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.

Losses of malathion postharvest residues were determined in various methods of processing gooseberries, plums, tomatoes, apples, and string beans, as well as after washing the fruits. The approximate losses were: canning, 50% or more; processes with a cooking period of 15 to 20 minutes, 30 to 50%; juice making by pressing or steaming, 70 to 90%; drying at 75° C. for 1 to 2 days, 90 to 100%; freezing, 40 to 50%. When fruits were washed in running water for 1 minute, the losses varied from 0 to 79%. When the processed materials were stored at 4° C., practically no malathion was lost.

Analytical Methods

Malathion was extracted from the plant products and residues were determined by methods described earlier (*3*). According to recovery tests in which stripping solutions were fortified with malathion before sample processing, the errors of this method usually remain within 10% with a standard deviation of 6.1% (*3, 5*).

The malathion residue on the raw material just before processing was determined by analyzing four 500-gram random samples. Subsequent analyses were made on two 500-gram samples of each processed material just before storage and sometimes also after certain intervals during storage of the products. The results of the analyses were corrected for control values obtained on corresponding plant material dipped in plain water. The total loss percentages of malathion given in the tables refer to real loss of the residue calculated on the fresh weight basis of the plant material.

Table I. Malathion[a] in Processed Strawberries and Total Malathion Losses Occurring in Processing

Process	P.P.M.	Loss, %
Canning		
Process I[b]	12.8	58
Process II[c]	16.3	47
Process III[d]	13.7	55
Jam I[e]	10.8	46
Jam II		
Before cooking	10.2	47
After cooking	11.9	66

[a] Residue on raw material, 30.6 p.p.m. [b] Canned with granulated sugar. [c] Canned with 30% sugar solution. [d] Canned with 50% sugar solution. [e] Processed by cooking.

Table II. Malathion[a] in Processed Gooseberries and Total Malathion Losses Occurring in Processing

Process	P.P.M.	Loss, %
Canning	8.3	63
Jam	9.5	31
Juice, steamed	9.3	72
Dried	2.2	90

[a] Residue on raw material, 22.2 p.p.m.

Table III. Malathion[a] in Processed Plums and Total Malathion Losses Occurring in Processing

Process	P.P.M.	Loss, %
Canning	0.4	89
Jam	1.4	45
Frozen[b]	2.2[c]	47
Dried	0.0	100

[a] Residue on raw material, 4.1 p.p.m. [b] Without blanching. [c] Assayed after storage for 1 month.

Processing Methods and Results

Strawberries. Strawberries were treated by dipping them in a 0.2% emulsion of malathion for 30 seconds (residue, 30.6 p.p.m.).

CANNING. Five hundred grams of strawberries with (Process I) 100 grams of granulated sugar, (Process II) 100 ml. of 30% sugar solution, or (Process III) 100 ml. of 50% sugar solution were placed in glass jars and autoclaved at 120° C. for 20 minutes.

JAM I. Berries and granulated sugar (600 grams per kg. of berries) were placed in layers in an aluminum kettle and boiled for 20 minutes.

JAM II. Berries and granulated sugar (600 grams per kg. of sugar) were placed in layers in a kettle, allowed to stand overnight at 4° C., and then boiled for 20 minutes. Jam II was analyzed both before and after cooking.

Table I shows that approximately equal amounts of malathion (45 to 66%) disappeared during both canning and preparation of jams. A considerable amount of malathion (47%) disappeared when the berries were allowed to stand overnight. Heating increased the losses by 19%.

Gooseberries. Gooseberries were dipped in a 0.2% emulsion of malathion for 30 seconds (residue, 22.2 p.p.m.).

CANNING. Five hundred grams of gooseberries and 200 ml. of 40% sugar solution were placed in glass jars and autoclaved at 120° C. for 20 minutes.

JAM. Berries and 70% sugar solution in the proportion 1 to 0.85 were boiled in an aluminum kettle for 20 minutes.

JUICE. Berries were steamed in an aluminum steam extraction kettle (Saftborn) for 45 minutes, after which the juice was collected and analyzed.

DRYING. Berries were dried at 75° C. for 1 day.

The results are presented in Table II. Canning and steaming were equally destructive to malathion, the losses amounting to about 60 to 70%. Malathion losses were smaller in jams (about 30%) but much higher in dried berries (90%).

Plums. Plums were dipped in a 0.1% emulsion of malathion for 30 seconds (residue, 4.1 p.p.m.).

CANNING. Five hundred-grams of plums with 200 ml. of a 23% sugar solution were placed in glass jars and autoclaved at 120° C. for 30 minutes.

JAM. Plums, sugar (600 grams per kg. of plums), and water (100 ml. per kg. of plums) were boiled in an aluminum kettle for 15 minutes.

