PYRAZOPHOS (153)

EXPLANATION

Pyrazophos was reviewed for the first time in 1985 but the data base at that time was inadequate for the estimation of an ADI; some Guideline Levels were recorded. Some additional data were reviewed in 1987 and in 1992, when the toxicological data were deemed sufficient for the estimation of an ADI, the previous Guideline Levels being converted, unchanged, into MRLs. However, the late submission of relevant information on GAP did not allow enough time to complete the evaluation of the residue data. This was therefore postponed until this Meeting.

Although full up-to-date GAP data were provided this year, only limited information was received relating to the previously expressed desiderata on the effects of processing on incurred residues of pyrazophos. No new data were presented on residues in animal products or the identities of plant metabolites.

USE PATTERN

Pyrazophos is a systemic fungicide especially active against powdery mildews and is generally used, both for preventive and curative treatments, as a 30% emulsifiable concentrate, with some use of a 30% wettable powder. Major uses are on cereals, cucurbits and some fruits, with lesser use on vegetables and hops and some applications in the culture of ornamentals and tobacco.

Information was provided on current GAP in 25 countries; this is summarized in Table 1.

Table 1. Pyrazophos - registered use rates and patterns. Nearly all formulations used are 30% EC; a very few are 15% WP mixtures.

Crop	Country	Appl. rate (kg ai/ha)	No. of appl.	PHI (days)	Comments
Apple	Argentina	0.09	-	21	10-14 day intervals
	Costa Rica	0.012-0.03	-	15	7-15 day intervals
	Egypt	0.45	1	-	Interval, 15 days
	France	0.3	3	15	
	Germany	0.221 or 0.331	15 or 12	28	7-14 day intervals
	Greece	0.135-0.48	1-2	14	
	Indonesia	0.1-0.2	4	14	
	Portugal	0.15-0.3	1-2	21	
	Rep. of Korea	1.35	unlim.	14	
	UK	0.165	-	ı	7-14 day intervals
Apricot	Egypt	0.45	1	-	Interval, 15 days
	France	0.3	3	15	

Crop	Country	Appl. rate (kg ai/ha)	No. of appl.	PHI (days)	Comments
Artichoke, Globe	Italy	0.04-0.08	2	7	
Barley	France	0.2	3	30	
	Germany	0.3 or 0.588	max. 2	49	
	Ireland	0.6	2		
	Rep. of Korea	0.36	unlim.	42	
Broccoli	Netherlands	0.15-0.3	-		
Brussels sprouts	Ireland	0.33-0.99	1	14	
	Netherlands	0.15-0.3	-	21 or 35	
	UK	0.33	1-3	14	
Cauliflower	Netherlands	0.15-0.3	-	-	
Cereals	Spain	0.045-0.12	1-2	15	
Chinese cabbage	Netherlands	0.15-0.3	-	21	
Citrus fruits	Indonesia	0.15-0.2	3	7-14	
Cole crops	Costa Rica	0.012-0.03	-	15	7-15 day intervals
	Dominican Republic	0.012-0.03	-	-	7-14 day intervals
Common bean	Spain	0.18-0.45	2-3	15	
Cucumber	Belgium	0.5-0.75	max. 10	3	
	Denmark	0.24	max. 10	3	
	France	0.15	3	3	
	Germany	0.07-0.141	max. 10	3	7 to 10 day intervals
	Greece	0.054-0.336	1-2	3	
	Netherlands	0.15-0.3	-	3	
	Portugal	0.15	2-3	3	
	Republic of Korea	0.45	unlim.	3	
Cucurbits	Argentina	0.09	-	7	10 day intervals
	Costa Rica	0.012-0.03	-	15	7-15 day intervals
	Dominican Republic	?	-	-	7-14 day intervals
	Egypt	0.12	1	-	Interval, 10- 14 days
	Guatemala	0.067	1	-	Local use only
	Italy	0.04-0.08	2-3	7	
	Philippines	Spot treatment	-	3	3-9 g ai/16 l
	Spain	0.18-0.45	2-4	15	
	Venezuela	0.075-0.18	-	3	7-14 day intervals
Egg plant	Spain	0.18-0.45	2-3	15	
Fruit trees	Denmark	0.3	4	14	
Fruits	Colombia	0.435	-	-	
	Ecuador	0.09	2	-	
	Venezuela	0.075-0.18	-	3	7-14 day intervals
Gherkin	Netherlands	0.12-0.15	-	3	
Grapes	Argentina	0.09-0.18	-	28	
	Dominican Republic	?	-	-	7-14 day intervals

