was included in the analysis, but the amounts recovered never exceeded 0.12 ppm; about 70% of the samples had only a trace or none. Total residues for the whole carrot ranged from 0.18 to 0.40 ppm. The residues were greater in the peel than in the pulp by a factor of approximately 10:1. Total residues in the top 3-cm section ranged from 0.33 to 1.47 ppm; in the upper 3–6 cm section residues were much less and ranged from 0.04 to 0.25. In the middle and bottom sections maximum residues were 0.13 and 0.05 ppm, respectively. Total residue levels for whole carrots did not differ appreciably for the four insecticides investigated (Table III). However, there was considerable variation in their distribution within the carrot, which may have some bearing on the efficacy of the insecticides for preventing carrot maggot damage.

Wheatley and Hardman (1967) suggested that larval toxicity results from translocation of the insecticides through the lateral roots to the lateral feeding sites, so that control is achieved by feeding rather than by contact action against eggs and larvae. Finlayson and Suett (1975) suggested that insecticide residues in the soil contribute more to the late protection of carrots from carrot maggot than do residues within the carrot because those within the carrot are diluted by growth. This study indicates that other factors may also be involved, for instance, the concentration of residues in the upper peel and the near absence of residues in the lower level of the root. Ethion was concentrated mostly in the peel and in the upper sections of the carrots which were well protected. But the roots were damaged more severely in the lower half than were carrots treated with carbofuran or fensulfothion (Finlayson et al., 1972). These treatments resulted in residues more than twice as high in the bottom 8 cm than those resulting from ethion treatment. The proportion of the total residue levels within the top 3 cm was calculated; for three of the insecticides more than 50% was present. Carbofuran residues in the same section were slightly more than 40%. This difference in distribution may be attributed to the greater water solubility of carbofuran allowing deeper penetration of the aqueous sprays in the soil. It is thus evident that the common practice of discarding the top 0.5 in. of the carrot and peeling the rest removes most of the residue.

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Degradation of Endosulfan and Ethion on Pears and Pear and Grape Foliage

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A mixture of endosulfan (6 lb of Thiodan-50 WP) and ethion (8 lb of Ethion-25 WP) recommended for control of pear psylla was applied to four experimental blocks of pear trees to study rates of degradation. In addition, two blocks of pears were treated with endosulfan (6 lb of Thiodan-50 WP) only and two blocks were treated with the endosulfan–ethion mixture to determine insecticide residues at harvest. Endosulfan residues on treated fruit were below the 2 ppm tolerance established for endosulfan on pears 14 days after application. Ethion residues were within the 1 ppm tolerance 20–35 days after application. Degradation rates of the two insecticides on pear and grape foliage are also reported.

Pear psylla (*Psylla pyricola* Foerster) is a major pest of pear orchards, causing discoloration and damage to both fruit and leaves. A major problem in controlling this insect is its rapid development of resistance to control materials. Present recommendations for summer control include endosulfan alone or in combination with ethion.

Endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methane-2,4,3-benzodioxathiepine 3-oxide) occurs in technical mixtures as two isomers, usually designated α and β in an approximate ratio of 70:30. The chemistry of endosulfan has been reviewed by Maier-Bode (1968). The only investigations he reported of residues of endosulfan on pears were those done by Cassil (1960) in California. Samples analyzed 1 and 3 weeks after final application of the insecticide (following applications in May, July, and August with a total of 3.5 lb of active ingredient per acre), showed total residues of α- and β-endosulfan to be 0.2 ppm 3 weeks after the August application.

Ethion, tetraethyl S,S^1-methylene bis(phosphorothiolethionate), is a nonsystemic insecticide and acaricide that is registered for control of a variety of fruit insects in Canada. The persistence of ethion in soil, water-borne silt, crops, and the atmosphere was studied by Hinden and Bennett (1970), who found no carryover of residues of ethion in soil from year to year and residues in crops at

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harvest greatly reduced from those measured at time of application. Gunther et al. (1962) studied the persistence of ethion on citrus fruit, finding the half-life for the insecticide on lemons and oranges to be 25–44 days.

