Table V. Amino Acid Content of Seed Coat Protein[a]

	C. foetidissima	*C. digitata*	*C. pepo*	*C. maxima*	*C. ficifolia*
Lys	7.7	5.3	7.3	5.0	7.5
His	2.6	3.1	2.6	3.2	5.4
Arg	9.3	13.2	6.4	3.7	2.7
Asp	12.5	11.4	9.8	9.2	11.4
Thr	1.1	2.1	1.0	0.5	0.4
Ser	3.3	3.0	2.1	1.3	2.6
Glu	15.1	17.4	9.1	9.0	10.8
Pro	2.5	1.2	1.2	0.5	0.7
Gly	14.2	9.6	10.1	11.9	20.6
Ala	1.8	3.1	2.5	1.2	1.6
Val	2.0	3.7	1.0	1.0	1.3
Met	0.6	1.3	0.5	0.3	0.3
Ile	1.5	3.2	1.5	0.7	0.7
Leu	2.5	5.3	2.7	1.0	1.0
Tyr	6.6	5.0	5.3	6.9	12.0
Phe	1.4	3.2	1.7	0.5	0.6
Cys	0.5	0.1	Tr[b]	Tr	Tr

[a] Data are reported as percent of protein. [b] Trace.

contain a mixture of heteropolymers consisting of xylose and arabinose, and xylose and glucose.

A possible way to utilize the carbohydrates of waste seed coats would be to hydrolyze them with microbial enzymes to form free sugars (Conrad and Palmer, 1976). Such treatments generally produce glucose and xylose.

Amino acid values (Table V) demonstrate that the crude protein levels in the xerophytic species are primarily protein nitrogen. The high levels of protein nitrogen found in these species suggest that a considerable portion of the protein may be present as glycoprotein. All seed coats had very low levels of leucine, phenylalanine, and the sulfur amino acids. In contrast, their lysine levels ranged from 5.0 to 7.7%.

A variety of technical studies involving processing and handling of these seed coats will be necessary before commercial feasibility can be demonstrated. In the case of the *C. foetidissima*, sufficient land is under cultivation to produce seed and plant material for evaluation as a ruminant feedstuff.

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Conversion of Parathion to Paraoxon on Soil Dusts and Clay Minerals as Affected by Ozone and UV Light

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The persistence of parathion and its conversion to the highly toxic paraoxon on soil dusts and monoionic clay minerals were measured in environmental chambers with various rates of atmospheric ozone with and without ultraviolet (UV) light. The oxidation of parathion to paraoxon on soil dust was controlled mainly by ozone concentrations and the type and thickness of soil dust. Rates of paraoxon production were maximum at high ozone levels in the presence of UV light. Neither ozone alone, nor UV light alone, effectively produced paraoxon on the soil dust. When dry monoionic clays were exposed to 300 ppb oxone and UV light, the kaolinite clays more effectively catalyzed the oxidation of parathion to paraoxon than the montmorillonite clays. In oxidizing parathion to paraoxon the Cu-saturated clays were most effective, and the Ca-saturated montmorillonite clay (the dominant species in many agricultural soils of California) was least effective.

The worker reentry problem associated with using organophosphate insecticides has been the topic of several studies and a recent review (Gunther et al., 1977). The infrequent episodes of workers becoming ill from exposure to residues of parathion under hot, dry, California conditions has been found to be caused mainly by the highly toxic alteration product, paraoxon, carried on dust particles to the worker's clothing or skin, from which it is dermally absorbed (Spear et al., 1977a,b). Considerable quantities of insecticides ultimately reach the soil surface—either by direct application or by runoff from crops in excess water applied with the insecticide. Parathion can persist on dry soil for long periods and can be oxidized to the highly toxic

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Table I. Characteristics of Soil Dusts Used in Chamber Studies

soil dust	org matter, %	pH	sand, %	silt, %	clay, %	predominant clay minerals
San Joaquin Sa. l.	2.4	7.0	22	58	19	kaolinite, mica
Madera Sa. l.	2.3	6.7	38	52	10	mica, kaolinite
Kaweah[a]	4.2	6.1	46	39	15	mica, kaolinite
Pikes Peak clay[b]	0.1	4.7	0.4	27	73	montmorillonite

[a] Dust collected from sandy loam soil in Kaweah Citrus Orchard Tulare County, CA. [b] An acid-washed commercial dust used in pesticide formulations.

paraoxon (Spencer et al., 1975). In addition, dislodgeable residues on foliage and fruit are predominately associated with dust particles (Gunther et al., 1977). The pesticide-bearing dust particles, originating from the leaf or soil surface, are mostly soil dust, but may also be commercial dust from insecticide formulations. Such dust can influence the oxidation of parathion to paraoxon (Adams et al., 1976) and stabilize adsorbed paraoxon (Adams et al., 1977).

