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MANCOZEB RESIDUES IN HIGHLAND AND LOWLAND TOMATOES

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RINGKASAN

Sisa-sisa mancozeb masih didapati dari tomato yang disembur sehingga kira-kira dua minggu selepas semburan. Bentuk pengurangan sisa yang sama juga dilihat pada tomato tanah pamah dan tanah tinggi pada kadar semburan yang disyorkan oleh pengilang-pengilang iaitu 0.2% bahan aktif dan pada sukatan yang lebih tinggi iaitu 0.4% bahan aktif. Masalah sisa tidak akan timbul jika masa selangan untuk memetik buah selama dua minggu diamalkan. Membasuh boleh mengurangkan 48% – 90% sisa permulaan dan seterusnya memasak dengan cara sistem 'reflux' boleh menghilangkan 12% – 79% daripada baki itu.

INTRODUCTION

Tomatoes are cultivated in both the lowland and highland areas in Malaysia. It is estimated that 940 hectares were under the cultivation of tomato in the lowlands in 1981, with an estimated production of 16 826 tonnes (LEMBAGA PEMASARAN PERTANIAN PERSEKUTUAN, 1985). The production of tomatoes in the highlands is also significant. Thirty per cent of the vegetable-growing areas in Cameron Highlands (approximately 876 hectares) are currently planted with tomatoes (CHAI, *pers comm.*, 1983). The estimated production of highland tomatoes in 1979 was 6 152 tonnes (FAMA, 1979).

Tomato is highly susceptible to fungal attack. Diseases such as early blight *(Alternaria solani),* late blight (*Phytophthora infestans)* and anthracnose [caused by *Colletotrichum phomoides* (Sacc.) (Chester)] are common, and broad spectrum fungicides such as the ethylenebis(dithiocarbamate) (EBDC) provide effective control. Although other fungicides are also recommended for the control of these diseases (KEMENTERIAN PERTANIAN MALAYSIA, 1981), they are not popularly used, usually because of high costs or lack of season-long and post-harvest control. A survey of fungicide usage in Cameron Highlands revealed that mancozeb, an ethylenebis(dithiocarbamate) fungicide, is the most popular among farmers. Approximately 450 tonnes of the fungicide are used annually, amounting to nearly 2.1 million ringgit.

The undesirable effect associated with mancozeb usage is the reported presence of ethylenethiourea (ETU), a weak carcinogen (BORGE, WEISBURGER, WEISBURGER, RICE and CYPHER, 1972) in the fungicide formulations (BONTOYAN, LOOKER, KAISER, GIANG and OLIVE, 1972). ETU may also be formed under conditions of aeration (HYLIN, 1973) or cooking (NEWSOME, 1976). Residues of mancozeb in tomatoes have been reported in several countries (NEWSOME, 1976; PEASE and HOLT, 1977; RIPLEY and COX, 1978) but such data are still lacking in Malaysia. The present study was conducted to determine the persistence of mancozeb in treated highland and lowland tomatoes. The effects of washing and heat treatment on the dissipation of the fungicide residues were also investigated.

MATERIALS AND METHODS

Field Lay-out and Treatment

Tomato plants (local selection) were cultivated at the MARDI Research Station in Cameron Highlands on 27 beds (3 m x 1 m) divided into three main plots; each plot consisting of three replicates (*i.e.* 3 beds/

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replicate). The three treatments in the experiment were : a) mancozeb spray treatment at the manufacturers' recommended rate of 0.2% a.i.; b) twice the recommended rate *i.e.* 0.4% a.i.; and c) untreated control. Bi-weekly treatment of mancozeb (*Dithane M−45,* 80% a.i. w/w' WP) applied with a nine-litre hand-sprayer, commenced before the flowering stage on April 23 1983 with the last spray treatment applied on June 27 1983.

A foliar spray of *Bacillus thuringiensis* was applied on in May 9 and May 20 1983 at a rate of 10 g/4.5 litres to control the tomato looper (*Plusia chalcites* Esq.) and budworm [*Chloridea (Heliothis) obsoleta* F.].

