Knaak, J. B., Tallant, M. J., Sullivan, L. J., *J. Agric. Food Chem.* **14**, 573 (1966).
Shaw, J. G., Espinosa, L. R., Hampton, R. B., *J. Econ. Entomol.* **63**, 1631 (1970).
Tashiro, H., Beaver, J. B., *J. Econ. Entomol.* **60**, 1187 (1967).
Tashiro, H., Chambers, D. L., Shaw, J. G., Beaver, J. B., Maitlen, J. C., *J. Econ. Entomol.* **62**, 443 (1969).
Westlake, W. E., Gunther, F. A., Carman, G. E., *Arch. Environ. Contam. Toxicol.* 1, 60 (1973).

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Residues of Dimethoate and Dimethoxon on Sweet Cherries Following Air Carrier Application

Robert W. Zwick, Ulo Kiigemagi,* and Gary J. Fields

Dimethoate was applied to sweet cherries at two Oregon locations using both the emulsifiable concentrate and the wettable powder formulations. The applications were made with an air carrier sprayer at rates ranging from 1.23 to 2.50 lb of active ingredient/acre. Only traces of dimethoate and its principal metabolite, dimethoxon, were present at harvest, 28 to 35 days after treatment. Total residues were reduced to levels below 2 ppm in 0 to 8 days after application. No differences in the initial residues or the rate of disappearance were observed between the emulsifiable concentrate and wettable powder formulations. This study indicates that dimethoate can be used for western cherry fruit fly control without excessive harvest residues.

Dimethoate [*O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorodithoate] is registered on pome fruits for the control of a variety of insect pests in the United States and Canada. Following investigations of Banham (1974) in Canada, we evaluated efficacy of dimethoate for western cherry fruit fly (*Rhagoletis indifferens* Curran) control on sweet cherries in Oregon (Zwick et al., 1975) and found that one application of dimethoate provided excellent protection over an entire season. Presently, dimethoate is registered for control of cherry fruit fly in Canada but not in the United States. We have been attempting to collect sufficient efficacy and residue data to support registration of this compound on cherries in the United States. Since previous residue studies of MacNeil et al. (1975) and Zwick et al. (1975) were based on hydraulic handgun applications which are not in general commerical use, we are presenting here the results of dimethoate residue analyses resulting from air carrier applications as would be applicable to commercial cherry orchards. In addition, residues resulting from the use of a wettable powder formulation are compared with those resulting from an emulsifiable concentrate application.

MATERIALS AND METHODS

Treatment and Sampling of Crop. In 1975 studies were conducted in two eastern Oregon areas, Hood River and The Dalles, both of which have commercial cherry acreages. Two rates of two dimethoate formulations [Cygon brand, 2.67 lb of active ingredient (AI)/gal of emulsifiable concentrate (EC) and 25% AI wettable powder (WP)] were applied once in each area to several varieties (Bing, Royal Anne, Van) of sweet cherries. Applications were made with a Berthoud VT 1500 Model air carrier sprayer calibrated to deliver 370 gal/acre (gpa) and 500 gpa in The Dalles and Hood River orchards, respectively. The differences in total gallonage applied per acre were due to the 26 ft rows and 1.40 mph tractor speed in The Dalles as compared with 20 ft rows and 1.36 mph speed in Hood River. Fan rpm, hydraulic pump pressure, and discharge nozzling remained constant for all applications. Although the dilution rates (lb of AI dimethoate/100 gal) for comparable plots were identical in each location, the lb of AI per acre applied were different in each location due to the different total gallonages applied (Table I). Individual plots were 3–12 trees in The Dalles and 4–10 trees in Hood River.

Applications in each area were made within a week after western cherry fruit fly had emerged. This was June 5 in The Dalles and June 9 in Hood River, at which time fruit was about 0.5 in. in diameter. About 1 lb random samples of fruit, three per plot at each sampling date, were individually bagged in plastic containers and stored at −10 °C until analysis. Samples were taken 0, 3, 7, 14, and 28 days after treatment and also at harvest. Control samples were from unsprayed trees at each location.

