

Residue Studies for (2,4,5-Trichlorophenoxy)acetic Acid and 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in Grass and Rice

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Grass in Texas was treated at an artificially high rate to give 12 lb/acre (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) which contained 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) as an impurity. Grass samples were analyzed for these compounds to determine their rate of dissipation. Residues decreased rapidly, having a half-life ($t_{1/2}$) of 17.4 days for 2,4,5-T and 5.6 days for TCDD. Rice grain and straw from rice fields in Arkansas, Louisiana, and Texas treated at maximum rates to give 2.25 lb/acre 2,4,5-T were analyzed for possible 2,4,5-T and TCDD residues. Samples of rice straw were analyzed for 2,4,5-T. There were small residues (<12 ppm) of 2,4,5-T in rice straw and no 2,4,5-T or TCDD was detected in rice grain with detection limits of 0.025 ppm and 2-7 ppt (parts per trillion), respectively. No TCDD residues (detection limits 2-10 ppt) were found in 30 samples of rice purchased in retail stores throughout the United States.

The herbicide (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), which may contain a measurable amount of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), can be used to control weeds in rice fields and rangeland in some areas of the United States. Concern has been expressed that TCDD contamination would occur in grass and rice grain from these treated areas. Several studies have shown that the level of herbicide 2,4,5-T, 2,4-D, silvex (Leng, 1972), and TCDD (Isensee and Jones, 1971; Young et al., 1978; Nash and Beall, 1980) rapidly decreases in plants following herbicide application. Isensee and Jones (1971) grew oat and soybean plants in solution or in soil in a microagroe-cosystem treated with ^{14}C -labeled TCDD at rates of 0.06-0.28 ppm (70 000 to about 200 000 times the level expected from a 2,4,5-T treatment at 2 lb/acre). They monitored ^{14}C only and found that TCDD was not continuously taken up by plants in solution but that radioactivity reached a maximum within 24 h followed by rapid decline at a rate to give a half-life between 2 and 4 days. In another experiment where soil was treated they found small quantities of radioactivity in soybean seeds from both control and treated soil. There was no detectable TCDD in oat seeds at maturity. This experiment at abnormally high application rates of TCDD presented optimum uptake conditions so they concluded that "accumulation of TCDD in plants from soil uptake is highly unlikely".

Isensee and Jones also applied TCDD to the first trifoliolate leaf of soybean plants and the first leaf blade of oats and allowed them to grow for another 3 weeks. There was no translocation of TCDD from the treated leaf.

Essentially no uptake of TCDD was found by Young et al. (1978) in an experiment where sorghum was grown in soil containing 14 ppm of [^{14}C]TCDD. They found that the rate of uptake of TCDD was approximately one-millionth of 1% of the TCDD soil level. Young et al. (1978) also found no TCDD in seeds from plants growing in an area where tons of 2,4,5-T-containing herbicides had been applied in tests of spraying equipment.

Dissipation of TCDD residues on grass was reported by Nash and Beall (1980). They applied an emulsifiable formulation of 2-(2,4,5-trichlorophenoxy)propionic acid (silvex) containing either 44 or 7500 ppb of [^3H]TCDD to grass in a microecosystem. They found silvex had a dissipation half-life of 4-5 days while for TCDD it was 3.9-7.1 days. They also reported field studies, but as they were

Table I. Specific Residues of 2,4,5-T and TCDD Found on Grass from Texas Treated with 3 gal/acre Esteron 245 Low Volatile Weed and Brush Killer (12 lb of 2,4,5-T/acre)^a

time after treatment, days	apparent 2,4,5-T found, ppm/lb of 2,4,5-T applied	apparent TCDD found, ppt ^b /lb of 2,4,5-T applied
	Untreated ^c	
	0.4	ND ^d (12) ^e
	0.3	7
	Treated	
0	95	35
	90	19
1	111	42
	104	43 ^f
7	57	11 ^f
	39	
14	39	6
	37	
28	32	3
	23	
64	11	2
	14	
112	0.7	1.3 ^f
	1.0	

^a This represents a treatment rate 6-12 times the normal rate with a product containing about 4 times the present specification limit of 0.1 ppm of TCDD. ^b ppt = parts per trillion. ^c Data are apparent residue and not calculated to specific residues as was done for the treated samples. ^d ND = not detected. ^e Limit of detection. ^f Average of data by batch extraction and Soxhlet extraction.

studying photodechlorination no comparison could be made on the rate of decline of TCDD residues in the microecosystem vs. in field plots.

