

Mobility and Persistence of Metolachlor and Aldicarb in Field Lysimeters

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ABSTRACT

The mobility and persistence of metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide], a herbicide, and aldicarb [2-methyl-2-(methylthio)propanaldehyde O-(methylcarbamoyl) oxime], an insecticide, were studied using field lysimeters containing 15 cm (diam.) by 70 cm (length) cores of Plainfield sand (mixed, mesic Typic Udipsamments). One-half of the cores received only rainfall, while the remainder received rainfall plus simulated 50.8-mm rainfalls on the second and eighth days after treatment, followed by simulated irrigation for the duration of the study. Metolachlor exhibited limited mobility, except in the supplementary watering treatment, in which there was rapid transport of some herbicide 40 cm down the core, with accompanying traces in the effluent. Metolachlor half-life was in the 3- to 4-wk range. Aldicarb rapidly converted to its sulfoxide [2-methyl-2-(methylsulfinyl)propanal O-(methylamino)carbonyl oxime] and sulfone [2-methyl-2-(methylsulfonyl)propanal O-(methylamino)carbonyl oxime] (50% in 3-5 d). Under normal rainfall, about 9% of the applied aldicarb leached out of the soil cores as sulfoxide or sulfone. In cores receiving supplementary watering, up to 64% of applied aldicarb appeared in the effluent principally as sulfoxide or sulfone.

Many different approaches to field persistence and mobility studies have been employed, ranging in scope from watershed studies (Norris et al., 1984) down to lysimeters (Fuhr, 1985) or soil columns (Leistra et al., 1976). The size of experimental area and the monitoring intensity selected for a study are influenced by the type of data required (accuracy, precision, detail). For example, many more detailed measurements are usually necessary for modeling studies than for routine monitoring situations.

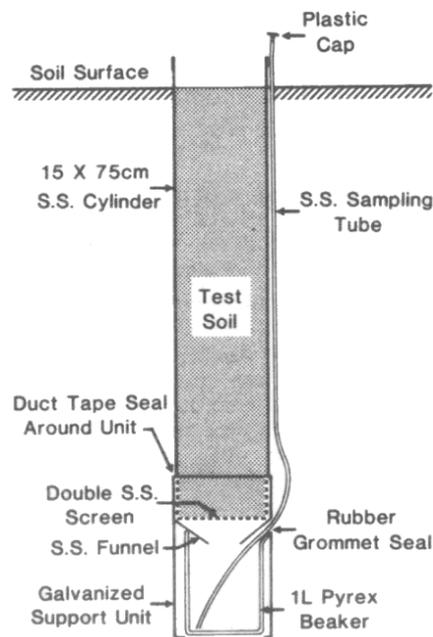
Field mobility studies are used routinely in pesticide screening and registration programs as a follow-up to laboratory studies that have identified potentially mobile compounds. Although these studies offer the advantage of examining pesticide behavior under field conditions, it is impossible to fully account for the disposition of mobile compounds that move below the soil-core sampling zone. A problem with field studies is the difficulty in predetermining how deep to take soil cores to include all of a mobile pesticide within the sampling zone. It is unrealistic to routinely take soil cores much below 30 to 40 cm because of soil penetration problems during dry summer months.

It was the objective of this study to evaluate a field replicated lysimeter system that would provide detailed mobility data not normally obtained with field plot techniques, as well as to provide soil persistence data for pesticides comparable with that obtained in field plot studies. Experimental conditions were created in some treatments to enhance pesticide transport in the lysimeters by using sandy soil cores that received two 50.8-mm water applications during the week after pesticide application, followed by a simulated irrigation program for the remainder of the study. Compounds that exhibit only limited mobility under such adverse conditions may not need much further field testing to ensure their environmental safety. Two commonly used pesticides, aldicarb [2-methyl-2-(methylthio)propanaldehyde O-(methylcarbamoyl) oxime], a highly mobile insecticide, and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide], a slightly mobile herbicide, were selected to evaluate the technique. The toxic mobile metabolites of aldicarb, aldicarb sulfoxide [2-methyl-2-(methylsulfinyl)propanal O-(methylamino)carbonyl oxime] (ALD.Sx.) and aldicarb sulfone [2-methyl-2-(methylsulfonyl)propanal O-(methylamino)carbonyl oxime] (ALD.Sn.), were also monitored throughout the study.

