

Removal of DDT, Malathion, and Carbaryl from Green Beans by Commercial and Home Preparative Procedures

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Green beans grown in California were field sprayed separately with DDT, malathion, and carbaryl, and prepared for serving by commercial and home preparative methods. Commercial water blanching removed more than 50% of the DDT residue. Additional commercial processing removed approximately 33% of the DDT residue. During home preparative methods, cold water washing and home canning removed a total of 80% of the original DDT residue. During commercial heat processing and home canning methods *p,p'*-DDT was converted

to *p,p'*-TDE. Commercial processing methods removed more than 94% of the original malathion residue. During home preparative procedures cold water washing removed 96% of the malathion. Only trace amounts remained in home cooked green beans. Commercial water blanching removed 68 to 73% of the carbaryl residue from the beans. Further processing removed no additional carbaryl. Home preparative procedures reduced carbaryl residues to trace amounts.

Until recently, little information could be found in the literature on the removal of pesticides from vegetables by commercial and home preparative procedures. Studies in this laboratory demonstrated the conversion of *p,p'*-DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] to *p,p'*-TDE [2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane] during the processing of canned spinach (Farrow *et al.*, 1966). The authors have also reported on the removal by commercial and home preparative methods of DDT, malathion (*O,O*-dimethyl dithiophosphate of diethyl mercaptosuccinate), and carbaryl (1-naphthyl *N*-methylcarbamate) from tomatoes (Farrow *et al.*, 1968a), the behavior of DDT in potatoes during these procedures (Lamb *et al.*, 1968a), the effect of these procedures on residues of DDT, parathion (*O,O*-diethyl-*O-p*-nitrophenyl phosphorothioate), and carbaryl in spinach (Lamb *et al.*, 1968b), and parathion and carbaryl in broccoli (Farrow *et al.*, 1968b). Previous references to work in this field are recorded in these publications.

The work described here is a further portion of a project designed to obtain information on the effects of commercial and home preparative procedures on permissible pesticide residues in selected commercially important crops.

EXPERIMENTAL

Pesticide Applications. Two crops of green beans were used in the course of this study. Spraying on both crops was done using two Hudson tank sprayers of 7.57-liter

capacity equipped with triple boom heads and flat spray nozzles.

The first crop of green beans was of the Tendergreen variety and was grown on the Gorman Ranch near Yolo, Calif. They were sprayed with Systox {mixture of *O,O*-diethyl *O*-[2-(ethylthio)ethyl] phosphorothioate and *O,O*-diethyl *S*-[2-(ethylthio)ethyl] phosphorothioate} by the grower during the week of July 19, 1965, for the control of mites. This control was unsatisfactory and on August 4, the field was sprayed with Kelthane [4,4'-dichloro- α -(trichloromethyl)benzhydrol] at 363 grams (0.8 pound) per acre of active ingredient. This treatment controlled the mites.

Three plots, each 0.1 acre, were staked out on July 26, 1965. The following treatments were applied:

- Plot No. 1. Carbaryl (Sevin) flowable emulsion (Stauffer) 2.27 kg. (5 pounds) per gallon 1.82 kg. (4 pounds) per acre of active ingredient applied on July 26 and August 2.
- Plot No. 2. DDT 50% wettable powder (Ortho) 2.27 kg. per acre of active ingredient applied on July 26 and August 4.
- Plot No. 3. Malathion 50% emulsifiable concentrate (Ortho). 817 grams (1.8 pounds) per acre of active ingredient applied on July 26 and 1.36 kg. (3 pounds) per acre applied on August 9.

On this crop of beans all pesticides were applied with a shorter application-to-harvest interval than is recommended on label registrations. The beans were harvested immediately after the second pesticide application.

The second crop was grown on a commercial field near

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the Niles division of Fremont, Calif. They were of the Blue Lake variety. The field was treated with Treflan (a,a,a-trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) herbicide prior to planting. Three plots (0.025 acre) were staked out and the following pesticide treatments were applied:

- Plot No. 1. DDT 50% wettable powder (Ortho) applied at 2.72 kg. (6 pounds) per acre on September 26, 1966. The beans were harvested on October 3, 1966.
- Plot No. 2. Carbaryl, Sevin, Stauffer flowable 1.82 kg. (4 pounds) per acre applied on September 26 and October 3, 1966. Harvested on October 3, 1966.
- Plot No. 3. Malathion 50% emulsifiable concentrate (Ortho) 1.36 kg. per acre applied on September 26 and October 3, 1966. Harvested on October 3, 1966.

