

## TOLYLFLUANID (162)

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### EXPLANATION

Tolylfluanid, a fungicide closely related to dichlofluanid, was first evaluated by the JMPR in 1988, with a subsequent residue evaluation in 1990. The compound was included in the Codex priority list at the 30th Session of the CCPR (1998; ALINORM 99/24, Appendix VII), and at the 31st Session was scheduled for periodic review in 2002 (1999; ALINORM 99/24A, para. 134 and Appendix VII). Currently there are Codex MRLs for black, red and white currants, gherkins, head lettuce, pome fruits, strawberry, and tomato.

The 29th CCPR was informed that dichlofluanid would not be supported beyond 2000. It was agreed that the Codex MRLs for dichlofluanid should be retained until its registration expires (ALINORM 97/24A, para. 58). The 33rd Session of the CCPR continued to retain the CXLs for dichlofluanid noting that the use of dichlofluanid would be replaced by that of tolylfluanid (ALINORM 01/24A, para. 129), and the 34th Session recommended the deletion of the CXLs for dichlofluanid in or on barley, cherries, common bean (pods and/or immature seeds), oats, rye, wheat and wheat straw and fodder (ALINORM 03/24, para. 113).

The Meeting received extensive information on the metabolism and environmental fate of tolylfluanid, methods of analysis for residues, freezer storage stability, national registered use patterns, and the results of supervised trials to support the existing CXLs for pome fruits, strawberry, blackcurrant, tomato and head lettuce and new maximum residue levels for blackberry, raspberry, grapes, cucumber, melons, sweet pepper, leek and hops. The fate of residues in processing and national MRLs were reported. The government of Poland provided information on GAP and trials on apples and strawberries, and the governments of Germany and The Netherlands provided information on GAP.

### IDENTITY

ISO Common name: tolylfluanid

#### Chemical name

IUPAC: *N*-dichlorofluoromethylthio-*N'*, *N'*-dimethyl-*N*-*p*-tolylsulfamide

CAS: 1,1-dichloro-*N*-[(dimethylamino)sulfonyl]-1-fluoro-*N*-(4-methylphenyl)-methanesulfenamide

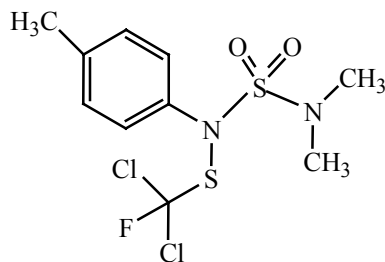
CAS Registry No.: 731-27-1

CIPAC No.: 275

#### Development code

and trade names: Bay 49854, Euparen M, Euparen Multi, Methyl-Euparen, , Elvaron M, Elvaron Multi

Structural formula:

Molecular formula:  $C_{10}H_{13}Cl_2FN_2O_2S_2$ 

Molecular weight: 347.25

**Physical and chemical properties**Pure active ingredient

Appearance: solid, colourless crystals (Schneider, 2002a)

Vapour pressure: 0.2 mPa at 20°C; 0.4 mPa at 25°C (Weber and Krohn, 1982)

Melting point: 93°C (Krohn, 1994)

Relative density: 1.520 at 20-25°C (Weber, 1984)

Henry's law constant:  $7.7 \times 10^{-2} \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$  at 20°C (Krohn, 1993)Octanol-water partition coefficient: 8000 (log  $P_{ow}$  3.90) at 21°C (Krohn, 1988a)

Solubility at 20°C: water, 0.90 mg/l (Krohn, 1985);

acetone, >250 g/l  
 acetonitrile, >250 g/l  
 dichloromethane, >250 g/l  
 dimethylsulfoxide, >250 g/l  
 ethyl acetate, >250 g/l  
 n-heptane, 54 g/l  
 1-octanol, 16 g/l  
 polyethylene glycol, 56 g/l  
 2-propanol, 22 g/l  
 xylene, 190 g/l (Krohn, 1996)

Hydrolysis at 22°C: half-life in sterile aqueous buffer solutions:  
 12 days at pH 4; 29 hours at pH 7; and << 10 minutes at pH 9 (Wilmes, 1982)

Photolysis: UV absorption data showed that tolylfluanid in aqueous solution does not absorb any light at wavelengths above 290 nm. No contribution of the direct photodegradation to the overall elimination of tolylfluanid in the environment is to be expected (Hellpointner, 1992)

Thermal stability: stable at room temperature (Mix and Berg, 1988)

Dissociation constant: aqueous solution of tolylfluanid does not show basic or acidic properties, so

it was not possible to specify pKa value in aqueous systems (Krohn, 1988).

#### Technical material

Purity:	≥96%; impurities total ≤4%
Appearance:	Whitish crystalline powder with lumpy parts (Schneider, 2002a)
Odour:	Weakly acidulous; musty (Schneider, 2002b)

### **METABOLISM AND ENVIRONMENTAL FATE**

#### **Animal metabolism**

The Meeting received information on the fate of tolyfluanid in rats, a lactating goat and laying hens using [U-phenyl-<sup>14</sup>C]tolylfluanid and [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid to trace the administered tolyfluanid. These studies were also reviewed by the WHO Core Assessment Group at the current Meeting.

Rats. When rats were dosed orally with [U-phenyl-<sup>14</sup>C]tolylfluanid (Ecker *et al.*, 1987; Weber, 1988; Abbink and Weber, 1988; Klein, 1991) or [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid (Weber *et al.*, 1977) at up to 100 mg/kg bw, more than 95% of the administered [U-phenyl-<sup>14</sup>C]tolylfluanid was absorbed and about 70 to 80% of the [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid. Virtually all the absorbed radioactivity was excreted rapidly, mainly in the urine and to a much lesser extent in the faeces. After two days less than 0.5% of the [U-phenyl-<sup>14</sup>C]tolylfluanid and less than 1.8% of the [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid was retained in the body excluding the gastrointestinal tract. This implies that no accumulation of tolyfluanid is to be expected. The main radioactive metabolites in the urine, from phenyl-labelled tolyfluanid were identified as 4-(dimethylaminosulfonylamino)benzoic acid (mean 68% of the TRR), and 4-(methylaminosulfonylamino)benzoic acid (mean 5%). The parent compound and *N,N*-dimethyl-*N'*-(4-methylphenyl)sulfamide (DMST) were found only in the faeces (8% and 7% respectively). When dichlorofluoromethyl-labelled tolyfluanid was used, the main metabolite in the urine was thiazolidine-2-thione-4-carboxylic acid (TTCA; 73-74% of the TRR).

Lactating goat. [U-phenyl-<sup>14</sup>C]tolylfluanid was administered orally by gavage to a single lactating goat at 10 mg/kg bw once daily for 3 days (equivalent to 250 ppm in the diet). Radioactivity was measured in the excreta, plasma and milk and in edible tissues at slaughter (Ecker and Weber, 1995).

50 hours after the first dose (2 hours after the last dose) 59.7% of the total administered dose had been excreted (49.4% in the urine and 10.1% in the faeces). The relatively high concentration in the liver indicates that a significant amount of the radioactivity in the faeces had been absorbed before secretion in the bile fluid. This was confirmed by plasma curve analysis. Only 0.24% of the total administered dose was secreted in the milk. At slaughter, the total radioactive residues in edible tissues and organs were estimated to be only 2.8% of the total administered dose.

Table 1. Distribution of [U-phenyl-<sup>14</sup>C]tolylfluanid in the edible tissues of a lactating goat (Ecker and Weber, 1995).

Parent compound equivalent (mg/kg)								
kidney	liver	perirenal fat	omental fat	Subcutaneous fat	flank muscle	loin muscle	round muscle	milk at slaughter
37.0	20.58	2.28	1.3	0.85	0.65	0.49	0.44	0.24

Since the goat was slaughtered about one hour after the peak plasma level was reached, these results represent maximum concentrations to be found in the tissues and organs.

No parent compound was detected in the tissues, organs or milk. The identity and distribution of metabolites in the organs, tissues and milk are shown in Table 2. DMST was formed, which was further metabolized by oxidation via the intermediate 4-hydroxymethyl-DMST to 4-(dimethylaminosulfonylamino)benzoic acid (XI) which was conjugated with glycine, yielding the corresponding hippuric acid (XIII). Metabolites XI and XIII, and in fat DMST, were the main degradation products. In addition, the corresponding demethylated metabolites IX, X, XII and XIV were formed in amounts below 10% of the total radioactive residues.

Table 2. Distribution of compounds in the edible tissues, organs and milk of a lactating goat after doses of [U-phenyl-<sup>14</sup>C]tolyfluanid at 10 mg /kg bw once daily for 3 days (Ecker and Weber, 1995). The results are from the third analysis, conducted to test the stability of residues during extraction and analysis (the first preliminary extraction and work-up trials were disregarded). Milk was analysed a fourth time for confirmation.

Compound	% of recovered radioactivity				
	Milk	Muscle <sup>1</sup>	Liver	Kidney	Fat <sup>2</sup>
Tolyfluanid	n.d.	n.d.	n.d.	n.d.	n.d.
DMST	n.d.	3.52	4.83	0.41	14.68
4-hydroxymethyl-DMST	- <sup>3</sup>	5.19	n.d.	n.d.	2.18
4-(methylaminosulfonylamino)benzyl alcohol (X)	- <sup>4</sup>	2.43	n.d.	n.d.	n.d.
4-(methylaminosulfonylamino)hippuric acid (XIV)	1.69	1.4	2.72	2.28	2.4
4-(methylaminosulfonylamino)benzoic acid (XII)	3.65	4.98	0.73	7.44	7.4
4-(dimethylaminosulfonylamino)hippuric acid (XIII)	35.41	37.36	57.67	45.2	42.12
4-(dimethylaminosulfonylamino)benzoic acid (XI)	23.92	22.84	15.11	37.41	22.11
Methylaminosulfotoluidide (IX)	1.06	6.21	0.96	0.8	3.9
Sum of identified metabolites	65.73	83.93	82.01	93.53	94.74
Sum of unidentified metabolites	11.62	4.51	2.22	3.49	-
Total radioactive residue (mg/kg in parent compound equivalents)	0.24	0.44-0.65	20.58	37.0	0.85-2.28

n.d.: not detected

<sup>1</sup> composite samples of flank, loin and round muscle

<sup>2</sup> composite samples of perirenal, omental and subcutaneous fat

<sup>3</sup> 4-(methylaminosulfonylamino)benzyl alcohol measured at 1.95% in milk sample at fourth analysis

<sup>4</sup> (X) measured at 4.38% in milk sample at second analysis

Laying hens. [U-phenyl-<sup>14</sup>C]tolyfluanid was administered to hens either as a single oral dose of 5 mg/kg bw or once daily for 3 days at a rate of 5 mg kg bw (equivalent to 83 ppm in the diet). Radioactivity was determined in the excreta, plasma and eggs at various intervals and in edible tissues and organs when the hens had been killed (Weber and Ecker, 1996).

56 hours after the first dose (i.e. 8 hours after the last) on average 83.9% of the total administered radioactivity had been excreted. The plasma curve analysis also indicated complete

absorption. On average less than 0.01% of the administered dose was in the eggs. At slaughter the total radioactive residues in the tissues and organs dissected from the body was estimated to be approximately 0.18% of the total administered dose. On the basis of these values, the calculated recovery was 84.1%.

The total residues in the organs, tissues and eggs were very low, with the highest levels in the excretory organs. The results are shown in Table 3.

Table 3. Distribution of  $^{14}\text{C}$  [U-phenyl- $^{14}\text{C}$ ]tolyfluanid in edible tissues of hens (Weber and Ecker, 1996).

Parent compound equivalent (mg/kg)							
kidney	liver	eggs dissected from the ovaries	skin without subcutaneous fat	breast muscle	thigh muscle	eggs collected during the last period before slaughter	Subcutaneous fat
0.47	0.23	0.048	0.045	0.037	0.027	0.024	0.019

Owing to the low levels of residues the work-up procedure and analyses were not repeated, except in liver. The main metabolites were DMST and the corresponding benzoic acid (XI), formed via 4-hydroxymethyl-DMST. In addition, the corresponding demethylated metabolites (IX, X and XII) were formed in minor quantities as well as 4-(dimethylaminosulfonylamino)hippuric acid (XIII) in eggs and 4-(methylaminosulfonylamino)benzoic acid (XII) in muscle and liver (Table 9).

Table 4. Identity and distribution of metabolites in the edible tissues, organs and eggs of laying hens after doses of [U-phenyl- $^{14}\text{C}$ ]tolyfluanid at a rate of 5 mg /kg bw once daily for 3 days (Weber and Ecker, 1996).

Compound	% of recovered radioactivity			
	Eggs	Muscle <sup>1</sup>	Fat	Liver <sup>2</sup>
Tolyfluanid	n.d.	n.d.	n.d.	n.d.
DMST	3.75	0.69	65.83	n.d.
4-hydroxymethyl-DMST	4.81	1.0	n.d.	1.74
4-(methylaminosulfonylamino)benzyl alcohol (X)	2.94	0.78	n.d.	n.d.
4-(methylaminosulfonylamino)benzoic acid (XII)	3.33	13.29	n.d.	11.47
4-(dimethylaminosulfonylamino)hippuric acid (XIII)	6.51	n.d.	n.d.	n.d.
4-(dimethylaminosulfonylamino)benzoic acid (XI)	37.0	55.53	15.32	10.59
Methylaminosulfotoluidide (IX)	3.63	0.83	n.d.	n.d.
Sum of identified metabolites	61.97	72.12	81.15	23.8
Total radioactive residues (mg/kg in parent compound equivalents)	0.024-0.048	0.027-0.037	0.019	0.23

n.d.: not detected

<sup>1</sup> Composite samples of breast and thigh muscle

<sup>2</sup> Combination of results from two analyses with different extraction procedures

Tolyfluanid is rapidly metabolized in rats, goats and hens by cleavage of the N-S bond to form DMST and in rats via a derivative of the  $-\text{SCCl}_2\text{F}$  side chain which becomes incorporated into TTCA. DMST is further metabolized into 4-hydroxymethyl-DMST which is subsequently oxidized to

form 4-(dimethylaminosulfonylamino)benzoic acid (XI), which may conjugate with glycine to form 4-(dimethylaminosulfonylamino)hippuric acid (XIII). In addition small amounts of the demethylated products of DMST, 4-hydroxymethyl-DMST, 4-(dimethylaminosulfonylamino)benzoic acid and 4-(dimethylaminosulfonylamino)hippuric acid are formed. The proposed metabolic pathways in animals are shown in Figure 1.

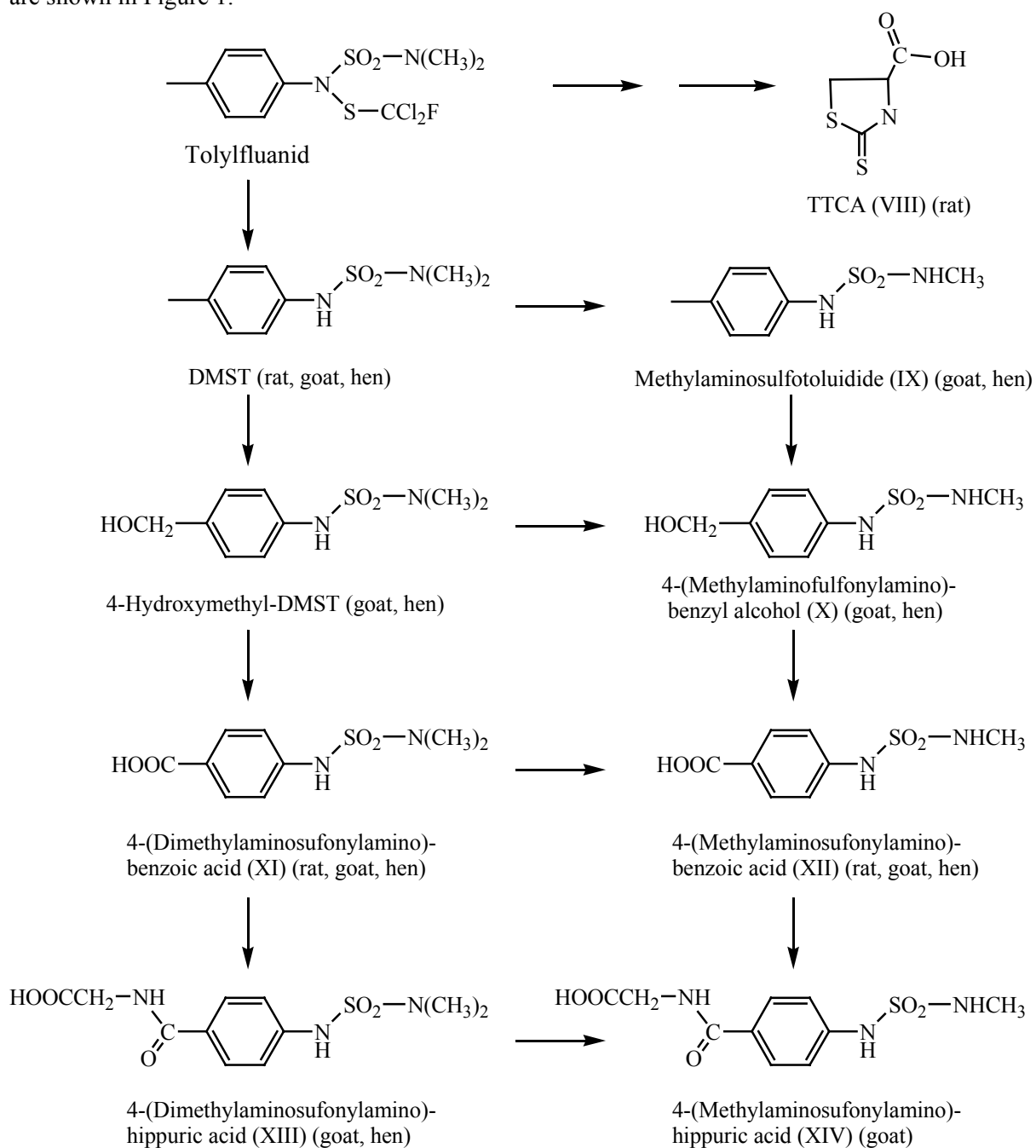


Figure 1. Proposed metabolic pathways of tolylfluanid in animals.

### Plant metabolism

The Meeting received information on the fate of [U-phenyl- $^{14}\text{C}$ ]tolylfluanid and/or [dichlorofluoromethyl- $^{14}\text{C}$ ]tolylfluanid after foliar application to apples, grapes strawberries and lettuce.

**Apples.** A solution of [U-phenyl-<sup>14</sup>C]tolyfluanid was applied to the surfaces of individual apples three times at a total rate of 0.5 mg ai/apple (Linke-Ritzer *et al.*, 1988). This resulted in a TRR of 2.62 mg parent compound equivalents/kg, corresponding to residue concentrations in the field trials (2-5 mg/kg on day of last application) at applications of 1.125 kg/ha for a maximum of 15 times per season. The TRR in apples harvested 7 and 14 days after the last application were 1.28 and 1.12 mg parent compound equivalents/kg respectively, the majority of which was on the surface (92% on day 7 and 88% on day 14) and was removed by surface washing. The sum of the TRR in the peel and pulp accounted for 8.4% on day 7 and 12.4% on day 14.

The parent compound accounted for 88% of the TRR on day 7 and 82% on day 14, and DMST 3.4% on day 7 and 7.9% on day 14. In total 94-97% of the TRR was characterized or identified. On average 0.5% of the TRR was not extracted by water or organic solvents (Table 5).

Table 5. Distribution and characterization of <sup>14</sup>C in apples treated three times on surface with [U-phenyl-<sup>14</sup>C]tolyfluanid (Linke-Ritzer *et al.*, 1988).

Compound	Radioactivity in/on treated apples (% of TRR)					
	PHI 7 days			PHI 14 days		
	Surface rinse	Peel + pulp	Total	Surface rinse	Peel + pulp	Total
Tolyfluanid	87.9	2.3	90.2	81.5	0.8	82.3
DMST	2.9	0.5	3.4	4.9	3.0	7.9
Sum of identified metabolites	90.8	2.8	93.6	86.4	3.8	90.2
Sum of unidentified metabolites	0.8	5.2	6.0	1.2	8.0	9.2
Sum of unextractable metabolites	-	0.4	0.4	-	0.6	0.6
Total	91.6	8.4	100	87.6	12.4	100
TRR (mg/kg parent compound equivalents)			1.28			1.12

In another trial [dichlorofluoromethyl-<sup>14</sup>C]tolyfluanid was sprayed on individual apples in a greenhouse (Vonk and den Daas, 1977). The TRR was approximately 1 mg parent compound equivalents/kg in apples picked immediately after treatment, which is consistent with concentrations in the field trials of 0.28-3.5 mg/kg on the day of last application. Apples were picked 0, 7, 14, 21 and 28 days after treatment. The TRR decreased to 58% of the initial value within 28 days, probably because of unidentified volatile compounds. Washing the apples with methanol removed 71% of the TRR on day 28. Unchanged tolyfluanid was the predominant component on the surface and accounted for 41% of the applied radioactivity (72% of the TRR) on day 28. The sum of the radioactivity in the peel and pulp accounted for 28% of the TRR. On day 28 a total of 4.4% (2.0% in peel and 2.4% in pulp) of the recovered radioactivity was not extracted with acetone-water (2:5).

**Grapes.** [U-phenyl-<sup>14</sup>C]tolyfluanid was sprayed directly onto bunches of grapes twice with a 21-day interval at a total rate of approximately 1.3 mg ai/bunch (Babczynski *et al.*, 1993), resulting in a TRR of 4.0 mg parent compound equivalents/kg in the bunches, including stems and stalks, collected immediately after the second application, which is similar to the residue concentrations in the field trials (0.65-11 mg/kg on the day of last application), indicating that the treatment corresponds to agricultural use (several applications at 0.5-2 kg ai/ha). The TRR in the bunches of grapes excluding stems and stalks decreased to 1.83 mg parent compound equivalents/kg 35 days after the second application, and unchanged tolyfluanid and DMST accounted for 13% (0.24 mg/kg) and 1.9% (0.04 mg/kg) respectively. The main metabolites in grapes were 4-hydroxymethyl-DMST glucoside (IV) (46% of the TRR, 0.84 mg parent compound equivalents/kg), 2-hydroxyphenyl-DMST glucoside (VI)

(13%, 0.24 mg/kg) and 3-hydroxyphenyl-DMST glucoside (VII) (1.8%, 0.03 mg/kg). There were eight minor metabolites, derived through further conjugation of the glucosides. In total 91.9% of the TRR was identified, and 2.9% not extracted by methanol, methanol-water (1:1) or dichloromethane.

Table 6. Distribution and characterization of  $^{14}\text{C}$  residues in grapes sprayed twice with [U-phenyl- $^{14}\text{C}$ ]tolyfluanid (Vonk and den Daas, 1977).

Compound	Radioactivity in/on treated grapes 35 days after last application (% of TRR)
Tolyfluanid	13.1
DMST	1.9
4-Hydroxymethyl-DMST	1.3
2-Hydroxyphenyl-DMST (V)	0.2
2-Hydroxyphenyl-DMST glucoside (VI)	13.1
Three other 2-Hydroxyphenyl-DMST-conjugates	6.0 (0.9, 2.3 and 2.8)
3-Hydroxyphenyl-DMST glucoside (VII)	1.8
Two other 3-Hydroxyphenyl-DMST-conjugates	1.7 (0.8 and 0.9)
4-Hydroxymethyl-DMST glucoside (IV)	46.0
Three other 4-Hydroxymethyl-DMST-conjugates	6.8 (0.8, 1.5 and 4.5)
Sum of identified metabolites	91.9
Sum of unidentified metabolites	5.2
Sum of unextractable metabolites	2.9
Total	100
TRR (mg/kg in parent compound equivalents)	1.83

No study was available on the fate of [dichlorofluoromethyl- $^{14}\text{C}$ ]tolyfluanid in grapes, but a study was conducted by Vogeler *et al.* (1979) on the fate of dichlofluanid, which has an identical side chain to tolyfluanid. [Dichlorofluoromethyl- $^{14}\text{C}$ ]dichlofluanid was applied once to bunches of grapes at a rate of 1 mg ai/bunch, corresponding to a normal concentration of a high volume spray application, common in viticulture. Dichlofluanid and two minor unidentified metabolites were found in grapes harvested after 35 days.

TTCA was not detected in grapes.

**Strawberries.** [U-phenyl- $^{14}\text{C}$ ]tolyfluanid was sprayed aerially twice on strawberries at a total rate of 0.485 g ai/0.6 m<sup>2</sup>, corresponding to 8.05 kg ai/ha (Reiner and Brauner, 1993). Although 2 applications were used and not 3, the use pattern was considered to be representative of the recommended use of tolyfluanid on strawberries. The TRR in and on berries harvested 14 days after the second application was 7.61 mg parent compound equivalents/kg; 72.5% was on the surface, of which 63.0% was unchanged tolyfluanid. The remaining 27.5% was recovered from the fruit. The main metabolites were DMST (6.2% of the TRR in surface rinse and 8.7% in fruit), 4-hydroxymethyl-DMST glucoside (IV) (1.0% in surface rinse and 5.6% in fruit), 4-hydroxymethyl-DMST (0.8% in surface rinse and 2.1% in fruit), and hydroxyphenyl-DMST glucoside (0.3% in surface rinse and 1.5% in fruit). The position of the hydroxyl group on the phenyl ring of the last metabolite was not determined owing to its low amount. A total of 91.9% of the TRR, corresponding to 6.99 mg/kg, was identified while 0.9% of the TRR was unextractable (Table 7).

Table 7. Distribution and characterization of  $^{14}\text{C}$  in strawberries sprayed twice with [U-phenyl- $^{14}\text{C}$ ]tolyfluanid (Reiner and Brauner, 1993).

Compound	Radioactivity in/on treated strawberries 14 days after the final treatment (% of TRR)		
	Surface rinse	Fruit	Total
Tolyfluanid	63.0	2.7	65.7
DMST	6.2	8.7	14.9
4-Hydroxymethyl-DMST	0.8	2.1	2.9
4-Hydroxymethyl-DMST glucoside (IV)	1.0	5.6	6.6



Compound	Radioactivity in/on treated strawberries 14 days after the final treatment (% of TRR)		
	Surface rinse	Fruit	Total
2-Hydroxyphenyl-DMST glucoside (VI) or 3-hydroxyphenyl-DMST glucoside	0.3	1.5	1.8
Sum of identified metabolites	71.3	20.6	91.9
Sum of unidentified metabolites	1.2	6.0	7.2
Sum of unextractable metabolites	-	0.9	0.9
Total	72.5	27.5	100
TRR (mg/kg parent compound equivalents)	7.61		

In two trials on strawberry plants grown in a closed air-flow system, fruit were sprayed once with 1.5 ml of either 0.125% (first experiment) or 0.65% ai solution (second experiment) of [dichlorofluoromethyl-<sup>13,14</sup>C]tolyfluanid (Hague *et al.*, 1979), corresponding to 1 or 5 times a common spray concentration of 0.125 kg ai/hl. Fruits at harvest 35 days after treatment contained 11.5% and 3.2% of the applied radioactivity respectively, and the release of <sup>14</sup>CO<sub>2</sub> was 4.3% and 11.7% respectively. COS was also detected, but to a much lesser extent. In the fruit in the second experiment the parent compound accounted for 1.3% of the TRR (0.04% of the applied radioactivity), and TTCA for 50.2% (1.6% of the applied radioactivity) (Schuphan *et al.*, 1979). TTCA was formed by the cleavage of the N-S bond and subsequent reaction between the released -SCCl<sub>2</sub>F moiety and cysteine. 68.2% of the TRR was identified and a total of 16.7% was unextractable with methanol, methanol/water or chloroform.

Lettuce. Lettuces at three different growth stages were sprayed twice with [U-phenyl-<sup>14</sup>C]tolyfluanid with an interval of 15 days at rates of 186 mg ai/m<sup>2</sup> and 184 mg ai/m<sup>2</sup> (Reiner, 2000), corresponding to a total of 3.70 kg ai/ha. Lettuces were harvested 7 (experiment A), 14 (experiment B) and 21 days (experiment C) after the second application. At harvest all the plants were similar in size.

Table 8. Growth stage of lettuce in the studies (Reiner, 2000).

	Days after transplant		
	Experiment A	Experiment B	Experiment C
Plants at the time of first spray application	15	8	1
Plants at the time of second spray application	30	23	16
Plants at harvest	37	37	37
Days after sowing			
Plants at harvest	57	58	57

The TRR decreased sharply with time after the second application. The size of the plants at the time of application may also have had some effect on the TRR. The main compound in the leaves was unchanged tolyfluanid, accounting for 95.4 (experiment A), 90.4 (experiment B) and 93.0% (experiment C) of the TRR. The metabolites DMST and 4-hydroxymethyl-DMST glucoside (IV) accounted for 2.0-5.2% and 0.6-2.0% of the TRR respectively. 97.0-99.1% of the TRR was identified and 0.2-0.9% was unextractable with methanol, methanol/water (1:1) or dichloromethane.

Table 9. Distribution and characterization of <sup>14</sup>C in lettuce sprayed twice with [U-phenyl-<sup>14</sup>C]tolyfluanid (Reiner, 2000).

Compound	Radioactivity in/on treated lettuce (% of TRR)		
	PHI 7 days	PHI 14 days	PHI 21 days
Tolyfluanid	95.4	90.4	93.0
DMST	3.1	5.2	2.0
4-Hydroxymethyl-DMST glucoside (IV)	0.6	1.9	2.0
Sum of identified metabolites	99.1	97.5	97.0
Sum of unidentified metabolites	0.7	1.9	2.1

Compound	Radioactivity in/on treated lettuce (% of TRR)		
	PHI 7 days	PHI 14 days	PHI 21 days
Sum of unextractable metabolites	0.2	0.6	0.9
Total	100	100	100
TRR (mg/kg in parent compound equivalents)	155	49.8	29.8

The metabolic patterns were similar in all plants studied. The metabolism in grapes showed a higher rate while most of the applied parent compound remained on the surface of apples and lettuce leaves. In grapes 4-hydroxymethyl-DMST glucoside and 2-hydroxyphenyl-DMST glucoside accounted for about 60% of the TRR.

The metabolism of tolylfluanid proceeds by cleavage of the N-S bond of tolylfluanid to form DMST and a derivative of the  $-SCCl_2F$  side chain. DMST is further metabolized to 4-hydroxymethyl-DMST and its glucoside and to a minor extent to 2-hydroxyphenyl-DMST and its glucoside and 3-hydroxyphenyl-DMST glucoside. These glucosides conjugate further with sugars to form more complex glycosides. As for the  $-SCCl_2F$  side chain, TTCA was identified in one study with [dichlorofluoromethyl- $^{14}C$ ]tolylfluanid on strawberries grown in a closed air-flow controlled system but not in studies on apples or grapes. The proposed metabolic pathways of tolylfluanid in plants are shown in Figure 2.

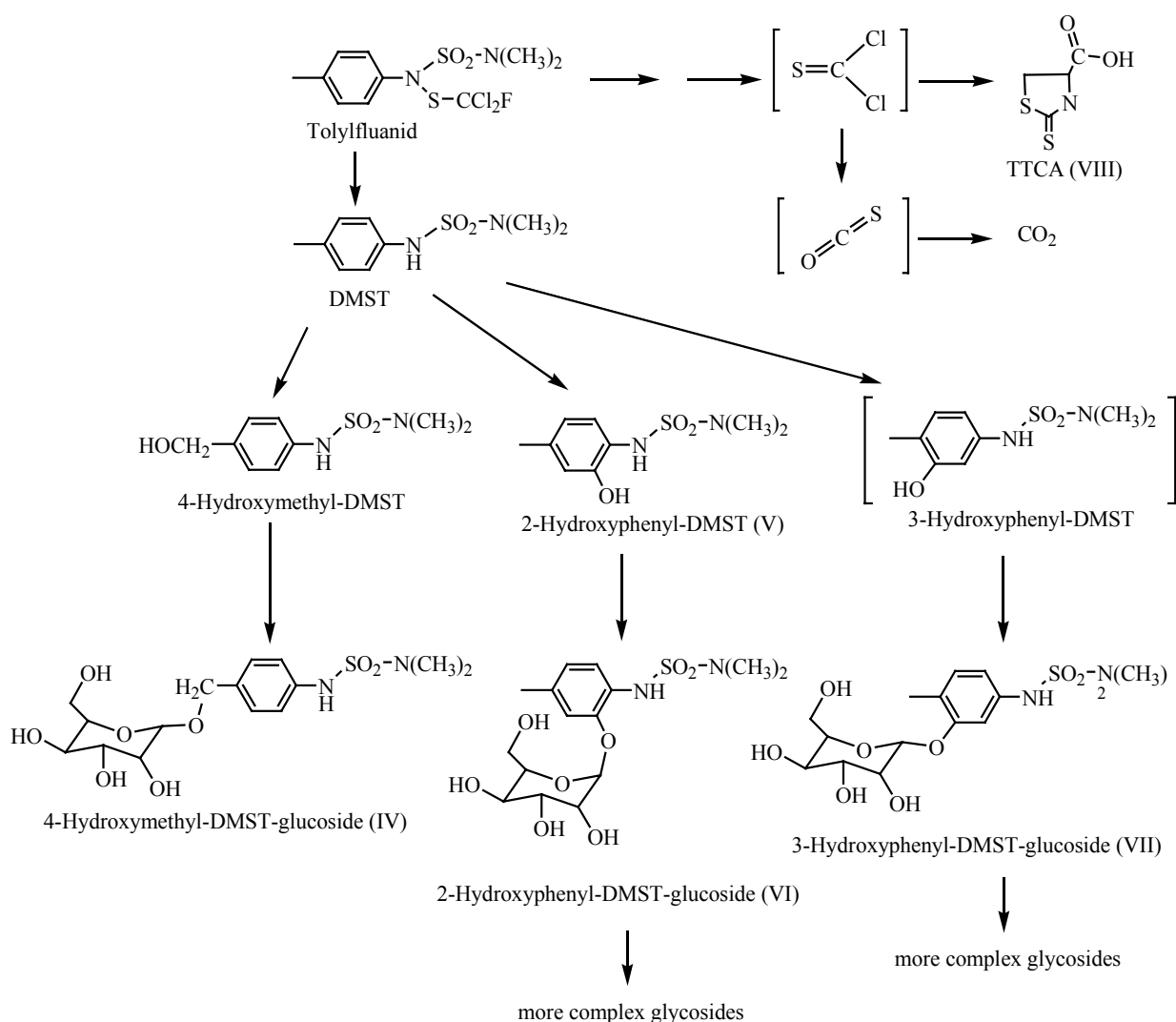


Figure 2. Proposed metabolic pathways of tolylfluanid in plants.

### Environmental fate in soil

The Meeting received information on the degradation, absorption and desorption, and mobility of tolyfluanid in soil.

Aerobic degradation. Scholz (1988a) incubated 3.0-3.5 mg [U-phenyl-<sup>14</sup>C]tolylfluanid/kg soil (on a dry basis) with four different soils in the dark at 22°C for 99 days. The moisture content of the samples was adjusted to 40% of the maximum water-holding capacity.

Tolyfluanid was degraded rapidly in soil under aerobic conditions mainly to DMST. The half-life was shorter than one day. DMST was further degraded through 4-(dimethylaminosulfonyl amino)benzoic acid (XI), 4-(methylaminosulfonylamino)benzoic acid (XII) and methylamino sulfotoluidide (IX) to CO<sub>2</sub> (24.7%-40.0% of the applied radioactivity on day 99). The amount of unextracted radioactivity increased with time, reaching a peak between days 15 and 64. On day 99 it accounted for 52.2-72.3% of the applied radioactivity, and was associated with fulvic and humic acid fractions. Only DMST could be identified from the unextracted residues (Table 10).

Table 10. Degradation of tolyfluanid under aerobic condition at 22°C after application of [U-phenyl-<sup>14</sup>C]tolylfluanid to soil (Scholz, 1988a).

