

MOVEMENT AND DISSIPATION OF TOXICANTS  
AND WATER IN NATURAL SOIL ENVIRONMENTS

by

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## ABSTRACT

Literature reviews were performed on the movement and dissipation of three chemically different herbicides, weakly basic atrazine, weakly acidic primisulfuron and nonionizable metolachlor. The former and latter compounds have been detected in ground water in many states. The other represents a new family of very low rate of application chemicals.

<sup>14</sup>C-labeled atrazine, metolachlor and primisulfuron, tritium, bromide and nitrate were applied to the surface of a Dothan loamy sand in a natural field environment and the movement and dissipation of the chemicals evaluated using a soil column lysimeter technique, which included monitoring soil and water. Factors examined included the effects of physicochemical and biological properties of the chemicals, addition of three water soluble acrylic polymers to each of the three herbicides, and surface cover and subsoil moisture tension on the movement and dissipation of metolachlor. Supplementary laboratory studies were conducted to characterize the degradation of the three herbicides and the sorption of metolachlor in surface and subsoil samples of the soil. Additionally, the dissipation and movement of <sup>14</sup>C-metolachlor and tritium in the field was compared with that predicted by a computer model.

Relative mobility of the chemicals studied was in the order water = tritium ≥ bromide = nitrate >> metolachlor > atrazine = primisulfuron. Soil movement of metolachlor as affected by surface cover was in the order mulch fallow > bare fallow > soybean seeded > sod. The presence of leachate collectors reduced subsurface moisture tension and water and herbicide movement slightly. Dissipation of the three herbicides was by way of four routes in the order volatilization >> fixation > degradation > leaching. Addition of three chemically different acrylic polymers, cationic, anionic and nonionic, to tank mixtures of the three herbicides did not affect mobility, loss or bioactivity of the herbicides in field lysimeter studies but some beneficial effects were observed in laboratory leaching column studies.

Metolachlor was degraded biologically while atrazine and primisulfuron were degraded biologically and chemically. Half-life values for the herbicides ranged from 3 to 6 days in the field lysimeters to 14 to 49 days in laboratory flasks.

Vertical movement of the three herbicides was inversely correlated with the organic matter content of the soil, while sorption of metolachlor by samples from different soil depths was directly correlated with organic carbon content of the soil. Prediction of tritium movement through the soil using the PRZM model was acceptable but prediction of metolachlor movement was not.

Soil column lysimeters proved to be useful in carrying out material balance studies on the movement and dissipation of chemicals in natural cores of Dothan loamy sand in the field. Further research using other soil types and other pesticides is needed. The technique is very useful in validating computer models but additional methodology needs to be developed to address volatilization losses of pesticides from the field lysimeter systems. Air, water and soil need to be monitored.



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## SUMMARY AND CONCLUSIONS

The use of  $^{14}\text{C}$ -labeled herbicides and tracers applied to soil in steel column field lysimeters supplemented by selected laboratory experiments and computer modeling techniques was found to be a successful way to measure the movement and dissipation of toxicants in a loamy sand under natural conditions.

Tritium, representing water, moved faster than chloride and bromide anions, which moved similarly and which were apparently involved in sorption/desorption processes. Tritium displaced only half of the water in natural soil cores over a 120 day period. All three chemicals moved much faster than  $^{14}\text{C}$ -labeled metolachlor, atrazine, primisulfuron or their metabolites, respectively. Movement of the most mobile herbicide, metolachlor, was greatest in mulched fallow systems followed by fallow, soybean seeded and sod systems suggesting that toxicant movement is dependent upon the soil moisture content as regulated by evaporation and evapotranspiration processes. It was also faster through lysimeters that were not equipped with leachate collectors than those with leachate collectors suggesting that capillary tension in the subsoil had a pronounced effect on the movement of toxicants. Addition of three water soluble acrylic polymers did not affect the movement, dissipation or bioactivity of the three herbicides in field studies, but laboratory studies indicated that other more lipophilic polymers did reduce movement of the chemicals.

Mass balance evaluation of the herbicides in the systems with time showed that nearly half of each of the herbicides dissipated from the soil as vapors suggesting that methodology for measuring volatilization of the chemicals and their breakdown products need to be developed. Of the  $^{14}\text{C}$ -metolachlor remaining in the soil after 90 days, 70%, most of which was nonextractable, was retained in the upper 15 cm and less than 2% of the  $^{14}\text{C}$ , none of which was parent or metabolite, appeared in the leachate. This is in contrast with nitrate where less than 5% was retained in the upper 23 cm of soil and 75% appeared in the leachate in the same time period.

Laboratory microbial studies showed that 30 to 67% of each of the three herbicides became bound and nonextractable from surface soil samples and was associated with the organic fraction of the soil. Metolachlor was degraded only biologically while atrazine and primisulfuron were degraded by biological and chemical processes. Degradation was much faster in surface than in subsurface soil samples. Lack of degradation of metolachlor in subsurface samples suggested that if the compound were leached into the subsoil under high rainfall conditions or in other soil types it is possible that it could contaminate ground water.

Laboratory sorption studies showed that metolachlor retention was directly related to the organic carbon content of the soil samples and decreased with soil depth. Sorption was shown to be a long-term, nonlinear equilibrium process. Movement of tritium in field lysimeters was shown to be predictable by the use of a computer model but that of metolachlor was not.



## RECOMMENDATIONS

The soil column lysimeter has been shown to be a useful technique for evaluating the potential of toxicants to contaminate ground water, examining the influence of soil parameters on toxicant movement, providing a holistic material balance assessment of toxicant dissipation in the environment and validating computer models in natural soils under field conditions. To make the system more complete, methodology should be developed for measuring volatilization losses of toxicant into the atmosphere from the system. Once this is done, the system should be used to examine the movement and dissipation of additional toxicants with widely differing physicochemical properties in selected soil types with widely differing profile characteristics. Because laboratory studies showed that selected lipophilic polymers reduced the movement and volatilization of organic herbicides, other related polymers should be examined using field lysimeters. Accumulated data of this type could then be used to elucidate interactions between specific toxicant structures and specific soil properties, validate computer models used to predict toxicant movement and dissipation in the environment, and evaluate polymers and other substances that might be used to reduce the movement of toxicants through the soil and their losses through volatilization.



## INTRODUCTION

### Pesticides in Groundwater

It is well documented that assorted pesticides have been detected in the nation's groundwater (Cohen et al. 1984, 1986, Frink and Hankin 1986, Patrick 1986, Williams et al. 1988, Ritter 1990, USEPA 1990a). This occurrence is of concern since there are approximately 13 million rural domestic wells and roughly 95% of all rural dwellings depend on groundwater for their drinking water supply (CAST 1985, USEPA 1990a). Furthermore, 55% of all North Carolinians and 97% of the state's rural residents depend on groundwater as their primary source of drinking water (McCarty et al. 1981, Cook and Zublena 1990, Severn and Ballard, 1990).

The majority of the compounds found in groundwater were preemergence herbicides with moderate to high water solubility and moderate-to-long half-lives. Many of the compounds are very persistent (DDT, aldrin, chlordane), are known or suspected carcinogens (DBCP, monuron, trifluralin), or are exceedingly toxic (aldicarb, endothal, paraquat (Smelt et al. 1978, Ware 1978, Nielson et al. 1985, Patrick 1986, Perry et al. 1989). Although use of the most persistent ones have been discontinued or restricted (Ware 1978, Wauchope 1978) some are degraded so slowly that residues left in the soil represent a reservoir for potential groundwater contamination (Junk et al. 1980). Even chemicals strongly sorbed to soil organic matter can be bioavailable (Weber 1972, Weber and Weed 1974, Quensen et al. 1984). The detection of these chemicals indicates that we do not fully understand the reactions that take place in the subsoil and groundwater systems.

### Pesticide Dissipation Processes

Pesticides introduced into the environment are normally subjected to many dissipation processes (Weber and Weed 1974, Bowman 1988, Weber 1991a). Transfer processes, in which the pesticide molecules remain intact, include absorption, exudation, and retention by weeds and crops, adsorption and desorption to soil colloids, movement in runoff, volatilization to the atmosphere, and leaching. Transformation processes, in which the pesticide molecules are modified, include chemical, photochemical and biological degradation. It is the combination of these processes, which may be influenced by the chemical and physical properties of the soil and pesticide and climatic conditions, that ultimately influence the movement of herbicides to groundwater (Hance 1980, Helling and Gish 1986, Weber and Miller 1989).

Leaching is one dissipation process that merits attentions since it has the potential for contaminating groundwater. A significant factor contributing to the difficulty of predicting pesticide behavior in subsurface systems is the heterogeneous nature of important physical and chemical properties of the subsurface environment. For example, water flow in the vadose zone is governed by soil hydraulic properties such as the relationship among hydraulic conductivity, volumetric water content and pressure head. However, Russo and Bresler (1981) reported that soil hydraulic properties may vary substantially over short distances in the vertical direction, adding significant complexity to the task of assessing merely the advective component of water flow in the unsaturated zone. Similar heterogeneities are hypothesized to exist with other important characteristics of an agroecosystem, which would be expected to profoundly affect pesticide transport and fate.

Sorption is an important process that strongly affects the behavior of a pesticide in the subsurface environment, by retarding pesticide movement and influencing availability for transformation reactions. Sorption reactions are also hypothesized as being affected by heterogeneities of the solid phase, and the concomitant changes in physical and chemical properties of the solid as a function of position. Failure to observe the extent of such variations and to include these variations in an appropriate modeling framework is expected to degrade the accuracy of predictions of pesticide transport and fate in subsurface environments.

#### Soil Management and Surface Cover Effects

Any soil management or agronomic practice that alters the chemical and physical properties of soil may influence pesticide mobility. No-till, a soil management practice, which accounts for over 202,500 ha in North Carolina (Cook 1989) denotes additional crop residues and reduced soil mixing when compared to conventional tillage. Crop residues or mulches on the soil surface of no-till fields are highly effective in increasing infiltration, reducing evaporation and subsequently increasing soil moisture (Blevins et al. 1971, Johnson et al. 1984, Radcliffe et al. 1988). The increased infiltration and soil water content associated with no-till and similar soil management systems warrant concern regarding pesticide mobility.

Recent studies in herbicide mobility under conventional and no-till practices suggest that preferential flow (macropores) is primarily responsible for increased herbicide mobility under no-till systems (Helling et al. 1988, Hall et al. 1989, Isensee et al. 1990, Steenhuis et al. 1990). These studies involved medium to heavy textured soils where preferential flow may be significant and would therefore not represent the dense, weak single-grain structure in the soil surface horizon commonly found in the Atlantic Coastal Plain. Also, Coastal Plain soils commonly have massive structure in the B horizon which would make it unlikely to contribute to preferential flow.

In row crop situations, whether in conventional or conservation practices, spatial and temporal distribution of soil water content exists (Van Wesenbeeck and Kachanoski 1988, Zhai et al. 1990). These researchers reported that throughout the growing season of corn (*Zea mays* L.), soil water content at 0- to 20-cm in the interrow position was almost always greater than the row position. Similarly, Arya et al. (1975) observed that soil water potentials were lowest in the rows during early soybean growth. Correspondingly, strong lateral soil water potential gradients have been reported at 10- to 30-cm depth during early soybean growth (Arya et al. 1975). Conditions such as reduced soil water and lateral soil water potential gradients (towards roots) will ultimately affect solute behavior and movement (Cassel 1983). Therefore, in crop-row zones, soil water movement downward and solute fluxes will be reduced as compared to interrow soil conditions. Interrow zones will favor greater downward fluxes due to a higher antecedent water content. Solutes in interrow zones will also move deeper due to a greater wetting-front advance from recent recharge events.

Very little research has been reported on solute movement, particularly pesticide movement in row and interrow zones in any crop. Recently, Timlin et al. (1992) reported that in a fine sandy loam corn plot, significantly more bromide was leached below the 50-cm depth in the interrow zone than in the row position. Timlin et al. (1992) also reported at 15-cm, significantly lower

matric potentials (suctions higher) in row zones than in the interrow zones in corn. The increased mobility of bromide in interrow zones depicts differential solute movement and thus lends credence to concerns of increased pesticide mobility under similar conditions.

Information concerning the mobility of pesticides and ultimate groundwater contamination in turf is limited. A study in Ohio by Krause and Niemczyk (1989) showed that over a 180 d period, 78 to 100% of the applied preemergent herbicides pendimethalin, bensulide, and oxadiazon were detected in the thatch layer. The same study also showed that in turf without thatch, 82 to 99% of the same herbicides were recovered in the 0- to 2.5-cm zone. These results are not surprising since these herbicides have an extremely low water solubility (WSSA 1989) and are strongly adsorbed to soil (WSSA 1989, Weber 1990). Bensulide, oxadiazon and pendimethalin in turf have been classified as having a medium, medium and low herbicide leaching potential, respectively (Weber 1991b,1991c). The mobility of two postemergent herbicides, 2,4-D and dicamba, has been evaluated in turf growing in a sandy loam soil (Gold et al., 1988). Gold et al. (1988) found that 0.4 and 1.0% of the applied 2,4-D and dicamba, respectively, was recovered in percolate. They concluded that, "Given the current water quality standards, routine applications of 2,4-D and dicamba to home lawns do not appear to threaten groundwater quality". Similarly, Cohen et al. (1990) monitored 2,4-D and dicamba movement in golf courses that represented a 'worst case scenario' for leaching of pesticides to groundwater. They found in sampling wells at various depths that 2,4-D and dicamba were not detected in toxicologically significant concentrations. Dicamba and 2,4-D are classified as leachers (Goodrich et al. 1991) and in turf have a high herbicide leaching potential (Weber 1991b).

#### **Pesticide Bioavailability and Degradation**

The slow availability of some chemicals in soils, coupled with reliance on groundwater for drinking water, show a need for understanding more about the breakdown and eventual fate of agricultural chemicals in subsoils as well as at the surface.

Degradation rates of agricultural chemicals generally are reported only for the top 15-20 cm of soil where microbial activity is the highest (Ghadiri et al. 1984, Alexander 1985, Frank and Sirons 1985, Brejda et al. 1988, Winkleman and Klaine 1991). While many studies have reported the dissipation of pesticides deeper in the soil, via binding to clay or organic matter, the format of the degradation products often is not mentioned.

Pesticide bioactivity in soils has been reported to be regulated by both the properties of the specific pesticide and the soil (Harris and Sheets 1965; Ballard and Santelmann 1973, Weber and Weed 1974, Peter and Weber 1985). Bioactivity is normally reduced when pesticides become bound to soil colloids or diffuse into inaccessible sites. Solid porous polymers used as controlled-release membranes for pesticides and drugs act to reduce chemical concentration at any given moment, thereby regulating chemical losses and utilization by organisms (Cardarelli 1976, Rosoff 1989).

#### **Effect of Polymers**

One method of reducing groundwater contamination by herbicides would be to keep them in the root zone, where they would be taken up by the weeds and

available for degradation for a longer period of time. Keeping higher amounts of the chemicals in the zone of germinating weeds might also allow farmers to apply herbicides at lower rates, thus reducing the amounts of herbicides introduced into the environment and reducing economic costs. Solid porous polymers have been used as controlled-release agents for insecticide vapors and fertilizer nutrients (Baker 1987), drugs (Rosoff 1989) and pesticides (Cardarelli 1976, Lewis and Coswar 1977, Scher 1984, 1988). Several solid porous polymers have been evaluated to determine their ability to decrease the downward movement of herbicides in soils (Cardarelli 1976). According to Hilton (1987), atrazine movement on soil thin-layer (TLC) plated was reduced by the addition of a water-soluble ASE-108 polymer obtained from the Rohm and Haas Co. (Philadelphia, PA). Weber et al. (1988) reported that the ASE-108 polymer reduced downward movement of atrazine, metolachlor and triasulfuron in soil leaching columns when applied at a rate of 86 kg of solid/ha.

### Soil Properties

Many of the soils in the upper Coastal Plain region of North Carolina, particularly the well-drained Kandiodults or Paleodults, have weak to single-grain structure in the surface horizons and nearly structureless B horizons (Gamble et al. 1970; Southard and Buol 1988). These conditions make it unlikely that preferential flow is a factor in enhanced solute movement. On the other hand, research in Delaware (Ghodrati and Jury 1990) and Nigeria (Wild and Babiker 1976) showed that preferential flow of dyes and anions was possible in nearly structureless loamy sand soils. Admittedly, Wild and Babiker (1976) attributed part of the preferential leaching of chloride and nitrate to earthworm channels. Models such as DRASTIC (Aller et al. 1985) HLP/SLP (Weber 1991b) and PRZM (Carsel et al. 1984) indicate that the Coastal Plain soils in North Carolina are susceptible to groundwater contamination by pesticides.

Examination of soil water and its components moving through the soil profile and ultimately into groundwater are enhanced by using a variety of tracers. Tracer studies in soil columns (White et al. 1984, Everts et al. 1989) or in the field (Blume et al. 1987, Jaynes et al. 1988, Everts et al. 1989) have commonly used chloride or bromide. These anions are used because they are not highly adsorbed and do not undergo biological transformations. Tritiated water is also commonly used as a tracer in column studies (McMahon and Thomas 1974, DeSmedt et al. 1986, Wierenga and Van Genuchten 1989). Similarly, Corey and Horton (1968) showed that tritiated water is insignificantly affected by chemical interactions with soils. Further information concerning tracer types is provided by Davis et al. (1980), Bowman (1984) and Nielsen and Cassel (1984).

To better understand herbicide mobility, numerous researchers have incorporated tracers in herbicide mobility studies using disturbed (O'Connor et al. 1980, Weber et al. 1986, Gamedinger et al. 1990, 1991, Czapar 1992) and undisturbed (White et al. 1986) soil columns or field situations (Smith et al. 1990, Starr and Glotfelty 1990, Steenhuis et al 1990).

The mobility of pesticides in soil is generally determined by several techniques with radiolabeled compounds under laboratory or greenhouse conditions. Techniques such as soil thin-layer chromatography (Helling 1971a), hand-packed soil columns (Weber and Whitacre 1982, Weber et al. 1986, Bowman 1988, Alhajjar et al. 1990) and undisturbed soil columns (Edwards and

Glass 1971, Cassel et al. 1974, Fermanich and Daniel 1991, Fermanich et al. 1991) are frequently used to assess the mobility of pesticides. Hand-packed or disturbed soils may be experimentally convenient; however, extrapolation of results to field conditions is quite debatable. Cassel et al. (1974) and McMahon and Thomas (1974) showed that undisturbed soil columns better represented field movement of water and solutes than hand-packed or disturbed columns. These techniques provide a measure of the relative mobility of pesticides; however, they do not measure the mobility of pesticides under actual field conditions. Furthermore, these techniques do not allow for other dissipating processes which occur in soil under actual field conditions.

Undisturbed soil columns have recently been used to assess the mobility of pesticides (White et al. 1986; Fermanich and Daniel 1991, Fermanich et al. 1991). Unfortunately, preferential flow of water and tracers have been observed in several experiments with undisturbed soil columns under saturated (Seyfried and Rao 1987, Singh and Kanwar 1991) and unsaturated (Richter and Jury 1986, White et al. 1986) conditions. These studies plus field observations (Thomas and Phillips 1979, Quisenberry and Phillips 1978, Everts et al. 1989) commonly report preferential flow occurring in structured soils. As an aftermath of preferential flow, solutes can bypass portions of the bulk soil, thus reducing the opportunity of adsorption. This enables solutes to move faster and deeper into the soil profile than would be expected based on piston flow (Thomas and Phillips 1979, Quisenberry and Phillips 1978, Rice et al. 1986).

Undisturbed soil columns, used in actual field conditions for monitoring herbicide mobility or other dissipation processes, are often referred to as lysimeters (SSSA 1987). Lysimeters, whether block or circular are commonly separated from the surrounding soil either by removal to a new location such as greenhouses or by encasement of the soil in place. In either case, the soil in the lysimeter is discontinuous from the original mass of soil. As a result of this discontinuity, atypical soil moisture conditions occur in the lysimeter (Neal et al. 1937, Wallihan 1940, Klocke et al. 1991). The abnormal soil moisture conditions result due to the retardation of downward water movement at the soil-air interface. This water will not be discharged from the lysimeter until the mass of accumulated non-capillary water overcomes the retention forces of soil particles. To help circumvent this problem vacuum drainage systems (Pruitt and Angus 1960, Tanner 1967, Fermanich et al. 1991, Klocke et al. 1991) are frequently installed to approximate soil moisture tensions.

In applying artificial tensions to lysimeters, Wallihan (1940) noted decreased evaporation of water from the lysimeter and increased volumes of percolate and nitrate and calcium levels. On the contrary, Dowdell and Webster (1980) evaluated lysimeters with two separate drainage systems: one had a 5-cm deep gravel bed and the other had six porous ceramic candles. These investigators found that water drained sooner from the suction (ceramic candle) drainage system and tended to flow continuously for longer periods contrasted to the gravity-drained (gravel bed) system; however, total amounts of percolated from both systems were comparable. Nitrate concentrations from both systems were also comparable. Other lysimeter studies, particularly experiments using <sup>14</sup>C-labeled herbicides have been shown to represent actual field conditions (Fuhr 1985, Bowman 1988, Kubiak et al. 1988, Fuhr et al. 1990). These researchers used filled 1-m<sup>2</sup> by 0.45 m deep lysimeters embedded in the ground which allowed for percolate collection. Kubiak et al. (1988) found that soil

moisture levels at 10 cm in 1-m<sup>2</sup> lysimeters recorded over a six month period in two separate years deviated slightly from values measured in the field. The researchers attributed this slight deviation to the lack of water supplied from underlying soil layers and the addition of irrigation. The use of lysimeters for estimating pesticide leaching is reviewed by Bergstrom (1990a, 1990b).

### Atrazine

Atrazine is a symmetrical triazine herbicide used to control broadleaf weeds in corn and some other crops (WSSA 1989). It has weakly basic properties with a pK<sub>a</sub> of 1.68 (Weber 1967a,b, 1970a), a low water solubility of 33 mg/L, and a low volatility with a vapor pressure of  $3.0 \times 10^{-7}$  mmHg at 20°C (WSSA 1989). It is readily adsorbed by a variety of clay minerals and organic colloids (Harris and Sheets 1965, Weber et al. 1965, 1969, Gunther and Gunther 1970). Adsorption increased with decreasing pH (Talbert and Fletchall 1965, McGlamery and Slife 1966, Weber 1970a, 1970b). This compound has been shown to leach in coarse-textured soils low in organic matter (Burnside et al. 1963, Rodgers 1968). Other researchers have detected atrazine and metabolites in soil at depths of up to 2 m with most occurring in the upper 30-cm (Klaine et al. 1988, Huang and Frink 1989, Starr and Glotfelty 1990, Adams and Thurman 1991).

In acidic soils atrazine spontaneously hydrolyzes to form hydroxyatrazine which has no herbicidal effect (Ghadiri et al. 1984). Atrazine and atrazine residues have been recovered from soils at depths of up to 2 m and ground water up to 9 years after application in Connecticut, Kansas, and elsewhere (Capriel et al. 1985, Klaine et al. 1988, Erickson and Lee 1989, Huang and Frink 1989).

In addition to hydroxylation and removal of chlorine at the 2 position, other reported reactions include: losses of the alkyl chains at the 4 and 6 positions forming de-ethyl and de-isopropyl atrazine (Jones et al. 1982, Erickson and Lee 1989, Winkleman and Klaine 1991) and loss of the amino groups at the 4 and 6 positions resulting in the formation of hydroxyatrazine and 2-hydroxy-6-amino-s-triazine. Because dechlorination can occur before or after dealkylation, the formation of the 2-chloro-de-alkylated and de-aminated molecules has also been reported (Esser and Marco 1975, Shocken and Speedie 1984, Giardi et al. 1985, Behki and Shahamat 1986, Erickson and Lee 1989). Most authors report between 0.1 to 1.6% of the ring-labeled carbon was evolved as carbon dioxide in studies lasting to 32 weeks (McCormick and Hiltbold 1966, Skipper et al. 1967, Roeth et al. 1969, Dao et al. 1979, Scheunert et al. 1986).

Gianessi and Puffer (1990) reported that between 1987 and 1989, 506,146 kg/yr of atrazine were applied in North Carolina. In addition, greater than 80% of the planted acreage in the Coastal Plain of North Carolina could, potentially, receive applications of the herbicide (North Carolina Agricultural Statistics 1991).

### Metolachlor

Metolachlor is an acetamide herbicide used to control annual grasses and several broadleaf weeds in corn, cotton, soybeans, and some other crops (WSSA 1989). Metolachlor is nonionic, has a high water solubility (530 mg/L at 20°C) and is moderately volatile (vapor pressure of  $1.3 \times 10^{-5}$  mm Hg at 20°C) (WSSA 1989).

Adsorption of metolachlor has been positively correlated with clay content (Ballard and Santelmann 1973, Weber and Peter 1982, Peter and Weber 1985, Braverman et al. 1986) and humic (CIBA-GEIGY 1978, Kozac et al. 1983) and organic matter content (Skipper et al. 1976, Weber and Peter 1982, Peter and Weber 1985, Rao et al. 1986, Wood et al. 1987) of soils. Metolachlor leaches moderately and has been found in groundwater (Braverman et al. 1986, Huang and Frink 1989, Weber 1991b). Several different organisms have been reported to partially degrade metolachlor (Krause et al. 1985, Saxena et al. 1987, Liu et al. 1988, Chesters et al. 1989, Liu et al. 1989). At least eight metabolites of metolachlor have been identified (McGahan and Tiedje 1978, Krause et al. 1985). However, no microorganism has been isolated that is able to degrade the substituted aniline ring probably due to steric hindrances and the presence of a tri-substituted amine group. Often < 5% of the labelled carbon is recovered as <sup>14</sup>Carbon dioxide (Cripps and Roberts 1978, Saxena et al. 1987, Lebaron et al. 1988). Gianessi and Puffer (1990) reported that between 1987 and 1989, 403,706 kg/yr of metolachlor were applied in North Carolina.

### Primisulfuron

Primisulfuron is a recently developed sulfonylurea postemergence herbicide used to control several grassy weeds including johnsongrass and many broadleaf weeds in corn (CIBA-GEIGY 1990). Primisulfuron has weakly acidic properties ( $pK_a=5.1$ ), a low water solubility of 70 mg/L (pH 7) at 20°C and a low volatility (vapor pressure of  $<7.5 \times 10^{-12}$  mm Hg at 20°C).

Retention of the sulfonylurea herbicides occurs in soils high in organic matter (Harvey et al. 1985, Mersie and Foy 1985, 1986, Goetz et al. 1989) and low soil pH (Harvey et al. 1985, Mersie and Foy 1986, Shea 1986). Further information concerning sulfonylurea herbicide-soil relations was reviewed by Beyer et al. (1987), Beyer et al. (1988) and Brown (1990). Soils with high contents of organic matter and low pH tended to reduce the bioactivity of sulfonylurea herbicides.

Chemical hydrolysis of a sulfonylurea bridge occurs readily in both aqueous solution and soils. Sulfonylurea bridges function as weak acids ( $pK_a$  3.3-5.2) and an equilibrium is established between the ionized and molecular forms. The ionized form is 250 to 1000 times less susceptible to hydrolysis than the molecular form. Ionization of the sulfonamide nitrogen and distribution of the resulting negative charge throughout the bridge reduces the electrophilic nature of the carbonyl carbon. In the molecular form, the carbonyl carbon is subject to nucleophilic attack by water cleaving the molecule into its constituent rings and releasing the carbonyl carbon as carbon dioxide. Chemical hydrolysis of the bridge decreased 15-fold for chlorsulfuron as soil acidity increased from a pH of 5.9 to 8.0 and up to 150-fold for chlorimuron-ethyl as solution pH rose from 4.0 to 7.0 (Beyer et al. 1988, Brown 1990). Sulfonylurea herbicides are reported to have degraded faster in acidic than neutral or basic soils (Thirunarayanan et al. 1985, Beyer et al. 1988, Beckie and McKercher 1989). Significant amounts of microbial degradation also occurred (Joshi et al. 1985, Beckie and McKercher 1989, Brown 1990). Microbial degradation involved the hydrolysis of the bridge and various hydroxylations and de-esterifications of the substitutions on the two rings (Beyer et al. 1988).

Binding of sulfonylurea herbicides to soil constituents increased with increasing organic matter content and acidity (Harvey et al. 1985, Mersie and Foy 1985, Mersie and Foy 1986, Beyer et al. 1988). Thus for basic soils with low organic matter content, significant contamination of groundwater with the sulfonylurea herbicides may occur.

## PURPOSE AND OBJECTIVES

The purpose of this research was to holistically characterize the movement and dissipation of physicochemically different toxicants and water in natural cores of a well-characterized Coastal Plain soil under field conditions.

The objectives were to: 1) measure the movement and dissipation of  $^{14}\text{C}$ -labeled atrazine, metolachlor, primisulfuron and their metabolites, and tritium, bromide and nitrate in fallow Dothan loamy sand steel column field lysimeters as influenced by the chemical and biological properties of the compounds and the soil, 2) determine the influence of three acrylic polymers on the soil movement, dissipation and bioactivity of the three herbicides, 3) determine the effects of transpiration (fallow versus soybean), surface cover (fallow bare, fallow mulch, soybean and sod) and subsurface moisture tension (leachate collectors versus no collectors) on the soil movement and dissipation of metolachlor, 4) characterize the degradation and determine the half-lives of the three herbicides in Dothan surface and subsoil samples in the laboratory, 5) determine the sorption of metolachlor in Dothan surface and subsoil samples as influenced by soil properties in the laboratory, and 6) compare the movement of metolachlor and tritium in Dothan loamy sand with that predicted by a computer model.

## PROCEDURES

### Lysimeter Studies

Installation. The field lysimeter experiment was conducted on a Dothan loamy sand (fine loamy, siliceous, thermic, *Plinthic Kandudult*) in 1988 through 1991 at the Central Crops Research Station, Clayton, NC. Steel cylinders (20-cm i.d. by 91-cm long) (Figure 1) were driven 30-cm apart in the conventionally tilled soil by an inverted tractor-mounted postdriver. Prior to insertion, a metal plate was placed atop each cylinder which prevented damage to the cylinder from the impact of the post driver. To protect against runoff, 2-cm of the cylinder remained above the soil surface of each soil column. After insertion, a secured trench was established parallel and 30-cm from the lysimeters. The trench enabled access to holes under selected lysimeters which allowed for continuous collection of leachate. Aluminum foil-lined funnels (20-cm i.d.) and 1-L glass jars were positioned under selected lysimeters to collect effluent. Remaining lysimeters maintained soil contact at the 89-cm depth.

Treatment. On July 1, 1988, June 30, 1989 and May 30, 1990,  $^{14}\text{C}$ -ring-labeled metolachlor (Figure 2) plus Dual 8 E (CIBA-Geigy Corp., Greensboro, NC) was

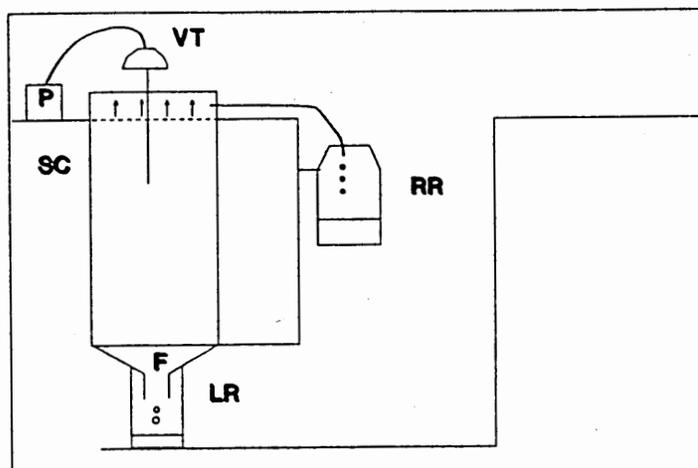


Figure 1. Steel column (SC) lysimeter equipped with funnel (F) and leachate receptacle (LR), runoff receptacle (RR, vacuum pump (P) and vapor trap (VT).

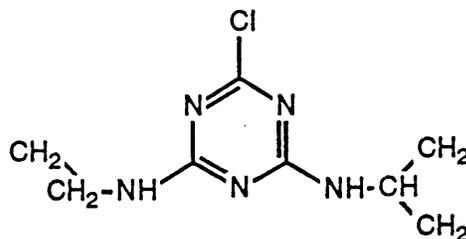
applied in 20 mL of water in a cross-hatch pattern to the soil surface, straw mulch or sod of each lysimeter. Quantities of  $^{14}\text{C}$ -labeled metolachlor applied were 0.75 MBq [sp. act. = 2.93 TBq/kg] for 1988, 0.56 MBq [sp. act. = 0.71 TBq/kg] for 1989 and 0.59 MBq [sp. act. = 2.64 TBq/kg] for 1990. On the same dates, in 1989 and 1990,  $^{14}\text{C}$ -ring-labeled atrazine [0.57 MBq (sp. act. = 0.72 TBq/kg) and 0.62 MBq (sp. act. = 1.98 TBq/kg), respectively] plus AATrex 4L and  $^{14}\text{C}$ -phenyl-labeled primisulfuron [0.54 MBq (sp. act. = 2.08 TBq/kg) and 0.37 MBq (sp. act. = 1.94 TBq/kg), respectively] (CIBA-Geigy Corporation, Greensboro, NC) were applied to the soil surfaces of selected lysimeters (Figure 2).

Radiochemical purity of all chemicals was > 97%. Application rates for atrazine and metolachlor were 1.12 and 2.24 kg ai/ha, respectively, both years. Rates for primisulfuron were 0.08 and 0.06 kg ai/ha for 1989 and 1990, respectively.

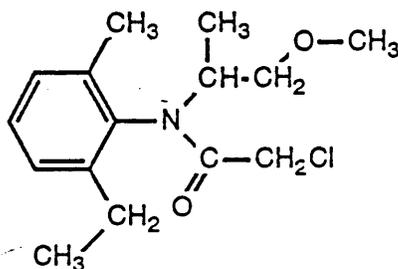
In 1989 and 1990, 18 h after herbicide application, instantaneous water ponding on the soil surface of selected lysimeters treated with  $^{14}\text{C}$ -labeled metolachlor was established by adding 825 mL of tritiated water [260 MBq in 1989 and 93 MBq in 1990 (sp. act. = 3.70 GBq/mL)] (equivalent to a height of 2.54 cm on the soil surface) (ICN Radiochemicals, Irvine, CA). In 1990 postassium bromide plus tritiated water were applied to duplicate lysimeters in the same manner as the herbicide solution.

On May 30, 1990, selected lysimeters were treated with each of one of the three herbicides, at the same rates, alone and mixed with each of three water-soluble acrylic polymers (ASE-108, HA-16 and E-1242 from Rohm and Haas Co.,

Atrazine



Metolachlor



Primisulfuron

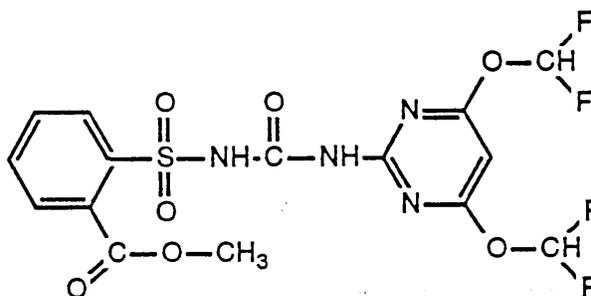


Figure 2. Molecular structures of atrazine, metolachlor and primisulfuron.

Philadelphia, PA). The three polymer/herbicide mixtures were pipeted onto the soil surface in a cross-hatch pattern in 10 mL of water at rates of 0.64, 1.64 and 1.80 kg/ha of solid polymer/ha, respectively. The amounts of polymer added would be equal to 2% of a water application volume of 168.4 L/ha, which is commonly used by farmers to apply herbicides. The density of all three polymers was 1.1 g/cm<sup>3</sup>. The polymers were selected to represent anionic, nonionic, and cationic charged materials, respectively. ACRYCOL ASE-108 (ASE-

108), described as a 20% solid suspension copolymer emulsion stabilizer, is used to stabilize liquid laundry and machine-dishwashing detergents and to formulate flowable pesticide products. It is shipped in an anionic acid form (pH 3.0) and must be neutralized to pH 8 to initiate polymerization and obtain high viscosity. RHOPLEX HA-16 (HA-16) is a nonionic 45% solid suspension, pH 3.0, self-cross-linking acrylic polymer used in a wide variety of textile applications. EMULSION E-1242 (E-1242) is a cationic 50% solid suspension, pH 4.5, self-cross-linking acrylic emulsion used in a wide variety of textile applications. The advantage of E-1242 is that it polymerizes at room temperature after drying.

After the herbicide or herbicide/polymer application, the soil was allowed to dry overnight (24 h), and water was added weekly, as necessary to maintain the 10-year average weekly precipitation.

On May 23, 1991, selected lysimeters were treated with nitrate at a rate of 200 kg/ha as calcium nitrate, and bromide at a rate of 300 kg/ha as potassium bromide. Approximately 1 cm of soil was removed from each lysimeter. The chemicals were applied to the exposed soil and then covered with the topsoil. Two days after treatment (DAT) lysimeters to which the nitrate and bromide were applied, were included as described above. After application, the 0 DAT lysimeters were immediately removed from the field, taken to the laboratory and separated into three layers (0-5 cm, 5-13 cm and 13-23 cm). The soil in each layer was thoroughly mixed and placed in a refrigerator (4-6°C) until analyzed for nitrate and bromide.

Removal and sectioning. For each year, duplicate fallow and soybean lysimeters with and without leachate collectors, were removed at 0, 30, 60, 90, 120, 180, and 360 DAT. In 1989 and 1990, replicated mulch, sod and polymer treated lysimeters were removed at 90 DAT. After removing soil from around the lysimeters by the use of a post-hole auger, the lysimeters were lifted by a winch to the soil surface. Lysimeter ends were secured with plastic and transported vertically to the laboratory. Lysimeters were cut lengthwise from bottom to top and the soil removed in twelve, 7.6-cm depth increments, placed in plastic bags, mixed thoroughly, labeled, weighed, sealed and stored at -20°C until analyzed. Zero-day (0 DAT) treated soil samples were prepared in the same manner except that only the 0-76 cm depth zone was taken for analysis. Background samples were taken from all depths at all time periods.

In 1989, duplicate lysimeters treated with tritiated water plus <sup>14</sup>C-labeled metolachor were removed at 0, 30, 60, 90, 120 DAT. In 1990, separate replicated soil lysimeters with herbicide and bromide plus tritiated water were removed at 120 DAT.

Leachate collection. Leachate was monitored daily and collected weekly from selected lysimeters. Leachate collection jars were weighed, two 1 mL samples were taken from each jar for immediate assay and the rest stored at -20°C.

<sup>14</sup>C, tritium, bromide and nitrate analysis. For total <sup>14</sup>C and tritium, four 1-g subsamples from each depth were combusted in a biological oxidizer (OX-300 Automated Biological Oxidizer, R. J. Harvey Instrument Corp., Hillsdale, NJ). Evolved <sup>14</sup>CO<sub>2</sub> and tritium were trapped in carbon (OX-161 Carbon 14 Cocktail, R. J. Harvey Instrument Corp., Hillsdale, NY) and tritium (OX-162 Tritium Cocktail, R. J. Harvey Instrument Corp., Hillsdale, NJ) cocktails,

respectively, and subsequently quantified by liquid scintillation spectrometry (LSS) in a liquid scintillation counter (Pack TRI-CARB Liquid Scintillation Analyzer, Model 2000CA, Packard Instrument Co., Downers Grove, IL). Soil moisture content for each section was determined by drying samples in the oven at 105°C for 24 h. Reproducibility among subsamples was  $\pm 3\%$ . Biological oxidizer efficiency was  $>96\%$ .  $^{14}\text{C}$  determination for each soil section was converted to percent of applied  $^{14}\text{C}$ .

In the 0- to 7.6-cm layer, metabolite and parent identification for each herbicide treatment was performed for the 1990 study. One hundred grams of air-dried soil were extracted with 100 mL of methanol on a horizontal shaker for 1 and 4 h for the metolachlor and atrazine treatments, respectively. Air-dried soil was used since the removal of water hastened the evaporation of methanol. Preliminary studies showed no loss of  $^{14}\text{C}$  from the soil during the air-drying process. One hundred grams of field moist soil from the primisulfuron treatment were extracted with 100 mL of acetonitrile on a horizontal shaker for 1 h. Slurries were filtered through glass fiber filters under reduced pressure. Filtrates were transferred to 500 mL round bottom boiling flasks and evaporated to less than 2 mL at 34°C under reduced pressure. Extractability of  $^{14}\text{C}$  varied for each herbicide and sampling date. Extracts were transferred to graduated test tubes and evaporated to 1 mL. A 0.1 mL aliquot of the extract was added to 15 mL of scintillation cocktail. (Scintiverse E, Fisher Scientific Co., Springfield, NJ). Radioactivity was quantified by LSS. Duplicate 1-g samples from the extracted soil were combusted to determine nonextractable  $^{14}\text{C}$ . Recovery of extractable plus nonextractable  $^{14}\text{C}$  was  $>93\%$ .

Concentrated extracts [150 to 500  $\mu\text{L}$ ;  $>3000$  disintegrations per min (DPM)] plus standard (parent compound) were subjected to thin-layer chromatography (TLC) to determine degradates and parent compound (Miller 1975). Primary solvent systems used were ethyl acetate:toluene (1:1 v/v) for atrazine, chloroform:methanol:formic acid:water (75:20:4:2 v/v/v/v) for metolachlor, and methylene chloride:ethyl acetate:acetic acid (50:50:1 v/v/v) for primisulfuron. To verify separations from primary solvent systems, randomly selected extracts were developed with secondary solvent systems. Secondary solvent systems were chloroform:acetone (95:5 v/v) for atrazine, methylene chloride:acetone (95:5 v/v) for metolachlor and toluene:methylene chloride:ethyl acetate (4:2:2 v/v/v) for primisulfuron. Radioactive zones, proportions, and corresponding  $R_f$  values were determined by scanning TLC plates (Whatman LK5F Linear TLC Plates, Whatman U.S.A., Hillsboro, OR) with an imaging TLC plate radiodensitometer (Bioscan System 400 Imaging Scanner, Bioscan Inc., Washington, DC). To verify proportions of radioactivity, zones were scraped from randomly selected TLC plates, combusted, and quantified by LSS.

For bromide analysis of bromide treated soils 10 g of air-dried soil and 50 mL of deionized water plus 1 mL of 5 M sodium nitrate was shaken for 1 h on a horizontal shaker. The suspension was then analyzed for bromide concentration by use of a bromide electrode (Corning Medical and Scientific, Corning Glass Works, Medfield, MA) and corrected for background bromide which ranged from 0.04 to 0.12 mg/kg (Adriano and Danner 1982). Bromide concentrations were converted to percent of applied.

A subsample from every section of nitrate treated soil was analyzed for nitrate. A 25-g wet soil sample was placed in a plastic vial and extracted

with 50 mL distilled water and 1 mL of ionic strength adjustor (2M ammonium sulfate); 0.5 mL of boric acid was added as a preservative. The soil and extractant were shaken for 30 min and analyzed with a nitrate electrode (Ionalyzer/901, Orion Research Inc., Cambridge, MS).

Total  $^{14}\text{C}$  and tritium in leachate were assayed by placing 1 mL aliquots of sample into 15 mL of scintillation cocktail and quantifying by dual-label LSS. Metabolite identification of leachates was done by filtering 90 mL of thawed sample through Sep-Pak  $\text{C}_{18}$  environmental cartridges (conditioned with 10 mL methanol and 50 mL deionized water) (Waters Chromatography Division/Millipore Corp., Milford, MA) by use of a vacuum pump and cartridge rack. Flow rate was 2 mL/min. Cartridges were then eluted with 20 mL 2-propanol and 30 mL of methanol. Eluates were combined and transferred to 250 mL round bottom boiling flasks and evaporated to <2 mL at 34°C under reduced pressure. Extracts were transferred to graduated test tubes and evaporated to 1 mL. A 0.1 mL aliquot of the extract was added to 15 mL of scintillation cocktail. Radioactivity was quantified by LSS. Extraction of  $^{14}\text{C}$  from leachate and recoveries of  $^{14}\text{C}$  from  $\text{C}_{18}$  cartridges were > 98%. Concentrated extracts (150 to 500  $\mu\text{l}$ : >3000 DPM) plus standard (parent compound) were subjected to TLC to determine degradates and parent compound (Miller 1975). Leachate from the six trench side lysimeters was analyzed for nitrate by adding 1 mL of ionic strength adjustor and 0.5 mL boric acid to 50 mL of leachate and use of the nitrate electrode. The limit of detection was about 1  $\mu\text{g}/\text{mL}$ .

For bromide analysis, 50 mL of leachate plus 1 mL of 5 M sodium nitrate was placed in a beaker, magnetically stirred with a Teflon-coated stirring bar, and bromide concentration determined by a bromide electrode and corrected for background bromide concentration. Bromide background levels in leachate varied from 0.12 to 0.22  $\mu\text{g}/\text{mL}$  and were in agreement with other researchers (Lein and Cassel 1991, unpublished data, Soil Science Dept., N.C. State University, Raleigh).

Vegetation establishment and analysis. Four 'Coker 368' soybeans, a maturity group VIII plant, were planted in eight lysimeters in 1988 and 1989 and 12 lysimeters in 1990 and upon plant emergence were thinned to one. In 1990, prior to planting soybeans, lysimeters were subsoiled to 50-cm with a crow-bar. Subsoiling was performed to fracture the tillage-induced pan that limits soybean root penetration in many of the Atlantic Coastal Plain soils (Kamprath et al. 1979, Martin et al. 1979). Transplanted bermudagrass, that had been established for 9 yr in an adjacent field, and wheat straw were placed on the surface of selected lysimeters 7 d prior to herbicide application to duplicate lysimeters in 1989 and 1990. Bermudagrass was clipped once in 1989 and twice in 1990, with clippings removed, stored at -20°C and composited at 90 d. Wheat straw was applied at a rate equivalent to 3200 and 2100 kg/ha in 1989 and 1990, respectively. Surface coverage was visually estimated to be >95%.

Vegetation fractions were separated from the soil, washed, dried at 80°C, weighed, and ground. Percent of applied  $^{14}\text{C}$  in the vegetative portions were determined by combusting two 0.1 g subsamples in a biological oxidizer, trapping the evolved  $^{14}\text{CO}_2$ , and quantifying by LSS.

Experimental design and data analysis. Herbicide treatments were arranged as a randomized complete block design with two replications and each experiment was run once in each of two years. Analysis of variance was conducted to

determine whether there were significant differences in measured parameters attributable to years, herbicides, surface cover, polymer addition, plant density and presence of leachate collector, for each depth and sampling date. The means of the herbicide concentrations (percent of applied  $^{14}\text{C}$ ) at each depth and sampling date were separated using Fisher's Protected Least Significant Difference (LSD) at the 5% level (Steel and Torrie 1980). Comparisons between depths and total recovery for each herbicide and sampling period were subjected to repeated measures using SAS procedures (SAS 1985). Regression analyses were used to predict herbicide longevity for the 0- to -15 cm depth. A single value called M-score developed by Mahnken (1989) to represent  $^{14}\text{C}$  distribution in soil was modified to represent  $^{14}\text{C}$ , tritium and soil water distribution within each lysimeter. This single value aided the statistical analysis of the treatments. A sample calculation for M-score is shown in Table 1. A large M-score indicated that more  $^{14}\text{C}$ , tritium or soil water was recovered in the lower depths of the lysimeter while a small M-score indicated that more of the materials were retained in the upper depths. Analysis of variance procedures (SAS 1985) for each lysimeter removal date were conducted to determine whether there were significant differences in total  $^{14}\text{C}$  and tritium in soil and water, M-scores and tensiometer readings. Treatment means were separated using the LSD.

Modified  $R_f$  values were calculated for each lysimeter to allow for comparison to be made among herbicide and polymer treatments using (Weber 1991a)

$$R_f = \sum_{i=1}^n (D_i F_i) / (MD \times TF)$$

where  $R_f$  is the index of herbicide mobility,  $n$  is the number of sections of the entire soil lysimeter,  $D$  is the mean depth of section  $i$  (total distance from soil surface to the midpoint of section  $i$  in cm),  $F$  is the fraction of herbicide applied in section  $i$ ,  $MD$  is the maximum mean depth (total distance from soil surface to the midpoint of the last section in cm), and  $TF = 1.0$  (total fraction of herbicide applied in the entire soil lysimeter).

A small  $R_f$  value indicates that the herbicide is nonmobile and travels a short distance in the soil lysimeter; a large  $R_f$  value indicates that the herbicide is very mobile and travels a long distance. [For instance the smallest  $R_f$  value possible for this lysimeter would be  $(3.8 \text{ cm} \times 1.0) \div (88 \text{ cm} \times 1.0) = 0.04$  which indicates that all applied herbicide was found in the first section (0-7.6 cm, mean = 3.8) of the lysimeter. A large  $R_f$  value of 1.0 from  $(88.0 \text{ cm} \times 1.0) \div (88.0 \text{ cm} \times 1.0)$  indicates that all of the herbicide was found at the bottom (83.6-90.0 cm, mean = 88.0 cm) section of the lysimeter]. The experiment was arranged as a randomized complete block with two replications. Total percent recovery data and  $R_f$  values were subjected to analysis of variance at the 5% confidence level.

To analyze the concentration changes of bromide and nitrate percolate, data are presented as a breakthrough curve. A breakthrough curve is a plot of the solute concentration versus the number of pore volumes of effluent collected or versus time. The pore volume, representing the volume of water each lysimeter could hold at field capacity, was calculated as the product of mass

Table 1. Example of M-score calculation for <sup>14</sup>C, tritium, or soil water distribution in the soil profile (from Mahnken 1989).

Mean depth	Fraction <sup>14</sup> C or tritium recovered	Normalized fraction <sup>14</sup> C or tritium recovered <sup>a</sup>	Fraction soil water present	Normalized fraction soil water present <sup>a</sup>	Depth x normalized <sup>14</sup> C or tritium	Soil water fraction
(D)	(F <sub>1</sub> )	(NF <sub>1</sub> )	(F <sub>2</sub> )	(NF <sub>2</sub> )	(DxNF <sub>1</sub> )	(DxNF <sub>1</sub> )
(Cm)						
4	0.182	0.446	0.07	0.05	1.78	0.20
11	0.079	0.194	0.06	0.05	2.13	0.55
19	0.028	0.069	0.07	0.05	1.31	0.95
27	0.028	0.069	0.07	0.05	1.86	1.35
34	0.012	0.029	0.07	0.06	0.99	2.04
42	0.009	0.022	0.08	0.06	0.92	2.52
49	0.009	0.022	0.09	0.07	1.08	3.43
57	0.008	0.019	0.11	0.08	1.08	4.56
65	0.009	0.022	0.14	0.11	1.43	7.15
72	0.012	0.029	0.16	0.12	2.09	8.64
80	0.018	0.045	0.18	0.14	3.60	11.20
86	0.014	0.034	0.21	0.16	2.92	13.76
Total	0.408	1.000	1.30	1.00	M-score=21.20	56.35

<sup>a</sup>Fraction recovered normalized to 100% recovered for comparative purposes.

wetness and bulk density for the 12 depth increments divided by the total volume at each depth, and then summing the 12 values.

#### Herbicide Degradation Studies

Soil sample collection. Samples of Dothan soil were taken from the side of a pit 1 meter deep at 0-5, 20-25, 45-50, and 70-75 cm. The type of clay appeared to change with depth. In samples from the upper 2 depths, the clay present was brownish-gray and did not flocculate well in organic solvents, while the clay from the 45-50 and 70-75 cm depths had a reddish-orange color and flocculated well in acetonitrile. Soils were air-dried and passed through a 2 mm sieve and stored dry in the plastic containers until needed.

For each experiment 5 kg of soil was placed in a plastic tub and moistened to approximately 40% of field capacity. The moist soil was then covered with plastic and incubated at least 7 d to develop an active microbial population.

Experimental design. The experiment was designed as a 2 x 4 factorial with sterility (sterile and non-sterile) and depth (0-5, 20-25, 45-50, and 70-75 cm) as variables. Treatment combinations were replicated three times. Each sample unit consisted of a 500 mL glass jar with a Teflon sheet lining the lid to prevent herbicide adsorption by the rubber gasket. Twenty five g of soil (on a dry wt basis) were added to one half of the units and 50 g to the remainder. The containers with 50 g soil were sterilized by autoclaving for 1 h at 121° C and 6.57 kPa on three successive days. Subsequently 1 mL of the radioactive-analytical grade solution was added to all units and the

application solvents allowed to evaporate overnight. To prevent chemical sterilization of microbial populations in the non-sterile treatment, applications were made to 25 g of soil and the application solvents allowed to evaporate overnight. Twenty-five g of microbially active soil were then added and thoroughly mixed with the soil in the containers. A 15-mL test tube containing 10 mL of 0.1 N sodium hydroxide was placed in each jar to trap carbon dioxide. Jars were capped and placed in a constant temperature room at 29°C (+/-1°) for incubation. The experiment was repeated and the results from each experiment averaged. Statistically there was no difference between the results of the two separate runs of the experiment except as noted in the results.

Treatment solutions. <sup>14</sup>C-labeled atrazine, metolachlor were mixed with their respective analytical grade material in methanol and primisulfuron with acetonitrile so that 1 mL of solution would deliver 5 x 10<sup>5</sup> DPM of radiolabeled material and a total of 4x field rates (16 kg/ha for atrazine and metolachlor and 80 g/ha for primisulfuron) to each soil sample.

Sampling and analysis. Contents of the jars containing herbicide-treated soils were analyzed at 0, 2, 4, 6, 9, 13, 17, and 22 wk after treatment for atrazine and at weekly intervals starting at time 0 and continuing through wk 7 for metolachlor and primisulfuron. For each sampling time the carbon dioxide traps were removed and sealed for later analysis. Subsequently, 250 mL of methanol was added to each of the sampling units for atrazine and metolachlor and acetonitrile for primisulfuron and their contents were shaken for 1 h on a reciprocal shaker, then suction filtered through glass fiber filter paper (Whatman GF/B). Extracts were transferred to flat bottom boiling flasks and evaporated under a vacuum of 700 mm of mercury at 32°C to dryness for atrazine at 32°C to a volume of 2-3 mL for metolachlor and to dryness at 40°C for primisulfuron. The extracts were re-dissolved in methanol for atrazine and metolachlor and in acetonitrile for primisulfuron, transferred to 15-mL volumetric test tubes, and brought to 10 mL. One milliliter of this extract was added to 10 mL of a liquid scintillation cocktail and quantitatively assayed for <sup>14</sup>C by LSS. An additional 150 µL of each extract was spotted on TLC plates (Whatman LK5F) to separate metabolites from the parent compounds. Two solvent systems, stated previously with differing polarities were utilized to ensure resolution of all metabolites.

Compounds were located on the TLC plates with an imaging scanner. Zones containing the parent compound or any metabolites were scrapped from the plate and suspended in 15 mL of scintillation cocktail and assayed by LSS.

Solvent-extracted soil was air-dried and finely ground. Duplicate 1-g samples were oxidized in a biological oxidizer, and assayed by LSS.

Duplicate 1-mL samples of sodium hydroxide from the carbon dioxide traps were titrated to determine the total carbon dioxide produced and another 1 mL aliquot was added to 15 mL of scintillation cocktail and assayed by LSS to determine the amount of <sup>14</sup>CO<sub>2</sub> produced. Sterile flasks remained sterile throughout the experimental period.

Statistical analyses were performed using SAS procedures a General Linear Models procedure (Proc GLM) for analysis of variance (SAS 1985). Separate statistical analyses were performed for values representing bound <sup>14</sup>C, <sup>14</sup>CO<sub>2</sub>, % extractable parent herbicide and % metabolites formed.

Significant differences between sterility treatments were detected using T tests (LSD) and differences among depth treatments detected using Duncan's Multiple Range Test. Half-lives were calculated using non-linear regression analysis.

### Metolachlor Sorption Studies

Soil sample collection. Two Dothan soil lysimeters were removed from the site and transported to the laboratory to be used for sorption studies of metolachlor by selected surface and subsoil samples. Lysimeter M11 was taken from the north end of the site and lysimeter M18 was taken from the south end of the site. The horizontal distance between the two locations was approximately 20 m. The lysimeters were divided horizontally into 12 sections, each 7.6-cm long. The mass of the soil in each section ranged from about 3 to 4 kg. The soil sections were air dried for one wk, sieved with a 2-mm standard sieve, and stored in labeled half gallon plastic containers.

Treatments. Bottle-point sorption rate studies were performed on all sections of lysimeters M11 and M18. A 2:1 ratio of soil mass (g) to solution volume (mL) was used for all sections except the uppermost section, for which a 1:1 soil to solution ratio was used. The reactors with a 2:1 soil to solution ratio contained 20 g of soil, while the reactors with a 1:1 soil to solution ratio contained 10 g of soil. Twenty-four bottle reactors (40-mL Kimax glass centrifuge bottles), consisting of 12 pairs of duplicate samples, were prepared for each soil section. Six blanks containing no soil were analyzed at each time step for comparison with the initial concentration.

The base aqueous solution consisted of distilled water, which was amended to a 0.005 M concentration of sodium azide and a 0.005 M concentration of calcium in the form of calcium chloride dihydrate. Soils samples were weighed and allowed to hydrate for about 12 h using 5-mL of the base solution. After hydration, 5 mL of the base solution with a constant concentration of analytical grade metolachlor was added to each bottle to create the desired soil to solution ratio at the desired concentration. The initial concentration of the experiments was approximately 8 mg/L, which is equivalent to the loading rate used in the field experiments. The reactors were tumbled to maintain completely mixed conditions until each pair was removed for solution-phase analysis at specified times throughout an eight wk experimental time period.

Bottle-point equilibrium studies were performed using methods similar to those used for the bottle-point rate studies on all sections of both columns. A six wk time period, based on results from rate studies, was allowed for equilibration. The equilibrium studies were run with 10 different initial concentrations of metolachlor. A scheme similar to that used for rate studies for sample replicates and blanks was followed for the equilibrium studies. Hydration, and mixing aspects of the equilibrium studies were identical to the methods used in the rate studies.

Analysis. Analysis of the metolachlor solution-phase concentration was carried out by isolating the supernatant from the soil, extracting it into hexane and using gas chromatography (GC) to quantify the concentration. Upon removal from the tumbler, the vessels were centrifuged at 100 x gravity for 30 min to separate the soil from the supernatant. Three mL of supernatant were extracted into 6 mL of analytical grade hexane that had been spiked with

hexachlorobenzene as an internal standard. GC analysis was performed using an electron capture detector on a Hewlett Packard 5890A gas chromatograph and a Hewlett Packard 3396A integrator (Packard Instrument Co., Downers Grove, IL). Each sample was injected twice and the ratios of the analyte to the internal standard peak areas were averaged and compared to known standards for quantification. GC conditions were: a 0.53-mm diameter, 2.65-m long HP-1 Megabore column with a crosslinked methyl silicone gum phase, an oven temperature 225° C, makeup gas flow rate of 60 mL/min, injector temperature of 250° C, carrier gas flow rate of 5 mL/min, a detector temperature of 300°C, and a run time of 4.5 min.

### Modeling Metolachlor Movement in Soil

Field and experimental data were used to investigate the predictive ability of the Pesticide Root Zone Model (PRZM) (Carsel et al. 1984). Field pesticide mobility studies were performed (Keller 1992) in which 90-cm lysimeters were sacrificed at selected time intervals for one year to determine the distribution of <sup>14</sup>C-metolachlor as a function of depth. Tracer studies using tritiated water were also run over a period of 4 months. Leachate at the lysimeter bottoms was collected and measured. Moisture content at wilting point and field capacity were measured on field samples as a function of depth for PRZM input.  $K_p$  data from the laboratory studies as well as bulk density data were also used for PRZM input. In the modeling effort, the 90 cm lysimeter was also divided into 12 horizons of 7.5 cm each. The spatial discretization was set at 1.5 cm leaving five discretizations per soil horizon.

PRZM was tested by first calibrating the measured field leaching data to model output based on known rainfall. Then, leaving the final leaching calibration the same, a nonreacting slug source was put into PRZM and the model's output was compared to the field tracer studies. Finally, a sorbing pesticide was simulated and the model's output compared to field pesticide data.

### Soil Analysis

Prior to study initiation, soil from each 7.6-cm depth was characterized by determining humic matter and organic carbon content, particle size distribution (texture), pH, cation exchange capacity (CEC), soil water characteristic, saturated hydraulic conductivity ( $K_{sat}$ ) and bulk density. Humic matter was determined using the sodium hydroxide extraction method (Mehlick 1984b) and organic carbon was determined by A & L Laboratories, Omaha, NE using the chromic acid colorimetric method (Walkley and Black 1934, Schulte 1988). Organic carbon content was determined by a modified medium-temperature dry combustion procedure (Nelson and Sommers 1982). A biological oxidizer, with a combustion tube and catalyst zone, was used to determine organic carbon. Combustion tube temperature was set at 860° C while the cupric oxide catalyst zone was set at 670° C. Eight 1-g samples from each depth were burned for 3 min with the carbon dioxide produced trapped in 15 mL of 0.2 N sodium hydroxide. The trapped carbon dioxide was precipitated as barium carbonate by the addition of excess 1.5 M barium chloride. The unreacted sodium hydroxide, plus a few drops of phenolphthalein as an indicator, was titrated with 0.02 N hydrochloric acid. Prior to soil combustion, samples plus water (w/w) were subjected to 1 hydrochloric acid until soil pH ranged from 3.5 to 4. This procedure removed any alkaline-earth carbonates which influence carbon dioxide levels. Combustion of carbon

standards was >98%. Total organic carbon (TOC) analysis was performed by the wet combustion method (Nelson and Summers 1982) using an Oceanographic International Corporation TOC Analyzer. Ten replicate analyses were performed on 5-mg samples taken from each section in lysimeters M11 (upper-slope) and M18 (lower slope). Linear regression of organic carbon content as a function of the dry mass of the soil for all replicates was used to assign an organic carbon fraction to each section. Soil profiles were also characterized at other intermediate-slope positions for soil water holding capacity, particle size distribution and  $K_{sat}$ .

Particle size analyses were performed by A & L Laboratories, Omaha, NE using the hydrometer method (Gee and Bauder 1986). Soil pH was measured in a 1:1 (w/w) soil:water mixture with a glass electrode pH meter (Eckert 1988). CEC of the soil was determined by the North Carolina Department of Agriculture, Raleigh, NC using the ammonium acetate replaced (Thomas 1982) and Mehlich 3 extracting solution (Mehlich 1984a). Soil cores, housed in aluminum rings, were taken from each depth using a hammer-driven core sampler to determine particle density (Blake and Hartge 1986). Four cores (7.62 cm diam. by 6.35 cm long) from each depth were placed in a pressure outflow system similar to one described by Danielson and Sutherland (1986), slowly water-saturated, and the soil water characteristic determined for soil water pressures of 0, -07, -1.6, -3.6, -5.4, -9.4, -17 and -42 kPa. Total porosity was assumed to be equal to water content at saturation. Macroporosity is defined as total porosity minus the water-filled porosity at the soil water pressure of -5.4 kPa. Upon removing each soil core from the pressure outflow system, it was resaturated with water and  $K_{sat}$  determined (Klute and Kirkson 1986). Upon the determination of  $K_{sat}$ , each soil core was used to obtain bulk density (Doering 1965, Blake and Hartge 1986a). Water content of soil samples from each depth and sampling period was determined by gravimetric methods (Gardner 1986).

