

USE OF FIELD LYSIMETERS FOR COMPARISON OF MOBILITY AND PERSISTENCE OF GRANULAR AND EC FORMULATIONS OF THE SOIL INSECTICIDE ISAZOFOS

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(Received 17 July 1990; Accepted 23 October 1990)

Abstract—Mobility and persistence of two formulations of the insecticide isazofos (emulsifiable concentrate (EC), granular) were compared by using 75-cm x 15-cm field lysimeters, packed with Plainfield sand, and two moisture regimes (natural rainfall, supplementary watering). Atrazine was applied to all lysimeters as an internal reference. Effluent was monitored for isazofos, its metabolite CGA17193, atrazine and desethylatrazine. Selected cores were sectioned and analyzed for each chemical at weeks 1, 2, 4, 8, 12 and 21. None of the applied chemicals or their metabolites leached from soil cores receiving only rainfall throughout the 21-week study. The mobility ranking under supplementary watering in Plainfield sand cores was CGA17193 » desethylatrazine > atrazine > isazofos EC > isazofos granular. The first-order half-life of isazofos was 2.0 and 2.7 weeks, respectively, in EC and granular formulations. Evaporative losses accounted for 44 to 67% and 72 to 100% of incident precipitation on the supplementary watering and rainfall lysimeters, respectively.

Keywords— Leaching Soil core CGA17193 Metabolite

INTRODUCTION

Each pesticide exhibits a unique combination of mobility and persistence in each soil-water system, which determines the potential to contaminate sub-surface or groundwater supplies. These mobility and persistence characteristics can be modified by selecting different formulations. As restrictive environmental controls make it increasingly difficult to register pesticides, it becomes advantageous to select carefully the optimum formulation for improved efficacy and environmental safety.

In the present scheme of pesticide evaluation, initial mobility and persistence testing tends to be done in the laboratory, whereas final testing is performed under actual field conditions. However, data gaps exist due to great differences in scale and experimental control between laboratory- and field-scale studies. Laboratory studies permit precise control over experimental variables (mass balance) but do not realistically simulate natural climatic factors such as diurnal temperature, moisture, light and wind variations.

At the other extreme, field dissipation studies suffer from two major limitations: (a) They limit researchers to a passive monitoring role, insofar as controlling climatic factors that drive leaching and dissipation processes. This results in a serious lack of consistency and repeatability from year to year, especially for studies conducted during extremes of heat or moisture. (b) They suffer from the lack of accountability (mass balances of parent and metabolites) in pesticide disposition due to the large sampling scale. Consequently, field-scale testing of pesticides is not a particularly efficient or sensitive means of establishing precise relationships among mechanistic variables, but rather is better suited to observing "net reactions" under existing environmental conditions.

The field lysimeter protocol [1,2] fits a specialized niche between laboratory and field studies, possessing some advantages of both environments while providing unique, detailed data not available from either. Because lysimeters are located outdoors, natural climatic factors control pesticide behavior. The smaller scale, although lacking the heterogeneity of the field, does permit control of moisture inputs and will generate detailed mass balance data for both parent compounds and metabolites. Being able to control important variables brings an essential degree of consistency and detail to field dissipation data that should assist in interpretation for registration purposes.

In this study, we intend to demonstrate the usefulness of the field lysimeter protocol in conducting side-by-side leaching and dissipation comparisons between two formulations of the soil insecticide isazofos.