The present experiment was planned to determine the persistence of endosulfan and ethion on pear fruit and foliage under local growing conditions. As endosulfan is recommended for control of grape leafhoppers and the winged form of grape phylloxera, residues on grape foliage were also studied for comparative purposes.

EXPERIMENTAL SECTION

Four plots of semi-dwarf pear trees (mixed varieties) were sprayed on July 26, 1974, with a mixture of 6 lb of Thiodan 50 WP (endosulfan) and 8 lb of Ethion 25 WP (ethion) per acre. Application was made with a Turbo-Mist low-volume air-blast sprayer. Two of the plots were on trickle irrigation, while the other two had over-tree sprinklers. Plots consisted of from 20 to 60 trees.

Three plots of grapes irrigated by overhead sprinklers containing approximately 100 vines per plot were sprayed with Thiodan 50 WP at a rate of 1 lb/acre. Some residual ethion was present in the spray tank from the mixture applied to the pears, as ethion residues were later found on the grape foliage sampled.

Composite samples of 50 leaves were taken from pear trees in each plot at time of application and then at intervals of 1, 3, 6, 14, 21, 28, and 35 days after application. A disk of surface area 7.26 cm^2 was cut from each leaf and the 50-disk composite was stripped of insecticide by washing in 50 ml of redistilled residue-free hexane (Caledon Laboratories). The surface strips were held under refrigeration until analyzed.

Samples of 18 pears were collected from two of the plots (one from trickle irrigation, one on overtree sprinklers) for each sampling date. In addition, samples of Anjou pears treated at a rate of 6 lb of Thiodan 50 WP per acre were harvested and analyzed 14 days after treatment. Other Anjou samples treated with 6 lb of Thiodan 50 WP and 8 lb of Ethion 25 WP were harvested and analyzed 20 days following treatment. These corresponded to the recommended time limitations from spray application to harvest for endosulfan (14 days) and ethion (20 days). Irrigation of these plots was by standard undertree sprinklers.

Composite samples from each plot were weighed and ground with a food chopper (Braun, Inc.) and a 50-g sub-sample was taken from each ground composite for analysis. A standard extraction procedure for fruit from "Analytical Methods for Pesticide Residues in Foods" (1969) was then followed. Briefly, the sample was extracted with acetonitrile in a high-speed Waring Blendor, partitioned into hexane, and chromatographed on a Florisil column. These are procedures 5.1 (a), 6.1, and 7.2 (b), respectively, from the analytical methods manual used. Fractions eluted from the Florisil column were reduced in volume to 10 ml for gas chromatographic analysis.

Composite samples of 25 leaves were collected from each of the grape plots. Two disks, each of surface area 7.26 cm^2, were cut from each leaf, washed with 50 ml of hexane, and stored under refrigeration until analyzed. Samples were collected on the same schedule as the pear leaves.

Analyses were performed with a Hewlett-Packard HP5713A gas chromatograph equipped with a linear ^{63}Ni electron capture detector. Separations were on a 4 ft × 0.25 in. i.d. glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcon AW-DMCS, 100–120 mesh (Supelco, Inc.). Carrier gas was 5% methane–95% argon at a flow rate of 35 ml/min. Oven temperature was 195°C; detector temperature was 300°C. The packing was conditioned at 225°C for 24 hr prior to use. Attenuation was set according to concentrations of insecticides in each sample. Standards were run at all attenuations used. Retention times for compounds analyzed on the column were: α-endosulfan, 4 min, 43 sec; β-endosulfan, 8 min, 50 sec; endosulfan sulfate, 14 min, 13 sec; ethion, 10 min, 55 sec. An injection volume of 1 μl was used for all samples.

