

Table II. Content of Phenolic Acids of Some Plant Material

acid	content, $\mu\text{g/g}$		
	Stuart pecans	instant tea	sphagnum moss
gallic	132.8 <sup>a</sup> (91.6) <sup>b</sup>	640.4 (422.6)	
gentisic	7.7		
vanillic	6.0		
protocatechuic	7.2 (5.4)		66.5 (51.2)
<i>p</i> -hydroxybenzoic ( <i>p</i> -hydroxyphenyl)- acetic	14.8 2.9		28
coumaric	tr	24.5 (36.9)	31.5 (47.2)
syringic	tr		
caffeic		255 (114.7)	
$\Sigma$ phenolic acids, %	0.0034	0.018	0.0025

<sup>a</sup> Results are given in micrograms per gram of dry plant material and are the means of triplicate analyses (pecan samples were also defatted). The sum of the identified phenolic acids are given as percent of dry weight of plant materials. <sup>b</sup> Values in parentheses were obtained from 4-h hydrolysis with 2 M aqueous NaOH.

cinnamic acids in the plant materials analyzed.

Due to its simplicity, reproducibility of reactions, and stability of the derivatives formed, the procedure herein reported for the GLC-MS analysis of plant phenolic acids

appears to be adequate for both qualitative and quantitative analysis.

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## Conversion of Parathion to Paraoxon on Soil Dusts As Related to Atmospheric Oxidants at Three California Locations

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Parathion-treated soil dusts were exposed outdoors near air-quality monitoring stations at three California locations. Results indicated that paraoxon production from parathion was controlled by atmospheric ozone concentration and type of soil dust. The ratio of paraoxon to parathion after 24 h ranged from an average of 0.117 with Mocho dust at a coastal site to 0.943 with Hanford dust at an inland site. The correlation coefficient ( $r$ ) between daily paraoxon production and daily peak ozone was 0.776, 0.701, and 0.773 for San Joaquin, Hanford, and Mocho dusts. Adding the additional variables of maximum temperature and minimum relative humidity only slightly improved correlations. In areas with relatively high ozone levels, the daily average, highest hourly average, and peak ozone concentration were equally good indicators of paraoxon formation rate. Neither total radiation nor UV was correlated with paraoxon production or with atmospheric ozone. Both parathion and paraoxon volatilized rapidly when no soil dust particles were present.

Exposure of agricultural workers to paraoxon residues has been shown to be responsible for the infrequent episodes of worker illnesses following parathion application to citrus in California (Spear et al., 1977a,b). Paraoxon, the highly toxic alteration product of parathion, is carried on dust particles originating from the soil or leaf surface to the workers' clothing or skin, from which it is dermally adsorbed. Under field conditions in the Central Valley of

California, parathion persists for long periods on dry soil and can be oxidized to the highly toxic paraoxon at the soil surface (Spencer et al., 1975). Dislodgeable residues on foliage are predominately associated with dust particles (Popendorf et al., 1975). Popendorf and Leffingwell (1978), who reported on natural variations in the decay and oxidation of parathion foliar residues in 17 central California orange groves, found that most of the parathion was converted to paraoxon during the first 2-4 days after application and that residue oxidation and decay were correlated strongly with dry, stable weather conditions. Adams et al. (1976, 1977) reported that dust can influence the oxidation of parathion to paraoxon and stabilize adsorbed paraoxon.

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Table I. Characteristics of Soil Dusts Used in Parathion Study

soil dust	organic matter, %	pH	sand, %	silt, %	clay, %	predominant clay minerals
Hanford (H)	2.7	6.5	36	46	18	<i>mica</i> , kaolinite
Moho (M)	1.0	7.3	51	27	21	<i>montmorillonite</i> , illite
San Joaquin (SJ)	2.4	7.0	22	58	19	<i>kaolinite</i> , illite

Table II. Average Temperatures, Relative Humidities, and Oxidant Levels Measured at the Experimental Sites during the Exposure Period

site	temp, °C		rel humidity, %		ozone, ppb		
	max	min	max	min	daily peak	highest hourly	daily
					(dp)	av (hha)	av (da)
inland I (Riverside)	35	19	86	37	199	180	55
inland II (Lindcove)	33	17	79	33	99	89	49
coastal (Costa Mesa)	23	17	100	58	65 <sup>a</sup>	56 <sup>a</sup>	24 <sup>a</sup>

<sup>a</sup> Total oxidant levels rather than ozone.