In 1989, tensiometers, which were used to measure the hydraulic and pressure head of the soil water, were installed horizontally at depths 8, 15, 30, 45, 60 and 75 cm below the soil surface in duplicate lysimeters with and without leachate collectors. Tensiometers were constructed with 2.86 cm long and 0.95 cm diameter cups (Arya et al. 1975, Cassel and Klute 1986) and were installed in the center of the lysimeters 53 DAT. Installation was carried out by removing soil adjacent to the outside wall at one side of each lysimeter exposing the outside wall of the steel cylinder. At the appropriate depths, holes were drilled through the cylinder walls to insert the tensiometer cup through the lysimeter wall. The guide hole in the soil was slightly less in diameter than the cup which ensured good contact between the cup and soil. Holes in the cylinder wall were sealed with silicon and the protruding tubing from each cup attached to a mercury manometer. Changes in mercury and water densities were assumed to be negligible throughout the study. Tensiometer readings were recorded weekly.

#### Climatic Data

Air temperature and rainfall were recorded by the Central Crops Research Station Weather Station (NOAA Site No. 31-1820-07). For the 1988 study, irrigation was added to each lysimeter on a weekly basis such that each unit received an amount of water equivalent to 20% greater than the 10 yr average rainfall for that same period. This watering scheme represented a 'worst case scenario'. For the 1989 study, irrigation was added to each lysimeter on a weekly basis such that each unit received an amount of water equivalent to the

10 yr average rainfall for that same period. For the 1990 study, irrigation was applied in the same manner but only during the first 150 d of the study. A US Weather Bureau Class A-type evaporation pan was installed adjacent to the lysimeter site. Cumulative pan evaporation was recorded at least twice weekly. Evaporation (E) or evapotranspiration (ET) from fallow and soybean lysimeters was determined for each sampling date. E and ET were calculated according to the following equation where SWCOD is the total soil water

$$E \text{ or } ET = (SWCOD + RI) - CL - SWC$$

content (cm) at 0 d, RI is cumulative rainfall plus irrigation (cm), CL is cumulative leachate (cm) and SWC is the total soil water content (cm). Soil temperatures were obtained by inserting 60-cm length dial thermometers into a pit wall dug adjacent to the lysimeters. Soil temperatures were recorded weekly at 8, 15, 30, 45, 60 and 75-cm below a bare surface.

## RESULTS AND DISCUSSION

### Soil Properties

Properties of soil profiles in the mid-slope position of the Dothan soil are shown in Table 2. Organic carbon and humic matter contents decreased with depth. Contents ranged from 1.1 to 0.4% for organic carbon determined by chromic acid oxidation, 0.5 to 0.1% organic carbon determined by combustion, and 0.4 to 0.0 humic matter. Nelson (1991), in analyzing the upper-slope and lower-slope positions of the same soil (Table 3) reported organic carbon contents, as determined by potassium persulfate oxidation (OC-3), of approximately the same magnitude as those determined by combustion (OC-2, Table 2). The lower-slope soil profile had slightly higher organic carbon contents than the upper-slope profile (Table 3).

Clay content increased with depth while silt content remained constant (Tables 2 to 4). The soil profile was shallower in upper-slope positions and deeper in lower-slope positions (Tables 3 and 4). Clay contents ranged from 2 to 9% at a depth of 38.0-4.56 in the upper-most slope positions (Sites A and B, Table 4) and from 2 to 7% at a depth of 53.2-60.8 cm in the lower-most slope positions (Sites E and F, Table 4). The clay content of the clayey subsoil ranged from 13 to 30% at 45.6 - 89.0 cm in the upper-most slope position to 14 to 30% at 60.8-89.0 cm in the lower-most slope position. Soil texture of the soil profiles also illustrated the deeper sand profiles in lower-slope positions compared with upper-slope positions (Tables 3 and 4).

CEC of the soil profile ranged from 1.3 to 3.9 cmol/kg and was a function of the organic carbon and clay content (Table 2). Soil pH ranged from slightly acid (pH 6.1-6.4) at the surface to extremely acid (pH 4.2-4.4) below 65 cm (Tables 2 and 3). Low CEC and pH values are typical for Ultisols in the southeastern USA (Adams and Moore 1983, Brady 1990). Bulk density ranged from 1.54 to 1.82 g/cm and increased with depth (Tables 2 to 4). The increased bulk density at 19- to 34-cm is a typical occurrence in Ultisols in the southeastern USA (Reicosky et al. 1977). Particle density ranged from 2.63 to 2.74 g/cm<sup>3</sup> and was relatively constant through the profile (Table 4). Total porosity ranged from 39% at the 0-7.6 cm depth to 27% at 22.8-30.4 cm depth (Table 2). Agreeably, total porosity was the smallest at depths with greatest

Table 2. Properties of Dothan loamy sand at the mid-slope position (Keller 1992).

Depth (cm)	Constituents <sup>a</sup>						Capacity/reactivity <sup>b</sup>							
	OC-1	OC-2	HM	S	SI	C	Texture	CEC	pH	Db	K <sub>sat</sub>	P	MP	
	----- (%) -----							(cmol/kg)		(g/cm <sup>3</sup> )	(cm/h)	----- (%) -----		
0-7.6	1.1	0.5	0.4	84	10	6	LS	2.3	6.1	1.54	9.64	38.8	23.6	
7.6-15.2	0.9	0.5	0.4	85	8	7	LS	2.0	5.7	1.66	5.94	31.8	18.2	
15.2-22.8	0.8	0.3	0.4	83	9	8	LS	1.6	5.2	1.71	3.55	28.6	15.4	
22.8-30.4	0.5	0.1	0.3	82	9	9	LS	1.3	5.1	1.70	3.10	27.0	14.2	
30.4-38.0	0.5	0.1	0.1	82	9	9	LS	1.4	5.1	1.71	1.95	27.7	13.4	
38.0-45.6	0.5	0.2	0.1	80	9	11	LS	1.9	5.0	1.65	2.81	29.1	13.7	
45.6-53.2	0.5	0.2	0.1	76	9	15	SL	2.0	5.0	1.67	4.63	29.8	14.0	
53.2-60.8	0.5	0.2	0.1	73	8	19	SL	2.5	4.6	1.64	3.25	31.2	13.6	
60.8-68.4	0.5	0.3	0.1	70	9	21	SCL	3.0	4.4	1.66	1.18	32.7	9.7	
68.4-76.0	0.5	0.3	0.1	67	9	24	SCL	3.0	4.3	1.61	1.27	33.6	8.3	
76.0-83.6	0.4	0.3	0.1	65	9	26	SCL	3.1	4.4	1.65	0.98	34.8	7.1	
83.6-89.0	0.4	0.3	0.0	60	11	29	SCL	3.9	4.4	1.63	0.31	36.8	5.2	

<sup>a</sup>OC-1 = organic carbon by chromic acid oxidation, OC-2 = organic carbon by combustion, HM = humic matter, S = sand, SI = silt, C = clay, LS = loamy sand, SL = sandy loam, and SCL = sandy clay loam.

<sup>b</sup>CEC = cation exchange capacity, pH = -log (H<sup>+</sup>), D<sub>b</sub> = bulk density, K<sub>sat</sub> = saturated hydraulic conductivity, p = total porosity and MP = macroporosity.

Table 3. Properties of Dothan loamy sand at the upper-slope and lower-slope positions (Nelson 1991).

Depth (cm)	Constituents <sup>a</sup>					Capacity/reactivity <sup>b</sup>		
	OC-3	S	SI	C	Texture	pH	D <sub>b</sub>	H <sub>2</sub> O
	------(%)-----						(g/cm <sup>3</sup> )	(%)
<u>M-11 Upper-slope position</u>								
0-7.6	0.5	84	10	6	LS	6.4	1.61	5.4
7.6-15.2	0.2	86	8	6	LS	5.8	1.58	5.9
15.2-22.8	0.2	84	8	8	LS	5.0	1.70	6.0
22.8-30.4	0.1	80	10	10	SL	5.0	1.70	5.9
30.4-38.0	0.1	80	10	10	SL	5.1	1.70	6.8
38.0-45.6	0.1	76	10	14	SL	5.3	1.67	7.6
45.6-53.2	0.1	72	8	20	SCL	5.7	1.67	8.6
53.2-60.8	0.1	68	8	24	SCL	5.0	1.70	9.8
60.8-68.4	0.2	68	8	24	SCL	4.5	1.72	13.3
68.4-76.0	0.1	66	10	24	SCL	4.3	1.69	14.2
76.0-83.6	0.1	66	10	24	SCL	4.3	1.60	14.9
83.6-89.0	0.1	66	8	26	SCL	4.4	1.59	17.1
<u>M-18 Lower-slope position</u>								
0-7.6	0.4	84	10	6	LS	5.8	1.49	6.2
7.6-15.2	0.3	84	8	8	LS	5.5	1.69	7.6
15.2-22.8	0.2	82	10	8	LS	5.3	1.75	6.7
22.8-30.4	0.2	84	8	8	LS	5.1	1.72	6.6
30.4-38.0	0.1	84	8	8	LS	5.1	1.73	8.1
38.0-45.6	0.2	84	8	8	LS	4.7	1.63	9.2
45.6-53.2	0.3	80	10	10	SL	4.4	1.64	10.7
53.2-60.8	0.2	78	8	14	SL	4.3	1.54	13.2
60.8-68.4	0.2	72	10	18	SL	4.2	1.53	12.6
68.4-76.0	0.2	68	8	24	SCL	4.3	1.58	14.6
76.0-83.6	0.2	64	8	28	SCL	4.4	1.63	17.1
83.6-89.0	0.2	54	14	32	SCL	4.4	1.57	18.3

<sup>a</sup>OC-3 = organic carbon by potassium persulfate oxidation, S = sand, SI = silt, C = clay, LS = loamy sand, SL = sandy loam and SCL = sandy clay loam.

<sup>b</sup>pH = log H<sup>+</sup>, D<sub>b</sub> = bulk density and H<sub>2</sub>O = soil moisture content.

Table 4. Properties of Dothan loamy sand at uppermost to lowermost slope positions (Lein and Cassel, 1991, unpublished, North Carolina State University, Raleigh, NC).

Depth	Constituents				Capacity/reactivity		
	Sand	Silt	Clay	Texture	Particle density	Bulk density	Hydraulic conductivity
cm	%	%	%		g/cm <sup>3</sup>	g/cm <sup>3</sup>	cm/h
Site A - Uppermost slope position							
0-7.6	90	8	2	S	2.65	1.61	3.66
7.6-15.2	93	4	3	S	2.66	1.55	6.67
15.2-22.8	90	7	3	S	2.68	1.70	1.47
22.8-30.4	89	6	5	S	2.67	1.82	0.18
30.4-38.0	87	8	5	LS	2.68	1.77	0.38
38.0-45.6	80	11	9	LS	2.66	1.71	1.04
45.6-53.2	78	9	13	SL	2.67	1.66	0.89
53.2-60.8	75	9	16	SL	2.66	1.68	0.91
60.8-68.4	76	9	15	SL	2.73	1.67	0.55
68.4-76.0	75	8	17	SL	2.73	1.73	1.07
76.0-83.6	70	8	22	SCL	2.74	1.62	0.55
83.6-89.0	63	10	27	SCL	2.73	1.60	0.18
						Mean	1.46
Site B							
0-7.6	89	8	3	S	2.64	1.56	7.25
7.6-15.2	90	7	3	S	2.67	1.72	2.27
15.2-22.8	90	7	3	S	2.66	1.63	4.17
22.8-30.4	89	6	5	S	2.67	1.76	0.32
30.4-38.0	86	8	6	LS	2.68	1.70	0.72
38.0-45.6	84	8	8	LS	2.69	1.75	0.26
45.6-53.2	75	7	18	SL	2.66	1.65	0.28
53.2-60.8	72	8	20	SL	2.63	1.61	0.50
60.8-68.4	76	7	17	SL	2.70	1.71	1.05
68.4-76.0	74	9	17	SL	2.70	1.75	0.72
76.0-83.6	66	9	25	SCL	2.69	1.61	0.57
83.6-89.0	60	10	30	SCL	2.69	1.59	0.36
						Mean	1.54
Site C							
0-7.6	89	7	4	S	2.65	1.66	4.78
7.6-15.2	90	6	4	S	2.66	1.70	2.98
15.2-22.8	90	6	4	S	2.67	1.78	1.05
22.8-30.4	86	9	6	LS	2.67	1.79	0.45
30.4-38.0	86	8	6	LS	2.66	1.72	1.35
38.0-45.6	86	8	6	LS	2.67	1.71	1.90
45.6-53.2	88	7	5	S	2.28	1.73	2.18
53.2-60.8	84	8	8	LS	2.67	1.75	1.17
60.8-68.4	78	7	15	SL	2.70	1.67	0.76
68.4-76.0	73	9	18	SL	2.70	1.78	0.15
76.0-83.6	66	10	24	SCL	2.70	1.61	0.22
83.6-89.0	54	11	35	SCL	2.68	1.49	0.96
						Mean	1.50

Table 4. continued

Depth	Constituents				Capacity/reactivity		
	Sand	Silt	Clay	Texture	Particle density	Bulk density	Hydraulic conductivity
cm	%	%	%		g/cm <sup>3</sup>	g/cm <sup>3</sup>	cm/h
Site D							
0-7.6	90	7	3	S	2.63	1.63	4.01
7.6-15.2	91	6	3	S	2.66	1.66	3.70
15.2-22.8	92	5	3	S	2.66	1.72	2.24
22.8-30.4	92	5	3	S	2.67	1.74	1.10
30.4-38.0	88	8	4	S	2.68	1.70	1.35
38.0-45.6	88	8	4	S	2.67	1.67	4.53
45.6-53.2	87	7	6	LS	2.68	1.74	2.43
53.2-60.8	85	8	7	LS	2.68	1.72	2.76
60.8-68.4	78	9	13	SL	2.75	1.70	0.82
68.4-76.0	73	9	18	SL	2.73	1.67	0.93
76.0-83.6	69	10	21	SCL	2.73	1.74	0.68
83.6-89.0	63	9	28	SCL	2.72	1.54	0.20
						Mean	2.06
Site E							
0-7.6	92	5	3	S	2.65	1.67	3.22
7.6-15.2	90	6	4	S	2.67	1.71	2.33
15.2-22.8	91	4	5	S	2.66	1.71	1.59
22.8-30.4	88	7	5	S	2.66	1.76	0.91
30.4-38.0	89	6	5	S	2.70	1.72	1.60
38.0-45.6	89	6	5	S	2.68	1.68	3.21
45.6-53.2	90	5	5	S	2.67	1.68	2.93
53.2-60.8	86	7	7	LS	2.68	1.72	0.85
60.8-68.4	77	9	14	SL	2.74	1.79	0.83
68.4-76.0	71	8	21	SCL	2.72	1.69	1.64
76.0-83.6	68	10	35	SCL	2.73	1.67	0.03
83.6-89.0	55	10	35	SCL	2.73	1.55	0.04
						Mean	1.60
Site F - Lowermost slope position							
0-7.6	93	5	2	S	2.66	1.66	2.69
7.6-15.2	93	5	2	S	2.69	1.68	2.83
15.2-22.8	92	5	3	S	2.67	1.70	1.98
22.8-30.4	92	5	3	S	2.66	1.73	1.68
30.4-38.0	89	7	4	S	2.68	1.71	2.55
38.0-45.6	90	6	4	S	2.68	1.64	2.88
45.6-53.2	89	7	4	S	2.69	1.66	5.21
53.2-60.8	85	8	7	LS	2.69	1.74	0.36
60.8-68.4	78	6	16	SL	2.73	1.77	2.28
68.4-76.0	72	9	19	SL	2.73	1.71	0.17
76.0-83.6	69	9	22	SCL	2.73	1.59	2.18
83.6-89.0	58	10	32	SCL	2.73	1.56	0.05
						Mean	2.07

bulk densities. Macroporosity, defined as air-filled pores at a soil water pressure of -5.4 kPa, ranged from 24% in the first depth to 5% in the 83.6-89.0 cm depth. Changes in macroporosity by depth were plainly related to the change in soil texture.

Soil moisture increased with depth and with increasing clay content of the soil (Table 3). ( $K_{sat}$ ) was the greatest in the shallower depths and decreased with depth (Tables 2 and 4). The general decrease in  $K_{sat}$  with depth is associated with increases in clay content; and decreases in macroporosity and sand content. Faster infiltration was observed in the field to occur in lower slope positions as compared with upper slope positions.

Water holding capacity of the Dothan soil increased with depth (Table 5) as it did with increased clay content (Tables 2 to 4). Mean moisture contents for each profile over the entire pressure head values ranged from 0.19 to 0.21 and did not appear to be related to slope position.

### Lysimeter Studies

Climatic conditions. Monthly water inputs, cumulative water inputs per respective DAT and average monthly air temperatures for 1988 to 1991 for lysimeter studies are shown in Tables 6, 7 and 8, respectively. Monthly pan evaporation data for 1988 to 1990 is shown in Table 9.

Even though 20% more water was applied for each week in 1988, only five of the months had totals greater than those in 1989 and 1990 (Table 6). Half of the monthly water inputs for the 1989 and 1990 studies were similar to the 10 yr average. Cumulative water inputs at 30 DAT were roughly twice as high in the 1988, 1989 and 1991 studies as compared to the 1990 study (15.49, 16.80 and 17.90 versus 8.64 respectively) (Table 7). Cumulative water inputs at 60 DAT were similar in 1989 and 1991 while at 90 DAT, 1988 and 1989 were comparable. Water inputs were alike at 120 and 180 DAT for 1989 and 1990 but were substantially higher than for 1988 for both periods. At the end of the three seasons, cumulative water inputs were 52, 34, 10 and 1% over the 10 yr average for the 1988, 1989, 1990 and 1991 studies, respectively (Table 6).

Mass balance of water inputs to fallow lysimeters with leachate collectors are shown in Table 10. Water inputs retained by soil is the difference in soil water content at sampling minus the 0 d water content. Evaporation was calculated by subtracting soil-retained water and percolate from water input.

During the 120 d study in 1989, on the average, 46% of the water added to fallow lysimeters evaporated, while an average of 53% of the water appeared as percolation and 1% was soil adsorbed (Table 10). At 120 DAT, a comparison of the 1989 and 1990 values shows slight differences in percolation and evaporation between the two years. This slight difference was probably due to daily differences in air temperature and relative humidity for each year. The amount of water lost through evaporation over the study period is in general agreement with other lysimeter studies (Kilmer et. al. 1944).

Fluctuating air temperatures were observed for each month, and in most instances, average maximum and minimum monthly readings were near the 10 yr average (Table 8). Maximum and minimum temperatures were relatively similar for the four seasons.

Table 5. Soil moisture holding characteristics of Dothan loamy sand at upper-most to lower-most slope positions (Lein and Cassel, 1991, unpublished, North Carolina State University, Raleigh, NC).

Pressure head (cm)	Soil depth (cm)											
	0-7.6	7.6-15.2	15.2-22.8	22.8-30.4	30.4-38.0	38.0-45.6	45.6-53.2	53.2-60.8	60.8-68.4	68.4-76.0	76.0-83.6	83.6-89.0
(%)												
Site A uppermost slope position												
0	0.38	0.42	0.32	0.27	0.31	0.33	0.30	0.32	0.32	0.33	0.35	0.33
-3.8	0.36	0.40	0.32	0.25	0.29	0.30	0.27	0.28	0.29	0.28	0.32	0.31
-10	0.36	0.36	0.31	0.25	0.29	0.30	0.27	0.28	0.28	0.28	0.31	0.31
-20	0.35	0.36	0.31	0.25	0.28	0.28	0.27	0.28	0.27	0.27	0.31	0.30
-30	0.34	0.32	0.30	0.24	0.27	0.26	0.26	0.27	0.27	0.27	0.30	0.30
-40	0.26	0.21	0.25	0.22	0.24	0.23	0.25	0.26	0.26	0.26	0.30	0.30
-50	0.19	0.16	0.19	0.20	0.20	0.21	0.23	0.25	0.25	0.25	0.29	0.29
-60	0.16	0.14	0.16	0.18	0.18	0.20	0.23	0.24	0.24	0.24	0.29	0.29
-100	0.13	0.11	0.13	0.15	0.16	0.18	0.20	0.23	0.23	0.24	0.28	0.28
-100*	0.14	0.11	0.13	0.15	0.15	0.20	0.23	0.30	0.27	0.30	0.32	0.43
-140	0.11	0.13	0.11	0.14	0.15	0.17	0.19	0.22	0.21	0.23	0.27	0.28
-180	0.10	0.10	0.10	0.13	0.14	0.17	0.18	0.22	0.21	0.22	0.26	0.27
-240	0.10	0.09	0.10	0.12	0.13	0.16	0.18	0.20	0.20	0.22	0.26	0.26
-320	0.09	0.09	0.09	0.12	0.13	0.16	0.17	0.19	0.19	0.20	0.25	0.26
-320*	0.05	0.04	0.05	0.06	0.06	0.09	0.11	0.13	0.14	0.16	0.17	0.24
-400	0.09	0.08	0.09	0.11	0.12	0.15	0.16	0.18	0.19	0.20	0.24	0.25
-15200*	0.03	0.02	0.02	0.03	0.03	0.05	0.08	0.10	0.10	0.12	0.14	0.19
Overall mean	= 0.21											
Site B												
0	0.42	0.34	0.37	0.30	0.31	0.31	0.29	0.31	0.30	0.29	0.36	0.36
3.8	0.37	0.32	0.35	0.28	0.29	0.28	0.26	0.29	0.27	0.27	0.32	0.33
-10	0.37	0.32	0.33	0.28	0.29	0.28	0.25	0.28	0.27	0.27	0.31	0.33
-20	0.36	0.32	0.32	0.27	0.28	0.27	0.24	0.28	0.27	0.26	0.31	0.32
-30	0.35	0.30	0.31	0.26	0.25	0.24	0.23	0.27	0.26	0.25	0.31	0.32
-40	0.27	0.28	0.25	0.22	0.19	0.21	0.22	0.26	0.25	0.24	0.30	0.31
-50	0.22	0.21	0.18	0.17	0.17	0.20	0.21	0.26	0.24	0.24	0.30	0.31
-60	0.19	0.16	0.16	0.16	0.16	0.19	0.21	0.25	0.23	0.23	0.30	0.31
-100	0.16	0.13	0.13	0.13	0.14	0.17	0.19	0.23	0.22	0.22	0.29	0.31
-100*	0.15	0.14	0.12	0.14	0.15	0.17	0.28	0.37	0.36	0.33	0.38	0.42
-140	0.14	0.11	0.12	0.12	0.13	0.16	0.18	0.22	0.20	0.20	0.28	0.30
-180	0.13	0.11	0.11	0.11	0.12	0.15	0.18	0.21	0.20	0.20	0.27	0.29
-240	0.12	0.10	0.10	0.11	0.12	0.14	0.17	0.20	0.19	0.19	0.27	0.29
-320	0.11	0.09	0.10	0.10	0.11	0.13	0.17	0.19	0.18	0.18	0.26	0.28
-320*	0.06	0.05	0.06	0.07	0.08	0.10	0.16	0.19	0.17	0.19	0.22	0.27
-400	0.11	0.09	0.09	0.10	0.11	0.13	0.16	0.19	0.18	0.18	0.25	0.28
-15200*	0.03	0.03	0.02	0.03	0.03	0.04	0.10	0.13	0.12	0.12	0.16	0.21
Overall mean	= 0.21											

Table 5. continued

Pressure head (cm)	Soil depth (cm)											
	0-7.6	7.6-15.2	15.2-22.8	22.8-30.4	30.4-38.0	38.0-45.6	45.6-53.2	53.2-60.8	60.8-68.4	68.4-76.0	76.0-83.6	83.6-89.0
	Site C											
0	0.38	0.35	0.30	0.26	0.30	0.30	0.26	0.26	0.35	0.30	0.35	0.41
-3.8	0.35	0.32	0.27	0.23	0.29	0.27	0.23	0.23	0.31	0.27	0.32	0.38
-10	0.35	0.32	0.27	0.23	0.29	0.27	0.23	0.23	0.31	0.27	0.31	0.37
-20	0.35	0.32	0.27	0.22	0.28	0.26	0.22	0.22	0.30	0.26	0.31	0.35
-30	0.34	0.30	0.26	0.21	0.27	0.23	0.19	0.21	0.29	0.25	0.30	0.35
-40	0.26	0.25	0.23	0.19	0.20	0.19	0.17	0.19	0.28	0.25	0.30	0.34
-50	0.19	0.17	0.18	0.17	0.17	0.16	0.15	0.18	0.27	0.25	0.29	0.34
-60	0.16	0.14	0.14	0.16	0.15	0.15	0.15	0.17	0.27	0.24	0.29	0.33
-100	0.12	0.10	0.11	0.13	0.12	0.12	0.11	0.16	0.25	0.23	0.28	0.32
-100*	0.14	0.12	0.14	0.15	0.14	0.13	0.15	0.20	0.31	0.38	0.40	0.52
-140	0.10	0.09	0.10	0.12	0.11	0.11	0.09	0.15	0.24	0.22	0.27	0.31
-180	0.09	0.08	0.10	0.12	0.10	0.10	0.08	0.14	0.23	0.22	0.27	0.31
-240	0.09	0.07	0.09	0.11	0.10	0.09	0.08	0.13	0.23	0.21	0.26	0.30
-320	0.08	0.07	0.08	0.11	0.09	0.09	0.07	0.12	0.22	0.21	0.25	0.29
-320*	0.07	0.07	0.07	0.09	0.07	0.08	0.08	0.11	0.16	0.20	0.24	0.31
-400	0.08	0.07	0.08	0.10	0.09	0.08	0.07	0.12	0.21	0.20	0.25	0.29
-15200*	0.02	0.02	0.02	0.03	0.04	0.05	0.06	0.07	0.12	0.15	0.19	0.26
Overall mean	= 0.20											

Table 5. continued

Pressure head (cm)	Soil depth (cm)											
	0-7.6	7.6-15.2	15.2-22.8	22.8-30.4	30.4-38.0	38.0-45.6	45.6-53.2	53.2-60.8	60.8-68.4	68.4-76.0	76.0-83.6	83.6-89.0
	Site D											
0	0.38	0.37	0.35	0.28	0.31	0.31	0.26	0.27	0.30	0.31	0.32	0.37
-3.8	0.35	0.35	0.33	0.26	0.29	0.29	0.23	0.24	0.26	0.28	0.27	0.34
-10	0.35	0.33	0.33	0.26	0.29	0.29	0.22	0.23	0.25	0.28	0.27	0.33
-20	0.35	0.33	0.33	0.25	0.28	0.27	0.22	0.23	0.25	0.27	0.26	0.33
-30	0.35	0.32	0.31	0.24	0.27	0.24	0.19	0.20	0.23	0.26	0.25	0.32
-40	0.29	0.24	0.28	0.20	0.20	0.18	0.16	0.19	0.22	0.26	0.25	0.32
-50	0.21	0.17	0.21	0.16	0.16	0.16	0.14	0.17	0.21	0.25	0.24	0.31
-60	0.15	0.14	0.18	0.15	0.15	0.14	0.13	0.16	0.20	0.24	0.24	0.31
-100	0.12	0.10	0.14	0.12	0.12	0.11	0.09	0.14	0.18	0.23	0.23	0.29
-100*	0.15	0.12	0.12	0.14	0.13	0.14	0.13	0.15	0.23	0.34	0.35	0.37
-140	0.10	0.09	0.13	0.11	0.10	0.10	0.09	0.13	0.17	0.22	0.21	0.29
-180	0.09	0.08	0.13	0.11	0.10	0.09	0.07	0.12	0.16	0.21	0.21	0.28
-240	0.08	0.08	0.12	0.10	0.09	0.09	0.07	0.11	0.15	0.20	0.20	0.27
-320	0.08	0.07	0.12	0.09	0.09	0.08	0.06	0.11	0.15	0.19	0.19	0.27
-320*	0.07	0.06	0.06	0.07	0.07	0.07	0.09	0.10	0.17	0.20	0.23	0.27
-400	0.08	0.07	0.12	0.09	0.08	0.08	0.06	0.10	0.14	0.19	0.18	0.26
-15200*	0.04	0.03	0.03	0.04	0.04	0.04	0.03	0.04	0.09	0.12	0.15	0.18
Overall mean	= 0.19											

Table 5. continued

Pressure head (cm)	Soil depth (cm)											
	0-7.6	7.6-15.2	15.2-22.8	22.8-30.4	30.4-38.0	38.0-45.6	45.6-53.2	53.2-60.8	60.8-68.4	68.4-76.0	76.0-83.6	83.6-89.0
	(8)											
	Site E											
0	0.36	0.35	0.34	0.28	0.31	0.31	0.29	0.27	0.30	0.33	0.34	0.39
-3.8	0.32	0.31	0.30	0.26	0.29	0.29	0.25	0.24	0.27	0.31	0.32	0.36
-10	0.32	0.31	0.30	0.26	0.29	0.29	0.25	0.24	0.26	0.30	0.32	0.36
-20	0.32	0.31	0.30	0.26	0.28	0.29	0.24	0.23	0.26	0.29	0.32	0.36
-30	0.32	0.29	0.29	0.24	0.27	0.25	0.22	0.22	0.25	0.28	0.32	0.35
-40	0.26	0.25	0.23	0.20	0.21	0.19	0.20	0.21	0.25	0.28	0.32	0.35
-50	0.19	0.18	0.18	0.16	0.17	0.17	0.17	0.19	0.24	0.27	0.31	0.35
-60	0.16	0.14	0.15	0.14	0.16	0.15	0.16	0.18	0.24	0.27	0.31	0.35
-100	0.12	0.10	0.11	0.12	0.12	0.12	0.12	0.17	0.22	0.25	0.30	0.34
-100*	0.14	0.12	0.11	0.14	0.14	0.11	0.14	0.26	0.26	0.32	0.38	0.38
-140	0.11	0.09	0.10	0.11	0.11	0.10	0.11	0.15	0.22	0.24	0.29	0.33
-180	0.10	0.08	0.10	0.10	0.10	0.09	0.10	0.14	0.21	0.23	0.29	0.33
-240	0.09	0.07	0.09	0.10	0.10	0.09	0.09	0.13	0.20	0.23	0.28	0.33
-320	0.09	0.07	0.09	0.09	0.09	0.09	0.09	0.12	0.20	0.23	0.27	0.32
-320*	0.08	0.07	0.07	0.08	0.08	0.06	0.07	0.09	0.15	0.18	0.20	0.26
-400	0.08	0.07	0.08	0.09	0.09	0.08	0.08	0.12	0.19	0.22	0.27	0.32
-15200*	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.06	0.14	0.16	0.22
Overall mean - 0.20												
	Site F- Lower-most slope position											
0	0.37	0.34	0.36	0.34	0.32	0.35	0.28	0.26	0.26	0.33	0.37	0.39
-3.8	0.34	0.32	0.33	0.30	0.30	0.34	0.25	0.22	0.22	0.29	0.33	0.37
-10	0.34	0.32	0.33	0.30	0.30	0.34	0.25	0.22	0.22	0.29	0.32	0.36
-20	0.34	0.32	0.33	0.30	0.30	0.34	0.25	0.21	0.21	0.29	0.31	0.36
-30	0.33	0.31	0.31	0.28	0.27	0.30	0.21	0.19	0.21	0.28	0.30	0.36
-40	0.28	0.24	0.28	0.22	0.20	0.21	0.18	0.18	0.20	0.28	0.29	0.36
-50	0.20	0.18	0.21	0.16	0.16	0.19	0.16	0.17	0.20	0.27	0.28	0.36
-60	0.17	0.15	0.17	0.14	0.15	0.17	0.14	0.16	0.19	0.27	0.28	0.35
-100	0.14	0.12	0.14	0.11	0.12	0.14	0.10	0.14	0.18	0.19	0.26	0.35
-100*	0.12	0.12	0.13	0.12	0.12	0.10	0.10	0.17	0.30	0.45	0.54	0.63
-140	0.12	0.10	0.13	0.10	0.11	0.13	0.08	0.13	0.17	0.25	0.25	0.34
-180	0.12	0.10	0.12	0.09	0.10	0.13	0.08	0.12	0.17	0.25	0.25	0.34
-240	0.10	0.09	0.12	0.09	0.09	0.12	0.07	0.11	0.16	0.23	0.23	0.33
-320	0.10	0.09	0.11	0.08	0.09	0.11	0.07	0.10	0.16	0.23	0.23	0.33
-320*	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.09	0.15	0.18	0.19	0.26
-400	0.10	0.08	0.10	0.08	0.08	0.11	0.06	0.10	0.16	0.23	0.22	0.32
-15200*	0.03	0.02	0.03	0.02	0.03	0.02	0.02	0.04	0.11	0.13	0.26	0.31
Overall mean - 0.21												

\*Pressure plate apparatus values.

Table 6. Monthly water inputs to field lysimeters for 1988 to 1991.

Month	Study				10-yr average <sup>a</sup>
	1988	1989	1990	1991	
	----- (cm) -----				
January	12.42	10.42	10.37	11.02	11.00
February	16.19	8.71	1.08	0.86	10.46
March	15.88	17.40	10.17	11.35	9.80
April	17.91	9.65	3.77	4.47	8.86
May	14.17	14.62	7.87	11.09	10.11
June	19.91	8.38	10.55	15.79	9.07
July	15.49	18.48	17.00	26.67	11.53
August	18.39	11.11	22.12	14.40	10.69
September	10.42	15.47	11.89	4.16	8.43
October	9.96	15.37	15.33	2.92	5.94
November	10.77	9.34	4.40	2.46	8.56
December	9.35	11.47	9.09	8.41	7.82
Total	170.86	150.42	123.64	113.62	112.27

<sup>a</sup>10-yr period, 1978-1987; Central Crops Research Station, Clayton, NC (NOAA Station No. 31-1820-07).

Table 7. Cumulative water input to field lysimeters for 1988 to 1991.

DAT <sup>a</sup>	Study			
	1988	1989	1990	1991
	----- (cm) -----			
30	15.49	16.80	8.64	17.90
60	33.88	29.59	27.55	30.60
90	43.72	43.99	47.44	57.50
120	52.28	58.30	58.82	
180	74.38	81.24	81.29	
360	170.86	150.42	123.64	

<sup>a</sup>DAT = days after treatment

Table 8. Average monthly maximum and minimum air temperature for 1988 to 1991.

Month	Study									
	1988		1989		1990		1991		10 yr average <sup>a</sup>	
	max	Min	Max	Min	Max	Min	Max	Min	Max	Min
	----- (°C) -----									
January	13	2	17	4	11	2	11	2	8	-3
February	12	1	17	5	16	4	16	3	11	-1
March	16	5	21	8	20	7	20	7	17	4
April	21	9	25	10	24	12	23	12	22	9
May	25	12	27	15	30	17	30	17	27	14
June	31	20	32	20	32	20	30	18	30	18
July	34	22	31	21	32	22	31	22	32	21
August	34	24	31	22	30	21	29	21	31	20
September	28	19	30	19	28	16	27	16	28	16
October	21	9	24	12	26	12	22	11	22	10
November	18	5	19	8	21	7	16	7	17	6
December	12	-1	8	-2	16	5	13	2	12	1

<sup>a</sup>10-yr period, 1978-1987; Central Crops Research Station, Clayton, NC (NOAA Station No. 31-1820-07).

Table 9. Monthly pan evaporation of water for 1988 to 1990.

Month	Study			10-yr
	1988	1989	1990	average <sup>a</sup>
	----- (cm) -----			
January	5.00	3.94	3.37	ND
February	5.00	5.28	4.47	ND
March	3.81	8.84	7.24	ND
April	10.18	12.50	9.22	13.75
May	9.14	11.20	10.95	16.88
June	13.59	15.82	15.82	18.62
July	15.32	13.16	16.61	19.06
August	17.50	8.23	10.03	17.13
September	10.21	8.28	11.12	13.22
October	6.98	6.63	9.70	9.41
November	3.96	5.18	5.56	6.64
December	4.06	1.37 <sup>b</sup>	6.73	ND
Total	104.75	100.43	111.18	114.71

<sup>a</sup>10-yr period, 1978-1987; Recorded 60 km NW of lysimeter site (NOAA Station No. 31-1677-03).

<sup>b</sup>Month partially frozen. ND = not determined.

Table 10. Mass balance of water input in fallow field lysimeters with leachate collectors at 30 to 120 DAT in 1989 and 120 DAT only in 1990 (Keller 1992).

DAT <sup>a</sup>	Water input	Retained by soil <sup>b</sup>		Percolation		Evaporation	
	(cm)	(cm)	(%)	(cm)	(%)	(cm)	(%)
30	16.80	0.08	0.47	8.31	49.46	8.41	50.07
60	29.59	0.22	0.76	13.38	45.20	15.99	54.04
90	43.99	1.28	2.92	24.35	55.36	18.36	41.73
120	58.30	0.25	0.43	35.01	60.06	23.03	39.50
120 <sup>c</sup>	58.82	0.21	0.36	30.17	51.29	28.44	48.35

<sup>a</sup>DAT = days after treatment.

<sup>b</sup>Water retained in lysimeter minus 0 d water content; water content at 0 d was 16.72 cm.

<sup>c</sup>1990 only.

Monthly pan evaporation for three seasons plus the 10 yr average are shown in Table 9. Apart from March and August 1988, pan evaporation values were relatively similar for the studies and were in general agreement with the 10 yr average. Recorded pan evaporation generally followed evapotranspiration losses for the region (Van Bavel and Verlinden 1956, Van Bavel 1961), however, pan evaporation was not adequate in estimating evaporation from fallow lysimeters (Figure 3). Cumulative evaporation was greater in soybean than fallow lysimeters. This difference was due to the transpiring soybean and agrees with other investigators using corn and fallow lysimeters (Musgrave 1935, Kilmer et al. 1944).

Mean monthly soil temperatures were similar for most months but considerable seasonal and monthly variations in soil temperature did occur (Figure 4). In April 1989, greater temperature fluctuations were observed between depths while no differences were noted in 1988 and 1990. In August, soil temperatures in 1988 were well above those registered in 1989 and 1990. Soil temperatures at 8 and 15-cm were generally warmer than the air above while temperatures at lower depths were commonly below the monthly air temperature. Soil temperature patterns over time were similar to those reported by Fluker (1958), however, temperature differences between depths were less than those reported by Fluker (1958) and Hillel (1982). Small temperature fluctuations between depths may be due to the bare soil surface and well-drained conditions of the Dothan soil which favor rapid warming and cooling.

Movement and dissipation of three <sup>14</sup>C-labeled herbicides. There was no significant year effect for any of the three herbicide treatments; therefore, the 1989 and 1990 studies were combined for atrazine, metolachlor and primisulfuron.

Recovery of <sup>14</sup>C from fallow lysimeters treated with <sup>14</sup>C-atrazine decreased with time in a curvilinear fashion (Figure 5). Total recovery of <sup>14</sup>C was 43% at 30 d, 41% at 90 d, 38% at 180 d, and 36% at 360 d which were nonsignificantly different (Table 11). Nonsignificant differences of the totals after 30 d indicated no further loss of atrazine or metabolites through volatilization, <sup>14</sup>CO<sub>2</sub> losses or leaching.

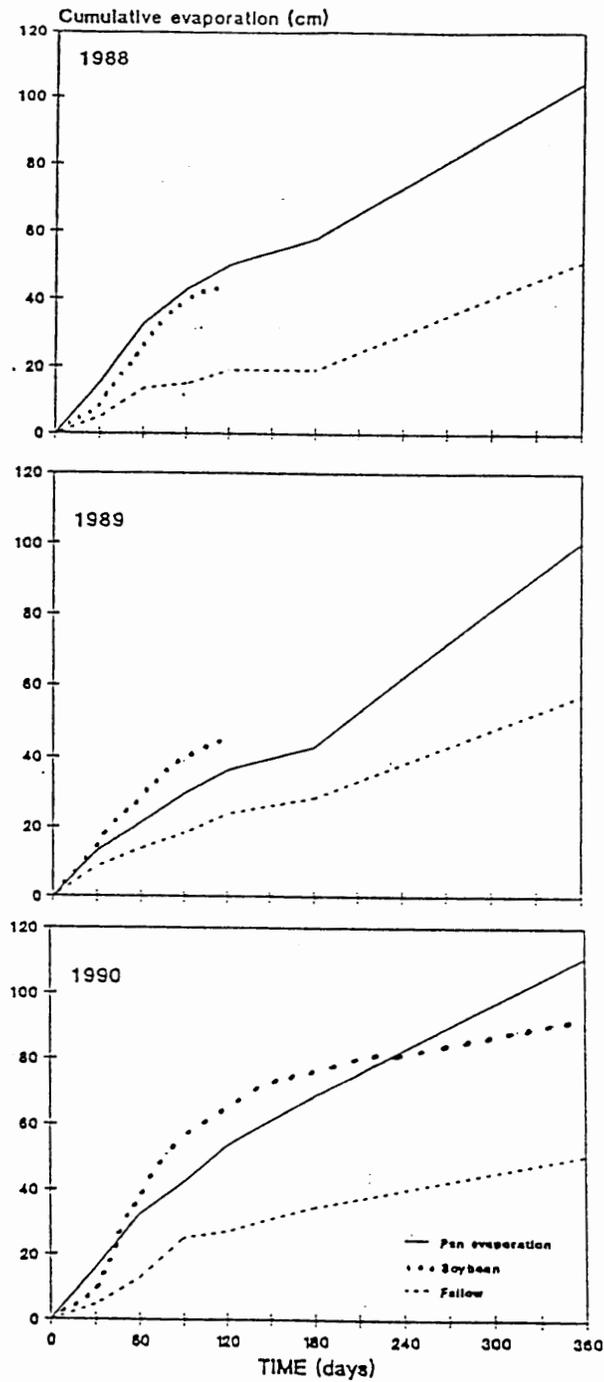


Figure 3. Cumulative evaporation from evaporation pan and fallow and soybean lysimeters in 1988 to 1990. (Keller 1992).

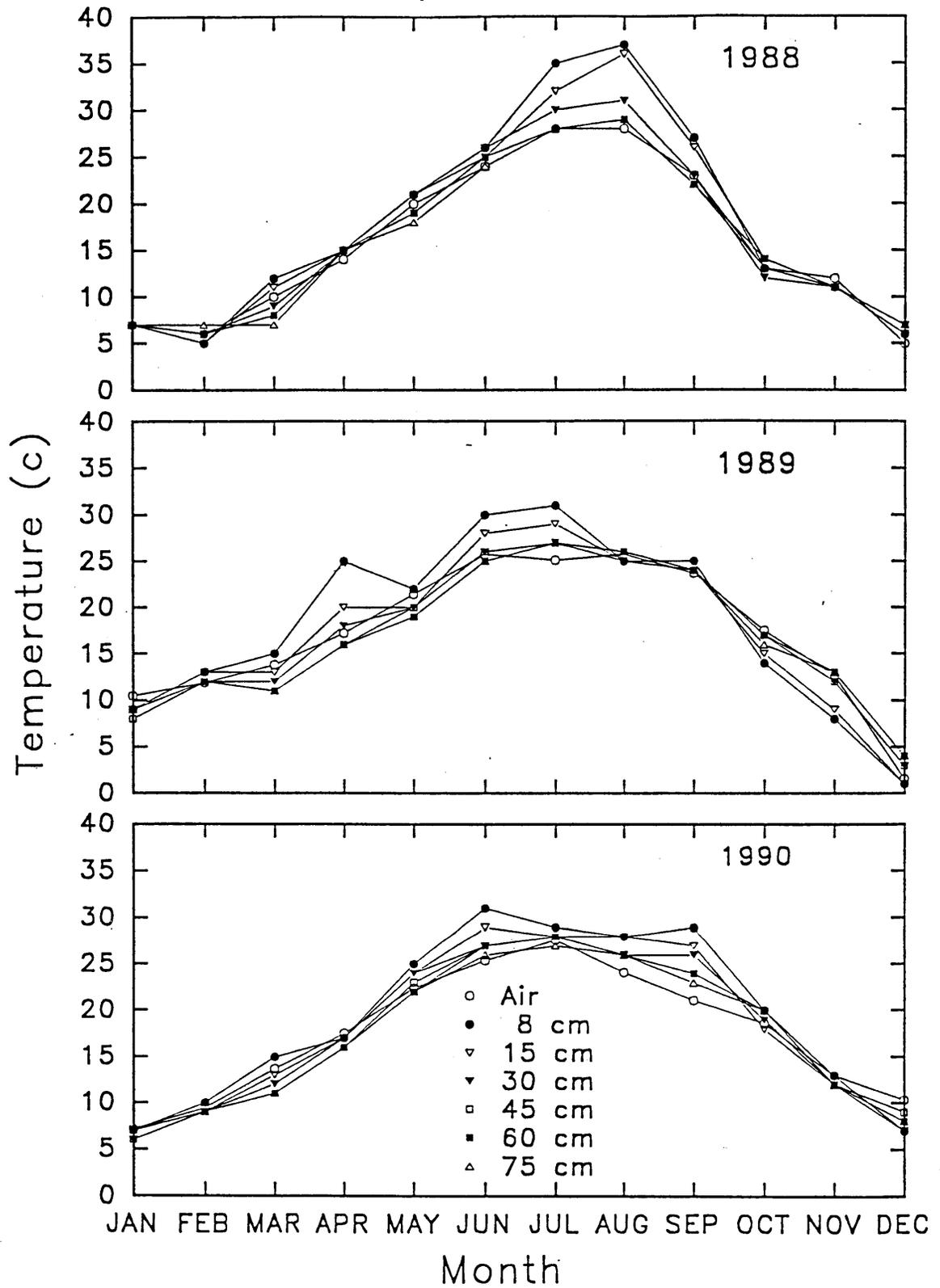


Figure 4. Average monthly air and soil temperatures for 1988 to 1990 (Keller 1992).

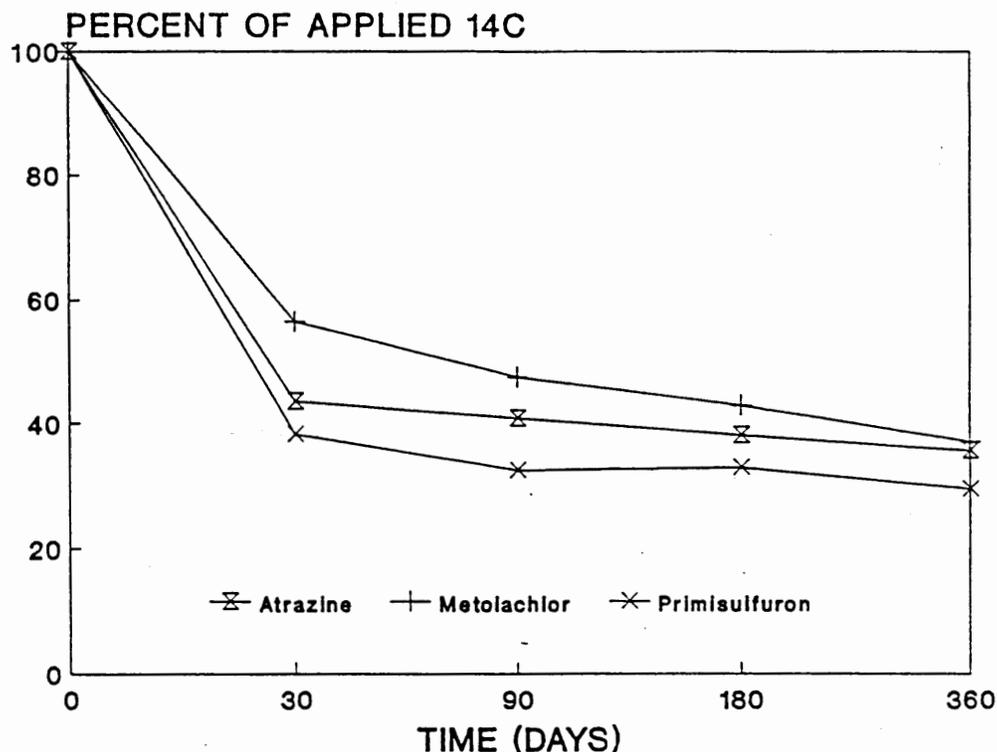


Figure 5. Total <sup>14</sup>C recovery with time in <sup>14</sup>C-labeled atrazine, metolachlor, and primisulfuron treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

Table 11. <sup>14</sup>C recovery and distribution in <sup>14</sup>C-atrazine treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

Depth (cm)	Days after treatment				
	0	30	90	180	360
	-----(% of applied <sup>14</sup> C)-----				
0.0 - 7.6	100.00**	30.49*	23.30**	20.36*	19.69*
7.6 - 15.2	0.00	9.98	9.43*	9.24*	8.28*
15.2 - 22.8	0.00*	2.33	4.20*	3.74	3.71*
22.8 - 30.4	0.00	0.43*	1.49*	2.20**	0.99*
30.4 - 38.0	0.00	0.11	0.53	0.63	0.41
38.0 - 45.6	0.00	0.10	0.35	0.45	0.42
45.6 - 53.2	0.00	0.02	0.27	0.30	0.28*
53.2 - 60.8	0.00	0.00	0.35	0.32	0.47
60.8 - 68.4	0.00	0.00	0.33	0.36	0.40
68.4 - 76.0	0.00	0.00	0.19	0.25	0.42
76.0 - 83.6	0.00	0.00	0.21	0.22	0.32*
83.6 - 89.0	0.00	0.00	0.08	0.12	0.19
Total	100.00*	43.46	40.73	38.01	35.58

\*Numbers followed by \* are significantly different from the number immediately below, while numbers followed by \*\* are significantly different from the number immediately to the right, as determined at the 0.05 level of probability.

Since 43% of the applied  $^{14}\text{C}$  was recovered in the soil profile at 30 d and no radioactivity was present below 30-cm, 57% of the applied  $^{14}\text{C}$  was lost through volatilization of the herbicide, metabolites or  $^{14}\text{CO}_2$ . Kearney et al. (1964) found that 30 and 60% of atrazine applied to a Tifton loamy sand under laboratory conditions volatilized in 72 h at 35° and 45° C, respectively. On the other hand, Glotfelty et al. (1989) found that 2.4% of atrazine applied to the field was lost within 21 d, while Hubbs and Lavy (1990) found that 7 and 10% of the atrazine applied to soil-coated glass slides was lost in 98 h under dark and ultraviolet conditions, respectively.

Atrazine volatilization or losses to the atmosphere while adsorbed to dust particles under field conditions can be substantiated. Atrazine has been detected in rainwater in Maryland (Wu 1981) and Indiana, Ohio, New York and West Virginia (Richards et al. 1987). Atrazine concentrations in rain reached their maxima in rainfall events immediately following applications.

At 30 d, the evolution of  $^{14}\text{CO}_2$  from  $^{14}\text{C}$  ring-labeled atrazine generally contributes to a small percentage (<3%) of the applied  $^{14}\text{C}$  lost from the soil (Best and Weber 1974, Winkelmann and Klaine 1991a, Miller 1992). After 180 d, however, 28% (Winkelmann and Klaine 1991a) and 36% (Miller 1992) of  $^{14}\text{C}$  ring-labeled atrazine applied to soil under laboratory conditions was lost as  $^{14}\text{CO}_2$ . In addition, Winkelmann and Klaine (1991b) applied four major  $^{14}\text{C}$ -ring-labeled atrazine metabolites to soil microcosms and found after 180 d that 25% of deethylatrazine, 16% of deisopropylatrazine, 59% of dealkylatrazine, and 21% of hydroxyatrazine was lost as  $^{14}\text{CO}_2$ .

$^{14}\text{C}$  distributions of atrazine and/or metabolites remaining in the lysimeters for the various sampling periods are shown in Table 11 and Figure 6.  $^{14}\text{C}$  distribution closely resembled that of soil organic carbon in the profile (Tables 2 and 3). Numerous researchers (Talbert and Fletchall 1964, McGlamery and Slife 1965, Blumhorst 1989) noted that atrazine adsorption was highly correlated with organic and humic matter contents of soils. In addition, they found that atrazine adsorption increased with decreasing pH. Weber et al. (1969) reported that maximum adsorption of *s*-triazines by organic matter occurred at pH levels in the locale of the  $\text{pK}_a$  values of the particular compounds. This scenario would favor the bonding of protonated *s*-triazine molecules to the negatively charged sites on soil organic matter.

Weed and Weber (1974) suggest that *s*-triazines may be physically and/or chemically adsorbed to soil organic matter depending on soil pH. Physical adsorption of atrazine in the Dothan soil surface was probably more prevalent than chemical adsorption, because at pH 6.1 most of the herbicide was in the nonionized form. Blumhorst (1989) found that atrazine was equally desorbed from a Norfolk sandy loam (5.7 pH, 6, 1.0 and 0.1% clay, organic carbon and humic matter, respectively) with either deionized water or 0.1 calcium chloride thus confirming physical adsorption.

Adsorption of atrazine metabolites must be also considered in the  $^{14}\text{C}$  distribution. Brouwer et al. (1990) and Clay and Koskinen (1990) reported that hydroxyatrazine was adsorbed in greater amounts than parent atrazine by soils of varying soil pH. Hydroxyatrazine ( $\text{pK}_a$  5.2; Weber 1967a,b, Vermeulen et al. 1982) is a stronger base than atrazine. Consequently, it becomes protonated at a higher pH resulting in a greater number of hydroxyatrazine cations. Weber et al. (1969) showed analogous behavior of hydroxypropazine versus propazine. Propazine and hydroxypropazine have  $\text{pK}_a$  values of 1.85 and

5.20, respectively, (Weber 1967b). Furthermore, protonation of hydroxyatrazine and small amounts of atrazine may occur even though the measured soil pH is greater than the compound's  $pK_a$ . The pH of colloidal surfaces has been reported to be several pH units less than that indicated by the pH of the surrounding aqueous matrix (Benesi 1956, Harter and Alrichs 1967, White and Cruz 1971). Brouwer et al. (1990) also reported that the adsorption of hydroxyatrazine > atrazine > deisopropylatrazine > deethylatrazine was consistent over a range of soil pH (5.0 to 7.3) and organic carbon levels (1 to 14%).

Thirty days after atrazine application, 98% of the  $^{14}C$  was present in the top 23-cm (Table 11; Figure 6). As previously discussed, this was the zone of highest organic matter content. Less than 0.5% of the applied  $^{14}C$  was detected below 23-cm, while no  $^{14}C$  was detected below 53-cm. At 90 d, 91% of the  $^{14}C$  remained in the top 23-cm. Seven percent of the radioactivity detected for this time period was distributed below 23-cm with less than 0.1% of the applied  $^{14}C$  observed at 84- to 90-cm.

At 180 and 360 d, 88 and 89% of the  $^{14}C$ , respectively, was present in the top 23-cm (Table 11; Figure 6). Also, below 30-cm there were no significant differences in  $^{14}C$  within depths between 90 and 360 d. Reduction in movement of  $^{14}C$  after 90 d indicates that the  $^{14}C$  was tightly adsorbed.

Extraction of the 0- to 7.6-cm layer (discussed later) at 30 d showed that atrazine, hydroxyatrazine, and deethylatrazine constituted 49, 15 and 16% of the extractable radioactivity, respectively. Since hydroxyatrazine is more tightly adsorbed than atrazine, the radioactivity present in the lower depths would likely be atrazine or deethylatrazine. In addition, hydroxyatrazine has been found to be less mobile than atrazine, especially in acidic soils (Helling 1971b). Deethylatrazine has a water solubility 13 times greater than atrazine (Beilstein et al. 1981) and, therefore, is probably more mobile than atrazine.

The immobility of  $^{14}C$  in the acidic sandy clay loam subsoil may be due to ionic adsorption of the protonated atrazine molecule. Atrazine in the acidic subsoil may be transformed via chemical hydrolysis to hydroxyatrazine (Armstrong et al. 1967, Skipper et al. 1967). On the other hand, Miller (1992) using the same Dothan subsoil under laboratory conditions, reported no chemical or microbial degradation of atrazine. Miller attributed the lack of atrazine degradation to insufficient organic matter and not soil pH. Armstrong et al. (1967) found that atrazine hydrolysis was largely controlled by soil pH and organic matter. Miller (1992) using Dothan soil under laboratory conditions, did report chemical and microbial degradation of atrazine in the 0- to 25-cm depth.

Recovery of  $^{14}C$  from lysimeters treated with  $^{14}C$ -metolachlor decreased with time in a curvilinear fashion similar to that of atrazine (Figure 5). Total recoveries of  $^{14}C$  were 56% at 30 d, 47% at 90 d, 43% at 180 d, and 37% at 360 d which were not significantly different (Table 12). Nonsignificant differences of the totals indicate no further loss of metolachlor and/or metabolites through volatilization,  $^{14}CO_2$  losses, or leaching.

At 30 d, 44% of the applied  $^{14}C$  was lost through volatilization of the herbicide and/or metabolites or possibly  $^{14}CO_2$  losses. Greenhouse lysimeter studies showed metolachlor volatilization from soil to be less than 0.01%

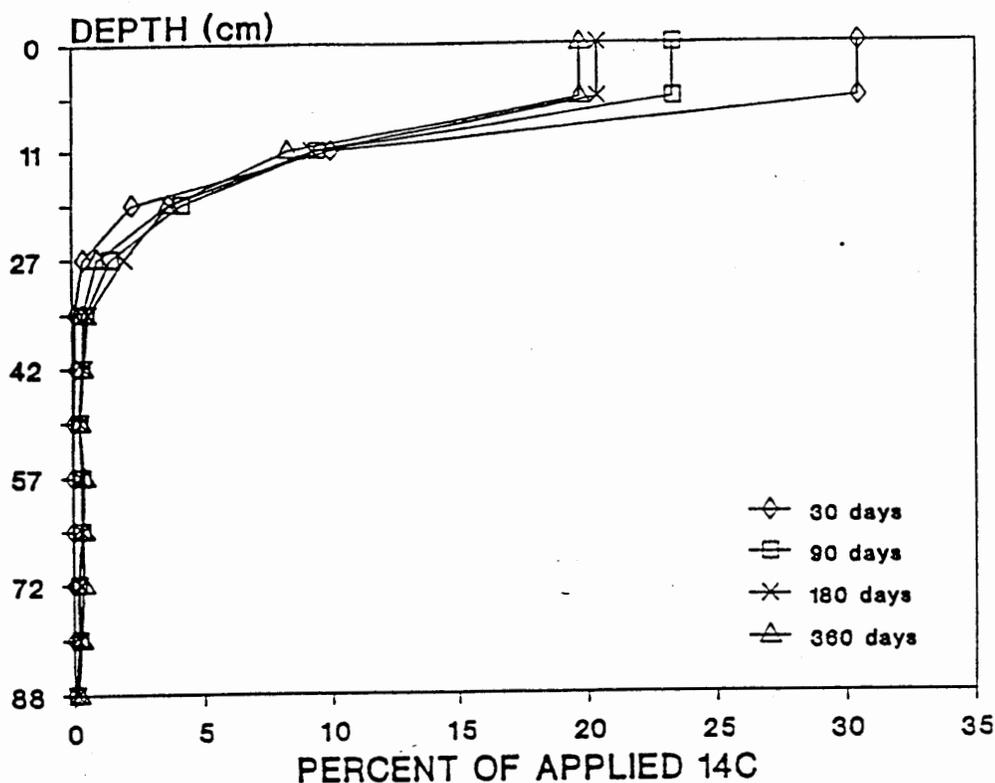


Figure 6. <sup>14</sup>C-distribution with time and depth <sup>14</sup>C-atrazine treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

after 11 wk (Alhajjar et al. 1990) while Parochetti (1978) observed that 0.1% of the applied metolachlor was lost from the soil surface after 8 d in greenhouse pot studies. Parochetti also noted that 17 and 53% of the applied metolachlor was lost from straw and glass, respectively. Streck and Weber (1982) reported that under greenhouse conditions, 38 and 19% of applied metolachlor was lost in 7 d from glass and straw, respectively. The researchers attributed the loss to volatilization.

Alachlor, a related chloracetamide herbicide, which has a similar vapor pressure to that of metolachlor (WSSA 1989), volatilized from a fallow soil in eastern Maryland (Glotfelty et al. 1989). The researchers reported that 19% of the alachlor was lost within 24 d after application. In addition, Beestman and Deming (1974) found under laboratory conditions that 50% of the applied alachlor was volatilized from a wet soil (10% clay, 1% organic carbon) within 12 d after application. Similarly, Hargrove and Merkle (1971) reported that 10 to 30% of alachlor applied to air-dry soil in closed systems at 38°C and relative humidities of 79 to 100%, volatilized within 48 h.

Metolachlor and alachlor have been detected in rainwater in Indiana, Ohio, New York and West Virginia (Richards et al. 1987). Furthermore, metolachlor and alachlor concentrations in rainfall reached their maxima in events immediately following applications.

The amount of <sup>14</sup>CO<sub>2</sub> produced from soil treated with <sup>14</sup>C-metolachlor is generally very low. Bailey and Coffey (1986) and LeBaron et al. (1988) found that

during a 12 wk period in soil under laboratory conditions, 4.8% of the  $^{14}\text{C}$ -metolachlor was released as  $^{14}\text{CO}_2$ . Similarly, Miller (1992) using Dothan soil under laboratory conditions, found that only 0.3 and 1.6% of the  $^{14}\text{C}$ -metolachlor was liberated as  $^{14}\text{CO}_2$  after 4 and 22 wk, respectively. On the other hand, after 28 d within a soil perfusion system, the evolved  $^{14}\text{CO}_2$  from a soil previously treated with metolachlor for 5 yr, accounted for 18.4% of the added  $^{14}\text{C}$ -metolachlor (Liu et al. 1988). The same researchers also found that the amount of  $^{14}\text{CO}_2$  produced from soil taken from the same field that had no history of metolachlor use, accounted for only 3.5% of the applied  $^{14}\text{C}$ -metolachlor.

Distributions of  $^{14}\text{C}$  from metolachlor and/or metabolites remaining in the lysimeters for the various sampling dates are shown in Table 12 and Figure 7. Like the atrazine treatment,  $^{14}\text{C}$  distribution closely resembled that of organic carbon in the soil profile (Tables 2 and 3). Various researchers (Jordan and Harvey 1978, Obrigawitch et al. 1981, Weber and Peter 1982, Peter and Weber 1985) determined that organic matter was the most important soil property that influenced metolachlor adsorption. Clay minerals were also reported to bind acetanilide herbicides to a limited extent (Peter and Weber 1985). Physical bonding of metolachlor on soil has been proposed by Obrigawitch et al. (1981) and Peter and Weber (1985). Wendt (1987) found that as much as 53% of the adsorbed metolachlor on a Norfolk soil was desorbed with water. Metolachlor desorbed by water would be available for dissipating processes.

At 30 d, 86% of the  $^{14}\text{C}$ -metolachlor was present in the top 23-cm (Table 12; Figure 7). Less than 3% of the applied  $^{14}\text{C}$  was detected below 23-cm, while none was detected below 68-cm. At 90 d, 63% of the  $^{14}\text{C}$  resided in the top 23-cm. Between 30 and 90 d, significant amounts of  $^{14}\text{C}$  in the 0- to 7.6-cm layer was either lost as  $^{14}\text{CO}_2$ , volatilization of the herbicide and/or metabolites or leaching. At 90 d, 1% of the applied  $^{14}\text{C}$  was detected at 84- to 90-cm.