It seemed desirable to obtain field data on the dissipation of 2,4,5-T and TCDD on grass to compare with the results of the microecosystem and also to confirm whether the absence of TCDD residue in the experiments with oats applies to rice grown in 2,4,5-T-treated fields. In addition a mini-market basket survey was conducted on rice in retail stores.

EXPERIMENTAL SECTION

Grass. Plots of a native grass mixture at the Pitchfork Ranch, Dickens, TX, were treated at the artificially high rate of 3 gal/acre with commercial formulation Esteron (Dow Chemical Co.) 245 Low Volatile Weed and Brush Killer (4 lb acid equiv of 2,4,5-T/gal as the propylene glycol butyl ether esters) when the grass was at the early seed-head stage of maturity. This treatment rate was 6-12

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times higher than normal treatment rates. The TCDD level in this product during the time of application was about half of the 1-ppm specification. This level correlates with residues in grass taken at zero time to 1 day, indicating the TCDD level was about 0.4 ppm in the 2,4,5-T (Table I). Grass was sampled the same day and at 1, 7, 14, 28, 64, and 112 days after application of the herbicide. Samples were immediately frozen in dry ice and shipped to the Midland, MI, laboratory of Dow Chemical U.S.A. where they were maintained frozen at -18°C . They were individually ground in a Hobart cutter on a Wiley mill. Each sample was well mixed and then divided into subsamples which were held frozen in polyethylene bags until analyzed.

Rice. Rice varieties typical of each area were planted in three locations: Beaumont, TX, Baton Rouge, LA, and Stuttgart, AR. Plots were 4×20 or 5×50 ft set up in a randomized block design and replicated 4 times. A commercial amine salt formulation of 2,4,5-T with a TCDD specification of 1 ppm was applied with ground equipment calibrated to give a 15–16 gal/acre spray. The plots were treated twice to simulate maximum use of 2,4,5-T. The first 2,4,5-T application was 0.75 lb/acre, 3–5 weeks after emergence of the rice; the second was 1.5 lb/acre just before panicle initiation, 7–8 weeks after emergence of the rice. The plots were harvested by cutting a 1.5–2-ft swath down the center of the plot. Rice grain and straw were collected from each plot and stored in polyethylene bags. Samples were ground through a Wiley mill with a 2-mm sieve before analysis. The samples were stored in a freezer except for a period of 4 months between the 2,4,5-T analyses and the start of the analyses for TCDD.

Market Basket Survey. Rice was purchased in retail stores by Dow Chemical Co. personnel and sent in the purchased container to Midland, MI. The samples included 14 different brands of rice and at least 15 different types of rice or rice product. They were purchased in 29 different cities across the Continental United States and Hawaii. All samples were ground in a Wiley mill equipped with a 2-mm sieve and stored in plastic bags in a freezer until analyzed. Since the herbicide treatment history, if any, of these samples was not known, two samples of rice were obtained by the Mississippi Rice Growers Association from fields that were treated with 2,4,5-T at the beginning of the growing season.

Analytical. Rice Grain and Straw: 2,4,5-T. Samples were analyzed by a modification of the method of Jensen and Glas (1980). The samples were extracted and hydrolyzed with 0.5 N aqueous sodium hydroxide at 80°C for 1 h, and the solids were separated by centrifugation, yielding a clear liquid extract. A 10-mL portion of the extract was acidified with sulfuric acid and saturated with sodium chloride, and the 2,4,5-T was extracted into ether. One milliliter of isooctane was added and the ether extract was concentrated to a volume of 1 mL. The methyl ester was prepared by using diazomethane and the ester cleaned up by shaking with 0.05 N NaOH for 15 s. The amount of 2,4,5-T in this solution was then determined by gas chromatography on an OV-3 column using electron capture detection. The recovery of 2,4,5-T added to rice grain over the range 0.025–0.5 ppm was 74% with a relative standard deviation of 14%. The average recovery from rice straw was 96% with a standard deviation of 17%.

