

Effect of formulation upon movement and dissipation of ¹⁴C-metolachlor and atrazine in field lysimeters

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Bowman, B. T. 1993. **Effect of formulation upon movement and dissipation of ¹⁴C-metolachlor and atrazine in field lysimeters.** *Can. J. Soil Sci.* 73: 309-316. One set of 12 lysimeters (75 cm x 15 cm, packed with 70 cm of Plainfield sand) was treated with ¹⁴C-labelled metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl ethyl)acetamide] in an emulsifiable concentrate (EC) while a second set was treated with a 25% granular (25G) formulation. Atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] was applied to all lysimeters as an internal reference. Duplicate soil cores from each treatment were removed and frozen at 1, 2, 4, 8, 12, and 21 wk following application. All lysimeters received supplementary water throughout the study, simulating 25-yr return storms on days 2 and 9, followed by a simulated irrigation practice thereafter. Soil cores were cut into seven 10-cm segments to obtain persistence data and concentration profiles. No metolachlor and only a few traces of atrazine appeared in the effluent throughout the study. Metolachlor EC disappeared more rapidly than metolachlor 25G, with 50% disappearance times of 2.2 and 4.0 wk, respectively. After 1 and 2 wk, 14.0 and 28.7% more metolachlor 25G than EC, respectively, remained in the top 10-cm layer. No metolachlor was detected below 40 cm in any soil core. Up to 22.3% of applied ¹⁴C accumulated in the effluent after 21 wk, with traces appearing in the effluent on day 2, following a 50-mm watering. ¹⁴C recovery in the lysimeter systems decreased to 78% after 21 wk, which may be partially ascribed to volatilization losses.

Key words: Leaching, degradation, radioisotope, mobility, herbicide

Bowman, B. T. 1993. **Étude des effets de la formulation sur le mouvement et sur la dissipation du ¹⁴C-métolachlore et de l'atrazine en lysimètres.** *Can. J. Soil Sci.* 73: 309-316. Une batterie de 12 lysimètres (75 cm x 15, remplis de 70 cm de sable Plainfield) a été traitée avec du métolachlore marqué au carbone-14 [2-chloro-N-(2-éthyl-6-méthylphényl)-N-(2-méthoxy-1-méthyl éthyl)acetamide] sous forme de concentré émulsionnable, cependant qu'une autre batterie recevait le même produit en préparation granulaire à 25% (25 G). L'atrazine [2-chloro-4-éthylamino-6-isopropylamino-1,3,5triazine] était appliquée dans tous les lysimètres, à titre de référence interne. Deux carottes de sol de chaque traitement ont été prélevées et mises en congélation 1, 2, 4, 8, 12 et 21 semaines après le traitement. Tous les lysimètres recevaient en outre un arrosage d'appoint, simulant une tempête cyclique de quart de siècle, aux jours 2 et 9 et un protocole d'irrigation simulée pour le restant du temps. Les carottes étaient tranchées en 7 segments de 10 cm, de façon à obtenir les données de rémanence et les profils de concentration. Aucune trace de métolachlore et quelques traces seulement d'atrazine ont été recouvrées dans l'effluent. Le métolachlore CE se dissipait plus rapidement que la présentation 25G, avec des délais respectifs de dissipation à 50% de 2,2 et de 4 semaines. Au bout d'une et deux semaines, les 10 cm supérieurs du sol conservaient, respectivement 14 et 28,7% plus de métolachlore sous la forme 25G que sous la forme CE. Aucune trace de métolachlore n'a pu être détectée à plus de 40 cm de profondeur. Jusqu'à 22,3% du ¹⁴C administré s'accumulait dans l'effluent au bout de 21 semaines, des traces apparaissant dans l'effluent au jour 2 à la suite d'un arrosage de 50 mm. La récupération du ¹⁴C dans les lysimètres est tombée à 78% au bout de 21 semaines, ce qui s'expliquerait en partie par les pertes par volatilisation.

Mots clés: Percolation, dégradation, radioisotope, mobilité, herbicide

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An ideal herbicide is one that persists near the soil surface in the plant root zone, providing effective weed control until the crop is mature, then degrading rapidly without leaching to the tile drains or groundwater. Because most herbicide degradation is microbially driven, and this activity resides primarily in the surface organic matter-rich plough layer, it is important that the herbicide be largely degraded before being leached into lower soil horizons. Therefore, a careful selection of the herbicide and its formulation, with regard to persistence and leachability for a given soil type, is an important step in implementing Best Management Practice routines for weed control. The objective is to use the least amount of herbicide that will provide effective weed control, where, and when it is most needed.