At 180 and 360 d, greater than 60% of the  $^{14}\text{C}$ -metolachlor was observed in the top 23-cm (Table 12; Figure 7). Distribution of  $^{14}\text{C}$  below 23-cm was similar at 90, 180, and 360 d. This occurrence suggests that there was no further movement of  $^{14}\text{C}$  and that the  $^{14}\text{C}$  was tightly adsorbed. At depths below 23-cm, low amounts of organic carbon and high amounts of clay were present for adsorptive processes (Table 2). Several investigators have reported that metolachlor adsorption has been correlated to clay content (Weber and Peter 1982, Peter and Weber 1985, Wood et al. 1987).  $^{14}\text{C}$  present at the lower depths was likely composed of metabolites of metolachlor. Extraction and analysis of  $^{14}\text{C}$  in the 0- to 7.6-cm layer (discussed later) showed that metolachlor constituted 90% of the extractable  $^{14}\text{C}$  at 30 d, 83% at 90 d, 77% for 180 d, and 70% at 360 d.

Like the atrazine and metolachlor treatments, total  $^{14}\text{C}$  in the primisulfuron columns declined with time in a curvilinear fashion and leveled off after 90 d (Figure 5). Total recovery of  $^{14}\text{C}$  was 38% at 30 d, 32% at 90 d, 33% at 180 d, and 29% at 360 d (Table 13). The 30 DAT samples were significantly different from the 90, 180, and 360 DAT treatments, while the 90, 180, and 360 DAT treatments were not significantly different. Similar totals at 90, 180, and 360 d indicate no further loss of  $^{14}\text{C}$  from the lysimeters.

As with atrazine and metolachlor, 62% of the applied  $^{14}\text{C}$ -primisulfuron disappeared within 30 d (Table 13). High surface soil temperatures and

Table 12. <sup>14</sup>C recovery and distribution in <sup>14</sup>C-metolachlor treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

Depth (cm)	Days after treatment				
	0	30	90	180	360
	-----(% of applied <sup>14</sup> C)-----				
0.0 - 7.6	100.00**	33.95**	18.37*	15.21*	14.61*
7.6 - 15.2	0.00*	9.67	8.06*	6.87*	5.95*
15.2 - 22.8	0.00*	5.29	3.68	3.76	2.73*
22.8 - 30.4	0.00*	2.78	2.79*	2.63	1.93
30.4 - 38.0	0.00	1.56	1.77	1.80	1.29
38.0 - 45.6	0.00	1.24*	1.49	1.37	1.12
45.6 - 53.2	0.00	0.81	1.67	1.91*	1.48
53.2 - 60.8	0.00	0.92	2.07	3.13	2.74
60.8 - 68.4	0.00	0.28*	2.34	2.36*	2.50*
68.4 - 76.0	0.00	0.00*	2.26	1.70	1.44
76.0 - 83.6	0.00	0.00*	1.86**	1.19**	0.75*
83.6 - 89.0	0.00	0.06*	1.02	0.81	0.52
Total	100.00*	56.56	47.38	42.74	37.06

\*Numbers followed by \* are significantly different from the number immediately below, while numbers followed by \*\* are significantly different from the number immediately to the right, as determined at the 0.05 level of probability.

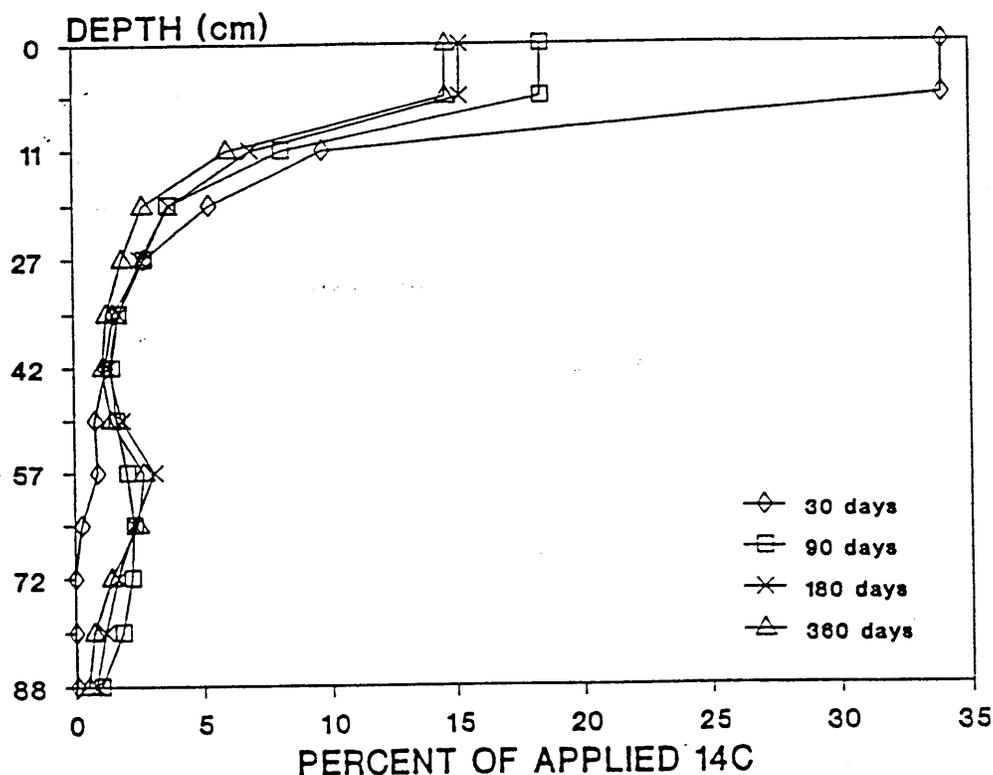


Figure 7. <sup>14</sup>C distribution with time and depth in <sup>14</sup>C-metolachlor treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

adequate moisture conditions, as established during frequent irrigation and rainfall, existed for the lysimeter study. These environmental factors produce conditions conducive for enhanced microbial and chemical reactions.

In this case, however, the herbicide was probably lost as  $^{14}\text{CO}_2$ . Phenyl- $^{14}\text{C}$ -labeled sulfonylurea herbicides, chlorimuron (Fuesler and Hanafey 1990) and sulfometuron methyl (Anderson and Dulka 1985), were applied to nonsterile soil under laboratory conditions and within 30 d, 20% of the radioactivity was converted to  $^{14}\text{CO}_2$ . Anderson and Dulka (1985) also reported that after 24 wk, 50% of the applied  $^{14}\text{C}$ -sulfometuron methyl was converted to  $^{14}\text{CO}_2$ . They concluded that in acid soils, a nonbiological hydrolysis process predominated. After hydrolysis, microorganisms then act on the  $^{14}\text{C}$ -phenyl hydrolysis products to convert them eventually to  $^{14}\text{CO}_2$ . These results are inconsistent with Miller (1992) who found that, over a 30 d period, less than 2% of the  $^{14}\text{C}$ -primisulfuron applied to a Dothan soil under laboratory conditions was converted to  $^{14}\text{CO}_2$ .

To add to the inconsistency in sulfonylurea dissipation, Anderson and Dulka (1985) applied  $^{14}\text{C}$ -sulfometuron methyl to undisturbed steel cylinders near Raleigh, NC, and presumed that the loss of  $^{14}\text{C}$  was due to  $^{14}\text{CO}_2$ . Total recovery of  $^{14}\text{C}$  was 87% at 30 d, 55% at 60 d, 35% at 120 d and 18% at 360 d. In still another study, Harvey et al. (1985) found that within 14 d, 50% of the  $^{14}\text{C}$ -sulfometuron methyl applied to river water with sediment was photolyzed to  $^{14}\text{CO}_2$  under aquatic photolysis conditions.

Between 30 and 90 d, an additional 6% of the applied  $^{14}\text{C}$ -primisulfuron was dissipated and was probably lost as  $^{14}\text{CO}_2$  (Table 13). Since primisulfuron has a vapor pressure 40 thousand times less than that of atrazine, losses due to volatilization were probably negligible. Furthermore, in reviewing the literature there are no reports of sulfonylurea volatilization.

Thirty days after application, 93% of the  $^{14}\text{C}$ -primisulfuron present in the top 23-cm (Table 13; Figure 8). This is in agreement with the  $^{14}\text{C}$ -sulfometuron methyl field dissipation study performed by Anderson and Dulka (1985). The large retention of  $^{14}\text{C}$  in this zone is probably directly related to the higher organic carbon content and acidic soil conditions present in this zone (Tables 2 and 3). Sulfonylurea adsorption increases with increasing organic matter content (Harvey et al. 1985, Mersie and Foy 1986) and acidic soil conditions (Harvey et al. 1985, Mersie and Foy 1986, Shea 1986). In acid soils, the undissociated sulfonylurea molecules are more lipophilic, thus sorption to organic matter increases. Neutral sulfonylurea molecules are lower in water solubility than the anionic forms.

At 90, 180, and 360 d, 78 to 81% of the  $^{14}\text{C}$ -primisulfuron which was present, remained in the top 23-cm while <1% of the applied  $^{14}\text{C}$  was noted at each depth below 30-cm (Table 13). Anderson and Dulka (1985) found similar results for a  $^{14}\text{C}$ -sulfometuron methyl field dissipation study. Radioactivity below 30-cm is likely in the form of the 3 metabolites commonly associated with sulfonylurea herbicides, saccharin, methyl-2-aminosulfonylbenzoate and 2-aminosulfonylbenzoic acid (Harvey et al. 1985, Anderson and Dulka 1985, USEPA 1992). Saccharin is more polar than the parent sulfonylurea compound (Harvey et al. 1985, Anderson and Dulka 1985) and would be more soluble and mobile in water. Small fractions of the radioactivity may be primisulfuron in the anionic form. Ionization of primisulfuron results in increased water solubility and mobility. However, the anionic form of primisulfuron and other sulfonylurea

Table 13. <sup>14</sup>C recovery and distribution in <sup>14</sup>C-primisulfuron treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

Depth (cm)	Days after treatment				
	0	30	90	180	360
	-----(% of applied <sup>14</sup> C)-----				
0.0 - 7.6	100.00**	23.90	10.95	12.03	11.50
7.6 - 15.2	0.00*	8.56*	10.88	9.22	8.06*
15.2 - 22.8	0.00	3.16	3.55	5.31	3.93*
22.8 - 30.4	0.00*	0.87*	2.33*	2.42	1.91
30.4 - 38.0	0.00	0.64	0.75	0.69	0.96
38.0 - 45.6	0.00	0.37*	0.75	0.79	0.64
45.6 - 53.2	0.00*	0.22	0.48	0.72*	0.49
53.2 - 60.8	0.00	0.07*	0.71*	0.53	0.39
60.8 - 68.4	0.00	0.24	0.55	0.50	0.47
68.4 - 76.0	0.00	0.12	0.57*	0.37	0.34
76.0 - 83.6	0.00	0.07	0.58*	0.17	0.33
83.6 - 89.0	0.00	0.06*	0.37	0.15	0.41
Total	100.00*	38.28*	32.47	32.90	29.43

\*Numbers followed by \* are significantly different from the number immediately below, while numbers followed by † are significantly different from the number immediately to the right, as determined at the 0.05 level of probability.

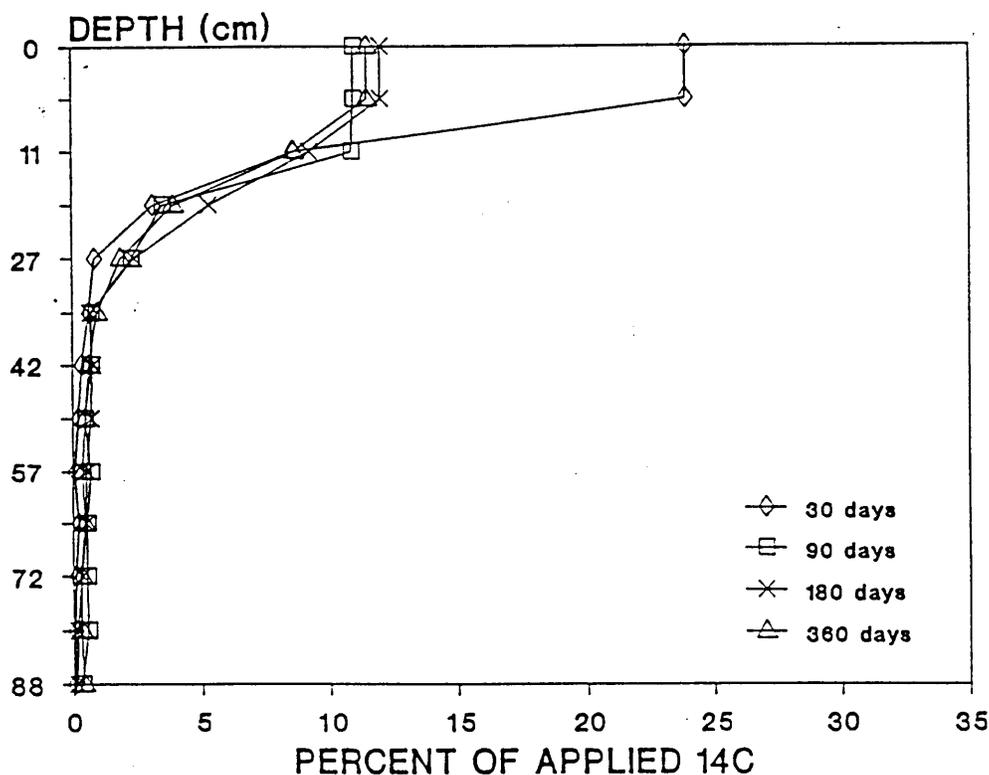


Figure 8. <sup>14</sup>C distribution with time and depth in <sup>14</sup>C-primisulfuron treated fallow field lysimeters (mean of 1989 and 1990) (Keller 1992).

herbicides may also be retained by the aluminum and iron hydrous oxides commonly associated with soils in the southeastern United States (Shea 1986, Goetz et al. 1989).

At 30 d, the total  $^{14}\text{C}$  recovered in lysimeters in decreasing order, was: metolachlor > atrazine primisulfuron (Figure 5). This trend was maintained throughout the remaining sampling dates. Differences in total  $^{14}\text{C}$  are due to herbicide and/or metabolite volatilization and/or  $^{14}\text{CO}_2$  losses.

Regardless of sampling time, the relative mobility of  $^{14}\text{C}$ -labeled herbicides and metabolites through the Dothan soil, in decreasing order, was: metolachlor > atrazine = primisulfuron (Figures 7, 6 and 8, respectively). Without knowing the structures of the  $^{14}\text{C}$ -labeled products in the subsoil, one can only speculate the reason on varying mobilities. Metolachlor and its metabolites are more water soluble and less sorbed than the other two herbicides and their by-products, which would result in increased  $^{14}\text{C}$  mobility of the former. Atrazine was less mobile due to its weakly basic character and tendency to be ionically bound to acidic soil colloids. Primisulfuron was lowest in mobility probably because of its low water solubility under acidic conditions and the high retention of its metabolites by organic matter.

Mass-balance dissipation of three  $^{14}\text{C}$ -labeled herbicides. Dissipation of pesticides in the environment is governed by transfer and transformation processes (Weber 1991a). Mass-balance distribution of  $^{14}\text{C}$ -labeled atrazine, metolachlor, and primisulfuron in the 1990 fallow lysimeter study is shown in Tables 14, 15, and 16, respectively. Metabolites identified in the degradation of the compounds are listed in Table 17.

Atrazine dissipation in the 1990 lysimeter study is presented in Table 14. As previously discussed, over 50% of the applied  $^{14}\text{C}$ -labeled atrazine was lost through volatilization of the herbicide or its metabolites or as  $^{14}\text{CO}_2$ . This conclusion was verified by the fact that  $^{14}\text{C}$  was absent below 53-cm at 30 d (Table 11). At 360 d, an additional 8% of the applied  $^{14}\text{C}$  was recorded as products lost to the atmosphere. This increase may be in part due to  $^{14}\text{C}$  that leached below 89-cm. Consistent amounts of  $^{14}\text{C}$  (bound + extracted) in the 0- to 7.6-cm zone and decreasing  $^{14}\text{C}$  in the subsurface suggests that  $^{14}\text{C}$  was leached below 89-cm.

$^{14}\text{C}$ -atrazine remaining in the 0- to 7.6-cm layer could not be completely extracted with methanol (Table 14). On the day of application, 14% of the applied  $^{14}\text{C}$ -labeled atrazine was bound. This was probably due to the closure of adsorptive sites (primarily the organic fraction) upon air-drying the soil prior to extraction. For the other sampling dates, there was no influence of air-drying on  $^{14}\text{C}$  extraction, and the lack of extractability was probably due to the inaccessibility of the herbicide and/or metabolites trapped in micropores within the soil colloids.

With time, the level of unextracted (bound)  $^{14}\text{C}$ -atrazine increased (Table 14). At 90, 180, and 360 d, bound  $^{14}\text{C}$  accounted for greater than 19% of the applied  $^{14}\text{C}$ . These observations are not surprising. A steady decrease in the extractable fraction of  $^{14}\text{C}$ -compounds from soils treated with  $^{14}\text{C}$ -labeled atrazine has frequently been observed (Best and Weber 1974, Capriel et al 1985, Winkelmann and Klaine 1991a). The bound residues generally included atrazine, deethylatrazine, deisopropylatrazine, hydroxyatrazine, and the dealkylated analogues of the latter (Capriel et al. 1985, Capriel et al.

Table 14. Mass-balance distribution of <sup>14</sup>C-atrazine in fallow field lysimeters(1990) (Keller 1992).

Distribution	Days after treatment				
	0	30	90	180	360
	-----(% of applied <sup>14</sup> C)-----				
Volatilization <sup>a</sup>	0.00	54.16	55.52	60.73	62.16
Soil (Ext) <sup>b</sup> 0- to 7.6-cm	85.43	10.82	1.98	1.36	1.66
Atrazine	73.68	5.32	0.56	0.34	0.32
Metabolite 1 <sup>c</sup>	6.06	1.68	0.73	0.66	0.92
Metabolite 2 <sup>c</sup>	0.38	1.22	0.16	0.07	0.06
Metabolite 3 <sup>c</sup>	1.49	0.75	0.11	0.06	0.07
Metabolite 4 <sup>c</sup>	3.20	1.64	0.23	0.08	0.11
Unknown	0.62	0.21	0.19	0.15	0.18
Bound <sup>d</sup>	14.57	17.57	21.42	19.67	20.39
Subsurface (7.6- to 89-cm)	0.00	17.45	21.08	18.24	15.79
Total	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Identified by TLC: Metabolite 1=hydroxyatrazine, Metabolite 2=unidentified, Metabolite 3=deisopropylatrazine, Metabolite 4=deethylatrazine.

<sup>d</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 15. Mass-balance distribution of <sup>14</sup>C-metolachlor in fallow field lysimeters(1990) (Keller 1992).

Distribution	Days after treatment				
	0	30	90	180	360
	-----(% of applied <sup>14</sup> C)-----				
Volatilization <sup>a</sup>	0.00	43.64	56.18	52.29	55.16
Soil (Ext) <sup>b</sup> 0- to 7.6-cm	91.53	8.57	1.13	0.60	0.50
Metolachlor	88.76	7.71	0.94	0.46	0.35
Metabolite 1	0.33	0.35	0.03	0.02	0.03
Metabolite 2	0.64	0.27	0.04	0.02	0.02
Unknown	1.80	0.24	0.12	0.10	0.10
Bound <sup>c</sup>	8.27	25.87	17.11	13.25	13.20
Subsurface (7.6- to 89-cm)	0.00	21.92	24.22	26.22	21.59
Leached	0.00	0.00	1.36	7.64	9.55
Total	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 16. Mass-balance distribution of <sup>14</sup>C-primisulfuron in fallow field lysimeters (1990) (Keller 1992).

Distribution	Days after treatment				
	0	30	90	180	360
	-----(% of applied <sup>14</sup> C)-----				
Volatilization <sup>a</sup>	0.00	71.37	76.81	78.52	78.43
Soil (Ext) <sup>b</sup>	96.45	1.55	0.34	0.22	0.34
0- to 7.6-cm					
Primisulfuron	94.95	1.14	0.25	0.15	0.25
Metabolite 1	0.73	0.15	0.02	0.02	0.02
Metabolite 2	0.00	0.03	0.01	0.01	0.01
Unknown	0.77	0.23	0.06	0.04	0.06
Bound <sup>c</sup>	3.55	11.86	7.26	8.01	10.26
Subsurface (7.6- to 89-cm)	0.00	15.22	15.59	13.25	10.97
Total	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with acetonitrile.

<sup>c</sup>Unextractable with acetonitrile, 0- to 7.6-cm depth.

Table 17. Chromatographic R<sub>f</sub> parameters for atrazine, metolachlor, primisulfuron and metabolites on silica TLC plates using selected solvent systems (Keller 1992).

Compound	Solvent systems <sup>a</sup>		
	A	B	C
	----- (R <sub>f</sub> ) -----		
Atrazine	0.66		
Metabolite 1 <sup>b</sup>	0.03		
Metabolite 2 <sup>b</sup>	0.13		
Metabolite 3 <sup>b</sup>	0.34		
Metabolite 4 <sup>b</sup>	0.44		
Metolachlor		0.81	
Metabolite 1		0.30	
Metabolite 2		0.43	
Primisulfuron			0.72
Metabolite 1			0.09
Metabolite 2			0.41

<sup>a</sup>(A) ethyl acetate:toulene (1:1 v/v) (B) chloroform:methanol:formic acid:water (75:20:4:2 v/v/v/v) (C) methylene chloride:ethyl acetate:acetic acid (50:50:1 v/v/v)

<sup>b</sup>Metabolite 1 - hydroxyatrazine, Metabolite 2 - unidentified, Metabolite 3 - unidentified, Metabolite 3 - deisopropylatrazine, Metabolite 4 - deethylatrazine.

1986). In addition, Best and Weber (1974) found that it was more difficult to extract hydroxyatrazine than atrazine from soil. Therefore, a greater fraction of the bound  $^{14}\text{C}$  is expected to be hydroxyatrazine.

The application solution was 96.5% atrazine, however, the 0 d soil extract contained 10% impurities. The increase in impurities was probably due to chemical hydrolysis. Armstrong et al. (1967) showed that atrazine hydrolysis to hydroxyatrazine in soil was catalyzed by adsorption and was accelerated in acid soils. Metabolite 1 was the most polar metabolite ( $R_f=0.03$ ; Table 17) and is probably hydroxyatrazine. Blumhorst and Weber (1992) used similar chromatographic techniques, and deemed a  $R_f=0$  as hydroxyatrazine. Matching  $R_f$  values to those of Blumhorst and Weber 1992, metabolites 3 and 4 were identified as deisopropylatrazine and deethylatrazine, respectively. Metabolite 2 was not identified, however, based on its polarity ( $R_f=0.13$ ; Table 17) it is likely a hydroxyatrazine analogue or dealkylatrazine. The unknown fraction (Table 14) refers to radioactivity that did not chromatograph into distinct peaks.

Thirty days after  $^{14}\text{C}$ -atrazine application, 11% of the applied  $^{14}\text{C}$  was extractable (Table 14). Half the extractable  $^{14}\text{C}$  was atrazine while hydroxyatrazine (metabolite 1), metabolite 2 (unidentified), and deethylatrazine (metabolite 4) constituted the majority of the remaining  $^{14}\text{C}$ . Hydroxyatrazine and deethylatrazine are commonly detected in greater concentrations than the other metabolites (Sironi et al. 1973; Muir and Baker 1978, Winkelmann and Klaine 1991a). Large amounts of hydroxyatrazine would be expected as hydroxylation is considered to be a major route of atrazine degradation (Armstrong et al. 1967, Skipper et al. 1967).

At 90, 180, and 360 d, less than 2% of the applied  $^{14}\text{C}$ -atrazine was extractable (Table 14). The decrease in extractable  $^{14}\text{C}$  was accompanied by increases in bound and subsurface (leached)  $^{14}\text{C}$ . The concentrations of extractable  $^{14}\text{C}$  over the sampling dates were: hydroxyatrazine > atrazine > deethylatrazine > metabolite 2 > deisopropylatrazine. The order of metabolite concentrations is similar to those of Sironi et al. (1973) and Winkelmann and Klaine (1991a).

At 30 d, 43% of the  $^{14}\text{C}$ -metolachlor was lost through volatilization of herbicide and/or metabolites or as  $^{14}\text{CO}_2$  (Table 15). Absence of  $^{14}\text{C}$  below 61-cm at 30 d confirms the loss of  $^{14}\text{C}$  through volatilization (Table 12, Figure 7). At 90 d, an additional 13% of the applied  $^{14}\text{C}$  was lost to the atmosphere (Table 15). After this period, loss of  $^{14}\text{C}$  to the air was negligible and indicates that  $^{14}\text{C}$ -labeled metolachlor and/or by-products were adsorbed to soil colloids and were no longer available for volatilization or mineralization.

Radioactivity of  $^{14}\text{C}$ -metolachlor treated lysimeters in the subsurface was rather constant for the four latter sampling periods (Table 15). These levels were maintained due to a reduction of  $^{14}\text{C}$  (extractable + bound) in the surface layer and evidence of  $^{14}\text{C}$  that leached beyond 89-cm.

On the day of application, 8% of the  $^{14}\text{C}$ -labeled metolachlor (99% pure) was bound (Table 15). As was the case for atrazine treatments, this was probably due to the closure of adsorptive sites upon air-drying the soil prior to extraction. For the other sampling periods, there was no influence of air-drying on  $^{14}\text{C}$  extraction. Bound  $^{14}\text{C}$  contained 26% of the applied  $^{14}\text{C}$  at 30 d,

17% at 90 d, and 13% at 180 d, indicating that the bound portion was available for other dissipating processes. The bound fractions at 90 d and 360 d were similar, indicating that the  $^{14}\text{C}$  was not available for further losses.

At 30 d, 9% of the applied  $^{14}\text{C}$ -metolachlor was extractable (Table 15). For this period, metolachlor constituted 90% of the extractable  $^{14}\text{C}$ , while two polar metabolites made-up the difference. This is in agreement with Miller (1992) who detected two metabolites in a Dothan soil. TLC procedures used in this study (Table 17) made it impossible to correlate the metabolites produced in this study to the metabolites observed by other researchers (McGahan and Tiedje 1978, Liu et al. 1988, 1991). Chesters et al. (1989) reported that at least 19 metabolites of metolachlor were possible in soil and soil cultures.

The amount of extractable metolachlor parent and metabolites declined with time (Table 15). Metolachlor concentrations were 0.94% of the applied  $^{14}\text{C}$  at 90 d, 0.46% at 180 d, and 0.35% at 360 d. Accordingly, metabolites composed less than 0.10% of the applied  $^{14}\text{C}$ . Since bound  $^{14}\text{C}$  did not increase with time, low quantities of extractable metabolites indicate that metolachlor was not present or degraded or that metabolites leached from the 0- to 7.6- cm depth. Metolachlor dissipation and movement in each of three years in fallow and soybean lysimeters is discussed in more detail later.

At 30 and 90 d in 1990, only very low levels of radioactivity were detected below 30-cm in the  $^{14}\text{C}$ -primisulfuron treated lysimeters (Table 13, Figure 8); therefore, more than 70% of the applied  $^{14}\text{C}$  was lost to the atmosphere. Primisulfuron and its major metabolite, saccharin (Anderson and Dulka 1985, USEPA 1992) are considered to be nonvolatile, hence, the majority of  $^{14}\text{C}$  was lost as  $^{14}\text{CO}_2$ .  $^{14}\text{CO}_2$  evolution continued throughout the study, however, slight losses of  $^{14}\text{C}$  due to leaching may have occurred.  $^{14}\text{CO}_2$  production from soil treated with a sulfonylurea herbicide was previously discussed.

Radioactivity in the subsurface of  $^{14}\text{C}$ -primisulfuron treated lysimeters was similar at 30 and 90 d and then declined after the latter (Table 16). Total  $^{14}\text{C}$  recoveries at 180 and 360 d (Table 13) were comparable; however, radioactivity in the 0- to 7.6-cm zone and subsurface (Table 16) were different suggesting that  $^{14}\text{C}$  may have moved upward by capillary flow. Two sulfonylurea herbicides, chlorsulfuron and triasulfuron have been shown to move readily by capillary flow in laboratory soil columns (Mahnken 1989).

Less than 4% of the  $^{14}\text{C}$ -primisulfuron application solution (97% pure) was bound in the soil on the day of application (Table 16). Bound  $^{14}\text{C}$  made-up 12% of the applied  $^{14}\text{C}$  at 30 d, 7% at 90 d, 8% at 180 d, and 10% at 360 d. A reduction in the bound fraction after 30 d implied that fixed  $^{14}\text{C}$  was available for other dissipating processes. The increase in bound  $^{14}\text{C}$  at 360 d was probably due to radioactivity that moved to the surface by capillary flow.

Thirty days after application, <2% of the applied  $^{14}\text{C}$ -primisulfuron was extractable (Table 16). For this sampling date, primisulfuron accounted for 73% of the extractable  $^{14}\text{C}$ , while two polar metabolites (Tables 17 and 16) made-up the difference. For the remaining sampling periods <0.5% of the applied  $^{14}\text{C}$  was extractable (Table 16). At least three metabolites have been determined in soil treated with primisulfuron (USEPA 1992). These products include saccharin, methyl-2-aminosulfonylbenzoate and 2-aminosulfonylbenzoic acid. Similarly, Anderson and Dulka (1985) used sulfometuron methyl, structurally comparable to primisulfuron, in a laboratory study and found the

same three metabolites plus methyl-2-[[N-(aminocarbonyl)amino]sulfonyl] benzoate. For this study, concentrations of extractable <sup>14</sup>C throughout the remaining periods were: primisulfuron > metabolite 1 > metabolite 2.

Atrazine, metolachlor and primisulfuron half-lives. Data presented in Tables 14, 15 and 16 indicate that the observed decreases in <sup>14</sup>C-labeled atrazine, metolachlor and primisulfuron in the 0- to 7.6-cm zone were the result of dissipating processes. These processes in decreasing order, were: volatilization of herbicides, metabolites, and/or <sup>14</sup>CO<sub>2</sub>, > subsurface (leaching) ≥ bound (adsorption) > nonvolatile metabolites (degradation). Extrapolating these dissipation processes, particularly the bound and extractable <sup>14</sup>C, to include the second depth, regression analyses were used to predict herbicide longevity in the 0- to 15-cm depth. The 0- to 15-cm depth has commonly been used in determining the half-life of a herbicide in soil (Sikka and Davis 1966, Kells et al. 1980).

A quadratic model was used to calculate the soil half-lives for the herbicides. Half-life is defined here as the time in days for one-half of "extractable" parent compound to disappear from the 0- to 15-cm zone. For this study, the half-life is dependent upon the previously mentioned dissipating processes. The quadratic model took the form of  $\ln(y) = a + bx + cx^2$ , where y is percent of applied herbicide remaining, x is time + 1 where time is in days, and a, b, and c are the parameter estimates. The equation is only valid for the range of independent variables used in the study. Parameter estimates, coefficients of determination and half-life values calculated from the quadratic model are presented in Table 18.

A soil half-life of 5 d for atrazine is strikingly less than the values obtained in fallow field studies performed in the southern United States. Half-life values of 14 d in Tennessee at 0- to 3-cm depth (Winklemann and Klaine 1991a), and 23 d in Alabama at 0- to 15-cm depth (Sikka and Davis 1966) were reported when formulated atrazine was applied. Kells et al. (1980) applied <sup>14</sup>C-atrazine to undisturbed aluminum cylinders (5-cm i.d. x 15-cm in length) in Kentucky and determined a half-life of 23 d in the 0- to 15-cm zone. The disparity in half-life values are likely due to differences in soil pH, sampling depth, environmental conditions and vaporization rates of formulated and radiolabeled atrazine and in definition of parent and in the method used to estimate half-life.

The half-life dissipation rate for metolachlor was 6 d (Table 18). This value is not in agreement with the 15 to 25 d reported for the herbicide in southern states (Skipper et al. 1976, WSSA 1989). The disparity in the half-life values are probably due to the soil differences discussed previously.

A soil half-life of 3 d for primisulfuron compares with the 3 to 12 d reported in the literature (USEPA 1990b) (Table 18). Unlike atrazine and metolachlor, the sulfonylurea herbicides degrade rapidly by chemical hydrolysis and microbial breakdown and are accelerated under warm, moist, light-textured, and low pH soils (Beyer et al. 1987). These conditions were maintained through the first 30 d.

Effects of surface cover on soil moisture. Analysis of variance of surface cover effects on soil water content indicated no year by treatment interaction at the 0- to 89-cm depth; therefore, years were combined and are shown in Figure 9. Lysimeters with soybean contained the least amount of soil water at

Table 18. Calculated soil half-life values for atrazine, metolachlor and primisulfuron in the 0- to 15-cm depth of fallow field lysimeters (Keller 1992).

Herbicide	Parameter estimates			R <sup>2</sup>	Half-life <sup>a</sup> (days)
	a	b	c		
Atrazine	4.68	-4.81	1.03	0.99	5
Metolachlor	4.68	-4.20	0.82	0.99	6
Primisulfuron	4.45	-5.90	1.46	0.99	3

<sup>a</sup>From  $\ln(y) = a + bx + cx^2$  where  $y = \%$  of applied herbicide remaining and  $x =$  time in months. Example: Calculate the % atrazine remaining at 5 DAT (0.166 month).  $\ln(y) = 4.68 - 4.81(0.166) + 1.03(0.166)^2 = 3.91$  and  $y = 50\%$ .

Table 19. Effect of surface cover on soil water distribution M-score values at 0- to 89-cm depth (mean of 1989 and 1990) and 0- to 46-cm depth (1989 and 1990 data) in filed lysimeters at 90 d. (Keller 1992).

Surface cover	M-score (mean 1989 and 1990)	
	0- to 89-cm depth	
Fallow	57.95a	
Mulch	65.29a	
Sod	59.89a	
Soybean	40.70b	
	0- to 46-cm depth	
	1989	1990
Fallow	7.68b	8.07b
Mulch	9.21a	10.21a
Sod	7.44b	7.97b
Soybean	6.55b	3.29c

<sup>a</sup>Within a column, means sharing the same letter are not significantly different, as determined by LSD (0.05).

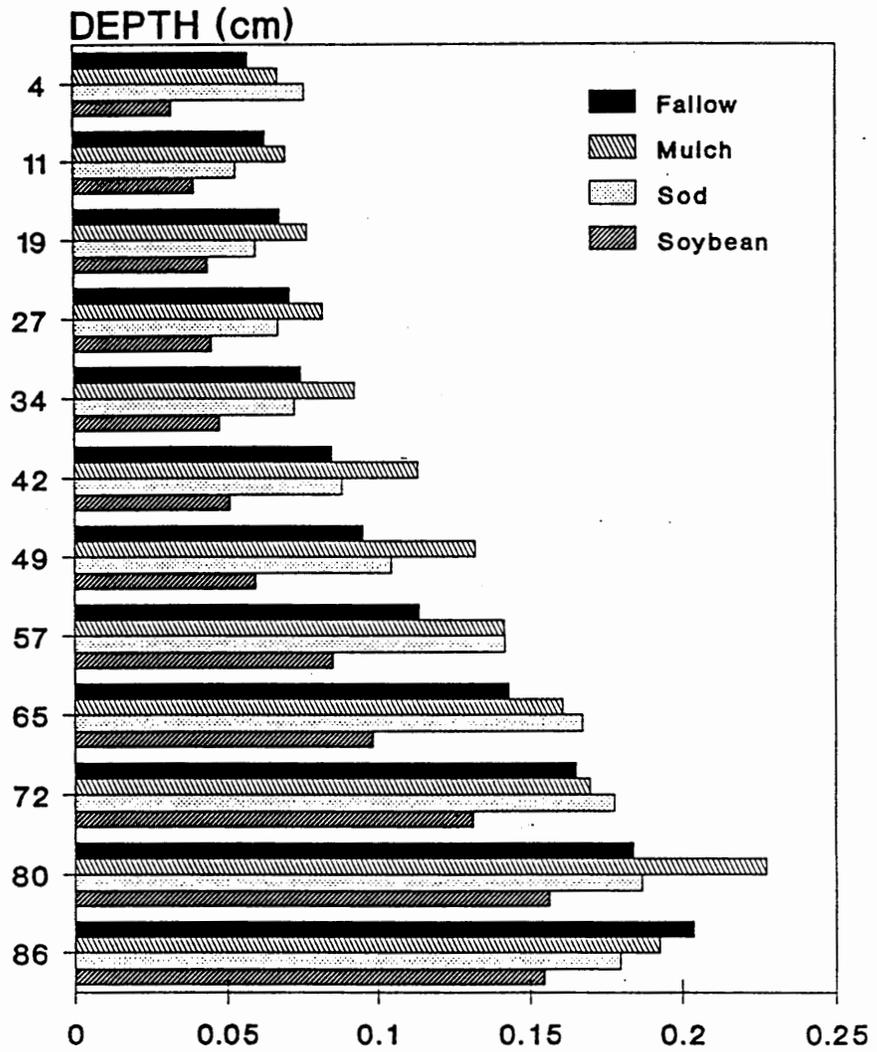


Figure 9. Soil water distribution in fallow, mulch, sod and soybean field lysimeters at 90 DAT (mean of 1989 and 1990) (Keller 1992).

rooting of soybean to 46-cm probably contributed to the significant reduction in soil water. Sod lysimeters contained roots only to 23-cm. Sod and mulch also contained a vegetative barrier that probably inhibited soil water evaporation.

Soil water M-scores calculated from the entire soil profile may have masked treatment effects in the 0- to 46-cm depth. Analysis of variance indicated a significant year by treatment interaction for M-scores calculated from the upper 46 cm; therefore, data are presented separately for each year (Figure 10). For both years, lysimeters with mulch generally contained greater amounts of soil water in each depth to 46 cm and as a result had significantly higher M-scores (Table 19). In 1990, soybean in lysimeters had a significant effect in reducing soil water content (Figure 10) and resulted in the lowest M-score (Table 19). The disparity in soybean M-scores in 1989 and 1990 was due to subsoiling performed in 1990 that resulted in 3.5 times more root mass (dry wt.) than that in 1989. M-score rankings for soil water content at 46- to 89-cm were comparable to those at 0- to 89-cm (data not shown). High soil water contents in fallow, mulch and sod columns as compared with soybean columns, suggest that greater herbicide mobility is likely under the latter surface conditions particularly near periods of herbicide application. Differences in soil water content between fallow (interrow), mulch and soybean (crop row) are consistent with other studies (Blevins et al. 1971, Van Wesenbeeck and Kachanoski 1988, Zhai et al. 1990).

#### Effects of surface cover on $^{14}\text{C}$ -metolachlor distribution and recovery.

Significant year by treatment interactions existed for total  $^{14}\text{C}$ -metolachlor in soil as influenced by surface cover (vegetation); therefore, data are presented separately for each year. In 1989, fallow, mulch and sod lysimeters retained comparable amounts of  $^{14}\text{C}$ , while only sod and soybean lysimeters were significantly different (Figure 11). In 1990, lysimeters with sod retained significantly more soil  $^{14}\text{C}$  than fallow, mulch, and soybean lysimeters.

Analogous amounts of  $^{14}\text{C}$  in vegetation were determined in 1989, while in 1990, mulch, soybean and sod contained significantly different amounts of  $^{14}\text{C}$  (Figure 11).  $^{14}\text{C}$  in mulch was less than that reported by other investigators in greenhouse (Strek and Weber 1982) and field studies (Banks and Robinson 1986). These researchers, however, used different metolachlor, straw and watering rates and sampling dates which could explain dissimilar results. Both research groups reported that 23 to 30% of the applied metolachlor was washed from straw by 1 to 3 cm rain. Furthermore, they attributed volatilization as a major loss mechanism of metolachlor from wheat straw. Banks and Robinson (1986) also reported that 17% of the metolachlor applied to 2240 kg/ha wheat straw reached the soil surface on day 0. Conceivably then, since the carrier volume was 22 times greater in the lysimeter study than in the Banks and Robinson study, more metolachlor may have reached the soil surface in the lysimeter. For the other surface covers, levels of  $^{14}\text{C}$  in sod and soybean were in general agreement with confined soil studies for s-triazines in corn, cotton and soybean (Best and Weber 1974), methabenzthiazuron, a urea derivative used in wheat (Fuhr 1985) and carbofuran, an insecticide used in corn (Fermanich and Daniel 1991).

$^{14}\text{C}$  distribution at 90 DAT in surface cover lysimeters is shown in Figure 12. Analysis of variance of the M-scores determined from the data in Figure 12 indicated a significant year by treatment interaction; therefore M-scores for each year are presented in Table 20. In 1989, lysimeters with sod contained

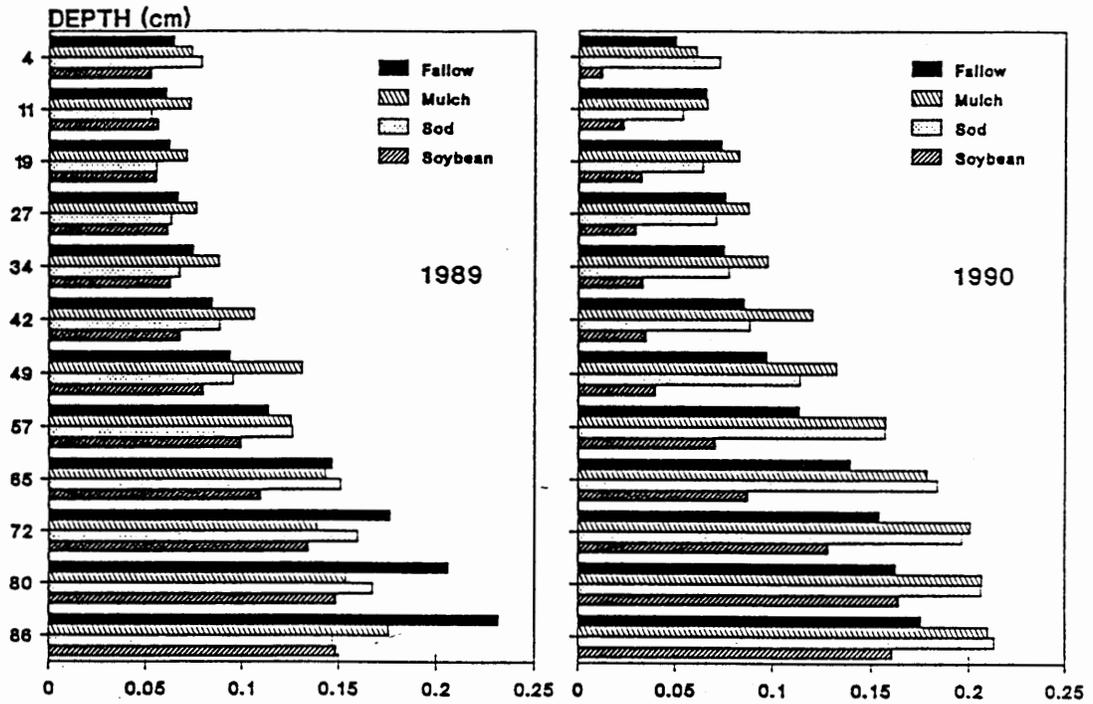


Figure 10. Soil water distribution in fallow, mulch, sod and soybean field lysimeters at 90 DAT in 1989 and 1990 (Keller 1992).

Table 20. Effect of surface cover on <sup>14</sup>C distribution M-score values at 0-89 cm depth in <sup>14</sup>C-metolachlor treated field lysimeters at 90 dat in 1989 and 1990<sup>a</sup> (Keller 1992).

Surface cover	M-score	
	1989	1990
Fallow	13.89a	9.77ab
Mulch	14.29a	11.11a
Sod	8.83	11.18a
Soybean	11.80ab	6.78b

<sup>a</sup>Within a column, means sharing the same letter are not significantly different, as determined by LSD (0.05).

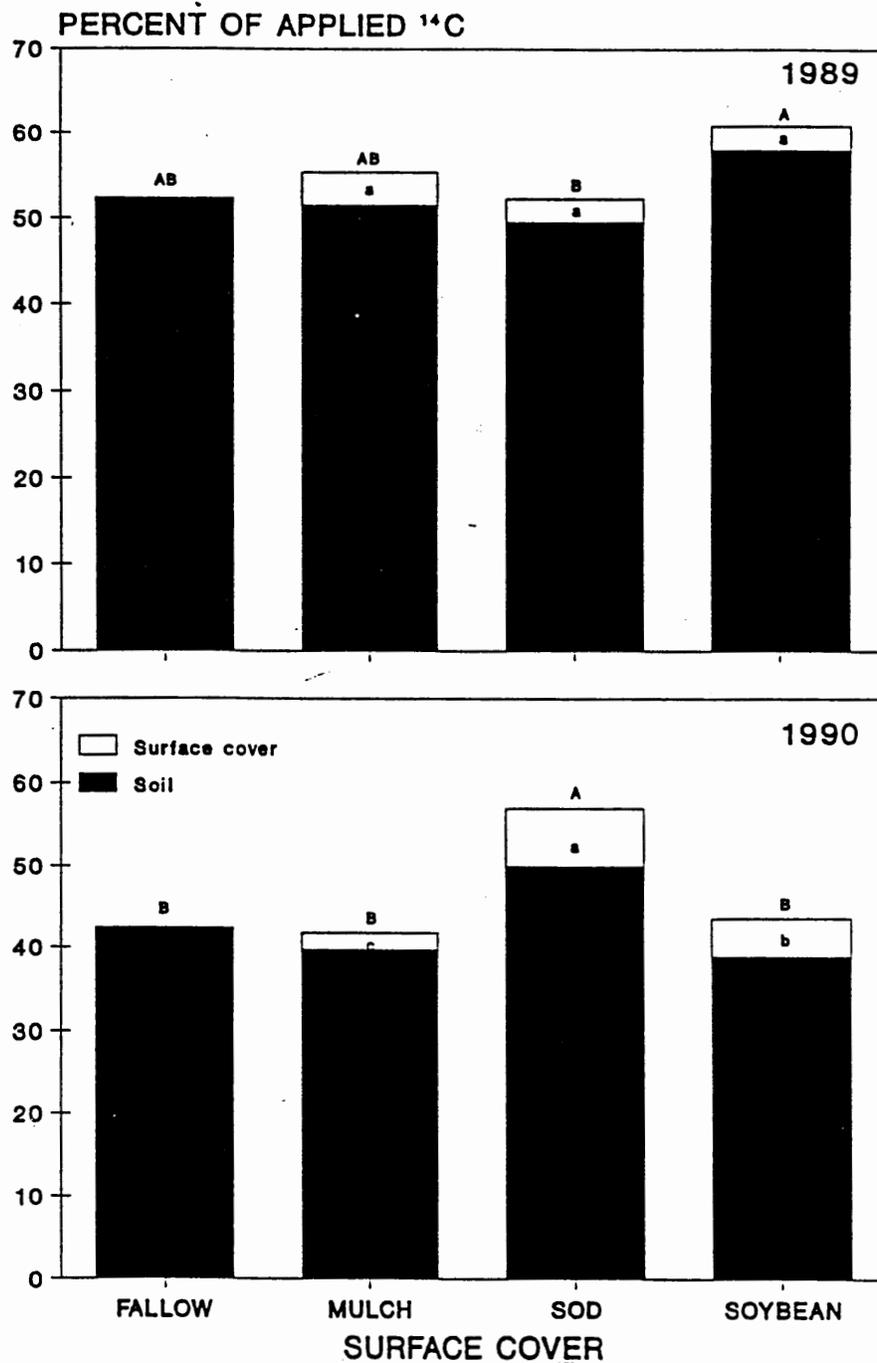


Figure 11. Total <sup>14</sup>C recovery in <sup>14</sup>C-metolachlor treated fallow, mulch, sod and soybean field lysimeters at 90 DAT in 1989 and 1990. (Means sharing the same letter are not significantly different, as determined by LSD (0.05). Upper and lowercase letters are for soil and surface cover comparisons, respectively) (Keller 1992).

the largest amount of  $^{14}\text{C}$  in the 0- to 7.6-cm depth and as a result contributed to the lowest M-score (Figure 12; Table 20). Accordingly, the mobility of  $^{14}\text{C}$  in sod lysimeters in 1989 was significantly less than the fallow and mulch systems. In 1990, lysimeters with soybean contained the least amount of  $^{14}\text{C}$  in the lower depths and as a result presented the lowest M-score. The mobility of  $^{14}\text{C}$  in soybean lysimeters was significantly less than the mulch and sod systems. For both years, sod lysimeters contained the largest amount of  $^{14}\text{C}$  in the first depth (Figure 12). This occurrence suggests that the adsorptive capacity (increase in soil organic carbon) of the soil was increased from the transplanted sod. Researchers have shown that sod, over a period of years, has a higher soil organic matter content than adjacent cultivated areas (McHenry et al. 1946; DeVane et al. 1952).

The distribution of  $^{14}\text{C}$  in each lysimeter (Figure 12) closely resembles the amount and distribution of organic carbon in the soil profile (Tables 2 and 3). Various researchers (Jordan and Harvey 1978; Obrigawitch et al. 1981; Weber and Peter 1982; Peter and Weber 1985) determined that organic matter was the most important soil property that influenced metolachlor adsorption. Clay minerals were also reported to bind chloracetamide herbicides to a limited extent (Peter and Weber 1985). A small fraction of the  $^{14}\text{C}$  in upper depths may be associated with microbial biomass. Liu et al. (1989) reported that bacteria absorbed and transformed  $^{14}\text{C}$ -metolachlor from a liquid medium. Eighty percent of the added  $^{14}\text{C}$ -ring-labeled metolachlor accumulated inside the cells.  $^{14}\text{C}$  absorbed by the bacteria was strongly bound with only 2% of the  $^{14}\text{C}$  being released into deionized water after shaking for 3 h. Bacteria biomass commonly accounts for 0.02 to 0.2% of the total soil weight in the 0- to 15-cm depth (Brady 1990). M-scores for fallow, mulch, sod, and soybean lysimeters were not significantly different at 0- to 46-cm (not shown). In 1990, soybean lysimeters had the lowest M-score at 46- to 89-cm, however, all lysimeters were not significantly different for both years (not shown).

Effects of soybean versus fallow on soil moisture. At 30 DAT, fallow and soybean lysimeters were nonsignificantly different in soil water content (Figure 13; Table 21). Differences in soil water content would not be expected since evapotranspiration would be insignificant. For this time period, soybean growth was at the V2 stage (15- to 20-cm tall).

Sixty days after treatment in 1989 and 1990, soil water content in fallow and soybean lysimeters were significantly different (Table 21; Figure 13). Difference in soil water content was attributable to the transpiring soybean. Soybean growth for this time period was at the V5 stage (40- to 50-cm tall). At 60 DAT in 1988, M-scores and soil water content distribution (not shown) for fallow and soybean lysimeters were similar. This agreement may have been due to a 5-cm rainfall event over a 3 d period just prior to sampling and may have masked treatment differences.

M-scores, soil water contents, and distributions at 90 DAT for each lysimeter were comparable to those at 60 DAT (Figure 13; Table 21). Similar soil water contents at 60 and 90 DAT indicate that water inputs between these time periods were used to maintain water vapor losses from the lysimeters. Consequently, very little percolate was measured between 60 and 90 DAT for fallow and soybean lysimeters (Figure 14).

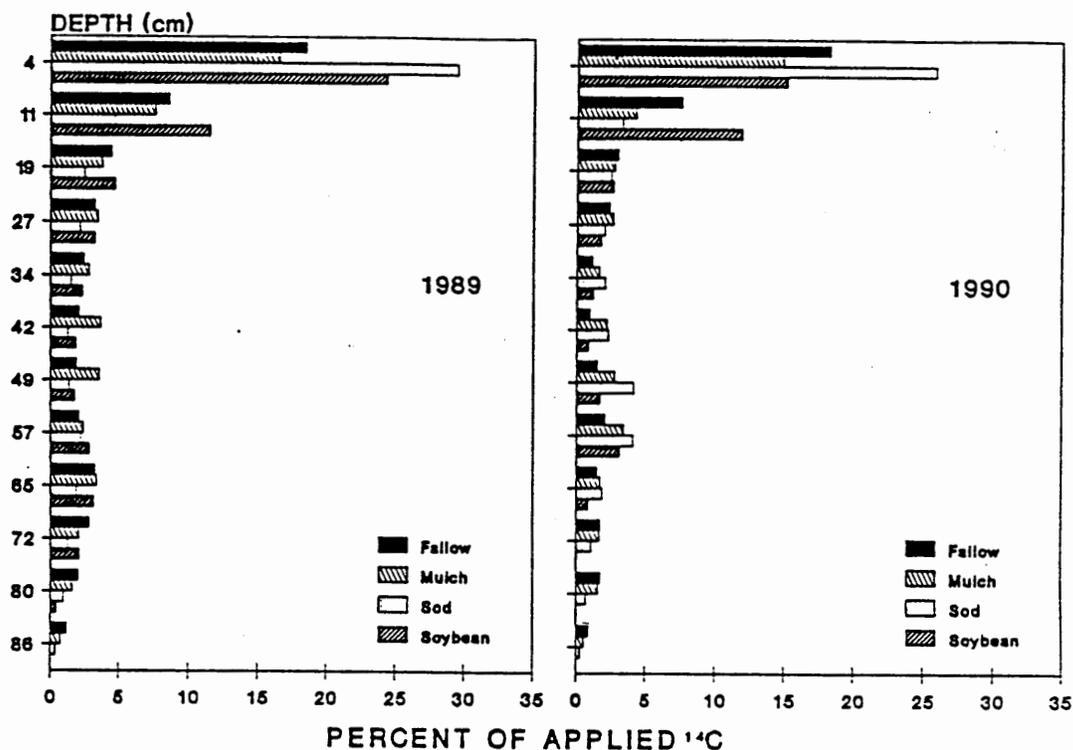


Figure 12.  $^{14}\text{C}$  distribution in  $^{14}\text{C}$ -metolachlor treated fallow, mulch, sod and soybean field lysimeters at 90 DAT in 1989 and 1990 (Keller 1992).

Table 21. Effect of fallow versus soybean on soil water distribution M-score values for the 0-89-cm soil depth in field lysimeters at 30 to 360 DAT (mean of 1988, 1989 and 1990)<sup>a</sup> (Keller 1992).

Surface cover	DAT <sup>b</sup>					
	30	60 <sup>c</sup>	90	120 <sup>d</sup>	180 <sup>d</sup>	360 <sup>d</sup>
Fallow	62.35a	64.19a	64.50a	64.72a	67.98a	70.31a
Soybean	60.78a	40.25b	40.27b	49.90b	66.73a	63.49a

<sup>a</sup>Within a column, means sharing the same letter are not significantly different, as determined by LSD (0.05).

<sup>b</sup>DAT = days after treatment.

<sup>c</sup>1989 and 1990 only.

<sup>d</sup>1990 only.

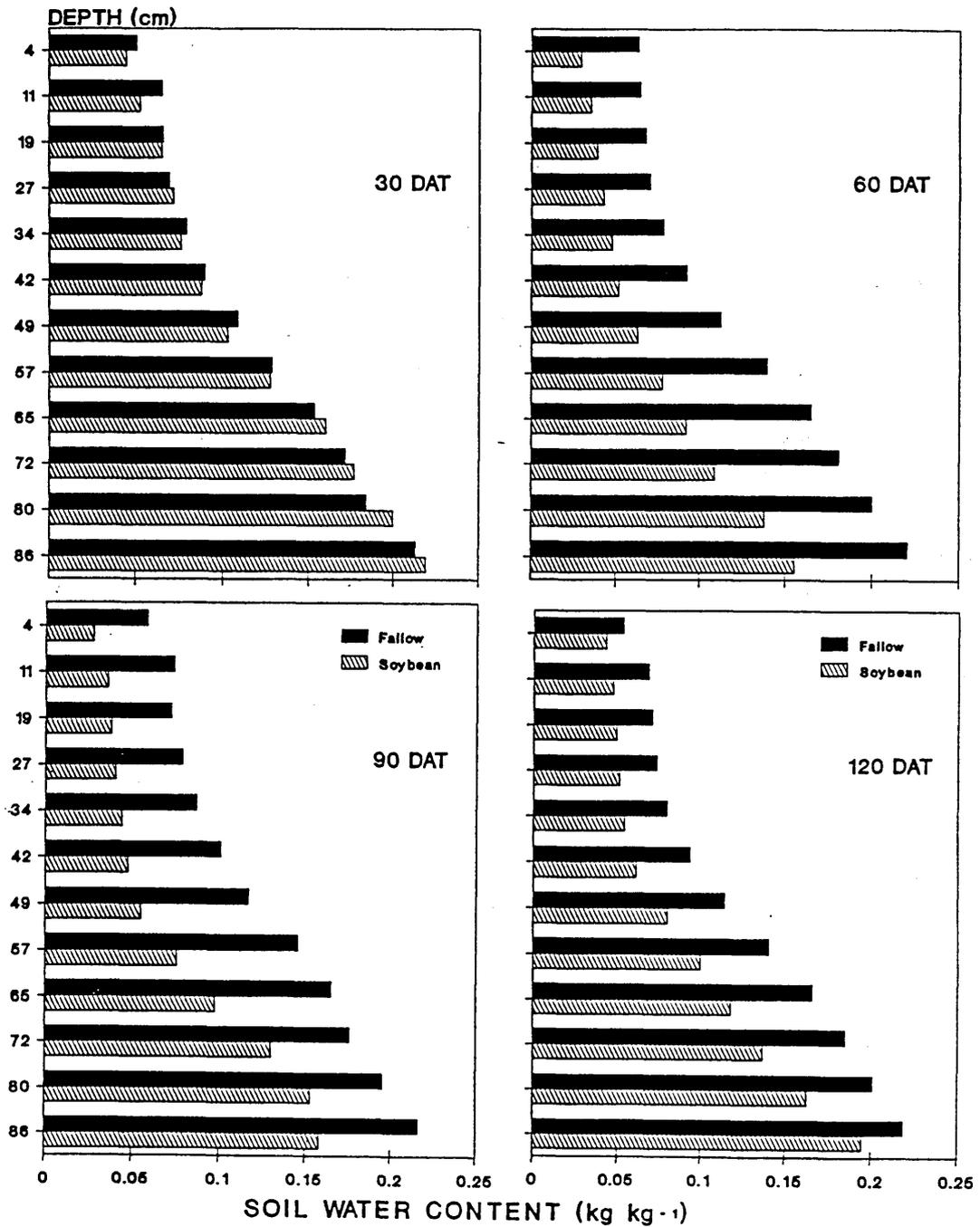


Figure 13. Soil water distribution in fallow and soybean field lysimeters at 30 to 120 DAT (mean of 1988, 1989 and 1990) (Keller 1992).

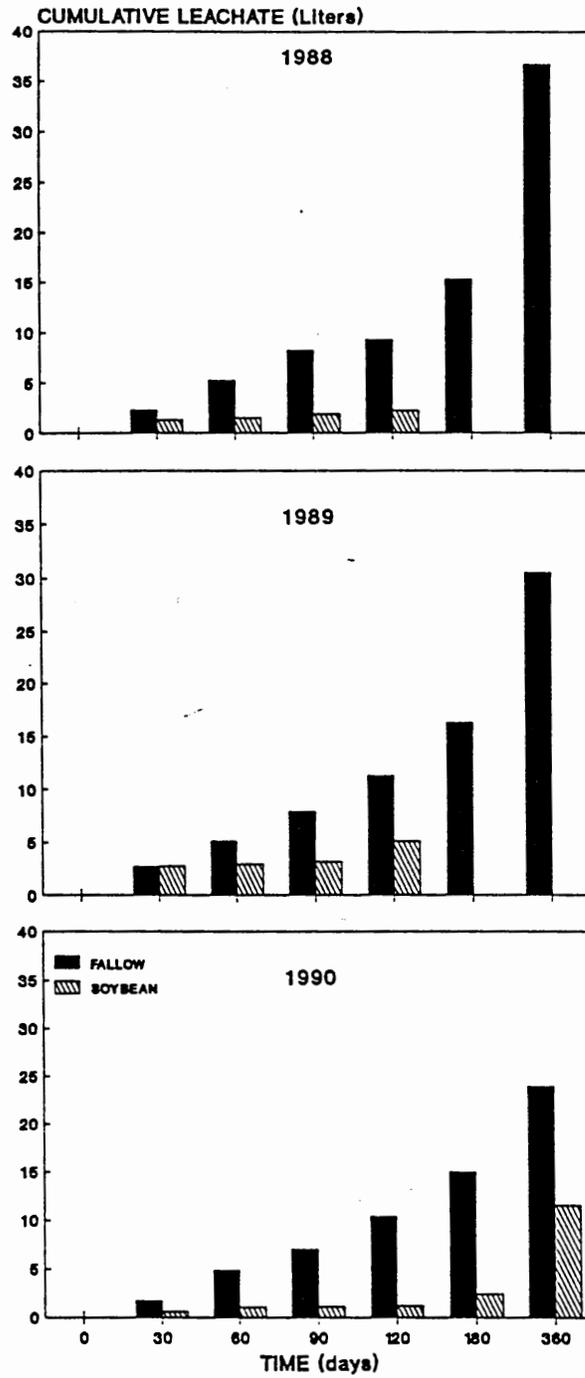


Figure 14. Cumulative leachate from fallow and soybean field lysimeters at 0 to 360 DAT in 1988, 1989, and 1990 (Keller 1992).

At 120 DAT, soil water contents in fallow and soybean lysimeters were significantly different in 1990 (Figure 13; Table 21) but were nonsignificantly different in 1988 and 1989 (not shown). The lack of significance in soil water content in both columns for 1988 and 1989 was probably due to differences in soybean growth characteristics. At 120 DAT, soybean plants were physiologically mature in 1988 and 1989, while in 1990, soybean growth was at the R3 stage. Soybeans in 1990 were planted 30 d earlier than those planted in 1988 and 1990. Researchers have reported that the rate of seed growth and maturity is accelerated when reproductive development occurs during successively shorter days, such as days after the summer solstice (Raper and Thomas 1978, Cure et al. 1982).

In 1990, soil water content in fallow and soybean lysimeters was nonsignificantly different at 180 and 360 DAT (Figure 15; Table 21). By 180 DAT, soybean had reached physiological maturity, and therefore enabled soil water recharge. Comparable leachate volumes (not shown) indicate that soil water recharge in soybean lysimeters, that is soil water contents similar to fallow, was finalized between 173 and 180 DAT. Beyond 180 DAT, leachate volumes were similar for both lysimeters.

