

## Leaching of Oxadiazon and Phosalone in Soils

The movement, on soil thin-layer chromatographic plates, of  $^{14}\text{C}$ -labeled oxadiazon [2-*tert*-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- $\Delta^2$ -1,3,4-oxadiazolin-5-one] and phosalone [*O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl)methyl phosphorodithioate] was compared with three standard pesticides, 2,4-D [(2,4-dichlorophenoxy)acetic acid], diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], and methylparathion [*O,O*-dimethyl *O*-(*p*-nitrophenyl) phosphorothioate]. Oxadiazon and phosalone were nearly immobile in four soils and moved to  $R_f \sim 0.3$  and  $\sim 0.25$ , respectively, in Lakeland sandy loam. Extracts from soils incubated 6 months with oxadiazon had a trace amount of highly mobile, unidentified radioactivity; most was immobile. Phosalone, aged 1 or 3 months in aerobic and flooded soils, was largely immobile but traces of radioactivity streaked to high  $R_f$  values. Phosalone predominated in both slightly mobile and highly mobile streaks, but was accompanied by several unknown components.

Oxadiazon [2-*tert*-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- $\Delta^2$ -1,3,4-oxadiazolin-5-one], a herbicide introduced in 1969 (Burgaud et al., 1969), has been used on soybeans, rice, cotton, peanuts, fruit trees, grapes, turfgrass, and carnations. Phosalone [*O,O*-diethyl *S*-(6-chloro-2-oxobenzoxazolin-3-yl)methyl phosphorodithioate] is an insecticide and acaricide introduced in 1963 (Desmoras et al., 1963). It has been used on fruit trees, grapes, corn, sorghum, potatoes, and tomatoes. Development and use of oxadiazon have been primarily in Japan; development of phosalone has been mainly in Europe.

Study of the leaching characteristics of oxadiazon and phosalone was part of a broader investigation concerning their fate in soil and water (Ambrosi and Isensee, 1977; Ambrosi et al., 1977a,b). There is very little information describing their movement in soil. Kittipong (1973) detected no leaching of oxadiazon, surface applied at 4.5 kg/ha, beyond 0–7.5 cm when up to 45 cm of water was added to Crowley silt loam. Oxadiazon penetrated only ca. 2.5 cm into a sand-peat mixture (Ahrens, 1976). Phosalone was apparently more mobile, because it was found at the 30–40 cm depth 20–25 days after 1000 l/ha of a 0.2% solution was applied (Nalbandyan, 1974). By comparison, carbaryl (1-naphthyl methylcarbamate) was observed at a maximum depth of 50–60 cm for 15–20 days after insecticide application.

### MATERIALS AND METHODS

Radioactive pesticides were used in the leaching experiments: [*U*-phenyl- $^{14}\text{C}$ ]oxadiazon (74.7  $\mu\text{Ci}/\text{mg}$ ); [*U*-phenyl- $^{14}\text{C}$ ]phosalone (69.1  $\mu\text{Ci}/\text{mg}$ ); [2,6- $^{14}\text{C}$ ]-methylparathion (*O,O*-dimethyl *O*-*p*-nitrophenyl phosphorothioate) (114  $\mu\text{Ci}/\text{mg}$ ); [2- $^{14}\text{C}$ ]diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] (4.1  $\mu\text{Ci}/\text{mg}$ ); and [*U*-phenyl- $^{14}\text{C}$ ]2,4-D [(2,4-dichlorophenoxy)acetic acid] (0.19  $\mu\text{Ci}/\text{mg}$ ).

Table I shows the soils used and their characteristics. Sterling loam is from Colorado, Benevola silty clay is from West Virginia, and the other soils are from Maryland. Dominant clay minerals are kaolinite and quartz (Lakeland), kaolinite and vermiculite (Norfolk, Hagerstown), illite (Benevola), and montmorillonite (Sterling).

