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Dislodgeable and Total Residues of Methomyl on Mint Foliage[1]

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Foliar residues of some cholinesterase-inhibiting pesticides can be hazardous to field workers performing tasks involving substantial contact with the crop (MILBY et al. 1974, SPEAR et al. 1975). Consequently, it is important to know the magnitude and fate of pesticide residues on the part of the crop contacted by the workers.

Methomyl [S-methyl N-(methylcarbamoyloxy) thioacetamidate] is used for the control of loopers and cutworms on mint in Oregon. At the time methomyl is applied, mint needs to be irrigated frequently because it is a vigorously growing crop. Workers who move the irrigation pipes may be exposed to mint foliage treated with methomyl, and for this reason a study was undertaken to determine the magnitude and fate of dislodgeable and total residues of methomyl when applied to mint. Dislodgeable residues are surface residues which may be incorporated into or onto particulate matter and are therefore easily transferrable to workers either by dislodgement into air or by direct transfer to workers' skin and clothing. Total residues also include material which has penetrated into the leaf.

EXPERIMENTAL METHODS

Treatment and Sampling: Fields (80 to 90 acres) of peppermint near Jefferson, Oregon, were treated with 0.9 or 1.8 lb ai/acre using a 90% WP Lannate brand formulation. Applications were made August 3, 1976, by airplane using 10 gal of water/acre and three 2-lb samples were collected/field at 4, 24 and 48 h after treatment.

Extraction and analysis of dislodgeable residues: The method was based on the method for dislodgeable residues of GUNTHER et al. (1973). Leaf discs, 1.3 cm in diameter, were punched from 100 leaves per sample immediately after collection and their weight determined. Samples were then stored at -10°C in 8-ounce jars until they were extracted. Discs were allowed to thaw for extraction and then stripped using 100 mL of water containing 4 drops of a 1:50 dilution of Sur-Ten wetting agent per sample. Jars were shaken end-to-end on a reciprocating shaker at 170 cycles/min for 20 min. The stripping solution was recovered by decantation and the procedure repeated two more times. The combined stripping solutions were acidified and extracted with three 100 mL portions of dichloromethane.

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Fifty mL of 0.1 N NaOH were added to the CH_2Cl_2 extract and the solvent evaporated on a steam bath followed by 15 min of additional heating. The hydrolysis mixture was acidified, extracted with three 50 mL portions of CH_2Cl_2, and the extract dried for gas chromatography.

Extraction and analysis of total residues: A 50 g sample of leaves was macerated with two successive 250 mL portions of ethyl acetate. The extract was recovered by filtering and the extraction jar and filter cake washed with additional 50 mL of ethyl acetate. Water was added and the organic solvent removed by evaporation. The aqueous phase was filtered, acidified, and washed three times with hexane followed by extraction of methomyl into CH_2Cl_2 with three 50 mL portions of the solvent. The sample was then hydrolyzed as described above.

Methomyl standard: Methomyl is hydrolyzed in the presence of alkali to the corresponding oxime, S-methyl N-hydroxythioacetimidate. In lieu of this compound as a standard, known amounts of methomyl were hydrolyzed along with the samples and used to calibrate the gas chromatograph.

Gas chromatography: Analyses were performed on a gas chromatograph equipped with a flame photometric detector operated with a 394 nm interference filter for sulfur. The 0.9 m x 2 mm ID Pyrex column was packed with 10% FFAP on 80/100 mesh acid washed HPW. Operating parameters were: column temperature 170°, injector temperature 190°, detector temperature 165°; nitrogen carrier gas flow 40 ml/min. Retention time of the oxime was about 4.2 min.

Validation of the analytical method: Untreated foliage showed no significant response to the analytical method. The sensitivity limits of the method were therefore estimated on the basis of the gas chromatographic response to the analytical standards, base line noise level, and sample size.

The reliability of the analytical method for dislodgeable residue measurements was tested by adding known amounts of methomyl in acetone solution to discs of untreated leaves. The solvent was allowed to evaporate and the samples were stored frozen for about the same length of time as the samples from treated fields. The fortified samples were extracted and analyzed as previously described along with treated samples. The results in Table 1 indicate a 78% average recovery.