Grass: 2,4,5-T. The samples were analyzed by the method of Jensen and Glas (1980) with the addition of a permanganate cleanup step prior to extraction of 2,4,5-T into ether. A 10-mL portion of the acidified alkaline extract was treated with 0.5 mL of saturated aqueous

tassium permanganate solution and allowed to stand for 5 min. The purple color was destroyed by dropwise addition of 5 M aqueous sodium bisulfite solution. The solution was then extracted with ether. The recovery of 2,4,5-T added over the range 1–1000 ppm averaged 87% with a standard deviation of 3%.

TCDD Determination. Caution: Analysis for the presence of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) requires the use of standard solutions. Since this compound is very toxic such preparation of standards should be carried out so that there is no contact with the compound and concentrated solutions of TCDD and that there is no contamination of the laboratory.

Rice: TCDD. Rice grain samples were further ground to a very fine powder in a blender at the time of analysis. The ground samples were extracted with hexane for 4 h in a Soxhlet apparatus, and the extracts evaporated, saponified, and cleaned up as described in the procedure for grain (Hummel, 1977). Since no rice grain was available with a TCDD residue, Soxhlet extraction was chosen because it is the more rigorous of the extraction procedures for DDT recommended by the Association of Official Agricultural Chemists (1965). It is assumed that effective extraction procedures for DDT will be equally efficient for TCDD, and it is further assumed that an extraction time that extracts essentially all of the oil from the ground rice will have extracted all of the TCDD if any is present. The concentrated extracts were examined for the presence of TCDD by gas chromatography–low-resolution mass spectrometry (GC–MS) as described by Shadoff and Hummel (1978). Since GC–low-resolution MS gave apparent positive results on a control and some treated sample extracts analyzed on the same day (Table II), they were reexamined by the more specific GC–high-resolution MS as described by Shadoff and Hummel (1978). Recovery of TCDD from rice grain fortified over the range 10–100 ppt averaged 79% with a standard deviation of 18% (Hummel, 1977).

Grass: TCDD. The grass samples were extracted with hexane and the hexane extracts cleaned up by the procedure reported by Hummel (1977). Two-gram samples of grass were used for the 0- and 1-day intervals, 5-g samples for the 1-, 2-, and 4-week intervals, and 10-g samples for the 8- and 16-week intervals after treatment. Batch extraction was carried out by boiling the grass with hexane for 15 min, decanting the hexane from the grass and repeating for a total of three extractions. A total of 50 mL of hexane was used for the 2-g samples and a total of 100 mL of hexane was used to extract the 5- and 10-g samples. Soxhlet extraction was carried out by placing the grass sample in a 25×80 mm cellulose extraction thimble and extracting 4 h by using 100 mL of hexane. After cleanup by the procedure described by Hummel (1977) the concentrated extract was analyzed for TCDD by GC–low-resolution MS, monitoring at *m/e* 320 and 322. Recovery of TCDD added to grass over the range 11–200 ppt (parts per trillion) averaged 97%.

Data Handling: Grass. These dissipation data for 2,4,5-T and TCDD were evaluated by using a one-compartment linear model or a two-compartment model based on the following assumptions:

$$V_1 = V_2 \quad (1)$$

$$\frac{dC_1}{dt} = -k_{10}C_1 - k_{12}C_1 + k_{21}C_2 \quad (2)$$

$$\frac{dC_2}{dt} = k_{12}C_1 - k_{21}C_2 \quad (3)$$

$$CT = C_1 + C_2 \quad (4)$$

Table II. Examination of Rice Straw and Rough Grain from Treated Fields for the Presence of 2,4,5-T and TCDD