MATERIALS AND METHODS

Compounds and application rates

Analytical-grade standards (99.7% purity), supplied by Ciba-Geigy Canada Ltd., were used to determine atrazine, desethylatrazine, isazofos and CGA17193 contents of soil and water samples. Commercially formulated products of these compounds were applied to the field lysimeters as follows: atrazine—Aatrex 480 L; isazofos— 10% granular and emulsifiable concentrate, 500 g/L (EC). Atrazine was applied at the maximum recommended rate of 2.25 kg active ingredient (a.i.)/ha (3,980 µg/core) [3]. Isazofos was applied at a rate of 4.25 kg/ha a.i. (7,530 µg/core) for both formulations. The granular formulation was applied 2.5 cm below the soil surface (at least 1.0 cm from outer edge of cylinder) by removing and replacing the top soil layer. Atrazine and isazofos EC formulations were carefully applied by pipet (10-ml aqueous suspensions) to the surface of each soil core in a spiral fashion, starting at least 1 cm away from the cylinder walls. Atrazine was applied to the granular isazofos core set after isazofos had been applied, and the surface soil layer was replaced.

Experimental setup

Details of the experimental procedures have been previously described [2]. Briefly, about 17 kg (dry weight) of Plainfield sand (87.5% sand, 6.5% silt, 6.0% clay, 1.5% organic matter) was loaded into each lysimeter, producing a 70-cm x 15-cm soil core packed to within 5 cm of the top of the stainless steel cylinder. Lysimeters were buried in an outdoor sandbox, and approximately 12 L of water were applied to each lysimeter over the two-week period preceding pesticide application on May 9, 1989. Each isazofos treatment required one lysimeter set (24 cores), which was divided into two moisture regimes of six pairs each. One-half of the lysimeters received natural rainfall only, whereas the remaining lysimeters received rainfall plus supplementary watering, simulating a 50-mm rainfall on days 2 and 9. After week 2, 25-mm water applications were made, simulating an irrigation protocol: (a) 2 d following less than 10 mm rainfall, (b) 3 d following 10 to 25 mm rainfall, (c) 4 d following >25 mm rainfall, or the last watering. Effluent from each lysimeter was analyzed for each chemical by HPLC or by GLC. One pair of cores from each moisture regime was retrieved from the field at 1, 2, 4, 8, 12 and 21 weeks and frozen for subsequent sectioning (7 x 10 cm) and residue analysis.

Soil core extraction and analysis

Soil core samples (100 g) were extracted with a 90:10 HPLC-grade methanol:water solvent mixture as reported earlier [2]. Extracts were filtered through vacuum Buchner funnels, and filtrates were quantitatively transferred to 250-ml volumetric flasks, made to volume with water, and centrifuged for 10 min to remove sediment traces before HPLC or GLC analysis.

Atrazine, desethylatrazine and isazofos analyses were done by GLC, using the following operating parameters: column, J&W DB-17, 0.53 µm x 15 m (megabore, 1.0-µm film); carrier gas, ultrapure He (15—20 ml/min); detector, nitrogen—phosphorus, 260°C; H₂ flow rate, 1 to 3 ml/min; injector temperature, 240°C; injection volume, 2.0 µl. Minimum detectable concentrations for atrazine, desethylatrazine and isazofos were, respectively, 2 to 5 µg/L, 5 to 10 µg/L and 0.2 to 0.5 µg/L.

CGA17193 was analyzed by HPLC, using the following operating parameters: column, 5 mm x 10 cm, 10-µm particle size, reversed-phase C₁₈; pump speed, 1.0 ml/min; detector wavelength, 215nm; mobile phase, 30/70 methanol/phosphate buffer containing 1 g/L of the ion-pairing reagent 1-octane sulfonic acid. The 0.02-M phosphate buffer was prepared with 500 ml of 0.02 M phosphoric acid mixed with 2.0 L of 0.02 M monobasic potassium phosphate (pH 3.25). The minimum detectable concentration was 15 to 30 µg/L. All mobile-phase solvents for HPLC analyses were degassed by vacuum-filtering through 0.7-µm glass microfiber filters. Peak areas of HPLC and GLC responses for the analytes were determined by a computing integrator using external standard solutions of the same solvent composition.

RESULTS AND DISCUSSION

Effluent data

About 42% of the 227 mm of rain received during the 21-week study fell within the first four weeks (Table 1). Despite this substantial rainfall, none of the applied chemicals (isazofos [both formulations], atrazine) or their metabolites (CGA17193, desethylatrazine) leached through cores receiving natural rainfall.

