1950; Leonard et al., 1967; Swanson, 1946), picloram (Leonard et al., 1967), and maleic hydrazide (Currier et al., 1951) also affect the phloem transport system.

Furthermore, treatment of wild oats with diclofop-methyl results in a large decrease in ATP production in the shoots (Table IV). Reduction in ATP production in the shoots of treated plants may restrain a number of physiological activities in the tissues. ATP is required to energize the movement of photosynthates in phloem tissues (Kursanov and Brochenko, 1961; Rathnam and Das, 1975). Reduced translocation of photosynthates to roots by reduced ATP may retard root development (Table I).

Sucrose is a major carbohydrate translocated by several plant species including wheat and barley (Edelman et al., 1959) and sugarcane (Hartt et al., 1963). Sucrose accumulated in the shoots of wild oats treated with diclofop-methyl (Table V), and this may be expected if sucrose is also the major carbohydrate translocated in wild oats. The conversion of glucose to sucrose also requires ATP (Edelman et al., 1959). Therefore, an accumulation of glucose in shoots of treated wild oats may be partly caused by a reduction in ATP synthesis.

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LITERATURE CITED

Arnon, D. I., *Plant Physiol.* **24**, 1 (1949).
Brezeanu, A. G., Davis, D. G., Shimabukuro, R. H., *Can. J. Bot.* **54**, 2038 (1976).
Bruinsma, J., *Photochem. Photobiol.* **2**, 241 (1963).
Ching, T. M., Ching, K. K., *Plant Physiol.* **50**, 536 (1972).
Chow, P. N. P., Burnside, O. C., Lavy, T. L., *Weeds* **14**, 58 (1966).
Chow, P. N. P., *Anal. Biochem.* **80**, 507 (1977).
Chow, P. N. P., *Weed Sci.* **26**, 352 (1978).
Currier, H. B., Day, B. E., Crafts, A. S., *Bot. Gaz.* **112**, 272 (1951).
Eames, A. J., *Am. J. Bot.* **37**, 840 (1950).
Edelman, J., Shibko, S. I., Keys, A. J., *J. Exp. Bot.* **10**, 178 (1959).
Gorbach, S. G., Kuenzler, K., Asshauer, *J. Agric. Food Chem.* **25**, 507 (1977).
Hartt, C. E., Kortschak, H. P., Forbes, A. J., Burr, G. O., *Plant Physiol.* **38**, 305 (1963).
Kursanov, A. L., Brochenko, V., *Physiol. Rast.* **8**, 265 (1961).
LaBerge, D. E., MacGregor, A. W., Meredith, W. O. S., *J. Inst. Brew., London* **79**, 471 (1973).
Leonard, O. A., Weaver, R. J., Glenn, R. K., *Weed Res.* **7**, 208 (1967).
Patterson, M. S., Greene, R. C., *Anal. Chem.* **37**, 854 (1965).
Rathnam, C. K. M., Das, V. S. R., *Biochem. Physiol. Fflanzen (BPP)* **167**, 565 (1975).
St. John, J. B., *Anal. Biochem.* **37**, 409 (1970).
Stewart, J. M., Guinn, G., *Plant Physiol.* **44**, 605 (1969).
Swanson, C. P., *Bot. Gaz.* **107**, 522 (1946).
Thurston, J. M., Phillipson, A., "Wild Oats in World Agriculture", Jones, D. P., Ed., Agricultural Research Council, London, 1976, p 19.
Todd, B. G., Stobbe, E. H., *Weed Sci.* **25**, 382 (1977).

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Residues of Ethylenebis(dithiocarbamate) and Ethylenethiourea in Treated Tomatoes and Commercial Tomato Products

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Residues of ethylenebis(dithiocarbamates) (EBDC) and ethylenethiourea (ETU) were monitored in tomatoes after application of several EBDC formulations from 1973 to 1977. After spraying at recommended rates, residues of EBDC on tomatoes were below the current Canadian tolerance of 4 ppm at the recommended harvest interval. ETU was detected during the analysis period at levels of <0.05 ppm on tomatoes whereas ETU residues in tomato juice and whole pack products, prepared from the treated tomatoes in the first 3 days after EBDC application, ranged from not detected (<0.01) to 0.17 ppm. Commercial tomato products contained traces of EBDC (<0.2 ppm) and ETU residues of ≤0.03 ppm. Boiling of some samples demonstrated additional ETU formation.

The ethylenebis(dithiocarbamates) (EBDC) are an agriculturally important group of fungicides, but their continued use is in jeopardy because ethylenethiourea (ETU; 2-imidazolidinethione) has been shown to be associated with these compounds. ETU is a degradation product in EBDC formulations, may be formed from EBDC by aeration or during cooking, and is present in most EBDC-treated crops (Federal Register, 1977). There is also evidence to suggest that long-term consumption of foods containing ETU could be inimical to health although Graham et al. (1975) concluded from a 2-year feeding study that ETU was not biologically deleterious to the rat at concentrations of 5 and 25 ppm.