MATERIALS AND METHODS

LYSIMETER UNIT

The mobility and persistence of aldicarb and metolachlor were obtained with field lysimeters that consisted of a 15 cm (diam) by 75 cm (length) stainless steel cylinder set into a support unit housing a 1-L Pyrex beaker, used for collecting effluent (Fig. 1). Each lysimeter was packed with a 70-cm core of Plainfield sand (mixed, mesic Typic Udipsamments). Lysimeters were buried in a sand-filled enclosure to within 5 cm of the top of the unit. Effluent was removed from the collection beaker below the soil core via a 0.48 cm i.d. stainless steel tube. In the 1985 studies, persistence data were obtained from 15 by 70 cm Plainfield sand cores packed into the stainless steel cylinders and buried in the ground (no base units). Effluent and mobility data in 1985 were obtained from soil cores in complete lysimeter units buried in the sand-filled enclosure.



S.S. = Stainless Steel

Fig. 1. Schematic representation of effluent-collecting field lysimeter.

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Received 12 Feb. 1987. * Corresponding author.

Published in *J. Environ. Qual.* 17:689-694 (1988).

PESTICIDE APPLICATION

The maximum recommended field-application rate for metolachlor (DUAL[®]960E) was 2.75 L/ha (OMAF, 1985a), equivalent to 5.27 mg/core. The required amount of EC product in a 10-mL aqueous aliquot was applied to the surface of each soil core. The maximum recommended rate for granular aldicarb (TEMIK[®]10G) was 200 g/100 m of row (OMAF, 1985b). Assuming a band width of 20 cm, the treatment rate represents 0.1 mg a.i./cm² on a cross-sectional column area of 177 cm², or 17.7 mg a.i./core. Aldicarb granules were applied in a uniform layer 2.5 cm below the core surface. The treated area of each soil core was kept at least 1 cm away from the cylinder walls to minimize "leakage" of the chemicals down the outside of the soil core.

SOIL CORE PREPARATION

Plainfield sand, used throughout the 1985 and 1986 leaching studies, contained 91.5% sand, 1.5% silt, and 7% clay, with an organic matter content of 0.7%. It was stored outside over-winter and was coarse-screened (1-cm sieve) and slightly air-dried until it flowed without caking. The lysimeters (packed to 70 cm mark) held approximately 18 kg (oven-dry basis) of soil. Four liters of water were leached through each packed unit to promote settling, and additional soil was added as necessary to maintain the level 5 cm below the top of the cylinder. The lysimeters were allowed to equilibrate for about 2 wk after packing before the cores were treated. On the day preceding pesticide application, 1 L of water was added to each core, which was then capped until treatment time to prevent evaporative losses. The water application allowed cores to start the study in a near-saturated condition, thereby making it easier to establish an accurate water balance.

RAINFALL/SUPPLEMENTARY WATERING PROTOCOL

In both years, one-half the soil cores received rainfall. In 1985, the remaining lysimeters received rainfall plus supplementary water, simulating an irrigation schedule in which a 20-mm water application was made.

1. Three days following < 10 mm rainfall
2. Four days following 10 to 20 mm rainfall or last watering
3. Five days following 20 to 30 mm rainfall
4. Six days following > 30 mm rainfall

In 1986, the remaining lysimeters received rainfall plus supplementary water to simulate two 50.8-mm rainfalls, on Day 2 and 8. A search of local weather records over the past 50 yr showed several instances where rainfalls of this magnitude occurred during late May or early June. After the second week, 25-mm water applications were made:

1. Two days following <10 mm rainfall
2. Three days following 10 to 25 mm rainfall
3. Four days following > 25 mm rainfall, or the last watering

EFFLUENT SAMPLING

On the morning following either a rainfall or watering, a 1-L vacuum flask with portable vacuum pump was used to transfer effluent from the collection beaker below the lysimeter to glass storage bottles. Effluent volumes were recorded and subsamples were centrifuged at 43 000 x g for 10 min to remove suspended material.

REMOVAL OF LYSIMETERS FROM FIELD SITE

Duplicate lysimeters from each treatment were removed from the field site after 1, 2, 4, 8, 12, and 21 wk. After lifting intact lysimeter units from the sandbox with the aid of a tractor-loader, the base support units were removed and the soil cores were capped and placed inside plastic bags for storage in the freezer.