A 50-mm supplementary water application on days 2 and 9 clearly differentiated isazofos mobility differences

Table 1. Precipitation amounts received May 10 to October 3, 1989, by lysimeters under both natural rainfall and supplementary watering treatments

Week	Cumulative precipitation (mm)	
	Rainfall	Watering
1	6.0	107.7
2	23.0	124.7
4	95.0	222.1
8	133.5	362.3
12	149.5	505.4
21	226.5	811.2

between the two formulations. In the granular-treated core set, isazofos first eluted on May 23 from two cores (1 µg), and only two further traces (total of four) were detected after that. In contrast, isazofos from EC-treated cores eluted from three cores after the first 50-mm water application and in total eluted on 22 occasions (total water input of 811 mm).

CGA17193 first appeared in the effluent of the eight remaining EC-treated cores on May 23 and eluted on a regular basis until early August (week 12) (total of 62 elution events). In contrast, CGA17193 did not elute from granular-treated cores until June 14 (total of 44 elution events), and in smaller amounts than those observed in the EC-treated cores. In total, 247 µg of CGA17193 was eluted from the EC-treated core set, compared with only 135 µg for the granular-treated core set.

Soil core mobility and persistence data

Only minute traces of any applied chemicals moved below 20 cm in cores receiving natural rain-fall throughout the 21-week study. In the maximum penetration bar graphs, which indicate only presence or absence of a chemical (not amounts) (Figs. 1 and 2), isazofos movement (granular application) reached a maximum of 30 cm at week 8 (Fig. 1B), compared with a 20-cm maximum at week 4 in the EC application (Fig. 2B). Maximum detectable penetration of CGA17193 occurred at four weeks in both isazofos applications (30 and 20 cm for the granular and EC applications, respectively). Greater isazofos penetration in cores receiving the granular application may have been a result of its greater persistence, relative to the EC application (Fig. 3). By week 12, the last remaining traces (0.0375 µg/g soil, using a 15-µg/L detection limit) of CGA17193 had disappeared from all cores.

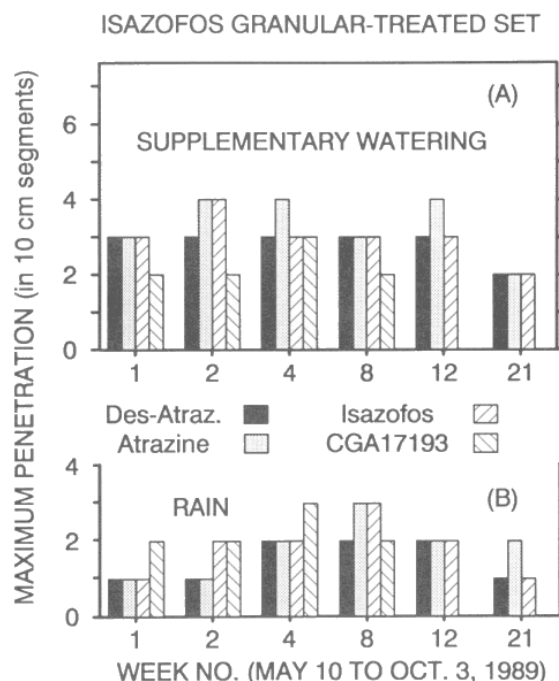


Fig. 1. Maximum penetration of atrazine, CGA17193, desethylatrazine (Des-Atraz.) and isazofos EC in Plainfield sand lysimeters: (A) supplementary watering; (B) rainfall.