One of the important crops requiring protection from fungal attack is tomatoes. Diseases such as early blight (*Alternaria solani*), late blight (*Phytophthora infestans*), and anthracnose (caused by *Colletotrichum phomoides*) are common on tomatoes, and broad spectrum fungicides such as the EBDC provide effective control. Although other fungicides are recommended (Publication 363, 1977) for the control of these diseases, they may not always be viable because of cost, the possibility of skin irritation, or the lack of season-long control.

Residues of EBDC and ETU in tomatoes have been reported (Engst et al., 1968; Newsome et al., 1975; Newsome, 1976; Pease and Holt, 1977), but because of the range of results and the need for additional data (Federal

Provincial Pesticide Residue Testing Laboratory, Ontario Ministry of Agriculture and Food, c/o University of Guelph, Guelph, Ontario, N1G 2W1, Canada.

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Table I. Residues of EBDC[a] and ETU on Tomato Foliage after Commercial Application of Fungicide at 2.69 kg of AI/ha in 1973

days after application (date)	Residue, ppm							
	Dithane M-22		Dithane M-45		Manzate D		Manzate 200	
	zineb	ETU	zineb	ETU	zineb	ETU	zineb	ETU
0 (July 5)	490	0.74	635	0.96	840	1.12	635	1.06
1	490	0.32	300	0.45	600	0.19	300	0.20
2	250	0.18	565	0.53	635	0.29	470	0.30
3	490	0.45	710	0.54	635	0.38	490	0.44
0 (July 17)	565	1.22	710	1.04	565	1.35	250	0.63
1	710	1.41	635	0.90	300	0.59	360	0.46
2	360	0.79	790	0.89	490	0.99	490	0.54
3	250	0.86	200	0.85	NA[b]	NA	NA	NA

[a] EBDC concentration expressed as zineb equivalent. [b] NA, not analyzed.

Table II. Residues of EBDC[a] on Tomato Foliage after Commercial Application[b] of Fungicide in 1974

days after application (date)	residue, ppm			
	Dithane M-22	Dithane M-45	Manzate D	Manzate 200
	zineb	zineb	zineb	zineb
fourth spray (Aug 10)				
0	300	145	500	185
1	415	260	575	306
2	200	390	310	157
3	305	410	380	780
4	315	245	490	500
5	180	170	450	320
6	140	104	230	245
8	315	35	117	145
sixth spray (Sept 10)				
0	NA[c]	NA	NA	NA
1	560	1150	560	680
2	NA	735	475	420
3	395	300	500	355
4	260	730	380	194
5	185	180	675	245
6	305	315	310	460
8	181	195	440	310

[a] EBDC concentration expressed as zineb equivalent. [b] Total of six applications of fungicide at 2.69 kg of AI/ha; sample taken after fourth and sixth spray. [c] NA, not analyzed.

Register, 1977), this study is presented. This study was initiated to determine the level of EBDC and ETU residues on commercially treated tomatoes from the commercial tomato growing area of southwestern Ontario, on hand-sprayed tomatoes from the area growing tomatoes for domestic use, in tomato products prepared using simulated commercial methods from the commercially treated tomatoes, in actual commercial tomato products, and in selected samples that were boiled to determine if further conversion of EBDC to ETU occurred as per home cooking.

EXPERIMENTAL CONDITIONS

Field Treatment. In the commercial tomato growing area of southwestern Ontario, 1.2 ha plots of Heinz 1630 tomatoes were treated with EBDC fungicides using a John Bean airblast sprayer operated to apply 2.69 kg of AI/ha in 526 L of H_2O/ha as per commercial recommendations (Publication 363, 1977) and label directions. The recommendations call for application of fungicide when the first fruits are almost walnut size, and sprays are repeated as required at 7–12 day intervals depending on weather conditions and the quality of disease control required. Spray histories are given in Tables I–V. The fungicides examined were Dithane M-22 and Dithane M-45 (Rohm and Haas Co.), and Manzate D and Manzate 200 (Dupont); the active ingredient in Dithane M-22 and Manzate D is manganese ethylenebisdithiocarbamate, and in Dithane M-45 and Manzate 200 the active ingredient is the coordination product of zinc ion and manganese ethylenebisdithiocarbamate. All formulations were 80% wettable powders.

At the Cambridge Research Station, Ontario Ministry of Agriculture and Food, 46.5 sq m plots of tomatoes were treated with Dithane M-22 (80%) at 2.58 kg of AI/ha using a 9-L hand sprayer. In 1975 Campbell 1327 variety tomatoes and in 1976 and 1977 New Yorker variety tomatoes were analyzed for residues at intervals after application of the fungicide.

Sampling. Foliage (100 g) and tomato fruit (10–15) were sampled after the spray dried and at intervals thereafter. The fresh samples were placed in sealed plastic bags and frozen until analysis; processed products, prepared from the treated tomatoes, were kept at room temperature until analysis. Commercial tomato products were randomly obtained from local supermarkets.