Research has been conducted under controlled conditions to establish environmental factors related to the production of paraoxon from parathion residues associated with the soil and foliar dust (Spear et al., 1978; Spencer et al., 1980). Spear et al. (1978) found that foliar dust levels and atmospheric ozone concentrations in environmental chambers greatly influenced the production of paraoxon from dislodgeable foliar parathion residues on dwarf Eureka lemon trees. Spencer et al. (1980) used a technique in environmental chambers whereby thin layers of parathion-treated soil dusts in Petri dishes were exposed to various concentrations of atmospheric ozone with and without ultraviolet light. The oxidation of parathion to paraoxon on soil dust was controlled mainly by ozone concentrations and the type and thickness of soil dust or clay mineral on which the parathion was adsorbed.

In this paper we report the results of a field study involving outdoor exposure of parathion-treated soil dusts in three climatic areas of California to determine the relationship between production of paraoxon from parathion and atmospheric or climatic conditions during or soon after pesticide application.

#### MATERIALS AND METHODS

Three soil dusts containing 439 µg/g parathion were exposed daily in Petri dishes (12.3 mg of dust/cm<sup>2</sup>) near air-quality monitoring stations at three California locations from July through Sept 1977. The amounts of paraoxon and parathion residues present after 24 or 72 h were correlated with atmospheric parameters. Two of the exposure sites were located inland, whereas the third site was located near the coast. Inland I site was located on the University of California (UC) Riverside campus near the air-quality monitoring station operated by the Statewide Air Pollution Research Center. Air-quality data from inland I site were collected by the Statewide Air Pollution Research Center (UC), Riverside. Inland II site was located in California's Central Valley at the UC Lindcove Field Station, in Tulare County about 23 km east of Visalia. Air-quality data from the inland II site were collected by R. C. Spear and co-workers, UC, Berkeley, and by Lindcove Field Station personnel. The coastal site was located within 3 km of the Pacific coast near the South Coast Air Quality Management District monitoring station on the grounds of the Fairview State Hospital, Costa Mesa, CA. Air-quality data were collected by the Orange County Zone, South Coast Air Quality Management District. At the coastal site, atmospheric oxidants were reported as total oxidants, rather than as ozone, as it was at the other sites.

Soil dust samples were collected by vacuuming the surface soil through a 100-mesh screen using a portable vacuum cleaner, following the procedure for determining

pesticide residues on the soil surface (Spencer et al., 1977). Some properties of the soil dusts derived from Hanford sandy loam (Typic Xerorthents) from the Riverside site, San Joaquin sandy loam (Abruptic Durixeralfs) from the Lindcove field station site, and Mocho sandy loam (Fluventic Haploxeroils) from a site near Costa Mesa are shown in Table I. The treatment of the dusts with parathion, their handling before, during, and after exposure, and their extraction was the same as that described for the exposure experiments conducted in environmental chambers (Spencer et al., 1980). An appropriate volume of 1 mg/mL ethyl parathion (technical, 98.4%) in a 1:1 hexane-acetone solution was added to ~300 g of dust in a 1-L flask. The suspension was mixed for 1 h, and the solvent removed under vacuum on a rotary evaporator. The resulting concentration of ethyl parathion, as determined by extraction of the dust, indicated that the concentrations were within ±2% of each other with an average concentration of 439 µg/g. Individual samples of 0.75 g of each dust were preweighed and placed into 30-mL screw-cap vials, sealed, and frozen. Periodic checks of the parathion concentration of the dust indicated no significant change in concentration throughout the experiment. Just before exposure, the dust samples were warmed to room temperature, placed in 8.8 cm i.d. glass Petri dishes, and spread uniformly with a hand-held, 5-cm wire screen.