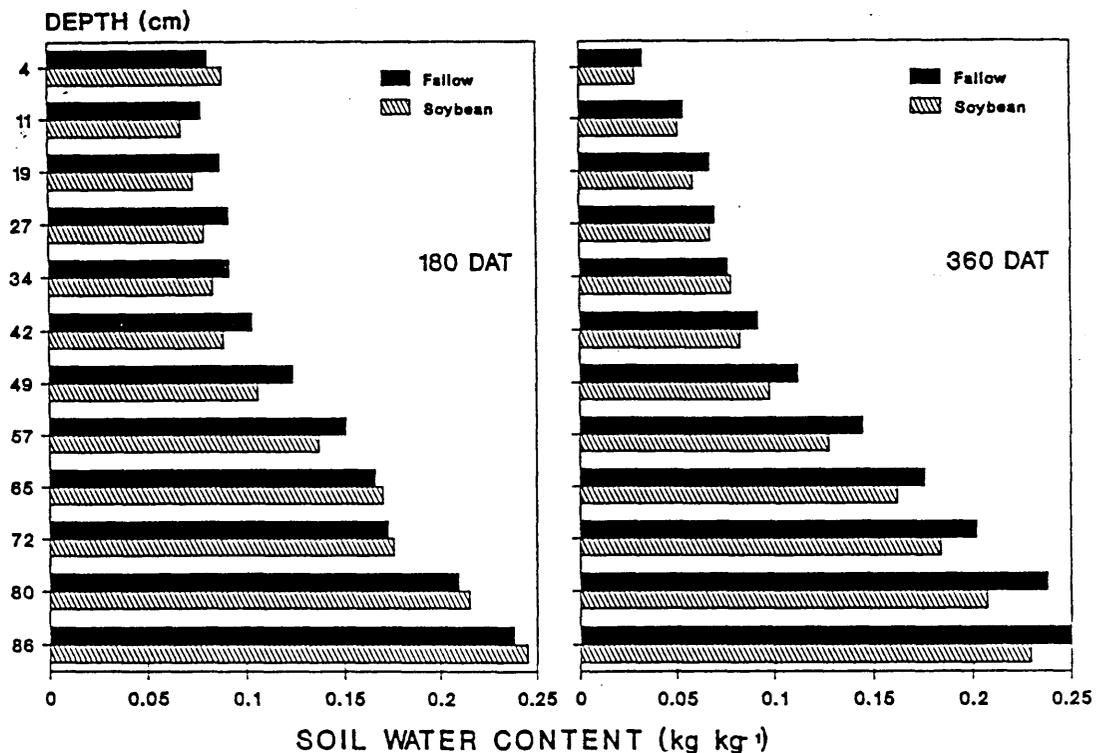


Figure 15. Soil water distribution in fallow and soybean field lysimeters at 180 and 360 DAT in 1990 (Keller 1992).

Effects of soybean versus fallow on  $^{14}\text{C}$ -metolachlor distribution and recovery. For all sampling dates, there was no significant year by treatment interaction for total  $^{14}\text{C}$ -metolachlor; however, large losses of  $^{14}\text{C}$  from year to year and significant year by treatment interactions for  $^{14}\text{C}$  in leachate, necessitated the need to present years separately for total  $^{14}\text{C}$ . In each year and sampling date, total  $^{14}\text{C}$  in fallow and soybean lysimeters were nonsignificantly different (Figure 16). For all sampling dates, greater amounts of total  $^{14}\text{C}$  were measured in 1988 and 1989. Differences in  $^{14}\text{C}$  are probably due to rates of volatilization and/or transformation and loss as  $^{14}\text{CO}_2$ . The absence of  $^{14}\text{C}$  in cumulative leachate from fallow and soybean lysimeters (Figure 17) at 30 DAT for each year substantiates vapor loss.

Volatilization of  $^{14}\text{C}$  was the highest in 1990. On the day of  $^{14}\text{C}$ -metolachlor application, water content in the 0- to 7.6-cm depth was 4.72 kg/kg in 1988, 6.18 in 1989, and 10.37 in 1990. Air temperature (Table 8), pan evaporation (Table 9), and soil temperature (Figure 4) at 8-cm for the first 14 d were similar for each year; however, 3.20 cm of water was added 7 d after herbicide application in 1988, 2.54 cm added after 24 h in 1989 and 1.91 cm added after 48 h in 1990. Total water inputs at 14 DAT were 5.36 cm in 1988, 7.52 in 1989 and 3.56 in 1990. Several researchers have reported that pesticides volatilized more rapidly from wet than dry soils (Kearney et al. 1964, Taylor 1978, Glotfelty et al. 1984).

Recovery of  $^{14}\text{C}$  from  $^{14}\text{C}$ -metolachlor treated lysimeters decreased with time in a curvilinear fashion (Figure 16). For each year, significant amounts of  $^{14}\text{C}$  were lost from fallow lysimeters at 0 to 30, 60 to 90 and 180 to 360 DAT. As previously mentioned, loss of  $^{14}\text{C}$  between 0 and 30 DAT was attributable to volatilization. In 1988  $^{14}\text{C}$  lost from fallow lysimeters between 60 to 90 DAT was accounted for in the leachate (Figure 17). On the other hand, for the same time span,  $^{14}\text{C}$  in leachate accounted for only 13 and 7% of the radioactivity lost from fallow systems in 1989 and 1990, respectively, with the balance attributable to vapor loss (Figures 16 and 17). At 180 DAT, 57, 46 and 40% of the applied  $^{14}\text{C}$  remained in fallow lysimeters in 1988, 1989 and 1990, respectively. After this time period, 8% of the applied  $^{14}\text{C}$  was lost in 1988 and 1989, and 4% lost in 1990. In lysimeters with soybean, significant amounts of  $^{14}\text{C}$  were lost at 0 to 30 DAT in the three years and 180 to 360 DAT in 1990 (Figure 16). Like the fallow lysimeters, loss of  $^{14}\text{C}$  in soybean lysimeters at 0 to 30 DAT was attributable to volatilization. After 180 DAT, leachate contained 20% of the  $^{14}\text{C}$  lost from soybean systems (Figure 17) while vapor losses made the balance.

Since no significant year by treatment interactions existed for  $^{14}\text{C}$  M-scores at each sampling date, data were combined and are presented in Figure 18 and Table 22. Distribution of  $^{14}\text{C}$  in fallow and soybean lysimeters closely resembled the amount and distribution of organic carbon in the soil profile (Tables 2 and 3).

At 30 DAT, distribution of  $^{14}\text{C}$  in fallow and soybean lysimeters was similar and was reflected by nonsignificant M-scores (Figure 18; Table 22). Similar distributions of  $^{14}\text{C}$  were due to insignificant water usage by soybean which led to comparable soil water contents (Figure 13). For this sampling date, 73 and 76% of the  $^{14}\text{C}$  remaining in fallow and soybean lysimeters, respectively, was retained in the upper 15 cm while <1% of the applied  $^{14}\text{C}$  was present below 68 cm.

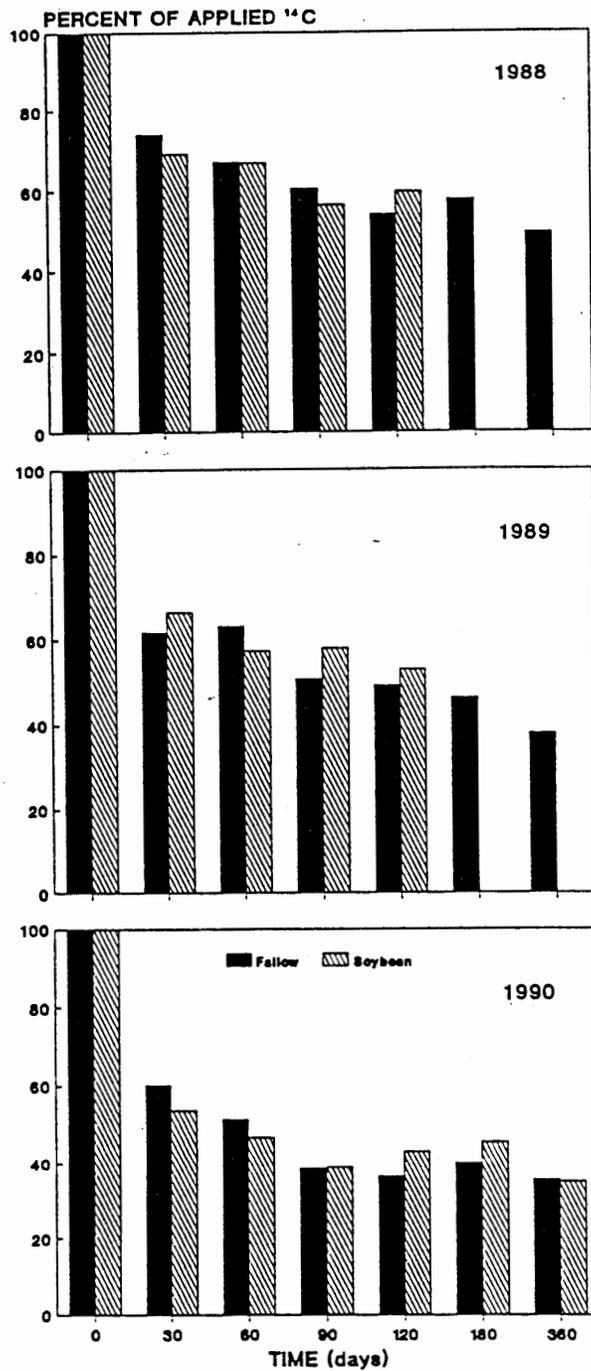


Figure 16. Total <sup>14</sup>C recovery in <sup>14</sup>C-metolachlor treated fallow and soybean field lysimeters at 0 to 360 DAT in 1988, 1989 and 1990 (Keller 1992).

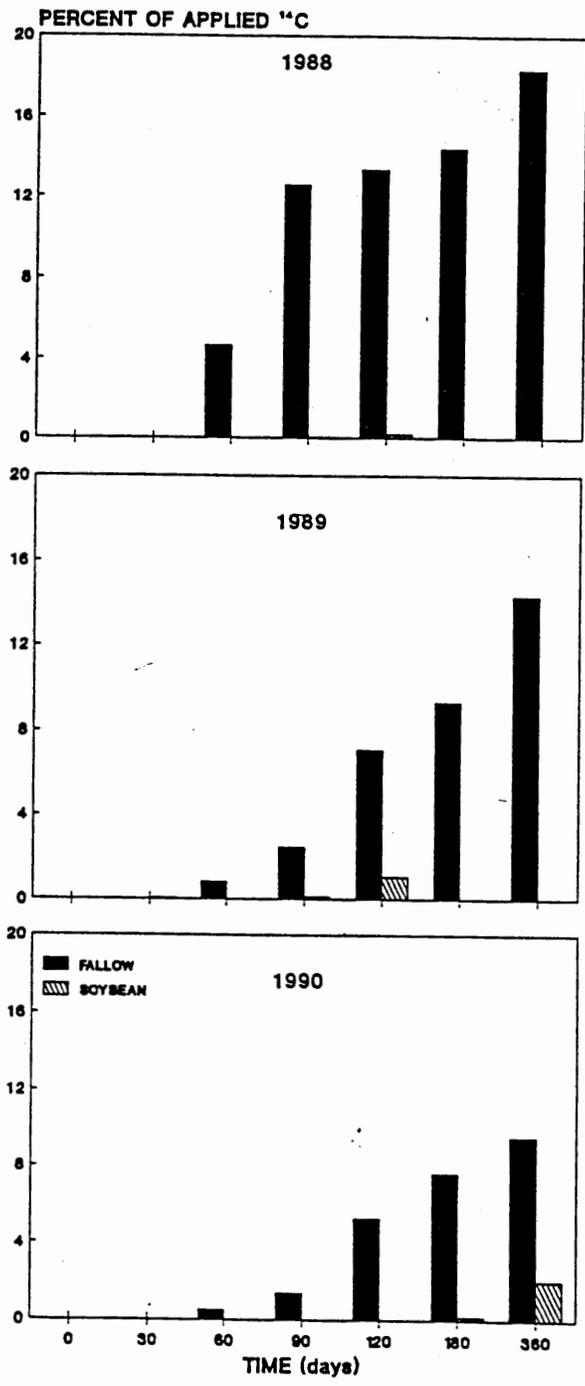


Figure 17. Cumulative <sup>14</sup>C in leachate from <sup>14</sup>C-metolachlor treated fallow and soybean field lysimeters at 0 to 360 DAT in 1988, 1989 and 1990 (Keller 1992).

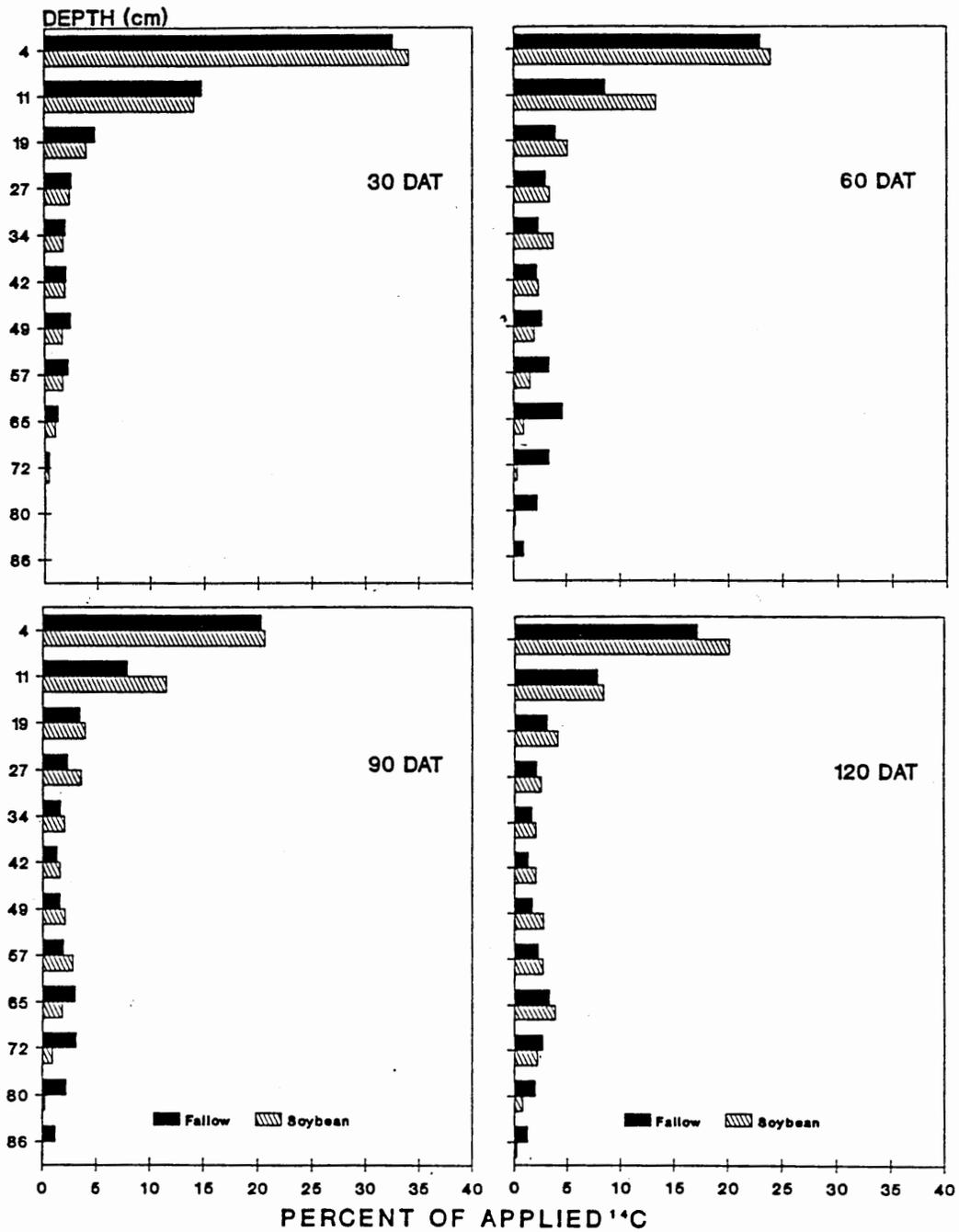


Figure 18. <sup>14</sup>C distribution in <sup>14</sup>C-metolachlor treated fallow and soybean field lysimeters at 30 to 120 DAT (mean of 1988, 1989 and 1990 studies) (Keller 1992).

Table 22. Effect of fallow versus soybean on <sup>14</sup>C distribution M-score values for 0- to 89-cm and 46- to 89-cm soil depths in <sup>14</sup>C-metolachlor treated field lysimeters at 30 to 360 DAT (mean of 1988, 1989 and 1990)<sup>a</sup> (Keller 1992).

Surface cover	DAT <sup>b</sup>					
	30	60	90	120	180 <sup>c</sup>	360 <sup>c</sup>
0- to 89-cm depth						
Fallow	9.79a	16.51a	12.93a	12.77a	11.23a	8.53a
Soybean	8.48a	9.56b	9.79a	12.65a	9.13a	7.31a
46- to 89-cm depth						
Fallow	3.71a	11.35a	8.89a	8.95a	5.04a	5.19a
Soybean	2.75a	2.97b	4.63b	7.89a	6.07a	3.60a

<sup>a</sup>Within a column, means sharing the same letter are not significantly different, as determined by LSD (0.05).

<sup>b</sup>DAT = days after treatment.

<sup>c</sup>1990 only.

Sixty days after treatment, <sup>14</sup>C mobility in fallow lysimeters was greater than that in soybean lysimeters (Figure 18) and was verified by significantly different M-scores (Table 22). The difference in apparent <sup>14</sup>C mobility was related to a reduction in soil water content (Figure 13) and subsequent lower water movement through soil columns containing soybean with high demands for water (Figure 14). Fifty two and 65% of the radioactivity retained in fallow and soybean systems, respectively, was located in the upper 15 cm, while >3% and 0% of the applied <sup>14</sup>C in fallow and soybean lysimeters appeared below 68 cm, respectively.

<sup>14</sup>C distribution for both systems at 90 DAT were comparable (Figure 18) and resulted in nonsignificantly different M-scores for 0- to 89-cm (Table 22). <sup>14</sup>C levels in the bottom six depths of each column were distributed differently and resulted in significantly different M-scores (Table 22). Similar to the earlier sampling dates, 55 and 65% of the <sup>14</sup>C remaining in fallow and soybean lysimeters, respectively, was retained in the first two depths.

At 120 DAT, <sup>14</sup>C distribution in fallow and soybean lysimeters was similar and was reflected by nonsignificant M-scores (Figure 18; Table 22). This occurrence suggests that <sup>14</sup>C-metolachlor and/or metabolites were sorbed and were not available for movement in soil water. Even though water inputs (Table 7) and leachate from fallow lysimeters (Figure 14) were greater from 120 to 180 DAT than 90 to 120 DAT, lesser amounts of <sup>14</sup>C were detected in leachate from the former (Figure 17) which confirms sorption processes. At 120 DAT, 48 and 61% of the <sup>14</sup>C remaining in fallow and soybean lysimeters, respectively, was retained in the top 15 cm.

In 1990, M-scores for fallow and soybean lysimeters at 180 and 360 DAT were nonsignificantly different (Table 22) and were represented by comparable  $^{14}\text{C}$  distributions (Figure 19). Similar  $^{14}\text{C}$  distributions and soil water contents (Figure 15) in both systems led to comparable amounts of  $^{14}\text{C}$  in leachate (Figure 17) between 180 to 360 DAT. For both sampling dates, <2% of the applied  $^{14}\text{C}$  was detected below 57 cm (Figure 19). In 1988 and 1989, distributions of  $^{14}\text{C}$  in fallow lysimeters at 180 and 360 were similar to 1990 and are therefore not shown.

Effects of soybean versus fallow on leachate. Significant year by treatment interactions existed for most of the sampling dates, therefore cumulative leachate data are presented separately for each year (Figure 14).

For the three years, cumulative water inputs to lysimeters were similar for the first five column removal dates (Table 7) and as a result, cumulative leachate from fallow lysimeters were comparable at each time period (Figure 14). Beyond 180 DAT, water inputs varied for each year and resulted in 37 L being collected from fallow lysimeters in 1988, 30 L in 1989 and 24 L in 1990. At 360 DAT, cumulative leachate (11.5 L) from soybean systems (Figure 14) accounted for 29% of the water inputs in 1990.

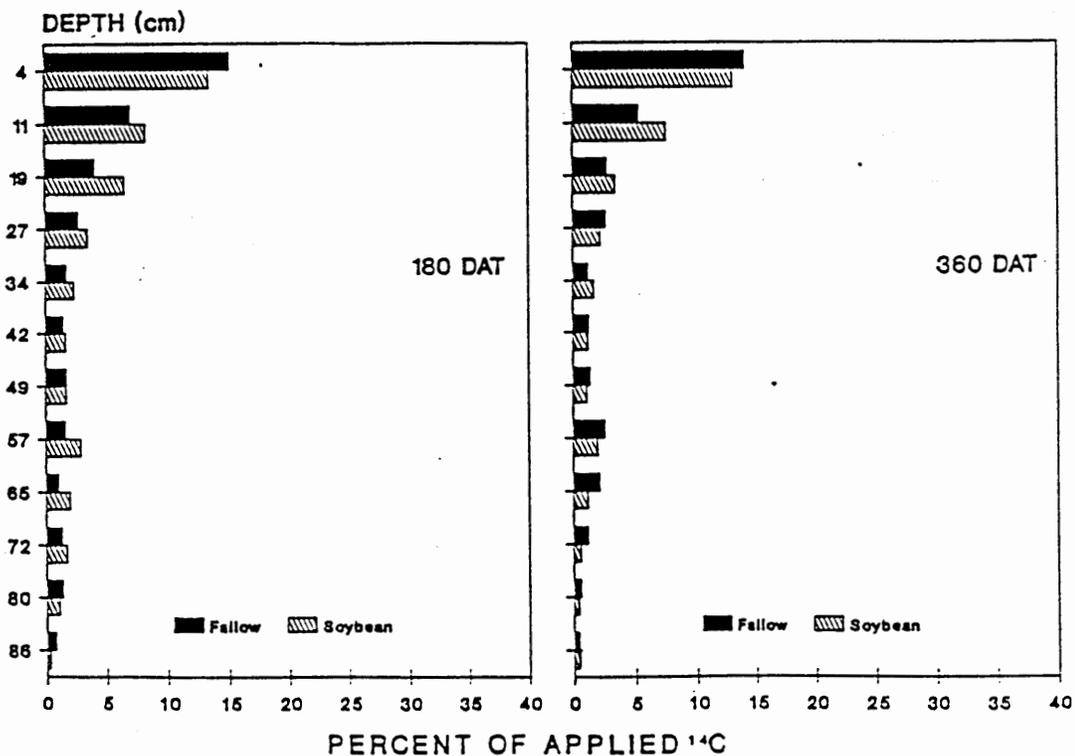


Figure 19.  $^{14}\text{C}$  distribution in  $^{14}\text{C}$ -metolachlor treated fallow and soybean field lysimeters at 180 and 360 DAT in 1990 (Keller 1992).

Fallow and soybean lysimeters were significantly different in cumulative leachate at each sampling date except at 30 DAT in 1989 (Figure 14). Also, the difference in leachate volume from date to date was higher in fallow systems, however, the difference in volume from 180 to 360 DAT in 1990 was equal for both lysimeters. Small differences in leachate volumes for the lysimeters were noted at 30 and 60 DAT, where demands for soil water by soybean were not as high as later dates. Differences in leachate volumes for both systems at 60 to 120 DAT were mirrored by soil water contents (Figure 13). Ratios of leachate volume from fallow and soybean column was in general agreement with studies performed by Kilmer et al. (1944). These researchers, using 91-cm diam. by 112-cm deep undisturbed cylindrical lysimeters, reported 6 to 10 times more percolate from fallow lysimeters than from lysimeters with corn.

Effects of soybean versus fallow on  $^{14}\text{C}$ -metolachlor in leachate. Excluding 30 DAT, year by treatment interactions existed at each lysimeter removal date for  $^{14}\text{C}$  in cumulative leachate; therefore data are presented separately for each year.

Leachate from fallow lysimeters in 1988 contained the greatest amount of radioactivity from  $^{14}\text{C}$ -metolachlor treatments (Figure 17). Since water inputs (Table 7) and leachate volumes (Figure 14) were similar for each study to 180 DAT, the high level of radioactivity in 1988 leachate was attributable to the amount of  $^{14}\text{C}$  present in the soil after 30 DAT (Figure 16). In 1988, the greatest increase in  $^{14}\text{C}$  in leachate from fallow lysimeters occurred between 60 and 90 DAT and 180 to 360 DAT, while, in 1989 and 1990, the greatest increase occurred between 90 to 120 DAT and 180 to 360 DAT in 1989 (Figure 17.) For all sampling dates, fallow and soybean lysimeters were significantly different in cumulative  $^{14}\text{C}$  as well as differences between dates; however, in 1990, equal amounts of  $^{14}\text{C}$  were detected for both systems at 180 to 360 DAT. At 360 DAT, cumulative leachate from fallow lysimeters contained 18% of the applied  $^{14}\text{C}$  in 1988, 14% in 1989, and 10% in 1990 (Figure 17). For the same time period, cumulative leachate from soybean lysimeters contained <2% of the applied  $^{14}\text{C}$ .

Data presented in Figure 17 does not adequately reflect the concentration and rate at which  $^{14}\text{C}$  moves through the lysimeters. The rate and concentration of  $^{14}\text{C}$  in leachate from lysimeters may best be depicted by breakthrough curves, where percent of applied  $^{14}\text{C}/\text{mL}$  is plotted against time (days) (Figure 20). Average maximum concentrations for fallow columns occurred at 83 Dat in 1988, 90 Dat in 1989, and 97 DAT in 1990. Peak concentrations for fallow lysimeters in 1989 and 1990 appeared about 34 d later than the peak concentrations for the nonreactive tracers, tritium and bromide, that were used in a study to be discussed later. Rate discrepancies for  $^{14}\text{C}$  and the tracers can be attributed to the sorptive behavior of  $^{14}\text{C}$ -metolachlor (Jordan and Harvey 1978, Obrigawitch et al. 1981, Weber and Peter 1982, Peter and Weber 1985). The "tailing" that is present after peak concentrations is probably due to adsorption-desorption processes (Wendt 1987 and  $^{14}\text{C}$ -metolachlor and/or metabolite exudates from microbial biomass (Liu et al. 1989). Some investigators, using soil columns, have reported that intraaggregation diffusion of the herbicides, 2,4,5-T and picloram, contributed to a "tailing" of the concentration in the effluent (Davidson and Chang 1972; Van Genuchten et al. 1977). Peak concentrations for soybean columns in 1988 and 1989 were insignificant and therefore are not shown, however, in 1990, a small peak occurred at 263 DAT (Figure 20).

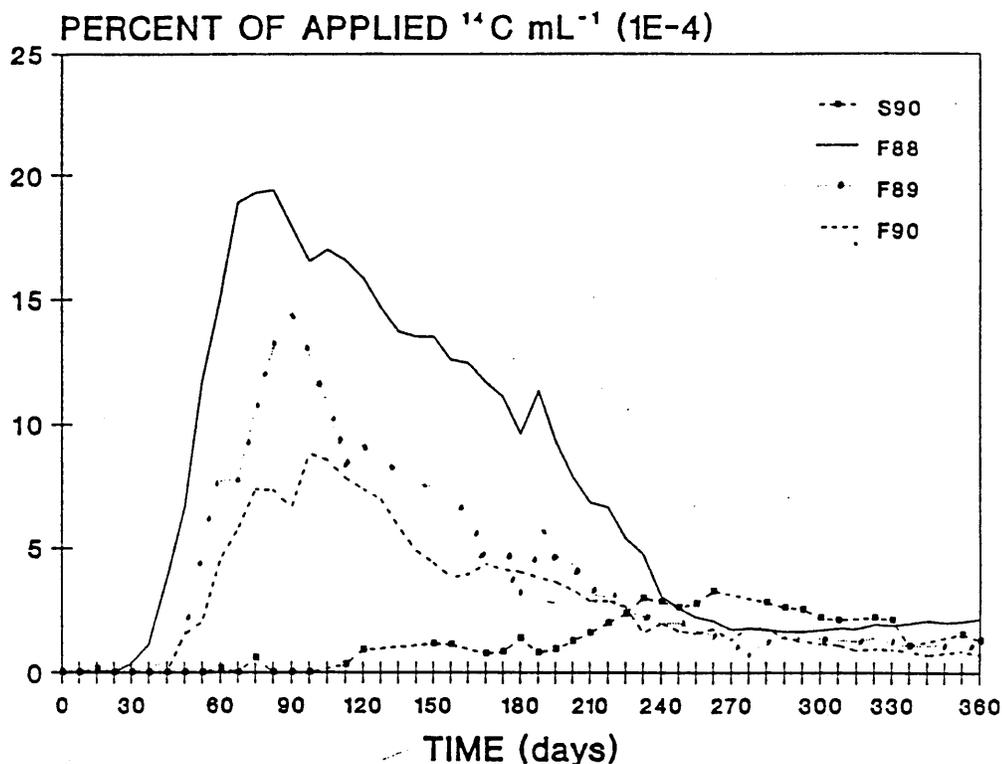


Figure 20. <sup>14</sup>C concentrations in leachate from <sup>14</sup>C-metolachlor treated fallow and soybean field lysimeters at 0 to 360 DAT in 1988, 1989 and 1990 (soybean lysimeters in 1990, S90; fallow lysimeters in 1988, F88; 1989, F89; 1990, F90) (Keller 1992).

Parent and metabolites were determined in leachate containing 100 dpm/mL. Results from composite samples over 7 d are presented in Figures 21 and 22 for fallow and soybean systems, respectively. For each year, in the earlier sampling periods, metabolite 1 constituted the largest percentage of radioactivity in leachate from fallow systems (Figure 21). Since the TLC plates used in this study were silica based; in theory then, polar compounds should be preferentially adsorbed with the most polar being retained near the application zone, therefore, metabolite 1 was the most polar ( $R_f=0.30$ ) of the radiolabeled compounds. The more polar nature of metabolite 1 probably led to an increased water solubility and mobility. Over time, metabolite 1 decreased while metabolite 2 ( $R_f=0.43$ ) increased. This occurrence suggests that metabolite 2 was less mobile or that metabolite 2 was formed from metabolite 1. Metabolites detected in leachate were most likely formed in the upper 5-cm of the soil profile, the region with the most biological activity. Miller (1992) using a Dothan soil under sterile and nonsterile laboratory conditions, found out of 4 depths down to 74-cm, that metolachlor was degraded only in the nonsterile 0- to 5-cm depth with 2 metabolites being produced. Similarly, Pothuluri et al. (1990), using a Coastal Plain soil under laboratory conditions, showed that degradation rates for alachlor, a related chloracetamide, decreased with depth, and that degradation was very slow in the subsoil. In general, the percentage of metolachlor reached peak levels between 240 and 300 DAT (Figure 21.) Metolachlor was the least polar ( $R_f=0.81$ ) of the radiolabeled compounds determined by TLC and therefore, would predict it to be the least mobile of the <sup>14</sup>C compounds. Also, between these time periods, cooler soil temperatures existed (Figure 4) which would have reduced microbial degradation of metolachlor (Bouchard et al. 1982, Zimdahl

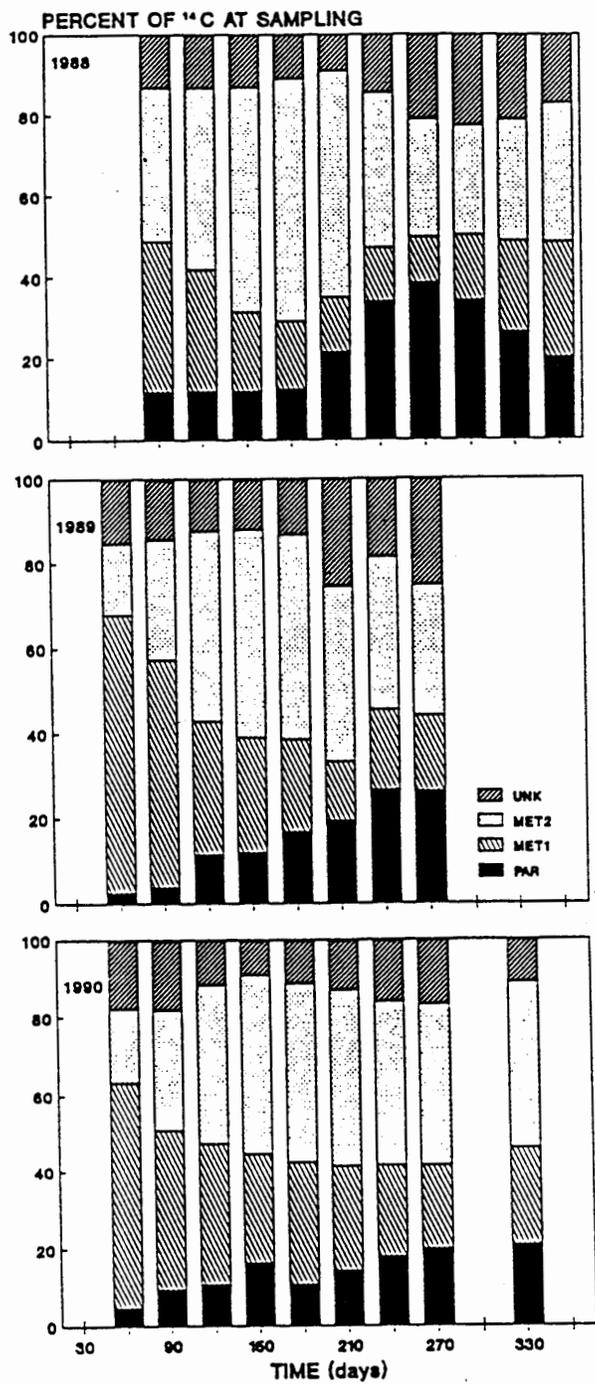


Figure 21. Composition of <sup>14</sup>C in leachate from <sup>14</sup>C-metolachlor treated fallow field lysimeters at 30 to 360 DAT in 1988, 1989 and 1990 (Keller 1992).

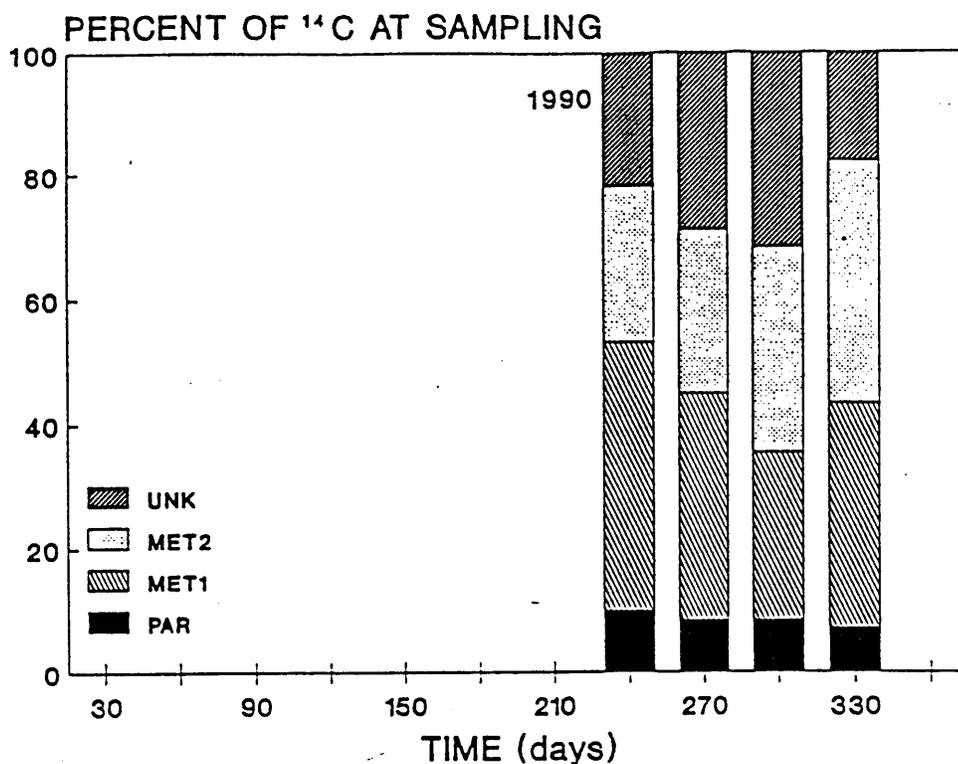


Figure 22. Composition of <sup>14</sup>C in leachate from <sup>14</sup>C-metolachlor treated soybean field lysimeters at 30 to 360 DAT in 1990 (Keller 1992).

and Clark 1982, Walker and Brown 1985). Reduced microbial degradation would sustain <sup>14</sup>C-metolachlor levels and would therefore make <sup>14</sup>C-metolachlor a large contributor to the <sup>14</sup>C pool. The number of metabolites detected in this study is in agreement with Alhajjar et al. (1990) who reported two to six metabolites of metolachlor in leachate from disturbed soil columns, however, at least 19 metabolites are possible in soil and soil cultures (Chesters et al. 1989).

Beyond 240 DAT in 1990, the composition of <sup>14</sup>C in leachate from lysimeters with soybean was similar to that of fallow lysimeters at the earlier sampling periods (Figures 21 and 22). This occurrence was probably due to delayed movement of <sup>14</sup>C in the soybean column that had been in the lower depths at 30 DAT. <sup>14</sup>C compositions were assumed to be equal for both columns at 30 DAT (Figure 18) and therefore, after 30 DAT, radioactivity in the lower depths of soybean lysimeters remained stationary due to reduction in soil water and effluent (Figures 13 and 14). After 180 DAT (soybean maturity), soil water contents were equal for both systems (Figure 15). Between 180 and 240 DAT, cumulative leachate from soybean lysimeters was 85% of the leachate volume from fallow systems at 30 to 90 DAT (not shown), so, conceivably <sup>14</sup>C composition from soybean lysimeters at 240 DAT was similar to the <sup>14</sup>C composition in the lower depths at 30 DAT. The "unknown" shown in Figures 21 and 22 is the radioactivity that did not chromatograph into distinct peaks. Generally, this component did not contribute to a large fraction of the <sup>14</sup>C.

Metolachlor concentration in leachate from fallow and soybean lysimeters was derived from data presented in Figures 20, 21, and 22. Metolachlor

concentration as  $\mu\text{g/L}$  was plotted against time (days) and is shown in Figure 23. Leachate in 1988 contained the highest concentration of metolachlor for the three years. Since water inputs to 180 DAT were similar for the three years (Table 7), differences in concentration are probably related to the levels of  $^{14}\text{C}$  in the lysimeters at 30 DAT (Figure 16). Peak concentrations of metolachlor in leachate from fallow lysimeters occurred at 120 DAT in 1988 ( $13 \mu\text{g/L}$ ) and 1989 ( $9 \mu\text{g/L}$ ) and at 90 DAT in 1990 ( $7 \mu\text{g/L}$ ), while consistent levels ( $<2 \mu\text{g/L}$ ) were detected from soybean lysimeters after 240 DAT in 1990 (Figure 23). Constant levels of metolachlor in the leachate are probably associated with adsorption-desorption processes and microbial exudates. All levels of metolachlor were well below the National Health Advisory level of  $100 \mu\text{g/L}$  in drinking water (USEPA 1989), however, these levels are much higher than those ( $0.1\text{-}0.4 \mu\text{g/L}$ ) detected in groundwater in Iowa and Pennsylvania (Cohen et al. 1986).

Effects of soybean versus fallow on  $^{14}\text{C}$ -metolachlor dissipation. A mass-balance approach was used to distinguish the dissipation pathways of  $^{14}\text{C}$ -metolachlor in fallow and soybean lysimeters. Since many year by treatment interactions existed for some of the  $^{14}\text{C}$  measurements, data for the mass-balance approach are presented separately for each year (Tables 23, 24, and 25). The 1990 data (Table 25) does not differ significantly from that for metolachlor in the three herbicide comparison study (Table 15).

At 30 DAT, averaged over both lysimeters (fallow and soybean), 28, 35, and 43% of the applied  $^{14}\text{C}$  in 1988, 1989 and 1990, respectively, was lost through volatilization of herbicide and/or metabolites or as  $^{14}\text{CO}_2$  (Tables 23, 24, and 25). The absence of  $^{14}\text{C}$  below 72 cm depths at 30 DAT confirms the loss of  $^{14}\text{C}$  through volatilization (Figure 18). Very little additional  $^{14}\text{C}$  was lost as vapor between 30 and 90 DAT in 1988 and 1989, (Tables 23 and 24, respectively); however, an additional 15% of the applied  $^{14}\text{C}$  was lost in 1990 (Table 25). Beyond 90 DAT for each year,  $^{14}\text{C}$  lost to the atmosphere was insignificant (Tables 22 to 24). Insignificant loss of  $^{14}\text{C}$  indicates that  $^{14}\text{C}$ -labeled metolachlor and/or by-products were adsorbed to soil colloids and were no longer available for volatilization.

The literature supports vapor losses of metolachlor after application. Although greenhouse lysimeter studies showed metolachlor volatilization from soil to be  $<0.01\%$  after 11 wk (Alhajjar et al. 1990), Parochetti (1978) reported that 0.1% of the applied metolachlor was lost from the soil surface after 8 d in greenhouse pot studies. Parochetti also noted that 17 and 53% of the applied metolachlor was lost from straw and glass, respectively. Streck and Weber (1982) reported that under greenhouse conditions, 38 and 19% of applied metolachlor was lost in 7 d from grass and straw, respectively. The researchers attributed the loss to volatilization.

Alachlor, a related chloracetamide herbicide, which has a similar vapor pressure to that of metolachlor (WSSA 1989) was volatilized from a fallow soil in eastern Maryland (Glotfelty et al. 1989). The researchers reported that 19% of the alachlor was lost through volatilization within 24 d after application. In addition, Beestman and Deming (1974) found under laboratory conditions that 50% of the applied alachlor was volatilized from a wet soil (10% clay, 1% organic carbon) within 12 d after application. Similarly, Hargrove and Merkle (1971) reported that 10 to 30% of alachlor applied to air-dry soil in closed systems at  $38^\circ\text{C}$  and relative humidities of 79 to 100%, volatilized within 48 h.

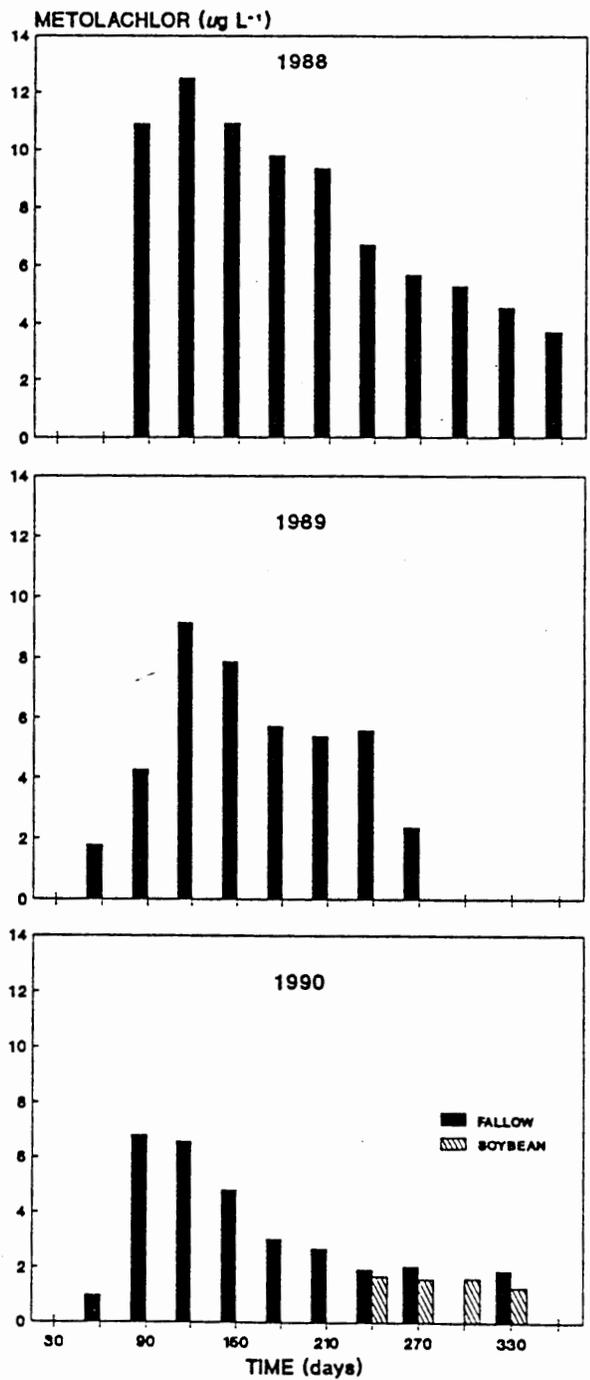


Figure 23. Concentration of metolachlor in leachate from  $^{14}\text{C}$ -metolachlor treated fallow and soybean-field lysimeters at 30 to 360 DAT in 1988, 1989 and 1990 (Keller 1992).

Table 23<sup>a</sup>. Mass balance distribution of <sup>14</sup>C-metolachlor in 0- to 7.6-cm zone at 30 to 90 DAT in fallow and soybean field lysimeters in 1988 (Keller 1992).

Distribution	Days after treatment					
	30		60		90	
	Fallow	Soybean	Fallow	Soybean	Fallow	Soybean
Volatilization <sup>a</sup>	25.93	30.41	28.25	29.31	26.96	36.58
	----- (% of applied <sup>14</sup> C) -----					
Plant uptake						
Top growth		0.54		2.99		5.76
Roots				0.77		1.19
Soil (Ext) <sup>b</sup>	8.90	11.09	2.42	3.12	2.55	2.33
0- to 7.6-cm						
Metolachlor	8.00	9.57	2.06	2.54	2.15	1.87
Metabolite 1	0.16	0.28	0.05	0.11	0.08	0.07
Metabolite 2	0.37	0.64	0.09	0.17	0.08	0.13
Unknown	0.37	0.60	0.22	0.30	0.24	0.26
Bound <sup>c</sup>	25.46	25.46	19.27	24.27	22.02	20.15
Subsurface (7.6- to 89-cm)	39.69	32.50	45.36	39.52	35.88	33.96
Leachate	0.02	0.00	4.70	0.02	12.59	0.03
Total	100.00	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 23<sup>b</sup>. Mass balance distribution of <sup>14</sup>C-metolachlor in 0- to 7.6-cm zone at 120 to 360 DAT in fallow and soybean field lysimeters in 1988 (Keller 1992).

Distribution	Days after treatment					
	120		180		360	
	Fallow	Soybean	Fallow	Soybean	Fallow	Soybean
Volatilization <sup>a</sup>	32.58	38.83	27.76	ND	32.31	ND
	----- (% of applied <sup>14</sup> C) -----					
Plant uptake						
Top growth		0.80		ND		ND
Roots		0.34		ND		ND
Beans		0.02		ND		ND
Soil (Ext) <sup>b</sup>	1.60	2.07	2.39	ND	1.81	ND
0- to 7.6-cm						
Metolachlor	1.37	1.73	2.09	ND	1.55	ND
Metabolite 1	0.03	0.06	0.06	ND	0.04	ND
Metabolite 2	0.04	0.07	0.05	ND	0.03	ND
Unknown	0.16	0.21	0.19	ND	0.19	ND
Bound <sup>c</sup>	16.17	18.75	16.95	ND	13.97	ND
Subsurface (7.6- to 89-cm)	36.27	38.97	38.50	ND	33.68	ND
Leachate	13.38	0.22	14.40	ND	18.33	ND
Total	100.00	100.00	100.00	100.00	100.00	ND

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 24<sup>a</sup>. Mass balance distribution of <sup>14</sup>C-metolachlor in 0- to 7.6-cm zone at 30 to 90 DAT in fallow and soybean field lysimeters in 1989 (Keller 1992).

Distribution	Days after treatment					
	30		60		90	
	Fallow	Soybean	Fallow	Soybean	Fallow	Soybean
Volatilization <sup>a</sup>	38.37	32.57	36.16	37.12	46.91	38.98
Plant uptake						
Top growth		0.99		5.10		2.49
Roots				0.44		0.40
Soil (Ext) <sup>b</sup>	6.89	8.18	3.60	3.09	2.20	2.29
0- to 7.6-cm						
Metolachlor	5.64	6.74	2.79	2.62	1.93	1.90
Metabolite 1	0.33	0.39	0.16	0.09	0.04	0.07
Metabolite 2	0.48	0.60	0.29	0.10	0.05	0.07
Unknown	0.44	0.45	0.36	0.28	0.18	0.25
Bound <sup>c</sup>	20.69	25.72	23.04	22.29	18.51	22.06
Subsurface (7.6- to 89-cm)	34.05	32.50	36.39	-31.94	29.91	33.64
Leachate	0.00	0.04	0.81	0.02	2.47	0.14
Total	100.00	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 24<sup>b</sup>. Mass balance distribution of <sup>14</sup>C-metolachlor in 0- to 7.6-cm zone at 120 to 360 DAT in fallow and soybean field lysimeters in 1989 (Keller 1992).

Distribution	Days after treatment					
	120		180		360	
	Fallow	Soybean	Fallow	Soybean	Fallow	Soybean
Volatilization <sup>a</sup>	43.76	43.68	44.34	ND	47.69	ND
Plant uptake						
Top growth		1.69		ND		ND
Roots		0.57		ND		ND
Beans		0.06		ND		ND
Soil (Ext) <sup>b</sup>	1.58	1.83	1.39	ND	0.82	ND
0- to 7.6-cm						
Metolachlor	1.33	1.53	1.21	ND	0.64	ND
Metabolite 1	0.04	0.06	0.30	ND	0.04	ND
Metabolite 2	0.03	0.07	0.02	ND	0.03	ND
Unknown	0.18	0.17	0.13	ND	0.11	ND
Bound <sup>c</sup>	16.53	22.18	17.60	ND	13.16	ND
Subsurface (7.6- to 89-cm)	31.05	28.92	27.36	ND	24.01	ND
Leachate	7.08	1.07	9.31	ND	14.32	ND
Total	100.00	100.00	100.00	100.00	100.00	ND

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 25<sup>a</sup>. Mass balance distribution of <sup>14</sup>C-metolachlor in 0- to 7.6-cm zone at 30 to 90 DAT in fallow and soybean field lysimeters in 1990 (Keller 1992).

Distribution	Days after treatment					
	30		60		90	
	Fallow	Soybean	Fallow	Soybean	Fallow	Soybean
Volatilization <sup>a</sup>	39.84	45.91	48.22	48.82	60.03	56.35
Plant uptake						
Top growth		0.41		3.62		3.34
Roots				0.87		1.28
Soil (Ext) <sup>b</sup> 0- to 7.6-cm	8.85	6.77	1.75	1.79	0.97	0.90
Metolachlor	7.97	5.46	1.45	1.44	0.81	0.74
Metabolite 1	0.36	0.42	0.08	0.07	0.03	0.02
Metabolite 2	0.28	0.53	0.05	0.04	0.03	0.03
Unknown	0.24	0.36	0.17	0.24	0.10	0.11
Bound <sup>c</sup>	26.76	24.93	18.72	17.02	14.67	14.23
Subsurface (7.6- to 89-cm)	24.55	21.98	30.80	27.88	22.97	23.90
Leachate	0.00	0.00	0.51	0.00	1.36	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

Table 25<sup>b</sup>. Mass balance distribution of <sup>14</sup>C-metolachlor in 0- to 7.6-cm zone at 120 to 360 DAT in fallow and soybean field lysimeters in 1990 (Keller 1992).

Distribution	Days after treatment					
	120		180		360	
	Fallow	Soybean	Fallow	Soybean	Fallow	Soybean
Volatilization <sup>a</sup>	58.26	54.23	52.42	53.29	54.78	62.22
Plant uptake						
Top growth		1.21		0.47		0.48 <sup>d</sup>
Roots		1.39		0.48		0.15
Beans				0.02		0.03 <sup>d</sup>
Soil (Ext) <sup>b</sup> 0- to 7.6-cm	0.90	0.74	0.66	0.55	0.52	0.57
Metolachlor	0.75	0.58	0.51	0.44	0.36	0.42
Metabolite 1	0.03	0.02	0.02	0.01	0.03	0.03
Metabolite 2	0.03	0.03	0.02	0.01	0.02	0.02
Unknown	0.09	0.11	0.11	0.09	0.11	0.10
Bound <sup>c</sup>	14.79	14.81	14.55	12.98	13.63	12.57
Subsurface (7.6- to 89-cm)	20.78	27.62	24.73	32.07	21.52	21.95
Leachate	5.27	0.00	7.64	0.14	9.55	2.03
Total	100.00	100.00	100.00	100.00	100.00	100.00

<sup>a</sup>Vapor losses of parent herbicide, metabolites, or <sup>14</sup>CO<sub>2</sub>.

<sup>b</sup>Extractable with methanol.

<sup>c</sup>Unextractable with methanol, 0- to 7.6-cm depth.

<sup>d</sup>Removed at 180 d.

Pendimethalin, a herbicide which has a similar vapor pressure to that of metolachlor (WSSA 1989), has been shown to be volatile when applied to turf (Cooper et al. 1990). The researchers reported that 4.8 and 13% of pendimethalin applied to Kentucky bluegrass (*Poa pratensis* L.) was volatilized after the first 24 h and 5 d, respectively.

Metolachlor, alachlor and pendimethalin have been detected in rainwater in Indiana, Ohio, New York and West Virginia (Richards et al. 1987) and Iowa (Nations and Hallberg 1992). Furthermore, metolachlor and alachlor concentrations in rainfall reached their maxima in events immediately following applications.

The amount of  $^{14}\text{CO}_2$  produced from soil treated with  $^{14}\text{C}$ -metolachlor is generally very low. Bailey and Coffey (1986) and LeBaron et al. (1988) found that during a 12 wk period in soil under laboratory conditions, 4.8% of the  $^{14}\text{C}$ -metolachlor was released as  $^{14}\text{CO}_2$ . Similarly, Miller (1992) using Dothan soil under laboratory conditions, found that only 0.3 and 1.6% of the  $^{14}\text{C}$ -metolachlor was liberated as  $^{14}\text{CO}_2$  after 4 and 22 wk, respectively. On the other hand, after 28 d within a soil perfusion system, the evolved  $^{14}\text{CO}_2$  from a soil previously treated with metolachlor for 5 yr, accounted for 18.4% of the added  $^{14}\text{C}$ -metolachlor (Liu et al 1988). The same researchers also found that the amount of  $^{14}\text{CO}_2$  produced from soil taken from the same field that had no history of metolachlor use, accounted for only 3.5% of the applied  $^{14}\text{C}$ -metolachlor.

The total accumulated  $^{14}\text{C}$  present in the various plant parts is presented in Tables 23 to 25. Maximum plant uptake of  $^{14}\text{C}$  occurred at 60 DAT in 1989 and 90 DAT in 1988 and 1990. These differences are probably related to  $^{14}\text{C}$  availability and/or stress conditions which may have influenced plant uptake. The reduction of  $^{14}\text{C}$  in the plant over time was probably due to the loss of water-soluble metabolites (LeBaron et al. 1988). The loss of  $^{14}\text{C}$  from the plant over time may have contributed to increased levels of soil  $^{14}\text{C}$  at the later sampling dates (Figure 16). For all years, plant uptake constituted <7% of the applied  $^{14}\text{C}$  and was in general agreement to other confined studies (Best and Weber 1974, Fuhr 1985, Fermanich and Daniel 1991).

For the three year period, on the day of application 5 to 8% of the  $^{14}\text{C}$ -labeled metolachlor (97% pure) applied to the 0- to 7.6-cm depth was nonextractable in methanol (not shown). This was probably due to the closure of adsorptive sites upon air-drying the soil prior to extraction. For the other sampling periods, there was no influence of air-drying on  $^{14}\text{C}$  extraction.

At 30 DAT, 7 to 11% of the  $^{14}\text{C}$  applied to the 0- to 7.6-cm zone was extractable with methanol (Tables 23, 24 and 25). For each year at 30 DAT, parent metolachlor constituted >80% of the extractable  $^{14}\text{C}$ , while two polar metabolites made-up the balance. These were the same metabolites found in leachate. This is in agreement with Miller (1992) who detected two metabolites in the 0- to 5- cm depth of a Dothan soil. TLC procedures used in this study made it impossible to correlate the metabolites produced in this study to the metabolites observed by other researchers (McGahen and Tiedje 1978, Liu et al. 1988, 1991).

The amount of extractable parent and metabolites declined with time (Tables 23, 24 and 25. Averaged over years and lysimeters, metolachlor concentrations

were 2.15% of the applied  $^{14}\text{C}$  at 60 DAT, 1.57% at 90 DAT, 1.22% at 120 DAT, 1.06% at 180 DAT, and 0.74% at 360 DAT. Accordingly, metabolite levels also decreased with time. Since bound  $^{14}\text{C}$  did not increase with time, low quantities of extractable metabolites indicate that metolachlor was not present or degraded or that the metabolites leached out of the 0- to 7.6-cm depth.

Fallow and soybean lysimeters contained contrasting amounts of  $^{14}\text{C}$  in the subsurface (7.6- to 89-cm) (Tables 23, 24, and 25). Differences in  $^{14}\text{C}$  in the subsurface were due to increased soil water contents in fallow lysimeters which provided a vehicle for  $^{14}\text{C}$  movement to the subsurface. Typically, levels of  $^{14}\text{C}$  in the subsurface of fallow lysimeters peaked at 60 DAT with a resulting decline of  $^{14}\text{C}$  being leached below 89-cm. Subsurface  $^{14}\text{C}$  in soybean systems was inconsistent from year to year, suggesting  $^{14}\text{C}$  was mobile in both vertical directions. Very little  $^{14}\text{C}$  was detected below 89-cm, however, supporting capillary movement upward of  $^{14}\text{C}$ .

Data presented in Tables 23, 24, and 25 indicate that the observed decrease of  $^{14}\text{C}$ -labeled metolachlor in the 0- to 7.6-cm depth was the result of several dissipating processes. These processes in decreasing order, were: volatilization of herbicides, metabolites, and/or  $^{14}\text{CO}_2$ ; > subsurface (leaching) > bound (adsorption) > nonvolatile metabolites (degradation).

#### Movement and dissipation of tritium, bromide and $^{14}\text{C}$ -metolachlor in the soil.

At 30, 60, 90, and 120 DAT in 1989, significantly different amounts of total radioactivity were recovered in fallow lysimeters treated with  $^{14}\text{C}$ -metolachlor and tritium (Figure 24). Recovery of tritium and  $^{14}\text{C}$  in soil declined with time and was an indication of vapor and leaching losses. Total recovery of  $^{14}\text{C}$  in soil was 62% of the applied at 30 d, 63 at 60 d, 51 at 90 d, and 49 at 120 d, while recovery of tritium was 36, 24, 6 and 0.25% for the same time periods. Adding the recoveries of tritium in leachate and soil and averaging the four sampling dates, 59% of the applied tritium (1.5 out of 2.54 cm tritium) evaporated within 30 DAT. On the other hand, only 38% of the applied  $^{14}\text{C}$  was lost to the atmosphere for the same time period. The disparity in radioactivity lost to the atmosphere can be attributed to differing vapor pressures and soil sorptive tendencies of water and metolachlor. At 20° C, water, in this case tritium, has a vapor pressure  $1.38 \times 10^6$  times greater than that of metolachlor (WSSA 1989, Weast et al. 1990).

As previously mentioned, within 30 DAT, 38% of the applied  $^{14}\text{C}$  was lost through volatilization of herbicide and/or metabolites or as  $^{14}\text{CO}_2$  (Figure 24). Absence of  $^{14}\text{C}$  below the 80 cm depth (Figure 25) or in leachate (Figure 24) at 30 DAT confirms vapor loss of  $^{14}\text{C}$ . Very little additional  $^{14}\text{C}$  was lost as vapor between 30 and 60 DAT, however, an additional 6 to 9% of the applied  $^{14}\text{C}$  was lost after 60 d.

$^{14}\text{C}$  and tritium distribution by mean soil depth at 30, 60, 90, and 120 d after application is shown in Figure 25. As expected, movement of the sorbing  $^{14}\text{C}$ -metolachlor and/or metabolite(s) in fallow lysimeters at 30 DAT was retarded relative to tritiated water. As anticipated, piston flow was negated by diffusion and more predominantly, by hydrodynamic dispersion processes (Hillel 1982) which resulted in a symmetrical distribution of tritium at 30 DAT (Figure 26). For this time period, 17 cm of cumulative water inputs (Table 7) displaced the tritium peak downward about 65 cm in 1989. Eighty-five percent of the tritiated water was at 49 to 72 cm, while 75% of the  $^{14}\text{C}$  was retained

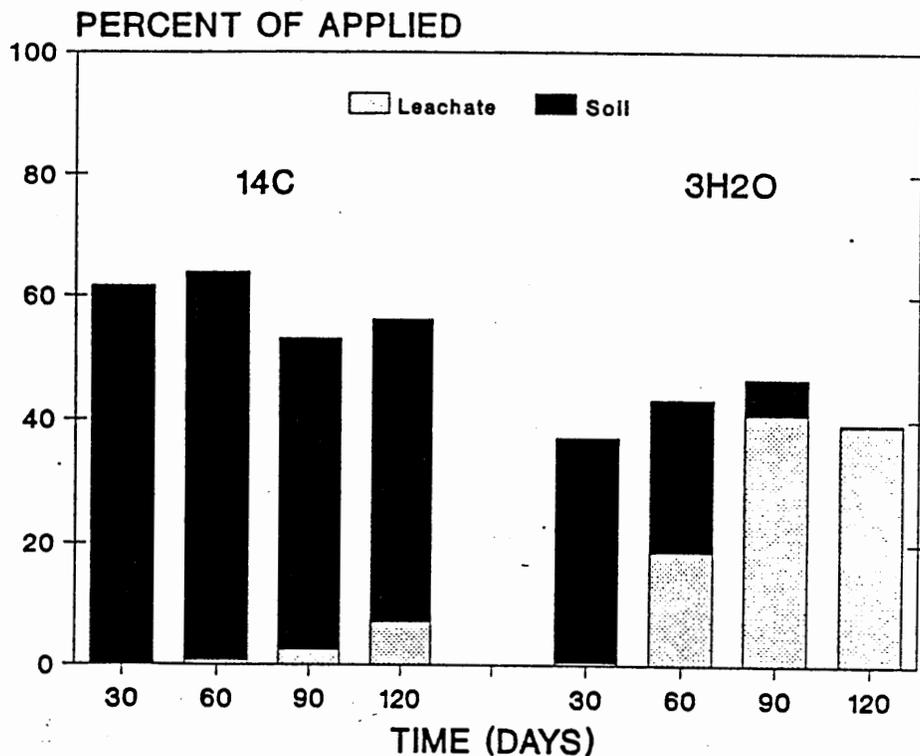


Figure 24. Percent of the applied <sup>14</sup>C and tritium recovered in cumulative leachate and soil in <sup>14</sup>C-metolachlor and tritium treated fallow lysimeters at 30 to 120 DAT in 1989 (Keller 1992).

in the first 3 depths (Figure 25). Sixty days after treatment, <sup>14</sup>C continued to be retained in the upper three depths; however, both radiolabeled peaks were displaced downward 12 cm. From 30 to 60 DAT in 1989, 13 cm of cumulative water (Table 7) was introduced to the lysimeters which resulted in the downward displacement of both peaks. It is interesting to note that both radiolabeled peaks were displaced to greater depths in the first 30 d, while only displaced an additional 12 cm at 30 to 60 d. The disparity in peak velocities for the sampling dates can be attributed to soil texture and the related  $K_{sat}$ , macroporosity (Table 2) and soil water contents. During the first 30 d, the tritium peak moved downward through more predominate loamy sand textures, while from 30 to 60 d it moved through sandy clay loam textures. Calculated velocities for the tritium peak were 2.17 cm/d for the first 30 d and 0.37 cm/d for the next 30 d. At 60 DAT, peak concentrations in the subsoil were 5 and 7% of the applied <sup>14</sup>C and tritium, respectively (Figure 25).