Commercial Processing. Samples of treated fruit were also taken from several of the commercial field studies and were processed immediately into tomato juice and whole pack tomatoes using simulated commercial methods. Two methods of preparing topping juice for the whole pack tomatoes were employed. One method consisted of using fruit from the same sample, and after it was washed, peeled, chopped, heated, and run through a finisher, it was placed on the peeled fruit in the can. Alternatively, topping juice was prepared, as above, from tomatoes that were peeled in an 18% lye solution.

Heat Treatment. Homogenates (20 g) of tomato or

Table III. Residues of EBDC[a] and ETU in Tomatoes, Sampled after the Sixth Application of Fungicide[b] in 1974, and in Products Processed from the Tomatoes

substrate	days after application	Residue, ppm							
		Dithane M-22		Dithane M-45		Manzate D		Manzate 200	
		zineb	ETU	zineb	ETU	zineb	ETU	zineb	ETU
fruit	0	2.85	NA[e]	0.96	NA	0.91	NA	1.05	NA
	1	3.56	NA	2.55	NA	6.61	NA	1.33	NA
	2	1.77	NA	1.80	NA	3.31	NA	1.29	NA
	3	2.30	NA	2.33	NA	3.49	NA	1.25	NA
juice	0	0.19	0.03	0.10	0.02	0.76	0.05	0.24	0.04
	1	0.44	0.06	0.30	0.15	0.94	0.17	0.40	0.04
	2	0.43	NA	0.44	0.02	0.70	0.15	0.53	0.11
	3	0.53	0.12	0.45	0.09	0.60	0.05	0.30	0.02
whole pack (not lye washed)	0	ND[c]	0.04	ND	0.02	ND	0.03	ND	0.02
	1	0.23	0.11	0.17	0.05	0.22	0.03	ND	Tr (0.01)
	2	ND	0.03	ND	0.08	0.26	0.08	ND	0.08
	3	0.18	0.05	ND	Tr (0.01)	ND	0.02	ND	0.02
whole pack (lye washed)	0	ND	0.01	ND	0.02	ND	0.02	ND	0.02
	1	ND	0.02	ND	0.02	ND	0.03	ND	0.03
	2	ND	0.01	ND	0.01	ND	0.03	ND	0.02
	3	ND	ND[d]	ND	0.02	ND	ND	ND	0.02

[a] EBDC concentration expressed as zineb equivalent. [b] Six sprays of fungicide at 2.69 kg of AI/ha. [c] Not detected (<0.1 ppm zineb). [d] Not detected (<0.01 ppm ETU). [e] NA, not analyzed.

Table IV. Residues of EBDC[a] in Tomatoes after Sixth Commercial Application of Fungicides in 1975

days after application	residue, ppm	
	Dithane M-22[b]	Dithane M-45[c]
	zineb	zineb
0	1.2	ND (<0.2)
1	5.7	1.6
2	4.8	4.1
3	2.8	4.0

[a] EBDC concentration expressed as zineb equivalent. [b] Six sprays of Dithane M-22 at 2.69 kg of AI/ha. [c] Three sprays of captafol (Difolatan) at 1.3 kg of AI/ha, followed by three sprays of Dithane M-45 at 2.69 kg of AI/ha.

processed product in a 125-mL round-bottom flask connected to a reflux condenser were heated for 10 min in a 100 °C water bath, then cooled and transferred with ethanol rinsing to blenders for extraction and ETU analysis.

Analytical Methods. The EBDC was analyzed using the CS_2 evolution technique (Pease, 1957) with modifications (Keppel, 1969; Ripley and Simpson, 1977). Recoveries in substrates fortified with EBDC (10–500 μg) prior to reflux were quantitative and had a coefficient of variation of ±10%.

ETU was determined by gas–liquid chromatography (GLC) of the *N*-trifluoroacetyl-*S*-(*m*-trifluoromethylbenzyl) derivative (King, 1977a; Ripley and Simpson, 1977) using a flame photometric detector in the sulfur mode and a 1.8 m × 3.5 mm i.d. glass column packed with 3% OV-275 on Chromosorb W, H.P. Temperatures (°C) were: column, 195; detector, 185; and injector, 225. Gas flows (mL/min) were: carrier (N_2), 60; H_2, 120; air, 40; and O_2, 20 These GLC conditions were optimized for a retention time of 3 min and linearity in the range 1–10 ng of the derivative. Substrates were fortified with ETU (0.01–0.25 ppm) prior to blending and were analyzed concurrently with samples. Quantitation was based on a calibration curve and results varied by ±0.01 ppm ETU.

