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Dislodgeable Residues of Parathion and Carbophenothion in Florida Citrus: A Weather Model[1]

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In 1973, the federal government promulgated emergency temporary reentry standards designed to protect agricultural laborers from organophosphorous pesticide residues in the agricultural workplace (STENDER 1973). These regulations were based on recurring harvester reentry illnesses in the western United States, particularly California (QUINBY and LEMMON 1958, SPEAR et al. 1975a).

MILBY et al. (1964) originally suggested the environmental conversion product, paraoxon, was the cause of worker illnesses where parathion had been applied. Recent California harvester reentry illnesses support this supposition as residue samples from fields where incidents occurred contained unexpectedly high levels of oxon metabolites (F. A. Gunther, K. T. Maddy, and R. C. Spear, personal communication). The current approach of residue studies for worker reentry information has been to investigate the decay of organophosphorus insecticide residue on leaves using dislodgeable or other surface techniques and also in soil with attention to analysis for oxon metabolites (ADAMS et al. 1976, IWATA et al. 1973, KIDO et al. 1975, LEFFINGWELL et al. 1975, SPEAR et al. 1975b, SPENCER et al. 1975, STAIFF et al. 1975, WARE et al. 1975, WESTLAKE et al. 1973, WINTERLIN et al. 1975). Although a weather model approach to pesticide decay is not generally used, it is generally agreed weather is a significant factor in pesticide decay (VAN DYK 1976) and subsequently to worker reentry illnesses (ANONYMOUS 1976, CARMAN 1976, MAY 1976, PAYNTER 1976, WARE and MORGAN 1976). The purpose of this study was to relate the disappearance of the dislodgeable residues of parathion, carbophenothion and their oxon metabolites on 'Valencia' orange leaves to weather.

EXPERIMENTAL

The 25% wettable powder (WP) parathion (Phoskil 25 spray, FMC Corp.) was a gift of the Utah Biomedical Test Laboratory,

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Salt Lake City, UT. The 15% WP parathion was provided by Helena Chem. Co., Memphis, TN. The 8E flowable parathion (Aqua 8 parathion) was a gift of FMC Corp., Middleport, NY and Carbophenothion 8EC emulsifiable concentrate was a gift of Stauffer Chem. Corp., Westport, CT. Analytical standards of carbophenothion (S-((p-chlorophenylthio)methyl) O,O-diethylphosphorothiolothionate) and carbophenothion oxon (S-((p-chlorophenylthio)methyl) O,O-diethylphosphorothiolate) were provided by Stauffer Chem. Co. Research Laboratories, Richmond, CA and parathion (O,O-diethyl O-p-nitrophenyl phosphorothionate) and paraoxon (O,O-diethyl O-p-nitrophenyl phosphate) analytical standards were from Chem. Service, West Chester, PA.

The experimental grove was a 12-year-old 'Valencia' orange grove on rough lemon rootstock. Trees were uniform in height and canopy density and were in excellent horticultural condition. Experimental plots were 4 trees each. Treatments were repeated 4 times in a random block design and 4 no-spray plots were included as controls. Experiment 1 was from 29 May--15 Jun 1975, a hot, wet weather period. Experiment 2 was from 10 Nov--15 Dec 1975, a cool, dry weather period.

Application methodology, sampling, extractions, gas-liquid chromatography, TLC and column chromatography, high-pressure liquid chromatography (HPLC), mass spectroscopy, weather monitoring, and statistical analyses were described by NIGG et al. (1977).

The mathematical decay model used was

$$\frac{dy}{dt} = (a_0 + a_1x_1 + a_2x_2 + \dots + a_nx_n)y \qquad (1)$$

where

y = pesticide residue (ng/cm^2 of leaf surface)

$x_1, \dots, x_n$ = environmental variables.