The reliability of the total residue method was tested in a similar manner. Known amounts of methomyl were added to untreated leaves, the solvent was allowed to evaporate and the samples stored frozen until analysis. The previously described method for total residues was used for extraction and analysis of these samples. The data in Table 1 show an average recovery of 89%.

The effect of frozen storage was further tested by reanalyzing the 4-h samples after 96 days of additional storage. The results

of this study are presented in Table 2 and show an average deviation from the earlier results of less than 5%. It is concluded that no significant losses of methomyl occur during 4 mo of frozen storage.

TABLE 1

RECOVERY OF ADDED METHOMYL FROM MINT LEAVES AFTER FROZEN STORAGE

Analytical method	Frozen storage, days	Methomyl, ppm Added	Found	Recovery, percent
dislodgeable	6	50	41	82
"	14	100	79	79
"	15	50	41	82
"	16	100	70	70
"	17	50	43	86
"	97	100	67	67
total	67	200	188	94
"	71	100	91	91
"	76	100	87	87
"	83	200	184	92
"	90	50	42	84
"	104	50	44	88

TABLE 2

EFFECT OF FROZEN STORAGE ON DISLODGEABLE RESIDUES IN FOUR-HOUR SAMPLES

Treatment, lb actual per acre	Frozen storage, days	Dislodgeable residue[1] ug/cm^2	ppm	Frozen storage, days	Dislodgeable residue[1] ug/cm^2	ppm
0.9	14	1.59	150	110	1.18	124
0.9	14	1.48	154	110	1.35	145
0.9	14	1.49	144	110	1.87	166
1.8	16	2.31	242	112	2.80	265
1.8	16	2.04	218	112	2.21	234
1.8	16	2.54	225	112	2.16	214

[1] Results not corrected for recoveries. Sensitivity of the analytical method: 0.01 ug/cm^2 or 0.4 ppm with 100 discs.

TABLE 3

DISLODGEABLE AND TOTAL RESIDUES OF METHOMYL ON MINT FOLIAGE

Treatment, lb actual per acre	Interval[1]	Dislodgeable residues[2]		Total residue[3]
		ug/cm^2	ppm	ppm
untreated	--	<0.01	<0.4	<0.1
0.9	4	1.59	150	220
0.9	4	1.48	154	161
0.9	4	1.49	144	180
0.9	24	0.77	71	135
0.9	24	0.63	53	87
0.9	24	0.72	56	100
0.9	48	0.36	35	78
0.9	48	0.32	31	64
0.9	48	0.32	24	67
1.8	4	2.31	242	309
1.8	4	2.04	218	258
1.8	4	2.54	225	321
1.8	24	1.72	164	195
1.8	24	0.95	75	112
1.8	24	1.03	104	178
1.8	48	0.69	55	110
1.8	48	0.66	57	97
1.8	48	0.53	46	76

[1] Interval between application and sampling, hours.

[2] Results not corrected for recoveries. Sensitivity of the analytical method: 0.01 ug/cm^2 or 0.4 ppm with 100 discs.

[3] Results not corrected for recoveries. Sensitivity of the analytical method: 0.1 ppm with a 50 g sample.

RESULTS

The results of the analyses are shown in Table 3. The data show that the dislodgeable residues diminished rapidly with a half-life of about 24 h and also that they diminished more rapidly than the penetrated residues. About 22% of the dislodgeable residue remained at 48 h as compared to 36% for total residue. The proportion of dislodgeable residue in total residue also declined with time: at 4 h 82% of the total residue was dislodgeable, at 48 h only 50%. It is the dislodgeable residue that is responsible for possible hazards to workers. The order of magnitude of dislodgeable residues of methomyl on mint was about the same on an area basis as reported in literature for other pesticides on other crops (WESTLAKE et al. 1973, LEFFINGWELL et al. 1975, WINTERLIN et al. 1975).

The weather during the sampling period was mild with very little precipitation. The maximum temperatures ranged from 20 to 30°C and the minimum temperature from 10 to 15°C. Rainfall was 0.05 cm on the last day of sampling.

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