

Effect of Commercial and Home Preparative Procedures on Parathion and Carbaryl Residues in Broccoli

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Broccoli grown in California was field-sprayed separately with parathion and carbaryl and prepared for serving by commercial and household procedures. No parathion was removed by commercial water washing or steam blanching. The detergent-washed samples were significantly lower in parathion residue than the water-washed sample. Only 30% of the parathion residue could be removed by commercial methods. Home preparative procedures removed

little or no parathion, and a slight increase in residue level might result if broccoli stalks are trimmed as in this experimental procedure. Data on commercially prepared broccoli containing carbaryl indicate almost complete removal of the residue by these methods. Over-all removal of carbaryl residue from broccoli by washing, blanching, and home freezing was about 90%; however, washing and home cooking removed only 55%.

This work is a continuation of a study of the effect of commercial and home preparative procedures on the removal of pesticide residues from vegetables. Data have been reported on the removal of DDT, malathion, and carbaryl from tomatoes (Farrow *et al.*, 1968), DDT from potatoes (Lamb *et al.*, 1968), and DDT, parathion, and carbaryl from spinach (Lamb *et al.*, 1969). References to previous work are given in these publications.

The studies reported in this paper are concerned with the effect of commercial freezing and home cooking and freezing on parathion and carbaryl residues in broccoli.

EXPERIMENTAL

Pesticide Application. Broccoli grown in the Salinas Valley in a field located near Castroville, Calif., was planted October 3, 1966, on a heavy loam soil. The field was sprayed on February 10, 1967, with phosdrin at 0.45 kg. (1 pound) per acre and with TEPP at 0.23 kg. (0.5 pound) per acre. Bufferol was added to the spray materials as a sticker. No other pesticides were applied prior to the experimental applications of parathion and carbaryl. The field was watered by overhead irrigation at roughly one-week intervals except during rainy periods. The broccoli was planted in double rows with 16 inches between plantings in each double row and 24 inches between rows.

Parathion and carbaryl were applied separately to two plots in the same field, each 327 feet long and 4 rows wide (13.33 feet), equal to 0.1 acre. The plots were sprayed with a Hudson 2-gallon spray tank equipped with flat spray nozzles on triple-boom heads. Four gallons of spray were applied to each plot in two tank loadings. Carbaryl was applied to one of the plots on March 6 and the broccoli was harvested on March 8. Parathion was applied on March 8 with the intention of harvesting on March 13, but heavy rain occurred from March 11 to 13. The plot was resprayed on March 17 and harvested on March 20. There was no rainfall during the latter period. The harvest on March 8 (carbaryl-treated plot) represented the first harvest of the field and consisted of somewhat overmature whole heads and side shoots. Samples of the parathion-treated plot were taken for analysis before and after each spraying.

The following spray treatments were given each plot:

CARBARYL. Stauffer Flowable Sevin 4 (4 pounds per gallon) applied March 6, 0.9 kg. (2 pounds) of carbaryl per acre; harvested March 8, 2 days after treatment.

PARATHION. Soil Serv parathion, 4 pounds per gallon of emulsifiable concentrate applied March 17, 0.23 kg. (0.5 pound) of parathion per acre. Residue before application 0.20 p.p.m.; residue after application 2.09 p.p.m.; harvest date March 20, 3 days after last treatment.

Although both pesticides were applied at the recommended dosage levels, the crop was harvested closer to application date than the minimum time specified in registered pesticide label recommendations for this crop.

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The residue levels at time of harvest, therefore, were higher than would be encountered commercially.

Approximately 68 kg. (150 pounds) of broccoli were harvested from each plot. One half of each lot was shipped to Washington, D. C., by air freight, arriving the following morning. The remainder was transported to the Berkeley laboratory and placed in cold storage at 2° C. (35° F.) until the following morning. Commercial processing experiments were conducted at the Berkeley Laboratory and home preparative experiments at the Washington, D. C., laboratory.