A similar trial was carried out at the MARDI Research Station in Serdang for lowland tomato (MT-1 variety) plants. Weekly treatment with *Dithane M-45* commenced from Jan 20 to March 17 1983. *Bacillus thuringiensis* was applied on Feb. 8 and March 22 1983.

Sample Processing

Tomatoes (±2 kg) from each replicate sub-plot were sampled after the spray dried and at specific intervals thereafter. Samples from the MARDI Research Station at Serdang were stored immediately in darkness in a cold room at − 4°Celsius. Those from the MARDI Research Station at Cameron Highlands were, however, processed at the station, kept in glass bottles and transported to Serdang. The samples were similarly stored and analysed within two months of storage. Plants from the untreated control plots were destroyed by fungal diseases before maturity.

Fruits were washed with tap water in a manner normally performed prior to cooking. For heat treatment, homogenate (50 g) of tomato placed in a 250-ml round-bottom flask connected to a reflux condenser was heated for 10 min in a heating mantle, and transferred with ethanol rinsing to a glass bottle for extraction and analysis.

Analytical Method

Mancozeb was analysed by using the headspace method of McLeod and McCully (1969). Hydrolysis of the dithiocarbamate compound yields carbon disulphide (CS_2), which is easily detected by a gas chromatograph. A linear relationship between the CS_2 evolved and the fungicide present was reported. Mancozeb residues can thus be readily determined by measuring the amount of CS_2 released upon hydrolysis.

The blended sample (50 g) was placed in a 250-ml glass reagent bottle with a Teflon stopper carrying a septum. Two per cent tin (II) chloride-hydrochloric acid solution (50 ml) was added. The bottle was placed in a water-bath at 80°C and shaken vigorously by hand for 2 min at quarter-hourly intervals for one hour. An aliquot of the headspace gas was examined by a gas-liquid chromatograph (Perkin-Elmer Sigma 1, P-E Corporation, Connecticut, USA) equipped with a flame-photometric detector. The glass column used (2 mm i.d. x 2.0 m) was packed with 5% OV-210 on 80/100 mesh Gas Chromosorb W, HP. The oven and detector temperatures were maintained at 60°C and 140°C respectively. The flow-rates of the carrier gas (oxygen-free nitrogen), air and hydrogen were 30 100 and 80 ml/min. respectively. Under these conditions, the limit of detection was 0.01 mg/kg carbon disulphide. A calibration curve was prepared by using CS_2 standards (30−180 μg range) treated similarly as for tomato samples.

RESULTS AND DISCUSSION

The headspace method of McLeod and McCully (1969) employed for the analysis of mancozeb residues in the present study was found to be simple, reliable and reproducible. There is a linear relationship between peak height and concentration of CS_2 in the range 30−180 μg CS_2 *(Figure 1)*. A collaborative study by laboratories in EEC countries had similarly found the results sufficiently encouraging for it to be considered by the EEC Commission for

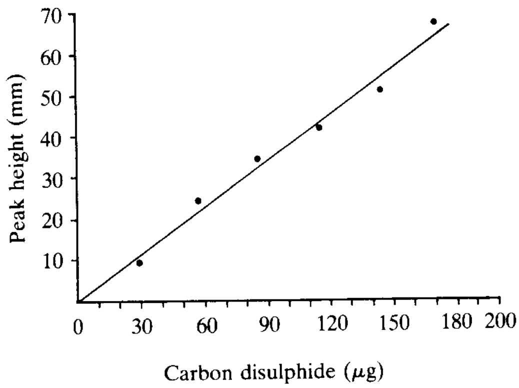

Figure 1. Calibration curve.

adoption as an official Community Method for dithiocarbamate residues (HILL and EDMUNDS, 1982). It has been reported that interference due to naturally occurring compounds decomposing to carbon disulphide may arise (HILL and EDMUNDS, 1982). Low levels of carbon disulphide (<0.1 mg/kg dithiocarbamate) in apparently untreated samples were detected. Using unsprayed tomatoes from various sources under the conditions employed, no carbon disulphide (<0.01 mg/kg) was detected in the current investigation indicating that the problem of interference did not arise.

