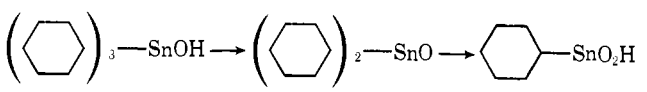
Residues on Apples and Pears from Use of Plictran Miticide

Milton E. Getzendaner* and Homer B. Corbin[1]

Apples and pears from trees in several experiments in various sections of the U.S., sprayed with Plictran miticide, were analyzed for residues of total and organic tin. Inorganic tin was calculated as the difference between total and organic tin. Residue levels were similar on the two fruits and a maximum of less than 2 ppm of organotin was found, calculated as tricyclohexyltin hydroxide (Cy_3SnOH) on the day of the last of four applications. Organotin decreased to about half of the initial value in 3 to 5 weeks. Most of the residue of total tin remaining 4 weeks after spraying was organic tin, and most of that was the active ingredient Cy_3SnOH. Nearly all the residue was on the peel of the fruit, and up to half of this was removed with a cold water wash.

Plictran miticide, containing the active ingredient tricyclohexyltin hydroxide (Cy_3SnOH), a product of The Dow Chemical Company, is effective for controlling plant-feeding mites on apples and pears. It may be applied up to four times a season, depending on conditions. As part of the information showing safety of the use of the chemical, apples and pears were treated in various sections of the United States from which samples were collected to study the residue deposition and degradation. This paper gives details and results of these experiments.

A study was conducted of products formed from irradiation of tricyclohexyltin hydroxide and dicyclohexyltin oxide (Starnes, 1966). The irradiation was carried out by sun lamp on thin-layer chromatographic plates, immediately before development of the plates with solvent. It was shown that the following degradation sequence takes place.



tricyclohexyltin hydroxide (Cy_3SnOH)	dicyclohexyltin oxide (Cy_2SnO)	cyclohexylstannoic acid ($CySnO_2H$)

Smith *et al.* (1970) have shown the same pattern for degradation of tricyclohexyltin hydroxide, with further degradation to inorganic tin.

To account for the major degradation products in crops, methods have been designed to determine all three of these organic tin compounds.

ANALYTICAL PROCEDURES

Initial work involved examination of whole fruit by a stripping procedure which has also been used and reported by Trombetti and Maini (1970). This separated the tin in the sample into three fractions: surface organic tin, surface inorganic tin, and interior tin. In one series the surface organic tin fraction was separated into the mono-, di-, and tri-substituted tin subfractions.

All of the later analytical work was done by methods permitting the use of macerated samples. This involved two methods: one determined total tin in the whole sample by wet-oxidation, separation of the tin (either by distillation as the bromide or by extraction as the iodide), and measurement by the colorimetric toluene-3,4-dithiol method (Corbin, 1970). A second method reported in this paper determines total organic tin in the fruit samples by solvent extraction of the three organic forms, wet oxidation, extractive separation as the iodide, and dithiol measurement. All method development and analyses were done under the direction of H. B. Corbin in the laboratories of M&T Chemicals, Inc.

Separate Cyclohexyltin Derivatives. (see Figure 1). 1. The fruit to be analyzed must fit loosely in a 1-qt wide-mouth extraction jar, must be free of cuts and holes, and not badly bruised. Bring the fruit to room temperature and remove surface moisture by storing overnight in a desiccator over $CaCl_2$.

2. Hexane Extraction of Organic Tin. Place two or three weighed fruits in a 32-oz jar, add 30 ml of acetic acid–hexane (1:99), and cap tightly. Roll the jar for 10 min on its side by hand or on a jar roller, allowing the solvent to wet the entire surface of the apples.

Open the jar and transfer the solvent through a glass funnel into a 300-ml Erlenmeyer flask. Rinse the fruit, place one at a time in the funnel, and also rinse the jar, using about 20 ml of acetic acid–hexane (1:99) from a wash bottle.

Replace the fruit in the jar and repeat the entire procedure twice more, allowing 10 min of contact each time. Return apples to the jar. The approximately 150 ml of acetic acid–hexane solution is treated as in Section 4.