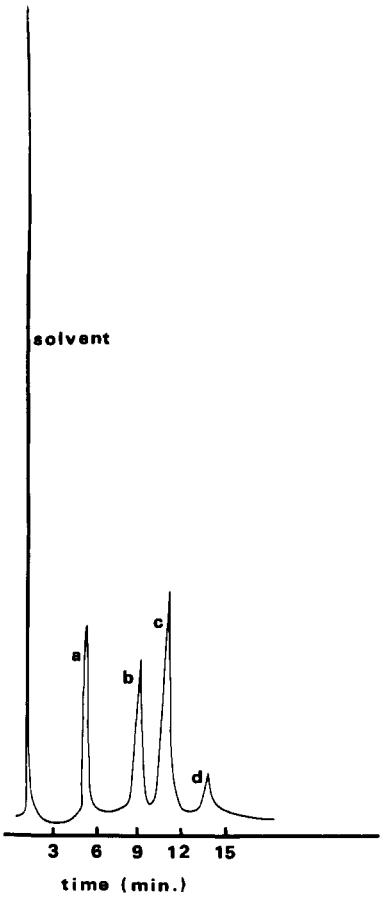

Figure 1. Typical chromatogram of separation of (a) α-endosulfan; (b) β-endosulfan; (c) ethion; (d) endosulfan sulfate. Chromatographic conditions: 4 ft × 0.25 in. glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcon AW-DMCS, 100–120 mesh; oven temperature, 195°C; detector temperature, 300°C; attenuation, 256; carrier, 5% methane-95% argon at 35 ml/min.

Results were confirmed using a 4 ft × 0.25 in. i.d. glass column packed with 3% OV-17 on Chromasorb W-HP, 80–100 mesh (Chemical Research Service, Inc.) at a carrier flow rate of 60 ml/min, oven temperature of 215°C, and detector temperature of 300°C. Retention times were: α-endosulfan, 7 min, 40 sec; β-endosulfan, 14 min, 20 sec; endosulfan sulfate, 20 min; ethion, 16 min, 40 sec.

Analytical standards of α-endosulfan, β-endosulfan, endosulfan sulfate, and ethion were provided by Niagara Chemicals.

RESULTS AND DISCUSSION

Ethion was found to be a more persistent compound than endosulfan, both on the fruit and on the foliage. Results in Table I show that β-endosulfan is more persistent on the fruit than its isomer, α-endosulfan. Endosulfan sulfate reached its maximum concentration 2–4 weeks following application. However, total endosulfan residues were well below accepted tolerances by this time. α-Endosulfan disappeared from the fruit very rapidly compared to the other compounds, with approximately 75% loss in the first week following application. Sample

Table I. Residues of Endosulfan and Ethion on Pears Sprayed with 6 lb/Acre Thiodan 50 WP and 8 lb/Acre Ethion 25 WP, July 26, 1974[a]

		Concentration, ppm			
t, weeks	Sample wt, g	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	Ethion
0	552 ± 15	4.02 ± 0.19	2.67 ± 0.03	0.04 ± 0.02	3.96 ± 0.31
1	579 ± 68	0.80 ± 0.11	1.68 ± 0.28	0.08 ± 0.02	2.54 ± 0.12
2	1042 ± 10	0.60 ± 0.15	0.80 ± 0.09	0.24 ± 0.03	1.95 ± 0.08
3	1317 ± 69	0.32 ± 0.02	0.44 ± 0.01	0.18 ± 0.01	1.18 ± 0.26
4	1620 ± 38	0.24 ± 0.03	0.30 ± 0.09	0.19 ± 0.06	1.19 ± 0.01
5	2132 ± 108	0.12 ± 0.01	0.20 ± 0.02	0.12 ± 0.06	0.67 ± 0.01

[a] Values are averages for two replicate plots, one on over-tree irrigation, the other on trickle irrigation. Variations reported are differences from the arithmetic mean.

Table II. Recoveries of α-Endosulfan, β-Endosulfan, Endosulfan Sulfate, and Ethion from Fortified Pear Samples (Average of Three Replicates)

Fortification level, all compds, ppm	α-Endosulfan, ppm	β-Endosulfan, ppm	Endosulfan sulfate, ppm	Ethion
0.10	0.13 ± 0.01	0.12 ± 0.01	0.13 ± 0.01	0.09 ± 0.01
1.00	0.95 ± 0.06	1.03 ± 0.06	0.98 ± 0.05	0.94 ± 0.05
Control	0	0	0	0

[a] Differences reported are standard deviations.

