

MOBILITY AND PERSISTENCE OF THE HERBICIDES ATRAZINE, METOLACHLOR AND TERBUTHYLAZINE IN PLAINFIELD SAND DETERMINED USING FIELD LYSIMETERS

B. T. BOWMAN

London Research Centre, Research Branch, Agriculture Canada,
London, Ontario N5V 4T3 Canada

(Received 23 June 1988; Accepted 13 December 1988)

Abstract—Field lysimeters (75 x 15 cm) packed with 18 kg (dry weight) Plainfield sand were used to study the mobility and persistence of commercial formulations of the herbicides atrazine, metolachlor and terbuthylazine under two precipitation regimes: rainfall, and rainfall with supplementary watering. Leachate from the 70-cm soil cores was monitored daily for each herbicide. Pairs of soil cores for each herbicide and each moisture regime were sectioned (7 x 10 cm) after 1, 2, 4, 8, 12 and 21 weeks to obtain both mobility and persistence data. After 21 weeks under rainfall, the maximum movements of atrazine, terbuthylazine and metolachlor were, respectively, 30, 20 and 10 cm, and under supplementary watering, were, respectively, 70, 50 and 40 cm. Only a single trace of atrazine appeared in the effluent of rainfall cores. Both atrazine and terbuthylazine appeared in the effluent following a 50-mm water application on day 2. Atrazine also appeared in the effluent on several occasions after week 12 under supplementary watering.

Keywords—Soil cores

Field lysimeters

Herbicide mobility/persistence

Leachates

INTRODUCTION

The risk of ground water contamination from agricultural pesticide use is ultimately determined by the relative rates of percolation and degradation within the soil profile, and by factors controlling these processes, such as climate, soil properties, microbial activity and chemical properties of the pesticides. Ground water contamination is less likely to occur if the degradation rates of parent compounds and their toxic metabolites exceed their percolation rates through the soil profile. The task of accurately predicting pesticide movement in soil can be complicated by "macropore" or "preferential" flow, in which the applied chemicals are flushed through small fissures, root channels or microflow channels to considerable depths in the soil profile. This can occur within a few hours following a heavy rainfall, bypassing most of the soil mass [1-41]. The variable nature of these fissures and microchannels, in both size and extent, makes it difficult to quantify or predict their contribution to ground water contamination.

Soil/water partitioning coefficients have been used for some time for predicting pesticide mobility in soils. There is evidence that these coefficients (K_d values) are not constant despite the fact that

they are usually treated as constant in modeling scenarios. Pesticide retention by soil appears to increase steadily for a considerable period following application [5-8]. Precipitation patterns, especially during the first week or so following application, have a major influence on the extent to which the pesticide will leach or be transported in runoff water [6,9]. If the pesticide moves below the organic matter-rich plough layer during this period, its leaching hazard is significantly increased because of decreased adsorption capabilities of the soil combined with lower biodegradation rates.

The objectives of this study were to investigate the relative mobility and persistence of the commercially formulated forms of the herbicides atrazine, metolachlor and terbuthylazine, using a field lysimeter test protocol.

MATERIALS AND METHODS

Compounds and application rates

Analytical-grade reference standards (99.7% purity), supplied by Ciba-Geigy Canada, were used in all analyses to evaluate the solution concentrations of atrazine, metolachlor and terbuthylazine. Commercially formulated products, supplied by Ciba-Geigy, were used in the field lysimeters as follows: atrazine, Aatrex 480L; metolachlor, Dual

960E; terbuthylazine, Gardoprim 80W. Both atrazine and terbuthylazine were applied to the soil cores at the maximum recommended field-application rate for atrazine of 2.25 kg/ha active ingredient (a.i.) [10], which is equivalent to 3,980 μg per core. Metolachlor was applied at its maximum recommended field application rate of 2.75 L/ha, which is equivalent to 4,500 μg a.i. per core. The required amount of formulated product in a 10-ml aqueous aliquot was applied uniformly over the surface of each soil core, at least 1 cm away from the cylinder walls.