PREPARATION OF SOIL CORES FOR ANALYSIS

A heat gun was used to warm the stainless steel cylinder sufficiently to allow the soil core to be ejected into a plastic bag. It was then sectioned into seven 10-cm segments using a band-saw. These segments were placed into plastic bags, weighed, and then allowed to thaw out before being thoroughly mixed and subsampled for pesticide and moisture analysis.

ZERO-DAY RECOVERY PROCEDURE

Lysimeters could not be removed from the field site immediately following pesticide application because of limited space and number of units. Instead, the efficiency of the analytical procedures were estimated using the same rate of pesticide applied to triplicate 2600-g lots of moist Plainfield sand inside plastic bags (soil weight comparable to top 10-cm core segment). The bags were sealed, equilibrated for 1 h, and then extracted following the standard procedure. (The initial persistence data point in Fig. 5, 9, 10, and 11 was taken to be the fraction recovered from the lab-fortified samples.)

EXTRACTION AND ANALYSIS

High pressure liquid chromatography (HPLC)-grade methanol (100 mL) was added to a 100-g soil sample (in duplicate) in a 250-mL screw-capped glass bottle that was tumbled for 40 min. The slurry was filtered using a vacuum Buchner funnel and the soil pad was washed with three 25-mL methanol washes, all of which were transferred to a 200-mL volumetric flask and made to volume. The resulting filtrate was diluted, or concentrated by rotoevaporator if necessary, and centrifuged at 43 000 x g for 10 min to remove suspended materials prior to analysis. All analyses were done by reversed-phase HPLC, using a 15.0 cm by 3.9 mm Waters 5µm spherical particle C18 column. Detection was by UV spectrophotometer at 200 nm. The carrier solvent composition (acetonitrile/water) and flow rates (mL/min) for metolachlor, aldicarb, and ALD.Sx./Sn. were, respectively, 55:45, 1.7; 35:65, 1.5; 13:87, 1.4.

Table 1. Water balance statistics for lysimeters in 1986, grouped by precipitation treatment and by termination data. †

Week no.	Precipitation received, mL	Avg. effluent volume, mL	Average water loss			
			Fraction	SD	Range	
			Min.	Max.		
<u>Cores receiving supplementary water</u>						
1	1 960	1 483	0.243‡	0.026	0.220	0.285
2	3 179	2 711	0.147	0.003	0.142	0.151
4	4 344	3 170	0.270	0.003	0.268	0.274
8	7 960	5 145	0.354	0.011	0.344	0.372
12	11 267	6 603	0.414	0.047	0.365	0.464
21	19 262	12 199	0.367	0.008	0.354	0.374
<u>Cores receiving natural rainfall</u>						
1	1 060	633	0.403‡	0.032	0.358	0.436
2	1 379	1 007	0.269	0.038	0.221	0.304
4	1 644	1 020	0.379	0.017	0.365	0.402
8	3 910	1 933	0.506	0.021	0.470	0.522
12	6 317	2 857	0.548	0.004	0.544	0.552
21	12 512	6 112	0.511	0.025	0.471	0.537

† Effluent data for four cores are averaged for each effluent volume and fractional water loss value shown.

‡ Higher fractional water loss for week 1 was anomalously high because cores were not totally saturated at treatment time.

Minimum detectable concentrations using 40- μL injection volumes were approximately 10 to 25 $\mu\text{g/L}$ for all compounds. All carrier solvents were degassed and filtered through 0.7- μm glass microfiber filters. Peak areas of HPLC responses of metolachlor, aldicarb, ALD.Sx., and ALD.Sn. were evaluated by a computing integrator using external standard solutions.

RESULTS AND DISCUSSION

The variability in fractional water losses among lysimeters, shown in terms of both standard deviation and range (Table 1), seem quite acceptable. Observed water losses after the first week appeared anomalously high because the cores were not fully saturated at treatment time. Although water losses were considerably greater for cores receiving supplementary water, average standard deviations were very similar for the two moisture regimes, viz. 0.025 vs. 0.023 for supplementary water and rain-fall, respectively. The average range was greater for rainfall cores (0.056) than for supplementary watered cores (0.038), which is to be expected since moisture extremes would have been less for the watered cores. These water losses were an important factor in reducing net downward water flow and hence pesticide transport. These values appear to be in agreement with Beese and Wierenga (1980), who stated that evaporative water losses can reduce net leaching by up to 40% or more under field conditions.