Crop	Country	Appl. rate (kg ai/ha)	No. of appl.	PHI (days)	Comments
	Egypt	0.714	1	-	Interval, 15 days
	Greece	0.054-0.192	2-3	21	
	Italy	0.14-0.21	1-2	21	
	Thailand	0.015-0.045	3	21	
Hops	UK	max 0.33	1-3	-	10-14 day intervals
Mango	Egypt	2.14	2	-	Interval, 15 days
	Thailand	0.027-0.09	10	14	
Melons	Belgium	0.5-0.75	max. 10	3	
	Brazil	0.18	2	7	
	France	0.15	3	3	
	Greece	0.054-0.336	1-2	3	
	Netherlands	0.12-0.15	-	3	
	Portugal	0.15	2-3	3	
Mushrooms	Netherlands	1.5	_	3	
Peach	Argentina	0.18	-	21	10 day intervals
	Costa Rica	0.012-0.03	-	15	7-15 day intervals
	Egypt	0.60	1	-	Interval, 15 days
	France	0.3	3	15	
	Italy	0.14-0.21	2	21	
Pear	Argentina	0.09	-	21	10-14 day intervals
	France	0.3	3	15	
Peppers, Sweet	Spain	0.18-0.45	2-3	15	
Pome fruit	Spain	0.15-0.3	1-3	15	
Rambutan	Thailand	0.027-0.09	5	14	
Rye	Germany	0.3 or 0.588	max. 2	49	
Scorzonera	Netherlands	0.15	-	7	
Spring barley	UK	0.6	1-3	-	
Squash, Summer	France	0.15	3	3	
	Netherlands	0.12-0.15	-	3	
Stone fruit	Spain	0.15-0.3	1-3	15	
Strawberry	Belgium	0.5-0.75	max. 7	-	Before flowering & after harvest
	Costa Rica	0.012-0.03	-	15	7-15 day intervals
	Denmark	0.24	2-3	21	Up to 3 weeks before harvest
	Dominican Republic	?	-	-	7-14 day intervals
	Germany	0.235	max. 7	-	After harvest
	Greece	0.036-0.096	1-3	7	
	Italy	0.036-0.06	2	7	
	Netherlands	0.06	5-10	14	
Swede	Netherlands	0.3	-	21	
Tomato	Spain	0.18-0.45	2-3	15	
Vegetables	Brazil	0.18	2	7	

Crop	Country	Appl. rate (kg ai/ha)	No. of appl.	PHI (days)	Comments
	Colombia	0.29-0.435	-	-	
	Ecuador	0.15	2	-	
	Greece	0.054-0.288	1-2	21	
	Philippines	Spot treatment	-	3	3-9 g ai/16 l
	Thailand	0.015-0.045	5	14	
	Venezuela	0.075-0.18	ı	3	7-14 day intervals
Watermelon	Indonesia	0.12-0.18	4	7	
	Philippines	Spot treatment	ı	3	3-9 g ai/16 l
	Taiwan	0.15	ı	-	
Wheat	Germany	0.3 or 0.588	2 or 1	49	
	Netherlands	0.15	ı	21	
Winter barley	Denmark	0.6	max. 2	42	
	UK	0.6	1-3	-	

RESIDUES RESULTING FROM SUPERVISED TRIALS

Additional residue data were provided by the manufacturer, Hoechst AG, from supervised trials on fruits, vegetables, and cereals. The earlier data recorded in 1985 (FAO/WHO 1986b) and 1987 (FAO/WHO 1988a) were also reconsidered at this Meeting. Some additional limited residue data were also provided by The Netherlands (Netherlands, 1993) and Spain (Spain, 1993). Summaries of the new data are given in Tables 2, 3 and 4. All reported residues are expressed as mg pyrazophos/kg sample; the analytical method determined only the parent molecule, no relevant levels of metabolites having been detected in plant products.