source ^f	sample type		apparent 2,4,5-T found, ppm		apparent TCDD found, ppt ^{a,b}		
			gross	corrected ^c	low resolution		high resolution
					gross	corrected ^c	
1	rough grain	control	0.08, 0.01				
		treated ^d	0.01, 0.01, 0.01, 0.01	ND ^e	4 (1) ^{f,g}	ND	ND (4)
1	straw	control	0.00, 1.8				
		treated ^d	2.0	1.1			
			4.1	3.2			
			3.0	2.1			
2	rough grain	control	0.06, 0.00				
		treated ^d	0.02, 0.02, 0.01, 0.02	ND	4 (1) ^{f,g}	ND	ND (7)
2	straw	control	0.0				
		treated ^d	10.1	10.1			
			3.8	3.8			
			7.8	7.8			
3	rough grain	control	0.01, 0.01, 0.00		5 (1) ^{f,g}		ND (7)
		treated ^d	0.01, 0.01, 0.02, 0.02	ND	5 (1) ^{f,g}	ND	ND (4)
3	straw	control	0.55, 1.1				
		treated	13.4	12.6			
			3.8	3.0			
			3.5	2.7			
			2.0	1.2			
4	rough grain	control			ND (4)		
4	rough grain	control			ND (7)		ND (4)
5	rough grain	treated ^h			4 (1)	ND	ND (3), ND (4)
6	rough grain	treated ⁱ			ND (6)	ND	

^a ppt = parts per trillion. ^b The sample analyzed was a composite of equal amounts from the four replicate plot samples taken in each experiment (except Moreland and Robertson, MS). ^c Corrected for apparent residue in control samples. ^d Treated at a rate to give 0.75 lb/acre 2,4,5-T about 30 days after plant emergence and a second treatment to give 1.5 lb/acre 2,4,5-T about 50 days after emergence. ^e ND = not detected. ^f Limit of detection is in parentheses, ppt, which is 2.5 times the recorder noise level. ^g These samples were run when the GC-MS sensitivity was greater than the level usually attained. ^h Field treated with a 2,4,5-T formulation at label rates in year of sampling and for 10 consecutive prior years. ⁱ Field treated at label rates with inverted 2,4,5-T formulated in year of sampling. ^j Source of samples. 1, USDA Rice Branch Experiment Station, Stuttgart, AR; 2, Louisiana State University, Baton Rouge, LA; 3, Agricultural Research and Extension Center, Texas A&M University, Beaumont, TX; 4, University of Arkansas, Stuttgart, AR; 5, Moreland, MS; 6, Robertson, MS.

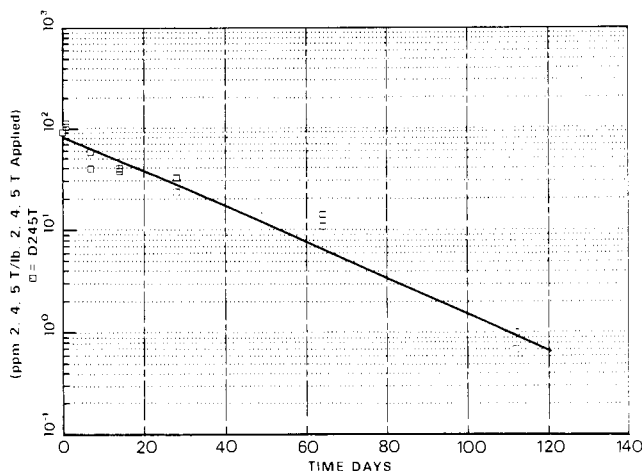


Figure 1. Dissipation of 2,4,5-T from treated grass.

where V_1 and V_2 are the volumes of the two compartments, C is the concentration in each compartment, k_{10} is the rate constant for the loss from compartment 1 which is not going to compartment 2, k_{12} is the rate constant for loss from compartment 1 to compartment 2, and k_{21} is the rate constant for loss from compartment 2 to compartment 1. The dissipation data were analyzed by using advanced continuous simulation language (ACSL) programming (Mitchell and Gauthin Associates, Inc., 1975). These calculations yielded computer-generated curves for dissipation of 2,4,5-T (Figure 1) and for TCDD (Figure 2). Estimates of the half-life ($t_{1/2}$) were also obtained. These calculated data were compared to the experimental data by using a weighted least-squares program, and the best parameters were determined by using the method de-

