Table I. DBCP Residues in South Carolina Fresh Peach Samples

DBCP treatment	no. of samples	mean DBCP concn, ppb	MS
treated 270 days prior to harvest	2	0.32	tentatively confirmed
treated 144 days prior to harvest	3	24.7	confirmed
treated 77 days prior to harvest	1	9.0	confirmed
treated 14 days prior to harvest	3	9.5	confirmed
treated 5 years prior to harvest	3	0.22	one not confirmed, two tentatively confirmed
never fumigated	2	0.13	tentatively confirmed
never fumigated	2	0.26	tentatively confirmed

Table II. DBCP Residues in Preserved Peaches in South Carolina

year preserved	replicates	mean DBCP concn, ppb	MS
1974	2	0.199	NR[a]
1963	2	0.057	NR
1959	2	ND[b]	NR
1953	2	0.083	tentatively confirmed
1948	4	0.252	confirmed

[a] NR = sample not run. Reagent blanks were shown to contain no DBCP. [b] ND = none detected.

to the release of DBCP (1953 and 1948) appeared to contain DBCP residues up to 0.3 ppb. Mass spectrometer analysis of selected samples extracted from fresh fruit and preserved fruit confirmed or tentatively confirmed DBCP in all the samples except one (Tables I and II). However, in the sample which was not confirmed, DBCP was tentatively confirmed in one replicate. No differentiation was obtained when the extract from the peaches preserved in 1948 was combined with a DBCP standard and injected into the mass spectrometer.

There appears to be either naturally occurring DBCP in peaches or a low level of a compound which cannot be distinguished from DBCP by the methods presently available. There may be a low-level residue of DBCP in peaches when it is applied while the peach fruit is on the tree. DBCP residues in peach fruit after the fall application were not different from the residues in peaches preserved in 1948. More research is required to determine the effect of fall fumigation on the presence of DBCP residues in peach fruit the following spring.

ACKNOWLEDGMENT

We gratefully acknowledge the services of the Agricultural Chemical Services Laboratory, Clemson University, for running duplicate samples with this laboratory and Kenneth Tomer and Edo Pellizzari, Research Triangle Institute, Research Triangle Park, NC, for mass spectrometer analysis.

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Received for review October 26, 1981. Accepted March 24, 1982. This research was partially funded by a grant from the Southern Region Pesticide Impact Assessment Advisory Committee. Contribution No. 1987 of the South Carolina Agricultural Experiment Station.

Preprocessing Oxidative Washes with Alkaline Hypochlorite To Remove Ethylenebis(dithiocarbamate) Fungicide Residues from Tomatoes and Green Beans

William D. Marshall

A four-minute preprocessing wash with dilute alkaline hydrochlorite followed by a 30-s dip into dilute sodium sulfite was demonstrated to reduce field residues of ethylenebis(dithiocarbamate) (EBDC) and ethylenethiourea (ETU) on green beans and tomatoes, to the limits of analytical significance. Subsequent processing of the washed tomatoes into juice did not raise levels of ETU whereas boiling unwashed green beans resulted in significant ETU residues on the beans and in the cooking water. This decontamination technique is thus demonstrated effective on a second crop and for a second EBDC fungicide.

Previous work (Marshall and Jarvis, 1979) has demonstrated the effectiveness of an oxidative wash with dilute hypochlorite as a technique for removing ethylenebis(dithiocarbamate) (I) (mancozeb) residues from field tomatoes. Concern regarding the continued use of EBDCs in vegetable production centers on the possibility that residues present on the surface of field-treated crops may be converted to 2-imidazolidinethione (II) (ethylenethiourea, ETU) during normal industrial processing of the crop. The nonbiological conversion of EBDCs to ETU is accelerated thermally (Newsome and Laver, 1973; Watts et al., 1974; Marshall, 1977). The conversion of surface residues of EBDC by cooking, blanching, or other processing (involving heat treatment) has been demonstrated on a variety of crops: on snap beans (Newsome et al., 1975;

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Cummings, 1977) on tomatoes, carrots, and spinach (Phillips et al., 1977), and on grapes (Gordon, 1977). Although the conversion of EBDC residues to ETU was considerably less than the theoretical maximum, it was appreciable in these trials.

ETU is a relatively potent oncogen (Innis et al., 1969; Ulland et al., 1972; Graham et al., 1975) and teratogen (Khera, 1973; Ruddick and Khera, 1975) when fed to rats and mice. In addition this toxicant possesses antithyroid properties (Rose et al., 1980). ETU is not considered to be persistent in the environment; its fate, however, in the sterile environment of a processed food has not been well documented.