The solution of (1) can be written

$$\ln(y) = \ln(y_0) + a_0\int dt + a_1\int x_1 dt + \dots + a_n\int x_n dt \qquad (2)$$

which is a multiple linear regression of ln(y) on accumulated environmental variables. y_0 is initial pesticide residue which appears as an "intercept" in the multiple regression equation.

Recoveries of pesticides at the 2.5 ng/cm^2 level from fortified Sur-Ten solutions were: parathion 97 ± 4%; paraoxon 93 ± 2%; carbophenothion 98 ± 3%; carbophenothion oxon 91 ± 2%. Quantitations on the GLC system described were consistent at 1.0 ng of paraoxon; 0.1 ng of parathion; 1.0 ng of carbophenothion oxon; 0.5 ng of carbophenothion per injection.

RESULTS

The evidence for the chemical identity of paraoxon and carbophenothion oxon is as follows: identical thin-layer R_f values and cochromatography with standards; paraoxon 0.16 and carbophenothion oxon 0.27; similar column chromatographic behavior--both compounds eluted in the 1:99 acetone: methylene chloride fraction, identical retention volumes and cochromatography with standards on HPLC, paraoxon 5.3 ml; carbophenothion oxon 7.5 ml; identical retention times to standards on a 0.61 m 5% OV-210 GC column and also on a 0.76 m 5% SP 2100 GC column and identical mass spectra to authentic paraoxon. Insufficient carbophenothion oxon was recovered for GC-mass spectral analysis.

As there was no significant difference in decay rates between amounts or formulations using an F test (LI 1964), the data for each compound were averaged within an experiment and this average was used for weather correlations. Since the object of these experiments was to provide one predictive model for each compound, data from experiments 1 and 2 were simultaneously correlated with their respective weather variables. Table 1 presents correlations against individual environmental variables for the data in Tables 3 and 4. The parathion data correlated most highly with cumulative leaf wetness (CLW) followed by cumulative heating degree days (HDD) and cumulative rainfall (CR) (Table 1). Time (T) was not significantly correlated with parathion decay at the 5% level. Time also was not significantly correlated with the carbophenothion data. Carbophenothion weather variable correlations were HDD>CLW>CR. Paraoxon decay was most highly correlated with CLW followed by T.

Table 2 presents similar correlations for the data of THOMPSON and BROOKS (1976). Correlations with parathion were not significant at the 5% level for any of the available environmental variables for THOMPSON and BROOKS' (1976) data. Significant correlations (at 5% level or better) with Thompson and Brooks' data were: carbophenothion T>HDD; ethion HD>T; azinphosmethyl HDD>T; dioxathion HDD>CR>T.

Table 5 presents the ln of the initial concentration and the coefficient of each environmental variable for a predictive equation for the data in Tables 3 and 4 and also for the data of THOMPSON and BROOKS (1976).

DISCUSSION

The absolute chemical identification of paraoxon and of carbophenothion oxon lends additional support to the general supposition that the oxon environmental products of the organophosphorus insecticides are produced in Florida as they are in California. However, the level of oxon metabolites remained below the parent residue throughout both experiments and the oxons did not remain at a steady level as reported in California

TABLE 1

Correlation matrixes of parathion, paraoxon, and carbophenothion decay on 'Valencia' orange leaves vs. environmental variables.

Parathion	Heating degree days^a	Time days	Cumulative rainfall in.	Cumulative leaf wetness hr
1.0000	-0.7822*	-0.5875	-0.7201*	-0.7989*
	1.0000	0.9446	0.3105	0.9540
		1.0000	0.0096	0.9008
			1.0000	0.2826
				1.0000
Paraoxon				
1.0000	-0.8636	-0.8921*	-0.7385	-0.9176*
Carbophenothion				
1.0000	-0.9303***	-0.6870	-0.7148*	-0.8617***

*Significant at 5% level.
**Significant at 1% level.
***Significant at < 1% level.

[a] 15° ≤ degree days ≤ 39°C.

