TRIADIMEFON (133)

EXPLANATION

Triadimefon was first evaluated in 1979 and has been reviewed 10 times since. Initially the CXLs were based on combined residues of triadimefon and triadimenol, triadimenol being the principal metabolite and a pesticide in its own right. Separate limits were later established for triadimenol to accommodate its direct use.

After the 1989 JMPR had recommended separate limits, the 1992 Meeting re-examined earlier data on triadimefon and triadimenol as well as new information. The data were limited and the review was dependent to a large extent on observed trends in the ratio of triadimefon to triadimenol in trials in which both compounds had been measured separately following applications of triadimefon.

At the 1995 CCPR one delegation reported additional residue data to support its view that the 1:1 ratio of triadimefon to triadimenol used by the 1992 JMPR in estimating a maximum residue level for pineapple was unrealistic. These data are the focus of attention at the present Meeting. Other information on GAP and data on residues which were submitted to the Meeting will be held on file for a future JMPR.

METHODS OF RESIDUE ANALYSIS

The analytical method used for the analysis of triadimefon and triadimenol (and their hydroxylated metabolites KWG 1323 and KWG 1342 respectively) was supplied to the Meeting (Obrist *et. al.*, 1982). A validated modification of this method was used for the analysis of pineapples in the reported trials (Burger, 1992). The basic method involves extraction by refluxing with methanol/water, concentration, and incubation with cellulase enzyme to release conjugated metabolites. The extract is then partitioned into methylene chloride, cleaned up by GPC, and separated into two fractions on a preparative HPLC column. The first contains triadimefon and triadimenol and the second KWG 1342 and KWG 1323.

Triadimefon and triadimenol residues are quantified by GLC with an NPD. KWG 1342 and KWG 1323 are derivatized with trifluoroacetic anhydride before determination. Recoveries from peel and pulp fortified at 0.01, 0.02 and 0.05 mg/kg with triadimefon, triadimenol, KWG 1342 and KWG 1323 were 80-100% for triadimefon, 80-105% for triadimenol and ≥ 62% for the other two metabolites with significantly more variability. Similar results were obtained at higher fortification levels. The limit of determination for pulp and peel was reported to be 0.01 mg/kg, the lowest level validated.

All peel and pulp control values were <0.01 mg/kg in the validations, but not in the field trials, where the apparent residues of triadimefon were 0.003-0.006 mg/kg in the pulp and 0.003-0.01 mg/kg in the peel, and those of triadimenol <0.01-0.004 mg/kg in the pulp and all <0.01 mg/kg in the peel. If the highest control values in the peel and pulp are assumed, the apparent triadimefon residues in the untreated whole fruit would be approximately 0.0024 mg/kg assuming 80% pulp and 20% peel. This, with the acceptable recoveries from 0.01 mg/kg added to peel and pulp, gives support for a limit of determination of 0.01 mg/kg for whole fruit.

Stability of pesticide residues in stored analytical samples

Pineapple samples from the field trials were shipped and stored deep frozen for periods of less than 9 months from treatment. No studies of the storage stability of analytical samples of pineapple containing triadimefon or triadimenol residues were provided to the Meeting, although summarized data were supplied from storage stability studies of triadimefon in grapes and of both compounds in tomatoes,

wheat grain and wheat forage.

Triadimefon was reported to show ≤ 7% loss in each of the commodities tested after 552 days of freezer storage. Triadimenol showed ≤4% loss after 552 days from tomato, wheat grain and wheat forage. The loss from grapes was reported to be 15% after 118 days with an unexplained 0% after 238 or 552 days. Residues in potatoes decreased by 12 and 4% after 113 and 234 days respectively.

USE PATTERN

Information on current uses of triadimefon on pineapples in five countries was provided and is summarized in Table 1. It confirms the information provided to the 1992 JMPR for the USA and Zaire.

Table 1. Approved uses of triadimefon on pineapples.