Our previous results had indicated that field-weathered EBDC residues were more difficult to remove by washing with water than were fresh residues. Washing with dilute hypochlorite, however, was equally effective at removing both field-weathered and fresh EBDC residues. This treatment reduced residues of both the parent EBDC and ETU to the limit of detection in juice prepared from tomatoes that had been treated in the field with up to nine successive sprays (during the growing season) at the maximum recommended rate. Blanching of the field tomatoes with hot acid also showed considerable promise as a decontamination technique. The objectives of the present study were (a) to extend the decontamination technique to a second crop and to a second EBDC fungicide (maneb), (b) to reduce the contact time of the crop with the hypochlorite wash, and (c) to test the decontamination technique on higher levels of EBDC residue. At the same time we wanted to measure the reduction in toxicant levels due solely to preprocessing washes and to separately measure reductions resulting from subsequent cooking or processing of the washed produce.

MATERIALS AND METHODS

Field Treatment. Maneb (Dithane M-22, 80% W.P., Rohm and Haas Co.) was applied to field green bean plants in four replicate plots at the rate of 6 lb/acre [2.69 kg of active ingredient (a.i.)/ha in 1120 L/ha water]. All plants were sprayed to the point of runoff. Two replicate plots each received a single spray of fungicide and ripe vegetable was harvested 9 days later whereas two replicate plots received no fungicide. The fresh produce was immediately frozen and stored at −4 °C.

In all experiments the sprayer used to apply the fungicide was a hand-operated "Zephir" knapsack type adapted to operate at constant pressure (3.4 atm, 345 kPa) by using an independent cylinder of compressed air as the propellant.

Field tomatoes, cv. Campbell 28, in three replicate plots, received either one or two sprays of the same fungicide at the maximum recommended rate ("Ontario Vegetable Production Recommendations", 1980): 3 lb/acre. Tomato plants, treated and controls, also received the insecticide carbaryl as Sevin 50% W.P. at the recommended rate of 2 lb/acre (1.79 kg of a.i./ha). Ripe fruit was harvested either 1, 4, or 22 days after the plants were sprayed. A second plot of treated tomato plants received a second application of the fungicide (at the same rate) 4 days preharvest. Tomatoes were transported immediately after harvest to the pilot plant and were frozen or subjected to one of three preprocessing treatments.

Preprocessing Washes. Subsamples of green beans from each plot were thawed and then analyzed directly or they were subjected to one of four preprocessing treatments. In treatment one, samples were bathed and agitated in cold tap water (400 mL for each 100-g sample) for 2 min followed by two rinses with 100 mL of fresh water (volume of combined washes, 600 mL). In the second treatment the beans were cooked in boiling water (500 mL for each 100-g sample) for 3 min. In the third treatment beans (100 g) were blanched in hot (95 °C) 1.0 M HCl (500 mL) for 2 min, strained, and rinsed by dipping into cold tap water (500 mL) for 2 min. In the fourth treatment 100-g samples of beans were bathed and agitated for 2 min in a 0.1% (v/v) solution of alkaline hypochlorite at ambient temperature. This hypochlorite solution was prepared by diluting a commercial bleaching solution (Javex, nominally 6% hypochlorite) 60-fold with 0.1 M NaOH solution. The final solution was thus nominally 1000 ppm of hypochlorite. The fourth treatment was followed by a dip of 30-s duration in 0.1% (w/v) sodium sulfite. Control beans which had received no fungicide were subjected to the same washing procedures. Samples were analyzed for EBDC and for ETU residue immediately after each treatment.

Tomatoes from each sampling date were immediately frozen after harvest or were subjected to one of three preprocessing washes. Samples were continuously washed (10 min) with fresh cold tap water or were agitated for 2 or 4 min in alkaline sodium hypochlorite [0.1% (v/v) solution]. Remaining traces of hypochlorite were removed by a subsequent dip of 30-s duration into 0.1% (w/v) sodium sulfite. The samples, in 2-kg lots, were drained and then frozen to await residue analysis, or they were processed into juice as described below.

Processing of Tomatoes. Following the washing procedures described above, tomatoes in 2-kg lots were macerated in a Hobart mixer, heated with stirring in a steam-jacketed kettle (90 °C), and passed through a Langsenkamp extractor fitted with a 0.027-in. (0.69-mm) screen. The resultant juice was canned (19-oz enameled cans) and held at 95 °C for 0.5 h prior to cooling. When the cans were cool they were stored at 4 °C until the produce was analyzed for pesticide residues.

Analyses. Analysis for EBDC residue was performed by using the carbon disulfide evolution method (Keppel, 1969, 1971) with only minor modification. Spectrophotometric quantitation was performed by using 5-cm cells and compensation techniques to reduce spectrophotometric error. The unit of analysis was 0.02 ppm for tomatoes and for green beans. Residues of ETU were measured by the method of King (1977).