Experimental setup

Details of the experimental setup, the leaching protocol and all analytical procedures have been described previously [11]. Briefly, about 18 kg (dry weight) Plainfield sand (91.5% sand, 1.5% silt, 7% clay, 0.7% organic matter) was loaded into each lysimeter, producing a 70 cm x 15 cm core of soil packed to within 5 cm of the top of the stainless steel cylinder (Fig. 1). Lysimeters were buried in an outdoor sand-filled enclosure to within 5 cm of the top of the unit. Provision was made for effluent removal from the 1-liter collection beaker

below the soil core via a 0.48 cm i.d. stainless steel tube. Approximately 6 to 8 liters of water was applied to cores to be treated with atrazine and metolachlor over a 2-week period preceding treatment to help pack the soil cores uniformly. For each chemical studied, 24 soil cores were used (12 pairs), which were divided into two moisture regime treatments of six pairs each. One pair of cores from each treatment was retrieved from the field at 1, 2, 4, 8, 12 and 21 weeks and frozen for subsequent sectioning (7 x 10 cm) and soil analysis. One-half the lysimeters received rainfall, while the remaining lysimeters received rainfall plus supplementary watering to simulate two 50.8-mm rainfalls, on days 2 and 8. After week 2, 25-mm water applications were made as follows: (a) 2 d following less than 10 mm of rainfall; (b) 3 d following 10 to 25 mm rainfall; and (c) 4 d following more than 25 mm rainfall, or the last watering. Effluent from each lysimeter was collected on the morning following a rain or water application, centrifuged at 40,000 g for 10 min, then analyzed for the respective chemicals by HPLC.

The atrazine and metolachlor leaching studies (48 cores), initiated on 12 May 1987, filled the field site to capacity. After week 4, half the cores from each treatment (24 total) had been removed, providing space to start the terbuthylazine study. Because it was desirable to complete this 21-week study before inclement weather arrived in November, only a 24-h equilibration period was used between packing and treating the lysimeters, rather than the normal 2-week period. Approximately 4 to 5 liters of water was percolated through the soil cores on the day previous to treatment to help uniformly pack the lysimeters. An additional short-term (4 weeks) leaching study was started in mid-August (12 lysimeters), which employed a combined atrazine-terbuthylazine application and received supplementary watering. The 12 lysimeters were divided into two pretreatment moisture regimes during the equilibration stage: In Treatment 1, cores received water on a daily basis for 12 d, with the last watering 18 h prior to treatment. In Treatment 2, cores received water on a daily basis for 7 d, at which time they were capped to prevent rain from entering the cores during the last 5 d prior to treatment.

Soil core extraction and analysis

HPLC-grade methanol (90 ml) was added to each of duplicate 100-g soil samples in 250-ml screw-capped glass bottles, which were then tumbled for 40 min. The slurries were filtered using

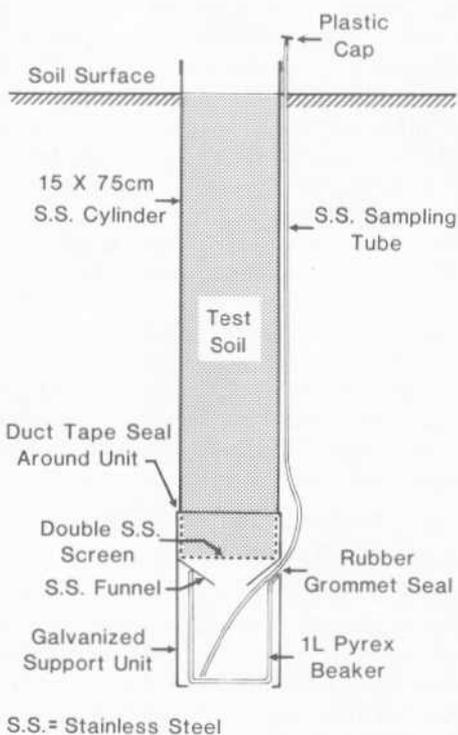


Fig. 1. Schematic representation of field lysimeter unit.