On this crop a 7-day interval was allowed between the DDT application and harvest, in accordance with label recommendations.

Commercial Procedures. In addition to providing information on the effect of washing, cooking, home canning, and home freezing, it was intended to provide data on the persistence of residues on the fresh produce.

The raw, unwashed beans were stored at 7° C. (45° F.). Samples were taken at intervals of 2 or 3 days, chopped separately in the Hobart mixer and two 100-gram portions from each extracted.

The entire lot of beans was cut into 2½- to 4-cm. lengths and mixed thoroughly. Three 454-gram samples were removed, placed in polyethylene bags, and frozen.

Approximately 6.82 kg. of beans were water blanched for 1½ minutes at 85° C. (185° F.) in the spray immersion unit of the experimental washer. The beans were then run through the spray washer section where they were sprayed with cold water for 50 seconds. Three 454-gram samples were taken.

The maximum retention time in the spray immersion unit is about 58 seconds, hence it was necessary to stop the conveyor belt while the beans were in the unit to obtain the desired blanch time.

The beans from each treatment were filled into No. 303 cans, a 2% salt brine solution was added at approximately 94° C., and the cans were closed immediately. They were processed 12 minutes at 121° C. in a still retort and cooled in the retort to about 38° C.

Another 6.82 kg. of beans were blanched in a steam chamber for 3 minutes at 99–100° C. followed by spraying for 1 minute with cold water.

All 454-gram laboratory samples were frozen and held in that form until analyzed.

Home Preparative Procedures. The unwashed beans were mixed thoroughly and three 454-gram samples chopped separately in a Hobart mixer. Two 100-gram portions from each sample were blended in a Waring Blendor and extracted.

Eleven kilograms of beans were washed with cold water in a clean sink. Three 454-gram samples of washed, cut beans were chopped in the Hobart mixer and two 100-gram portions from each sample were blended and extracted. Nine pint jars were packed with the washed, cut

green beans. One-half teaspoon of salt was added and each jar filled with boiling water leaving 13 mm. of headspace. The jars were processed in a pressure canner at 10 pounds at 115° C. for 20 minutes.

The remaining washed, cut green beans were blanched 3 minutes in boiling water in 1.35-kg. batches. One 100-gram sample from each blanch was removed and extracted and a similar sample taken for the total solids determination. The remaining blanched beans were packed into 8-ounce freezer containers. A total of six samples was extracted from the blanched beans and 14 samples were frozen in a home freezer at -17.8° C. (0° F.).

In parallel with the first sampling interval, three 454-gram portions of beans were washed in cold water. One measuring cup of water containing 1 teaspoon of salt was brought to boil in a saucepan. The beans were added to the boiling water and boiled for 14 minutes. The cooking water was drained off, measured, and extracted. The cooked beans were weighed, homogenized, and two 100-gram portions from each sample extracted.

At the same time three 454-gram samples were prepared for pressure cooking. One-half cup of water was brought to boil in a pressure saucepan. Beans were added, the cover was fastened, and beans were cooked for 2½ minutes at 15 pounds of pressure. The pressure was brought down as quickly as possible by running cold water over the saucepan. The cooking water was drained, measured, and extracted. The cooked beans were weighed, homogenized, and two 100-gram portions from each sample were extracted.

Analytical Methods. DDT and its degradation products were determined by electron-capture gas liquid chromatography. Malathion was determined by gas chromatography using a thermionic detector and carbaryl was determined colorimetrically. The analytical procedures have been discussed and referenced in our previous publication (Farrow *et al.*, 1968).

RESULTS AND DISCUSSION

Sample Variation and Residue Content during Storage. The effect of short storage periods at 7° C. on DDT, malathion, and carbaryl residues in fresh green beans is shown in Tables I and II. An analysis of variance was performed on these data to isolate the sample variation and to investigate the significance of differences in pesticide content. Confidence limits at the 95% level have been calculated to describe the variability of sample averages.

Removal of DDT from Green Beans by Commercial Processing Procedures. Data on removal of DDT residues during commercial processing procedures were collected from the second green bean crop (Table III).

The unwashed green beans contained an average of 4.08 p.p.m. of DDT of which 3.52 p.p.m. or 86% was the *p,p'*-isomer and 0.56 p.p.m. or 14% was the *o,p'*-isomer.

