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Abstract
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Disciplines
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Chapter 7

Mobility and Degradation of Pesticides and Their Degradates in Intact Soil Columns

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Laboratory studies were conducted to determine the mobility of parent pesticides and degradation products through the use of large undisturbed soil columns. The influence of vegetation on the mobility of pesticide adjuvants was also investigated. Modifications to the laboratory setup of soil columns for studying various pesticides, degradation products, and adjuvants were done to fit the needs of the particular compound being studied. To improve mass balances of volatile parent compounds, such as methyl bromide, as well as biodegradable (mineralizable) pesticide degradation products such as deethylatrazine, modifications of columns to accommodate isolation of volatile degradation products were accomplished by enclosure of the column head space and use of flow-through systems. Evidence of preferential flow of atrazine, deethylatrazine, metolachlor, and methyl bromide were indicated by the presence of either the \(^{14}\)C-compound or Br\(^{-}\) (in the case of methyl bromide-applied soil columns) after the first leaching event. Diffusion through the soil matrix was also evident with a peak of \(^{14}\)C in the leachate several weeks after pesticide (or degradate) application to the soil column. Deethylatrazine, a major degradate of atrazine, was more mobile than the parent compound. Vegetation had a significant positive effect on reducing the mobility of the adjuvants propylene glycol and ethylene glycol.

The fate of any pesticide in the environment is important to understand because of any potential detrimental effect; thus the environmental chemistry and environmental toxicology of a pesticide are inextricably linked. Similarly, the environmental fate of a pesticide encompasses both the

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movement and transformation of the compound. There is an interdependent linkage between these two processes: (1) the transformation products have mobilities that differ from the parent molecule, and (2) conversely, the mobility of a compound can have great impact on the transformation processes since the location of a molecule influences the types and rates of transformations that occur.

Depending on their structure and physicochemical properties, soil-applied pesticides can move through runoff, leaching, volatilization, uptake into plants or microbes, or adsorption to the soil matrix. The conditions at each site are different, and the various agents that act upon the pesticide molecule can effect different types of transformations. The transformation products are typically degradates, although occasionally other types of transformations occur, such as conjugations, rearrangements, dimerizations, or isomerizations. The toxicological significance of any transformation product obviously needs to be considered for each compound. Recently there has been a realization that pesticide degradates are sometimes as important or more important than the parent pesticide in environmental settings. Although only a small minority of transformation products are of toxicological significance, serious consideration must be given to their formation mechanisms, quantities present, persistence, and mobility in the environment.

Investigations that focus on soil incubations, plant metabolism, or other component-based experiments have several distinct advantages, such as closely controlled environmental variables, low space requirements, and low cost per experimental unit which allows for more treatments and more replication. On the other hand, there are several shortcomings of very specific laboratory experiments, especially the lack of realistic environmental conditions variability and the scale. Research on larger scales, including field plots, fields, watersheds, or regions allows ample realism in conditions, variability, and scale, but such research has obvious limitations in investigators' capacity to control the variables such as climate; also, the costs of research are much higher at the larger scales.

Lysimeter research, as presented in this volume, represents a concept that optimizes the process of evaluating the environmental fate of pesticides. It incorporates many of the advantages of the laboratory approach, but retains essential elements of the realistic conditions encountered in the field. The scale is midway between the lab and the field, allowing for adequate replication, excellent sensitivity through the use of radiotracers, and manageable costs, but it also takes advantage of an intact soil monolith and natural weather conditions.

Utilization of intact soil columns for studying environmental fate of pesticides has some of the same advantages as the lysimeter concept. These are field-collected but studied under laboratory conditions. There are, of course, trade-offs once again, but they have one important advantage in common with the lysimeters. They provide an integrated evaluation of a compound's persistence, binding, degradation, and mobility in one experimental unit.

Laboratory mobility studies are often carried out using soil columns that have been created by packing sieved soils from various soil profiles into a PVC pipe or other cylindrical container. Pesticides applied at the surface move through the column with simulated rainfall. Pesticides or degradation products that are able to move by diffusion through the soil matrix along with water are retrieved at the bottom of the column. Concentrations are often measured by either gas chromatography (GC) or radiotracer techniques. The use of packed soil columns does not take into consideration the natural formation of macropores such as those created by plant roots or earthworm channels, and, thus, the contribution of preferential flow
from rapid movement of the pesticides through such channels can not be determined. Czapar et al. (1) compared mobilities of alachlor, cyanazine, and pendimethalin in soil columns with and without artificial macropores. These herbicides were detected in leachates from only those columns with continuous macropores, and they state that leaching studies that use packed soil columns may underestimate herbicide mobility. With the use of undisturbed soil columns in laboratory studies, one can obtain a more realistic understanding of parent pesticide and degradation product mobility under less variable conditions than in the field. Maintaining the integrity of naturally occurring macropores allows for not only measurement of the mobility of compounds due to diffusion through the soil matrix, but also mobility due to preferential flow of compounds with water.

Methods for acquiring and setting up large undisturbed soil columns for studies conducted in this laboratory were modified from (2), who had used such methods to investigate solute transport through macropores in large undisturbed soil columns. The earliest studies in our laboratory using this method were conducted to determined the mobility of atrazine and major degradation products (3). In earlier fate studies of atrazine, volatility and evolution of CO₂ from its degradation were reported to be minimal (4,5), thus completely enclosing the headspace of the columns for this study was not necessary.

For a deethylatrazine mobility study (6), the soil column set up was modified to enable trapping of ^14^CO₂ in order to improve the mass balance of ^14^C-deethylatrazine applied to the column. Evolution of the modification of the soil column continued with the study of metolachlor mobility (7). A preliminary study indicated a poor mass balance, and, thus, modification to make the system completely enclosed was carried out. A flow-through system was incorporated into the study so that the column was never opened to the atmosphere. Aerobicity was maintained, however, through a port that contained a charcoal trap to allow for air exchange while trapping organic ^14^C that was generated from metolachlor degradation. In the mobility study of highly volatile methyl bromide (8), additional modifications to soil columns were undertaken. Instead of adding another separate section to the top of the soil column, a continuous PVC pipe was used, thus eliminating the seam between the column and the head space. Additionally, a charcoal trap was suspended in the column to trap methyl bromide that volatilized above the soil.

The influence of vegetation on the mobility of pesticide adjuvants was also investigated. For these studies, undisturbed soil columns were either seeded with alfalfa or rye grass or left unvegetated. During the establishment of vegetation, soil columns were maintained under controlled temperature and lighting conditions for 4 months, with water added to the columns as needed. After sufficient growth of plants had been achieved, as noted by the observation of roots at the bottom of the columns, adjuvants were applied to the soil, and a leaching study was begun.