Ninety days after treatment, 89% of the tritium remaining in the soil profile was located below 72 cm, while a large percentage of the <sup>14</sup>C continued to be located in the first 3 depths (Figure 25). The apparent distribution of tritium in the subsoil, with a maximum concentration of 2% of the applied radioactivity, is the tail of the moving front which was present at 30 and 60 d. The <sup>14</sup>C pulse at the 65 cm depth at 60 DAT was no longer present at 90 DAT

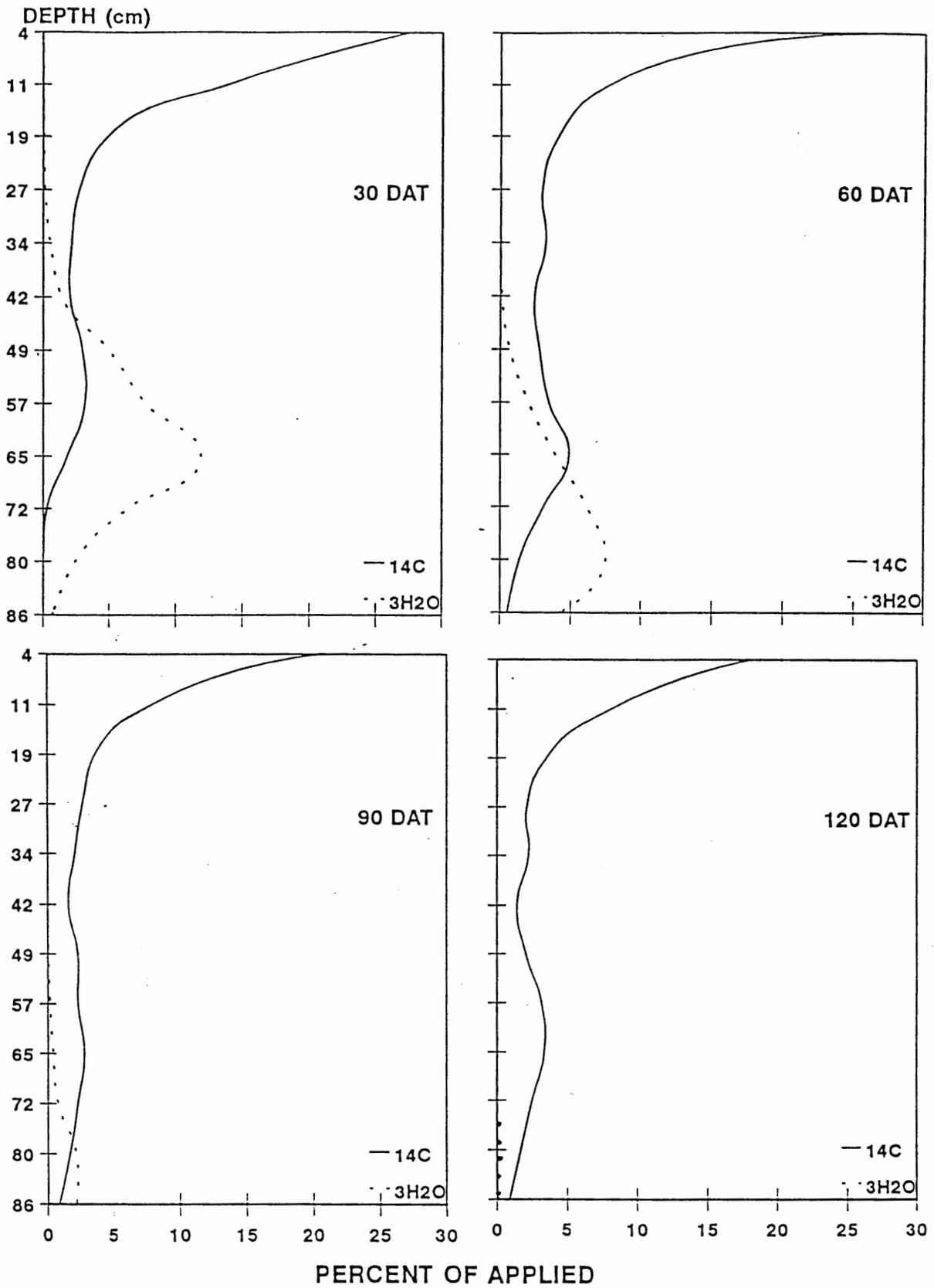


Figure 25.  $^{14}\text{C}$  and tritium distribution in  $^{14}\text{C}$ -metolachlor and tritium treated fallow field lysimeters at 30 to 120 DAT in 1989 (Keller 1992).

and was correspondingly eluted from the column. The elution of the  $^{14}\text{C}$  front at or just prior to 90 d is quite apparent as shown by the breakthrough curve in Figure 26.

At 120 DAT, tritium was still detected in the subsoil, however, the total amount detected was  $<0.25\%$  of the applied (2 mL) (Figures 25 and 26). Remaining radioactivity may be due to immobile water (Van Genuchten and Wierenga 1977, De Smedt et al. 1986), sorption (Stewart 1972, Van de Pol et al. 1977, Nkedi-Kizza et al. 1982) or isotopic exchange (Stewart and Baker 1973). Stewart and Baker (1973) note that 2% of the hydroxyl groups in kaolinite, a prominent clay mineral in Ultisols, exchanged with tritium. The retention of tritium and/or tritiated water in the subsoil had a slight effect on the symmetrical breakthrough curve that will be discussed later.

Movement of tritium, bromide and  $^{14}\text{C}$ -metolachlor in leachate. As previously mentioned, leachate or percolation accounted for 45 to 60% of the water inputs to fallow lysimeters treated with tritium and  $^{14}\text{C}$ -metolachlor (Table 10). In this leachate, significantly more tritium was detected at 60 to 120 DAT (Figure 24). This occurrence was expected and reflects the mobility and distribution of tritium and  $^{14}\text{C}$  in the soil profile (Figure 25).

At 30 DAT, no  $^{14}\text{C}$  was detected in leachate, while  $<1\%$  of the applied tritium was collected (Figure 24). Total recovery of  $^{14}\text{C}$  in cumulative leachate was 1% of the applied at 60 d, 2% at 90 d, and 7% at 120 d, while recovery of tritium was 19, 41, and 40% for the same time periods, respectively.

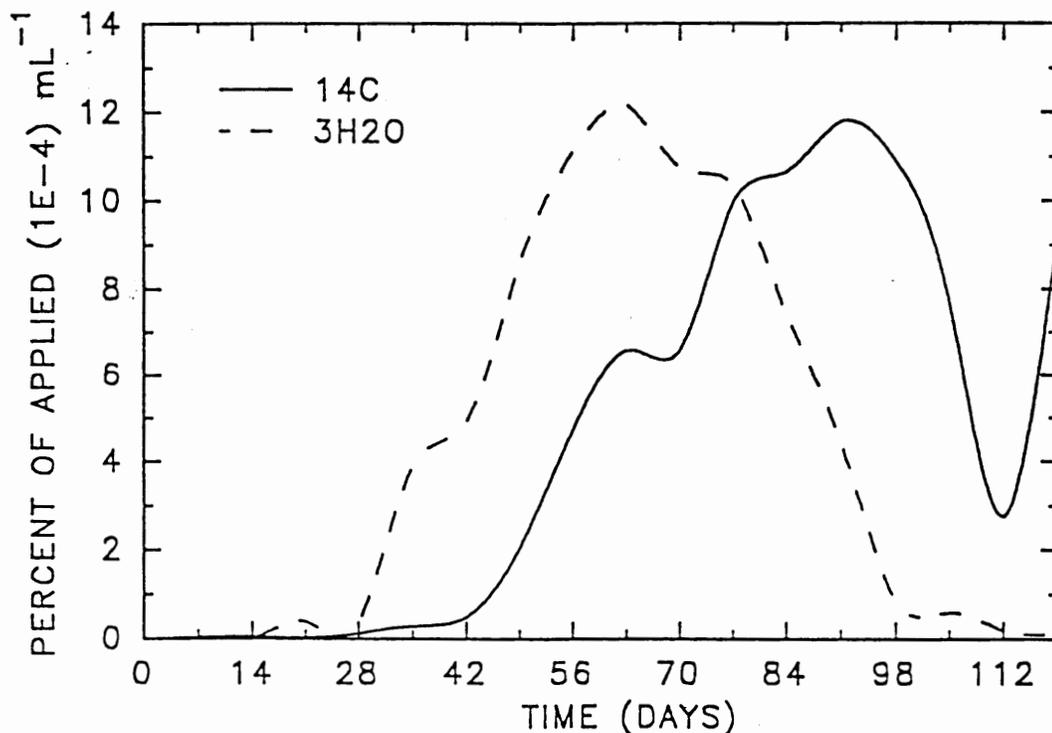


Figure 26. Breakthrough curves of  $^{14}\text{C}$  and tritium in leachate with time from  $^{14}\text{C}$ -metolachlor and tritium treated fallow field lysimeters in 1989. (Concentration of tritium reduced by a factor of 10 for comparative purposes) (Keller 1992).

The manner in which the concentration of a solute, in this case radioactivity, changes in leachate and not total solute, provides information about the soil profile and the behavior of the fluids moving through the profile. A breakthrough curve (BTC) allows for the assessment in concentration changes of a solute(s) in the leachate from a lysimeter. For this study, a breakthrough curve is a plot of the concentration (percent of applied/mL) versus the number of pore volumes of leachate collected or time. As stated earlier, pore volume was determined from soil water contents at field capacity.

BTCs for displacement of  $^{14}\text{C}$ -metolachlor and/or metabolites and tritium through fallow lysimeters are shown in Figures 26 and 27. Mean tritium and  $^{14}\text{C}$  concentrations and pore volumes were calculated from 8 lysimeters ( $n=8$ ) to 30 d, 6 to 60 d, 4 to 90 d, and 2 at 120 d. These time periods were equivalent to 0.5, 1.0, 1.4, and 2.1 pore volumes of leachate, respectively. Over the 120 d study, coefficients of variation (CV) for tritium and  $^{14}\text{C}$  concentration in 25 leachate collections, ranged from 10 to 104 and 17 to 283%, respectively, with an overall average CV of 58% for tritium and 120% for  $^{14}\text{C}$ . It is not surprising to observe the large range of CVs in this study because both radiolabeled compounds are susceptible to vapor loss, sorption and other dissipation processes. Large CVs for solute concentrates in soils have been reported (Starr et al. 1986, Agus and Cassel 1992) and estimated

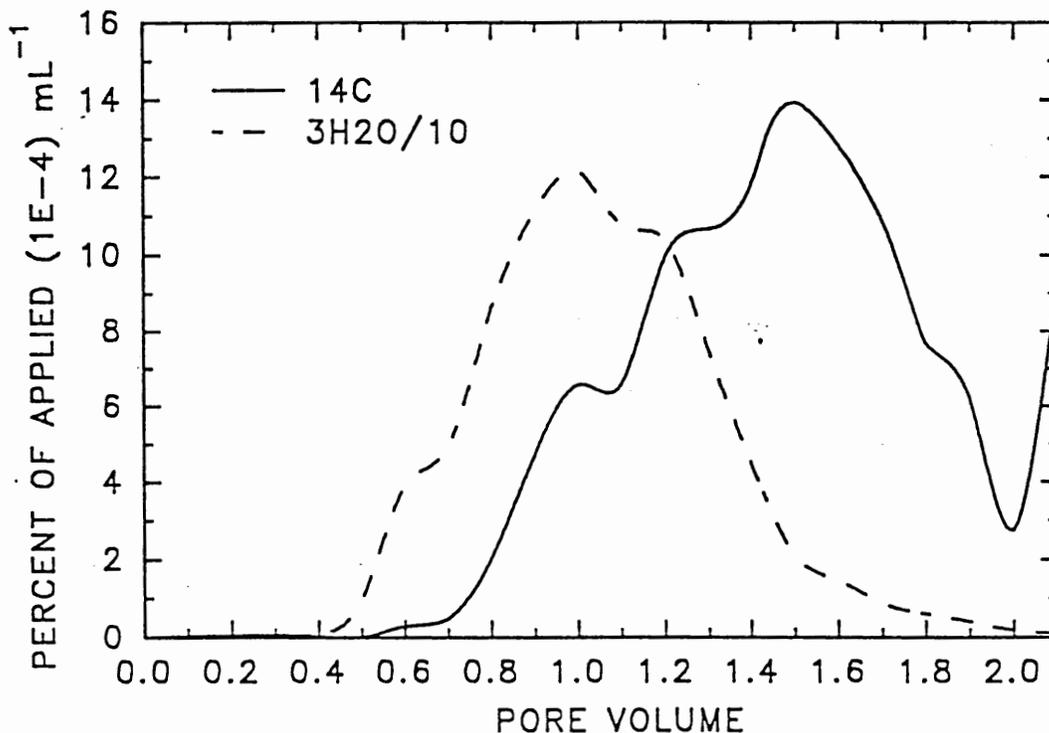


Figure 27. Breakthrough curves of  $^{14}\text{C}$  and tritium in leachate with pore volumes from  $^{14}\text{C}$ -metolachlor and tritium treated fallow field lysimeters in 1989. (Concentration of tritium reduced by a factor of 10 for comparative purposes) (Keller 1992).

(Silvertooth et al. 1992) in field and undisturbed column studies (Cassel et al. 1974). Even though CVs were high for concentration, CVs for pore volume ranged from 1 to 23% with an average of 6% for the 120 d study. Low CVs for pore volume indicate that water flow was rather uniform through the lysimeters for the 25 leachate collections, and further substantiates tritium and  $^{14}\text{C}$  concentration differences were influenced more by other dissipation processes.

The breakthrough curve for tritium was fairly symmetrical with slight "tailing" (Figure 27) and rightly mirrors the tritium distribution in the soil profile at 30 DAT (Figure 25). The peak tritium concentration at one pore volume (Figure 27) agrees favorably with data collected by Brown et al. (1985) who applied bromide to undisturbed, unsaturated soil columns to characterize water flow. Even though a 2.5 cm head of tritium occurred on d 0, the absence of tritium prior to 0.4 pore volumes indicates that wall-flow did not occur through cracks and channels or was not critical. Results by Tindall et al. (1992) also support the findings in this study. To characterize water flow, Tindall et al. (1992) added bromide to 30 cm diam. by 38 cm long columns containing an undisturbed, unsaturated Kanhapludult and concluded that the lack of bromide prior to 0.4 pore volumes indicated no interface flow along the edge of the core. The slight "tailing" of the tritium BTC may be due to immobile water (Van Genuchten and Wierenga 1977, De Smedt et al. 1986), sorption (Stewart 1972, Van de Pol et al. 1977, Nkedi-Kizza et al. 1982) or isotopic exchange (Stewart and Baker 1973). The most prominent influence was probably immobile water (Van Genuchten and Wierenga 1977, White et al. 1984, De Smedt et al. 1986). The low  $K_{sat}$  and preponderance of micropores in the bottom four depths (Table 2) makes soil conditions susceptible to immobile water. Van Genuchten and Wierenga (1977), using packed soil columns, found that the amount of immobile water increased as the pore-size distribution became narrower and the related flow velocity decreased. Conversely, Nkedi-Kizza et al. (1983) found that immobile water fractions increased with increasing water velocities. For whatever reasons, the presence of immobile water (<1%) indicates water bypass or preferential flow which subsequently reduces the capacity of the soil profile to adsorb and retain solutes.

$^{14}\text{C}$  and tritium concentrations in leachate peaked 91 and 63 d after application, respectively (Figure 26). The occurrence of the BTC for  $^{14}\text{C}$  to the right of the tritium BTC is due to an adsorption-induced retardation (Nielsen and Biggar 1962, Rao and Davidson 1979). The retardation of  $^{14}\text{C}$  is apparent by the  $^{14}\text{C}$  distribution in the soil profile over the 120 d period (Figure 25) and the subsequent need for an additional 0.6 pore volumes to reach peak  $^{14}\text{C}$  concentration (Figure 27).

At 120 DAT, in 1990, there was considerable variation among replications for total  $^{14}\text{C}$  and bromide in fallow lysimeters (Figure 28). For duplicate lysimeters, there were similar amounts of  $^{14}\text{C}$  in leachate; however,  $^{14}\text{C}$  in soil varied greatly and was probably due to vapor loss differences. Similarly, bromide in leachate was comparable for duplicate systems; however, bromide in soil varied greatly. The large variation in bromide recovery plus discrepancies in bromide BTCs for the two replications (Figure 29) deems that discussion be focused on the second replication. The low recovery of bromide in the second replication was probably due to anion adsorption and subsequent low desorption of bromide in the acidic, kaolinitic subsoil (Berg and Thomas 1959, Thomas 1963, Brady 1990).

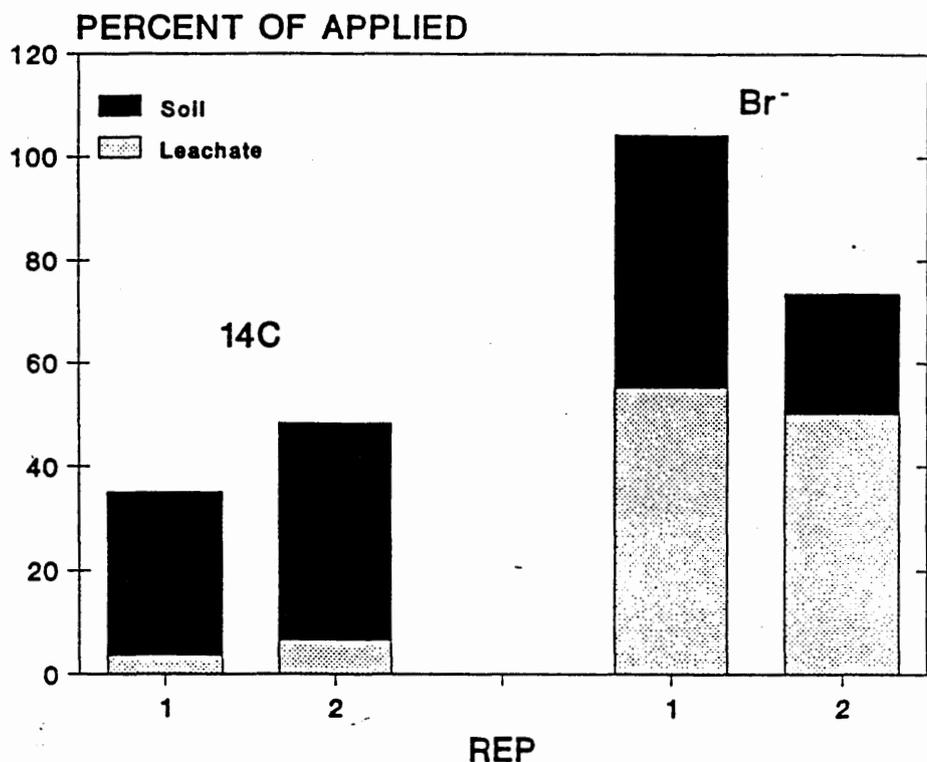


Figure 28. Percent of applied <sup>14</sup>C and bromide recovered in cumulative leachate and soil in <sup>14</sup>C-metolachlor and bromide treated fallow field lysimeters at 120 DAT in 1990 (Keller 1992).

The distribution of <sup>14</sup>C-metolachlor and/or metabolite(s) and bromide remaining in the soil profile at 120 DAT in 1990 is shown in Figure 30. Even though bromide recoveries were variable (Figure 28), maximum levels of bromide were at depths below 65 cm (Figure 30). These levels of bromide are most likely a reflection of the anionic adsorption capabilities of the acidic, kaolinitic subsoil (Berg and Thomas 1959, Thomas 1963, Brady 1990). Supportably, bromide in the subsoil was not considered to be in "stagnant pockets of water" as evidenced by minute amounts of immobile water in the tritium and <sup>14</sup>C study in 1989 and the absence of tritium in the soil profile of this study (Figure 30). Furthermore, the peak level of bromide in the soil was not considered a moving "pulse" as evidenced by the bromide peak in leachate from the second replication at 70 d (Figure 31). The distribution of bromide in the lysimeters closely resembles the amount and distribution of clay in the soil profile (Tables 2 and 3).

<sup>14</sup>C was less mobile than bromide (Figure 30) and this difference was attributed to adsorptive differences previously discussed.

At 120 DAT in 1990, 59 cm of water was added to each column (Table 7) with percolation (leachate) accounting for 51% of the water inputs (Table 10). In this cumulative leachate, greater amounts of bromide than <sup>14</sup>C were collected after 120 d (Figure 28). This order was expected and reflects the mobility and distribution of bromide and <sup>14</sup>C in the soil profile (Figure 30). Due to evaporation of tritium from the soil surface, <1% of the applied tritium was detected in cumulative leachate at 120 DAT (not shown).

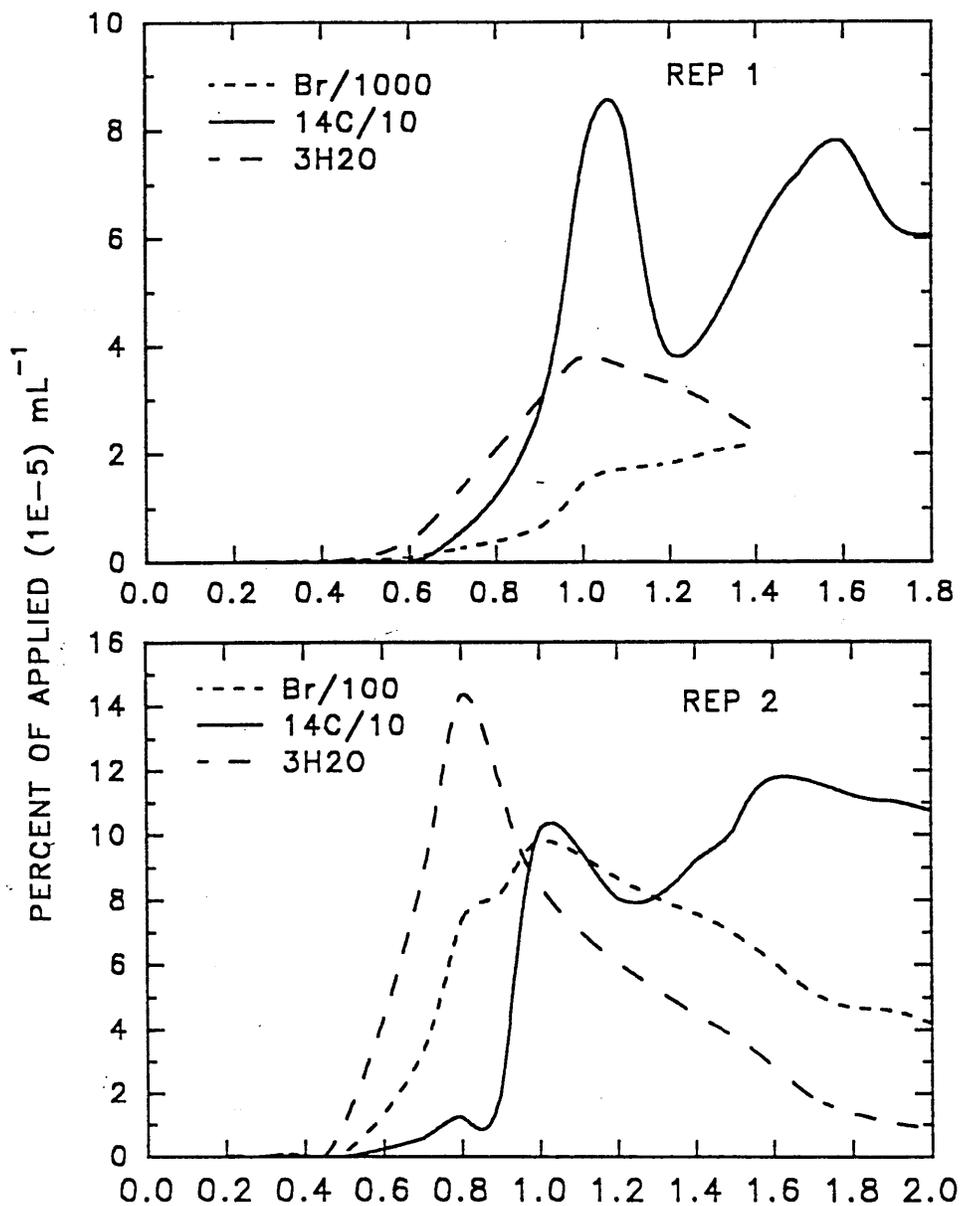


Figure 29. Breakthrough curves of <sup>14</sup>C, bromide and tritium with pore volumes from <sup>14</sup>C-metolachlor, bromide and tritium treated fallow field lysimeters in 1990 (<sup>14</sup>C and bromide reduced for comparative purposes) (Keller 1992).

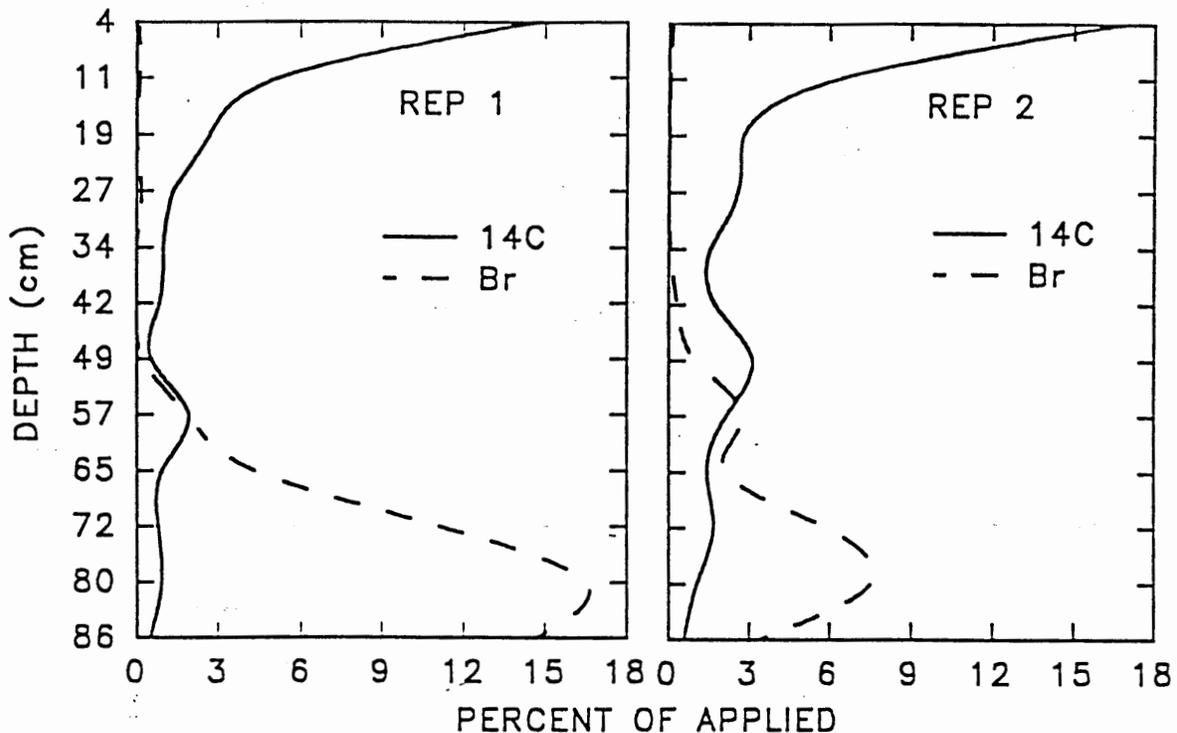


Figure 30.  $^{14}\text{C}$  and bromide distribution in  $^{14}\text{C}$ -metolachlor and bromide treated fallow field lysimeters at 120 DAT in 1990 (Keller 1992).

Breakthrough curves for  $^{14}\text{C}$ , bromide, and tritium in 1990 were diluted for comparative purposes and are shown in Figures 29 and 31. In the second replication, the BTC for tritium had considerable tailing (Figure 29) suggesting immobile water (Van Genuchten and Wierenga 1977, White et al. 1984, De Smedt et al. 1986) and/or intrasorbent diffusion (Brusseau and Rao 1989). Intrasorbent diffusion, in this case, intraorganic matter diffusion, most likely contributed to the tailing of the tritium BTC. Upon the evaporation of tritium prior to irrigation, a small portion of tritium probably diffused into the organic matter matrix which provided a "source" for continued tritium movement in the soil profile during rainfall or irrigation.

As evidenced from Figures 29 and 31, the BTCs for bromide and  $^{14}\text{C}$  were shifted to the right of the tritium BTC. Generally, when anionic tracers, such as chloride and bromide are used with tritium, the BTC for the anion is eluted first (McMahon and Thomas 1974, Gamedinger et al. 1990) indicating anion exclusion or bypassing of soil by water and anion (Nielsen and Biggar 1962, McMahon and Thomas 1974); however, this was not the case in this study. The asymmetrical shape and shift to the right of the BTCs for bromide and  $^{14}\text{C}$  indicated adsorption-desorption processes (Nielsen and Biggar 1962, Rao and Davidson 1979) with the principal clay and organic matter fractions, respectively. The shift of the  $^{14}\text{C}$  BTC to the right of the tritium BTC is in agreement with other studies utilizing tritium, atrazine and 2,4-D in water-saturated soil columns (Rao and Davidson 1979). Peak and fluctuating

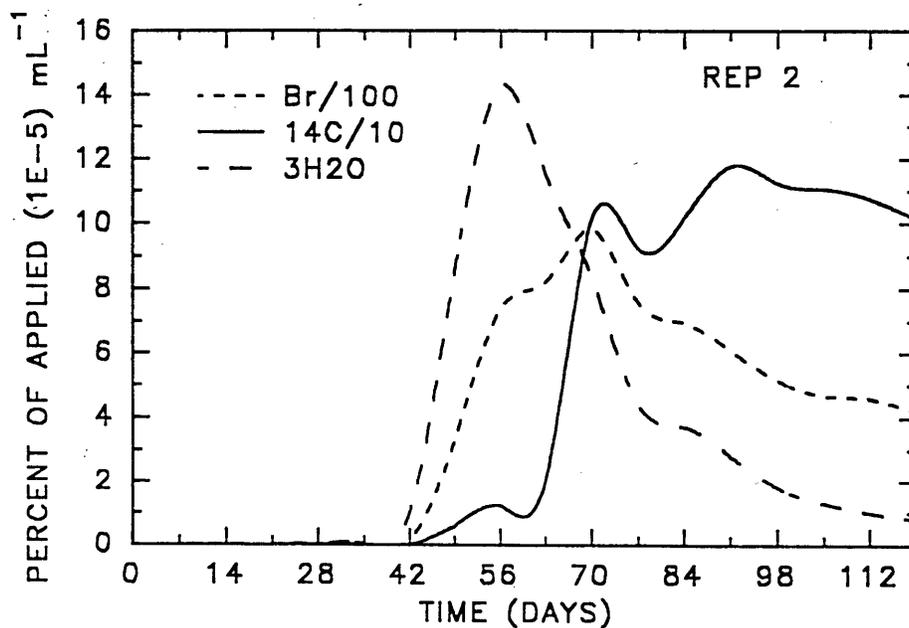
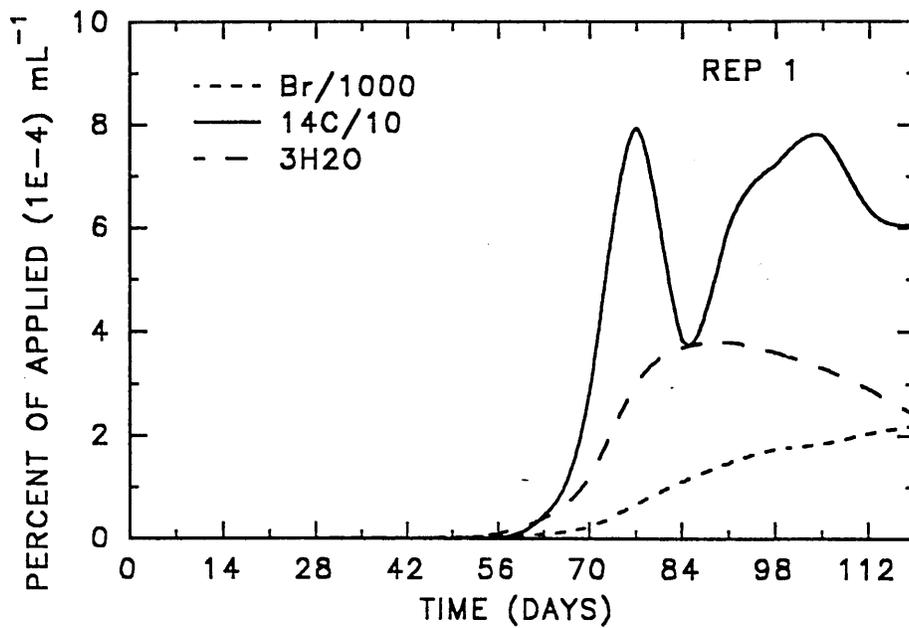


Figure 31. Breakthrough curves of <sup>14</sup>C, bromide and tritium with time from <sup>14</sup>C-metolachlor and bromide treated fallow field lysimeters in 1990 (<sup>14</sup>C and bromide reduced for comparative purposes). (Keller 1992).

concentrations of the BTC for  $^{14}\text{C}$  were probably a result of adsorption-desorption processes of the parent compound with subsequent metabolism to more polar metabolites. It is interesting to note that peak concentrations of  $^{14}\text{C}$  in leachate occurred at 91 DAT in 1989 and the second replication in 1990 (Figures 26 and 31).

Bromide distribution in independent KBr treated fallow lysimeters at 91 DAT in 1991 (Tables 26 and 27) was similar to that observed in 1990 (Figure 30).

Effects of leachate collectors on water and  $^{14}\text{C}$ -metolachlor distribution in soils. M-scores for soil water were calculated as shown in Table 1 with fraction of soil water multiplied by the mean soil depth. For all sampling dates, analysis of variance of total soil water and M-scores indicated a nonsignificant year by treatment interaction, therefore years were combined. Total soil water in lysimeters with and without leachate collectors were nonsignificantly different for all sampling dates (not shown); however, this occurrence does not give an indication of the distribution of soil water.

At 30 and 180 DAT, lysimeters with and without leachate collectors had similar distributions of soil water (Figure 32), which resulted in nonsignificantly different M-scores (Table 28). For the other sampling dates, lysimeters with collectors tended to have higher levels of soil water (Figure 32), however, these levels were nonsignificantly different as indicated by M-scores at 90 and 360 DAT (Table 28). Even though soil water contents were similar in the

Table 26. Bromide distribution in bromide treated (#15) and control fallow field lysimeters at 91 DAT in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

Depth	Bromide			Total Br	Percent of applied <sup>a</sup>
	In sample	In control	Difference		
cm	----- $\mu\text{g}/\text{ml}$ -----			$\mu\text{g} \times 10^4$	
0-8	0.008	0.007	0.007	0.0013	0.00
8-15	0.008	0.005	0.003	0.0049	0.02
15-23	0.009	0.004	0.005	0.0088	0.03
23-31	0.012	0.005	0.007	0.0172	0.06
31-38	0.013	0.005	0.008	0.0197	0.07
38-46	0.021	0.003	0.018	0.0311	0.11
46-53	0.015	0.009	0.006	0.0127	0.05
53-61	0.024	0.007	0.017	0.0339	0.12
61-69	0.058	0.008	0.050	0.1264	0.46
69-76	0.537	0.011	0.526	1.1374	4.14
76-84	2.940	0.017	2.923	6.9408	24.24
84-91	8.850	0.027	8.823	19.1643	<u>69.69</u>
Total	12.490	0.108	12.393		100.00

<sup>a</sup>101% recovered in day zero columns.

Table 27. Bromide recovered in the leachate of a bromide treated fallow field lysimeter (#15) at 7 to 91 DAT in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

Days after application	Cumulative rainfall	Cumulative leachate	Br in leachate			Total Br	Percent Br recovered	
			In sample	In control*	Difference		Indiv.	Cumulative
	-----mm-----		-----µg/ml-----			µg	-----%-----	
7	102 <sup>b</sup>	4	0.2	0.1	0.1	12	0	0
14	123	7	0.1	0.1	0	0	0	0
21	144	14	0.1	0.1	0	0	0	0
31	175	45	0.5	0.0	0.5	507	0.1	0.1
35	260	45	2.1	0.1	2.0	31	0	0.1
41	307	74	1.0	0.1	0.9	845	0.2	0.3
46	328	103	4.5	0.1	4.4	4064	0.7	1.0
50	328	113	4.6	0.1	4.5	1597	0.3	1.3
56	363	118	38.0	0.1	37.9	5233	0.9	2.2
64	387	125	85.0	0.1	84.9	19192	3.5	5.7
68	527	155	178.0	0.1	177.9	177906	32.3	38.0
71	527	173	172.0	0.1	171.9	96962	17.6	55.6
77	540	177	125.0	0.1	124.9	16115	2.9	58.5
82	614	188	172.0	0.1	171.9	61373	11.1	69.6
84	614	205	169.0	0.1	168.9	94423	17.1	86.7
89	660	219	136.0	0.1	135.9	60489	11.0	97.7
91	660	222	113.0	0.1	112.9	12197	2.2	99.9
Total µg Br recovered from leachate						550946		
% Br recovered from leachate						45.2%		
Total µg Br recovered from soil						274985		
% Br recovered from leachate						22.6%		
Total µg Br recovered from leachate and soil						825931		
Total % Br recovered, leachate and soil						67.8%		

\*The µg/ml bromide present in samples collected during same time period from control column #17.

<sup>b</sup>Includes rainfall which occurred in week 0, the week before experiment began.

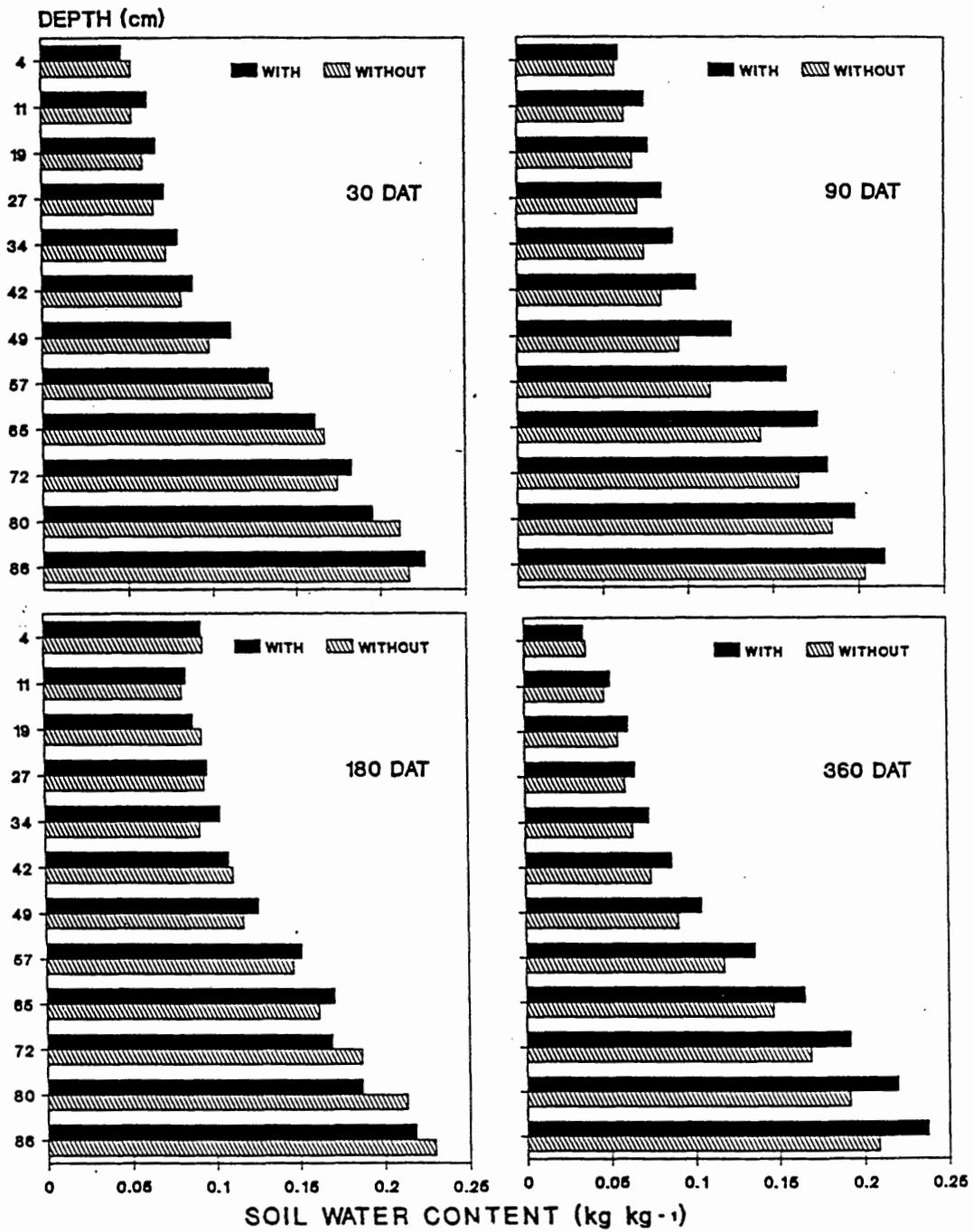


Figure 32. Soil water distribution in fallow field lysimeters with and without leachate collectors at 30 to 360 DAT (mean of 1989 and 1990) (Keller 1992).

Table 28. Effect of leachate collectors on soil water and <sup>14</sup>C distribution M-scores at 0- to 89-cm soil depth of <sup>14</sup>C-metolachlor treated fallow field lysimeters at 30 to 360 DAT (mean of 1989 and 1990) (Keller 1992).

Leachate collectors	DAT			
	30	90	180	360
M-scores for soil water distribution				
With	63.81a	66.98a	66.03a	65.96a
Without	62.88a	57.95a	66.19a	57.84a
M-scores for <sup>14</sup> C distribution				
With	8.22a	10.62a	10.06a	9.03a
Without	6.35b	11.83a	11.12a	9.18a

<sup>a</sup>Within a column, means sharing the same letter are not significantly different, as determined by LSD (0.05).

two types of lysimeters, four sampling periods may not be sufficient to detect treatment differences.

To monitor soil water status on a frequent basis over the 360 d study in 1989, tensiometers were installed at six depths in duplicate columns with and without leachate collectors. Tensiometers were used to measure the hydraulic head and pressure head of the soil water. Pressure head, particularly when negative, represents the matric potential which is related to soil water content. Generally speaking, when soils become drier, matric potential gets lower (becomes more negative) and vice versa when soils become wetter. The applications and characteristics of tensiometers are discussed in more detail by Cassel and Klute (1986).

Soil matric potential in lysimeters with and without leachate collectors at six depths over the 360 d study is shown in Figures 33 and 34. Each vertical bar is the mean of two observations with a plus sign indicating significantly different values. For both types of lysimeters, the lowest matric potential was frequently observed at the 8 cm depth (Figure 33), which was expected due to the low water holding capacity of the loamy sand and its proximity to the soil surface and subsequent opportunity for water evaporation. At the 8- and 15-cm depths, matric potential tended to be equal for the lysimeters with the lowest occurring at 342 d. At the 30 cm depth, matric potential tended to be lower in lysimeters without leachate collectors, with two dates recording significantly different matric potentials. In 1989, irrigation was applied weekly which probably contributed to the lack of treatment effects in the first three depths.

At the 45, 60, and 75 cm depths, matric potential was frequently lower in lysimeters that sustained soil contact (no collectors) with significant differences occurring between 60 and 90 d (Figure 34). Lower matric

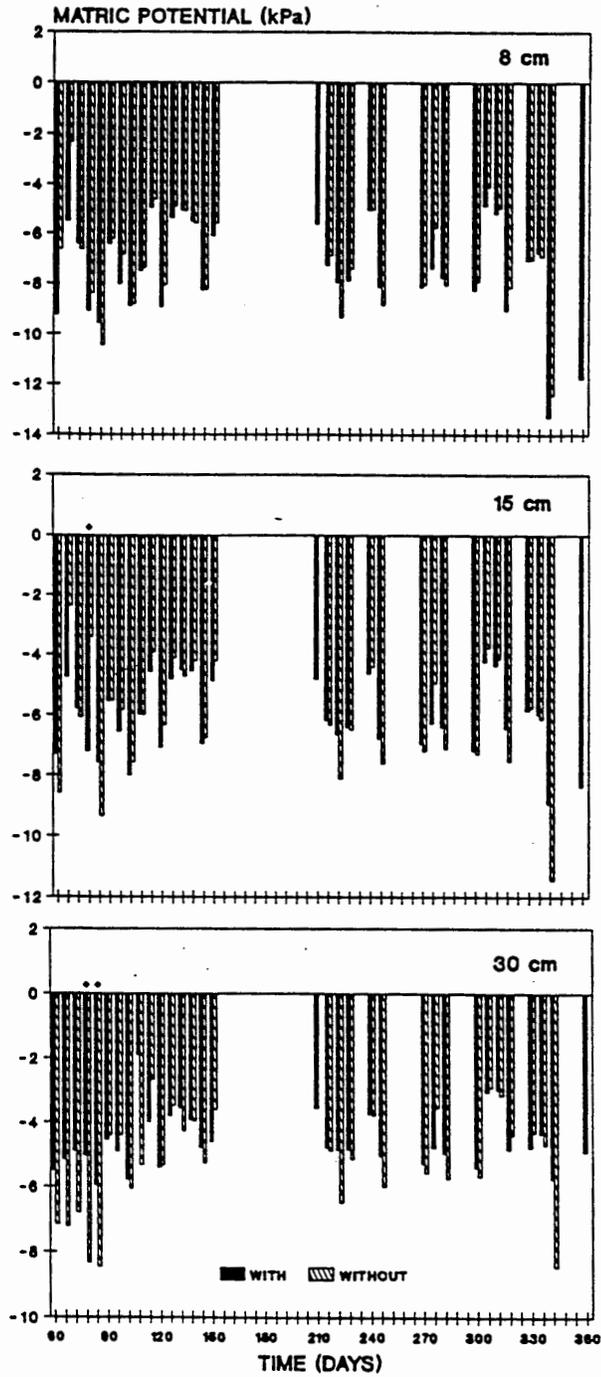


Figure 33. Soil matric potential at 8, 15 and 30 cm soil depths with time in fallow field lysimeters with and without leachate collectors in 1989 (Keller 1992).

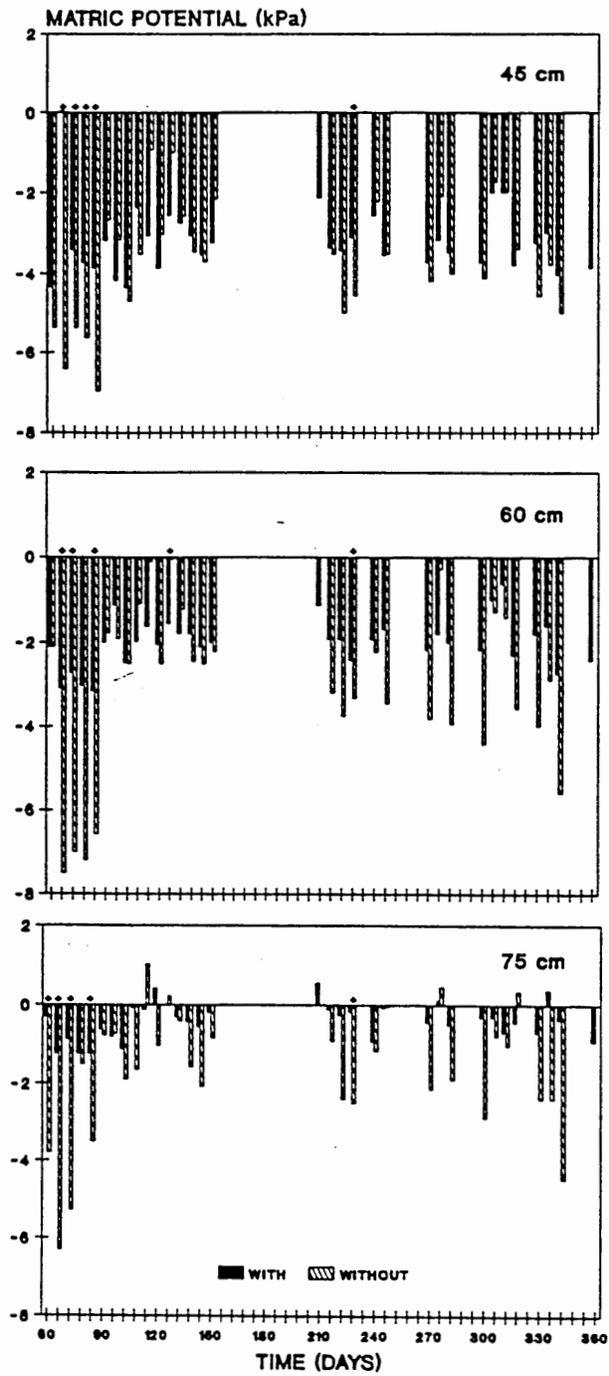


Figure 34. Soil matric potential at 45, 60 and 75 cm soil depths with time in fallow field lysimeters with and without leachate collectors in 1989 (Keller 1992).

potentials in lysimeters without collectors indicate drier soil conditions than that in lysimeters with collectors. The difference in soil water content for the two types of lysimeters at the lower depths, particularly at 75 cm, agrees with other investigators (Neal et al. 1937, Wallihan 1940, Klocke et al. 1991). Capillary tension (lysimeters without collectors) provides increased drainage and subsequent lower soil water contents. Drainage or downward water flow is best explained by hydraulic head differences between depths occurring in the two types of lysimeters. The small sample size probably restricted the opportunity to distinguish more treatment effects. The determination of hydraulic head at different depths allows for the calculation of hydraulic gradients which assist in determining the direction and magnitude of water movement in the soil profile. For this paper, discussion will be focused only on the direction of water flow. The flow of soil water is caused by a driving force resulting from a potential gradient, in this case determined by hydraulic head, with flow occurring in the direction of decreasing potential.

Hydraulic head at six depths in lysimeters with and without leachate collectors at 60, 71, 145, and 336 DAT is shown in Figure 35. At 60 DAT, four out of five possible gradients in lysimeters without collectors indicated downward soil water flow (negative values) while the opposite occurred in lysimeters with collectors. Irrigation (2.4 cm) 24 h prior to tensiometer readings at 71 DAT contributed to elevated hydraulic heads; nonetheless, soil water flow downward was prominent in lysimeters that maintained soil contact. At 145 and 336 DAT, soil water flow downward continued in lysimeters without leachate collectors. Supportably, 46 and 63% of the 155 possible gradients in 31 time periods (5 gradients per time period) indicated downward flow in lysimeters with and without leachate collectors, respectively (not shown). Furthermore, lysimeters without collectors had 14 more time periods indicating downward flow between the 60 and 75 cm depths (not shown). The predominance of downward soil water flow in lysimeters with capillary tension and upward flow in lysimeters with collectors, supports the reported decrease of evaporation and increased volume of percolate in lysimeters with tension (Wallihan 1940).

For all sampling dates, there was no significant year by treatment (with or without leachate collectors) interaction for total  $^{14}\text{C}$  or M-scores; therefore years were combined. At the four sampling dates, lysimeters with and without leachate collectors were not significantly different in total  $^{14}\text{C}$ , with 59% of the applied  $^{14}\text{C}$  recovered at 30 DAT, 46% at 90 DAT, 43% at 180 DAT, and 37% at 360 DAT (not shown). Similar recoveries of  $^{14}\text{C}$  implied that vapor and/or leaching losses of  $^{14}\text{C}$  were equal in the two types of lysimeters; however,  $^{14}\text{C}$  recoveries do not reflect the distribution of  $^{14}\text{C}$  in the soil profile.

At 30 DAT,  $^{14}\text{C}$  distribution in lysimeters with and without collectors was significantly different as reflected by significant M-scores (Figure 36; Table 28). Although there was no year by treatment interaction, the difference in  $^{14}\text{C}$  distribution at 30 DAT was attributable to the  $^{14}\text{C}$  distribution in 1989 which resulted in M-scores of 11 and 8 for lysimeters with and without leachate collectors, respectively (not shown). At 30 DAT in 1990, M-scores were equal for the two lysimeters (not shown). Since total  $^{14}\text{C}$ ,  $^{14}\text{C}$  distributions, and M-scores were similar for the remaining sampling dates (Figure 36; Table 28), the significantly different distribution of  $^{14}\text{C}$  in the two lysimeters at 30 DAT may have occurred by chance alone. At 90, 180 and 360 DAT,  $^{14}\text{C}$  distribution was similar in both lysimeters (Figure 36) and was

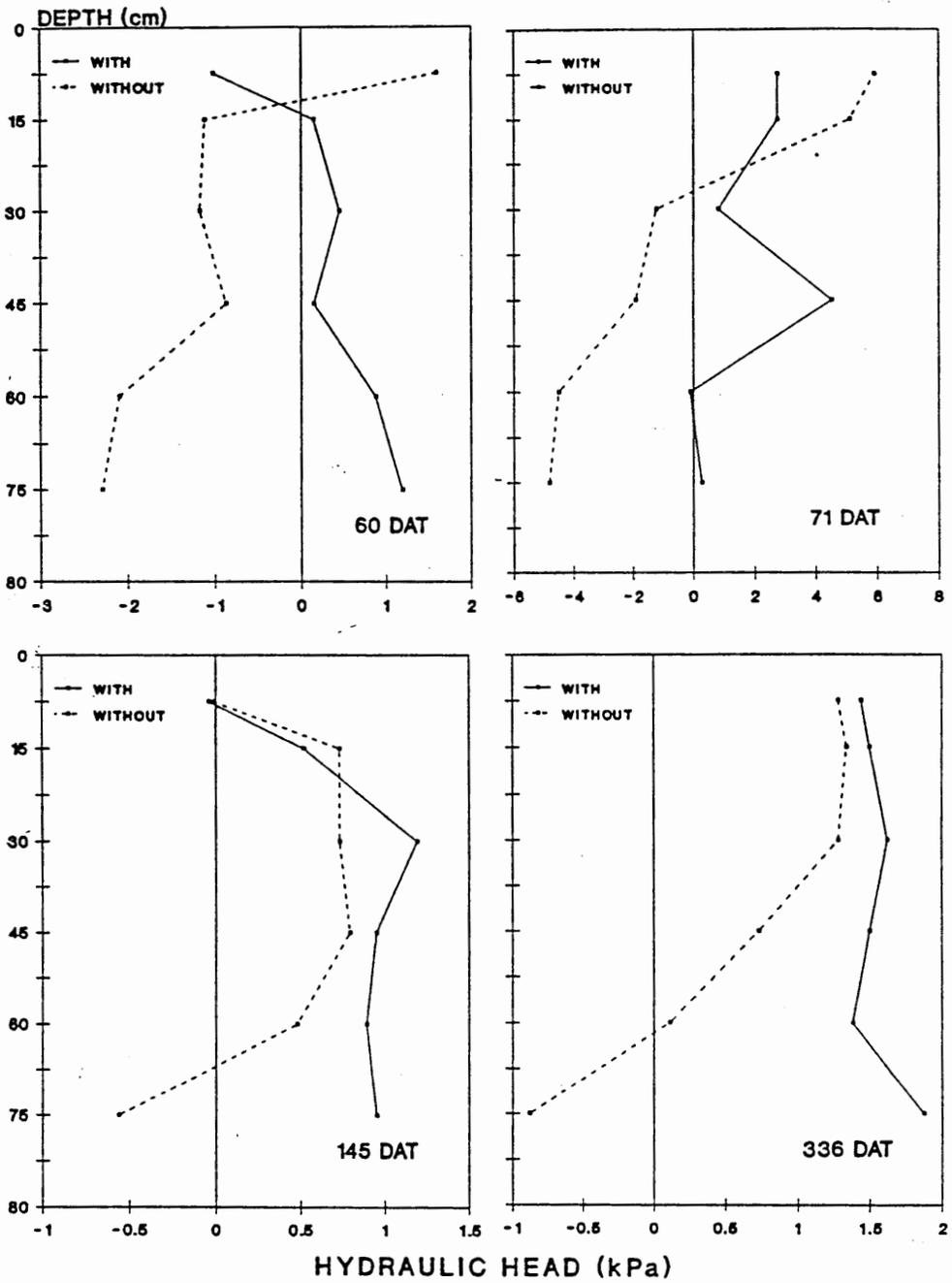


Figure 35. Soil hydraulic head at 8 to 75 cm soil depths at 60 to 336 DAT in fallow field lysimeters with and without leachate collectors in 1989 (Keller 1992).

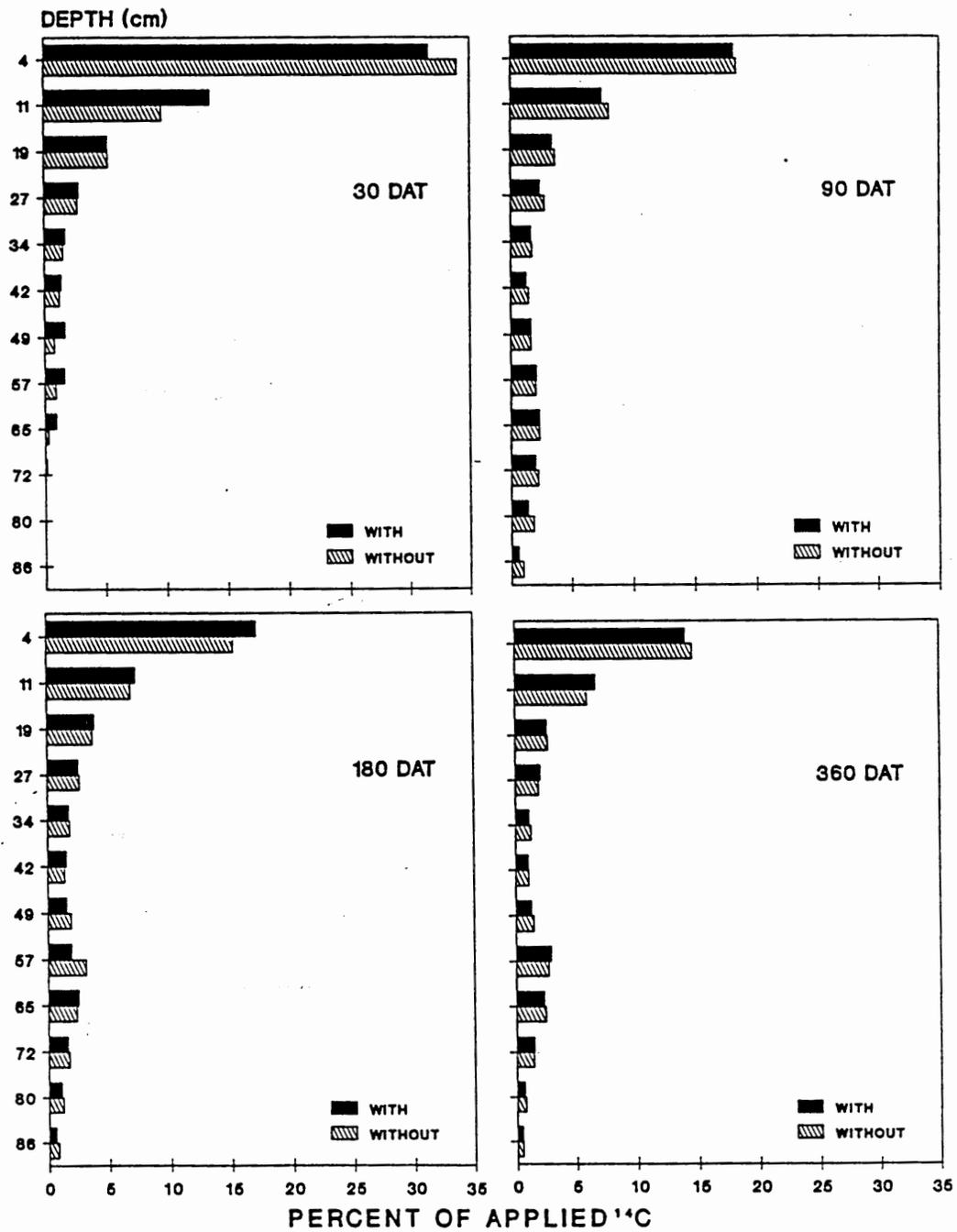


Figure 36.  $^{14}\text{C}$  distribution in  $^{14}\text{C}$ -metolachlor treated fallow field lysimeters with and without leachate collectors at 30 to 360 DAT (mean of 1989 and 1990) (Keller 1992).

verified by nonsignificant M-scores (Table 28). For the four sampling periods, <3% of the applied <sup>14</sup>C was present below 34 cm with a majority of the <sup>14</sup>C retained in the upper 3 depths (Figure 36).

Nitrate movement and dissipation in soil. The amount of nitrate recovered from 0 DAT fallow lysimeters was 54.3% of applied. The low recovery rate was thought to be due to the method of calcium nitrate application. Small droplets of water were observed inside the "salt-shaker type" applicator used to apply the calcium nitrate to the soil. Though the appearance of these small water droplets seemed minor at the time, apparently only 54% of the nitrate placed in the shaker was applied to the soil surface; the remainder stayed in the shaker dissolved in the water droplets. All reported percent recoveries for nitrate which follow are based on the average  $1.923 \times 10^6 \mu\text{g}$  of nitrate recovered in the 0 DAT lysimeters. Nitrate present in the 5- to 13-cm and 13- to 23-cm depths of control (untreated) lysimeters was taken as background concentration (Table 29).

Details showing the calculation of the nitrate mass balance for lysimeter #5 are shown in Table 29. Reported in column 2 of Table 29 is nitrate concentration in  $\mu\text{g/ml}$  in the subsamples. The entry in column 4 is corrected for background nitrate, using data from lysimeter #4. The entry in column 5 in Table 29 was calculated by multiplying the data in column 4 by 51.5 ml, the total volume of extraction solution, by the mass of oven-dried soil in the section, and dividing by the oven dry mass of soil in the subsample. Percent total recovery was obtained by dividing the data in column 4 by the total  $\mu\text{g}$  nitrate recovered in the entire lysimeter. Also shown in Table 29 are the total masses of nitrate recovered in the 12 sections. Based on the amount of

Table 29. Nitrate distribution in a nitrate treated fallow field lysimeter (#15) at 32 DAT in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

Depth cm	Nitrate			Recover %	Total nitrate <sup>a</sup> $\mu\text{g} \times 10^4$
	In sample $\mu\text{g/ml}$	In control $\mu\text{g/ml}$	Difference $\mu\text{g/ml}$		
0-8	15.4	14.5	0.9	0.3	0.46
8-15	10.9	4.6	6.3	2.0	3.70
15-23	6.0	3.6	2.4	1.2	2.15
23-31	21.7	2.0	19.7	11.6	21.45
31-38	45.8	2.1	43.7	21.1	39.05
38-46	36.9	4.0	32.9	15.0	27.65
46-53	37.3	2.5	34.8	17.1	31.63
53-61	31.7	6.7	25.0	12.3	22.77
61-69	21.8	4.1	17.7	8.5	15.69
69-76	13.7	2.2	11.5	6.0	11.07
76-84	7.3	1.3	6.0	2.9	5.31
84-91	6.8	1.1	5.7	2.2	4.03
Total				100.0	184.97

<sup>a</sup>Nitrate recovered in zero day lysimeters (0 DAT) was 54.3% of applied.

nitrate recovered from the 0 DAT lysimeters immediately after applying calcium nitrate, 96.2% of the nitrate was recovered in this lysimeter. Results indicate that more than 53% of the nitrate was located between the 38- and 53-cm depths 32 d (180 mm rainfall) after nitrate was applied. Less than 5 percent of the nitrate remained in the top 23 cm. It appears that the leading edge of the nitrate pulse had already reached the 91-cm depth.