Soil/application rate	% of applied radioactivity										
	DAT	Tolyfluanid	DMST	IX	XI	XII	Others	CO <sub>2</sub>	Ex-traced	Unex-traced	Total
loamy sand <sup>1</sup> (sand, 58.6%; silt, 28.1%; clay, 13.2%)/ 3.5 mg ai/kg	0	49.2	41.0	-	-	-	-	-	90.2	9.8	100.0
	1	23.7	57.1	-	1.1	-	-	0.4	81.3	18.1	99.8
	4	17.8	40.3	2.4	3.2	0.2	1.7	3.0	65.6	37.1	105.7
	8	14.5	23.1	1.5	1.8	1.4	1.9	8.3	43.3	51.0	102.6
	15	8.5	15.6	1.0	0.6	-	2.5	16.0	28.0	58.6	102.6
	32	9.2	6.1	0.3	0.2	0.2	2.3	23.4	18.1	60.9	102.4
	64	7.7	3.6	0.4	0.3	-	3.5	29.6	15.4	63.5	108.5
	99	6.8	2.8	0.2	0.2	-	2.8	34.0 <sup>2</sup>	12.7	56.0	102.7
clay silt <sup>2</sup> (sand, 2.6%; silt, 84.4%; clay, 13.0%)/ 3.1 mg ai/kg	0	22.0	61.2	-	0.7	-	0.4	-	84.3	15.7	100.0
	1	4.0	45.8	0.7	2.2	0.7	2.2	1.2	55.6	35.2	92.0
	4	4.8	12.9	0.8	1.7	0.7	2.5	9.2	23.4	65.5	98.1
	8	0.8	3.3	-	0.4	-	3.4	20.0	7.9	65.8	93.7
	15	1.8	2.7	1.7	-	-	2.1	25.1	8.3	68.2	101.6
	32	1.2	1.8	0.1	0.1	<0.1	2.4	27.6	5.6	60.1	93.3
	64	0.2	0.4	0.1	0.2	-	2.2	32.2	3.1	58.6	93.9
	99	0.4	0.6	0.2	0.2	-	1.8	38.8	3.2	61.0	103.0
clay silt <sup>2</sup> (sand, 36.5%; silt, 55.0%; clay, 8.5%)/ 3.0 mg ai/kg	0	28.2	58.9	-	1.4	-	0.9	-	89.4	10.6	100.0
	1	2.1	55.3	-	1.8	-	2.2	0.3	61.4	40.1	101.8
	4	1.2	14.8	1.3	4.1	-	2.5	2.9	23.9	70.0	96.8
	8	1.0	4.7	-	1.0	-	4.0	9.7	10.7	79.9	100.3
	15	0.9	1.9	0.4	-	-	3.4	14.0	6.6	83.7	104.3
	32	0.1	2.0	0.3	-	-	2.8	17.8	5.2	77.3	100.3
	64	0.1	1.0	0.2	0.4	0.1	2.1	21.1	3.9	71.0	96.0
	99	0.1	0.8	0.3	0.1	-	2.3	24.7	3.6	72.3	100.6
loamy silt <sup>2</sup> (sand, 79.6%; silt, 12.1%; clay, 8.3%)/ 3.4 mg ai/kg	0	26.0	60.2	-	-	-	3.0	-	89.2	10.8	100.0
	1	5.9	73.7	-	1.0	-	2.8	0.6	83.4	17.4	101.4
	4	2.8	52.5	1.3	2.6	1.4	4.6	3.7	65.2	33.4	102.3
	8	2.4	33.4	0.2	2.6	1.0	5.4	11.2	45.0	47.7	103.9
	15	2.1	14.8	0.7	0.5	-	6.2	21.4	24.3	56.1	101.8
	32	1.3	3.4	0.4	0.2	0.2	5.3	32.2	10.8	58.9	101.9
	64	1.0	1.7	0.5	0.2	-	4.2	29.9	7.6	57.7	95.2
	99	0.8	1.0	0.3	0.2	-	3.9	40.0	6.2	52.2	98.4

<sup>1</sup> mean of two values

IX: methylaminosulfotoluidide

<sup>2</sup> only one value  
 DAT: days after treatment

XI: 4-(dimethylaminosulfonylamino)benzoic acid  
 XII: 4-(methylaminosulfonylamino)benzoic acid

In another experiment [dichlorofluoromethyl-<sup>13,14</sup>C]tolyfluanid was incubated with two different soils at a concentration of 10 mg/kg soil (on a dry basis) in the dark at 22°C for 65 days (Schuphan and Ebing, 1979). The moisture content was adjusted to 40% of maximum capacity. The main degradation product in both soils was <sup>14</sup>CO<sub>2</sub>, which accounted for 65% and 77% of the applied radioactivity after 65 days. The half-life of tolyfluanid was estimated to be 1 day for one soil and 2-3 days for the other. Unextracted residues ranged from 20-40% and 7-10% of the applied radioactivity. Most of the extracted radioactivity was associated with tolyfluanid and less than 1% was attributed to unknown degradation products.

Table 11. Degradation of tolyfluanid under aerobic condition at 22°C after application of [dichlorofluoromethyl-<sup>13,14</sup>C]tolyfluanid to two soils (Schuphan & Ebing, 1979).

Soil	% of applied radioactivity							
	Organic carbon	DAT	Tolyfluanid	Others	<sup>14</sup> CO <sub>2</sub>	Extracted	Unextracted	Total
loamy sand	2.5%	2	13.4	0.8	24.0	14.2	~30	~68.2
		5	1.4	0.8	40.2	2.2	~40	~82.4
		9	0.4	0.6	49.2	1.0	~29	~79.2
		14	0.3	0.5	55.5	0.9	~26	~82.4
		33	0.3	0.4	62.2	0.6	~27	~89.8
		65	0.2	0.2	64.8	0.4	~23	~88.2
loamy sand	1.0%	2	52.8	0.6	25.6	53.4	~6	~85
		5	30.8	0.0	46.2	30.8	~7	~84
		9	20.4	0.7	56.7	21.1	~9	~86.8
		14	8.7	0.5	64.9	9.2	~10	~84.1
		33	1.5	0.4	74.5	1.9	~10	~86.4
		65	0.5	0.6	76.7	1.0	~7	~84.7

On the basis of these studies the half-life of tolyfluanid, assuming first-order kinetics, was ≤3 days regardless of the type of soil, (Schäfer, 1995; Schad, 2001; Shuphan and Ebing, 1979).

Table 12. Half-lives of [U-phenyl-<sup>14</sup>C]tolyfluanid (ph) and [dichlorofluoromethyl-<sup>13,14</sup>C]tolyfluanid (dic) in soils in aerobic condition (first-order kinetics assumed).

Radiolabel/ Incubation conditions	Soil	Org. C (%)	pH	Concentration (mg ai/100 g soil (dry wt))	Half-life (days)	Reference
Ph/ 22°C, 99 days, 40% WHC	loamy sand	1.3	5.6 <sup>1</sup>	3.5	22°C: 2.2 20°C: 2.6	Scholz, 1988a Schäfer 1995 Schad, 2001
	clay silt	2.2	6.7 <sup>1</sup>	3.1	22°C: 1.7 20°C: 2.0	
	clay silt	0.9	7.1 <sup>1</sup>	3.0	22°C: 1.6 20°C: 1.9	
	loamy silt	2.4	7.1 <sup>1</sup>	3.4	22°C: 0.4 20°C: 0.5	
Dic/ 22°C, 65 days, 40% WHC	loamy sand	2.5	5.5-7.5	10	22°C: <1	Schuphan and Ebing, 1979
	loamy sand	1.0	5.5-7.5	10	22°C: 2-3	

<sup>1</sup> in KCl

The half-life of DMST was less than 6.7 days.

Table 13. Half-life of DMST in soils in aerobic condition (first-order kinetics assumed).

Soil	org. C (%)	pH	Half-life (days)	Reference
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Soil	org. C (%)	pH	Half-life (days)	Reference
loamy sand	1.3	5.6	22°C: 3.7 20°C: 4.3	Scholz, 1988a Schäfer 1995
clay silt	2.2	6.7	22°C: 1.4 20°C: 1.6	Schad, 2001
clay silt	0.9	7.1	22°C: 1.3 20°C: 1.9	
loamy silt	2.4	7.1 <sup>1</sup>	22°C: 5.7 20°C: 6.7	

The aerobic degradation pathways of tolyfluanid in soil are shown in Figure 3.

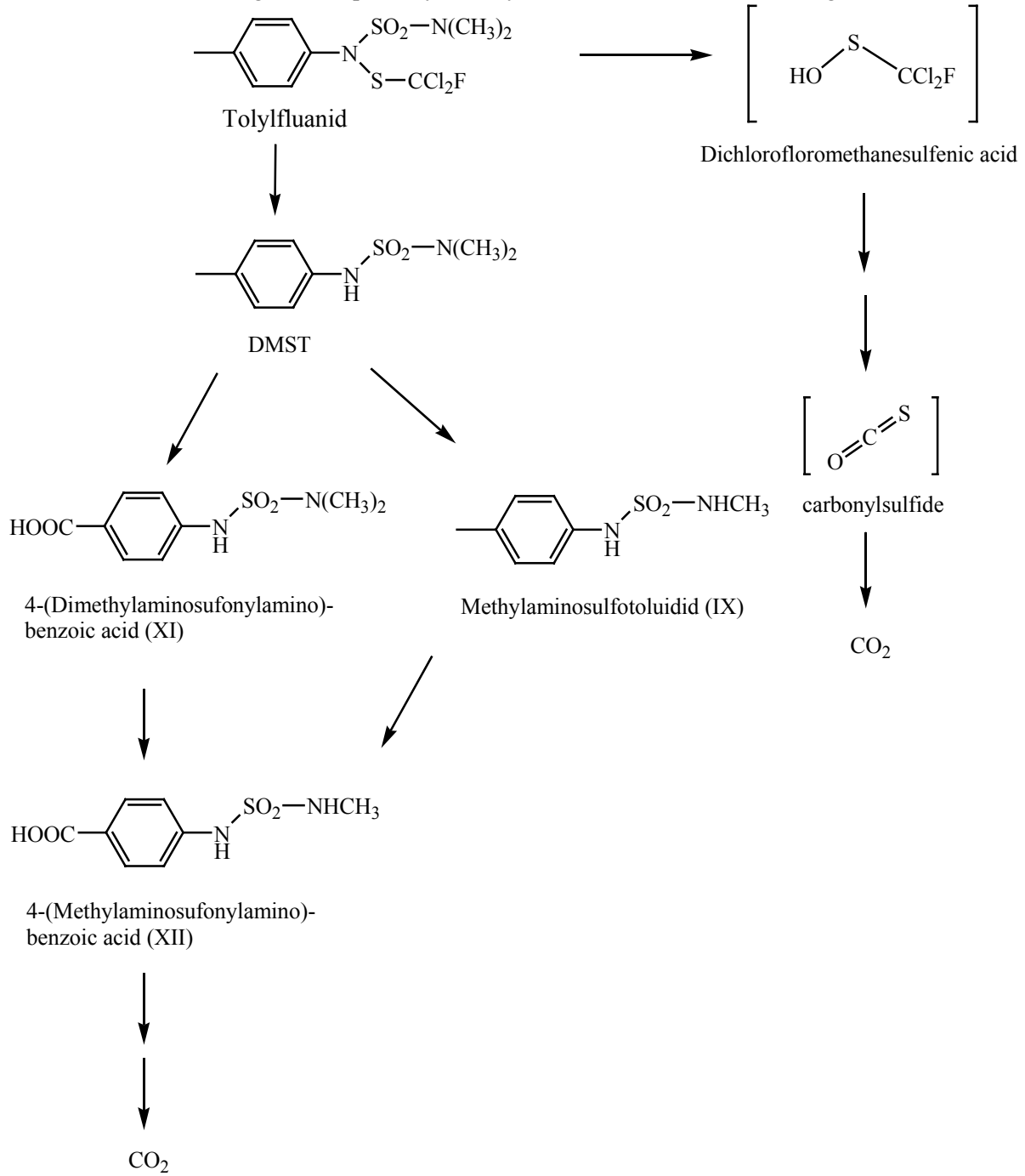


Figure 3. Aerobic degradation pathways of tolyfluanid.

**Anaerobic degradation.** No study was conducted on anaerobic degradation as it was not regarded as necessary owing to the proposed use pattern of spray application and the rapid degradation of tolylfluanid.

**Photolysis in soil.** The photodegradation of [U-phenyl-<sup>14</sup>C]tolylfluanid was studied on thin layers (2 mm) of silt loam soil (sand 3.6%, silt 80.8%, clay 15.6%, organic carbon 2.4%, pH in water 6.0) at a rate of 6.67 µg/g soil on a dry basis by Hellpointner (2000a). The moisture content of the samples was adjusted to 50% of maximum capacity. The soil layers were stored at 20°C and irradiated for 18 days with light from a Xenon lamp with the cut-off wavelength at 290 nm and an intensity of 756 mW/m<sup>2</sup>. Tolyfluanid was degraded with a half-life of 4.9 days in the irradiated samples and 4.3 days in the control samples stored in the dark at the same temperature. At the end of the experiment unextracted residues reached 39% of the applied radioactivity in the irradiated and 52% in the control samples. DMST and 4-(dimethylaminosulfonylamino)benzoic acid were the main degradation products with the minor products methylaminosulfotoluidide (IX) and 4-(methylaminosulfonylamino)benzoic acid (XII). Because of the very thin layer of soil, desiccation was very fast and microbial activities were reduced so that it was not possible to relate the rate of degradation to the influence of irradiation.

No field studies were conducted as tolylfluanid and its main degradation products have short half lives.

**Adsorption and desorption.** Adsorption/desorption experiments with soil/water systems were not applicable to tolylfluanid owing to its rapid hydrolysis. A  $K_{oc}$  value of tolylfluanid was estimated by an HPLC method in which tolylfluanid and 13 reference standards with  $K_{oc}$  values ranging from 17.8 to 64300 were chromatographed, giving a value of 2220 ml/g with the log of 3.35, which indicates that tolylfluanid could be classified as immobile (Sommer, 2000).

An adsorption/desorption study was carried out with DMST in four soils (Brumhard, 1997). Two, 4 or 10 g dry weight of the soils were equilibrated with 20 ml of [phenyl-U-<sup>14</sup>C]DMST at 7, 50, 500 and 5000 µg/l in 0.01 M CaCl<sub>2</sub> by shaking for 24 hours. The radioactivity was measured in the supernatant after centrifugation. Desorption was determined by equilibrating the residual soil sediment with 0.01 M CaCl<sub>2</sub> and measuring the released radioactivity. The stability of [phenyl-U-<sup>14</sup>C]DMST in 0.01 M CaCl<sub>2</sub> for 6 days was examined by TLC. The distribution coefficient  $K_d$  was calculated by the Freundlich equation for adsorption and desorption in each soil.  $K_{oc}$  values were also calculated from the organic carbon content.

Table 14.  $K_d$  and  $K_{oc}$  values for DMST in four soils (Brumhard, 1997).

Soil	pH	Organic Carbon (%)	Absorption		Desorption		Mobility
			$K_d$ (ml/g)	$K_{oc}$ (ml/g)	$K_d$ (ml/g)	$K_{oc}$ (ml/g)	
Loamy sand	7.0	1.8	1.01	56	2.27	126	Low
Sand	5.9	0.7	0.41	59	1.11	159	Low-intermediate
Silt loam	6.0	2.4	1.73	72	2.63	110	Low
Silty clay	7.6	0.6	0.76	118	1.99	311	Low-intermediate

**Mobility.** Scholz (1987a) studied the leaching of aged [U-phenyl-<sup>14</sup>C]tolylfluanid residues in BBA standard soil 2.1 (Organic carbon 0.69%; pH in KCl 7.0, Biomass 92 mg microbial C/kg dry soil; WHC 18.2%) at a rate of 5.2 mg/kg dry soil. The samples were aged at 20°C for 12 or 40 days, then placed on top of a saturated soil column 27 cm long and 5cm in diameter which was irrigated for 48 h with 400 ml of deionized water, corresponding to 200 mm precipitation. The leachate was collected as 2 fractions of approximately 200 ml from each column and contained 6.6% of the applied radioactivity from the 12-day aging and 4.9% from the 40-day aging, associated with DMST (1.1% 12-day and 0.2% 40-day), 4-(dimethylaminosulfonylamino)benzoic acid (XI) (0.9% 12-day), methylaminosulfotoluidide (IX) (<0.4% 12-day), and <sup>14</sup>CO<sub>2</sub> (7.5% 12-day and 17.1% 40-day).

Unchanged tolyfluanid accounted for less than 0.1% of the applied radioactivity. During irrigation 61% and 75% of the radioactivity remained in the upper third of the soil column. On the basis of these results tolyfluanid was classified as immobile in soil and DMST slightly mobile.

Environmental concentrations of tolyfluanid and DMST in groundwater recharge were calculated using the simulation model FOCUS-PELMO from version 1.1.1 (Schad, 2001) from the results of Scholz's aerobic degradation study (1988a), Sommer's  $K_{oc}$  value for tolyfluanid (2000) and Brumhard's values for DMST (1997). Environmental concentrations of tolyfluanid and DMST resulting from the use of tolyfluanid on apples, strawberries and grapes in Europe for 20 years were predicted to be below 0.01  $\mu\text{g/l}$ , which would include their concentrations in groundwater recharge below the predefined soil depth of 1.10 m.

### Environmental fate in water-sediment systems

The Meeting received information on the hydrolysis of tolyfluanid in buffers, in aquatic systems, and volatilization and photolysis in air.

#### Degradation in aquatic systems

**Hydrolysis.** The hydrolysis of tolyfluanid was examined at a concentration of 1 mg/l in buffer solutions (pH 4, 7 and 9) incubated at 20, 30 and/or 40°C (Wilmes, 1982). Tolyfluanid was unstable under all conditions, so much so that at pH 9 at room temperature the parent compound was immediately undetectable. The half-life was calculated to be 11.7 days at pH 4 and 29.1 hours at pH 7 at 22°C.

Table 15. Hydrolytic degradation of tolyfluanid in aqueous buffer solutions at 20, 30, and 40°C (Wilmes, 1982).

pH	Time	Tolyfluanid (mg/l)	Time	Tolyfluanid (mg/l)
4	30°C		40°C	
	0 day	1.00	0 day	1.00
	1 day	0.81	3 days	0.47
	4 days	0.68	3.2 days	0.45
	5 days	0.57	4 days	0.33
	6 days	0.49	4.3 days	0.30
	8 days	0.37	5 days	0.24
			6 days	0.19
			7 days	0.13
	7	20°C		30°C
0 hour		1.00	0 hour	1.00
1.5 hours		0.90	0.4 hour	0.97
2.8 hours		0.85	1.8 hours	0.81
4.4 hours		0.82	2.5 hours	0.79
6.1 hours		0.80	3.8 hours	0.70
22.8 hours		0.63	4.9 hours	0.63
24.4 hours		0.62	7.4 hours	0.54
30.4 hours		0.53	22.3 hours	0.14
46.9 hours		0.43		

Wilmes (1982) also investigated the hydrolysis of DMST in buffer solutions (pH 4, 7 and 9) at a concentration of 8-9 mg/l when incubated for one week at 55°C or in refrigerator. No hydrolysis was observed in the incubated or refrigerated samples, indicating a half-life of >1 year at 22°C at pH 4, 7 and 9.

Suzuki and Yoshida (1994) studied the degradation of tolyfluanid in a pH 7.2 buffer solution at a concentration of 100 mg/l incubated at 25°C for eight weeks. As the concentration was much higher than the solubility of tolyfluanid, the rate-limiting factor for transformation was the

dissolving of the compound in the buffer. No reliable half-life was therefore estimated but the study demonstrated that tolyfluanid was hydrolyzed to DMST, fluoride ion, chloride ion, sulfur and carbon dioxide.

Photolysis. The UV-visible spectrum of tolyfluanid in 1:1 acetonitrile-water (4.99 mg/l) showed an absorption maximum at 193 nm ( $\epsilon=36748 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and a shoulder at 220-230 nm but no absorption at wavelengths above 290 nm ( $\epsilon<10 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) (Hellpointner, 1992). Photolysis in aqueous solution is not expected to occur.

The UV-visible spectrum of DMST in water (10 mg/l) showed absorption maxima at 196 nm ( $\epsilon=69388 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and about 232 nm (Hellpointner, 2000b). The quantum yield of direct photodegradation of DMST in aqueous solution was determined according to the ECETOC method using polychromatic light. Unlabelled DMST in water at ca. 5 mg/l was tested for a maximum period of 420 min at 25°C under irradiation by Hg lamp with a Duran 50 filter. The concentration of the test compound was determined by reversed-phase HPLC with external standards. The results indicated that DMST was stable under direct photodegradation in aqueous solution without yielding major degradation products. The quantum yield was calculated from the UV absorption data and the degradation kinetics to be  $4.66 \times 10^{-3}$ . The quantum yield and UV absorption data in water were used to estimate the environmental half-life of DMST in water using two different simulation models. One predicated a half-life of a minimum of approximately 2 months at 30°N and 3 months at 50°N for July-August, the period of main use, the other a half-life of more than 1 year. These results indicate that direct photodegradation in aqueous solution was expected to contribute little to the elimination of DMST in the environment.

Biological degradation in water/sediment systems. The biological degradation of tolyfluanid was examined in three aqueous sediment systems: Ijzendoorn, The Netherlands (organic carbon, 2.5%; pH of aqueous phase, 7.7; pH of sediment, 7.14), Lienden, The Netherlands (organic carbon, 0.8%; pH of aqueous phase, 8.0; pH of soil, 7.39) and the Rhine (Scholz, 1987b, 1988b). [U-phenyl- $^{14}\text{C}$ ]tolylfluanid was applied directly to water of a depth of 10 cm at a concentration of 2.5 mg/l, equivalent to a spray application rate of 2.5 kg ai/ha, and the systems incubated at 22°C in the dark for 120 days. Aerobic conditions in the supernatant water were maintained throughout the study. Samples were analysed by TLC.

The mean recovery of radioactivity from all systems was 96.2% (91.9-100.8%) indicating that almost no dissipation occurred. Tolyfluanid was degraded so rapidly in the three systems that it was not detected in the sample taken on day 14 and its half-life could not be estimated. The radioactivity in the water decreased and the unextracted radioactivity increased continuously. In addition to DMST, a predominant metabolite in both the water and sediment,  $\text{CO}_2$  and methylaminosulfotoluidide were detected. DMST was degraded into methylaminosulfotoluidide (IX) which was finally mineralized to  $\text{CO}_2$ . The half-life of DMST was calculated by Krauskopf (1995) from the results of the Ijzendoorn and Lienden systems to be 42.1 and 75.8 days in the supernatant water respectively. The results from the Rhine system indicated that the degradation of tolyfluanid and DMST was similar in the three systems.



Table 16. Distribution of radioactivity from [U-phenyl-<sup>14</sup>C]tolyfluanid in water/sediment systems (Scholz, 1987b, 1988b).

System	Compound	% of applied radioactivity				
		14 days	30 days	75 days	90 days	120 days
<b>Ijzendoorn, NL</b>						
Surface water	Tolyfluanid	<0.1	<0.1	<0.1	<0.1	<0.1
	DMST	67.5	58.9	42.1	40.1	23.5
	IX	<0.1	<0.1	4.3	5.1	6.1
	Others	<0.1	<0.1	2.1	2.1	1.5
	Total	67.5	58.9	48.5	47.3	31.1
Sediment	Tolyfluanid	<0.1	<0.1	<0.1	<0.1	<0.1
	DMST	28.3	28.5	19.6	13.5	10.4
	IX	<0.1	<0.1	1.6	1.3	1.5
	Others	<0.1	<0.1	3.6	3.9	3.2
	Total	28.3	28.5	21.2	15.4	12.3
	Unextracted	4.8	8.4	20.1	25.1	34.0
	<sup>14</sup> CO <sub>2</sub>	0.2	0.9	6.7	8.0	14.5
<b>Lienden, NL</b>						
Surface water	Tolyfluanid	<0.1	<0.1	<0.1	<0.1	<0.1
	DMST	72.7	64.0	32.7	20.9	13.4
	IX	0.1	0.1	3.0	3.4	4.3
	Others	<0.1	<0.1	3.6	3.9	3.2
	Total	72.9	64.0	39.2	28.2	20.9
Sediment	Tolyfluanid	<0.1	<0.1	<0.1	<0.1	<0.1
	DMST	19.8	12.3	5.6	4.2	2.9
	IX	<0.1	<0.1	1.0	0.5	0.7
	Others	<0.1	<0.1	0.8	0.8	0.6
	Total	19.8	12.3	7.4	5.5	4.2
	Unextracted	3.9	16.7	32.1	37.8	40.1
	<sup>14</sup> CO <sub>2</sub>	0.2	3.9	15.7	26.7	28.0
<b>Rhine, Germany</b>						
Surface water	Tolyfluanid			<0.1		<0.1
	DMST			32.2		19.1
	IX			3.5		4.5
	Others			3.4		2.9
	Total			39.1		26.5
Sediment	Tolyfluanid			<0.1		<0.1
	DMST			15.0		10.2
	IX			1.4		2.2
	Others			3.7		1.0
	Total			20.1		13.4
	Unextracted			14.6		24.2
	<sup>14</sup> CO <sub>2</sub>			22.3		32.7

IX: methylaminosulfotoluidide

In another degradation study in Germany by Scholz (1997) with the sediment and water from two ponds, one in Hönniger-Weiher (organic carbon 4.07%, pH in water 7.4-7.7 and in soil 5.8) and the other in Angler-Weiher (organic carbon 2.31%, pH in water 8.0-8.2 and in soil 7.3), [U-phenyl-<sup>14</sup>C]tolyfluanid was applied at a concentration of 0.4 mg/l and the systems incubated at 20°C in the dark for 7 days. In experiment I only surface water and in II the complete water/sediment systems were used. Aerobic conditions in the supernatant water were maintained throughout the study. Samples were analysed by TLC.

In both systems tolyfluanid was degraded rapidly and after 7 days it was not detected. Its half-life was 1.4-5 hours. DMST was found in both the water layer and sediment with higher levels in the water.

Table 17. Distribution of radioactivity from [U-phenyl-<sup>14</sup>C]tolyfluanid in water/sediment systems (Scholz, 1997).

System	Compound	% of applied radioactivity				
<b>Experiment I (surface water only)</b>						
		0h	4h	12h	24h	7d
<b>Hönniger-Weiher, Germany</b>						
Surface water	Tolyfluanid	99.2	57.4	10.6	0.9	<0.1
	DMST	0.6	42.8	87.5	100.8	99.6
	Others	n.d.	n.d.	n.d.	n.d.	n.d.
<b>Angler-Weiher, Germany</b>						
Surface water	Tolyfluanid	99.3	25.8	1.3	0.2	<0.1
	DMST	0.6	72.2	97.6	99.5	99.3
	Others	n.d.	n.d.	n.d.	0.1	n.d.
<b>Experiment II (complete water/sediment system)</b>						
		0 h	5 h <sup>1</sup>	12 h	24 h <sup>1</sup>	7 d
<b>Hönniger-Weiher, Germany</b>						
Surface water	Tolyfluanid	99.2	39.5	17.4	1.1	n.d.
	DMST	0.6	36.5	56.0	66.0	46.6
	Others	n.d.	0.4	0.5	0.7	2.8
Sediment	Tolyfluanid	-	8.4	6.7	0.4	n.d.
	DMST	-	9.5	14.2	24.3	41.3
	Others	-	n.d.	n.d.	n.d.	0.6
	Unextracted	-	0.4	0.6	1.2	3.0
	<sup>14</sup> CO <sub>2</sub>					0.4
<b>Angler-Weiher, Germany</b>						
Surface water	Tolyfluanid	99.3	28.6	8.4	n.d.	n.d.
	DMST	0.6	53.4	71.4	72.2	46.7
	Others	n.d.	0.4	0.4	1.0	2.7
Sediment	Tolyfluanid	-	2.2	1.5	n.d.	n.d.
	DMST	-	10.6	12.1	20.8	39.3
	Others	-	n.d.	n.d.	n.d.	n.d.
	Unextracted	-	0.4	0.3	0.7	2.6
	<sup>14</sup> CO <sub>2</sub>					0.4

n.d.: not detected

<sup>1</sup> mean of two values

4. The proposed degradation pathways of tolyfluanid in aqueous systems are shown in Figure

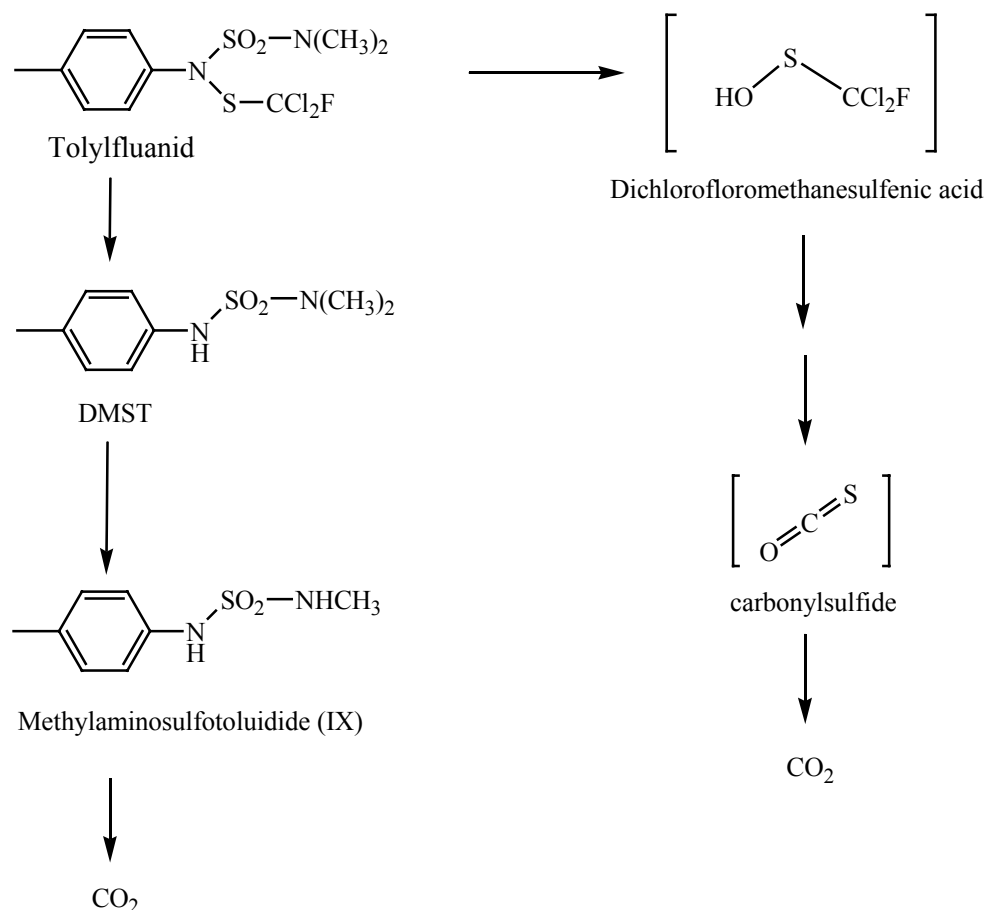


Figure 4. Degradation of tolyfluanid in aqueous systems.

### Degradation in air

**Volatilization.** The vapour pressures of tolyfluanid and DMST were determined to be  $2 \times 10^{-4}$  Pa and  $2.5 \times 10^{-4}$  Pa respectively at 20°C (Weber and Krohn, 1982; Krohn, 1999).

The Henry's Law constants of tolyfluanid and DMST were  $7.7 \times 10^{-2} \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$  and  $7.7 \times 10^{-5} \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$  respectively at 20°C (Krohn, 1993). These values suggest that volatilization of tolyfluanid driven by evaporating water might need to be taken into consideration but in practice, owing to the rapid hydrolysis, volatilization should not be of significant concern. Significant volatilization of DMST is also unlikely.

**Photolysis.** The half-lives of tolyfluanid and DMST in air using the Atkinson model and AOPWIN software were calculated to be 7.2 hours and 2.3 hours respectively (Hellpointner, 1995), corresponding to chemical lifetimes of 10.4 hours and 3.3 hours respectively. It is therefore unlikely that these compounds would be transported in the gaseous phase over long distances or that they would accumulate in air.

### **Residues in succeeding crops**

As the half-lives of tolyfluanid and DMST are very short in soil, residues were not expected to be significant in succeeding crops so no studies on succeeding crops were carried out.

## RESIDUE ANALYSIS

### Analytical methods

The Meeting received information on analytical methods for the determination of residues of tolylfluanid and DMST in a variety of crops and processed commodities.

#### Analysis of plant commodities

Gas chromatographic methods. Becker and Schug (1987) developed a multi-residue method in which tolylfluanid and DMST, together with organohalogen, organophosphorus and triazine compounds, are extracted from plant samples with acetone and the extract filtered. After dilution with water, the compounds are extracted with dichloromethane from an aliquot of the filtrate. The organic phase is dried and rotary-evaporated, and the residue is dissolved in dichloromethane. Interfering substances are separated on an activated carbon-silica gel column. The compounds are eluted with a mixture of dichloromethane, toluene and acetone. The eluate is rotary-evaporated, and the residue diluted with n-hexane to a known volume. The residues in this solution are identified and quantified by GC with EC and NP detection. The mean recovery from samples of grapes and strawberries fortified with tolylfluanid at 0.2 mg/kg was 70% and the LOQ was 0.02 mg/kg. The GC-NPD method is suitable for enforcement and confirmatory analyses.

Specht and Thier (1987) also described a method using GC with NP (suitable for enforcement analysis) or CG with EC detection (suitable for confirmatory analysis) for the determination of organochlorine, organophosphorus, nitrogen-containing and other pesticides. The extraction is with acetone/water (2:1). After filtration, sodium chloride and dichloromethane are added. The organic phase is evaporated and the residues are dissolved in cyclohexane/ethyl acetate. After gel permeation chromatography on Bio-Beads S-X3, quantification is by GC with NP or GC with EC detection. The mean recovery from apple samples fortified with 0.01 mg/kg tolylfluanid was 90% and the LOQ for tolylfluanid is 0.01 mg/kg.

Weeren and Pelz (1999a) used this method for the determination of tolylfluanid in rape seed with extraction as described by Ernst *et al.* (1974). Recoveries from canola seed fortified with tolylfluanid at 0.02-0.2 mg/kg were 70-110% and the LOQ was 0.02 mg/kg. This method is also suitable for enforcement analysis of rape seed.

Weeren *et al.* (1999) also revised the method developed by Specht and Thier by modifying the extraction and partition steps to make them less laborious and replacing dichloromethane for toxicological and ecological reasons. Recovery from water-containing samples fortified at 0.05-0.1 mg/kg was 84% and the LOQ was 0.05 mg/kg. The method is suitable for enforcement analysis of such samples.

Brennecke (1988) developed a method in which tolylfluanid and DMST are extracted with acetone from fruit and vegetables with a high water content. The extracts are filtered and then concentrated until only aqueous phase remains, and this is then diluted to a defined volume with water. An aliquot of this solution is applied to a disposable extraction column. Aqueous samples (beverages) are applied directly to the extraction column. Tolyfluanid and DMST are eluted with a cyclohexane/ethyl acetate mixture. After the eluates have been evaporated, the residue is purified by chromatography on a minicolumn of silica gel and active charcoal. Tolyfluanid and DMST are determined by GC-FPD or GC-NPD. Recoveries from samples fortified with tolylfluanid or DMST at 0.05-5.0 mg/kg were 84-104% and 81-105% from apples, 82-99% and 82-104% from grapes, 79-103% and 74-104% from strawberries, 79-98% and 86-107% from tomatoes, and 84-107% and 89-108% from lettuce respectively. The LOQ was 0.05 mg/kg.

Brennecke (1989) described a method to determine dichlofluanid, DMSA, tolylfluanid, DMST and tebuconazole, which is basically the same as his 1988 method except that an acetone/water

mixture can be used for extraction, and a silica gel minicolumn is used for clean-up. Recoveries from samples fortified with tolyfluanid or DMST at 0.02-5.0 mg/kg were 84-102% and 82-109% from leeks and 93-108% (Brennecke, 1989) and 95-104% (Koehler, 1989) from apples respectively. The LOQ was 0.02 mg/kg for both compounds.

Brennecke (1993a) modified his 1988 method for the analysis of jams and preserves by homogenizing preserve samples with a triturator and stirring jam samples with an equal amount of water before acetone extraction and the other procedures. Recoveries from samples fortified with tolyfluanid and DMST at 0.02-0.5 mg/kg were 93-99% and 93-99% from blackcurrants, 96-114% and 72-94% from blackcurrant jam and juice, and 74-110% and 78-105% from strawberry jam and preserve. The LOQ was 0.02 mg/kg.

Brennecke (1993b) incorporated automated sample clean-up to reduce losses in the analysis of tomatoes. After filtration, the acetone extract is concentrated to the aqueous remainder which is subsequently made up with dichloromethane to a defined volume. An aliquot of this solution is transferred to the laboratory robot in a centrifuge tube with a screw cap. Aqueous samples are transferred directly to the robot which then carries out liquid-solid extraction on diatomaceous earth, collection and evaporation of the eluate, dissolution of the residue, column chromatography on silica gel, elution of two fractions, collection and evaporation of the two eluates, and dissolution of the residues. The resulting analytical solutions are analysed by GC-NPD. Recoveries from tomatoes fortified with 0.02-5.0 mg/kg tolyfluanid and DMST were 71-99% and 78-95% respectively. The LOQ is 0.02 mg/kg.

Brennecke (1995e) reported the determination of tolyfluanid and its metabolites in grapes and their products with a modified version of his 1988 method. Liquid samples (such as beverages) are directly applied to the extraction column or directly subjected to enzymatic hydrolysis and then processed as aqueous extract of solids. Recoveries from samples fortified with tolyfluanid and DMST at 0.02-2.0 mg/kg were respectively 80-118% and 87-118% from table and wine grapes, and 72-118% and 79-106% from processed grape products. The LOQ was 0.02 mg/kg.

