pearance rate of malathion from strawberries on the field was very high; the RL_{50} was only 1 day or less, and over 80% of the malathion disappeared in 2 days. Similar observations were made in the present study. The RL_{50} values of all the postharvest residues on strawberries were less than 24 hours. After 2 days 80 to 90% had disappeared at both 10° and 20° C. Likewise, malathion residues on gooseberries disappeared under field conditions very rapidly (*4*), with an RL_{50} of 2 days and 80% loss in 1 week. Disappearance values obtained in the present investigation on gooseberries stored at 20° C. were of the same order. Gunther and Blinn (*3*) calculated a RL_{50} value of 3 days for residues on tomatoes in the investigations by Smith, Giang, and Fulton (*6*). In the present work the RL_{50} values varied from 1 to $5^1/_2$ days, depending on the type of treatment and storage temperature.

Since malathion residues seem to disappear from fruits at practically the same rate both under field conditions and in the laboratory, this suggests that external weathering forces play no important role in the rapid disappearance of malathion field residues. It can also be assumed, on the basis of these similar disappearance rates, that too high malathion residues from field treatments could effectively be brought down to safe levels by simply holding the crop for a certain time.

When judging the suitability of malathion as a postharvest insecticide on fruits, it may be concluded from the present investigation that the residual effect of malathion is short, at least on plant products of the type used here. This is both a disadvantage and an advantage; malathion will give only short-lasting protection against pests, but the rapid disappearance of its residues guarantees that even relatively high initial deposits will decrease to a safe level after only short storage.

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INSECTICIDE RESIDUES

Disappearance Rates of Malathion Residues as Affected by Previous Treatments with Paraoxon, Parathion, and Malathion

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Studies were made to determine whether the disappearance rate of malathion residues on fruits and vegetables is affected by previous treatments with paraoxon, parathion, or malathion. Paraoxon applied to plums, tomatoes, and string beans after harvest clearly retarded the disappearance rate of postharvest residues of malathion. Application of parathion or malathion one or more times during the week before the postharvest treatment of string beans or the field treatment of New Zealand spinach had no detectable effects on the disappearance of malathion from the bean pods during storage or from spinach leaves *in situ*. It is evident that paraoxon retards the disappearance rate of malathion by inhibiting carboxyesterases, one of the enzymatic systems responsible for the decomposition of malathion in the plant tissues.

In a previous investigation (*2*) it was found that paraoxon (*O,O*-diethyl *O*-*p*-nitrophenyl phosphate) had a retarding effect on the rates of malathion disappearance [*O,O*-dimethyl *S*-(1,2-dicarbethoxyethyl) phosphorodithioate] in fresh plant homogenates. This was assumed to be due to the fact that paraoxon inhibited the carboxyesterase enzymes, which normally cleave one of the carboxyethyl bonds and produce the so-called monoacid derivative of malathion [*O,O*-dimethyl *S*-(1-carboxy-2-carbethoxy)ethyl phosphorodithioate] or its isomer [*O,O*-dimethyl *S*-(1-carbethoxy-2-carboxy)ethyl phosphorodithioate]. The same type of degradation mechanism in animal tissues was earlier demonstrated by Cook *et al.* (*1*) and subsequently found by many other workers (*4*). The object of this investigation was to determine whether the disappearance rate of malathion residues on certain intact fruits and vegetables was affected by previous treatments with paraoxon, parathion (*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothionate), and

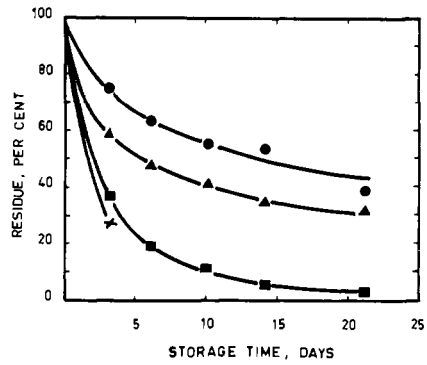

Figure 1. Disappearance of malathion postharvest residues from stored plums at 4° C. with different treatments

×-× Malathion emulsion alone
●-● Paraoxon + malathion emulsion
■-■ Malathion suspension alone
▲-▲ Parooxon + malathion suspension

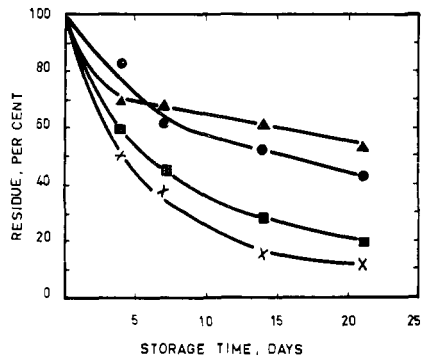

Figure 2. Disappearance of malathion postharvest residues from stored tomatoes at 4° C. with different treatments

