Malathion Residues on Fruit Treated by Dipping

PEKKA KOIVISTOINEN, ANJA KARINPÄÄ, MAILA KÖNÖNEN, and PAAVO ROINE

Department of Nutritional Chemistry, University of Helsinki, Helsinki, Finland

Disappearance rates of malathion postharvest residues were chemically determined on strawberries, plums, tomatoes, and gooseberries which had been treated after harvest by dipping in a water emulsion or suspension of the pesticide. Dipping as an application method was tested with respect to the uniformity of residues and the effect of dip concentration, dipping time, and size of fruit on the amount of initial deposits. The disappearance rates of the residues on the stored fresh fruits were very high, in many cases as high as *in situ* on the corresponding plant parts. Malathion seems to be a promising insecticide for eradicating pests from stored fresh fruit and their surroundings if a short residual life is desired.

MALATHION [*O,O*-dimethyl *S*-(1,2-dicarbethoxyethyl)phosphorodithioate] is one of the most commonly used pesticides in the world. It has been accepted for control of pests on vegetables and field crops, fruits and nuts, ornamentals, stored grain, and domestic animals, and it is also used in controlling insect pests in dwellings and other buildings (*1*, *8*). Its wide use is based on its low toxicity to mammals, its relatively strong pesticidal qualities, and its residual behavior in plants, which is characterized by a high disappearance rate and low residues remaining in the harvested crops (*4*, *8*).

The present paper deals with malathion residues on fruits and vegetables treated after harvest by dipping. Special attention is given to dipping as a postharvest application method and to stability of residues on stored fresh commodities. This study is a part of a larger research project on postharvest residues of insecticides and fungicides on horticultural crops. The results of this research will be published in several subsequent papers in the near future.

Materials

Malathion was applied to the fruits as both water emulsions and water suspensions. The emulsions were prepared from a 57% emulsifiable concentrate (*2*) containing, by weight, 60% of 95% premium grade malathion technical (American Cyanamid Co., New York, N. Y.), 8% emulsifier Triton X-100 (Rohm and Haas Co., Philadelphia, Pa.), and 32% xylene. The suspensions were prepared from a 25% commercial wettable powder formulation (Ligtermoet & Zoon, Holland). The standard calibration curve was prepared from 99.6% pure malathion (American Cyanamid Co.).

Four kinds of fruits were used: strawberries (var. Ydun or Senga Sengana), gooseberries (var. Houghton), plums (var. Victoria), and tomatoes (var. Selentia or Grower's Pride); they were harvest-ripe at the time of malathion treatment. The stipes of the strawberries and both the stipes and the perianth remnants of the gooseberries were included in the analyses.

Analytical Methods

About 500 grams of the plant material, carefully weighed, was used for each extraction. The material was extracted without maceration, since preliminary trials had indicated that malathion recoveries were about the same from both macerated and unmacerated materials. The material was placed in 2-liter glass jars provided with cellophane-protected caps and extracted with 500 ml. of benzene (Pharm. Fennica VI) in a drum-tumbler stripper at 44 r.p.m. for 1 hour.

After extraction the benzene was decanted. If an emulsion had formed during extraction, it was eliminated before decanting by centrifuging, usually for 5 minutes at a relative centrifugal force of about 800 (International centrifuge, Size 2, Model V, with 600-ml. cups). The stripping benzene was purified with a mixture consisting of 50% activated charcoal, Nuchar C-190-N (Industrial Chemical Sales Division, West Virginia Pulp & Paper Co., New York, N. Y.), 25% Hyflo Super-Cel (L. Light and Co., Ltd., England), and 25% anhydrous sodium sulfate. This mixture was added to the stripping benzene in the ratio of 4 grams per 100 ml. of benzene and immediately agitated for 5 minutes on the drum-tumbler stripper, after which the mixture was filtered through filter paper. The filtrate was collected in glass bottles and stored in a refrigerator until analyzed. The analytical results were corrected for the control values obtained for corresponding plant material treated with plain water.

Malathion was determined by a modification of the method of Norris, Vail, and Averell (*5*) described in detail by Koivistoinen (*4*). This modification has proved during continuous laboratory practice of about 5 years to be rapid and very precise and to give highly reproducible results.

According to previous recovery tests the errors were usually under 10% when apples, gooseberries, cabbage, and spinach were fortified by adding malathion to stripping solvents before sample processing, so that the samples contained 0.2, 1.0, 2.0, or 25.0 p.p.m. of malathion. No noteworthy effects on the analysis results were caused by maceration of the plant material or by dilution or concentration of the purified stripping benzene.

