

- Holmstead, R. L., Casida, J. E., Ruzo, L. O., *Adv. Chem. Ser. No.* **42**, 137 (1977).
- Holmstead, R. L., Casida, J. E., Ruzo, L. O., Fullmer, D. G., *J. Agric. Food Chem.* **26**, 590 (1978).
- Holmstead, R. L., Fullmer, D. G., *J. Agric. Food Chem.* **25**, 56 (1977).
- Kuivila, H. G., Beumel, O. F., *J. Am. Chem. Soc.* **83**, 1246 (1961).
- Matuszewski, B., Givens, R. S., Neywick, C., *J. Am. Chem. Soc.* **95**, 595 (1973).
- Miyakado, M., Ohno, N., Okuno, Y., Hirano, M., Fujimoto, K., Yoshioka, H., *Agric. Biol. Chem.* **39**, 267 (1975).
- Oakwood, T. S., Weisgerber, C. A., *Org. Synth.* **24**, 14 (1944).
- Ohkawa, H., Ohkawa, R., Yamamoto, I., Casida, J. E., *Pestic. Biochem. Physiol.* **2**, 95 (1972).
- Ratcliffe, R., Rodehorst, R., *J. Org. Chem.* **35**, 4000 (1970).
- Ruzo, L. O., Holmstead, R. L., Casida, J. E., *Tetrahedron. Lett.*, 3045 (1976).
- Ruzo, L. O., Holmstead, R. L., Casida, J. E., *J. Agric. Food Chem.* **25**, 1385 (1977).
- Ueda, K., Gaughan, L. C., Casida, J. E., *J. Agric. Food Chem.* **22**, 212 (1974).
- Vogel, A. I., in "A Textbook of Practical Organic Chemistry", Longman Group Limited, London, England, 1970, p 902.
- Zweifel, G., Horng, A., Snow, J. T., *J. Am. Chem. Soc.* **92**, 1427 (1970).

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Conversion and Disappearance of Methidathion on Thin Layers of Dry Soil

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A technique has been developed for the production of reproducible thin layers of pesticide-containing soil for studies involving residue behavior on air-dry soil under different environmental conditions. The method has been applied to the study of methidathion on six different soils under conditions simulating those occurring on arid land soil surfaces and under abnormally high ozone levels in air. In contrast to results found for methidathion in moist soils, a very slow rate of disappearance occurs in dry soils in the absence of atmospheric oxidants or sunlight. The initial disappearance of methidathion appears to follow first-order kinetics, but with wide rate variations ($t_{1/2} = 19$ to 110 days for the particular types of soils tested). Considerable quantities of methidathion oxygen analogue are produced and retained in dry soil, in contrast to very low amounts found by others for moist soil.

The use of pesticides leads to unavoidable contamination of the surrounding soil. Thus, information on pesticide interaction with the soil and its associated soil microorganisms is necessary even for pesticides which were never intended for use as soil treatment chemicals. As water provides a medium for chemical reactions such as hydrolysis and is required for the active existence of soil microorganisms, soil studies generally are conducted under moist soil conditions. Flooded soil conditions, such as encountered in rice paddies, are recognized to yield quite dissimilar results compared to nonflooded conditions (Sethunathan, 1972). The other extreme, represented by air-dry soil, is also a fruitful area of research, as in many areas of the country much of the soil surface remains dry throughout the year. The conversion of organophosphorus compounds containing the P=S moiety to their more toxic cholinesterase-inhibiting P=O oxygen analogues, often called "oxons", on dust adhering to crop foliage (Gunther et al., 1977) demonstrates the importance of this line of investigations. Air-dry soil exposed to sunlight may produce and retain alteration products, such as the oxons, which are not found in any significant quantities in moist soil laboratory conditions. Exposure of agricultural workers to residues of organophosphorus oxons on foliage is speculated to be responsible for the occasional episodes of worker illnesses reported in California (Spear et al., 1975).

Adams et al. (1976) studied the behavior of different parathion-bearing soil dusts resident on citrus leaves. They

found that the rate of dissipation of parathion and its extent of conversion to paraoxon were dependent on the characteristics of the soil dust used. Spencer et al. (1975) reported on a sampling technique for soil dust in the field and on the levels of parathion and paraoxon found on the loose surface dust after parathion application to citrus trees.