vacuum Buchner funnels and the soil pads were washed with three 25-ml methanol washes, all of which were transferred to 200-ml volumetric flasks and made to volume. The resulting filtrates were centrifuged at 40,000 g for 10 min to remove suspended materials prior to analysis. All analyses were done by HPLC, using a 15.0 cm x 3.9 mm Waters reversed-phase 5- μ m spherical particle C_{18} column. Detection was by UV spectrophotometer at 200 nm for metolachlor, and 220 nm for atrazine and terbuthylazine. The carrier solvent composition (acetonitrile:water) and flow rates for metolachlor were, respectively, 55:45 and 1.7 ml/min, and for both atrazine and terbuthylazine, respectively, 50:50 and 1.2 ml/min. All carrier solvents were degassed by vacuum filtering through 0.7- μ m glass microfiber filters. A minimum detectable concentration of 15 μ g/L was achieved for metolachlor using a 40- μ l injection volume. Peak areas of HPLC responses for atrazine, metolachlor and terbuthylazine were determined by a computing integrator using external standard solutions of the same solvent composition.

RESULTS AND DISCUSSION

Effluent data

Only a single trace of atrazine (0.2 μ g), and no metolachlor or terbuthylazine appeared in the effluent of lysimeters in the rainfall treatment throughout the 21-week study. No metolachlor eluted during the previous study in 1986, despite receiving more than double the 1987 rainfall amount during the 12 May to 6 October period (707 mm [11] vs. 325 mm, Fig 2). For lysimeters receiving supplementary watering, no metolachlor eluted, whereas atrazine eluted from 4 of the 12 cores in amounts ranging from 1.9 to 32.4 μ g (<0.8 % of 3, 980 μ g a.i. application). In comparison, 8 of the 12 terbuthylazine cores eluted amounts of from 1.6

to 42.8 μ g, primarily following the 50-mm water application on day 2, and to a much lesser extent following the second 50-mm application on day 8. Since terbuthylazine has a K_d value for Plainfield sand that is 2.4 times that for atrazine (Table 1), its greater elution from these cores was unexpected.

Because of the short time (24 h) available for equilibrating the terbuthylazine cores prior to treatment, the cores were in a more saturated state than their atrazine counterparts, which were equilibrated for almost two weeks prior to treatment. There is evidence in the literature suggesting that soil moisture levels at the time of pesticide application can measurably affect subsequent leachability [12]. To study the possible effects of soil moisture content at treatment time on subsequent leachability, we initiated a four-week lysimeter study using a combined atrazine-terbuthylazine application, and two pretreatment moisture regimes during equilibration of the cores (Treatment 1, daily watering until 18 h prior to herbicide application; Treatment 2, no watering for 5 d prior to herbicide application).

Neither atrazine nor terbuthylazine eluted from cores harvested 1 week following the combined application, despite the 50-mm water application on day 2. In cores harvested after two weeks, 6 to 7 μ g atrazine, in total, eluted from both cores in Treatment 1, and 8 μ g of atrazine eluted from one core in Treatment 2 following the 50-mm water application on day 2. In cores harvested after four weeks, 8.2 μ g atrazine and 6.7 μ g terbuthylazine eluted from one core in Treatment 1, while 10.8 μ g atrazine and 3.7 μ g terbuthylazine eluted from one core in Treatment 2. There was some variability in elution patterns among replicate cores in this study, as was the case in the separate atrazine (Figs. 3A and 4A) and terbuthylazine (Figs. 3C and 4C) leaching studies. However, it is significant that atrazine appeared more often in the effluent than terbuthylazine (five cores vs. two cores,

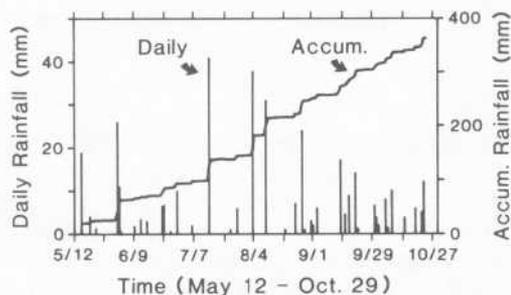


Fig. 2. Rainfall record for Fanshawe field station: Daily and accumulative rainfall, 1987.