In earlier field lysimeter studies involving the soil insecticide isazofos (Bowman 1992) I demonstrated that the formulation strongly influenced both the leachability and chemical persistence of the insecticide. Both microencapsulated (ME) and granular formulations of isazofos were considerably less susceptible to leaching than was the emulsifiable concentrate (EC) formulation. Huang and Ahrens (1991) found that a controlled-release alachlor formulation was much more persistent in soil than a conventional formulation 1 yr after application. Wilson et al. (1988) found in field studies over 3 yr that ME-alachlor generally provided superior annual grass control to EC-alachlor, and the ME- and EC-formulated metolachlor provided similar annual grass control. The efficacy of any formulation in a given year is quite dependent upon factors such as soil (type and organic matter), crop management practices (tillage, crop residue), as well as climatic effects (temperature and moisture).

In this study, the mobility and persistence of two formulations of ^{14}C -labelled metolachlor were compared in Plainfield sand using field lysimeters. Such information should be useful in selecting herbicide formulations for weed control.

MATERIALS AND METHODS

Compounds and Application Rates

Atrazine (Aatrex 480SC) [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] plus ring-labelled ^{14}C -metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl ethyl)acetamide] (specific activity of $1.94 \times 10^9 \text{ Bq g}^{-1}$), formulated as either 960E emulsifiable concentrate (960 g L^{-1}) or 25% granular (25G), were applied to the soil cores (see below). The radiochemical purity of the ^{14}C -metolachlor was 98.7% and the chemical purity was 96.1% (GLC analysis). Atrazine was applied at $2.25 \text{ kg a.i. ha}^{-1}$ (3.98 mg per core) while metolachlor was applied at $2.6 \text{ kg a.i. ha}^{-1}$.

Experimental Setup

Two sets of 12 lysimeters (75 cm high x 15 cm diameter, packed with a 70-cm core of Plainfield sand, 87.5% sand, 6.5% silt, 6.0% clay, 1.5% organic matter) were established as follows: Set 1: metolachlor EC, Set 2: metolachlor 25G. (The term lysimeter includes the soil core and the hardware.) The lysimeters (in a 4 x 6 grid) were placed vertically in an outdoor, aboveground plywood box (1.2 m high x 1.5 m wide x 6 m long) filled with fine sand and embanked with soil on three sides for thermal stability (north side open for access). The granular metolachlor formulation was applied 2.5 cm below the soil surface (at least 1.0 cm from the cylinder wall) by removing and replacing the top soil layer. Liquid formulations were applied by pipette (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 all soil cores as an internal reference.

Details of experimental procedures have been previously reported (Bowman 1988, 1990, 1992). Briefly, about 12 L of water were applied to each lysimeter for 2 wk preceding pesticide application on 14 May 1991. Both lysimeter sets received a 50-mm water application on days 2 and 9, simulating a 25-yr return storm. After the second week, both sets received natural rainfall plus 25-mm water applications (simulating an irrigation protocol) as follows: (a) 2 d following less than a 10-mm rainfall, (b) 3 d following a 10- to 15-mm rainfall, (c) 4 d following a > 25-mm rainfall or the previous watering. The effluent was collected in a 1-L beaker placed below the soil core, and removed through a stainless steel tube into a vacuum collector flask on the day following a rain or water application. One pair of duplicate soil cores from each lysimeter set was retrieved from the field at 1, 2, 4, 8, 12 and 21 wk, and frozen for subsequent sectioning into seven 10-cm segments and for residue analysis.