Here we have used a modification of the soil thin-layer chromatography method of Helling and Turner (1968), who used finely sieved soil in place of conventional adsorbents to produce soil thin-layer plates. By "spotting" a pesticide on the plate and developing it with water, Helling (1971a,b,c) conveniently studied pesticide mobility in soil. In our work, the pesticide was mixed with soil and water and the slurry was spread to produce a 1-mm thickness of soil on glass plates; the soil was allowed to dry and was analyzed at various times for the pesticide and its conversion product. This technique provides a more convenient and reproducible tool for the evaluation of environmental effects such as solar radiation, humidity, and atmospheric oxidants on air-dry soil than is possible with field application studies. The soil thin-layers give an indication of what may occur to pesticides sorbed to dust particles adhering to foliage and on the surface soil of agricultural land. Reported here are tests conducted with methidathion (Supracide, GS-13005, S-[5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl]-methyl] O,O-dimethyl phosphorodithioate) to determine what effects different soil types and ozone have on its dissipation and its conversion to methidathion oxon under air-dry conditions. This compound was selected as it is currently the third most-used organophosphorus pesticide in California citrus production. Its use here is primarily as a research tool for

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Table I. Characteristics of Soils Used

Soil	pH	Organic matter, %	Water saturation, %	Particle size distribution, %		
				Sand (>0.05 mm)	Silt (0.002-0.05 mm)	Clay (<0.002 mm)
Madera sandy loam	6.7	1.4	27	60	28	12
Windy loam	6.0	11	54	51	40	9
Laveen loamy sand	8.7	0.1	21	94	1	5
Santa Lucia silt loam	5.6	20	94	34	42	24
"Visalia" silt loam ^a	5.2	2.5	35	24	57	19
Arlington fine sandy loam	6.8	0.7	28	55	33	12

^a Collected from an orange grove near Visalia, Calif.

demonstrating the utility of the soil thin-layer technique. However, since its residues are a potential hazard to agricultural workers entering treated groves, information of its behavior on dry soil is desirable. The degradation of methidathion in moist soil was reported by Getzin (1970) and by Eberle and Hörmann (1971).

EXPERIMENTAL SECTION

Materials. The ozone generator was an OREC Ozonator, Model 03B3-0, made by Ozone Research and Equipment Corp., Phoenix, Ariz. The thin-layer plates were exposed to ozone in a glasshouse of approximately 50 m³ volume. A Mast ozone meter was obtained from the Mast Development Corp., Davenport, Iowa. Supracide 2E and analytical standards of methidathion and its oxon were donated by Ciba-Geigy Corp., Greensboro, N.C.

Preparation of Soil Thin-Layer Plates. Six soils collected from different areas of California and selected to represent diverse soil types were used. The characteristics of these soils are listed in Table I. An initial concentration of about 700 µg of methidathion/g of soil dust was chosen as a realistic concentration of soil residues to be expected following a pesticide application (Spencer et al., 1975; Gunther et al., 1977). The soils used were sieved to pass through a 100-mesh screen. To 100 g of the sieved soil was added 0.29 mL of a 2 lb of AI/gal of Supracide 2E emulsifiable concentrate formulation which was suspended in 20 mL of water, giving a concentration of approximately 700 µg of methidathion/g of dry soil. Additional water was added to produce a slurry with a consistency similar to heavy cream. This was then poured into the reservoir of the TLC coating applicator, previously adjusted to deliver a 1.0-mm thick layer. The slurry was immediately applied to 20-cm square glass plates and allowed to air dry. The area which could be covered with 100 g of soil varied greatly depending on the bulk density of the soil; in general, at least 1000 cm² could be covered. The weight of the air-dry soil per unit area of glass ranged from 0.04 to 0.12 g/cm².

Exposure Conditions. Three sets of plates were used. One set was kept in a darkened laboratory storage room and served as a control. A second set was placed on a flat roof where it was exposed to sunlight throughout the day. A third set was placed in a controlled air-quality greenhouse equipped with an ozone generator adjusted to produce a concentration of 0.5 ppm O₃, corresponding to a severe smog episode. This concentration was maintained for 8 h each day and was monitored with a Mast ozone meter.