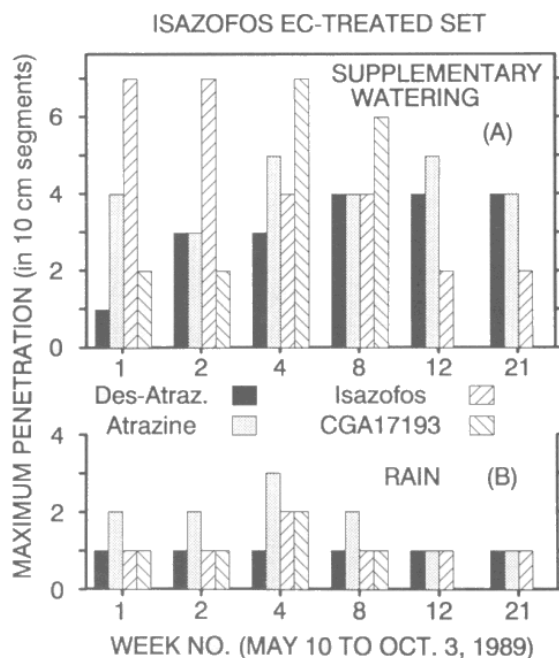


Fig. 2. Maximum penetration of atrazine, CGA17193, desethylatrazine (Des-Atraz.) and isazofos granular in Plainfield sand lysimeters: (A) supplementary watering; (B) rainfall.

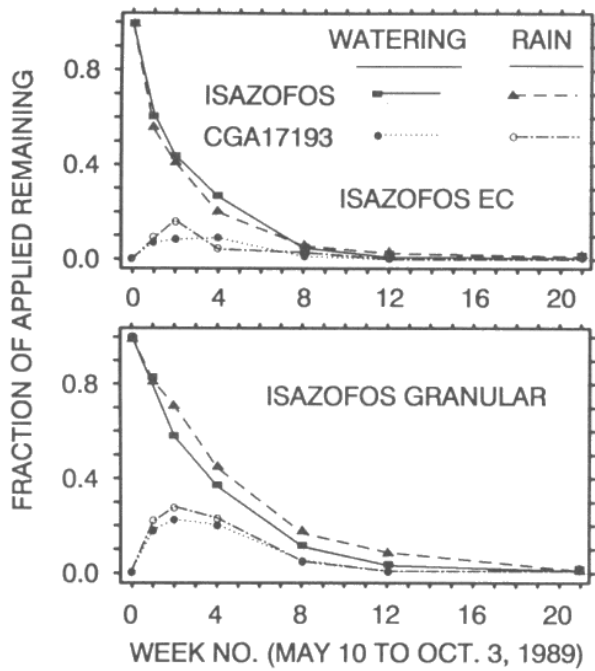


Fig. 3. Persistence of isazofos granular, isazofos EC and CGA17193 in Plainfield sand lysimeters, under both supplementary watering and rainfall.