FREEZING. Five hundred-gram portions of plums were sealed in plastic bags, frozen, and stored at about −18° C.

DRYING. Plums were dried at 75° C. for 2 days.

The results in Table III show that malathion losses during canning were higher from plums than from either strawberries or gooseberries, probably because of the longer autoclaving time (30 minutes instead of 20). The losses from plum jam were similar to those from jams prepared from the other plant materials. A considerable proportion of malathion (47%) disappeared during freezing. After drying for 2 days, all of the malathion on plums disappeared.

Tomatoes. Green tomatoes were dipped in a 0.5% emulsion of malathion for 1 minute (residue, 5.4 p.p.m.).

PICKLING. Tomatoes were boiled for 20 minutes in a solution (750 ml. per kg. of tomatoes) containing vinegar (3.3%) and sugar (600 grams per liter of solution).

When the tomatoes and the vinegar-sugar solution were analyzed separately, it was found that the fruit contained 2.6 p.p.m. of malathion and the solution 2.1 p.p.m. Thus the loss of malathion was 16% if both processed fruit and solution are taken into account, and 51%

Table IV. Malathion[a] in Processed Apples at Different Times during Storage and Total Malathion Losses Occurring in Processing and Storage

Time of Storage, Months	Canning[b] P.p.m.	Canning[b] Loss, %	Mash P.p.m.	Mash Loss, %	Steam Juice P.p.m.	Steam Juice Loss, %	Pressed Juice P.p.m.	Pressed Juice Loss, %	Frozen[c] P.p.m.	Frozen[c] Loss, %
0	2.1	90	4.8	87	4.8	92	2.3	96	...	..
1	3.0	86	4.9	88	4.9	92	2.1	97	21.1	37
2	6.8	67	8.0	78	4.9	92	2.1	97	23.0	29
4	4.3	79	7.4	79	5.1	92	2.3	96	19.1	41
8	5.7	72	4.9	86	5.1	92	2.5	96	21.7	33

[a] Residue on raw material, 32.6 p.p.m. [b] Both fruits and solution. [c] Without blanching.

if only the malathion found on fruit is included.

Apples. Apples were dipped in a 0.02% emulsion of malathion for 1 minute (residue, 32.6 p.p.m.).

CANNING. One-kilogram portions of the apples were weighed, and a half of each apple was included in each sample. The 500-gram samples were put in glass jars and 300 ml. of a 40% sugar solution were added. The jars were autoclaved at 120° C. for 30 minutes and stored at about 4° C. After autoclaving and subsequently after 1, 2, 4, and 8 months of storage the apples and sugar solution in each jar were analyzed separately.

MASH. Apples were cut into four segments and boiled in water (100 ml. per kg. of apples) for 40 minutes, after which they were pressed through a mash strainer. The mash was heated to boiling. Sugar (400 grams per 1 kg. of mash) was added, and the mixture was stored in 0.5-liter glass jars at about 4° C. The mash was analyzed at the same intervals as the canned apples.

STEAM JUICE. Apples were cut into four segments and steamed in an aluminum steam extraction kettle (Saftborn) for 1 hour, after which the juice was poured into 0.5-liter glass bottles and stored at about 4° C. Analyses were carried out as before.

PRESSED JUICE. Apples were macerated and pressed in a hand-operated screw press. The juice obtained was pasteurized in 0.5-liter glass bottles at 80° C. for 10 minutes and then stored at about 4° C. Analyses were carried out as before.

FREEZING. Five hundred-gram samples were obtained by taking a quarter segment of each apple from a 2-kg. portion; these were put in plastic bags, frozen, and stored at about −18° C. Analyses were made after 1, 2, 4, and 8 months of storage.

The results are given in Table IV. The analyses made immediately after processing as well as at different times during storage showed high malathion losses in all the processes, with the exception of freezing which resulted in a loss of about 40%.

String Beans. Whole pods of string beans were dipped in a 0.5% emulsion of malathion for 1 minute (residue, 33.2 p.p.m.).

CANNING. Whole pods of string beans were boiled for 2 minutes in a 1.5% NaCl solution and allowed to cool, after which 1-kg. portions were put in 2-liter glass jars with 700 ml. of 1.5% NaCl solution. The jars were autoclaved at 120° C. for 30 minutes. Immediately afterwards the beans and the solution from each jar were separately analyzed.

SALTING. Bean pods were cut into pieces of 1 cm. or less and packed with salt (300 grams per 1 kg. of beans) in glass jars. The jars were stored at about 4° C. and the beans were analyzed after 2, 4, and 8 months of storage.

