Behavior of Aldicarb in Soil Relative to Control of Heterodera schachtii[1]

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Abstact: The adsorption characteristics of two soils for aldicarb sulfoxide were similar to that described by the Freundlich equation. The adsorption constant for the Holtville clay was 3.3, and that of the Buren silt loam, 0.34. Planting beds in a field of Holtville clay and another of Buren silt loam were side-dressed at 25 kg and 50 kg/ha 10% aldicarb (Temik® 10G). Comparison of field measurements of aldicarb concentrations with previous laboratory determinations of aldicarb effects on *Heterodera schachtii* allowed predictions of soil zones in which hatching, infectivity, and orientation of males to females would be affected. Aldicarb in the soil water of Holtville clay sufficient to interfere with male orientation extended through most of the bed profile to a depth of 46 cm 1 week after the first irrigation. Orientation could be affected in only the top 20 cm of the bed 37 days after treatment and application of 712 mm of irrigation water. In Buren silt loam, disorientation of males was estimated to occur throughout the bed 42 days after treatment and 600 mm irrigation water. Aldicarb persisted in extensive areas of the bed at concentrations sufficient to prevent infection. In small areas of the profile, aldicarb sufficient to inhibit hatching persisted. Amounts of aldicarb in soil water samples obtained directly from beds agreed well with those from the analysis of the air dried soil samples. *Key Words:* nematicide, adsorption isotherm, movement, persistence.

The behavior of nonfumigant-type nematicides in soil has not been investigated as thoroughly as that of the fumigant-type nematicides. The persistence of various organophosphate and carbamate nematicides has received considerable attention, (4) but little data are available on the movement of these pesticides in soil. These nematicides of low volatility move mainly by mass transfer in soil.

Soil chemical and physical characteristics, and the amount of rainfall and/or the method of irrigation, are important factors which govern the movement and persistence of the

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nematicides. Appreciable effort has been made in recent years to determine the factors which regulate the movement and persistence of pesticides in soil. Some of this information is now being applied to the problem of environmental contamination. Unfortunately, little of this data has been used in predicting biological performance of pesticides (7).

Nematodes are aquatic animals and they are subjected to pesticides in soil water. It would therefore be valuable to know how much of a nematicide is present in the soil water, and how it is distributed in the soil profile. With toxicological data at hand, as well as knowledge of the relative amount of pesticide in the soil water versus that absorbed to the soil phase, one should be able to estimate the degree of control afforded by a given pesticide based on the analysis of the pesticide in soil samples.

The behavior of many pesticides appears to be largely governed by the adsorption characteristics of the soil. One of the methods frequently used to describe the magnitude of adsorption of a pesticide is the adsorption isotherm.

The objectives of this study were: to determine the adsorption of aldicarb sulfoxide in a clay soil and a silt loam; to use the adsorption data to estimate the amount of aldicarb present in soil water; and to predict the effects of aldicarb in the soil water on nematodes as it relates to control from available toxicological data.

MATERIALS AND METHODS

Adsorption isotherms: Aqueous stock solutions which contained 50 and 500 μg aldicarb sulfoxide per ml solution were prepared. Standard aldicarb sulfoxide solutions were prepared from these stock solutions to obtain concentrations of 0.1, 0.3, 1.0, 3.0, 10.0, and 100.0 μg/ml in 0.01M $CaCl_2$.

The physical and chemical properties of the Holtville clay and Buren silt loam are presented in Table 1. In order to determine the adsorption characteristics of the two soils, a slurry was obtained by mixing 20 g dry (60 C, 72h) soil, the adsorbent, with 20 ml of the prepared aldicarb sulfoxide solutions. The slurry was shaken for 8 h in centrifuge tubes at 22 C to equilibrate the aldicarb sulfoxide in the adsorbent and solution phases. The adsorbent and solution were separated by

TABLE 1. Physical and chemical characteristics of two soils used in experiments to evaluate the behavior of aldicarb in soils relative to the control of *Heterodera schachtii*.