TABLE 2

Correlation matrixes of parathion, carbophenothion, ethion, azinphosmethyl, and dioxathion decay on 'Valencia' orange leaves vs. weather variables using data of THOMPSON and BROOKS (1976).

Parathion	Heating degree days^a	Time days	Cumulative rainfall in.
1.0000	-0.6678	-0.6755	-0.4591
	1.0000	0.9173	0.8649
		1.0000	0.6135
			1.0000
Carbophenothion			
1.0000	-0.7929*	-0.8254**	-0.5188
Ethion			
1.0000	-0.7800*	-0.7763*	-0.5526
Azinphosmethyl			
1.0000	-0.8144**	-0.7625*	-0.6114
Dioxathion			
1.0000	-0.9170***	-0.7353*	-0.8809***

*Significant at 5% level.
**Significant at 1% level.
***Significant at < 1% level.

[a] 50° ≤ degree days ≤ 100°F.

TABLE 3

Dislodgeable residues of parathion and paraoxon on 'Valencia' orange leaves (ng/cm^2 ± SD[a]).

Days after treatment	0	1	3	5	7	14	21	28	35
Exp. 1 (Hot-Wet)									
8 oz 4E/ 100 gal									
Parathion	--	14.7 ± 2.0	4.7 ± 8.3	0.04 ± .02	0[b]	0	--	--	--
Paraoxon	--	0.03 ± 0.01	0.03 ± 0.03	0	0	0	--	--	--
Oxon/thion	--	0.002	0.006	--	--	--	--	--	--
1.5 lb 25 WP/ 100 gal									
Parathion	--	17.8 ± 31.2	11.0 ± 21.3	.47 ± .77	0	0	--	--	--
Paraoxon	--	4.5 ± 4.5	2.2 ± 4.5	0	0	0	--	--	--
Oxon/thion	--	0.25	0.20	--	--	--	--	--	--
Exp. 2 (Cool-Dry)									
4 oz 8E/ 100 gal									
Parathion	219.9 ± 30.1	20.0 ± 3.2	12.5 ± 1.5	10.4 ± 4.1	5.4 ± 1.8	3.9 ± 1.0	4.0 ± 0.9	1.7 ± 0.3	1.2 ± 0.6
Paraoxon	11.1 ± 4.6	7.4 ± 2.4	6.3 ± 4.3	5.5 ± 2.9	2.7 ± 2.2	0.9 ± 0.3	1.9 ± 2.2	0	0
Oxon/thion	0.05	0.37	0.50	0.53	0.50	0.23	0.48	--	--
6.3 lb 15 WP/ 100 gal									
Parathion	1359.4 ± 269.8	275.3 ± 95.8	87.2 ± 15.7	50.9 ± 34.6	20.6 ± 5.6	11.5 ± 4.4	9.3 ± 4.3	3.9 ± 0.9	1.1 ± 1.4
Paraoxon	42.7 ± 2.5	17.2 ± 5.6	15.0 ± 7.5	8.1 ± 2.7	3.1 ± 1.0	2.9 ± 2.1	1.7 ± 2.5	0	0
Oxon/thion	0.03	0.06	0.17	0.16	0.15	0.25	0.18	--	--

[a] SD = Standard Deviation.

[b] Analysis performed, no pesticide detected.

TABLE 4

Dislodgeable residues of carbophenothion and carbophenothion oxon on 'Valencia' orange leaves (ng/cm^2 ± SD[a]).