The soil thin-layer chromatographic (soil TLC) method of Helling and Turner (1968) was used to evaluate pesticide mobility. This procedure is also described in the current guidelines for pesticide registrants (U.S. Environmental Protection Agency, 1975a). Four plates per soil were used. To each was applied 2 and 5  $\mu\text{l}$  (0.08 to 0.20  $\mu\text{g}$ ) of oxadiazon, 5 and 10  $\mu\text{l}$  (0.07 to 0.14  $\mu\text{g}$ ) of phosalone, 25  $\mu\text{l}$  (0.13  $\mu\text{g}$ ) of methylparathion, 5  $\mu\text{l}$  (1.95  $\mu\text{g}$ ) of diuron, and 25  $\mu\text{l}$  (132  $\mu\text{g}$ ) of 2,4-D. The spotting order was varied among plates. Autoradiograms were obtained after 8 to

15 days contact with the leached plates.

Concentrated organic solvent extracts, from soil incubated with 10 ppm of oxadiazon and phosalone, were also tested for mobile components. Details of the oxadiazon (Ambrosi et al., 1977a) and phosalone (Ambrosi et al., 1977b) metabolism studies are reported elsewhere. Extract O(6) was from oxadiazon incubated 6 months in Matapeake loam at 75% FMC; this soil was extracted with acetone-methanol, 1:1 (v/v). Phosalone extracts were from Monmouth fine sandy loam: PH(1) represented a 1-month incubation at 75% FMC, then extraction with benzene-ethyl acetate-acetone (1:1:2); PF(1) represented 1-month incubation under flooded conditions, benzene-ethyl acetate-acetone extraction; and PF(3) represented 3-month incubation under flooded conditions, acetone-methanol extraction. Duplicate plates of Lakeland, Sterling, and Hagerstown soils were spotted with oxadiazon (0.20  $\mu\text{g}$ ), phosalone (0.07 and 0.14  $\mu\text{g}$ ), and the extracts O(6), PH(1), PF(1), and PF(3).

Zones from portions of the leached plates were removed and then extracted with 5 ml of methanol. The total soil TLC extracts, after concentration, were applied as single spots to precoated silica gel F-254 TLC plates. Standard and aged oxadiazon were developed with hexane-acetone (60:40). Phosalone samples were developed with ethyl acetate-chloroform-triethylamine (50:50:2.5). Some chromatographically separated components were later scraped from the plates and counted by direct addition to a liquid scintillation solution.

### RESULTS AND DISCUSSION

**Leaching of Standard Pesticides.** The soils used for soil TLC were selected to represent a range of texture, organic matter content, pH, and clay mineralogy characteristics (Table I). All soils except Benevola were previously used to evaluate the mobility of 13 pesticides (Helling, 1971b), and Hagerstown was used additionally in studies with 38 pesticides (Helling, 1971a). Since  $R_f$  values on soil TLC are reproducible, we could reasonably compare the results from the present study with mobilities of these other compounds.

In soil TLC studies, it is judicious to include internal standards. Ideally, these are pesticides whose field and laboratory behavior is well known, whose mobilities on soil TLC plates bracket those of the newer pesticide, and which may be alternative or companion compounds to this pesticide. Methylparathion, diuron, and 2,4-D partially fulfilled the suggested criteria and were used as reference standards. A further advantage is that these three pesticides are among a series of benchmark pesticides proposed by the U.S. Environmental Protection Agency (1976).

Table I. Soils Used and Their Characteristics

Type	Soil		pH	%			
	No.	Subgroup		OM <sup>a</sup>	Clay	Silt	FMC <sup>b</sup>
Norfolk sandy loam	26	Typic paleudults	5.1	0.14	11.3	25.3	6.5
Lakeland sandy loam	51	Typic quartzipammments	6.4	0.90	12.0	16.4	8.5
Sterling loam	13	Typic calcixerolls	7.7	1.64	21.7	29.9	23.8
Hagerstown silty clay loam	48	Typic hapludalfs	6.7	2.10	39.5	44.1	34.1
Benevola silty clay	35	Mollic hapludalfs (typic)	7.2	4.68	43.6	47.4	27.0

<sup>a</sup> Organic matter. <sup>b</sup> Water retention at 1/3-bar pressure (FMC = field moisture capacity); Benevola value obtained by draining excess water from a soil column.