3. HCl Extraction of Inorganic Tin. To the jar containing the hexane-extracted fruit add 30 ml of HCl (1:4) containing 0.01% sodium lauryl sulfate and cap tightly. Extract with the HCl three times for 10-min periods exactly as was done with hexane. Collect in a 500-ml Erlenmeyer flask. The 150 ml of HCl extract is treated as in Section 7. The fruit are retained in the jar and treated as in Section 6.

4. Separation of Monocyclohexyl Stannoic Acid. Add 40 ml of HCl (1:4) to the 150 ml of acetic acid–hexane solution, stopper tightly, and agitate vigorously for 10 min on the shaker. Transfer to a 250-ml separatory funnel (No. 1). Stopper and allow to separate for 10–15 min.

Draw off the lower layer including any unseparated emulsion into a 250-ml separatory funnel (No. 2). Transfer the clear hexane back to the 300-ml Erlenmeyer. Rinse the emptied separatory funnel (No. 1) with 40 ml of HCl (1:4) and add to the flask. Return to the shaker and agitate vigorously for 10 min. Transfer hexane and acid to separatory funnel No. 1 and let settle for 10–15 min.

Draw off the lower layer including any unseparated emulsion into separatory funnel 2. Repeat the washing of the hexane with a third 40-ml portion of HCl (1:4). Retain the hexane solution in funnel No. 1 for Section 5.

Add 25 ml of hexane to the 120 ml of HCl extract in funnel No. 2. Shake manually for 3 min and allow to separate. Draw the aqueous HCl layer into a 250-ml separatory funnel

Ag-Organics Department, Dow Chemical U.S.A., Midland, Michigan 48640.
[1] M&T Chemicals Inc., Rahway, New Jersey 07065.

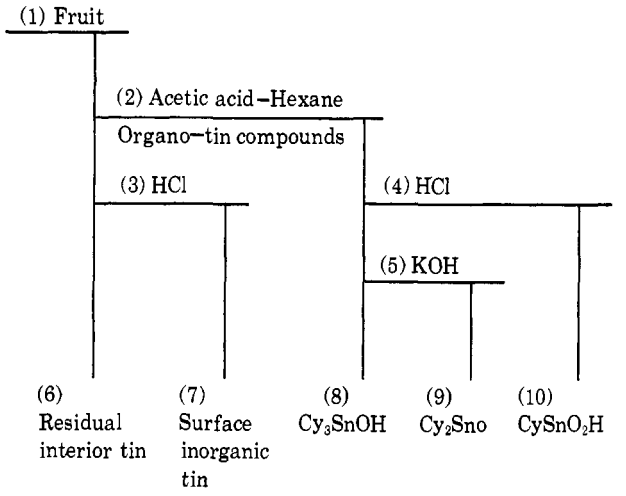


Figure 1. Separation flow chart. Numbers refer to sections of the procedure

(No. 3). Add 25 ml of hexane to funnel 3, stopper, and shake for 1 min. Allow to separate and draw off the aqueous HCl layer into a 500-ml flask.

Transfer the hexane from No. 3 to No. 2 and wash the combined hexane portions with 25 ml of HCl (1:4). Draw the HCl into the main portion in the 500-ml flask and treat as in Section 10. Transfer the 50 ml of hexane from No. 2 to the main hexane extract in No. 1. Treat as in Section 5.

5. Separation of Dicyclohexyltin Oxide. To the 150–200 ml of hexane in funnel No. 1, add 20 ml of KOH (5% in 50% alcohol). Stopper and shake manually for 2 min. Let separate 20 min and draw into a 250-ml separatory funnel (No. 4). Repeat the extraction of the hexane with the alcoholic KOH, using again 20 ml and allowing to settle for 20 min. Combine the alcoholic KOH solutions in funnel No. 4. Wash the hexane in funnel No. 1 with 40 ml of H_2O, avoiding vigorous shaking. Transfer the H_2O to funnel No. 4. Treat the hexane as in Section 8.

To the KOH–alcohol–water solution (funnel No. 4) add 40 ml of concentrated HCl and 50 ml of hexane. Shake for 2 min and let separate. Transfer the aqueous layer to a 200-ml tall form beaker. Pour off the hexane into a second 200-ml tall form beaker. Return the aqueous solution to the funnel. Rinse the first 200-ml beaker with 30 ml of hexane and transfer to the funnel. Extract for 2 min, separate, and discard the aqueous layer. Transfer the hexane to the second 200-ml beaker. Treat as in Section 9.