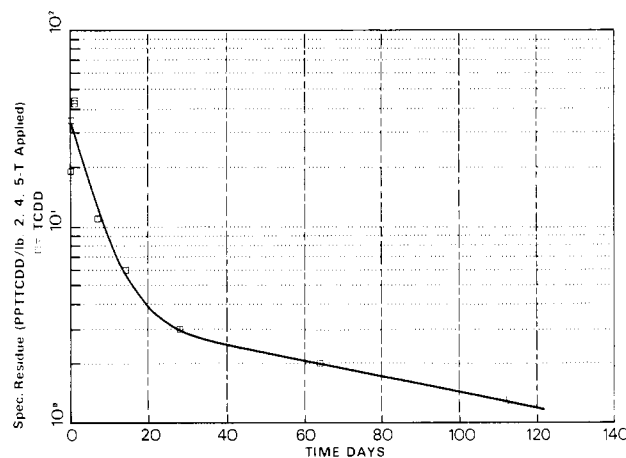


Figure 2. Dissipation of TCDD from treated grass.

scribed by Lasdon et al. (1978).

RESULTS AND DISCUSSION

Grass: 2,4,5-T. An alkaline extraction step was reported to be needed for extraction of herbicide acids from grass (Chow et al., 1971). Therefore, this extraction step was included in the analysis of grass samples for 2,4,5-T to ensure that all forms of 2,4,5-T would be determined. The 2,4,5-T residues on grass at various times after spraying have been normalized by dividing them by the 2,4,5-T application rate (Table I). These specific residues can be used to estimate the residues that would occur from any specified 2,4,5-T treatment rate.

A single-compartment model adequately described the dissipation data for 2,4,5-T. Residues of 2,4,5-T declined rapidly (Figure 1), having a half-life ($t_{1/2}$) of 17.4 days.

Table III. Examination of Rice Grain Purchased in Retail Stores throughout the United States for the Presence of TCDD

sample no.	description	location	TCDD, ppt ^a	limit of detection ^b
1	natural brown long grain	Palatine, IL	ND ^c	2
2	natural brown long grain	Arlington Heights, IL	ND	6
3	natural brown long grain	Aurora, CO	ND	9
4	enriched plump tender grain	Memphis, TN	ND	6
5	enriched extra long grain	Brinkley, AR	ND	2
6	enriched extra long grain	Wickliffe, OH	ND	4
7	enriched extra long grain	Fayetteville, AR	ND	10
8	enriched extra long grain	Indianapolis, IN	ND	10
9	enriched plump tender grain	Williamsville, NY	ND	5
10	converted rice	Montrale, NJ	ND	4
11	converted rice	St. Louis, MO	ND	10
12	converted rice	Natick, MS	ND	10
13	converted rice	Memphis, TN	ND	8
14	converted rice	Minneapolis, MN	ND	6
15	converted rice	Houston, TX	ND	7
16	enriched rice	Houston, TX	ND	2
17	enriched precooked	Forrest City, AR	ND	6
18	enriched long grain	Walnut Creek, CA	ND	10
19	rice	Donham Springs, LA	ND	3
20	rice	Lubbock, TX	ND	5
21	long grain	San Antonio, TX	ND	2
22	natural brown long grain	Cincinnati, OH	ND	8
23	long grain white rice	Honolulu, HI	ND	4
24	enriched long grain	El Centro, CA	ND	6
25	enriched extra long grain	Stamford, CT	ND	3
26	enriched extra long grain	Flushing, NY	ND	7
27	enriched long grain	Kingston, NH	ND	5
28	long grain	Moorhead, MN	ND	7
29	long grain	Overland Park, KS	ND	4
30	long grain	Charlotte, NC	ND	9

^a ppt = parts per trillion. ^b Limit of detection, ppt, is 2.5 times the recorder noise level. ^c ND = not detected.