RESULTS AND DISCUSSION

The origin and treatments for samples of green beans are outlined schematically in Figure 1. A similar flow diagram detailing experiments with field tomatoes is presented in Figure 2.

Washing of Green Beans. The efficiency of various decontamination procedures may be obtained by comparing residual EBDC and ETU levels on beans before and after washing (Table I). Each recorded value in Table I represented the average of at least seven samples. The variability in the spray coverage is reflected in the high standard deviations. Repeated analysis of the same subsample led to considerably lower standard deviations. Unwashed samples from plots treated with maneb contained an average of 1.49 ± 0.12 ppm of the parent fungicide but only very low levels of ETU. Taking into account the probable conversion of EBDC residues to ETU during analyses for the latter (Pease and Holt, 1977; Phillips et al., 1977), this level of ETU is not considered to be significant. If the beans were agitated in cold water for 2 min, an average of 55% of the EBDC residue initially present remained on the washed beans. A further 26% of the EBDC residue was detected in the combined water

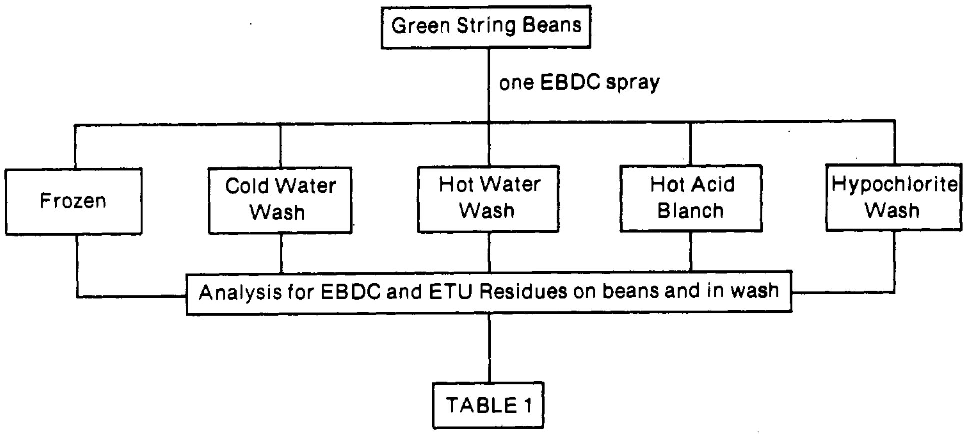

Figure 1. Postharvest treatments of green beans which had been field treated with maneb.

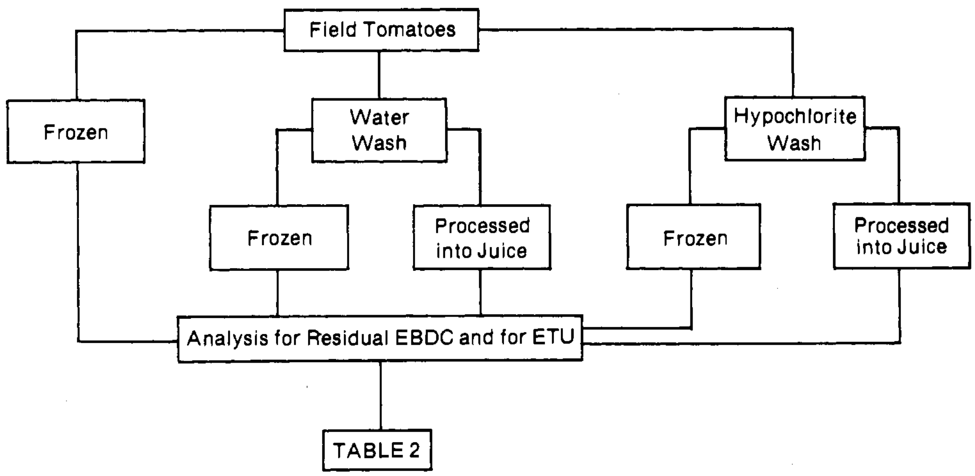

Figure 2. Postharvest treatments of tomatoes which had been field treated with maneb.

Table I. Mean Residues (ppm of a.i.) of Maneb (Dithane M-22) and of ETU on Green Beans and in Wash Water following Various Preprocessing Treatments

residues	washing procedure	unwashed	cold water wash	hot water wash	hot acid treatment	hypochlorite treatment
EBDC	beans	1.49 ± 0.12	0.82 ± 0.05	ND[a]	0.04 ± 0.03	ND
	wash water		0.39 ± 0.06			
ETU	beans	0.030 ± 0.009	0.021 ± 0.005	0.144 ± 0.032	0.059 ± 0.014	ND
	wash water		0.039 ± 0.009	0.170 ± 0.035		

[a] ND = none detected = less than 0.02 ppm of EBDC or less than 0.01 ppm of ETU.

