials carried out in 1985/86 and evaluated in 1992, the Meeting received data on 7 trials on sour cherries and 5 trials on sweet cherries in Germany from 1967 to 1972, which could be evaluated on the basis of Swiss GAP. Dithianon was applied three to ten times at 0.05 kg ai/hl (0.4-1.4 kg ai/ha). After PHIs of 21-23 days the residues in the fruit ranged from 0.62 to 4.3 mg/kg.

In 1993 two further trials were conducted on sour cherries in Germany which included analyses of processed products. After three applications at 0.56 kg ai/ha and a 27-day PHI the residues in the fruit were 0.48 and 0.77 mg/kg, reduced by washing to 0.24 and 0.28 mg/kg respectively. No residues above the limit of determination (0.05 mg/kg) could be detected in preserves, jam or juice.

Two new trials on sweet cherries were carried out in France in 1992 (3 treatments, 0.38 kg ai/ha, 0.038 kg ai/hl). The residues 14 or 28 days after application were 0.11 and 0.05 mg/kg.

After re-evaluation of all results from application rates of 0.038-0.075 kg ai/hl or 0.49-0.78 kg ai/ha according to the reported European GAP the Meeting estimated a maximum residue level of 5 mg/kg for cherries to replace the previous recommendation (1 mg/kg).

Apples. A short summary report of trials on apples was made available by Finland. Dithianon was applied four or five times a year at application rates from 0.5 to 2 kg ai/ha. Residues after a PHI of 21 days ranged from 0.5 to 16 mg/kg. The high residue occurred because the last treatment was carried out about 30 days later than usual. The data do not reflect GAP in Finland but may be considered as supplementing the results provided in 1992 on which an estimated maximum residue level for pome fruit was based. The Meeting considered that they supported the previous estimate of 5 mg/kg.

RECOMMENDATIONS

The Meeting estimated the revised maximum residue level for cherries shown below, which is recommended for use as an MRL.

Definition of the residue: dithianon

Commodity		Recommended MRL		PHI on which based, days
CCN	Name	New	Previous	
FS 0013	Cherries	5	1	21

dithianon

FURTHER WORK OR INFORMATION

Desirable

Additional studies on the fate of residues in farm animals (metabolism and transfer studies), and on plant metabolism and soil degradation (from 1992).

REFERENCES

Anon. 1994a. Information on GAP, residue data and explanatory notes on dithianon for the 1995 JMPR. Federal Biological Research Centre for Agriculture and Forestry, Federal Republic of Germany, May 1994. Unpublished.

Anon. 1994b. Information on residues of dithianon in apples for the 1995 JMPR. Ministry of Trade and Industry, Advisory Committee on Foodstuffs, Finland, November 30, 1994. Unpublished.

Anon. 1994c. Information on GAP for dithianon for the 1995 JMPR. Pesticides Safety Directorate UK, November 31, 1994. Unpublished.

Carlou, R. 1992. Residues of dithianon in cherries from France treated with delan - 1992 trials. Betr. 93.006, budget code 876.72.700.

Sieper, H. and Pies, H. 1968. Verfahren zur Bestimmung des Fungizids Dithianon auf Äpfeln. Z. Anal. Chem. 242, 234-245.

Specht, W. 1994. HPLC- Bestimmung von Dithianon in pflanzlichem Material.

In: Determination of residues of dithianon in cherries and their processed products after application of SAG 107 11 F. SHELL trial No. SKG-9303-01 and SKG-9303-02, project identity SHE-9301 Az. 13932/93. Unpublished.

Weeren, R.D. Weber, H. and Kwasnick, A. 1994. Determination of residues of dithianon in cherries and their processed products after application of SAG 107 11 F. SHELL trial No. SKG-9303-01 and SKG-9303-02, project identity SHE-9301 Az. 13932/93. Unpublished.