Residue levels of mancozeb in fresh tomatoes are summarised in *Tables 1* and *2*. At the manufacturers' recommendation of 0.2% a.i. treatment level, a high residue level of 5.5 mg/kg CS_2 was recorded. The decline of mancozeb residues commenced only one week after spraying and levelled out 14–18 days after. There was no appreciable decrease in residues until after about two weeks when residues fell below 3 mg/kg, the maximum residue limit recommended by the Joint Meeting of the FAO Working Party of Experts on Pesticide Residues and the WHO Expert Committee on Pesticide Residues (FAO/WHO, 1978). This suggests that residue problems are unlikely to arise if the manufacturers' recommended pre-harvest interval of two weeks is followed. However, this practice is usually not adhered to by farmers who frequently apply dithiocarbamate fungicides a day before harvesting for post-harvest protection against fungal diseases.

The practice of applying pesticides at rates higher than the manufacturers' recommendation is common among farmers in the country. Residue studies were therefore conducted using a higher application rate of 0.4% active ingredient. At this higher treatment level, a similar pattern of residue dissipation was observed, although the rate, not unexpectedly, is slightly slower. There was no significant difference in the residue levels immediately after spraying. Residues dropped to 4.5 mg/kg CS_2 14 days after treatment and appreciable decrease was recorded after 14 – 20 days. Results therefore, indicate that application at double the recommended dosage does not improve the cost-effectiveness of mancozeb application and that a slightly longer pre-harvest interval has to be observed.

RIPLEY and COX (1978) also observed initial high residues in tomatoes although the residue dissipation rate was slightly faster. Only 27% of the initial residues remained five days after spraying and thereafter residues declined gradually and levelled out 10–15 days at a low level. NEWSOME (1976) found 37% of the initial mancozeb remaining after 14 days. It has been suggested that foliage cover, temperature, and rainfall showed no apparent effect on the dissipation of EBDC residues (RIPLEY and COX, 1978). It was also demonstrated by RIPLEY and SIMPSON (1977) that there was no apparent effect of temperature or rainfall on the dissipation of zineb residues in pear foliage or fruit. Therefore, the differences in the residue dissipation patterns observed may have been due to differences in application rates and tomato variety used in the study.

Results show that washing removed a substantial proportion of mancozeb residues. About 48% to 90% of the initial mancozeb residues were removed by wash-

Table 1. Persistence of mancozeb in highland tomatoes and residue dissipation as affected by washing and heat treatment

Spray concentration (% a.i.)	Period after treatment (days)	Mancozeb residues* (mg/kg CS_2)± s.d.		
		Before washing	After washing	After heat treatment
0.2	0	5.5 ± 0.87	0.65 ± 0.17	0.31 ± 0.10
	1	5.2 ± 0.57	0.81 ± 0.52	0.23 ± 0.06
	2	4.2 ± 0.46	0.44 ± 0.13	0.32 ± 0.02
	3	5.4 ± 0.60	0.90 ± 0.36	0.68 ± 0.28
	5	5.6 ± 0.60	0.96 ± 0.47	0.29 ± 0.12
	7	4.5 ± 0.85	0.80 ± 0.27	0.30 ± 0.01
	10	3.8 ± 0.68	0.68 ± 0.27	0.23 ± 0.01
	14	3.8 ± 0.15	0.58 ± 0.17	0.27 ± 0.02
	18	0.44 ± 0.10	0.07 ± 0.03	0.03 ± 0.05
	21	0.44 ± 0.18	0.07 ± 0.03	0.03 ± 0.05
0.4	0	5.9 ± 0.42	0.82 ± 0.24	0.34 ± 0.21
	1	5.3 ± 0.67	1.1 ± 0.52	0.37 ± 0.11
	2	5.0 ± 0.45	1.2 ± 0.07	0.53 ± 0.19
	3	6.3 ± 0.31	1.4 ± 0.21	0.94 ± 0.1
	5	5.4 ± 0.36	0.64 ± 0.33	0.27 ± 0.19
	7	5.1 ± 0.60	0.81 ± 0.16	0.29 ± 0.03
	10	4.8 ± 0.30	1.2 ± 0.15	0.25 ± 0.10
	14	4.5 ± 0.52	0.86 ± 0.21	0.35 ± 0.10
	18	1.4 ± 0.27	0.28 ± 0.10	0.12 ± 0.05
	21	0.37 ± 0.12	0.07 ± 0.01	0.03 ± 0.02