Fruits - see Table 2.

 $\overline{\text{Apples}}$. In a number of supervised trials carried out in France, $\overline{\text{Germany}}$ and the UK, residues ranged up to about 0.4 mg/kg at the normal PHI of 28 days, consistent with the current MRL of 0.5 mg/kg, although one result of 0.9 mg/kg was observed.

<u>Peaches and nectarines</u>. Four residue trials were carried out in Italy in 1977 at rates of 0.23 and 0.45 kg ai/ha. Residues were up to 0.30 mg/kg, 28 days after treatment at the higher rate. There is no current MRL for peaches.

In one glasshouse trial in Spain in 1988 (Spain, 1993) residues were 0.27 to 0.40 mg/kg, mean 0.33 mg/kg, after 14 days and 0.13 to 0.25 mg/kg, mean 0.19 mg/kg, after 21 days.

Strawberries. Data submitted from three trials in 1967, 1970 and $\overline{1976}$, not previously evaluated, showed that residues were below 0.07 mg/kg after 19-32 days, within the existing MRL of 0.2 mg/kg.

Four trials on strawberries in Spain from 1986 to 1990 (Spain, 1993) showed residues from 0.13 to 0.64 mg/kg after 14 days. Two trials in The Netherlands in 1977 showed residues ranging from 0.04 to 0.08 mg/kg after 7 days, and 0.01 to 0.03 mg/kg after 14/15 days (Netherlands, 1993).

Table 2. Residues of pyrazophos in fruit from supervised trials. All trials were with 30% EC unless otherwise noted.

Crop/ Country/Year	Applica	Application		Residues, mg/kg, at days after last appl.	Ref.
	kg/ha	kg/ha No.			
Apple					
France '73	0.36	9	1	0.03 (32)	A 01354
' 75	0.42	9	2	0.06, 0.07 (34)	A 07780,07782
	0.84	9	2	0.07, 0.07 (34)	A 07781,07783
Germany'74	0.23	14	2	<0.05 (21) [30% WP]	A 04072,04074
	0.3	12	2	0.10 (21) [WP]; 0.20 (21)	A 04070,04076
	0.45	9	2	0.40 (14); 0.20 (21) [30% WP]	A 04073,04075
	0.6	10	1	1.0 (10), 0.40 (14), 0.20 (21) [30% WP]	A 04071
	0.6	9	1	6.0 (10), 0.3 (14), 0.2 (21)	A 04077
'80	0.15	12	1	0.40 (17), 0.40 (22), 0.10 (27)	A 21359
'81	0.22 -0.44	12	1	0.90 (14), 0.60 (21), 0.40 (28)	A 27694
	0.44	12	1	1.0 (14), 2.0 (21), 0.90 (28)	A 27693
'82	0.33	3	2	0.30, 0.40 (21), 0.04, 0.20 (28)	A 25641,25642
' 87	0.13 -0.33	7	4	0.10-0.39 (21), 0.02-0.06 (70)	A 39422-3, 38797-8
UK '74	0.18	4	2	<0.05 (72)	A 05726,05728
	0.18	7	1	<0.05 (90)	A 05727
Nectarine					
Italy '77	0.23	2	1	0.30 (14), 0.07 (21), 0.05 (28)	A 12478
	0.45	2	1	0.40 (14), 0.10 (21), 0.30 (28)	A 12477
Peach					
Italy '77	0.23	2	1	0.90 (14), 0.30 (21), 0.20 (28)	A 12566
	0.45	2	1	0.40 (14), 0.30 (21), 0.20 (28)	A 12567
Spain '88	1.1	1	1	0.70 (7), 0.33 (14), 0.19 (21) [G'house]	Spain 1993
Strawberry					
Finland'76	0.26	3	1	<0.03 (19)	A 14176
N'lands'67	0.15	4	1	0.06 (26), 0.07 (32)	A 00324
' 70	0.12	4	1	0.01 (14), <0.007 (21)	A 01209
Spain '86	0.03	1	1	0.18 (0), 0.95 (3), 0.37 (7), 0.17 (14)	Spain 1993
Spain '87	0.03	1	1	0.72 (0), 0.58 (3), 0.29 (7), 0.17 (14)	Spain 1993
Spain '88	0.03	1	1	1.7 (0). 1.1 (3), 0.92 (7), 0.64 (14)	Spain 1993

Crop/ Country/Year	Application		No. of trials	Residues, mg/kg, at days after last appl.	Ref.
	kg/ha	No.			
Spain '90	0.03	1	1	0.98 (0), 0.95 (3), 0.78 (7), 0.36 (14)	Spain 1993

Vegetables - See Table 3.