Days after treatment Carbophenothion 8EC	0	1	3	5	7	14	21	28	35
<u>3/8 pt/100 gal</u>									
<u>Exp. 1</u> (Hot-Wet)									
Carbophenothion	236.0 ± 74.2	41.5 ± 25.2	8.9 ± 2.3	3.6 ± 1.5	2.3 ± 1.8	.68 ± 0.5			
Carbophenothion oxon	14.2 ± 3.8	5.9 ± 4.1	0[b]	0	0	0			
Oxon/thion	0.06	0.14	--	--	--	--			
<u>Exp. 2</u> (Cool-Dry)									
Carbophenothion	167.9 ± 14.8	63.9 ± 10.7	38.3 ± 14.1	38.0 ± 9.0	15.3 ± 3.8	7.9 ± 2.6	5.6 ± 1.2	4.1 ± 1.2	2.4 ± 1.0
Carbophenothion oxon	0	0	0	0	0	0	0	0	0
Oxon/thion	--	--	--	--	--	--	--	--	--
<u>3/4 pt/100 gal</u>									
<u>Exp. 1</u>									
Carbophenothion	407.1 ± 45.0	205.9 ± 18.2	30.0 ± 9.0	10.3 ± 5.5	4.7 ± 1.6	1.5 ± 0.7			
Carbophenothion oxon	20.2 ± 4.2	18.5 ± 8.6	0	0	0	0			
Oxon/thion	0.05	0.09	--	--	--	--			
<u>Exp. 2</u>									
Carbophenothion	233.3 ± 36.1	113.9 ± 26.1	52.5 ± 13.4	40.7 ± 3.1	31.9 ± 9.4	14.6 ± 3.8	12.8 ± 1.3	5.7 ± 1.6	5.3 ± 2.6
Carbophenothion oxon	9.3 ± 1.2	0	0	0	0	0	0	0	0
Oxon/thion	0.04	--	--	--	--	--	--	--	--

[a] SD = Standard Deviation.

[b] Analysis performed, no pesticide detected.

TABLE 5

Variable coefficients for parathion, paraoxon, carbophenothion, ethion, azinphosmethyl, and dioxathion decay on 'Valencia' orange leaves (see equation (1)).

Compound	Ln initial conc.	HDD	CR	CLW	T	% variation explained	
						Time	Weather + time
Parathion[a]	2.2816	-0.0177	0.6791	--	0.1515	46	52*
Parathion	3.4511	0.0069	-1.2311	-0.0916	-0.0159	35	90***
Paraoxon	3.2822	0.0825	-1.0610	-0.0424	-0.2975	79*	98**
Carbophenothion[a]	2.9962	-0.0206	0.8344	--	0.1536	68**	75***
Carbophenothion	4.2014	0.0201	-0.9280	-0.0205	-0.1336	47	93***
Ethion[a]	2.9170	-0.0201	0.7479	--	0.1801	60*	69**
Azinphosmethyl[a]	3.3568	-0.0310	1.1144	--	0.3654	58*	78***
Dioxathion[a]	3.9349	-0.0220	0.4474	--	0.2914	54*	93***

HDD = Cumulative heating degree days; CR = Cumulative rainfall(in.); CLW = Cumulative leaf wetness (hr); T = Time (days).

*Significant at 5% level.

**Significant at 1% level.

***Significant at $<$ 1% level.

[a] Data from THOMPSON and BROOKS (1976).

(ADAMS et al. 1976, SPENCER et al. 1975). This may represent an important difference in residue patterns between California and Florida which may be related to the lack of acute pesticide illness reports among citrus harvesters in Florida.

We found no difference in the rate of decay of WP and EC parathion. WINTERLIN et al. (1975) also present data on parathion on California peaches that indicate no difference in the rate of decay of WP and EC formulations. Theoretically, the understanding of the effect of weather on pesticide decay could provide a key to the design of formulations to slow or to accelerate the effect of a particular variable. This approach to pesticide decay is compatible with the weather variable time base already in universal use in pest management models and becomes increasingly important as the residual action of pesticides on economic pests is included in pest management strategies. As shown in Table 5, the prediction of the residue level of the organophosphates is improved when weather is included with time.

Our data correlate much better with weather variables (Table 1) than the data of THOMPSON and BROOKS (1976) (Table 2). We interpret much of this difference to be the use of weather variables collected 10 miles from the experimental site in their case, whereas our weather data were collected at the experimental site. Nonetheless, the explanation of their data is improved compared to time alone even with distant weather data (Table 5).