FREEZING. Beans were boiled as described in connection with canning. After cooling, 1-kg. portions were put in plastic bags, frozen, and stored at about −18° C. The beans were analyzed immediately after freezing and subsequently after 1, 2, 4, and 8 months.

A malathion residue of 0.32 p.p.m. was found in the beans preserved by canning, whereas the salt solution gave no response to the method used (residue, <0.1 p.p.m.). The total loss of malathion during canning was 99%. The analyses of the salted beans showed that nearly 90% of the malathion disappeared during processing and the first two subsequent months of storage, and that the losses increased with additional storage (Table V). Over 95% of the malathion disappeared in the freezing process, which included preliminary boiling of the beans; no further losses occurred during storage (Table V).

Effect of Washing on Residues. Since raw plant materials are often washed before preserving, some experiments were carried out to determine the losses of malathion residues caused by washing. The plant materials used were apples, plums, and tomatoes, all of which had been dipped into an emulsion or suspension of malathion after harvest. The fruits were washed in a strainer under running tap water for 1 minute.

The results (Table VI) indicate that the residues from emulsion applications resisted washing considerably better than those from the suspensions. None of the emulsion residues disappeared from apples during washing, whereas 15% disappeared from plums and 36% from tomatoes, which indicates differences in the affinity of malathion toward the different fruits. When determined half a day after pesticide treatment, the suspension residue losses amounted to 79% from tomatoes and 64% from plums. The effect of washing on the suspension residues on tomatoes diminished as the age of the residues increased.

Table V. Malathion[a] in Processed String Beans at Different Times during Storage and Total Malathion Losses Occurring in Processing and Storage

Time of Storage, Months	Salted P.p.m.	Salted Loss, %	Frozen[b] P.p.m.	Frozen[b] Loss, %
0	...	..	0.7	98
1	...	..	0.9	97
2	3.0	88	1.8	95
4	2.0	92	1.0	97
8	1.1	96	1.0	97

[a] Residue on raw material, 33.2 p.p.m.
[b] With previous boiling.

Table VI. Effect of Washing on Malathion Residues

Fruit	Treatment	Age of Residue, Days	Residue, P.P.M. Before washing	Residue, P.P.M. After washing	Loss of Residue, %
Apples	Emulsion	1	32.7	33.8	0 (+3)
		7	12.4	12.7	0 (+2)
Plums	Emulsion	1/2	4.1	3.5	15
	Suspension	1/2	29.3	10.4	64
Tomatoes	Emulsion	1/2	3.6	2.3	36
		7	1.4	0.9	36
Tomatoes	Suspension	1/2	12.8	2.7	79
		7	5.8	2.8	52
		14	3.5	2.1	40

Discussion

The present experiments indicated that the effect of food processing in destroying malathion residues in fresh plant products was dependent on at least three factors. First, even a short heating period of 15 to 30 minutes in the form of boiling or autoclaving destroyed a considerable proportion of the malathion. This is probably because of the relatively rapid hydrolysis of malathion at higher temperatures, an effect which will be dealt with more closely in later publications. Secondly, considerable malathion was lost even when fresh plant material was allowed to stand during the preservation process (jam II, Table I). This is probably the same phenomenon as the disappearance of malathion from fresh-stored fruits (*5*), and it may be attributed to the enzymatic disintegration of malathion in fresh plant material (*3*). This same process might have been responsible for the reduction of residues on the fresh frozen plums (Table III) and apples (Table IV) even before they became frozen. Thus the validity of residue analyses made after freezing the sample is questionable. The third important observation was that when juice was prepared mechanically—for instance, by pressing—it contained relatively little malathion (Table IV). This may be due to the fact that malathion, at least in the case of older residues, is bound firmly to the plant material, probably dissolved in the cuticle.

These results agree almost identically with those found in a previous investigation (*6*), in which black currants with a malathion residue from a field treatment were made into steam juice and two kinds of jam. The losses of malathion during corresponding stages as well as its stability during the storage of the finished products were practically the same as in the present investigation.

The effect of washing on the malathion residues in fruits depended on both the kind of formulation and the type of fruit (Table VI). It is evident that suspension residues, which partly consist of solid material adhering to the surface, are easier to wash off than emulsion residues, which are firmly bound to and dissolved in the cuticle of the fruit (*2*). The fact that the kind of fruit seems to affect the disappearance is probably due to differences in the structure of the cuticle. The losses due to washing found in this study were considerably lower than those of Smith, Giang, and Taylor (*7*). In their trials with several field-treated samples of vegetables and tomatoes, washing removed from 84 to 100% of the malathion residues.

The stability of malathion in stored processed materials is a result of the relatively slow hydrolysis of malathion at the temperatures investigated. The rates of the hydrolysis of malathion in water solution will be reported in a later publication.

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