Sample exposure began and ended at 0900 h, and Petri dishes were changed daily Monday through Friday with a 3-day exposure each weekend. Duplicate Petri dishes with each soil dust were placed on wooden tables ~20 cm above the ground surface and exposed to the outdoor atmosphere for 24 or 72 h. The dust samples were then removed from the Petri dishes and placed into 30-mL screw-cap vials and kept frozen until weighed for analysis. The parathion and paraoxon were extracted from the dust by eluting 0.1-g samples of dust in plastic syringe tips with 25 mL of a 1:1 hexane-acetone solution. Paraoxon and parathion in extracts were quantitated with a Tracor gas-liquid chromatograph using glass columns packed with 3% OV-1 columns and a flame photometric detector (Spencer et al., 1980).

For determination of the effect of soil dust on persistence, parathion and paraoxon without dust were exposed in clean Petri dishes, and paraoxon alone added to dust from San Joaquin sandy loam was exposed outdoors at the inland I site for 24 or 72 h during several days.

#### RESULTS

Average temperatures, relative humidities, and oxidant levels measured at the experimental sites are shown in Table II. The conversion of parathion to paraoxon and their persistence on the three soils at each site for the 24-

**Table III. Paraoxon (Oxon) and Parathion (Thion) Residues after 24-h Exposure of Various Dusts Containing 5.41 µg/cm<sup>2</sup> (439 µg/g) Parathion at Three Sites in California**

site	dust	no. obsvd, n	residues			oxon/thion ratio
			µg/cm <sup>2</sup>			
			oxon	thion	total	
inland I	H	57	1.60	1.88	3.48	0.943
	M	58	0.97	2.85	3.82	0.362
	SJ	58	1.10	3.07	4.17	0.383
inland II	H	65	1.38	2.55	3.93	0.585
	M	65	0.64	3.47	4.12	0.193
	SJ	64	0.74	3.68	4.42	0.209
coastal	H	63	0.90	2.45	3.35	0.403
	M	64	0.39	3.36	3.75	0.117
	SJ	63	0.54	3.57	4.11	0.156

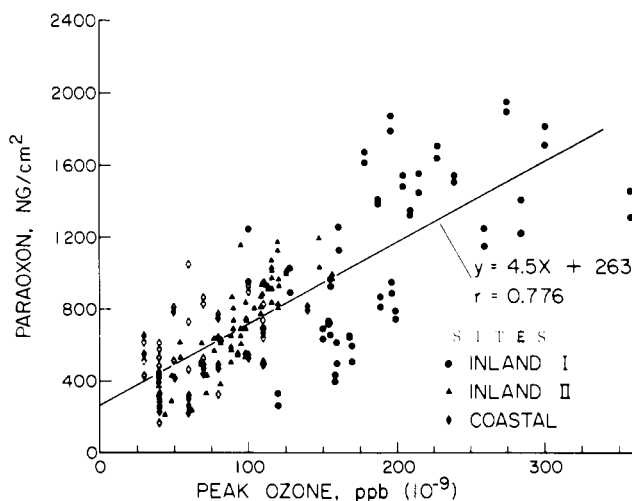
**Table IV. Paraoxon (Oxon) and Parathion (Thion) Residues after 72-h Exposure of Various Dusts Containing 5.41 µg/cm<sup>2</sup> or San Joaquin Dust Containing 13.46 µg/cm<sup>2</sup> Parathion at Three California Sites**

site	dust	no. obsvd, n	residue			oxon/thion ratio
			µg/cm <sup>2</sup>			
			oxon	thion	total	
inland I	H	16	1.48	0.44	1.92	5.50
	M	16	1.09	0.85	1.94	1.99
	SJ	16	1.44	0.88	2.32	2.57
	SJ <sup>a</sup>	18	2.94	2.29	5.23	1.96
inland II	H	18	1.90	0.53	2.43	5.26
	M	18	1.27	1.40	2.67	1.04
	SJ	17	1.67	1.45	3.12	1.32
	SJ <sup>a</sup>	22	3.07	3.47	6.55	1.09
coastal	H	20	1.29	0.86	2.15	2.15
	M	20	0.58	1.53	2.11	0.38
	SJ	20	0.98	1.46	2.44	0.89
	SJ <sup>a</sup>	16	2.22	4.30	6.52	0.52