RESULTS AND DISCUSSION

Part of the controversy associated with EBDC–ETU residue studies is the question of ETU methodology with respect to conversion of EBDC to ETU during workup of samples, variable background levels in untreated crop samples, and variable recoveries. Pease and Holt (1977) discuss these problems and conclude "that apparent levels of ETU below 0.05 ppm are not significant". In our preliminary studies, these problems were observed particularly with the Newsome (1972) method based on S-benzylation of ETU and EC detection and also after subsequent N-trifluoroacetylation to the second derivative

Table V. Residues of EBDC[a] and ETU in Fruit and Processed Tomato Juice after Seventh Application of Fungicide in 1976[b]

substrate	days after application (date)	residue, ppm		
		zineb	ETU	ETU (after boiling 10 min)
fruit	0 (Sept 11)	0.53	0.02	0.04
	1	4.09	0.04	0.36
	2	1.18	0.02	0.07
	3	1.47	0.02	0.11
processed tomato juice	0	0.14 ± 0.03[c]	0.01 ± 0.01	0.05 ± 0.01
	1	0.27 ± 0.03	0.04 ± 0.01	0.10 ± 0.02

[a] EBDC concentration expressed as zineb equivalent. [b] Three applications of Dithane M-45 at 2.69 kg of AI/ha plus 3.36 kg of AI/ha fixed copper, followed by applications of Dithane M-45 at 2.69, 2.69, 3.58, and 2.69 kg of AI/ha. [c] Mean of four sample replicates ± standard deviation.

and FPD detection in the sulfur mode. The King (1977a) method based on S-(*m*-trifluoromethyl)benzylation also showed "dirty" chromatograms on EC examination. Formation of the second derivative [*N*-trifluoroacetyl-*S*-(*m*-trifluoromethylbenzyl)ethylenethiourea] and the use of the FPD in the sulfur mode were definite improvements. After repeated trials, a technique was established that produced consistent results although they varied by ±0.01 ppm ETU. The variability of ETU results was observed for both fortified samples and with repeated injections of the same sample; part of the injection variability may have been caused by fluctuations in gas flows to the FPD and the low attenuation required for the detection of trace levels of ETU.

Certain points in the analytical technique appeared to give more consistent results. In the liquid–liquid partitioning of the acid solution containing the *S*-(*m*-trifluoromethylbenzyl)ethylenethiourea, the use of anhydrous ethyl ether was found superior to distilled-in-glass ethyl ether. After removal of the ether in a warm water bath (60 °C), the benzene was added first, then the base was added dropwise down the side of the tube which was shaken immediately. For quantitative recovery, the solution must be alkaline and because of variable sample pH, the pH of the solution was checked at this step. Only a portion of the supernatant (250 μL) was removed and transferred to a screw-top test tube. Prior to GLC analysis, fresh trifluoroacetic anhydride (TFAA, 10% in benzene, 50 μL) was added and after 5 min the solution was injected. The use of 1-mL ampules of TFAA (Pierce) demonstrated better reproducibilities than the use of TFAA in large-volume bottles, presumably because opening and closing the bottle causes hydrolysis of the anhydride to the acid due to moisture in the air. We also found that samples should be injected on the same day as workup. Three runs of six samples or standards could easily be handled by one analyst in 1 day.

Care must be taken to optimize the GLC conditions for retention time, linearity in the low concentration range (1–10 ng of derivative injected), and sensitivity. As noted above, some variability was found with the GLC determination, but by analyzing fortified substrate concurrently with samples and quantitating using a calibration curve, good results were obtained. Two or three preliminary injections of the TFAA solution also aided the reproducibility, since there is probably some on-column derivatization. Unfortunately, after repeated injections of sample extracts containing TFAA, the GLC column was depleted as noted by the increased retention time under the same GLC conditions. Column life varied from 2–6 weeks.

Interferences, from substrate background (Figure 1), were eliminated by varying the GLC conditions. Although not specifically examined in this study, there appears to be little, if any, formation of ETU during sample workup (Ripley and Simpson, 1977; King, 1977b).

Residues of EBDC (as zineb equivalent) in tomato fruit and foliage, following application in 1973 through 1976 of four recommended EBDC fungicides as per commercial practice, are presented in Tables I–V. Analysis of variance of the EBDC data from each trial showed that the variance of residue from the four compounds was not significant at the 95% confidence level, whereas the variance for serial application was sometimes significant. Since there was no apparent difference in the residues from the four formulations, the data for EBDC residues on tomatoes were collated and are presented in Table VI. Analysis of variance of these data indicate a significant difference in