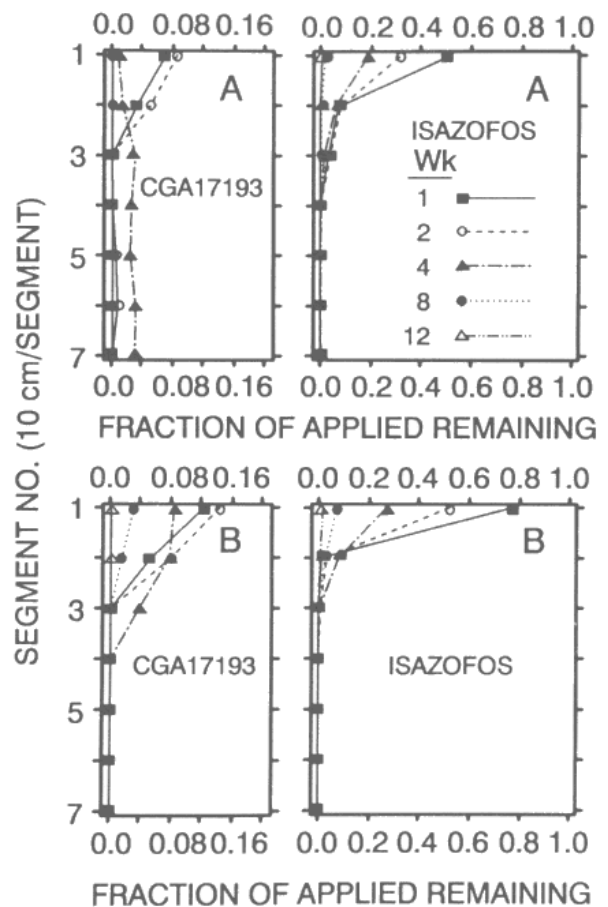


Fig. 4. Mobility profiles for isazofos EC and CGA17193 in Plainfield sand lysimeters under supplementary watering: (A) EC formulation; (B) granular formulation.

Under natural rainfall, maximum movement of atrazine and desethylatrazine was always within 10cm (one core segment) of that observed for both isazofos formulations. Mobility profiles are not shown for cores receiving only rainfall, due to minimal movement of the chemicals.

Following the first 50-mm supplementary water application, traces of isazofos from the EC application quickly reached the base of the cores (Fig. 1A) and continued to be detected there until degradation effects became significant by week 8. In contrast, isazofos (granular) (Fig. 2A) was never detected below 40 cm in the soil cores. These data agree with the effluent data that show only four isolated traces of isazofos (granular) eluted, compared with 22 elutions from the EC-treated cores. Considerably more isazofos from the EC than from the granular application moved into the second (20 cm) and third segments (30 cm) (Fig. 4).

Mobility profiles for CGA17193 in the two isazofos formulations were quite different due to apparent differences in leachability and persistence (Fig. 4). This may have been a result of greater isazofos stability in the granules combined with a controlled-release rate. In Figure 4, note the reduced scale ranges for the fraction of applied CGA17193 remaining (0- 0.16). More CGA17193 in granular-treated cores remained in the top 30 cm despite its obvious mobility, as observed in both EC-treated cores and from the effluent data. A considerable fraction of isazofos may have degraded while associated with the granules, with resulting CGA17193 also being retained and protected from degradation and leaching by the granules.

Mobility profiles for atrazine and desethylatrazine were similar in both lysimeter sets, indicating consistent soil cores (Fig. 5). Maximum penetration for each chemical generally did not vary by more than one 10-cm segment between lysimeter sets for respective moisture treatments, with exceptions of week 1 for desethylatrazine and of week 21 where traces of both chemicals moved 20 cm deeper in the EC lysimeter set (Figs. 1 and 2).

In an earlier field leaching study [2] using Honeywood silt loam, we observed the following mobility ranking under supplementary watering: desethylatrazine > atrazine > isazofos (granular). In this study, using Plainfield sand, the mobility ranking under supplementary watering was CGA-17193 » desethylatrazine > atrazine > isazofos (EC) > isazofos (granular). Although desethylatrazine moved deeper into the cores (Fig. 5) than CGA17193 from isazofos

granular, CGA17193 was judged to be the more mobile compound, based on its greater elution frequency. This discrepancy in observed mobilities was probably a result of a lower minimum detection limit for desethylatrazine (5-10 µg/L vs. 15-30 µg/L for CGA17193). Mobility rankings for these compounds in Plainfield sand were inversely related with their respective soil/water partitioning coefficients (K_d), obtained by batch adsorption: isazofos, 1.436; atrazine, 0.843; desethylatrazine, 0.489; CGA17193, $<0.10 \mu\text{g}^{-1}\text{N}^{-1}\text{ml}^{\text{N}}$, where N is the Freundlich exponent. When using K_d values to predict mobility in modeling scenarios, one should consider that adsorption K_d values were generated with analytical-grade chemicals and that formulation can greatly modify observed mobility characteristics, as observed here. To our knowledge, no modeling programs as yet allow input K_d values to be adjusted for different formulations.