Water blanching removed slightly over one half of the total residue. The steam blanch removed about one third of the total residue, significantly less than that removed by the water blanching. The steam blanch in this instance was followed by a spray rinse, in keeping with ordinary commercial practice in freezing plants using a steam blanch. These results are consistent with those obtained on tomatoes and with those on spinach reported

Table I. Behavior of DDT Residues in Green Beans during Storage at 7° C.^a

Days after Harvest	Kelthane	<i>p,p'</i> -DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	Total DDT
1	0.9(0.29) ^b	0.15(0.04) ^b	2.0(0.46) ^b	10.5(1.5) ^b	12.7(1.9) ^b
5	1.1(0.41)	0.14(0.04)	2.3(0.22)	10.7(0.56)	13.2(0.7)
9	1.6(0.15)	0.18(0.03)	2.7(0.27)	11.8(0.6)	14.7(0.9)
13	1.4(0.49)	0.15(0.02)	2.8(0.21)	11.8(0.5)	14.9(0.7)
16	1.1(0.68)	0.15(0.05)	2.6(0.15)	11.6(1.0)	14.4(0.8)

^a Residues in p.p.m., wet basis. Average of five determinations for 1 and 5 days after harvest, average of six determinations for 9 and 13 days after harvest, and average of four determinations for 16 days after harvest.

^b 95% confidence limits (wet basis) = S.D. (Student's *t* at 0.05)√*N*.

Table II. Behavior of Malathion and Carbaryl Residues in Green Beans during Storage at 7° C.^a

Days after Harvest	Malathion	Carbaryl
1	1.12 (0.52) ^b	11.0 (1.54) ^b
4	0.41 (0.15)	8.0 (1.16)
6		
8	0.06 (0.02)	
11		8.5 (0.75)

^a Residues in p.p.m., average of six determinations.

^b 95% confidence limits (wet basis) = S.D. (Student's *t* at 0.05)/√*N*.

earlier. In every case more of the *p,p'*-isomer has been removed by washing and blanching than the *o,p'*-isomer.

Processing caused an overall reduction of total DDT of approximately 83%. A part of the *p,p'*-DDT was converted to *p,p'*-TDE, but the major portion of it was transformed to degradation products not detected in the ordinary scheme of analysis for chlorinated hydrocarbon pesticides.

Removal of DDT from Green Beans by Home Preparative Procedures. The first crop of green beans was used for the home preparative procedures (Table IV).

The beans contained 0.9 p.p.m. of Kelthane. A cold water wash removed virtually all of this residue. A second series of analyses was carried out on the raw unwashed beans on the fifth day after harvest in parallel with the cooking experiments. The mean Kelthane content was 1.1 p.p.m., a result in satisfactory agreement with that obtained 1 day after harvest. Kelthane residues were not detectable in the boiled or pressure cooked samples.

A cold water wash similar to that used by housewives in preparing their product for the table or for home canning or freezing may remove up to three fourths of the DDT and related compounds from green beans. In generalizing on the susceptibility of various residues to removal by washing, the method of application of spray must be kept in mind. The wettable powder formulations similar to that used in this experiment probably result in residues which are more easily removed by a water wash than formulations in oil base solvents. The beans used for the home preparative studies contained about 13 p.p.m. of total DDT, whereas the beans in the commercial studies contained only about 4 p.p.m. This may account in part for the somewhat better removal obtained in the home preparative experiments.

Washing plus blanching removed relatively little more of the pesticide residues than cold water washing alone. This seems to suggest that the loosely adhering surface residue is removed by the cold water wash, while the more inaccessible portions of the DDT and related compounds that may have penetrated into the surface of the beans are not appreciably reduced by blanching for 3 minutes⁷ in boiling water.

Boiling and pressure cooking did not remove significantly larger quantities of residue than the cold water wash. This reinforces the suggestion that it is the surface residue that is removed in the washing operation and that the cooking operation, which by comparison is much more severe, is not effective in removing portions of the compounds that have been absorbed by the beans.