Metolachlor

Although metolachlor is a moderately water-soluble compound (530 $\mu\text{g/mL}$; Worthing, 1983), which might be expected to exhibit some mobility in a light-textured soil, no movement below 10 cm was observed in Plainfield sand cores during 1985 field studies. The soil-water partitioning coefficient for metolachlor in Plainfield sand was $0.7 \mu\text{g}^{1-N} \text{g}^{-1} \text{mL}^N$, where N = the Freundlich isotherm slope (unpublished data, this laboratory). These cores used only the upper cylinder portion of the lysimeter unit, being directly interfaced with loam field soil below and receiving only rainfall (Fig. 2), totalling 386 mm from 14 May to 8 October. All leaching studies in 1986 used complete lysimeter units. With almost double the 1985 rainfall (Fig. 3), only limited movement of metolachlor occurred (20 cm max.) in those soil cores receiving rainfall (Fig. 4A). The first water application (50.8 mm) on the day following treatment produced almost immediately downward transport of metolachlor (40 cm max, Fig. 4B). Small amounts of metolachlor appeared in the effluent during the week following the first 50.8-mm water application but not thereafter. In total, amounts appearing in the effluent from the

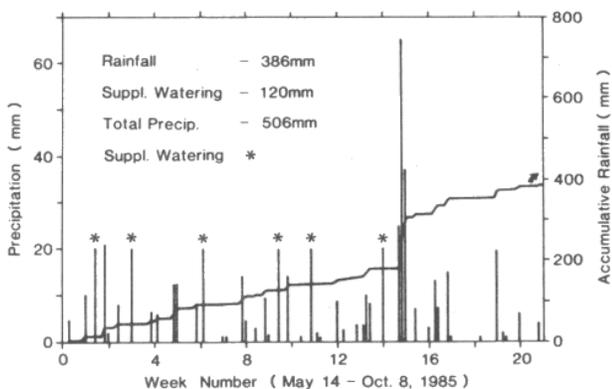


Fig. 2. Daily precipitation and accumulative rainfall records for London Research Centre, 1985. Includes supplementary watering.

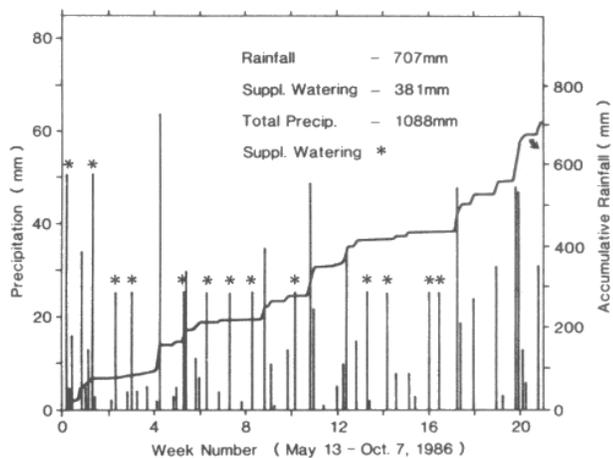


Fig. 3. Daily precipitation and accumulative rainfall records for London Research Centre, 1986. Includes supplementary watering.