Soil Core Extraction and Chemical Analyses

Soil core subsamples (100 g) were extracted sequentially with two 80-mL aliquots of a HPLC-grade methanol:water (90:10 vol vol⁻¹) solvent mixture (Bowman 1990). The samples were sonicated for 15 min following each addition of the solvent (before tumbling). 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, GLC or liquid scintillation analyses. Metolachlor and atrazine analyses which were performed by GLC used the following operating parameters: column, J&W DB-17, 0.53 μm x 15 m (megabore, 1.0- μm film); carrier gas: ultra-pure He (15-20 mL min⁻¹); detector: nitrogen-phosphorus, 260°C; H₂ flow rate: 1-3 mL min⁻¹; injector temperature: 240°C; injection volume: 2.0 μL . Minimum detectable concentrations for metolachlor and atrazine were, respectively: 50 $\mu\text{g L}^{-1}$ and 20 $\mu\text{g L}^{-1}$ ($\pm 3\%$ error). Samples were pre-concentrated by 12-fold using solid-phase octadecyl C18 - 14% cartridges, giving an effective minimum detectable concentration of approximately 4 and 1.5 $\mu\text{g L}^{-1}$, respectively, for metolachlor and atrazine. Metolachlor and atrazine analyses were confirmed by HPLC. The operating parameters were: Waters Resolve Column 15.0 cm x 3.9 mm reversed-phase C18, 3 μm ; pump speed: 0.9 mL min⁻¹; injection volume: 40 μL ; detector wavelength: 205 nm for metolachlor, 220 nm for atrazine; mobile phase: acetonitrile:water (1:1). Minimum detectable concentrations for both compounds were in the 15-20 $\mu\text{g L}^{-1}$ range ($\pm 1\%$ error). After sample pre-concentration, this provided an effective minimum detectable limit of approximately 1.0-1.5 $\mu\text{g L}^{-1}$ for both compounds. Extraction recoveries from soil always exceeded 95% of applied amounts.

Soil Sample Combustion Analyses

Well-mixed 1-g subsamples of each core segment for all treatments were combusted (R. J. Harvey Biological Oxidizer) for 4 min at about 850°C, with the ¹⁴CO₂ being trapped in a liquid scintillation cocktail (R. J. Harvey). The trapping efficiency was determined periodically by comparing the disintegrations per minute (DPM) from a counting standard applied to a moistened filter paper which was then combusted, with the DPM from the same volume of counting standard added to the counting vial containing the cocktail. All samples were counted with a Beckman liquid scintillation counter (courtesy of University of Guelph, Guelph, ON).

Liquid Scintillation Analyses

Liquid scintillation analyses of the effluent were performed with a LKB 1217 RackBeta, using Program Mode 1 (cpm/dpm program package), and Counting Mode 4 (single label Carbon, using ESR (External Standardization Ratio)). The following parameters were used for counting samples: counting channel windows: Ch 1, 50-170; Ch 2, 0-0; Ch 3, 100-135; Ch 4, 135-184; counting time: 600 s; maximum counts: 100,000; external standard counting time: 30 s; external standard maximum counts: 100,000. An aqueous counting cocktail was used (Ready Gel[®], Beckman) to count all samples, which permitted aqueous loads approaching 50% and which resulted in a stable, uniform counting gel with high counting efficiencies. The standard vial composition was: 9 mL of Ready Gel, 7 mL of sample. For the quench curve, the following vial composition was employed: 9 mL of Ready Gel, 6 mL of either soil extract or core effluent, and 1 mL (in methanol) of a stock solution of ¹⁴C-metolachlor, having a theoretical DPM count of 145,525. Counting efficiencies were recorded for each of the following additions of CCl₄ to the counting vial: 0, 10, 20, 30, 50, 90, 140, 200 μL .

RESULTS AND DISCUSSION

Effluent Data

Throughout the 21-wk study no metolachlor and only a few traces of atrazine were detected in the effluent from the soil cores. This result was similar to an earlier lysimeter study (Bowman 1990) in which only two traces of metolachlor (< 20 $\mu\text{g L}^{-1}$) were found in the effluent. However, low concentrations of ¹⁴C (0.06 and 1.0 $\mu\text{g L}^{-1}$, respectively, for the 25G and EC formulations) appeared in the effluent immediately following the first 50-mm water application on day 2. Those low ¹⁴C levels in the effluent could be accounted for by the 1.3% of unidentified radiochemical impurities present in the metolachlor formulations. However, we cannot discount the possibility that minute amounts of metolachlor rapidly leached through the 70-cm soil cores since measured ¹⁴C effluent concentrations were below the analytical detection limits of the parent metolachlor. A larger fraction of applied ¹⁴C appeared sooner in

the effluent from the EC-treated cores, than from the 25G-treated cores (see inset, Fig. 1). By the end of the study 18.7 and 22.3 % of the applied ^{14}C appeared in the effluent of the EC and 25G treatments, respectively.