Table II. Mean Residues[a] (ppm of a.i.) of Maneb (Dithane M-22) in Tomatoes or Juice following Preprocessing Washes

		sprayed Aug 14		resprayed Sept 1	
harvested	postharvest treatment	and juiced	and frozen	and juiced	and frozen
1 day postspray	not washed		0.65		
	10 min with H_2O	0.15, 0.21	0.42		
	2 min with OCl	ND,[b] ND	ND		
	4 min with OCl	ND, ND	ND		
4 days postspray	not washed		0.45		
	10 min with H_2O	0.25, 0.15	0.30		
	2 min with OCl	0.0, 0.06	0.09		
	4 min with OCl	0.03, 0.02	0.03		
22 days post 1st spray	not washed		0.36		2.15
	10 min with H_2O	0.17, 0.22	0.28	0.19, 0.21	0.98
	2 min with OCl	0.07, 0.13	0.17	0.05, 0.08	0.12
	4 min with OCl	0.02, ND	0.03	ND, ND	0.07

[a] Each entry represents the average of at least three replicate analyses of each tin or 2-kg composite sample of macerated whole tomatoes. Analyses were repeated until the standard deviation was below 0.06 ppm for frozen tomatoes and below 0.03 ppm for juiced samples. [b] ND = none detected (less than 0.02 ppm).

washes. This treatment did not affect the levels of ETU present in the beans or wash water. If the beans were boiled in hot water for 3 min, no EBDC residue above background could be detected on the cooked vegetable or in the cooking water. However, the beans contained an average of 0.144 ppm (seven samples, duplicate analyses), and the cooking water contained an average of 0.170 ppm of ETU. Analogous conversions of field EBDC residues to ETU have been observed by several investigators (Baron, 1976; Newsome, 1976; Gordon, 1977; Phillips et al., 1977) when a variety of crops (tomatoes, carrots, spinach, and grapes) were cooked or processed. Blanching of the beans in hot (95 °C) 1.0 M hydrochloric acid for 2 min followed by a 2-min cold water wash removed virtually all the EBDC (95% reduction) but left small amounts of ETU on the beans (0.059 ± 0.014 ppm). Although this washing procedure was successful at removing/decomposing EBDC, residue traces of ETU were formed during the process. The wash with alkaline hypochlorite followed by dipping in dilute sodium sulfite left no detectable residue of maneb or of ETU on the treated beans.

Washing of Tomatoes. The efficiency of water washing as compared to washing with alkaline hypochlorite for 2 or 4 min may be observed in Table II if one compares toxicant levels on tomatoes before and after treatment. Each entry in Table II represented the average of three or more replicate analyses on separate cans or 2-kg homogenates of whole tomato. Levels of maneb residues were lower in all produce that had been washed compared to those of unwashed fruit. Washing with water (10 min) was only moderately effective (30–55% removal) at reducing toxicant levels. Processing the washed fruit into juice further reduced these levels (40–77% reduction relative to that of unwashed fruit). Treatment with hypochlorite was considerably more effective than water washing; however, aged residues (samples harvested 22 days postspray) were less efficiently removed by the 2-min wash than were fresh residues (samples harvested 1 day postspray). In all instances maneb residues were reduced virtually to the limit of detection by the 4-min hypochlorite wash and were only slightly higher on samples from the 2-min hypochlorite wash. ETU levels were measured on juiced samples only. No ETU residue was detected in any of these samples.

Previous studies with tomatoes (Marshall and Jarvis, 1979) involved the use of an aqueous hypochlorite wash to remove mancozeb residues; in the present work commercial hypochlorite was diluted with 0.1 M NaOH. No improvement was observed with this modification.

It is concluded that EBDC and ETU residues on tomatoes and beans may be controlled effectively by washing the fresh produce with a dilute solution of hypochlorite. In the present studies the hypochlorite washing technique has been demonstrated to be effective at removing a second EBDC residue (maneb) from a second crop matrix (green beans).

ACKNOWLEDGMENT

Our sincere appreciation is extended to D. Pohlman (Harrow Research Station) for conducting the field trials and processing tomato samples into juice. It is also a pleasure to acknowledge the excellent technical assistance of M. Simon (Chemistry and Biology Research Institute, Agriculture Canada) and H. Mineau-Tees and the contribution of Dr. S. U. Khan (CBRI), which made the completion of this work possible.

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Received for review September 29, 1981. Accepted March 1, 1982. This work received financial support from the National Science and Engineering Research Council of Canada.