

Avdovich and D. Legault for the NMR spectra, and K. Khera for the gross pathological examination of the rats.

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Received for review March 11, 1975. Accepted May 16, 1975.

Dissipation of Parathion and Related Compounds from Field-Sprayed Lettuce

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In June 1974 in Yolo County, California, duplicate plots of Climax lettuce were sprayed at the rate of application of active ingredient of 0.5 lb and 1 lb per acre 7 days before harvest with Thiophos parathion 4 E.C. A control plot was also established and sampled before the other plots were sprayed and daily thereafter with the sprayed plots. The sprayed lettuce was analyzed for parathion and related compounds as the field head, trimmed head, and trimmings from the initial day of pesticide application through the harvest sample, 7 days later at both rates of spray application. To determine the depth of penetration and

amounts of residue present at each level within the head of the field lettuce, the outer 12 leaves were analyzed as a composite, the next 6 inner leaves, the next 6 inner leaves, and the remaining head. The sum total residues of parathion and related compounds on the untrimmed harvested lettuce samples 7 days after pesticide application were below the tolerance level of 1 ppm at the 0.5 lb rate of active ingredient per acre spray application. The trimmed heads at both rates of pesticide application were below 1 ppm residue levels at harvest.

Parathion applications have been recommended for the control of leaf-feeding aphids and leafminers on lettuce at the rate of 0.5 lb of actual material per acre not less than 7 days before harvest (*Calif. Agric. Exp. Stn. Bull.*, 1973). Storherr et al. (1964) have reported the identification and analysis of five organophosphate pesticides, including parathion, and their recoveries from crops fortified at 5.0, 1.0, and 0.1 ppm from eight different crops including lettuce. Coffin (1966) studied the oxidative metabolism and persistence of parathion and malathion on field-sprayed lettuce. Parathion was applied at a rate of 400 g of active ingredient per acre and was sampled at various intervals after spraying and was analyzed by paper chromatography for residues. Parathion residues decreased from 1.9 to 0.1 ppm in 4 days and detectable quantities were present at 15 days and longer. Small quantities of paraoxon and two unidentified metabolites were detected, at times within 2 days and longer after the parathion application. The effects of some climatic factors on the degradation of parathion and methylparathion residues on lettuce were investigated by Polizu et al. (1963). Parathion and methylparathion were sprayed in doses of 240 and 600 g/ha on lettuce in field and greenhouse tests followed by the determination of the toxic residues on the leaves. The degradation of the parathion and methylparathion was affected by exposure to sunshine and high temperature. The period between spraying and safe harvesting was 10-16 days in the field and 14-19 days in greenhouses.

Although parathion levels were determined by the above workers, most of the other possible related compounds

were not determined. The purpose of the present investigations was to determine quantitatively the fate of the levels of parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) as well as possible related compounds such as paraoxon (*O,O*-diethyl *O-p*-nitrophenyl phosphate), aminoparathion (*O,O*-diethyl *O-p*-aminophenyl phosphorothioate), *S*-phenylparathion (*O,O*-diethyl *S-p*-nitrophenyl phosphorothioate), *S*-ethylparathion (*O,S*-diethyl *O-p*-nitrophenyl phosphorothioate), *p*-nitrophenol, *O,O*-diethyl phosphate, and *O,O*-diethyl phosphorothioate in the environment on field-sprayed lettuce sampled daily from application through harvest.

EXPERIMENTAL SECTION

Lettuce Plots. In June 1974 in Yolo County, California, rows of Climax lettuce 40 in. wide and 48 ft in length were selected for duplicate spray applications of Thiophos parathion 4 E.C. at the rates of 0.5 (plot B) and 1 lb (plot C) of active ingredient per acre. Another plot of similar dimensions upwind from the others was established as a control plot (plot A). The lettuce selected was at the stage of maturity 7 days before harvest since the recommended spray application is 0.5 lb of active ingredient/acre 7 days before harvest. The first sampling of the control plot was taken before spraying the other plots. Each of the other plots was sampled immediately after spraying, and all plots were randomly sampled (approximately 6 kg) thereafter at the same time of day during the experiments' duration and extracted for analysis after subsampling composites. At the harvest sampling all the lettuce from each plot was completely harvested and random subsamples were immediately extracted for analysis. Samples were taken daily from time of pesticide application to time of harvest 7 days later. The