Soil Core Mobility and Persistence Data

Metolachlor from the 25G formulation was considerably more persistent than from the EC formulation in the Plainfield sand cores, giving 50% disappearance times (DT_{50}) of 4.0 and 2.2 wk, respectively (Fig. 2). It is of interest that each data point in a disappearance curve represented the averaged data from a different set of duplicate soil cores, with data from 12 cores (one lysimeter set) being used to construct one dissipation curve. The lack of discontinuities in the curves is an indication of the uniformity of the soil cores in a lysimeter set and also a measure of the repeatability of the technique. DT_{50} values for atrazine were 3.7 and 4.0 wk, in the EC and 25G treatments. During the first week, 21.4 and 13.4% of applied metolachlor disappeared from the EC- and 25G-treated lysimeters, respectively. At that time, the top 10-cm layer of the 25G-treated cores contained 14.0% more metolachlor than the EC-treated cores (Table 1). The residual differences between the two formulations in the top 10-cm layer [25G - EC] increased to 28.7% and 25.8% at 2 and 4 wk, respectively, and was still 3.0% greater after 21 wk, reflecting greater mobility and lesser persistence of metolachlor in the EC formulation. These large differences in disappearance rates were evident in the surface segment (top 10 cm) of the respective concentration profiles (Fig. 3). The DT_{50} value of 2.2 wk for the EC metolachlor in Plainfield sand was similar to that reported using a similar experimental setup (Bowman 1988) but shorter than the 3-3.5 wk reported in 1986 and 1988 (Bowman 1989).

Despite the considerably larger amounts of metolachlor remaining in the 25G-treated cores relative to the EC-treated cores, none had reached the 40-cm level after 8 wk, compared with 1.5 % of the amount applied in the EC treatment (Fig. 3). No metolachlor from either formulation was detected below 40 cm throughout the study, which confirms previous results (Bowman 1990). Essentially 100% of

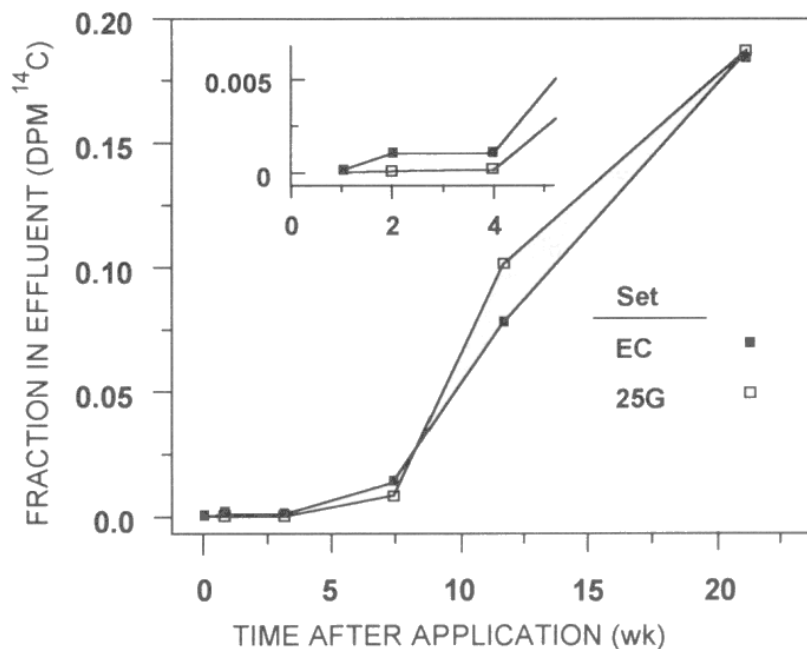


Fig. 1. Accumulative fraction of applied ^{14}C from the EC and 25G metolachlor formulations collected in effluent during the 21-wk study (DPM = disintegrations per min).