**Fate Studies in Intact Soil Columns**

**Mobility and Degradation of Atrazine.** The fate of atrazine was determined in a laboratory study using large undisturbed soil columns taken from a field with no previous pesticide history (3). Intact soil columns were obtained from a field with no previous pesticide history at the Iowa State University Agronomy and Agricultural Engineering Farm, Till Hydrology Site, near Ames, IA. In order to obtain the undisturbed soil columns, a circular trench 70 cm deep was...
dug by using shovels, leaving a soil pedestal of approximately 40 cm in diameter in the middle of the trench. A furnace pipe measuring 15 cm in diameter and 60 cm tall was pressed gently into the top 2 to 3 cm of the soil pedestal, and soil was carved away at a depth of 5 to 10 cm in the same diameter as the furnace pipe before pushing the pipe further into the soil. In this way, compaction was avoided within the soil column. Physical and chemical characteristics of soils throughout the profile were determined (A & L Midwest Laboratory, Omaha) on subsamples of soils taken during column extraction.

**Laboratory Preparation.** In the laboratory, soil columns were prepared for laboratory experiments (Figure 1A). A polyvinyl chloride (PVC) pipe, measuring 20 cm in diameter and 60 cm in length, was centered around the soil column and the space was filled with molten paraffin wax to prevent boundary flow along the outer edges of the columns during the leaching study (9). Prior to this step, the vertical surfaces of the soil columns were sealed with Plasti-Dip® spray (P.D.I., Inc., Circle Pines, MN) to prevent paraffin from penetrating the soil column. An aluminum collar (15 cm tall) was fixed around the top of the soil column to prevent leachate from spreading over the wax during the leaching study. Once the wax was cooled and hardened, the bottom 1 cm of soil was removed, and a wire screen was placed in contact with the bottom of the soil column. A perforated Plexiglas™ plate (20-cm diameter) with six metal washers glued to it was mounted on the bottom of the PVC pipe. The washers served as spacers between the screen and the plate to prevent air locks and to assure continuous flow of leachate during the leaching study.

In order for the soil moisture of replicate columns to be equivalent at the beginning of the study, columns were saturated with 0.005 M CaSO₄. This solution was chosen for soil saturation as its characteristics more closely resemble those of soil pore water than would ultrapure water. Each column was placed in a large metal garbage can, and CaSO₄ solution was added until columns were completely submerged. This submersion was done at a slow rate so that no air would be trapped within the soil column, with complete saturation accomplished over a 48-h period. Soil columns were then mounted in stands in a temperature-controlled room held at 25 °C and allowed to drain to field capacity. Ultrapure water was added to the top of each soil column and was then collected at the bottom to obtain a background leachate sample. A chloride tracer was applied to the top of the soil columns, which were then leached with ultrapure water to verify their performance (9). A qualitative comparison of the precipitate, arising from the drop-wise addition of 1 M AgNO₃ to the leachate, was made with background samples to ensure that the amount of chloride in the leachate was above the background level found normally in soil.

**Soil Treatment.** A solution was prepared with a mixture of Aatrex Nine-0® and [U-ring-¹⁴C]ATR (98.2% radiopurity; Novartis Crop Protection, Greensboro, NC) dissolved in deionized water. Each column was applied with ATR at a soil concentration of 2.24 kg (active ingredient) per hectare and radioactivity level of 15 μCi of ¹⁴C. The atrazine treatment was incorporated into the top 2 cm of soil. To minimize evaporation, the top of each soil column was covered loosely with aluminum foil. No attempt was made to trap for CO₂, since a previous soil metabolism study in this laboratory indicated minimal mineralization of ATR (< 1%) in soil the same field plot (4).
Figure 1. Preparation and subsequent modifications of intact soil columns for laboratory experiments
Leaching Study. So that mobility of not only the parent compound but also degradation products could be determined, a leaching study was not begun until three weeks after ATR treatment to allow for degradation formation from ATR. Soil columns were then leached weekly for 12 weeks with 3.8 cm of simulated rain (a quantity chosen to represent comparable rainfall amounts received during the spring in Iowa). The quantity of radioactivity recovered in leachate each week was determined by radioassaying subsamples of leachate by using liquid scintillation techniques.

Soil Extractions and Analyses. Following the leaching study, soil columns were cut into 10-cm increments. Subsamples from each depth (50-g dry weight) were extracted three times with 150 ml methanol/water (9:1), with an extraction efficiency for ATR of 100%. The extract was partitioned with dichloromethane, and subsamples of the concentrated organic fraction were radioassayed and used for thin-layer chromatography and autoradiography to determine the proportions of ATR and degradates. To determine the quantities of unextractable 14C-residues, subsamples of extracted soils were combusted in a Packard sample oxidizer (Packard Instrument Co.).

Mobility and Degradation of Atrazine. In the leaching study, radioactivity was recovered in the leachate with the first rain event, indicating preferential (macropore) flow. Each week, approximately 0.1% of the applied radioactivity was detected in the leachate and, cumulatively, at the end of the 12-week period, 1.2% of the applied 14C-ATR was recovered. With such a low amount of 14C recovered in the leachate, no attempt was made to characterize the radioactivity (parent versus degradation products). Based on the proportion of 14C to active ingredient in the treating solution, the cumulative concentration of ATR in the leachate was 7.6 μg/L.

The majority of the radioactivity remained in the top 10 cm of soil (77% of the applied 14C), with the greatest proportion of 14C as soil-bound (unextractable) residues (57%) (Figure 2). Deethylatrazine (DEA) was the most predominant degradate, with 3.6% of the applied 14C characterized as DEA in the top 10 cm of soil. Deisopropylatrazine (DIA) was the second most predominant identified degradate. Polar degradation products (from the aqueous fraction after partitioning of the soil extracts) were greater in the top 10 cm of soil than in other depths.

In this study, ATR, along with the two degradation products DEA and DIA, exhibited the greatest mobility as they were detected at all depths. Their presence in soils of all depths of the column might also be attributed to degradation of ATR after reaching these depths.

Mobility and Degradation of Deethylatrazine. A study was conducted to determine the fate of deethylatrazine (DEA), a major metabolite of ATR, in large undisturbed soil columns (6). Soil columns (15-cm diameter x 60-cm length) were obtained from a field with no previous ATR history, as described in the ATR section. Two soil columns were prepared for laboratory experiments by using a modification of the method described by (3) (Figure 1B). In order to obtain a mass balance of the applied 14C, the top of the column was sealed with an additional section of PVC pipe (20-cm diameter by 20-cm length), and the top of this section was capped with a plexiglas plate and sealed with silicon rubber adhesive sealant (General Electric Co., Waterford, NY) (6). Within the Plexiglas™ plate, three holes were cut. A large central
hole, or port, was sealed with a neoprene stopper and used to access the top of the soil column during the leaching experiment. The stopper had a glass rod through the center which served as an attachment site for a polyurethane foam trap for trapping $^{14}$C-organic volatiles. In order to trap $^{14}$CO$_2$ arising from complete mineralization of $^{14}$C-DEA, a sodium hydroxide (NaOH) trap was suspended from a neoprene stopper in a second port. In order to assure that aerobic conditions were maintained, a perforated plastic centrifuge tube (capped with a neoprene stopper) containing 5 ml ultrapure water and two drops of a 4% resazurin solution was inserted to serve as a monitor for the aerobicity of the headspace over the soil column. All neoprene stoppers were wrapped with Teflon® tape.

