Fate of Kelthane Residues on Apple Pomace Exposed to Drying in the Dark, Sunlight and Ultraviolet Light Irradiation

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Apple pomace (stems, cores, seeds and peelings) is that byproduct which remains after preparation of apple juice and sauce for human consumption from whole apples. The nutritive value of apple waste for livestock has been reported by several researchers (4, 6, 7).

The problems of pesticide accumulation in adipose tissue of beef cattle fed contaminated apple processing wastes and investigations for the alleviation of these problems has been published (5, 8, 9).

Kelthane (dicofol; 1,1-bis-(p-chloropehny1)-2,2,2-trichloro-ethanol) has been used on apples in California for the control of the European Red Mite, Two Spotted Mite, McDaniel Mite and Brown Mite. The possibility exists that Kelthane residues are present on apples at the time of harvest and would be found in the pomace by-product of the processed apples. Decontamination procedures for removing Kelthane contaminants from whole apples have been reported (1).

The present investigations were undertaken to determine the fate of Kelthane residues intentionally applied to apples under controlled laboratory conditions and the reduction of these residues in the pomace by exposure to drying in the dark, in sunlight and ultraviolet light irradiation.

Materials and Methods

Apple Sample and Pesticide Application. Red Delicious apples which had not been treated with Kelthane were purchased from Placerville, California in October. One hundred-twenty apples were sprayed with one liter of acetone containing 1.6 of Kelthane by using a Hudson hand sprayer. After air drying for approximately five minutes, the sprayed apples were stored at 4C in 1 gal. glass pickle jars containing 6 apples per jar. These apples served as starting materials for the research investigators.

To obtain the pomace, the contaminated apples were cut into quarters and placed in a laboratory scale pulper-finisher equipped with a 1.52 mm screen (Food Processing Equipment Co., Kalamazoo, Michigan, Model #LP100). The pomace was separated from the pulp

Levels of Kelthane and 4,4'-Dichlorobenzophenone on Apples after Air Drying in the Dark; Drying by Ultraviolet Light; Drying by Sunlight

co 29C)		Total	Kelthane (PPM)	713.4	520.0	472.2	454.3	438.7	368.7
Lot III rying (16 t	4,4'-D	as	Water Kelthane Kelthane (%) (PPM)	10.9	15.0	18.5	12.3	7.7	9.2
Lo Light Dry	,		Kelthane (PPM)	702.5	505.0	453.7	442.0	431.0	359.5
9C) Sur			Water (%)	73	41	24	12	12	12
Lot II Lot III Ultraviolet Light Drying $(35 \text{ to } 39\text{C})$ Sunlight Drying $(16 \text{ to } 29\text{C})$		Total	Kelthane (PPM)	713.4	742.6	463.8	367.2	302.5	194.1
Lot II ght Drying	4,4'-D	as	(PPM) (%) (PPM) (PPM) (PPM)	10.9	28.6	6.2	2.0	2.2	2.7
riolet Li			Kelthane (PPM)	702.5	714.0	457.6	365.2	300.0	191.4
Ultra			Water (%)	73	33	24	12	12	12
		Total	Kelthane (PPM)	713.4	508.6	419.3	362.7	354.0	384.9
to 26C)	4,4'-D	as	Kelthane (PPM)	10.9	4.0	1.3	1.3	1.0	6.0
Lot I Dark Drying (23 to 26C)			Time Water Kelthane (Day) (%) (PPM)	702.5	504.6	418.0	361.4	353.0	384.0
Dark I			Time Water (Day) (%)	73	65	48	28	16	15
			Time (Day)	0	7	7	7	6	14

 $^{^{\}rm a}$ All ppm data presented on a dry weight basis.

 $^{^{}b} \mathrm{Ultraviolet}$ light exposure (2537Å) at approximately 1.1x10 $^{4} \mathrm{ergs/cm.}^{2}$

^CSunlight exposure to nondefined type ultraviolet light at approximately >5x10⁴ergs/cm².

containing the juice. Each apple weighed approximately 212 g and contained 8% pomace resulting in 928 g of pomace from 54 apples. The pomace was divided into 3 equal amounts and transferred to 3 aluminum foil-lined containers of such size that the pomace could be spread in a 1-cm layer for drying which decreased in thickness as drying occurred. The plant material was mixed twice daily and sampled as shown in the schedule of Table I. Lot I was dried in the dark, Lot II was dried under ultraviolet light and Lot III was dried in the sunlight. After the initial drying period, the samples were cross transferred to the other light treatments (Table II), with the exception of no further dark drying, for sampling periods of 3, 6 and 9 days. Specific details for the various drying treatments were previously described for alfalfa hay (3).