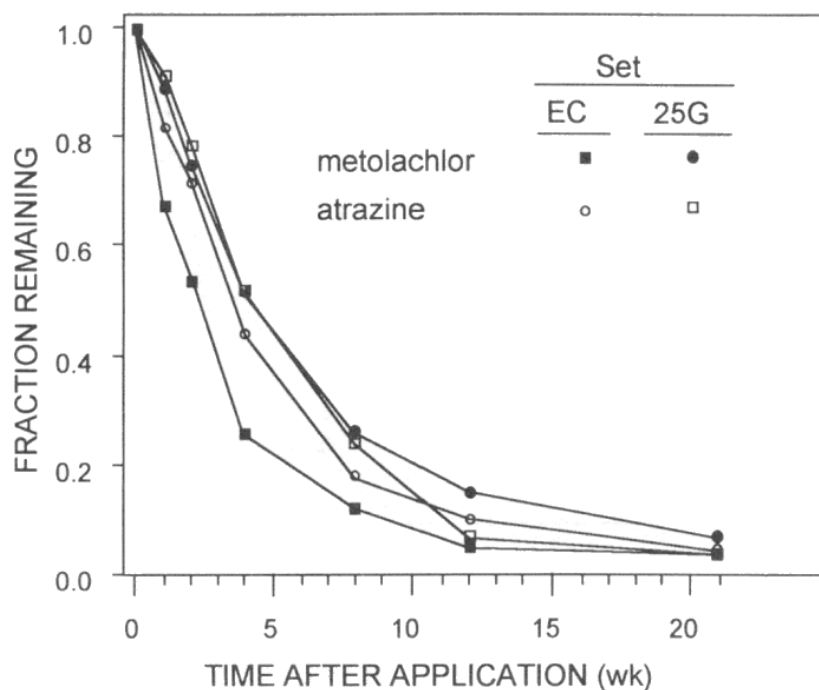


Fig. 2. Persistence of metolachlor (EC and 25G formulations) and atrazine in Plainfield sand lysimeters during the 21-week study..

Table 1. Relative amounts of metolachlor throughout the 21-wk study in the top 10 cm of soil in the 25G- and EC-treatments in Plainfield sand lysimeters

Week	Percent of applied metolachlor in top 10 cm of soil		
	25G	EC	Difference (25G - EC)
1	86.4	72.4	14.0
2	67.8	39.1	28.7
4	45.0	19.2	25.8
8	20.2	9.3	10.9
12	9.4	3.6	5.8
21	4.9	1.9	3.0

applied ^{14}C in the lysimeters (soil and effluent) was accounted for after the first week using the standard solvent extraction procedure, after which ^{14}C recoveries steadily decreased to just under 40% by week 21. Much of this "apparent" loss may have been the result of formation of "bound" residues, not readily extractable by the methanol/water solvent. Khan (1991) and Smith et al. (1992) reported that bound residue formation can account for a significant fraction (> 50%) of many soil-applied ^{14}C -labelled herbicides. It was somewhat unexpected, however, that such a large fraction of the herbicide appeared to be bound in a sandy textured soil, containing only 1.5% organic matter distributed uniformly throughout the entire core.

Combustion analysis of the treated soil cores permitted a mass balance for ^{14}C to be calculated for both lysimeter sets throughout the study (Table 2). With the exception of one set of lysimeters (25G, week 4) which gave anomalously low recoveries, over 95 % of applied ^{14}C was accounted for during the first 4 wk (including amounts in the effluent), after which recoveries decreased to 77-79% by 21 wk. The

downward redistribution of applied ^{14}C (including labelled metolachlor) occurred more rapidly than the redistribution of metolachlor (determined analytically), with 2.2 and 15.7% of the ^{14}C in the 25G and