Nüsslein (1996i) and Brennecke (1996i) made slight modifications to the method developed by Brennecke in 1988: following maceration the pH of the mixture is adjusted to <5, the residues are eluted with a 7:3, instead of 85:15, cyclohexane/ethyl acetate mixture, the quantity of charcoal for clean-up on the silica gel column is reduced, and the elution volume of dichloromethane doubled to 20 ml. Nüsslein reported the following recoveries from samples fortified with tolyfluanid or DMST at 0.02-2.0 mg/kg: for tolyfluanid, 84-116% (apple and pear), 83-96% (apple pomace, dry), 106-112% (apple pomace, wet), 89-118% (apple juice and sauce), 85-118% (strawberry), 83-112% (tomato), 70-105% (tomato pomace, wet), 82-103% (tomato pomace, dry), 68-117 (processed tomato products), 90-107% (cucumber), 101-109% (pepper), 64-121% (melon, pulp and peel); for DMST, 88-103% (apple and pear), 86-101% (apple pomace, dry), 91-105% (apple pomace, wet), 64-112% (apple juice and sauce), 87-126% (strawberry), 83-110% (tomato), 84-108% (tomato pomace, wet), 82-89% (tomato pomace, dry), 69-112 (processed tomato products), 89-106% (cucumber), 102-110% (pepper), 63-99% (melon, pulp and peel). The LOQ is 0.02 mg/kg except in dry and wet apple pomace and dry tomato pomace in which it is 0.05 mg/kg. Brennecke reported recoveries from blackberries and raspberries fortified with tolyfluanid or DMST at 0.02-2.0 mg/kg of 63-113% (tolylfluanid) and 70-121% (DMST), with an LOQ of 0.02 mg/kg.

Brennecke (1996b) further modified his original 1988 method. The pH of the homogenate is checked with a meter, and, if higher than 5, adjusted to 3-5 with a small amount of 10% hydrochloric acid. If it is known that the sample material will have a pH-value higher than 5, a small amount of 10% hydrochloric acid should be added directly to the analytical sample after the addition of acetone. For dried hop cones, spent hops, hops draff and brewer's yeast slightly modified extraction procedures have to be used. An alternative clean-up procedure was developed for the determination of the parent compound only, because tolyfluanid is the only residue of concern for regulatory purposes. Recoveries from fortified hops and related products were 72-93% (green cones and dried cones, 0.5-

50 mg/kg), 77-92% (spent hops, 0.1-1.0 mg/kg), 95-105% (hops draff, 0.5-5.0 mg/kg), 75-86% (yeast 0.1-1.0 mg/kg) and 96-105% (beer, 0.02-0.2 mg/kg), for tolylfluanid, and 81-98% (green cones and dried cones, 0.5-50 mg/kg), 86-94% (spent hops, 0.1-1.0 mg/kg), 92-100% (hops draff, 0.5-5.0 mg/kg), 86-96% (yeast, 0.1-1.0 mg/kg) and 100-109% (beer, 0.02-0.2 mg/kg). The LOQ for tolylfluanid and DMST was 1.0 mg/kg in dried hop cones, 0.5 mg/kg in green cones and hops draff, 0.1 mg/kg in spent hops and yeast, and 0.02 mg/kg in beer.

Brennecke (1997c) reported the determination of tolylfluanid in green hops and dried cones by a modified 1988 method. An alternative clean-up procedure with a 5-g silica gel column is used instead of the activated charcoal/silica gel mini-column. Residues are eluted with a cyclohexane-ethyl acetate mixture. Tolyfluanid is determined by GC-NPD. According to Brennecke (1997c) and Schrier (1996) the recovery from dry hop cones fortified with tolylfluanid at 1 and 30 mg/kg was 87-122% and the LOQ 1.0 mg/kg. This method is suitable for enforcement purposes.

HPLC-MS-MS methods. Brennecke (1997b) modified an existing method for the determination of tolylfluanid and DMST. Sample weights are reduced to five g because samples for residue analysis are usually available in a well-prepared and homogeneous form for many raw agricultural and processed commodities. Residues of tolylfluanid and DMST are extracted with an acetone/water mixture. After filtration, most of the acetone is removed from the extract by evaporation in a vacuum rotary evaporator. The aqueous remainder is then applied to a conditioned pre-packed 6-ml reversed phase (C18) column, the column washed with water and the eluate discarded. Subsequent elution is with 5 ml of methanol and the eluate (analytical solution) is collected in a 10-ml test tube. The residues of tolylfluanid and DMST are determined in the same run by LC-MS-MS using a triple-stage quadrupole mass spectrometer with an electrospray interface in the multiple-reaction monitoring mode. In this mode the protonated parent ions are separated and immediately impulsed with nitrogen to yield their characteristic daughter ions (tolylfluanid 347 to 238; DMST 215 to 106). These ions are separated and used for quantification. Recoveries from samples fortified with tolylfluanid or DMST at 0.02-2.0 mg/kg were 77-109% and 82-116% respectively from tomato and head lettuce. The LOQ was 0.02 mg/kg for both compounds.

Brennecke (1998b,c) used the above method, but with argon instead of nitrogen for impulse, for the determination of tolylfluanid and DMST in blackcurrants, strawberries and lettuces. Recoveries from samples fortified with tolylfluanid or DMST at 0.02-2.0 mg/kg were respectively 89-106% and 85-104% from blackcurrants, 91-102% and 110-117% from strawberries, and 71-102% and 99-114% from lettuce. The LOQ was 0.02 mg/kg for both compounds.

Schoening (1999) used acetone/water/hydrochloric acid for the extraction of tolylfluanid and DMST from plant material. After extraction, concentration, and column-partitioning, the residues are quantified by reverse-phase HPLC with electrospray MS-MS detection. The instrumental response was linear over the range of 0.0005 to 0.5 mg/l in solvent, cucumbers and head lettuce weighted 1/x. Recoveries from samples fortified with tolylfluanid and DMST at 0.02-0.2 mg/kg were respectively 80-92% and 94-104% for tomatoes and tomato juice, 69-80% and 76-88% for tomato paste, and 71-93% and 77-96% for lettuce. The LOQ was 0.02 mg/kg.

Owing to the significant matrix effect observed in the determination of tolylfluanid in leeks with the above method, Sur (2001) used matrix-matched standards for the analysis of leeks. Recoveries from leeks and pepper fortified with tolylfluanid and DMST at 0.02-0.2 mg/kg were 76-101% and 89-101% respectively. The LOQ was 0.02 mg/kg.

#### Analysis of animal commodities

Maasfeld and Brennecke (1996) described a method for the determination of tolylfluanid in eggs, fat, muscle and milk. Samples are homogenized with either n-hexane or acetonitrile and then with n-hexane. After centrifugation the extract is partitioned between n-hexane and acetonitrile. The acetonitrile phase is evaporated to dryness. The residue is dissolved in acetonitrile/acidic water and

transferred to an RP-1 8 disposable column, which is eluted with a few millilitres of acetonitrile. After evaporation to dryness the residue is dissolved in n-hexane and transferred to a silica gel disposable column. Elution is with n-hexane/ethyl acetate. The eluate is brought to dryness and the residue is finally dissolved in ethyl acetate. Tolyfluanid is determined by GC-ECD. Recoveries from samples fortified with tolyfluanid were 76-97% from milk (fortification at 0.01-0.10 mg/kg) and 71-130% from meat, eggs and fat (fortification at 0.05-0.5 mg/kg). The LOQ was 0.05 mg/kg for muscle, fat and eggs and 0.01 mg/kg for milk. This method is suitable for enforcement purposes (Maasfeld and Brennecke, 1996; Weeren and Schmidt, 1996).

In a method described by Weeren and Pelz (1998) milk, meat and eggs are extracted with acetone after addition of sulfuric acid. Water is added previously in an amount that takes full account of the natural water content of the sample so that during extraction the acetone:water ratio remains constant at 2:1. For liquid/liquid partition ethyl acetate/cyclohexane (1 + 1) and sodium chloride are added and after repeated mixing excess water is separated. The evaporated residue of an aliquot of the organic phase is cleaned up by gel permeation chromatography on Bio Beads S-X3 polystyrene gel using a mixture of ethyl acetate and cyclohexane (1 + 1) as eluant on an automated gel permeation chromatograph. The residue fraction is concentrated and analysed by gas chromatography with a fused silica capillary column (DB-1) and an electron capture detector (ECD). Fat is dissolved in acetone and mixed vigorously with acetonitrile and synthetic calcium silicate. The mixture is filtered twice, the volume of the filtrate is measured, and the solution is rotary-evaporated. The evaporated residue of an aliquot of the organic phase is cleaned up by GPC and analysed by gas chromatography as described above. Recoveries of tolyfluanid were 70-113% from milk (fortification at 0.01-0.1 mg/kg) and 73-99% from meat, fat and egg (fortification at 0.05-0.5 mg/kg). The LOQ was 0.05 mg/kg for muscle, fat and eggs and 0.01 mg/kg for milk. This method is suitable for enforcement purposes.

#### Analysis of soil

Specht (1990) and Specht *et al.* (1995) described a method for the determination of tolyfluanid and DMST in soil. Extraction with an acetone-water mixture is followed by liquid-liquid partition with acetone-water-dichloromethane (or ethyl acetate/cyclohexane instead of dichloromethane), with saturation of the water with sodium chloride, and gel chromatographic purification on bio-beads S-X3 with ethyl acetate/cyclohexane (1 + 1) as eluant. Determination of residues is by GC-NPD. The mean recoveries from soil fortified with tolyfluanid and DMST at 0.02-0.40 mg/kg were 91% and 85% respectively. The method is suitable for both enforcement and confirmatory purposes.

#### Analysis of water

The water sample is extracted three times with 50 ml dichloromethane. The organic phases are filtered through sodium sulfate and the combined filtrates evaporated. The residue is dissolved in ethyl acetate and cyclohexane. An aliquot of this solution is cleaned up by gel permeation chromatography on Bio Beads S-X3 polystyrene gel with ethyl acetate/cyclohexane (1 + 1) as eluant on an automated gel permeation chromatograph. The concentrated solution is analysed for tolyfluanid and DMST by gas chromatography using a fused silica capillary column (DB-S MS) and a mass selective detector (MSD). The LOQ for both analytes is 0.05 µg/l. The mean recoveries from surface water fortified with tolyfluanid and DMST at 0.05-0.50 µg/l were 95% and 108% respectively. The method is suitable for enforcement and confirmatory purposes (Weeren and Pelz, 1999b).

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

The Meeting received data on the freezer storage stability of tolyfluanid and DMST in apples, grapes, grape juice and wine, tomatoes, tomato juice and purée, and hops (green and dry). In the studies reported below, tolyfluanid and DMST were determined in all samples. In grapes and grape products 4-hydroxymethyl-DMST glucoside and 2-hydroxyphenyl-DMST glucoside were also determined.

Recoveries from freshly fortified samples were determined concurrently with the analysis of stored fortified samples and used to validate the analytical results at each interval.

Brennecke (1997j) shredded untreated apples, spiked them with tolylfluanid or DMST at 0.50 mg/kg and stored them at or below  $-18^{\circ}\text{C}$ . Samples were taken for analysis after 27, 91, 182, 342 and 560 days. Tolyfluanid and DMST were stable for up to about 1.5 years (Table 18).

Table 18. Storage stability of tolylfluanid and DMST in apples fortified at 0.50 mg/kg and stored at or below  $-18^{\circ}\text{C}$  in a deep freeze (Brennecke, 1997j).

Storage period (days)	Tolyfluanid, %		DMST, %	
	Remaining	Procedural recovery	Remaining	Procedural recovery
0	120	115	105	105
27	90	115	81	108
91	86	93	89	96
182	95	94	103	98
342	99	85	86	72
560	102	95	96	89

Brennecke (1997f-h) fortified shredded grapes, grape juice and wine with tolylfluanid, DMST, 4-hydroxymethyl-DMST glucoside or 2-hydroxyphenyl-DMST glucoside at 1 mg/kg and stored them in a deep freezer at or below  $-18^{\circ}\text{C}$  for about 2.2 years. The four compounds were stable for up to 805 days in the grapes and juice although the tolylfluanid remaining in the grapes was below 70% of the fortified amount at 196 days. In wine, the two hydroxylated metabolites of DMST were stable throughout, but tolylfluanid decreased and DMST increased in general with time. However, the sum of tolylfluanid and DMST remained relatively constant with a minimum total of 78% of the fortified amount on day 197 and 114% on day 790, indicating that DMST is stable in wine at  $-18^{\circ}\text{C}$  and tolylfluanid is degraded to DMST during vinification and will not be detected in wine. All three metabolites potentially present in wine were regarded as stable for over 2 years.



Table 19. Storage stability of tolylfluanid and its metabolites in grapes, juice and wine fortified at 1.0 mg/kg and stored at or below -18°C.

Sample	Storage, days	Tolyfluanid		DMST		4-hydroxymethyl-DMST glucoside <sup>3</sup>		2-hydroxyphenyl-DMST glucoside <sup>3</sup>		Ref.
		% Rem <sup>1</sup>	% Proc recov <sup>2</sup>	% Rem <sup>1</sup>	% Proc recov <sup>2</sup>	% Rem <sup>1</sup>	% Proc recov <sup>2</sup>	% Rem <sup>1</sup>	% Proc recov <sup>2</sup>	
Fruit	0	92	85	98	95	87	85	100	102	Brennecke, 1997f
	28	74	81	94	102	89	80	105	111	
	83	75	87	77	82	77	69	90	85	
	196	69	76	74	78	78	78	83	82	
	369	79	89	102	99	81	86	96	104	
	574	83	99	101	107	77	73	102	95	
	805	76	75	100	76	85	75	99	101	
Juice	0	98	97	98	96	78	74	105	103	Brennecke, 1997g
	28	69	72	96	98	90	90	98	88	
	56	70	67	78	63	72	64	70	59	
	91	82	96	102	94	76	73	86	85	
	196	59	95	73	86	85	80	93	91	
	266	67	77	83	82	82	85	91	88	
	357	69	77	83	72	84	79	98	83	
	564	64	97	88	94	79	78	93	97	
	789	106	95	100	95	78	84	109	92	
Wine	0	104	100	113	108	86	80	106	102	Brennecke, 1997h
	29	68	75	108	102	99	89	111	106	
	57	39	74	107	75	72	84	82	80	
	91	42	100	118	104	74	56	87	74	
	127	33	80	119	81	84	86	97	97	
	197	21	81	113	88	92	88	97	107	
	358	13	81	123	91	88	85	99	84	
	565	28	93	144	97	96	97	92	88	
	790	39	100	161	101	81	70	99	92	

<sup>1</sup>% remaining

<sup>2</sup>% procedural recovery

<sup>3</sup> aglycone determined

Brennecke (1997i) studied the freezer storage stability of tolylfluanid and DMST in tomatoes and Nüsslein (1996c) in tomato juice and purée. Homogenized tomato samples were fortified with tolylfluanid or DMST at 0.5 mg/kg and juice and purée samples at 0.2 mg/kg, and stored in a deep freezer at or below -18°C for 553 days (tomatoes), 125 days (juice) or 119 days (purée). Tolylfluanid and DMST were stable in tomatoes, juice and purée for the duration of storage (Table 20). 4-hydroxymethyl-DMST glucoside and 2 hydroxyphenyl-DMST glucoside were stable for 1.5 years in tomatoes.

Table 20. Storage stability of tolylfluanid and DMST in tomatoes and tomato products stored at or below -18°C.

Sample	Fortification mg/kg	Storage, days	Tolyfluanid, %		DMST, %		Reference
			Remaining	Procedural recovery	Remaining	Procedural recovery	
Tomato	0.5	0	71	77	74	78	Brennecke (1997i)
		30	66	70	88	80	
		92	77	78	100	76	
		182	64	91	86	93	
		366	68	94	104	99	
553	71	76	115	85			
Juice	0.2	0	112		111		Nüsslein (1996c)
		28	108	124	123	126	
		90	87	104	89	102	
125	97	105	84	83			
Purée	0.2	0	90		95		Nüsslein

Sample	Fortification mg/kg	Storage, days	Tolyfluanid, %		DMST, %		Reference
			Remaining	Procedural recovery	Remaining	Procedural recovery	
		28	65	93	113	94	(1996c)
		92	81	116	128	104	
		119	82	115	108	117	

Brennecke (1997l) studied the freezer storage stability of tolyfluanid and DMST in green hop cones and dry hops. Green hop cones from a field trial on day 0 contained concentrations of tolyfluanid and DMST of 17 and 2.5 mg/kg respectively; these values were taken as 100%. For the determination of procedural recovery, green hop cone samples were spiked with 10 mg/kg. Untreated dry hops were fortified with tolyfluanid and DMST at 20 mg/kg and stored in a deep freeze at or below  $-18^{\circ}\text{C}$  for 363 days. No significant degradation of tolyfluanid or DMST was observed in the green hop cones or dry hops although there was greater variation in the residues remaining in the cones probably owing to the lower homogeneity of the residues. The results indicate that residues of tolyfluanid and DMST are stable for 1 year in frozen green and dry hop cones.

Table 21. Storage stability of tolyfluanid and DMST in hops stored at or below  $-18^{\circ}\text{C}$  (Brennecke, 1997l).

Sample	Fortification mg/kg	Storage, days	Tolyfluanid		DMST	
			% Remaining	% Procedural recovery	% Remaining	% Procedural recovery
Green hop cones	*	0	100 <sup>1</sup>	100	100 <sup>2</sup>	100
		32	76 <sup>1</sup>	76	80 <sup>2</sup>	87
		90	65 <sup>1</sup>	93	64 <sup>2</sup>	94
		119	129 <sup>1</sup>	91	176 <sup>2</sup>	92
		144	76 <sup>1</sup>	97	124 <sup>2</sup>	107
		181	106 <sup>1</sup>	92	100 <sup>2</sup>	96
		363	94 <sup>1</sup>	84	76 <sup>2</sup>	95
Dry hops	20	0	81	90	88	94
		30	83	84	90	91
		90	85	88	93	93
		181	89	93	97	99
		363	81	80	89	91

\* 10 mg/kg was used for the concurrent analysis of freshly fortified samples

<sup>1</sup> incurred residues measured at 0, 32, 90, 119, 181 and 363 days were 17 (100%), 13, 11, 22, 13, 18, and 16 mg/kg.

<sup>2</sup> incurred residues measured at 0, 32, 90, 119, 181 and 363 days were 2.5 (100%), 2.0, 1.6, 4.4, 3.1, 2.5, and 1.9 mg/kg.

Brennecke (1995d) determined the stability of tolyfluanid and three metabolites in aqueous extracts of grapes and in grape juice and wine samples fortified with tolyfluanid at 0.2 mg/kg, DMST at 0.2 mg/kg, 4-hydroxymethyl-DMST glucoside at 0.5 mg/kg or 2-hydroxyphenyl-DMST glucoside at 0.5 mg/kg and stored at  $4-8^{\circ}\text{C}$  for 21 to 31 days. After 21 days only DMST was stable in the aqueous extract; both glucosides were stable in grape juice and wine. Only 5-6% of the tolyfluanid remained in wine samples while 126-141% of DMST was measured, indicating the degradation of tolyfluanid into DMST in wine. The results show that aqueous extracts and samples must be analysed at once and not stored in a refrigerator.

Brennecke (1995d) also investigated the stability of tolyfluanid and the same three metabolites in analytical extracts of grapes, grape juice and wine fortified with 1 mg/kg of one of the compounds and stored at  $4-8^{\circ}\text{C}$  for 80 days. Tolyfluanid, DMST, 4-hydroxymethyl-DMST and 2-hydroxyphenyl-DMST were stable in the analytical solutions throughout the test period. The disilyl derivative of 4-hydroxymethyl-DMST and 2-hydroxyphenyl-DMST were stable at room temperature over the test period of 6 days.

Brennecke (1996) tested the stability of tolyfluanid and DMST in analytical extracts of green and dry hop cones fortified at 5.0 mg/kg and stored at 4-8°C for 3 weeks (green) or 4 weeks (dry). Both compounds were stable throughout the test periods.

### Definition of the residue

Tolyfluanid is metabolized in plants by cleavage of an N-S bond to form DMST and a derivative of the dichlorofluoromethylthio side chain. DMST is further metabolized to hydroxylated metabolites and their glucosides. Tolyfluanid is generally the main residue found after application except in grapes when 4-hydroxymethyl-DMST glucoside and 2-hydroxymethyl-DMST glucoside accounted for about 60% of the TRR. Thiazolidine-2-thione-4-carboxylic acid (TTCA), a substance of toxicological concern, was identified in one strawberry study under artificial test conditions and is not expected under normal agricultural conditions.

In animals, tolyfluanid is rapidly metabolized and no parent compound was detected in the tissues and organs of farm animals. DMST, 4-(dimethylaminosulfonylamino)benzoic acid and 4-(dimethylaminosulfonylamino)hippuric acid are significant metabolites present in tissues and organs.

Products of further metabolism of DMST are not of toxicological significance. Owing to the rapid metabolism of tolyfluanid to DMST, it was not possible to distinguish long-term effects of DMST from those of tolyfluanid except for fluoride deposition. The acute oral toxicity of DMST is comparable to that of tolyfluanid.

The Meeting recommended that the definition of the residue for commodities derived from plants should be as follows:

For compliance with MRLs: tolyfluanid

For the estimation of dietary intake: sum of tolyfluanid and DMST, expressed as tolyfluanid.

### USE PATTERN

Tolyfluanid is registered mainly in European countries. It is a broad-spectrum fungicide with a protective mode of action and is effective against many plant diseases. It is used for the simultaneous control of scab (*Venturia* spp.), eye rots and storage diseases in orchard fruits, and for the control of grey mould (*Botrytis cinerea*) in strawberries and other berries, grapes, vegetables and hops. When sprayed repeatedly, tolyfluanid is also effective against spider mites (*Panonychus ulmi*). The information available to the Meeting on registered uses is summarized in Table 22. Official labels of Belgium, Chile, Denmark, Finland, France, Germany, Ireland, The Netherlands, Poland, Slovenia, Sweden, Switzerland, Turkey, the UK and Uruguay have been provided to the Meeting.

Table 22. Registered uses of tolyfluanid (all foliar).

Crop <sup>1</sup>	Country	Form	Application <sup>2</sup>				PHI, days
			Spray conc. kg ai/hl	Water vol l/ha	Rate, kg ai/ha	No.	
Almond	France	WP50	0.075		n.s.	n.s.	7
Apple	Finland	WG50	n.s.	800-2500	1.5-2.5 <sup>3</sup>	n.s.	21
Apple	Netherlands	WG50 WP50	0.075	1000-1500	0.75-1.12	6-7	7
Apple	Sweden	WG50	0.05-0.075		n.s.	n.s.	7
Apricot	Turkey	WP50	0.125		n.s.	2	14
Arctic bramble	Finland	WG50	0.075	400	0.3	2	30

Crop <sup>1</sup>	Country	Form	Application <sup>2</sup>				PHI, days
			Spray conc. kg ai/hl	Water vol l/ha	Rate, kg ai/ha	No.	
Bilberries ( <i>Vaccinium</i> spp)	Netherlands	WG50 WP50	0.125	1000-1200	1.25-1.50	2	21
Blackberry	Belgium	WG50	0.125		n.s.	n.s.	7
Blackberry	Ireland	WG50	n.s.	≥2000	1.7 2 2.25 3.38	4 <sup>4</sup> 3 3 <sup>4</sup> 2 <sup>4</sup>	21
Blackberry	Netherlands	WG50 WP50	0.125	1000-1200	1.25-1.50	4-5 2	14
Blackberry	Switzerland	WG50	0.1-0.125		n.s.	3-4	14
Blackberry	UK	WG50	n.s.	≥2000	1.7	4	14
Blueberry	Belgium	WG50	0.125		n.s.	n.s.	21
Cabbage	Sweden	WG50	0.075 <sup>5</sup> 0.125 <sup>6</sup>	1000	n.s.	4-5	14
Celery	Sweden	WG50	0.075 <sup>5</sup> 0.125 <sup>6</sup>	1000	n.s.	4-5	14
Cucumber (F, G)	Belgium	WG50	0.075		n.s.	n.s.	3
Cucumber (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	4-5	3
Cucumber	Poland	WG50 WP50	n.s.	600-800	0.75	2-3	3
Cucumber (G)	Poland	WG50 WP50	0.1	1500-2000	n.s.	3-4	3
Cucumber	Sweden	WG50	n.s.		1.5	3-4	3
Cucumber (G)	Sweden	WG50	0.075		n.s.	3-4	7
Currants (black)	Ireland	WG50	0.075	≥1000 <sup>7</sup> ≥2000 <sup>8</sup>	n.s.	6	21
Currants (black, red, white)	Belgium	WG50	0.125		n.s.	n.s.	21
Currants	Finland	WG50	0.125		1.25-1.5	2	<sup>9</sup>
Currants (black, red, white)	Netherlands	WG50 WP50	0.125	1000-1200	1.25-1.50	4-5 2	21
Currants	Poland	WG50 WP50	0.1-0.2	500-900	1	n.s.	21
Currants	Sweden	WG50	0.125		n.s.	2-3	<sup>24</sup>
Currants (black, red, white)	UK	WG50	n.s.	1000-2000	0.75 <sup>10</sup> 1.0 <sup>11</sup>	3	21
Egg plant (G)	Belgium	WG50	0.075		n.s.	n.s.	3
Egg plant (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	4-5	3
Endive	Germany	WG50	0.1	600	0.6	6	21
Endive (G)	Netherlands	WG50 WP50	n.s.	500-1000	1.0-1.5	1	21
Gherkin	Belgium	WG50	0.075		n.s.	n.s.	3
Gherkin (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	4-5	3
Gooseberry	Belgium	WG50	0.125		n.s.	n.s.	21
Gooseberry	Finland	WG50	0.125		1.25-1.5	2	<sup>9</sup>
Gooseberry	Ireland	WG50	0.075	≥1000	n.s.	4	21
Gooseberry	Netherlands	WG50 WP50	0.125	1000-1200	1.25-1.50	4-5 2	21
Gooseberry	UK	WG50	n.s.	1000-2000	0.75 <sup>10</sup> 1.0 <sup>11</sup>	3	21
Grape, Wine (for downy mildew)	Germany	WG50	0.019-0.3	400-1600	0.3-1.2	3 <sup>12</sup>	35
Grape, Wine (for powdery mildew, <i>Botrytis cinerea</i> and downy mildew)	Germany	WG50	0.025-0.4	400-1600	0.4-1.6	6 <sup>12</sup>	35

Crop <sup>1</sup>	Country	Form	Application <sup>2</sup>				PHI, days
			Spray conc. kg ai/hl	Water vol l/ha	Rate, kg ai/ha	No.	
Grapes	Chile	WP50	0.1-0.125		1-1.5	n.s.	21
Grapes	Netherlands	WG50 WP50	0.125	500-1500	0.625- 1.875	4-5	35
Grapes	Slovenia	WP50	0.1-0.125		n.s.	n.s.	35
Grapes	Spain	WP50	0.1		n.s.	n.s.	15 <sup>13</sup>
Grapes	Switzerland	WG50	0.1-0.125		n.s.	n.s.	14
Grapes	Turkey	WP50	0.1		n.s.	n.s.	21
Grapes	Uruguay	WG50	0.125		n.s.	n.s.	14
Hazelnut	France	WP50	0.075		n.s.	n.s.	7
Hop	Poland	WG50 WP50	0.075	600- 3000 <sup>15</sup>	n.s.	n.s.	14
Leek	Netherlands	WG50 WP50	n.s.	500-1000	1.25	4-5	21
Lettuce	Belgium	WG50	n.s.		1.25	3	16
Lettuce	Germany	WG50	0.1	600	0.6	6	21
Lettuce	Slovenia	WP50	n.s.	n.s.	1-1.25	n.s.	21
Lettuce	Sweden	WG50	0.075 <sup>5</sup> 0.125 <sup>6</sup>	1000	n.s.	4-5	14
Lettuce	Uruguay	WG50	0.125		n.s.	3	5
Lettuce (G)	Poland	WG50 WP50	0.1	600-800	n.s.	Max. 3	21
Lettuce, Head (G)	Netherlands	WG50 WP50	n.s.	500-1000	1.0-1.5	1	21
Loganberry	Ireland	WG50	n.s.	≥2000	1.7 2 2.25 3.38	4 <sup>4</sup> 3 3 <sup>4</sup> 2 <sup>4</sup>	21
Loganberry	UK	WG50	n.s.	≥2000	1.7	4	14
Melons	Belgium	WG50	0.075		n.s.	n.s.	3
Melons (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	4-5	3
Melons	Spain	WP50	0.075-0.1		n.s.	n.s.	15
Melons	Sweden	WG50	n.s.		1.5	3-4	3
Melons (G)	Sweden	WG50	0.075		n.s.	3-4	7
Onion	Sweden	WG50	0.075 <sup>5</sup> 0.125 <sup>6</sup>	1000	n.s.	4-5	14
Onion	Uruguay	WG50	0.125		n.s.	n.s.	5
Pear	Netherlands	WG50 WP50	0.075	1000-1200	0.75-0.90	6-7	7
Peppers (G)	Belgium	WG50	0.075		n.s.	n.s.	3
Peppers (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	3	3
Pome fruits	Belgium	WG50	0.075	1500	1.125	n.s.	7
Pome fruits	Chile	WP50	0.075-0.1		n.s.	n.s.	7
Pome fruits	France	WP50	0.075		n.s.	n.s.	7
Pome fruits (for fungal storage decay)	Germany	WG50 WP50	0.076	500 <sup>18</sup>	0.38 <sup>18</sup>	5 <sup>17</sup> (8-14)	7
Pome fruits (for scab)	Germany	WG50 WP50	0.076	500 <sup>18</sup>	0.38 <sup>18</sup>	12	7
Pome fruits	Poland	WG50 WP50	0.13-0.20	500-750	1	1-2	7
Pome fruits	Slovenia	WP50	0.1	1000 <sup>19</sup>	n.s.	n.s.	7
Pome fruits	Spain	WP50	0.075-0.1		n.s.	n.s.	15
Pome fruits	Switzerland	WG50	0.1		n.s.	n.s.	21
Potato	Chile	WP50	0.1-0.15		n.s.	n.s.	3
Potato	Finland	WG50	n.s.	≥400	0.75-1.0	3	14
Potato	Sweden	WG50	n.s.	300-400 <sup>20</sup> 500-600 <sup>21</sup>	0.75 <sup>22</sup> 1 <sup>23</sup>	4-6	7

Crop <sup>1</sup>	Country	Form	Application <sup>2</sup>				PHI, days
			Spray conc. kg ai/hl	Water vol l/ha	Rate, kg ai/ha	No.	
Raspberry	Belgium	WG50	0.125		n.s.	n.s.	7
Raspberry	Finland	WG50	0.125	1000-1200	1.25-1.5	3	21
Raspberry	Ireland	WG50	n.s.	≥2000	1.7 2 2.25 3.38	4 <sup>4</sup> 3 3 <sup>4</sup> 2 <sup>4</sup>	7
Raspberry	Netherlands	WG50 WP50	0.125	1000-1200	1.25-1.50	4-5 2	14
Raspberry	Poland	WG50 WP50	0.1-0.2	500-900	1	n.s.	7
Raspberry	Sweden	WG50	0.125		n.s.	2-3	2 <sup>4</sup>
Raspberry	Switzerland	WG50	0.1-0.125		n.s.	3-4	14
Raspberry	UK	WG50	n.s.	≥2000	1.7	4	14
Rubus hybrids <sup>25</sup>	UK	WG50	n.s.	≥2000	1.7	4	14
Squash	Sweden	WG50	n.s.		1.5	3-4	3
Squash (G)	Sweden	WG50	0.075		n.s.	3-4	7
Squash, Summer	Belgium	WG50	0.075		n.s.	n.s.	3
Squash, Summer (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	4-5	3
Strawberry	Belgium	WG50	n.s.		1.25	n.s.	7
Strawberry (G)	Belgium	WG50	n.s.		1.25	n.s.	14
Strawberry (F. G)	Chile	WP50	0.1-0.125		n.s.	n.s.	7 <sup>26</sup>
Strawberry	Finland	WG50	0.125	1000-1500	1.25-1.9	2-3	14
Strawberry	Germany	WG50	0.125	2500	2.5	3	7
Strawberry	Ireland	WG50	n.s.	≥1000	1.7 2.25 3.38	4 <sup>27</sup> 3 <sup>27</sup> 2 <sup>27</sup>	14
Strawberry	Netherlands	WG50 WP50	0.125	600-1000	0.75-1.25	4-5 2	7
Strawberry	Poland	WG50 WP50	0.17-0.5	500-1500	2.5	2-3	7
Strawberry	Slovenia	WP50	0.1-0.125	n.s.	n.s.	n.s.	7
Strawberry	Spain	WP50	0.075-0.1		n.s.	n.s.	15
Strawberry	Sweden	WG50	n.s.	500-1000	2	2-3	7
Strawberry	Switzerland	WG50	0.1-0.125		n.s.	3-4	14
Strawberry	UK	WG50	n.s.		1.7	4	14
Strawberry	Uruguay	WG50	0.10-0.125		n.s.	3	1
Tomato (F, G)	Belgium	WG50	0.075		n.s.	n.s.	3
Tomato (F. G)	Chile	WP50	0.1-0.125		n.s.	n.s.	3 <sup>26</sup>
Tomato (G)	Denmark	WG50	0.075		n.s.	10	3
Tomato	Germany	WG50	0.1	600-1200	0.6-1.2	6 (8-10)	3
Tomato (G)	Ireland	WG50	0.05	≥2000	n.s.	6	3
Tomato (G)	Netherlands	WG50 WP50	0.075	500-1500	0.37-1.12	4-5	3
Tomato	Poland	WG50 WP50	n.s.	600-800	0.75	2-3	3
Tomato (G)	Poland	WG50 WP50	0.1	1500-2000	n.s.	3-4	3
Tomato	Slovenia	WP50	n.s.	n.s.	1-1.25	n.s.	3
Tomato	Sweden	WG50	0.075		n.s.	n.s.	4
Tomato	Turkey	WP50	0.1		n.s.	n.s.	7
Vegetables (including tomato (G))	Spain	WP50	0.075-0.1		n.s.	n.s.	15

<sup>1</sup> (G): cultivation in greenhouse. (F, G). cultivation outdoor and in greenhouse. No indication: cultivation outdoor

- <sup>2</sup> Not specified on the label
- <sup>3</sup> For fruit orchards
- <sup>4</sup> Using the combined programme for the control of cane diseases and Botrytis, up to 7 applications may be made in a season
- <sup>5</sup> On small plants
- <sup>6</sup> On larger plants
- <sup>7</sup> At late grape stage
- <sup>8</sup> For later sprays
- <sup>9</sup> May not be sprayed later than one week after the end of flowering
- <sup>10</sup> For first 2 sprays
- <sup>11</sup> For third spray
- <sup>12</sup> No more than a total of 8 applications on production areas, and, of these, a maximum of 6 between end of flowering and onset of maturity.
- <sup>13</sup> For wine grapes, 21 days
- <sup>14</sup> Last date for application: 15 August
- <sup>15</sup> Depending growth stage: 600-1000 l, 1500-2000 l or 2500-3000 l
- <sup>16</sup> Not to be used after the plant weighs 40 g or when the stage “covering of the soil by the leaves” has been reached. If the plant is to be cut at a final weight of 200-250 g, the treatment has to be carried out 3 days earlier
- <sup>17</sup> In combination with the application against scabs, no more than 15 applications in total
- <sup>18</sup> Application rate for standard tree of 3 m height equivalent to 1.1 kg ai/ha and 1500 l water/ha
- <sup>19</sup> For apples
- <sup>20</sup> At early spraying before the canopy rows close themselves
- <sup>21</sup> Later in the season and during unfavourable conditions
- <sup>22</sup> For sprays 1 and 2
- <sup>23</sup> For spray 3
- <sup>24</sup> Final treatment at the latest before green fruit formation
- <sup>25</sup> Other than raspberries, loganberries and blackberries
- <sup>26</sup> For vegetables in greenhouses, the PHI is at least double that for field-grown vegetables
- <sup>27</sup> Where necessary an additional spray of 1.7 kg/ha may be made following the recommended programme provided that the pre-harvest interval is observed

## RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information from the manufacturer on supervised field trials on:

Fruits	Table 23.	Apples and pears in France, Germany, Italy, The Netherlands, Poland and Spain	
	Table 24.	Grapes in Chile, France, Germany, Italy and Spain	
	Table 25.	Blackcurrants in Germany and the UK	
	Table 26.	Blackberries in Germany and the UK	
	Table 27.	Raspberries in Germany and the UK	
	Table 28.	Strawberries in France, Germany, The Netherlands, Poland and Spain	
	Vegetables	Table 29.	Cucumbers in Germany, Italy and Spain
		Table 30.	Melons in France and Greece
Table 31.		Tomatoes in France, Germany, Italy, Mexico and Spain	
Table 32.		Peppers in Italy, The Netherlands and Spain	
Table 33.		Lettuce in Belgium, France, Germany, Greece, Italy, Portugal, Spain and the UK	
Table 34.		Leeks in Germany, The Netherlands and the UK	
Dried vegetables	Table 35.	Hops in Germany	

Residue levels were reported for tolyfluanid and its main metabolite DMST. For supervised trials on grapes, 4-hydroxymethyl-DMST glucoside (230.3 g/mol) and 2-hydroxymethyl-DMST glucoside (230.3 g/mol) were determined as the disilyl derivatives of the aglycones and expressed as aglycones. The sum of tolyfluanid and DMST was calculated and expressed as tolyfluanid on the

basis of the molecular weight of tolyfluanid (347.3 g/mol) and DMST (214.3 g/mol). When tolyfluanid and/or DMST was found to be below the limit of quantification, the sum of tolyfluanid and DMST was calculated as follows and expressed as tolyfluanid.