Soil series	Mechanical Analysis			Organic matter (%)	pH[a]	C.E.C. (me/100 g)
	Sand (%)	Silt (%)	Clay (%)			
Holtville clay	6.4	42.1	51.5	1.4	7.6	32.7
Buren silt loam	37.7	51.3	11.0	1.4	7.2	10.8

[a]Soil pH was measured in a soil slurry at 61% saturation for the Holtville clay and at 39% for the Buren silt loam.

TABLE 2. Dates (1973) for aldicarb (Temik® 10G) application, irrigation, soil sampling, and soil water sampling from experimental plots in El Centro (Holtville clay) and Riverside (Buren silt loam).

	Holtville Clay	Buren silt loam
Aldicarb application:	7 May	11 July
Irrigation:		
1st	12-13 May	11 July
2nd	22 May	24 July
3rd	6 June	9 August
Soil sampling:		
1st	20 May	18 July
2nd	29 May	1 August
3rd	13 June	22 August
Soil water sampling:		
1st	24 May	13 July
2nd		12 August

centrifugation for 20 min at 22 C. A 10-ml aliquant of the solution phase was analyzed for aldicarb sulfoxide and the amount of nematicide adsorbed per gram adsorbent was calculated from the determined equilibrium concentration of the solution. The aldicarb removed from solution was assumed to be adsorbed. The amount of aldicarb sulfoxide