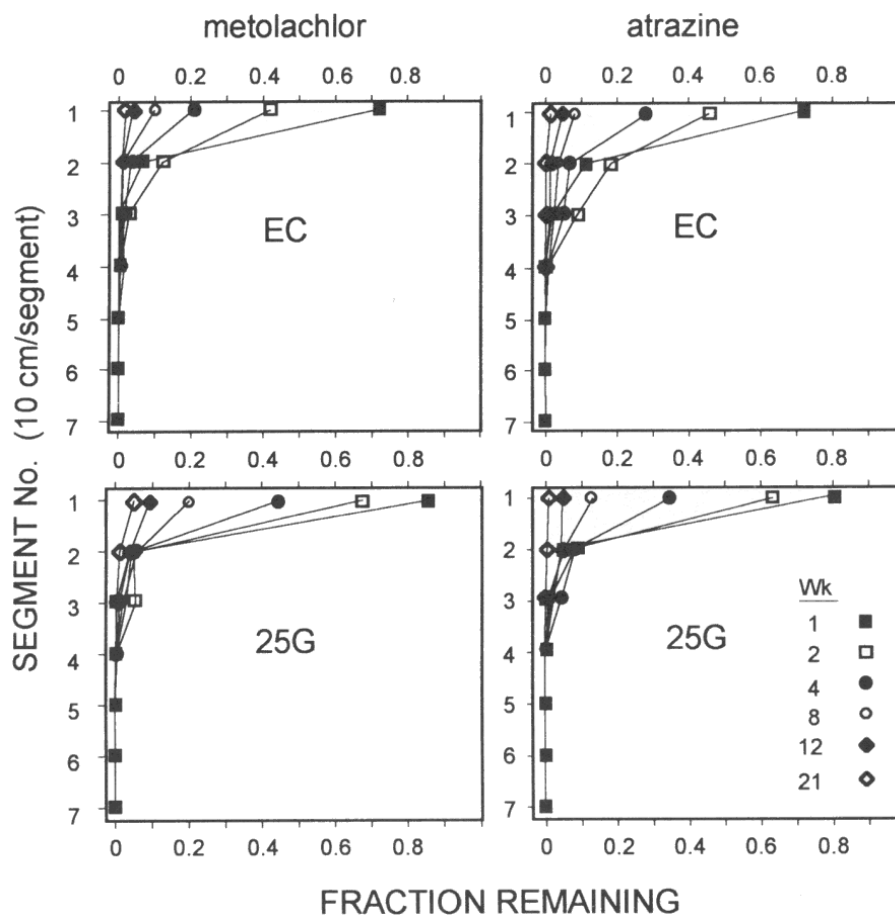


Fig. 3. Concentration profiles throughout the 21-wk study for metolachlor and atrazine in the EC- and 25G-treated Plainfield sand lysimeter sets.

Table 2. Mass balance of applied ^{14}C in field lysimeters treated with EC- and 25G-formulations of ^{14}C -labelled metolachlor, expressed as fraction of applied metolachlor

Week	Fraction of applied metolachlor					
	EC			25G		
	Soil ^z	Effluent ^y	Total	Soil	Effluent	Total
1	1.075	0.000	1.075	0.974	0.000	0.974
2	0.973	0.001	0.974	1.039	0.000	1.039
4	0.977	0.001	0.979	0.797	0.000	0.797
8	0.872	0.016	0.888	0.904	0.009	0.912
12	0.714	0.092	0.806	0.808	0.101	0.910
21	0.569	0.223	0.792	0.578	0.187	0.765

^z Fraction of applied ^{14}C remaining in soil, determined by combustion analysis.

^y Fraction of applied ^{14}C collected in effluent.

EC treatments, respectively, moving below the 10-cm level after the first week, and with traces (0.1-0.2% of applied) reaching the lower extremities of both core sets.

Concentration profiles for "metabolites + bound parent" (METBP) were calculated as "fraction remaining [total ^{14}C -extractable metolachlor]" (Fig. 4). The METBP fraction in the surface segment of the EC-treated cores increased from 0.18 at week 1 to a maximum of 0.45 at week 4, decreasing thereafter. The increasing METBP fraction in the surface segments of EC cores, primarily a result of parent metolachlor degradation, was approximately twice that in the 25G-treated cores. Any observed movement of the METBP fraction below the top 10-cm segment would be almost exclusively metabolites, since bound residues would have been attached to soil aggregates. After week 1, approximately 1.4% of METBP, which is believed to be primarily metabolites, reached 60 cm in the EC cores, compared with just traces at this depth in the 25G cores. Throughout the remainder of the study, up to 5% of applied ^{14}C , primarily metabolites, was present in all the lower segments (below 40 cm) of both formulations at all sampling dates.

