ACKNOWLEDGMENT

The authors are grateful to L. H. Lyall and R. Main of the Ottawa Research Station, Research Branch, Agriculture Canada, for close cooperation in the provision of the crops and spray equipment used in the study.

LITERATURE CITED

Engst, R., Schnaak, W., Rattba, H., *Nachrichtenbl. Dtsch. Pflanzenschutzdienstes (Braunschweig)* **22,** 26 (1968).
Hylin, J. W., *Bull. Environ. Contam. Toxicol.* **10,** 227 (1973).
Ludwig, R. A., Thorn, G. D., Miller, D. M., *Can. J. Bot.* **32,** 48 (1954).
Newsome, W. H., *J. Agric. Food Chem.* **20,** 967 (1972).
Newsome, W. H., *J. Agric. Food Chem.* **22,** 886 (1974).
Newsome, W. H., *J. Agric. Food Chem.* **23,** 348 (1975).
Newsome, W. H., Laver, G. W., *Bull. Environ. Contam. Toxicol.* **10,** 151 (1973).
Pecka, Z., Baulu, P., Newsome, H., *Pestic. Monit. J.,* in press (1975).
Watts, R. R., Storherr, R. W., Onley, J. H., *Bull. Environ. Contam. Toxicol.* **12,** 224 (1974).
Yip, G., Onley, J. H., Howard, S. F., *J. Assoc. Off. Anal. Chem.* **54,** 1373 (1971).

Received for review December 23, 1974. Accepted March 31, 1975.

Persistence of Dimethoate and Dimethoxon on Cherries

James D. MacNeil,* Mitsuru Hikichi, and Fred L. Banham

Two sprays of dimethoate, 10 fluid oz per 100 gal, applied 28 and 14 days prior to harvest on sweet and sour cherry trees, resulted in residues of less than 2.0 ppm of combined dimethoate and dimethoxon at harvest. The recommended use pattern of dimethoate for control of black and western cherry fruit flies in British Columbia should not result in residues at harvest exceeding tolerance levels.

Dimethoate, *O,O*-dimethyl *S*-(*N*-methylcarbamoyl)-methyl phosphorodithioate, is a broad spectrum contact and systemic insecticide that is registered in Canada for control of a wide variety of insect pests. Recently, the use pattern for this material was extended to include control of black cherry fruit fly and western cherry fruit fly. A preharvest interval of 15 days for the last spray application has been set and a residue tolerance of 2 ppm of dimethoate has been established.

Residue studies with dimethoate applied to cherries have previously been conducted in Europe. Beitz et al. (1969) in Germany reported that a 7-day interval to harvest following aerial application of the insecticide should be sufficient, but a further study (Beitz, 1973) indicated that ground spraying led to more persistent residues. Mitic-Muzina et al. (1971) reported that dimethoate degraded more slowly than diazinon and carbaryl on cherries. Residues of dimethoate have also been studied on other tree-fruit crops, including peaches (Mestres and Barrois, 1964) and citrus crops (Woodham et al., 1974a,b).

Experiments were carried out during 1973 to determine the degradation rate of dimethoate and the persistence of its oxygen analog, dimethoxon, on cherries in the Okanagan Valley of British Columbia.

EXPERIMENTAL SECTION

Plots of sweet cherries (Lamberts) and sour cherries (Meteor, Northstar, and English Morello) were treated with dimethoate (Rogor 40% EC) at the recommended rate of 10 fluid oz per 100 Imperial gal. Trees were sprayed to the point of run-off using a portable plot sprayer operated at 300 psi. The first cover spray was applied 6 days after the first cherry fruit fly was trapped and a second cover spray was applied 14 days later. Samples of fruit were taken 14 days after the application of the first cover spray (prior to application of the second cover spray), and then at intervals of 1, 2, 4, 7, and 14 days after the second spray was applied. Sample fruit was frozen and held for later analysis. The sweet cherry test plot consisted of six trees while the sour cherry plot consisted of five trees. Fruit used as controls was picked from trees separated from treated plots by an unsprayed buffer row. The plot pattern (six sweets, five sours) was duplicated for the controls.