**Soil Treatment and Leaching.** Each column received an application of DEA equivalent to 0.5 lb a.i./acre and approximately 20 μCi of [$^{14}$C]DEA by applying a treating solution prepared with a mixture of analytical grade DEA and [U-$^\text{ring-}$]$^{14}$C]DEA (94.8% radiopurity) [$^{14}$C]DEA dissolved in ultrapure water. The DEA treatment was incorporated into the top 2 cm of soil to minimize volatilization of DEA. Three days after treatment, a leaching study was initiated with an equivalent of 3.8 cm of rainfall (675 ml ultrapure water) applied slowly to the top of each column per week for 13 weeks. Rainfall applications usually took between 40 and 60 min. Leachate from each rain event was collected at the bottom of columns in 100-ml aliquots which were analyzed for radioactivity by liquid scintillation counting techniques (LSC).

**Solid-phase Extraction (SPE) of Leachate.** A modified SPE method was used to isolate DEA and degradates from the leachate (10). After filtering the leachates through a glass-microfiber filter, the pH was adjusted within the range of 7.0 to 7.5 by drop-wise addition of aqueous ammonia or phosphoric acid. For this procedure, Bond Elut® (Varian, Harbor City, CA) cyclohexyl SPE cartridges were used. After conditioning the cartridges with methanol and ultrapure water, leachates were passed through the SPE cartridges at a rate of approximately 5 ml/min, and then the cartridges were air-dried. DEA and degradates were eluted from the cartridges with 10 ml of acetonitrile. Effluent volumes were taken, and subsamples of the effluent and eluate were counted by using liquid scintillation spectroscopy, with radioactivity in the effluent categorized as unidentified polar degradates. DEA and degradates in the acetonitrile eluate were characterized by thin-layer chromatography on normal phase silica gel plates in a solvent system of chloroform: methanol: formic acid: water (100:20:4:2) (Novartis Crop Protection). Autoradiography was used to visualize the radioactive spots associated with $^{14}$C-standards. TLC plates were scraped and counted using LSC techniques.

**Soil Extractions and Analyses.** At the conclusion of the leaching experiment, soil columns were cut into 10-cm increments, and subsamples were extracted and analyzed as described in the ATR section and in (3).

**Statistical Analysis.** For components of the leachate, an analysis of variance (ANOVA) was performed on the repeated measures design. Orthogonal contrasts were also determined for specific comparisons of leaching events. To determine the effect of soil depth, an ANOVA which used soil columns as a blocking variable was conducted on the components determined in soil extractions and analyses.
Mass Balance of DEA in Leachate and Soil. For this experiment, the overall mean recovery of radioactivity was 97%, with 89% of the applied radioactivity distributed throughout soil columns at the end of the leaching study. Less than 0.2% of the applied $^{14}$C was recovered as $^{14}$CO$_2$, and no $^{14}$C-organic volatiles were detected.

Preferential flow was noted during the first leaching event, with a significantly greater percentage of $^{14}$C being leached in this rain event (2.3% of the applied $^{14}$C) compared with all other rain events ($p = 0.0002$) (Figure 3). Of this amount, 1.3% was a characterized as DEA. There were no significant differences in the quantities of DEA leached from the columns for rain events 2 through 13. Unidentified polar degradates made up 1% of the radioactivity from the first rain event. After the sixth rain event, the concentration of polar degradates exceeded that of DEA in the leachate. Trace amounts ($< 0.01\%$) of didealkylatrazine (DDA) and deethylhydroxatrazine (DEHYA) occurred in the leachate throughout the leaching study. With the eleventh rain event, significantly greater DDA and DEHYA concentrations were noted, compared with all of the other rain events ($p = 0.002$ and $p = 0.004$, respectively).

Cumulatively, 7.5% of the radioactivity applied to the top of soil columns was recovered in the leachate over the course of the 13-wk leaching experiment. In consideration of the unlabeled analytical grade DEA associated with this quantity of radioactivity in the treating solution and taking into account the total volume of the leachate, this corresponds to a total DEA/degradate concentration of 10 μg/L (in DEA equivalents). With 3.6% as DEA, this corresponds to a concentration of 4.9 mg/L. The percentages of DDA and DEHYA in the leachate over the 13-wk study were less than 0.02% of the applied, while unidentified polar degradates accounted for 3.8% of the applied radioactivity. The unidentified polar degradates may have included DDA and DEHYA since the SPE method used may not have been as efficient for polar degradates including DDA and DEHYA, although it was efficient for isolating DEA. Recent research by (11) has focused on methods for isolation of polar degradates. In comparing the ATR-applied and DEA-applied soil column studies, it was noted that DEA was more mobile than ATR. After 12 weeks, 6% of the applied DEA was leached (DEA and degradates), compared with only 1% in ATR-applied soil columns (Figure 4).

Distribution of $^{14}$C-DEA and Degradates in the Soil Profile. The top 10 cm of soil columns retained the majority of the applied $^{14}$C (67%). The percentage of DEA was significantly greater in this depth (5.5%) than in the remaining depths $\leq 1.2\%$ ($p = 0.0001$). There were no significant differences in the quantities of DDA and DEHYA extracted from all depths. Significantly larger quantities of unidentified polar degradates were formed in the top 10 cm (12%) compared with deeper soils $\leq 2.6\%$ ($p = 0.001$). Fifty-seven percent of the applied radioactivity was unextractable (soil bound) from soil columns (sum of all depths). In the top 10 cm, 48% of the applied radioactivity was unextractable, and this quantity was significantly greater than in soils deeper than 10 cm $\leq 4.8\%$ ($p = 0.0001$). The quantities of bound residues in the 10 to 20-cm depth were an order of magnitude below those formed in the top 10 cm (4.8%), and there were no significant differences in bound residue quantities among soils below 20-cm depth.

Mobility and Degradation of Metolachlor. Metolachlor (2-chlor-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl)acetamide) is one of the most widely used herbicides in the Midwestern United States (12). This moderately soluble (530 mg/L at 20°C) nonionizable
Figure 2. Percentages of applied \(^{14}\text{C}\) as ATR, DEA, polar degradates, and soil-bound residues in the top 10 cm of intact soil columns treated with \(^{14}\text{C}\)-ATR. Bars represent standard errors (n = 2).