The sporadic occurrence of worker illness and the atypical paraoxon residue levels occasionally observed in the field (Spear et al., 1977b) make it necessary to determine what environmental factors are related to the production of paraoxon from parathion residues associated with the soil surfaces or foliar dusts. Parathion in solution can reportedly be converted to paraoxon by ozone (Gunther et al., 1970) and by ultraviolet (UV) light (Grunwell and Erickson, 1973), but little is known about the effect of these agents on soil-adsorbed parathion. Woodrow et al., (1977) reported that conversion of parathion to paraoxon can occur in the atmosphere, and Moilanen et al, (1978) found that atmospheric oxidants increased photooxidation of molinate. Spencer et al. (1978) reported that atmospheric conditions, especially oxidant concentrations, affected the rate of conversion of parathion to paraoxon.

This paper reports the results of a study conducted to examine the effects of ozone and longwave UV light under controlled conditions in environmental chambers on the conversion of parathion to paraoxon adsorbed on various soil dusts and monoionic clay minerals. Spear and coworkers (1978) previously reported on the synergistic effects of foliar dust and ozone in some complementary investigations on foliar residues.

MATERIALS AND METHODS

To identify the environmental factors important in paraoxon production and persistence, parathion-treated soil dust and clay minerals were exposed to various atmospheric ozone levels and UV light conditions in environmental chambers in three experiments.

Paraoxon Production on Soil Dusts. Parathion-treated soil dusts were exposed in two types of environmental chambers to various levels of ozone and UV light. Four dusts were used in both chambers. Three were derived from California soils by vacuuming the surface soil through a 100-mesh screen (Spencer et al., 1977), and the fourth (Pikes Peak clay) was a commercial dust used in some pesticide formulations. Some properties of the soil dusts and Pikes Peak clay are shown in Table I.

About 500 μg/g parathion was added to each dust. An appropriate volume of 1 mg/mL parathion in 1:1 hexane/acetone solution was added to 50 g of dust suspended in 200 mL of 1:1 hexane/acetone in a 1-L flask. The suspension was mixed for 1 h and the solvent removed under vacuum on a rotary evaporator. The dried dusts were then passed through a 100-mesh screen to break up aggregates. Individual samples for exposure were weighed into 30-mL screw-cap vials, sealed, and frozen. Just before exposure, the samples were warmed to room temperature, placed in 8.8-cm i.d. petri dishes, and spread uniformly with a hand-held, 5-cm wire screen. After the dust samples were exposed within the chambers for the specified time, they were removed from the petri dishes and placed into 30-mL screw-cap vials and kept frozen until weighed for analysis.

Experiment 1 (Intermittent Ozone and UV). The four dusts in petri dishes were exposed simultaneously with parathion-treated dwarf lemon trees in an environmental chamber as described by Spear et al. (1978). To better simulate outdoor plant growth conditions, the UV lamps were on for 8 h, at the same time that the ozone was introduced into the chamber, and off for 16 h. Dust samples were removed from the chamber on an 8- and 16-h schedule, just before and after UV lights were turned on and ozone was introduced. Dust samples were exposed to ozone with and without UV light simultaneously by placing two sets of petri dishes within the chamber, half of which were shielded from the UV light with an aluminum foil shade, but not from the ozone. Each petri dish contained 3.0 g of dust in 8.8-cm petri dishes equivalent to a dust loading density of 49.3 mg of dust/cm^2.