6. Determination of Tin in Extracted Fruit. Determine tin as previously reported (Corbin, 1970).

7. Determination of Surface Inorganic Tin. The 150 ml of HCl extract of the fruit from Section 3 is treated in the 500-ml flask as follows. Add 20 to 30 glass beads (4 mm, solid) and 150 ml of nitric acid. Mix, add 40 ml of concentrated sulfuric acid, and again mix. Heat to boiling and boil down to fumes of H_2SO_4. Wash down the neck and walls with 75 ml of H_2O, mix, and boil to fumes. Fume on the hot plate, and free flame 1 min. Cool to room temperature. Distil and determine the tin.

8. Determination of Tricyclohexyltin Hydroxide. Transfer the hexane solution (Section 5) to a 300-ml tall form beaker. Set in the hood uncovered and allow to evaporate at room temperature in a good draft of air.

To the residue add 10 ml of HNO_3 and 4 ml of H_2SO_4. Cover with a flat watch glass and heat to reflux the HNO_3 for a few minutes. Remove the cover and take to fumes of H_2SO_4. Cool slightly and slowly add 5 ml of HNO_3 to the hot solution. Take to fumes, cover, and flame lightly. Cool a few minutes, add 5 ml of HNO_3 and ten drops of $HClO_4$ (70%). Swirl on the hot plate and boil off HNO_3. Cover and allow to reflux to the top by heating strongly. Remove the cover, fume off all water, and fume covered.

Cool, rinse down with 10–15 ml of H_2O, and evaporate to fumes without boiling. Fume off traces of H_2O, cover, and fume strongly for 1 min. Allow to cool to room temperature. Determine the tin. It is not usually necessary to distil the tin.

9. Determination of Dicylohexyltin Oxide. Evaporate the hexane in the 200-ml beaker (Section 5), oxidize with $HNO_3H_2SO_4$, and determine tin as in Section 8.

10. Determination of Monocyclohexyl Stannoic Acid. To the HCl solution in the 500-ml flask (Section 4) add 150 ml of HNO_3, 4 ml of H_2SO_4, and a roughened stirring rod. Boil down on the hot plate to 25–50 ml volume. Transfer to a clean 200-ml tall form beaker using HNO_3 to complete the transfer. Insert the stirring rod and take down to fumes. Fume off H_2O, cover, and fume at reflux. Cool a few minutes, and add 5 ml of HNO_3 and ten drops of $HClO_4$ (70%). Swirl on the hot plate boiling off HNO_3. Cover, heat strongly to reflux, then remove cover and fume off all water. Finally cover and fume strongly.

Cool, rinse down with 10–15 ml of H_2O, and evaporate to fumes without boiling. Fume off traces of H_2O, cover, and fume strongly for 1 min. Cool to room temperature and determine the tin. It is not usually necessary to distil the tin.

Calculations: ppm $CySnO_2H$ = 2.0 × ppm Sn; ppm Cy_2SnO = 2.5 × ppm Sn; ppm Cy_3SnOH = 3.25 × ppm Sn; ppm SnO_2 = 1.3 × ppm Sn.

Total Organic Tin. Weigh 60 to 120 g of macerated fruit into a 1000-ml glass stoppered flask. Add 240 ml of concentrated HCl and mix. Add 360 ml of $CHCl_3$. Stopper and shake manually for about 0.5 min. Place in a water bath maintained at 45 to 50°C with the stopper loosened. Leave in the bath 45 to 60 min, shaking about a minute at 10- to 15-min intervals.

Centrifuge and decant the liquid layers into a 500-ml separatory funnel. After separation of the phases, remove the $CHCl_3$ layer. Measure the volume of recovered $CHCl_3$ into a beaker (A ml). Allow to evaporate at room temperature to or near dryness. (Sample weight × A/360 is the actual weight of sample used in final tin determination.)

