

Table IV. $^{14}\text{CO}_2$ and [^{14}C]Alkylarsine Recovered from Plant and Soil, 2 Weeks after Treatment with [^{14}C]MSMA^a

Sample	% applied radioact. recovd
Plant	59.4 ^b
Soil	19.8 ^b
$^{14}\text{CO}_2$	0.8 ^c
[^{14}C]Alkylarsines	0.1 ^c

^a Values are means of two replications. ^b Determined by combustion and liquid-scintillation counting of the trapped $^{14}\text{CO}_2$. ^c Determined by liquid-scintillation counting.

Table V. Arsenic Residue in Wheat Seeds^a

Experiment	Arsenic residue ^b
Control	0.39
MSMA treated expt I	1.52
MSMA treated expt III	1.16

^a These values represent mean of duplicates for each of the samples. ^b Analysis by atomic absorption spectrometry.

[^{14}C]MSMA since at the end of 1 week neither $^{14}\text{CO}_2$ nor [^{14}C]alkylarsine was detected. Detection occurred only after 2 weeks, sufficient time for root exudation. Von Endt et al. (1968) and Woolson (1976) showed that [^{14}C]MSMA is degraded in soil to release $^{14}\text{CO}_2$ or is methylated and reduced to dimethyl- and trimethylarsines.

Experiment III. Application of MSMA at 3.36 kg/ha under greenhouse conditions at the two-three leaf development stage resulted in an increase in the arsenic content of the wheat crop relative to the control (Table V). The shallowness of the soil and the greenhouse environment itself may have enhanced the arsenic residues in the seed. Field studies conducted by Moore (1975) indicated that use of MSMA resulted in a small but in-

significant increase in the arsenical content of wheat seeds.

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Pesticide Residue Reduction by the Process of Preparing Whole Orange Puree

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Bearing Marrs orange trees [*Citrus sinensis* (L.) Osbeck] sprayed with a mixture of pesticides (az-inphosmethyl, carbophenothion, ethion, parathion, malathion, dioxathion, dimethoate, dicofol, and chlorobenzilate) were harvested at 1, 7, and 21 days after application. Samples from each harvest were analyzed for pesticide residues: (1) unwashed; (2) after washing by a common processing plant method; and (3) after being processed into whole orange puree. Washing eliminated from 8 to 35% of the residue initially present on the unwashed fruit. The whole orange puree had a residue level 71 to 95% less than the unwashed fruit. Individual pesticide residues did not exceed the tolerances established by the Environmental Protection Agency (EPA), even on the unwashed fruit harvested 1 day after the spray application. Residues on fruit harvested 3 months after the last spray application in a normal pesticide program were no higher than 1.4% of the tolerance limit. We concluded that residues in oranges received by processors probably would not exceed EPA tolerances for the pesticides tested, and also that pesticide residues in whole orange puree were substantially less than that of the unwashed fruit and well within the established tolerances for whole fruit.

The fate of pesticide residues on citrus fruits which are processed into whole citrus fruit puree has not been investigated previously. The puree process of Cruse and Lime (1970) incorporates from 85 to 90% of the entire fruit

into the final product. In their process whole fruits are water blanched at 100 °C for 10 min before grinding. This blanch and the removal of hard portions of tissue in the finisher would be expected to eliminate a considerable portion of any pesticide residue that might be present in the field-run fruit. Gunther (1969) discussed residues and their removal in the processing of other citrus products.

The purpose of this study was to determine the effects of the puree process on the content of pesticide residues in the puree and to determine whether or not pesticide

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Table I. Composition of Nine-Pesticide Spray Mixture Applied November 9, 1972

Chemical	Act. ingredient in formulation, lb/gal	Quarts of formulation per 500 gal of spray mixture	Act. Ingredient applied, ^a lb/acre
Dioxathion	4	2	8
Ethion	4	2	8
Chlorobenzilate	4	1	4
Parathion	4	1.25	5
Carbophenothion	4	1.25	5
Dicofol	4	1	4
Azinphosmethyl	2	2.5	5
Malathion	5	3	15
Dimethoate	2.67	2	5.3

^a These values are based on a coverage of 2000 gal of spray mixture per acre of mature 20-ft high trees planted 100 trees/acre. Gallonage, and consequently active ingredient applied per acre, will differ for different groves with differing tree height and planting density. These factors are likely to vary between different growing areas with different environmental and cultural factors. Comparison of residue data in terms of application rates must be done with due consideration of the limitations imposed by these variations.

residues on fruit used to prepare purees exceeded established tolerances.