Country	Application			PHI, days	Notes
	Formu-lation	No.	g ai/ha (g ai/hl)		
Brazil	WP	--	(7.5)	-	1 min. plant dip
Mexico	WP	1-2	125	50	field spray
Philippines	WP	1	25-50	-	field use
USA	WG or WP	1	(50)	-	Post-harvest, 3 min. dip
Zaire	EC	1	(10)	0	field use

RESIDUES RESULTING FROM SUPERVISED TRIALS

Pineapples. The current CXL of 3 mg/kg for the combined residues of triadimefon and triadimenol was based on the 1986 JMPR review showing total residues up to 2.2 mg/kg. Two other post-harvest trials in which the two compounds were determined separately indicated residues of triadimefon and triadimenol of 0.25 and 0.33 mg/kg (1979 JMPR) and 0.25 and 0.2 mg/kg (1983 JMPR). It was on the basis of these approximately 1:1 ratios and the observation that residues of triadimenol from dip uses are generally equal to or less than those of triadimefon that the 1992 JMPR estimated separate maximum residue levels of 1 mg/kg each for triadimefon and triadimenol. Another trial had indicated a 2.5:1 ratio, but this was from ten times the GAP application rate. The 1992 Meeting recognized the limitations of the data and concluded that additional trials were desirable.

The Meeting reviewed substantial new residue data (Burger, 1992) and relevant information on GAP. Two separate trials were conducted, both with three-minute dips (30 sec. in two cases) at a rate of 50 g ai/hl. In each case pineapples were treated separately on five successive days to allow for variability. Although the concentration was the same in both trials the volume of dip was 1 gallon in one trial and 7 gallons in the other. Samples were handled and stored under frozen conditions until analysis no more than 9 months after treatment. The results are shown in Table 2.

Table 2. Triadimefon and triadimenol residues in pineapples after post-harvest dip treatments with a 50% Dry Flowable formulation at 50 g ai/hl (Burger, 1992).

Day	Sample	% of Total Weight	Residues, mg/kg[1]			Ratio triadimefon/triadimenol
			Triadimefon	Triadimenol [2]	Total	
Experiment 1 (Miles 458-BL005, 1 gall dip)						
1	Pulp Peel Whole[3]	77 23 100	0.06 4.46 1.07	0.01 0.30 0.08	0.07 4.76 1.2	6 14.9 13.4
2	Pulp Peel Whole	74 26 100	0.1 5.58 1.52	<0.01 0.31 0.09	0.10 5.89 1.6	>10 18 16.9
3	Pulp Peel Whole	78 22 100	0.13 5.50 1.31	<0.01 0.40 0.1	0.13 5.91 1.4	>13 13.9 13.6
4	Pulp Peel Whole	77 23 100	0.14 7.03 1.73	<0.01 0.24 0.06	0.14 7.27 1.8	14 29.3 28.8
5	Pulp Peel Whole	78 22 100	0.15 6.28 1.5	<0.01 0.24 0.06	0.15 6.52 1.6	15 26.2 25
Experiment 2 (Miles 458-BL006, 7 galls dip)						
1[4]	Pulp Peel Whole	91 9 100	0.10 7.59 0.77	<0.01 0.49 0.05	0.10 8.08 0.82	>10 15.5 15.4
2[4]	Pulp Peel Whole	88 12 100	0.12 6.83 0.93	<0.01 0.36 0.05	0.12 7.19 0.98	>12 119 18.6
3	Pulp Peel Whole	88 12 100	0.07 6.26 0.81	<0.01 0.35 0.05	0.07 6.61 0.86	>7 17.9 16.2
4	Pulp Peel Whole	76 24 100	0.09 5.45 1.38	<0.01 0.37 0.1	0.09 5.82 1.50	>9 14.7 14.4
5	Pulp Peel Whole	83 17 100	0.06 5.56 1.0	<0.01 0.34 0.07	0.06 5.90 1.1	>6 16.3 14.3

[1] Samples were also analyzed for metabolites KWG 1342 and KWG 1323: no residues (<0.01 mg/kg) were found.
[2] <0.01 mg/kg treated as 0.01 mg/kg for calculation. [3] Calculated from weights of peel and pulp after removal of crown.
[4] 30 sec. dip.

APPRAISAL

Triadimefon has been reviewed many times since the first evaluation in 1979. MRLs were recommended for combined residues of triadimefon and triadimenol until 1989. Triadimenol being the principal metabolite of triadimefon and a pesticide in its own right. Triadimenol was evaluated for the first time in 1989, when a number of maximum residue levels were estimated to accommodate its direct use. On the basis of somewhat limited data the 1992 JMPR recommended separate MRLs for triadimefon and triadimenol. That Meeting considered additional data desirable.

triadimefon

The present Meeting reviewed comprehensive new data on the post-harvest use of triadimefon on pineapples to address a concern expressed at the 1994 CCPR (ALINORM 95/24, para 244) that the separate maximum residue levels of 1 mg/kg estimated for triadimefon and triadimenol were not supported by recent data. Other residue data and information on GAP submitted to the 1995 JMPR will be held on file in the FAO for evaluation by a future Meeting.