The 2.3 × 2.4 × 4.3 m long environmental chamber was constructed of enameled plywood. Temperature and relative humidity were controlled at 38 °C and 30% RH. The UV light source was xenon arc lamps with an intensity in the critical region from 280 to 450 nm, equivalent to about 75% of the radiant flux at summer noon in the Central Valley of California. Ozone [0, 50 ppb (representative of low ambient oxidant levels) and 300 ppb (representative of high ambient oxidant levels)] was introduced into the chamber from a Wellsbach P-23 Laboratory Ozonator. Ozone levels were continuously monitored with a Dashibi 1003-AH UV photometer and also frequently with a Mast meter. The "0 level" had no added ozone; however, because ozone could not be completely eliminated during UV radiation, it was reduced to less than 10 ppb by cycling chamber air through a carbon filter.

Experiment 2 (Continuous Ozone and UV). The four parathion-treated dusts in petri dishes at three dust densities (2.5, 12.3, and 49.3 mg of dust/cm^2) were exposed continuously to UV light and to 30 or 300 ppb ozone. The lowest dust density resembled the amount of loose dust vacuumed from the soil surface in parathion-treated citrus groves (Spencer et al. 1975), but is much higher than that normally observed (0.3 mg/cm^2) on dusty citrus leaves (Popendorf et al., 1975). Exposed dust samples were removed from the chamber periodically during the first 72 h for the 2.5 and 12.3 mg of dust/cm^2 and 432 h for 49.3 mg of dust/cm^2.

For experiment 2 the chamber was a painted plywood box (1.5 × 1.0 × 0.6 m high). A bank of 12 UV fluorescent lamps, 1.22 m long, were mounted above the chamber with the light filtered through a sheet of borosilicate glass to provide a UV light spectra similar to sunlight over the 300–400 nm range. Ozone was generated externally with an ozonator and metered into the chamber. The distance between the samples and the light source was adjusted to provide about the same UV intensity as in experiment 1, i.e., about 1460 μW/cm^2.

Paraoxon Production on Monoionic Clays. To determine the reason for differences in catalytic activity of

Table II. Effect of Atmospheric Ozone Concentration and UV Light on Conversion of Parathion (thion) to Paraoxon (oxon) on Dust from San Joaquin Sandy Loam (49.3 mg of Dust/cm^2[a] at 38 °C and 30% RH with Intermittent Ozone and UV Light)

	residue concentration, ppm								
	no ozone			50 ppb ozone			300 ppb ozone		
time, h	oxon	thion	total	oxon	thion	total	oxon	thion	total
				With UV Light					
0	0	357	357	0	357	357	5	397	402
8	4	334	338	9			78	318	396
24	5	323	328	9			65	274	339
32	7	323	330	7	289	296	91	251	342
48	9	316	325	10	340	350	95	231	326
56	8	335	343	12	341	353	117	218	335
72	7	274	281	13	381	394	127	217	344
80	8	272	280	15	322	337	126	188	314
96	8	280	288	15	280	295	137	189	326
104	8	308	316	16	235	251	124	153	277
				Without UV Light					
0	0	357	357	0	357	357	5	397	402
8	2	338	340	2	272	274	12	430	442
24	2	306	308	3	320	323	11	398	409
32	3	314	317	3	333	336	26	378	404
48	4	317	321	2	323	325	16	356	372
56	4	309	313	4	324	328	43	365	408
72	4	342	346	3	342	345	38	351	389
80	3	303	306	6	350	356	58	318	376
96	3	331	334	4	380	384	45	299	344
104	3	332	335	5	343	348	54	322	376

[a] Three grams of dust in 8.8-cm diameter petri dish or 49.3 mg/cm^2.

the soil dusts, parathion-treated kaolinite and montmorillonite clays, saturated with Ca, Na, or Cu, were exposed to ozone and UV light in the same environmental chamber as that used for experiment 2. The clays used were montmorillonite No. 31 (Bentonite) from Cameron, AZ, and Kaolinite No. 4 from the O'Neal Pit in Macon, GA. The <2 μm fraction, separated from each clay, was treated with concentrated HCl to remove adsorbed cations and washed with distilled, deionized water. A 1% suspension of each clay was treated with NaCl, $CaCl_2$, or $CuCl_2$ twice to saturate the sites with Na, Ca, or Cu, and the excess chloride was washed from the clay by centrifugation and dialysis with deionized water. Copper-saturated clays were included since sprays containing Cu are applied to citrus groves, and Popendorf and Leffingwell (1978) found increased conversion and dissipation of parathion when easily ionized $ZnSO_4$ was added to the spray application. Also, Mortland and Raman (1967) reported that some organophosphate pesticides are catalytically hydrolyzed by copper.