The nitrate mass balance for all lysimeters initially receiving application of calcium nitrate are summarized in Table 30. After 32 d, approximately 12% of the nitrate had leached from the lysimeters and 76 to 96% remained in the soil. After 61 d (310 mm rainfall), about 30 percent had leached from the lysimeters and 48 to 96% was retained, and after 91 d (580 mm rainfall), approximately 75% had been removed and only 10 to 35% remained. At 32 DAT, there was a trend for a greater fraction of the nitrate to be leached from the lysimeter at the upper-slope position of the field compared to the lower-slope position. For all three dates, the amount of nitrate remaining in the soil was always greatest for the lower-slope position lysimeter. A comparison of the distribution of nitrate (Table 30) and bromide (Table 26) retained in the soil at 91 DAT shows both anions leached similarly and nearly all of each is retained in the bottom three soil sections.

Nitrate in leachate. The mass balance of nitrate in leachate collected from trenchside lysimeter #16 is shown in Table 31. The nitrate concentrations reported for the leachate samples for each date are corrected for background nitrate. The average background nitrate concentration for control lysimeter #17 throughout the 91-day-long period was  $15\mu\text{g/ml}$ . The mass of nitrate in each leachate sample was calculated by multiplying the corrected nitrate concentration by the volume of leachate collected. The % nitrate recovered in each leachate sample was obtained by dividing nitrate content of each leachate sample by the total mass of nitrate recovered in the leachate over the duration of the study (i.e.  $1.347 \times 10^6 \mu\text{g}$ ). Based on the amount of nitrate recovered from the 0 DAT lysimeters immediately after applying calcium nitrate, 70% of the applied nitrate was recovered in the leachate for lysimeter #16.

The nitrate mass balances for leachate from the four treated, trenchside lysimeters, including #16 are summarized in Table 32. The appearance of a significant amount of applied nitrate (>25%) did not occur until over 139 mm of leachate had drained from lysimeter #13, 155 mm for lysimeter #15, 113 mm for lysimeter #16 and 118 mm for lysimeter #18. Nitrate concentration versus volume of leachate (or time) collected is shown for each column in Figures 37, 38, 39, 40, 41 and 42. The pulse of nitrate appeared in the leachate of lysimeters #16 and #18 at approximately 60 DAT and in the leachate of lysimeters #13 and #15, at approximately 70 DAT, even though it appeared after nearly the same volume of water (5000 mL) had passed through each lysimeter. This suggests that the soil in lysimeters #13 and 15 was slightly more retentive to nitrate than soil in lysimeters #16 and 18. This may have been because soil in the former two lysimeters had slightly higher organic carbon contents in their profiles than soils in the latter two lysimeters (Table 3). Factors which may have played minor roles in less than complete nitrate recoveries (Table 32) include the overflow of leachate from collection containers during two rain events, June 23 and July 30. The June 23 event likely contained only "background" amounts of nitrate and would have little effect on total  $\text{NO}_3$  recovery. The magnitude of leachate loss on July 30 is unknown.

Table 30. Soil nitrate mass balance for all nitrate treated fallow field lysimeters in 1991 (Lein and Cassel 1991, unpublished, N.C. State University, Raleigh, NC).

Depth	After 32 days (480 mm rainfall)			After 61 days (310 mm rainfall)			After 91 days (510 mm rainfall)			Trenchside Columns			
	Lower # 1	Middle # 5	Upper # 9	Lower # 2	Middle # 6	Upper # 10	Lower # 3	Middle # 8	Upper # 12	Lower	NB*	Middle	NM*
0-8	0.2	0	0	0.8	1.2	0.8	0	0	0	0	0	0	0
8-13	2.0	0.4	1.2	1.4	0.5	0.7	0	0	0	0	0	0	0
13-23	1.2	0	0.7	0.7	0.2	0.3	0	0	0	0	0	0	0
23-31	11.6	0.5	3.1	0.7	0.4	0.5	0	0	0	0	0	1.9	0
31-38	21.1	1.6	6.1	0.6	0	0.2	0	0	0	0	0	0	0
38-46	14.9	5.2	9.0	0.7	0.4	0.4	0	0	0	0	0	0	0
46-53	17.1	13.8	14.8	7.5	0.3	0.1	2.2	0	0	0	0	0	0
53-61	12.3	22.3	19.6	25.3	0.5	0.4	7.2	0	0	3.0	0	0	0
61-69	8.5	32.1	25.9	28.2	8.6	13.7	10.4	0	0	14.3	0	0	9.6
69-76	6.0	15.1	10.7	16.3	26.9	21.9	17.3	21.5	15.1	29.8	9.5	4.0	8.5
76-84	2.9	5.7	5.4	10.5	34.8	30.8	24.3	32.7	31.7	33.8	40.6	36.0	30.7
84-91	2.2	3.2	3.3	7.4	26.3	29.9	38.6	45.8	53.2	19.1	49.9	58.2	51.2
% of applied recovered	96.2	90.9	76.5	96.5	48.8	66.8	34.8	10.4	19.1	38.0	26.7	8.0	23.0

\*NB = nitrate/bromide, NM = nitrate/metolachlor  
 \*Normalized to 100% recovered.

Table 31. Nitrate recovery in the leachate of a nitrate treated fallow field lysimeter (#16) at 7 to 91 DAT in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

Days after application	Cumulative rainfall	Cumulative leachate	NO <sub>3</sub> conc* corr.	Nitrate in leachate	Nitrate recovered	
					Indiv.	Cumulative
	-----mm-----		µg/ml	µg		
7	103 <sup>b</sup>	7	8	1832	0.1	0.1
14	123	14	11	2497	0.2	0.3
21	144	18	5	695	0.1	0.4
27	175	27	2	580	0	0.4
31	175	58	28	28000	2.1	2.5
35	260	51	93	5580	0.4	2.9
41	307	79	95	59375	4.4	7.3
46	328	94	189	91098	6.8	14.1
50	328	109	267	126558	9.4	23.5
56	363	113	341	46717	3.5	27.0
64	387	121	325	85150	6.3	33.3
68	527	152	421	421000	31.2	64.5
71	527	173	285	192660	14.3	78.5
77	540	178	138	24288	1.8	80.6
82	614	191	187	79662	5.9	86.5
84	614	211	157	97340	7.2	93.7
89	660	226	138	69000	5.1	98.8
91	660	230	124	15376	1.1	99.9
Total µg NO <sub>3</sub> recovered from leachate				1348408	99.9	
% NO <sub>3</sub> recovered from leachate				70.1		
Total µg NO <sub>3</sub> recovered from soil				154242		
% NO <sub>3</sub> recovered from soil				8		
Total µg NO <sub>3</sub> from leachate and soil				1501650		
Total % NO <sub>3</sub> recovered, leachate & soil				78.1		

\*Average background nitrate level, collected over entire experiment from control column #17 was 15 µg/ml.

<sup>b</sup> Some rainfall during the week before NO<sub>3</sub> was applied is included.

Influence of acrylic polymers on the movement and dissipation of three herbicides. The influence of several water soluble acrylic polymers on the mobility and loss of <sup>14</sup>C-labeled atrazine, metolachlor and primisulfuron is discussed in detail elsewhere (Lee and Weber 1993) (Appendix 1). Briefly, it was reported that none of the polymers (ASE-108, HA-16 and E-1242) added to tank mixtures of each of the three herbicides significantly affected the losses on the mobility of the compounds in the soil in fallow field lysimeter studies.

#### Herbicide Degradation Study

General. The total recoverable radioactivity could be divided into three pools: 1) Extractable <sup>14</sup>C removed from the soil by organic solvents, 2) Bound <sup>14</sup>C not removed by solvents, and 3) <sup>14</sup>CO<sub>2</sub> produced by mineralization to

Table 32. Nitrate mass balances for leachate collected from nitrate treated fallow field lysimeters (#13, 15, 16 and 18) at 7 to 91 DAT in 1991 (Lain and Cassel, 1991, unpublished, N.C., State University, Raleigh, NC).

Days after application	#13 lower end				#15 lower end				#16 upper end				#18 upper end			
	Cumulative leachate	Nitrate conc.	Nitrate recovery		Cumulative leachate	Nitrate conc.	Nitrate recovery		Cumulative leachate	Nitrate conc.	Nitrate recovery		Cumulative leachate	Nitrate conc.	Nitrate recovery	
			Sample	Cumulative												
	mm	µg/ml			mm	µg/ml			mm	µg/ml			mm	µg/ml		
7	3	5	0.1	0.1	4	5	0.1	0.1	7	8	0.1	0.1	7	12	0.3	0.3
14	4	0	0	0.1	7	58	0.6	0.7	14	11	0.2	0.3	14	4	0.1	0.4
21	5	0	0	0.1	14	4	0.1	0.8	18	5	0.1	0.4	18	4	0	0.4
27	5	0	0	0.1	--	--	--	--	27	2	0	0.4	23	0	0	0.4
31	36	0	0	0.1	45	<0	0	0.8	58	28	2.1	2.5	54	22	2.0	2.4
35	36	0	0	0.1	45	<0	0	0.8	60	93	0.4	2.9	60	65	1.2	3.6
41	63	0	0	0.1	74	<0	0	0.8	79	95	4.4	7.3	69	67	1.9	5.3
46	90	0	0	0.1	103	<0	0	0.8	94	189	6.8	14.1	93	113	7.9	13.4
49	--	--	--	--	--	--	--	--	--	--	--	--	95	95	0.6	14.0
50	104	5	0.6	0.7	113	83	3.4	4.2	109	267	9.4	23.5	103	168	4.1	18.1
56	107	14	0.3	1.0	118	52	0.8	5.0	113	356	3.5	27.0	109	148	2.9	21.0
64	112	6	0.3	1.3	125	104	2.7	7.7	121	325	6.3	33.3	118	196	4.9	25.9
68	139	107	25.0	26.3	155	283	32.7	40.4	152	421	31.2	64.5	148	308	28.4	54.3
71	152	176	18.1	44.4	173	315	20.5	60.9	173	285	14.3	78.8	166	321	17.1	71.4
77	153	72	0.8	45.2	177	140	2.1	63.0	178	138	1.8	80.6	172	276	2.8	74.2
82	176	67	13.2	58.4	188	234	9.6	72.6	191	187	5.9	86.5	180	199	5.1	79.3
84	203	89	20.8	79.2	205	231	14.9	87.5	211	157	7.2	93.7	197	196	5.1	79.3
89	215	166	16.6	95.8	219	202	10.4	97.9	226	138	5.1	98.8	212	194	9.0	97.9
91	218	167	4.1	99.9	222	164	2.0	99.9	230	124	1.1	99.9	216	191	2.1	100.0
Lysimeter number					#13		#15		#16		#18					
Total µg NO <sub>3</sub> recovered from leachate					391,712		865,841		1,347,408		1,085,088					
%NO <sub>3</sub> recovered from leachate					20.4%		45.0%		70.1%		56.4%					
Total µg NO <sub>3</sub> recovered from soil					730,945		513,196		154,242		442,198					
%NO <sub>3</sub> recovered from soil					38.0%		26.7%		8.0%		22.9%					
Total µg NO <sub>3</sub> recovered from leachate plus soil					1,122,657		1,379,037		1,501,650		1,527,286					
Total % NO <sub>3</sub> recovered from leachate plus soil					58.4%		71.7%		78.1%		79.4%					

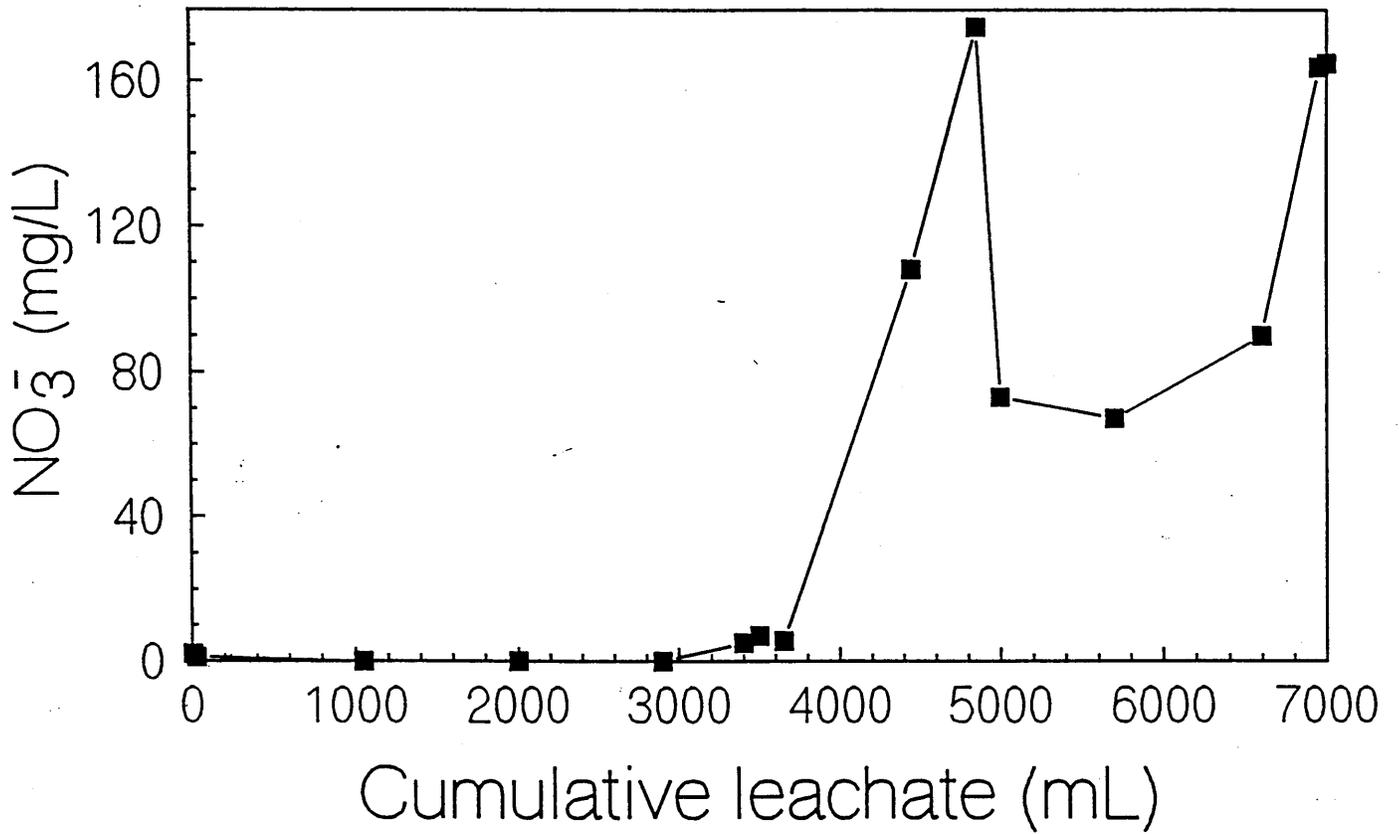


Figure 37. Breakthrough curve of nitrate in leachate with leachate volume from a nitrate treated fallow field lysimeter (#13, lower slope position) in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

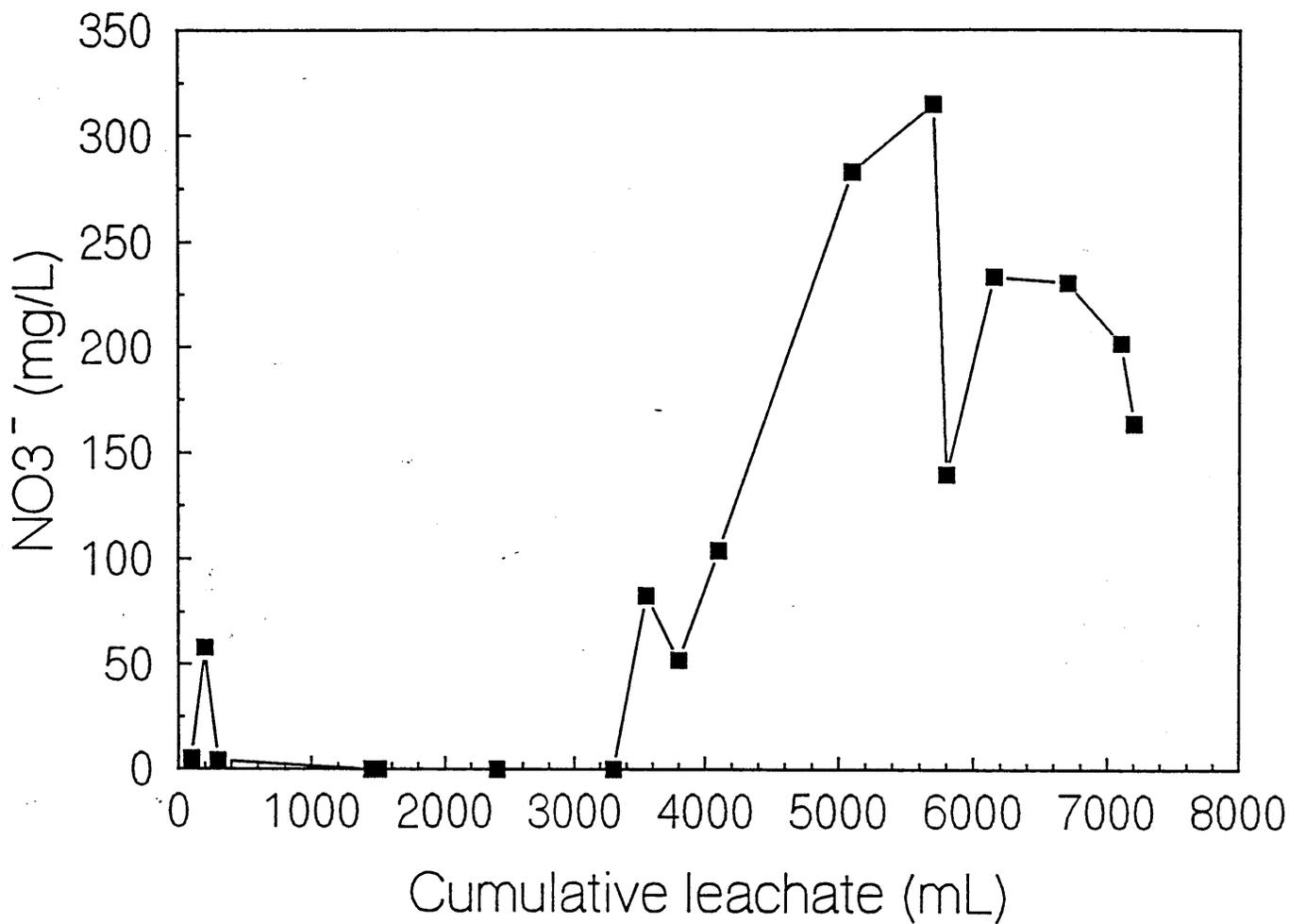


Figure 38. Breakthrough curve of nitrate in leachate with leachate volume from a nitrate treated fallow field lysimeter (#15, lower slope position) in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

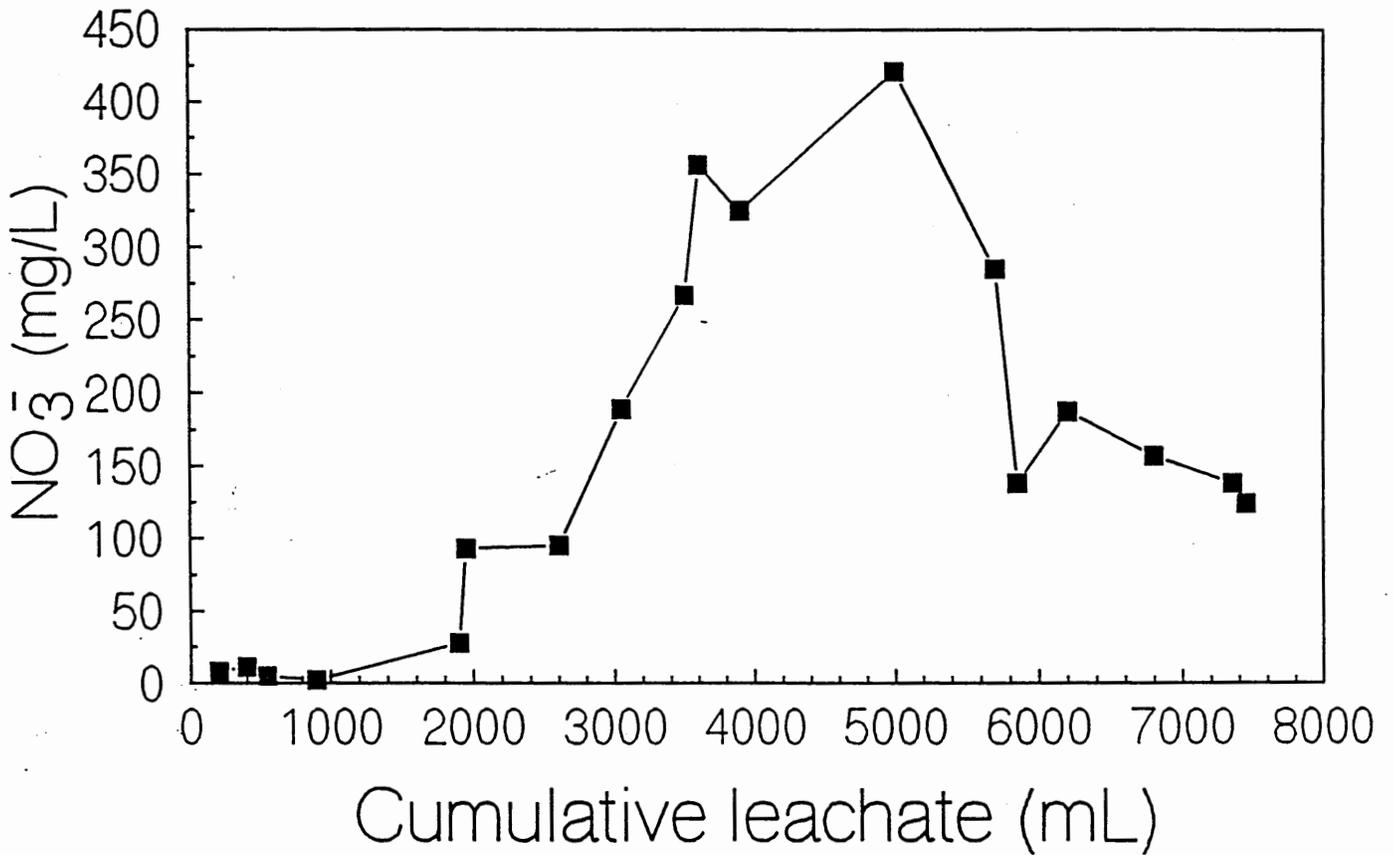


Figure 39. Breakthrough curve of nitrate in leachate with leachate volume from a nitrate treated fallow field lysimeter (#16, upper slope position) in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

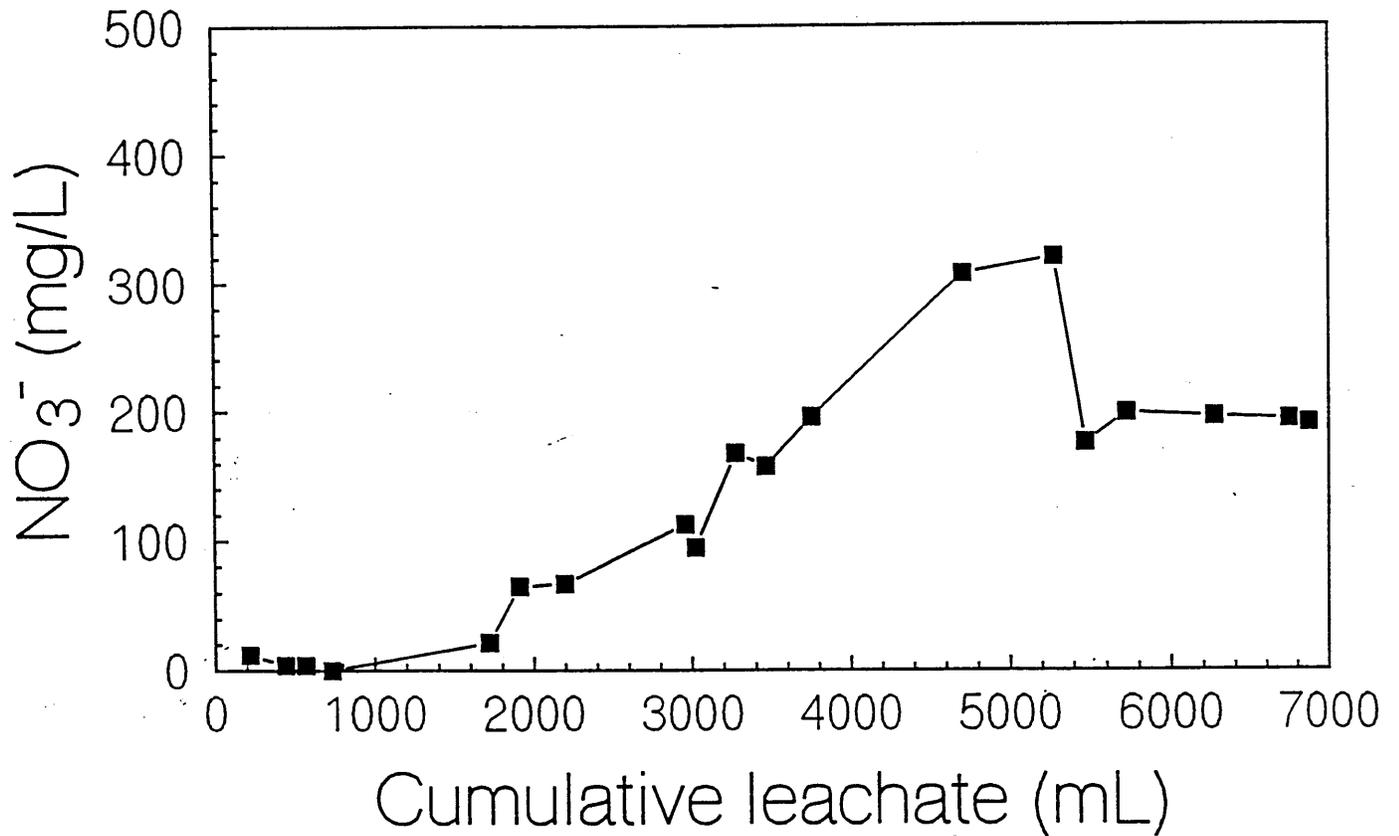


Figure 40. Breakthrough curve of nitrate in leachate with leachate volume from a nitrate treated fallow field lysimeter (#18, upper slope position) in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

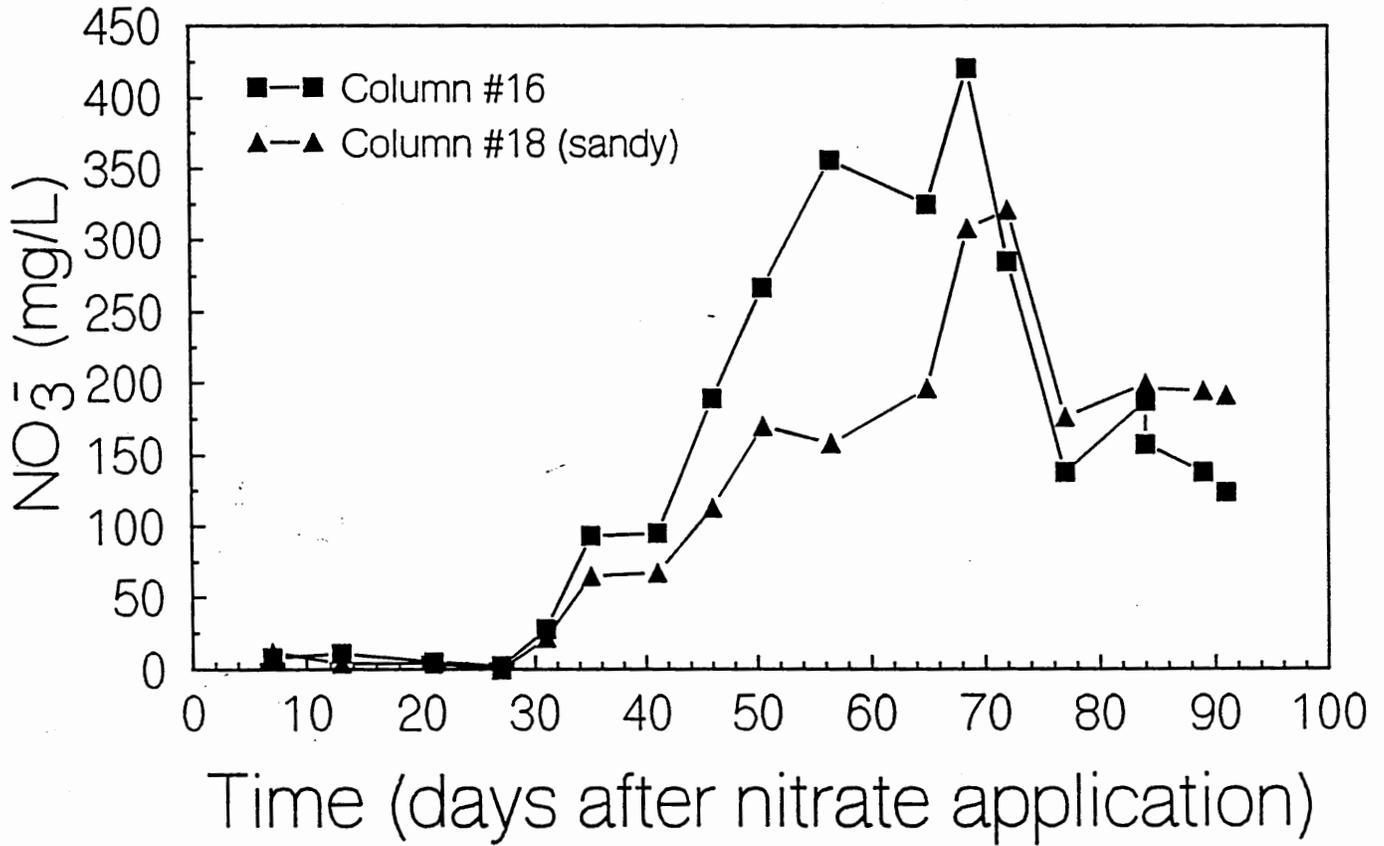


Figure 41. Breakthrough curves of nitrate in leachate with time from nitrate treated fallow field lysimeter (# 16 ■, #18 ▲, upper slope position) in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

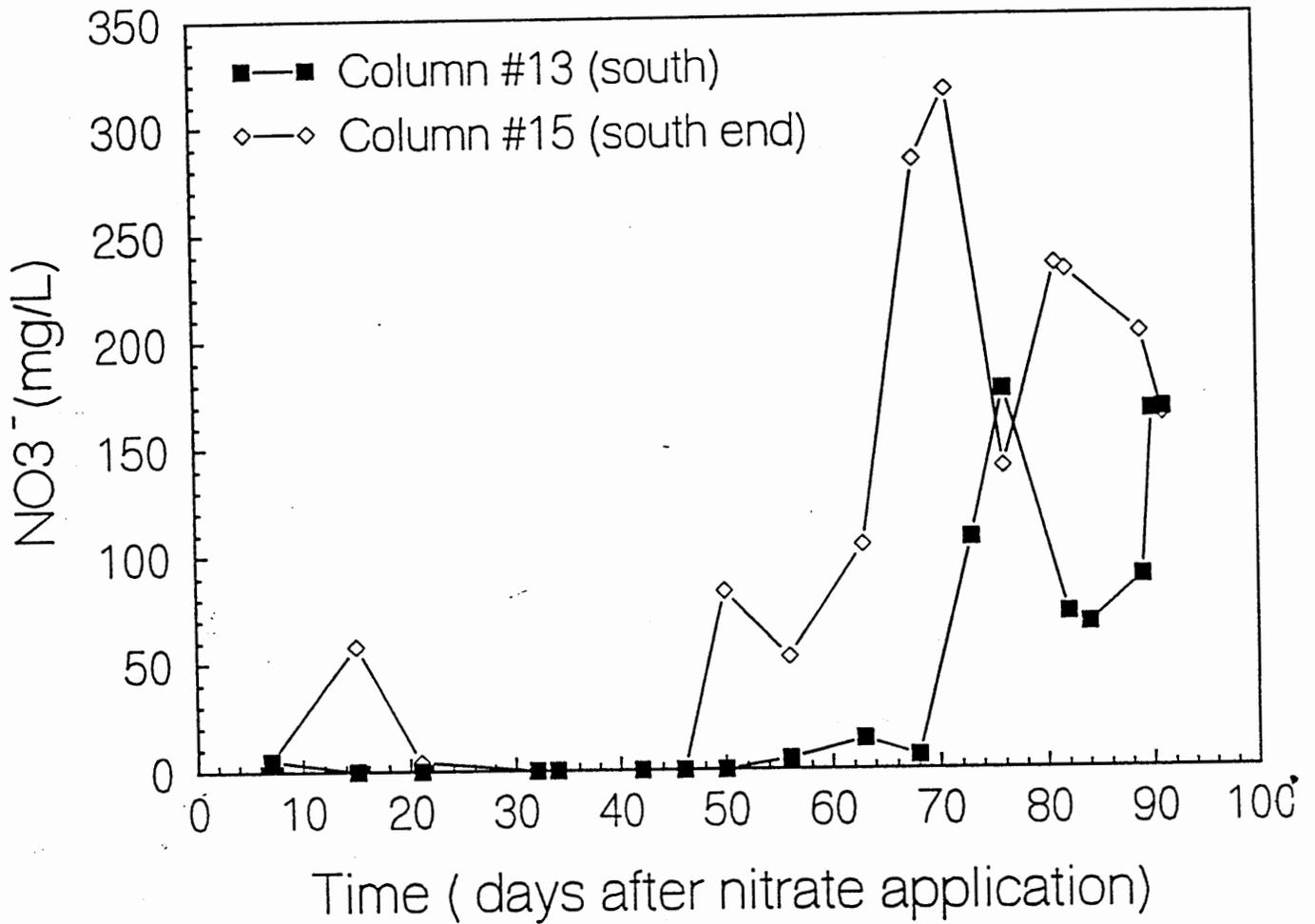


Figure 42. Breakthrough curves of nitrate in leachate with time from nitrate treated fallow field lysimeter (# 13 ■, #15 ◇ , lower slope position) in 1991 (Lein and Cassel, 1991, unpublished, N.C. State University, Raleigh, NC).

CO<sub>2</sub> and H<sub>2</sub>O. Balance sheets were constructed from the <sup>14</sup>C data. Total recoveries for the three herbicides ranged from 90.5 to 100.7% and averaged 96.9%.

Atrazine. Total recovery of applied <sup>14</sup>C for atrazine averaged across the sterile and non-sterile treatments and all depths, was 99.2% at time 0. Atrazine dissipation and binding, as affected by sterilization and soil depth are shown in Figures 43 to 51. Binding of atrazine to the soil increased with time for all samples (Figures 43 to 46). This is consistent with reports of others (Ghadiri et al. 1984, Scheunert 1986, Schiavon 1988, Huang and Frink 1989, Bowman 1989). Soil samples from horizons which had higher levels of organic matter had higher levels of bound residues. In non-sterile soil, atrazine binding decreased with increasing depth in the order, 0cm > 20cm > 45cm > 70cm (Figures 43 to 46). In 0-5cm samples, however, binding decreased after 9 weeks (Figure 43). In the sterile treatment, however, the order was 0cm > 45cm > 20cm > 70cm (Figures 43 to 46).

At 22 weeks there were significant differences in the amount of bound radioactivity between sterile and non-sterile samples from 0-5, 20-25, and 45-50 cm, but not 70-75 cm (Figures 43 to 46). This reflects the fact that autoclaving the soil affects some, but not all, of the binding sites of atrazine. Samples from 70-75 cm apparently did not contain enough organic matter to be influenced by autoclaving.

Autoclaving the soil produced two different effects on binding to soil constituents. For samples from 0-5, 20-25 and 70-75 cm, binding was highest in the non-sterile treatment where the soil had not been autoclaved (Figures 43, 44 and 46). Non-sterile samples from the 0-5 cm depth had higher levels of bound residues for the first 9 weeks vs the sterile treatment until these residues started to be mineralized to <sup>14</sup>CO<sub>2</sub>, (Figures 43 and 51). Sterile samples from 45-50 cm had higher levels of bound residues than the non-sterile treatment; however, the reason for this is unclear (Figure 45). It is possible that autoclaving the soil affected the structure or reactivity of either the clay or iron oxides present at this depth. Degradation of atrazine to extractable <sup>14</sup>C-polar compounds (Table 17) occurred in samples from 0-5 cm and 20-25 cm in both the sterile and non-sterile treatments (Figures 47 and 48, respectively). Production of hydroxy products was evident within 2 wk, ranging from 5.9 to 8.5% of the total applied radioactivity. Degradation in sterile samples indicates that the initial degradation step of atrazine is chemical rather than a biological process. This indicates that soil conditions which are conducive to chemical degradation of atrazine were similar in samples from 0-5 and 20-25 cm and in both sterile and non-sterile soil.

Most authors have reported that chemical rather than biological degradation is the primary degradation route of atrazine (McCormick and Hiltbold 1966, Skipper et al. 1967, Dao et al. 1979, Geller 1980). Degradation of atrazine to hydroxyatrazine is catalyzed by bonding to soil constituents, notably organic matter (Armstrong et al. 1967, Armstrong and Chesters 1967, Skipper et al. 1967, Gamble and Khan 1985). This may occur through ionic bonds, hydrogen bonding or charge transfer complexes (Senesi and Chen 1989). Binding appears to increase the electron deficiency of carbons in the triazine ring allowing nucleophilic attack by water on the chlorine-carbon bond at the #2 position (Esser et al. 1975, Erickson and Lee 1989).

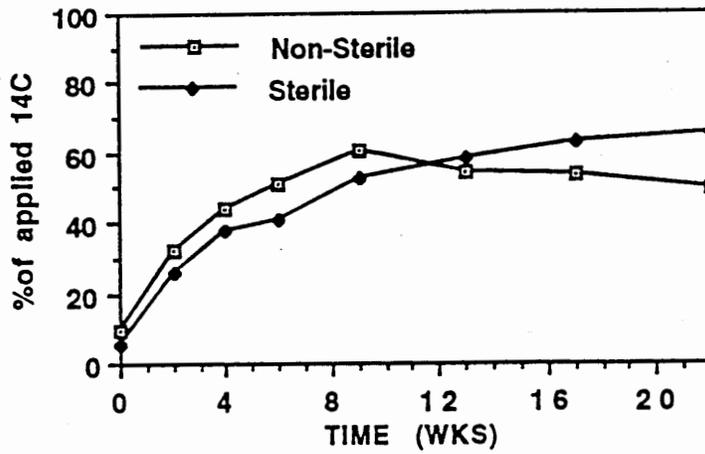


Figure 43. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 0- to 5-cm depth soil (Miller 1992).

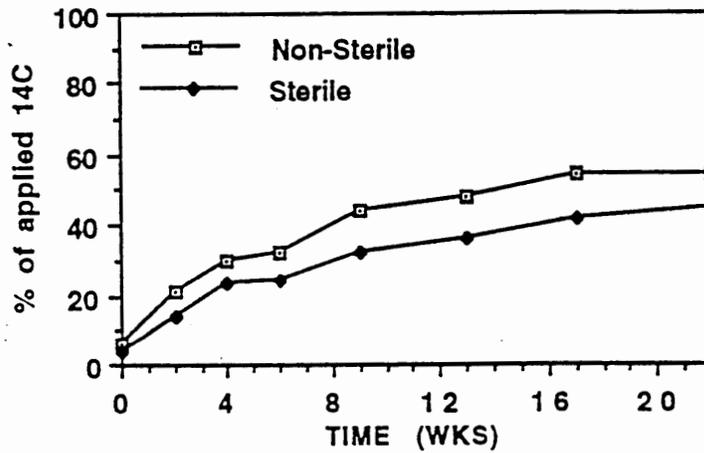


Figure 44. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 20- to 25-cm depth soil (Miller 1992).

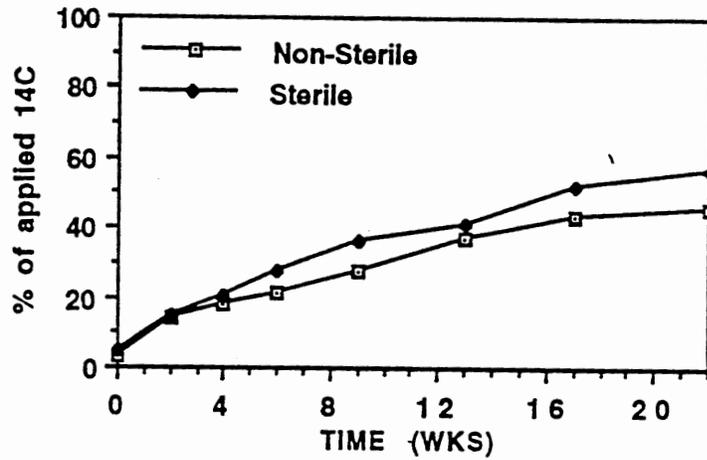


Figure 45. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 45- to 50-cm depth soil (Miller 1992).

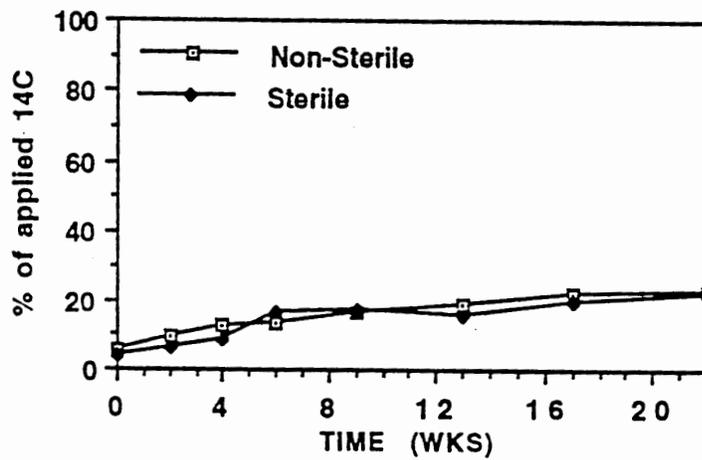


Figure 46. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 70- to 75-cm depth soil (Miller 1992).

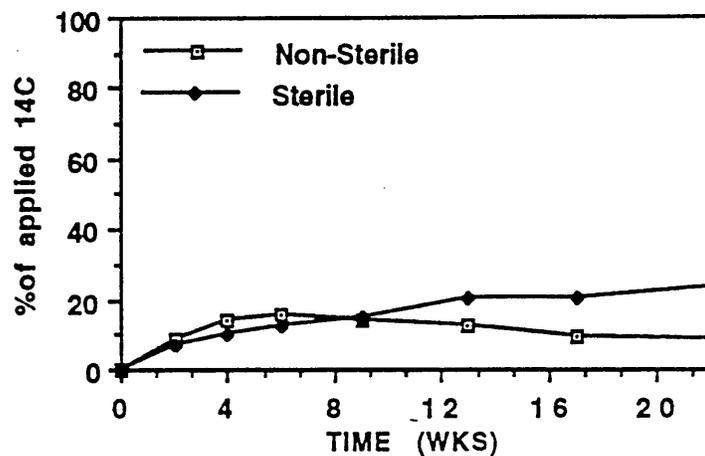


Figure 47. Extractable atrazine metabolite production with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 0- to 5-cm depth soil (Miller 1992).

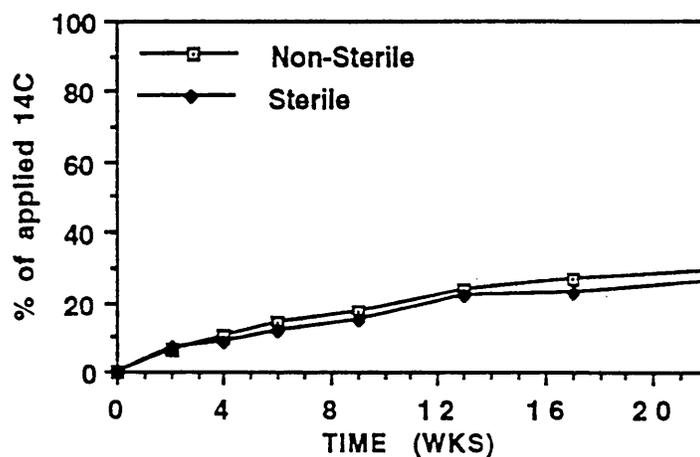


Figure 48. Extractable atrazine metabolite production with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 20- to 25-cm depth soil (Miller 1992).

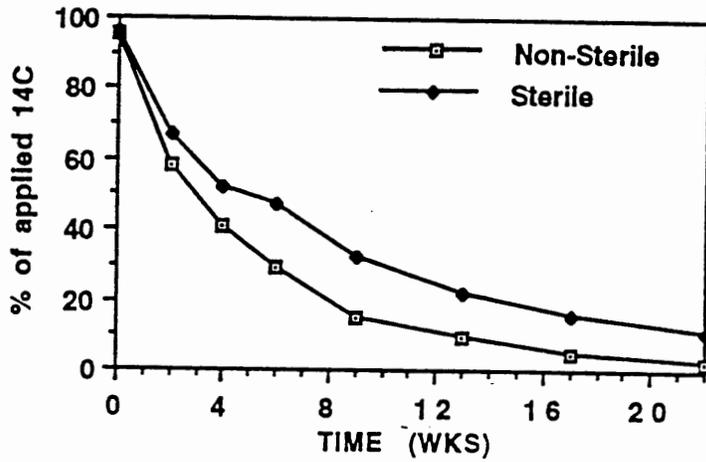


Figure 49. Atrazine dissipation with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 0- to 5-cm depth soil (Miller 1992).

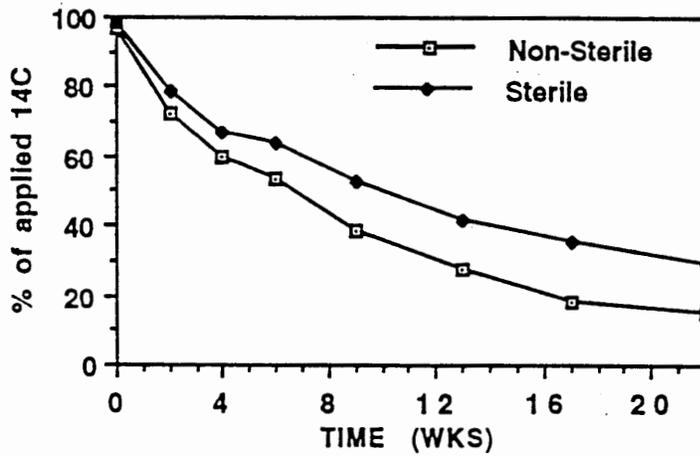


Figure 50. Atrazine dissipation with time in sterile and non-sterile <sup>14</sup>C-atrazine treated 20- to 25-cm depth soil (Miller 1992).

Chemical degradation to hydroxyatrazine was lacking in samples from the lower depths in both the sterile and non-sterile treatments (not shown). This was unexpected since reports of acid hydrolysis are present in the literature (Armstrong et al. 1967, Benyon et al. 1972, Chadiri et al. 1984) and due to the fact that the pH at these depths was 4.3 - 4.7 (Tables 2 and 3). However, the soils used by Armstrong et al. (1967) and Ghadiri et al. (1984) had organic carbon contents up to 13% while the organic carbon contents at the 45-50 and 70-75 cm depths in this study were 0.5 and 0.4, respectively (Tables 2 and 3). Organic matter seems to greatly influence atrazine degradation more than pH or the two factors may interact synergistically. Other authors have also reported decreasing degradation of atrazine at deeper soil depths (Roeth et al. 1969, Frank and Sirons 1985, Schiavon 1988).

The major polar metabolite was probably hydroxyatrazine, but thin layer chromatography could not distinguish between this and hydroxy-deethyl or hydroxy-diisopropyl atrazine since all three have an  $R_f = 0$  to 0.09 in the solvent systems used (Table 17). However, deethyl and diisopropyl atrazine were not detected in this study

Biologically available atrazine degraded in soil from the 0-5 and 20-25 cm depths in both the sterile and non-sterile treatments (Figures 49 and 50) but not in samples from the 45-50 or 70-75 cm depths (not shown). Available atrazine declined to 2.5% after 22 weeks in the non-sterile treatment and to 10.8% in the sterile treatment for the 0-5 cm depth samples as binding and degradation increased (Figure 49). For the 20-25 cm depth samples, 15.3 and 29.0% of the applied radioactivity was recovered as atrazine after 22 wk for the non-sterile and sterile treatments, respectively (Figure 50). After 22 wk, there were significant differences in the amount of atrazine remaining between sterile and non-sterile samples from 0-5, 20-25, and 45-50 cm but not in samples from 70-75 cm. The main difference in recoverable parent between the sterile and non-sterile surface samples was due to the increasing amount of radioactivity recovered as  $^{14}\text{CO}_2$  in the non-sterile samples. The organic matter content at each depth appeared to have the most influence on the speed of dissipation. Samples which had higher levels of organic matter dissipated atrazine faster than samples with low levels. In all samples, except non-sterile surface samples, more  $^{14}\text{C}$  was recovered in the bound fraction than was recovered as degradation products.

For the lower three depths in both sterile and nonsterile treatments, less than 2% of the applied radioactivity was recovered as  $^{14}\text{CO}_2$  (data not shown). For the non-sterile surface samples, an average of 36% of the applied radioactivity was recovered as  $^{14}\text{CO}_2$  after 22 wk (Figure 51) compared to less than 0.5% for the sterile sample (not shown). This is greater than most previous reports where the average  $^{14}\text{CO}_2$  recoveries range from 3-5% with one report of 28% (Skipper et al. 1967, Scheunert et al. 1986, Winkleman and Klaine 1991a,b). The difference between the results of this study and those reported by other authors may be due to enhanced degradation. Atrazine (as AAtrex) had been applied at this site in 1980 and 1985 (G. B. Clark, Superintendent - Central Crops Research Station, 1992, personal communication). Therefore, the development of a population of microorganisms capable of degrading atrazine is a possibility.

The production of hydroxy-compounds in the sterile treatment indicates that atrazine is chemically degraded while the production of  $^{14}\text{CO}_2$  in the non-sterile treatment indicates that further biological degradation is also

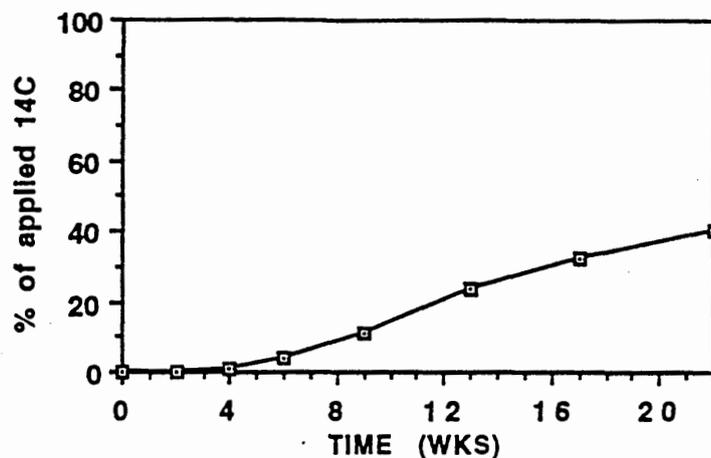


Figure 51. <sup>14</sup>CO<sub>2</sub> production with time in non-sterile <sup>14</sup>C-atrazine treated 0- to 5-cm depth soil (Miller 1992).

occurring. The lack of <sup>14</sup>CO<sub>2</sub> production in sterile samples indicates that cleavage of the triazine ring is a microbial process.

In non-sterile 0-5 cm samples, as levels of <sup>14</sup>CO<sub>2</sub> production were increasing (Figure 51), levels of both bound radioactivity (Figure 43) and hydroxyatrazine were declining. This decrease in the bound fraction, as hydroxyatrazine was being mineralized to <sup>14</sup>CO<sub>2</sub>, indicates that the bound fraction was also available for mineralization. Small amounts (3-4%) of the bound fraction of chemicals such as metolachlor have been reported to be microbially degraded to <sup>14</sup>CO<sub>2</sub> when soils containing unextractable residues were mixed with microbially active soil (LeBaron et al. 1988). The observation that bound residues declined after 9 weeks only in non-sterile samples from 0-5 cm (Figure 43), coupled with the large amounts of <sup>14</sup>CO<sub>2</sub> produced by microbial activity, suggests that degradation of these residues was due to microbial rather than chemical processes. The fact that bound residues can be mineralized indicates that current concepts of "bound" or "unextractable" residues are inadequate.

The half-life of a chemical is defined as the time required for 50% of the chemical to dissipate. This is not a true kinetic half-life and is dependant upon many parameters including volatilization, binding to soil constituents, plant uptake, leaching and degradation. Therefore, even if no degradation occurs, a half-life can be calculated if 50% or more of the applied compound becomes available for any of the above reasons. However, the definition of unavailable is still open to debate. Compounds which are bound to the soil may still be available to both plants and microbes. This represents a procedural problem related to an inability to characterize bound residues. Bound residues can still be phytotoxic (Weber and Weed, 1974), indicating that the parent molecule may still be intact and is slowly available for uptake by plants. In this study only binding to the soil and degradation into metabolites contributed to the dissipation of the applied chemical and the half-lives presented reflect the time required for 50% of the parent compound to become unextractable with organic solvents.

The time required for dissipation of 50% of the applied atrazine varied among soil depths and treatments (Table 33). Regardless of treatment, soil samples from the surface had shorter half-lives than samples taken from lower in the profile. This was due to higher amounts of bound residues formed in samples with higher levels of organic matter. With the exception of samples from 45-50 cm, non-sterile samples dissipated atrazine faster than sterile samples. This was also due to binding of the herbicide to organic matter, except for samples from 0-5 cm where significant microbial degradation occurred.

Half-lives ranged from 3.6 weeks in non-sterile 0-5 cm samples to >22 weeks in all subsurface samples deeper than 45 cm. Atrazine was not chemically or biologically degraded in samples from 45-50 or 70-75 cm in either treatment.

Metolachlor. Total recovery of applied  $^{14}\text{C}$  for metolachlor averaged across the sterile and non-sterile treatments and all depths, was 93.3% at time 0. Metolachlor degraded only in non-sterile surface samples, as shown in Figures 52 to 55.

As occurred with atrazine, binding of metolachlor to the soil increased with time and was lower for samples from deeper in the profile than in samples from the surface (Figures 52 and 53). For the sterile treatment, binding was virtually identical among all depths: after 7 weeks between 3 and 8% of the applied  $^{14}\text{C}$  was recovered as bound residues. In the non-sterile treatment, the bound fraction from 0-5 and 20-25 cm samples was 30 and 11% of the applied  $^{14}\text{C}$ , respectively, significantly higher than in samples from the lower depths.

The significant effect of autoclaving in sterile samples from 0-5 and 20-25 cm indicates that autoclaving alters or destroys most of the binding sites for metolachlor (Figures 52 and 53). Binding of metolachlor in small amounts in sterile samples suggests that autoclaving does not destroy all of the sites to which metolachlor normally binds or that the metolachlor molecule is capable of binding to different kinds of sites. Sites most highly affected by autoclaving were most prevalent in the surface 0-5 cm samples where organic matter content was the highest (Tables 2 and 3).

In the non-sterile treatment, there were statistical differences among depths for bound residues (Figure 53) but the only difference of biological significance was between samples from 0-5 cm (Figure 52) and samples from the lower depths (Figure 53). Samples from lower in the profile were very similar. All of this suggests, consistent with the reports of others, that organic matter is probably the primary adsorbing surface for metolachlor in this soil, which lacks any expanding-type clay minerals (CIBA-Geigy 1978, Peter and Weber 1985, Rao et al. 1986, Wood et al. 1987).

The only soil samples in which metolachlor metabolites were formed were taken from the 0-5 cm depth in the non-sterile treatment (Figure 54). This is consistent with other reports that metolachlor degradation is a biological rather than a chemical process (Bouchard et al. 1982, LeBaron et al. 1988). During the study, two metabolites were detected. Metabolite 1 is a polar metabolite with  $R_f = 0$  in the solvent system used and comprised 12.9% of the applied radioactivity after 7 weeks. Metabolite 2 is a less polar product ( $R_f = 0.45$ ) (Table 17) and made up 4.1% of the applied radioactivity after 7 wk. It was not possible using the methods described to correlate the metabolites produced in this study to any of the eight metabolites of metolachlor which

Table 33. Time required for dissipation of 50% of applied <sup>14</sup>C-labeled atrazine and primisulfuron, as influenced by sterilization and depth of soil sample (Miller 1992).

Depth	Treatment <sup>a</sup>	
	Non-Sterile	Sterile
cm	----- (wk) -----	
	Atrazine	
0-5	3.6 Aa	6.2 Aa
20-25	7.4 Ab	12.1 Bb
45-50	25.1 Ac (est)	18.6 Bc
70-75	>> 22.0 Ad	>> 22.0 Ad
	Primisulfuron	
0-5	2.1 A <sup>1</sup> a <sup>2</sup>	> 7.0 Ba
20-25	3.4 Aa	> 7.0 Ba
45-50	> 7.0 Ab	> 7.0 Ba
70-75	> 7.0 Ab	6.7 Ab

<sup>a</sup>Sterile/Non-sterile comparisons followed by the same capital letter are not different at the 0.5% level of significance using standard T-tests. Numbers in each column followed by the same lowercase letter are not different at the 0.5% level of significance using Duncan's multiple range test.

have been identified by other investigators (McGahen and Tiedje 1978, Krause et al. 1985).

After 7 wk, in non-sterile samples from 0-5 cm, 52% of the applied <sup>14</sup>C-metolachlor was recovered as metolachlor and a half-life of 7.3 wk was estimated (Figure 54). The combined amount of metolachlor bound and degraded in sterile samples and samples from all other depths was much less than 50% of the applied chemical; thus dissipation half-lives could not be calculated (Figure 55). The fact that degradation occurred only in the non-sterile surface samples indicates that degradation was microbial rather than chemical.

Only small amounts of <sup>14</sup>CO<sub>2</sub> were produced from any of the samples during the 7 wk of the experiment with a maximum of 1.6% from the non-sterile 0-5 cm depth sample (not shown). Because metolachlor was labeled in the aniline ring, the absence of <sup>14</sup>CO<sub>2</sub> production suggests that any metabolites formed during incubation came from modifications of the alkyl side chains rather than from cleavage of the aniline ring. Other authors have reported up to 18.4% of applied metolachlor mineralized to CO<sub>2</sub> in soil previously exposed to metolachlor but less than 5% from soil having no history of metolachlor application. Pure cultures of organisms capable of degrading metolachlor do not appear capable of producing <sup>14</sup>CO<sub>2</sub> from extensive cleavage of the aniline ring (Saxena et al. 1987, Liu et al. 1988).

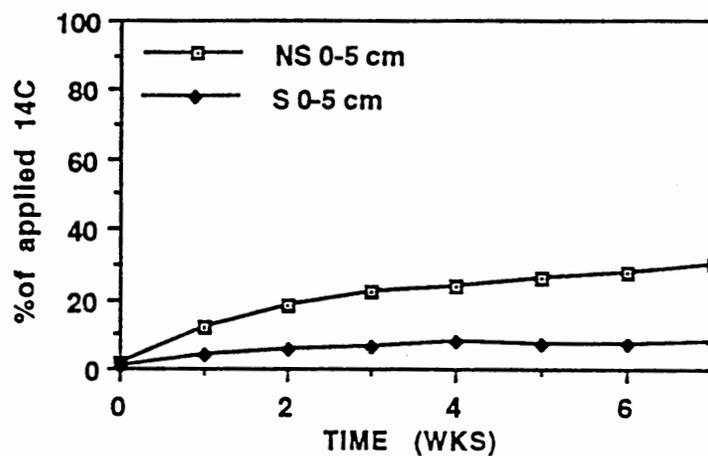


Figure 52. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-metolachlor treated 0-to 5-cm depth soil (Miller 1992).

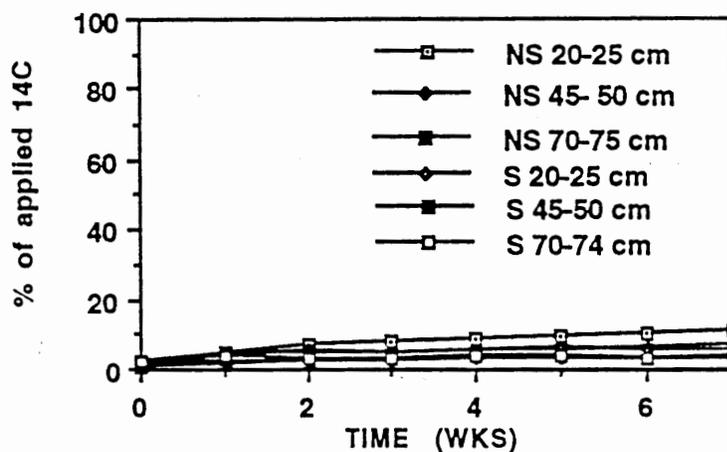


Figure 53. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-metolachlor treated 20-25, 45,50, and 70-75 cm depth soil (Miller 1992).

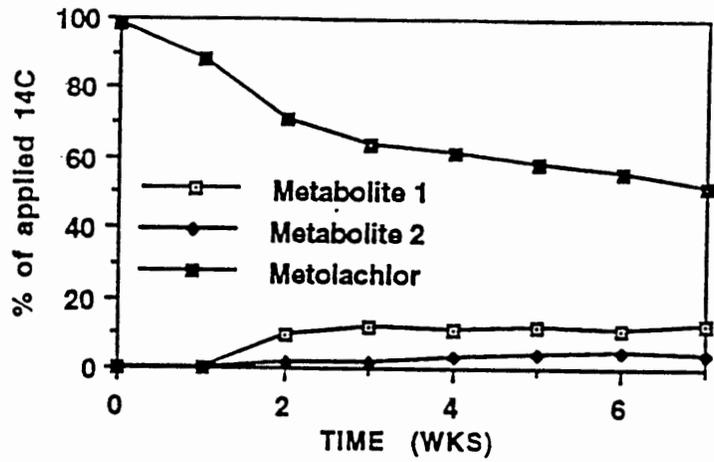


Figure 54. Metolachlor dissipation with time and metabolite appearance in <sup>14</sup>C-metolachlor treated non-sterile 0-5 cm depth soil (Miller 1992).

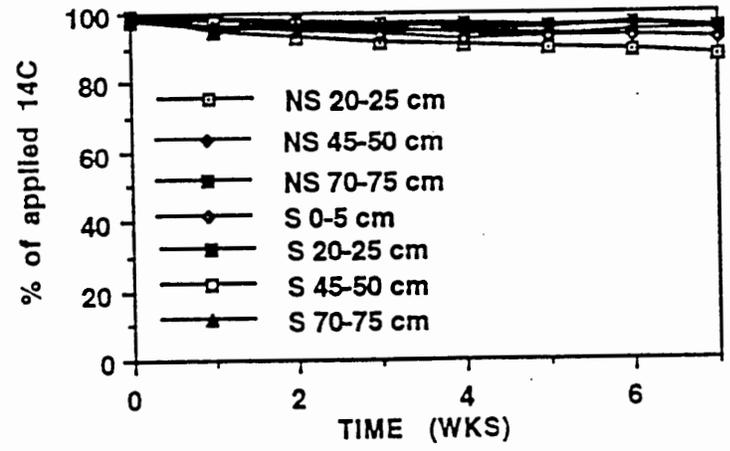


Figure 55. Metolachlor dissipation with time in sterile and non-sterile <sup>14</sup>C-metolachlor treated 0-5, 20-25, 45-50 and 70-75 cm depth soil (Miller 1992).

