

A Computer Simulation Model for Predicting Pesticide Losses from Agricultural Lands

by

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(ABSTRACT)

A field scale model for predicting the surface losses of pesticides (Pesticide Losses In Erosion and Runoff Simulator, PLIERS) was developed. PLIERS accounts for pesticide losses by degradation and volatilization, the washoff of pesticides from plant canopy and surface residue, the adsorption and desorption of pesticides to and from soil particles, and the movement of pesticides in the dissolved and adsorbed phases. Hydrologic data are generated by the comprehensive watershed model, FESHM; which contains an extended sediment detachment and transport algorithm. PLIERS uses first order rate equations to describe degradation and volatilization, and pesticide washoff. The adsorption of pesticides to individual particle size classes is estimated using the Freundlich equation.

Movement of atrazine and 2,4-D in runoff and sediment was measured on twelve field plots under simulated rainfall. The plots were treated with conventional or no-tillage in combination with one of three residue levels (0, 750, and 1500 kg/ha). Runoff and sediment losses were found to increase with decreasing residue cover for both tillage systems. No-till reduced sediment loss and total runoff volume by 98 and 92 percent, respectively, compared to conventional tillage. Concentrations of atrazine and 2,4-D in runoff and sediment were greater from the no-till plots than from the conventional plots but the total losses were less. Both pesticides were carried predominately in the dissolved phase. Averaged over all plots, the atrazine losses were 2.9 percent of applied amount for conventional tillage and 0.3 percent for no-tillage. The corresponding values for 2,4-D were 0.3 percent and 0.02 percent.

PLIERS was validated using data from the rainfall simulator field plot studies. Agreement between predicted and observed data was very good for dissolved pesticide losses and satisfactory for adsorbed pesticide losses. In addition, the effects of tillage type and residue level were reflected

in PLIERS predictions. PLIERS shows great potential as a flexible planning tool since it could be used with any comprehensive hydrologic model and is able to predict the losses of pesticides under various field conditions.

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INTRODUCTION

In recent years much public attention has been focused on pesticides and their effects on the environment. Of particular concern are the effects of pesticides on surface and ground waters. A major source of pesticide pollution is the loss of these chemicals from agricultural lands (Rao et al., 1983). In 1986, agricultural pesticide usage was 341,000 metric tons of active ingredient which accounted for 68% of the total pesticide used in the United States (Pimentel and Levitan, 1986). Once in the soil, these pesticides are subject to movement by runoff and leaching.

The pesticides lost by runoff and leaching create hazards within the environment. Pimentel and Levitan (1986) estimated that less than 0.1 % of the pesticides applied to crops actually reach the target pest, and they concluded that most of the pesticide applied enters the environment, contaminating the soil, water and air and potentially poisoning or adversely affecting nontarget organisms. Nontarget pesticide poisoning has been held accountable for fish kills, reproductive failure in birds, and illness in humans (Rao et al., 1983). Biomagnification, the concentration of persistent pesticides within the food chain, is responsible for occasionally high levels of chemicals within an organism's body tissues. These pesticide concentrations are often many times larger than the concentrations of pesticides in the surrounding environment (Brewer, 1979).

Some recent studies (Allen and Davis, 1979; Gile, 1983; Wehtje et al., 1983) indicate that pesticides are now detectable in the lowest trophic levels of the food chain. Hence, measures must

be taken to control the losses of pesticides from agricultural lands. The increase in agricultural production dictated by urbanization and an expanding population will lead to greater use of agricultural chemicals. This trend is enhanced by the positive correlation between increased pesticide use and crop yield (Stewart et al., 1975). If this increase in pesticide usage is not counterbalanced by methods of pollution control, the resulting contamination of surface and ground waters may render these resources useless.

On farm Best Management Practices (BMPs) may prove helpful in the reduction of pesticide losses from agricultural lands. Conservation tillage is one BMP commonly identified as a method for improving water quality (Bailey et al., 1985). However, pesticide application rates are usually higher for conservation tillage than for conventional tillage systems. Thus, the potential pesticide loss from conservation tillage is higher. In addition, the degree of soil incorporation of agricultural chemicals is reduced or eliminated in conservation tillage systems. This lack of incorporation may result in higher chemical concentrations in both runoff and sediment (Baker, 1985).

It is apparent that BMPs should not be recommended unless their effectiveness in reducing nonpoint source pollution has been established. Computer simulation is a practical method by which the effectiveness of various BMPs can be determined. Computer models can be adapted to many field situations and may include the effects of different land uses and soil types in ungaged watersheds, thus reducing the need for expensive and difficult field data collection. If physically based and adequately tested with field data, computer models can be used for the simulation and evaluation of various combinations of practices in the selection of the most cost-effective soil and water conservation program.

Many simulation models have been developed for predicting pesticide losses from agricultural lands, using both empirical and mathematical expressions. However, most of these models do not adequately describe one or more of the pesticide movement processes. In addition, existing models often rely on inadequate hydrologic components for the generation of runoff and sediment information.

Objectives

The overall goal of this project was to develop a computer simulation model for predicting the losses of selected pesticides from agricultural lands. A comprehensive watershed model was incorporated into the pesticide model to include the effects of runoff and erosion on pesticide losses from agricultural lands. The specific objectives of this study were:

1. To measure pesticide losses in sediment and runoff from field plots. In particular, the effects of various crop residue levels and tillage systems were investigated.
2. To develop a field scale pesticide loss model for predicting the transport of pesticides in runoff and sediment which accounts for pesticide degradation and volatilization, washoff of pesticides from crop residue, and the movement of pesticides in runoff water and eroded sediment. A comprehensive watershed model was used to generate the required hydrologic data.
3. To evaluate the accuracy of the model by comparing its predictions with observed data from the field plot experiments.

LITERATURE REVIEW

Hydrologic Models

Many approaches to hydrologic modeling have been undertaken, each approach having distinct advantages and disadvantages. The applicability of any modeling approach is determined by the needs of the model user. However, some model features are universally desirable. The model should be reliable, adequately tested and verified, simple to use and understand, inexpensive to run, and applicable to both short term and long term changes in watershed characteristics (Smolen, 1983). Most models can be classified as one of three conceptual types: 1) empirical, 2) lumped parameter, and 3) distributed parameter.

Empirical models are generally equations developed from experimental data. These models are time efficient and easy to use; however, their application is limited depending on the source of the experimental data used in model development. In addition, the model cannot be further developed or verified without the accumulation of large amounts of data.