EXPERIMENTAL PROCEDURE

The investigation was divided into two experiments. In experiment 1 trees bearing mature fruit were sprayed with a mixture of nine pesticides and then the fruits were harvested at various times after exposure. The aim was to obtain mature fruit which had been subjected immediately before harvest to what would constitute a grossly negligent, uneconomical, and illegal application of pesticides.

Experiment 2 aimed to obtain mature fruit from trees which had undergone a documented normal pesticide program during the season before harvest.

In both experiments the fruits were analyzed for pesticide residues at stages in the post-harvest handling and processing.

Trees. The trees treated were in a grove of 9-year-old Marrs orange trees located at Texas A&I University's Citrus Center, Weslaco, Tex. This grove had been divided into blocks which were maintained on documented schedules of pest-control management. One group of three trees which had not received any pesticide treatment during the prior year was selected to be sprayed with the nine-pesticide mixture (experiment 1). Another group of three trees, from a block which received a documented spray program of the type generally used in commercial groves in Texas, was selected for experiment 2.

Spray Treatment. In experiment 1 the mixture of nine pesticides in a single tank was applied with a high-pressure commercial sprayer on Nov 9, 1972. The spray mixture included mutually compatible insecticides and miticides in the concentrations indicated in Table I. A spreader-sticker also was added to the formulation (Triton B-1956 at 1 oz per 100 gal). Sufficient spray was applied to each tree to provide complete wetting of the foliage as indicated by the initiation of run-off.

In experiment 2 trees received the treatment listed in Table II during the 6 months prior to harvest. Those applications included a spreader-sticker (Triton B-1956 at 1 oz per 100 gal) and were applied with a high-pressure oscillating boom sprayer.

Table II. Composition of Pesticide Mixtures Applied for the Normal Spray Program

Date	Chemical	Act. ingredient in formulation, lb/gal	Quarts of formulation per 500 gal of spray mixture	Act. ingredient applied, ^a lb/acre
June 30	Parathion	4	2	8
	Carbophenothion	4	3	12
Aug 17	Azinphosmethyl	2	8	16
	Chlorobenzilate	4	1.5	6
Oct 12	Dicofol	4	2	8
	Carbaryl ^b	(80%)	(7 lb)	(22.4)

^a These values are based on a coverage of 2000 gal of spray mixture per acre of mature 20-ft high trees planted 100 trees/acre. Gallonage, and consequently active ingredient applied per acre, will differ for different groves with differing tree height and planting density. These factors are likely to vary between different growing areas with different environmental and cultural factors. Comparison of residue data in terms of application rates must be done with due consideration of the limitations imposed by these variations. ^b Carbaryl residues were not determined in this investigation.

Harvest and Processing. In experiment 1 samples of fruit were harvested 1 day before spraying (Control, D - 1), and then 1 (D + 1), 7 (D + 7), and 21 days (D + 21) after spraying. At each harvest date six samples of 21 fruits each (a random selection of 7 fruits from each of the three times) were obtained. The six samples for each harvest date were divided into three post-harvest treatment stages of two replications each. The three treatment stages were: unwashed, fruit prepared for analysis after undergoing normal harvest handling; washed, fruit washed in a manner similar to that used in commercial processing plants as follows: soak in fresh water (1 min), scrub on rotary brushes under a high-pressure water spray (1 min), and drain (1 min); pureed, fruits were washed as above and then made into whole orange puree by the method of Cruse and Lime (1970).

In experiment 2 fruit from the three trees which had undergone the normal spray program was harvested on Jan 8, 1973. Six samples of fruit were harvested and divided into two replications for each of the three post-harvest treatment stages.

Pesticide Analysis. After each of the first two post-harvest treatment stages the samples were ground up to a homogeneous consistency and a portion was sealed in 46-oz cans and frozen immediately. The pureed samples were also sealed in 46-oz cans and frozen. These frozen samples were submitted to a certified commercial analytical laboratory experienced in pesticide analysis. The laboratory used the standardized acetonitrile isolation procedure developed by the U.S. Department of Health, Education and Welfare (1968a). The dicofol and chlorobenzilate residues in the extract fractions were determined by gas chromatography with an electron capture detector (U.S. Department of Health, Education and Welfare, 1968b). The remaining pesticides were determined by gas chromatography with a flame photometric detector (Zweig, 1972).