Table 1. Adsorption and solubility data for atrazine, metolachlor and terbuthylazine

Compound	Solubility (μ g/ml)	Freundlich constants (a)	
		K_d (b)	Slope
Atrazine	30	0.350	0.852
Metolachlor	530	0.661	0.840
Terbuthylazine	6	0.844	0.889

(a) Freundlich constants determined using Plainfield sand.

(b) Units: μ g (l^{-N}) ml N g $^{-1}$, where N = slope.

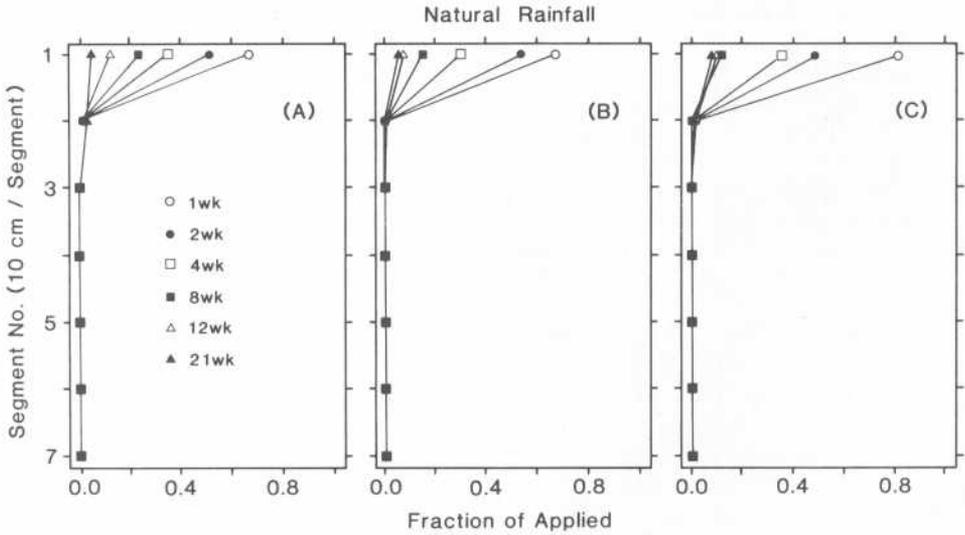


Fig. 3. Mobility in Plainfield sand lysimeters in 1987, receiving only rainfall. A: Atrazine. B: Metolachlor. C: Terbutylazine.

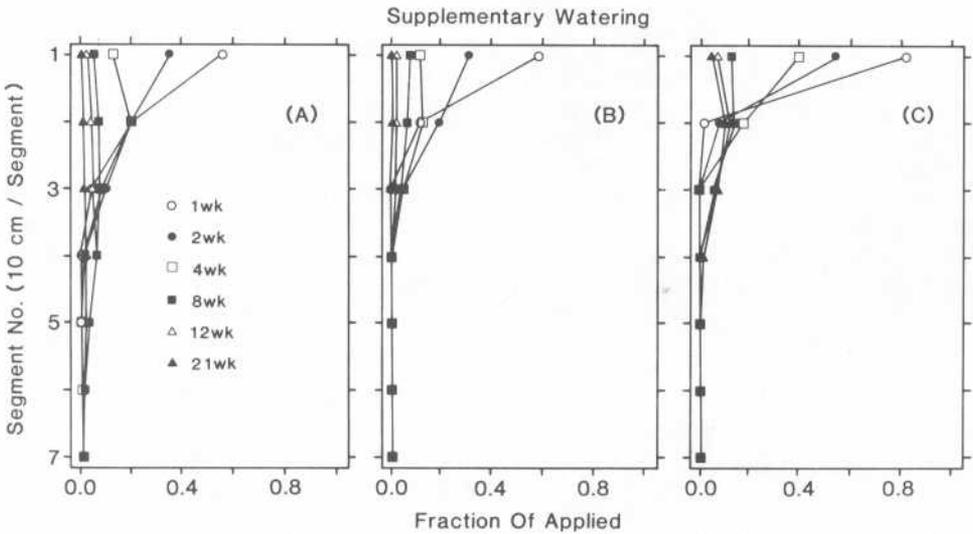


Fig. 4. Mobility in Plainfield sand lysimeters in 1987, receiving only supplementary watering. A: Atrazine. B: Metolachlor. C: Terbutylazine.