×-× Malathion emulsion alone
●-● Paraoxon + malathion emulsion
■-■ Malathion suspension alone
▲-▲ Paraoxon + molathion suspension

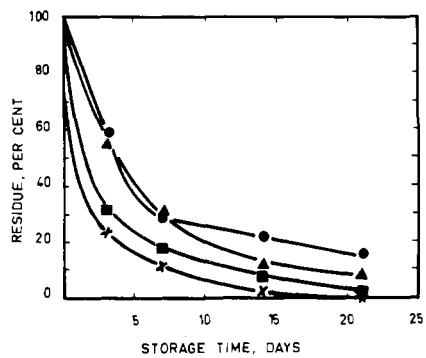

Figure 3. Disappearance of malathion postharvest residues from stored tomatoes at 20° C. with different treatments

×-× Malathion emulsion alone
●-● Paraoxon + molathion emulsion
■-■ Malathion suspension alone
▲-▲ Paraoxon + malathion suspension

Table I. Disappearance of Malathion Postharvest Residues from Stored String Beans

I. No previous treatment
II. Malathion on field 2 and 6 days before
III. Parathion on field 6 days before
IV. Parathion on field 2 days before
V. Paraoxon in laboratory 1 day before

Storage Time, Days	Loss of Residue, %				
	I	II	III	IV	V
2	73	67	64	74	67
4	88	86	84	88	76
7	92	92	89	92	83

malathion. In their oxon forms these compounds might be expected to inhibit carboxyesterases and thus possibly retard the disappearance of malathion residues in plant tissues.

Materials

Plums (var. Victoria), tomatoes (var. Selentia), string beans (var. Hinrichs Kaenpe), and New Zealand spinach were used.

The pesticide solutions employed were made from four formulations: 57% emulsifiable concentrate of malathion (*3*), 25% wettable powder of malathion (Ligtermoet & Zoon, Holland), 50% emulsifiable concentrate of paraoxon (Farbenfabriken Bayer, Germany), and 50% emulsifiable concentrate of parathion (Farbenfabriken Bayer, Germany).

Methods and Results

Malathion was extracted with benzene from the unmacerated plant materials immediately after sampling and residues were determined by methods described earlier (*2*, *3*). Each residue value reported here is a mean of duplicate determinations made on two or more 500-gram samples of each material.

Plums. The plums were treated with the pesticides after harvest. Paraoxon was applied by dipping the plums in a 0.2% paraoxon emulsion for 1 minute. Six hours later both these and the untreated plums were immersed in a 0.1% malathion emulsion or a 0.2% malathion suspension for 30 seconds. After drying for about 2 hours, initial deposits of malathion were determined. These were found to be 3.8 p.p.m. on the plums treated with emulsion and 23.6 p.p.m. on those treated with suspension. The plums were stored at about 4° C.

The disappearance curves of malathion residues obtained in these experiments are shown in Figure 1. Paraoxon retarded the disappearance rate only during the first week of storage, after which the curves run parallel. On the suspension-treated plums paraoxon reduced the loss percentages by about 30%, and on emulsion-treated plums, even more.

Tomatoes. These experiments were carried out in the same manner as those withplums, except that malathion was applied to the tomatoes as a 0.5% emulsion or a 0.2% suspension. The initial deposits of malathion were 3.8 and 14.7 p.p.m., respectively. The fruits were stored at about 4° and 20° C.

The disappearance curves of malathion residues from tomatoes stored at 4° C. are shown in Figure 2 and from those stored at 20° C. in Figure 3. Paraoxon distinctly retarded the disappearance rate at both temperatures, with a greater effect at the lower temperature. At 4° C. the reduction in residue losses during the first 2 weeks of storage was about 30% on both the emulsion- and suspension-treated fruits. At 20° C. the greatest difference in the loss percentages caused by paraoxon was found 3 days after treatment. Later the differences decreased, amounting in the latter part of the experiment to about 20% on the emulsion-treated plums and about 5% on the suspension-treated plums.

String Beans. String beans were treated either *in situ* or in the laboratory before the postharvest application of malathion.