RESULTS AND DISCUSSION

Data in Table III show that in no case did residues of any individual pesticide exceed the tolerance limits established by the U.S. Environmental Protection Agency

Table III. Pesticide Residues in Marrs Oranges from Trees Receiving a Spray Application of a Nine-Pesticide Mixture

Pesticide	Minimum detectable amount, ppm	EPA tolerance, ppm	Treatment	Time of harvest ^a Pesticide residue in ppm ^{b,c}			
				D - 1	D + 1	D + 7	D + 21
Azinphosmethyl	0.33	2.0	Unwashed	*	*	*	*
			Washed	*	*	*	*
			Pureed	*	*	*	*
Carbophenothion	0.02	2.0	Unwashed	*	0.27	0.24	*
			Washed	*	0.20	0.19	*
			Pureed	*	0.08	0.03	*
Ethion	0.009	2.0	Unwashed	*	0.58	0.56	*
			Washed	*	0.38	0.43	*
			Pureed	*	0.12	0.05	*
Parathion	0.005	1.0	Unwashed	*	0.60	0.41	*
			Washed	*	0.48	0.32	*
			Pureed	*	0.04	0.02	*
Malathion	0.007	8.0	Unwashed	*	0.75	0.54	*
			Washed	*	0.52	0.40	*
			Pureed	*	0.04	0.04	*
Dioxathion	0.17	2.8	Unwashed	*	*	*	*
			Washed	*	*	*	*
			Pureed	*	*	*	*
Dimethoate	0.17	2.0	Unwashed	*	*	*	*
			Washed	*	*	*	*
			Pureed	*	*	*	*
Dicofol	0.60	10.0	Unwashed	*	*	*	*
			Washed	*	*	*	*
			Pureed	*	*	*	*
Chlorobenzilate	0.13	5.0	Unwashed	*	1.00	1.00	*
			Washed	*	0.78	0.92	*
			Pureed	*	0.22	0.16	*

^a Days before or after pesticide application. ^b Average of two replications. ^c All residues are uncorrected for absolute recovery but have been corrected for analytical recovery from the point of first extraction. An asterisk indicates the residue is less than the minimum detectable amount.

(Code of Federal Regulations, 1975). This was true even of unwashed fruit harvested the day immediately after spraying. Of course the tolerances for pesticides within the same class are not additive and the presence of one member of a class causes a proportional decrease in the amount of residue which may be allowed for other members of the same class. It must be emphasized that the residues reported in Table III represent samples harvested very soon after spraying which would not be found in commercial practice. The residues found here only represent the upper limits of residues which can be induced by early harvest under environmental conditions which are not conducive to rapid pesticide degradation. Figure 1 summarizes the climatic conditions which prevailed during the two experiments. The weather was mild with no rainfall until just before harvest of fruit at D + 21 days. Day length during November is approaching the minimum.

Residue values reported here are generally less than those reported by other workers (see Gunther, 1969). These differences are principally due to the reference point at which residues are being determined on the fruit. Residue studies for pesticide label registry are aimed at determining the residue on the fruit as it exists on the tree. Consequently great care is taken in these developmental studies to sample the fruit on the tree without losing any residues from the fruit surface. This is in contrast to our own studies which seek to determine residues on the fruit after having undergone normal commercial harvesting and handling, up to the point of arrival at a processing plant.

Gunther (1969, p 96) points out that it would be interesting to compare residue data obtained in developmental studies with residue data actually being found in current commercial practice. The present study provides an indication of how developmental data taken at one location and climate can contrast with those data taken