Residue Analysis. The analytical method used was based on that developed by Stellar and Pasarela (1972). The fruit was subsampled in the laboratory as received, and randomly selected 100-g aliquots, were taken for extraction. In most cases the three replicates taken were combined, mixed well, and then one subsample taken. One subsample per replicate was taken from one plot at each location. Whole fruits were macerated with 400 mL of acetone in the presence of 50 g of anhydrous sodium sulfate for 5 min using an Omnimixer. The extract was recovered by filtering with suction, and the extraction jar, pulp, and filter paper were washed with additional 50 mL of acetone. The acetone extract was concentrated to 100 mL on a steam bath, 100 mL of water added, and the aqueous solution extracted with three 100-mL portions of dichloromethane. The dichloromethane extract was dried with 50 g of anhydrous sodium sulfate and purified with 3 g of activated charcoal (Nuchar C-190-N). The absorbent

Mid-Columbia Experiment Station, Oregon State University, Hood River, Oregon 97031 (R.W.Z., G.J.F.) and the Department of Agricultural Chemistry, Oregon State University, Corvallis, Oregon 97331 (U.K.).

Table I. Amounts of Dimethoate Applied to Sweet Cherries by Air Carrier Sprayer in The Dalles and Hood River, Oregon, 1975

		Amount of dimethoate applied			
		25% WP		2.67 EC	
Area	gpa	lb/100 gal	lb AI/acre	pt/100 gal	lb AI/acre
The Dalles	370	1.33	1.23	1.0	1.23
		2.00	1.85	1.5	1.85
Hood River	500	1.33	1.67	1.0	1.67
		2.00	2.50	1.5	2.50

Table II. Residues of Dimethoate and Dimethoxon (in ppm) Resulting from Air Carrier Sprayer Applications to Sweet Cherries in The Dalles and Hood River, Oregon, 1975[a]

		Dimethoate applied, lb of AI/acre											
		25% WP						2.67 EC					
		1.23[b]			1.85			1.23			1.85		
Area	Days after treatment	Di[c]	Dx[d]	Total	Di	Dx	Total	Di	Dx	Total	Di	Dx	Total
The Dalles	0	4.20	<0.02	4.20	7.76	<0.02	7.76	4.28	<0.02	4.28	7.14	0.02	7.16
	3	2.15	0.09	2.24	4.15	0.09	4.24	2.34	0.12	2.46	4.73	0.15	4.88
	7	0.44	0.09	0.53	1.77	0.16	1.93	0.84	0.18	1.02	1.94	0.13	2.07
	14	0.13	0.10	0.23	0.65	0.25	0.90	0.14	0.12	0.26	0.79	0.11	0.90
	28	0.06	0.06	0.12	0.05	0.12	0.17	0.02	0.10	0.12	0.06	0.04	0.10
	35	<0.02	0.05	0.05	0.02	0.11	0.13	<0.02	0.04	0.04	0.02	0.02	0.04
			1.67			2.50			1.67[b]			2.50	
Hood River	0	2.21	0.02	2.23	3.33	0.04	3.37	1.54	0.03	1.57	3.33	0.03	3.36
	3	0.37	0.07	0.44	1.45	0.17	1.62	0.63	0.07	0.70	0.73	0.10	0.83
	7	0.21	0.10	0.31	0.27	0.12	0.39	0.15	0.06	0.21	0.36	0.11	0.47
	14	0.04	0.06	0.10	0.08	0.07	0.15	0.06	0.05	0.11	0.03	0.03	0.06
	28	0.02	0.04	0.06	0.02	0.04	0.06	<0.02	<0.02	<0.02	<0.02	0.03	0.03

[a] Sensitivity of the analytical method with a 100-g sample: 0.02 ppm for dimethoate and dimethoxon. The values have not been corrected for recoveries. [b] Average of three replicates. [c] Dimethoate. [d] Dimethoxon.

was removed by filtering and the filtrate concentrated for gas chromatography using a rotary evaporator.