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Table I. Levels^a of Parathion and Related Compounds Applied to Head Lettuce in the Field in an Emulsifiable Concentrate Formulation

Sample day	Parathion, ppm ^b			Aminoparathion, ppm ^b			Paraoxon, ppm ^c			<i>p</i> -Nitrophenol, ppm ^b		
	Head	Trim	Total	Head	Trim	Total	Head	Trim	Total	Head	Trim	Total
Application Rate 1 lb per Acre of Active Ingredient												
0	2.68	25.8	11.7	0.259	2.27	0.709	0.006	0.072	0.026	0.046	0.140	0.072
1	1.10	14.2	7.39	0.113	1.16	0.547	0.003	0.070	0.021	0.030	0.113	0.076
2	0.760	9.62	4.89	0.093	0.763	0.520	0.004	0.070	0.025	0.026	0.094	0.082
3	0.695	7.47	3.71	0.087	0.652	0.438	0.006	0.080	0.031	0.027	0.073	0.064
4	0.527	5.59	2.87	0.070	0.549	0.334	0.005	0.073	0.023	0.038	0.066	0.055
5	0.377	4.98	2.24	0.076	0.520	0.212	0.004	0.067	0.014	0.044	0.067	0.050
6	0.224	4.34	1.96	0.058	0.385	0.137	0.007	0.066	0.014	0.043	0.065	0.054
7	0.083	2.20	1.62	0.012	0.118	0.085	0.010	0.060	0.019	0.048	0.072	0.059
Application Rate 0.5 lb per Acre of Active Ingredient												
0	1.21	11.3	4.88	0.152	1.13	0.394	0.006	0.041	0.031	0.053	0.108	0.071
1	0.586	7.14	3.64	0.085	0.776	0.255	0.004	0.024	0.022	0.050	0.084	0.070
2	0.293	4.70	2.35	0.037	0.422	0.214	0.004	0.032	0.027	0.044	0.069	0.063
3	0.205	3.09	1.47	0.057	0.263	0.168	0.005	0.042	0.023	0.028	0.056	0.048
4	0.189	2.30	1.12	0.069	0.153	0.132	0.006	0.041	0.020	0.022	0.046	0.038
5	0.136	1.69	1.04	0.045	0.128	0.112	0.005	0.033	0.021	0.024	0.049	0.040
6	0.104	1.26	0.880	0.029	0.129	0.090	0.005	0.030	0.017	0.021	0.057	0.043
7	0.059	1.01	0.650	0.010	0.084	0.043	0.006	0.032	0.015	0.010	0.061	0.045

^a Parts per million calculated on a fresh weight basis; trimmed head 56.2% and trim 43.8% of total head weight; percent moisture head, 94.8 ± 0.4; percent moisture trim, 91.2 ± 0.1; percent moisture total head, 92.5 ± 1.0. ^b Ppm method sensitivity, 0.001. ^c Ppm method sensitivity, 0.002.

sprayed plots were duplicated and the analytical data represent average values for the duplicate plots. The percent moisture content of the field lettuce head was 92.5 ± 1.0, the trimmed lettuce head was 94.8 ± 0.4, and the lettuce trim was 91.2 ± 0.1.

Sampled Lettuce Analyzed. The sampled sprayed lettuce heads were analyzed by the following procedures. (1) The total head and trim leaves were chopped, mixed, and analyzed (field lettuce head, trim, and head, 909 g). (2) The edible head was separated from the trim and each portion analyzed separately after chopping and mixing (trimmed lettuce head, 501 g; lettuce trim, 408 g). (3) To determine the depth of penetration of the pesticide spray into the field lettuce head, the trim leaves were removed in groups of 12 leaves, 6 and 6, and each group of leaves and each remaining lettuce head was chopped, mixed, and analyzed separately.