Brussels sprouts. Trials data from Germany, The Netherlands and the UK obtained between 1969 and 1984 showed no residues above 0.09 mg/kg after about 21 days, within the current MRL of 0.1 mg/kg.

<u>Cucumbers</u>. Data from field and greenhouse culture studies in Japan showed residues to be generally below 0.01~mg/kg in the whole fruit, 7 or more days after treatment. The current MRL is 0.1~mg/kg.

Egg plant. In two trials in Spain in 1990, residues of 0.05 and
<0.01 mg/kg were found 15 days after treatment.</pre>

<u>Peppers</u>. Data from 4 trials in Japan in 1970 and 4 in Spain in 1990 were made available to the Meeting. At the usual PHI of 14 days, residues were 0.04 mg/kg or less; at 7 days, a maximum of 0.32 mg/kg was found in Japan.

Tomato. In one trial in Spain in 1989 (Spain, 1993) residues ranged from 0.70 mg/kg at 2 days to 0.25 mg/kg at 15 days.

Beetroot. Residues in beetroot 27 days after application were below 0.02 mg/kg in one trial (Netherlands, 1993).

<u>Carrots</u>. No new data on trials on carrots were supplied by Hoeschst. Data from one trial in The Netherlands in 1984 (Netherlands, 1993) showed no residue above the limit of determination of 0.02 mg/kg. The existing MRL is 0.2 mg/kg.

<u>Witloof chicory</u>. In a trial in 1984 in The Netherlands, residues were below 0.02 mg/kg after 60 days (Netherlands, 1993).

Table 3. Residues in vegetables from supervised trials with 30% EC.

Crop/	Application		Residues, mg/kg, at days after	Ref.
Country/Year		trials	last appl.	1

	kg ai/ha	No.			
Brussels sprouts	3				
Germany '84	0.07	4	1	0.25 (7), 0.13 (14), 0.09 (21)	A 33447
N'lands '69	0.3	1	1	0.05 (12), 0.03 (20)	A 00377
'70	0.12	4	1	<0.02 (7), 0.06 (10), 0.05 (14)	A 01047
	0.12-0.3	4	1	0.05 (7), 0.05(10), <0.02 (14)	A 01046
UK '72	0.34	4	1	0.05 (17)	A 01178
Cucumber					
Japan '73	0.45	3	2	<0.01 (7-21) [Field]	A 15610-1
	0.45	3	2	<0.01 (7-21) [Greenhouse]	A 15615,15620
	0.45	5	2	<0.01 (7-21) [Field]	A 15614,15617
	0.45	5	2	<0.01 (7-21) [Greenhouse]	A 15612,15621
	0.75	3	2	<0.01 (7-21)	A 15613,15618
	0.75	5	2	<0.01 (7-21)	A 15616,15619
Spain '92	0.24	1	1	0.09 (3), <0.01 (7, 15) [G'house]	Spain 1993
Melon					
Spain '92	0.2-0.25	1	4	0.03-0.05 (7), 0.02-0.04 (15) [G'house]	Spain 1993
	0.45	1	2	0.08, 0.22 (7);0.05, 0.12 (15) [G'house]	Spain 1993
Squash, Summer		•			
Spain '92	0.26	1	1	0.17 (3), <0.01 (7, 15) [G'house]	Spain 1993
	0.30	1	1	0.07 (3), 0.01(7), <0.01 (15) [G'house]	Spain 1993
	0.36	1	1	0.06 (3), 0.02 (7), <0.01 (15) [G'house]	Spain 1993
	0.38	1	1	0.06 (3), <0.01 (7, 15) [G'house]	Spain 1993
	0.39	1	1	0.01 (3), <0.01 (7, 15)	Spain 1993
Watermelon		1			1
Spain '92	0.21	1	1	0.03 (7), 0.04 (15)	Spain 1993
	0.22	1	1	0.01 (7), <0.01 (15)	Spain 1993
	0.23	1	1	<0.01 (7, 15)	Spain 1993
	0.26	1	1	0.01 (7), <0.01 (15)	Spain 1993
Egg plant		•			
Spain '90	0.34	1	2	0.07,0.10 (7), <0.01,0.05 (15)	Spain 1993
Pepper					
Spain '90	0.22	1	4	0.08-0.17 (7), 0.02-0.04 (14)	Spain 1993
Tomato					
Spain '89	0.45	1	1	0.57 (7), 0.32 (10), 0.25 (15) [G'house]	Spain 1993
Beetroot					
N'lands '84	0.15	2	1	<0.02 (27)	N'lands 1993
Carrot	•	•	•		
N'lands '84	0.15	2	1	<0.02 (27)	N'lands 1993
Witloof chicory	•				
N'lands'84	0.15	2	1	<0.02 (60)	N'lands 1993