*Average of 3 replicates

Table 2. Persistence of mancozeb in lowland tomatoes, and residue dissipation as affected by washing and heat treatment

Spray concentration (% a.i.)	Period after treatment (days)	Mancozeb residues* (mg/kg CS_2) ± s.d.		
		Before washing	After washing	After heat treatment
0.2	0	5.0 ± 0.4	0.79 ± 0.12	0.39 ± 0.01
	1	5.4 ± 0.9	1.0 ± 0.2	0.53 ± 0.09
	2	5.6 ± 0.6	1.5 ± 0.5	0.70 ± 0.01
	3	5.2 ± 0.8	1.2 ± 0.0	0.69 ± 0.13
	5	5.1 ± 0.1	1.5 ± 0.6	0.62 ± 0.13
	7	4.4 ± 0.6	0.89 ± 0.24	0.38 ± 0.11
	14	3.6 ± 0.1	0.79 ± 0.27	0.50 ± 0.13
	21	0.78 ± 0.23	0.41 ± 0.07	0.36 ± 0.19
0.4	0	5.0 ± 0.6	1.8 ± 0.6	0.59 ± 0.14
	1	5.3 ± 1.0	2.2 ± 0.6	0.89 ± 0.08
	2	6.2 ± 0.1	2.5 ± 0.8	0.79 ± 0.12
	3	5.4 ± 0.8	1.7 ± 0.3	0.70 ± 0.12
	5	5.3 ± 0.5	2.3 ± 0.1	0.61 ± 0.09
	7	5.6 ± 0.8	2.4 ± 0.1	0.80 ± 0.03
	14	5.6 ± 0.6	2.4 ± 0.1	0.80 ± 0.03
	21	1.8 ± 0.52	0.75 ± 0.25	0.52 ± 0.10

*Average of 3 replicates

ing, as most of the residues were reportedly concentrated in the peels (LIM, ONG and CHEAH, 1983). This was not unexpected as dithiocarbamate fungicides are not systemic in nature and therefore remain as surface deposits. Washing prior to cooking or raw consumption, as practised in most households, would undoubtedly minimise hazards as indicated. Washing, therefore, is beneficial in reducing mancozeb residues from tomatoes.

Boiling under reflux for 10 min further removed 12% – 79% of mancozeb residues from tomatoes. This does not, however, necessarily mean that a 'safe level' will be attained. Ethylenethiourea is metabolised from EBDC fungicides (MARSHALL, 1977; RIPLEY and COX, 1978) and this can be relatively substantial; for instance, NEWSOME (1976) found that the mean percentage yield (molar basis) of ETU from mancozeb was 48.8 per cent.

On the pattern of dissipation of mancozeb residues in tomatoes, little difference was found between the highland and lowland situations. This suggests that the marked differences in rainfall and temperature of highland and lowland situations have no apparent effect on the dissipation of mancozeb residues, as indicated in the studies by RIPLEY and SIMPSON (1977) and RIPLEY and COX (1978). However, since diseases are more prevalent in the highlands, mancozeb is used more widely and frequently there. Thus the occurrence of mancozeb residues is more likely to arise in the highlands.