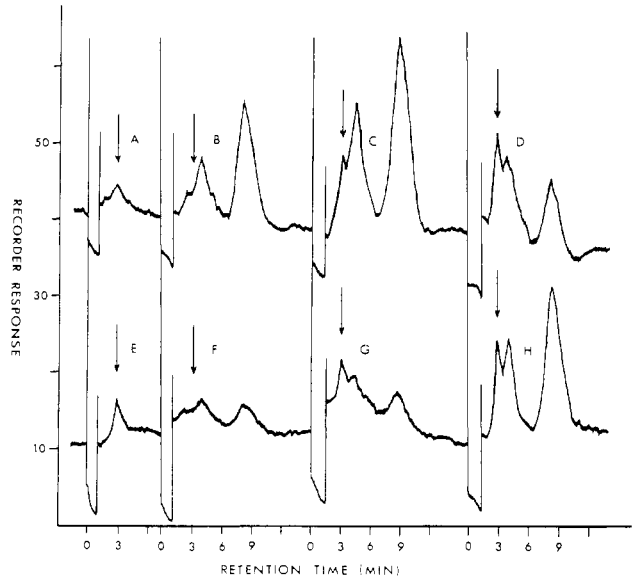

Figure 1. Chromatograms of *N*-trifluoroacetyl-*S*-(*m*-trifluoromethylbenzyl)ethylenethiourea. Conditions as in text; 1.024×10^{-8} amps full scale; final tomato extract, 4 g/mL. (A) 10 μL, standard 0.10 μg/mL; (B) 20 μL, fresh tomato, control; (C) 20 μL, treated tomato; (D) 20 μL, processed tomato juice; (E) 10 μL, standard 0.25 μg/mL; (F) 20 μL, commercial whole pack, "control"; (G) 20 μL, commercial whole pack fortified with 0.02 ppm ETU; (H) 20 μL, whole pack tomato prepared from treated tomatoes.

Table VI. Summary of EBDC[a] Residues on Commercially Treated Field Tomatoes for 1974–1976

days after application	zineb, ppm
0	1.10 ± 0.84[b]
1	3.63 ± 2.00
2	2.61 ± 1.45
3	2.52 ± 1.00

[a] EBDC concentration expressed as zineb equivalent. [b] Mean of seven sample replicates ± standard deviation.

EBDC residues from the four EBDC formulations, but this presumably is due to yearly variation.

To compare the commercial field treatment with small-scale, hand-spraying trials, a study on the dissipation of Dithane M-22 (maneb) was conducted at Cambridge (Table VII, Figure 2). Examination of these data indicate a similarity for the two methods of fungicide application. Yearly variations in hand-spraying data may be attributable to the difference in tomato variety or to the poor tomato growth observed in 1976 and 1977.

The purpose of the 1975 Cambridge study was to determine the effect of serial application of EBDC on the presence of residues in the tomatoes. Over the trial period (July–October) the foliage cover changed from high and dense to low and sparse. Levels of EBDC residue found in the tomatoes during the serial applications are shown in Figure 2 and the data are summarized in Table VII. Foliage cover, temperature, and rainfall showed no apparent effect on the dissipation of EBDC residues; however, one anomaly was observed the day following a mild night frost when the EBDC residue, in all plots, rose to double the expected value, but returned on subsequent days to the levels anticipated from the dissipation curve.

In 1975, EBDC residues and the rate of dissipation of residue were also examined after application of maneb at 0.5, 2, and 3 times the recommended rate (Figure 3). Data points for 2 and 3 times the rate represent the mean of two applications. There appears to be little increase in the

Table VII. Residues of EBDC[a] on Tomatoes after Hand Spraying at Cambridge with Dithane M-22 at 2.58 kg of AI/ha

	zineb residue, ppm					
	1975[b]				3-year average	
days after application	no. of samples	mean ± SD	1976[c]	1977[d]	no. of samples	mean ± SD
0	15	2.27 ± 0.45	7.6	4.1	18	2.69 ± 1.40
1	13	1.87 ± 0.62	8.2	1.7	16	2.59 ± 2.28
2	13	1.42 ± 0.61	4.0	3.4	16	1.88 ± 1.14
3	13	0.94 ± 0.29	6.8	1.2	16	1.68 ± 2.21
4	9	1.00 ± 0.43	0.4		11	0.94 ± 0.44
5	8	0.62 ± 0.19	0.5		10	0.61 ± 0.19
6	13	0.54 ± 0.23	1.4	0.60	16	0.64 ± 0.40
7	11	0.47 ± 0.14	2.5	0.86	14	0.79 ± 1.05
8	5	0.83 ± 0.17			5	0.83 ± 0.17
9	6	0.76 ± 0.10			6	0.76 ± 0.10
10	5	0.70 ± 0.15			5	0.70 ± 0.15
11	1	0.58			1	0.58
12	1	0.59			1	0.59
13	5	0.50 ± 0.08			5	0.50 ± 0.08
14	1	0.55	0.5		3	0.53 ± 0.04
17	1	0.24			1	0.24

[a] EBDC concentration expressed as zineb equivalent. [b] See text and Figure 2. [c] Mean of two applications. [d] Only one application.