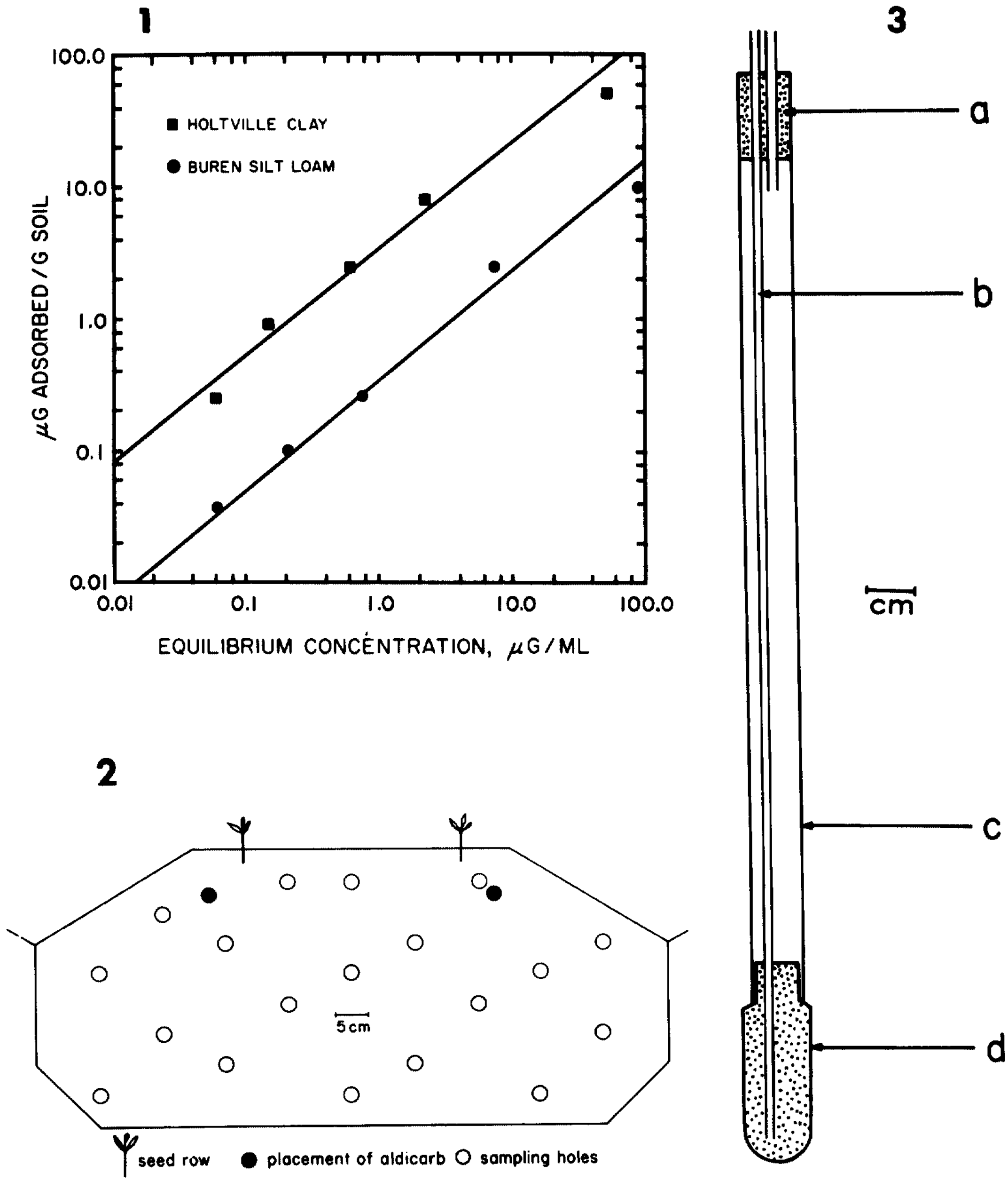

FIG. 1-3. 1) Freundlich adsorption isotherms of aldicarb sulfoxide for a Holtville clay and Buren silt loam. The aldicarb sulfoxide in 0.01M $CaCl_2$ was equilibrated with the soil for 8 h at 22 C. A 1:1 adsorbent-solution ratio was used. 2) Steel soil sampling template, with holes through which horizontal soil samples were taken for analysis. The plate was driven into the profile of the sugarbeet bed, the soil was removed from one side of the plate, and samples were taken from each of the holes with a soil-sampling tube. Position of seedrow and placement of aldicarb (Temik® 10G) are illustrated. 3) Soil water sampling tube. Legend: (a) rubber stopper, (b) vinyl tube, (c) polyethylene tube, (d) ceramic (tensiometer) cup. The tube is pushed into wet soil, a vacuum is created, and the tube is left in place for 12 h to allow the soil solution to pass through the porous wall of the ceramic cup.

adsorbed per gram adsorbent was plotted against the equilibrium concentration of the solution on a log-log scale (Fig. 1).

Field application of aldicarb: The experimental plots were ploughed to a depth of 20-30 cm, disked, and leveled. The beds measured 105 cm from center to center and were shaped with mechanical bed shapers. The top of the beds were 51-56 cm across. The irrigation furrows were approximately 15 cm deep.

A field of Holtville clay at El Centro, California, and a Buren silt loam at Riverside, California, were side-dressed with a granular formulation of aldicarb, Temik® 10G, using a tractor-drawn Noble® applicator. Aldicarb was applied at both sides of the beds about 2.5 cm to the inside of the shoulder of the beds to a depth of 7.5 cm (Fig. 2). There were three treatments, 0.0, 2.5, and 5.0 kg aldicarb/ha. Each treatment used two beds 10 m long and was replicated three times in randomized complete blocks.

Irrigation of the experimental plots was by furrow irrigation. The normal irrigation schedule of the grower for the field at El Centro (Holtville clay) was followed where 1 day's irrigation was equivalent to approximately 178 mm of water. The Holtville clay was dry during the period from aldicarb application to irrigation. The plot at Riverside (Buren silt loam) was irrigated similarly, but metal gates were installed in order to raise the level of the water in the furrows since the slope of this field would have been too great to wet the beds properly. One day's irrigation in this case was equivalent to 200 mm of water. The irrigation schedule for the field plots is given in Table 2 along with the schedule for when soil and soil water samples were taken for chemical analysis of aldicarb and its sulfoxide and sulfone derivatives. Soil temperature at different depths was recorded during the experiment.

Soil sampling procedures: Soil samples were taken from the two experimental plots as follows: steel plates were constructed to conform to the sugarbeet bed configuration; 19 3.2-cm diam holes were drilled in plates to give a systematic pattern through which soil samples were taken (Fig. 2); the plates were driven vertically into the beds, the soil was removed from one side of the plates, exposing the holes in the plates; and soil samples were taken horizontally and parallel with the direction of the beds to a depth of 46 cm by pushing an Oakfield sampling tube (2.5-cm diam) into the soil through the holes in the plates.