respectively), and that in those cores for which a chemical leached into the effluent, atrazine always eluted in greater quantities than terbutylazine.

The two pretreatment moisture regimes did not produce different elution patterns, with chemicals eluting from three cores that were kept saturated (Treatment 1) and from two cores that were kept dry before treatment (Treatment 2). It may be

significant that no terbutylazine eluted from 10 of the 12 cores during this four-week study, compared with the first terbutylazine study in which it eluted from 8 of the 12 cores, primarily following the first 50-mm water application in week 1. The distinct difference in terbutylazine elution tendencies between the first study and the combined application study may be ascribed to the

longer pretreatment equilibration time in the combined application study (12 d vs. 1 d). Longer equilibration periods between packing and treatment of the lysimeters appear necessary to produce more uniform leaching patterns among lysimeters.

The moisture contents of soil cores under both moisture regimes increased steadily with increasing depth, to approximately 20% (w/w) in the bottom segment of each core. The saturation moisture percentage for this soil was measured at 29.7% (w/w). The moisture content of the top segments of the rainfall cores were in the 9 to 10% range during the first few weeks of the study, but gradually decreased to the 6 to 7% range during the very dry weather in late June and July. By week 21, the moisture content in the top segments had returned to 10% as a result of several rains in September. The moisture content of the top segments of the supplementary watering cores remained in the 8.5 to 11% range throughout the entire study, since water was applied at regular intervals (excepting, of course, for brief intervals following water applications).

Soil core mobility data

Soil mobility profiles for those cores receiving rainfall, as a function of time following treatment, are shown in Figure 3A (atrazine), Figure 3B (metolachlor) and Figure 3C (terbuthylazine). Since the summer of 1987 was rather dry (Fig. 2), none of the chemicals moved to any great extent down the cores. By week 21, there was slight movement of atrazine into the 20 to 30 cm zone (Fig. 3A, Segment 3), whereas terbuthylazine did not move beyond 20 cm (Fig. 3C, Segment 2) and metolachlor did not move beyond 10 cm (Fig. 3B, Segment 1). As noted above, no chemical eluted from the rainfall cores, with the exception of a single trace of atrazine (0.2 μg).

There was substantially greater downward transport in those cores receiving supplementary water (Fig. 4A, B and C) than in those receiving rainfall (Fig. 3A, B and C). This was especially true for atrazine, which began eluting in small amounts during week 12 and which by week 21 had penetrated the full 70-cm core length. In contrast, metolachlor did not move below 30 cm (Fig. 4B) and terbuthylazine did not penetrate below 40 cm (Fig. 4C). Soil mobility data for atrazine and terbuthylazine in Treatment 1 of the combined four-week study (Fig. 5) were very similar to profiles obtained in the separate studies (Fig. 4A and C).

It is of interest that long before atrazine or terbuthylazine reached the lower core segments in

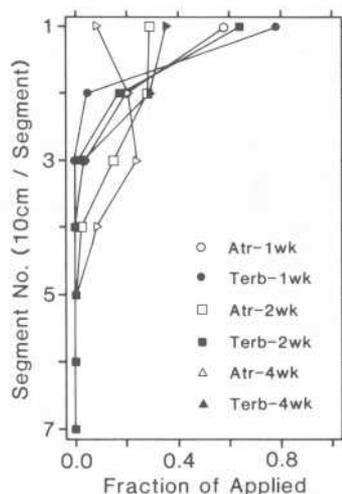


Fig. 5. Atrazine and terbuthylazine mobility in Plainfield sand lysimeters in 1987. A 5-d pretreatment dry period was followed by supplementary watering.

analytically detectable amounts (greater than 2 to 3 ng/g soil), variable trace levels of both chemicals had eluted from several cores, primarily following the first 50-mm water application on day 2 and to a much lesser extent following the second 50-mm application on day 8. Metolachlor did not exhibit sudden elution behavior in this study, although it did in a previous study [11]. Although this sudden elution behavior exhibited some similarities to macropore flow in soil profiles, such flow seems unlikely to be the case in this study, since only minimal elution of chemicals occurred following the second 50-mm water application on day 8.