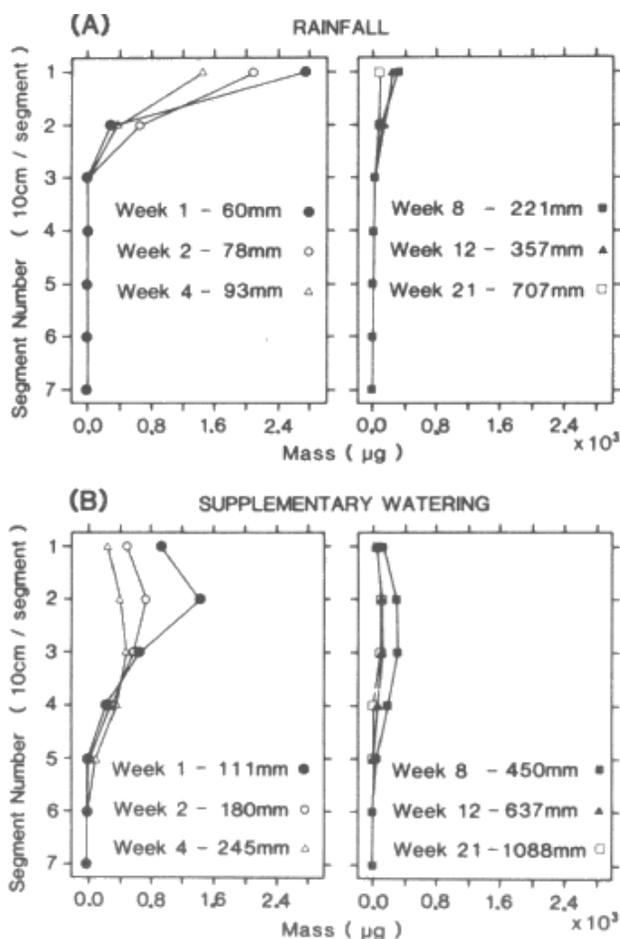


Fig. 4. Metolachlor mobility and dissipation in field lysimeters containing Plainfield sand, 1986. A. Received only rainfall, B. Received supplementary water.

12 replicate cores were small (range: 0.3-28 μg ; total applied: 4480 μg). It is unlikely that this rapid transport of metolachlor could have been leakage down the inner wall of the cylinder since the application area was away from the cylinder wall. If indeed there were a leakage problem, it is not apparent why metolachlor did not continue to be transported further down the core with the second 50.8-mm water application on Day 8.

The rapid movement of a portion of the metolachlor following a large post-application rain concurred with similar observations made by Wauchop (1978) and by Leonard et al. (1979) for some other compounds. In this study there is suspicion that some component of the metolachlor formulation may have temporarily reduced soil retention of metolachlor during the first few days following application, because the solute front moved only slightly deeper during the remainder of the study (Fig. 4B) despite some heavy watering. The point of maximum metolachlor concentration did shift about 10 cm deeper during the study.

Based on the assumption that metolachlor disappearance followed first-order kinetics, the calculated half-life, decay constant (k), and R^2 values for the soil cores receiving only rainfall and supplementary watering were, respectively, 4.0 wk, 0.171 wk^{-1} , 0.993; and 3.3 wk, 0.212 wk^{-1} , 0.974. Only data points (5) up to 12 wk were used, as the disappearance rate appeared to decrease after this time. The average of these two data sets appears as the single disappearance line for 1986 cores in Fig. 5. These half-life values compare well with 3.8 wk reported by Braverman et al. (1986), and 3 to 5 wk reported by Walker and Zimdahl (1981), under similar temperature and moisture regimes.

Aldicarb

Aldicarb (solubility, 6000 $\mu\text{g}/\text{mL}$; Worthing, 1983) and its two very soluble metabolites, the sulfoxide (ALD.Sx.) and the sulfone

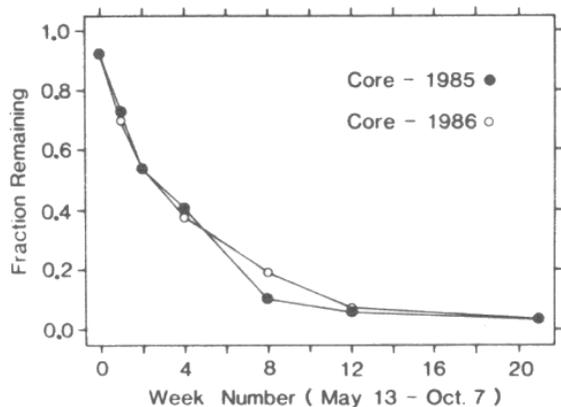


Fig. 5. Metolachlor persistence in Plainfield sand cores, 1985 and 1986.

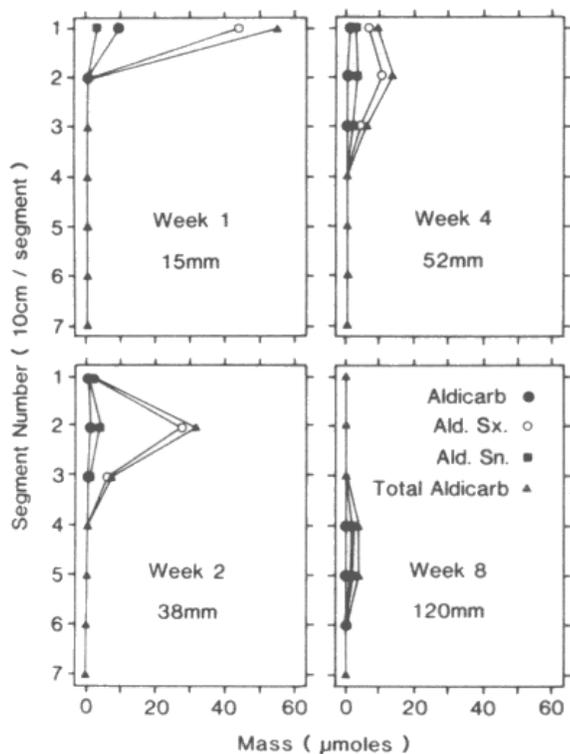


Fig. 6. Aldicarb mobility and dissipation in noneffluent collecting Plainfield sand cores, 1985. Received only rainfall.