Lumped parameter models represent watershed response with a series of differential equations. Input parameters for these models are averaged over the entire watershed. Since model parameters are not easily measured, values are assumed and then calibrated against observed rainfall

and runoff data. Therefore, lumped parameter models, like empirical models, rely on data from gaged watersheds. If sufficient watershed data is not available, such as for ungaged watersheds or in situations involving various land uses, the confidence of the model is reduced.

Distributed parameter models allow the description of spatial variations of watershed characteristics such as soil type, vegetation and topography. Parameter estimates can be obtained from measured watershed characteristics; therefore, calibration is generally unnecessary. However, compared to lumped parameter models, distributed parameter models have large data requirements, and require more computer time. These disadvantages are counterbalanced by three major advantages. First, the model's ability to depict spatial variation increases the potential for greater prediction accuracy. Second, since distributed parameter models do not generally require calibration, they are suitable for use on ungaged watersheds. Third, these models are well adapted for simulating chemical transport. Many distributed parameter hydrologic models have been developed, some of these are described below.

Description of Selected Hydrologic Models

ANSWERS

The ANSWERS (Areal Nonpoint Source Watershed Environment Response Simulation) model is a single event model developed to be used as a planning tool for watersheds having agriculture as their predominant land use. The original hydrologic model (Huggins and Monke, 1966) accounted for interception, infiltration, surface storage, interflow and surface storage. The model has since been expanded to include erosion, sediment transport, tile drainage and channel flow (Beasley, 1977), and best management practices such as parallel tile outlet terraces, sediment basins, grasses waterways and field borders (Beasley and Huggins, 1981).

Surface runoff and tile flow are described using the continuity equations. A variation of the infiltration equations developed by Holtan (1961) and Overton (1965) is used to estimate infiltration. An extended sediment detachment and transport routine based on relationships described by Yalin (1963) and Meyer and Wischmeier (1969) was added by Dillaha (1981). ANSWERS simulates hydrologic response for square elements in which watershed characteristics are assumed constant. The size of the elements depends on the degree of nonhomogeneity of the watershed. Element output is routed as dictated by element slope.

CREAMS

The Chemical, Runoff, and Erosion from Agricultural Management Systems model (CREAMS; Knisel, 1980) simulates continuous hydrologic response of agricultural fields. CREAMS includes submodels for simulating infiltration, soil water movement, surface runoff and erosion during rainfall events, and evapotranspiration between rainfall events. In addition, CREAMS is capable of predicting the transport of nutrients and pesticides.

Surface runoff is estimated using the SCS curve number technique (U. S. Soil Conservation Service, 1973). Subsurface water movement is described with the Green-Ampt model (Green and Ampt, 1911). A model described by Ritchie (1972) is used to describe evapotranspiration. The sediment detachment and transport algorithms are based on established relationships such as the USLE (Wischmeier and Smith, 1978). CREAMS assumes homogeneous land use and soil type, and thus cannot be applied to nonhomogeneous areas.

USDAHL

The USDAHL-74 Revised Model of Watershed Hydrology (USDAHL; Holtan et al., 1975) was developed to describe the continuous hydrologic response of small agricultural

watersheds under natural rainfall conditions. Widely accepted mathematical relationships are used to describe the component processes which constitute the major hydrologic processes within a watershed. The model uses the kinematic wave approximation to estimate overland flow rates. Infiltration is predicted by Holtan's infiltration equation (Holtan, 1961). Potential evapotranspiration is determined as a function of the weekly pan evaporation. The model assumes that a watershed can be represented by hydrologic response zones having homogeneous hydrologic and soil characteristics.

USDAHL is capable of continuously simulating water quantity and flow rates. However, the model does not predict sediment yield. In addition, there are no provisions for describing the impact of hydrologic structures on surface runoff. As presently written, USDAHL is not capable of performing water quality simulations. However, the model may be interfaced with water quality components.

FESHM

The Finite Element Storm Hydrograph Model (FESHM; Judah et al., 1975; Ross et al., 1978; Shanholtz et al., 1981a, Heatwole et al., 1982) is an event oriented distributed parameter model which simulates surface runoff from ungaged watersheds. The model contains an extended sediment detachment and transport function (Wolfe, 1982). The model assumes that a watershed can be discretized into flow elements. Each of these flow elements, which constitute the finite element matrix, are defined such that they have a uniform land use and soil type.

The runoff simulator in FESHM consists of two major components, a precipitation excess generator and a flow routing routine. The calculation of rainfall excess depends on the spatial distribution of land use and soil-mapping units as described by the flow elements. Precipitation excess, which varies between the elements, is determined using the Holtan infiltration equation (Holtan, 1961). The infiltration rate, F , is computed as a function of the unused pore space, S , and the final infiltration rate, f_c :

$$F = \text{GINDEX} \times a \times S^n + f_c \quad [1]$$

Equation constants include the growth index, GINDEX, the cover density index, a, and the equation exponent, n. Excess precipitation generated for each overland flow element is routed through overland flow elements and into channel elements using a finite element approximation of the kinematic wave equation. FESHM assumes that evaporation during rainfall, interception and subsurface flow have negligible effects on hydrologic response. However, these components are generally negligible when simulating short intense storms (Smolen, 1983).

The erosion component of FESHM is a two part process consisting of the detachment of particles from the soil mass and the transport of the particles in overland flow. The detachment of soil particles is a function of both the kinematic energy of rainfall and the lift forces generated by overland flow. Interrill and rill detachment is computed based on equations developed by Foster et al. (1980):

$$DI = 0.210 EI (s + 0.014) K C P (q_p / V_u) \quad [2]$$

$$DR = 37983 m V_u q_p^{1/3} (x / 72.6)^{m-1} s^2 K C P (q_p / V_u) \quad [3]$$

where DI is the interrill detachment rate, DR is the rill detachment rate capacity, EI is Wischmeier's rainfall erosivity index, x is the length of the flow element, s is the sine of the slope angle, m is the slope length exponent, K, C and P are the USLE soil erodibility factor, crop management factor and erosion control practice factor, respectively, q_p is the peak runoff rate, and V_u is the runoff volume. The transport capacity of the overland flow is calculated using a version of the Yalin equation (Yalin, 1963) as presented by Foster and Meyer (1972). This modified relationship allows for modeling the particle size distribution of eroded sediment.

Pesticides in the Environment

The movement of pesticides from agricultural lands to the environment not only poses a threat to nontarget organisms, but also represents an economic loss to the farmer. While application techniques and other cultural practices are geared towards lowering pesticide losses for the minimization of cost, studies show that pesticides are still leaving agricultural lands and entering surface and ground waters (Hall et al., 1972; Leonard et al., 1979; Rohde et al., 1981; Frank et al., 1982; Wu et al., 1983; Wehtje et al., 1983; Cohen et al., 1984; O'Hare et al., 1985).