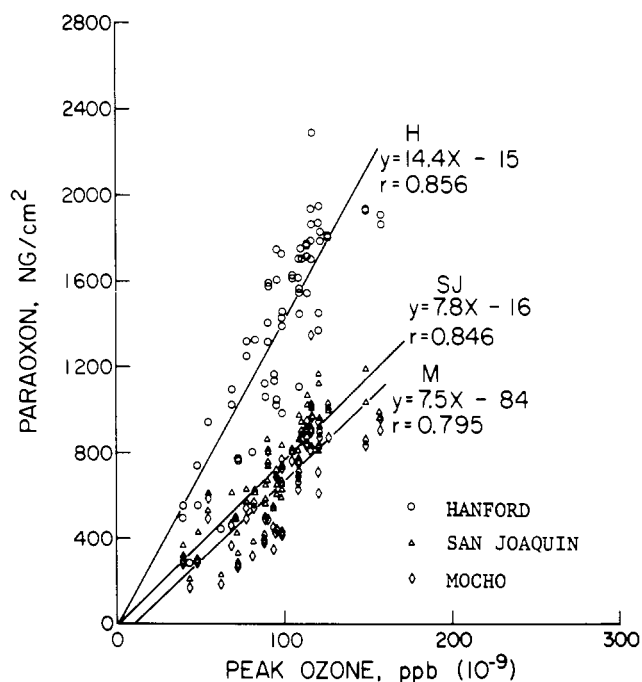
<sup>a</sup> San Joaquin dust at 13.46 µg/cm<sup>2</sup> (1090 µg/g) parathion.

and 72-h periods are shown in Tables III and IV, respectively. More paraoxon was produced at the inland sites than at the coastal site, and the dust from Hanford sandy loam oxidized more parathion to paraoxon than did the other two soil dusts. The average paraoxon/parathion ratio was highest for the Hanford dust which had 24 and 72-h average values of 0.94 and 5.5, respectively, at the inland I site. For the Hanford dust at the inland I site, the paraoxon/parathion ratio after 72 h ranged from 1.1 to 17, whereas the highest paraoxon/parathion ratio after 24 h was 2.1. Considering the total residues, parathion seemed to be slightly more persistent on San Joaquin than on the other two dusts.

Figure 1 shows the relationship between paraoxon produced within 24 h in dust from San Joaquin sandy loam at all three sites plotted against the daily peak ozone concentration of the atmosphere. The overall correlation between paraoxon and daily peak ozone concentrations resembled that for the other two dusts which had overall



**Figure 1. Relationship between 24-h paraoxon production in San Joaquin dust and daily peak ozone concentrations at all three sites.**



**Figure 2. Relationship between 24-h paraoxon production in three soil dusts and peak ozone concentration at the inland II site.**

correlation coefficients (*r*) of 0.701 and 0.773 for Hanford and Mocho dust, respectively. Figure 2 illustrates the interaction between soil dusts and peak ozone concentration on paraoxon production as observed at the inland II site. Paraoxon produced is plotted vs. the instantaneous peak ozone level recorded during the 24-h period. The correlation coefficient between paraoxon production and peak ozone were highly significant for all three dusts.

**Table V. Simple Correlations (*r*) for 24-h Paraoxon Production vs. Daily Peak (dp), Highest Hourly Average (hha), and Daily Average (da) Ozone Concentrations at the Three Sites**

dust	site								
	inland I, n = 48			inland II, n = 50			coastal, n = 63		
	dp	hha	da	dp	hha	da	dp	hha	da <sup>a</sup>
Hanford	0.680	0.688	0.670	0.868	0.823	0.773	0.556	0.505	0.296
Mocho	0.681	0.667	0.675	0.827	0.796	0.740	0.377	0.351	0.121
San Joaquin	0.699	0.710	0.780	0.890	0.854	0.745	0.464	0.417	0.260

<sup>a</sup> All *r* values are significant at the 1% level, except the da values at the coastal site.