The soil samples were placed in plastic bags labeled and stored at −15 C. Following storage, all samples were air-dried on plastic sheets in a greenhouse at a temperature of approximately 27-40 C for 3 days. The soil was pulverized and sieved through a 3-mm screen to remove large stones and organic debris. A composite sample of the three replicates was made. Fifty grams of each sample were weighed and kept in a plastic bag at −15 C until extracted and analyzed for aldicarb and its cholinesterase-inhibiting analogs (the total amount of aldicarb, aldicarb sulfoxide, and aldicarb sulfone was analyzed by a method supplied by Union Carbide Corporation, utilizing a gas chromatograph equipped with a flame detector). Following removal of soil samples for pesticide analysis, a similar number of soil samples were taken according to the pattern of holes in the steel plates for bulk density and water content measurements. Data from the three replicates of each treatment were averaged.

Soil water sampling procedures: Polyethylene tubes fitted with ceramic cups were constructed to facilitate the sampling of water in the soil (Fig. 3). The tubes were pushed into place at different depths in the seedrow shortly after irrigation when the soil was still fluid. At sampling time, a tension of 80 centibars was pulled in the tubes with a hand vacuum pump. The tubes were sealed to maintain the vacuum for 12 h during which time the soil water from the surrounding area moved through the ceramic cup and into the tubes. The water samples were obtained by removing the tubes from the soil, the soil solution was drained into 60-ml polyethylene bottles, and kept at −15 C until analyzed for aldicarb and its cholinesterase-inhibiting analogs. Water samples from the three replicates of each treatment were analyzed separately.

RESULTS AND DISCUSSION

The log-log plot of the adsorption isotherms obtained with aldicarb on the Holtville clay and Buren silt loam (Fig. 1) are straight lines indicating that the adsorption of aldicarb sulfoxide conforms to the Freundlich equation where:

$$x/m = KC^{1/n} \quad \text{(eq.-1)}$$

x/m = amount of aldicarb sulfoxide adsorbed per given amount of adsorbent (μg/g), C is the equilibrium concentration of the adsorbate in solution (μg/ml), and K and n are constants. The Freundlich K value can be determined graphically as the intercept where the equilibrium concentration equals 1 μg/ml since:

$$\log x/m = 1/n \log C + \log K \quad \text{(eq.-2)}$$

With the equilibirum concentration at 1 μg/ml the equation reduces to log x/m = log K. The Freundlich K value for aldicarb sulfoxide is 3.3 for the Holtville clay and 0.34 for the Buren silt loam. These K values indicate the adsorption of aldicarb sulfoxide is considerably greater by the Holtville clay than by the Buren silt loam.

The Freundlich constants determined from the adsorption isotherm studies were used to calculate nematicide concentrations in the soil solution, C, in the field from the total nematicide analyzed on the dry soil samples. To facilitate the calculations, the value of 1/n was assumed to be one (unity). This would appear to be a reasonable assumption over narrow concentration ranges. When 1/n approaches one (unity) the Freundlich equation is reduced to the linear isotherm:

$$x/m = KC \quad \text{(eq.-3)}$$

The analysis of the field soil samples gives, C_T (μg/g), the total aldicarb plus its sulfoxide and sulfone concentrations on an air-dry soil basis. It is necessary to express all concentrations on a total soil volume basis, so values will be comparable. This yields the