Pesticides in Surface Waters

Hall et al. (1972) studied the fate of atrazine for three years following a single application. The study was conducted on 14 field plots (1.8 m by 22.3 m) to which atrazine was applied at six rates, ranging from 0.6 to 9.0 kg/ha (all pesticide application rates in this thesis are in active ingredient per ha and are designated as kg/ha), plus two control plots to which no atrazine was applied. Average losses of atrazine in runoff water and sediment were 2.4 and 0.16 % of the total applied amount, respectively, regardless of the application rate. They indicated that the concentration of atrazine in runoff water and sediment increased as the application rate increased. In addition, atrazine concentrations in sediment decreased with each consecutive runoff event.

Herbicide runoff from four upland watersheds located in the Georgia piedmont was studied by Leonard et al. (1979). The watershed areas ranged from 1.3 to 2.7 ha with average slopes of 3 to 4%. Each year the watersheds were planted with either grain sorghum, corn, or soybeans. Herbicides commonly used for each crop (atrazine, cyanazine, diphenamide, paraquat, propazine, and/or trifluralin) were applied at recommended rates. With the exception of paraquat, total seasonal herbicide losses in runoff and sediment were generally less than 2% of the applied amount.

Paraquat losses were higher due to strong soil sorption and slow degradation. Herbicide concentration in runoff generally decreased exponentially with time after application.

Rohde et al. (1981) examined the movement of atrazine from field plots (14.1 m by 25.9 m) to which atrazine had been applied at rates of either 2.24 or 4.48 kg/ha. Total losses for the two rates varied from 0.22 to 2.24% of the applied amount. Initial atrazine concentrations in the soil were approximately twice as large for the higher application rate as compared to the lower application rate. Furthermore, atrazine concentrations in the soil and surface runoff were directly related to the application rate.

Eleven watersheds in Ontario's Great Lakes Basin were monitored over a two year period (Frank et al., 1982). The watersheds ranged in size from 1860 to 1913 ha with an average of 93.6% of the land devoted to agriculture. Crops cultivated in the watersheds varied from forage crops for livestock to high value cash crops. A total of 81 different pesticides were applied to the eleven watersheds. Of these, 41 were investigated and 18 were identified in surface water.

A three year study of pesticide runoff from eight experimental watersheds was conducted in Maryland's Rhode River Basin (Wu et al., 1983). Watershed areas ranged from 16 to 250 ha and consisted of cropland, pasture, forest, residential land, and marshland. Runoff water was tested for atrazine and alachlor. Maximum herbicide concentrations in winter runoff from the eight watersheds were 10 µg/L and 0.5 µg/L for atrazine and alachlor, respectively. Atrazine lost from the watersheds was primarily in the dissolved phase.

Pesticides in Groundwater

Groundwater contamination may result from the loss of pesticides from agricultural lands. Atrazine was detected in most irrigation wells used for the gravity irrigation of corn in the central Platte Valley of Nebraska (Wehtje et al., 1983). Their investigation of 41 monitoring wells in two Nebraska counties showed atrazine concentrations of 0.01 to 8.29 µg/L. Bioassays involving the well water indicated that current contamination levels were below the levels of phytotoxicity.

Cohen et al. (1984) reported the results of a study which investigated current pesticide concentrations in groundwater. Twelve different pesticides were detected in the groundwater of 18 states. Typical concentrations reported by Cohen et al. (1984) include aldicarb at 50 ppb in 13 states including Virginia, 300 ppb bromacil in Florida, 700 ppb DCPA and 65 ppb oxamyl in New York.

A summary of the occurrence of groundwater pollution in the United States resulting from the use of agricultural chemicals was reported by O'Hare et al. (1985). The authors found that 33 states had confirmed or suspected groundwater pollution by pesticides. Of these 33 states, 26 had either adequate legislative awareness or were preparing to evaluate the threat of pesticides to their groundwater.

Recent studies which further discuss the contamination of groundwater by pesticides have been presented by Baier and Robbins, (1982), Beck (1985), and Poinke and Urban (1985). Pesticide transport in groundwater is described, among others, by Carsel et al. (1984) and Leonard et al. (1986).

Controlling Pesticide Losses

Conservation practices, such as conservation tillage and increased residue cover, have been shown to influence pesticide transport. Researchers have projected that over 90% of United States farmland will be under conservation tillage by the end of this century (Croson, 1981). Because pesticide application rates are higher for conservation tillage than for conventional tillage systems, the potential pesticide loss from conservation tillage is greater. Furthermore, conservation tillage may increase infiltration and thus the downward movement of soluble pesticides. Some of the research aimed at describing the relationship between tillage systems and pesticide loss is summarized below.

Ritter et al. (1974) measured pesticide losses in runoff and by leaching from four small Iowa agricultural watersheds ranging in size from 0.53 to 1.54 ha. During the four years of the study, two

watersheds were planted in contour corn and the other two in ridge planted corn. Atrazine and propachlor were applied at rates of 2.24 and 4.48 kg/ha, respectively, the first two years, and 3.36 and 6.72 kg/ha the following two years. Diazinon was applied in a band application 2.5 to 5.0 cm deep once a year at 1.12 kg/ha. No traces of diazinon were found in runoff or sediment when the pesticide was applied at the recommended rates and incorporated into the soil. Atrazine was found to move slowly in the soil profile and to penetrate the soil to depths of 20.3 to 25.4 cm by the end of one year. Only traces of propachlor remained in the soil after 4 to 6 weeks.

Baker et al. (1978) investigated the effect of conservation tillage in pesticide runoff losses from 3.05 m by 10.67 m plots under simulated rainfall. The plots contained either conventional or no-till corn planted up and down the slope. Fonofos was applied at 1.12 kg/ha and alachlor and cyanazine were applied at 2.24 kg/ha each. Rainfall was simulated for 1.4 hr at 6.35 cm/hr, 1.0 hr at 6.35 cm/hr, and 0.5 hr at 12.70 cm/hr. Under these extreme conditions, pesticide losses were not affected by tillage method.

The effects of conventional tillage, till-plant, and ridge-plant systems on pesticide runoff from six small watersheds in Iowa ranging in size from 0.55 to 1.75 ha were studied by Baker and Johnson (1979). The study was conducted over a four year period during which fonofos was incorporated into the top 5 cm of the soil at 1.12 kg/ha and alachlor, atrazine, and cyanazine were surface applied at 2.24 kg/ha each. The authors concluded that conservation tillage reduced the runoff of pesticides from agricultural lands, and that the time of application was a significant factor in determining pesticide losses in runoff.