Composite samples of sweet cherries and sour cherries were prepared by pooling fruit collected from each plot for each sampling date. The extraction procedure was adapted from that reviewed by Zweig and Sherma (1972). A 1-kg sample of the composite was chopped in a kitchen meat grinder and two 100-g sub-samples were then taken. Each was macerated in an explosion-proof Waring Blendor (Waring Products, Inc.) with 150 ml of residue quality dichloromethane (Caledon Laboratories, Inc., Georgetown, Ontario, Canada) for 5 min. Fifty grams of anhydrous sodium sulfate was then added to the macerate and the mixture was left to stand for 30 min with periodic swirling. Six grams of activated charcoal was added and mixed, and the mixture left to stand for another 2 min. The macerate was filtered through a Millipore glass pad under suction and washed with two 50-ml volumes of dichloromethane. The filtered solution was evaporated to dryness using a rotary evaporator (Buchi Rotavapor-R) and the residue taken up in 1 ml of residue quality acetone (Caledon Laboratories, Inc.).

Chromatographic analyses were carried out on a HP 5715A gas chromatograph (Hewlett-Packard) equipped with a flame photometric detector (Tracor, Inc.) operated in the phosphorus mode (526 nm) and with the following set conditions: oven temperature, 190°; detector temperature, 200°; nitrogen flow rate, 30 ml/min; hydrogen, oxygen, and air flow rates, 125, 25, and 45 ml/min, respectively; attenuation, 1000 × 32. The detector was modified as suggested by Burgett and Green (1974) to prevent solvent flame-out and provide an improved signal-to-noise ratio. On column injection was used.

Chromatography was carried out on a glass column, 6 ft × ⅛ in., packed with 3% OV-17 on Chromosorb W-HP, 80–100 mesh (Chemical Research Services, Inc.). The column was conditioned overnight at 250°, following which re-

Research Station, Agriculture Canada, Summerland, British Columbia, Canada VOH IZO.

Table I. Rate of Degradation of Dimethoate and Dimethoxon on Cherries

	Sweet cherries			Sour cherries		
Day	Dimethoate, ppm	Dimethoxon, ppm	Total ppm	Dimethoate, ppm	Dimethoxon, ppm	Total ppm
0[a]	0.24	0.14	0.38	0.48	0.22	0.70
1	2.30	0.24	2.54	2.76	0.23	2.99
2	1.65	0.21	1.86	1.91	0.23	2.14
4	1.24	0.23	1.47	1.56	0.31	1.87
7	0.89	0.21	1.10	0.80	0.28	1.08
14	0.53	0.19	0.72	0.38	0.33	0.71

[a] Residues measured at day 0 are those remaining from first cover spray applied 14 days earlier on samples taken prior to the application of the second cover spray.

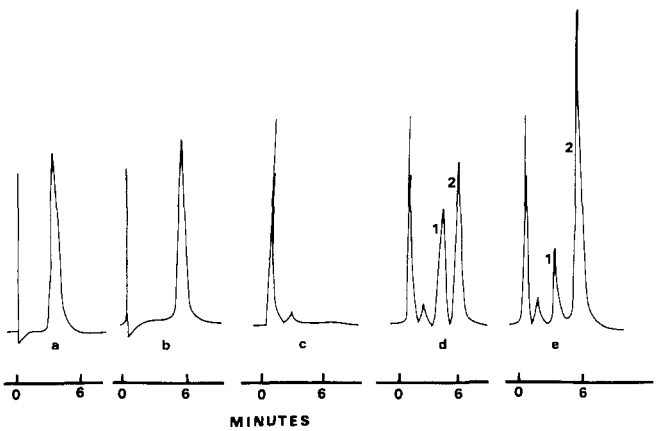

Figure 1. Chromatograms of: (a) dimethoxon (t_R = 3.7 min); (b) dimethoate (t_R = 6.0 min); (c) sweet cherry control; (d) sweet cherry control fortified at 0.5 ppm with dimethoxon (1) and dimethoate (2); (e) day 7 sweet cherry sample showing dimethoxon (1) and dimethoate (2). Injection volume for all samples, 5 μl; column, 3% OV-17 on 80–100 mesh Chromosorb W-HP; N_2 flow rate, 30 ml/min; oven temperature, 190°.

peated injections of dimethoate and dimethoxon were made until good reproducibility was obtained. A 5-μl aliquot of each cherry extract was injected for all samples analyzed. Calibration curves were prepared using solutions prepared from analytical standards of dimethoate and dimethoxon.

The detector signal was integrated using a Model 477 digital integrator (Varian Associates) and recorded on a 1-mV Speed Servo II recorder (Esterline Angus). The integrator was operated at the following settings: peak width one-half height, 30; slope sensitivity, 5; digital base-line corrector rate, 5; count rate, 500 Hz/min. Signals were fed to the recorder as logarithmic outputs and recorded at a chart speed of 7.5 in./hr.