Table VI. Simple Correlations (*r*) for 72-h Paraoxon Production vs. Daily Peak (dp), Highest Hourly Average (hha), and Daily Average (da) Ozone during the First 24 h after Application

dust	site								
	inland I, <i>n</i> = 48			inland II, <i>n</i> = 50			coastal, <i>n</i> = 63		
	dp	hha	da	dp	hha	da	dp	hha	da
H <sup>a</sup>	0.445	0.421	-0.103	0.565 <sup>c</sup>	0.586 <sup>d</sup>	0.715 <sup>d</sup>	0.269	0.223	0.022
M <sup>a</sup>	0.549 <sup>c</sup>	0.496 <sup>c</sup>	0.328	0.704 <sup>d</sup>	0.672 <sup>d</sup>	0.795 <sup>d</sup>	0.338	0.283	-0.144
SJ <sup>a</sup>	0.541 <sup>c</sup>	0.522 <sup>c</sup>	0.379	0.636 <sup>d</sup>	0.594 <sup>d</sup>	0.721 <sup>d</sup>	0.340	0.286	-0.012
SJ <sup>b</sup>	0.676 <sup>d</sup>	0.659 <sup>d</sup>	0.618 <sup>d</sup>	0.614 <sup>d</sup>	0.641 <sup>d</sup>	0.736 <sup>d</sup>	0.830 <sup>d</sup>	0.813 <sup>d</sup>	0.745 <sup>d</sup>

<sup>a</sup> Parathion applied at 5.41 μg/cm<sup>2</sup>. <sup>b</sup> Parathion applied at 13.46 μg/cm<sup>2</sup>. <sup>c</sup> Value is significant at the 5% level according to Snedecor (1956). <sup>d</sup> Value is significant at the 1% level, according to Snedecor (1956).

Table VII. Simple and Multiple<sup>a</sup> Linear Regressions of Paraoxon (Oxon) and Parathion (Thion) Residues (ng/cm<sup>2</sup>) after 24 h and Peak Values of Environmental Variables at All Three Sites

<i>y</i>	dust	no. obsvd, <i>n</i>	<i>r</i>					eq coeff			
			ozone	max temp	min % RH <sup>b</sup>	<i>R</i>	<i>R</i> <sup>2</sup>	<i>A</i> <sub>0</sub>	<i>A</i> <sub>1</sub>	<i>A</i> <sub>2</sub>	<i>A</i> <sub>3</sub>
oxon	H	185	0.701	0.723	-0.649	0.792	0.628	572	3.31	21.9	-8.38
	M	187	0.773	0.732	-0.621	0.826	0.683	34	3.00	14.5	-4.22
	SJ	185	0.776	0.638	-0.519	0.792	0.627	304	3.81	5.21	-2.97
thion	H	185	-0.631	-0.445	0.246	0.641	0.411	3661	-5.03	-17.3	-5.75
	M	187	-0.625	-0.462	0.270	0.633	0.401	4326	-3.89	-15.0	-4.04
	SJ	185	-0.694	-0.455	0.266	0.701	0.492	4385	-5.17	-5.56	-3.93
oxon/thion ratio	H	185	0.722	0.634	-0.501	0.787	0.619	0.078	0.004	0.007	-0.002
	M	187	0.783	0.676	-0.565	0.810	0.657	0.021	0.015	0.003	-0.002
	SJ	185	0.796	0.587	-0.456	0.799	0.638	0.079	0.002	0.001	-0.001

<sup>a</sup> Residue *y* = *A*<sub>0</sub> + *A*<sub>1</sub>(dp ozone or oxidant, ppb) + *A*<sub>2</sub>(maximum temperature, °C) + *A*<sub>3</sub>(minimum RH, %). <sup>b</sup> RH = relative humidity.

Again, the greater reactivity of the Hanford dust was readily apparent.