Another factor, in addition to tillage systems, which may affect pesticide movement is the amount of crop residue left on or incorporated into the soil. While crop residue improves infiltration and reduces erosion, pesticides may be intercepted by residue and thus be more susceptible to washoff.

The impact of corn residue on the losses of propachlor, atrazine, and alachlor from field plots (1.5 m by 1.9 m) subjected to simulated rain was examined by Baker et al. (1982). Pesticides were applied at a rate of 2.09 kg/ha to plots having residue cover of 0, 375, 750, or 1500 kg/ha.

Simulated rain was then applied at 6.35 cm/hr for 2 hours. Crop residue was found to reduce and delay surface runoff, thus reducing herbicide losses.

Pathways of Pesticide Movement

Pesticides applied to agricultural land are exposed to many modes of displacement including photochemical, chemical and microbial degradation, volatilization, uptake and metabolism by plants, and movement in water and on sediment. A diagram of these processes is shown in Figure 1. The following section summarizes some of the research aimed at describing the processes of displacement.

Pesticide Degradation

Pesticide degradation refers to the breakdown of pesticides within the environment. A pesticide is susceptible to photochemical, chemical, and microbial decomposition. Photochemical degradation, breakdown under the influence of ultraviolet light, is common for organic pesticides. Chemical decomposition may occur through the presence of excess acidity or alkalinity, and is therefore related to pH. Biological degradation is the result of microbial metabolism of pesticides, and is often the main source of pesticide degradation in soils (Haque and Freed, 1974).

Pesticide degradation, as affected by various soil parameters, has been studied by several researchers. Kells et al. (1980) and Moreale and van Bladel (1980) studied the influence of soil pH on the dissipation of atrazine and 2,4-D, respectively. Kells et al. (1980) concluded that degradation rates are lower when soil pH is above 6.5 and higher for soil pH values below 5.0. Conversely, Moreale and van Bladel (1980) reported that 2,4-D losses were greater in soils having a pH above

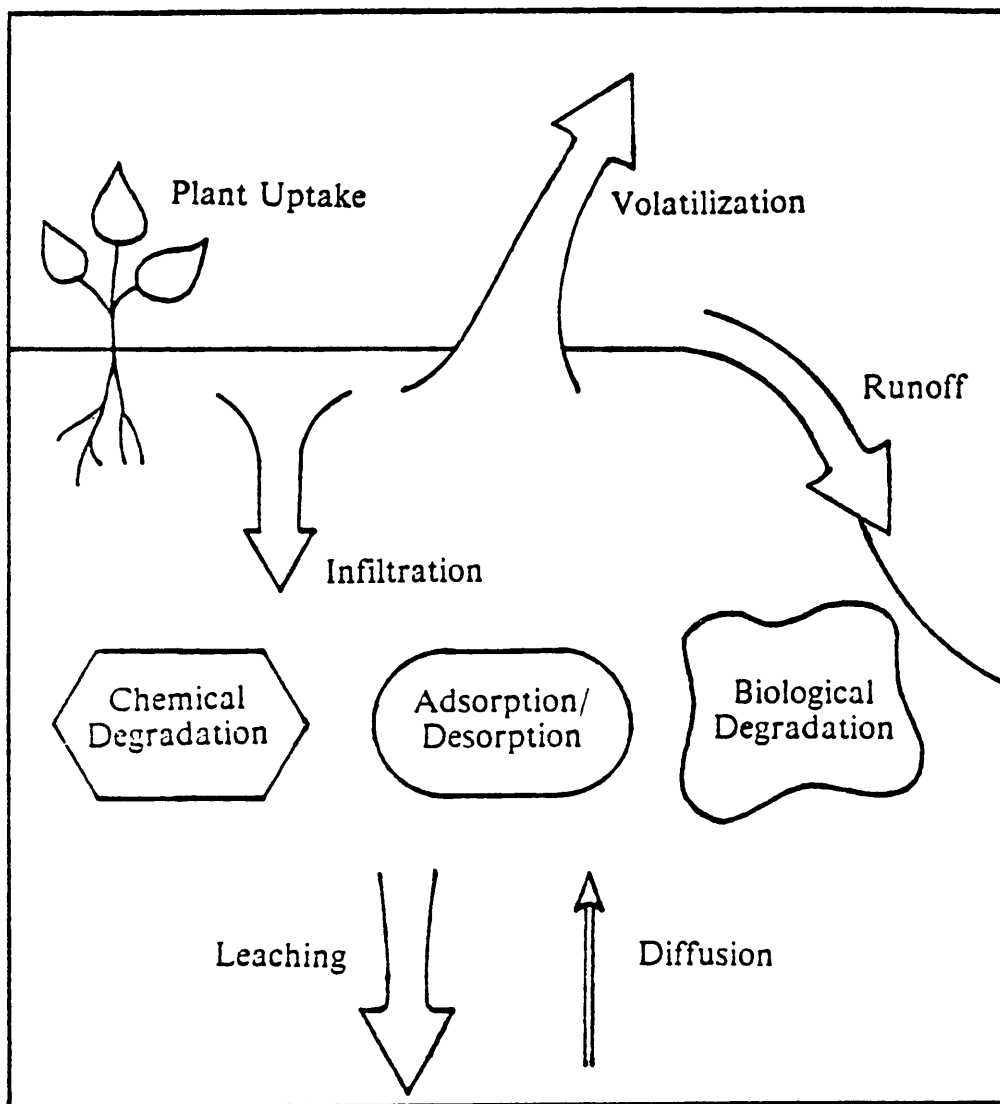


Figure 1. Methods of pesticide transport.

6.0 than those having a lower pH. In addition, degradation was found to be independent of the tillage type and remaining crop residue (Kells et al., 1980).

The effects of soil moisture and temperature on the degradation of carbofuran and 2,4-D has been reported by Ou et al. (1982) and Parker and Doxtader (1983), respectively. Both studies indicate that degradation peaks for soil temperatures ranging from 27 to 35 °C. In addition, Ou et al. (1982) found that a soil temperature increase from 15 to 27 °C had a greater impact on carbofuran degradation than did a temperature increase from 27 to 35 °C. Ou et al. (1982) also found a correlation between the degradation rate and the product of the soil temperature and moisture content for homogeneous data sets. This relation, however, performed poorly when soil-water tension was considered instead of soil moisture content, nor when used to describe the grouped data. Parker and Doxtader (1983) concluded that the rate of decomposition of 2,4-D decreased with increasing soil water tension between soil temperatures of 20 and 35 °C.