Subsequent recovery tests made in the present investigation (Table I) also indicate that the errors were generally under 10%, irrespective of whether the benzene-extracted plant material was macerated in ethanol as cosolvent or not. The average percentage yields in both the present and earlier recovery tests (*4*) were 100 and the standard deviation of the errors was 6.1%. In the present studies, two or more extractions from each batch of plant material and two determinations of malathion from each extract were used.

Dipping as Application Method

Postharvest application of malathion was made by dipping the plant materials into water emulsions or suspensions of the pesticide. This method was chosen because it is simple and easy and because it evidently provides more uniform initial deposits on the plant material than spraying, fog generating, or dusting. Experiments were made to determine the

Table I. Recoveries[a] of Malathion from Fortified[b] Samples

Plant Materiol	Malathion Added, p.p.m.	Malathion Recovered, p.p.m.	Malathion Recovery, %	Maceration[c]
Strawberries	2.0	2.2	110	−
	2.0	2.0	100	+
	10.0	9.4	94	−
	10.0	10.7	107	+
	50.0	56.4	113	−
	50.0	52.8	106	+
Plums	2.0	2.1	105	−
	2.0	2.0	100	+
	10.0	10.5	105	−
	10.0	9.5	95	+
	50.0	51.0	102	−
	50.0	52.6	105	+
Tomatoes	2.0	2.2	110	−
	2.0	2.1	105	+
	10.0	9.7	97	−
	10.0	9.4	94	+
	50.0	48.3	97	−
	50.0	51.0	102	+

[a] Mean value of two determinations from same benzene extract. [b] Malathion added to ethanol before maceration (macerated samples) or to stripping benzene before extract on (unmacerated samples). [c] 500 grams of plant material blended in 250 ml. of ethanol or 1 minute. Benzene extract washed with saturated NaCl solution.

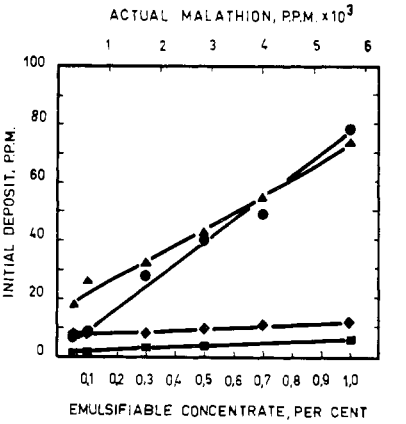

Figure 1. Effect of concentration of dip emulsions on initial deposits of malathion

● Strawberries
▲ Gooseberries
◆ Plums
■ Tomatoes

Table II. Variations of Initial Deposits of Malathion on Strawberries and Tomatoes Dipped in Emulsions or Suspensions

Fruit	Treatment[a]	No. of Portions	Initial Deposit[b] Mean, p.p.m.	Range,[c] p.p.m.	Standard Deviation, s, P.p.m.	Standard Deviation, s, %
Strawberries	Emulsion, 0.20%	5	31.56	5.80	2.32	7.4
Tomatoes	Emulsion, 0.05%	10	2.34	1.35	0.39	16.7
	Emulsion, 0.50%	10	4.54	1.55	0.60	13.2
Strawberries	Suspension, 0.10%	5	16.88	2.70	1.15	6.8
Tomatoes	Suspension, 0.05%	9	0.90	0.70	0.24	26.7
	Suspension, 0.50%	10	5.04	1.73	0.52	10.3

[a] Percentages refer to formulations. [b] From each dip portion two 500-gram samples analyzed by duplicate determinations. [c] Difference between highest and lowest value.

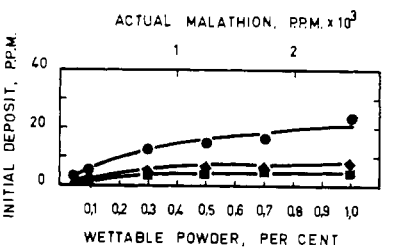

Figure 2. Effect of concentration of dip suspensions on initial deposits of malathion

● Strawberries
◆ Plums
■ Tomatoes

uniformity of the initial deposits as well as the effects of concentration of dip solution, time of dipping, and size of fruits on the initial deposits.

Uniformity of Initial Deposits. Strawberries and tomatoes having average unit weights of about 10 and 65 grams, respectively, were tested. Five 1-kg. portions of strawberries in each dip series were successively placed in a wire basket and immersed for 30 seconds in 10 liters of dip solution at 20° C. Between and during the dippings the solution was agitated. When tomatoes were used, ten 2-kg. portions in each series were treated in the same manner as the strawberries. After having dried, each portion was analyzed for malathion.