Primisulfuron. The total recovery of applied  $^{14}\text{C}$ -primisulfuron during the sampling periods ranged from 91.5 to 100.1% and averaged 97.5%. Primisulfuron has two aromatic rings, however, only one of the rings was radiolabeled. This created problems in detection of metabolites as only compounds formed from one of the rings could be traced. Metabolites produced by degradation of the other ring may have been present but could not be detected. Primisulfuron dissipation and binding as affected by sterilization and soil depth are shown in Figures 56 to 64.

In the non-sterile treatment, more primisulfuron was bound in samples from the surface than in samples from the lower depths (Figures 56 and 57), probably directed related to organic carbon content (Tables 2 and 3). In samples from the 0-5, 20-25 and 45-50 cm depths, autoclaving may have destroyed primisulfuron binding sites, resulting in significantly lower levels of bound radioactivity in the sterile samples when compared to the corresponding non-sterile samples. Sterile samples from the 70-75 cm depth had a higher level of bound radioactivity, but part of this difference from the non-sterile samples may have been due in part to the different clay type and oxide deposits observed during the original sampling. The fact that bound residues decline with declining organic carbon content in non-sterile samples suggests that organic matter is a primary binding site for primisulfuron in undisturbed soils. The differences noted for autoclaved samples, point out that clay is capable of binding primisulfuron and that there maybe an important interaction between clay and organic matter for binding primisulfuron.

Two metabolites of primisulfuron were produced at every depth and for both the sterile and non-sterile treatments (Figures 58 to 61, Table 17). The initial production of metabolite 1 was similar in both the sterile and non-sterile treatment (Figures 58 and 59). In the sterile treatment a second metabolite appeared rapidly, within 1 to 2 wk, increasing to nearly 20% of the applied radioactivity (Figure 60). The increase in metabolite 2 appeared to be at the expense of metabolite 1 and at the end of the 7 wk incubation only small amounts of metabolite 1 were detected (<9%) (Figure 58). For all samples in the sterile treatment, the total level of  $^{14}\text{C}$  recovered as metabolites increased for the first 2 wk but then remained relatively constant (Figures 58 and 60). After 2 wk very little additional  $^{14}\text{C}$  was metabolized, but levels of metabolite 1 declined as it was transformed into metabolite 2.

In the non-sterile samples, primisulfuron metabolite 1 was transformed into metabolite 2 at a much slower rate than sterile samples (Figures 59 and 61). At the end of 7 wk of incubation most of the  $^{14}\text{C}$  was still present as metabolite 1 and only small portions were detected as metabolite 2. Total  $^{14}\text{C}$  recovered as metabolites in non-sterile samples continued to rise steadily throughout the experiment. In the non-sterile treatment, samples from the 20-25 cm depth produced higher levels of metabolites than did samples from the surface. This difference may be due to differences in soil pH and organic carbon contents between the two depths (Tables 2 and 3). Samples from the upper two horizons had pH levels from 5.7 to 6.4 and organic carbon contents of 0.9 to 1.1% while the second two depths had pH levels from 5.0 to 5.2 and organic carbon contents of 0.5 to 0.8. It may be that in the 20-25 cm depth samples, hydrolysis occurred more readily compared to other depths. Organic carbon and pH levels decreased with depth. Even though non-sterile samples from 20-25 cm contained more metabolites than those from the 0-5 cm depth, disappearance of primisulfuron in non-sterile 0-5 cm samples was faster

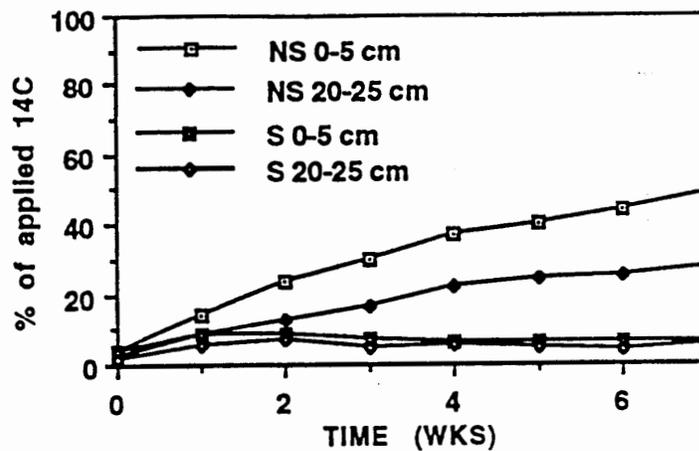


Figure 56. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-primisulfuron treated 0-5 and 20-25 cm depth soil (Miller 1992).

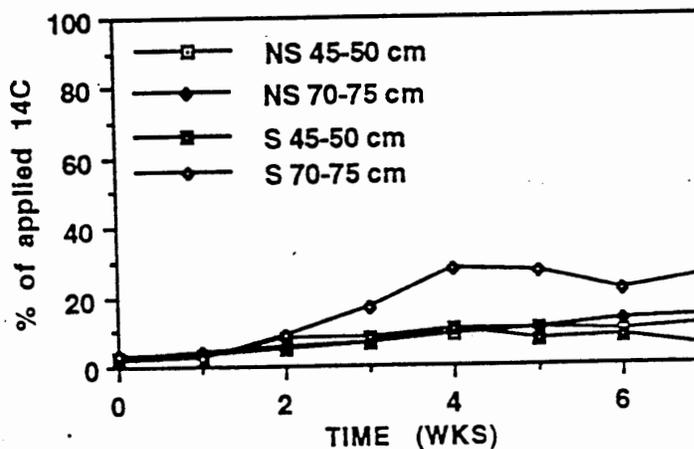


Figure 57. Bound <sup>14</sup>C with time in sterile and non-sterile <sup>14</sup>C-primisulfuron treated 45-50 and 70-75 cm depth soil (Miller 1992).

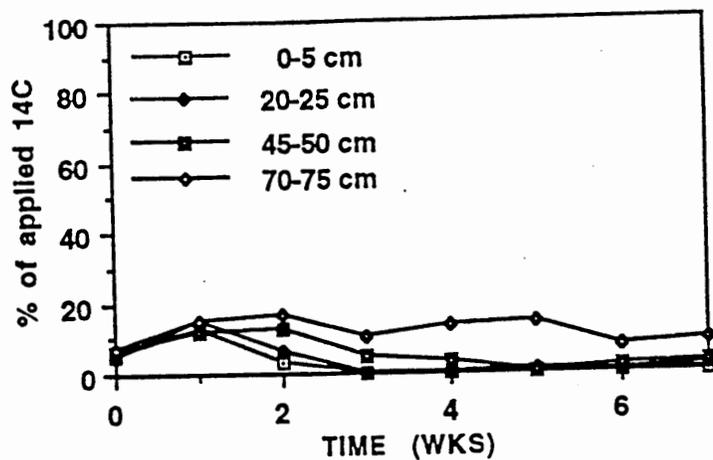


Figure 58. Extractable metabolite 1 production in sterile <sup>14</sup>C-primisulfuron treated 0-5, 20-25, 45-50 and 70-75 cm depth soil (Miller 1992).

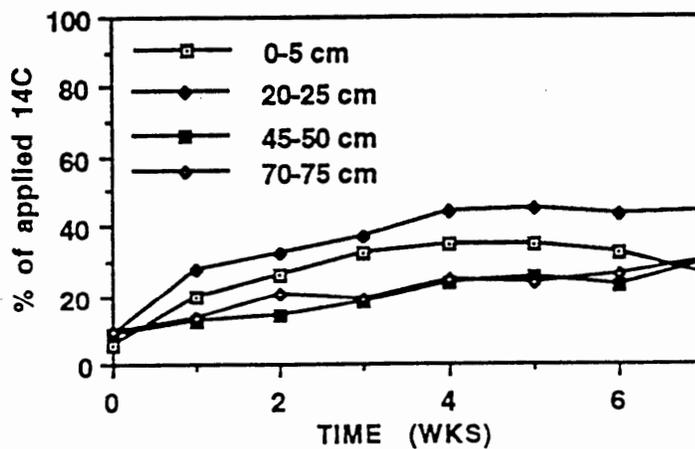


Figure 59. Extractable metabolite 1 production in non-sterile <sup>14</sup>C-primisulfuron treated 0-5, 20-25, 45-50 and 70-75 cm depth soil (Miller 1992).

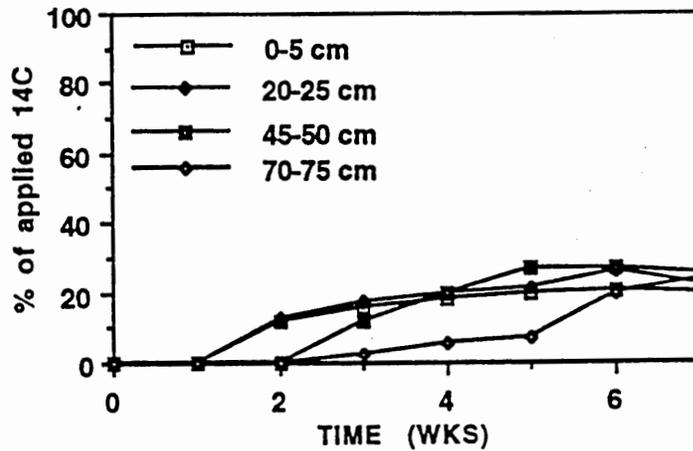


Figure 60. Extractable metabolite 2 production in sterile <sup>14</sup>C-primisulfuron treated 0-5, 20-25, 45-50 and 70-75 cm depth soil (Miller 1992).

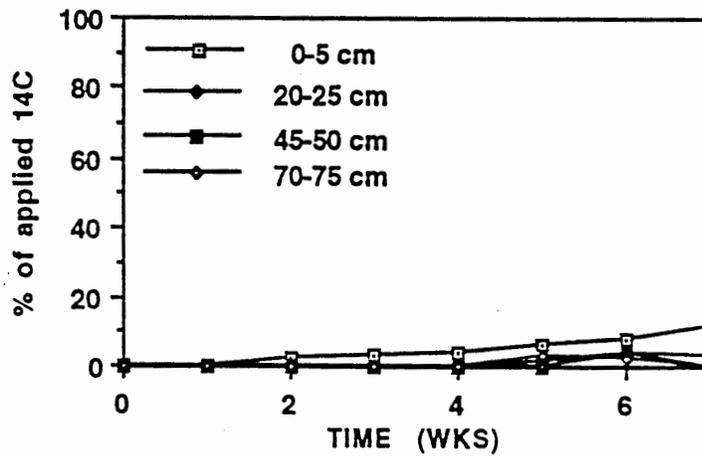


Figure 61. Extractable metabolite 2 production in non-sterile <sup>14</sup>C-primisulfuron treated 0-5, 20-25, 45-50 and 70-75 cm depth soil (Miller 1992).

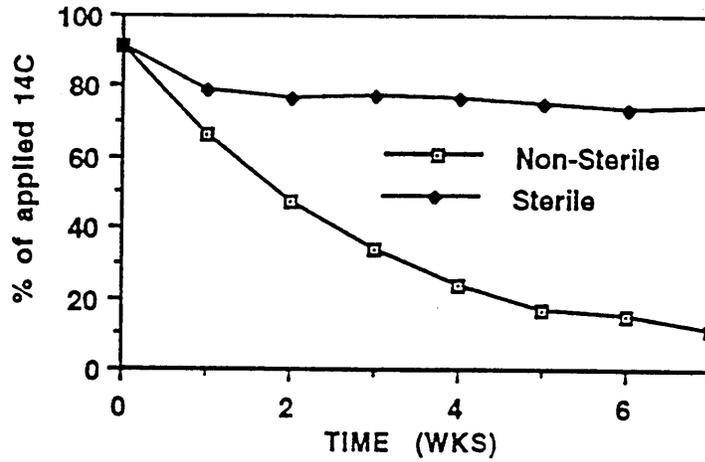


Figure 62. Primisulfuron dissipation with time in sterile and non-sterile <sup>14</sup>C-primisulfuron treated 0-5 depth soil (Miller 1992).

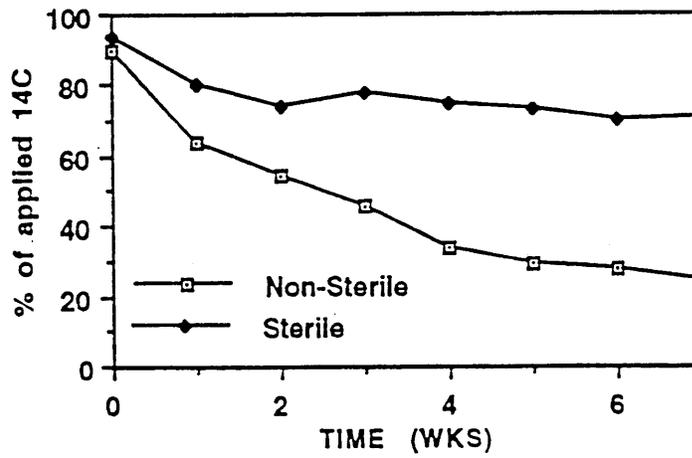


Figure 63. Primisulfuron dissipation with time in sterile and non-sterile <sup>14</sup>C-primisulfuron treated 20-25 depth soil (Miller 1992).

because the rate of formation of bound residues was higher in surface samples than in subsurface samples (Figures 56 and 57).

The disappearance of primisulfuron appeared to proceed in a much faster fashion in the non-sterile media as compared with sterile conditions (Figures 62 to 64). Initially, the parent molecule was spontaneously hydrolyzed on contact with the soil to form an initial metabolite (metabolite 1). As much as 11.6% of the applied radioactivity was recovered as metabolite 1 at time 0 (non-sterile samples from 20-25 cm). The first step is likely to be the chemical hydrolysis of the urea bond, although some microbial processes appear to have supplemented chemical hydrolysis as evidenced by significantly greater amounts of metabolite 1 in the non-sterile samples vs sterile ones (Figures 58 and 59). Metabolite 1 was then transformed to a more polar compound (metabolite 2). Metabolite 2 was detected only as the amount of metabolite 1 declined (Figures 58 and 60). Therefore, it is surmised that metabolite 2 was formed by alteration of metabolite 1 rather than being produced directly from the alteration of primisulfuron. A second chemical step occurred as levels of metabolite 2 increased dramatically in the sterile samples but not in the non-sterile ones (Figures 60 and 61). Despite this, a greater proportion of the radioactivity was recovered as metabolites from the non-sterile treatment compared to sterile samples.

The production of metabolite 1 was very similar in magnitude and timing for the two experiments but metabolite 2 appeared later in experiment 1 than experiment 2. This was the only major difference between the two runs of the experiment. At the end of 7 wk, however, the total amount of metabolite 2 produced in each experiment was similar.

Primisulfuron disappeared faster in surface 0-5 cm samples than samples from deeper in the profile and faster in non-sterile samples vs sterile ones (Figures 62 to 64). Significantly less primisulfuron remained in the upper horizons of the non-sterile treatment than in soils from lower depths after a 7 wk incubation. For the sterile samples there were essentially no differences in the amounts of primisulfuron remaining among the different depths except that lower amounts of extractable primisulfuron were found in 70-75 cm depth samples due to binding.

There was very little production of  $^{14}\text{CO}_2$  in either sterile or non-sterile treatments. A maximum of 2.7% of the applied radioactivity was recovered as  $^{14}\text{CO}_2$  in the non-sterile samples and less than 0.05% from the sterile samples. The lack of  $^{14}\text{CO}_2$  production indicated that there was little cleavage of the radiolabeled ring.

Non-radioactive  $\text{CO}_2$  was detected in samples from every depth from both the sterile and non-sterile. Since bacteriological analyses indicate that sterile treatments had remained sterile during incubation some non-radioactive  $\text{CO}_2$  could have come from the hydrolysis of the urea bond and the subsequent release of the carbonyl carbon as  $\text{CO}_2$ . Evolution of the carbonyl carbon as  $\text{CO}_2$  has been reported for diuron and for other sulfonylurea herbicides (McCormick and Hiltbold 1966, Beyer et al. 1988, Brown 1990).

The half-life of primisulfuron was similar for the sterile and non-sterile soil samples except for the non-sterile upper horizons where half-lives ranged from 2.1 to 3.4 wk (Table 33). No difference in disappearance could be detected in sterile samples where half-lives were greater than the 7 wk

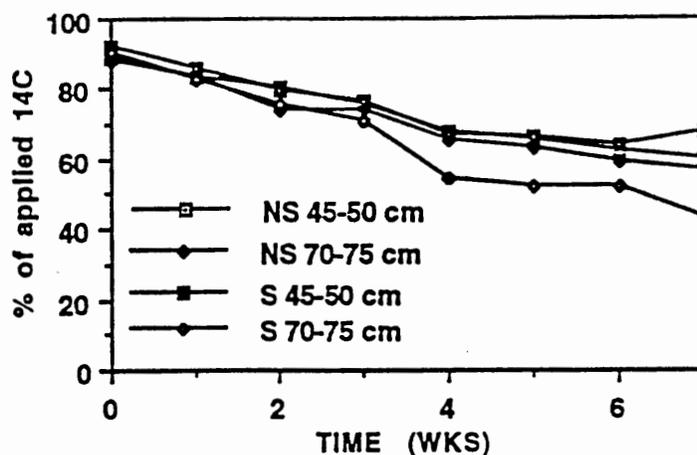


Figure 64. Primisulfuron dissipation with time in sterile and non-sterile  $^{14}\text{C}$ -primisulfuron treated 45-50 and 70-75 cm depth soil (Miller 1992).

duration of the experiment except for samples from 70-75 cm for which a half-life of 6.7 weeks was observed. For the non-sterile treatment, half-lives were shorter for surface samples when compared to samples from the lower horizons. Samples from 0-5 cm had the highest level of bound residues as well as the shortest half-life.

Primisulfuron was degraded in both the sterile and non-sterile samples and in samples from all four depths but very little was mineralized to  $^{14}\text{CO}_2$ . Differences in metabolite production between sterile and non-sterile samples suggest that microbial activity plays a major role in primisulfuron degradation. Primisulfuron appeared to bind well to organic matter with about 50% of the applied  $^{14}\text{C}$  recovered as bound residues in the surface samples. Very little  $^{14}\text{CO}_2$  was produced indicating little cleavage of the ringed structure of the molecule. In subsoil samples primisulfuron did not bind in large amounts and while there was some microbial degradation, the total amount was lower than what occurred in the surface samples. While the processes of degradation and binding do occur in subsoil samples, the rates of these processes are low. Primisulfuron that reaches the lower soil horizons may continue to leach to the ground water, posing a threat to the groundwater supplies, before it is degraded.

#### Metolachlor Sorption by Surface Soil and Subsoil

A total of 25 sorption rate studies were performed utilizing metolachlor and soils from selected depths of lysimeters M11 and M18. Two experiments were performed with the 7.5 to 15-cm section of the M11 lysimeter to investigate the effect of changing the initial metolachlor concentration by about a factor of ten, on the rate of sorption.

Figures 65 and 66 show metolachlor sorption rate results for an equivalent set of three representative sections from cores M11 and M18. Recall that the solids concentration used for all experiments was 2:1 (g of solids:mL of solution), except the upper most section for which a 1:1 solids concentration

was used. These ratios were chosen to yield intermediate final concentrations of metolachlor in solution, which allows for the clearest interpretation of data trends. A rapid initial decrease in fluid-phase metolachlor concentration followed by a slower, sustained rate of fluid-phase metolachlor decrease was observed for all experiments. Such results are consistent with previous reports (Karickhoff 1984, Miller and Weber 1986, Wu and Gschwend 1986).

A comparison of results from Figures 65 and 66 shows similar trends and extents of metolachlor sorption for both the 0 to 7.5-cm and the 82.5 to 90.0-cm sections. However, a significant variation existed in the sorption rate profile observed for the 37.5 to 45.0-cm section, with a greater extent of metolachlor sorption exhibited in Figure 65 for the sample from M11. This is surprising because the TOC of this section was only about a third of the TOC for the same depth section in the M18 lysimeter. The correlation of increasing sorption of an organic solute with increasing organic carbon content of a natural solid material is well-known in the literature (Karickhoff 1981).

Results plotted in Figures 65 and 66 show an approach to apparent equilibrium that is slower as the final fluid-phase metolachlor concentration decreases. This observation has support in the literature (Weber and Miller 1989, Brusseau and Rao 1989). Sufficient data does not exist to conclude that a final equilibrium was approached for all cases. Examination of the sorption rate profiles in Figure 65 shows that sorption of metolachlor seems to be continuing at times in excess of 1000 hours. It should be noted that this is much longer than most equilibrium studies are allowed to equilibrate.

Figure 67 shows a comparison of two rate studies performed on the 7.5 to 15.0-cm section of the M11 lysimeter, but varying in initial metolachlor concentration in the fluid phase. These results show a decreasing fluid phase concentration that persists for the duration of the experiments--times in excess of 1300 hours. A uniform trend in these results is the direct correlation between initial metolachlor concentration and normalized metolachlor concentration as a function of time during the experiment. These results are consistent with a nonlinear equilibrium distribution, whereby proportionately less sorption occurs in equivalent systems as the initial concentration of metolachlor in solution increases--a concave or favorable equilibrium model. This of course assumes that the results are not obscured by variations in the fractional approach to equilibrium as a function of time. Based upon previous observations, such a result would not be expected (Weber and Miller 1989, Brusseau and Rao 1989).

Sorption equilibrium distributions were achieved by keeping the soil to solution ratios constant while varying the initial metolachlor concentrations between 1 mg/L and 200 mg/L. In general, the reactors were allowed 1000 to 1100 hours to reach equilibrium. The results of the rate studies, however, indicate that this time allotment is not sufficient in most cases for the reactors to reach equilibrium.

As predicted from the data in Figure 67 for the varying initial concentration rate experiments, the equilibrium distribution relationships for metolachlor on these soils appear to be nonlinear. The Freundlich Model was used to describe the experimental relationships. The data were plotted using the linearized version of the Freundlich equation, and the empirical constants,  $K_f$

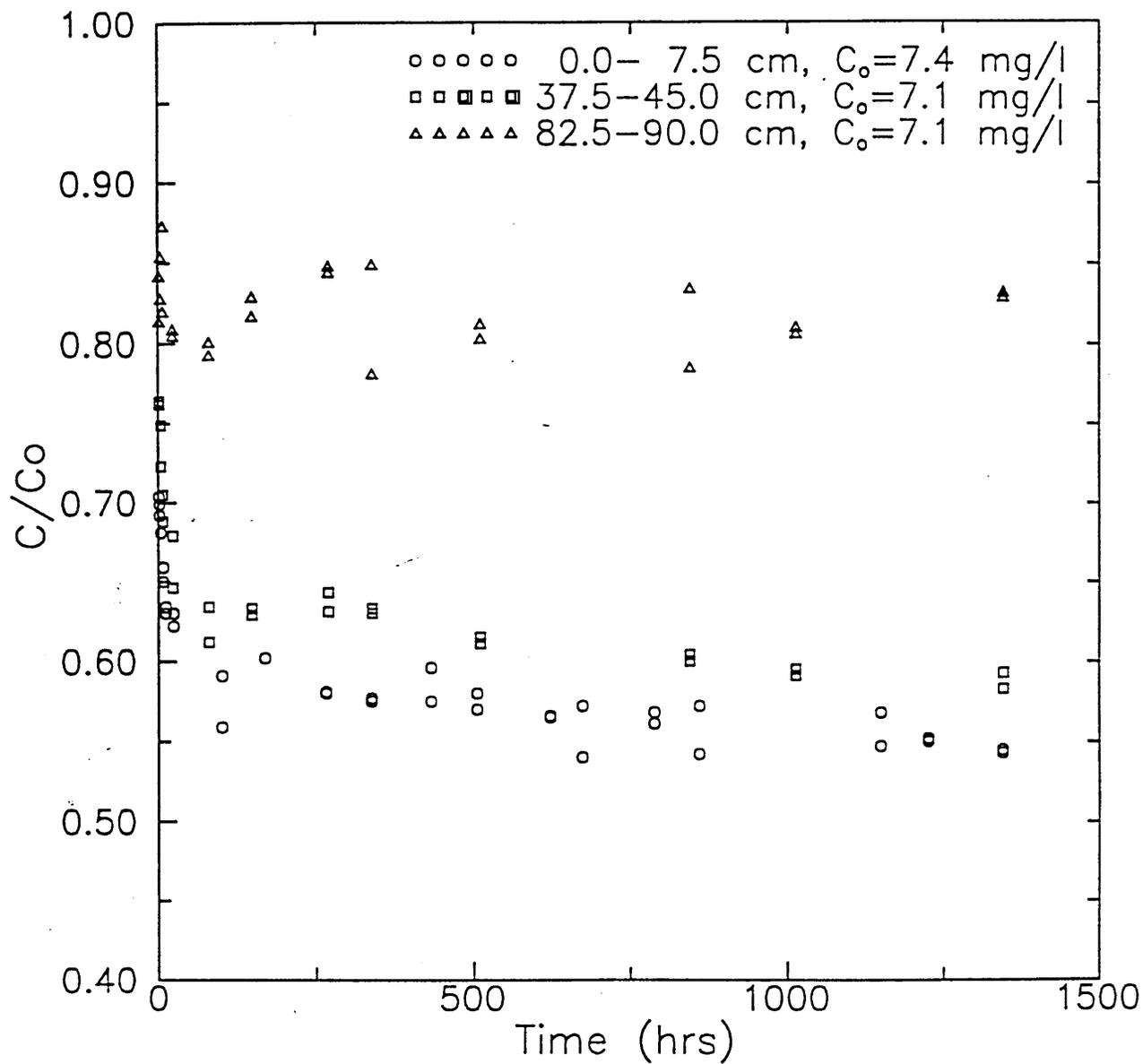


Figure 65. Kinetic data for the sorption of metolachlor, at initial concentrations of 7.1-7.4 mg/L on 0-7.5, 37.5-45.0 and 82.5-90.0 cm depth soil (M11) (Nelson 1991).

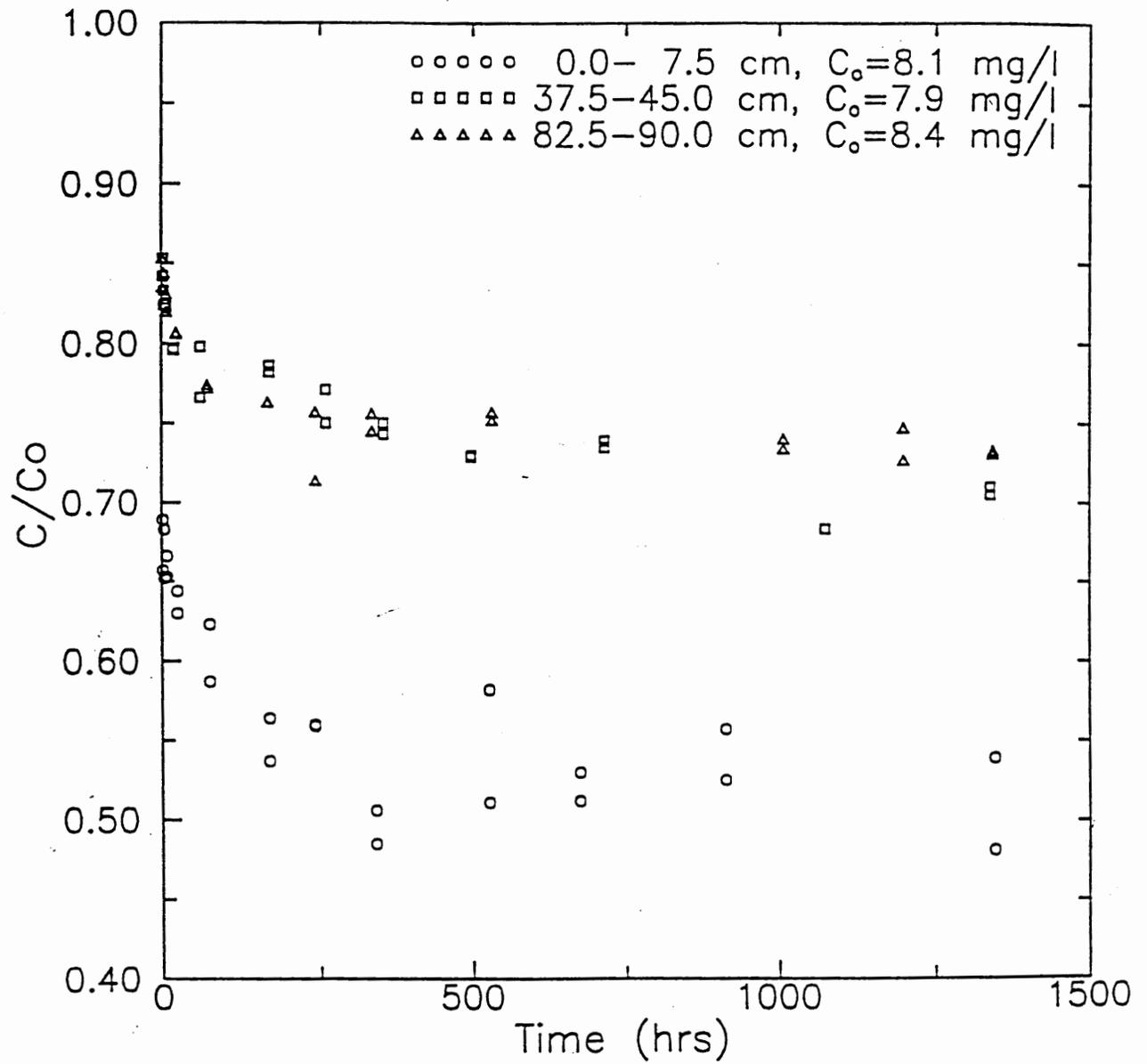


Figure 66. Kinetic data for the sorption of metolachlor, at initial concentrations of 7.9-8.4 mg/L, on 0-7.5, 37.5-45.0 and 82.5-90.0 cm depth soil (M18) (Nelson 1991).

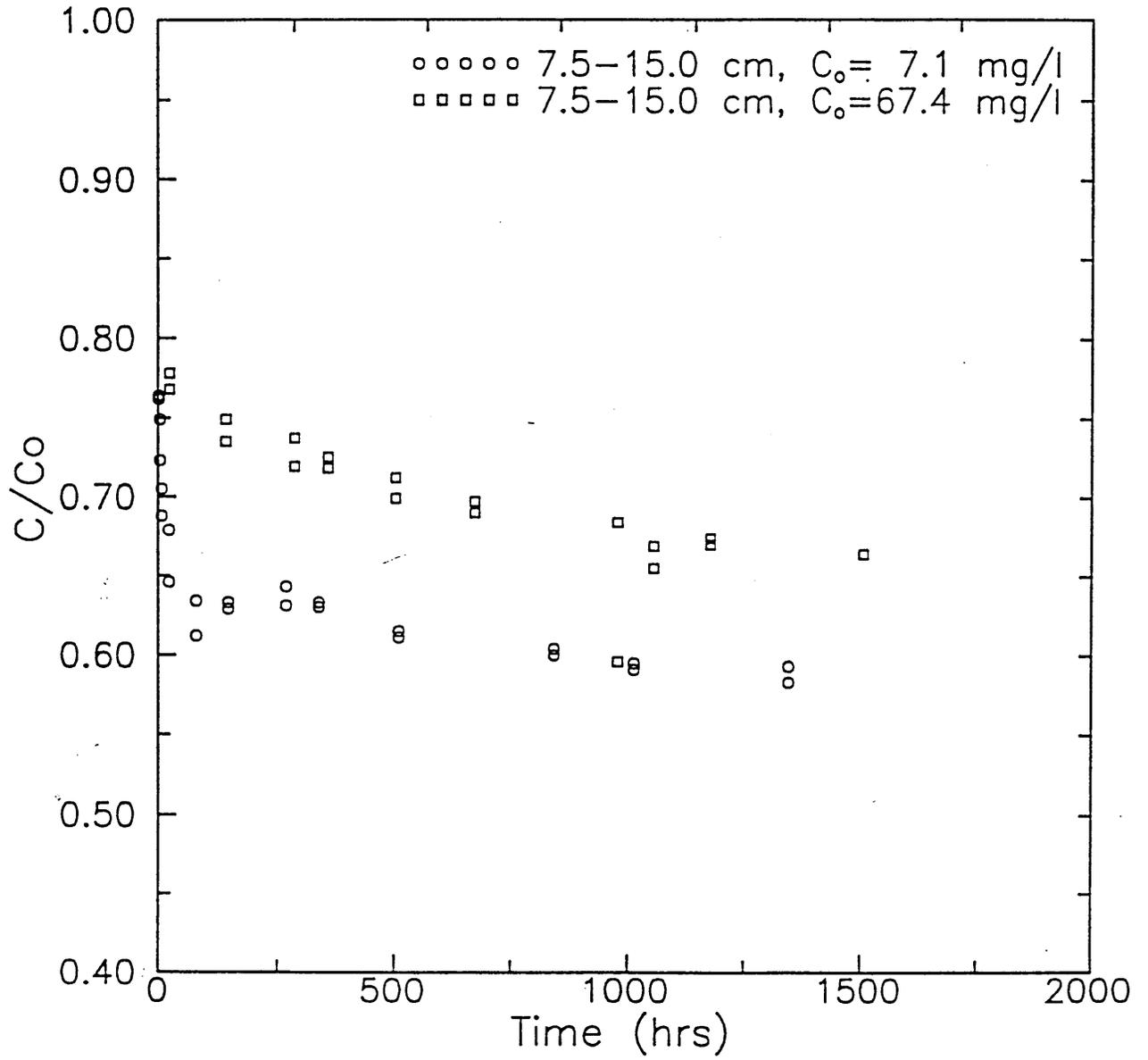


Figure 67. Kinetic data for the sorption of metolachlor, at initial concentrations of 7.1 and 67.4 mg/L on 7.5-15.0 cm depth soil (M11) (Nelson 1991).

and  $n$ , were obtained from linear regression in log space. Table 34 lists the best fit parameter values and their standard errors from the log fits. The Freundlich exponent ranged from 0.79 to 1.05, and the sorption capacity coefficient ranged from 0.0138 to 0.198 (note accompanying variation in the units because of exponent variations). Pignatello and Huang (1991) reported a similar range of Freundlich exponents for equilibrium experiments of metolachlor on four soils that ranged from 0.81 to 1.14. Typical results of sorption isotherm data and Freundlich model fits are given on Figure 68.

The large amount of data obtained in these experiments made it possible to determine the correlation between soil organic carbon content and the linear sorption partition coefficient for these soils. This was accomplished by assuming the equilibrium distribution relationships were linear and fitting a least squares fit with a zero intercept to the data. The values obtained for  $K_p$  and their corresponding  $r^2$  values are reported in Table 34. The plot of  $K_p$  as a function of TOC shown in Figure 69 illustrates the expected linear correlation (Karickhoff 1981, Voice and Weber 1985, Pignatello and Huang 1991). The slope of the line in Figure 69 corresponds to  $K_{oc}$  and has a value of 104 (range of 66 to 145). This is on the low end of values reported in the literature which were as follows: Mean 121 and range 88-141 (Pignatello and Huang 1991), mean 171 and range 101-242 (Peter and Weber 1985), mean 258 (Gerstl 1990) and mean 266 and range 263-269 (Bouchard et al. 1982). This was surprising in that relatively long periods of time were allowed for equilibration compared to other studies, which increased the extent of sorption, hence the value of  $K_{oc}$ .

The variations in equilibrium coefficient with spatial location are further indicative of the heterogeneities in the soil columns, especially with regard to the ability of solutes to move downward (Table 34). The trend shows that if local equilibrium were occurring, the contaminants would move more slowly through the upper layers and more quickly through the middle and lower layers.

#### Modeling Metolachlor Movement in Soil

The PRZM model was calibrated to the 1990 field leaching data for fallow soil lysimeters from Keller (1992) by inputting known rainfall and adjusting evapotranspiration (ET) levels. Field leaching data was available on a monthly basis for columns with plants and lysimeters without plants (Keller 1992). Flow calibration involved an iterative procedure in which ET was adjusted so that leaching flows output by PRZM had fairly good agreement with field data. The iterative procedure consisted of adjusting depth of soil evaporation and method of ET calculation. Field tracer flow data matched well with PRZM flow data when the maximum depth of soil evaporation was set at 12 cm. Field pan evaporation data were available on a nearly weekly basis. For the simulations in this study, it was found that the water balance more favorably compared to field data when temperature data were used to calculate ET during growing months and when average pan evaporation data were used to calculate ET when no plants were present. The pan factor for the no-plant case was selected from Carsel et al. (1984) to be 0.75. The results of the leaching output calibration efforts are shown in the bargraphs in Figure 70.

The flow calibration was validated by comparing PRZM output to field tracer data. Tritiated water was used on several lysimeters in the field to check for preferential flow patterns (Keller 1992). The studies were begun on the same day as the pesticide studies, so rainfall and temperature data were the

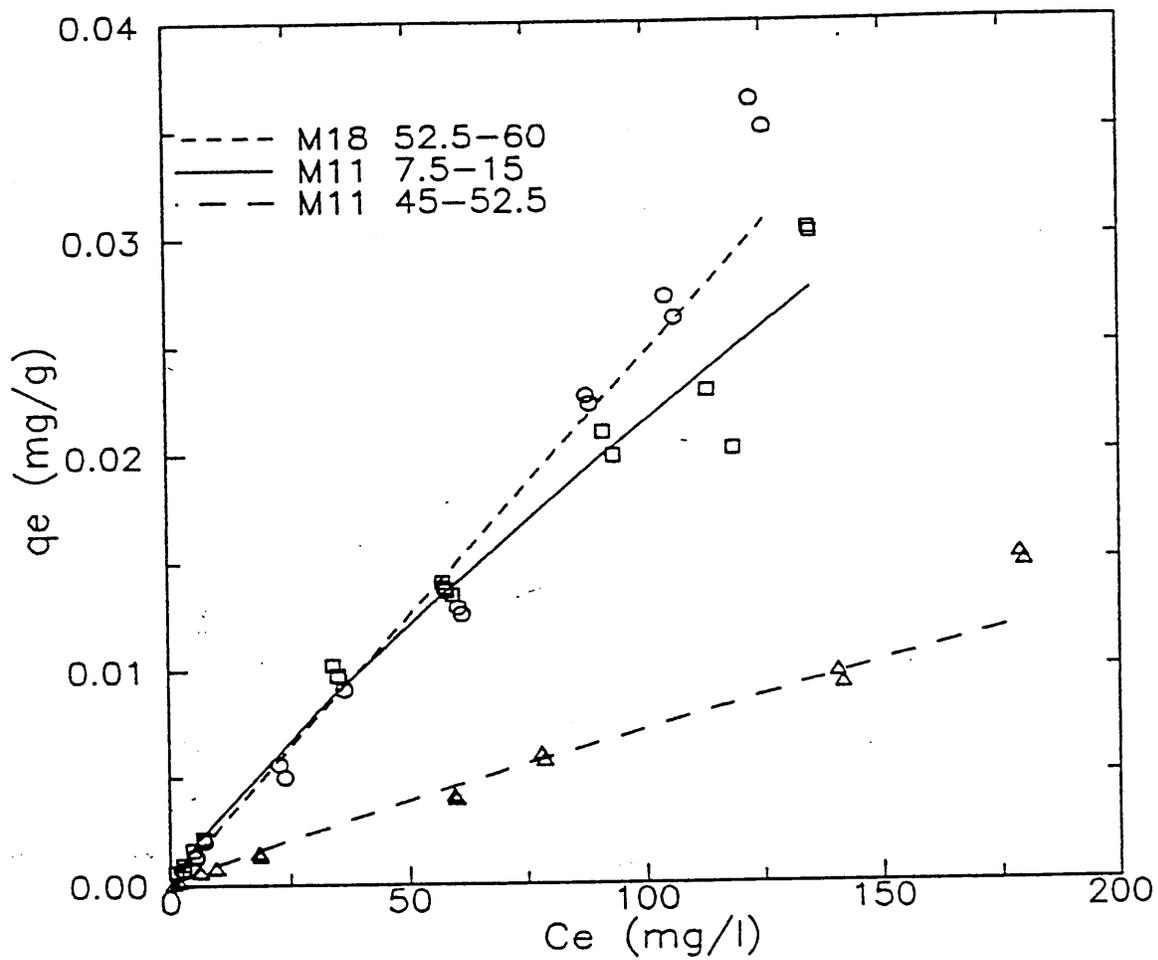


Figure 68. Sorption isotherms for metolachlor on 7.5-15.0 and 45.0-52.5 cm depth soil (M11) and 52.5-60.0 cm depth soil (M18) (Nelson 1991).

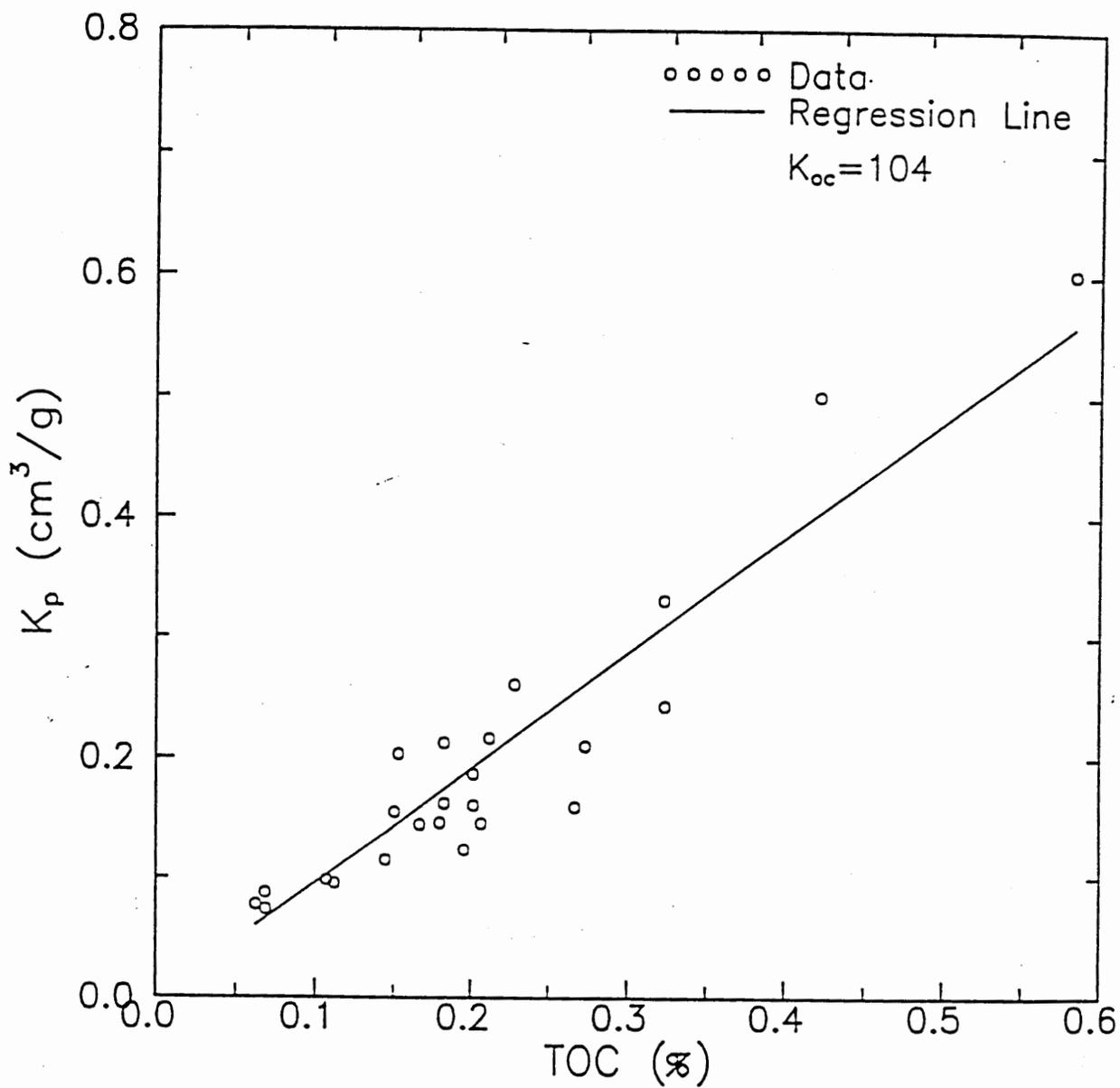


Figure 69.  $K_p$  versus % TOC for metolachlor sorption on 24 depth soil samples from varying depths (Nelson 1991).

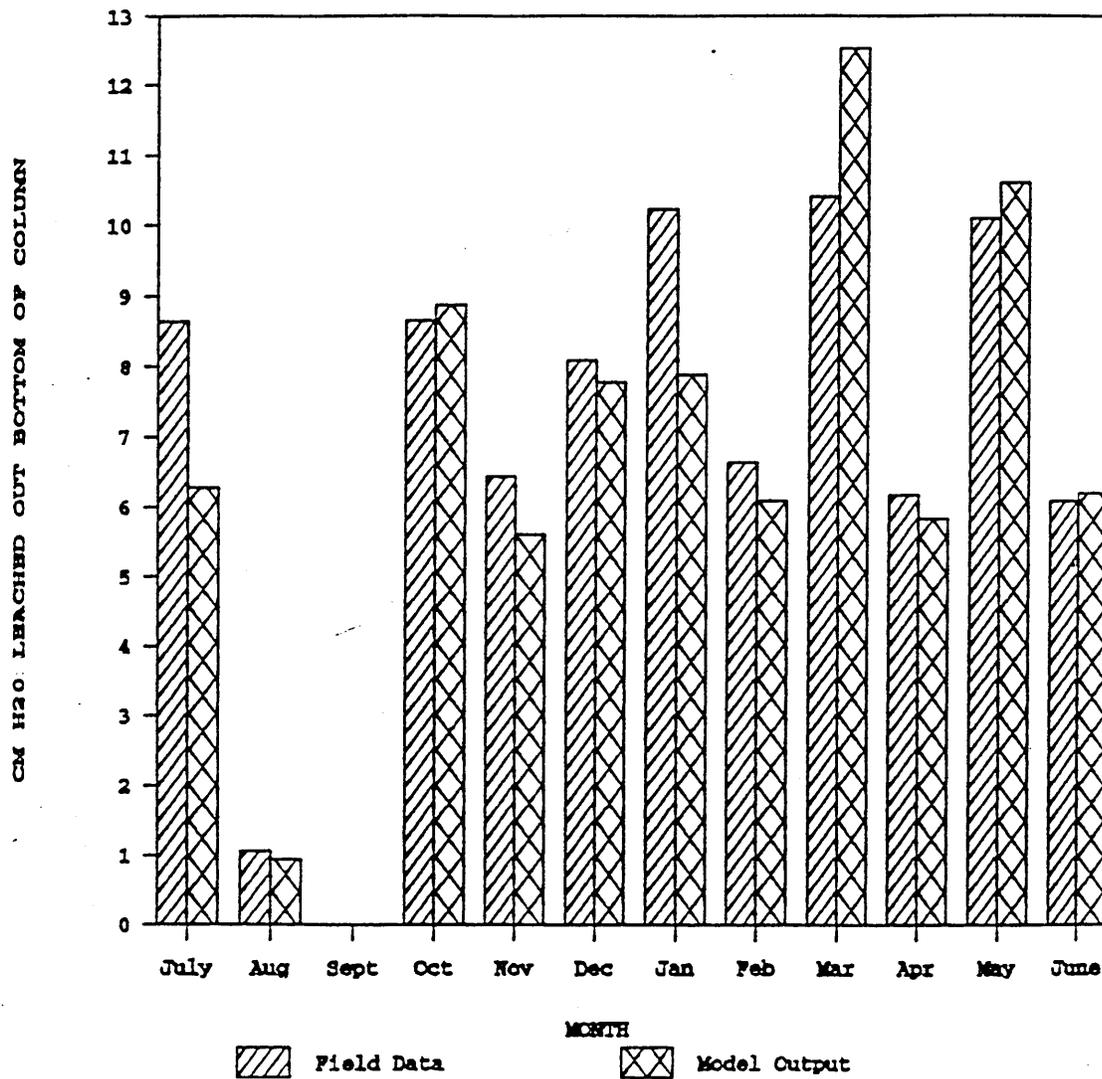


Figure 70. A comparison of leaching flow through soil column lysimeters as measured in the field and predicted using PRZM (with plants present, from Keller, 1992) (Nelson 1991).

Table 34. Equilibrium model parameters for the sorption of metolachlor on soil from varying depths (Nelson 1991).

Soil Depth (cm)	Linear Model		Freundlich Model			
	$K_p$ (cm <sup>3</sup> /g)	$r^2$	$K_f$ (cm <sup>3</sup> /g <sup><math>n_f</math></sup> (g/g)	Standard Error <sup>1</sup>	$n_f$	Standard Error <sup>1</sup>
Core: M11						
0-7.5	0.602	0.990	0.1770	0.0981	0.872	0.0110
7.5-15	0.216	0.971	0.0462	0.0960	0.833	0.0131
15-22.5	0.187	0.986	0.0664	0.0971	0.892	0.0106
22.5-30	0.098	0.990	0.0138	0.1850	0.790	0.0255
30-37.5	0.087	0.935	0.0415	0.1660	0.926	0.0186
37.5-45	0.073	0.958	0.0180	0.2070	0.855	0.0294
45-52.5	0.077	0.983	0.0240	0.1470	0.881	0.0163
52.5-60	0.095	0.968	0.0369	0.2180	0.906	0.0311
60-67.5	0.203	0.941	0.0879	0.2830	0.935	0.0342
67.5-75	0.161	0.977	0.0615	0.1760	0.906	0.0249
75-82.5	0.155	0.984	0.1040	0.1510	0.968	0.0169
82.5-90	0.124	0.980	0.1860	0.1030	1.050	0.0184
Core: M18						
0-7.5	0.500	0.988	0.1260	0.0514	0.851	0.0072
7.5-15	0.330	0.992	0.0644	0.0679	0.828	0.0108
15-22.5	0.210	0.989	0.0404	0.1020	0.822	0.0135
22.5-30	0.163	0.963	0.0446	0.1210	0.865	0.0201
30-37.5	0.115	0.997	0.0458	0.1090	0.902	0.0150
37.5-45	0.147	0.981	0.0526	0.1020	0.893	0.0172
45-52.5	0.243	0.998	0.0709	0.0762	0.872	0.0102
52.5-60	0.261	0.979	0.1980	0.1070	0.976	0.0183
60-67.5	0.213	0.988	0.1450	0.0563	0.964	0.0085
67.5-75	0.145	0.991	0.1070	0.0922	0.972	0.0158
75-82.5	0.146	0.992	0.0730	0.1120	0.932	0.0156
82.5-90	0.160	0.970	0.1180	0.1560	0.975	0.0268

same. Leachate was collected on a monthly basis for 4 months and most of the water had moved through the lysimeter at the end of the four month period. Several lysimeters were analyzed for tracer across their diameters at certain depths to investigate the possibility of preferential flow. The results indicated a fairly uniform tracer concentration profile across the lysimeter diameter at 25, 50 and 75 cm depths. Volatilization led to loss of approximately 62 percent of the tracer mass as tritiated water by the end of the experiment. Field data were normalized to create 100% mass for comparison to the model. PRZM can be used to simulate the tracer study by setting sorption and degradation to zero and modeling for a no-plant case. The results of the comparison between the model and field tracer leaching data at the end of 1 and 2 months are shown in Figures 71 and 72, respectively. The PRZM output is in phase with the tracer data, further indicating that PRZM can effectively model flow.

Field data on metolachlor movement were available on a monthly basis for lysimeters without plants (Keller 1992). The field studies were carried out using ring labeled <sup>14</sup>C-metolachlor. For these experiments, a lysimeter was sacrificed approximately once a month and the total <sup>14</sup>C within each segment

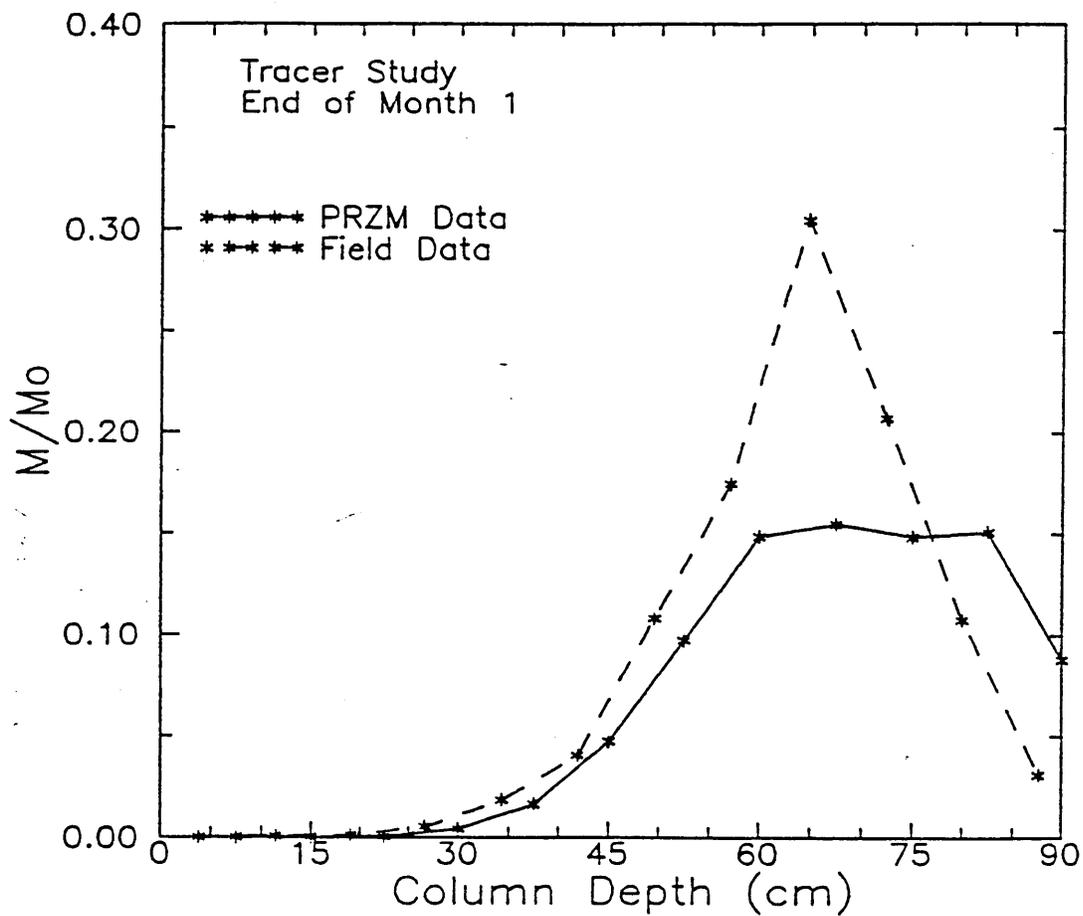


Figure 71. Experimental field data (Keller 1992) versus PRZM-predicted tritium concentration profile in a Dothan loamy sand at 1 month after treatment (Nelson 1991).

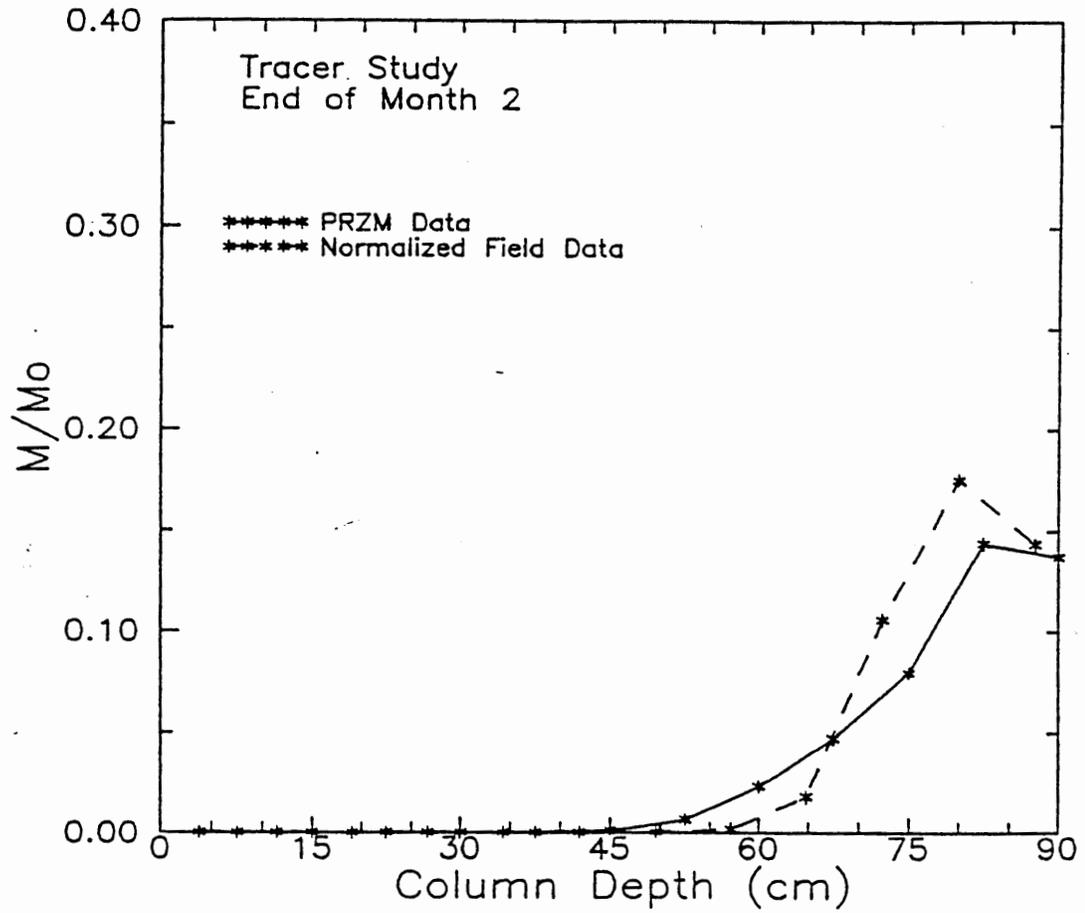


Figure 72. Experimental field data (Keller 1992) versus PRZM-predicted tritium concentration profile in a Dothan loamy sand at 2 months after treatment (Nelson 1991).

was determined without regard to whether it was parent compound or metabolite, fluid-phase or sorbed-phase. Approximately 40% of the metolachlor applied in the field lysimeter was lost to volatilization, probably as  $^{14}\text{CO}_2$  and  $^{14}\text{C}$ -metolachlor vapors (LeBaron et al. 1988), so these data were normalized to create a 100% mass balance for comparison to PRZM output. Since the field data were representative of total  $^{14}\text{C}$  remaining at any given time period, a comparable PRZM run would include no degradation. An attempt was made to compare the field data by running PRZM with and without sorption. A comparison of such data for one month, three months and six months is shown in Figures 73 to 75. PRZM is not adequate to predict what actually happens in the field. The field data depict a compound that is highly retained in the upper layers of the soil profile, probably an anilide, acetanilide, and aniline metabolites (LeBaron et al. 1988), with small amounts evenly dispersed through the lower layers. Anilides, amides, and aniline compounds have been reported to be readily bound by organic soil colloids (Schnitzer and Khan 1978) and clay minerals (Theng 1974). Keller (1992) reported that while 92% of the  $^{14}\text{C}$  was extracted in methanol at 0 DAT, (98% of it was parent metabolite), 21% was extractable at 30 DAT, and only 4% was extractable at 90 and 180 DAT. The PRZM prediction appears to be typical of a slug source moving through porous media and it considers only the movement of parent metolachlor.

The mismatch between the model and the field data may also exist because, under unsaturated conditions, some of the soil water does not readily move within the soil. The mass transfer of solute between the immobile and mobile regions of the soil is a diffusion limited process. Following Russo et al. (1989), the immobile water occupies only a small percentage of water-filled pore space during infiltration. This percentage increases during redistribution and becomes quite large during periods of evaporation. Consequently, the total solute concentration in the top of the soil profile increases considerably during evaporation periods between rainfalls, because evaporation causes solute to move upward, and is not completely leached during infiltration periods. Furthermore, the rate of solute desorption is affected by these transient moisture conditions. Rate-limited desorption would also retard solute movement in unsaturated conditions. Loague and Green (1991) compared field data of atrazine movement in vertical soil columns with PRZM output. Their field data were similar to the field data reported in Figures 73 to 75, and their PRZM predictions also showed poor comparison with field data. The measured data showed that atrazine was retained in the upper layers of the soil columns but PRZM predicted that the slug of herbicide moved downward. The authors reported that the poor PRZM performance was not unexpected because the inputs were not characterized at each site.

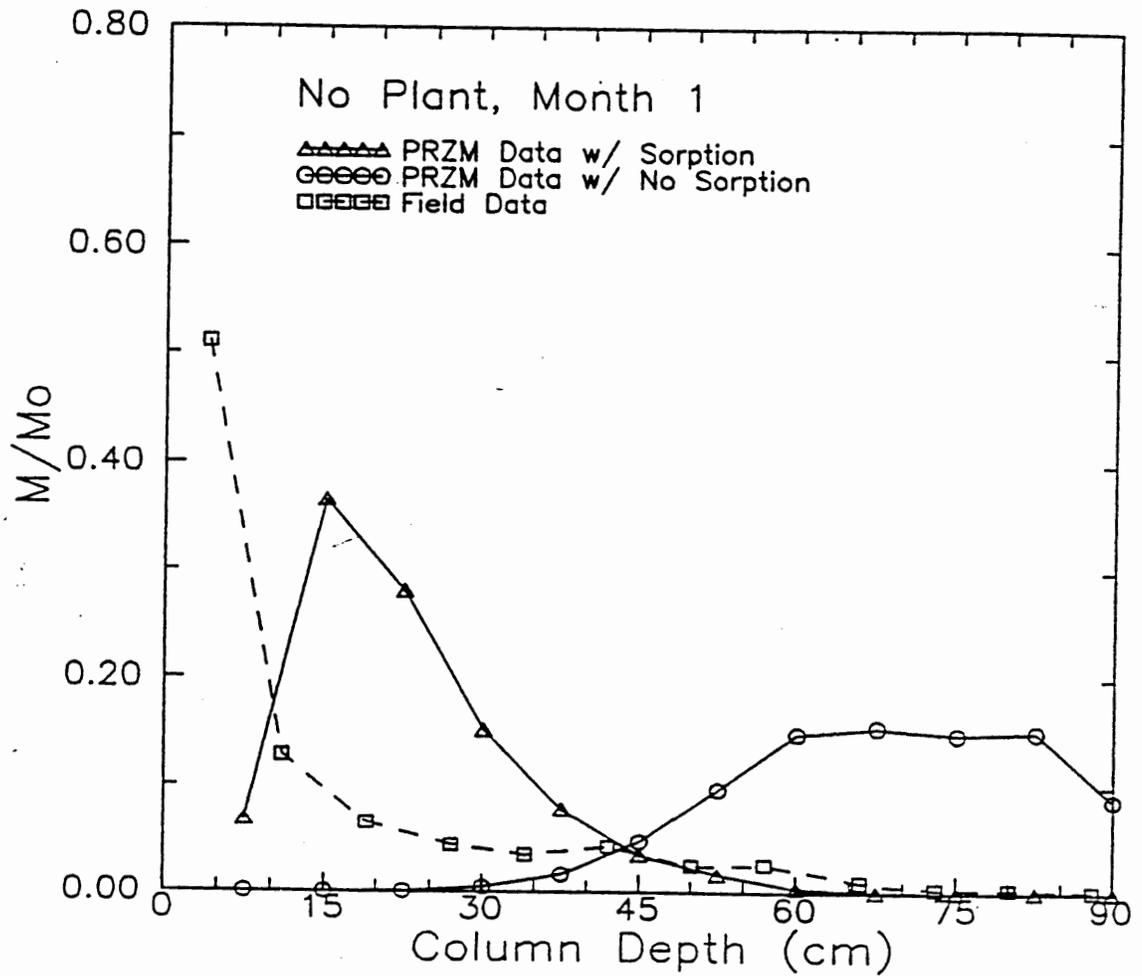


Figure 73. Experimental field data (Keller 1992) versus PRZM-predicted metolachlor concentration profile in a Dothan loamy sand at 1 month after treatment (Nelson 1991).