This half-life obtained under field conditions compares favorably with the 5-day half-life found for silvex sprayed on bluegrass turf in a microecosystem (Nash and Beall, 1980) and the value of 14 days in field experiments for all phenoxy herbicides applied to grass (Leng, 1972).

Rice: 2,4,5-T. Alkaline hydrolysis was used in the analytical procedure for rice grain and for straw because of concerns for missing conjugated forms of 2,4,5-T. It was later discovered that simple alkaline extraction would have given the same results (Jensen and Glas, 1980). There was no detectable 2,4,5-T (with a detection limit of 0.025 ppm) in rice grain from fields treated to maximize the potential for residues (Table II). There were small amounts of 2,4,5-T (≈ 10 ppm) in rice straw (Table II).

Grass: TCDD. The specific TCDD residues [residue(s) found per 2,4,5-T application rate] are given in Table II.

The two-compartment model was necessary to explain these TCDD data. The dissipation curve (Figure 2) shows that during the first few weeks following application of herbicide there was rapid loss of TCDD, giving a $t_{1/2}$ of 5.6 days. This rate of loss was about twice that found for 2,4,5-T. Then the rate of loss slows and the $t_{1/2}$ changes to 52 days. The initial half-life compares very favorably with the $t_{1/2}$ of 3.9–7.1 days for TCDD on bluegrass turf in a microecosystem (Nash and Beall, 1980).

The second slower rate process was not observed by Nash and Beall (1980) presumably because they applied extremely high levels of TCDD in their tests. Apparently TCDD residues must be quite low before this slower process can be observed. The half-lives obtained in both this work and by Nash and Beall are much longer than the half-life of 4 h obtained for excised leaf tissues (Crosby and Wong, 1977).

Rice: TCDD. No residues of TCDD were found in rice grain from 2,4,5-T treated fields (Table II). These experiments were conducted at twice the recommended 2,4,5-T rate which may have contained up to 5 times the currently specified level of TCDD. The low-resolution MS result on the Texas control (Table II) can be used in interpreting the Arkansas and Louisiana results for TCDD because the Texas control was stored and analyzed at the same time as the Texas, Arkansas, and Louisiana samples. The Arkansas control further down in the table was analyzed at a different time.

Composites of the four replicates from the experiments in Arkansas, Louisiana, and Texas were analyzed. By use of GC-low-resolution mass spectrometry apparent positive results were obtained for TCDD in the control (5 ppt with a detection limit of 1 ppt) and in the treated samples analyzed at the same time (4 or 5 ppt of TCDD with a detection limit of 1 ppt). Finding the same level of TCDD in all samples whether they were control or treated raises extreme doubt that TCDD was actually in these samples. However, the samples were reexamined by GC-high-resolution MS and no TCDD was detected in any of these samples. The limit of detection for these additional assays were at or below the apparent level of TCDD found by the less-specific GC-low-resolution MS technique for all but one sample. In that sample the apparent TCDD level found by GC-low-resolution MS was 4 ppt while GC-high resolution MS gave a result of none detected at a detection limit of 7 ppt. Other researchers (Isensee and Jones, 1971; Young et al., 1978) have concluded that accumulation of TCDD in plants and seeds was highly unlikely especially considering that water solubility is needed for transport in the plant and TCDD is relatively water insoluble. Finding no detectable TCDD in rice fit the pattern seen by other workers.

No TCDD residues were found in rice from the market basket survey covering most of the United States (Table III). The detection limit varied from 2 to 10 ppt.

These studies in rice coupled with previous work further confirm that harmful residues do not occur in food as a result of 2,4,5-T use in rice fields. No 2,4,5-T or TCDD was found in rice grain. In addition, 20 fish from a pond containing rice flood water from 2,4,5-T-treated fields had no detectable TCDD when analyzed by a method with a detection limit of 1–22 ppt (Shadoff et al., 1977).