Tolyfluanid	DMST	Total (expressed as tolyfluanid)
<0.02	<0.02	<0.02
0.10	<0.02	0.10
<0.02	0.10	0.16
0.10	0.10	0.26

When residues were not detected they are shown as below the limit of quantification, e.g. <0.05 mg/kg. Residues and spray concentrations were rounded to two significant figures except for residues near the limit of quantification when one significant figure was used. Residues in the trials according to maximum GAP were used for the estimation of maximum residue levels. These results are double underlined.

Most trials were well documented. Laboratory reports included method validation with recovery experiments conducted at 10 times the limit of quantification, and/or at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of sample storage were also provided. Field reports provided data on the sprayers used, plot size, soil characteristics, climatic data, application dates, residue sample size and sampling date. Although trials included control plots, no control data are recorded in the Tables except where residues in control samples exceeded the limit of quantification. Residues determined before the last application are reported for some trials. The results are not adjusted for recovery.

The government of Poland submitted the summary reports of supervised trials in Poland on apples and strawberries.

Table 23. Residues in apples and pears from supervised trials in France, Germany, Italy, The Netherlands, Poland and Spain.

Country, Year (Variety)	Application				PHI (days)	Residues, mg/kg			Report no.
	Form	kg ai/ha	kg ai/hl	No		T	D	T+D <sup>1</sup>	
APPLE									
Germany 1983 (James Grieve)	WP50	1.125	0.075	15	0	0.6	0.4	1.2	8200-83
					7	<u>0.5</u>	0.2	<u>0.8</u>	
					14	0.3	0.1	0.5	
					21	0.1	<0.1	0.1	
Germany 1983 (Cox Orange)	WP50	1.125	0.075	15	0	2.1	0.5	2.9	8201-83
					7	<u>2.3</u>	0.5	<u>3.1</u>	
					14	1.9	0.5	2.7	
					21	1.1	0.3	1.6	
Germany 1987 (Golden Delicious)	WG50	1.125	0.075	15	0	1.9	0.20	2.2	8239-87
					1	1.7	0.26	2.1	
					3	2.0	0.18	2.3	
					7	0.82	0.11	1.00	
					10	<u>0.92</u>	0.11	<u>1.10</u>	
Germany 1987 (Jonathan)	WG50	1.125	0.075	15	0	1.6	<0.05	1.6	8240-87
					1	1.5	<0.05	1.5	
					3	1.0	<0.05	1.0	
					7	<u>0.46</u>	<0.05	<u>0.46</u>	
Germany 1988 (Jonagold)	WG50	1.125	0.225	15	0	3.5	0.21	3.8	0251-88
					1	2.7	0.19	3.0	
					3	2.2	0.28	2.7	
					7	<u>2.0</u>	0.35	<u>2.6</u>	
					10	1.8	0.39	2.4	



Country, Year (Variety)	Application				PHI (days)	Residues, mg/kg			Report no.
	Form	kg ai/ha	kg ai/hl	No		T	D	T+D <sup>1</sup>	
Germany 1988 (Cox Orange)	WG50	1.125	0.225	15	0	1.4	0.13	1.6	0252-88
					1	1.0	0.11	1.2	
					3	1.0	0.17	1.3	
					7	<u>0.55</u>	0.20	<u>0.87</u>	
					10	<u>0.35</u>	0.15	<u>0.59</u>	
Germany 1989 (Cox Orange)	WG50	1.125	0.225	15	0	0.98	0.07	1.09	0507-89
					1	1.2	0.09	1.3	
					3	0.66	0.13	0.87	
					7	0.44	0.11	0.62	
					10	<u>0.48</u>	0.11	<u>0.66</u>	
Germany 1989 (Cox Orange)	WG50	1.125	0.075	15	0	1.8	0.15	2.0	0508-89
					1	1.1	0.10	1.3	
					3	0.8	0.15	1.0	
					7	0.59	0.13	0.80	
					10	<u>0.60</u>	0.14	<u>0.83</u>	
Germany 1995 (Discovery)	WG50	1.125	0.225	7	0 <sup>3</sup>	0.19	0.03	0.24	RA- 2095/95 0380-95
					0	0.99	0.06	1.09	
					3	0.98	0.09	1.13	
					7 <sup>2</sup>	<u>0.35</u> , 0.28	0.04, 0.04	<u>0.41</u> , 0.34	
					14	<u>0.26</u>	0.06	<u>0.36</u>	
Germany 1995 (James Grieve)	WG50	1.125	0.075	7	0 <sup>4</sup>	0.03	< 0.02	0.03	RA- 2095/95 0381-95
					0 <sup>3</sup>	0.78	0.05	0.86	
					0	2.9	0.14	3.1	
					3	2.0	0.12	2.2	
					7 <sup>2</sup>	1.5, <u>1.7</u>	0.11, 0.10	1.68, <u>1.86</u>	
14	1.0	0.08	1.1						
Germany 1995 (Elstar)	WG50	1.21	0.225	7	0 <sup>3</sup>	0.48	0.09	0.63	RA- 2095/95 0584-95
					0	1.6	0.10	1.8	
					3	0.74	0.10	0.90	
					7	0.47, <u>0.59</u>	0.11, 0.09	0.65, <u>0.74</u>	
					14	0.45	0.06	0.55	
Germany 1995 (Melrose)	WG50	1.125	0.225	7	0 <sup>3</sup>	0.36	0.03	0.41	RA- 2095/95 0585-95
					0	1.4	0.05	1.5	
					3	0.61	0.03	0.66	
					7 <sup>2</sup>	0.46, <u>0.46</u>	0.03, 0.03	0.51, <u>0.51</u>	
					14	0.41	0.03	0.46	
Germany 1995 (Jamba)	WG50	1.125	0.225	7	0	0.67	0.03	0.72	RA- 2095/95 0586-95
					7 <sup>2</sup>	0.16, <u>0.18</u>	<0.02, <0.02	0.16, <u>0.18</u>	
Germany 1995 (Golden Delicious)	WG50	1.125	0.075	7	0	0.28	0.02	0.31	RA- 2095/95 0587-95
					7 <sup>2</sup>	0.23, <u>0.24</u>	0.03, 0.03	0.28, <u>0.29</u>	
Netherlands 1995 (Elstar)	WG50	1.125	0.225	7	0	0.41	<0.02	0.41	RA- 2095/95 0378-95
					7 <sup>2</sup>	0.16, <u>0.19</u>	<0.02, 0.02	0.16, <u>0.19</u>	
Netherlands 1995 (Schone van Boskoop)	WG50	1.125	0.225	7	0	1.6	0.10	1.8	RA- 2095/95 0590-95
					7 <sup>2</sup>	0.40, <u>0.58</u>	0.09, 0.11	0.55, <u>0.76</u>	
Poland 1997	WP50	1.0		3	1	1.30			Government submis- sion
					3	0.75			
					7	<u>0.44</u>			
					10	0.39			
					14	0.35			
France (south) 1995 (Golden)	WG50	1.5 1.35 <sup>5</sup>	0.1	3	0 <sup>3</sup>	0.23	<0.02	0.23	RA- 2096/95 0301-95
					0	0.72	0.03	0.77	
					3	0.66	0.04	0.72	
					7 <sup>2</sup>	<u>0.50</u> , 0.48	0.04, 0.04	<u>0.56</u> , 0.54	
					14	0.22	0.04	0.28	
France (south) 1995 (Granny Smith)	WG50	1.5	0.1	3	0 <sup>3</sup>	0.28	0.02	0.31	RA- 2096/95 0588-95
					0	0.60	0.03	0.65	
					3	0.95	0.04	1.01	
					7 <sup>2</sup>	<u>0.65</u> , 0.55	0.03, 0.03	<u>0.70</u> , 0.60	
					14	0.45	0.03	0.50	

Country, Year (Variety)	Application				PHI (days)	Residues, mg/kg			Report no.
	Form	kg ai/ha	kg ai/hl	No		T	D	T+D <sup>1</sup>	
Italy 1994 (Red Chief)	WG50	1.5	0.1	3	0 <sup>3</sup>	0.10	<0.02	0.10	RA- 2064/94 0262-94
					0	0.88	<0.02	0.88	
					3	0.37	0.03	0.42	
					5	0.42	0.03	0.47	
					7	<u>0.22</u>	0.03	<u>0.27</u>	
Italy 1994 (Annurca)	WG50	1.5	0.1	3	0 <sup>3</sup>	0.39	0.04	0.45	RA- 2064/94 0264-94
					0	1.3	0.07	1.4	
					3	0.37	0.04	0.43	
					5	0.35	0.05	0.43	
					7	<u>0.14</u>	0.03	<u>0.19</u>	
Italy 1995 (Fiorina)	WG50	1.5	0.1	3	0	1.1	0.07	1.2	RA- 2096/95 0379-95
					7 <sup>2</sup>	0.47, <u>0.51</u>	0.07, 0.08	0.58, <u>0.64</u>	
Italy 1995 (Granny Smith)	WG50	1.5	0.1	3	0	1.9	0.20	2.2	RA- 2096/95 0589-95
					7 <sup>2</sup>	<u>2.3</u> , 2.2	0.25, 0.28	<u>2.7</u> , 2.7	
Spain 1994 (Golden Smooting)	WG50	1.3	0.1	3	0 <sup>3</sup>	0.42	0.04	0.48	RA- 2064/94 0265-94
					0	2.9	0.13	3.1	
					3	2.3	0.09	2.4	
					5	1.2	0.09	1.3	
					7	<u>1.2</u>	0.06	<u>1.3</u>	
PEAR									
Germany 1983 (Alexander Lucas)	WP50	1.125	0.075	15	0	3.6	0.5	4.4	8202-83
					7	<u>1.5</u>	0.3	<u>2.0</u>	
					14	0.7	0.2	1.0	
					21	0.7	0.2	1.0	
Germany 1983 (Alexander Lucas)	WP50	1.125	0.075	15	0	8.1	0.9	9.6	8203-83
					7	<u>3.4</u>	0.4	<u>4.0</u>	
					14	2.2	0.2	2.5	
					21	1.9	0.2	2.2	
Italy 1994 (William)	WG50	1.5	0.1	3	0 <sup>3</sup>	0.10	<0.02	0.10	RA- 2150/94 0266-94
					0	0.73	0.03	0.78	
					3	0.30	0.02	0.33	
					5	0.22	<0.02	0.22	
					7	<u>0.26</u>	<0.02	<u>0.26</u>	
Italy 1994 (Precoce di Fiorano)	WG50	1.5	0.1	3	0 <sup>3</sup>	0.47	0.03	0.52	RA- 2150/94 0267-94
					0	1.9	0.05	1.98	
					3	0.78	0.05	0.86	
					5	0.53	0.04	0.59	
					7	<u>0.40</u>	0.04	<u>0.46</u>	
Spain 1994 (Ercolini)	WG50	1.5	0.1	3	0 <sup>3</sup>	0.31	0.03	0.36	RA- 2150/94 0268-94
					0	2.1	0.17	2.4	
					3	0.89	0.07	1.00	
					5	0.77	0.05	0.85	
					7	<u>0.54</u>	0.04	<u>0.60</u>	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid<sup>2</sup> Two independent composite samples collected per site<sup>3</sup> Before last application<sup>4</sup> Control sample<sup>5</sup> Last application

Table 24. Residues in grapes from supervised trials in Chile, France, Germany, Italy and Spain.

Country, Year (Variety)	Application				Sample	PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
Germany 1987 (Riesling)	WG50	0.5- 2.5	0.1	8	bunch of grapes	0	3.3	0.33	3.8	8200-87
						14	0.34	0.10	0.50	
						21	0.16	0.25	0.57	
						28	0.19	<0.05	0.19	
						35	0.24	0.07	0.35	
						42	0.25	0.06	0.35	
Germany 1987 (Spätburgunder)	WG50	0.5- 1.8	0.1	8	bunch of grapes	0	5.0	0.39	5.6	8201-87
						14	1.1	0.19	1.4	
						21	0.49	0.14	0.72	
						28	0.82	0.14	1.05	
						35	0.41	0.10	0.57	
						42	<u>0.63</u>	0.13	<u>0.84</u>	
Germany 1987 (Müller-thurgau)	WG50	0.6- 1.8	0.3	8	bunch of grapes	0	9.2	0.45	9.9	8202-87
						14	2.4	0.22	2.8	
						21	1.7	0.24	2.1	
						28	1.4	0.21	1.7	
						35	0.47	0.07	0.58	
						42	<u>0.49</u>	0.11	<u>0.67</u>	
Germany 1987 (Spätburgunder)	WG50	0.6- 1.8	0.3	8	bunch of grapes	0	11	0.23	11	8203-87
						14	4.3	0.20	4.6	
						21	2.3	0.20	2.6	
						28	2.0	0.18	2.3	
						35	<u>1.7</u>	0.15	<u>1.9</u>	
						42	0.41	0.05	0.49	
Germany 1988 (Müller-thurgau)	WG50	0.75- 1.8	0.3	8	bunch of grapes	0	1.5	0.07	1.6	0212-88
						14	0.13	<0.05	0.13	
						21	0.07	<0.05	0.07	
						28	<0.05	<0.05	<0.05	
						35	<u>0.06</u>	<0.05	<u>0.06</u>	
						42	0.06	<0.05	0.06	
Germany 1988 (Müller-thurgau)	WG50	0.6- 1.8	0.3	8	bunch of grapes	0	4.3	0.23	4.67	0213-88
						14	1.5	0.20	1.82	
						21	1.0	0.11	1.18	
						28	0.59	0.12	0.78	
						35	<u>0.67</u>	0.10	<u>0.83</u>	
						42	0.63	0.07	0.74	
Germany 1988 (Müller-thurgau)	WG50	0.6- 1.8	0.1	8	bunch of grapes	0	3.3	0.19	3.6	0211-88
						14	0.78	0.12	0.97	
						21	0.53	0.07	0.64	
						28	0.34	0.08	0.47	
						35	<u>0.35</u>	0.07	<u>0.46</u>	
						42	0.26	<0.05	0.26	
Germany 1988 (Riesling)	WG50	0.6- 2.0	0.1	8	bunch of grapes	0	6.0	0.34	6.6	210-88
						14	1.4	0.18	1.7	
						21	1.3	0.21	1.6	
						28	1.1	0.18	1.4	
						35	<u>0.91</u>	0.17	<u>1.19</u>	
						42	0.91	0.14	1.14	
France (south) 1992 (Grenache)	WG50	2.0	2.0	5	bunch of grapes	0 <sup>3</sup>	0.71	0.07	0.82	RA-2007/92 0423-92
						0	4.2	0.12	4.4	
						7	1.9	0.14	2.1	
						14	0.77	0.07	0.88	
						21	0.36	0.04	0.42	
France (south) 1992 (Carignan)	WG50	2.0	2.0	5	bunch of grapes	0 <sup>3</sup>	1.8	0.09	1.9	RA-2007/92 0424-92
						0	3.5	0.11	3.7	
						7	2.3	0.14	2.5	
						14	1.4	0.08	1.5	
21	0.57	0.11	0.75							
France (south) 1992 (Syrah)	WG50	2.0	2.0	5	bunch of grapes	0	5.4	0.14	5.6	RA-2007/92 0425-92
						21	0.33	0.05	0.41	

Country, Year (Variety)	Application				Sample	PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
France (south) 1992 (Cinsault)	WG50	2.0	2.0	5	bunch of grapes	0 21	4.7 1.4	0.19 0.14	5.0 1.6	RA-2007/92 0426-92
France (south) 1993 (Grenache)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21 39	0.12 1.2 1.2 0.33 0.46 0.11	<0.02 0.07 0.09 0.05 0.09 0.02	0.12 1.3 1.3 0.41 0.61 0.14	RA-2049/93 0085-93
France (south) 1993 (Chardonnay)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21 35	0.05 0.65 0.11 0.08 0.06 0.05	0.02 0.05 0.04 0.04 0.06 0.03	0.08 0.73 0.17 0.14 0.16 0.10	RA-2049/93 0320-93
France (south) 1993 (Grenache)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup> 0 21 35	0.74 7.3 2.1 1.2	0.08 0.24 0.17 0.09	0.87 7.7 2.4 1.3	RA-2049/93 0321-93
France (south) 1993 (Grenache Blanc)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup> 0 21 35	1.2 5.8 1.4 0.6	0.08 0.19 0.07 0.04	1.3 6.1 1.5 0.7	RA-2049/93 0322-93
France (south) 1995 (Grenache)	WG50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21 <sup>2</sup> 35	1.1 4.1 2.7 1.3 2.6, 1.1 0.43	0.07 0.13 0.19 0.12 0.22, 0.13 0.09	1.2 4.3 3.0 1.5 3.0, 1.3 0.58	RA-2093/95 0015-95
France (south) 1995 (Mouvèdre)	WG50	2.0	2.0	3	bunch of grapes	0 <sup>4</sup> 0 <sup>3</sup> 0 7 14 21 <sup>2</sup> 35	0.02 1.7 5.9 4.7 3.4 3.5, 2.7 0.62	<0.02 0.10 0.16 0.14 0.16 0.20, 0.13 0.08	0.02 1.9 6.2 4.9 3.7 3.8, 2.9 0.75	RA-2093/95 0599-95
Italy 1994 (Pampanuto)	WG50	1.0	0.2	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21	0.10 0.65 0.18 0.06 0.04	<0.02 0.04 <0.02 <0.02 <0.02	0.10 0.71 0.18 0.06 0.04	RA-2065/94 0270-94
Italy 1994 (Sangiovese)	WG50	1.0	0.2	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21	0.12 1.1 0.13 0.06 0.04	<0.02 0.07 0.03 <0.02 <0.02	0.12 1.2 0.18 0.06 0.04	RA-2065/94 0671-94
Italy 1994 (Blusch)	WP50	1.0	0.1	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21	0.15 2.4 0.36 <u>0.13</u> 0.05	<0.02 0.05 0.04 <0.02 <0.02	0.15 2.5 0.42 <u>0.13</u> 0.05	RA-2065/94 0269-94
Italy 1994 (Centenial)	WP50	1.0	0.1	3	bunch of grapes	0 <sup>3</sup> 0 7 14 21	0.13 2.0 0.13 <u>0.11</u> 0.03	<0.02 0.06 <0.02 <0.02 <0.02	0.13 2.1 0.13 <u>0.11</u> 0.03	RA-2065/94 0669-94
Spain 1993 (Xarello)	WP50	1.0	0.16	3	bunch of grapes	0 <sup>3</sup> 0 8 14 21	0.63 6.5 3.3 2.7 1.7	0.11 0.17 0.17 0.12 0.11	0.81 6.8 3.6 2.9 1.9	RA-2050/93 0353-93

Country, Year (Variety)	Application				Sample	PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
Spain 1993 (Macabeo)	WP50	1.0	0.16	3	bunch of grapes	0 <sup>3</sup>	1.6	0.26	2.0	RA-2050/93 0354-93
						0	10	0.68	11	
						6	8.0	0.31	8.5	
						14	6.9	0.37	7.5	
						21	5.1	0.23	5.5	
Chile 1994 (Thompson Seedless)	WP50	1.5	0.075	2	bunch of grapes	0 <sup>3</sup>	0.32	0.04	0.38	RA-2146/94 0791-94
						0	5.2	0.15	5.4	
						7	2.9	0.15	3.1	
						14 <sup>2</sup>	1.7,1.8	0.12,0.17	1.9,2.1	
						21	<u>1.8</u>	0.13	<u>2.0</u>	
Chile 1994 (Thompson Seedless)	WP50	1.65	0.075	2	bunch of grapes	0 <sup>3</sup>	0.61	0.03	0.66	RA-2146/94 0792-94
						0	2.5	0.12	2.7	
						7	1.5	0.08	1.6	
						14 <sup>2</sup>	1.2,2.0	0.04,0.07	1.3,2.1	
						21	<u>0.98</u>	0.04	<u>1.04</u>	
Chile 1994 (Thompson Seedless)	WP50	1.65	0.075	2	bunch of grapes	0 <sup>3</sup>	0.40	0.03	0.45	RA-2146/94 0793-94
		1.5				0	1.1	0.08	1.2	
						7	0.58	0.02	0.61	
						14 <sup>2</sup>	0.51	0.04,0.05	0.57,0.74	
						21	0.66	0.03	<u>0.29</u>	

Country Year (Variety)	Application				Sample	PHI (days)	Residues, mg/kg			Report no.
	Form	kg ai/ha	kg ai/hl	No			4-HMD	2-HPD	T+ 3 metabolites <sup>5</sup>	
France (south) 1992 (Grenache)	WG50	2.0	2.0	5	bunch of grapes	0 <sup>3</sup>	0.68	0.17	2.10	RA- 2007/92 0423-92
						0	0.79	0.23	5.93	
						7	0.74	0.15	3.47	
						14	0.59	0.11	1.94	
						21	0.60	0.11	1.49	
France (south) 1992 (Carignan)	WG50	2.0	2.0	5	bunch of grapes	0 <sup>3</sup>	1.1	0.12	3.79	RA- 2007/92 0424-92
						0	0.70	0.07	4.84	
						7	0.94	0.10	4.10	
						14	0.80	0.09	2.87	
						21	0.84	0.07	2.12	
France (south) 1992 (Syrah)	WG50	2.0	2.0	5	bunch of grapes	0	1.3	<0.05	7.59	RA- 2007/92 0425-92
						21	1.2	<0.05	2.22	
France (south) 1992 (Cinsault)	WG50	2.0	2.0	5	bunch of grapes	0	1.0	0.11	6.68	RA- 2007/92 0426-92
						21	1.1	0.08	3.41	
France (south) 1993 (Grenache)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup>	0.08	<0.05	0.24	RA- 2049/93 0085-93
						0	0.24	<0.05	1.67	
						7	0.22	<0.05	1.68	
						14	0.22	<0.05	0.74	
						21	0.37	<0.05	1.17	
						39	0.19	<0.05	0.43	
France (south) 1993 (Chardonnay)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup>	<0.05	<0.05	0.08	RA- 2049/93 0320-93
						0	0.06	<0.05	0.82	
						7	0.18	<0.05	0.44	
						14	0.20	<0.05	0.44	
						21	0.18	<0.05	0.43	
						35	0.19	<0.05	0.39	
France (south) 1993 (Grenache)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup>	0.43	0.09	1.65	RA- 2049/93 0321-93
						0	0.55	0.11	8.69	
						21	0.57	0.11	3.41	
						35	0.63	0.10	2.45	
France (south) 1993 (Grenache Blanc)	WP50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup>	0.40	0.08	2.05	RA- 2049/93 0322-93
						0	0.53	0.13	7.11	
						21	0.50	0.07	2.37	
						35	0.50	<0.05	1.41	

Country Year (Variety)	Application				Sample	PHI (days)	Residues, mg/kg			Report no.
	Form	kg ai/ha	kg ai/hl	No			4-HMD	2-HPD	T+ 3 metabolites <sup>5</sup>	
France (south) 1995 (Grenache)	WG50	2.0	2.0	3	bunch of grapes	0 <sup>3</sup>	0.28	<0.05	1.63	RA- 2093/95 0015-95
						0	0.37	<0.05	4.87	
						7	0.59	0.06	3.99	
						14	0.38	<0.05	2.06	
						21 <sup>2</sup>	0.52,0.47	<0.05, <0.05	3.74,2.02	
35	0.61	0.05	1.58							
France (south) 1995 (Mouvèdre)	WG50	2.0	2.0	3	bunch of grapes	0 <sup>4</sup>	<0.05	<0.05	0.02	RA- 2093/95 0599-95
						0 <sup>3</sup>	0.32	<0.05	2.34	
						0	0.35	<0.05	6.69	
						7	0.32	<0.05	5.41	
						14	0.40	<0.05	4.26	
21 <sup>2</sup>	0.47,0.41	<0.05, <0.05	4.53,3.53							
35	0.35	<0.05	1.28							
Italy 1994 (Pampanuto)	WG50	1.0	0.2	3	bunch of grapes	0 <sup>3</sup>	0.26	<0.05	0.49	RA- 2065/94 0270-94
						0	0.33	<0.05	1.21	
						7	0.42	<0.05	0.81	
						14	0.31	<0.05	0.54	
						21	0.22	<0.05	0.37	
Italy 1994 (Sangiovese)	WG50	1.0	0.2	3	bunch of grapes	0 <sup>3</sup>	0.15	<0.05	0.35	RA- 2065/94 0671-94
						0	0.20	<0.05	1.51	
						7	0.24	<0.05	0.54	
						14	0.17	<0.05	0.32	
						21	0.19	<0.05	0.33	
Italy 1994 (Blusch)	WP50	1.0	0.1	3	bunch of grapes	0 <sup>3</sup>	0.29	<0.05	0.59	RA- 2065/94 0269-94
						0	0.23	<0.05	2.83	
						7	0.42	<0.05	1.05	
						14	0.38	0.06	0.79	
						21	0.29	<0.05	0.49	
Italy 1994 (Centenial)	WP50	1.0	0.1	3	bunch of grapes	0 <sup>3</sup>	0.14	<0.05	0.34	RA- 2065/94 0669-94
						0	0.23	<0.05	2.45	
						7	0.25	<0.05	0.51	
						14	0.26	<0.05	0.50	
						21	0.22	<0.05	0.36	
Spain 1993 (Xarello)	WP50	1.0	0.16	3	bunch of grapes	0 <sup>3</sup>	0.41	0.06	1.52	RA- 2050/93 0353-93
						0	0.43	<0.05	7.43	
						8	0.43	0.06	4.32	
						14	0.65	0.08	3.99	
						21	0.61	0.06	2.89	
Spain 1993 (Macabeo)	WP50	1.0	0.16	3	bunch of grapes	0 <sup>3</sup>	0.33	0.08	2.64	RA- 2050/93 0354-93
						0	0.39	0.13	11.89	
						6	0.51	0.16	9.51	
						14	0.70	0.27	8.96	
						21	0.87	0.24	7.14	
Chile 1994 (Thompson Seedless)	WP50	1.5	0.075	2	berry	0 <sup>3</sup>	0.37	<0.05	0.94	RA- 2146/94 0791-94
						0	0.48	<0.05	6.16	
						7	0.53	<0.05	3.94	
						14 <sup>2</sup>	0.49,0.54	<0.05, <0.05	2.63,2.89	
						21	0.56	<0.05	2.85	
Chile 1994 (Thompson Seedless)	WP50	1.65	0.075	2	berry	0 <sup>3</sup>	0.13	<0.05	0.86	RA- 2146/94 0792-94
						0	0.14	<0.05	2.90	
						7	0.23	<0.05	1.98	
						14 <sup>2</sup>	0.36,0.36	<0.05, <0.05	1.80,2.65	
						21	0.36	<0.05	1.58	
Chile 1994 (Thompson Seedless)	WP50	1.65	0.075	2	berry	0 <sup>3</sup>	0.21	<0.05	0.77	RA- 2146/94 0793-94
		1.5				0	0.26	<0.05	1.62	
						7	0.41	<0.05	1.23	
						14 <sup>2</sup>	0.48,0.55	<0.05, <0.05	1.29,1.57	
						21	0.46	<0.05	0.98	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

<sup>2</sup> PHI at which two independent composite samples were collected per site

<sup>3</sup> Before last application

Control sample

<sup>5</sup> Sum of tolyfluanid, DMST, 4-hydroxymethyl-DMST (230.3 g/mol) and 2-hydroxyphenyl-DMST (230.3 g/mol) expressed as tolyfluanid

Table 25. Residues in blackcurrants from supervised trials in Germany and the UK.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1996 (Titania)	WG50	1.25	0.125	2	0 <sup>3</sup>	0.26	0.19	0.57	RA-2061/96 0411-96
					0	4.3	0.49	5.1	
					7	1.8	0.33	2.3	
					14	1.3	0.33	1.8	
					21	<u>0.21</u>	0.08	<u>0.34</u>	
					28	0.06	0.02	0.09	
Germany 1999 (Rosenthals Langtraubige)	WG50	1.25 <sup>2</sup>	0.125	2	0 <sup>3</sup>	0.14	0.13	0.35	RA-2007/99 0112-99
					0	1.5	0.41	2.2	
					14	0.50	0.17	0.78	
					21	<u>0.17</u>	0.10	<u>0.33</u>	
Germany 1996 (Titania)	WG50	1.25	0.125	2	0 <sup>3</sup>	0.36	0.11	0.54	RA-2007/99 0202-99
					0	2.1	0.27	2.5	
					14	0.57	0.15	0.81	
					22	<u>0.10</u>	0.09	<u>0.25</u>	
UK 1995 (Ben Tirran)	WG50	1.25	0.25	2	0 <sup>3</sup>	0.32	0.14	0.55	RA-2108/95 0007-95
					0	1.4	0.26	1.8	
					7	0.70	0.20	1.02	
					14	0.24	0.24	0.63	
					21	<u>0.12</u>	0.14	<u>0.35</u>	
					28	0.06	0.11	0.24	
UK 1995 (Ben Tirran)	WG50	1.25	0.25	2	0 <sup>3</sup>	0.30	0.22	0.66	RA-2108/95 0591-95
					0	0.81	0.28	1.26	
					7	0.54	0.39	1.17	
					14	0.43	0.23	0.80	
					21	0.27	0.15	0.51	
					28	<u>0.28</u>	0.18	<u>0.57</u>	
UK 1996 (Ben Tirran)	WG50	1.25	0.125	2	0 <sup>3</sup>	0.54	0.07	0.65	RA-2061/96 0412-96
					0	2.4	0.16	2.7	
					7	1.5	0.30	2.0	
					14	0.90	0.29	1.37	
					21	<u>0.31</u>	0.23	<u>0.68</u>	
					28	0.18	0.15	0.42	
UK 1999 (Ben Tirran)	WG50	1.25	0.125	2	0 <sup>3</sup>	0.06	0.04	0.12	RA-2007/99 0203-99
					0	1.1	0.12	1.3	
					14	0.32	0.08	0.45	
					21	<u>0.28</u>	0.07	<u>0.39</u>	
UK 1999 (Ben Tirran)	WG50	1.25	0.125	2	0 <sup>3</sup>	0.03	0.03	0.08	RA-2007/99 0204-99
					0	0.42	0.06	0.52	
					14	0.24	0.08	0.37	
					21	<u>0.07</u>	0.07	<u>0.18</u>	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

<sup>2</sup> The second application was about 6% under-dosed

<sup>3</sup> Before last application

Table 26. Residues in blackberries from supervised trials in Germany and the UK.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1995 (Theodor Reimers)	WG50	1.7	0.113	4	0	8.2	0.18	8.5	RA-2107/95 0533-95
					14	<u>2.0</u>	0.12	<u>2.2</u>	

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1997 (Theodor Reimers)	WG50	1.7	0.113	4	0 <sup>2</sup>	3.6	0.41	4.3	RA-2045/97 0095-97
					0	19	1.0	21	
					14	<u>1.7</u>	0.22	<u>2.1</u>	
UK 1995 (Bedford Giant)	WG50	1.7	0.34	4	0 <sup>2</sup>	1.3	0.33	1.8	RA-2107/95 0028-95
					0	7.0	0.80	8.3	
					7	1.9	0.26	2.3	
					10	0.71	0.18	1.00	
					14	<u>0.61</u>	0.07	<u>0.72</u>	
					21	0.40	0.08	0.53	
UK 1997 (Fantasia)	WG50	1.7	0.34	4	0 <sup>2</sup>	1.5	0.22	1.9	RA-2045/97 0440-97
					0	5.5	0.51	6.3	
					14	<u>1.6</u>	0.17	<u>1.9</u>	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

<sup>2</sup> Before last application

Table 27. Residues in raspberries from supervised trials in Germany and the UK.

Country Year	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1995 (Schönemann)	WG50	1.7	0.113	4	0	8.5	0.26	8.9	RA-2107/95 0027-95
					14	<u>1.7</u>	0.21	<u>2.0</u>	
Germany 1995 (Zewa 2)	WG50	1.7	0.113	4	0	11.0	0.23	11.4	RA-2107/95 0597-95
					14	<u>2.4</u>	0.29	<u>2.9</u>	
UK 1995 (Malling Jewel)	WG50	1.7	0.34	4	0 <sup>2</sup>	4.8	0.18	5.1	RA-2107/95 0006-95
					0	12.0	0.32	12.5	
					7	3.5	0.14	3.7	
					10	1.9	0.10	2.1	
					14	<u>1.4</u>	0.09	<u>1.5</u>	
					21	0.39	0.07	0.50	
UK 1995 (Glen Prosen)	WG50	1.7	0.34	4	0 <sup>2</sup>	1.5	0.13	1.7	RA-2107/95 0598-95
					0	2.8	0.19	3.1	
					7	1.7	0.09	1.8	
					10	0.92	0.13	1.13	
					14	<u>0.42</u>	0.04	<u>0.48</u>	
					21	0.21	0.04	0.27	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

<sup>2</sup> Before last application

Table 28. Residues in strawberries from supervised trials in France, Germany, Italy, The Netherlands, Poland and Spain.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1972 (Regina)	WP50	2.5	0.125	3	10	<u>0.90</u>	0.10	<u>1.06</u>	0087-72
					14	0.55	0.10	0.71	
					23	0.20	0.15	0.44	
Germany 1972 (Senga Praecosa)	WP50	2.5	0.125	3	10	<u>0.75</u>	0.15	<u>0.99</u>	0088-72
					14	0.60	0.15	0.84	
					23	0.15	0.20	0.47	
Germany 1972 (Senga Sengana)	WP50	2.5	0.125	3	11	<u>1.4</u>	0.20	<u>1.7</u>	0089-72
					14	1.4	0.25	1.8	
					23	0.40	0.20	0.72	



Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1987 (Tenira)	WG50	2.5	0.125	3	0	6.2	0.61	7.2	8250-87
					3	1.4	0.43	2.1	
					5	1.4	0.43	2.1	
					7	<u>0.77</u>	0.34	<u>1.32</u>	
					10	<0.05	0.47	0.76	
					12	<0.05	0.61	0.99	
					14	<0.05	0.39	0.63	
Germany 1987 (Gorella)	WG50	2.5	0.125	3	0	7.4	0.51	8.2	8251-87
					3	3.3	0.63	4.3	
					5	1.3	0.45	2.0	
					7	<u>0.77</u>	0.26	<u>1.20</u>	
					10	0.61	0.33	1.14	
					12	0.28	0.20	0.60	
					14	0.18	0.12	0.37	
Germany 1987 (Senga Sengana)	WG50	2.5	0.125	3	0	5.5	0.39	6.1	8252-87
					3	4.0	0.33	4.5	
					5	1.4	0.24	1.8	
					7	<u>1.1</u>	0.23	<u>1.5</u>	
					10	1.0	0.14	1.2	
					12	0.40	0.12	0.59	
					14	0.28	0.13	0.49	
Germany 1987 (Karina)	WG50	2.5	0.125	3	0	7.9	0.42	8.6	8253-87
					3	6.0	0.51	6.8	
					5	3.8	0.46	4.5	
					7	<u>1.9</u>	0.50	<u>2.7</u>	
					10	1.4	0.44	2.1	
					12	0.71	0.32	1.22	
					17	0.51	0.35	1.08	
Germany 1987 (Elvira)	WG50	2.5	0.125	3	0	2.6	0.20	2.9	8254-87
					3	0.74	0.16	1.00	
					5	0.45	0.13	0.66	
					7	<u>0.05</u>	0.13	<u>0.26</u>	
					10	0.07	<0.05	0.07	
					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<0.05	
Germany 1987 (Senga Sengana)	WG50	2.5	0.125	3	0	4.3	0.21	4.6	8255-87
					3	1.6	0.18	1.9	
					5	0.31	0.12	0.50	
					7	<u>0.47</u>	0.15	<u>0.71</u>	
					10	0.28	0.13	0.49	
					14	0.22	0.08	0.35	
					21	0.07	<0.05	0.07	
Netherlands 1988 (Elsanta)	WG50	1.0	0.125	5	0	2.4	<0.05	2.4	0013-88
					3	1.5	0.14	1.7	
					7	<u>0.73</u>	0.24	<u>1.12</u>	
					10	0.70	0.08	0.83	
Poland 1994	WP50	2.5		4	1	5.90			Government submission
					7	1.49			
					10	<u>2.65</u>			
					14	0.99			
France (south) 1995 (Selva)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.02	0.09	0.17	RA-2097/95 0013-95
					0	1.0	0.75	2.2	
					3	0.61	0.51	1.44	
					7	<u>0.08</u>	0.17	<u>0.36</u>	
					10	<0.02	0.04	0.06	
France (south) 1995 (Mara des Bois)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.03	0.09	0.18	RA-2097/95 0592-95
					0	0.21	0.39	0.84	
					3	0.04	0.19	0.35	
					7	<u>0.03</u>	0.15	<u>0.27</u>	
					10	<u>0.02</u>	0.07	0.13	