Plant Extraction and Cleanup. All plant samples (10 g/150 ml benzene) were extracted by three ½-hr. refluxes with benzene; the solvent was pooled, concentrated, and analyzed (2). The solvent extracts were cleaned-up on Florisil (activated at 270 C for 3 hr.). Kelthane and 4,4'-dichlorobenzophenone (4,4'-D) were eluted from the Florisil with 390 ml of 30% diethyl ether and 70% pentane and recoveries were in excess of 90% as checked by standards and fortified samples through the analytical procedures.

Gas-Liquid Chromatography (GLC) and Thin-Layer Chromatography (TLC). These procedures were employed routinely, either separately or in combination (2). All chemicals used in these studies were reagent grade. The pesticides were analytical standards; the reagent grade solvents were redistilled shortly before use. The data reported are on a dry weight basis.

Results and Discussion

Table I shows the decline of Kelthane residues on the apples from zero to 14 days drying treatment during dark (Lot I), uItraviolet light (Lot II) and sunlight (Lot III) exposure. Maximal loss of residue (Lot I, approximately 46%) occurred between 7 and 14 days after application.

Upon 9 days exposure of Lot I to sunlight (Table II) there was an additional loss of total Kelthane residues equivalent to approximately 42% after the initial 14 day exposure.

Upon exposure of Lot I to ultraviolet light (Table II) an additional loss of total Kelthane residues occurred equivalent to approximately 46% after the initial 14 day exposure.

Traces of 4,4'-D were detected in all of the above samples and the total Kelthane residue losses included in the 14 day exposure plus the additional 9 day treatment of either sunlight or ultraviolet light was approximately 70%.

Maximal loss of residue (Lot II, approximately 73%) occurred

Levels of Kelthane and 4,4'-Dichlorobenzophenone on Apples Lots I,II,III as shown TABLE II

1. 10. 1.01 1.01	+ 0+ 0-	1	in Table I and Subsequently Exposed to Ultraviolet Light and Sunlight.	I and Sub	sequen	tly Expos	ed to Ult	raviolet	Light a	nd Sunlig	Sunlight.	11
Dark to Sunlight (16 to 35C)	to Sunlight to 35C)	·· ht			III	traviolet (16 t	Ultraviolet to Sunlight (16 to 35C)	ight	Sunl	ight to (32	Sunlight to Ultraviolet Light (32 to 40C)	et Light
4,4'-D		4,4'-D					4,4'-D				4,4'-D	
as	as	as	Ĭ	Total			as	Total			as	total
Time Water Kelthane Kelthane Kelthane Kelthane Kelthane (Day) (%) (PPM) (PPM) (PPM) (PPM) (PPM)	Kelthane Kelthane Kel (PPM) (PPM) (Kelthane Kel (PPM) (Kel	(PPM)	Water (%)	Kelthane (PPM)	Kelthane (PPM)		Water (%)	Kelthane (PPM)	Water Kelthane Kelthane (%) (PPM) (PPM)	Kelthane (PPM)
14+3 13 242.0 12.5 25	12.5		25	254.5	12	251.9	2.0	253.9	13	375.1	13.4	388.5
14+6 13 308.0 3.6 31	3.6		31	311.6	12	251.9	1,8	253.7	13	380.6	2.8	383.4
13 220.0 1.8 221	1.8		221	221.8	12	297.0	2.0	299.0	13	319.0	1.4	320.4
Lot I to Lot II	Lot I to Lot II	Lot II										
Dark to Ultraviolet Light (32 to 40C)	o Ultraviolet Light (32 to 40C)	olet Light OC)	. 1									
14+3 12 380.6 1.8 382.4	1.8		382	4.								
14+6 12 270.6 0.46 27	97.0		27.	271.1								
14+9 12 209.6 0.24 209.8	0.24		209	8.								

all ppm data presented on a dry weight basis.

 $^{\rm O}$ Ultraviolet light exposure (2537A) at approximately 1.1X10 ergs/cm.

 $^{\text{C}}$ Sunlight exposure to nondefined type ultraviolet light at approximately $5\text{X}10^{\text{+}}$ ergs/cm. $^{\text{2}}$

14 days after application. Upon exposure of Lot II to sunlight (Table II) no significant additional loss occurred. Traces of 4,4'-D were found in all samples.

Maximal loss of residue (Lot III, approximately 47%) occurred 14 days after application. Upon exposure of Lot III to ultraviolet light (Table II) an additional loss of total Kelthane residues occurred equivalent to approximately 13% after the initial 14 day exposure. Traces of 4,4'-D were found in all samples.

The possibility of the presence of other decomposition products exists. However, due to the relative short treatment and the type of "solvent" present (wax-like materials of the plant cuticle) amounts of these products would be small and undetectable. The loss of Kelthane residues during apple pomace drying is mainly due to volatility rather than photodecomposition.

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