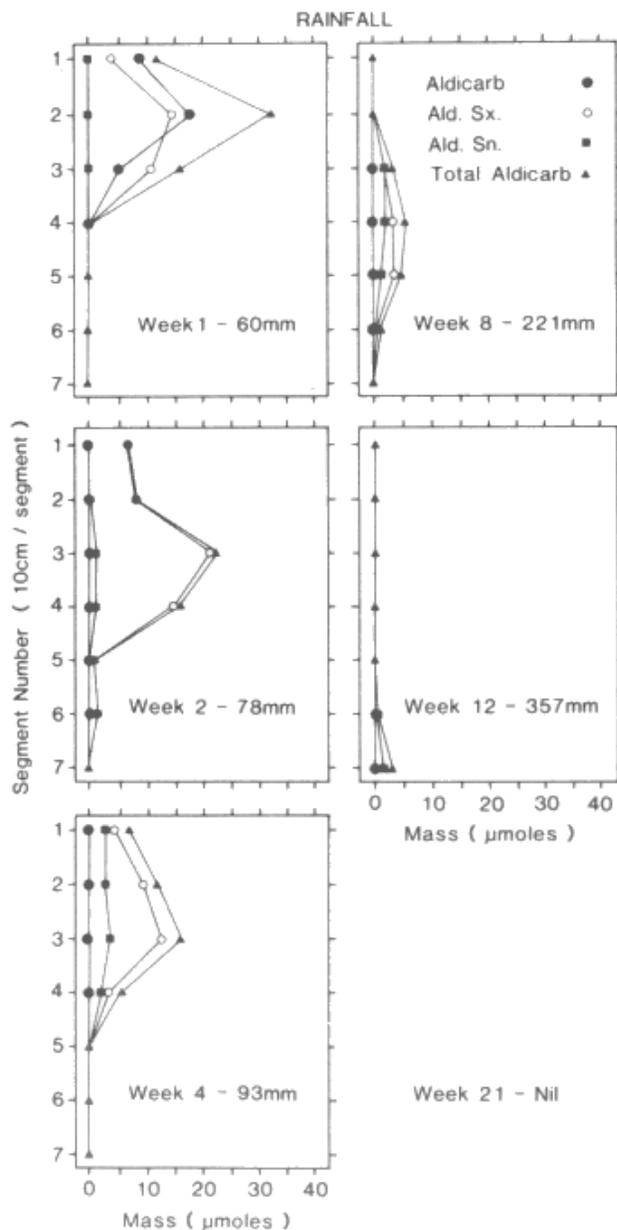


Fig. 7. Aldicarb mobility and dissipation in field lysimeters containing Plainfield sand, 1986. Received only rainfall.

(ALD.Sn.) were quite mobile in Plainfield sand cores under rainfall in both 1985 and 1986. The soil-water partitioning coefficients for aldicarb, ALD.Sx., and ALD.Sn. in Plainfield sand were all $<0.1 \mu\text{g}^{-1}\text{N g}^{-1}\text{mL}^{\text{N}}$ (unpublished data, this laboratory), indicating minimal adsorption by this soil. In 1985, little rainfall was received during the first week (Fig. 2) when most aldicarb was converted to ALD.Sx., which in turn moved down 10 to 30 cm during the second week (Fig. 6). Initial day recovery accounted for 95.4% of applied aldicarb, with no detectable ALD.Sx. or ALD.Sn. present. In 1986, two substantial rainfalls (16 and 34 mm) during the week following application quickly moved the concentration maxima of both aldicarb and ALD.Sx. to the 10- to 20-cm zone (Fig. 7). No aldicarb was detected in the effluent in either year because of its short half-life. Traces of ALD.Sx. and ALD.Sn. started eluting after 6 wk, although most eluted between Weeks 8 and 18. In total, less than 9% of the applied aldicarb eluted as ALD.Sx. or ALD.Sn. in 1986.