Isazofos was more persistent in the granular than in the EC application (Table 2). First-order half-life ($t_{1/2}$) value for the granular (first eight weeks' data, average of both moisture regimes) was 2.7 weeks, compared with 1.95 weeks for the EC formulation. Atrazine persistence appeared to increase in the presence of the isazofos granular formulation. In Table 2, atrazine persistence data are included from another concurrent lysimeter study in which the herbicide metribuzin was applied with atrazine. Atrazine $t_{1/2}$ values were similar in both the EC- and the metribuzin-treated core sets (4.1-4.9 weeks), compared with the values of the granular-treated core sets (both moisture regimes) (5.4-6.9 weeks). Further studies are required to confirm possible interactions between the granular isazofos and atrazine formulations.

Soil moisture relationships and consequences

Moisture profiles for both moisture regimes were similar to those observed earlier [2]. Moisture contents of surface core segments were near 11.5% at treatment time and fluctuated much more throughout the study for cores receiving only rainfall than in supplementary watering lysimeters. Moisture contents of bottom core segments ranged from 20 to 24% and 22 to 25% (w/w), respectively, for the rainfall and supplementary watering core sets, which were several percent below water-holding capacity for this soil.

Evaporative water losses from soil surfaces greatly reduced vertical pesticide transport by reducing net downward water flow. Daily water losses in this study (computed from monthly averages) ranged from 2.6 to 3.7 mm/d for supplementary watering cores and from 0.74 to 2.2 mm/d for rainfall cores over the 21-week study period. Expressed in different terms, evaporative losses accounted for 44 to 67% and 72 to 100% of incident precipitation on the supplementary watering and rainfall lysimeters, respectively. Under natural rainfall, potential evaporation far exceeded rainfall throughout most of the study, and in fact no effluent was collected from these lysimeters from early July until mid-September. Such daily evaporative water losses are normal for this climatic zone [4], and when expressed in percent of incident precipitation, serve to illustrate the impact of evaporation on reduced pesticide leaching. The lack of a plant canopy was of minor consequence, as the most important mobility and persistence data were collected before a plant canopy would have been large enough to influence water losses.

Evaporative losses not only reduce net downward water movement, but may, during drying periods, create an upward flux

Table 2. Persistence data in Plainfield sand for atrazine and isazofos in three lysimeter sets (isazofos EC, granular, and a third set from another concurrent study)

	Half-life (week) ^a	
	Watering	Rainfall
EC set		
Isazofos	1.9	2.0
Atrazine	4.1	4.9
Granular set		
Isazofos	2.4	3.0
Atrazine	5.4	6.9
Third set		
Atrazine	4.9	4.3

^a First-order half-life (first eight weeks' data).

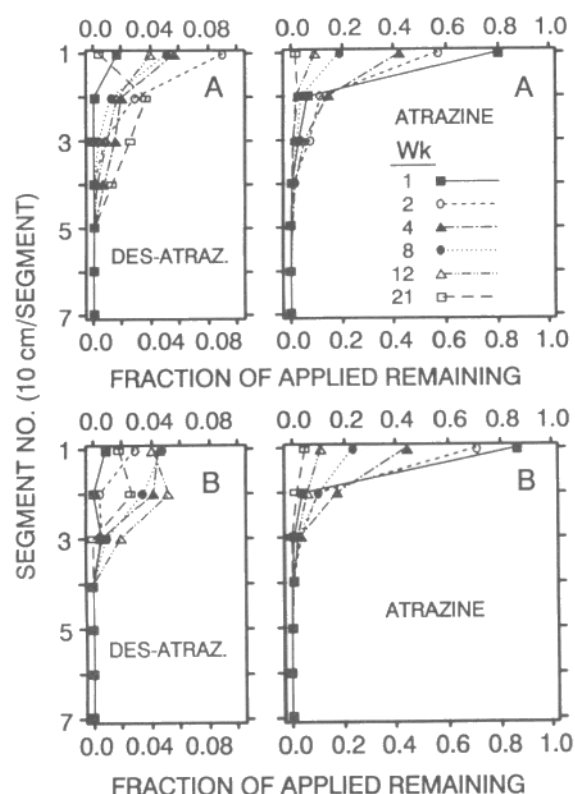


Fig. 5. Mobility profiles for atrazine and desethylatrazine (Des-Atraz.) in Plainfield sand lysimeters treated with isazofos under supplementary watering: (A) EC-treated core set; (B) granular-treated core set.