Table III. Residues of Endosulfan and Ethion on Pear Leaves Resulting from Application of 6 lb/Acre Thiodan 50 WP and 8 lb/Acre Ethion 25 WP, July 26, 1974

	Concentration of insecticide, μg/cm²			
Sample[a]	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	Ethion
Control	0	0	0	0
Day 0	3.42 ± 0.42	2.14 ± 0.34	0	3.37 ± 0.56
Day 1	2.05 ± 0.60	2.04 ± 0.36	0	3.41 ± 1.78
Day 3	0.88 ± 0.38	2.06 ± 0.44	0	2.43 ± 0.72
Day 6	0.25 ± 0.09	1.05 ± 0.40	0.08 ± 0.04	1.21 ± 0.26
Day 14	0.08 ± 0.04	0.30 ± 0.14	0.07 ± 0.02	1.46 ± 0.18
Day 21	0.04 ± 0.02	0.14 ± 0.08	0.06 ± 0.03	0.40 ± 0.19
Day 28	0.06 ± 0.04	0.13 ± 0.04	0.10 ± 0.05	0.34 ± 0.07
Day 35	0.03 ± 0.01	0.08 ± 0.02	0.12 ± 0.05	0.27 ± 0.09

[a] Values reported are averages for four replicate plots, each plot sample consisting of 50 leaves. Analyses performed on composites of 50 leaf disks, each 7.26 cm² in surface area, 1 disk per leaf. Differences reported are standard deviations. Two plots were on over-tree sprinklers; two were on trickle irrigation.

Table IV. Residues of Endosulfan and Ethion on Grape Leaves Resulting from Application of 1 lb/Acre Thiodan 50 WP and Approximately 1 lb/Acre Ethion 25 WP, July 26, 1974

	Concentration of insecticide, μg/cm²			
Sample[a]	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	Ethion
Control	0	0	0	0
Day 0	1.13 ± 0.30	0.92 ± 0.12	0	0.59 ± 0.07
Day 1	0.75 ± 0.22	0.85 ± 0.16	0	0.40 ± 0.07
Day 3	0.21 ± 0.12	0.62 ± 0.38	0.01 ± 0.00	0.20 ± 0.14
Day 6	0.09 ± 0.07	0.49 ± 0.36	0.02 ± 0.00	0.10 ± 0.06
Day 14	0.05 ± 0.04	0.19 ± 0.22	0.05 ± 0.02	0.10 ± 0.11
Day 21	0.02 ± 0.02	0.06 ± 0.05	0.03 ± 0.02	0.02 ± 0.01
Day 28	0.02 ± 0.01	0.04 ± 0.04	0.03 ± 0.02	0.02 ± 0.02
Day 35	0.01 ± 0.02	0.03 ± 0.03	0.04 ± 0.02	0.01 ± 0.01

[a] Values reported are averages for three replicate plots, 25 leaves sampled per plot. Analyses performed on composites of 50 leaf disks, each 7.26 cm² in surface area, two disks per leaf. Differences reported are standard deviations.

weights per fruit showed about a fourfold increase from week 1 to week 5. Ethion concentrations in the fruit for the same period showed approximately a fourfold decrease. It therefore appears that the apparent decrease in ethion residues in this period was due to dilution by increase in fruit size rather than any actual loss or degradation.

During this experiment, there were approximately 390 total sunshine hours and 0.80 in. of rain. The mean temperature was 70°F, with daytime highs of 75–95°F and overnight lows of 50–65°F. No good correlation between rainfall and removal of deposits could be found.