Add 10 ml of HNO_3 and 15 ml of H_2SO_4. Cover with a flat watch-glass and heat on the hot plate (low heat) so that HNO_3 condenses and washes down the walls. Remove the watch-glass and take to fumes of SO_3. Complete the oxidation with a further amount of HNO_3 and 10 to 30 drops of $HClO_4$. When colorless and free of H_2O and $HClO_4$, cover and heat at high heat to reflux H_2SO_4 on the beaker walls. Cool, rinse down with 15 ml of H_2O, and evaporate below boiling to fumes. Heat to drive off H_2O, cover, and fume strongly. The solution should be clear and water-white.

Add 30 ml of H_2O, mix, and cool in an ice bath to below room temperature. Transfer the solution as completely as possible to a 250-ml separatory funnel, leaving the glass beads in the flask. Rinse down the walls of the beaker with 15 ml of KI (20% w/v) and swirl. Transfer to the separatory funnel and swirl to mix.

Rinse the flask and beads with 50 ml of *n*-hexane and transfer to the separatory funnel. Stopper and shake vigorously for 1.5 min. Allow to stand until separated and draw off the

aqueous solution to the digestion flask. Transfer the hexane to a clean 200-ml tall form beaker. Rinse the funnel with 5 ml of hexane.

Combine the hexane washing with the first extract in the beaker and add 5 ml of HNO_3. Set the beaker in the hood and allow the hexane to evaporate (without heating) in a good draft.

Add 4 ml of H_2SO_4 to the HNO_3 in the beaker. Cover with a flat watch-glass and warm on the hot plate until the HNO_3 condenses on the watch-glass. Remove the cover and evaporate to fumes. Cool somewhat, add a few milliliters of HNO_3, and five to six drops of $HClO_4$. Heat to fumes, driving off all H_2O. Cover and fume strongly on the hot plate. Then remove and cool.

Wash down the beaker walls with about 10 ml of H_2O and add three drops of $HClO_4$. Evaporate below boiling to fumes, fume off H_2O, and cover the fume strongly for a minute or two. Remove from heat and cool. Determine tin content of extract.

Although most of the results on total organic tin in the apple and pear samples were determined as detailed above, later work has been done by a somewhat more direct modification.

After the hexane extraction of SnI_4, take the following steps. Transfer the hexane extract to a second 125-ml separatory funnel by pouring from the neck. Rinse the first funnel with 5 ml of hexane and combine. Add to the second funnel exactly (pipet) 20 ml of a solution containing 0.2 mg of Sn and 150 ml of concentrated H_2SO_4 in each liter. Stopper, extract for 1 min, and allow to separate for 5 min. Transfer the aqueous layer directly into a 50-ml volumetric flask. Rinse down the funnel twice with 5-ml portions of distilled water. Transfer the washings successively into the volumetric flask. Allow the volumetric flask containing the Sn to stand overnight before developing and measuring the color.

Results of recovery studies to verify the methods are given in Table I. Known amounts of listed tin compounds in solution were added to weighed subsamples of the substrate immediately before the analysis was started.

$$\text{Residue found (corrected)} = \frac{\text{ppm found}}{\%\ \text{recovery}} \times 100$$

It is apparent that the total tin method works well for all of the compounds tested. Although the recovery of $CySnO_2H$ is somewhat lower than recovery of the other derivatives, this is not very important in the total organotin recovery because of the relatively lower content of the Cy_3SnO_2H (Table II). Inorganic tin does not interfere with the determination of organotin.

In Table II, recovery factors were used in calculating the values of specific tin compounds found. In the tables following, no recovery factors are used because of the nearly quantitative recovery demonstrated for the organic tin method.