Table V shows simple correlation coefficients for the 24-h paraoxon production vs. the daily peak, highest hourly average, and daily average ozone concentrations. At inland I and II sites, which are areas with relatively high ozone concentrations, paraoxon production was equally correlated with each value, but at the coastal site it was most highly correlated with peak values. The correlations for individual soil dusts indicated that, even though some dust may be more reactive than others in producing paraoxon, the degree of correlation between paraoxon production and ozone levels is similar for all soil dusts. Additional research is required to pinpoint the soil variables responsible for the different rates of paraoxon production with different soils.

Simple correlation coefficients for 72-h paraoxon production vs. daily peak, highest hourly average, and daily average ozone (or total oxidant) concentrations during the first 24-h of exposure are shown in Table VI. Except for the higher rate of applied parathion, the correlation coefficients between atmospheric oxidant concentrations during the first day and amounts of paraoxon after 72 h were lower than those for paraoxon present after 24 h (Table V). These lower correlation coefficients after 72 h were probably caused by (1) loss of paraoxon along with the parathion and because (2) the initial conversion rate of parathion to paraoxon could not be maintained and paraoxon production was limited by the availability of parathion and not the concentration of atmospheric oxidant. These conclusions are supported by the fact that, for the higher parathion rate, correlation coefficients between oxidants and paraoxon after 72 h remained relatively high. The relationship between rates of formation and dissipation of parathion and paraoxon residues over the 3-day period and the environmental parameters needs to be examined more closely and will be the subject of a subsequent paper.

The high relative humidity at the coastal site, which reached 100% every day (Table II), is typical for coastal

regions and was responsible for wetting the samples enough to cause the dust to adhere to the glass Petri dishes so that the dust had to be scraped from the sides of the Petri dish to remove it. The combination of low oxidant concentrations (Table II) and high relative humidity at the coastal site resulted in the low observed paraoxon production and the correspondingly low correlation coefficients relating paraoxon production to oxidant levels.

Table VII shows simple and multiple correlation coefficients for daily paraoxon production and parathion persistence in the three dusts vs. daily peak ozone, maximum temperature, and minimum relative humidity. The daily peak ozone variations accounted for much of the variation in paraoxon production. Adding the additional variables of maximum temperature and minimum relative humidity only slightly improved correlations. Also, the disappearance of parathion was more highly correlated with oxidant level than with maximum temperature or minimum relative humidity. For all sites during the same days of observation, the correlation coefficients (*r*) were 0.698 between ozone and maximum temperature, -0.494 between ozone and minimum relative humidity, and -0.783 between maximum temperature and minimum relative humidity.

Simple correlation coefficients among peak values of additional atmospheric parameters measured at the inland I site and paraoxon production in San Joaquin dust are shown in Table VIII. There was a high degree of inter-correlation between atmospheric ozone and peroxyacetyl nitrate but not between ozone and nitrogen oxides. The correlation coefficient was higher than expected between paraoxon production and nitrogen oxides which indicates that oxidizing species other than ozone may be important in paraoxon formation. Ultraviolet and total radiation did not seem to be correlated with paraoxon production or atmospheric ozone. Maximum temperatures and ozone levels were highly correlated (*r* = 0.759) (data not shown).

Table IX shows the amounts of parathion and paraoxon residues remaining in clean Petri dishes as compared with that in parathion- or paraoxon-treated dust after outdoor

Table VIII. Simple Correlation Coefficients ( $r$ )<sup>a</sup> among Peak Values of Additional Atmospheric Parameters at the Inland I Site and Paraoxon in San Joaquin Dust after 24 h

Y	X							
	paraoxon	ozone	NO	NO <sub>2</sub>	NO <sub>x</sub>	PAN <sup>b</sup>	radiation	
							UV	total
paraoxon	1	0.699	0.542	0.685	0.606	0.552	-0.097	0.332
ozone		1	0.107	0.195	0.106	0.825	-0.534	-0.176
NO			1	0.867	0.958	0.116	0.279	0.504
NO <sub>2</sub>				1	0.953	0.140	0.244	0.583
NO <sub>x</sub>					1	0.090	0.312	0.565
PAN <sup>b</sup>						1	0.339	-0.089
UV radiation							1	0.812
total radiation								1

<sup>a</sup> 48 observations:  $r > 0.276$ , significant at the 5% level. <sup>b</sup> Peroxyacetyl nitrate.