The analyses were performed on a Varian Aerograph 204B gas chromatograph equipped with a MicroTek flame photometric detector operated with a 526-nm interference filter for phosphorus. The 60 cm × 3 mm glass column was packed with 11% DC-200 and 0.01% Versamid 900 on 60/80 mesh Gas-Chrom Q and conditioned overnight at 190 °C. The operating parameters were: column temperature, 160 °C; injector temperature, 190 °C; detector temperature, 165 °C; nitrogen carrier gas flow, 33 mL/min; hydrogen, oxygen, and air flows to the detector, 150, 20, and 40 mL/min, respectively. The detector was modified according to Burgett and Green (1974) to prevent solvent flame-out and to improve signal-to-noise ratios.

Considerable amounts of plant waxes were present in the cleaned-up extract which increasingly contaminated the injection port and the column as the analyses progressed. This influenced the performance of the gas chromatograph by lowering the peak heights and by increasing the retention times. We compensated for these changes in the column performance by injecting standards after each sample and calculating the concentration of dimethoate and its oxon on the basis of the subsequently eluting standard. In addition, the injection port was cleaned daily and the column packing replaced whenever the instrument sensitivity became too low for use. The average retention times were 5.9 min for dimethoate and 3.9 min for dimethoxon. The detection limits for dimethoate or dimethoxon were about 7 ng at 2× attenuation. Untreated cherries showed no significant response to the analytical method.

The precision of the gas chromatographic measurements was estimated by determining the relative standard deviation of peak heights of standards injected during 1 day selected at random. The relative standard deviations averaged 3.35% for dimethoate and 3.89% for dimethoxon. The greater variation with dimethoxon was expected because of the lesser stability of this compound.

The reliability of the analytical method was tested by adding known amounts of dimethoate and dimethoxon to untreated cherries, followed by extraction and analysis. Twenty-eight 100-g samples were fortified with 0.06 to 5.0 ppm of dimethoate and dimethoxon in 1 mL of acetone, and the average recovery was 97% ± 12 for dimethoate and 79% ± 13 for dimethoxon. Since the cherries were fortified with an acetone solution of the insecticides which was allowed to be absorbed before extraction, these results should approximate the recoveries to be expected from field samples.

The identity of dimethoate residues in some samples was confirmed by gas chromatography–mass spectrometry (GC–MS). A Varian CH-7 mass spectrograph was used in conjunction with a Varian Aerograph 1200 gas chromatograph and System Industries Data System 150. The ionizing voltage was 70 eV, the source temperature, 171 °C, and the single stage glass jet separator temperature, 260 °C. The gas chromatograph was equipped with a 120 cm × 3 mm glass column packed with 2% OV-210 on 100/120 mesh Chromosorb W.

RESULTS AND DISCUSSION

The results (Table II) show that the harvest residues of dimethoate and its toxic metabolite, dimethoxon [*O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorothiolate], on cherries were considerably below the 2 ppm tolerance for dimethoate established for many crops. The results reported for The Dalles 1.23 lb/acre WP plot and for Hood River 1.67 lb/acre EC plot were averages of three replicates, all other values were the results of a single analysis. Harvest residues found by this study were lower than those previously reported (Zwick et al., 1975), where the total harvest residues ranged from 0.15 to 0.36 ppm.