Good recoveries were obtained when the extraction procedure was followed with pear samples fortified at 0.10 and 1.00 ppm of α-endosulfan, β-endosulfan, endosulfan sulfate, and ethion (see Table II). Results reported are averages for three replicates containing each material at the fortification level. No interferences were encountered in the controls. A typical chromatogram is shown in Figure 1.

No significant differences were found in concentrations of insecticides on leaves for the two irrigation practices. Results for the four plots were averaged and are reported in Table III. Again, β-endosulfan was more persistent than α-endosulfan and ethion was the most persistent material. However, in contrast with the findings for the fruit, a net loss of ethion did occur over the sampling

Table V. Residues of Insecticides Endosulfan and Ethion Found in Anjou Pears Harvested Following Normal Time Limitation from Last Application to Harvest

Sample	Concentration of insecticide, ppm			
	α-Endosulfan	β-Endosulfan	Endosulfan sulfate	Ethion
(1) 6 lb/acre Thiodan 50 WP (14 days application to harvest)				
A	0.36	1.13	0	0
B	0.33	0.89	0	0
(2) 6 lb/acre Thiodan 50 WP + 8 lb/acre Ethion 25 WP (20 days application to harvest)				
A	0.45	0.57	0.06	0.62
B	0.43	0.58	0.04	0.61
(3) Control	0	0	0	0

period. Results on pear leaves may be compared with the degradation rates on grape leaves in Table IV. While the grapes received a much lower treatment rate than the pears, the higher final residues on the pear leaves may be due in part to the heavily waxed surface of the latter. Final or hard residues would tend to be trapped in this wax layer and therefore would be less vulnerable to physical or chemical attack.

Anjou pears sampled 14 days after treatment with endosulfan and 20 days after treatment with endosulfan–ethion were found to have insecticide residues within tolerances. Results are reported in Table V. While residues of each of these materials individually are considered acceptable, questions of possible potentiation and of acceptable total pesticide residues should be given careful consideration in the future.

The greater persistence of ethion on pears sprayed in July than on those sprayed 20 days prior to harvest may be due in part to the irrigation practices followed. Residues on the pears in the block under trickle irrigation tended to be higher than in the other blocks, as the influence of sprinklers washing off deposits was removed. Results could also have been influenced by the fact that the Anjou pears were sprayed later in the season than those in the first four test blocks by a different operator using a second sprayer of the same make (Turbo-Mist) as that used in the initial application. The effect of various irrigation practices on residue persistence is a subject requiring further study.

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Effect of Phosphatases on the Persistence of Organophosphorus Insecticides in Soil and Water

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The degradation of some organophosphorus insecticides by phosphatases was studied in water, soil, and soil extract. There is an obvious effect of the phosphatases in solution, but no effect of the enzymes was noted on the insecticides which were adsorbed on the soil surface, even after multiple enzyme applications.

The degradation of organophosphorus insecticides consists of chemical and biological processes (Lichtenstein and Schulz, 1964; Menzer and Dauterman, 1970). The chemical degradation of parathion, guthion, and pyrimiphos-methyl was recently studied in our laboratory (Yaron et al., 1974; Yaron, 1975; Mingelgrin and Yaron, 1973), but very little information is available on the biological decomposition of these insecticides. It is assumed that the decomposition stems from the secretion of microbial enzymes, and more specifically phosphatases, into the soil (Skujins, 1967; Kaufman, 1970). The establishment of phosphatase activity was shown only indirectly by determining the breakdown products which result from incubation of soil samples with different phenyl phosphate substrates (Kramer, 1957; Halstead, 1964; Ramirez-Martinez and McLaren, 1966; Tabatabai and Bremner, 1969). The aim of our study was to determine whether and to what extent one can attribute the biological degradation to the phosphatases by examining directly the effect of different phosphatases on three common organophosphorus insecticides. Since the phosphatases are the most likely enzymes to affect the organophosphorus metabolism, it was interesting to establish which of them are the more effective, and on which substrate.

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MATERIALS AND METHODS

The soil used throughout the experiments was a loamy loessial sierozem (from the Gilat Regional Experiment Station) with an organic matter content of less than 1%,