The paraoxon data were 98% explained by time + weather (Table 5). This reflects essentially a correlation against experiment 2 data (dry period) since there are only 3 points for paraoxon in experiment 1 (wet period). The paraoxon and parathion correlations differ due to the strong paraoxon correlation with cumulative leaf wetness (-0.9176, Table 1). In Florida, there is an average of 2 hours of free water on citrus foliage from September through May and an average of 8 hours of free water from May through August in central Florida (McCOY et al. 1971, McCOY 1973). Although correlations may not be cause and effect, the paraoxon decay correlation with cumulative leaf wetness supports the theory of environmental hydrolysis of this compound (SPENCER et al. 1975). WESTLAKE et al. (1973) report up to a 56% reduction in dioxathion residue levels by washing trees with water. CARMAN et al. (1976) report up to a 73% reduction by washing for parathion. R. C. Spear (personal communication) noted similar decreases in paraoxon levels after washing trees without a reduction in dust loads.

Based on these observations and our weather correlations, it appears that although dusty conditions may serve as the primary transfer mechanism of pesticides to field workers in California (ADAMS et al. 1976, F. A. Gunther, personal communication, IWATA et al. 1975, SPEAR et al. 1975a,b, SPENCER et al. 1975, WESTLAKE et al. 1973), the primary reason for high parathion and paraoxon levels in California crops and worker reentry illnesses may be the lack of water (dew or rainfall) under California weather conditions to support a rapid hydrolysis of these pesticides.

An important consideration when using a multiple regression program is that a weather variable may correlate at a significant level (5 or 1%) on an individual basis but not contribute significantly to a multiple correlation. This is because the program uses the weather variable most highly correlated with the data and subsequently uses the other weather variables to correlate with the residual differences of the 1st correlation. If THOMPSON and BROOKS (1976) had collected leaf wetness data (Table 5), the sign of their coefficients might be the same as ours. For a previous ethion decay weather model (NIGG et al. 1977), although cumulative leaf wetness was more highly correlated with the data than cumulative rainfall or time, it did not contribute to the multiple correlation and was not included. In the future, we recommend as many weather variables as practical be included in a model until there is evidence that a variable is unimportant to a pesticide's disappearance or until a more easily measured variable can be used. Since weather variables are confounded, use of simple weather measurements to predict residue decay is a distinct possibility. Obviously, solar radiation data are missing in these experiments.

Experiments to model pesticide decay according to weather must be run under different weather conditions. For instance in experiment 1, heavy rainfall was highly correlated with pesticide decay, but temperature was more important during a dry period (exp. 2). It is clear that one experiment is not satisfactory for weather modeling and models will have to be updated as data become available.

Another advantage of weather modeling suggested by D. L. Houseworth (personal communication) is an accurate estimate of residues at harvest to meet Environmental Protection Agency tolerances. This could save a pesticide manufacturer many thousands of dollars where a tolerance has been set under one set of weather conditions but residues do not meet the tolerance under another set of weather conditions. Weather relationships plus time should overcome this difficulty of using a static time-based regulation in a dynamic situation. A recent loss of this type occurred in California alfalfa (D. L. Houseworth, personal communication).

It seems that harvester acute intoxications by organophosphates are the exception rather than the rule. The available data on worker reentry illnesses implicate the oxon environmental conversion products of the organophosphate pesticides rather than the parent compound. Identification of those weather factors leading to abnormal oxon levels in the agricultural workplace should allow prediction of the quality and quantity of residues dangerous to farm labor.

Other researchers have taken a mathematical approach to calculate worker safety reentry times to circumvent expensive human monitoring studies (SERAT 1973, SERAT et al. 1975). The effect of weather on pesticide residues was an important unresolved issue in his approach. As soon as the appropriate correlations between residue levels in the agricultural workplace and human physiological responses are made, a weather model of pesticide decay may allow the prediction of safe reentry times.

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