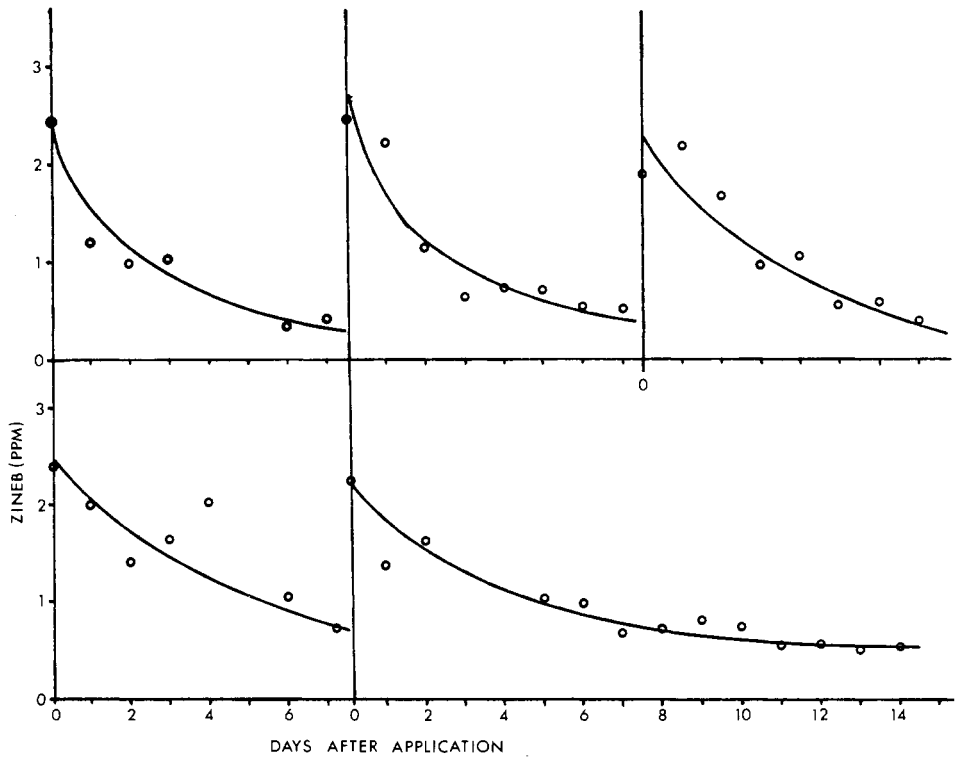

Figure 2. Maneb residues, expressed as zineb equivalent, present on tomatoes at Cambridge following serial application of Dithane M-22 at 2.58 kg of AI/ha using a hand sprayer.

deposit of residue beyond a certain spray rate. Residues declined as expected and leveled out after 10–15 days at a low level.

In all cases of EBDC application to tomatoes at the recommended rates (Tables I–VII), the EBDC residues present at harvest were below the current Canadian tolerance of 4 ppm as the zineb equivalent. From the data, however, the reason for the difference in days to harvest, after terminal application of the EBDC, of 1 day for the coordination product and 3 days for the maneb is not clear.

ETU residues in the tomato foliage and fruit are presented in Tables I and V. The percentage of ETU to EBDC was 0.15 ± 0.09 in the foliage and 1.95 ± 1.25 in the fruit; in previous studies by the authors, the ratios were generally less than 1%. These values are closer to those expected from ETU "impurity" in the formulations (Johnson and Tyler, 1962; Czeglédi-Jankó and Hallő, 1967; Bontoyan et al., 1972) than those that might be formed during analysis (Pease and Holt, 1977). From our experience with EBDC–ETU monitoring studies, it appears that most of the ETU residues arise from the presence of ETU in formulations. ETU does not appear to be formed or accumulated in significant amounts in the field after spraying; the rate of dissipation of ETU residues, either through weathering or dilution due to growth, appears to be similar to that of the EBDC residues.

ETU has been shown to be formed from EBDC (Ludwig et al., 1954; Hylin, 1973; Newsome and Laver, 1973; Watts et al., 1974; Marshall, 1977) under elevated temperature and oxidative conditions, as in home cooking. ETU has