In cores receiving supplementary water (Fig. 8), most aldicarb converted to ALD.Sx. during the first week, during which time the ALD.Sx. concentration maximum moved to the 20- to 30-cm zone, whereas the remaining aldicarb maximum moved to the 30- to 40-cm zone. Both aldicarb and ALD.Sx. first appeared in the effluent just preceding the second 50.8-mm water application. By the end of the second week, the effluent contained primarily ALD.Sx., with traces of ALD.Sn. The ALD.Sx. and ALD.Sn. completely disappeared from both cores (Fig. 8) and effluent by the tenth week. Up to 64% of applied aldicarb was recovered in the effluent, primarily as ALD.Sx., with small amounts of ALD.Sn. and traces of aldicarb that appeared during the second week.

Aldicarb persistence patterns in the cores receiving rainfall were very similar in both 1985 (Fig. 9) and in 1986 (Fig. 10). Aldicarb completely disappeared within 2 wk, largely converting to ALD.Sx., part of which oxidized to ALD.Sn. Aldicarb half-life in this soil was estimated at 3 to 5 d in both years, which compares well with persistence data of Smelt et al. (1978), Bromilow et al. (1980), and Leistra et al. (1984). In both years there were about 15, 5, and 0% total aldicarb residues remaining after 8, 12, and 21 wk, respectively. Rates of transformation of aldicarb and its metabolites appeared similar during the first 4 wk under both rainfall (Fig. 10) and supplementary watering regimes (Fig. 11), despite large differences in water volumes applied. A substantial portion of the residues eluted from the the cores receiving supplementary water during the first 8 wk, by which time no residue traces remained in the cores themselves.

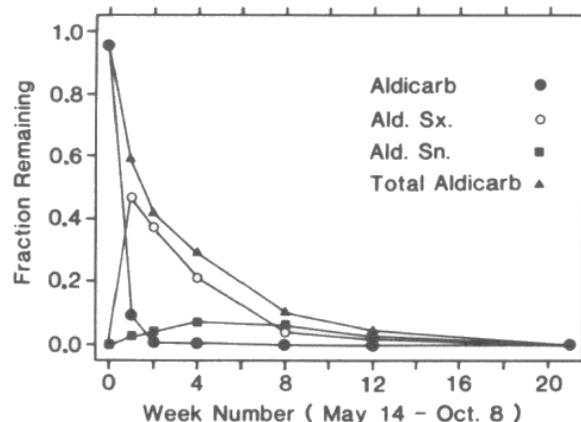


Fig. 9. Aldicarb persistence in noneffluent collecting Plainfield sand cores, 1985. Received only rainfall.

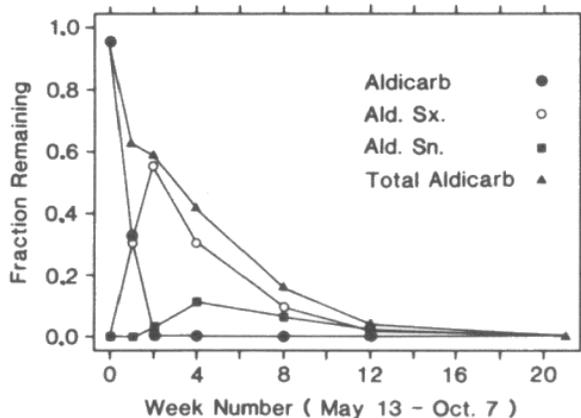


Fig. 10. Aldicarb persistence in field lysimeters containing Plainfield sand cores, 1986. Received only rainfall.