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
France (south) 1996 (Elsanta)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.45	0.06	0.55	RA-2062/96 0177-96
					0	1.6	0.14	1.8	
					3	0.64	0.14	0.87	
					7	<u>0.23</u>	0.22	<u>0.59</u>	
					10	0.25	0.14	0.48	
France (south) 1996 (Elsantha)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.12	0.26	0.54	RA-2062/96 0571-96
					0	0.36	0.90	1.82	
					3	0.44	0.22	0.80	
					7	<u>0.35</u>	0.12	<u>0.54</u>	
					10	0.21	0.06	0.31	
France (south) 1996 (Mano des Bais)	WG50	1.25	0.125	3	0 <sup>4</sup>	1.5	0.27	1.9	RA-2062/96 0815-96
					0	3.3	0.51	4.1	
					7	<u>2.6</u>	0.22	<u>3.0</u>	
France (south) 1996 (Mano des Bais)	WG50	1.25	0.125	3	0	2.3	0.55	3.2	RA-2062/96 0816-96
					7	<u>1.7</u>	0.18	<u>2.0</u>	
France (south) 1997 (Pageroect)	WP50	1.25	0.125	3	0 <sup>4</sup>	0.16	0.27	0.60	RA-2048/97 0285-97
					0	1.3	0.61	2.3	
					3	0.41	0.22	0.77	
					7	<u>0.14</u>	0.13	<u>0.35</u>	
					10	0.09	0.06	0.19	
France (south) 1997 (Darselect)	WP50	1.25 <sup>2</sup>	0.29- 0.34	3	0 <sup>4</sup>	0.46	0.41	1.12	RA-2048/97 0286-97
					0	2.0	0.79	3.3	
					3	0.71	0.99	2.31	
					7	<u>0.55</u>	0.53	<u>1.41</u>	
					10	0.37	0.60	1.34	
France (south) 1997 (Elsanta)	WP50	1.25 <sup>3</sup>	0.31- 0.35	3	0 <sup>4</sup>	0.31	0.35	0.88	RA-2048/97 0386-97
					0	1.1	0.51	1.9	
					7	<u>0.20</u>	0.24	<u>0.59</u>	
Italy 1996 (Chandler)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.42	0.22	0.78	RA-2062/96 0306-96
					0	0.60	0.18	0.89	
					7	<u>0.41</u>	0.33	<u>0.95</u>	
Italy 1996 (Pajaro)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.52	0.15	0.76	RA-2062/96 0572-96
					0	1.1	0.28	1.6	
					7	<u>0.43</u>	0.13	<u>0.64</u>	
Spain 1994 (Seascape)	WG50	1.0	0.1	3	0 <sup>5</sup>	<0.02	0.07	0.11	RA-2086/94 0351-94
					0 <sup>4</sup>	0.13	0.21	0.47	
					0	1.5	0.44	2.2	
					3	0.45	0.19	0.76	
					5	0.15	0.11	0.33	
					7 <sup>5</sup>	<0.02	0.11	0.18	
					7	<u>0.12</u>	0.09	<u>0.27</u>	
Spain 1995 (Seascape)	WG50	1.0	0.125	3	0 <sup>4</sup>	0.04	0.06	0.14	RA-2097/95 0012-95
					0	0.19	0.12	0.38	
					3	0.11	0.07	0.22	
					7	<u>0.03</u>	0.07	<u>0.14</u>	
					10	<0.02	0.05	0.8	
Spain 1996 (Seascape)	WG50	1.25	0.125	3	0 <sup>4</sup>	0.17	0.07	0.28	RA-2062/96 0418-96
					0	2.0	0.57	2.9	
					7	<u>0.32</u>	0.12	<u>0.51</u>	

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid<sup>2</sup> First application about 6% under-dosed<sup>3</sup> First and last applications about 6 or 7% under-dosed<sup>4</sup> Before last application<sup>5</sup> Control sample

Table 29. Residues in cucumbers from supervised outdoor and indoor trials in Germany, Italy and Spain.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Field									
Germany 1995 (Hokus)	WG50	0.6	0.1	6	0 <sup>2</sup>	<0.02	<0.02	<0.02	RA-2103/95 0096-95
					0	0.39	0.11	0.57	
					1	<0.02	<0.02	<0.02	
					3	<u>0.02</u>	<0.02	<u>0.02</u>	
					7	<0.02	<0.02	<0.02	
Germany 1995 (Vorge- birgstraube)	WG50	0.6	0.1	6	0 <sup>2</sup>	<0.02	<0.02	<0.02	RA-2103/95 0604-95
					0	0.44	0.09	0.59	
					1	<0.02	<0.02	<0.02	
					3	<u>&lt;0.02</u>	<0.02	<u>&lt;0.02</u>	
					7	<0.02	<0.02	<0.02	
Germany 1995 (Pioneer)	WG50	0.6	0.1	5	0	0.19	0.07	0.30	RA-2103/95 0605-95
					3	<u>0.02</u>	<0.02	<u>0.02</u>	
					7	<0.02	<0.02	<0.02	
					7	<0.02	<0.02	<0.02	
Germany 1995 (Trepplecrown)	WG50	0.6	0.1	5	0	0.20	0.07	0.31	RA-2103/95 0606-95
					3	<u>0.02</u>	<0.02	<u>0.02</u>	
					7	<0.02	<0.02	<0.02	
					7	<0.02	<0.02	<0.02	
Greenhouse									
Germany 1995 (Cumlaude)	WG50	0.9- 1.2	0.1	6	0 <sup>2</sup>	0.07	0.03	0.12	RA-2104/95 0026-95
					0	0.48	0.16	0.74	
					1	0.29	0.14	0.52	
					3	<u>0.18</u>	0.10	<u>0.34</u>	
					7	<u>0.03</u>	<0.02	<u>0.03</u>	
Germany 1995 (Bellissima)	WG50	0.9- 1.2	0.1	6	0	0.28	0.06	0.38	RA-2104/95 0600-95
					3	<u>0.05</u>	<0.02	<u>0.05</u>	
					7	<0.02	<0.02	<0.02	
					7	<0.02	<0.02	<0.02	
Germany 1995 (Bella)	WG50	0.9- 1.2	0.1	6	0	0.25	0.05	0.33	RA-2104/95 0602-95
					3	<u>0.11</u>	0.03	<u>0.16</u>	
					7	<0.02	<0.02	<0.02	
					7	<0.02	<0.02	<0.02	
Germany 1995 (Cumlaude)	WG50	0.9- 1.2	0.1	6	0	0.91	0.10	1.07	RA-2104/95 0603-95
					3	<u>0.57</u>	0.06	<u>0.67</u>	
					7	0.24	0.03	0.29	
					7	0.24	0.03	0.29	
Spain 1995 (Dakota)	WG50	1.5	0.1	6	0 <sup>2</sup>	0.02	<0.02	0.02	RA-2104/95 0302-95
					0	1.1	0.16	1.4	
					1	0.62	0.10	0.78	
					3	<u>0.30</u>	0.06	<u>0.40</u>	
					7	0.29	0.06	0.39	
Italy 1995 (Darina)	WG50	1.5	0.15	6	0	0.33	0.07	0.44	RA-2104/95 0303-95
					3	<u>0.18</u>	0.08	<u>0.31</u>	
					7	0.08	0.02	0.11	
					7	0.08	0.02	0.11	
Spain 1996 (Alaska)	WG50	1.5	0.1	6	0 <sup>2</sup>	0.07	<0.02	0.07	RA-2063/96 0179-96
					0	0.48	0.07	0.59	
					1	0.87	0.10	1.03	
					3	<u>0.55</u>	0.08	<u>0.68</u>	
					7	0.28	0.04	0.34	
Italy 1996 (Market- more 70)	WG50	1.5	0.1	6	0 <sup>2</sup>	0.28	0.08	0.41	RA-2063/96 0419-96
					0	0.61	0.15	0.85	
					1	0.49	0.14	0.72	
					3	<u>0.64</u>	0.20	<u>0.96</u>	
					7	<u>0.33</u>	0.08	<u>0.46</u>	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid<sup>2</sup> Before last application

Table 30. Residues in melons from supervised trials in France and Greece.

Country, Year (Variety)	Application				Sample	PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.			T	D	T+D <sup>1</sup>	
France (north) 1996 (Galoubet)	WG50	1.25	0.45	3	Whole fruit	0 <sup>4</sup>	<0.02	0.02	0.03	RA- 2064/96 0415-96
						0	0.30	0.18	0.59	
						2	<u>0.08</u>	0.07	<u>0.19</u>	
						6	0.05	0.04	0.11	
						13	0.02	0.05	0.10	
						20	<0.02	0.03	0.05	
					Pulp	13	<0.02	0.02	0.03	
Peel	13	0.03	0.09	0.18						
Whole fruit, calculated	13	<0.02	0.04	0.06						
France (north) 1996 (Diego)	WG50	1.25	0.45	3	Whole fruit	0 <sup>4</sup>	0.04	0.04	0.10	RA- 2064/96 0417-96
						0	0.21	0.10	0.37	
						14	0.10	0.09	0.25	
					Pulp	14	<0.02	<0.02	<0.02	
Peel	14	0.27	0.26	0.69						
Whole fruit, calculated	14	0.09	0.08	0.22						
France (north) 1997 (Figaro)	WG50	1.25	0.45	3	Whole fruit	0 <sup>4</sup>	<0.02	0.02	0.03	RA- 2046/97 0096-97
						0	0.05	0.08	0.18	
						3	<u>0.03</u>	0.07	<u>0.14</u>	
						7	0.02	0.05	0.10	
						14	0.02	0.05	0.10	
						21	0.02	0.04	0.08	
					Pulp	14	<0.02	0.04	0.06	
Peel	14	0.18	0.31	0.68						
Whole fruit, calculated	14	0.04	0.08	0.17						
France (north) 1997 (Diego)	WG50	1.25	0.45	3	Whole fruit	0 <sup>4</sup>	<0.02	0.03	0.05	RA- 2046/97 0097-97
						0	0.08	0.15	0.32	
						14	<0.02	0.03	0.05	
					Pulp	14	<0.02	0.02	0.03	
Peel	14	0.04	0.11	0.22						
Whole fruit, calculated	14	<0.02	0.04	0.06						
France (south) 1993 (Delta)	WG50	1.25 <sup>2</sup>	0.45	3	Pulp	0 <sup>5</sup>	<0.02	0.03	0.05	RA- 2045/93 0086-93
						0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	<0.02	0.04	0.06	
						3	<0.02	<0.02	<0.02	
						7	<0.02	<0.02	<0.02	
						14	<0.02	<0.02	<0.02	
						24	<0.02	<0.02	<0.02	
						Peel	0 <sup>5</sup>	0.03	0.06	
					0 <sup>4</sup>	<0.02	0.04	0.06		
					0	0.37	0.33	0.90		
					3	0.12	0.12	0.31		
					7	0.02	0.07	0.13		
					14	<0.02	<0.02	<0.02		
					24	<0.02	<0.02	<0.02		
					Whole fruit, calculated	0 <sup>5</sup>	<0.02	0.04	0.06	
					0 <sup>4</sup>	<0.02	0.02	0.03		
0	0.16	0.16	0.42							
3	0.05	0.05	0.13							
7	<0.02	0.04	0.06							
14	<0.02	<0.02	<0.02							
24	<0.02	<0.02	<0.02							

Country, Year (Variety)	Application				Sample	PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.			T	D	T+D <sup>1</sup>	
France (south) 1993 (Delta)	WG50	1.25	0.45	3	Pulp	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2045/93 0313-93
						0	<0.02	0.02	0.03	
						3	<0.02	0.02	0.03	
						7	<0.02	<0.02	<0.02	
						14	<0.02	<0.02	<0.02	
					22	<0.02	<0.02	<0.02		
					Peel	0 <sup>4</sup>	<0.02	0.02	0.03	
						0	0.20	0.23	0.57	
						3	0.15	0.14	0.38	
						7	0.03	0.04	0.09	
						14	<0.02	<0.02	<0.02	
					Whole fruit, calculated	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.08	0.10	0.24	
						3	0.07	0.07	0.18	
						7	<0.02	0.02	0.03	
14	<0.02	<0.02	<0.02							
France (south) 1993 (Delta)	WG50	1.25	0.45	3	Pulp	0 <sup>5</sup>	<0.02	0.03	0.05	RA- 2045/93 0314-93
						0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	<0.02	<0.02	<0.02	
						3	<0.02	<0.02	<0.02	
						7	<0.02	<0.02	<0.02	
					14	<0.02	<0.02	<0.02		
					Peel	0 <sup>5</sup>	0.03	0.04	0.09	
						0 <sup>4</sup>	<0.02	0.03	0.05	
						0	0.14	0.15	0.38	
						3	0.03	0.05	0.11	
						7	<0.02	0.03	0.05	
					Whole fruit, calculated	0 <sup>5</sup>	0.03	0.03	0.08	
						0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.06	0.07	0.17	
						3	<0.02	0.03	0.05	
7	<0.02	<0.02	<0.02							
France (south) 1993 (Alpha)	WG50	1.25	0.45	3	Pulp	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2045/93 0315-93
						0	<0.02	0.03	0.05	
						3	<0.02	<0.02	<0.02	
						7	<0.02	0.03	0.05	
						14	<0.02	0.04	0.06	
					Peel	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.16	0.18	0.45	
						3	0.08	0.09	0.23	
						7	<0.02	0.06	0.10	
						14	<0.02	0.05	0.08	
					Whole fruit, calculated	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.06	0.08	0.19	
						3	0.04	0.04	0.10	
						7	<0.02	0.04	0.06	
						14	<0.02	0.04	0.06	
France (south) 1994 (Alpha)	WG50	1.25 <sup>3</sup>	0.45	3	Pulp	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2052/94 0199-94
						0	<0.02	<0.02	<0.02	
						3	<0.02	<0.02	<0.02	
						7	<0.02	<0.02	<0.02	
						14	<0.02	<0.02	<0.02	
					21	<0.02	<0.02	<0.02		
					Peel	0 <sup>4</sup>	<0.02	0.03	0.05	
						0	0.06	0.07	0.17	
						3	0.03	0.03	0.08	
						7	0.03	0.04	0.09	
						14	<0.02	0.02	0.03	
					21	<0.02	<0.02	<0.02		

Country, Year (Variety)	Application				Sample	PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.			T	D	T+D <sup>1</sup>	
					Whole fruit, calculated	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.03	0.04	0.09	
						3	<0.02	<0.02	<0.02	
						7	0.02	0.03	0.07	
						14	<0.02	<0.02	<0.02	
21	<0.02	<0.02	<0.02							
France (south) 1993 (Delta)	WG50	1.25 <sup>3</sup>	0.45	3	Pulp	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2052/94 0200-94
						0	0.03	0.05	0.11	
						14	<0.02	<0.02	<0.02	
					Peel	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.10	0.12	0.29	
						14	<0.02	0.05	0.08	
					Whole fruit, calculated	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.06	0.08	0.19	
						14	<0.02	0.03	0.05	
Greece 1994 (Thrakiotika)	WG50	1.25	0.45	3	Pulp	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2052/94 0202-94
						0	<0.02	0.05	0.08	
						3	<0.02	<0.02	<0.02	
						7	<0.02	<0.02	<0.02	
						14	<0.02	<0.02	<0.02	
					21	<0.02	<0.02	<0.02		
					Peel	0 <sup>4</sup>	<0.02	0.02	0.03	
						0	0.32	0.40	0.97	
						3	<0.02	0.04	0.06	
						7	<0.02	0.02	0.03	
						14	<0.02	<0.02	<0.02	
					21	<0.02	<0.02	<0.02		
					Whole fruit, calculated	0 <sup>4</sup>	<0.02	<0.02	<0.02	
						0	0.14	0.20	0.46	
						3	<0.02	<0.02	<0.02	
						7	<0.02	0.02	0.03	
						14	<0.02	<0.02	<0.02	
					21	<0.02	<0.02	<0.02		
Greece 1994 (Thrakiotika)	WG50	1.25	0.45	3	Pulp	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2052/94 0203-94
						0	0.04	0.06	0.14	
						14	<0.02	<0.02	<0.02	
					Peel	0 <sup>4</sup>	0.07	0.05	0.15	
						0	1.3	0.49	2.1	
						14	0.47	0.26	0.89	
					Whole fruit, calculated	0 <sup>4</sup>	0.02	<0.02	0.02	
						0	0.20	0.11	0.38	
						14	0.08	0.05	0.16	

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid

<sup>2</sup> First application about 8% under-dosed

<sup>3</sup> First application about 6 or 7% over-dosed

<sup>4</sup> Before last application

<sup>5</sup> Control sample

Table 31. Residues in tomatoes from supervised outdoor and indoor trials in France, Germany, Italy, Mexico and Spain.

Country, Year (variety)	Application				PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
<i>Field</i>									
Germany 1987 (Sioux)	WG50	0.6- 1.2	0.1	6	0	3.0	0.17	3.3	8204-87
					2	1.6	0.19	1.9	
					3	<u>0.99</u>	0.17	<u>1.27</u>	
					5	0.55	0.12	0.74	
					7	0.52	0.08	0.65	

Country, Year (variety)	Application				PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1987 (Moneymaker)	WG50	0.6- 1.2	0.1	4	0	1.1	0.11	1.3	8205-87
					2	0.51	0.07	0.62	
					3	<u>0.34</u>	0.09	<u>0.49</u>	
					5	0.17	<0.05	0.17	
					7	0.13	0.07	0.24	
Germany 1987 (Grosse Fleisch- tomate)	WG50	0.9	0.1	6	0	0.72	0.35	1.29	8206-87
					2	0.14	0.07	0.25	
					3	<u>0.15</u>	0.09	<u>0.30</u>	
					5	0.07	0.06	0.17	
					7	0.06	<0.05	0.06	
Germany 1987 (Hilds- Hellfrucht)	WG50	0.9	0.1	6	0	1.3	0.37	1.9	8207-87
					2	0.65	0.21	0.99	
					3	<u>0.20</u>	0.09	<u>0.35</u>	
					5	0.15	<0.05	0.15	
					7	0.07	<0.05	0.07	
Germany 1988 (Sioux)	WG50	0.9- 1.2	0.1	6	0	0.38	0.12	0.57	0219-88
					2	0.30	0.16	0.56	
					3	0.12	0.13	0.33	
					5	<u>0.15</u>	0.12	<u>0.34</u>	
					7	0.10	<0.05	0.10	
Germany 1988 (Sioux)	WG50	0.6- 1.2	0.1	6	0	4.2	0.22	4.56	0220-88
					2	0.60	<0.05	0.60	
					3	<u>0.47</u>	<0.05	<u>0.47</u>	
					5	0.33	<0.05	0.33	
					7	0.42	<0.05	0.42	
Germany 1988 (Hilds- Hellfrucht)	WG50	0.9	0.1	6	0	0.97	0.30	1.46	0221-88
					2	0.30	0.13	0.51	
					3	<u>0.27</u>	0.08	<u>0.40</u>	
					5	0.14	0.06	0.24	
					7	0.08	<0.05	0.08	
Germany 1988 (Hilds- Hellfrucht)	WG50	0.9	0.1	6	0	0.50	0.16	0.76	0222-88
					2	0.27	0.12	0.46	
					3	<u>0.18</u>	<0.05	<u>0.18</u>	
					5	0.10	<0.05	0.10	
					7	<0.05	<0.05	<0.05	
France (south) 1992 (Zenith)	WG50	1.25 <sup>2</sup>	0.25	4	0 <sup>7</sup>	<0.02	<0.02	<0.02	RA- 2006/92 0418-92
					0	0.14	0.05	0.22	
					3	<u>0.05</u>	<0.02	<u>0.05</u>	
					7	0.03	<0.02	0.03	
					0 <sup>7</sup>	0.03	<0.02	0.03	
France (south) 1992 (Maséro)	WG50	1.25	0.25	4	0 <sup>7</sup>	0.03	<0.02	0.03	RA- 2006/92 0419-92
					0	0.34	0.08	0.47	
					3	<u>0.27</u>	0.05	<u>0.35</u>	
					7	0.13	0.02	0.16	
					0 <sup>7</sup>	0.09	0.03	0.14	
France (south) 1992 (Canary)	WG50	1.25	0.25	4	0	0.65	0.09	0.80	RA- 2006/92 0421-92
					3	<0.02	<0.02	<0.02	
					7	<u>0.05</u>	<0.02	<u>0.05</u>	
					0 <sup>7</sup>	0.02	<0.02	0.02	
					0	0.63	0.12	0.82	
France (south) 1992 (Zenith)	WG50	1.25	0.25	4	0 <sup>7</sup>	0.02	<0.02	0.02	RA- 2006/92 0422-92
					0	0.63	0.12	0.82	
					3	<u>0.34</u>	0.05	<u>0.42</u>	
					7	0.10	<0.02	0.10	
					0 <sup>7</sup>	0.09	0.02	0.12	
France (south) 1993 (Lerica)	WG50	1.25	0.45	4	0	0.36	0.07	0.47	RA- 2125/93 0084-93
					3	0.24	0.04	0.30	
					7	<u>0.31</u>	0.05	<u>0.39</u>	
					0 <sup>7</sup>	0.12	0.02	0.15	
					0	0.60	0.06	0.70	
France (south) 1993 (Zenith)	WG50	1.25	0.45	4	0 <sup>7</sup>	0.12	0.02	0.15	RA- 2125/93 0317-93
					0	0.60	0.06	0.70	
					3	<u>0.49</u>	0.07	<u>0.60</u>	
					7	0.31	0.05	0.39	
					0 <sup>7</sup>	0.19	0.03	0.24	
France (south) 1993 (Masséro 2)	WG50	1.25	0.45	4	0	0.58	0.07	0.69	RA- 2125/93 0318-93
					3	<u>0.48</u>	0.04	<u>0.54</u>	
					7	0.28	0.03	0.33	
					0 <sup>7</sup>	0.19	0.03	0.24	
					0	0.58	0.07	0.69	

Country, Year (variety)	Application				PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
France (south) 1993 (Cannery row)	WG50	1.25	0.45	4	0 <sup>7</sup>	0.18	<0.02	0.18	RA- 2125/93 0319-93
					0	0.62	0.06	0.72	
					3	<u>0.50</u>	0.04	<u>0.56</u>	
					7	0.32	0.03	0.37	
Italy 1994 (Hypeel 244)	WG50	1.0	0.1	3	0 <sup>7</sup>	0.20	0.03	0.25	RA- 2063/94 0259-94
					0	1.0	0.11	1.2	
					3	0.16	0.05	0.24	
					5	<u>0.23</u>	0.04	<u>0.29</u>	
7	0.21	0.03	0.26						
Italy 1994 (Hypeel 244)	WG50	1.0	0.1	3	0 <sup>7</sup>	0.15	0.04	0.21	RA- 2063/94 0260-94
					0	0.48	0.10	0.64	
					3	<u>0.42</u>	0.10	<u>0.58</u>	
					5	0.21	0.06	0.31	
7	0.05	<0.02	0.05						
Italy 1994 (Red Peel)	WG50	6	0.6	1	0	1.2	0.13	1.4	RA- 2063/94 0668-94
					3	1.2	0.16	1.5	
					7	0.37	0.06	0.47	
Italy 1995 (EXH)	WG50	1.5	0.15	3	0	0.77	0.19	1.08	RA- 2100/95 0581-95
					3	<u>0.19</u>	0.03	<u>0.24</u>	
					7 <sup>3</sup>	0.14,0.16	0.02,0.02	0.17,0.19	
Italy 1995 (Marmande)	WG50	1.5	0.15	3	0	0.10	0.02	0.13	RA- 2100/95 0583-95
					3	<u>0.04</u>	0.02	<u>0.07</u>	
					7 <sup>3</sup>	0.04,0.03	0.02,0.02	0.07,0.06	
Italy 1995 (Canaria)	WG50	1.5	0.15	3	0 <sup>7</sup>	0.62	0.13	0.83	RA- 2100/95 0678-95
					0	1.0	0.20	1.3	
					3	<u>0.07</u>	0.02	<u>0.10</u>	
					7 <sup>3</sup>	0.04,0.04	0.02,0.02	0.07,0.08	
10	0.05	0.02	0.08						
Italy 1995 (Red Setter)	WG50	1.5	0.15	3	0 <sup>7</sup>	0.05	<0.02	0.05	RA- 2100/95 0681-95
					0	0.50	0.04	0.56	
					3	<u>0.21</u>	0.04	<u>0.27</u>	
					7 <sup>3</sup>	0.04,0.05	<0.02, <0.02	0.04,0.05	
10	0.05	<0.02	0.05						
Spain 1995 (Nikita)	WG50	1.5	0.15	3	0	0.64	0.21	0.98	RA- 2100/95 0679-95
					3	<u>0.40</u>	0.06	<u>0.50</u>	
					7 <sup>3</sup>	0.54,0.38	0.09,0.06	0.69,0.48	
Spain 1995 (Royesta)	WG50	1.5	0.15	3	0	0.54	0.09	0.69	RA- 2100/95 0682-95
					3	<u>0.47</u>	0.08	<u>0.60</u>	
					7 <sup>3</sup>	0.34,0.19	0.11,0.09	0.52,0.34	
Mexico 1995 (NVH 4473)	WP50	1.5	0.375	4	0 <sup>7</sup>	0.24	0.03	0.29	RA- 2157/95 0734-95
					0	0.19	0.08	0.32	
					3 <sup>3</sup>	0.21,0.14	0.06,0.07	0.31,0.25	
					5 <sup>3</sup>	0.19,0.14	0.04,0.08	0.25,0.27	
7 <sup>3</sup>	0.11,0.09	0.04,0.06	0.17,0.19						
Mexico 1995 (BR-84)	WP50	1.5	0.333	4	0 <sup>7</sup>	0.08	0.02	0.11	RA- 2157/95 0735-95
					0	0.09	0.02	0.12	
					3 <sup>3</sup>	0.11,0.12	<0.02,0.02	0.11,0.15	
					6 <sup>3</sup>	0.13,0.08	0.02,<0.02	0.16,0.08	
7 <sup>3</sup>	0.12,0.03	0.02,<0.02	0.15,0.03						
Mexico 1995 (Gala)	WP50	1.5	0.375	4	0 <sup>7</sup>	0.30	0.08	0.43	RA- 2157/95 0736-95
					0	0.45	0.11	0.63	
					3 <sup>3</sup>	0.24,0.15	0.07,0.06	0.35,0.25	
					5 <sup>3</sup>	0.33,0.13	0.08,0.05	0.46,0.21	
7 <sup>3</sup>	0.09,0.09	0.05,0.03	0.17,0.14						
Mexico 1995 (189 BHN Divino)	WP50	1.5	0.375	4	0 <sup>7</sup>	0.24	0.04	0.30	RA- 2157/95 0737-95
					0	0.85	0.08	0.98	
					3 <sup>3</sup>	0.43,0.42	0.04,0.05	0.49,0.50	
					5 <sup>3</sup>	0.40,0.34	0.05,0.04	0.48,0.40	
7 <sup>3</sup>	0.23,0.14	0.04,0.02	0.29,0.17						



Country, Year (variety)	Application				PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Mexico 1995 (Solimar)	WP50	1.5	0.375	4	0 <sup>7</sup>	0.35	0.04	0.41	RA- 2157/95 0738-95
					0	0.58	0.06	0.68	
					3 <sup>3</sup>	0.66,0.51	0.06,0.04	0.76,0.57	
					5 <sup>3</sup>	0.51,0.19	0.08,0.03	0.64,0.24	
					7 <sup>3</sup>	0.40,0.30	0.05,0.05	0.48,0.38	
Mexico 1995 (Yaqui)	WP50	1.5	0.375	4	0 <sup>7</sup>	0.25	0.05	0.33	RA- 2157/95 0739-95
					0	0.52	0.09	0.67	
					3 <sup>3</sup>	0.57,0.23	0.12,0.09	0.76,0.38	
					5 <sup>3</sup>	0.21,0.21	0.05,0.04	0.29,0.27	
					7 <sup>3</sup>	0.29,0.52	0.04,0.06	0.35,0.62	
<i>Greenhouse</i>									
Belgium 1997 (Blitz)	WG 43.5	2.13- 2.25 <sup>5</sup>	0.11	5	0 <sup>7</sup>	0.62	0.17	0.90	RA- 2126/97 0697-97
					0	1.2	0.23	1.6	
					3	0.91	0.19	1.22	
					5	0.85	0.18	1.14	
					7	0.74	0.15	0.98	
10	0.48	0.13	0.69						
Belgium 1998 (Blitz)	WG 43.5	2.25	0.11	8	0	1.4	0.29	1.9	RA- 2135/98 1619-98
					5	0.59	0.20	0.91	
					7	0.52	0.15	0.76	
Belgium 2000 (Elegance)	WG50	1.41- 1.5 <sup>4</sup>	0.1	6	0 <sup>7</sup>	0.24	0.02	0.27	RA- 2097/00 0502-00
					0	0.90	0.04	0.96	
					3	<u>0.72</u>	0.03	<u>0.77</u>	
					7	0.59	0.03	0.64	
					14	0.33	0.02	0.36	
Germany 1995 (Piranto)	WG50	0.6- 1.2	0.1	6	0 <sup>7</sup>	0.02	<0.02	0.02	RA- 2101/95 0035-95
					0	0.21	0.06	0.31	
					3	<u>0.24</u>	0.10	<u>0.40</u>	
					7 <sup>3</sup>	0.09,0.10	0.03,0.05	0.14,0.18	
					14	0.04	0.02	0.07	
Germany 1995 (Ferrari)	WG50	0.9- 1.2	0.1	6	0 <sup>7</sup>	0.51	0.06	0.61	RA- 2101/95 0607-95
					0	0.86	0.18	1.15	
					3	<u>0.59</u>	0.07	<u>0.70</u>	
					7 <sup>3</sup>	0.22,0.28	0.04,0.04	0.28,0.34	
					14	0.19	0.03	0.24	
Germany 1995 (Venessa)	WG50	0.9- 1.2	0.1	6	0	0.25	0.06	0.35	RA- 2101/95 0608-95
					3	<u>0.08</u>	0.04	<u>0.14</u>	
					7 <sup>3</sup>	0.08,0.05	0.02,0.02	0.11,0.08	
Germany 1995 (Aranka)	WG50	0.9- 1.2	0.1	6	0	0.14	0.06	0.24	RA- 2101/95 0609-95
					3	<u>0.16</u>	0.04	<u>0.22</u>	
					7 <sup>3</sup>	0.10,0.12	0.02,0.03	0.13,0.17	
Germany 1997 (Susso)	WG 43.5	1.8- 2.25	0.11	5	0 <sup>7</sup>	0.26	0.06	0.36	RA- 2126/97 0213-97
					0	1.1	0.17	1.4	
					3	0.31	0.06	0.41	
					6	0.33	0.06	0.43	
					7	0.36	0.07	0.47	
10	0.31	0.08	0.44						
Germany 1998 (Rogella)	WG 43.5	1.46- 2.25	0.11	8	0	1.5	0.22	1.9	RA- 2135/98 1621-98
					5	0.97	0.18	1.26	
					7	0.86	0.13	1.07	
Germany 1998 (Ferrari)	WG 43.5	1.46- 2.25	0.11	8	0	2.3	0.26	2.7	RA- 2135/98 1308-98
					5	1.6	0.24	2.0	
					7 <sup>8</sup>	0.02	<0.02	0.02	
					7	0.79	0.14	1.02	
Germany 2000 (Rogella)	WG50	1.2- 1.5 <sup>4</sup>	0.1	6	0 <sup>7</sup>	0.25	0.02	0.28	RA- 2097/00 0500-00
					0	0.74	0.05	0.82	
					3	<u>0.42</u>	0.03	<u>0.47</u>	
France 1997 (Cecilia)	WG 43.5	2.03- 2.25	0.11	5	0 <sup>7</sup>	0.51	0.13	0.72	RA- 2126/97 0700-97
					0	1.0	0.24	1.4	
					3	1.1	0.23	1.5	
					5	0.93	0.16	1.19	
					7	0.82	0.15	1.06	
10	0.50	0.12	0.69						

Country, Year (variety)	Application				PHI (days)	Residues (mg/kg)			Ref.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Italy 1994 (Max))	WG50	1.5	0.15	3	0 <sup>7</sup>	0.07	0.03	0.12	RA- 2063/94 0261-94
					0	0.38	0.16	0.64	
					3	0.26	0.07	0.37	
					5	0.20	0.05	0.28	
					7	0.12	0.06	0.22	
Italy 1997 (Fedra)	WG 43.5	1.8- 2.03	0.11	5	0 <sup>7</sup>	1.7	0.48	2.48	RA- 2126/97 0698-97
					0	2.2	0.56	3.1	
					3	1.5	0.58	2.4	
					5	2.0	0.96	3.6	
					7	1.2	0.47	2.0	
10	0.93	0.36	1.51						
Italy 1998 (Sidonia)	WG 43.5	0.68- 2.03	0.11	8	0	1.3	0.36	1.9	RA- 2135/98 1620-98
					5	1.0	0.29	1.5	
					7	0.63	0.27	1.07	
Italy 2000 (PS 110)	WG50	1.12- 1.34 <sup>4</sup>	0.1	6	0 <sup>7</sup>	0.60	0.06	0.70	RA- 2097/00 0501-00
					0	1.2	0.09	1.3	
					3	<u>1.4</u>	0.06	<u>1.5</u>	
Italy 2000 (PS 110)	WG50	1.16- 1.35 <sup>4</sup>	0.1	6	0 <sup>7</sup>	1.0	0.11	1.2	RA- 2097/00 0503-00
					0	1.4	0.15	1.6	
					3	1.4	0.10	1.6	
					7	<u>2.0</u>	0.11	<u>2.2</u>	
					14	1.4	0.07	1.5	
Spain 1993 (Daniela)	WP50	1.2- 1.4	0.1	3	0 <sup>7</sup>	0.07	0.02	0.10	RA- 2048/93 0352-93
					0	0.67	0.13	0.88	
					3	<u>0.49</u>	0.11	<u>0.67</u>	
					5	0.10	0.03	0.15	
					7	0.15	0.03	0.20	
Spain 1998 (Rento)	WG 43.5	1.46- 2.27 <sup>6</sup>	0.11	8	0	0.91	0.43	1.61	RA- 2135/98 1073-98
					5	0.64	0.41	1.30	
					7	0.83	0.15	1.07	

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid

<sup>2</sup> First application about 13% overdosed

<sup>3</sup> PHI at which two independent composite samples were collected per site

<sup>4</sup> For some treatments application rate was under-dosed by 10-25% owing to calculation of water volume in relation to plant height: instead of 1.5m, a standard height of 2m was inadvertently used

<sup>5</sup> Fourth application about 6% under-dosed with respect to the intended use of 3 kg product per ha and m plant height

<sup>6</sup> Third application about 6% over-dosed with respect to the same use

<sup>7</sup> Before last application

<sup>8</sup> Control sample

Table 32. Residues in peppers from supervised greenhouse trials in Italy, The Netherlands and Spain.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Ref
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Netherlands 2000 (Spirit)	WG50	1.15- 1.25	0.1	3	0 <sup>2</sup>	0.18	0.18	0.47	RA-2094/00 0441-00
					0	0.36	0.33	0.89	
					3	<u>0.26</u>	0.22	<u>0.62</u>	
Netherlands 2000 (Tiffany)	WG50	1.2- 1.3	0.1	3	0 <sup>2</sup>	0.08	0.06	0.18	RA-2094/00 0442-00
					0	0.39	0.23	0.76	
					3	<u>0.20</u>	0.15	<u>0.44</u>	
Italy 1994 (Rubro)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.04	0.02	0.07	RA-2028/94 0256-94
					0	0.32	0.08	0.45	
					3	<u>0.07</u>	0.03	<u>0.12</u>	
					5	0.08	0.03	0.13	
					7	0.03	<0.02	0.03	
Italy 1994 (Pathos)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.12	0.04	0.18	RA-2028/94 0257-94
					0	0.53	0.10	0.69	
					3	<u>0.28</u>	0.04	<u>0.34</u>	
					5	0.18	0.03	0.23	
					7	0.06	<0.02	0.06	

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Ref
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Italy 1994 (Soldi)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.21	0.18	0.50	RA-2028/94 0258-94
					0	0.52	0.27	0.96	
					3	<u>0.61</u>	0.21	<u>0.95</u>	
					5	<u>0.42</u>	0.13	<u>0.63</u>	
					7	0.16	0.09	0.31	
Italy 1994 (Soldi)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.45	0.34	1.0	RA-2028/94 0665-94
					0	0.39	0.17	0.67	
					3	<u>0.49</u>	0.14	<u>0.72</u>	
					5	0.43	0.13	0.64	
					7	0.39	0.13	0.60	
Spain 1994 (Italiano)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.19	0.04	0.25	RA-2028/94 0356-94
					0	0.93	0.16	1.19	
					3	<u>0.66</u>	0.12	<u>0.85</u>	
					5	0.52	0.07	0.63	
					7	0.30	0.06	0.40	
Spain 1994 (Jedeon)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.07	0.04	0.13	RA-2028/94 0357-94
					0	0.74	0.17	1.02	
					3	<u>0.24</u>	0.12	<u>0.43</u>	
					5	<u>0.36</u>	0.05	<u>0.44</u>	
					7	0.23	0.04	0.29	
Spain 1994 (Espartaco)	WG50	1.0	0.1	3	0 <sup>2</sup>	0.98	0.17	1.26	RA-2028/94 0359-94
					0	2.8	0.36	3.4	
					3	<u>0.77</u>	0.15	<u>1.01</u>	
					5	1.2	0.13	1.4	
					7	1.2	0.12	1.4	
Spain 1994 (Mazurka)	WG50	0.73- 1.0	0.1	3	0 <sup>2</sup>	0.16	0.05	0.24	RA-2028/94 0667-94
					0	1.1	0.26	1.5	
					3	<u>1.3</u>	0.21	<u>1.6</u>	
					5	0.25	0.07	0.36	
					7	0.33	0.09	0.48	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