Figure 3. Percentages of applied \(^{14}\text{C}\)-DEA recovered in leachate as DEA or polar degradates. Bars represent standard deviations of the mean (n = 2).
herbicide is primarily transported in the water phase and is more mobile and persistent than other chloroacetamide herbicides (13-16). Researchers have detected metolachlor in subsurface soils (2.28 m deep) (14,17), subsurface tile drain water, and groundwater (18-20). Based on the water solubility, sorption behavior, and moderate persistence of this herbicide, the United States Environmental Protection Agency (USEPA) has listed metolachlor as having a potential to leach through soil and contaminate groundwater (21). The following undisturbed soil column studies were conducted to evaluate the fate of radiolabeled metolachlor in the soil profile. The depth to which metolachlor leached in the soil and the quantity of metolachlor and metolachlor degradation products in the soil column and the leachate were determined.

**Laboratory Preparation.** Undisturbed soil columns were extracted from a pesticide-free field, prepared in the laboratory, and saturated with 0.005 M CaSO\(_4\) as previously described (Figure 1A). The performance of each column and the reproducibility between the replicate soil columns were evaluated with a bromide ion tracer. A potassium bromide solution containing 17.5 mg of potassium bromide (9.903 kg/ha) was applied to the surface of each column. The soil columns were leached with 675 ml of ultrapure water to simulate 3.8 cm of rainfall. Leachates were collected in fractions, and the concentration of bromide ion in each fraction was measured using an ion-selective electrode.

**Soil Treatment and Modification of the Soil Column for a Flow-through System.** Technical grade metolachlor and [U-\(\text{ring}^{-14}\text{C}\)]metolachlor (100 \(\mu\text{Ci}\)) were dissolved in water and uniformly applied to the surface of each soil column at the rate of 3.36 kg ai/ha. The treating solution was incorporated into the top 2 cm with a spatula, and glass wool was placed over the top of each soil column to maintain the integrity of the surface. The top of the PVC pipe was sealed with a Plexiglas™ plate containing a polytetrafluoroethylene-covered neoprene stopper (#13) with three glass tube ports (Figure 1C). The center port was connected to a separatory funnel that allowed ultrapure water to be applied to the soil column weekly. The second port contained a charcoal trap that allowed air into the column and trapped organic volatiles from the headspace of the column. The final port led to a 0.1 N sodium hydroxide trap, followed by an Ultima Gold™ trap. A vacuum pump was used to create a suction that bubbled the contents of each column headspace through 0.1 N sodium hydroxide and Ultima Gold™ traps to absorb \(14\text{CO}_2\) and \(14\text{C}\)-organic volatiles, respectively. The radioactivity of the trapping solutions was measured with a liquid scintillation spectrometer. A vial containing a resazurin solution (several drops of a 4% resazurin solution in ethanol + water) was used to determine when the enclosed headspace of the soil column became anaerobic. When the column headspace became anaerobic, the headspace of the column was exchanged more frequently (22).

**Leaching Study.** Beginning 3 weeks after the treatment of the soil columns, each column was leached weekly for 12 weeks. The initial leaching of the columns was begun 3 weeks after the herbicide treatment to allow metolachlor to begin to degrade in order to observe the mobility of metolachlor and metolachlor degradation products through the soil profile. The leachates were collected, and the radioactivity in each leachate was determined by LSC.
Solid-phase Extraction (SPE) and Analyses of the Leachate. A portion of each leachate was vacuum filtered (glass fiber filter paper) and drawn through a solid phase extraction cartridge (Supelclean Envi-18™). The quantity of [14C]metolachlor and [14C]metolachlor degradation products in the methanol eluates were characterized by thin-layer chromatography (250-mm silica gel 60 F-254; hexane/methylene chloride/ethyl acetate (6:1:3, v/v/v) solvent system) (23) and autoradiography (X-Omat™ Kodak diagnostic film). The location of the non-radiolabeled standards were identified with an ultraviolet lamp (254 nm), and the percent of radioactivity characterized as metolachlor or metolachlor degradation products was measured by LSC.

Soil Extraction and Analysis. At the completion of the leaching study, soil columns were disassembled and divided into 10-cm sections. Three 50-g subsamples were taken from each 10-cm section and extracted three times with 150 ml of methanol/water (9:1 v/v). The quantity of metolachlor and metolachlor degradation products in the soil extracts were determined by thin-layer chromatography and autoradiography as described in the analysis of the leachates. Extracted soils were combusted with hydrolyzed starch in a Packard sample oxidizer (Packard Instrument Co., Downer’s Grove, IL.) to determine the quantity of [14C]soil bound residues. Radiolabeled CO₂ resulting from the combustion of the soil was trapped in Carbo-Sorb® E and Permafluor® V (Packard Instruments Co.) and the radioactivity in each sample was quantified using LSC. Percentages of [14C]metolachlor mineralized to 14CO₂, leached through the soil column, and the amount remaining in the soil (bound and extractable) was calculated. Analysis of variance (ANOVA) was used to determine significant differences between metolachlor and metolachlor degradation products in the soil extracts and significant differences between soil-bound residues in the 10-cm sections of the extracted soil column.

Mobility and Degradation of Metolachlor. The initial metolachlor mobility studies were conducted with undisturbed soil columns similar to the deethylatrazine-treated columns (Figure 1B). At the completion of the analysis only 42% of the applied radioactivity had been recovered. Additional soil columns were treated with [14C]metolachlor, and modifications were made to the soil columns to reduce chemical loss and improve the final mass balance. Despite the addition of the flow-through system (Figure 1C) and attempts to account for all radioactivity, the recovery of the applied 14C in the modified soil columns was 44%. The results of this study are reported in percentage of recovered radioactivity.

Twenty-five percent of the recovered 14C leached through the soil profile of the undisturbed soil columns. The quantity of radioactivity detected in the leachate gradually declined with the leaching events from 3.34% in the first leachate to 1.09% in the final leachate (Figure 5). Only trace amounts (<1%) of the recovered radioactivity were characterized as the parent compound, [14C]metolachlor, in each of the leachates. At the completion of the leaching study, greater than 6,500 ml of leachate had been collected at the bottom of each column. The calculated concentration of metolachlor in the total leachate was 4.5 μg/L.

Metolachlor was degraded in the soil to a number of degradation products. Between six and eleven degradation products were detected in each leachate. Our findings are in agreement with those of (24) who detected metolachlor and six unidentified metolachlor metabolites in the leachate of greenhouse lysimeters. The presence of eight degradation products in the first leaching event indicates that some of the degradation products of metolachlor were as mobile or more mobile than the parent compound.
Figure 4. Radioactivity recovered in leachate from atrazine- or deethylatrazine-treated soil columns. Bars represent standard deviations of the mean (n = 2).