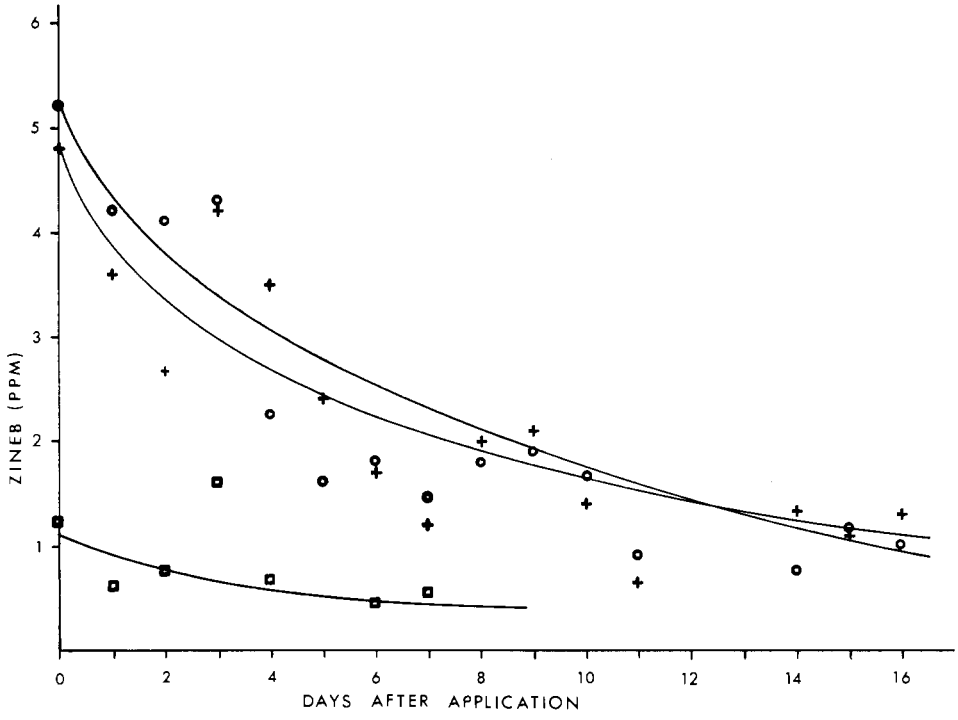

Figure 3. Maneb residues, expressed as zineb equivalent, present on tomatoes at Cambridge following application of Dithane M-22 at various rates using a hand sprayer. Application rates (kg of AI/ha) were 1.29 (-○-○-), 5.15 (-+-+-), and 7.73 (-□-□-).

Table VIII. Residues of EBDC[a] and ETU in Commercial Tomato Products[b]

		residue, ppm		
product	manufacturer	zineb	ETU	ETU (after boiling 10 min)
whole pack	A	NA[c]	ND (<0.01)	NA
whole pack	B	NA	Tr (0.01)	0.02
paste	C	NA	Tr (0.01)	0.05
paste	C	Tr (0.15)	ND (<0.01)	NA
paste	D	ND (<0.1)	Tr (0.01)	NA
paste	E	Tr (0.17)	0.03	0.05
paste	F	ND (<0.1)	ND (<0.01)	ND (<0.01)
juice	C	ND (<0.1)	ND (<0.01)	Tr (0.02)
juice	C	Tr (0.18)	ND (<0.01)	Tr (0.01)
juice	C	NA	ND (<0.01)	0.03
soup	C	NA	Tr (0.01)	Tr (0.01)
ketchup	C	ND (<0.1)	ND (<0.01)	Tr (0.02)

[a] EBDC concentration expressed as zineb equivalent. [b] Purchased locally; amount of EBDC treatment unknown. All products were processed in Ontario, except D (U.S.A.), E (Italy), and F (Spain). [c] NA, not analyzed; Tr, trace; ND not detected.

also been shown to be present in commercially processed products (Pecka et al., 1975; Pease and Holt, 1977; Phillips et al., 1977; Ripley and Simpson, 1977; Ripley et al., 1978). Because of the possibility of high ETU concentrations being found in commercial products prepared from EBDC-treated crops, the commercially treated tomatoes were processed using simulated commercial methods into whole pack tomatoes and tomato juice and these products were analyzed for EBDC and ETU residues (Tables III and V). In the processed products, the EBDC concentration was reduced by 50–75% and the ETU concentration was about the same or slightly elevated compared to the fruit levels. A good correlation existed between higher EBDC concentrations and higher ETU concentrations in the same samples. However, the variability of results indicate a wide range of conversion due to processing; it should be noted that some samples showed no detectable EBDC residue, but had ETU levels as high as 0.08 ppm.

The topping juice for the whole pack tomatoes was prepared from treated tomatoes in two ways: some were run through an 18% lye solution/peeler and some were not. The data indicate that lye washing was beneficial in reducing both EBDC and ETU concentrations in the whole pack tomatoes. Marshall (1977) observed that the formation of ETU from EBDC increased as the pH was raised, although in a subsequent study Marshall and Singh (1977) conclude that "oxidation using basic hypochlorite prior to industrial processing of vegetables which have been treated with EBDC fungicides would seem to be an effective means of removing contaminating surface residues of ETU".

Commercial tomato products were purchased at local supermarkets and were analyzed for EBDC and ETU residues (Table VIII). Low concentrations of both compounds were found in all commodities and these levels agree with previous data for processed tomato products (Pecka et al., 1975; Pease and Holt, 1977). In general, it appeared that slightly higher residues are found in those products that are concentrated by water removal. The lower residue levels present in the commercial products, relative to those in the simulated processing study, is probably due to dilution of the product with tomatoes

harvested at various intervals after the terminal EBDC application.

Since many households cook with fresh tomatoes and commercial tomato products, some samples were heated for 10 min in the laboratory and then analyzed for ETU (Tables V and VIII). Elevated ETU levels were found in all but one sample after cooking; in three samples ETU was found after cooking at trace levels (0.01–0.02 ppm) in samples that previously showed no apparent ETU residues.

In conclusion, field tomatoes treated at the recommended rate for EBDC fungicides contain EBDC residues of <4 ppm and ETU residues that were detectable, but <0.05 ppm, at the suggested harvest date. Tomato products prepared from treated fruit had EBDC concentrations of <1 ppm and ETU concentrations of <0.1 ppm; commercial tomato products had trace levels of EBDC and ETU concentrations of <0.05 ppm. Lye washing to remove tomato skins appeared to be beneficial in reducing both EBDC and ETU residues. Boiling of fresh fruit and commercial products resulted in increased levels of ETU.