ACKNOWLEDGMENT

We thank Roy Smith, Jr., USDA Rice Branch Experiment Station, Stuttgart, AR, John B. Baker, Louisiana State University, Baton Rouge, LA, Wayne T. Flinchum, Texas A&M University, Agricultural Research and Extension Center at Beaumont, TX, and Bobby A. Huey,

University of Arkansas, Stuttgart, AR, for conducting rice experiments, Mississippi Rice Growers Association, Cleveland, MS, Charles Heinsz, Moreland, MS, and Penn Owen, Robertson, MS, for rice samples, all persons who purchased rice samples in the market basket survey, L. Shadoff, H. S. Higgins, L. L. Lamparski, E. Madrid, and D. K. Ervick of Dow Chemical U.S.A. for analytical assistance, and G. Agin of Dow Chemical U.S.A. for assistance in the analysis of dissipation data.

Registry No. 2,4,5-T, 93-76-5; TCDD, 1746-01-6.

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Received for review February 24, 1982. Accepted September 27, 1982.

Residues of Phenthoate (Cidial) and Its Oxon on Grapefruit, Lemons, Oranges, Their Fractionated Products, and Soil

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An analytical procedure for the analysis of phenthoate insecticide [*O,O*-dimethyl *S*-(α -carboethoxybenzyl) phosphorodithioate, Cidial] and its oxon is described for fresh grapefruit, lemons, and oranges as well as for 15 fractionated products and soil. The phenthoate, in the form of an emulsifiable concentrate (Cidial), was applied to the citrus trees at 4 and 8 oz of active ingredient/100 gal. Fresh fruit and soil exhibited typical first-order decay for phenthoate, with levels after 7 days in peel below 1 ppm; pulp levels never exceeded 0.04 ppm (orange, 7 days). Maximum phenthoate soil levels occurred at the tree drip line near the surface (0.55 ppm) but decayed to 0.12 ppm after 28 days; maximum oxon occurred at 14 days for these samples (0.04 ppm). Lemon peel oil, resulting from the 8 oz/100 gal treatment, incurred the highest phenthoate residues (16 ppm) as well as oxon (2.2 ppm). Wash water (after-water rinse) contained negligible residues of phenthoate and oxon.

Phenthoate [*O,O*-dimethyl *S*-(α -carboethoxybenzyl) phosphorodithioate, Cidial] is a broad spectrum organophosphorous insecticide effective in controlling various mites, thrips, and scale insects. It has an LD₅₀ for the rat of 4728 mg/kg and for the common housefly of 5 mg/kg (Pellegrini and Santi, 1972). Phenthoate oxon has been shown to be the major metabolite removable from orange peel surfaces by solvent extraction (Takade et al., 1976) while the major bound residues released by enzymatic and hydrolytic conditions were shown to be ethyl mandelate and mandelic acid (Mallipudi and Fukuto, 1981). The two bound residues are toxicologically innocuous and can be dismissed.

Most Florida citrus production is used for processed products, such as juice concentrate, peel oil, and dried peel and molasses which are combined into cattle feed. The

safety of these products in terms of freedom from hazardous pesticide residues is a concern particularly since the potential exists for concentrating the residues by processing. In addition, significant amounts of water are used in a typical citrus processor as the fruit is washed prior to being sized; water contaminated with pesticide could present a problem in its disposal, whether it be returned to a natural body of surface water or to the aquifer or otherwise. Consequently, the ability to ensure safe foods and environment requires analytical procedures for all of the above-named materials.

A method for measuring residues of phenthoate and phenthoate oxon on fresh citrus fruit and leaves, as well as soil, has been reported (Iwata et al., 1977). Acetonitrile was used for extracting citrus fruit, while acetone was used for extracting soil; after partitioning the extracts were concentrated and analyzed by gas chromatography employing either alkali flame ionization detection (AFID) or flame photometric detection (FPD). Gas chromatographic columns used were 3% OV-1, 3% DC-200, or 5% DC-200-7.5% QF-1.

The method described here, while employing gas chromatography with FPD detection, uses modified extraction

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