The mean and range values of the initial deposits of each dip series are presented in Table II. On the strawberries, which had rather high initial deposits (about 32 and 17 p.p.m.), the distribution from the mean was rather small in both dipping series. On the other hand, in tomatoes, where the initial deposits were very low (about 5 p.p.m. or less), the distribution was much higher. The tomatoes dipped in the 0.05% suspension had the highest standard deviation value, 0.24 p.p.m., or about 27% of the mean. The reason for this was that when 10 portions of tomatoes were dipped in the same solution, a statistically significant ($P < 0.001$) decrease in the initial deposits occurred with the sequence number of the dip portion. The standard deviation calculated from the regression (7) was 0.12 p.p.m. or 13%, which is only half of that calculated from the mean. Actually, this distribution due to dipping was similar to that in the other tomato series, which showed no statistically significant regression of initial deposits with the sequence number of the dip portion.

Since the analytical method used for the estimation of malathion caused a standard deviation of 6.1% in the results, it can roughly be estimated that the unhomogeneous formation of the initial deposits in the different dip portions of the same batch resulted in practically no increase in the standard deviation on strawberries and only a very small one on tomatoes.

Dip Concentration. Four kinds of fruit were tested: strawberries, gooseberries, tomatoes, and plums. Both malathion emulsions and suspensions were used. Duplicate 1-kg. portions of the fruits were dipped for 30 seconds in the dip solutions of each concentration. A 500-gram random sample from both of the duplicate portions was analyzed for initial deposits, and the mean values of the results for each concentration were calculated.

The initial deposits of malathion resulting from dip solutions of different concentration are shown in Figures 1 and 2. When emulsions were used, there was a rectilinear correlation between the dip concentrations and the initial deposits (Figure 1), but when dip suspensions were used, a curvilinear correlation existed (Figure 2).

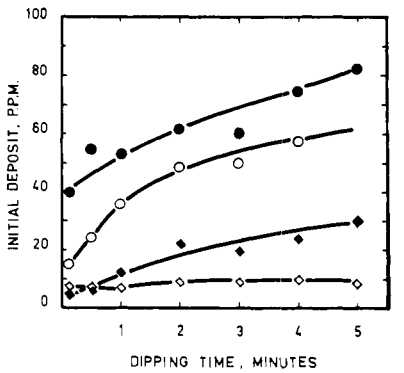

Figure 3. Effect of dipping time on amount of malathion initial deposit from emulsions of two concentrations

● Strawberries, 0.5%
○ Strawberries, 0.05%
◆ Plums, 0.5%
◇ Plums, 0.05%

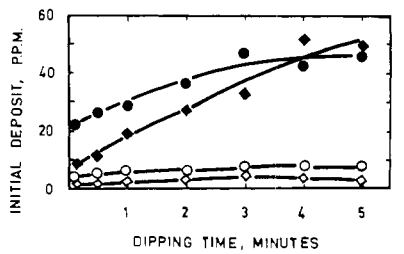

Figure 4. Effect of dipping time on amount of malathion initial deposit from suspensions of two concentrations

● Strawberries, 0.5%
○ Strawberries, 0.05%
● Plums, 0.5%
◇ Plums, 0.05%

When emulsions were used, the 20-fold increase of dip concentration had the greatest effect on strawberries, increasing the malathion deposits 13.7-fold, and the smallest on plums with a 1.5-fold increase. On tomatoes the corresponding figure was 7.6 and on gooseberries 4.2.

When dip suspensions were used, the effect of concentration was again greatest on strawberries, but the increase on the deposit for the 20-fold concentration change was markedly less than in emulsion treatments, only 6.9-fold. On tomatoes and plums these increase factors were a little less, 5.3 and 4.6, respectively.

Therefore, an increase in concentration of the dip solution had different effects on the amounts of the initial deposits, depending greatly on the kind of fruit. This effect varied more in the emulsion than in the suspension treatments.

Dipping Time. Strawberries and plums were dipped for different periods of time in emulsions and suspensions of two concentrations. The malathion treatments and the analyses were made as described above.

The effect of dipping time on the initial deposits is illustrated in Figures 3 and 4. There was a curvilinear correlation between dipping time and the amounts of initial deposits, although the gradual decrease of the curve slopes was very small in some cases.

Generally, increasing the dipping time from 5 seconds to 5 minutes did not very greatly increase the initial deposit. When the higher concentrations (0.5%) were used, this increase was 2.1-fold on strawberries and 6.0-fold on plums for both formulations. When the lower concentrations (0.05%) were used, the increases varied from 1.2-fold to 4.2-fold. Thus the effect of dipping time depends on both the concentration of dip solution and the kind of fruit but probably not at all on whether emulsions or suspensions are used.