Table IX. Comparison of Paraoxon Formation and Persistence of Parathion (Thion) and Paraoxon (Oxon) in Petri Dishes with and without 0.75 g of Soil Dust from San Joaquin Sandy Loam (SJ) Placed Outdoors at Riverside, CA

medium	chemical applied	amount applied, $\mu\text{g}$	no. obsvd, $n$	residues			
				thion, $\mu\text{g}$	oxon, $\mu\text{g}$	total	
						$\mu\text{g}$	% applied
24 h after Application							
SJ dust	thion <sup>a</sup>	329	58	187	67	254	77
SJ dust	oxon <sup>b</sup>	686	12		507	507	74
glass <sup>d</sup>	thion	330	12	38	6	44	13
glass <sup>d</sup>	oxon	622	12		173	173	28
72 h after Application							
SJ dust	thion <sup>a</sup>	329	18	53	88	141	43
SJ dust	thion <sup>c</sup>	819	18	139	178	317	39
SJ dust	oxon <sup>b</sup>	686	4		382	382	56
glass <sup>d</sup>	thion	330	4	ND <sup>e</sup>	ND <sup>e</sup>		
glass <sup>d</sup>	oxon	622	4		ND <sup>e</sup>		

<sup>a</sup> 439 ppm of parathion on SJ dust. <sup>b</sup> 915 ppm of paraoxon on SJ dust. <sup>c</sup> 1092 ppm of parathion on SJ dust. <sup>d</sup> Applied in 1-mL of acetone-hexane solution to clean a 8.8 cm diameter petri dish. <sup>e</sup> Not detected.

exposure for 24 and 72 h at the inland I site. Without soil dust, 87% of the parathion residue disappeared from the glass surfaces with less than 2% of it present as paraoxon after 24 h. Paraoxon disappeared somewhat more slowly from glass surfaces with only 72% dissipated in 24 h. Both parathion and paraoxon disappeared completely from glass surfaces in less than 72 h. Parathion and paraoxon residues were equally persistent when San Joaquin dust was present. These data indicate that both parathion and paraoxon will dissipate rapidly, undoubtedly by volatilization (Spencer et al., 1979), without soil dust particles acting as adsorbents. The observed behavior of parathion and paraoxon in clean Petri dishes resembled that on clean leaves (Spear et al., 1978). Their persistence will depend in large part on the foliar dust load of the leaves, as reported by Pependorf and Leffingwell (1978) and Spear et al. (1978).

The high degree of correlation between paraoxon production and atmospheric oxidants observed in this study indicates that the oxidant content of the outdoor atmosphere greatly affects the rate of paraoxon formation from parathion. This finding agrees with results observed under controlled conditions in environmental chambers (Spear et al., 1978; Spencer et al., 1980). However, even though a correlation may exist between atmospheric variables and the production or persistence of toxic oxons from organophosphates, documenting such a relationship under field-use conditions is difficult because of the many variables affecting pesticide persistence, such as initial residue concentrations, application method, formulation, site characteristics, and soil type (Gunther et al., 1977; Iwata et al., 1979; Nigg et al., 1979).

In this work, we attempted to examine a limited number of variables affecting paraoxon production under constant

conditions of soil, parathion concentration, and sampling site. Our results conclusively demonstrated that the rate of conversion of parathion to paraoxon in soil surface dust is controlled by the type of adsorbing dust and atmospheric conditions, particularly the oxidant levels at which the dusts are exposed. These data explain the rapid formation of paraoxon soon after parathion application on foliage (Pependorf and Leffingwell, 1978) and on soil dust (Spencer et al., 1975). However, whether or not this early ozone effect will result in high oxon levels when workers reenter fields several weeks after parathion application will depend on atmospheric and weather conditions between application and reentry. Additional studies are needed to pinpoint and intergrate all the parameters affecting rates of organophosphate residue dissipation to account for the differing oxon concentrations observed several weeks after spraying (Spear et al., 1977b; Pependorf and Leffingwell, 1978; Iwata et al., 1979).