Figure 5. Metolachlor and metolachlor degradation products in the leachate of the undisturbed soil columns.
Distribution of Metolachlor and Metolachlor Degradation Products in the Soil Profile. Seventy-five percent of the recovered 14C remained in the soil column. Surface soils (0-10 cm) contained more than five times the amount of radioactivity detected in any of the subsurface soils (10-60 cm) (Table I). The significantly greater (p < 0.05) percentage of radioactivity detected in the surface soils and the significant decline in the quantity of 14C in the subsurface soils are similar to the findings of in the observations of (24,25) the fate of [14C]metolachlor in greenhouse lysimeters and field lysimeters, respectively.

Soil-bound residues accounted for the largest percentage of radioactivity detected in the surface soils (Table I). Subsurface soils contained significantly less (p < 0.05) nonextractable residues than surface soils. The quantity of radioactivity bound to the surface soil was between eight and twenty-five times the amount found in the subsurface sections. The fate of agricultural chemicals in the soil and their potential to leach through the soil profile and contaminate groundwater is dependent on the persistence of the compounds and their sorption to the soil (26). Adsorption of metolachlor to soil is correlated with increasing organic carbon content (r = 0.72), percent clay (r = 0.80), and cation exchange capacity (r = 0.94) of the soil (9, 13, 27-29). Surface soils often contain greater quantities of organic matter than subsurface soils. Laboratory and greenhouse studies have reported metolachlor is weakly adsorbed and highly mobile in low-organic matter soils (<1% organic matter) (27). Examination of this Iowa soil reveals a 2.3% to 3.0% organic matter content in the soil from 0 to 45 cm. The presence of 48.7% of the recovered 14C (31.9% nonextractable bound residues) in the top ten centimeters of our columns is believed to be the result, in part, of metolachlor and metolachlor degradation products adsorption to the humic fraction of this soil (30).

The greatest quantity (p < 0.05) of extractable [14C]metolachlor and [14C]metolachlor dégradâtes were detected in the top 10 cm of the soil column (Table I). Less than 2% of the recovered 14C was identified as [14C]metolachlor in the soil extract of the surface soils, while 14% was identified as extractable metolachlor degradation products. Negligible quantities of metolachlor were measured in the soil extracts of the subsurface soils (< 0.07%). Extractable metolachlor degradation products ranged from 0.88% in the 40-50 cm section to 3.49% in the 10-20 cm section.

Mineralization and Volatilization of Metolachlor. Ultima Gold™ traps and sodium hydroxide traps were used to collect organic volatiles and 14CO2 produced from the mineralization of [14C]metolachlor. Mineralization of [14C]metolachlor to 14CO2 was minimal. Less than one percent of the recovered 14C was detected in the NaOH traps. Organic volatiles were not detected in the headspace of the columns.

Volatility and Mobility of Methyl Bromide. Undisturbed soil columns were used to study the volatility, mobility, and degradation of methyl bromide (MeBr) in soil (7,31). Two undisturbed soil columns (15-cm diameter x 38-cm length) were obtained from an agricultural field site (no previous pesticide history) near Ames, IA. Procedures for the collection, removal, and storage of the columns were previously described by (2) and in this chapter. Additional soil samples were collected at the same depths as the column to determine the soil physicochemical properties. A composite of these soil samples consisted of sandy clay loam soil with a pH of 5.4 and 54% sand, 25% silt, 21% clay, and 2.5% organic matter.
Table I. Distribution of $^{14}$C-metolachlor and $^{14}$C-metolachlor degradation products in undisturbed soil columns

<table>
<thead>
<tr>
<th>Soil depth:</th>
<th>0-10 cm</th>
<th>10-20 cm</th>
<th>20-30 cm</th>
<th>30-40 cm</th>
<th>40-50 cm</th>
<th>50-60 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractable residues</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor</td>
<td>1.30 A</td>
<td>0.02 B</td>
<td>0.06 B</td>
<td>0.06 B</td>
<td>0.07 B</td>
<td>0.05 B</td>
</tr>
<tr>
<td></td>
<td>(0.102)</td>
<td>(0.007)</td>
<td>(0.003)</td>
<td>(0.009)</td>
<td>(0.016)</td>
<td>(0.011)</td>
</tr>
<tr>
<td>Degradation products</td>
<td>14.0 A</td>
<td>3.49 B</td>
<td>2.38 C</td>
<td>1.55 D</td>
<td>0.88 D</td>
<td>0.96 D</td>
</tr>
<tr>
<td></td>
<td>(0.76)</td>
<td>(0.19)</td>
<td>(0.078)</td>
<td>(0.055)</td>
<td>(0.098)</td>
<td>(0.086)</td>
</tr>
<tr>
<td></td>
<td>(2.1)</td>
<td>(0.12)</td>
<td>(0.16)</td>
<td>(0.088)</td>
<td>(0.044)</td>
<td>(0.039)</td>
</tr>
<tr>
<td>Total$^b$</td>
<td>48.7 A</td>
<td>8.35 B</td>
<td>6.09 B</td>
<td>5.22 CD</td>
<td>3.62 CD</td>
<td>3.07 C</td>
</tr>
<tr>
<td></td>
<td>(2.07)</td>
<td>(0.73)</td>
<td>(0.25)</td>
<td>(0.43)</td>
<td>(0.69)</td>
<td>(0.51)</td>
</tr>
</tbody>
</table>

$^a$Means in each row followed by the same letter are not statistically different (p=0.05).

$^b$Summation of metolachlor, metolachlor degradation products, and soil-bound residues.
Undisturbed soil columns were prepared for laboratory studies as described by (3,6) and in this chapter (Fig. 1A-1B). Modifications were made to collect the MeBr that volatilized from the soil (Fig. 1D) (7). The PVC pipe on the exterior of the column was longer than the soil column to ensure sufficient headspace for the addition of an activated carbon trap. A Plexiglas™ plate with three openings was mounted to the top of each PVC pipe and sealed with silicon rubber adhesive sealant. These openings were sealed with polytetrafluoroethylene-covered neoprene stoppers containing either a granular-activated carbon trap, resazurin trap, or glass tube sealed with a septum (for addition of water). Granular-activated carbon traps were suspended in the headspace of each column to adsorb MeBr that volatilized from the soil. Each trap consisted of 8 g activated charcoal wrapped in 5 x 5-cm, 100% cotton net (1-mm mesh). Resazurin traps (0.5 ml 4% resazurin in ethanol, with 4.95 ml deionized water) were used to indicate if the column headspace was becoming anaerobic. Soil columns were initially saturated with 0.005 M CaSO$_4$ then drained to field capacity as previously described in this chapter. Four 500-mL increments of deionized water were leached through the columns to determine the naturally occurring bromide ion (Br$^-$) background concentration.