Spray Application. The lettuce was sprayed with Thiophos 4 E.C. using a Hudson Climax 6335 Simplex Sprayer, 8.5-l. capacity, equipped with a Hudson 149-403 spray control valve and a nozzle extension. A 0.95 cm i.d. flexible neoprene, Teflon-lined rubber tubing for chemical inertness was attached between the pressure tank and the Roto-Spray Nozzle.

Parathion Applied. The parathion was in the formulation of American Cyanamide Co. designated as Thiophos parathion 4 E.C. (1 gal contains 4 lb of parathion).

Active ingredients were: parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate), 46.7%; xylene-range aromatic hydrocarbon solvent, 47.6%; inert ingredients, 5.7%. Plot B (0.5 lb of active parathion/acre) was sprayed with 1 gal of water containing 1.666 g of parathion using the equipment described above and plot C (1 lb of active parathion/acre) was sprayed with 1 gal of water containing 3.334 g of parathion.

The formulation was found to contain, by analysis and calculated as the parathion active ingredient equivalent, 95.4% parathion, 3.88% aminoparathion, 0.12% paraoxon, 0.11% *O,S*-diethyl *O-p*-nitrophenyl phosphorothiolate, 0.05% *O,O*-diethyl *S-p*-nitrophenyl phosphorothiolate,

0.43% *p*-nitrophenol, and 0.01% *O,O*-diethyl phosphorothioate.

Sample Extraction. Twenty-five grams of lettuce was extracted by refluxing in 250 ml of a solvent mixture containing 5% 2-propanol-95% benzene (v/v) for 30 min. The refluxed sample was cooled in an ice bath and the solvent was filtered through Whatman No. 1 filter paper. The extraction was repeated by refluxing the lettuce two times further after the addition of 2 ml of 0.1 *N* HCl before each reflux and the filtered solvent was pooled and stored for cleanup and analysis. The extracted plant material was discarded. All solvents used in the experiment were reagent grade freshly distilled prior to use.

Diazomethane Preparation and Methylation of the Sample Extract. The laboratory preparation of diazomethane is detailed on the label of the Diazald reagent bottle obtained from the Aldrich Chemical Co. (Milwaukee, Wisc.).

The extractives from 10 g of lettuce (300 ml of solvent extract) were concentrated *in vacuo* at 50-60° to approximately 1 ml and the volume was quantitatively adjusted to 5 ml with *n*-hexane. The extractives equivalent to 5 g of lettuce were added to 5 ml of ethereal diazomethane solution at room temperature and allowed to stand for at least 15 min prior to sample cleanup.

Sample Cleanup and Analysis. The parathion and related compounds in the lettuce samples were cleaned up on Florisil and analyzed by gas-liquid chromatography as previously described for these compounds as residues on spinach (Archer, 1974). The parts per million data are based on fresh weight calculations since the percent moisture content of the total head, trim, and trimmed head did not change significantly during the 7-day experiment (Table I).

RESULTS AND DISCUSSION

The control field lettuce head 7 days preharvest contained trace amounts of the following compounds at parts per million concentrations: parathion, 0.012; aminoparathion, 0.002; *p*-nitrophenol, 0.042; paraoxon, 0.001; *S*-ethylparathion, <0.010; *S*-phenylparathion, <0.010; diethyl

Table II. Levels and Depth of Penetration of Parathion and Major Related Compounds on Head Lettuce Sprayed with Two Rates of Thiophos Parathion 4 E.C.

Sample analyzed	ppm residue ^a					
	Initial sampling			Harvest sampling		
	Parathion	Amino-parathion	<i>p</i> -Nitro-phenol	Parathion	Amino-parathion	<i>p</i> -Nitro-phenol
Application Rate 1 lb of Active Ingredient per Acre						
Outer 12 leaves ^b	14.7	0.910	0.076	2.80	0.062	0.084
Next inner 6 leaves ^b	21.9	1.52	0.077	3.18	0.224	0.056
Next inner 6 leaves ^b	3.95	0.238	0.068	2.91	0.172	0.060
Trimmed head ^c	0.016	0.003	0.082	0.134	0.004	0.045
Application Rate 0.5 lb of Active Ingredient per Acre						
Outer 12 leaves ^b	7.85	0.444	0.031	1.82	0.076	0.081
Next inner 6 leaves ^b	9.87	0.492	0.055	1.05	0.112	0.085
Next inner 6 leaves ^b	11.4	0.846	0.027	0.123	0.025	0.086
Trimmed head ^c	0.152	0.009	0.008	0.004	<0.001	0.061