Cereals - See Table 4.

 $\overline{\text{Barley}}$. Data from an additional 15 trials on barley were submitted. In all cases residues in the grain were below the current MRL of 0.05 mg/kg.

Rye. No new residue data for rye were available; the previous data were re-evaluated but again deemed insufficient for any recommendation for an MRL.

 $\overline{\text{Wheat}}$. Details of a total of 54 additional trials were made available to the Meeting, all of which were conducted in Germany in 1975-76. The current MRL is 0.05 mg/kg and the new data only served to confirm that figure.

Table 4. Residues of pyrazophos in cereals from supervised trials, all with 30% EC unless otherwise noted.

Crop/ Country/Year	Application		No. of trials	Residues, mg/kg, at days after last appl.	Ref.
	kg/ha	No.			
Barley (grain)					
Germany '74	0.15	1	1	<0.01 (112)	A 04557
'76	0.3	2	4	<0.01-0.04 (49-56) [30% WP]	A 12789,90,92,95
'83-84	0.59	2	2	<0.05 (66, 76)	A 31247-8
' 89	2.25	2	2	<0.01; 0.23 (49)	A 46994-5
Barley (straw)					
'74	0.15	1	3	<0.05, 0.05 (75); <0.01 (112)	A 10177,10179,04557
'76	0.3	2	4	<0.05, 0.10, 0.20, 0.20 (50-56) [30% WP]	A 12788,91,93,94
Wheat (grain)					
Germany '75	0.15	1	4	<0.02 (34-58)	A 05740-3
' 76	0.3	1	16	<0.01-0.02 (33-47) [30% WP]	See {1} below
	0.3	2	5	<0.01-<0.02 (55-56) [30% WP]	A 09276-90
	0.6	2	3	<0.02 (55-56) [30% WP]	A 09278,83,84
Wheat (straw)					
Germany '75	0.15	1	4	<0.06-0.20 (34-58)	A 05740-3
'76	0.3	1	16	0.20-4.7 (33-47) [30% WP]	See {2} below
	0.3	2	5	0.07-1.3 (55-56) [30% WP]	A 09277,80,87,98,91
	0.6	2	3	0.20-2.8 (55-56) [30% WP]	A 09279,83,85

 $^{\{1\} \ \}texttt{References:-} \ \texttt{A} \ \texttt{09194,96,98,9200,38,41,42.44,93,95,96,98,9317,18,20,22}$

Dried herbs

<u>Hops</u>. No new data on residues in dry hops were provided. The existing MRL for hops (dry) is 10 mg/kg.

^{2} References:- A 09193,95,97,99,9239,40,43,45,92,94,97,99,9316,19,21,66

FATE OF RESIDUES

In storage and processing

In two processing studies on apples in Germany in 1987, residues in pressed apple juice and in a cooked mash were below the limit of determination, 0.01 mg/kg (Hoechst, A 38797, 38798).