that can transport weakly adsorbed pesticides back toward the soil surface (wick effect) [5]. Simulation runs with the pesticide root zone model (PRZM) [6], using our lysimeter data, predicted that within a relatively short period following pesticide application the surface concentration of a moderately mobile compound such as atrazine or isazofos would be depleted, forming a concentration bulge a short distance below the application point. This concentration bulge was predicted to migrate downward, gradually spreading and diminishing as degradation and leaching progressed. However, we have observed that concentrations continuously decrease with depth until late in the study (Figs. 4 and 5).

The PRZM model does not realistically simulate evaporative water losses from soil because it sequentially extracts water to the wilting point from each soil compartment before starting the next compartment [6, p.16]. PRZM also does not allow for upward migration of water or pesticides with it during drying periods. Small concentration bulges predicted by PRZM may be redistributed upward during drying periods, producing the exponentially decreasing concentration profiles normally observed in our soil cores. Walker and Welch [7] have observed similar transport anomalies, in which their model predicted much more surface depletion of sulfonylurea residues than that actually observed. Their study included extended periods when total potential evaporation greatly exceeded actual rainfall.

CONCLUSIONS

The manner in which pesticides are formulated can dramatically affect both their leaching and degradation behavior in soil under certain climatic conditions. Differences in mobility between the two isazofos formulations were clearly accentuated under supplementary watering. In summary, the following important observations were made:

1. Under existing rainfall patterns of 1989, none of the applied chemicals leached through the 70-cm Plainfield sand cores during the 21-week study. In fact, only limited chemical movement occurred (30 cm maximum). Under these conditions, no differences in isazofos mobility between the two formulations would have been observed in a conventional field study.
2. The supplementary water treatment accentuated small mobility differences among chemicals and formulations that would normally be observed only during wet weather and/or under an ongoing irrigation program. The observed mobility ranking under supplementary watering was CGA17193 » desethylatrazine > atrazine > isazofos EC > isazofos granular. Relative magnitudes of Freundlich K_d values were inversely related to their mobility ranking.
3. CGA17193 appeared to persist longer and accumulate more in soil cores treated with isazofos granular than with the EC formulation. The formulation matrix may have played a role in this effect.
4. Isazofos was more persistent in the granular than it was in the EC formulation, with $t_{1/2}$ values being 0.5 and 1.0 week longer for supplementary watering and rainfall, respectively.
5. Evaporative losses accounted for 44 to 67% and 72 to 100% of incident precipitation on the supplementary watering and rainfall lysimeters, respectively. This appeared to be a major factor in reducing net downward water flow and pesticide movement in the lysimeters.

The field lysimeter protocol has demonstrated its usefulness in distinguishing between mobilities of two pesticide formulations that would have been evident in field trials only under much wetter climatic conditions. From an environmental safety viewpoint, the granular formulation of isazofos would appear to be the more desirable product because of its greater persistence and lower mobility. Isazofos EC might be useful in certain turf applications where greater soil penetration is desirable.

Acknowledgement— The author wishes to acknowledge the assistance of John Armistead and LouAnn Verellen in the collection and analysis of the data used in the preparation of this manuscript; and the assistance of Dr. Shiv Prasher and Ward Smith of Macdonald College, McGill University, St. Anne de Bellevue, Quebec, Canada, for the PRZM simulations. The author expresses his appreciation to Ciba-Geigy Corporation, USA, for providing partial funding for this study and for their technical collaboration.

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