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ABSTRACT

There was no significant dissipation of mancozeb residues from treated tomatoes until about two weeks after treatment. The same pattern of residue dissipation was observed for lowland and highland tomatoes at the manufacturers' recommended application rate of 0.2% a.i. and at a higher dosage of 0.4% active ingredient. Residue problem is not likely to arise if a pre-harvest interval of two weeks is followed. Washing removed 48% – 90% of initial residues while boiling under reflux removed a further 12% – 79% of the remaining residues.

REFERENCES

BONTOYAN, W.R., LOOKER, J.B., KAISER, T.E., GIANG, P. and OLIVE, B.M. (1972). Survey of ethylenethiourea in commercial ethylenebis-dithiocarbamate. *J.A.O.A.C.* ***55***, 923–5.

BORGE, M.U., WEISBURGER, J.H., WEISBURGER, E.K., RICE, J.M. and CYPHER, R.J. (1972). Thyroid cancer in rats from ethylenethiourea intake. *US Natn. Cancer Inst.* ***49***, 583–4.

FAO/WHO (1978). *Guide to Codex Maximum Limits for Pesticide Residues* CAC/PRI. p. 158.

FEDERAL AGRICULTURAL and MARKETING AUTHORITY (1979). *Market Potential for Selected Commodities.* p. 39.

HILL, A.R.C. and EDMUNDS, J.W. (1982). Headspace methods for the analysis of dithiocarbamate pesticide residues in foodstuffs. *Analytical Proceedings* 19, 433–5.

HYLIN, J.W. (1973). *Bull. Env. Cont. Toxicol.* ***10***, 227. Cited in RIPLEY B.D. and SIMPSON, C.M. (1977) in Residues of zineb and ethylenethiourea in orchard-treated pears and commercial pear products. *Pesti. Sci.* ***8***, 487–91.

LEMBAGA PEMASARAN PERTANIAN PERSEKUTUAN (1985). *Kajian potensi pasaran bagi barangan pertanian terpilih.* Jabatan Perisik Persekutuan. pp. 15–6.

KEMENTERIAN PERTANIAN MALAYSIA, (1981). *Syor-syor kawalan tanaman.* Section D6.1.1. Kementerian Pertanian Malaysia, Kuala Lumpur.

LIM, G.S., ONG, S.H. and CHEAH, U.B. (1983). Environmental hazards associated with pesticide usage on vegetables in Malaysia. *Proc. Int. Conf. Env. Haz. Agrochem.* ***1***, 372–92.

MARSHALL, W.D. (1977). Thermal decomposition of ethylenebis(dithiocarbamate) fungicides to ethylenethiourea in aqueous media. *J. agric. Fd Chem.* ***25***, 357–61.

MCLEOD, H.A. and MCCULLY, K.A. (1969). Headspace gas procedure for screening food samples for dithiocarbamate pesticide residues. *J.A.O.A.C.* ***52***, 1 226–30.

NEWSOME, W.H. (1976). Residues of four ethylenebis-(dithiocarbamates) and their decomposition products on field-sprayed tomatoes. *J. agric. Fd Chem.* ***24***, 999–1 001.

PEASE, H.L. and HOLT, R.F. (1977). Manganese ethylenebis(dithiocarbamate) (Maneb)/Ethylenethiourea (ETU) residue studies on five crops treated with ethylenebis(dithiocarbamate) (EBDC) fungicides. *J. agric. Fd Chem.* ***25***, 561–7.

RIPLEY, B.D. and COX, D.F. (1978). Residues of ethylenebis(dithiocarbamate) and ethylenethiourea in treated tomatoes and commercial tomato products. *J. agric. Fd Chem.* ***26***, 1 137–43.

RIPLEY, B.D. and SIMPSON, C.M. (1977). Residues of zineb and ethylenethiourea in orchard treated pears and commercial pear products. *Pesti. Sci.* ***8***, 487–91.

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