Size of Fruits. Two size groups of tomatoes were used. Their average weights were: "large tomatoes" 100 grams for emulsion treatment and 71 grams for suspension treatment and "small tomatoes" 21 grams for both treatments. Three 1-kg. portions from both size groups were dipped for 1 minute in a 0.5% malathion emulsion (2850 p.p.m. of actual malathion) or in a 0.2% malathion suspension (500 p.p.m. of actual malathion).

The results, presented in Table III, show that the size of the tomatoes had no noteworthy effect on the amount of malathion per unit of surface area, whereas the deposits expressed in terms of parts per million varied inversely with the weight of the fruit.

Disappearance Rates of Residues

The disappearance rates of malathion postharvest residues on fresh fruits during storage were studied on four kinds of fruit, which were treated by dipping in a malathion emulsion or suspension of a specified concentration and then stored for different periods of time. The disappearance rates of residues were determined by analyzing samples of the stored fruits for malathion at certain intervals.

Residue Losses. The losses of postharvest residues of malathion from these fruits are presented in Tables IV to VI. It can be concluded from the data that malathion disappeared very rapidly from all the fruits. The losses on strawberries were about 50 to 80% in 1 day and 60 to 90% in 2 days, with the lowest percentages at 4° C. and the highest at 20° C. The corresponding losses on plums were 60 to 90% in 3 days, or slightly slower than on strawberries. Malathion disappeared from tomatoes somewhat more slowly than from plums: 40 to 80% loss in 3 days and 80 to 100% in 3 weeks. Gooseberries treated with emulsion and stored at 20° C. showed malathion losses of more than 50% in 2 days and 80% in 1 week.

Both types of treatment, suspension and emulsion, resulted in approximately the same rates of residue disappearance from strawberries (Figure 5) and plums (Table V), whereas on tomatoes the residues from emulsion treatment disappeared more rapidly than those from suspension (Figure 6).

The temperature had a noteworthy effect on the disappearance rate of the residues. For instance, after emulsion-treated strawberries were stored for 2

Table III. Initial Deposits of Malathion on Tomatoes of Different Size

Treatment	Av. Weight, Grams	Av. Surface Area,[a] Sq. Cm.	Initial Deposit P.p.m.	Initial Deposit μG./sq. cm.
Emulsion	100	104.2	3.7	3.6
	21	36.9	5.9	3.4
Suspension	71	83.2	13.2	11.2
	21	36.9	19.7	11.2

[a] In calculation tomatoes assumed spherical with specific gravity of 1.0.

Table IV. Malathion Residues on Strawberries Stored at Different Temperatures

Time after Application, Hours	4° C. Residue, p.p.m.	4° C. Loss, %	10° C. Residue, p.p.m.	10° C. Loss, %	20° C. Residue, p.p.m.	20° C. Loss, %
	Treated with Emulsion[a]					
1	22.9	0	22.9	0	22.0	0
18	11.9	48	9.1	60	6.3	72
24	11.3	51	7.2	69	4.7	79
48	7.7	66	3.7	84	3.0	87
	Treated with Suspension[b]					
1	9.8	0	9.8	0	9.8	0
18	5.5	44	3.6	63	2.9	70
24	4.0	59	2.3	76	2.1	79
48	3.9	60	2.0	80	1.2	88

[a] Concentration 0.2%. [b] Concentration 0.1%.

Table V. Malathion Residues on Plums and Tomatoes Treated with Emulsion or Suspension and Stored at Different Temperatures

Time after Application, Days	4° C. Emulsion Residue, p.p.m.	4° C. Emulsion Loss, %	4° C. Suspension Residue, p.p.m.	4° C. Suspension Loss, %	20° C. Emulsion Residue, p.p.m.	20° C. Emulsion Loss, %	20° C. Suspension Residue, p.p.m.	20° C. Suspension Loss, %
				Plums[a]				
0	4.1	0	29.3	0	4.1	0	29.3	0
3	1.2	71	10.9	63	0.6	85	4.2	86
7	...	..	5.6	81	...	...	...	..
10	...	..	3.5	88	...	...	...	..
14	...	..	1.6	95	...	...	...	..
21	...	..	0.9	97	...	...	...	..
				Tomatoes[b]				
0	3.6	0	12.8	0	3.6	0	12.8	0
3	1.7	53	7.5	41	0.9	75	4.1	68
7	1.3	64	5.8	55	0.4	89	2.1	84
14	0.5	86	3.5	73	0.0	100	0.9	93
21	0.4	89	2.3	82	0.0	100	0.5	96
28	...	..	0.5	96	...	...	0.4	97

[a] Emulsion concentration 0.1%. Suspension concentration 0.2%. [b] Concentration 0.5%.