Detectable quantities of *p,p'*-TDE were found in ex-

Table III. Removal of DDT from Green Beans by Commercial Procedures^a

Treatment	Total Solids	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	<i>p,p'</i> -TDE	Total DDT and Related Compounds	Confidence Limits	Percentage Decrease	
							Wet	Dry
Unwashed	17.4	0.56	3.52		4.08	(0.57)		
WB 1 ^b	15.7	0.36	1.12		1.48	(0.34)	64	60
WB 2 ^c	16.9	0.49	1.47		1.96	(0.38)	52	50
SB 2 ^d	14.5	0.44	1.90		2.33	(0.08)	43	31
Processed								
WB 1	7.5		0.06	0.31	0.37	(0.08)	91	79
WB 2	8.4		0.09	0.28	0.37	(0.08)	91	83

^a Residues in p.p.m., wet basis. Average of six determinations.

^b Water blanched 1.5 minutes at 85° C.

^c Water blanched 3.0 minutes at 85° C.

^d Steam blanched 3.0 minutes at 100° C.

Table IV. Removal of DDT from Green Beans by Home Canning, Home Freezing, and Home Cooking^a

Treatment	Total Solids	Kelthane	<i>p,p'</i> -DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	<i>p,p'</i> -TDE	Total DDT and Related Compounds	Confidence Limits	% Decrease	
									Wet	Dry
Unwashed	17.40	0.90	0.15	2.0	10.5		12.7	(1.94)		
Washed	17.98	Trace ^b	0.09	1.0	2.6		3.7	(0.88)	71	71
Blanched	13.32	Trace ^b	0.07	0.79	1.6		2.5	(0.51)	80	74
Home canned	9.35	ND ^c	0.08	0.79	ND ^c	0.55	1.41	...	89	80
Home frozen	12.00	Trace ^b	0.08	0.30	2.6		2.9	...	77	67
Unwashed ^d	17.40	1.10	0.14	2.3	10.7		13.2	(0.76)		
Boiled	18.77	ND ^c	0.15	1.2	4.4	0.64	6.4	(1.65)	52	55
Pressure cooked	17.98	ND ^c	0.11	1.2	3.2		4.5	(0.65)	66	67

^a Residues in p.p.m., wet basis. Average of six determinations except for home canned and home frozen which was an average of three determinations.

^b Trace = Less than 0.05 p.p.m.

^c ND = Not detected.

^d Unwashed samples stored at 7° C. for 4 days

tracts of the boiled samples. These beans were boiled in water for 14 minutes. Shorter heat treatments in the 3-minute blanching experiment did not result in the formation of detectable quantities of TDE. Pressure cooking the samples at a higher temperature for 2½ minutes at 15 pounds of pressure also did not result in the formation of detectable quantities of this compound.

The cooking water in the boiled samples and also in the pressure cooked samples contained only very small quantities of DDT-related compounds. Measurable quantities of the *o,p'*-isomer and the *p,p'*-isomer were present in both cases. In the cooking water from the boiled samples, very small amounts of *p,p'*-TDE were present.

The cold water wash carried out 1 day after harvest removed 71% of the total DDT-related compounds. Five days after harvest the cold water wash and boiling 14 minutes removed only 52% of the residue. During the

4-day storage interval at 7° C. a somewhat greater percentage of the total DDT residue seemed to be converted from a "surface" residue to an "internal" residue, or otherwise became somewhat less accessible to a gentle washing procedure. The existence of a real difference between the two results, however, is open to question.

The initial residue of 12.7 p.p.m. is considerably in excess of the legal tolerance, 7 p.p.m., for DDT on green beans. In ordinary commercial practice the legal tolerance is very seldom approached at harvest time. Additional pesticide treatments were applied to the beans to make certain that at harvest, residues would equal or exceed the legal tolerances.

Removal of Malathion from Green Beans by Commercial Processing Procedures. These results were obtained from the second crop of green beans and are recorded in Table V. In this experiment, blanching removed somewhat smaller

Table V. Removal of Malathion from Green Beans by Home and Commercial Preparative Procedures^a

Treatment	Total Solids, %	Average of Six Determinations	Confidence Limits	Percentage Decrease	
				Wet	Dry
Commercial					
Unwashed ^b	14.3	0.52	(0.16)		
B1 ^c	14.3	0.25	(0.04)	52	52
B2 ^d	13.6	0.15	(0.03)	71	71
SB ^e	13.6	0.59	(0.16)	(13) ^f	(21) ^f
Canned					
B1 ^c	7.6	Trace ^g		94+	94+
B2 ^d	7.5	Trace ^g		94+	94+
Home					
Unwashed	15.73	1.12	(0.50)		
Washed	16.23	0.05		96	96
Blanched	13.06	Trace ^g		99+	99+
Frozen		Trace ^g		99+	99+
Canned	8.87			99+	99+
Unwashed ^h		0.41	(0.15)		
Cooked	17.83	Trace ^g		99+	
Pressure cooked	15.66	Trace ^g		99+	

^a Residues in p.p.m., wet basis.