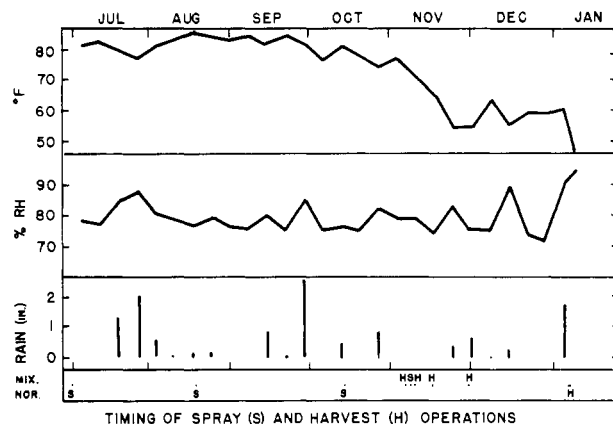


Figure 1. Relationship of weekly average climatic conditions: temperature ($^{\circ}$ F), percent relative humidity (% RH), and rain (inches); to the timing of spray (S) and harvest (H) operations for trees receiving an application of the nine-pesticide mixture (Mix.) and for trees receiving a normal (Nor.) pesticide spray program.

at a different location with different variety, climate, spray schedule, and point of sampling during the commercial handling of fruit.

Simple washing of the fruit removed from 8 to 35% of the residue initially present on the unwashed fruit. Simple washing plus the puree process reduced residues 71 to 95% from that of the unwashed fruit.

The larger reductions in pesticide residues due to washing found by Gunther in contrast to those reported here are again most likely a consequence of the point at which the first residue analyses are made. Since the samples analyzed here had undergone simulated commercial handling prior to the first analysis much of the dislodgable residue had already been lost. As a conse-

Table IV. Pesticide Residues in Marrs Oranges from Trees Receiving a Normal Pesticide Spray Program

Pesticide	Application to harvest interval, days	Min detectable amount, ppm	EPA tolerance ppm	Treatment	Pesticide residue, ppm ^{a, b}
Azinphosmethyl	144	0.09	2.0	Unwashed	*
				Washed	*
				Pureed	*
Carbophenothion	192	0.03	2.0	Unwashed	*
				Washed	*
				Pureed	*
Parathion	192	0.005	1.0	Unwashed	0.007
				Washed	0.008
				Pureed	0.006
Dicofol	88	0.06	10.0	Unwashed	0.12
				Washed	0.14
				Pureed	0.08
Chlorobenzilate	144	0.04	5.0	Unwashed	*
				Washed	*
				Pureed	*

^a Average of two replications. ^b All residues are uncorrected for the absolute recovery but have been corrected for analytical recovery from the point of first extraction. An asterisk indicates the residue is less than the minimum detectable amount.

quence less residue was available for removal by washing.

Even under the extreme conditions of these experiments the puree never exceeded 6% of the EPA tolerances established for raw fresh citrus fruits.

Since harvesting fruit without waiting a prescribed time after pesticide application is contrary to good grove management and labeling restrictions, and because no residue tolerances were exceeded on fruit harvested only 1 day after pesticide treatment, we tentatively conclude that: if label restrictions are followed it is improbable that any oranges having pesticide residues exceeding the EPA tolerances would reach the processor. Furthermore, pesticide residues in whole orange purees, prepared as described, are substantially less than that of the unwashed fruit and well within the established tolerances for whole fruit.

Such a conclusion is supported by the results of experiment 2 (Table IV). None of the samples contained residues greater than 1.4% of the EPA-established tolerances for citrus.

NOMENCLATURE

Azinphosmethyl	<i>O,O</i> -Dimethyl <i>S</i> -[4-oxo-1,2,3-benzotriazin-3(4 <i>H</i>)-yl methyl] phosphorodithioate
Carbophenothion	<i>S</i> -[<i>p</i> -(Chlorophenylthio)methyl] <i>O,O</i> -diethyl phosphorodithioate
Ethion	<i>O,O,O',O'</i> -Tetraethyl <i>S,S'</i> -methylenebisphosphorodithioate
Parathion	<i>O,O</i> -Diethyl <i>O-p</i> -nitrophenyl phosphorothioate
Malathion	Diethyl mercaptosuccinate <i>S</i> -(<i>O,O</i> -dimethyl phosphorodithioate)

Dioxathion	2,3- <i>p</i> -Dioxanedithiol <i>S,S</i> -bis(<i>O,O'</i> -diethyl phosphorodithioate)
Dimethoate	<i>O,O</i> -Dimethyl <i>S</i> -(<i>N</i> -methylcarbamoyl)methyl phosphorodithioate
Dicofol	1,1-Bis(<i>p</i> -chlorophenyl)-2,2,2-trichloroethanol
Chlorobenzilate	Ethyl 4,4'-dichlorobenzilate

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