Table I. Recovery of Known Amounts of Tin Compounds Added to Apples and Pears

Compound	Added ppm range	No. of runs	Avg % recovered[a]	Method
Cy_3SnOH	0.2–5	8	99 ± 11	Total tin
Cy_2SnO	0.2–5	19	99 ± 13	Total tin
$CySnO_2H$	0.3–3	6	100 ± 14	Total tin
Cy_2SnO + $CySnO_2H$ (1:1)	0.4–8	16	98 ± 9	Total tin
Tin[b]	0.04–4	26	93 ± 20	Total tin
Cy_3SnOH	0.1–5	23	93 ± 12	Total organotin
Cy_2SnO	0.1–10	13	90 ± 14	Total organotin
$CySnO_2H$	0.1–9	23	78 ± 12	Total organotin
Sn	1–4	12	1[c]	Total organotin
Cy_3SnOH	0.01–3.2	11	93 ± 22	Specific[d]
Cy_2SnO	0.05–1.2	7	85 ± 35	Specific[e]
$CySnO_2H$	0.3–0.7	6	77 ± 33	Specific[f]

[a] ± Figures are 95% confidence limits for individual values. [b] Metallic Sn dissolved in HCl added. [c] Maximum % of inorganic tin found in the total organic tin procedure. [d] Cy_2SnO and $CySnO_2H$ added in some of these analyses were not recovered. [e] Cy_3SnOH and $CySNO_2H$ added in some of these analyses were not recovered. [f] Cy_3SnOH and Cy_2SnO added in some of these analyses were not recovered.

Table II. Residues of Tin Compounds in and on Apples Harvested at Intervals after Applications of Plictran 50W

Oz Plictran 50W per 100 gal	Days application to harvest	Residue found, ppm of compound[a] 0	8	16	32
	Cumulative rainfall, in.	0.05	0.07	2.24	2.36
4	Surface				
	Cy_3SnOH	0.61	0.66	0.25	0.17
	Cy_2SnO	0.02	0.04	0.01	0.03
	$CySnO_2H$	0.02	0.03	<0.02	<0.02
	SnO_2	0.02	0.03	0.04	0.05
	Interior total SnO_2	0.03	0.06	0.06	0.08
	Total	0.69	0.82	0.36	0.32
	% Reduction	...	0	56	61
8	Surface				
	Cy_3SnOH	1.9	1.5	0.92	0.71
	Cy_2SnO	0.10	0.10	0.08	0.07
	$CySnO_2H$	<0.02	0.06	0.05	0.07
	SnO_2	0.01	0.05	0.08	0.12
	Interior total SnO_2	0.06	0.14	0.14	0.14
	Total	2.0	1.9	1.3	1.1
	% Reduction	0	5	35	45
Control	Surface				
	Cy_3SnOH	0.02	0.02	0.01	0.01
	Cy_2SnO	<0.01	0.01	<0.01	0.01
	$CySnO_2H$	0.01	0.02	0.01	0.03
	SnO_2	0.01	0.01	0.01	...
	Interior total SnO_2	0.01	0.02	0.02	0.02
	Total	0.06	0.07	0.06	...

[a] $\frac{[\text{Residue (treated)} - \text{Residue (control)}] \times 100}{\text{Avg \% recovery}}$ = residue found Avg % recovery (Table I). Cy_3SnOH, 93; Cy_2SnO, 85; $CySnO_2H$, 77; SnO_2, 93.

FIELD EXPERIMENTS AND RESULTS

A preliminary experiment was conducted to determine the relative amounts of Cy_3SnOH, Cy_2SnO, and $CySnO_2H$ on apples harvested at intervals after being sprayed in the field with the miticide. Mature Delicious apples were treated on September 30, 1966, with Plictran 50W, a wettable powder formulation containing 50% of Cy_3SnOH, spraying to runoff with 4 and 8 oz of formulation per 100 gal by means of a high pressure hand gun. Apples were collected randomly from the trees the day of spraying, 8, 16, and 32 days after spraying. Untreated control apples were also collected.

The apples were analyzed by the method for determining individual tin compounds. The data (Table II) show that there was a decrease of residue with time. The residue remaining was primarily Cy_3SnOH, with relatively small amounts of the degradation products appearing as residues. Apparently some of the loss of residue was caused by rain, which fell during the experimental period. Nearly all of the tin was confined to the surface. Because the organotin residue on fruit was nearly all Cy_3SnOH, in subsequent experiments total organotin was determined, and all calculated as Cy_3SnOH.