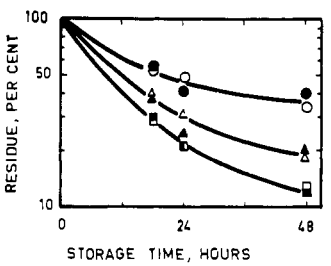

Figure 5. Disappearance of malathion residues from strawberries with two different treatments and at three storage temperatures

□ Emulsion, 20° C.
■ Suspension, 20° C.
△ Emulsion, 10° C.
▲ Suspension, 10° C.
○ Emulsion, 4° C.
● Suspension, 4° C.

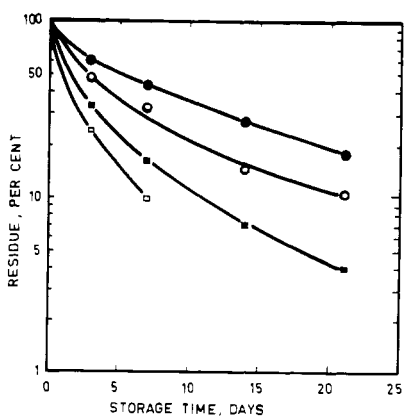

Figure 6. Disappearance of malathion residues from tomatoes with two different treatments and at two storage temperatures

□ Emulsion, 20° C.
■ Suspension, 20° C.
○ Emulsion, 4° C.
● Suspension, 4° C.

days, the residue at 40° C. (7.7 p.p.m.) was about twice that at 10° C. (3.7 p.p.m.) and about $2^1/_2$ times greater than that at +20° C. (3.0 p.p.m.) (Table IV). Similar differences were obtained on strawberries treated with suspension. In the case of plums and tomatoes treated in either way, after 3 days the residues at +4° C. were about two times greater than those at +20° C. (Table V).

Table VI. Malathion Residues on Gooseberries Treated with Emulsion[a] and Stored at 20° C.

Time after Applicotion, Days	Residue, P.P.M.	Loss, %
0	26.5	0
1	17.6	34
2	11.8	55
4	7.0	74
7	4.7	82

[a] Concentration 0.1%.

However, the disappearance was also rapid at 4° C. This indicates that the mechanism responsible for the disappearance process is not greatly dependent on the temperature in the range +4° to +20° C.

RL_{50} **Values.** Table VII gives the RL_{50} values (time required for half of the residue to disappear) of the malathion postharvest residues at different temperatures, calculated from the disappearance curves according to Gunther and Blinn (*3*). These values agree well with those obtained in earlier field experiments (*4*).

Disappearance Curves. Figures 5 and 6 illustrate the disappearance behavior of postharvest residues of malathion on stored strawberries and tomatoes. These disappearance curves plotted on a semilogarithmic scale are not linear as expected; instead, their slope gradually decreases with time. This indicates that the rate of residue disappearance does not exactly follow the chemical kinetics of first-order reactions, but is somewhat slower. Thus the disappearance curves have the typical characteristics of neither degradation nor persistence behavior of residues (*3*). A similar curvilinear behavior in residue disappearance was observed in the case of suspension-treated plums stored at 4° C. and emulsion-treated gooseberries stored at 20° C.

Discussion

Postharvest residues of malathion disappeared rapidly from all fruits studied. The disappearance rate seemed to be dependent on the type of the pesticide preparation used (emulsion or suspension), the kind of fruit, and the storage temperature. According to a previous study by Koivistoinen (*4*), malathion residues on apples and beans treated after harvest and stored at 20° C. disappeared at practically the same rate as under field conditions. The disap-

Table VII. RL_{50}[a] Values of Malathion Postharvest Residues at Different Temperatures

Fruit	Treatment	Temp., ° C.	RL_{50} Hours	RL_{50} Days
Strawberries	Emulsion	20	9	
		10	12	
		4	20	
	Suspension	20	9	
		10	12	
		4	20	
Plums	Emulsion	20		1
		4		$1^1/_2$
	Suspension	20		1
		4		$2^1/_2$
Tomatoes	Emulsion	20		1
		4		3
	Suspension	20		$1^1/_2$
		4		$5^1/_2$
Gooseberries	Emulsion	20		$1^1/_2$

[a] Time required for half of residue to disappear.

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

PEKKA KOIVISTOINEN, ANJA KARINPÄÄ, and MAILA KÖNÖNEN

Department of Nutritional Chemistry, University of Helsinki, Helsinki, Finland

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