Clays were treated with parathion by adding 25 mL of aqueous solution of 20 μg/mL of parathion to 75 mL of a dilute suspension of each clay to provide a concentration equivalent to 1000 μg/g of parathion on the clay. After shaking the parathion-treated clay suspension for 1.5 h, 10-mL aliquots of the 0.5% clay suspension were pipetted into 8.8-cm petri dishes. This provided a clay loading density of 0.822 mg of clay/cm^2. The clay suspensions were dried for about 2 h in a fume hood with the sash down to provide a relatively high flow of laboratory air over the dish surface. Replicate samples of each dried clay were analyzed for the preexposure "O time" parathion and paraoxon residues. After transferring the petri dishes with the dry clays to the chamber, they were exposed to 300 ppb ozone with UV light for various periods.

Extraction and Analysis. The organophosphate insecticide residues were extracted from the dust and clay subsamples by an elution procedure. About 0.04 g of glass wool was pressed into the end of a polypropylene syringe tip (1000-μL Eppendorf pipetter tip). The tip was tared; 0.1 ± 0.04 g of previously exposed dust was placed in the tip; and the tip was reweighed. The dust-loaded tips were fitted to the bottom of 65-mm glass funnels, volumetric flasks were placed under the tips, and 25 mL of 1:1 hexane/acetone was added to the funnel. The funnels were covered to minimize solvent evaporation. After elution, which was usually complete in 2–4 h, the extracts were made up to 25 mL.

Table III. Percent of Parathion Oxidized to Paraoxon on Various Dusts after 48-h Intermittent Exposure to Ozone and UV Light

	paraoxon, as % of added parathion					
	no ozone		50 ppb ozone		300 ppb ozone	
dust	−UV	+UV	−UV	+UV	−UV	+UV
San Joaquin	1.1	2.5	0.6	2.8	3.9	23.6
Madera	0.9	2.4	0.9	3.8	7.3	24.0
Kaweah	1.4	3.4	1.2	2.7	6.6	25.4
Pikes Peak	1.6	2.2	1.4	4.4	8.5	27.6
mean	1.3	2.6	1.0	3.4	6.6	25.2

Parathion and paraoxon in the extracts were quantitated by gas–liquid chromotography using a Tracor flame photometric detector operated in the phosphorus mode (Spencer et al., 1975). Residue levels were calculated from the average peak heights from duplicated injections of each sample as compared with peak heights of reference standards. Data form triplicate samples were averaged. Analysis of blanks showed no interference from the extraction procedure, and analysis of unexposed samples showed that elution of the organophosphorus compounds were quantitative.

RESULTS

Paraoxon Production on Soil Dust. Our results indicated that ozone and UV light are important factors in converting parathion to paraoxon adsorbed on soil dust.

Experiment 1 (Intermittent Ozone and UV Light). Table II presents the effects of atmospheric ozone concentrations with and without UV light on rates of con-

Table IV. Paraoxon Formation and Persistence on San Joaquin (A) and Kaweah (B) Soil Dusts Exposed to 30 and 300 ppb Continuous Ozone, with UV Light, as Affected by Thickness of Dust in Petri Dishes at 38 °C and 30% RH