Efficiency of extraction was studied using 50-g samples of controls (whole cherries) fortified with both dimethoate and dimethoxon standards prior to addition of dichloromethane and maceration in the blender. Identical analytical procedures were followed with fortified extracts as with all other samples, with the exception that the grinding procedure was omitted as this was used only to obtain a more uniform sample of treated fruit.

RESULTS AND DISCUSSION

Table I shows that total residues of dimethoate and dimethoxon were below the accepted tolerance levels for dimethoate prior to the end of the 15-day interval between last application and harvest. Values reported are averages for two replicates. Rates of degradation were similar on both sweet and sour cherries.

Table II. Recovery of Dimethoate and Dimethoxon from Fortified Samples (Sweet Cherry Controls) Containing Both Dimethoate and Dimethoxon

Compd added	Fortification level, ppm	Apparent residues, ppm	Recovery, %
Dimethoate	0.40	0.43	108
Dimethoxon	0.40	0.43	103
Dimethoate	1.00	1.03	103
Dimethoxon	1.00	0.85	85

Residues measured in this experiment are higher than would often be encountered with normal use of dimethoate for cherry fruit fly control. In most cases, one early season cover spray is effective in providing control until harvest. Thus, the monitoring of trees treated with two cover sprays provides data on residues where extreme control measures are needed. The results for "day 0" in Table I are indicative of residues that would result where only one spray is required. These would be further diminished by the further aging of the spray deposits in the final 2 weeks to harvest and by dilution effect of the ripening cherries increasing in size. Sweet cherries show about a twofold weight increase during the 2 weeks prior to harvest, while sour cherries show a somewhat greater increase.

The OV-17 packing was chosen for analyses in preference to the DC-200 packing used by other researchers such as Stellar and Pasarella (1972) and Woodham et al. (1974a,b) due to the higher temperature stability of OV-17. Also, inclusion of polyethylene glycol in the sample and its injection on the column (Stellar and Pasarella, 1972) to obtain good separation of dimethoate and dimethoxon is not required on OV-17. Good sensitivity was obtained with excellent resolution of the two peaks at 190°. Retention time for dimethoxon was 3.7 min, while that for dimethoate was 6.0 min. Samples contained dimethoate at 10–50 ng/5 μl injection and dimethoxon at 10–30 ng/5 μl injection. Linear calibration plots were obtained for both compounds in these respective ranges. Detection limits were about 5 ng for dimethoxon and 1–2 ng for dimethoate. Typical chromatograms are shown in Figure 1.

The cherry extracts did not contain any significant interfering peaks. Analysis of controls taken each sampling date revealed no dimethoate or dimethoxon. It should be noted, however, that diazinon and dimethoxon were found to have equal retention times on the 3% OV-17 column used in this study. Samples which may contain diazinon should therefore be run on the DC-200 packing, at least for confirmation purposes. None of the other organophosphorus insecticides commonly used in the orchard industry, such as azinphos-methyl, ethion, malathion, parathion, and phosmet,

were found to interfere in the analysis. Some peak broadening and tailing were observed after a number of cherry extracts had been run through the column. This was produced by a build-up of co-extractives on the glass wool end plug of the column at the injection port. Replacement of this plug with a new one whenever the problem developed returned the column to its former efficiency.

Studies performed on samples fortified prior to extraction with both dimethoate and dimethoxon showed good recoveries, as reported in Table II. As dimethoate and dimethoxon were applied and allowed to dry on the surface of the fruit prior to extraction, these results should approximate the recoveries to be expected from the surface of cherries.

The results indicate that residues in excess of accepted tolerances will not be found in cherries treated with dimethoate if recommended treatment rates and application practices are followed.

ACKNOWLEDGMENTS

We thank G. S. Cooper of Cyanamid of Canada for supplying analytical standards of dimethoate and dimethoxon and W. A. Charnetski, Agriculture Canada, Research Station, Lethbridge, Alberta, for a standard of dimethoxon.