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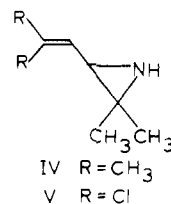
## Aziridine Analogues of Some Synthetic Pyrethroids

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The aziridines 2,2-dimethyl-3-(2-methylpropenyl)aziridine and 2,2-dimethyl-3-(2,2-dichlorovinyl)aziridine were synthesized. These aziridines were coupled with chloroformates prepared from 3-phenoxybenzyl alcohol, 5-benzyl-3-furylmethyl alcohol, and allethrolone. These couplings yielded aziridine analogues (C-1 carbon in the cyclopropane ring has been replaced with a nitrogen atom) of resmethrin, allethrin, phenothrin, NRDC 134, and permethrin. Other aziridinecarbamates were prepared from a variety of chloroformates. Preliminary insecticidal tests on these compounds have been performed. A general mortality rate of less than 10% at the 500-ppm level was found for the majority of the compounds synthesized. A notable exception is the compound containing the 5-benzyl-3-furylmethyl alcohol moiety, which had a mortality rate of 100% at the 500-ppm level in a number of insects.

Recent development in new synthetic pyrethroids have been primarily concerned with the synthesis of either photostabilized alcohol moieties or the replacement of the isobutenyl methyl groups of the acid moiety by functions that are resistant to oxidative degradation (Soderlund and Casida, 1977). There has been very little work reported on structural or compositional variations of the cyclopropane ring with the exception of the acyclic compounds such as in fenvalerate (Ohno et al., 1974). A compositional variation that we have been concerned with recently is the replacement of the C-1 carbon in the cyclopropane ring with a nitrogen atom to form an aziridinecarbamate linkage between the "acid" and alcohol components of the pyrethroid. It has been established that the configuration of the C-1 carbon in the cyclopropane ring must be *R* for insecticidal activity; the *S* configuration confers little or no toxicity (Elliott and Janes, 1973). Replacement of the C-1 carbon with a nitrogen would remove this aspect of configuration; however, the ease of inversion about the nitrogen atom in the aziridine ring system (Acheson, 1976) would allow the molecule to possess, part of the time, the same molecular conformation as that of a pyrethroid having the *R* configuration at the C-1 carbon. Casida and Berteau (1969) reported the synthesis of 5-benzyl-3-furylmethyl 2,2,3,3-tetramethylaziridine-1-carboxylate. Toxicity test data revealed a housefly topical LD<sub>50</sub> of 13 mg/kg with synergist and 228 mg/kg without synergist. Sammes and Rahman (1972) synthesized methyl and ethyl 2,2-dimethyl-3-(2-methylpropenyl)aziridine-1-carboxylates by means of photochemical decomposition of azido-

formates in the presence of 2,5-dimethyl-2,4-hexadiene but did not extend their studies by employing alcohol moieties that would be expected to produce analogues of known active pyrethroids. No additional pyrethroid-like compounds containing the aziridine ring in lieu of the cyclopropane ring have been found in the literature. We wish to report the synthesis and certain toxicity data for compounds obtained from the coupling of 2,2-dimethyl-3-(2-methylpropenyl)aziridine (IV) and 2,2-dimethyl-3-(2,



dichlorovinyl)aziridine (V) with various chloroformates. Initial insecticidal test data have been obtained for the aziridine analogues of resmethrin, allethrin, phenothrin, NRDC 134, and permethrin (Table I). The aziridine moieties were also coupled with chloroformates prepared from *o*-, *m*-, and *p*-cresols, sesamol, phenol, benzyl alcohol, and piperonyl alcohol. Insect toxicity for most of these analogues was low with a general mortality rate of less than 10% at 500 ppm.

### EXPERIMENTAL SECTION

Infrared spectra were determined with a Beckman IR-33. <sup>1</sup>H NMR spectra were recorded by using a Hitachi Perkin-Elmer R-24B NMR spectrometer. A Hitachi Perkin-Elmer RMU-6E mass spectrometer was used in obtaining the mass spectra. The photolysis was conducted with a Hanovia, No. 7825-36, mercury-vapor lamp of medium

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