At selected time intervals during the experiment, a 50 cm² area of soil was removed from each plate. The soil sample was placed in a 2-oz (60-mL) screw-cap vial and 5.0 mL of a 5% water-acetone (v:v) mixture followed by 5.0 mL of hexane were added. The bottle, closed with a Teflon-lined cap, was then shaken at 200 cycles/min on an Eberbach reciprocating shaker for 20 min. Then, 3.0 g of anhydrous Na₂SO₄ was added and the vial was shaken

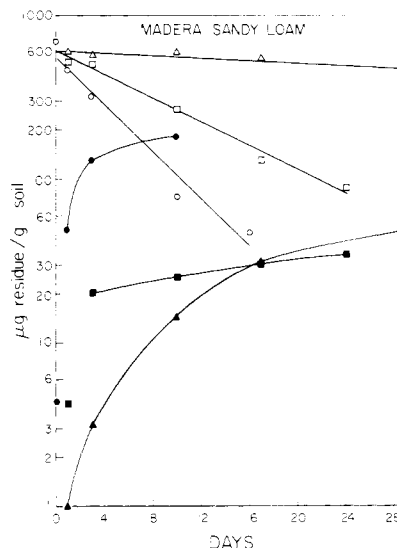


Figure 1. Residues of methidathion (open symbols) and its oxygen analogues (closed symbols) on Madera sandy loam treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

for an additional 5 min. The contents were filtered through a 5.5-cm Whatman No. 1 filter, diluted as needed, and analyzed. Average recoveries for methidathion and its oxon were 107 and 86%, respectively.

Analysis. Quantitation of methidathion and its oxon was by gas chromatography using a Tracor MT-220 gas chromatograph equipped with a flame photometric detector. A 30 cm × 4 mm i.d. glass column packed with 5% Apiezon N on 60/80 mesh Gas-Chrom Q was used with inlet, column, and detector temperatures of 228, 205, and 220 °C, respectively, and a nitrogen carrier gas flow rate of 80 mL/min.

RESULTS AND DISCUSSION

Figure 1 shows the dissipation curves for methidathion and the formation and subsequent dissipation of methidathion oxon under the three test conditions. First-order kinetics were assumed in comparing rates of methidathion disappearance for the six different soils and three different exposure conditions plotted in Figures 1-6. The best straight lines were drawn and the first-order rate constants and corresponding half-lives calculated. These values are given in Table II. For the laboratory-stored control soils, the only evident relationship to methidathion stability was to the soil pH; the greatest methidathion persistence occurred on soils having the highest pH (Laveen loamy sand, Figure 3, and Madera sandy loam, Figure 1), and the lowest persistence for those with the lowest pH ("Visalia" silt loam, Figure 5). This relationship was also observed for parathion dissipation on dry soil by Adams et al. (1976).

Weathering tests simulating what may occur under actual outdoor field conditions were conducted on soil

Table II. Pseudo-First-Order Rate Constants (k_1) and Corresponding Half-Lives ($t_{1/2}$) for Methidathion on Air-Dry Soil

Soil	Exposure condition					
	Control		Weathered		Ozone	
	k_1 (day ⁻¹)	$t_{1/2}$ (day)	k_1 (day ⁻¹)	$t_{1/2}$ (day)	k_1 (day ⁻¹)	$t_{1/2}$ (day)
Madera sandy loam	-0.010	72	-0.082	8.5	-0.16	4.2
Windy loam	-0.014	51	-0.065	11	-0.10	7.0
Laveen loamy sand	-0.0062	110	-0.064	11	-0.27	2.5
Santa Lucia silt loam	-0.011	62	-0.105	6.6	-0.15	4.6
"Visalia" silt loam	-0.036	20	-0.15	4.5	-0.14	4.8
Arlington fine sandy loam	-0.019	36	-0.088	7.9	-0.18	3.8

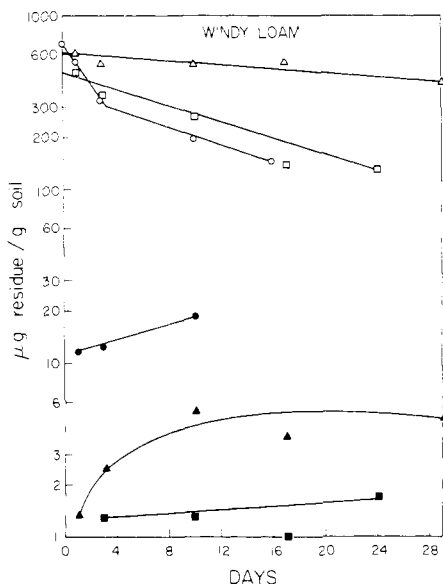


Figure 2. Residues of methidathion (open symbols) and its oxygen analogue (closed symbols) on Windy loam treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