Commercial Processing. The broccoli was trimmed to 12.5-cm. (5-inch) lengths and the individual shoots were separated. After mixing, six 450-gram (1-pound) samples were taken for analysis. The remainder of the lot was divided into two portions of about 13.5 to 16.0 kg. (30 to 35 pounds).

A diagram of the sampling points is shown in Figure 1.

WATER WASH, NO DETERGENT. The broccoli was in the spray immersion unit of the pilot plant washer (Farrow *et al.*, 1968) using approximately 120 liters of water. Residence time was 30 seconds and the spray pressure was 30 pounds. The broccoli was then passed through the spray wash unit, where it was sprayed with 60 liters of water for 15 seconds. Three 450-gram samples were taken for laboratory analysis and the remainder was divided into three equal portions, each consisting of 3.5 to 4.5 kg. (8 to 10 pounds.).

WATER WASH, DETERGENT. The second portion of broccoli was washed in exactly the same manner, except that 0.1% Tergitol 07 (Union Carbide Chemical Co.) was added to the water in the spray immersion unit. The second spray rinse consisted of pure water. Three additional 450-gram samples were taken and the remainder was divided into three equal portions.

STEAM BLANCH. The water-washed and detergent-washed broccoli was steamed blanched for 4 and 8 minutes at 99° to 100° C. (210° to 212° F.). Three samples were taken for analysis and the remaining broccoli was passed through the spray unit, where it was sprayed with cold water for 15 seconds.

WATER BLANCH. Water-washed and detergent-washed broccoli was immersed in 100 liters of water at 85° C.

(185° F.) in the blanch unit of the pilot equipment for 6 minutes, followed by passage under cold sprays for 15 seconds in the spray unit. No samples for analysis were taken before the spray rinse because of the difficulty of removing samples at this stage.

WATER BLANCHED WITH ADDED PESTICIDE. Following water blanching of the detergent-washed broccoli, parathion or carbaryl was added to the same blanch water to produce a concentration of approximately 1.5 and 10 p.p.m., respectively. The blanch water was then allowed to circulate through the blancher for 30 minutes at 85° C. (185° F.) before final lots of broccoli were blanched. Following a 6-minute blanch, the broccoli was sprayed with cold water as before. A sample of the blanch water was taken for analysis immediately after blanching.

FREEZING. The blanched broccoli was drained and packed into cardboard freezing cartons, 5½ × 4 × 1¾ inch I.D., holding approximately 280 grams (10 ounces) of broccoli. Each lot consisted of 10 cartons. The broccoli was frozen in a plate freezer at approximately -26° C. (-15° F.), then transferred to a cold room at approximately -18° C. (0° F.), and stored until the analytical work was completed.

Home Preparation. Each of the two lots of broccoli was received in Washington, D. C., on the day following harvest. On arrival the entire lot was thoroughly mixed and three 450-gram samples were taken for analysis. These were chopped separately in a Hobart food chopper and two 100-gram subsamples from each sample were extracted. A 13.5-kg. (30-pound) portion was washed in cold water and three 450-gram samples were removed for extraction. The remainder of each lot was placed in storage at 0° C.

A diagram of the sampling points is shown in Figure 2.

BLANCHING. The washed broccoli was prepared for blanching by cutting lengthwise into uniform pieces, leaving heads about 3.8 cm. (1½ inches) in diameter. Since the stalks were somewhat longer than a housewife would customarily use, from 1.3 to 3.8 cm. were trimmed from the ends. The trimmed stalks were placed in a wire basket, blanched in boiling water for 3 minutes, and then cooled by plunging into cold water. This procedure was repeated three times, changing the blanch water each