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LITERATURE CITED

Bontoyan, W. R., Looker, J. B., Kaiser, T. E., Giang, P., Olive, B. M., *J. Assoc. Off. Anal. Chem.* **55**, 923 (1972).
Czeglédi-Jankó, G., Halló, A., *J. Chromatogr.* **31**, 89 (1967).
Engst, R., Schnaak, W., Rattba, H., *Nachrichtenbl. Dtsch. Pflanzenschutzdienstes (Braunschweig)* **22**, 26 (1968).
Fed. Regist. **42**, 40618 (1977).
Graham, S. L., Davis, K. J., Hansen, W. H., Graham, C. H., *Food Cosmet. Toxicol.* **13**, 493 (1975).
Hylin, J. W., *Bull. Environ. Contam. Toxicol.* **10**, 227 (1973).
Johnson, E. I., Tyler, J. F. C., *Chem. Ind.*, 305 (1962).
Keppel, G. F., *J. Assoc. Off. Anal. Chem.* **52**, 162 (1969).
King, R. R., *J. Agric. Food Chem.* **25**, 73 (1977a).
King, R. R., Fredericton Research Station, Agriculture Canada, Fredericton, New Brunswick, Canada, personal communication, 1977b.
Ludwig, R. A., Thorn, G. D., Miller, D. M., *Can. J. Bot.* **32**, 48 (1954).
Marshall, W. D., *J. Agric. Food Chem.* **25**, 357 (1977).
Marshall, W. D., Singh, J., *J. Agric. Food Chem.* **25**, 1316 (1977).
Newsome, W. H., *J. Agric. Food Chem.* **20**, 967 (1972).
Newsome, W. H., *J. Agric. Food Chem.* **24**, 999 (1976).
Newsome, W. H., Laver, G. W., *Bull. Environ. Contam. Toxicol.* **10**, 151 (1973).
Newsome, W. H., Shields, J. B., Villeneuve, D. C., *J. Agric. Food Chem.* **23**, 756 (1975).
Pease, H. L., *J. Assoc. Off. Anal. Chem.* **40**, 1113 (1957).
Pease, H. L., Holt, R. F., *J. Agric. Food Chem.* **25**, 561 (1977).
Pecka, Z., Baulu, P., Newsome, H., *Pestic. Monit. J.* **8**, 232 (1975).
Phillips, W. F., Grady, M. D., Freudenthal, R., "Effects of Food Processing on Residues of Ethylenebisdithiocarbamate Fungicides and Ethylenethiourea", Environmental Health Effects Research Series, Report EPA-600/1-77-021 (April 1977), U.S. Environmental Protection Agency.
Publication 363, Vegetable Production Recommendations 1977, Ontario Ministry of Agriculture and Food, Information Branch, Legislative Buildings, Toronto, Ontario K7A 1A5.
Ripley, B. D., Simpson, C. M., *Pestic. Sci.* **8**, 487 (1977).
Ripley, B. D., Cox, D. F., Wiebe, J., Frank,-R., *J. Agric. Food Chem.* **26**, 134 (1978).
Watts, R. R., Storherr, R. W., Onley, J. H., *Bull. Environ. Contam. Toxicol.* **12**, 224 (1974).

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Residues in Crops Irrigated with Water Containing Simazine

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Annual ditchbank vegetation growing on the inside slopes of irrigation canals can be managed with low-rate applications of simazine. When a herbicide is applied to the bank of either a flowing or a dry canal, some residue might be expected in the irrigation water applied to crops. Six crops representing nine commodity groupings were irrigated with water containing simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine] at 0.01 and 0.10 mg/L. The treatment levels were selected to simulate the maximum amount and ten times the maximum that might be expected to enter irrigation water after bank application for weed control. Herbicide was applied to randomized test plots through sprinkler and furrow irrigation, and crops were harvested 7 and 30 days after treatment. Samples were analyzed for residues with a gas chromatograph equipped with a nitrogen and phosphorus detector. No simazine residue was found in corn grain and pinto bean pods while trace amounts were found in pinto bean foliage and cucumbers. Amounts ranging from 0.6 to 2.9 μg/kg were found in sugar beets, corn foliage, and tomatoes. Sugarbeet foliage collected 7 days after application of simazine at 0.01 and 0.10 mg/L by sprinkler irrigation contained 5 μg/kg. Alfalfa contained the most residue of the crops tested; samples collected from plots that were sprinkler-irrigated with water containing simazine at 0.10 mg/L contained 6.4 μg/kg.

Simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine] is one of the most widely used preemergence herbicides for the control of annual grasses and broadleaf weeds in orchards and in such crops as corn, alfalfa, and sugar cane. The persistence and movement of simazine after such applications have been extensively studied, but less effort has been directed to following its accumulation and dissipation after use for weed control in or along irrigation channels (Smith et al., 1975). In 1957, B. H. Grigsby of Michigan

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