Table III. Details of Experimental Application of Plictran 50W to Apples and Pears

Experiment No.	Year	Location	Variety	Soil type	Treatment dates 1	2	3	4	5	Reps	Oz Plictran 50W[a] per 100 gal
Apples											
1	1965	Midland, Mich.	Golden Delicious	Sandy loam	7/7	8/18	9/14			1	8[a]
2	1968	Saginaw, Mich.	Red Delicious and Northern Spy	Sandy loam	5/20	6/3	9/25	10/30[b]		2	6[a]
3	1968	Joy, N.Y.	Wealthy		5/27	6/10	7/1	9/3[b]		2	6[a]
4	1968	Puyallup, Wash.	Golden Delicious	Sandy loam	5/15	6/11	7/1	10/10[b]		2	6[a]
5	1968	Winchester, Va.	Red Delicious	Clay loam	5/13	6/7	7/16	9/16[b]		4	6[a]
6	1967	Watsonville, Calif.	Red Delicious	Adobe	4/13	5/2	5/25	7/27	9/7	4	6[a]
Pears											
7	1968	Midland, Mich.	Bartlett	Sandy loam	5/17	5/31	9/4[b]			4	6[a]
8	1967	Midland, Mich.	Bartlett	Sandy loam	8/3	8/17				4	6[a]
					8/13	8/17	8/31				6[a]
					8/17	8/31	9/15				6[a]
					8/17						6[a]
					8/31						6[a]
					9/15						6[a]
9	1967	Marysville, Calif.		Sandy						4	6[b,a]
10	1966	Courtland, Calif.	Bartlett	Columbia	4/12					3	4[b]
					4/12						6[b]
					4/12						8[b]
11	1968	Davis, Calif.	Bartlett	Sandy	4/10	5/9	7/31[b]			3–4	6[b,a]
12	1968	Marysville, Calif.	Bartlett	Sandy	4/11	5/9	7/30[b]			4	6[b,a]

[a] Plictran 50W contains 50% Cy_3SnOH. Method of application: a. Hand spray gun; b. Air blast sprayer. [b] Variable last spray date to give various intervals from last application to harvest. Last spray and harvest date given.

Experiments were set up on both apples and pears, covering the major areas of the United States where these are important crops. Table III shows the experimental conditions under which they were carried out.

In many of the tests the last application was timed on different plots so that all samples could be taken on the same day, with different intervals between last application and harvest. Most applications were made by hand gun, and all were made to run-off. The experiments were conducted with four replicates in most cases. Samples consisted of 30 fruit picked randomly from the plots. They were placed in polyethylene bags and shipped to Midland, Michigan, where they were prepared for analysis, either in a meat grinder or salad shredder. Stainless steel grinders were used, after thoroughly cleaning with HCl. Care was taken in sampling and grinding of samples to avoid contamination by tin or tin compounds. Polyethylene bags were used, too, because tin compounds are used as stabilizer in some other types.

In most of the work the entire sample of fruit was macerated and well mixed, and subsamples were stored in plastic bags in the freezer. Prepared samples were shipped frozen to Rahway, New Jersey, where they were held frozen until analyzed.

The experiment, in which the cyclohexyltin derivatives were determined separately (Table II), demonstrates the formation of Cy_2SnO, $CySnO_2H$, and inorganic tin (expressed as SnO_2) from the Cy_3SnOH applied. In this experiment where the apples were fully developed at time of application, large decreases of residue are apparently due to rainfall.

Experiment 1 (Table IV) consisted of a single sample from each treatment, all of which were peeled and cored before analysis for total tin content. Essentially all of the residue was found on the peel.

In an experiment from both the apples and pears (Table IV) some of the fruits from two of the four replicates were prepared for analysis without washing, and some were washed before preparation. In addition, some of the unwashed fruits were peeled, and the peeling and peeled fruit were prepared and analyzed as separate samples. The washing was done in cold water without detergent, with gentle brushing. When the fruit was peeled by hand no effort was made to prevent transfer of residues by handling from the peel to the peeled fruit.

The data (Table IV) show that after application of Plictran 50W miticide, there is a nearly steady-state inorganic tin residue of 0.1 to 0.2 ppm, which is relatively independent of total number of applications, in excess of one, and independent of time between last application and harvest, within 1 month of last application. The average level of inorganic tin on apples and pears from multiple applications is 0.1 ppm, equivalent to 0.3 ppm when calculated as Cy_3SnOH. An inorganic tin residue as high as 0.3 ppm, equivalent to 1.0 ppm of Cy_3SnOH, was found on pears.