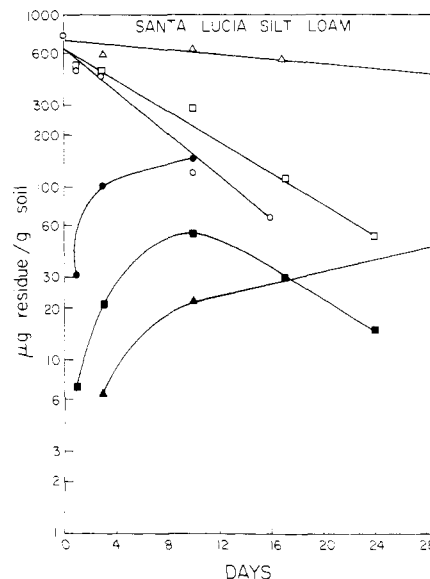


Figure 4. Residues of methidathion (open symbols) and its oxygen analogue (closed symbols) on Santa Lucia silt loam treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

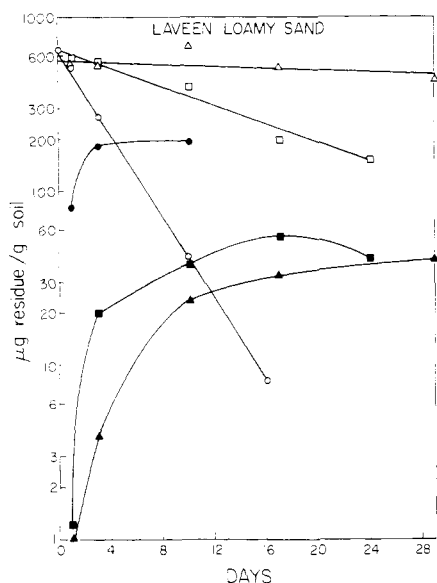


Figure 3. Residues of methidathion (open symbols) and its oxygen analogue (closed symbols) on Laveen loamy sand treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

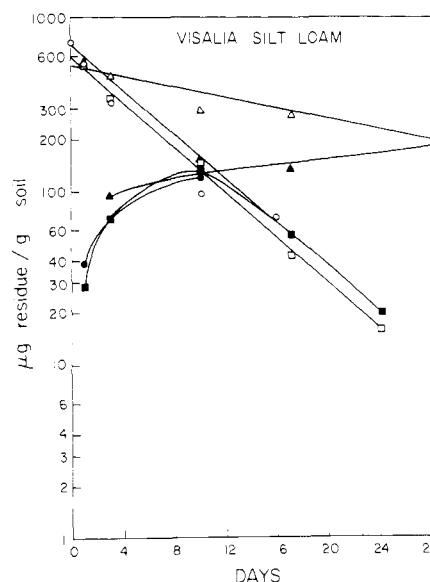


Figure 5. Residues of methidathion (open symbols) and its oxygen analogue (closed symbols) on "Visalia" silt loam treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

samples from 12 April to 12 May, 1977. During this time the average ambient air ozone concentration was a low value of 0.07 ppm and the average daily maximum air temperature was 78 °F (26 °C). The actual soil sample temperature was, however, considerably higher due to

absorption of the incident sunlight. Since the same phenomenon occurs under normal field conditions, the experimental conditions used were realistic. In general, the samples exposed to weathering showed methidathion