^a Parts per million on fresh weight basis. ^b Lettuce trim 91.2 ± 0.1% moisture; 51.7% of total field lettuce head by weight. ^c Lettuce head 94.8 ± 0.4% moisture; 48.3% of total field lettuce head by weight.

phosphate, <0.001; and *O,O*-diethyl phosphorothioate, <0.001.

The four major compounds detected in all samples were parathion, aminoparathion, paraoxon, and *p*-nitrophenol with the other compounds listed above present, if at all, in concentrations below the limit of method detection. The aminoparathion and other compounds as detected in the spray formulation were applied as contaminants and were not degradation products as shown by the formulation analysis above. Table I shows the levels of parathion and related compounds on the lettuce sprayed at the rate of 0.5 and 1 lb of active ingredient per acre based upon 46.7% active ingredient. At the 0.5 lb/acre rate the total residue as parathion was approximately 5.4 ppm on the field lettuce head, 1.4 ppm on the trimmed head, and 12.6 ppm on the trimmings on the initial sample and 0.75, 0.09, and 1.2 ppm, respectively, on the harvest sample. At the 1 lb/acre rate the residues were 12.5, 3.0, and 28.3 ppm, respectively, on the initial sampling and 1.8, 0.15, and 2.5 ppm on the harvest sampling. At the 1 lb/acre rate *S*-ethylparathion was present at concentrations of 0.026 ppm on the untrimmed head, 0.019 on the trimmed head, and 0.136 ppm on the trimmings and at the 0.5 lb/acre rate 0.023, 0.018, and 0.102 ppm, respectively. After day 2, these residues dropped to <0.010 ppm. At both rates of application, *S*-phenylparathion, *O,O*-diethyl phosphate, and *O,O*-diethyl phosphorothioate were not detected in any of the lettuce samples (<0.001 ppm).

Table II shows the levels and depth of penetration of the parathion and major related compounds on the field lettuce sprayed at the two rates of application with Thiophos parathion 4 E.C. In all cases of initial and harvest samples at the 0.5 and 1 lb rates of application, the pesticide levels under the conditions of these experiments on the trimmed heads which had the outer 24 leaves removed were well below the 1-ppm tolerance levels. Since the average weight of the field heads was 909 g and the trim weighed 469 g, an ample amount of lettuce head (440 g) remained after 24 leaves were removed from the field head as trim. The first

12 leaves represented 26.0% of the total field head weight and the next two trim levels represented 13.8 and 11.9%, respectively, with the trimmed head representing 48.3% of the total field weight. Although it is usually customary during marketing of lettuce to remove approximately 12 trim leaves, the present data indicate that the removal of approximately 24 leaves was necessary to eliminate practically all of the pesticide residues (Table II). At the 0.5 lb rate of parathion application on the lettuce, 40.7% of the total initial residue was found on the first 12 leaves of trim, 25.9% on the next 6 leaves, 32.0% on the final 6 leaves, and 1.4% on the trimmed head. On the harvest sample, 71.6, 20.3, 3.1, and 5.0% of the total residue was found on each level of trim and head, respectively. At the 1 lb rate of parathion application on the lettuce, the initial residue fractions of the total level were 52.0, 41.8, 5.8, and 0.4% and on the harvest sample 40.1, 29.8, 23.4, and 6.7%, respectively. As shown by the above data, pesticide residues can be effectively removed from sprayed field lettuce by proper trimming at harvest.

ACKNOWLEDGMENT

The technical assistance of James D. Stokes and Christopher Potter in aspects of this work is gratefully acknowledged; appreciation is given to the Department of Vegetable Crops and especially J. Clostermyer of the Mann Laboratory, University of California, Davis, for providing the lettuce plots.

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Received for review March 31, 1975. Accepted June 6, 1975.