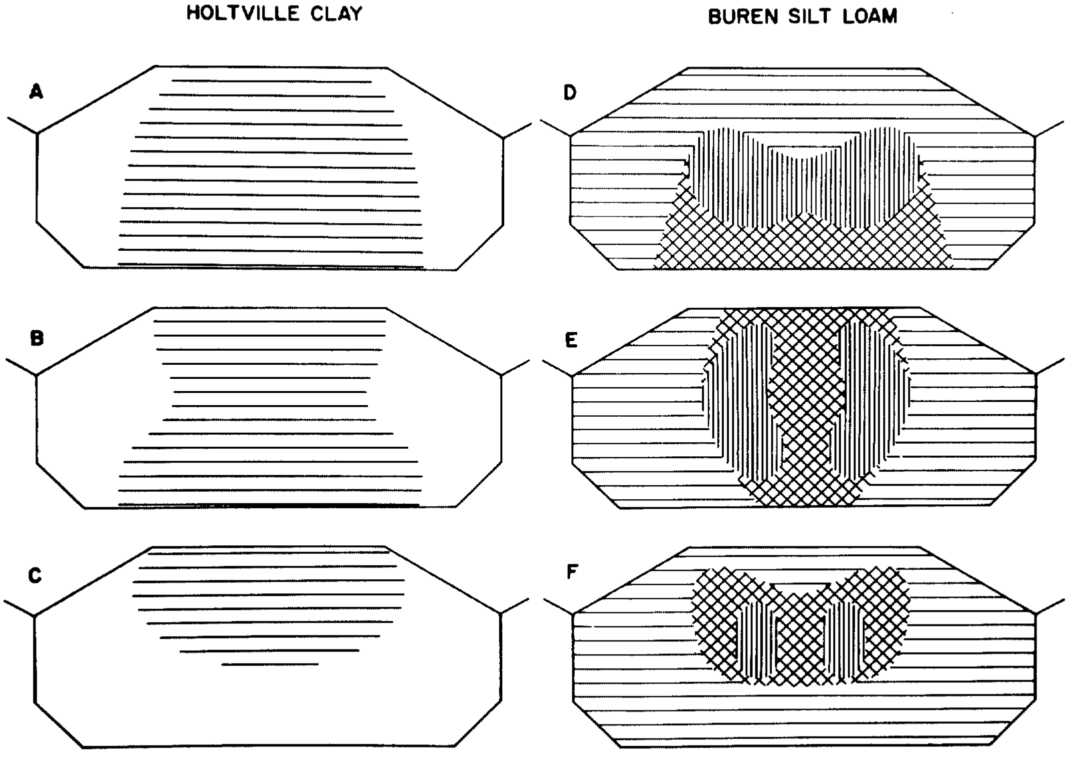

FIG. 4. Diagram of a vertical section of a sugarbeet bed, indicating areas in the profile where 0.01 μg/ml (horizontal lines), 1.0 μg/ml (cross hatched lines), and 5.0 μg/ml aldicarb sulfoxide (vertical lines) occurred in the soil water. [These concentrations of aldicarb sulfoxide (0.01, 1.0, and 5.0 μg/ml) corresponded to areas where orientation of males to females of *Heterodera schachtii* might be disrupted, infection by larvae inhibited, and hatching of eggs inhibited, respectively]. A, B, and C are 13, 22, and 37 days after treatment and application of 356, 534, and 712 mm of irrigation water, respectively. D, E, and F are 7, 21, and 42 days after treatment and application of 200, 400, and 600 mm irrigation water, respectively.

following relationship between the total soil pesticide concentration, C_T, the equilibrium solution concentration, and the amount adsorbed:

$$\beta C_T = \beta\,(x/m) + C\theta \qquad \text{(eq.-4)}$$

where β = soil bulk density (g/cc total soil) and θ = volumetric soil water content (g/cc total soil) = β times the soil water content (w/w). Substitution of equation 3 in 4 gives

$$C\theta = \frac{\beta C_T}{1 + (\beta K/\theta)} \qquad \text{(eq.-5)}$$

which gives the solution concentration on a total-soil-volume basis. Dividing the quantity $C\theta$ by θ yields the solution concentration in units of μg per ml of soil solution. Equation 5 was used to calculate aldicarb sulfoxide concentrations, C, in the field soil solutions. The gravimetric soil moisture content was 29.2% for the Holtville clay and 16.9% for the Buren silt loam 1 week after the second irrigation in each of the fields. It must be noted that the chemical analysis of the soil samples from the experimental plots did not discriminate between aldicarb, aldicarb sulfoxide, and aldicarb sulfone; however reports in the literature (1, 2, 3) suggest that aldicarb sulfoxide comprises the bulk of the toxic metabolites of aldicarb in soil. That is also the reason why the adsorption characteristics of the soils were determined for aldicarb sulfoxide.