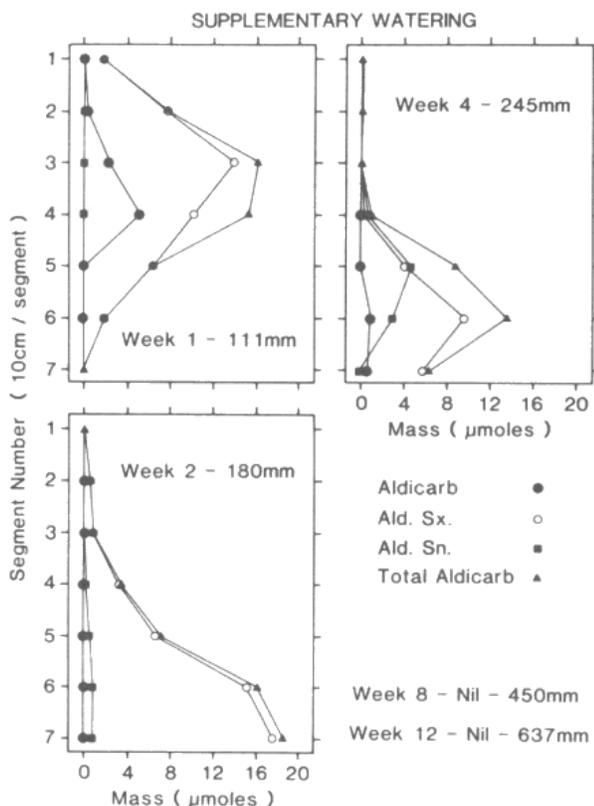


Fig. 8. Aldicarb mobility and dissipation in field lysimeters containing Plainfield sand, 1986. Received supplementary water.

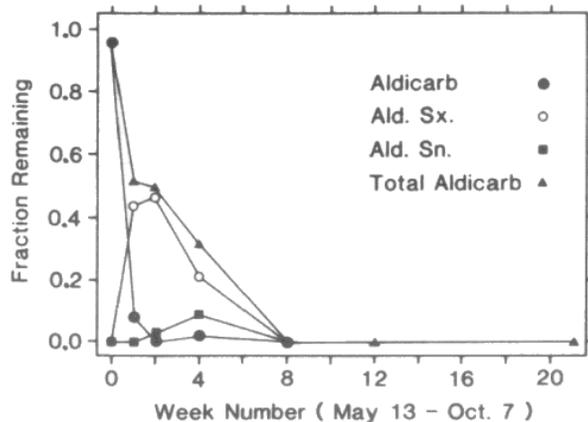


Fig. 11. Aldicarb persistence in field lysimeters containing Plainfield sand cores, 1986. Received supplementary water.

CONCLUSIONS

Leaching and mobility data obtained using field-based lysimeters were comparable to conventional field data reported in the literature for metolachlor and aldicarb. Although separate core units were used for each sampling data, they were sufficiently uniform to provide both consistent mobility and persistence with no discontinuities in either disappearance curves or in distribution profiles. This technique offers several advantages over conventional dissipation studies of pesticides in the field, which follow:

1. The lysimeters provide accurate effluent volume data, which allows monitoring of amounts of solutes leaving the core. These data are necessary to accurately describe the persistence of mobile compounds, such as that of aldicarb in soil profiles.
2. The simultaneous use of both rainfall and supplementary watering treatments with the lysimeters permits the assessment of pesticide persistence and mobility behavior under two very different moisture regimes during one season, rather than repeating field studies over a number of years.
3. Because the lysimeters provide a more complete record of pesticide behavior than do field microplot studies, it may be easier to adapt a modeling program to allow reasonably accurate predictions of pesticide mobility based on only a relatively few inputs, such as daily temperatures and rainfall amounts, compound stability, and soil-water partitioning coefficients. This might allow simulations to be made for various lengths of soil cores under rainfall distributions from different years or locations.

From the results of this study, it is suggested that metolachlor, applied to agricultural soils at recommended rates, would be minimally leached under normal Ontario weather conditions, unless a heavy rainfall occurred shortly after application. In contrast, aldicarb was converted rapidly to its more soluble sulfoxide and sulfone metabolites which, under moderate rainfall, can move considerably in light to medium textured soils.

There are two points of caution to be exercised when interpreting the leaching data of this study.

1. No crop cover was used over the lysimeters throughout the study. Although crop covers tend to reduce net downward water flow in soil by evapotranspiration, and hence reduce pesticide transport, they are often not well enough established during the most susceptible period following pesticide application to have an appreciable effect. The presence of a crop cover later in the study could have had some influence on pesticide movement down the soil cores.
2. The heavy supplementary watering schedule was used to simulate weather conditions that might be expected to occur only occasionally over a 50-yr period. Mobility data obtained under these conditions are quite useful in pesticide screening programs. Pesticides that show only limited mobility under such adverse conditions may require only limited large-scale field trials.

ACKNOWLEDGMENTS

The author greatly appreciates the assistance of Dr. R.A. Chapman and Dr. J.H. Tolman in the preparation and review of this article.

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