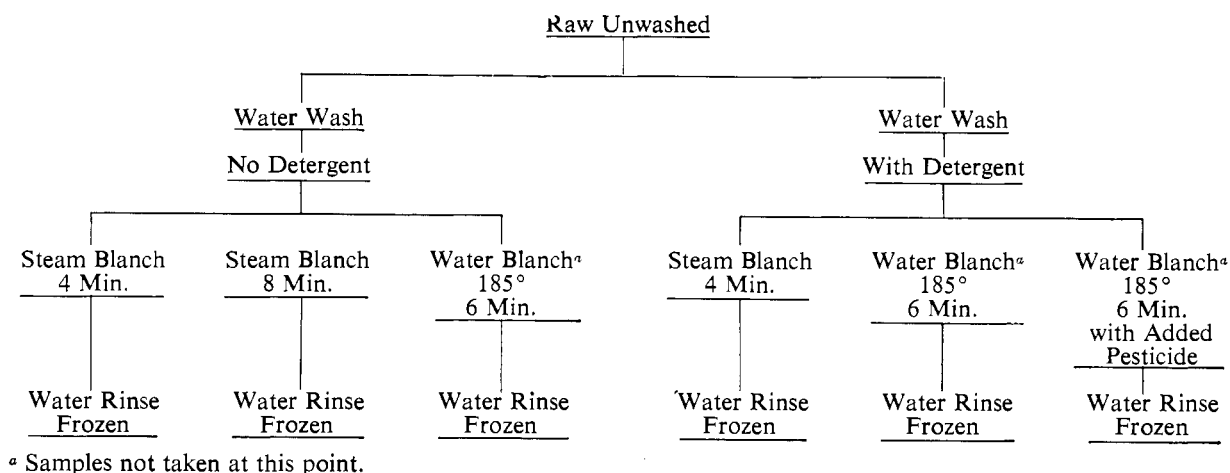


Figure 1. Sampling points for commercial processing procedures

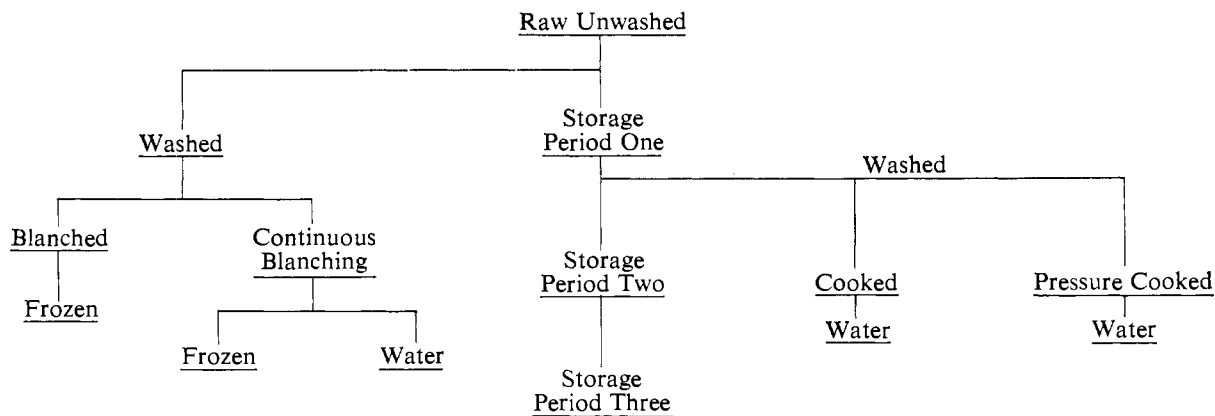


Figure 2. Sampling points for home preparative procedures

time. Duplicate 100-gram portions were extracted. A sample of the blanch water was taken for analysis after each blanching. The remainder of the broccoli was frozen.

CONTINUOUS BLANCHING. The blanching was conducted in exactly the manner described previously, except that the three separate portions were blanched in the same water. Samples of the water were taken for analysis after each blanching.

STORAGE. The broccoli not used in the blanching experiment was placed in cold storage at 0° C. and three 450-gram samples were removed from storage at 2- or 3-day intervals for a total storage period of 12 days.

COOKED. Three 450-gram samples were taken from cold storage after one day and prepared for home cooking by washing in cold water, trimming the ends, and cutting lengthwise into uniform pieces. One measuring cup of water containing one-half teaspoon of salt was brought to a boil in a saucepan, the broccoli was added, the saucepan covered, and the broccoli cooked 10 to 15 minutes after the water returned to a boil. After cooking, the water from each sample was drained off and extracted for residue analysis. The cooked broccoli was blended and two 100-gram subsamples of each sample were analyzed.