Pesticide Volatilization

Volatilization, the diffusion of pesticides through the soil to the soil surface and the movement of a pesticide into and through the atmosphere, is dependent on the vapor pressure and heat of vaporization of the chemical, the partition coefficient between the atmosphere and any other phase, and the air flow mass which will transport the airborne chemical (Haque and Freed, 1974). In addition to these factors, pesticide volatilization is affected by the method of pesticide application. Pesticides which are surface applied are more susceptible to volatilization, than those which are incorporated into the soil.

The diffusion characteristics of lindane and metribuzin as affected by various soil parameters have been studied by Ehlers et al. (1969a) and Scott et al. (1974), respectively. Ehlers et al. (1969a) reported that the diffusion coefficient of lindane increased as the bulk density of the soil decreased and as the soil temperature increased. These findings agreed well with predictions made by theoretical calculations (Ehlers et al., 1969a). Both Ehlers et al. (1969a) and Scott et al. (1974)

concluded that diffusion rates increased with increasing soil moisture content. However, Ehlers et al. (1969a) found that after the water content surpassed 3% (by weight) the diffusion rate remained constant. The increases in diffusivity resulting from increases in the soil moisture content may have been due to displacement of the pesticide from the soil surface by water (Ehlers et al., 1969a), or by movement of the pesticide by soil water (Scott et al., 1974).

The volatilization of surface applied 2,4-D from wheat has been investigated by Gile (1983) and Grover et al. (1985). Both studies indicated that volatilization losses were highest for the first few days following application and declined sharply thereafter. In addition, only a small fraction of the 2,4-D entering the air, two days following application, was the original applied compound, the remainder was composed of metabolites of the parent compound (Gile, 1983; Grover et al., 1985). Gile (1983) studied the effect of formulation on 2,4-D volatilization and determined that ester formulations are much more volatile than amine formulations. Diurnal variations in pesticide volatilization rates were detected by Grover et al. (1985) who reported that the highest volatilization rates occur in the early afternoon due to higher temperatures.

Pesticide Absorption and Metabolism

Although many consumers are concerned about ingestion of pesticides with food, only a few of the synthetic organic compounds manufactured have been studied in plant uptake investigations (Kaufman, 1983). The uptake of pesticides by plants is affected by many factors. The most important factors are the plant species, growth stage, and intended use (Finlayson and MacCarthy, 1973). Soil characteristics such as pH, temperature, clay fraction, moisture content, and particularly organic matter content also influence the uptake of pesticides by plants (Finlayson and MacCarthy, 1973). In addition, the type of pesticide, the pesticide formulation, the method of application, and the mode of action affect plant uptake (Kaufman, 1983).

The mode of action of a herbicide refers to the sequence of events which cause injury or death to the plant (Kirkwood, 1983). If a pesticide is systemic, uptake and translocation of the

pesticide is necessary. Once absorbed by the plant a pesticide can be metabolized and is lost. Two commonly used systemic herbicides which have been used in plant uptake and metabolism studies are atrazine and 2,4-D (WSSA, 1974).

The uptake of atrazine by sudangrass, sorghum, and corn was studied by Roeth and Lavy (1971). The authors found that atrazine uptake by the roots and shoots of young plants is mainly dependent on the herbicide concentration in the soil and the amount of water used by the plant. In addition, uptake rates as percent of the applied amounts were 6, 9, and 15% for sudangrass, sorghum, and corn, respectively.

Uptake of 2,4-D has been examined for corn and soybeans (Montgomery et al., 1971), wheat (Gile, 1983), and turfgrass (Thompson et al., 1984). Montgomery et al., (1971) found that 2,4-D uptake by beans and corn was 65% of the applied amount eleven days following the application. These rates are high, however, since Montgomery et al. (1971) used a 200 ppm pesticide solution which included additives to enhance pesticide uptake by plants. This pesticide solution was not only very concentrated, but was also foliarly applied. Furthermore, the experiment was conducted in a laboratory environment. Thus, there was no opportunity for the herbicide to move out of the system via runoff or leachate.

Gile (1983) also conducted a plant uptake investigation in a closed environment, and like Montgomery et al. (1971), Gile applied 2,4-D foliarly. However, the application rate used in Gile's (1983) investigation was only 1 kg/ha. The amount of 2,4-D recovered in wheat was 27% of the amount applied.

Thompson et al. (1984) foliarly applied 2,4-D to turfgrass at 1 kg/ha. The researchers washed the grass with methanol and toluene to remove all herbicide present on the plant surface. Analysis of the plant material revealed an uptake rate of 6% of that applied.

Washoff

Pesticides which are foliarly applied or applied to crop residues are subject to interception by the plant material. These pesticides remain on the plant surface until they are removed by intercepted rainfall or volatilize. The washoff of these pesticides will amend the pesticide load in the soil and thus will alter the amount of pesticide available for movement by runoff and sediment.

Several studies have been conducted on the movement of pesticides from plant material. The washoff of cyanazine, alachlor, atrazine, and propachlor from corn residue as a function of the cumulative amount of water applied, herbicide solubility, and application rates was investigated by Martin et al. (1978). Baker and Shiers (1985) studied the effects of herbicide type, formulation, and application method on the washoff of alachlor, cyanazine, and propachlor from corn residues. In both studies, the pesticides were applied to corn residue contained in shallow trays and subsequently subjected to simulated rainfall. Martin et al. (1978) used application rates of 0.56 kg/ha and 2.24 kg/ha, and Baker and Shiers (1985) applied herbicides at a rate of 1.0 kg/ha. Rainfall intensities applied by Martin et al. (1978) were 2 and 3 cm/hr, while that employed by Baker and Shiers (1985) was 2.5 cm/hr. Both investigations indicated that herbicide concentrations in washoff water were initially high and decreased rapidly as washoff continued. Martin et al. (1978) found that as much herbicide was lost in the first 0.5 cm of washoff as in the next 3.0 cm, with an average of 71 % of the applied pesticide load washed off after 3.5 cm. Herbicide concentrations in washoff water were found to be greater for higher application rates (Martin et al., 1978), but were not affected by herbicide formulation or application method (Baker and Shiers, 1985). Herbicide washoff as a percent of the applied amount was determined to be independent of herbicide type and application rate (Martin et al., 1978). Baker and Shiers (1985) concluded that alachlor was more resistant to washoff than either cyanazine or propachlor, however, the difference was slight.