Table II. Mobility of Five Pesticides in Soil TLC Systems

Soil	Average $R_f$ ( $\pm$ SD) of				
	Oxadiazon	Phosalone	Methylparathion	Diuron	2,4-D
Norfolk	0.08 $\pm$ 0.03	0.07 $\pm$ 0.02	0.40 $\pm$ 0.02	0.72 $\pm$ 0.05	0.95 $\pm$ 0.08
Lakeland	0.29 $\pm$ 0.06	0.26 $\pm$ 0.04	0.50 $\pm$ 0.06	0.57 $\pm$ 0.06	0.89 $\pm$ 0.04
Sterling	0.08 $\pm$ 0.01	0.05 $\pm$ 0.01	0.21 $\pm$ 0.01	0.37 $\pm$ 0.01	1.00 $\pm$ 0
Hagerstown	0.04 $\pm$ 0.01	0.02 $\pm$ 0.01	0.14 $\pm$ 0.01	0.22 $\pm$ 0.02	0.85 $\pm$ 0.05
Benevola	0.02 $\pm$ 0	0.02 $\pm$ 0	0.14 $\pm$ 0.01	0.22 $\pm$ 0.02	0.83 $\pm$ 0.08

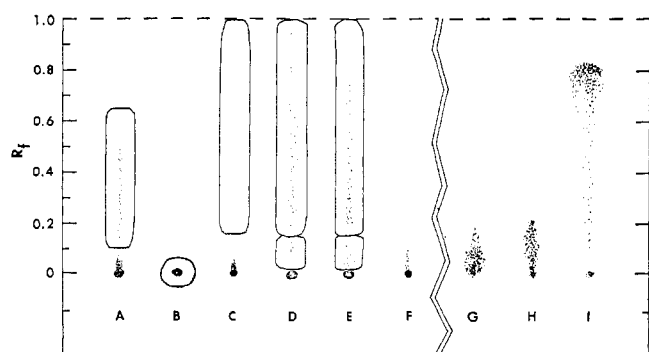


Figure 1. Representation of pesticide movement on Hagerstown soil TLC plates. The samples are: (A) oxadiazon; (B) oxadiazon extract O(6); (C) phosalone; (D) phosalone extract PH(1); (E) phosalone extract PF(1); (F) phosalone extract PF(3); (G) methylparathion; (H) diuron; and (I) 2,4-D. The circled regions were later removed, extracted, and analyzed by conventional TLC.

Table II summarizes the results of the soil TLC analyses. Representation of their movement on Hagerstown soil appears in Figure 1.  $R_f$  values of oxadiazon and phosalone are averages of both rates, because their movement at the higher rate never exceeded 0.01  $R_f$  unit over that of the lower rate, except in Lakeland soil. Oxadiazon and phosalone were essentially immobile in four soils, but were somewhat mobile in Lakeland. Thus, oxadiazon's behavior is consistent with Kittipong's (1973) field observations in a silt loam. Its substantial adsorption by isolated organic matter (Carringer et al., 1975) has been demonstrated. There is a trend to even less movement as soil organic matter increases, except for Lakeland. This apparent anomaly has been recognized previously (Helling, 1971b) and may be related to the much-higher water flux through Lakeland.

Phosalone's leaching was always slightly less than that of oxadiazon. Both phosalone and oxadiazon have very low water solubility, 10 and 0.7 ppm, respectively. This is usually associated with pesticide immobility. Our observations of phosalone movement on soil TLC plates do not seem to match the field results of Nalbandyan (1974). Unfortunately, no information was given as to soil type, rainfall, or irrigation in the abstract of this paper. Earlier (Helling et al., 1971), the  $R_f$  of carbaryl on Hagerstown soil TLC plates was reported as 0.35–0.38. This is much greater than phosalone ( $R_f$  0.02), which seemed to be ca.

half as mobile as carbaryl in the field study (Nalbandyan, 1974).

The reference pesticides facilitate comparison of our present results (Table II) with past soil TLC on the same soils. Previously published (Helling, 1971b)  $R_f$  values of 2,4-D for the Norfolk–Lakeland–Sterling–Hagerstown group were 0.88, 1.00, 0.94, and 0.69, respectively. Except for Lakeland sandy loam, movement of 2,4-D tended to be somewhat higher in the present study. Previously published (Helling, 1971b)  $R_f$  values for diuron were 0.61, 0.60, 0.36, and 0.24, respectively, which compare well with mobilities listed in Table II.