PRESSURE-COOKED. After one day of cold storage, three 450-gram samples were washed and trimmed as described above. One-third cup of water was added to the pressure cooker, and the broccoli was placed in the cooker, covered, and placed on the burner at high heat. When steam began to escape, the heat was reduced and the broccoli cooked for 1½ minutes. Pressure was reduced as quickly as possible, and the cooling water was drained off and saved for analysis. Two 100-gram subsamples of broccoli were analyzed.

Analytical Methods. The extraction, cleanup, and analytical procedures used for carbaryl in these studies have been described (Farrow *et al.*, 1968). Parathion was determined in the Washington laboratory by GLC (Guifrida, 1964) following a sweep codistillation cleanup procedure (Storherr and Watts, 1965). In the Berkeley laboratory, parathion was determined by the official AOAC method (Association of Official Agricultural Chemists, 1965). Samples of commercially blanched broccoli were given an additional cleanup using cylindrical thin-layer

chromatography (Hirayama, 1967). Recoveries of parathion from broccoli ranged from 8 to 101% and of carbaryl from 80 to 113%.

RESULTS AND DISCUSSION

Removal of Parathion by Commercial Procedures. Table I presents the results of the commercial processing experiments. The level of parathion in the unwashed broccoli averages 0.56 p.p.m. This starting level must be borne in mind in evaluating the results, since the per cent removal may be influenced by the initial level of residue. Low levels of residue are generally more difficult to re-

Table I. Parathion Residues in Broccoli Residues in P.P.M.

| Treatment | Total Solids, % | Av. Parathion, 6 Samples | Confidence Limits ^a | Per Cent Decrease | |
|---|-----------------|--------------------------|--------------------------------|-------------------|-------------------|
| | | | | Wet | Dry |
| EFFECT OF COMMERCIAL PREPARATIVE PROCEDURES | | | | | |
| Unwashed | 11.61 | 0.65 | (0.15) | ... | ... |
| Water-washed | 10.16 | 0.63 | (0.11) | 3 | (11) ^b |
| Steam-blanched 4 min. | 10.32 | 0.60 | (0.11) | 8 | (5) ^b |
| Steam-blanched 8 min. | 10.05 | 0.66 | (0.05) | (2) ^b | (20) ^b |
| Water-blanched 6 min. | 8.89 | 0.44 | (0.08) | 32 | 10 |
| Detergent-washed | 11.61 | 0.43 | (0.08) | 34 | 33 |
| Steam-blanched 8 min. | 10.47 | 0.46 | (0.07) | 29 | 21 |
| Water-blanched 6 min. | 8.86 | 0.40 | (0.06) | 39 | 18 |
| EFFECT OF HOME PREPARATIVE PROCEDURES | | | | | |
| Unwashed | 10.51 | 0.39 | (0.20) | ... | ... |
| Washed | 9.92 | 0.41 | (0.24) | (5) ^b | (11) ^b |
| Blanched | 8.71 | 0.39 | (0.14) | 0 | (22) ^b |
| Cont. blanching | 8.64 | 0.41 | (0.32) | (5) ^b | (27) ^b |
| Frozen | 7.88 | 0.39 | (0.15) | 0 | (32) ^b |
| Home-cooked | 10.07 | 0.58 | (0.25) | (49) ^b | (47) ^b |
| Pressure-cooked | 11.50 | 0.76 | (0.22) | (95) ^b | (78) ^b |

^a 95% confidence limits (wet basis) = SD (Student's *t* at 0.05)/√*N*₁
^b Per cent increase.

move than higher levels. Considerable variability was encountered among samples given the same processing treatment.

These data show that, at this level of initial residue, not more than 20 to 30% of the parathion can be removed by washing and blanching. Since the initial level is well within tolerance limits, this degree of removal can be considered satisfactory.