The toxicological data developed by Hough and Thomason (6) indicated that hatching of the sugarbeet cyst nematode, *Heterodera schachtii* Schmidt, is inhibited at approximately 5.0 μg/ml aldicarb in water, larval movement and infection are impaired at 1.0 μg/ml, and orientation of males to females is disrupted at 0.01 μg/ml. This information was used to determine those areas in the soil profile in which various effects of aldicarb could be operative over a period of time. The approximate zones in the soil profile where concentrations of aldicarb in the soil solution, having various behavioral effects on nematodes, might occur were determined and illustrated. Figures 4-A, B, C represent the potentail area of action of aldicarb in the Holtville clay. The data in these figures are based on soil solution concentrations as determined from adsorption data, soil analysis (Fig. 5), and equation 5. Data illustrated for both fields are for rates of 5.0 kg aldicarb per ha.

Little aldicarb and toxic derivatives were found in the Holtville clay after 13 days (Fig. 4-A). This could be due to the adsorption characteristics of the clay as well as leaching of the aldicarb by 356 mm irrigation water. The areas next to the furrows did not have enough residual aldicarb to interfere with male orientation to females of *H. schachtii*, and the aldicarb concentrations in the soil water did not reach levels anywhere in the soil profile where hatching or infectivity would be expected to be inhibited. A biological assay conducted in the field to a depth of 15-20 cm, confirmed this prediction (5). The soil water sample analysis also indicate that hatching and infectivity should not be affected (Table 3). Soil samples taken 22 days after treatment and after application of another 178 mm of

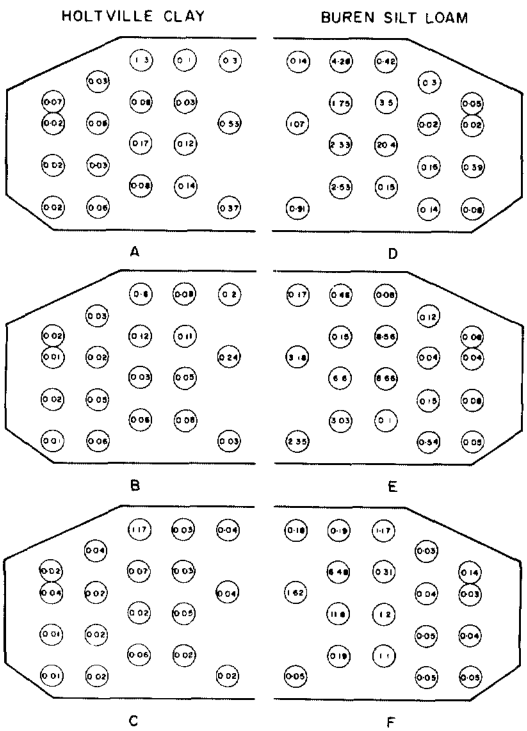

FIG. 5. Total aldicarb (sulfoxide and sulfone derivatives) concentrations (μg/g in dry soil) in the bed profile of two soils. The beds were side-dressed at the rate of 5.0 kg/ha aldicarb. Data are given according to symmetrical transpositions of the 19 soil sample locations as illustrated in Fig. 2. Values are means of three replications. For an explanation of A through F see Fig. 4.

TABLE 3. Concentration of aldicarb (Temik® 10G) and total cholinesterase-inhibiting analogs in soil water (μg/ml) sampled at various depths in two soils.

Application rate (kg/hectare)	Aldicarb concn in soil water at various depths under seedrow (cm)						
	Holtville clay[a]				Buren silt loam		
	10	20	30	50	10	30	50
25	0.13	0.16	0.20	0.03	0.17	5.30	0.57[b]
					1.20	3.50	0.10[c]
50	0.71	0.28	0.18	0.10	1.42	18.75	1.17[b]
					0.5	8.4	1.60[c]

[a]Samples taken 17 days after chemical application and addition of 534 mm of irrigation water.
[b]First samples taken 2 days after chemical application and addition of 200 mm of irrigation water.
[c]Second samples taken 32 days after chemical application and addition of 600 mm of irrigation water.