Pesticide washoff from cotton plants was reported for methyl parathion, toxaphene, and fenvalerate by McDowell and Willis (1985) and for permethrin by Willis et al. (1986). Both experiments involved the foliar application of pesticides to mature cotton plants at rates of 1.15, 2.30,

and 0.11 kg/ha methyl parathion, toxaphene, and fenvalerate, respectively (McDowell and Willis, 1985) and 0.224 kg/ha permethrin (Willis et al., 1986). Simulated rainfall was applied to the treated cotton plants at rates varying between 0.66 cm/hr to 10.64 cm/hr (Willis et al., 1986) and at 5.28 cm/hr (McDowell and Willis, 1985). Both investigations utilized trays situated below the crop canopy for the collection of washoff water. Like the studies conducted by Martin et al. (1978) and Baker and Shiers (1985), these studies also indicated that herbicide washoff was rapid during the first few increments of rainfall and diminished quickly thereafter. In addition, Willis et al. (1986) concluded that the amount of rainfall rather than the rainfall intensity was the predominant factor in herbicide washoff.

Adsorption/Desorption

Pesticides released into the environment eventually come into contact with soil. Among the processes acting on the pesticide in the soil is the adsorption of the pesticide by the solid constituents of the soil (Freed and Haque, 1973). Adsorption is affected by soil characteristics such as organic matter content, pH, soil particle size distribution, temperature, and moisture content.

Atrazine adsorption as affected by soil characteristics has been studied by Dao and Lavy (1978) and Wauchope and Myers (1985). Dao and Lavy (1978) investigated the effects of soil temperature, moisture content and electrolyte concentration of atrazine adsorption on four soils. Decreasing soil moisture content was found to increase atrazine adsorption regardless of soil type. Increasing electrolyte concentrations increased atrazine adsorption. Finally, adsorption decreased as the soil temperature increased. Wauchope and Myers (1985) found that adsorption of atrazine by soil was positively correlated with both the organic matter and the clay content of the soil.

The effects of soil characteristics on 2,4-D adsorption have been studied by Helling (1971) and Moreale and van Bladel (1980). Both investigations indicated that 2,4-D adsorption increases with increasing organic matter content, increasing electrolyte concentrations, and decreasing pH.

The impact of soil particle size distribution on pesticide adsorption has been examined by Nkedi-Kizza (1983) and Huang et al. (1984). Nkedi-Kizza (1983) concluded that adsorption of diuron and 2,4,5-T was stronger to particles smaller than 50 μm than to particles larger than 50 μm . Similarly, Huang et al. (1984) found that adsorption of atrazine was stronger on soil particles smaller than 20 μm in diameter.

Modeling Pesticide Movement

Modeling Degradation

To characterize the degradation of pesticides in soil, one must understand the factors which influence the degradation process. Thus, the mechanics and pathways of degradation, the kinetics of degradation, the characteristics of the pesticide and the soil, the ambient conditions, and the agricultural management practices must be considered. Experiments to separate the photochemical, microbial, and chemical components of degradation are difficult and unreliable (Cheng and Lehmen, 1985). Therefore, the modeling of degradation must consider all of the breakdown processes at one time.

A first order rate equation has been used by several researchers to describe degradation (Freed and Haque, 1973; Frere, 1975; Parker and Doxtader, 1982; Cheng and Lehmen, 1985). This expression relates dA/dt , the change in pesticide loading with respect to time, to the current pesticide loading A :

$$\frac{dA}{dt} = -k(A) \quad [4]$$

where k is the decay rate constant.

Crawford and Donigian (1974) incorporated an algorithm describing the influence of soil moisture and temperature into the first order decay rate equation. This algorithm, which estimated the actual degradation rate of the pesticide was expected to be quite sensitive to the daily fluctuations of soil moisture and temperature. However, test results indicated that these small fluctuations were negligible. Crawford and Donigian (1974) concluded that the insensitivity of the expanded model to daily changes in soil temperature and moisture did not justify the additional computations required.

Parker and Duxtader (1982) compared the ability of the first order rate equation to predict 2,4-D degradation to that of the Michaelis-Menten rate equation. The researchers found that the first order rate equation did not satisfactorily predict the degradation of 2,4-D for some initial conditions. On the other hand, the Michaelis-Menten rate equation was found to be satisfactory only when relationships depicting enzymatic changes during microbial degradation were included.

Modeling Volatilization

The volatilization of pesticides includes two processes — diffusion within the soil and diffusion in the atmosphere. Models have been developed to describe both of these processes. This section briefly describes some of these models.

Pesticide diffusion in the soil has been studied by Ehlers et al. (1969a) and Scott et al. (1974). Ehlers et al. (1969a) considered the movement of lindane in both the vapor and nonvapor phases. The resulting model incorporated the principles of steady-state vapor diffusion, continuity, and sorption. Ehlers et al. (1969a) concluded that their model predicted lindane diffusion well for low pesticide concentrations in the soil, but that the model's prediction ability decreased as pesticide concentrations increased.

Scott et al. (1974) examined the adsorbed phase diffusion of herbicides in soil. The authors utilized mass balance techniques and the law of continuity as the basis of their expression. A constant volume fraction of each phase at any given concentration, non-volatility, linear adsorption,

and no pesticide precipitation was assumed. The equation developed by Scott et al. (1974) was found to overpredict actual diffusion. In addition, predicted diffusion coefficients were negative for the lowest of the soil moisture contents tested.

Volatilization of both surface applied and soil incorporated pesticides has been described by Farmer and Letley (1974) in six separate models. One model describes the volatilization of surface applied pesticides. Fick's law was used as a basis of this model which also incorporated the vapor pressure of the herbicide, the ambient temperature, and the wind speed. The remaining five models estimate volatilization of soil incorporated pesticides. These models are derived from mass flow and diffusion equations and assume that the adsorbed pesticide concentration is equal to the difference between the total and dissolved pesticide concentrations. The first of these soil incorporation models assumes that pesticides volatilize as soon as they reach the soil surface. The second model is based on the first, but is simplified by assuming a large depth of pesticide incorporation. Pesticide diffusion into soil below the depth of incorporation is described in the third model. The fourth model provides for incomplete depletion of pesticides at the soil surface. All four of these soil incorporation models assume that the air above the soil surface is a perfect sink for evaporating pesticides. The fifth model assumes that a non-moving air layer is in contact with the soil surface, allowing pesticides to accumulate in the air.

Farmer and Letley (1974) compared the volatilization losses of trifluralin, lindane, DDE, and DDT with values estimated by the surface application model and concluded that the model adequately described the observed phenomena. The results given by the diffusion based soil incorporation volatilization models were compared to the observed dielthen volatilization values. There was good agreement between the measured and calculated values, although the model overestimated pesticide flux for short times following pesticide application.