Steam-blanching samples were also taken directly from the blancher without spray cooling, placed in plastic bags, and frozen. These samples contained consistently from one half to two thirds of the amount of parathion found in the samples frozen in the cartons, whether the results were calculated on the wet or the dry basis. The only difference in treatment was that the samples packed in cartons were given an additional spray rinse and cooled to approximately room temperature before packing in the cartons. The only explanation that can be offered is that since the samples taken directly from the blancher and placed in plastic bags remained warm for longer than those packed in cartons, thermal destruction of parathion occurred during this period.

Removal of Parathion by Home Preparative Procedures. The results on parathion residues after home preparation are shown in Table I.

The unwashed broccoli had a level of parathion (0.39 p.p.m.) slightly less than the raw material used for commercial processing. This low level led to a high degree of sample variability, and probably to less efficient removal than if the initial level had been higher.

None of the treatments produced any apparent decrease in the level of parathion and the average values for each treatment variable were higher than the average for the unwashed sample. Although the magnitude of these increases was within the confidence limits in most instances, an actual increase in residue may have resulted from the trimming of the lower 0.5 inch of the stalk after washing and before blanching and cooking. This was done on advice of home economists, who considered that it would be a likely household practice in this instance. This would have a concentrating effect on the parathion residue, since the manner in which the spray was applied would have deposited most of the residue in the head of the broccoli.

Storage of the raw broccoli for up to 12 days at 0° C. did not indicate a decrease in parathion during this period.

Removal of Carbaryl by Commercial Procedures. The results on carbaryl residues after commercial processing are shown in Table II. Unlike the results obtained on parathion, there was no difference between the samples taken directly from the blancher and frozen in plastic bags and those obtained from the freezer cartons, which were given an additional spraying with cold water. Exactly the same methods of sample preparation were used in both instances. This would indicate that carbaryl has a greater degree of heat stability than parathion. Furthermore, there was no indication that the long (8-minute) steam blanch might give higher residue than the short (4-minute) blanch as was the case with parathion.

There was no significant difference between the water- and the detergent-blanching broccoli after water blanching and freezing.

Table II. Carbaryl Residues in Broccoli Residues in P.P.M.

| Treatment | Total Solids, % | Av. Carbaryl, 6 Samples | Confidence Limits | Per Cent Decrease | |
|---|-----------------|-------------------------|-------------------|-------------------|-----|
| | | | | Wet | Dry |
| EFFECT OF COMMERCIAL PREPARATIVE PROCEDURES | | | | | |
| Unwashed | 12.23 | 12.4 | (0.8) | ... | ... |
| Water-washed | 11.36 | 2.7 | (0.4) | 78 | 77 |
| Steam-blanching | | | | | |
| 4 min. | 11.00 | 2.0 | (0.4) | 84 | 82 |
| Rinsed | 10.72 | 1.9 | (0.2) | 85 | 83 |
| Steam-blanching | | | | | |
| 8 min. | 11.63 | 1.6 | (0.6) | 87 | 86 |
| Rinsed | 10.74 | 1.8 | (0.4) | 86 | 84 |
| Water-blanching | | | | | |
| 6 min. | 8.81 | 0.19 | (0.06) | 99 | 98 |
| Detergent-washed | 11.05 | 3.0 | (0.4) | 76 | 73 |
| Steam-blanching | | | | | |
| 8 min. | 10.84 | 1.7 | (0.2) | 86 | 85 |
| Rinsed | 10.94 | 2.1 | (0.2) | 83 | 82 |
| Water-blanching | | | | | |
| 6 min. | 8.80 | 0.28 | (0.06) | 98 | 97 |
| EFFECT OF HOME PREPARATIVE PROCEDURES | | | | | |
| Unwashed | 11.51 | 8.5 | (0.77) | ... | ... |
| Washed | 11.93 | 5.2 | (2.9) | 39 | 41 |
| Blanched | 9.18 | 1.2 | (0.5) | 86 | 82 |
| Blanch water | ... | 0.52 | (0.18) | ... | ... |
| Cont. blanch | 8.83 | 0.65 | (0.22) | 92 | 90 |
| Cont. blanch | | | | | |
| water | ... | 0.28 | (0.14) | ... | ... |
| Frozen | ... | 1.1 | (0.29) | 87 | ... |
| Frozen cooked | ... | 0.93 | (0.12) | 89 | ... |
| Cooking water, | | | | | |
| frozen samples | ... | 0.47 | ... | ... | ... |
| Home-cooked, | | | | | |
| saucepan | 10.75 | 3.6 | (1.0) | 58 | 55 |
| Pressure-cooked | 10.75 | 6.3 | (5.4) | 26 | 25 |
| Pressure-cooking | | | | | |
| water | ... | 3.5 | ... | ... | ... |
| Cooking water, | | | | | |
| saucepan | ... | 1.2 | ... | ... | ... |