^b Average of 12 determinations.

^c B1, water blanched 1.5 minutes at 85° C.

^d B2, water blanched 3.0 minutes at 85° C.

^e SB, steam blanched 3.0 minutes at 100° C.

^f Per cent increase.

^g Trace, less than 0.05 p.p.m.

^h Unwashed, stored 3 days at 7° C.

portions of malathion from green beans than in the home washing experiments described in the next section. The low initial level of malathion in this experiment may have been a factor in the less efficient removal.

In all instances, residues of malathion after processing were negligible. There appears to be a high rate of thermal breakdown of this pesticide. The breakdown products have not been identified.

In studies of malathion residues variations between subsamples representing the same treatment variables are high as compared with other pesticides studied. This may be partly ascribed to greater analytical uncertainty resulting from a low level of residue found in most of the samples. A portion of the variability, however, may be related to the high instability of surface residues as compared with residues that have penetrated into the plant tissues. The proportion of malathion that has penetrated may be quite variable from sample to sample.

Removal of Malathion from Green Beans by Home Preparative Procedures. The first crop of green beans was used for these experiments (Table V). The raw, unwashed fresh green beans contained an average of 1.12 p.p.m. of malathion.

Home cooking of green beans in a 2-quart saucepan also resulted in removal of malathion residue. Only trace amounts of the pesticide were found in these samples. The water which was used to cook the beans in the saucepan was extracted and analyzed, and found to contain no residue. Residues in amounts of 10 p.p.b. would have been detected.

After pressure cooking for 2 minutes at 15 pounds of pressure, the residue was less than 0.05 p.p.m., a decrease of 99% or more from the original level. The water used in the pressure saucepan contained residues of borderline detectability.

Samples of frozen green beans after one month of storage showed only trace amounts of malathion. Most of the residue was removed by washing and blanching.

Removal of Carbaryl from Green Beans by Commercial Preparative Procedures. Results described here were obtained from the first green bean crop (Table VI). The unwashed beans contained an average of 7.6 p.p.m. of carbaryl.

The residue in frozen beans would be approximately equal to that found in steam blanched beans, since steam blanching is customarily employed in this method of preservation.

Removal of Carbaryl from Green Beans by Home Preparative Procedures. These results were obtained from the second green bean crop (Table VI). No carbaryl residue was found in home canned green beans. Although the analytical method leaves something to be desired at carbaryl concentrations of 1 or 2 p.p.m., some indications of its presence should have been obtained if more than 0.2 or 0.3 p.p.m. had been present. For all practical purposes, 100% of the carbaryl residue was removed by home canning methods.

Table VI. Removal of Carbaryl from Green Beans by Home and Commercial Preparative Procedures^a

Treatment	Total Solids Per Cent	Average Six Determinations	Confidence Limits	Percentage Decrease	
				Wet	Dry
Commercial					
Unwashed	18.36	7.6	(0.2)		
B1 ^b	17.53	2.0	(0.2)	74	73
B2 ^c	15.27	2.0	(0.1)	74	68
SB ^d	15.77	3.8	(0.3)	50	52
Canned					
B1 ^b	8.91 ^e	1.1	(0.1)	86	71
B2 ^c	8.75 ^e	1.0	(0.1)	87	73
Home					
Unwashed		11.0	(1.5)		
Washed		5.3	(0.7)	52	
Blanched		2.1	(0.4)	81	
Frozen		0.7	(0.6)	94	
Canned		ND ^f	...	100	
Unwashed ^g		8.0	(1.1)		
Washed		4.7	(0.5)	41	
Cooked		1.7	(0.7)	77	
Pressure cooked		2.5	(0.4)	69	

^a Residues in p.p.m., wet basis.

^b B1, water blanched 1.5 minutes at 85° C.

^c B2, water blanched 3.0 minutes at 85° C.

^d SB, steam blanched 3.0 minutes at 100° C.

^e Corrected for added salt.

^f ND, not detected.

^g Unwashed, stored 5 days at 7° C.

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