It is more likely that there was insufficient time between the herbicide application and the 50-mm water application on day 2 for the soil to attain its full retention capacity for the herbicide. In related laboratory partitioning studies using the same lysimeter application technique for the herbicides, we found that the soil retention increased substantially over a several-week period (unpublished data). These soil/water partitioning data are different from those obtained by the slurry adsorption technique because the herbicide was applied to air-dried soil and allowed to equilibrate for varying periods before addition of the bulk water phase. These time-dependent partitioning coefficients, which are actually desorption coefficients, more realistically represent partitioning processes under field conditions than do the slurry partitioning soil/water coefficients.

Soil core persistence data

Although atrazine (Fig. 6A) and metolachlor (Fig. 6B) persistence in the rainfall cores were almost identical during the first three weeks of the study (50 % remaining after 2.5 weeks), atrazine became relatively more persistent throughout the remainder of the study. Under supplementary watering, atrazine was considerably more persistent than metolachlor (50 % remaining after 3.5 and 2.5 weeks, respectively). These differences may be a result of the greater movement of atrazine away from the soil surface (Fig. 4A) where maximum temperatures exceeded 40°C (at 2.5 cm) on several occasions. Terbutylazine persistence

(Fig. 6C) in the rainfall treatment (50 % remaining after 2 weeks) was somewhat similar to that for atrazine. However, terbutylazine was much more persistent in the supplementary watering treatment (50 % remaining after 5.5 weeks), with 30% of applied chemical still present after week 21. The increased persistence of terbutylazine may, in part, be a result of lower soil temperatures later in the season, since the terbutylazine study started and ended a month later than the atrazine and metolachlor studies (soil temperatures after mid-August were significantly lower than those measured in June and July).

CONCLUSIONS

Based on effluent and soil core data, the three herbicides exhibited limited movement in light-textured Plainfield sand cores under the moderate rainfall patterns of 1987. All three compounds exhibited the same relative mobilities under both precipitation regimes after 21 weeks, in decreasing order as follows (maximum penetration in parentheses): rainfall - atrazine (30 cm) > terbutylazine (20 cm) > metolachlor (10 cm); supplementary watering - atrazine (70 cm) > terbutylazine (50 cm) > metolachlor (40 cm). Terbutylazine may have moved deeper into the soil cores than metolachlor, not necessarily because of greater mobility but because it persisted longer (Fig. 6B and C), partially as a result of being applied a month later when soil temperatures were lower. The trends in adsorption and solubility data for atrazine and terbutylazine (Table 1) are consistent with the mobility data, but the data for metolachlor, a member of another chemical class, does not fit these trends.

The sudden elution behavior of atrazine and terbutylazine resulting from a heavy water application within 24 h following application suggests that agricultural chemicals may be quite vulnerable to leaching for a period following application. A second 50-mm water application after one week eluted much less chemical because of the greater contact time. These data suggest that soil/water partitioning coefficients obtained by traditional slurry methods may not accurately reflect the restricted soil-pesticide contact available in normally unsaturated soils, especially for the first week or so following soil application of the pesticide.