<sup>2</sup> Before last application

Table 33. Residues in head lettuce from supervised trials in Belgium, France, Germany, Greece, Italy, Portugal, Spain and the UK.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1987 (Attraktion)	WG50	0.6	0.1	6	0	17	14	40	8208-87
					7	0.36	0.19	0.67	
					14	<0.05	<0.05	<0.05	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
Germany 1987 (Attraktion)	WG50	0.6	0.1	6	0	29	11	47	8209-87
					7	1.2	0.48	2.0	
					14	0.12	<0.05	0.12	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
Germany 1987 (Victoria Typ King)	WG50	0.6	0.1	6	0	26	6.5	37	8210-87
					7	1.0	0.20	1.3	
					14	<0.05	<0.05	<0.05	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
Germany 1987 (Victoria Typ King)	WG50	0.6	0.1	6	0	20	5.6	29	8211-87
					7	1.3	0.47	2.1	
					14	0.58	<0.05	0.58	
					21	<u>0.17</u>	<0.05	<u>0.17</u>	
					28	<0.05	<0.05	<0.05	

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Germany 1988 (Attraktion)	WG50	0.6	0.1	6	0	17	8.2	30	0215-88
					7	0.96	0.53	1.82	
					14	<0.05	<0.05	<0.05	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
Germany 1988 (Ovation)	WG50	0.6	0.1	6	0	24	6.0	34	0216-88
					7	0.39	0.21	0.73	
					14	0.15	0.06	0.25	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
Germany 1988 (Victoria King)	WG50	0.6	0.1	6	0	30	1.3	32	0217-88
					7	13	0.37	14	
					14	0.63	0.06	0.73	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
Germany 1988 (Victoria King)	WG50	0.6	0.1	6	0	36	3.9	42	0218-88
					7	2.6	0.41	3.3	
					14	<0.05	<0.05	<0.05	
					21	<u>&lt;0.05</u>	<0.05	<u>&lt;0.05</u>	
					28	<0.05	<0.05	<0.05	
France (south) 1996 (Massaida)	WG50	1.0	0.1	3	0 <sup>4</sup>	0.03	<0.02	0.03	RA- 2066/96 0474-96
					0	16	1.5	18	
					3	3.9	0.60	4.9	
					7	0.98	0.11	1.16	
					10	0.71	0.11	0.89	
Italy 1996 (Audran)	WG50	1.0	0.1	3	0 <sup>4</sup>	0.08	0.02	0.11	RA- 2066/96 0310-96
					0	16	1.2	18	
					7	3.1	0.29	3.6	
Portugal 1996 (Vanity)	WG50	1.0	0.1	3	0 <sup>4</sup>	0.11	0.04	0.17	RA- 2066/96 0421-96
					0	16	2.3	20	
					7	1.9	1.6	4.5	
Spain 1994 (Rob)	WG50	1.0	0.1	3	0 <sup>4</sup>	<0.02	<0.02	<0.02	RA- 2090/94 0360-94
					0	17	4.6	25	
					3	8.8	2.1	12.2	
					5	4.0	1.2	5.9	
					7	2.4	0.93	3.9	
Spain 1994 (Inverna Typ)	WG50	1.0	0.1	3	0 <sup>4</sup>	1.1	0.32	1.6	RA- 2090/94 0362-94
					0	9.0	1.8	11.9	
					3	5.1	0.85	6.5	
					5	3.5	0.74	4.7	
					7	2.1	0.52	2.9	
Spain 1995 (Hiverna)	WG50	1.0 <sup>2</sup>	0.1	3	0 <sup>4</sup>	1.5	0.36	2.1	RA- 2105/95 0005-95
					0	12	1.5	14	
					3	7.9	0.99	9.5	
					7	3.2	0.67	4.29	
					10	2.3	0.46	3.05	
Spain 1995 (Francesca)	WG50	1.0	0.1	3	0	9.1	0.96	10.7	RA- 2105/95 0008-95
					7	6.0	0.69	7.1	
Spain 1996 (Francesca)	WG50	1.0 <sup>3</sup>	0.1	3	0 <sup>4</sup>	0.31	0.07	0.42	RA- 2066/96 0178-96
					0	15	1.3	17	
					3	6.9	0.59	7.9	
					7	3.8	0.40	4.4	
					10	0.93	0.16	1.19	
Belgium 1998 (Soraya)	WG 43.5	1.125	0.19	6	0 <sup>4</sup>	0.76	0.30	1.25	RA- 2136/98 1622-98
					0	11	1.1	13	
					3	1.6	0.33	2.1	
					7	1.1	0.18	1.4	
					10	1.1	0.15	1.3	
France (north) 1997 (Titan)	WG 43.5	1.125	0.19	5	0	14	2.4	18	RA- 2121/97 0209-97
					7	0.38	0.10	0.54	

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
France (north) 1998 (Remeo)	WG 43.5	1.125	0.19	6	0	34	1.3	36	RA- 2136/98 1625-98
					6	11	0.56	12	
					8	13	0.42	14	
Germany 1997 (Nadine)	WG 43.5	1.125	0.19	5	0 <sup>4</sup>	2.7	0.35	3.3	RA- 2121/97 0208-97
					0	26	0.75	27	
					3	2.5	0.52	3.3	
					7	1.4	0.19	1.7	
					10	0.72	0.12	0.91	
Germany 1997 (Nadine)	WG 43.5	1.125	0.19	5	0 <sup>4</sup>	6.9	0.47	7.7	RA- 2121/97 0639-97
					0	27	1.0	29	
					3	0.4	0.07	0.51	
					7	0.26	0.02	0.29	
					10	0.15	<0.02	0.15	
Germany 1998 (Nadine)	WG 43.5	1.125	0.19	6	0 <sup>4</sup>	1.3	0.20	1.6	RA- 2136/98 1074-98
					0	9.2	0.67	10.3	
					2	4.0	0.44	4.7	
					7	2.0,1.9	0.21,0.21	2.3,2.2	
					10	1.5	0.12	1.7	
Germany 1998 (Nadine)	WG 43.5	1.125	0.19	6	0	10	0.39	11	RA- 2136/98 1077-98
					6	2.3	0.30	2.8	
					7	2.1,2.1	0.16,0.19	2.4, 2.4	
Germany 1998 (Nadine)	WG 43.5	1.125	0.19	6	0	16	1.1	18	RA- 2136/98 1624-98
					5	5.8	0.71	7.0	
					7	3.7	0.51	4.5	
UK 1997 (Siletta)	WG 43.5	1.125	0.19	5	0 <sup>4</sup>	9.8	0.34	10.4	RA- 2121/97 0638-97
					0	28	0.77	29	
					3	12	0.45	13	
					7	2.8	0.14	3.0	
					10	1.8	0.10	2.0	
France (south) 1998 (Batavia Nevada)	WP50	0.8	0.08	2	0 <sup>4</sup>	0.10	<0.02	0.10	RA- 2039/98 1410-98
					0	15	1.8	18	
					3	1.8	0.55	2.7	
					7	0.26	0.10	0.42	
					10	0.12	0.05	0.20	
France (south) 1999 (Princesse)	WP50	1.0	0.1	2	0 <sup>4</sup>	0.43	0.13	0.64	RA- 2039/99 0032-99
					0	6.7	1.2	8.6	
					3	4.5	0.72	5.7	
					7	2.9	0.38	3.5	
					10	1.3	0.24	1.7	
Greece 1999 (Acacia)	WP50	1.0	0.1	2	0 <sup>4</sup>	0.46	0.11	0.64	RA- 2039/99 0510-99
					0	11	1.2	13	
					3	11	0.53	12	
					7	4.6	0.45	5.3	
					10	1.9	0.19	2.2	
Italy 1998 (Messalina)	WP50	0.8	0.08	2	0	14	2.1	17	RA- 2039/98 1409-98
					7	0.11	0.06	0.21	
Italy 1999 (Bionda Lenta a Montare)	WP50	1.0	0.1	2	0	5.1	0.39	5.7	RA- 2039/99 0033-99
					7	1.3	0.12	1.5	
Portugal 1999 (Grand Rapid)	WP50	1.0	0.1	2	0	9.7	0.77	11.0	RA- 2039/99 0034-99
					7	2.3	0.25	2.7	
Spain 1999 (Daguan)	WP50	1.0 <sup>5</sup>	0.1	2	0 <sup>4</sup>	4.8	0.95	6.3	RA- 2039/99 0031-99
					0	12	1.8	15	
					3	12	1.2	14	
					7	8.5	1.2	10.4	
					10	8.4	1.1	10.2	
Spain 1999 (Daguan)	WP50	1.0	0.1	2	0 <sup>4</sup>	4.0	0.68	5.1	RA- 2039/99 0509-99
					0	14	1.5	16	
					6	9.7	1.2	12	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

<sup>2</sup> First application about 9% under-dosed

<sup>3</sup> First application about 5% over-dosed

<sup>4</sup> Before last application

<sup>5</sup> Last application about 7% under-dosed.

Table 34. Residues in leek shoots from supervised trials in France, Germany, The Netherlands and the UK.

Country, Year (Variety)	Application				PHI (days)	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No.		T	D	T+D <sup>1</sup>	
Belgium 1997 (Arkansa)	WG50	1.25 <sup>3</sup>	0.21	5	0 <sup>2</sup>	0.24	0.09	0.39	RA-2047/97 0242-97
					0	3.1	1.9	6.2	
					7	0.06	0.03	0.11	
					14	0.02	<0.02	0.05	
					21	<u>&lt;0.02</u>	<0.02	<u>&lt;0.02</u>	
28	<0.02	<0.02	<0.02						
France (north) 1997 (Adrea)	WG50	1.25	0.21	5	0	5.8	1.0	7.4	RA-2047/97 0243-97
					14	3.5	0.74	4.7	
					21	<u>0.94</u>	0.36	<u>1.52</u>	
Germany 1997 (Paragon)	WG50	1.25	0.21	5	0 <sup>2</sup>	0.42	0.09	0.57	RA-2047/97 0241-97
					0	7.5	1.2	9.4	
					7	2.5	0.49	3.3	
					14	1.4	0.30	1.9	
					21	<u>0.84</u>	0.20	<u>1.16</u>	
28	0.42	0.12	0.61						
Germany 1997 (Paragon)	WG50	1.25	0.21	5	0 <sup>2</sup>	0.40	0.09	0.55	RA-2047/97 0441-97
					0	5.0	1.1	6.8	
					7	1.5	0.40	2.1	
					14	0.79	0.32	1.31	
					21	<u>0.58</u>	0.24	<u>0.97</u>	
28	0.47	0.14	0.70						
Netherlands 1989 (Gauia)	WG50	1.25	0.21	5	0	1.7	0.29	2.2	0514-89
					14	0.61	0.10	0.77	
					21	0.29	0.06	0.39	
					27	<u>0.34</u>	0.07	<u>0.45</u>	
Netherlands 1989 (Porino)	WG50	1.25	0.21	5	0	1.8	0.18	2.1	0515-89
					14	0.63	0.07	0.74	
					21	<u>0.92</u>	0.09	<u>1.07</u>	
					28	0.51	0.08	0.64	
Netherlands 1989 (Cortina)	WG50	1.25	0.21	5	0	1.9	0.22	2.3	0517-89
					15	0.74	0.08	0.87	
					22	<u>0.17</u>	<0.05	<u>0.17</u>	
					30	0.11	<0.05	0.11	
UK 1997 (Verina)	WG50	1.25	0.21	5	0	8.7	1.3	10.8	RA-2047/97 0442-97
					14	2.4	0.48	3.2	
					21	<u>1.2</u>	0.37	<u>1.8</u>	
UK 2000 (Primera)	WG50	1.25	0.21	5	0 <sup>2</sup>	0.51	0.10	0.67	RA-2008/00 0132-00
					0	7.6	0.74	8.8	
					1	7.0	0.71	8.2	
					8	1.3	0.16	1.6	
					14	0.52	0.06	0.62	
					21	<u>0.36</u>	0.03	<u>0.41</u>	
					29	0.29	0.03	0.34	

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid.

<sup>2</sup> Before last application

<sup>3</sup> First application 7% over-dosed

Table 35. Residues in hops from supervised trials in Germany.

Country, Year (Variety)	Form	Application			Sample	PHI (days)	Residues (mg/kg)			Report no.
		kg ai/ha	kg ai/hl	No.			T	D	T+D <sup>1</sup>	
Germany 1995 (Hallertauer Tradition)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	<0.5	<0.5	<0.5	RA- 2102/95 0029-95
						0	32	2.4	36	
						4	15	1.3	17	
						8	13	1.1	15	
						14 <sup>2</sup>	3.8,3.9	1.1,0.81	5.6, 5.2	
						21	4.3	<0.5	4.3	
					Cone, Dried	14 <sup>2</sup>	<u>7.8</u> ,3.3	3.5,2.7	<u>13.5</u> , 7.7	
						21	5.0	4.7	12.6	
Germany 1995 (Perle)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	0.68	<0.5	0.68	RA- 2102/95 0535-95
						0	35	3.9	41	
						3	21	2.2	25	
						7	15	1.6	18	
						14 <sup>2</sup>	9.2,6.1	1.0,0.72	10.8, 7.3	
						20	7.5	0.71	8.7	
					Cone, Dried	14 <sup>2</sup>	<u>9.1</u> ,8.5	14,11	<u>31.8</u> ,26.3	
						20	7.3	6.1	17.2	
Germany 1995 (Northern Brewer)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	1.6	<0.5	1.6	RA- 2102/95 0613-95
						0	27	4.1	34	
						2	28	6.2	38	
						7	29	4.6	36	
						14 <sup>2</sup>	15,17	1.5,1.5	17, 19	
						22	11	1.7	14	
					Cone, Dried	14 <sup>2</sup>	<u>11</u> ,11	13,11	<u>32</u> , 29	
						22	8.0	9.2	22.9	
Germany 1995 (Spalter Select)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	1.6	0.69	2.7	RA- 2102/95 0614-95
						0	57	12	76	
						3	35	3.8	41	
						7	25	2.8	30	
						14 <sup>2</sup>	7.8,18	1.1,1.9	9.6, 21	
					Cone, Dried	14 <sup>2</sup>	<u>27</u> ,17	27,29	<u>71</u> , 64	
Germany 1996 (Hallertauer Tradition)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	2.4	<0.5	2.4	RA- 2067/96 0167-96
						0	24	3.1	29	
						2	25	3.6	31	
						6	11	1.2	13	
						13	4.1	<0.5	4.1	
						20	4.6	<0.5	4.6	
					Cone, Dried	13	<u>2.8</u>	3.7	<u>8.8</u>	
						20	2.2	2.1	5.6	
Germany 1996 (Spalter Select)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	8.3	0.70	9.4	RA- 2067/96 0568-96
						0	53	3.7	59	
						2	36	4.3	43	
						6	26	2.0	29	
						13	19	1.5	21	
						20	11	0.86	12	
					Cone, Dried	13	<u>8.9</u>	13	<u>30.0</u>	
						20	5.6	8.9	20.0	
Germany 1996 (Perle)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	4.3	<0.5	4.3	RA- 2067/96 0569-96
						0	24	1.3	26	
						2	19	3.0	24	
						6	11	0.86	12	
						13	<u>6.9</u>	0.55	7.8	
						20	9.1	0.62	10.1	
					Cone, Dried	13	<u>5.4</u>	8.6	<u>19.3</u>	
						20	4.0	4.9	11.9	

Country, Year (Variety)	Form	Application			Sample	PHI (days)	Residues (mg/kg)			Report no.
		kg ai/ha	kg ai/hl	No.			T	D	T+D <sup>1</sup>	
Germany 1996 (Northern Brewer)	WG 50	1.0- 3.0	0.1	6	Cone, Green	0 <sup>3</sup>	6.5	<0.5	6.5	RA- 2067/96 0570-96
						0	26	1.5	28	
						2	23	3.47	29	
						6	17	1.7	20	
						13	12	1.1	14	
					20	5.3	0.93	6.8		
					Cone, Dried	13	<u>10</u>	4.8	<u>18</u>	
						20	4.4	4.3	11.4	

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid

<sup>2</sup> PHI at which two independent composite samples were collected per site

<sup>3</sup> Before last application

## FATE OF RESIDUES IN STORAGE AND PROCESSING

### In processing

The Meeting received information on the fate of incurred residues of tolylfluanid and DMST during the processing of apples, pears, grapes, blackcurrants, strawberries, tomatoes, lettuce and hops, and also of the glucosides of 4-hydroxymethyl-DMST and 2-hydroxyphenyl-DMST during the processing of grapes. Information on the fate of incurred residues during drying of hops is included in Table 35 above.

Sneikus (2000) demonstrated that tolylfluanid is hydrolyzed in simulated cooking conditions. When added to buffered drinking water at 0.5 mg/l it was completely hydrolyzed to DMST (recovery of radioactivity of >99.9%) when heated at 100°C for 60 min at pH 5 or at 120°C for 20 min at pH 6. No products other than DMST were detected.

Apples and pears. Nüsslein and Walz-Tylla (1996) harvested 24 to 26 kg of apples from supervised trials in Italy in 1994 (Table 23) 7 days after the last treatment and processed them into juice, sauce and pomace in accordance with industrial practices, except that household practices were also used to prepare sauce from Annurca apples (Figure 5). Residues of tolylfluanid were mainly transferred to pomace. They were below the limit of quantification (0.02 mg/kg) in the juice and sauce, and in wet pomace were about 3 times those in the fruit. Conversion of tolylfluanid into DMST was observed in the heated products, sauce and dry pomace.

Apples and pears from supervised trials in Germany in 1983 were also processed into sauce, juice and canned fruit but only summary details were reported (Anon., 1984).

Table 36. Residues in apples and their processed commodities from supervised trials in Italy and Germany.

Country, Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Reference
	Form	kg ai/ha	kg ai/hl	No.			T	D	T+D <sup>1</sup>	
<b>APPLE</b>										
Italy 1994 (Red Chief)	WG	1.5	0.1	3	7	Fruit	0.22	0.03	0.27	Nüsslein and Walz- Tylla, 1996 RA-3064/94 0262-94
						Juice	□0.02	0.02	0.03	
						Sauce	<0.02	0.06	0.10	
						Pomace, wet	0.64	0.08	0.77	
						Pomace, dry	1.15	0.54	2.02	



Country, Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Reference
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
Italy 1994 (Annurca)	WG	1.5	0.1	3	7	Fruit	0.14	0.03	0.19	Nüsslein and Walz- Tylla, 1996 RA-3064/94 0264-94
						Juice	<0.02	0.02	0.03	
						Sauce	<0.02	0.09	0.15	
						Pomace, wet	0.61	0.08	0.74	
						Pomace, dry	1.55	0.47	2.31	
Italy 1994 (Red Chief)	WG	7.5	0.2	1	7	Fruit	2.56	0.12	2.75	Nüsslein and Walz- Tylla, 1996 RA-3064/94 0783-94
						Juice	<0.02	0.16	0.26	
						Pomace, wet	3.73	0.14	3.96	
Germany 1983 (James Grieve)	WP	1.125	0.075	15	7	Fruit	0.6	0.4	1.2	Anon., 1984 8200-83
						Sauce	<0.1	<0.1	<0.1	
						Juice	<0.1	<0.1	<0.1	
						Canned fruit	<0.1	<0.1	<0.1	
Germany 1983 (Cox Orange)	WP	1.125	0.075	15	7	Fruit	2.1	0.5	2.9	Anon., 1984 8201-83
						Sauce	<0.1	<0.1	<0.1	
						Juice	<0.1	<0.1	<0.1	
						Canned fruit	<0.1	<0.1	<0.1	
PEAR										
Germany 1983 (Alexander Lucas)	WP	1.125	0.075	15	7	Fruit	3.5	0.5	4.3	Anon., 1984 8202-83
						Juice	<0.1	<0.1	<0.1	
						Canned fruit	<0.1	<0.1	<0.1	
Germany 1983 (Alexander Lucas)	WP	1.125	0.075	15	7	Fruit	8.1	0.9	9.6	Anon., 1984 8203-83
						Juice	<0.1	0.2	0.3	
						Canned fruit	<0.1	<0.1	<0.1	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

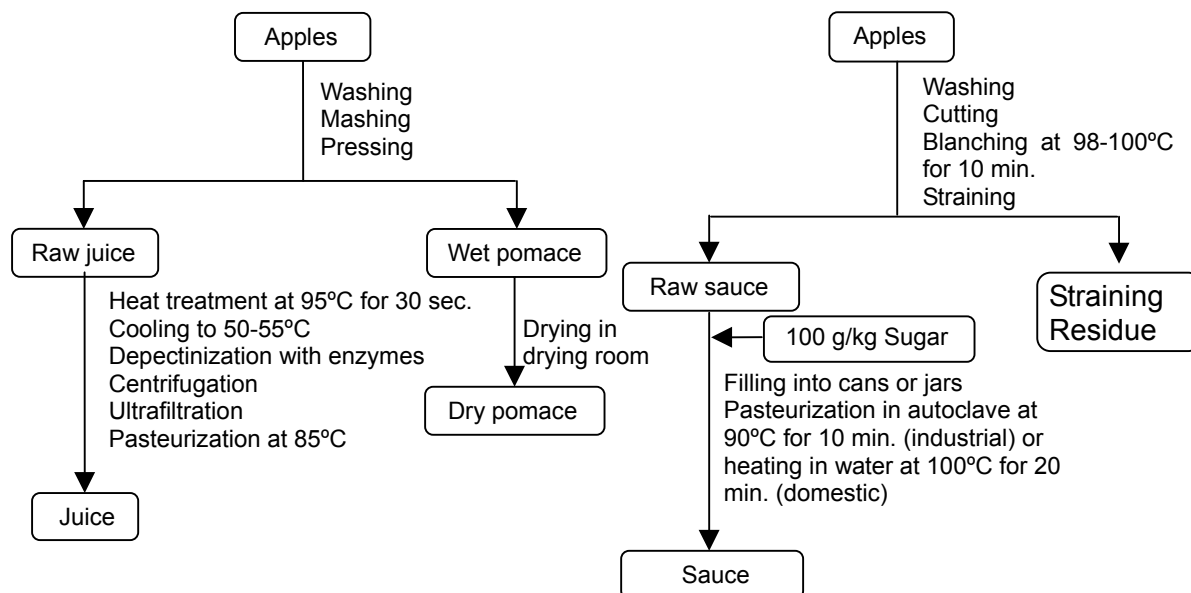


Figure 5. Processing of apples to juice, sauce and pomace (Nüsslein and Walz-Tylla, 1996).

**Grapes.** Bunches of grapes from supervised trials in Germany in 1987 (Anon., 1988) and in France in 1992 and 1993 (Brennecke, 1996a,g) were processed into wine and must as in commercial practice. In the German studies bunches of grapes were collected 35 days after the last application. Although no details of the processing were given in the study reports, one report indicated that 127 kg of grapes were processed. In French studies, bunches of grapes were harvested 21 days after the last application. About 43-50 kg of grapes were processed into wine and must as in commercial processing on a pilot

plant scale as in Figure 6, or processed by the French “Institute Technique de la Vigne et du Vin”. Both red and white grape varieties were used in these studies.

The residues of tolyfluanid were below the limit of quantification in wine in all studies, and also in must in the German studies but higher in must in four of the six French studies. The concentrations of DMST in wine were slightly higher than those in grapes in the German studies and significantly higher in 5 of the French studies, and were higher in must. The differences were probably caused by the degradation of tolyfluanid into DMST during fermentation. The sum of tolyfluanid and DMST was lower in wine than in grapes in the German but higher in the French studies. In the French studies 4-hydroxymethyl-DMST and 2-hydroxyphenyl-DMST were determined. The former was the main metabolite in wine and at higher concentrations than in grapes when tolyfluanid concentrations were high in grapes ( $\geq 0.60$  mg/kg) but lower when tolyfluanid concentrations were low. It showed a decrease in must. 2-Hydroxyphenyl-DMST increased slightly in wine when its concentration was above the limit of quantification in grapes. It is not found in must in all the French studies.

About 21 to 25 kg of grapes from supervised trials in Italy in 1994 were processed to juice and pomace and about 4 kg into dried grapes and raisin waste by simulated industrial practices as in Figure 6 (Brennecke, 1996e). The residues of tolyfluanid were below the limit of quantification in juice in all studies including one in which 5 times the maximum application rate was used. In dried grapes there was a slight decrease but concentrations were higher in raisin waste and wet and dry pomace. DMST showed an increase in dried grapes, raisin waste and pomace, and a decrease in juice from grapes harvested 21 days after receiving 5 times the maximum dose. The sum of tolyfluanid and DMST is slightly less in juice, but significantly higher in other commodities than in grapes. The concentrations of 4-hydroxymethyl-DMST increased in all processed fractions, and those of 2-hydroxyphenyl-DMST were generally below or slightly above the limit of quantification.

Table 37. Residues in grapes and their processed products from supervised trials in France, Germany and Italy.

Country, Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
Germany 1987 (Riesling)	WG	0.5-2.5	0.1	8	35	Bunch	0.24	0.07	0.35	8200-87 (white)
						Wine	<0.05	0.13	0.21	
						Must	<0.05	0.09	0.15	
Germany 1987 (Spätburgunder)	WG	0.5-1.8	0.1	8	35	Bunch	0.41	0.10	0.57	8201-87 (red)
						Wine	<0.05	0.31	0.50	
						Must	<0.05	0.20	0.32	
Germany 1987 (Müller-thurgau)	WG	0.6-1.8	0.3	8	35	Bunch	0.47	0.07	0.58	8202-87 (white)
						Wine	<0.05	0.16	0.26	
						Must	<0.05	0.09	0.15	
Germany 1987 (Spätburgunder)	WG	0.6-1.8	0.3	8	35	Bunch	1.7	0.15	1.94	8203-87 (red)
						Wine	<0.05	0.36	0.58	
						Must	<0.05	0.40	0.65	
Germany 1988 (Müller-thurgau)	WG	0.75- 1.8	0.3	8	35	Bunch	0.06	<0.05	0.06	0212-88 (white)
						Wine	<0.05	<0.05	<0.05	
						Must	<0.05	<0.05	<0.05	
Germany 1988 (Müller-thurgau)	WG	0.6-1.8	0.3	8	35	Bunch	0.67	0.10	0.83	0213-88 (white)
						Wine	<0.05	0.15	0.24	
						Must	<0.05	0.13	0.21	
Germany 1988 (Müller-thurgau)	WG	0.6-1.8	0.1	8	35	Bunch	0.35	0.07	0.46	0211-88 (white)
						Wine	<0.05	0.08	0.13	
						Must	<0.05	0.09	0.15	
Germany 1988 (Riesling)	WG	0.6-2.0	0.1	8	35	Bunch	0.91	0.17	1.19	210-88 (white)
						Wine	<0.05	0.35	0.57	
						Must	0.29	0.33	0.82	

Country, Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
France (south) 1992 (Grenache)	WG	2.0	2.0	5	21	Bunch Wine Must	0.36 <0.02 0.57	0.04 0.50 0.18	0.42 0.81 0.86	RA- 2007/92 0423-92 (red)
France (south) 1992 (Carignan)	WG	2.0	2.0	5	21	Bunch Wine Must	0.57 <0.02 0.93	0.11 0.67 0.46	0.75 1.09 1.68	RA- 2007/92 0424-92 (red)
France (south) 1992 (Syrah)	WG	2.0	2.0	5	21	Bunch Wine Must	0.33 <0.02 0.80	0.05 0.93 0.33	0.41 1.51 1.33	RA- 2007/92 0425-92 (red)
France (south) 1992 (Cinsault)	WG	2.0	2.0	5	21	Bunch Wine Must	1.4 <0.02 1.74	0.14 1.1 0.60	1.63 1.78 2.71	RA- 2007/92 0426-92 (red)
France (south) 1993 (Grenache)	WP	2.0	2.0	3	21	Bunch Wine Must	0.46 <0.02 <0.02	0.09 0.14 0.25	0.61 0.23 0.41	RA- 2049/93 0085-93 (red)
					39	Bunch Wine Must	0.11 <0.02 <0.02	0.02 0.43 0.06	0.14 0.70 0.10	
France (south) 1993 (Chardonnay)	WP	2.0	2.0	3	21	Bunch Wine Must	0.06 <0.02 <0.02	0.06 0.12 0.05	0.16 0.19 0.08	RA- 2049/93 0320-93 (white)
					35	Bunch Wine Must	0.05 <0.02 <0.02	0.03 0.04 0.03	0.10 0.06 0.05	
Italy 1994 (Blusch)	WP	1.0	0.1	3	21	Bunch	0.05	<0.02	0.05	RA-3065- 94 0269-94 (red)
						Juice	<0.02	<0.02	<0.02	
						Pomace, wet	0.12	0.12	0.31	
						Pomace, dry	0.13	0.13	0.34	
						Dried grape	<0.05	<0.05	<0.05	
Raisin waste	0.51	0.47	1.27							
Italy 1994 (Centenial)	WP	1.0	0.1	3	21	Bunch	0.03	<0.02	0.03	RA-3065- 94 0669-94 (white)
						Juice	<0.02	<0.02	<0.02	
						Pomace, wet	0.50	0.15	0.74	
						Pomace, dry	0.53	0.48	1.31	
						Dried grape	<0.05	0.10	0.16	
Raisin waste	0.39	0.34	0.94							
Italy 1994 (Trebiano)	WO	5.0	0.5	1	21	Bunch	0.69	0.10	0.85	RA-3065- 94 0670-94 (white)
						Juice	<0.02	0.03	0.05	
						Pomace, wet	0.71	0.29	1.18	
						Pomace, dry	0.80	0.97	2.37	
						Dried grape	0.56	1.25	2.59	
Raisin waste	3.77	4.45	10.98							

Country, Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			4-HMD	2-HPD	T+3 metabolites <sup>1</sup>	
France (south) 1992 (Grenache)	WG	2.0	2.0	5	21	Bunch Wine Must	0.60 0.89 0.29	0.11 0.19 <0.05	1.49 2.44 1.30	RA- 2007/92 0423-92 (red)
France (south) 1992 (Carignan)	WG	2.0	2.0	5	21	Bunch Wine Must	0.84 1.06 0.39	0.07 0.13 <0.05	2.12 2.88 2.29	RA- 2007/92 0424-92 (red)
France (south) 1992 (Syrah)	WG	2.0	2.0	5	21	Bunch Wine Must	1.23 1.58 0.46	<0.05 <0.05 <0.05	2.26 3.89 2.02	RA- 2007/92 0425-92 (red)

Country, Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			4-HMD	2-HPD	T+ 3 metabolites <sup>1</sup>	
France (south) 1992 (Cinsault)	WG	2.0	2.0	5	21	Bunch	1.06	0.08	3.35	RA- 2007/92 0426-92 (red)
						Wine	1.40	0.10	4.04	
						Must	0.39	<0.05	3.30	
France (south) 1993 (Grenache)	WP	2.0	2.0	3	21	Bunch	0.37	<0.05	1.17	RA- 2049/93 0085-93 (red)
						Wine	0.24	<0.05	0.59	
						Must	0.15	<0.05	0.64	
					39	Bunch	0.19	<0.05	0.43	
						Wine	0.31	<0.05	1.17	
						Must	0.20	<0.05	0.40	
France (south) 1993 (Chardonnay)	WP	2.0	2.0	3	21	Bunch	0.18	<0.05	0.43	RA- 2049/93 0320-93 (white)
						Wine	0.09	<0.05	0.33	
						Must	0.09	<0.05	0.22	
					39	Bunch	0.19	<0.05	0.39	
						Wine	0.11	<0.05	0.23	
						Must	0.09	<0.05	0.19	
Italy 1994 (Blusch)	WP	1.0	0.1	3	21	Bunch	0.29	<0.05	0.49	RA- 3065/94 0269-94 (red)
						Juice	0.30	0.05	0.53	
						Pomace, wet	0.38	0.05	0.96	
						Pomace, dry	0.58	<0.10	1.21	
						Dried grape	1.08	0.11	1.79	
						Raisin waste	0.92	<0.10	2.66	
Italy 1994 (Centenial)	WP	1.0	0.1	3	21	Bunch	0.22	<0.05	0.36	RA- 3065/94 0669-94 (white)
						Juice	0.30	<0.05	0.30	
						Pomace, wet	0.42	<0.05	1.37	
						Pomace, dry	0.97	<0.10	2.77	
						Dried grape	0.88	<0.10	1.49	
						Raisin waste	0.48	<0.10	1.66	
Italy 1994 (Trebiano)	WO	5.0	0.5	1	21	Bunch	0.33	<0.05	1.35	RA- 3065/94 0670-94 (white)
						Juice	0.33	<0.05	0.55	
						Pomace, wet	0.35	<0.10	1.71	
						Pomace, dry	0.70	<0.10	3.43	
						Dried grape	1.00	<0.10	4.10	
						Raisin waste	1.21	<0.05	12.80	

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid

<sup>2</sup> Sum of tolylfluanid, DMST, 4-hydroxymethyl-DMST (230.3 g/mol) and 2-hydroxyphenyl-DMST (230.3 g/mol) expressed as tolylfluanid

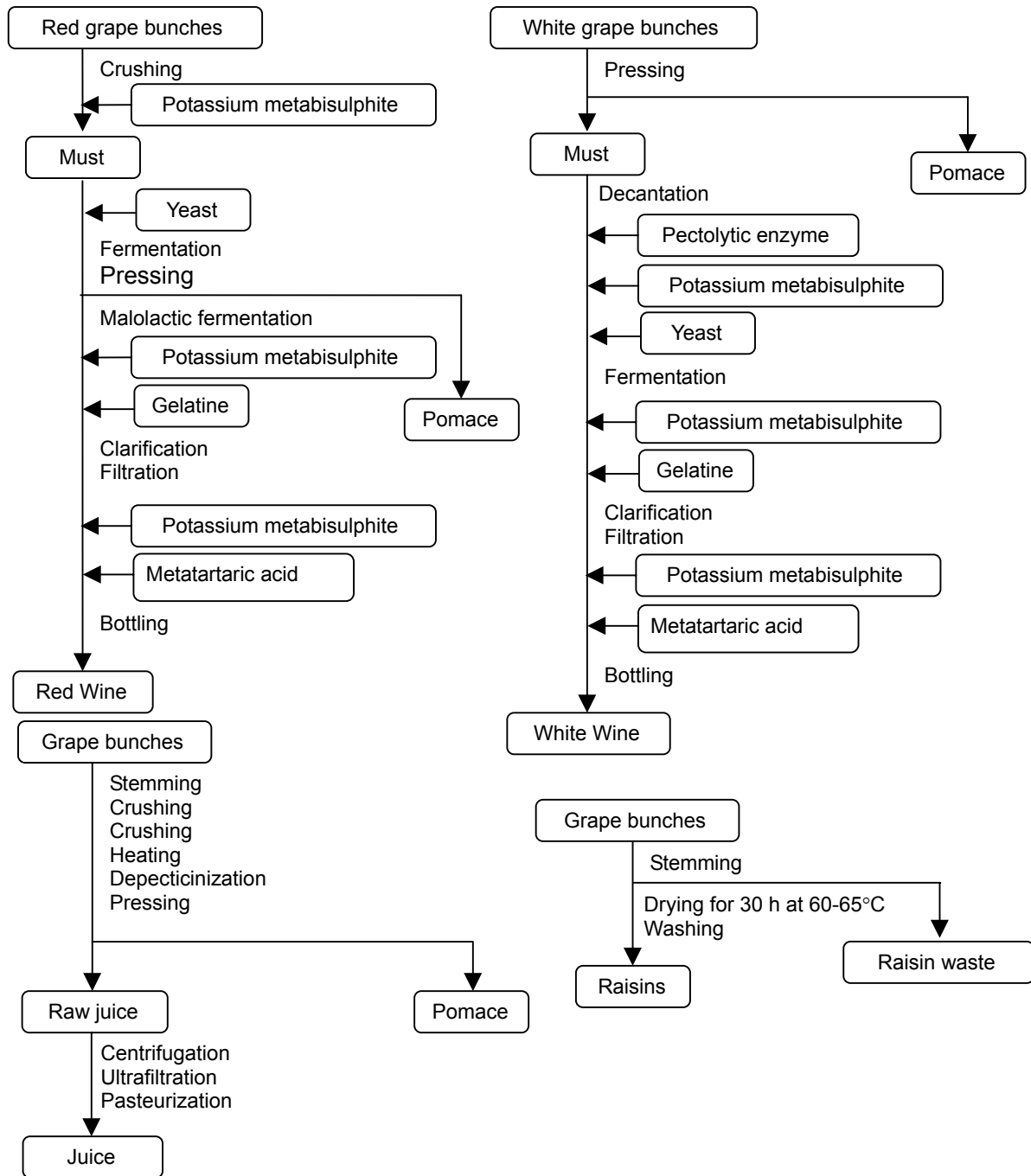


Figure 6. Processing of grapes to wine, juice and raisins (Brennecke, 1996e).