The bean plants, growing in 2 × 2.5 meter plots, were sprayed with 0.2% malathion or parathion emulsion at a rate of 1 liter per square meter at different time intervals, as indicated in Table I, before the postharvest application of malathion in the laboratory. One day before this application untreated bean pods were dipped in 0.2% paraoxon emulsion for 1 minute. On the following day malathion was applied to all the pods by dipping them in 0.5% malathion emulsion for 30 seconds. After drying for about 2 hours, the initial deposits of malathion were determined and found to range from 24.9 to 34.4 p.p.m. The pods were stored at about 20° C., and the disappearance of the malathion residue from the different lots was followed for a week.

Table I shows that the field treatments with malathion and parathion had only a very slight, if any, effect on the disappearance rate of malathion postharvest residues on the bean pods during storage. Paraoxon applied to the pods after harvest retarded the disappearance rate, although much less than on the plums and tomatoes.

New Zealand Spinach. New Zealand spinach, growing in 2 × 2.5 meter plots, was given a malathion or parathion treatment before the actual application of malathion in the field. The disappearance of malathion residues from the leaves *in situ* was followed under field conditions.

Before the actual malathion treatment, the plants were sprayed with 0.2% malathion emulsion or with 0.2% parathion emulsion at a rate of 1 liter per square meter at different time intervals (Table II). The actual malathion treat-

Table II. Disappearance of Malathion Residues from New Zealand Spinach *in situ* Treated with Malathion or Parathion before Actual Malathion Spray

I. No previous treatment
II. Malathion 7 days before
III. Malathion 4 days before
IV. Malathion 1 day before
V. Malathion 7 + 4 + 1 days before
VI. Parathion 7 days before
VII. Parathion 4 days before
VIII. Parathion 1 day before

Time after Application, Days	Loss of Residue, %							
	I	II	III	IV	V	VI	VII	VIII
3	79	79	75	80	80	78	75	72
5	90	95	90	89	83	89	90	85
7	98	99	98	97	98	97	98	96

ment of all the plots took place on the same day and consisted of 0.2% emulsion sprayed at a rate of 1 liter per square meter. After drying for about 2 hours, leaf samples from each plot were analyzed for initial deposits of malathion, which ranged from 125 to 184 p.p.m. Three further analyses were made during the first week.

Table II indicates that previous treatments with malathion or parathion applied to growing spinach plants in the field had no detectable effects on the disappearance rate of malathion residues on the leaves *in situ*.

Discussion

The experiments reported in the present paper indicate that the biologically active form of parathion—paraoxon—retards the disappearance of malathion postharvest residues from fruits during storage (Figures 1, 2, and 3 and Table I). This observation supports the view that the disappearance of malathion residues, at least from stored fruits, is partly due to carboxyesterase enzymes, which normally decompose malathion but are at least partially inactivated by paraoxon. Paraoxon did not, however, completely prevent the disappearance of malathion residues, as was the case with fresh plant homogenates (*2*), which indicates that intact fruits probably have also other enzymatic systems which decompose malathion.

Parathion or multiple malathion treatments of growing plants in the field did not detectably reduce the disappearance of malathion postharvest residues on bean pods or field residues on spinach leaves. This result does not support the theoretical possibility that parathion and malathion in growing plants, after having been converted to their oxon forms, might interfere through enzyme inhibition with the disappearance of malathion. There may be at least three reasons for this observation: a low rate of oxidation of parathion and malathion to the oxon forms, a rapid elimination of the oxon compounds in growing plants, and a degradation mechanism in growing plants which greatly differs from that in stored fruits and vegetables as well as plant homogenates.

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POSTHARVEST INSECTICIDE RESIDUES

Stability of Malathion Residues in Food Processing and Storage

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IN EVALUATING the hazard to the consumer caused by pesticide residues in food, it is important to know the stability of the residues during processing of plant materials. From the health standpoint the pesticides should lose their toxicity as completely as possible during preservation. Since this problem has great practical significance, it was studied in a research project concerning the fate and effects of postharvest pesticide residues on fruits and vegetables. The present publication deals with the fate of malathion [*O,O*-dimethyl *S*-(1,2-dicarbethoxyethyl) phosphorodithioate] residues derived from postharvest treatments in plant commodities during food processing.

Materials

Six kinds of plant products were used: strawberries (var. Ydun or Senga Sengana), gooseberries (var. Houghton), plums (var. Victoria), tomatoes (var. Selentia), apples (var. Wealthy), and string beans (var. Hinrichs Kaenpe). The plant products were harvest-ripe when the experiments were started.

When ripe, the plant products were harvested and treated with malathion in the laboratory by dipping them in a water emulsion or suspension of the pesticide. The emulsions were prepared from a 57% emulsifiable concentrate (*1*) and the suspensions from a 25% commercial wettable powder formulation (*5*). The time elapsing between malathion application and food processing was less than 1 day.