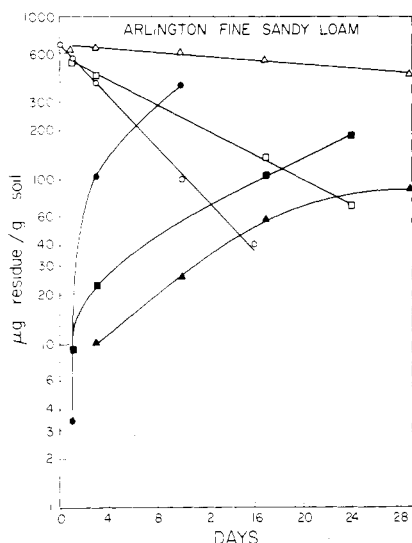


Figure 6. Residues of methidathion (open symbols) and its oxygen analogue (closed symbols) on Arlington fine sandy loam treated with 700 ppm methidathion under dark storage (triangles), ambient air and sunlight (squares), or 0.5 ppm ozone and sunlight (circles).

degradation and oxon production intermediate between the control samples and those exposed to 0.5 ppm ozone. On the weathered samples some of the effects were probably due to ultraviolet radiation, which has been observed by Spear (1976) to cause the thion-to-oxon conversion with parathion.

Ozone exposure experiments were conducted during March, 1977; the average maximum air temperature during this time was 66 °F (19 °C); soil sample temperatures again were considerably higher. The rate of disappearance of methidathion was greatly accelerated by 0.5 ppm ozone compared to the laboratory control samples. In general, the rate of oxon formation was increased by ozone, but this was not consistently the case, as shown by the results for the "Visalia" silt loam (Figure 1), where there is no sig-

nificant difference between the ozone exposure and normal weathering in oxon formation rates. In the cases of the Laveen loamy sand and the Arlington fine sandy loam soil, the concentration of oxon after 10 days was far greater than the concentration of parent compound.

The soil thin-layer technique is a convenient method for studying the dissipation, degradation, and alteration of pesticides on air-dry soil. Any pesticide can be incorporated into the soil and soil type and environmental variables can be altered to determine what effects are produced.

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LITERATURE CITED

- Adams, J. D., Iwata, Y., Gunther, F. A., *Bull. Environ. Contam. Toxicol.* **15**, 547 (1976).
 Eberle, D. O., Hörmann, W. D., *J. Assoc. Off. Anal. Chem.* **54**, 150 (1971).
 Getzin, L. W., *Bull. Environ. Contam. Toxicol.* **5**, 104 (1970).
 Gunther, F. A., Iwata, Y., Carman, G. E., Smith, C. A., *Residue Rev.* **67**, 1 (1977).
 Helling, C. S., *Soil Sci. Am., Proc.* **35**, 732 (1971a).
 Helling, C. S., *Soil Sci. Am., Proc.* **35**, 737 (1971b).
 Helling, C. S., *Soil Sci. Am., Proc.* **35**, 743 (1971c).
 Helling, C. S., Turner, B. C., *Science* **162**, 562 (1968).
 Sethunathan, N., in "Fate of Organic Pesticides in the Aquatic Environment", Gould, R. F., Ed., American Chemical Society, Washington, D.C., 1972 p 244.
 Spear, R. C., Jenkins, D. L., Milby, T. H., *Environ. Sci. Technol.* **9**, 308 (1975).
 Spear, R. C., School of Public Health, University of California, Berkeley, Calif., personal communication, 1976.
 Spencer, W. F., Cliath, M. M., Davis, K. R., Spear, R. C., Pendorff, W. J., *Bull. Environ. Contam. Toxicol.* **14**, 265 (1975).

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Determination of Phosphine in Wheat by Headspace Gas-Liquid Chromatography

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A relatively fast gas chromatographic method has been developed for the determination of residual phosphine (PH₃) in wheat. The phosphine was released by grinding the grain in a gas-tight blender jar. After equilibrium had been reached, samples from the headspace gas were injected directly into the gas-liquid chromatograph and measured against standards.

Hydrogen phosphide, or phosphine, PH₃, has been used to control stored grain pests for a number of years (Dieterich et al., 1967). The gas is generated by the action of moisture on aluminum phosphide preparations.

Phostoxin, manufactured by Degesch, Frankfurt/Main, Germany, is available in tablets or pellets. A 3-g tablet or 0.6-g pellet releases 1 g or 0.2 g of phosphine, respectively.

As phosphine is toxic at low levels (LCLo: 8 ppm; Christensen and Luginbyhl, 1974), it is necessary to monitor any residual gas in the grain. This has previously been done by colorimetric (Bruce et al., 1962) or chemical

Australian Government Analytical Laboratory, Melbourne, 3000, Australia.