LITERATURE CITED

Beitz, H., *Gartenbau* **20,** 106 (1973)
Beitz, H., Seefeld, F., Geissler, K., *Nachrichtenbl. Dtsch. Pflanzenschutzdienst (Berlin)* **23,** 103 (1969).
Burgett, C. A., Green, L. E., *J. Chromatogr. Sci.* **12,** 356 (1974).
Mestres, R., Barrois, C., *Trav. Soc. Pharm. Montpellier* **24,** 176 (1964)
Mitic-Muzina, N., Adamovic, V., Pantovic, D., Petrovic, O., Sokic, B., *Zast. Bilja* **22,** 43 (1971).
Stellar, W. A., Pasarella, N. R., *J. Assoc. Off. Anal. Chem.* **55,** 1280 (1972).
Woodham, D. W., Hatchett, J. C., Bond, C. A., *J. Agric. Food Chem.* **22,** 239 (1974a).
Woodham, D. W., Reeves, R. G., Williams, C. B., Richardson, H., Bond, C. A., *J. Agric. Food Chem.* **22,** 731 (1974b).
Zweig, G., Sherma, J., "Analytical Methods for Pesticides and Plant Growth Regulators. VI. Gas Chromatographic Analysis", Zweig, G., Ed., Academic Press, New York, N.Y., 1972, pp 357–375.

Received for review November 25, 1974. Accepted February 24, 1975. Contribution No. 405 from Agriculture Canada.

Distribution of Carbaryl and 3,5-Xylyl Methylcarbamate in an Aquatic Model Ecosystem

Jun Kanazawa,[1] Allan R. Isensee, and Philip C. Kearney*

The distribution and metabolism of ^{14}C-1-naphthyl-labeled methylcarbamate (carbaryl) and ^{14}C-*N*-methyl-labeled 3,5-xylyl methylcarbamate (XMC) were studied in an aquatic model ecosystem containing 10 kg of Matapeake soil, 80 l. of water, and catfish, crayfish, daphnids, snails, algae, and duckweed. Maximum carbaryl concentration (based on total radioactivity) in water was 16 ppb after 7 days, and decreased to 9.5 ppb after 22 days. XMC increased gradually to 35.8 ppb after 34 days. Bioaccumulation ratios were relatively large (2000–4000) for algae and duckweed, but those for snails, catfish, and crayfish were low (100–500). Soil was the major repository for ^{14}C in these microecosystems; the biomass contained between 0.11 and 1.59% of the ^{14}C. Forty-five percent of residual ^{14}C from carbaryl and 38% residual ^{14}C from XMC could not be extracted from soils and appeared to be bound. Bound insecticide residues in soil were nontoxic to daphnids. Only α-naphthol, carbaryl, and XMC were identified in soils.

Organochlorine insecticides have been used intensively worldwide for more than 20 years. Some of these insecticides are very persistent in the environment and have resulted in widespread contamination. Moreover, certain of these insecticides are bioconcentrated in aquatic and terrestial food chains. Organochlorines are being increasingly supplanted by organophosphorus and carbamate insecticides. Since these insecticides are esters, they are likely to be degraded in the environment, metabolized in organisms, or excreted after conversion to water-soluble metabolites. Therefore, significant bioaccumulation of these insecticides would not be expected, but they should be investigated because of their extensive use.

The metabolic pathways of 1-naphthyl methylcarbamate (carbaryl) in animals (Dorough, 1970), plants and insects (Kuhr, 1970), and a soil fungus (Liu and Bollag, 1971) have been studied extensively. However, the fate and metabolism of methylcarbamate insecticides in the aquatic environment and in aquatic organisms have not been investigated extensively. Eichelberger and Lichtenberg (1971) examined the persistence of carbaryl in Ohio river water and showed only 5% remained after 1 week and nondetectable levels by 2 weeks. Johnson (1968) reported that the 48-hr LD_{50} of carbaryl for goldfish was 1.75 ppm. It is more toxic to crustacea than to fish and mollusks, but the reverse is true for its metabolites. Koren (1973) studied the uptake and persistence of carbaryl in channel catfish (*Ictalurus punctatus*). Kazano et al. (1972) found that hydrolysis was the main degradation pathway of carbaryl and 3,5-xylyl methylcarbamate (XMC) in five Japanese paddy field soils. They reported that ring opening of ^{14}C-1,4,5,8-ring-labeled naphthol was relatively slow, and more than 70% of the radioactivity was bound to soil humic substances. In Japan, more than ten methylcarbamate insecticides, including carbaryl and substituted phenyl methylcarbamates, have been used successfully for control of leaf hoppers on rice plants. These insecticides are applied directly to water near streams. When applied in upland fields, they adsorb on soil particles which may be transported into streams by runoff.

Agricultural Environmental Quality Institute, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Beltsville, Maryland 20705.
[1] Present address: National Institute of Agricultural Sciences, 2-1 Nishigahara, Kita-Ku, Tokyo, 114 Japan.