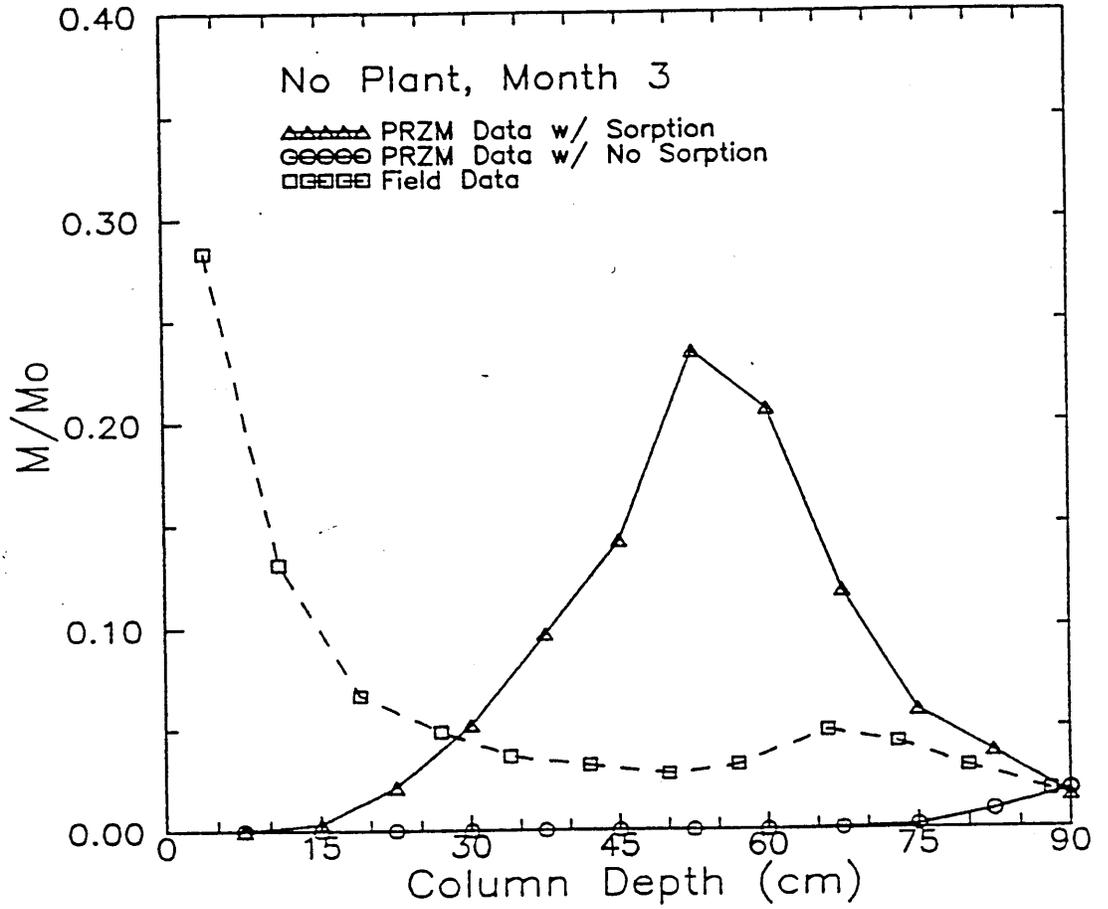


Figure 74. Experimental field data (Keller 1992) versus PRZM-predicted metolachlor concentration profile in a Dothan loamy sand at 3 months after treatment (Nelson 1991).

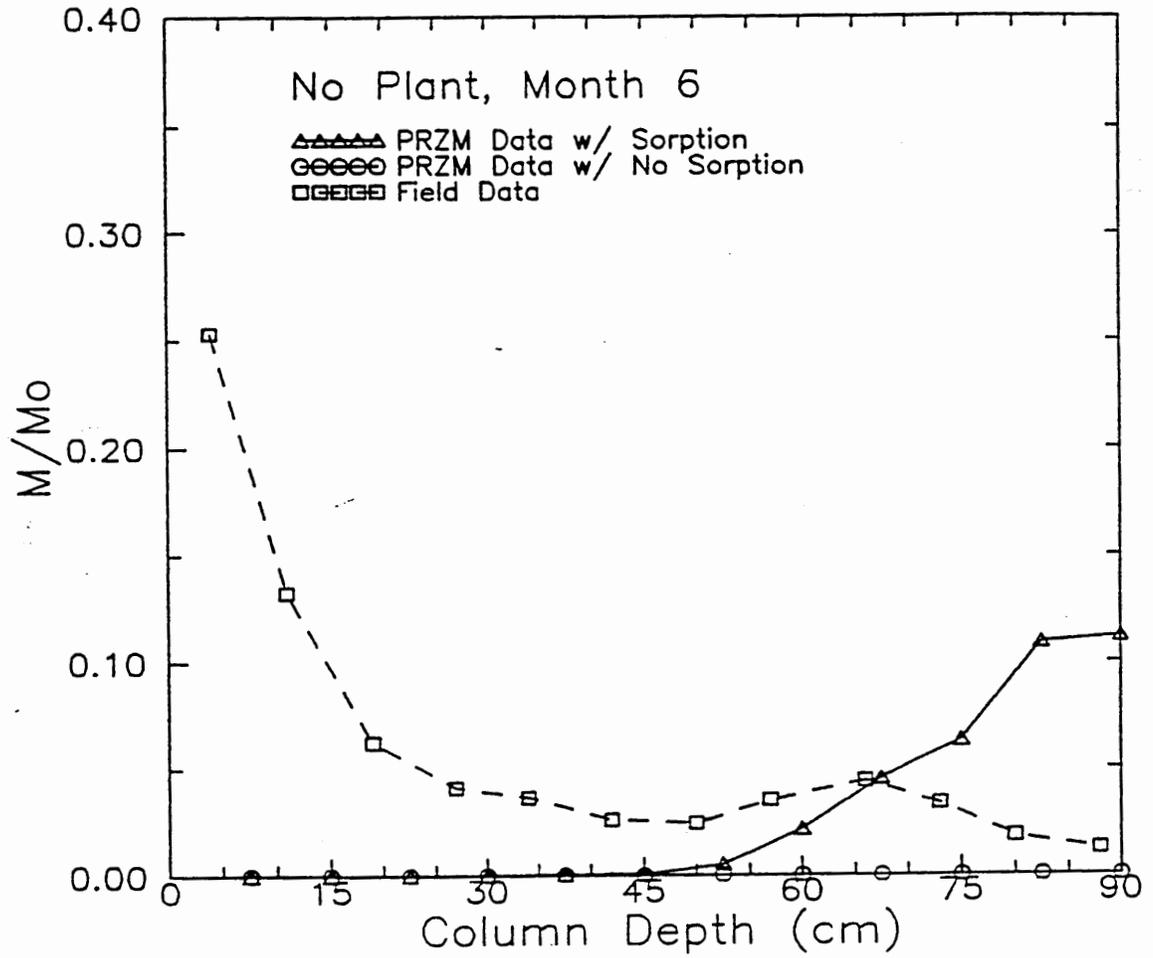


Figure 75. Experimental field data (Keller 1992) versus PRZM-predicted metolachlor concentration profile in a Dothan loamy sand 6 months after treatment (Nelson 1991).

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## GLOSSARY

### Abbreviations (units of measurement)

Bq	becquerel	meq	milliequivalent
°C	degrees centigrade	mg	milligram
cm	centimeter	min	minute
cmol	centimole	mL	milliliter
d	day	mon	month
g	gram	mm	millimeter
h	hour	mol	mole
ha	hectare	TBq	terabecquerel
Kg	kilogram	µg	microgram
KPa	kilopascal	µL	microliter
L	liter	wk	week
m	meter	%	percent
MBq	megabecquerel		

### Terms

<u>Acetic acid:</u>	CH <sub>3</sub> COOH
<u>Acetonitrile:</u>	CH <sub>3</sub> C≡N
<u>ai:</u>	Active ingredient in percent.
<u>Alachlor:</u>	2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide herbicide (LASSO).
<u>Aldicarb:</u>	2-Methyl-2-methylthio propionaldehyde O-(methylcarbamoyl) oxime insecticide (TEMIK).
<u>Aldrin:</u>	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro- <u>exo</u> -1,4- <u>endo</u> -5,8-dimethanonaphthalene insecticide (OCTALENE).
<u>Ammonium hydroxide:</u>	NH <sub>4</sub> OH
<u>Ammonium sulfate:</u>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
<u>Atrazine:</u>	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine herbicide (AATREX).
<u>Barium carbonate:</u>	BaCO <sub>3</sub>
<u>Barium chloride:</u>	BaCl <sub>2</sub>
<u>Bensulide:</u>	O,O-Bis (1-methylethyl) S-[2-(phenylsulfonyl) aminoethyl] phosphorodithioate herbicide (BETASAN).
<u>Bioavailable:</u>	Biologically available to organisms.
<u>Boric acid:</u>	H <sub>3</sub> BO <sub>3</sub>
<u>Bromide:</u>	Br <sup>-</sup> ion.
<u>BTC:</u>	Breakthrough curve for a chemical leaching from a column.
<u>C:</u>	Carbon of mass number 12.
<sup>14</sup> C:	Radioactive carbon isotope of mass number 14.
<u>Calcium:</u>	Ca <sup>+2</sup> ion.

<u>Calcium chloride dihydrate:</u>	CaCl <sub>2</sub> ·H <sub>2</sub> O
<u>Carbofuran:</u>	2,3-Dihydro-2,2-dimethyl-7-benzofuranyl mehtylcarbamate insecticide (FURADAN).
<u>CAST:</u>	Council for Agricultural Science and Technology
<u>CEC:</u>	Cation exchange capacity of a soil or colloid
<u>Chlordane:</u>	1,2,4,5,6,7,8,8-Octachloro-3a,4,7,7a-tetrahydro- 4,7-methanoindane insecticide (OCTACHLOR).
<u>Chloride:</u>	Cl <sup>-</sup> ion.
<u>Chloroform:</u>	CHCl <sub>3</sub>
<sup>14</sup> CO <sub>2</sub> :	Radiolabeled carbon dioxide.
<u>Cotton:</u>	<u>Gossypium hirsutum</u> L.
<u>Cupric oxide:</u>	CuO
<u>CV:</u>	Coefficient of variation is an expression of the standard deviation per experimental unit as a percent of the general mean of the experiment.
<u>2,4-D:</u>	2,4-Dichlorophenoxy acetic acid herbicide (WEEDAR).
<u>DAT:</u>	Days after treatment.
<u>D<sub>b</sub>:</u>	Bulk density in grams per milliliter or cubic centimeter.
<u>DBCP:</u>	1,2-Dibromo-3-chloropropane
<u>DDT:</u>	1,1,1-Trichloro-2,2-bis (chlorophenyl)ethane insecticide (GESAROL).
<u>Dealkylatrazine:</u>	2-Chloro-4,6-diamino- <u>s</u> -triazine
<u>Deethylatrazine:</u>	2-Chloro-4-amino-6-isopropylamino- <u>s</u> -triazine
<u>Deisopropylatrazine:</u>	2-Chloro-4-ethylamino-6-amino- <u>s</u> -triazine
<u>Diammonium orthophosphate:</u>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>
<u>Dicamba:</u>	3,6-Dichloro-2-methoxybenzoic acid herbicide (BANVEL).
<u>Dichloromethane:</u>	CH <sub>2</sub> Cl <sub>2</sub>
<u>DPM:</u>	Disintegrations per minute of a decaying element.
<u>DRASTIC:</u>	Depth to water table, net Recharge, Aquifer media, Soil media, Topography, Impact of the vadose zone, hydraulic Conductivity of the aquifer
<u>DTPA:</u>	Diethylenetriamine pentaacetic acid, pentasodium salt.
<u>E:</u>	Evaporation of water vapor from soil or free water to the atmosphere.
<u>EDB:</u>	Ethylene dibromide
<u>8E:</u>	8 Pounds per gallon emulsified formulation
<u>Endothal:</u>	7-Oxabicyclo-2,2,1-heptane-2,3-dicarboxylic acid herbicide (ENDOTHALL).
<u>ET:</u>	Evapotranspiration of water through a plant plus evaporation.
<u>Ethyl acetate:</u>	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>
<u>Formic acid:</u>	HCOOH
<u>GC:</u>	Gas chromatography.
<u>GLEAMS:</u>	Groundwater Leaching Effects of Agricultural Management Systems model
<u>Hexachlorobenzene:</u>	C <sub>6</sub> Cl <sub>6</sub>
<u>Hg:</u>	Mercury
<u>HLP/SLP:</u>	Herbicide Leaching Potential/Soil Leaching Potential model.

<u>Hydrochloric acid:</u>	HCl
<u>Hydroxyatrazine:</u>	2-Hydroxy-4-ethylamino-6-isopropylamino- <u>s</u> -triazine
<u>Hydroxypropazine:</u>	2-Hydroxy-4,6-isopropylamino- <u>s</u> -triazine
<u>i.d.:</u>	Internal diameter
<u>K<sub>A</sub>:</u>	Ionization constant
<u>K<sub>d</sub>:</u>	Distribution coefficient is the ratio of the amount of chemical sorbed to a sorbent to the concentration of the chemical in the solution phase.
<u>K<sub>f</sub>:</u>	Sorption capacity constant from Freundlich equation.
<u>K<sub>oc</sub>:</u>	K <sub>f</sub> or K <sub>d</sub> divided by the fraction of organic carbon in the media.
<u>K<sub>sat</sub>:</u>	Saturated hydraulic conductivity is the rate of water flowing through saturated soil media.
<u>4L:</u>	4 Pounds per gallon liquid.
<u>LSD:</u>	Least significant difference between a treatment mean and the mean of the control.
<u>Lysimeter:</u>	A device for measuring water gains and losses by a mass of soil under controlled conditions
<u>LSS:</u>	Liquid scintillation spectrometry measures the photons given off by photosensitive chemicals in the scintillation cocktail.
<u>M:</u>	Molar solution contains one molecular weight of substance dissolved per liter of solution.
<u>Methabenzthiazuron:</u>	1-Benzothiazol-2-yl-1,3-dimethylurea herbicide (TRIBUNIL).
<u>Methanol:</u>	CH <sub>3</sub> OH
<u>Methylene chloride:</u>	CH <sub>2</sub> Cl <sub>2</sub>
<u>Metolachlor:</u>	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide herbicide (DUAL).
<u>Monuron:</u>	N'-4-chlorophenyl-N,N-dimethylurea herbicide (TELVAR).
<u>M-score:</u>	Index of chemical movement through soil media obtained by multiplying the fraction of applied chemical present times the distance moved.
<u>n:</u>	Sorption intensity constant from Freundlich equation.
<u>N:</u>	Normal solution contains one equivalent weight of a substance dissolved per liter of solution.
<u>Nitrate:</u>	NO <sub>3</sub> <sup>-</sup> ion.
<u>NOAA:</u>	National Oceanic and Atmospheric Administration
<u>Oxidiazon:</u>	3-[2,4-Dichloro-5-(1-methylethoxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2-(3H)-one herbicide (RONSTAR)
<u>Paraquat:</u>	1,1'-Dimethyl-4,4'-bipyridinium ion herbicide (GRAMOXONE).
<u>Pendimethalin:</u>	N-1-ethylpropyl-3,4-dimethyl-2,6-dinitrobenzenamine herbicide (PROWL).
<u>pH:</u>	-Log H <sup>+</sup> concentration in solution.
<u>Phenolphthalein:</u>	(C <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub> C <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>4</sub>
<u>Picloram:</u>	4-Amino-3,5,6-trichloro-2-pyridinecarboxylic acid herbicide (TORDON).

<u>pK<sub>a</sub></u> :	-Log K <sub>a</sub>
<u>Potassium bromide</u> :	KBr
<u>Potassium persulfate</u> :	K <sub>2</sub> O <sub>8</sub> S <sub>2</sub>
<u>Primisulfuron</u> :	2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl] benzoic acid herbicide (BEACON).
<u>2-Propanol</u> :	CH <sub>3</sub> CH <sub>2</sub> (OH)CH <sub>3</sub>
<u>Propazine</u> :	2-chloro-4,6-isopropylamino-s-triazine
<u>PRZM</u> :	Pesticide Root Zone Model
<u>R<sub>r</sub></u> :	Retention or retardation factor for a chemical moving through media, i.e., the ratio of the distance that a chemical moved to the distance the solvent moved.
<u>R3 stage</u> :	Reproductive stage of soybean (beginning pod formation)
<u>Sodium azide</u> :	NaN <sub>3</sub>
<u>Sodium hydroxide</u> :	NaOH
<u>Sodium nitrate</u> :	NaNO <sub>3</sub>
<u>Soybean</u> :	<u>Glycine max</u> L. Merr.
<u>Sp. Act.</u> :	Specific activity is the rate of decay per unit mass of an element.
<u>SSSA</u> :	Soil Science Society of America
<u>2,4,5-T</u> :	2,4,5-Trichlorophenoxy acetic acid herbicide (WEEDONE).
<u>TLC</u> :	Thin-layer chromatography
<u>TOC</u> :	Total carbon analysis
<u>Toluene</u> :	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>
<u>Triasulfuron</u> :	2-(2-chloroethoxy)-N-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl] benzenesulfonamide herbicide (AMBER).
<u>Trifluralin</u> :	2,6-Dinitro-N,N-dipropyl-4-trifluoromethylaniline herbicide (TREFLAN).
<u>Tritium</u> :	Radioactive isotope of hydrogen with mass 3.
<u>U.S.</u> :	United States
<u>USEPA</u> :	United States Environmental Protection Agency
<u>V2 stage</u> :	Vegetative growth stage of soybean (second node).
<u>V3 stage</u> :	Vegetative growth stage of soybean (third node).
<u>V/V</u> :	Volume/volume
<u>V/V/V</u> :	Volume/volume/volume
<u>WSSA</u> :	Weed Science Society of America
<u>W/W</u> :	Weight/weight



APPENDIX



# Influence of Polymers on the Mobility, Loss, and Bioactivity of $^{14}\text{C}$ from $^{14}\text{C}$ -Labeled Atrazine, Metolachlor, and Primisulfuron†

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Neither soil mobility nor relative losses of  $^{14}\text{C}$  from  $^{14}\text{C}$ -labeled atrazine, metolachlor, or primisulfuron were influenced by tank-mix applications of ASE-108, HA-16, or E-1242 polymer in a 92-day field lysimeter study. In a 3-day soil column laboratory study, however, CGA-A polymer reduced losses of [ $^{14}\text{C}$ ]atrazine by 7% and addition of E-CELL, CGA-A, CGA-F, or CGA-G polymer increased [ $^{14}\text{C}$ ]atrazine mobility by 14–23%. Additions of ASE-108, CGA-A, or CGA-F polymer reduced [ $^{14}\text{C}$ ]metolachlor losses by 15–23%. G-110, E-CELL, or CGA-C addition reduced [ $^{14}\text{C}$ ]metolachlor mobility by 10%, and addition of ASE-108, CGA-A, or CGA-F polymer reduced [ $^{14}\text{C}$ ]metolachlor mobility by 16–21%. Addition of ASE-108 or CGA-B polymer to [ $^{14}\text{C}$ ]primisulfuron reduced mobility of the herbicide by 8–14%, and addition of CARBO, E-CELL, CGA-F, or CGA-G increased mobility by 8–14%. None of the polymers affected [ $^{14}\text{C}$ ]primisulfuron losses by more than 7%. Tank-mix additions of G-110 polymer reduced the preemergence bioactivity of atrazine and metolachlor by 20–50% in field studies, but addition of ASE-108, CARBO, or E-CELL polymer had little or no effect. E-CELL polymer additions reduced the postemergence bioactivity of primisulfuron slightly, but the other polymers had little or no effect.

## INTRODUCTION

Because nearly 50% of Americans depend on groundwater daily (Severn and Ballard, 1990), groundwater contamination has been a major issue to the public. Approximately 46 pesticides have been found in the groundwater of 26 states (Williams et al., 1988). The majority of the compounds found were preemergence herbicides with moderate to high water solubility and moderate to long half-lives.

Herbicide movement through soil is dependent upon many factors including the chemical and physical properties of the herbicide, the properties of the soil, and climatic conditions (Helling and Gish, 1986; Weber and Miller, 1989).

Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N'*-(2-methoxy-1-methylethyl)acetamide] are two major preemergence crop herbicides that have been found in groundwater of many states (Cohen et al., 1985; Williams et al., 1988). Atrazine is a symmetrical triazine herbicide used to control broadleaf weeds in corn and some other crops (*Herbicide Handbook of the Weed Science Society of America*, 1989). It has weakly basic properties with a  $pK_A$  of 1.68 (Weber, 1970), a low water solubility of 33 mg/L, and a low volatility with a vapor pressure of  $3.0 \times 10^{-7}$  mmHg at 20 °C (*Herbicide Handbook of the Weed Science Society of America*, 1989). Triazine herbicide sorption in soil has been attributed to binding to organic matter (Harris and Sheets, 1965; Weber et al., 1969) and expanding-type clay minerals (Weber et al., 1965; Weber, 1966) and to be pH dependent (Talbert and Fletchall, 1965; McGlamery and Slife, 1966; Weber, 1966; Weber et al., 1969).

Metolachlor is an acetamide herbicide used to control annual grasses and several broadleaf weeds in corn, cotton,

soybeans, and some other crops (*Herbicide Handbook of the Weed Science Society of America*, 1989). Metolachlor is nonionic, has a high water solubility (530 mg/L at 20 °C), and is moderately volatile (vapor pressure of  $1.3 \times 10^{-5}$  mmHg at 20 °C) (*Herbicide Handbook of the Weed Science Society of America*, 1989). Major soil constituents reported to inactivate metolachlor included organic matter and expanding-type clay (Ballard and Santelmann, 1973; Kozak et al., 1983; Peter and Weber, 1985).

Primisulfuron [2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoic acid] is a recently developed sulfonylurea postemergence herbicide used to control several grassy weeds including johnsongrass and many broadleaf weeds in corn (Ciba-Geigy, 1990). Primisulfuron has weakly acidic properties ( $pK_A = 5.1$ ), a low water solubility of 70 mg/L (pH 7) at 20 °C, and a low volatility (vapor pressure of  $<7.5 \times 10^{-12}$  mmHg at 20 °C). The mobility of sulfonylurea herbicides in the soil has been correlated with organic matter content and pH (Harvey et al., 1985; Mersie and Foy, 1985, 1986; Goetz et al., 1989). Soils with high contents of organic matter and low pH tended to reduce the bioactivity of sulfonylurea herbicides.

The mobility of nutrients and pesticides in soils has been shown to be dependent on the properties of the chemicals and the soils using soil leaching columns and lysimeters (Edwards and Glass, 1971; Cassel et al., 1974; Weber and Whitacre, 1982; White et al., 1986; Bowman, 1988). By definition, a lysimeter is a device for measuring water gains (irrigation, precipitation) and losses (evapotranspiration) by a mass of soil under controlled conditions (*Glossary of Soil Science Terms*, 1987). Water and solute movements in disturbed and undisturbed soil lysimeters have also been reported to be different due to the differences in macro- and micropore distributions (Cassel et al., 1974; McMahon and Thomas, 1974).

One method of reducing groundwater contamination by herbicides would be to keep them in the root zone, where they would be taken up by the weeds and available for degradation for a longer period of time. Keeping higher amounts of the chemicals in the zone of germinating weeds might also allow farmers to apply herbicides at lower rates,

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thus reducing the amounts of herbicides introduced into the environment and reducing economic costs. Solid porous polymers have been used as controlled-release agents for insecticide vapors and fertilizer nutrients (Baker, 1987), drugs (Rosoff, 1989), and pesticides (Cardarelli, 1976; Lewis and Cowsar, 1977; Scher, 1984, 1988). Several solid porous polymers have been evaluated to determine their ability to decrease the downward movement of herbicides in soils (Cardarelli, 1976). According to Hilton (1987), atrazine movement on soil thin-layer plates was reduced by the addition of a water-soluble ASE-108 polymer obtained from the Rohm and Haas Co. (Philadelphia, PA). Weber et al. (1988) reported that the ASE-108 polymer reduced downward movement of atrazine, metolachlor, and triasulfuron [2-(2-chloroethoxy)-*N*-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]amino]carbonyl]benzenesulfonamide in soil leaching columns when applied at a rate of 86 kg of solid/ha. Approximately 90% of each of the three herbicides was recovered in the 0–5-cm section of the leaching columns when ASE-108 was mixed with herbicide prior to application, compared with only 40% when the herbicides were applied alone.

Pesticide bioactivity in soils has been reported to be regulated by both the properties of the specific pesticide and the soil (Harris and Sheets, 1965; Ballard and Santelmann, 1973; Weber and Weed, 1974; Peter and Weber, 1985). Bioactivity is normally reduced when pesticides become bound to soil colloids or diffuse into inaccessible sites. Solid porous polymers used as controlled-release membranes for pesticides and drugs act to reduce chemical concentration at any given moment, thereby regulating chemical losses and utilization by organisms (Cardarelli, 1976; Rosoff, 1989).

The objectives of this experiment were to investigate the effects of three water-soluble acrylic polymers (ASE-108, HA-16, E-1242) on the mobility of atrazine, metolachlor, and primisulfuron in undisturbed soil cores using field soil column lysimeters, to investigate the effects of eight water-soluble acrylic polymers [ASE-108, G-110, CARBOSET-H (CARBO), CGA-A, CGA-B, CGA-C, CGA-F, CGA-G], as well as expanded cellulose (E-CELL), on the mobility of the three herbicides using laboratory soil leaching columns, and to determine the effects of four of the polymers (ASE-108, G-110, CARBO, E-CELL) on the bioactivity of the three herbicides in the field.

## MATERIALS AND METHODS

**Lysimeter Study.** The field lysimeter experiment was conducted on a Dothan loamy sand (fine loamy, siliceous, thermic, *Plinthic Kandudult*) in 1989 at the Central Crops Research Station, Clayton, NC. Soil properties including percent organic matter (chromic acid oxidation method) (Walkley and Black, 1934), pH (1:1 soil:water), soil texture (hydrometer method; Gee and Bauder, 1986), and cation-exchange capacity (CEC) (1.0 N ammonium acetate replacement method; Thomas, 1982) were determined by A&L Agricultural Laboratories, Omaha, NE. Percent soil humic matter was determined by the North Carolina Department of Agriculture, Raleigh, NC (Mehlich, 1984).

Lysimeters consisted of 0.129 cm (16 gauge) thick steel columns (20.3 cm i.d. and 95 cm in length), which were driven 90 cm into the soil using a tractor-mounted post driver.

Atrazine, as a mixture of formulated AAtrex 4L and <sup>14</sup>C-ring-labeled atrazine (specific activity = 19.5 μCi/mg, 99.5%) and each polymer, was applied uniformly in a cross-hatch pattern in 10 mL of water at the rate of 1.12 kg of ai/ha to the soil surface in the lysimeter using a pipet. Total radioactivity for each atrazine-treated column was 15.4 μCi. Metolachlor, as a mixture of Dual 8E and <sup>14</sup>C-ring-labeled metolachlor (specific activity = 19.3 μCi/mg, 99.7%) and each polymer, was applied in the same manner as for atrazine at the rate of 2.24 kg of ai/ha. Total

radioactivity applied was 15.1 μCi per lysimeter. Primisulfuron, as <sup>14</sup>C-ring-labeled primisulfuron (specific activity = 56.2 μCi/mg, 99.5%) and each polymer, was applied in the same manner as for the other herbicides at the rate of 0.08 kg of ai/ha. Total radioactivity applied was 14.7 μCi per lysimeter. In addition to the herbicide/polymer mixtures, each herbicide was applied without polymer for comparison.

Three Rohm and Haas Co. water-soluble acrylic polymers (ASE-108, HA-16, E-1242) were mixed with the respective herbicides and applied to the soil surface in the lysimeter at rates of 0.64, 1.63, and 1.80 kg of solid/ha, respectively. The amounts of polymer added would be equal to 2% of a water application volume of 168.4 L/ha, which is commonly used by farmers to apply herbicides. The density of all three polymers was 1.1 g/cm<sup>3</sup>. The polymers were selected to represent anionic, nonionic, and cationic charged materials, respectively. ACRY SOL ASE-108 (ASE-108), described as a 20% solid suspension copolymer emulsion stabilizer, is used to stabilize liquid laundry and machine-dishwashing detergents and to formulate flowable pesticide products. It is shipped in an anionic acid form (pH 3.0) and must be neutralized to pH 8 to initiate polymerization and obtain high viscosity. RHOPLEX HA-16 (HA-16) is a nonionic 45% solid suspension, pH 3.0, self-cross-linking acrylic polymer used in a wide variety of textile applications. EMULSION E-1242 (E-1242) is a cationic 50% solid suspension, pH 4.5, self-cross-linking acrylic emulsion used in a wide variety of textile applications. The advantage of E-1242 is that it polymerizes at room temperature after drying.

After the herbicide or herbicide/polymer application, the soil was allowed to dry overnight (24 h), and water was added weekly, as necessary to maintain the 10-year average weekly precipitation. Lysimeters were removed from the field and sectioned horizontally at the end of 92 days. Soil samples from each 7.6-cm section were placed in plastic bags, mixed thoroughly, and stored in the freezer at -20 °C until analyzed. <sup>14</sup>C radioactivity for each soil section was determined by using four 1-g subsamples which were combusted in a biological oxidizer (Model OX-300, R. J. Harvey Instrument Corp., Hillsdale, NJ), and the <sup>14</sup>CO<sub>2</sub> was trapped in 15 mL of Harvey <sup>14</sup>C scintillation cocktail. <sup>14</sup>C radioactivity was assayed using a liquid scintillation analyzer (Packard Model 2000 CA, Packard Instrument Co., Downers Grove, IL) and converted to total <sup>14</sup>C activity recovered for each section. Soil moisture content for each section was determined by drying samples in the oven at 105 °C for 24 h. Reproducibility among subsamples was ±3%.

Modified *R<sub>f</sub>* values were calculated for each column to allow for comparison to be made among herbicide and polymer treatments using (Weber, 1991)

$$R_f = \sum_{i=1}^n (D_i F_i) / (MD \times TF) \quad (1)$$

where *R<sub>f</sub>* is the index of herbicide mobility, *n* is the number of sections of the entire soil column, *D* is the mean depth of section *i* (total distance from soil surface to the midpoint of section *i* in cm), *F* is the fraction of herbicide applied in section *i*, *MD* is the maximum mean depth (total distance from soil surface to the midpoint of the last section in cm), and *TF* = 1.0 (total fraction of herbicide applied in the entire soil column).

A small *R<sub>f</sub>* value indicates that the herbicide is nonmobile and travels a short distance in the soil column; a large *R<sub>f</sub>* value indicates that the herbicide is very mobile and travels a long distance. [For instance, the smallest *R<sub>f</sub>* value possible for this lysimeter would be (3.8 cm × 1.0) ÷ (88.0 cm × 1.0) = 0.04, which indicates that all applied herbicide was found in the first section (0–7.6 cm, mean = 3.8 cm) of the lysimeter. A large *R<sub>f</sub>* value of 1.0 from (88.0 cm × 1.0) ÷ (88.0 cm × 1.0) indicates that all of the herbicide was found at the bottom (83.6–90.0 cm, mean = 88.0 cm) section of the lysimeter.] The experiment was arranged as a randomized complete block with two replications. Total percent recovery data and *R<sub>f</sub>* values were subjected to analysis of variance at the 5% confidence level.

**Leaching Column Study.** The A horizon (0–15-cm depth) of Dothan loamy sand was air-dried and passed through a 2-mm sieve mesh before being packed into the 5.1 cm i.d. by 20 cm long cellulose tubing soil leaching columns. One end of each column

was covered with a vinyl cap with a centered 1 cm diameter hole. Three layers of cheesecloth followed by 68 g of quartz sand were put in the bottom of each column to prevent soil loss. Dothan soil was added in 70-g increments to each column. Each increment (2 cm) of soil was evenly distributed in the column by tapping the side of the column until a 12-cm soil core with a bulk density of 1.71 g/cm<sup>3</sup> was obtained.

All polymer solutions were prepared with 0.01 M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, pH 8, buffer solution to meet the polymerization requirement of ASE-108.

Atrazine, as a mixture of formulated AAtrex 4L and <sup>14</sup>C-ring-labeled atrazine (specific activity = 53.5 μCi/mg, 99.5%) and each polymer, was applied uniformly to the soil surface of each column in a cross-hatch pattern in 5 mL of water at the rate of 1.12 kg of ai/ha.

Metolachlor, as a mixture of formulated DUAL 8E and <sup>14</sup>C-ring-labeled metolachlor (specific activity = 71.5 μCi/mg, 99.7%) and each polymer, was applied in the same manner as for atrazine at the rate of 2.24 kg of ai/ha.

Primisulfuron, as a mixture of formulated BEACON and <sup>14</sup>C-ring-labeled primisulfuron (specific activity = 52.4 μCi/mg, 99.5%) and each polymer, was applied as for the other herbicides at the rate of 0.04 kg of ai/ha. Each column received 0.4 μCi of each herbicide.

Polymers used in this experiment were ASE-108, G-110, CARBO, E-CELL, CGA-A, CGA-B, CGA-C, CGA-F, and CGA-G. All polymers were mixed with the respective herbicide and applied at a rate of 1.12 kg of solid/ha. In addition to the herbicide/polymer mixtures, herbicides were applied without polymer for comparison.

ASE-108 and G-110 are products of Rohm and Haas Co. G-110, has a density of 1.1 g/cm<sup>3</sup>. It is an anionic, pH 9.5, ammonium polyacrylate solution that is used in the textile industry for thickening synthetic and natural lattices. CARBOSET-H (CARBO), a low molecular weight (density of 1.1 g/cm<sup>3</sup>), anionic, 40% solid suspension, pH 7.0, acrylic resin which produces a film adhesive to all kinds of materials after drying, is manufactured by BF Goodrich Co. (Cleveland, OH). Expanded cellulose (E-CELL) is a product of the Procter and Gamble Cellulose Co. (Memphis, TN) and is made by dispersing natural fibers in water. The nonionic, 4% solid suspension, pH 7.0, cellulose has a myriad of voids among fibers; however, all fibers collapse upon drying due to the formation of hydrogen bonds, and redispersion is impossible. CGA-A, CGA-B, CGA-C, CGA-F, and CGA-G, with percent solid suspensions of 25, 19, 25, 19, and 17, respectively, were synthesized specifically for this project by Ciba-Geigy Corp. (Greensboro, NC). CGA-A, CGA-B, and CGA-F were described as 50/50, 10/90, and 20/80 butyl esters of acrylic acid, respectively. The polymers CGA-C and CGA-G were described as 50/50 and 20/80 ethyl esters of acrylic acid. Lipophilicity of the CGA polymers was in the order A >> C > F >> G = B.

After herbicide/polymer applications, the columns were allowed to air-dry for 48 h. One container-capacity volume [approximately 1 field-capacity (FC) pore volume of distilled-deionized water (72 mL, equivalent to 3.3 cm)] was added to each column to distribute water and the applied chemicals chromatographically throughout the soil profile. Twelve hours later each soil column was cut into six 2-cm sections, and each section was placed into a plastic bag and mixed thoroughly. <sup>14</sup>C activity and moisture content of each section were determined as described above. *R<sub>f</sub>* values were calculated using eq 1.

The smallest *R<sub>f</sub>* value possible in this experiment was  $(DF) \div (MD \times TF) = (1.0 \text{ cm} \times 1.0) \div (11.0 \text{ cm} \times 1.0) = 0.09$ , which indicates that all of the applied herbicide was found in the first section (0–2 cm, mean depth = 1.0 cm). The maximum *R<sub>f</sub>* value of 1.0 would indicate that all of the herbicide was found at the bottom section of the column  $(11.0 \text{ cm} \times 1.0) \div (11.0 \text{ cm} \times 1.0)$ .

The experiment was arranged as a randomized complete block design with two replications. Total percent recovery data and *R<sub>f</sub>* values were subjected to analysis of variance at the 5% confidence level, using the Statistical Analyses System (*User's Guide: Statistics*, 1985). All <sup>14</sup>C wastes were disposed of by the North Carolina State University Life Safety Services following proper procedures (*Manual For Chemical Waste Management*, 1991).

**Herbicide/Polymer Bioactivity Study.** Corn was planted on a Rains sandy loam soil (fine-loamy, siliceous, thermic *Typic Palequilt*) at the Upper Coastal Plains Research Station, Rocky Mount, NY, on May 14, 1990. Soil property analyses, including soil texture (13, 34, and 54% clay, silt, and sand, respectively), pH (5.2), organic matter content (1.9%), and cation-exchange capacity (CEC = 5.3) were determined on A horizon (0–15-cm depth) soil samples as described previously. Four corn row test plots (3.6 × 6.1 m), with two weed species planted on either side of the two center corn rows, were arranged as a randomized complete block design (three replicates). The weeds included barnyardgrass (BG) [*Echinochloa crus-galli* (L.) Beauv.], prickly sida (PS) (*Sida spinosa* L.), green foxtail (GF) [*Setaria glauca* (L.) Beauv.], and velvetleaf (VL) (*Abutilon theophrasti* Medik.). Dense, uniform weed populations were obtained with few indigenous weeds present.

Atrazine and metolachlor/polymer tank-mix treatments were applied preemergence, and primisulfuron/polymer tank-mix treatments were applied postemergence when corn was at the 6-leaf stage (ca. 15 days after the preemergence treatments). Commercial atrazine (AAtrex Nine-0) and metolachlor (DUAL 8E) and experimental primisulfuron (BEACON) were applied at rates of 0, 0.67, 0.90, and 1.12 kg/ha; 0, 0.45, 0.67, and 0.90 kg/ha; and 0, 0.009, 0.011, and 0.013 kg/ha, respectively, alone and in tank-mix combination with polymers ASE-108, G-110, CARBO, and E-CELL, at rates of 0.06, 0.08, and 0.11 kg/ha; 1.12, 2.24, and 3.36 kg/ha; 1.12, 5.60, and 11.21 kg/ha; and 1.12, 2.24, and 3.36 kg/ha, respectively. ASE-108 solutions were adjusted to pH 8.0 with 0.01 M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and NH<sub>4</sub>OH. All herbicide/polymer treatments were applied with a CO<sub>2</sub> backpack sprayer with hollow cone "whirl chamber" nozzles (Monarch 49 × 49) at a pressure of 236 kPa.

Weeds were rated visually using a scale of 0% (no injury) to 100% (complete termination) 30 days after application. Injury ratings were subjected to analysis of variance at the 5% confidence level using the Statistical Analysis System (*User's Guide: Statistics*, 1985).

## RESULTS AND DISCUSSION

**Soil Properties.** The soil clay content increased with depth from 6% in the surface to 29% at 90 cm in the lysimeter study. Soil texture changed from loamy sand at the soil surface (0–45.6 cm) to sandy loam (45.6–60.8 cm) and sandy clay loam (60.8–90 cm) in the subsoil. Soil pH was 6.1 in the surface and decreased with depth to 4.4 at 90 cm. Soil organic matter and humic matter contents also decreased with depth from 1.1 and 0.4%, respectively, in the surface, to 0.4 and 0.1%, respectively, at 90 cm. Soil moisture content inside the lysimeter was determined at the time of column removal, 3 months after treatment. Water content in the lysimeter ranged from a low of 5.4% in the surface soil to a high of 16.5% in the subsoil at the bottom of the lysimeter. CEC in the soil profile was relatively uniform throughout the profile, ranging from 1.0 to 2.1 mequiv/100 g of soil due to the higher organic matter content in the surface soil and higher clay content in the subsoil.

**Lysimeter Study.** Mean temperature for the period of the study was 27.1 °C, and precipitation and irrigation input for July, August, and September 1989 was 18.5, 11.1, and 15.5 cm/month, respectively, which was 47% above the 10-year average for the area.

Total <sup>14</sup>C recoveries in the <sup>14</sup>C-labeled atrazine, metolachlor, and primisulfuron treatment without polymer addition (control) after 92 days in the field were 40.6, 54.8, and 40.5%, respectively (Table I). On the basis of *R<sub>f</sub>* values from treatments with herbicide alone (control), <sup>14</sup>C from [<sup>14</sup>C]metolachlor (*R<sub>f</sub>* = 0.30) was the most mobile material in this experiment due to metolachlor's nonionic nature and higher water solubility compared to the other two compounds. The major extractable metabolite of metolachlor is an oxalic acid derivative of metolachlor [*N*-(2-

Table I. Effect of Water-Soluble Acrylic Polymers on the <sup>14</sup>C Distribution and Recovery from <sup>14</sup>C-Labeled Herbicides over a 92-Day Period

mean depth, cm	total recovery, %				normalized recovery, <sup>a</sup> %			
	control	ASE-108	HA-16	E-1242	control	ASE-108	HA-16	E-1242
Atrazine								
3.8	23.6	22.0	16.3	25.1	58.0	58.6	42.3	60.8
11.4	10.3	7.0	13.5	11.0	25.5	18.8	34.9	26.7
19.0	4.4	5.2	4.8	3.1	10.8	13.8	12.4	7.4
26.8	1.4	1.8	1.4	0.9	3.5	4.9	3.7	2.2
34.4	0.3	0.6	0.9	0.3	0.7	1.5	2.3	0.8
42.1	0.1	0.3	0.4	0.2	0.3	0.8	1.0	0.6
49.7	0.1	0.2	0.3	0.1	0.2	0.6	0.9	0.2
57.4	0.1	0.1	0.3	0.1	0.3	0.3	0.8	0.3
65.0	0.1	0.1	0.6	0.1	0.3	0.2	1.4	0.3
72.7	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.3
80.3	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
88.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.1
total	40.6	37.5	38.5	41.3	100.0	100.0	100.0	100.0
LSD <sub>0.05</sub> =	8.9				R <sub>f</sub> = 0.10	0.11	0.14	0.10
					LSD <sub>0.05</sub> = 0.05			
Metolachlor								
3.8	20.0	17.4	15.9	15.5	36.4	34.4	30.8	29.2
11.4	8.7	8.2	7.3	7.1	15.8	16.3	14.0	13.4
19.0	4.9	4.3	5.7	3.8	8.9	8.6	11.0	7.3
26.8	3.4	3.7	3.6	3.0	6.3	7.2	7.0	5.6
34.4	2.5	2.9	2.4	2.2	4.5	5.8	4.7	4.1
42.1	2.0	2.6	2.7	2.1	3.7	5.1	5.2	3.9
49.7	2.0	2.5	2.6	2.1	3.6	4.9	5.1	4.0
57.4	2.0	2.0	2.9	3.6	3.7	3.9	5.5	6.9
65.0	3.4	2.7	2.7	4.4	6.1	5.3	5.2	8.3
72.7	2.8	2.1	2.7	4.4	5.1	4.3	5.2	8.3
80.3	1.9	1.4	2.2	3.4	3.5	2.8	4.2	6.5
88.0	1.2	0.7	1.1	1.4	2.2	1.3	2.0	2.6
total	54.8	50.4	51.7	53.0	100.0	100.0	100.0	100.0
LSD <sub>0.05</sub> =	10.0				R <sub>f</sub> = 0.30	0.29	0.32	0.37
					LSD <sub>0.05</sub> = 0.11			
Primisulfuron								
3.8	14.0	15.4	19.3	14.4	34.5	24.8	34.6	25.4
11.4	14.3	22.4	20.3	26.5	35.3	36.2	36.3	46.7
19.0	4.4	11.2	6.8	9.3	10.8	18.0	12.3	16.4
26.8	2.8	7.0	2.8	1.9	6.9	11.3	5.0	3.3
34.4	1.1	1.2	0.6	1.1	2.7	1.8	1.1	1.9
42.1	0.8	0.5	1.0	0.8	2.0	0.8	1.7	1.4
49.7	0.4	1.2	0.6	0.6	1.0	1.9	1.0	1.1
57.4	0.8	0.8	1.1	0.6	2.0	1.4	1.9	1.0
65.0	0.5	0.6	1.3	0.5	1.4	1.0	2.3	1.0
72.7	0.4	0.8	1.0	0.2	1.1	1.4	1.7	0.3
80.3	0.6	0.6	0.8	0.5	1.5	0.9	1.5	0.9
88.0	0.3	0.2	0.3	0.3	0.8	0.4	0.6	0.6
total	40.5	61.9	55.8	56.7	100.0	100.0	100.0	100.0
LSD <sub>0.05</sub> =	21.7				R <sub>f</sub> = 0.18	0.19	0.18	0.17
					LSD <sub>0.05</sub> = 0.07			

<sup>a</sup> Normalized to 100% recovered, assuming equivalent losses from all depths, so as to compare herbicide mobility and effects of polymers.

methoxy-1-methylethyl)-2-ethyl-6-methyloxalic acid anilide] (Lebaron et al., 1988). As an acid, it was probably repelled by soil clay. <sup>14</sup>C from [<sup>14</sup>C]primisulfuron (R<sub>f</sub> = 0.18) was less mobile than <sup>14</sup>C from [<sup>14</sup>C]metolachlor but more mobile than <sup>14</sup>C from [<sup>14</sup>C]atrazine (R<sub>f</sub> = 0.10). Beyer et al. (1988) reported that the major metabolite from the hydrolysis of sulfonylurea herbicides, such as primisulfuron, is a sulfonamide derivative, which is less mobile than the parent in the soil profile due to its weakly basic properties. In addition, Mersie and Foy (1985, 1986) reported that moderately high soil sorption and low phytotoxicity of chlorsulfuron [2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide], a similar sulfonylurea herbicide, were observed in an acid soil. Atrazine has weakly basic properties and was reported to be sorbed in high amounts on acidic soil surfaces due to its subsequent sorption to exchangeable

sites by Coulombic forces (Weber, 1969, 1970). It was, therefore, the least mobile herbicide in this study over the 92-day period.

Approximately 40% of the total <sup>14</sup>C applied was recovered in the [<sup>14</sup>C]atrazine treatment regardless of the addition of polymers, indicating none of the polymers affected the loss of the herbicide (Table I). Most of the <sup>14</sup>C activity (approximately 20% of applied) was retained in the upper 7.6-cm (mean = 3.8 cm) sections of the columns. For a polymer to be effective in either reducing herbicide movement or reducing herbicide loss, the amounts recovered in the 3.8-cm section of herbicide/polymer treatments must be higher than those from control soils (no polymer). Of the polymers, HA-16 influenced <sup>14</sup>C from [<sup>14</sup>C]atrazine mobility the most, increasing it slightly; however, the differences were not significantly

different [16.3% recovered (3.8-cm zone) vs 23.6% for the control and an  $R_f$  value of 0.14 with HA-16 vs 0.10 for the control].

Calculated  $R_f$  values for the various [ $^{14}\text{C}$ ]atrazine/polymer treatments showed that none of the polymers affected the [ $^{14}\text{C}$ ]atrazine leaching pattern, and thus atrazine mobility, to a significant degree (Table I).

Since the organic matter content was very low throughout the soil column, [ $^{14}\text{C}$ ]metolachlor activity found throughout the lysimeters was not surprising (Table I). Metolachlor was a much higher water solubility than atrazine, and sorption is not pH dependent as is the case for atrazine. Extraction and thin-layer separation of parent herbicides and metabolites in similar lysimeter studies suggest that the  $^{14}\text{C}$  was not parent herbicide (Keller, 1992).

None of the polymers was effective in influencing the loss or mobility of [ $^{14}\text{C}$ ]metolachlor (Table I). Approximately 50% of the total  $^{14}\text{C}$  applied was recovered regardless of polymer treatment. Of that recovered, approximately one-third was found in the upper 7.6-cm (mean = 3.8 cm) section regardless of the polymer added or not added. The highest calculated  $R_f$  value was obtained in the E-1242 treatment due to the higher  $^{14}\text{C}$  activity recovered in the 61–90-cm depth; however, the value was not statistically different from the control.

Total  $^{14}\text{C}$  recovered in the [ $^{14}\text{C}$ ]primisulfuron control treatment was 40%, and although lower than where each of the polymers was added, the differences were not significant (Table I). Approximately 30% of the recovered  $^{14}\text{C}$  was located in the upper 7.6-cm (mean depth = 3.8 cm) zone regardless of whether polymer was added or not. Calculated  $R_f$  values for polymer vs no polymer treatments were not significantly different, suggesting that the added polymers did not affect [ $^{14}\text{C}$ ]primisulfuron mobility in the soil. Since differences in herbicide mobility and losses attributable to polymers were minor, the herbicide molecules appeared to be weakly bound and easily desorbed by infiltrating water. There was no relationship between the properties of the polymers (Table I) and the properties of the herbicides as expressed in the amounts of herbicides recovered or their calculated  $R_f$  values.

**Leaching Column Study.** Since the herbicide/polymer applications (48 h on dry soil) and leaching processes (12 h) were completed in approximately 60 h total in this study, it is likely that all detected  $^{14}\text{C}$  was parent compound, so loss and mobility are of parent compounds only, in contrast with the 92-day lysimeter study in which metabolites were involved. In addition, only the Dothan A horizon (0–15-cm depth) soil was used in the leaching study, while the entire 0–90-cm surface and subsoil were involved in the lysimeter study.

$^{14}\text{C}$ -labeled herbicide distributions, as affected by polymer additions, are shown in Table II. Total recoveries of atrazine, metolachlor, and primisulfuron alone (control) were 81.3, 74.6, and 74.5%, respectively. Calculated  $R_f$  values for atrazine, metolachlor, and primisulfuron alone (control) were 0.22, 0.19, and 0.50, respectively; thus, the relative mobility in descending order was primisulfuron >> atrazine  $\geq$  metolachlor. Primisulfuron was present primarily in the parent anion form and was probably repelled by the negatively charged soil clay, as it was carried chromatographically through the soil over the 12-h period; therefore, primisulfuron was the most mobile herbicide in this study. The pH of the Dothan A horizon soil was approximately 6, so parent atrazine was present primarily in the molecular form. Therefore, both parent atrazine and metolachlor were nonionic in this study and had similar

mobilities ( $R_f = 0.22$  and 0.19, respectively). They were much less mobile than primisulfuron, which had an  $R_f$  value more than twice that of the two herbicides.

Total  $^{14}\text{C}$  recovery data showed that the total amount of atrazine recovered increased significantly from 81.3% without polymer to 89.5% with the addition of CGA-A polymer (Table II). It appears that this polymer reduced atrazine losses by approximately 7%. The eight other polymers had no effect. According to calculated  $R_f$  values, the addition of E-CELL ( $R_f = 0.25$ ), CGA-A ( $R_f = 0.27$ ), CGA-F ( $R_f = 0.25$ ), and CGA-G ( $R_f = 0.26$ ) increased atrazine mobility significantly over that of atrazine applied alone (control) ( $R_f = 0.22$ ), but the other four polymers (G-110, CARBO, CGA-A, CGA-C) had no effect. Higher herbicide mobility by polymer additions suggests that the chemicals were more easily released from the polymers than from the Dothan soil itself or that the herbicide and polymers moved together more readily than the herbicide moved alone.

Two-thirds of the polymers increased the total recovery of metolachlor, while the others had no effect (Table II). Total recovery of metolachlor was significantly higher than the metolachlor control alone (74.6%) when polymer ASE-108 (97.9%), CGA-F (93.4%), CGA-A (89.9%), G-110 (79.5), CGA-G (79.4%), or CARBO (78.9%) was added. Apparently the polymers bound metolachlor more effectively against losses than did the Dothan A horizon soil. The other three polymers (E-CELL, CGA-B, CGA-C) had no effect.

On the basis of calculated  $R_f$  values, polymer ASE-108 ( $R_f = 0.15$ ), G-110 ( $R_f = 0.17$ ), E-CELL ( $R_f = 0.17$ ), CGA-A ( $R_f = 0.16$ ), CGA-C ( $R_f = 0.17$ ), and CGA-F ( $R_f = 0.16$ ) additions reduced metolachlor movement as compared to metolachlor applied alone ( $R_f = 0.19$ ) (Table II). The quantity of metolachlor retained in the 0–2-cm soil zone (mean depth = 1.0 cm) was also higher and ranged from 47.8 to 74.1% for columns where these polymers were added compared with the control column (43.9%). The polymers were apparently more effective in binding metolachlor against desorption by water than was the Dothan soil. The other three polymers (CARBO, CGA-B, CGA-G) had no effect.

Total recovery of primisulfuron was not increased by polymer additions ( $74.5 \pm 5.0\%$ ), but two polymers (G-110, CGA-C) did significantly reduce primisulfuron recovery by 5.7 and 6.9%, respectively (Table II). This suggests that primisulfuron was lost from these two polymers more readily than it was from the Dothan soil; i.e., the polymers were less sorptive for the herbicide than the soil was.

The addition of ASE-108 and CGA-B resulted in significantly smaller  $R_f$  values for primisulfuron,  $R_f = 0.43$  and 0.46, respectively, than the primisulfuron control,  $R_f = 0.50$ , indicating that the two polymers retained primisulfuron against leaching more effectively than did the soil (Table II). A significantly greater amount of primisulfuron was retained in the 1.0- and 3.0-cm zones when ASE-108 was added (33%) than when no polymer was added (24%), also suggesting that the polymer retarded movement of the herbicide. Four of the polymers (CARBO, E-CELL, CGA-F, CGA-G) increased  $R_f$  values,  $R_f = 0.56, 0.54, 0.55$ , respectively, over primisulfuron alone,  $R_f = 0.50$ , suggesting that these polymers retained the herbicide against desorption by water less effectively than did the soil or that they moved through the soil along with herbicide. None of these four polymers affected the quantity of primisulfuron that was retained in the 1.0- or 3.0-cm zones of the soil, however. The other three polymers (G-110, CGA-A, CGA-C) had no effect.

**Table II. Effect of Water-Soluble Acrylic Polymers and E-CELL on the Mobility of Soil-Applied <sup>14</sup>C-Labeled Herbicides in Laboratory Leaching Columns**

mean depth, cm	total recovery, %					normalized recovery,* %					total recovery, %					normalized recovery,* %				
	control	ASE-108	G-110	CARBO	E-CELL	control	ASE-108	G-110	CARBO	E-CELL	CGA-A	CGA-B	CGA-C	CGA-F	CGA-G	CGA-A	CGA-B	CGA-C	CGA-F	CGA-G
<b>Atrazine</b>																				
1.0	38.6	43.9	37.9	41.3	37.4	47.5	51.2	45.7	46.9	42.3	38.15	35.8	37.4	36.1	33.8	42.6	46.3	46.6	42.9	41.0
3.0	28.5	30.4	27.2	29.3	27.3	35.1	35.4	32.8	33.3	30.9	26.3	26.7	25.0	27.9	25.2	29.3	34.6	31.2	33.1	30.6
5.0	11.8	9.7	15.1	14.2	19.5	14.6	11.3	18.2	16.2	22.7	19.3	11.5	14.0	15.9	18.1	21.6	14.9	17.5	18.9	21.9
7.0	2.0	1.6	2.5	2.8	3.8	2.5	1.9	3.1	3.2	4.3	5.4	2.8	3.4	3.8	4.7	6.1	3.7	4.2	4.6	5.7
9.0	0.3	0.2	0.2	0.4	0.4	0.3	0.2	0.2	0.5	0.4	0.3	0.3	0.5	0.4	0.6	0.4	0.4	0.6	0.5	0.7
11.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	81.3	85.7	82.9	88.0	88.4	100.0	100.0	100.0	100.0	100.0	89.5	77.2	80.2	84.2	82.4	100.0	100.0	100.0	100.0	100.0
LSD <sub>0.05</sub> =	7.30					$R_f = 0.22$	0.21	0.24	0.23	0.25	LSD <sub>0.05</sub> =	7.30				$R_f = 0.27$	0.23	0.24	0.25	0.26
						LSD <sub>0.05</sub> =	0.03									LSD <sub>0.05</sub> =	0.03			
<b>Metolachlor</b>																				
1.0	43.9	74.1	50.5	45.9	47.8	58.9	75.7	63.6	58.1	61.2	61.7	44.1	47.2	62.6	44.8	68.7	58.0	62.6	67.0	58.4
3.0	22.8	19.2	24.1	25.4	25.2	30.6	19.5	30.4	32.2	32.2	22.0	25.2	21.8	24.6	26.6	24.5	33.2	29.0	26.4	33.5
5.0	6.8	3.5	4.2	6.4	4.4	9.1	3.6	5.3	8.1	5.6	4.9	5.7	5.5	4.8	6.5	5.4	7.5	7.2	5.1	8.2
7.0	0.8	0.7	0.5	0.9	0.6	1.1	0.7	0.7	1.2	0.8	0.9	0.8	0.7	0.9	1.1	1.0	1.0	1.0	1.0	1.4
9.0	0.2	0.1	0.1	0.3	0.1	0.3	0.1	0.1	0.4	0.2	0.3	0.2	0.2	0.4	0.2	0.4	0.3	0.2	0.4	0.3
11.0	0.0	0.3	0.0	0.1	0.0	0.0	0.3	0.0	0.1	0.0	0.1	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.2	0.2
total	74.6	97.9	79.5	78.9	78.2	100.0	100.0	100.0	100.0	100.0	89.9	76.0	75.4	93.4	79.4	100.0	100.0	100.0	100.0	100.0
LSD <sub>0.05</sub> =	4.20					$R_f = 0.19$	0.15	0.17	0.19	0.17	LSD <sub>0.05</sub> =	4.20				$R_f = 0.16$	0.18	0.17	0.16	0.19
						LSD <sub>0.05</sub> =	0.01									LSD <sub>0.05</sub> =	0.01			
<b>Primisulfuron</b>																				
1.0	17.8	22.1	17.6	16.9	16.7	23.8	28.3	25.6	23.8	22.8	17.2	19.8	16.3	15.6	15.7	23.1	27.0	24.1	20.9	20.6
3.0	6.3	10.9	6.1	4.8	5.4	8.4	13.9	8.8	6.2	7.4	5.8	8.5	5.8	5.7	7.4	7.7	11.8	8.6	7.6	9.8
5.0	13.6	16.2	12.7	7.9	9.8	18.2	20.7	17.6	11.2	13.4	11.5	13.5	10.6	10.0	12.2	15.4	18.4	15.7	13.6	16.0
7.0	18.9	16.4	16.2	15.5	17.5	25.4	21.0	23.6	21.9	23.9	18.6	17.1	15.1	18.5	17.1	24.9	23.2	22.4	24.8	22.5
9.0	12.7	8.9	11.7	13.9	15.6	17.1	11.4	17.4	18.6	21.4	14.9	9.6	12.7	15.7	14.6	20.0	13.1	18.9	21.0	19.2
11.0	5.3	3.7	5.1	12.3	8.1	7.1	4.7	7.4	17.4	11.1	6.6	4.9	6.9	9.1	9.0	8.9	6.7	10.3	12.2	11.9
total	74.5	78.2	68.8	71.0	73.1	100.0	100.0	100.0	100.0	100.0	74.6	73.4	67.6	74.5	76.0	100.0	100.0	100.0	100.0	100.0
LSD <sub>0.05</sub> =	5.0					$R_f = 0.50$	0.43	0.49	0.56	0.54	LSD <sub>0.05</sub> =	5.0				$R_f = 0.52$	0.46	0.52	0.55	0.54
						LSD <sub>0.05</sub> =	0.03									LSD <sub>0.05</sub> =	0.03			

\* Normalized to 100% recovered, assuming equivalent losses from all depths, so as to compare herbicide mobility and effects of polymers.

**Herbicide/Polymer Bioactivity Study.** The mean temperature for the period of the study (May 14–June 14, 1990) was 23 °C (normal) and total precipitation was 10 cm (normal). Weed and crop growth was excellent, and herbicide injury to the weeds from atrazine and metolachlor was above normal, while that from primisulfuron was generally below normal.

Herbicide/polymer interactions were observed throughout the experiment; however, there were no obvious trends (data not shown). ASE-108 and E-CELL polymers had little or no effect on the bioactivity of any of the herbicides. G-110 reduced the bioactivity of atrazine and metolachlor by 20–50% but had no effect on primisulfuron. CARBO reduced the bioactivity of atrazine by 18–20% but had no effect on metolachlor or primisulfuron.

## CONCLUSIONS

Pesticides that are applied to plants or soils may be lost through photodecomposition, volatilization to the atmosphere, or leaching through the soil to groundwater or be carried off the soil in runoff water. If polymers could be added to pesticides to reduce their losses or movement and not detrimentally affect bioactivity, it would improve their efficacy and/or environmental safety. In a 92-day field lysimeter study on a Dothan soil, three differently charged water-soluble polymers [ASE-108 (anionic), HA-16 (nonionic), E-1242 (cationic)] added to three ionically different <sup>14</sup>C-labeled herbicides [atrazine (weak base), metolachlor (nonionizable), primisulfuron (weak acid)] had no effect on the soil mobility or losses of <sup>14</sup>C from the <sup>14</sup>C-labeled herbicides. Apparently, the charge properties of the herbicides and polymers made little difference.

In a 3-day soil column laboratory study, nine nonionic or anionic polymers (ASE-108, G-110, CARBO, E-CELL, CGA-A, CGA-B, CGA-C, CGA-F, CGA-G) added to the three <sup>14</sup>C-labeled herbicides had differing effects on soil mobility and/or losses of the chemicals. The most lipophilic of the CGA polymers, CGA-A, reduced the loss of metolachlor by 15% and reduced soil mobility by 15% but increased the soil mobility of atrazine by 23% and had no effect on primisulfuron. ASE-108 polymer reduced the loss and mobility of metolachlor by 22% and little or no effect (<10%) on atrazine or primisulfuron. CGA-F polymer also reduced the loss of metolachlor by 19% and soil mobility by 16% but had no effect on loss of the other herbicides and increased mobility of atrazine and primisulfuron by 12%. CGA-G and E-CELL polymers, two of the most hydrophilic polymers, increased the soil mobility of atrazine by 14–18% and that of primisulfuron by 8% but had little effect on metolachlor. The two polymers had no effect on losses of any of the three herbicides. CGA-B, CGA-C, G-110, and CARBO polymers had little or no effect on the loss or mobility of the three herbicides.

The observation that the ASE-108 polymer reduced the loss and soil mobility of [<sup>14</sup>C]metolachlor in the 3-day laboratory study but did not influence the loss or mobility of <sup>14</sup>C from [<sup>14</sup>C]metolachlor in the 92-day field study suggests that the polymer may influence the loss and mobility of parent metolachlor but has no influence on degradation products of metolachlor. This is highly likely since the polymer has an influence on herbicide behavior only for the short time the two are in the immediate vicinity of one another. The polymer exerts little or no influence on the herbicide once the two are separated. The observation that the most lipophilic of the CGA polymers, CGA-A, had the most influence on reducing the loss and mobility of metolachlor and that the more hydrophilic

polymers, E-CELL, CGA-B, and CGA-G, had no influence on metolachlor loss or mobility suggests that if more polymers are to be examined, they should probably be of the more lipophilic type. The herbicide/polymer field bioactivity study showed that the polymers had little or no effect on the bioactivity of the three herbicides. G-110 was the only polymer that consistently reduced the bioactivity of atrazine and metolachlor, but it had no effect on primisulfuron.

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