**Blackcurrants.** Blackcurrants from a trial in 1992 in the UK were harvested and frozen 34 days after the last treatment (Brennecke and Walz-Tylla, 1994b). Seven kilograms of frozen blackcurrants were processed into juice and jelly according to household practices (Figure 7). Washing of the frozen fruits reduced residues of tolyfluanid by about half while the amount of DMST increased slightly by hydrolysis of the parent compound. Residues of tolyfluanid were not found in either the juice or jelly. The total of tolyfluanid and DMST was also less in juice and jelly than in the fruit.

Table 38. Residues in blackcurrants and their processed commodities from supervised trials in the UK.

Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D	
1992 (Baldwin)	WG	1.5	0.3	4	34	Fruit	1.1	0.41	1.76	RA-2010/92 0189-92
						Fruit, washed	0.64	0.52	1.48	
						Juice	<0.02	0.28	0.45	
						Jelly	<0.02	0.61	0.99	
1992 (Baldwin)	WG	1.5	0.3	4	34	Fruit	1.1	0.41	1.76	RA-2010/92 0190-92

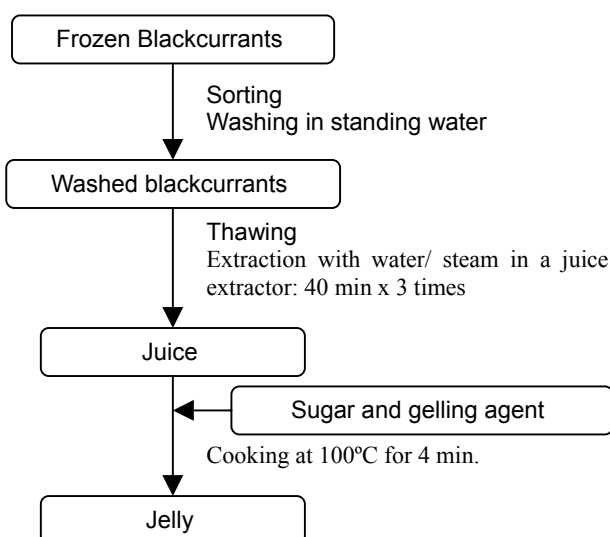


Figure 7. Processing of blackcurrants into juice and jelly (Brennecke and Walz-Tylla, 1994b).

**Strawberries.** In processing studies in the UK in 1992, strawberries were harvested 14 days after the last application (Brennecke and Walz-Tylla, 1994a). About 1.4 kg were processed into jam as in household practice and 2 kg into preserves following industrial practice (Figure 8). Washing the strawberries reduced residues of tolylfluanid by about half, and processing the washed fruit into jam and preserve reduced tolylfluanid significantly without increasing the DMST. The total tolylfluanid and DMST was decreased significantly by washing and processing.

Table 39. Residues in strawberries and their processed commodities from supervised trials in the UK.

Year (Variety)	Application				PHI (days)	Sample	Residues (mg/kg)			Report no.
	Form	kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
1992 (Elsanta)	WG	2.0- 2.25 <sup>2</sup>	0.1- 0.45	4	14	Fruit	3.0	0.58	3.94	RA-2009/92 0180-92
						Fruit, washed	1.6	0.50	2.41	
						Jam	<0.02	0.54	0.87	
						Canned fruit	0.20	0.40	0.85	
1992 (Cambridge Favourite)	WG	2.0- 2.25	0.1- 0.45	4	14	Fruit	2.4	0.48	3.18	RA-2009/92 0198-92
						Fruit, washed	1.2	0.36	1.78	
						Jam	0.02	0.42	0.70	
						Canned fruit	0.18	0.29	0.65	
1992 (Hapil)	WG	2.0- 2.25	0.1- 0.45	4	14	Fruit	1.5	0.24	1.89	RA-2009/92 0178-92

<sup>1</sup> Sum of tolylfluanid and DMST expressed as tolylfluanid<sup>2</sup> 1st application at 0.2 kg ai/hl and 2000 l; 2nd-4th applications at 0.45 kg ai/hl and 500 l.

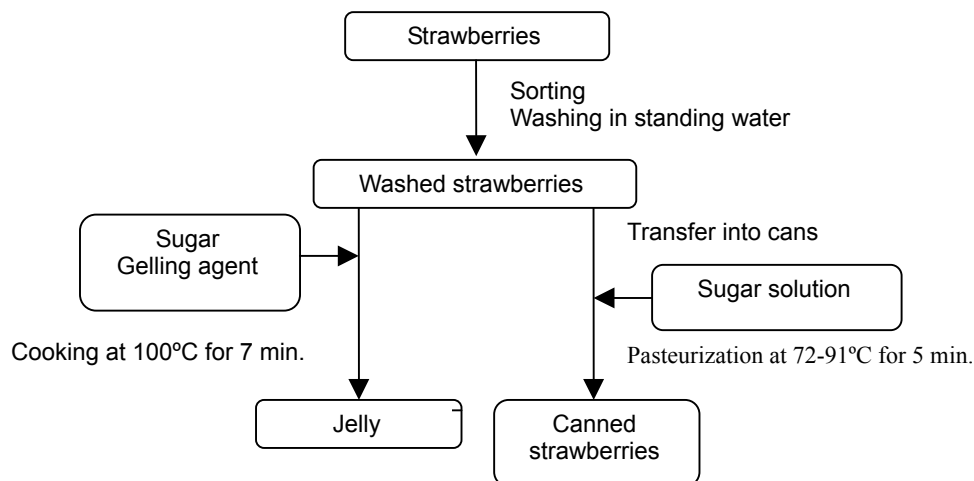


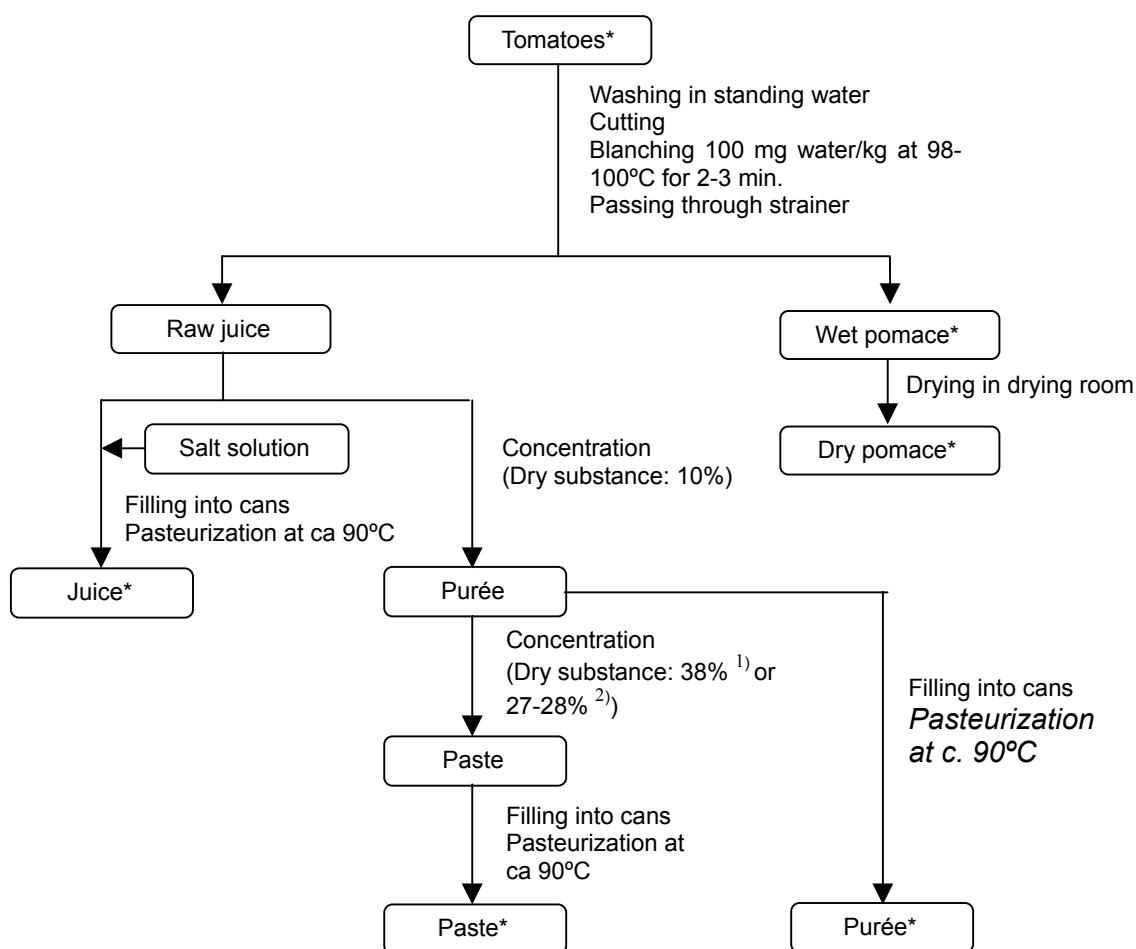
Figure 8. Processing of strawberries into jam and preserve (Brennecke and Walz-Tylla, 1994a).

**Tomatoes.** In processing studies in Italy in 1994 (Nüsslein, 1996e) and in greenhouses in Germany in 1998 (Brennecke, 1999), tomatoes were picked 7 days after the last application. About 30 to 50 kg were processed into juice, paste, purée and pomace in accordance with industrial practices (Figure 9). The residues of tolyfluanid were markedly less in the processed food commodities, but higher in pomace. DMST was generally concentrated in the processed foods with the highest concentration in the paste. The residues of tolyfluanid in the fruit were mostly transferred to pomace and there hydrolysed to DMST. The total residue of tolyfluanid and DMST decreased in juice and purée but showed a tendency to increase in paste, and the highest concentrations of both compounds were in the dry pomace.

Table 40. Residues in tomatoes and their processed commodities from supervised trials in Germany and Italy.

Country, Year (Variety)	Form	Application			PHI (days)	Sample	Residues (mg/kg)			Report no.
		kg ai/ha	kg ai/hl	No			T	D	T+D <sup>1</sup>	
Italy 1994 (Hypeel 244)	WG	1.0	0.1	3	7	Fruit	0.21	0.03	0.26	RA- 3063/94 0259-94
						Juice	<0.02	0.02	0.03	
						Paste	<0.02	0.10	0.16	
						Purée	<0.02	0.07	0.11	
						Pomace, wet	0.13	0.13	0.34	
						Pomace, dry	0.47	1.5	2.90	
Italy 1994 (Hypeel 224)	WG	1.0	0.1	3	7	Fruit	0.05	<0.02	0.05	RA- 3063/94 0260-94
						Juice	<0.02	0.03	0.05	
						Paste	<0.02	0.29	0.47	
						Purée	<0.02	0.16	0.21	
						Pomace, wet	0.27	0.16	0.53	
						Pomace, dry	0.66	2.4	4.55	
Italy 1994 (Red Peel)	WG	6.0	0.6	1	7	Fruit	0.37	0.06	0.47	RA- 3063/94 0668-94
						Juice	<0.02	0.10	0.16	
						Paste	<0.02	0.50	0.81	
						Purée	<0.02	0.16	0.26	
						Pomace, wet	0.45	0.41	1.11	
						Pomace, dry	3.1	4.4	10.23	
Germany 1998 (Ferrari)	WG	1.46- 2.25	0.11	8		Fruit	0.79	0.14	1.02	RA- 3135/98 1308-98
						Juice	<0.02	0.28	0.45	
						Paste	<0.02	1.2	1.94	
						Purée	<0.02	0.33	0.53	
Germany 1998 (Panovi)	WG	11.5	0.56	1		Fruit	1.7	0.14	1.93	RA- 3135/98 1703-98
						Juice	<0.02	0.12	0.19	
						Paste	<0.02	0.56	0.91	
						Purée	<0.02	0.21	0.34	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid



\* analysed sample

<sup>1</sup> Nüsslein, 1996e

<sup>2</sup> Brennecke, 1999

Figure 9. Processing of tomatoes into juice, purée, paste and pomace.

**Lettuce.** The effects of washing on residues on lettuce leaves and the distribution of residues in outer and inner leaves were studied by Brennecke and Block (1999d). In supervised trials 24 lettuce heads were harvested 7 days after the last treatment and processed according to household practice (Figure 10). The residues of tolylfluanid and DMST were both reduced by removing outer leaves and further reduced by removing stems and washing. The residues of tolylfluanid were mainly present in the outer leaves.

Table 41. Residues in lettuce and their processed commodities from supervised trials in Germany. 7-day PHI.

Year (Variety)	Form	Application			Sample	Residues (mg/kg)			Report no.
		kg ai/ha	kg ai/hl	No		T	D	T+D <sup>1</sup>	
1998 (Nadine)	WG	1.125	0.19	6	Head	2.0, 1.9	0.21, 0.21	2.3, 2.2	RA- 3136/98 1074-98
					Head, inner	1.7, 1.1	0.17, 0.16	2.0, 1.4	
					Leaf, outer	7.5, 6.9	0.50, 0.50	8.3, 7.7	
					Leaf, inner	1.2, 0.87	0.16, 0.13	1.5, 1.1	
					Leaf, inner, washed	0.31, 0.29	0.08, 0.06	0.44, 0.39	
					Washing water	0.009, 0.009	0.05, 0.04	0.09, 0.07	



Year (Variety)	Form	Application			Sample	Residues (mg/kg)			Report no.
		kg ai/ha	kg ai/hl	No		T	D	T+D <sup>1</sup>	
1998 (Nadine)	WG	1.125	0.19	6	Head	2.1, 2.1	0.16, 0.19	2.36, 2.41	RA-3136/98 1077-98
					Head, inner	1.6, 1.4	0.15, 0.17	1.84, 1.68	
					Leaf, outer	6.1, 8.0	0.51, 0.57	6.93, 8.92	
					Leaf, inner	1.2, 1.1	0.13, 0.13	1.41, 1.31	
					Leaf, inner, washed	0.54, 0.59	0.08, 0.08	0.67, 0.72	
					Washing water	0.05, 0.06	0.02, 0.01	0.08, 0.08	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

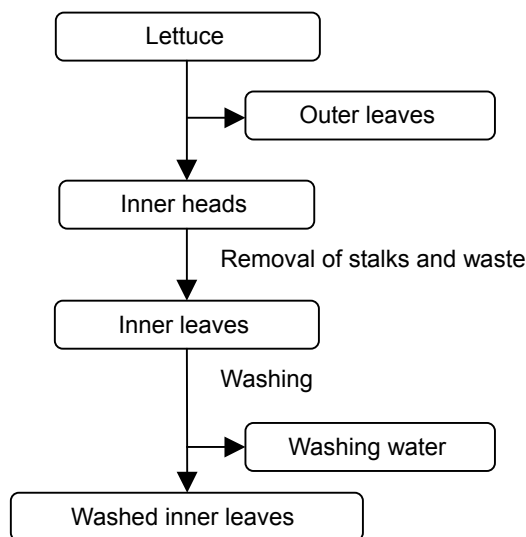


Figure 10. Washing and separation of lettuce (Brennecke and Block, 1999d).

Hops. Hops harvested 14 days after the last treatment in supervised trials in Germany in 1995 were kiln-dried and 1.6-1.7 kg of dried hops were used for brewing in accordance with commercial practice as in Figure 11 (Brennecke, 1997d). The residues of tolyfluanid and DMST were markedly reduced in beer and were below the limit of quantification or at a very low level. Tolyfluanid and DMST significantly above the LOQ were found only in spent hops.

Table 42. Residues in hops and brewing products from supervised trials in Germany. 14-day PHI.

Year (Variety)	Form	Application			Sample	Residues (mg/kg)			Report no.
		kg ai/ha	kg ai/hl	No		T	D	T+D <sup>1</sup>	
1995 (Hallertauer Tradition)	WG	1.0	0.1	6	Cone, dried	3.8, 3.3	3.5, 2.7	5.6, 5.2	RA-3102/95 0029-95
					Beer	<0.02	<0.02	<0.02	
					Spent hops	0.28	1.5	2.71	
					Hops draff	<0.50	<0.50	<0.50	
					Brewer's yeast	<0.10	<0.10	<0.10	
1995 (Northern Brewer)	WG	1.0	0.1	6	Cone, dried	11, 11	13, 11	17, 19	RA-3102/95 0613-95
					Beer	<0.02	0.04	0.04	
					Spent hops	0.32	1.8	3.24	
					Hops draff	<0.50	<0.50	<0.50	
					Brewer's yeast	<0.10	<0.10	<0.10	

<sup>1</sup> Sum of tolyfluanid and DMST expressed as tolyfluanid

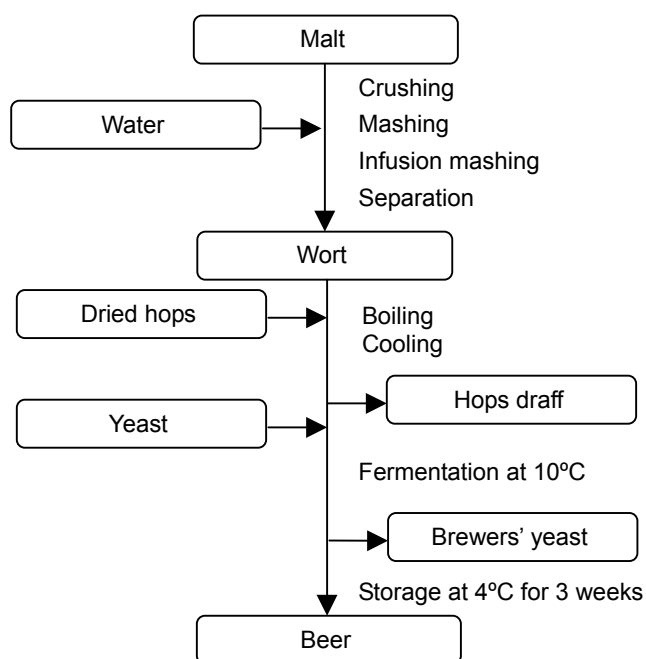


Figure 11. Brewing beer (Brennecke, 1997d).

Processing factors for all the processed commodities were calculated for tolyfluanid only and for the sum of tolyfluanid and DMST expressed as tolyfluanid. In the tolyfluanid-only calculation, where the residue in the processed commodity was below the limit of quantification the processing factor is reported as  $<[\text{LOQ}/(\text{residue in RAC})]$ . In the calculation of the sum of tolyfluanid and DMST, where both the residues of tolyfluanid and DMST were below the LOQ, the processing factor is reported as  $<[(\text{sum of LOQs})/(\text{residue in RAC})]$  (Table 43).

Table 43. Processing factors for tolyfluanid residues in apples, pears, grapes, blackcurrants, strawberries, tomatoes, lettuces and hops.

APPLE										
	Study 1	Study 2	Study 3	Study 4	Mean	Study 1	Study 2	Study 3	Study 4	Mean
	Tolyfluanid (mg/kg)					Tolyfluanid+DMST (mg/kg <sup>1</sup> )				
Fruit	0.22	0.14	0.6	2.1		0.27	0.19	1.2	2.9	
Juice	<0.02	<0.02	<0.1	<0.1		0.03	0.03	<0.1	<0.1	
Sauce	<0.02	<0.02	<0.1	<0.1		0.10	0.15	<0.1	<0.1	
Canned fruit			<0.1	<0.1				<0.1	<0.1	
Pomace, wet	0.64	0.61				0.77	0.74			
Pomace, dry	1.15	1.55				2.02	2.31			
	Processing factor					Processing factor				
Juice	<0.09	<0.14	<0.17	<0.05	<0.09	0.11	0.15	<0.08	<0.03	0.09
Sauce	<0.09	<0.14	<0.17	<0.05	<0.11	0.37	0.79	<0.08	<0.03	0.32
Canned fruit			<0.17	<0.05	<0.11			<0.08	<0.03	<0.06
Pomace, wet	2.9	4.4			2.9	2.9	3.9			2.7
Pomace, dry	5.2	11			8.1	7.5	12			9.8
PEAR										
	Tolyfluanid (mg/kg)					Tolyfluanid+DMST (mg/kg <sup>1</sup> )				
	Study 1	Study 2				Study 1	Study 2			Mean
Fruit	3.5	8.1				4.3	9.6			
Juice	<0.1	<0.1				<0.1	0.3			
Canned fruit	<0.1	<0.1				<0.1	<0.1			
	Processing factor					Processing factor				
Juice	<0.03	<0.01			<0.02	<0.02	0.03			0.03
Canned fruit	<0.03	<0.01			<0.02	<0.02	<0.01			<0.02

GRAPE															
	Study 1	Study 2	Study 3	Study 4	Study 5	Study 6	Study 7	Study 8	Study 9	Study 10	Study 11	Study 12	Study 13	Study 14	Mean
Tolyfluanid (mg/kg)															
Bunch	0.24	0.41	0.47	1.7	0.06	0.67	0.35	0.91	0.36	0.57	0.33	1.4	0.46	0.06	
Wine	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	
Must	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.29	0.57	0.93	0.8	1.74	<0.02	<0.02	
Processing factor															
Wine	<0.21	<0.11	<0.11	<0.03	<0.83	<0.07	<0.14	<0.05	<0.06	<0.04	<0.06	<0.01	<0.04	<0.33	<0.16
Must	<0.21	<0.11	<0.11	<0.03	<0.83	<0.07	<0.14	0.32	1.6	1.6	2.4	1.2	<0.04	<0.33	0.57
Tolyfluanid+DMST (mg/kg <sup>1</sup> )															
Bunch	0.35	0.57	0.58	1.94	0.06	0.83	0.46	1.19	0.42	0.75	0.41	1.63	0.61	0.16	
Wine	0.21	0.50	0.26	0.58	<0.05	0.24	0.13	0.57	0.81	1.09	1.51	1.78	0.23	0.19	
Must	0.15	0.32	0.15	0.65	<0.05	0.21	0.15	0.82	0.86	1.68	1.33	2.71	0.41	0.08	
Processing factor															
Wine	0.60	0.87	0.45	0.30	0.83	0.29	0.28	0.48	1.9	1.5	3.7	1.1	0.38	1.2	1.0
Must	0.43	0.56	0.26	0.34	0.83	0.25	0.33	0.70	2.0	2.2	3.2	1.7	0.67	0.50	1.0
Tolyfluanid+DMST+4HMD+2HPD (mg/kg)															
Bunch									1.49	2.12	2.26	3.35	1.17	0.43	
Wine									2.44	2.88	3.89	4.04	0.59	0.33	
Must									1.30	2.29	2.02	3.30	0.64	0.22	
Processing factor															
Wine									1.6	1.4	1.7	1.2	0.50	0.76	1.2
Must									0.87	1.1	0.89	1.0	0.55	0.51	0.82
	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean
	Tolyfluanid (mg/kg)			Tolyfluanid+DMST (mg/kg <sup>1</sup> )			Tolyfluanid+DMST+4HMD+2HPD (mg/kg)			Study 1	Study 2	Mean	Study 1	Study 2	Mean
Bunch	0.05	0.03		0.05	0.03		0.49	0.36							
Juice	<0.02	<0.02		<0.02	<0.02		0.53	0.30							
Pomace, wet	0.12	0.5		0.31	0.74		0.96	1.37							
Pomace, dry	0.13	0.53		0.34	1.31		1.21	2.77							
Dried grape	<0.05	<0.05		<0.05	0.16		1.79	1.49							
Raisin waste	0.51	0.39		1.27	0.94		2.66	1.66							
	Processing factor			Processing factor			Processing factor			Study 1	Study 2	Mean	Study 1	Study 2	Mean
Juice	<0.4	<0.7	<0.5	<0.4	<0.7	<0.53	1.1	0.83	1.0						
Pomace, wet	2.4	17	9.7	6.2	25	16	2.0	3.8	2.9						
Pomace, dry	2.6	18	10	6.8	43	25	2.5	7.6	5.1						
Dried grape	<1.0	<1.7	<1.3	1	5.3	3.2	3.7	4.1	3.9						
Raisin waste	10	13	12	25	31	28	5.4	4.6	5.0						
BLACKCURRANT															
	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean
	Tolyfluanid (mg/kg)			Tolyfluanid+DMST (mg/kg <sup>1</sup> )			Tolyfluanid+DMST (mg/kg <sup>1</sup> )			Study 1	Study 2	Mean	Study 1	Study 2	Mean
Fruit	1.1			1.76			1.76								
Fruit, washed	0.64			1.48			1.48								
Juice	<0.02			0.45			0.45								
Jelly	<0.02			0.99			0.99								
	Processing factor			Processing factor			Processing factor			Study 1	Study 2	Mean	Study 1	Study 2	Mean
Fruit, washed	0.58			0.84			0.84								
Juice	<0.02			0.26			0.26								
Jelly	<0.02			0.56			0.56								
STRAWBERRY															
	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean	Study 1	Study 2	Mean
	Tolyfluanid (mg/kg)			Tolyfluanid+DMST (mg/kg <sup>1</sup> )			Tolyfluanid+DMST (mg/kg <sup>1</sup> )			Study 1	Study 2	Mean	Study 1	Study 2	Mean
Fruit	3.0	2.4		3.94	3.18		3.94	3.18							
Fruit, washed	1.6	1.2		2.41	1.78		2.41	1.78							
Jam	<0.02	0.02		0.87	0.70		0.87	0.70							
Canned fruits	0.20	0.18		0.85	0.65		0.85	0.65							
	Processing factor			Processing factor			Processing factor			Study 1	Study 2	Mean	Study 1	Study 2	Mean
Fruit, washed	0.53	0.50		0.61	0.56		0.61	0.56							
Jam	<0.007	<0.008		0.22	0.22		0.22	0.22							
Canned fruits	0.067	0.075		0.22	0.20		0.22	0.20							

TOMATO								
	Study 1	Study 2	Study 3		Study 1	Study 2	Study 3	Mean
	Tolyfluanid (mg/kg)				Tolyfluanid+DMST (mg/kg <sup>1</sup> )			
Fruit	0.21	0.05	0.79		0.26	0.05	1.02	
Juice	<0.02	<0.02	<0.02		0.03	0.05	0.45	
Paste	<0.02	<0.02	<0.02		0.16	0.47	1.94	
Purée	<0.02	<0.02	<0.02		0.11	0.21	0.53	
Pomace, wet	0.13	0.27			0.34	0.53		
Pomace, dry	0.47	0.66			2.90	4.55		
	Processing factor				Processing factor			
Juice	<0.1	<0.4	<0.03	<0.2	0.12	1.0	0.44	0.52
Paste	<0.1	<0.4	<0.03	<0.2	0.62	9.4	1.9	4.0
Purée	<0.1	<0.4	<0.03	<0.2	0.42	4.2	0.52	1.7
Pomace, wet	0.62	5.4		3.0	1.3	11		6.2
Pomace, dry	2.2	13		7.7	11	91		51
HOP								
	Study 1	Study 2			Study 1	Study 2		Mean
	Tolyfluanid (mg/kg)				Tolyfluanid+DMST (mg/kg <sup>1</sup> )			
Cone, dried	3.6	11			5.4	18		
Beer	<0.02	<0.02			<0.02	0.04		
Spent hops	0.28	0.32			2.71	3.24		
Hops draff	<0.50	<0.50			<0.50	<0.50		
Brewer's yeast	<0.10	<0.10			<0.10	<0.10		
	Processing factor				Processing factor			
Beer	<0.006	<0.002		<0.004	<0.003	0.002		0.003
Spent hops	0.078	0.029		0.053	0.50	0.18		0.34
Hops draff	<0.14	<0.045		<0.092	<0.093	<0.027		0.060
Brewer's yeast	<0.028	<0.009		<0.018	<0.018	<0.0056		0.012

<sup>1</sup> Expressed as tolyfluanid

### Residues in the edible portion of food commodities

The information on residues in the edible portion of melons is in Table 30 (supervised trials).

The plant metabolism studies on apples and strawberries indicate that washing them removes most of the tolyfluanid on their surfaces (see Tables 5 and 7).

### RESIDUES IN ANIMAL COMMODITIES

#### Farm animal feeding studies

Of those commodities for which maximum residue levels were estimated, apple pomace is used as feed for cattle, but no feeding studies were reported on cattle. A metabolism study with one lactating goat reported in the animal metabolism section showed no tolyfluanid residue in edible tissues or milk but significant amounts of DMST in the muscle, liver and fat.

No RAC or its processed products are used as feed for pigs or poultry.

### NATIONAL MAXIMUM RESIDUE LIMITS

National MRLs were reported by Bayer AG and by the governments of Germany and The Netherlands.

Country Residue definition (if not tolyfluanid)	Commodity	MRL mg/kg	Note
Australia	Strawberry	3	
Austria	Pome fruits	5	

Country Reside definition (if not tolyfluanid)	Commodity	MRL mg/kg	Note
	Strawberry	5	
	Other commodities of plant origin	0.1	
Belgium	Fruiting vegetables	5	
	Lettuce and similar commodities	5	
	Other fruits	5	
	Other commodities of plant origin	0	Below the limit of determination (0.05 mg/kg)
	Pome fruits	2	
	Strawberry	3	
Brazil	Beans	0.5	
	Cotton	0.5	
	Maize	0.5	
	Soya beans	0.5	
Denmark	Berries and small fruits	5	
	Other fruits	5	
	Pome fruits	5	
	Stone fruits	5	
Finland Sum of dichlofluanid and tolyfluanid	Berries	10	
	Grape	10	
	Lettuce	10	
	Other fruits	5	
	Other vegetables	5	
France	Apple	2	
	Other pome fruits	2	
	Pear	2	
Germany	Berries and other small fruits (other than wild)	5	Including strawberry, <i>Rubus</i> spp. and grapes
	Cucumber and gherkin	2	
	Hop	30	
	Lettuce and similar commodities	1	
	Melons	2	
	Other commodities of plant origin	0.1	
	Pome fruits	5	
	Tomato	2	
Netherlands Dimethylaminosulfotolui- dide	Blackberry	10	
	Cucurbits (with edible peel)	5	
	Cucurbits (without edible peel)	5	
	Endive	1	
	Grapes	5	
	Kohlrabi	0.1	
	Lettuce	1	
	Other berries and small fruits	10	
	Other commodities of plant origin	0.1 *	
	Pome fruits	2	
	Raspberry	10	
	Solanaceae	5	
	Strawberry	10	
Republic of Korea	Apple	5	
	Grape	5	
	Lettuce	1	
	Pear	5	
	Strawberry	3	
	Tomato	2	
Spain	Beet, sugar	0.1	
	Berry, wild	0.1	
	Brassica vegetables	0.1	
	Bulb vegetables	0.1	
	Cacao	0.1	
	Cereals	0.1	
	Citrus fruit	0.1	
	Coffee	0.1	

Country Residue definition (if not tolyfluanid)	Commodity	MRL mg/kg	Note
	Cola	0.1	
	Corn, sweet	0.1	
	Cucurbits with edible peel	0.1	
	Cucurbits with inedible peel	0.1	
	Forage crops and straw	0.1	
	Fruit and vegetables, dried	0.1	
	Grape	0.1	
	Herbs	0.1	
	Hop	0.1	
	Leafy vegetables	0.1	
	Legume vegetables	0.1	
	Mushroom	0.1	
	Nuts	0.1	
	Oil plants seed	0.1	
	Other berries and small fruits	0.1	
	Other solanacea	0.1	
	Pome fruits	3	
	Potato	0.1	
	Pulses	0.1	
	Root and tuber vegetables	0.1	
	Rubus-Species (Cane fruit)	0.1	
	Spices	0.1	
	Stem vegetables	0.1	
	Stone fruit	0.1	
	Strawberry	3	
	Sugarcane	0.1	
Tea	0.1		
Tomato	1		
Trop. and subtrop. Fruit	0.1		
Sweden	Fruit	3	
	Vegetables	3	
Switzerland	Blackberry	5	T
	Cucumber	2	T
	Grape	5	T
	Grape, wine	1	T
	Lettuce	1	T
	Pome fruits	2	T
	Raspberry	5	T
	Strawberry	3	T
	Tomato	2	T

T: temporary tolerance

## APPRAISAL

Tolyfluanid, fungicide closely related to dichlofluanid, was first evaluated for toxicology and residues by the Meeting in 1988, with subsequent residue evaluation in 1990. The Meeting in 1988 recommended the residue definition of tolyfluanid. Currently there are Codex MRLs for currants, black, red, white; gherkin; lettuce, head; pome fruits; strawberry; and tomato. The compound was included in the Codex priority list for periodic review included in the Codex priority list at the 30th Session of the CCPR (1998; ALINORM 99/24, Appendix VII).

The Meeting received extensive information on the metabolism and environmental fate of tolyfluanid, methods of analysis for residues, stability in freezer storage, national registered use patterns, the results of supervised trials in support of the existing CXLs for pome fruits, strawberry, black currant, tomato and head lettuce and new maximum residue levels for blackberry, raspberry, grapes, cucumber, melons, sweet pepper, leek and hop, the fate of residues in processing and national

MRLs. Poland provided the GAP information and summary trial data on apple and strawberry. Germany and the Netherlands provided the GAP information.

### Animal metabolism

The metabolism of tolyfluanid was studied in rats, a lactating goat and laying hens using [phenyl-U-<sup>14</sup>C]tolylfluanid and [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid.

When rats were dosed orally with [phenyl-U-<sup>14</sup>C]tolylfluanid or [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid at up to 100 mg/kg bw, radioactivity was rapidly absorbed; higher than 95% of the administered [phenyl-U-<sup>14</sup>C]tolylfluanid was absorbed and about 70 to 80% of the administered [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid was absorbed. The absorbed radioactivity, whether [phenyl-U-<sup>14</sup>C]tolylfluanid or [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid was used, was eliminated almost completely at a fast rate, mainly via urine and to much lesser extent via faeces. Two days after oral administration, only a small portion (less than 0.5% in the case of [phenyl-U-<sup>14</sup>C]tolylfluanid and less than 1.8% in the case of [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid) of the administered radioactivity was retained in body excluding gastrointestinal tract. This implies that no accumulation of tolyfluanid was expected. The main radioactive metabolites in urine, when phenyl-labelled tolyfluanid was used, were identified as 4-(dimethylaminosulfonylamino)benzoic acid (mean, 68% of the recovered radioactivity), and 4-(methylaminosulfonylamino)benzoic acid (mean, 5%). The parent compound, tolyfluanid, and *N,N*-dimethyl-*N'*-*p*-tolylsulfamide. (dimethylaminosulfonotoluidine DMST) were found only in faeces (8% and 7% respectively). When dichlorofluoromethyl-labelled tolyfluanid was used, the main metabolite in urine was thiazolidine-2-thioxo-4-carboxylic acid (TTCA)(73-74% of the recovered radioactivity).

[Phenyl-U-<sup>14</sup>C]tolylfluanid administered by gavage to a lactating goat at a rate equivalent to 250 ppm in diet was also rapidly absorbed and then eliminated in urine (49% of the administered radioactivity 2 hours after the last dose) and faeces (10% of the administered radioactivity). At the time of slaughter, only 2.8% of the administered dose remained in edible tissues and organs: mostly in kidney and liver with only a small portion (0.24%) in milk. The main metabolites in organs and milk were 4-(dimethylaminosulfonylamino)hippuric acid and 4-(dimethylaminosulfonylamino)benzoic acid. Smaller amounts of 4-(methylaminosulfonylamino)benzoic acid and 4-(methylaminosulfonylamino)hippuric acid were also found. The parent compound was not detected in any of edible tissues/organs or milk while DMST was present at a significant amount in muscle, liver and fat.

[Phenyl-U-<sup>14</sup>C]tolylfluanid administered orally to laying hens at a rate equivalent to 83 ppm in diet was readily absorbed and eliminated (84% of the administered radioactivity 8 hours after the last dose). On average less than 0.01% of the administered radioactivity was found in eggs. At sacrifice the total radioactive residues in the tissues and organs were about 0.18% of the administered radioactivity, highest levels being found in kidney and liver. The main metabolite in tissues/organs was 4-(dimethylaminosulfonylamino)benzoic acid. The parent compound was not detected in muscle, fat, liver or eggs. DMST was the major metabolite in fat.

### Plant metabolism

The Meeting received information on the fate of tolyfluanid after application to apples, grapes, strawberries and lettuce.

Individual apples were sprayed with radio-labelled tolyfluanid. A majority of the total radioactive residues (TRR) was located on the surface of apples collected (92% of TRR on day 7 and 88% on day 14 in a study using [phenyl-U-<sup>14</sup>C]tolylfluanid and 71% on day 28 in a study using [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid). These residues on the surface were removed by surface washing. The predominant radioactive component on apples was identified as the parent compound (88% of TRR on day 7 and 82% on day 14 in a study using [phenyl-U-<sup>14</sup>C]tolylfluanid and 72% on

day 28 in a study using [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid). A small amount of DMST was formed on the surface and in the peel plus pulp after the application of tolylfluanid.

Grape bunches were sprayed twice with [phenyl-U-<sup>14</sup>C]tolylfluanid at a total rate of approximately 1.3 mg a.i./bunch. Thirty-five days after the last application, the TRR in the bunch of grapes (excluding stems and stalks) declined to about 50% of the applied dose, in which unchanged tolylfluanid and DMST accounted only for 13% and 1.9% of the TRR. The major metabolites on/in grapes were identified as 4-hydroxymethyl-DMST-glucoside (46% of the TRR), 2-hydroxyphenyl-DMST-glucoside (13%) and 3-hydroxyphenyl-DMST-glucoside (1.8%). Eight minor metabolites were identified which were derived through further conjugation of the above-mentioned glucosides.