The third reference pesticide, methylparathion, had not been previously analyzed by soil TLC. Methylparathion, parathion [*O,O*-diethyl *O*-(*p*-nitrophenyl)phosphorothioate], and disulfoton [*O,O*-ethyl *S*-2-(ethylthio)ethyl phosphorodithioate] all appeared in the effluent from a gravelly sand loam column (McCarty and King, 1966), yet were incompletely leached even after adding >20 column volumes of water. In more typical agricultural soils, they would likely be far less mobile (Baida, 1970; Harris, 1969; Lichtenstein et al., 1967; Swoboda and Thomas, 1968; U.S. Environmental Protection Agency, 1975b). In previously unpublished research (Helling, 1972, 1973), the  $R_f$  values of parathion and disulfoton were 0.08 and 0.02, respectively, on Hagerstown soil. In other soils, disulfoton was always immobile and parathion movement reached  $R_f$  0.30–0.35 only in sandy soils. The water solubility of methylparathion is ca. twice that of parathion, so it seems reasonable that it would be more mobile than its diethyl homologue, parathion.

**Leaching of Aged Soil Extracts.** Oxadiazon and phosalone are unlikely to be advectively transported any significant distance into soils, except possibly for Lakeland-type profiles. However, metabolism may radically modify a pesticide's polarity and molecular weight. When such degradation products are persistent, the potential for leaching may be enhanced. Therefore, leaching studies with stable metabolites or extracts from aerobically "aged" soil have been suggested (U.S. Environmental Protection Agency, 1975a).

We used a 6-month aerobic extract of oxadiazon and 1- and 3-month aerobic and flooded extracts of phosalone. Aged oxadiazon was immobile (Figure 1), based on autoradiograms exposed for 1 week. Single plates of Lakeland, Hagerstown, and Sterling were exposed again for 6 weeks; these autoradiograms revealed a trace com-

ponent that leached to  $R_f$  0.86 (Hagerstown) to  $R_f$  1.00 (Sterling). This zone was distinctly more mobile than the faint streak seen in standard oxadiazon, but was in too small quantity to identify further.

Aged phosalone was largely immobile, but in addition showed faint, but extensive, streaking. This was greatest for PH(1), which reached  $R_f$  1.0 in Sterling soil. The  $R_f$  value of this streak seemed to decrease in flooded soil extracts, especially with the 3-month sample.

Standard oxadiazon had shown faint streaking far above the dominant movement nearer the origin (Figure 1). Extraction and TLC analysis of this mobile zone indicated oxadiazon predominated, but three-four other components were also present. Their  $R_f$  values in the hexane-acetone system were 0.50 (parent), 0.37, 0.28 (?), 0.24, and 0. We believe the 0.24 component is a known metabolite, 2-*tert*-butyl-4-(2,4-dichloro-5-hydroxyphenyl)- $\Delta^2$ -1,3,4-oxadiazolin-5-one. These components were apparently impurities in the standard oxadiazon or were products of nonbiological breakdown during leaching. The more interesting observation, however, is the demonstration that a trace of relatively immobile pesticide is transported through the soil layer profile. This may occur by: (a) rapid transport of a small portion of solubilized pesticide through larger pores; (b) physical movement (perhaps on the plate surface) of dispersed fine clay particles containing the pesticide; or (c) movement of solubilized organic matter, also containing adsorbed pesticide. It should be emphasized that this streaking represents only a small part of the pesticide residue and may be an artifact of laboratory leaching studies.

Phosalone had trace streaking movement, identified by TLC as the parent, just as oxadiazon did. The combined 1-month aged extracts, from the soil TLC zone associated with phosalone, contained phosalone ( $R_f$  0.68 in the conventional TLC system) and two other components ( $R_f$  0.70 and 0) at a 2:1:1 ratio, respectively. When the mobile streak on soil TLC plates was analyzed, phosalone was present, as expected, but unknown  $R_f$  0.08 and 0 bands also appeared, in the same relative amounts as the parent. The various phosalone unknowns did not correspond with an impurity in the [ $^{14}\text{C}$ ]phosalone standard, nor with the metabolites phosalone-oxon, 6-chloro-2-benzoxazolinone, and 2-amino-7-chloro-3*H*-phenoxazin-3-one (Ambrosi et al., 1977b).

Because of the relatively large amount of soil organic matter extracted from the original aged soils and from soil TLC plates, it is perhaps not unreasonable to attribute some immobility (perhaps in both soil and silica gel) to pesticide association with nonmobile organic fractions. This may be particularly true in oxadiazon extract O(6).

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