After 21 wk about 22% of the applied ^{14}C in both lysimeter sets was unaccounted for. Alhajar et al. (1990) reported that ^{14}C -metolachlor volatility losses from their large soil cores were only in the order of 0.01 % of applied amounts. Chesters et al. (1989) in a comprehensive review of the environmental fate of alachlor and metolachlor, reported that metolachlor was not as volatile as alachlor. In an earlier study, Burkhard and Guth (1981) measured volatilization rates for metolachlor in a sand and silt loam soil with 2.2 and 3.6% organic matter, and in a closed temperature- controlled airflow system. They reported volatilization fluxes of 4.5 and 1.5 $\text{ng cm}^{-2} \text{h}^{-1}$, respectively, for the two soils. In this study, the 22% unaccounted-for portion of applied metolachlor was about 1000 μg . Over the 21-wk study, this translated into an average vapour loss of 1.6 $\text{ng cm}^{-2} \text{h}^{-1}$ on a soil with only 1.5% organic matter, well within the range reported by Burkhard and Guth (1981).

In summary, no detectable metolachlor from either the EC or 25G formulations, or atrazine leached through the 70-cm Plainfield sand lysimeters throughout the 21-wk study. The disappearance rate for metolachlor in the EC formulation in Plainfield sand was considerably greater than that for the 25G formulation (DT_{50} values were 2.2 and 4.0 wk, respectively). Approximately 20% of the applied ^{14}C in both metolachlor formulations accumulated in the leachate from the lysimeters at the completion of the 21-wk study. The metolachlor metabolites containing

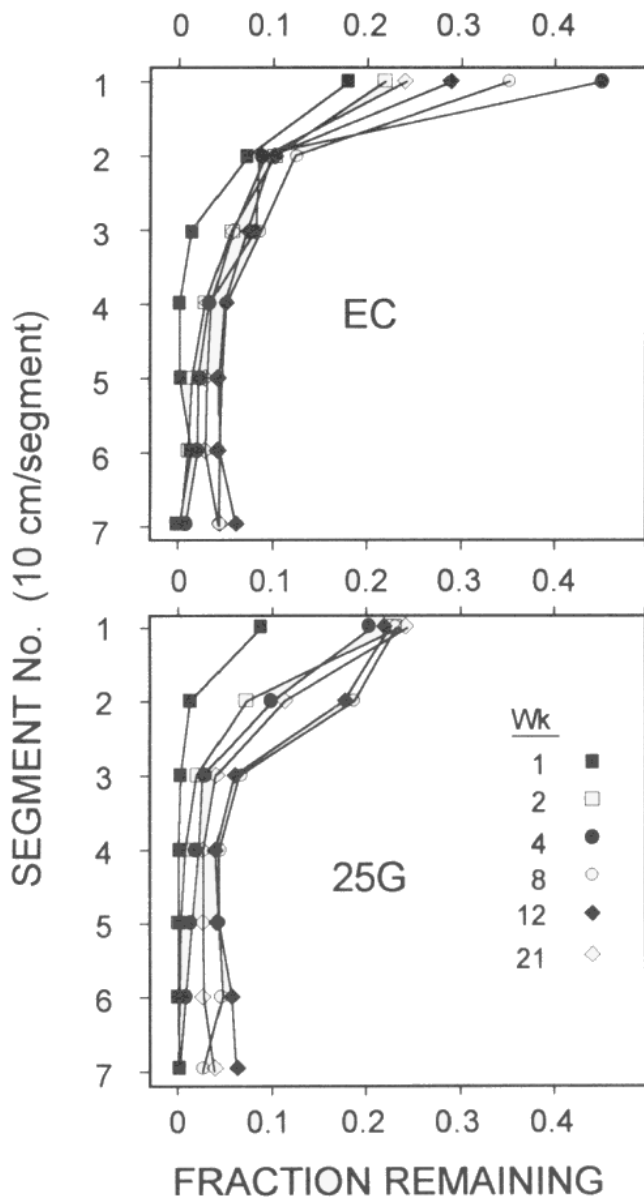


Fig. 4. Concentration profiles for ^{14}C - containing "metabolites + bound parent" (EC, 25G) in Plainfield sand, calculated as: fraction remaining [total ^{14}C - extractable metolachlor].

the ^{14}C label appeared much more susceptible to leaching than did the parent compound. Although metolachlor from the EC formulation was more mobile than from the 25G formulation, none was detected in the soil below 40 cm during the study. The greater persistence of the metolachlor 25G, combined with a lower mobility, make it potentially a much more effective weed control agent than the EC formulation strictly from a chemical residue point of view. However, other factors such as increasing crop canopy competition with the weed population later in the season, and the dosage required for effective weed control may lessen the impact of these differences in behaviour between formulations.

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