**Soil Treatment and Leaching.** Liquid MeBr (at 0.57 kg/m$^3$, or 1 lb/yard$^3$) was applied to the soil surface, and the columns were immediately sealed. Soil columns were incubated at 24 ± 1 °C for 48 h to allow this fumigant to penetrate the soil and reach an equilibrium between the air/soil/water. After the 48-h equilibration period, MeBr-fumigated columns were place in column stands, maintained at 24 ±1 °C, and leached weekly (for 23 weeks) with 500 mL deionized water to represent 2.5 cm of rainfall (7). Leachates were collected at the bottom of the columns and analyzed for MeBr and its degradation product, Br$^-$. 

**Collection and Analysis of Volatilized Methyl Bromide.** Forty-eight hours after the application of MeBr, activated carbon and resazurin traps were suspended in the headspace of each soil column. Carbon traps were replaced periodically and used to determine the amount of MeBr in the headspace of the column. Upon removal, these traps were placed in 45-mL glass bottles equipped with screw caps and polytetrafluoroethylene-lined septa and stored at -60 °C until analysis. The headspace of these bottles was analyzed prior to the desorption of MeBr from the carbon. Procedures used to desorb MeBr from the carbon traps were modified from (32). Two gram-carbon subsamples from each trap were placed in 7-mL glass vials and sealed with a polytetrafluoroethylene-lined septa. Three mL of air was evacuated from the vials with a gas-tight syringe and replaced with 3 mL benzyl alcohol (Fisher Scientific, Pittsburgh, PA). Samples were warmed to 110 °C for 15 minutes and the headspace was analyzed by gas chromatography (GC). The quantities of MeBr detected in the headspace of the bottles and desorbed off the carbon were considered in the final calculation of MeBr that volatilized from the soil.

Procedures for the analytical standards and analysis of sample and standard headspace were modified from (32). Methyl bromide standards were made in benzyl alcohol, stored at -60 °C, and replaced every 2 weeks. Samples were analyzed on a Varian 3740 gas chromatograph equipped with a $^{60}$Ni electron-capture detector. The glass column (0.912 m x 2.0 mm i.d.) was packed with 100/120 mesh Porapak Q (Supelco Inc., Bellefonte, PA) on Carbopack with a carrier gas consisting of ultrapure nitrogen (26 mL/min). Injector, column,
and detector temperatures were 170 °C, 140 °C, and 350 °C, respectively. Peak heights were used to construct a calibration curve and quantify the samples.

**Analysis of Leachate.** Soil column leachates were analyzed for MeBr and Br⁻ by using GC headspace analysis as described above and a bromide-specific electrode attached to pH meter (Fisher Scientific, Pittsburgh, PA). Br⁻ standards were prepared with NaBr, deionized water, and 5 M NaNO₃ (ionic strength buffer). Calibration curves were constructed from the standards and used to determine the sample concentrations.

**Soil Extractions and Analysis.** At the completion of the study, undisturbed soil columns were cut into 5-cm increments and analyzed for MeBr and Br⁻ residues. Three 10-g subsamples from each soil profile were placed in 45-mL glass vials, and the headspace was analyzed on a GC as described above. These soil samples were then extracted with 20 mL deionized water by mechanical agitation and centrifugation. The supernatant was removed and analyzed for Br⁻ using a bromide-specific electrode.

**Volatility, Mobility, and Degradation of Methyl Bromide.** MeBr volatilized rapidly from the soil. The flux of MeBr from the undisturbed soil columns is shown in Figure 6. Greater than 75% of the MeBr flux occurred within 48 h after the fumigation period. After 7 days, MeBr was not detected in the soil column headspace. The volatilization of MeBr from our undisturbed soil column study was comparable to the MeBr field study results reported by (31,33-34). Anderson et al., (31), also observed greater than 75% of the MeBr flux occurred within 4 days after MeBr application. Negligible quantities of soil gas MeBr were detected after 7 d (31,33).

Soil column leachates from each rain event were analyzed for Br⁻ and MeBr. Within the first rain event following the MeBr fumigation, Br⁻ increased from a background level of 0.01 μg/g to 0.4 μg/g (Figure 7) The concentration of Br⁻ in the leachate continued to increase, peaked at 3 weeks (4.3 μg/g), and gradually decreased with subsequent rain events. A total of 28.8 μg/g Br⁻ leached through the soil column, which represents > 5% of the MeBr initially applied. MeBr was not detected in any of the soil column leachates throughout the 23-week study. Wegman et al. (35) detected MeBr and Br⁻ in drainage water from fumigated glasshouse soils. They observed a sharp increase in the concentration of Br⁻ during the initial irrigation of greenhouse soils, followed by a steady decrease. The increase of Br⁻ and the absence of MeBr in the soil column leachates indicate MeBr will degrade in the soil and will not leach through this soil profile.

After the final rain event, soil columns were divided into 5-cm fractions and analyzed for MeBr and Br⁻. Residuals of this fumigant and the metabolite were not detected in the soil profile. Levels of Br⁻ were similar to control (untreated) soil samples. Persistence of MeBr in soil appears to be low, primarily due to its rapid volatilization, as well as biological and chemical degradation. Based on these results MeBr would not be expected to contaminate groundwater unless preferential flow was involved.
Figure 6. Volatility of methyl bromide in undisturbed soil columns following a 48-h fumigation period. Data points are the mean ± one standard deviation.

Figure 7. Bromide ion breakthrough from an undisturbed soil column treated with methyl bromide. Soil columns were leached weekly after the 48-h fumigation period.
Pesticide Adjuvants.

Pesticide applications invariably include the use of various adjuvants in the commercial formulations. This broad category can include solvents, emulsifiers, sticking agents (adhesives), UV-light protectants and dyes, among others. They are mostly considered to be inert ingredients, but their environmental fate should also be addressed. Most of them have other industrial uses and, hence, other environmental inputs.

Ethylene glycol and propylene glycol have been used as solvents in pesticide formulations as well as antifreeze in vehicles and deicing agents for airplanes and runways. Their environmental impact is often expressed as an excess nutrient input into bodies of water, leading to a eutrophic anoxic system in which fish and other species with high oxygen requirements die. Their degradation and mobility have not been previously investigated in a soil column experiment.

Effects of Plants on the Degradation of Pesticide Adjuvants in the Intact Soil Column.

Rhizosphere is the region of soil directly influenced by the roots. Plant roots secrete energy-rich exudates (sugars, amino acids, vitamins, and keto acids) and mucilages (polysaccharides) that support large and diverse populations of microorganisms. Root-influenced soils have a greater microbial biomass (10 to 100 times) and activity than bulk soils; therefore, enhanced degradation of organic compounds may occur in the rhizosphere (36-39). In addition, the interaction between plants and their associated microbial communities is mutually beneficial for both types of organisms. Soil microorganisms have a positive influence on plants by 1) solubilizing inorganic nutrients and secreting organic compounds (gibberellins, auxins, amino acids, and vitamins) that stimulate plant growth and 2) potentially deterring plant pathogens through competition and production of antibiotics (36, 38, 40).