Fourteen days after the last aerial application of [phenyl-U-<sup>14</sup>C]tolylfluanid to strawberries, a total of 72.5% of the TRR was located on the surface of berries, of which 63% was attributed to unchanged tolylfluanid. The washed fruit contained 27.5% of the TRR. The major metabolites were identified as DMST (6.2% of the TRR in surface rinse and 8.7% in fruit), 4-hydroxymethyl-DMST-glucoside (1.0% in surface rinse and 5.6% in fruit), 4-hydroxymethyl-DMST (0.8% in surface rinse and 2.1% in fruit), and hydroxyphenyl-DMST-glucoside (0.3% in surface rinse and 1.5% in fruit; the position of hydroxyl group not determined). When strawberry plants were sprayed with [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid in a form of spray in a closed air-flow controlled system, <sup>14</sup>CO<sub>2</sub> was released (4.3-12% of the applied radioactivity). The analysis of radioactive compounds in fruits showed that the parent compound accounted for 1.3% of the TRR and TTCA 50% of the TRR. However, the presence of TTCA was detected only in one study employing artificial conditions of closed chamber. TTCA was not detected in studies more reflective of agricultural practices.

Lettuce plants at three different growth stages were sprayed with [phenyl-U-<sup>14</sup>C]tolylfluanid. The TRR in lettuce declined sharply with longer period after the last application. The predominant residue component in lettuce leaves was unchanged tolylfluanid accounting for more than 90% of the TRR on 7, 14 and 21 days after the last application. DMST, 4-hydroxymethyl-DMST-glucoside were identified as minor metabolites.

In plant metabolism, tolylfluanid was the major residue component except in the case of grapes in which the major component was 4-hydroxymethyl-DMST-glucoside followed by tolylfluanid and 2-hydroxyphenyl-DMST-glucoside. Tolylfluanid was found mostly on the surface of crops tested. The metabolic patterns were similar in all plants studied although the metabolic rates differed from species to species with a higher rate seen in grapes.

## Environmental fate

### *Soil*

The incubation of [phenyl-U-<sup>14</sup>C]tolylfluanid in four different soils in the dark under aerobic conditions at 22°C for 99 days revealed rapid degradation of tolylfluanid mainly to DMST, which was further degraded to 4-(dimethylaminosulfonylamino)benzoic acid, 4-(methylaminosulfonylamino)benzoic acid and methyltolylsulfamide and to CO<sub>2</sub> (25-40% of the applied radioactivity on day 99). The increase of unextractable radioactivity was observed over time after the application (52-72% of the applied radioactivity on day 99). The incubation of [dichlorofluoromethyl-<sup>14</sup>C]tolylfluanid in two different soils in the dark under aerobic conditions at 22°C for 65 days showed the degradation of tolylfluanid to CO<sub>2</sub> (65-77% of the applied radioactivity after 65 days) while formation of unextractable residues occurred over time (7-40% of the applied radioactivity). The calculated half life of tolylfluanid at 20 or 22°C was shorter than 3 days in all studies conducted and that of DMST at 20 or 22°C was in a range of 1.3-6.7 days indicating that the degradation of DMST was also fast.

Adsorption/desorption experiments with soil/water systems were not applicable to tolylfluanid due to its rapid hydrolysis. A K<sub>oc</sub> value of tolylfluanid was estimated using an HPLC



method to be 2220 ml/g and  $\log K_{oc}$  was 3.35. This result indicates that tolyfluanid could be classified as an immobile substance. Absorption/desorption studies were carried out for DMST, the only major metabolite of tolyfluanid formed in the aerobic soil degradation studies (see above). DMST was classified as a substance with low to intermediate mobility.

In leaching studies in which soil samples were aged with [phenyl-U-<sup>14</sup>C]tolylfluanid and then placed on top of a saturated column, tolyfluanid was demonstrated to be immobile in soil while DMST slightly mobile. These results indicate that the leachate of either tolyfluanid or DMST was not likely to contaminate groundwater. This was confirmed by a computer simulation of environmental concentrations of tolyfluanid and DMST in groundwater recharge.

Due to the very short half-life of tolyfluanid, no studies could be conducted on photolysis in the field conditions.

#### *Water-sediment systems*

In a study of hydrolysis, tolyfluanid was readily hydrolyzed into DMST under all conditions used (pH 4, 7 and 9; 20, 30 and 40°C). The half life of tolyfluanid was calculated to be 11.7 days at pH 4 and 29.1 hours at pH 7 at 22°C in respective sterile buffer solutions. Tolyfluanid was so unstable at pH 9 that no parent compound was left to be detected even in immediate analysis of the sample making the estimation of half life impossible. Another hydrolysis study demonstrated that tolyfluanid was hydrolyzed into DMST, fluoride ion, chloride ion, sulfur and carbon dioxide. DMST, on the other hand, was stable at pH 4, 7 and 9 up to 55°C in respective sterile buffer solutions. The half life of DMST was calculated to be >1 year at 22°C at pH 4, 7 and 9.

The major degradation product in aqueous hydrolysis, DMST, showed resistance against direct photodegradation in aqueous solution without yielding major degradation products. The half life of environmental direct photolysis of DMST was estimated using one modelling to be a minimum of approximately 2 months (at 30° N) or 3 months (at 50° N) for the period of main use (July-August) and using another to be longer than 1 year. These results indicate that direct photodegradation in aqueous solution was expected to contribute little to the elimination of DMST in the environment.

The biological degradation of tolyfluanid and DMST was examined in three aqueous sediment systems. Tolyfluanid was degraded so rapidly in the three systems tested that it was not detected in the sample taken on day 14 and therefore its half life could not be estimated. The radioactivity in the water decreased and the unextractable radioactivity increased continuously. DMST, the predominant degradation product in water and sediment, was further degraded to demethylated compound, methyltolylsulfamide, and finally mineralized to CO<sub>2</sub>. The half life of DMST in the supernatant water was calculated to be 42 – 76 days. In another aerobic aquatic degradation study using aquatic model water/sediment systems, the half life of tolyfluanid was calculated to be 1.4-5 hours.

#### **METHODS OF ANALYSIS**

For the determination of residues of tolyfluanid and DMST, gas chromatographic methods with various detectors and HPLC/MS/MS methods were reported for various matrices.

The gas chromatographic methods generally employ extraction, partition, clean-up and determination using electron capture detector, flame photometric detector, nitrogen-phosphorus detector, or mass spectrometry. Most methods are capable of determining both tolyfluanid and DMST residues in supervised trials. Some methods were developed to determine residues arising from the use of not only tolyfluanid but also organohalogen, organophosphorus, triazine, etc.. The limit of quantification for tolyfluanid or DMST was in most cases, either 0.02 mg/kg or 0.05 mg/kg. For enforcement purposes, gas chromatographic methods were validated for apple, grapes, strawberry,

canola seed/rape seed, hops, water-containing matrices and commodities of animal origin. Confirmatory methods are available for all of these matrices. Gas chromatographic methods have also been validated for enforcement and confirmatory purposes for soil, water and air.

HPLC/MS/MS methods generally employ extraction, evaporation, partition/clean-up and determination using liquid chromatography with a triple-stage quadrupole mass spectrometer with an electrospray interface in the multiple-reaction monitoring mode. The limit of quantification is 0.02 mg/kg for tolylfluanid and DMST in black currant, strawberry, tomato and tomato products, lettuce, peppers and leek.

### **STABILITY OF RESIDUES IN STORED ANALYTICAL SAMPLES**

Stability of tolylfluanid and metabolites in freezer storage was tested for a range of plant commodities under conditions representative of intended uses of tolylfluanid. Studies were conducted on apples (fruit), grapes (fruit, juice and wine), tomatoes (fruit, puree and juice), and hops (green and dry hop cones). In all studies, tolylfluanid and DMST were determined. In studies on grapes 4-hydroxymethyl-DMST-glucoside and 2-hydroxyphenyl-DMST-glucoside were determined as well as tolylfluanid and DMST because these two glucosides were also major residue components found in bunches of grapes treated with tolylfluanid. Tolyfluanid and DMST were generally stable in samples for the intervals tested:

- ✓ 2.2 years: grapes and grape juice
- ✓ 1.5 years: apples and tomatoes
- ✓ 1 year: green hop cones and dry hop cones
- ✓ 4 months: tomato juice and tomato puree

In grape wine, the degradation of tolylfluanid into DMST was observed. The sum of tolylfluanid and DMST remained relatively constant over 2.2 years. However, the concentration of tolylfluanid showed some decrease already on day 29 of storage. 4-Hydroxymethyl-DMST-glucoside and 2-hydroxyphenyl-DMST-glucoside were stable for up to 2.2 years in grapes, grape juice and grape wine in deep freezer.

Tolyfluanid is very susceptible to hydrolysis. Aqueous extracts of grapes and aqueous samples (grape juice and wine) were fortified with tolylfluanid, DMST, 4-hydroxymethyl-DMST-glucoside or 2-hydroxyphenyl-DMST-glucoside and kept at 4-8°C for 21 to 31 days. In aqueous extracts only DMST was stable and in juice and wine the two glucosides were also stable. The degradation of tolylfluanid into DMST was observed also in this study. This indicates that aqueous extracts and aqueous samples must be analyzed at once for determining tolylfluanid without storing them in refrigerator.

### **DEFINITION OF THE RESIDUE**

When applied to crops, tolylfluanid is metabolized to form DMST. DMST is further metabolized to hydroxylated metabolites and their glucosides. Generally tolylfluanid is the main residue found in plants after application of tolylfluanid except that in grape 4-hydroxymethyl-DMST-glucoside and 2-hydroxymethyl-DMST-glucoside accounted for about 60% of the TRR. Thiazolidine-2-thione-4-carboxylic acid (TTCA), a substance of toxicological concern, was identified in one strawberry study under an artificial test condition and is not expected to arise under normal agricultural conditions.

In animals, tolylfluanid is rapidly metabolized and no parent compound was detected in tissues and organs of farm animals. DMST, 4-(dimethylaminosulfonylamino)benzoic acid and 4-(dimethylaminosulfonylamino)hippuric acid are significant metabolites present in tissues and organs.

Products of further metabolism of DMST are not of toxicological significance. Due to the rapid metabolism of tolylfluanid to DMST, it is not possible to distinguish long term effects of DMST

from those of tolyfluanid except for fluoride deposition. The acute oral toxicity of DMST is comparable to that of tolyfluanid.

The Meeting recommended that definition of the residue for commodities derived from plants should be as follows:

For compliance with MRLs: tolyfluanid

For the estimation of dietary intake: tolyfluanid and DMST expressed as tolyfluanid.

## RESULTS OF SUPERVISED TRIALS

The results of supervised trials were available for use of tolyfluanid on apples and pears, grapes, black currants, blackberries, raspberries, strawberries, cucumber, melons, tomato, peppers, lettuce, leek and hop. Relevant GAP information is available for all of the above crops.

The sum of tolyfluanid and DMST was calculated and expressed as tolyfluanid on the basis of the molecular weight of tolyfluanid (347.3 g/mol) and DMST (214.3 g/mol). When tolyfluanid or DMST was found to be below the respective limit of quantification or when both were below their respective limits of quantification, the sum of tolyfluanid and DMST was calculated following the examples below and expressed as tolyfluanid:

Tolyfluanid	DMST	Total (expressed as tolyfluanid)
<0.02	<0.02	<0.02
0.10	<0.02	0.10
<0.02	0.10	0.16
0.10	0.10	0.26

Pome fruits. Trials on pome fruits were conducted in France, Germany, Italy, the Netherlands, Poland and Spain.

In Germany, tolyfluanid is registered for use on pome fruits up to a total of 15 applications at 1.1 kg a.i./ha or 0.076 kg a.i./hl with a PHI of 7 days. The concentrations of tolyfluanid residues, in ranked order, in apples from 14 trials in Germany that matched GAP were: 0.18, 0.24, 0.35, 0.46 (2), 0.48, 0.5, 0.55, 0.59, 0.60, 0.92, 1.7, 2.0 and 2.3 mg/kg.

The GAP in the Netherlands allows tolyfluanid application of a maximum of 1.12 kg a.i./ha or 0.075 kg a.i./hl, 7 applications and a PHI of 7 days on apples. The concentrations of tolyfluanid residues in apples from 2 trials in the Netherlands that matched the GAP, in ranked order, were: 0.19 and 0.58 mg/kg.

The residue concentration of tolyfluanid in apples in a trial conducted in Poland in accordance with its GAP (1 kg a.i./ha or 0.20 kg a.i./hl, 2 applications, PHI of 7 days) was 0.44 mg/kg. DMST was not determined in this trial.

The French use pattern on pome fruits allows tolyfluanid to be sprayed at 0.075 kg a.i./hl with a PHI of 7 days. Two apple trials in France, 4 trials in Italy and 1 trial in Spain were evaluated against the French GAP. The concentrations of tolyfluanid residues, in ranked order, were: 0.14, 0.22, 0.50, 0.51, 0.65, 1.2 and 2.3 mg/kg.

The concentrations of tolyfluanid residues, in ranked order, in pears from 2 trials in Germany that matched GAP were: 1.5 and 3.4 mg/kg.

Two pear trials in Italy and one in Spain were evaluated against the French GAP for pome fruits. The concentrations of tolyfluanid residues, in ranked order, were: 0.26, 0.40 and 0.54 mg/kg.

The Meeting agreed to combine the above results for estimating a maximum residue level for pome fruits. The combined results of 29 trials were, in ranked order: 0.14, 0.18, 0.19, 0.22, 0.24, 0.26, 0.35, 0.40, 0.44, 0.46 (2), 0.48, 0.5, 0.50, 0.51, 0.54, 0.55, 0.58, 0.59, 0.60, 0.65, 0.92, 1.2, 1.5, 1.7, 2.0, 2.3 (2) and 3.4 mg/kg for tolyfluanid; and 0.18, 0.19 (2), 0.26, 0.27, 0.29, 0.41, 0.46 (2), 0.51, 0.56, 0.60, 0.64, 0.66, 0.70, 0.74, 0.76, 0.8, 0.83, 0.87, 1.10, 1.3, 1.86, 2.0, 2.6, 2.7, 3.1 and 4.0 mg/kg for the sum of tolyfluanid and DMST expressed as tolyfluanid.

The Meeting confirmed the previous recommendation for maximum residue level of 5 mg/kg for pome fruits and estimated an STMR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 0.68 mg/kg and an HR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 4.0 mg/kg.

Grapes. Trials on grapes were conducted in Chile, France, Italy and Spain.

In Germany tolyfluanid was registered for use on wine grapes up to a total of 8 applications at a maximum of 1.6 kg a.i./ha with a PHI of 35 days. The concentrations of tolyfluanid in ranked order in grapes in 7 trials in Germany that matched GAP were: 0.06, 0.35, 0.49, 0.63, 0.67, 0.91 and 1.7 mg/kg.

The results of trials in Southern France, Italy and Spain were evaluated against the GAP reported for Spain (0.1 kg a.i./hl, PHI of 15 days for table grape and 21 days for wine grape). The concentrations of tolyfluanid residue in grapes in 2 trials that matched the GAP were, in ranked order: 0.11 and 0.13 mg/kg.

The concentrations of tolyfluanid in 3 trials in Chile that matched the GAP in Chile (1.5 kg a.i./ha or 0.125 kg a.i./hl, PHI of 21 days), in rank order, were: 0.24, 0.98 and 1.8 mg/kg.

The above results were regarded to come from similar populations. The combined concentrations from 12 trials, in ranked order, were: 0.06, 0.11, 0.13, 0.24, 0.35, 0.49, 0.63, 0.67, 0.91, 0.98, 1.7 and 1.8 mg/kg for tolyfluanid; and 0.06, 0.11, 0.13, 0.29, 0.46, 0.67, 0.83, 0.84, 1.04, 1.19, 1.9 and 2.0 mg/kg for the sum of tolyfluanid and DMST expressed as tolyfluanid.

The Meeting estimated a maximum residue level of 3 mg/kg, an STMR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 0.75 mg/kg, and an HR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 2.0 mg/kg.

Black currant. Trials were conducted on black currants in Germany and in the United Kingdom.

The GAP in the Netherlands allows the use of tolyfluanid on currants two applications at 1.50 kg a.i./ha or 0.125 kg a.i./hl with a PHI of 21 days. The results of 4 trials in Germany and 4 trials in the United Kingdom were evaluated against GAP in the Netherlands. The concentrations of tolyfluanid in black currants in 8 trials in ranked order were: 0.07, 0.10, 0.12, 0.17, 0.21, 0.28 (2) and 0.31 mg/kg; and the sum of tolyfluanid and DMST expressed as tolyfluanid were: 0.18, 0.25, 0.33, 0.34, 0.35, 0.39, 0.57 and 0.68 m/kg.

The Meeting estimated maximum residue level at 0.5 mg/kg for currants, black, red, white to replace the previous recommendation of 5 mg/kg. It also estimated an STMR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 0.345 m/kg and an HR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 0.68 mg/kg.

Blackberry and raspberry. Trials were conducted on blackberry and raspberry in Germany and the United Kingdom.

The UK GAP allows the use of tolyfluanid on blackberry and raspberry up to 4 applications at 1.7 kg a.i./ha with a PHI of 14 days. The results of blackberry trials conducted in Germany and the United Kingdom were evaluated against the UK GAP. The concentrations of tolyfluanid in blackberries in 2 trials in Germany and 2 trials in the United Kingdom were, in ranked order: 0.61, 1.6, 1.7 and 2.0 mg/kg; and the sum of tolyfluanid and DMST expressed as tolyfluanid: 0.72, 1.9, 2.1 and 2.2 mg/kg.

The results of raspberry trials in Germany and the United Kingdom were evaluated against the above-mentioned UK GAP. The concentrations of tolyfluanid in raspberries in 2 trials in Germany and 2 trials in the United Kingdom were, in ranked order: 0.42, 1.4, 1.7 and 2.4 mg/kg; and the sum of tolyfluanid and DMST expressed as tolyfluanid: 0.48, 1.5, 2.0 and 2.9 mg/kg.

The results of blackberry trials and those of raspberry trials were mutually supportive. The combined results in ranked order were: 0.42, 0.61, 1.4, 1.6, 1.7 (2), 2.0 and 2.4 mg/kg for tolyfluanid; 0.48, 0.72, 1.5, 1.9, 2.0, 2.1, 2.2 and 2.9 mg/kg for the sum of tolyfluanid and DMST expressed as tolyfluanid.

The Meeting estimated the following values for both blackberry and raspberry: maximum residue level, 5 mg/kg; an STMR (sum of tolyfluanid and DMST expressed as tolyfluanid), 1.95 mg/kg; and an HR (sum of tolyfluanid and DMST expressed as tolyfluanid), 2.9 mg/kg.

Strawberry. Trials were conducted outdoors in France, Germany, Italy, the Netherlands, Poland and Spain.

The concentrations of tolyfluanid in 9 trials in Germany matching the German GAP (0.125 kg a.i./hl, 2.5 kg a.i./ha, 3 applications, PHI of 7 days) were, in ranked order: 0.05, 0.47, 0.75, 0.77(2), 0.90, 1.1, 1.4 and 1.9 mg/kg.

The concentration of tolyfluanid in one trial in the Netherlands matching the GAP in the Netherlands (0.125 kg a.i./hl, 0.75-1.25 kg a.i./ha, 5 applications, PHI of 7 days) was: 0.73 mg/kg.

The concentration of tolyfluanid in one trial in Poland matching the GAP in Poland (0.5 kg a.i./hl, 2.5 kg a.i./ha, 3 applications, PHI of 7 days) was: 2.65 mg/kg (DMST not determined).

The results of trials conducted in Southern France, Italy and Spain were evaluated against the GAP in Slovenia (0.1-0.125 kg a.i./hl, PHI of 7 days). The concentrations of tolyfluanid in 14 trials matching the GAP were, in ranked order: 0.03(2), 0.08, 0.12, 0.14, 0.20, 0.23, 0.32, 0.35, 0.41, 0.43, 0.55, 1.7 and 2.6 mg/kg.

These two sets of results seem to belong to similar populations. The combined concentrations from 25 trials in ranked order were: 0.03(2), 0.05, 0.08, 0.12, 0.14, 0.20, 0.23, 0.32, 0.35, 0.41, 0.43, 0.47, 0.55, 0.73, 0.75, 0.77(2), 0.90, 1.1, 1.4, 1.5, 1.7, 1.9, 2.6 and 2.65 mg/kg for tolyfluanid; and 0.14, 0.26, 0.27 (2), 0.35, 0.36, 0.51, 0.54, 0.59 (2), 0.64, 0.71, 0.95, 0.99, 1.06, 1.12, 1.20, 1.32, 1.41, 1.5, 1.7, 2.0, 2.7 and 3.0 mg/kg for the sum of tolyfluanid and DMST expressed in tolyfluanid. The Meeting estimated a maximum residue level of 5 mg/kg to replace the previous recommendation of 3 mg/kg. It also estimated an STMR (sum of tolyfluanid and DMST expressed in tolyfluanid) of 0.84 mg/kg and HR (sum of tolyfluanid and DMST expressed in tolyfluanid) of 3.0 m/kg.

Cucumber. Trials were conducted in Germany (outdoor and indoor), Italy (indoor) and Spain (indoor).

The results of trials conducted outdoors in Germany were evaluated against the GAP in Belgium (both indoor and outdoor; 0.075 kg a.i./hl, PHI of 3 days). The concentrations of tolyfluanid residue found in 4 trials that matched the GAP were, in ranked order: <0.02 and 0.02(3) mg/kg. These

values were not used for the estimation of maximum residue level as these values and those obtained in indoor trials seem to belong to two different populations.

The results of trials conducted indoors in Germany, Italy and Spain were evaluated against the GAP in Belgium (both indoor and outdoor; 0.075 kg a.i./hl, PHI of 3 days). The concentrations of tolyfluanid residue found in 8 trials that matched the GAP were, in ranked order: 0.05, 0.11, 0.18 (2), 0.30, 0.55, 0.57 and 0.64 mg/kg. The sum of tolyfluanid and DMST expressed as tolyfluanid were, in ranked order: 0.05, 0.16, 0.31, 0.34, 0.40, 0.67, 0.68 and 0.96 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg, STMR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 0.37 mg/kg, and HR (sum of tolyfluanid and DMST expressed as tolyfluanid) of 0.96 mg/kg.

The Meeting withdrew the MRL of 2 mg/kg for gherkin as no data were submitted.

Melons except watermelon. Trials were conducted in France and Greece.

The trials were conducted using a spray concentration of 0.45 kg a.i./hl, which is much higher than any of approved use pattern (except those not specified). Only those trials conducted in Northern France could be evaluated against the GAP of Sweden (1.5 kg a.i./ha, 3-4 applications, PHI of 3 days). The concentrations of tolyfluanid in trials that matched the GAP were: 0.03 and 0.08 mg/kg. There is no reported GAP that supports trials conducted in Southern France or Greece.

The Meeting concluded that there is not sufficient data to estimate a maximum residue level, STMR or HR at present.

Tomato. Trials were conducted in Belgium (indoor), France (outdoor, indoor), Germany (outdoor, indoor), Italy (outdoor, indoor), Mexico (outdoor) and Spain (outdoor, indoor).

The results of trials conducted outdoors in Germany were evaluated against the GAP in Germany (1.2 kg a.i./ha, 6 applications, PHI of 3 days). The concentrations of tolyfluanid in 8 trials matching the GAP are, in ranked order: 0.15(2), 0.18, 0.20, 0.27, 0.34, 0.47 and 0.99 mg/kg.

The results of trials conducted outdoors in Southern France, Italy and Spain were evaluated against the GAP in Slovenia (1.25 kg a.i./ha, PHI of 3 days). The concentrations of tolyfluanid in 16 trials matching the GAP are, in ranked order: 0.04, 0.05(2), 0.07, 0.19, 0.21, 0.23, 0.27, 0.31, 0.34, 0.40, 0.42, 0.47, 0.48, 0.49 and 0.50 mg/kg.

The results of trials conducted in greenhouse in Belgium, France, Germany, Italy and Spain were evaluated against the GAP in Belgium (0.075 kg a.i./hl, PHI of 3 days). The concentrations of tolyfluanid in 9 trials matching the GAP are, in ranked order: 0.08, 0.16, 0.24, 0.42, 0.49, 0.59 and 0.72, 1.4 and 2.0 mg/kg.

There is no matching GAP reported for outdoor trials conducted in Mexico.

The Meeting concluded that the results of trials conducted indoors and outdoors were regarded to come from similar populations. The combined results from 33 trials were, in ranked order: 0.04, 0.05 (2), 0.07, 0.08, 0.15 (2), 0.16, 0.18, 0.19, 0.20, 0.21, 0.23, 0.24, 0.27 (2), 0.31, 0.34 (2), 0.40, 0.42 (2), 0.47 (2), 0.48, 0.49 (2), 0.50, 0.59, 0.72, 0.99, 1.4 and 2.0 mg/kg for tolyfluanid; and 0.05 (2), 0.07, 0.10, 0.14, 0.18, 0.22, 0.24, 0.27, 0.29, 0.30, 0.34, 0.35 (2), 0.39, 0.40 (2), 0.42, 0.47 (2), 0.49, 0.50, 0.54, 0.56, 0.58, 0.60 (2), 0.67, 0.70, 0.77, 1.27, 1.5 and 2.2 mg/kg for the sum of tolyfluanid and DMST expressed as tolyfluanid.

The Meeting estimated a maximum residue level of 3 mg/kg to replace the previous recommendation at 2 mg/kg, an STMR (sum of tolyfluanid and DMST expressed in tolyfluanid), 0.39 mg/kg and an HR (sum of tolyfluanid and DMST expressed in tolyfluanid), 2.2 mg/kg.

Peppers. Trials were conducted on sweet peppers indoors in Italy, the Netherlands and Spain.

The results of trials conducted in greenhouse in Italy, the Netherlands and Spain were evaluated against the GAP in the Netherlands for peppers in greenhouse (up to 1.12 kg a.i./ha, 0.075 kg a.i./hl, 3 applications, PHI of 3 days). The concentrations of tolyfluanid residue in 10 trials matching the GAP were, in ranked order: 0.07, 0.20, 0.24, 0.26, 0.28, 0.49, 0.61, 0.66, 0.77 and 1.3 mg/kg for tolyfluanid; and 0.12, 0.34, 0.43, 0.44, 0.62, 0.72, 0.85, 0.95, 1.01 and 1.6 mg/kg for the sum of tolyfluanid and DMST expressed as tolyfluanid.

The Meeting estimated a maximum residue level of 2 mg/kg for peppers, sweet and an STMR (sum of tolyfluanid and DMST expressed in tolyfluanid) of 0.67 mg/kg and an HR (sum of tolyfluanid and DMST expressed in tolyfluanid) of 1.6 mg/kg.

Lettuce, head. Trials were conducted in Belgium, France, Germany, Greece, Italy, Portugal, Spain and the United Kingdom.

The results of trials conducted in Germany were evaluated against the GAP of Germany (0.1 kg a.i./hl, 0.6 kg a.i./ha, 6 applications, PHI of 21 days). The concentrations of tolyfluanid in 8 trials that matched the GAP were, in ranked order: <0.05 (7) and 0.17 mg/kg. The results of trials carried out in Southern France, Italy and Spain could not be evaluated as the closest GAP, which was of Slovenia, requires a PHI of 21 days while the maximum sampling interval of these trials was 10 days. The concentrations of the sum of tolyfluanid and DMST expressed in tolyfluanid were: <0.07 (7) and 0.17 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg to replace the previous recommendation of 1 mg/kg. It also estimated an STMR of 0.05 mg/kg and an HR of 0.17 mg/kg.

Leek. Trials were conducted in Belgium, Northern France, Germany, the Netherlands and the United Kingdom.

The results of these trials were evaluated against the GAP in the Netherlands (1.25 kg a.i./ha, 4-5 applications, PHI of 21 days). The concentrations of residues in 9 trials were, in ranked order: <0.02, 0.17, 0.34, 0.36, 0.58, 0.84, 0.92, 0.94 and 1.2 mg/kg for tolyfluanid; and <0.02, 0.17, 0.41, 0.45, 0.97, 1.07, 1.16, 1.52 and 1.8 mg/kg for the sum of tolyfluanid and DMST expressed in tolyfluanid.

The Meeting estimated a maximum residue level of 2 mg/kg; an STMR (sum of tolyfluanid and DMST expressed in tolyfluanid) of 0.97 mg/kg; and an HR (sum of tolyfluanid and DMST expressed in tolyfluanid), 1.8 mg/kg.

Hops, dry. Trials were conducted in Germany.

The results of trials in Germany were evaluated against GAP in Poland (0.075 kg a.i./hl, 600-3000 l/hl depending on the growth stage, PHI of 14 days). The concentrations of residues in dry hops in 8 trials were, in ranked order: 2.8, 5.4, 7.8, 8.9, 9.1, 10, 11 and 27 mg/kg for tolyfluanid; and 8.8, 13.5, 18, 19.3, 30.0, 31.8, 32 and 71 mg/kg for the sum of tolyfluanid and DMST expressed in tolyfluanid.

The Meeting estimated a maximum residue level of 50 mg/kg, an STMR (sum of tolyfluanid and DMST expressed in tolyfluanid), 25 mg/kg, and an HR (sum of tolyfluanid and DMST expressed in tolyfluanid), 71 mg/kg.

## FATE OF RESIDUES DURING PROCESSING

According to plant metabolism studies, tolylfluanid residue is mainly located on the surface of apples and strawberries and surface washing significantly removed the residues from these fruits (92% in the case of apples harvested 7 days after spray in experimental application; and 73% in the case of strawberries harvested 14 days after spray.).

Processing studies were conducted using apples, black currants, grapes, hops, lettuce, strawberries and tomatoes.

For those commodities for which MRLs were estimated, STMR-P and HR of processed products are calculated using the mean processing factors as follows, except that for the calculation of STMR-P of beer, a processing factor of 0.001 was used:

	Processing factor	STMR/STMR-P <sup>1</sup> (mg/kg)	HR/HR-P <sup>1</sup> (mg/kg)
Pome fruits	-	0.68	4.0
Apple juice	0.09	0.06	
Apple sauce	0.32	0.22	
Canned apple	<0.06	0.04	
Apple pomace, wet	2.7	1.8	
Apple pomace, dry	9.8	6.7	
Pear juice	0.03	0.02	
Canned pear	<0.02	0.01	
Grapes		0.75	2.0
Grape wine	1.0	0.75	
Grape juice	<0.53	0.40	
Grape pomace, wet	16	12	
Grape pomace, dry	25	19	
Dried grape	3.2	2.3	
Currants		0.345	0.68
Black currant, washed	0.84	0.29	0.57
Black currant juice	0.26	0.09	
Black currant jelly	0.56	0.19	
Strawberry		0.84	3.0
Strawberry, washed	0.59	0.50	1.8
Strawberry jam	0.22	0.18	
Canned strawberry	0.21	0.18	
Tomato		0.39	2.2
Tomato juice	0.52	0.20	
Tomato paste	4.0	1.6	
Tomato puree	1.7	0.66	
Tomato pomace, wet	6.2	2.4	
Tomato pomace, dry	51	20	
Hops, dry		25	71
Beer	0.001	0.025	

<sup>1</sup> sum of tolylfluanid and DMST expressed as tolylfluanid

## RESIDUES IN ANIMAL COMMODITIES

### Dietary burden in animals

The Meeting estimated the dietary burden of tolylfluanid residues in farm animals on the basis of the feeding stuffs listed in Appendix IX of the FAO Manual. Among processed products of commodities for which maximum residue levels were estimated, wet apple pomace is used as feed for cattle. No



maximum residue levels were estimated for commodities which or the products of which can be used as feed for pigs or poultry.

Commodity	STM <sup>R</sup> -P <sup>1</sup> mg/kg	Group	Dry matter %	Residue on dry basis mg/kg	% of diet		Residue contribution, mg/kg	
					Beef cattle	Dairy cattle	Beef cattle	Dairy cattle
Apple pomace, wet	1.8	AB	40	4.5	40	20	1.8	0.9
				<b>TOTAL</b>			<b>1.8</b>	<b>0.9</b>

<sup>1</sup> sum of tolyfluanid and DMST expressed as tolyfluanid

**Animal feeding studies**

Although no animal feeding studies were performed, a metabolism study on a lactating goat dosed daily for three days with 10 mg/kg bw of tolyfluanid which is equivalent of 250 ppm in feed, and slaughtered about one hour after the plasma peak level was reached (2 hours after the last dose) showed no tolyfluanid residue in muscle, liver, kidney or milk. Although the goat was fed for only three days, the amount of tolyfluanid administered was far higher than the calculated animal dietary burden. Therefore, the Meeting concluded that residues of tolyfluanid were unlikely to occur in edible tissues/organs or milk of cattle when beef cattle and dairy cattle ingest tolyfluanid and DMST (expressed as tolyfluanid) at 1.8 mg/kg and 0.9 mg/kg in wet apple pomace respectively.

The liver and fat (perirenal, omental and subcutaneous fat) of the goat mentioned above contained total radioactivity of 20.58 and 0.85-2.28 mg/kg in tolyfluanid equivalents, among which 4.83% and 14.68% was identified as DMST respectively. DMST concentrations in the liver and fat tissues were calculated to be 0.613 and 0.077-0.207 mg/kg respectively after the 3 day oral administration of tolyfluanid at a level equivalent to 250 ppm in feed. It was estimated that concentrations of DMST in liver and fat would be very low when cattle ingests wet apple pomace containing 1.8 or 0.9 mg/kg of residues of tolyfluanid and DMST and unlikely to pose risk to health as the estimated dietary intake of tolyfluanid and DMST from liver containing 0.613 mg/kg of DMST (0.993 mg/kg in tolyfluanid equivalents) was less than 0.01% of the ADI, and 1% and 2% of the acute reference dose for general population and for children respectively. The concentrations of DMST in other tissues/organs were expected to be even much lower according to the metabolism study. No DMST was detected in milk in the study. Because the metabolism study was conducted using only one administration level, the Meeting was not able to estimate the concentrations of DMST in edible tissues at the calculated animal dietary burden.

**RECOMMENDATIONS**

On the basis of the data from supervised trials, the Meeting concluded that the maximum residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of residue for compliance with MRLs for plant commodities: tolyfluanid

Definition of residue for the estimation of dietary intake for plant commodities: tolyfluanid and DMST expressed as tolyfluanid

Commodity		Recommended MRL mg/kg <sup>1</sup>		STM <sup>R</sup> /STM <sup>R</sup> -P <sup>2</sup> mg/kg	HR/HR-P <sup>2</sup> mg/kg
CCN	Name	New	Previous		
FB 0264	Blackberries	5	-	1.95	2.9
VC 0424	Cucumber	1	-	0.37	0.96
FB 0021	Currants, Black, Red, White	0.5	5	0.345	0.68
	Black currant, washed			0.29	0.57

Commodity		Recommended MRL mg/kg <sup>1</sup>		STMR/STMR-P <sup>2</sup> mg/kg	HR/HR-P <sup>2</sup> mg/kg
CCN	Name	New	Previous		
JF 1140	Black currant juice			0.09	
	Black currant jelly			0.19	
	Gherkin	W	2		
FB 0269	Grapes	3	-	0.75	2.0
	Grape wine			0.75	
JF 0269	Grape juice			0.40	
DF 0269	Dried grapes			2.3	
DH 1100	Hops, dry	50	-	25	71
	Beer			0.025	
VA 0384	Leek	2	-	0.97	1.8
VL 0482	Lettuce, Head	0.2	1	0.05	0.17
VO 0445	Peppers, sweet	2	-	0.67	1.6
FP 0009	Pome fruits	5	5	0.68	4.0
JF 0226	Apple juice			0.06	
	Apple sauce			0.22	
	Canned apple			0.04	
	Pear juice			0.02	
	Canned pear			0.01	
FB 0272	Raspberries, Red, Black	5	-	1.95	2.9
FB 0272	Strawberry	5	3	0.84	3.0
	Strawberry, washed			0.50	1.8
	Strawberry jam			0.18	
	Canned strawberry			0.18	
VO 0448	Tomato	3	2	0.39	2.2
JF 0448	Tomato juice			0.20	
	Tomato paste			1.6	
	Tomato puree			0.66	

<sup>1</sup> tolylfluanid

<sup>2</sup> sum of tolylfluanid and DMST expressed as tolylfluanid

## DIETARY RISK ASSESSMENT

### Long-term intake

The International Estimated Dietary Intakes (IEDIs) were calculated for the five GEMS/Food regional diets using STMRs for 12 commodities and STMR-P for dried grapes, tomato juice and tomato paste estimated by the current Meeting (Appendix III). A new ADI of 0-0.08 mg/kg bw was proposed by the current Meeting. The calculated IEDIs were 0-2% of the ADI. The Meeting concluded that the intake of residues of tolylfluanid and DMST resulting from the uses considered by the current JMPR was unlikely to present a public health concern.

### Short-term intake

The International Estimated Short-Term Intakes (IESTI) for tolylfluanid and DMST were calculated for commodities for which STMRs and/or HRs were estimated by the current Meeting. An acute reference dose of 0.5 mg/kg bw was proposed by the current Meeting. The IESTIs for children range from 0 to 68% of the acute reference dose and those for general population range from 0 to 24% of the acute reference dose. The Meeting concluded that the short-term intake of residues of tolylfluanid and DMST from uses considered by the current JMPR was unlikely to present a public health concern.

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