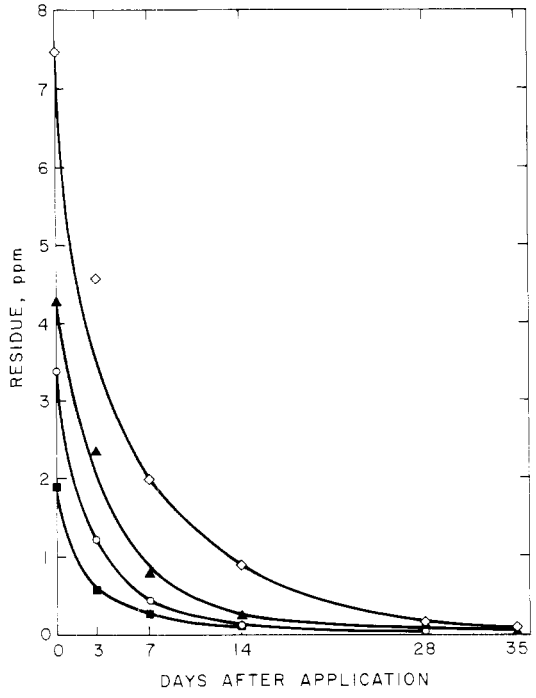

Figure 1. Persistence of total dimethoate on cherries at The Dalles and Hood River, Oregon. Residues of dimethoate and dimethoxon have been added and residues from plots treated with EC and WP formulations have been averaged: (◇) The Dalles, 1.85 lb of AI/acre; (▲) The Dalles, 1.23 lb of AI/acre; (○) Hood River, 2.50 lb of AI/acre; (■) Hood River, 1.67 lb of AI/acre.

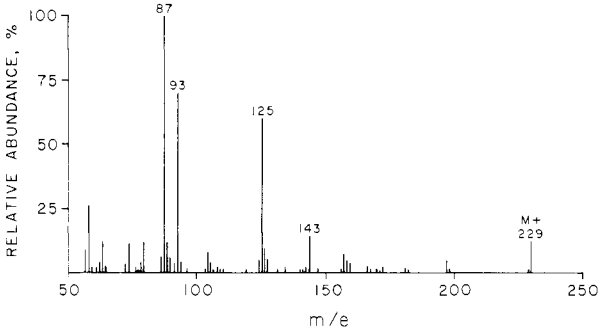

Figure 2. Mass spectrum of authentic dimethoate.

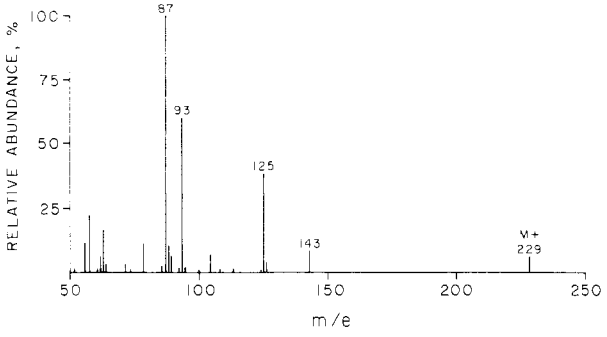

Figure 3. Mass spectrum of sample no. 84, 1.74 ppm dimethoate.

The 14-day residues at the lower application rates were also lower than the residues reported by MacNeil et al. (1975). The explanation for these differences probably lies in the application method. In both of the earlier studies the pesticide was applied by handgun to the point of runoff. This practice will result in more thorough coverage of the trees and therefore in higher residues than the air carrier application. Since the air carrier sprayers represent the prevalent commercial practice of today, the data presented in this paper would be more indicative of residues expected than the data obtained with handgun applications.

Another factor influencing the persistence of pesticides is climate, particularly rainfall. However, if the rainfall data for 1971 and 1975 for these two locations were compared, very little difference was evident, indicating that the difference in residues must be due to the application method. Residues of the principal toxic metabolite, dimethoxon, remained relatively constant, suggesting that dimethoxon was formed and degraded at about the same rate. A slight peak in the dimethoxon formation occurred between 3 and 14 days after application and the highest residue found was 0.25 ppm 14 days after application.