Modeling Plant Uptake

The mechanics by which pesticides are absorbed by plants is not understood well enough to support extensive modeling efforts. However, a model based on the principles of mass flow and cylindrical geometry was developed by Scott and Philips (1973) to estimate the absorption of pesticides by plant roots. The authors assumed that plant roots were cylindrical and were far enough apart that competition between roots was eliminated. In addition, roots were assumed to be perfect sinks for pesticides. This model was validated with actual uptake data for chlorpropham and atrazine by soybean roots. The adsorption model was found to underestimate pesticide uptake for the first few hours after generation. For all other times, the model was found to overestimate pesticide uptake, and the overestimation worsened as time elapsed.

Modeling Washoff

The process of pesticide washoff from plant material is not well understood. Thus, mathematical models describing pesticide washoff do not exist. Several studies have been conducted, however, which have resulted in the development of empirical equation for describing washoff.

McDowell and Willis (1985) described the fractional cumulative loss (CL) of methyl parathion, toxaphene, and fenvalerate from cotton plants as a function of applied rainfall, P, in the general form:

$$CL = a + b \times \ln(P) \quad [5]$$

where a and b are constants and should be determined experimentally for each pesticide. Depending on the pesticide, the washoff equations were able to account for 87 to 93% of the variability of the data.

Willis et al. (1986) described the washoff concentration of permethrin (C) from a cotton plant canopy in terms of washoff amount (R). The equation took the general form:

$$C = [a/(b + R)] - c \quad [6]$$

where a, b, and c are regression constants. Comparison of the washoff equations with the observed data yielded an R² value of 0.98.

Modeling Adsorption

Soil represents a heterogeneous mixture of various constituents such as organic matter, sand, clays, and inorganic salts. These components often present a large surface area with a number of sites onto which pesticides can adsorb (Haque and Freed, 1974). Several models describing the adsorption of pesticides on soil under both equilibrium and nonequilibrium conditions have been developed. Some of these models are reviewed in this section.

The most commonly used of the equilibrium adsorption models is the Freundlich equation (Freundlich, 1926). This model has been described by many researchers (Hance, 1974; Haque and Freed, 1974; Grover, 1977; Dao and Lavy, 1978; Rao and Davidson, 1979; Moreale and van Bladel, 1980; Burkhard and Guth, 1981; Nkedi-Kizza et al., 1983, Huang et al., 1984), and generally takes the form:

$$\frac{x}{m} = K(C)^{\frac{1}{n}} \quad [7]$$

where: x is the weight of the adsorbate, m is the weight of the adsorbent, C is the equilibrium concentration of the chemical, and K and n are constants. The Freundlich equation has been found to be appropriate for nonionic pesticides and other chemicals which exhibit multilayer adsorption in soils (Wauchope and Koskinen, 1983). This equation assumes that the adsorption process is fully reversible. In addition, the Freundlich equation constants, k and n, have been related to the

thermochemical properties of the adsorbing chemical (Swanson and Dutt, 1973; Wauchope and Koskinen, 1983).

Freed and Haque (1973) reviewed two other equilibrium equations which have been used to describe pesticide adsorption. The first of these is the Langmuir equation. This equation assumes monolayer adsorption and takes the form:

$$\frac{x}{m} = \frac{abC}{1 + aC} \quad [8]$$

where x , m and C are as defined previously, and a and b are constants. The Langmuir equation is not frequently used for pesticide-soil adsorption since the monolayer adsorption assumption is rarely valid. The other equilibrium equation cited by Freed and Haque (1973) is the Brunauer, Emmett, and Taylor (B.E.T.) isotherm, commonly used to describe the adsorption of gases to solids. Like the Langmuir equation, the B.E.T. isotherm is rarely used for pesticide-soil adsorption because of a monolayer adsorption assumption.

Several researchers have derived nonequilibrium models for describing pesticide-soil adsorption. Lindstrom et al. (1970) used the Langmuir equation as the basis for their nonequilibrium model. Their equation also accounts for the possibility that the adsorbate will stick to the surface as a function of the availability of adsorption sites and the simultaneous desorption rate. The model developed by Lindstrom et al. (1970) was found to give reasonable results for pesticides with low solubilities.

The nonequilibrium equation developed by Davidson and McDougal (1973) reduces to the Freundlich equation when pointwise equilibrium is assumed. This model is derived from mass balance and chemical thermodynamics theories. The authors tested their model with adsorption data of picloram, fluometuron, and prometryne and found that the nonequilibrium model did not adequately describe adsorption. Furthermore, Davidson and McDougal (1973) concluded that the adsorption isotherms of the three pesticides fit the Freundlich equation.

Rao et al. (1979) divided the adsorption sites of the soil into two groups — one group where adsorption was assumed instantaneous and the other where adsorption either followed nonlinear

reversible kinetics (Model I) or was diffusion controlled (Model II). Atrazine and 2,4-D adsorption data were used to evaluate the two models. The researchers concluded that Model II was not applicable for all soils and that Model I provided only a fair prediction of pesticide adsorption to soils.

The models developed by Lindstrom et al. (1970) and Davidson and McDougal (1973) and the Freundlich equation were compared for their ability to predict picloram adsorption by van Genuchten et al. (1974). The researchers determined that the nonequilibrium models were inadequate at describing picloram adsorption under some circumstances. The Freundlich equation was generally more applicable. However, the reversible adsorption assumption required by the Freundlich equation was disputed.

Pesticide Transport Models

A wide variety of pesticide transport models are currently available, and these models can be categorized into three general classes: a) empirical models, b) theoretical models and c) comprehensive computer simulation models. Empirical models are generally single equations which have been developed from large sources of data, and are limited by the data used for model development. Theoretical models incorporate mathematical expressions for describing pesticide transport processes, and generally obtain hydrologic information from lumped parameter watershed models. Computer simulation models for predicting pesticide transport are frequently incorporated into comprehensive watershed models. Like theoretical models, computer simulation models use mathematical relationships to describe surface pesticide transport. Computer simulation models also allow the spatial description of watersheds to further refine pesticide loss predictions.

Empirical Models

Bruce et al. (1975) described a parametric structured empirical model for estimating sediment, water, and pesticide losses from a watershed during a runoff event. Pesticide runoff was divided into three classes: dissolved, suspended in overland flow, and adsorbed to soil particles. An empirical equation was developed to calculate pesticide concentrations. Soil pesticide concentrations were assumed to remain constant throughout the runoff event at the initial level. Although predicted losses agreed reasonably well with observed losses for paraquat, trifluralin, and diphenamide, the model is severely limited in that it does not account for losses of pesticides by volatilization or degradation, and the amount of pesticide present in the soil is not reduced by losses in runoff water or eroded sediment. Also, the empirical nature of the model limits its usefulness.