Vegetation can enhance the removal of human-made organic compounds and pollutants in soil environments by microbial degradation in the rhizosphere and plant uptake (41,42). Previous research has shown enhanced degradation of industrial chemicals such as trichloroethylene (43) polycyclic aromatic hydrocarbons (44), and petroleum (45) in the rhizosphere soil as compared to root-free soil. Increased mineralization of the pesticides parathion (46) and carbofuran (47) has been reported in the rhizosphere of rice plants. Hsu and Bartha (48) noted similar results for parathion in the bean rhizosphere. Accelerated mineralization of pesticides has also been found in the rhizosphere of plants from pesticide-contaminated sites. Anderson et al. (49) observed greater microbial biomass and enhanced degradation of atrazine, trifluralin, and metolachlor (after 14 d) in the rhizosphere soil of herbicide-resistant Kochia sp. in comparison to nonrhizosphere and sterile soils, respectively. In addition to enhanced degradation in the rhizosphere, plants may take up contaminants as part of their transpiration stream (41). Lee and Kyung (47) monitored the uptake of fresh and aged carbofuran residues by rice plants. Approximately 60 to 70 % of the “C detected in the shoots was the intact parent compound in both the freshly applied and aged soils. Anderson and Walton (50) studied the fate of [14C]TCE in soil-plant systems collected from a contaminated site. They reported that 1 to 21% of the recovered radiocarbon (depending on the plant species) was detected in the plant tissues, particularly in the roots. Vegetation may play a vital role in reclaiming polluted ecosystems and preventing further contamination by enhancing degradation and uptake into tissues, thereby reducing migration to surface waters and groundwater aquifers.
Effect of Vegetation on Mobility of Pesticide Adjuvants. Vegetated undisturbed soil columns were used to study the influence of plants on the mobility of propylene glycol (PG) and ethylene glycol (EG) through the soil profile. High concentrations were applied to nonvegetated and vegetated undisturbed soil columns to simulate spills of these solvents used as antifreezes, airplane deicing agents, and pesticide adjuvants.

Undisturbed soil columns (15-cm x 38-cm length) were collected from an agricultural field site and prepared for laboratory studies as previously described in this chapter (Figure 1A) and by (2,3).

Eight soil columns (4 each) were planted with alfalfa (Medicago sativa) or ryegrass (Lolium perenne L.) (Figure 1E). Nonvegetated and vegetated columns were maintained in a greenhouse (25 °C, 16:8 light:dark) for 4 months to allow sufficient growth of the plants. Water was added to the columns as needed. Roots of *M. sativa* and *L. perenne* were observed through the clear perforated Plexiglas™ bottom of the columns. This indicated that *M. sativa* and *L. perenne* roots were established through the length of the columns. Following the four-month growth period, soil columns were saturated with 0.005 M CaSO₄ (2), then drained to field capacity.

Soil columns were moved to an incubator set at 25 °C, and the temperature was slowly decreased (approximately 3 °C/24h) to 10 °C to represent spring conditions. Soil columns were maintained at 10 °C with a 16:8 light:dark cycle for 96 h prior to the treatment to acclimate plants to this temperature. During this 96-h time period, soil columns were leached with 400 ml deionized water. These leachates were analyzed on a gas chromatograph equipped with a flame ionization detector (GC-FID) and with a bromide-specific electrode attached to a pH meter (Fisher Scientific, Pittsburgh, PA) to determine background levels of propylene glycol and Br⁻, respectively. A KBr tracer was applied to the soil surface and leached through the soil columns with deionized water. Breakthrough curves were determined for each column by analyzing the quantity of Br⁻ in the leachate. Br⁻ standards were prepared with NaBr, deionized water, and 5M NaNO₃ (ionic strength buffer). Calibration curves were constructed from the standards and used to determine the sample concentrations (8).

Soil Treatment and Leaching. Propylene glycol (Fisher Scientific, Fair Lawn, NJ) solution (1.76 ml PG/364 ml water) was applied to the soil surface. Twenty-four hours after the treatment, soil columns were leached with 400 ml deionized water daily. Water was applied to the columns in four 100-ml increments. This application caused a temporary pooling of water each time. Soil columns were leached repeatedly throughout the studies (see Figures 8 & 9). Leachates were collected at the bottom of each column and analyzed on a gas chromatograph (GC) to determine the quantity of PG and EG that moved through the soil profile. Samples were stored in a freezer until the analysis.

Analysis of Leachates. Undisturbed soil column leachates were analyzed following procedures modified from (51). Propylene glycol and ethylene glycol standards were made every two weeks in deionized water and stored in a freezer. Leachate samples were analyzed on a Varian model 3740 GC (Varian Associates, Sunnyvale, CA, USA), equipped with a flame ionization detector (FID) and 2.7 m x 2 mm (i.d.) glass column containing 5% Carbowax 20M on 100/120 mesh Supelcoport® (Supelco Inc., Bellefonte, PA). Ultrapure nitrogen (99.9%) was used as the carrier gas at a flow rate of 20 ml/min. The injector and oven
Figure 8. Concentration of propylene glycol detected in the leachate of vegetated and nonvegetated soil columns.

Figure 9. Cumulative concentration of propylene glycol detected in the leachate of vegetated and nonvegetated soil columns.
temperatures were 250 °C and 160 or 200 °C. Propylene glycol samples were also analyzed on a Shimadzu GC-9A GC-FID (Shimadzu Corp., Kyoto, Japan) equipped with a 5% Carbowax 20M packed column (1.2 m x 3 mm i.d.). The carrier gas was helium, and the injector and oven temperatures were 300 °C and 160 °C, respectively. Peak heights were used to construct each calibration curve and to quantitate the glycol in the samples. All the standard curves had correlation coefficients exceeding 0.990. One-way analysis of variance (ANOVA) and the least squared means were used to test for significant differences among the treatments (52).

Influence of Vegetation on the Mobility of Glycols in Soil Columns. Propylene glycol and ethylene glycol were detected in the leachates of all the soil columns studied (Figure 8 and 9). The greatest PG concentrations occurred within the first four leaching events and continued to decrease with time. Approximately 53 to 86% of the recovered PG was detected in the leachates within 7 d.

Greater than 500, 300, and 200 μg/ml EG was noted in leachates of the nonvegetated, M. sativa and L. perenne soil columns. After 10 days, 64 to 92% of the recovered EG had leached through the soil columns. Movement of PG and EG through the soil profile depends on its properties and adsorptive characteristics, soil characteristics, soil temperature, and the quantity and frequency of runoff or precipitation (53).

Previous research has shown EG does not adsorb to soil (51). Lokke (51) reported little or no adsorption of EG to sandy till, muddy till, or clayey soils. Propylene glycol and ethylene glycol are water soluble and appear to be mobile within the 38-cm soil profile.