	residue concentration, ppm								
	2.5 mg of dust/cm^2			12.3 mg of dust/cm^2			49.3 mg of dust/cm^2		
time, h	oxon	thion	total	oxon	thion	total	oxon	thion	total
				A. San Joaquin Dust					
				30 ppb Ozone					
0	0	455	455	0	455	455	0	455	455
4	7	402	409	4	440	444	1	456	457
8	10	354	364	6	412	418	2	443	445
24	16	227	243	9	358	367	4	431	435
48							5	392	397
72	26	89	115	18	277	295			
96							10	371	381
144							18	340	358
216							32	301	333
288							39	276	315
360							55	241	296
432							69	216	285
				300 ppb Ozone					
0	2	498	500	2	498	500	2	498	500
4	169	221	390	75	365	440	17	529	546
8	224	132	376	180	244	424	31	478	509
24	224	70	294	279	79	358	138	321	459
48							231	170	401
72	172	25	197	267	40	307			
96							246	83	329
144							279	50	329
216							247	69	316
288							235	37	272
360							246	34	280
432							239	14	253
				B. Kaweah Dust					
				30 ppb Ozone					
0	0	410	410	0	410	410	0	410	410
4	11	316	327	5	370	375	1	372	373
8	14	266	280	8	339	347	4	393	397
24	27	211	238	12	302	314	6	363	369
48							7	375	382
72	26	112	138	24	256	280			
96							11	332	343
144							15	297	312
216							21	289	310
288							23	267	290
360							32	234	266
432							36	228	264
				300 ppb Ozone					
0	3	485	488	3	485	488	3	485	488
4	32	253	285	28	384	412	18	493	511
8	48	217	265	42	337	379	28	457	485
24	51	101	152	70	282	352	61	408	469
48							69	354	423
72	49	101	150	76	205	281			
96							65	305	370
144							75	282	357
216							85	264	349
288							87	254	341
360							86	255	341
432							88	239	327

version of adsorbed parathion to paraoxon for the San Joaquin sandy loam soil dust. Rates of paraoxon production were maximum at high ozone levels with UV light. Ultraviolet light alone was relatively ineffective in converting parathion to paraoxon. But, with added ozone, UV increased the total conversion by a factor of two–three times and greatly increased the rate of conversion as well. Most of the adsorbed parathion remained at the end of the 4-day experiment, either as paraoxon or parathion, although the total residues dissipated more rapidly with UV light, possibly due to a surface temperature effect of the xenon arc lamps.

In this short-term experiment with relatively high dust loading levels, similar amounts of paraoxon were produced on all soil dusts. Table III shows the percent of added parathion oxidized to paraoxon in various dusts after 48 h of exposure to intermittent levels of ozone with and without UV light.

Experiment 2 (*Continuous Ozone and UV*). At high ozone levels, the type and thickness of dust markedly affected paraoxon production. The effect of dust type was most apparent at the lower dust loadings. The extreme contrasts between the rates of paraoxon formation and residue persistence between the most (San Joaquin) and least (Kaweah) reactive dust are shown in Table IVA and IVB, respectively. At the 2.5 mg/cm^2 dust level, paraoxon accounted for essentially all of the residue on the San Joaquin dust (and also Pikes Peak clay) within less than

Table V. Percent of Added Parathion Oxidized to Paraoxon after 8 h of 30 and 300 ppb Continuous Ozone, with UV Light, as Affected by Dust Type and Thickness

	paraoxon, as % of added parathion					
	30 ppb ozone			300 ppb ozone		
type of dust	2.5 mg/cm² of dust	12.3 mg/cm² of dust	49.3 mg/cm² of dust	2.5 mg/cm² of dust	12.3 mg/cm² of dust	49.3 mg/cm² of dust
San Joaquin	2.2	1.3	0.4	49	36	6
Madera	2.1	1.4	0.7	22	22	6
Kaweah	3.4	2.0	1.0	10	9	6
Pikes Peak	4.1	1.8	0.7	65	30	5
mean	3.0	1.6	0.7	37	24	6

24 h at 300 ppb ozone. The maximum ratio of paraoxon/parathion on San Joaquin dust was 17.1 after 432 h of exposure to 300 ppb ozone at 49.3 mg/cm^2 of dust. The maximum ratio of paraoxon/parathion with Kaweah dust never exceeded 0.5 at any dust level.

The maximum rates of paraoxon production observed with San Joaquin dust during the first 24 h at the highest dust density (49.3 mg/cm^2) were equivalent to 0.28 μg/cm^2 h. With this thicker dust, the rate of paraoxon production remained essentially the same for the first 48 h, indicating that parathion oxidation was controlled by the availability of oxidant or its rate of movement to the reaction site. Paraoxon was very persistent on the dust, even though concentrations tended to decrease on the thinner dust layers within 72 h. The maximum amounts of paraoxon present during the 432 h measurement were 13.8, 10.7, 4.3, and 10.2 μg/cm^2 of paraoxon for San Joaquin, Madera, Kaweah, and the Pike Peak's clay, respectively. While the level of ozone did not have an appreciable effect upon the total residue, the highest dust loading decreased the rates of total residue dissipation by two–three times.