water, revealed that the total area in the soil profile where male behavior might be affected, was reduced (Fig. 4-B). The area in the soil profile where male orientation could be affected, decreased even more 37 days after treatment and was limited to the upper parts of the soil profile at the center of the beds (Fig. 4-C). These data were obtained from soil samples taken after the field was irrigated with a total of 712 mm water. Most of the aldicarb was degraded by this time to a level where it had no adverse effect on *H. schachtii*. Soil temperatures during this period were high in the Holtville clay with a mean maximum and minimum of 25.4 and 23.2 C at 30-cm depth, and this probably increased the degradation of the pesticide in this clay soil. The pH of the Holtville clay was 7.6, which is below the levels at which significant alkaline degradation of aldicarb would occur.

The behavior of aldicarb was quite different in the Buren silt loam. Figure 4-D shows that the entire bed profile has an estimated concentration of aldicarb in the soil water that exceeded 0.01 μg/ml 7 days after application of Temik 10G and after 200 mm irrigation water. Male orientation toward females would be expected to be disrupted throughout the soil profile. A substantial area of the soil profile had concentrations higher than 1.0 μg/ml, which would inhibit infection by *H. schachtii*. It must be noted that a considerable amount of aldicarb leached toward the center of the bed. The movement of the aldicarb was downward and towards the center of the bed, indicating that it moved by mass transfer in the water. A substantial area in the soil profile with aldicarb concentrations in the soil solution higher than 5.0 μg/ml persisted. This area was below the seedrow and could be important in inhibiting hatch temporarily.

Considerable redistribution of aldicarb took place after another 200 mm of water was used to wet the soil (Fig. 4-E). The soil samples were taken 21 days after application of aldicarb. Aldicarb concentrations which would disorient males persisted through the entire profile. The areas where infectivity would be impaired redistributed more towards the surface of the soil. The areas containing excess of 5.0 μg/ml redistributed upwards and toward the sides of the profile.

A third set of soil samples was taken 42 days after application of aldicarb and after the field received a total of 600 mm irrigation water. The areas in the soil profile where the soil water concentration exceeded 1.0 and 5.0 μg/ml had diminished but persisted in the center areas of the soil profile (Fig. 4-F). Concentrations which will affect males, however, were found to persist throughout the profile. Soil temperatures during this experiment were also high, with a mean maximum of 29.6 C and minimum of 21.2 C at the 30-cm depth.

The most striking difference between the clay and the loam soil was the higher concentration and greater persistence of aldicarb in the silt loam than in the clay. The soil organic matter content, pH, salinity, and temperatures of the two soils were very similar. The adsorption characteristics of the soils were assumed to be major factors which determined the fate of aldicarb in the soil. However, significant differences in soil biological activity are known to affect persistence of pesticides and was not eliminated in these trials.

Fifty-three soil water samples were taken in an attempt to estimate the concentration of aldicarb in the soil water more directly. The soil water was recovered from the vicinity of the ceramic cup, but the exact volume of the soil profile sampled could not be determined.

These samples were analyzed for total aldicarb, aldicarb sulfoxide, and aldicarb sulfone (Table 3). Much less aldicarb was present in the soil water from the Holtville clay than from that of the Buren silt loam. This is in agreement with data calculated from the adsorption isotherms. The concentrations of aldicarb measured in the soil water samples agreed closely with that calculated for the soil water on the basis of analysis of air-dried soil samples. Soil water samples were taken within 2-3 days after irrigation, whereas the soil samples were taken 6-12 days after irrigation. Redistribution of aldicarb could have occurred in the profile, and may account for the differences in aldicarb concentrations between the soil water samples and soil samples taken from a similar location in the soil profile. Nevertheless, the data from the soil water samples add support to the hypothesis concerning the manner by which aldicarb affected the nematodes in the soils during the period of investigation.

There are many physical, chemical, and biological factors which govern the movement and persistence of a pesticide in soil. We have not considered all of them; however, it seems possible to make a reasonably accurate prediction of the biological performance of this pesticide in soil with the information obtained.

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