Results from this study indicate vegetation reduced the quantity of PG and EG that moved through the soil profile. Leachates from the vegetated soil columns contained significantly (p = 0.05) less PG than leachates from the nonvegetated columns (Figure 8). Measured quantities of 91.5, 73.0, and 73.0 mg of PG were detected in leachates of nonvegetated, M. sativa, and L. perenne soil columns, respectively. Similar results were noted with the EG-treated soil columns (Fig. 9). The total quantity of EG that infiltrated through nonvegetated, M. sativa, and L. perenne, and soil columns was 1195, 519, and 722 mg, respectively. The results of the nonvegetated column shown in Figure 9 contain only one replication due to the loss of the second nonvegetated soil column. Less EG was detected in the leachate from M. sativa soil columns than L. perenne, but they were not significantly (p = 0.05) different. Plants can decrease the concentration of PG and EG in soil and reduce their movement through the soil profile to groundwater by plant uptake, enhanced degradation in root-associated soils, and reduction of the soil water status (41). Results from previous research show enhanced degradation of EG and PG in the M. sativa and L. perenne rhizosphere soils compared to nonvegetated soil (54). In the current study, we observed a 9 to 12% decrease in the quantity of water that leached through vegetated soil columns relative to the nonvegetated soil columns, together with even greater reductions in the percentages of PG and EG that leached in the nonvegetated columns. Overall, vegetation can clearly reduce the leaching of PG and EG through the soil profile.
Comparisons With Other Methods

Incubation Studies. While soil column studies provide important information on the mobility of parent compounds and degradation products, comparisons of data from pesticide-applied columns to that of controlled soil metabolism studies gives a better understanding of the fate of the compounds. In studies conducted using intact soil columns, such as described in this chapter, the presence of degradation products at various depths may be due either to movement of degradation products formed in upper layers or to the degradation of the parent compound once it has reached a particular depth. This is not the case in controlled soil metabolism studies using contained soils from various depths, where the presence of degradation products cannot be due to movement from another depth. Soil metabolism studies with a time series of analyses can also give information on half-lives for applied pesticides.

From the ATR-applied soil column study (3), it was noted that DEA was present in subsurface soils which could be due not only to degradation of ATR in all depths, but also to movement after formation in upper layers. DEA was more mobile than ATR in the soil column studies (3, 6). The comparative fate of ATR and DEA in surface (0 to 30 cm) and subsurface (65 to 90 cm) soils was studied in the laboratory (55). The concentration of DEA arising from ATR degradation in subsurface soil increased 3-fold from a 60- to 120-d incubation period. The half-lives of DEA and ATR were significantly greater in subsurface soils than in the surface soils. However, in soil from the 90- to 120-cm depth (held at -33 kPa soil moisture tension), the half-lives for DEA and ATR were 178 and 161 d, respectively (55, 56).

Soil Thin-layer Chromatography. Studies on the mobility of pesticides have been carried out by using a method of thin-layer chromatography (TLC) that incorporates a thin film of soil onto a glass plate. Soil TLC (STLC) plates applied with radiolabeled pesticides are then submitted to ascending chromatography by placing the plates in developing chambers containing water as a mobile phase. The differential affinity of a pesticide for soils of various characteristics and water can easily and economically be determined. While the assessment of pesticide mobility in large, intact soil columns is more true to field conditions, space requirements, time, and cost are considerations for running multiple columns of various soil characteristics. Concerns, however, with using STLC are that no indication of preferential flow can be obtained, and in the process of making STLC plates, pulverization of soil can alter soil characteristics such that care must be taken with inferences to the real world.

In comparing the ATR- and DEA-applied soil column studies with an STLC study, all conducted in this laboratory, it was noted that relative mobilities of ATR and DEA were consistent. The relative mobilities of ATR, DEA, other pesticides, and degradates were determined in an STLC experiment that used soils from the surface (0 to 30 cm) and subsurface (65 to 90 cm) from ten soil types (2 depths, 5 locations) of Iowa (57). In this study, DEA was the most mobile compound in 8 of the 10 soils. These results agree with the soil column studies in which DEA was recovered in greater quantities in leachate than was ATR (Figure 4).

Field Box Lysimeters. With the use of field box lysimeters, it is possible to study the fate of pesticides under field conditions, while maintaining a somewhat contained system. Box-type lysimeters (Figure 10) had been constructed using polyethylene sheets for sides and bottom that were assembled by using stainless-steel bolts to secure aluminum angle-iron corners onto
Figure 10. Field box lysimeter used to study pesticide concentrations in leachate and in soil water.
the sheets (58). The corner seams were treated with silicone sealant to make them waterproof, and styrofoam sheets (2.5-cm thick) were placed against each side. Heavy-duty duct tape was used to join each foam sheet, and a 0.5 mm-thick box-shaped, impermeable plastic liner, with the same shape and dimensions as the lysimeter box, was placed inside each lysimeter, pulled tightly over the styrofoam sheets, and attached to the outside of the lysimeter with duct tape. The sides of the lysimeter extended above the soil surface. Through the use of a grave-digging machine, the soil profile was excavated to make a hole that measured 234 cm by 92 cm by 137 cm. For the top 60 cm, soils were separated into 15-cm layers, and for soils between 60 and 150-cm depth, soils were separated into 30-cm layers. A bentonite layer (5-cm thick) was placed at the bottom of each excavated area. The lysimeter box was lowered into the hole, and the gaps between the lysimeter and the soil were fill with bentonite. A drainage-tile sump apparatus was installed, and the soil was replaced in the lysimeter layer by layer, according to the original vertical soil profile. Two stainless steel suction lysimeter tubes were installed, one on each side of the sump. One suction tube was installed at a depth of 60 cm and the other at 90 cm. A two-year study of atrazine mobility and degradation in box lysimeters showed that rate of application had an influence on the detection of residues in water collected in the soil profile (59, 60).

This approach to studying the mobility of pesticides is advantageous in that one can conduct rain simulations over the lysimeters, use various cropping systems, monitor pesticide movement to tile drains, and determine concentrations in soil water by using the suction lysimeters. With the excavation of the soil profile, however, it takes some time to reestablish soil structure, and the box lysimeters are too large to remove to analyze.

Conclusion

It is clear that several of the advantages of the lysimeter as an experimental unit are also expressed in the intact soil column. The focus on intact soil columns in this chapter provides some degree of comparison in the techniques. Both maintain the crucial capacity to integrate the fate of the pesticide, measuring both degradation and mobility of the parent compound and transformation products. As analytical methods become more sophisticated, as public concern over pesticides grows, and as requirements for pesticide registration data expand, it is important that our understanding of pesticide degradation and movement in the environment continues to advance. The advancement of our knowledge is, to a large degree, limited by the tools we possess to make the assessments of the behavior of agrochemicals in our environment. It is therefore imperative that we constantly strive to develop and improve our methodology, such as the lysimeter approach, to aid in the production and protection of a safe and bountiful food supply, while affording protection of the environment.

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Literature Cited