Acknowledgement-The author acknowledges the assistance of Mrs. Leah Lyubechansky and Mr. John Armistead in the collection and analysis of the data used in the preparation of the manuscript. Additional funding sup-

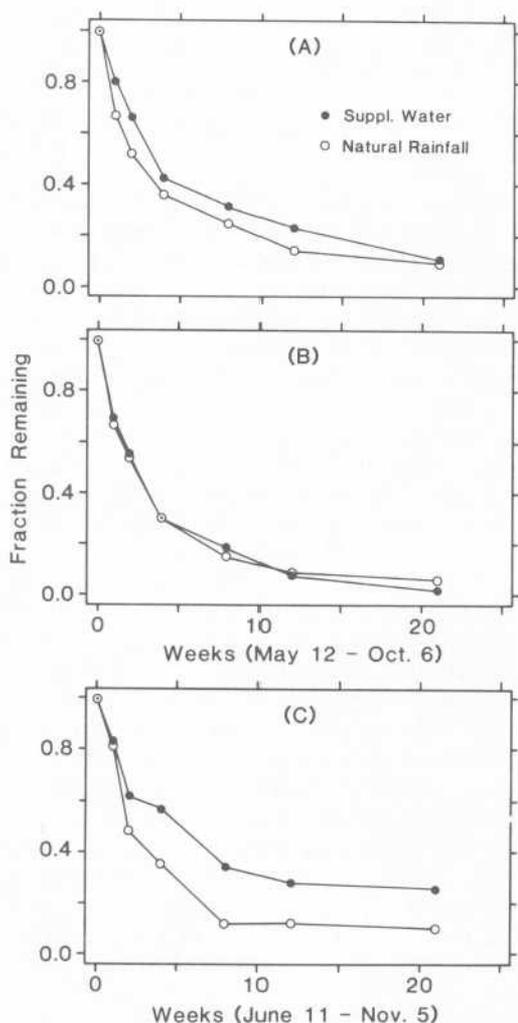


Fig. 6. Persistence in Plainfield sand lysimeters in 1987. A: Atrazine. B: Metolachlor. C: Terbutylazine.

port for this study was provided by both Ciba-Geigy Canada, Ltd., and the Ontario Ministry of Agriculture and Food.

REFERENCES

1. Beven, K. and **P. Germann**. 1981. Water flow in soil macropores. II. A combined flow model. *J. Soil Sci.* 32: 15-29.
2. **Ehlers, W.** 1975. Observations on earthworm channels and infiltration on tilled and untilled loess soil. *Soil Sci.* 119:242-249.
3. **Rice, R.C., R.S. Bowman** and **D.B. Jaynes**. 1986. Percolation of water below an irrigated field. *Soil Sci. Soc. Am. J.* 50:855-859.
4. **Richter, G.** and **W.A. Jury**. 1986. A microlysimeter field study of solute transport through a structured sandy loam soil. *Soil Sci. Soc. Am. J.* 50:863-868.
5. **Boesten, J.J.T.I.** and **L.J.T. Van der Pas**. 1983. Test of some aspects of a model for the adsorption/desorption of herbicides in field soil. *Aspects Appl. Biol.* 4: 495-501.
6. **Karickhoff, S.W.** and **J.R. Morris**. 1985. Sorption dynamics of hydrophobic pollutants in sediment suspensions. *Environ. Toxicol. Chem.* 4:469-479.
7. **McCall, P.J.** and **G.L. Agin**. 1985. Desorption kinetics of picloram as affected by residence time in the soil. *Environ. Toxicol. Chem.* 4:37-44.
8. **Walker, A.** 1987. Evaluation of a simulation model for prediction of herbicide movement and persistence in soil. *Weed Res.* 27:143-152.
9. **Wauchope, R.D.** 1978. The pesticide content of surface water draining from agricultural fields-A review. *J. Environ. Qual.* 7:459-472.
10. **Ontario Ministry of Agriculture and Food**. 1985. OMAF Guide to Chemical Weed Control. Publication 75. Toronto, Ontario.
11. **Bowman, B.T.** 1988. Mobility and persistence of metolachlor and aldicarb in field lysimeters. *J. Environ. Qual.* 17:689-694.
12. **Leonard, R.A., G.W. Langdale** and **W.G. Fleming**. 1979. Herbicide runoff from upland Piedmont watersheds -Data and implications for modeling pesticide transport. *J. Environ. Qual.* 8:223-229.