If residues resulting from the application of wettable powder or emulsifiable concentrate formulations were compared, no differences in initial residues or the rate of disappearance could be seen. This shows that the physical differences in the two formulations apparently did not influence the volatility or degradation of dimethoate. The dissipation curves for total dimethoate residues (dimethoate plus dimethoxon) are shown in Figure 1. Because of the very small differences between the formulations, the values for the two formulations at each rate and at each location were averaged. The degradation and persistence half-lives (Gunther and Blinn, 1955) were estimated graphically and the degradation half-life for total residue at The Dalles was about 3.5 to 4 days and at Hood River about 2.25 days. The persistence half-life of total dimethoate was about 13 days for Hood River and 6 to 13 days for The Dalles. In addition, the initial residues at The Dalles were about twice as high as those at Hood River, despite the fact that the amount of pesticide used at The Dalles was lower. No explanation can be offered for this discrepancy.

Special studies were carried out to determine the source of errors in the analytical procedure. Three replicates were taken from one field plot at each location and analyzed separately. The average relative standard deviation of these two series of samples was found to be about 15%. When a field sample was subsampled in the laboratory and the subsamples analyzed separately, the relative standard deviation was 6.8%. When aliquots were taken from the extract of a single sample and analyzed, the relative standard deviation was 3.3%. These results thus indicated that the major source of variations in the analytical results was in the field sampling.

The mass spectra of a dimethoate standard and that of a field sample are shown in Figures 2 and 3. The mass number data provided by the GC–MS system for the treated samples corresponded to the mass spectrum of a dimethoate standard which showed prominent peaks at masses 87, 93, 125, 143, and 229. This spectrum also corresponds to the mass spectrum of dimethoate previously published (Damico, 1966). It was not possible to confirm the presence of dimethoxon residues in this manner because of the low residues present in the cherries.

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LITERATURE CITED

Banham, F. L., *Proc. 5th Annu. B.C. Fruit Growers Assoc. Hortic. Forum* **5**, 13 (1974).

Burgett, C. A., Green, L. E., *J. Chromatogr. Sci.* **12**, 356 (1974).
Damico, J. N., *J. Assoc. Off. Anal. Chem.* **49**, 1027 (1966).
Gunther, F. A., Blinn, R. C., "Analysis of Insecticides and Acaricides", Interscience, New York, N.Y., 1955, pp 135–141.
MacNeil, J. D., Hikichi, M., Banham, F. L., *J. Agric. Food Chem.* **23**, 758 (1975).
Stellar, W. A., Pasarela, N. R., *J. Assoc. Off. Anal. Chem.* **55**, 1280 (1972).
Zwick, R. W., Fields, G. J., Kiigemagi, U., *J. Econ. Entomol.* **68**, 383 (1975).

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Dissipation of Molinate in a Rice Field

Charles J. Soderquist, James B. Bowers, and Donald G. Crosby*

The dissipation of the herbicide molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate) in a California rice field was investigated. Laboratory experiments indicated that while dilute aqueous solutions of molinate were stable in sunlight, irradiation in the presence of tryptophan resulted in decomposition primarily to 1-[(ethylsulfinyl)carbonyl]hexahydro-1*H*-azepine, *S*-ethyl hexahydro-2-oxo-1*H*-azepine-1-carbothioate, and hexamethyleneimine. Analysis for molinate and its degradation products at sub-ppm levels in water, soil, and air samples collected from a commercially treated field, together with laboratory studies, showed that volatilization of molinate from water was the primary mode of dissipation, although photodecomposition products were present in field water.

Molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate, I) is the active ingredient in the commercial herbicide Ordram. About one million pounds of molinate were used in California in 1975 (California Department of Food and Agriculture, 1976), essentially all of which was applied in rice culture to control barnyard grass (*Echinochloa* spp.). As part of a study of the effects of chemicals used in rice culture on environmental quality of California's Sacramento Basin (Soderquist and Crosby, 1975), the fate of molinate under typical use conditions was examined.