The Meeting confirmed that the limited data available to the 1992 JMPR were consistent with a ratio of triadimefon to triadimenol in the residue of 1:1 (or at most 2.5:1 from excessive applications). However, more recent results from 10 supervised post-harvest trials according to GAP support the views expressed at the CCPR that the ratio should be higher. The new data indicated that the triadimefon:triadimenol ratio from post-harvest dips according to GAP with a dry flowable formulation is 18 ± 5:1 under the conditions of the experiments in which samples were taken for analysis immediately after treatment.

The average residues of triadimefon in the whole fruit (calculated from separate analyses of peel and pulp) were 12.5 times those in the pulp and triadimenol residues were over 7 times those in the pulp, although the latter estimate is not exact since only one residue in pulp was measurable (0.01 mg/kg). The calculated residues in the whole fruit (peel + pulp, crown removed) of triadimefon ranged from 0.8 to 1.7 mg/kg (mean, 1.2 S.D. ± 0.33) and those of triadimenol from 0.05 to 0.1 mg/kg (mean 0.07 ± 0.02). The Meeting gave greater weight to the new data which show that shortly after dipping triadimefon residues are likely to exceed 1 mg/kg, and recommended that the current 1 mg/kg proposal be increased to 2 mg/kg.

The situation with triadimenol is less clear. The recent data clearly show that the triadimefon:triadimenol ratio shortly after treatment is much higher than in the 3 studies reviewed previously, which indicated a ratio of 1:1 or at the most 2.5:1. The recent data alone would support a maximum residue level of triadimenol of 0.1 mg/kg or perhaps 0.2 mg/kg, since most of the residues are close to 0.1 mg/kg. A level of 0.2 mg/kg might also be supported in view of the variability shown in the 10 trials (the ratio of triadimefon to triadimenol varied from 13.6:1 to 29:1).

However, because samples were taken immediately after treatment, the Meeting was concerned that the results did not reflect the maximum triadimenol residues likely to occur in commercial practice after storage. The Meeting therefore concluded that the new trials did not provide an adequate basis for revising the MRL of 1 mg/kg recommended by the 1992 JMPR for triadimenol and confirmed that recommendation.

Because it seemed that triadimenol residues could increase during commercial storage after treatment, the Meeting considered that information on triadimefon and triadimenol residues in commerce or at consumption was desirable for further confirmation of the estimates.

The analytical method used for triadimefon included enzymatic incubation to allow the determination of conjugated residues. Determination was by GLC with NP detection and the limit of determination was approximately 0.01 mg/kg in whole pineapples.

Only summary data from studies of the storage stability of analytical samples were provided with the report of the pineapple trials. These were not with pineapples, but with triadimefon or triadimenol on grapes, wheat grain and forage, tomatoes and potatoes. Generally the results would give credence to the pineapple trials if confirmed by the original reports. The Meeting concluded that any future periodic review of triadimefon and triadimenol would require submission of the full reports of storage stability studies, not only summary data.

RECOMMENDATIONS

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

Definition of the residue: triadimefon

Commodity		Recommendation (mg/kg)	
CCN	Name	Name	Current
FI 0353	Pineapple	2 Po	1 Po

FURTHER WORK OR INFORMATION

Desirable

Information on residues of triadimefon and triadimenol in pineapples in commerce or at consumption.

REFERENCES

Burger, R., 1992. Triadimefon (50DF) - Magnitude of the Residue on Pineapple. Data Requirements. EPA Guideline Ref. No: 171-4(d) Magnitude of the Residue Post harvest Treatments. Unpublished Miles Report No. 102649, May 15, 1992, submitted by Bayer AG.

Obrist, J., Leimkuehler, W. and Coffman, M., 1982. Phase 3 reformat of MRID 00149163: Residue Analysis Procedure for Bayleton and Metabolites in Barley and Wheat: Project Report No. 80488. Unpublished report, Mobay Corporation, original study data January 20, 1982.