After a trial on barley, in which an application rate of 4 times the normal was used, residues in the grain were 0.23 mg/kg; conversion of this grain to malt showed a residue of 0.09 mg/kg, while residues in the beer prepared from this were below the limit of determination of 0.01 mg/kg (Hoechst, A 46995).

Processing studies were carried out on wheat in Germany in 1989 in order to investigate the possible residue contamination of flour, bran and bread. Wheat was treated at 5 times the usual application rate (2.9 kg ai/ha) and at harvest, 49 to 51 days after treatment, the residues in the grain ranged from 0.038 to 0.048 mg/kg. After normal processing, the whole wheat flour showed 0.014 mg/kg, bran contained 0.02 to 0.035 mg/kg, while wholemeal bread had residues which were only just above the limit of determination of 0.01 mg/kg. At normal rates of application, residues in all of these products are unlikely to be measurable (Hoechst, A 46996, 46997).

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting received information on the following MRLs in Spain.

Commodity	MRL,	mg/kg
Apple	0.20	
Cereals	0.10	
Common bean		0.10
Cucurbits	0.10	
Peach	0.20	
Peppers	0.20	
Tomatoes	0.20	

APPRAISAL

Owing to the late submission of GAP information, evaluation of the residue data for pyrazophos was postponed from the 1992 Meeting, at which an ADI was estimated and the existing Guideline Levels became MRLs. Full GAP information has now been recorded and some previously unreported data on residues resulting from supervised trials on fruits, vegetables and cereals have been evaluated, together with those included in the 1985 and 1987 reviews. In general, these additional data served only to reinforce the conclusions reached earlier. There were insufficient new data to support any recommendations on new crops, other than on barley and wheat straw.

For apples, the additional data were deemed adequate to

support a recommendation to increase the MRL from 0.5 to 1 mg/kg. Data for strawberries, Brussels sprouts, cucumbers, barley and wheat supported the recommendations previously made for those crops. MRLs could also now be recommended for barley and wheat straw, based mainly on the ample trials data on wheat treatments. No additional data were received for carrots and hops, but a review of the data previously reported led to confirmation of the existing recommendations.

Data on residues in a few crops for which MRLs had not previously been recommended, namely nectarine, peach, summer squash, watermelon, egg plant, peppers, tomato, beetroot and Witloof chicory, were mostly only in summary form and, in any event, they were deemed insufficient as a basis for any MRL recommendation.

Some limited data on residue changes during the processing of barley and wheat were made available in response to previous requests. These showed that residues of pyrazophos were unlikely to be found in beer or bread produced from crops treated according to GAP. Residues in pressed apple juice and in a cooked mash from treated apples were below 0.01 mg/kg. Data on residues in animal products and the identities of plant metabolites were still not available.

RECOMMENDATIONS

On the basis of the data on residues resulting from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits.

Definition of the residue: pyrazophos.

PHI on which con based, day	ich Name	Recommended New	MRL (mg/kg) Previous
FP 0226 28	Apple	1	0.5
GC 0640 49-56	Barley	0.05	0.05
AS 0640 49-56	Barley straw and fodder, dr	cy 5	-
VB 0402 21	Brussels sprouts	0.1	0.1
VR 0577 28	Carrot	0.2	0.2
VC 0424	Cucumber	0.1	0.1
DH 1100 16	Hops, dry	10	10
	Melons, except Watermelon	0.1	0.1
FB 0275	Strawberry	0.2	0.2

14-21			
GC 0654	Wheat	0.05	0.05
33-58			
AS 0654	Wheat straw and fodder, dry	5	_
33-58			

FURTHER WORK OR INFORMATION

Desirable

- 1. Information on residues in meat and milk from cattle, meat from pigs, and meat and eggs from poultry, fed on a diet containing pyrazophos.
- 2. Additional information on the identities and quantities of metabolites in plants after treatment with pyrazophos.
- 3. Full reports of the residue trials supplied in summary form by Spain and The Netherlands.

REFERENCES

(All references are unpublished)

Hoechst AG, 1993. A large number of residue reports in the A..... series, as indicated in the Tables or text as appropriate.

Netherlands, 1993. Data on GAP and residues supplied by The Netherlands for the JMPR.

Spain, 1993. Data on GAP and residues supplied by Spain for the JMPR.