The objectives of the present investigation were to examine, under controlled laboratory conditions, the processes such as volatilization, hydrolysis, and photolysis responsible for molinate dissipation; to devise analytical methods sensitive to sub-ppm levels for the identification and quantitation of molinate and its degradation products; and to monitor these compounds in the water, soil, and air from an Ordram-treated rice field.

EXPERIMENTAL SECTION

Chemicals. Technical molinate (96.5%) was purified by distillation under vacuum; the highly volatile forerun (about 1% of the molinate) was trapped at −80 °C and identified as diethyl disulfide by gas chromatography–mass spectroscopy (GC–MS). The purified molinate was homogeneous to both thin-layer (TLC) and gas-liquid chromatography (GLC) and was used throughout this study unless otherwise noted. Solvents were distilled twice in glass, and all other commercial chemicals were used as received except as noted. Analysis of a sample of the Ordram 10G to be applied to the field showed 11% molinate but no other products exceeding 20 ppm.

1-[(Ethylsulfinyl)carbonyl]hexahydro-1H-azepine (II). Commercial (5.3%) sodium hypochlorite solution (8.5 mL, 6 mmol of NaOCl) and 1.5 mL of 0.01 M HCl were added with stirring to a solution of I (1.0 g, 5.3 mmol) in 1.5 L of water. After 1 h, the solution was extracted with four 100-mL portions of dichloromethane. The combined extracts were dried briefly over anhydrous sodium sulfate and concentrated under vacuum at less than 40 °C to a clear, viscous liquid. Trituration with hexane at 0 °C followed by drying at room temperature under vacuum yielded white crystals (0.98 g, 90% yield), mp 39–41 °C. The product was free of I and was homogeneous to thin-layer chromatography (TLC), with an R_f (0.21, solvent A) and ninhydrin response similar to that reported by Casida et al. (1975). Spectral data were consistent with structure II: infrared spectrum (IR) 2950, 1690 (CO), 1070 (SO) cm^{-1}; mass spectrum (solid probe) *m/e* 126 (base, $C_6H_{12}NCO$), 98 ($C_6H_{12}N$), no M^+. Published methods (Casida et al., 1975; Tilles and Casida, 1975) utilizing 3-chloroperoxybenzoic acid were less satisfactory.

1-[(Ethylsulfonyl)carbonyl]hexahydro-1H-azepine (III). Hydrogen peroxide (90%) (0.3 mL, 6 mmol) was added to a solution of II (75 mg, 0.37 mmol) in 0.5 mL of formic acid at 20 °C. After 1 h, 50 mL of water was added and the solution extracted with 5 mL of hexane. The hexane was washed with 1 mL of water and then concentrated under nitrogen to yield a white solid (mp 88–90 °C) which was homogeneous to TLC with an R_f (0.61, solvent A) and ninhydrin response similar to that reported by Casida et al. (1975): IR 2940, 1680 (CO), 1310, 1130 (SO_2) cm^{-1}; mass spectrum (GC–MS) *m/e* 126 (base, $C_6H_{12}NCO$), 98 ($C_6H_{12}N$), no M^+.

S-Ethyl Hexahydro-2-oxo-1H-azepine-1-carbothioate (IV). Ethyl chlorothiolformate (95% pure) (35.5 g, 0.27 mol) was added dropwise to a vigorously stirred mixture of caprolactam (VI) (31.6 g, 0.28 mol), 200 mL of 1.8 M sodium hydroxide (0.35 mol), and 100 mL of hexane. After stirring for 2 h, the aqueous phase was discarded and the hexane phase washed successively with 50-mL portions of 1.0 M sodium hydroxide, 2.0 M HCl, and water and dried briefly with anhydrous sodium sulfate. The hexane and excess ethyl chlorothiolformate were removed by vacuum distillation (35 °C, 0.1 Torr) and the residue purified by column chromatography on Florisil using hexane–diethyl ether (9:1 v/v). While the yield of IV (a viscous oil) was

Department of Environmental Toxicology, University of California, Davis, California 95616.