The percent of the added parathion oxidized to paraoxon during the first 8 h of continuous exposure to 30 and 300 ppb ozone as affected by all dust types and thickness are shown in Table V. At 300 ppb ozone, even after only 8 h, the lesser oxidation of parathion from the Kaweah soil was readily apparent. At 30 ppb ozone paraoxon production was very low for all dusts and differences between dusts were insignificant.

Paraoxon Production on Monoionic Clays. The effects of various montmorillonite (M) and kaolinite (K) clays on paraoxon formation and residue persistence at 300 ppb ozone, with UV light, are shown in Table VI. The residue concentrations at "0 time" were those present after drying and before chamber exposure to 300 ppb ozone. During drying of the clay suspensions in the fume hood, much of the parathion residues disappeared from the clay suspensions, and considerable amounts of parathion were converted to paraoxon, particularly for some clays. Paraoxon constituted 6.0, 28.9, 50.7, 1.6, 26.3, and 32.8% of the residue remaining after drying for CaK, NaK, CuK, CaM, NaM, and CuM, respectively. The total residue remaining after drying ranged from 28.2% of that applied with CuK to 41.9% with CaK. Volatilization (Spencer et al., 1973) and hydrolysis of drying clays (Yaron, 1978) are the most logical routes of parathion residue loss during the drying of the suspensions.

During exposure of the dry clays to ozone and UV light, the kaolinite clays were generally more effective than the montmorillonite clays in oxidizing parathion to paraoxon. Since the clays contained variable amounts of paraoxon and parathion at the beginning of the ozone exposure, the actual rates of paraoxon formation can not be readily seen in Table VI. Table VII shows rates of paraoxon formation normalized for the amount of parathion present at the beginning of the exposure period along with data on paraoxon formed during drying. Both during the drying and ozone exposure periods, the Cu-saturated clays were most effective and the Ca-saturated montmorillonite clay (CaM) least effective in oxidizing parathion to paraoxon. Table VIII shows changes in the ratio of paraoxon to parathion with length of exposure to ozone. With CaM, the ratio of paraoxon to parathion remained below 0.5, similar to that in the dust from the Kaweah soil in the previous experiments.

Paraoxon and parathion dissipated quite rapidly, especially from the Ca-saturated clays. The more rapid dissipation from clays than from soil dusts probably was caused by the smaller amounts of clay in the petri dishes, resulting in much thinner layer thicknesses of adsorbent.

DISCUSSION

Spencer et al. (1975) reported that paraoxon concentrations in the loose dust at the soil surface after parathion applications to citrus trees were much higher than those in the soil just below the surface. For example, 4 days after the application of 9 kg/ha parathion, samples of loose dust contained 114 μg/g paraoxon and the total amount of paraoxon in the 1-cm soil depth could be contained in dust only 0.009 cm deep. They concluded that paraoxon was being produced only at the soil surface. On the basis of the results reported here, the oxidation of parathion to paraoxon by ozone in the presence of UV light logically explains their observations.

Spear et al. (1978) reported that foliar dust level and atmospheric ozone concentration controlled paraoxon production from foliar parathion residues. High ozone levels effectively increased paraoxon production only at high dust levels. The effects of ozone are the same on foliar-dust residues as on soil-dust residues. However, a high percentage of the foliar residues rapidly dissappeared due to volatilization of the parathion, particularly at the

Table VI. Conversion of Parathion to Paraoxon on Monoionic Kaolinite (K) and Montmorillonite (M) Clays[a] Saturated with Ca, Na, or Cu When Exposed Continuously to 300 ppb Ozone and UV Light

	residue concentration, ppm											
	CaK		NaK		CuK		CaM		NaM		CuM	
time, h	oxon	thion	oxon	thion	oxon	thion	oxon	thion	oxon	thion	oxon	thion
0[b]	25	394	116	286	143	139	6	361	86	241	98	201
1	172	137	234	65	210	34	45	295	120	185	197	44
2	141	65	259	31	231	28	58	213	117	121	202	30
4	182	29	272	52	191	23	49	149	101	103	230	30
8	117	21	233	62	172	16	38	76	97	67	184	20
24	22	8	72	5	73	3	9	24	25	27	82	9
48	20	5	56	4	71	5	7	27	12	22	67	9
96	11	4	34	5	50	5	3	16	4	14	64	11

[a] A 0.05-g clay sample in 8.8-cm-diameter petri dish or 0.822 mg/cm^2. [b] After drying for 2 h in fume hood.