In evaluation of these results, one must bear in mind the higher initial residues which may produce a more favorable picture than with parathion; however, carbaryl is much easier to remove by commercial procedures than parathion, and very little residue should remain after commercial freezing.

Removal of Carbaryl by Home Preparative Procedures. The results on carbaryl removal after home preparation are shown in Table II.

Home washing and water blanching were less effective in removal of carbaryl than the comparable commercial operations; however, after commercial steam blanching, the residues were similar to those obtained after home water blanching. Freezing resulted in no loss of carbaryl and cooking the frozen broccoli did not lower the residue significantly.

The results indicate that washing, blanching, and freezing by home preparative procedures remove a high proportion of the carbaryl residue from broccoli. There was no significant change in carbaryl residue level after storage of broccoli at 0° C. for up to 12 days.

BLANCHING IN CONTAMINATED BLANCH WATER AND CONTINUOUS BLANCHING. It was considered possible that continuous passage of a product through the same blanch water would contaminate the water to such an extent that removal of residue would be seriously impaired and that certain lots of raw product might become contaminated with more residue than was initially present if other lots, higher in residue, had previously been blanched in the same water. To obtain information on the pickup of residue from blanch water, pesticides were added to the water in an amount that might conceivably accumulate through repeated use.

In one experiment parathion was added in an amount sufficient to produce a concentration of 1.55 p.p.m. in the experimental blancher. The water maintained at a temperature of 85° C. (185° F.) was then allowed to circulate in the blancher for 30 minutes, to determine parathion breakdown over a prolonged period. An additional lot of broccoli was then blanched and the broccoli and blanch water were analyzed for parathion. In a similar experiment carbaryl was added to the blanch water in an amount sufficient to produce a concentration of 10.2 p.p.m.

Broccoli blanched in water contaminated with parathion picks up a large proportion of the parathion. The concentration found in the broccoli was almost twice that originally present in the water and 16 times higher than the amount remaining in the blanch water. About 70% of the added parathion was unaccounted for and presumably was destroyed during the 30-minute heating period.

Much less carbaryl was picked up by the broccoli from the blanch water, the concentrations in broccoli and blanch water being approximately equal after blanching. Carbaryl appears to have a higher degree of heat stability than parathion, since over 50% was recovered after the 30-minute heating.

It would appear unlikely that high concentrations of parathion would build up in the blanch water, since experiments have shown that it is not readily removed by blanching. Its lack of heat stability would also prevent it from accumulating in the blancher. In spite of the lesser affinity of broccoli for carbaryl, there is a somewhat greater possibility of its transfer from one lot of broccoli to another. It is removed to a much greater extent by

blanching and has greater heat stability. Since washing in cold water also is highly efficient in removing carbaryl from broccoli, it is unlikely that much residue would accumulate in the blanch water if a thorough water wash was applied before blanching.

In the home preparation series of experiments, three successive portions of broccoli were blanched in the same water. This did not appear to result in less efficient removal of either parathion or carbaryl than when the blanch water was changed between lots. No more than a trace of parathion was found in the blanch water after the final blanch and no more carbaryl was found after the final blanch than after a single lot was blanched in fresh water. Under these conditions, continuous blanching would not appear to result in higher residues in the final product.

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