The location of the residue existing predominantly, if not entirely, on the surface of apples and pears is demonstrated by the experiments in which peel and pulp were analyzed separately. The small amount of residue found inside of the fruit could have resulted from transfer from the skin during peeling.

Some of the residue of organotin was removed from both applies and pears by mild washing, up to 50% on pears (Table IV). Presumably a more rigorous washing would have removed more of the residue. This also points out the nonsystemic nature of the residue. Washing some of the residue from the fruit by rain probably accounts for some of the decrease of residue after application and before harvest. Some of the decrease in residue after application can also be accounted for by dilution caused by increased weight of the fruit.

The conclusions of Trombetti and Maini that residue levels on pears are higher than on apples is not supported here. In

Table IV. Residues of Tin in or on Apples and Pears from Applications of Plictran Miticide

Expt. no.	Location	Application data: Times sprayed	Oz Cy_3Sn-OH per 100 gal	Days last spray to harvest	Range of residues found, ppm[a]: Unwashed fruit: Whole fruit: Inorg Sn	Whole fruit: Org Sn	Peel, total Sn	Pulp, total Sn	Cores, total Sn	Washed fruit whole fruit, total Sn
1A	Michigan	1	4	17			5.9	0.1	<0.1	
		3	4	17			16	0.1	0.1	
2A	Michigan	4	3	0	0.1	0.9–1.5				
				14	0.1	1.1–1.2				
				28	<0.1–0.1	0.3–0.7				
3A	New York	4	3	0	0.1–0.2	1.2–2.0				
				14	0.1–0.2	1.5–1.6				
				28	<0.1–0.1	0.8–1.2				
4A	Washington	4	3	0	0.1	1.6–1.9				
				14	0.1–0.2	1.3				
				28	0.1	0.8–1.1				
5A	Virginia	4	3	0	0.1	1.1–1.5	7–8	0.1		1.1–1.4
				7	0.1–0.2	1.0–1.2				
				14	0.1	0.7–1.0	5–6	0.1		0.8–0.9
				21	0.1	0.4–0.7				
				28	<0.1–0.1	0.5–1.0	4–5	<0.1		0.7
				35	0.1	0.6–0.7				
6A	California	5	3	0	0.5–0.6[b]					
7P	Michigan	3	3	0	<0.1	1.3–1.6	5–7[c]	0.3[c]		0.6–0.7[c]
				7	<0.1	0.6	4[c]	0.2[c]		0.5[c]
				28	0.2	0.2	0.5–0.6[c]	<0.1[c]		0.1[c]
8P	Michigan	1	3	0	<0.1	0.3–0.7				
				15	0.1	0.4–0.6				
				29	0.1	<0.1–0.2				
		2	3	29	0.1	0.1				
		3	3	0	0.1–0.2	0.5–1.4				
				15	0.2	0.4–0.5				
9P	California	3	3	0	0.1	0.8–0.9				
				7	0.1–0.2	0.6–1.0				
				14	0.1–0.2	0.7–0.8				
				21	0.1–0.3	0.4–1.2				
				28	<0.1–0.1	0.2–0.3				
				42	<0.1–0.2	0.2–0.3				
				61	<0.1–0.1	0.2–0.3				
10P	California	1	2	85	<0.1	<0.1				
		1	4	85	<0.1	<0.1				
		1	8	85	<0.1	<0.1				
11P	California	3	3	0	0.1–0.2	0.9–1.4				
				28	0.1–0.2	0.4–0.6				
12P	California	3	1	0	0.1	0.9–1.4				
				28	0.1	0.5–0.7				

A = apples; P = pears.

[a] Organic and total tin calculated as Cy_3SnOH. [b] Total tin determined only, reported as inorganic tin. [c] Organic tin calculated as Cy_3SnOH.

this work there was as much difference between experiments on the same fruit as there was between apples and pears. The half-value level of organotin generally falls between 3 and 5 weeks, although in the New York and Virginia experiments on apples it is somewhat longer. Differences of residue level on the day of last application and of rate of loss of residue are probably due to differences of application and environmental conditions, rather than to variety or species differences.

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