Table VII. Rates of Paraoxon Formation from Parathion during Drying of Monoionic Clay Suspensions and during the Initial Exposure Period to 300 ppb Ozone

	paraoxon, ng/cm² h					
time period	CaK	NaK	CuK	CaM	NaM	CuM
drying[a]	11	48	59	3	36	41
0-1 h	120	97	55	32	28	81
0-1 h, per ng of thion, t_0[b]	0.37	0.41	0.48	0.11	0.14	0.49

[a] Dried for 2 h in fume hood. [b] Rate of paraoxon formation expressed as ng/cm²-h of paraoxon per ng of parathion at the beginning of the exposure period (t_0).

Table VIII. Ratio of Paraoxon to Parathion on Monoionic Kaolinite (K) and Montmorillonite (M) Clays after Continuous Exposure to 300 ppb Ozone and UV Light

time,	ratio oxon/thion					
h	CaK	NaK	CuK	CaM	NaM	CuM
0	0.063	0.405	1.03	0.016	0.356	0.487
1	1.26	3.60	6.18	0.152	0.648	4.48
2	2.17	8.35	8.25	0.272	0.966	6.73
4	6.28	5.23	8.30	0.328	0.980	7.67
8	5.57	3.76	10.8	0.500	1.45	9.20
24	2.75	14.4	24.3	0.375	0.925	9.11
48	4.00	14.0	14.2	0.259	0.545	7.44
96	2.75	6.8	10.0	0.187	0.285	5.82

low foliar dust levels. In the case of the soil dust, a high percentage of the added parathion residue remained at the end of the experiment. Thus, the major difference between foliar residues and soil dust residues is the greater persistence of the residues on the soil dusts, which ultimately results in a much higher percentage of the added parathion being converted to paraoxon on soil dust than on foliage. This difference is caused by difference in dust loadings between soil and foliage and not by differences in the nature of the dust or the parathion residues.

The results with the monoionic clay minerals indicated that kaolinite clays are more effective than montmorillonite clays in oxidizing parathion to paraoxon and this would be expected to carry over into soil dusts if organic matter contents were similar. The dominant clay mineral in the Kaweah and Madera dust was mica with small amounts of kaolinite. The dominant clay in San Joaquin dust was kaolinite with smaller amounts of mica; whereas, the Pike Peak clay was predominately montmorillonite. Differences in catalytic activity between the various soil dusts seem to be more related to differences in organic matter content than to type of clay mineral. The ratios of paraoxon to parathion (46, 6.85, 2.05, and 0.48 for Pikes Peak clay, San Joaquin, Madera, and Kaweah dust, respectively) after 72 h of exposure of 2.5 mg of dust/cm² to 300 ppb ozone were inversely related to the organic matter contents of the dusts. If parathion adsorption on clays in the soil is required in the oxidation, it is reasonable to conclude that parathion adsorbed on soil organic matter will be protected from oxidation by ozone, and organic matter coatings on clay surfaces will probably decrease their catalytic activity.

These organic matter effects agreed with results of Adams et al. (1976), who indicated the initial dissipation rate of parathion was inversely related to the soil organic matter content of several parathion-treated dusts applied to citrus leaves; also, the parathion-residue level at which the dissipation rate decreased to a lower rate was directly related to soil organic matter. The difference in catalytic activity between the San Joaquin dust and the Madera dust with similar organic matter contents in this study can possibly be accounted for by the greater amount of kaolinite in the San Joaquin dust. The dominant clay mineral is kaolinite as compared with mica and the clay content is 19.4% for San Joaquin dust as compared with 10.3% for Madera dust.

Our results indicated that the conversion of parathion to paraoxon and its persistence is controlled by atmospheric ozone concentrations, UV light, and the nature of the adsorbing dust surface. Organic matter content and type of clay mineral both seem to be important in determining the catalytic activity of the soil dust. However, these findings need to be confirmed under field conditions. We are presently studying the production of toxic oxons from organophosphate insecticides in relation to atmospheric or climatic conditions during or soon after pesticide application under field conditions.

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