The runoff and persistence of selected herbicides in four Georgia Piedmont watersheds was studied for four years by Leonard et al. (1979). The data obtained was used to develop relationships for soil-based herbicide transfer to runoff water. The average herbicide concentrations in storm runoff were correlated with the concentration of herbicide in the top cm of soil at the time the runoff event occurred. An exponential equation was found to describe the transfer of sediment-bound herbicides to runoff water.

Theoretical Models

A mathematical model described by Frere (1975) calculates the movement of a chemical as it is transported through or from an agricultural watershed. Frere (1975) separated the processes of pesticide movement into two groups — those occurring during rainfall events and those occurring between rainfall events. The model uses the first order rate equation (Equation 4) to approximate degradation. The model assumes that all pesticides intercepted by vegetation are washed off completely to the soil surface during initial rainfall. The concentration of pesticides in runoff water is

estimated with the aid of the degradation relationship. The pesticides lost by sediment are estimated by multiplying the amount of pesticides present in the soil at the time in question by an adsorption coefficient.

A simple mathematical model for predicting the loss of pesticides in runoff was developed by Haith (1980) for use on ungaged watersheds. Haith's model is based on a mass balance of the top cm of the soil. The amount of pesticide present in the soil at any time was determined and was separated into adsorbed and dissolved phases according to the Freundlich equation (Equation 7). Pesticide losses in the adsorbed and dissolved phases were computed knowing the volumes of runoff and eroded sediment and the separation of pesticides between phases. The estimates of runoff and soil loss at any time increment were obtained using the SCS Curve Number (U. S. Soil Conservation Service, 1973) and the Universal Soil Loss Equation (Wischmeier and Smith, 1978), respectively. The model was verified against actual atrazine losses from two small Georgia watersheds. The model produced large errors for some single event simulations, but was reasonably accurate at predicting long term total pesticide losses. The separation of pesticide losses into dissolved and adsorbed phase components was reflected by better model predictions.

Steenhuis and Walter (1980) developed a simple mathematical model for predicting pesticide losses in runoff. They assumed that the adsorbed and dissolved phases of a pesticide are in equilibrium at all times and that the concentrations of pesticides in leachate, runoff, and soil water are equal in the mixing zone — a layer of soil near the soil surface where rain, shallow flow, and pesticides intermix. Steenhuis and Walter (1980) described pesticide loss models for two stages occurring during a rainfall event. The first stage occurs while water infiltrates without ponding or runoff. The second stage was defined as that time when ponding starts, and was further broken down into periods of surface storage and surface runoff with percolation. The model was verified with data collected by Baker et al. (1978) for alachlor and cyanazine losses from field plots. The model proved to be sensitive to changes in the estimate of the mixing zone depth, but produced trends similar to those given by the observed data.

Computer Simulation Models

PTR

The Pesticide Transport and Runoff (PTR) model for agricultural lands was described by Crawford and Donigian (1974). The PTR model estimates the loss of pesticides from agricultural lands over extended periods of time using mathematical models for surface runoff, erosion, pesticide adsorption and desorption, and pesticide volatilization and degradation. Hydrologic watershed responses are simulated by a subroutine within the PTR model. The adsorption/desorption model used in the PTR model is based on the Freundlich equation (Equation 7) and is expressed as:

$$\frac{x}{m} = K \times C^{\left(\frac{1}{n}\right)} + \frac{F}{M} \quad [9]$$

where the additional term, F/M , is defined as the pesticide adsorbed in a permanent fixed state per unit of soil. This adsorption model, like the Freundlich equation, assumes an equilibrium condition and that pH and ion competition are insignificant. Two volatilization models are described — one for volatilization of soil incorporated pesticides and the other for surface broadcast pesticides. Degradation estimates in the PTR model are based on daily degradation factors supplied by the model user. These factors are used to lower the pesticide storage values once daily. Pesticide losses in sediment and runoff water are estimated using the results from the hydrologic response subroutine and the adsorption model.

The PTR model was tested with data from two small watersheds and two runoff plots. The PTR model provided reasonable estimates of paraquat losses when it was assumed that the paraquat was 100 % adsorbed to soil particles. For conditions in which the pesticide was in both the adsorbed and dissolved phase, the model produced only fair estimates of pesticide loss. This poor performance may be caused by inadequacies of the single-value Freundlich equation used in the adsorption model.

ARM

The Agricultural Runoff Management (ARM) model (Donigian et al., 1977) simulates hydrologic reaction, erosion, nutrient losses, and pesticide movement across the soil surface and in the soil profile. Refinements to the model currently include soil moisture and temperature simulation and pesticide degradation. A first order rate equation was chosen to represent pesticide degradation as well as pesticide adsorption to soil. No allowance is made for pesticide volatilization or soil environmental conditions. The authors verified the pesticide transport model of the ARM model against observed runoff of paraquat and atrazine from watersheds in Georgia and Michigan. Both one month long and storm event simulations were tested. Monthly pesticide yield estimates were acceptable for paraquat, but were only fair for atrazine. Pesticide loss estimates for single storm events were acceptable for both atrazine and paraquat. These results indicate that dissolved pesticide movement is not simulated well by the ARM model, and that the effects of the environmental conditions of the top 1 cm of soil on pesticide behavior warrants further study.

CPM

The Cornell Pesticide Model (CPM) is an event based model which approximates pesticide losses in runoff and percolating waters (Anonymous, 1979). The model assumes that the soil can be divided into four layers or zones. Zone 1 is the top 5 cm of the soil. Zone 2 extends from 5 cm depth to the bottom of the current root zone. Zone 3 reaches from the bottom of the current root zone to the maximum depth of rooting. Zone 4 extends from the maximum depth of rooting to the impermeable layer. The hydrologic sub-model in CPM defines the soil moisture for the three upper soil zones assuming that no water moves downward when the soil is below field capacity. Runoff is computed using the SCS Curve Number and sediment losses with the USLE. Pesticide losses caused by degradation and volatilization are computed using a the first order rate equation for degradation (Equation 4). The simulation of pesticide losses during a storm and the remaining

concentration of pesticide in the top 0.9 cm of soil, the mixing zone, is the same as the one described by Steenhuis and Walter (1980).

CREAMS

The pesticide submodel of the Chemical, Runoff, and Erosion from Agricultural Management (CREAMS) model (Leonard and Wauchope, 1980) is based on simplified concepts of pesticide transport processes and was designed to be responsive to various agricultural management practices. The submodel is able to predict the movement of both foliar and soil applied pesticides. The degradation of pesticides on leaf surfaces and in the soil is described by the first order rate equation (Equation 4). An arbitrary percentage of the pesticides on the plant surface was assumed to be washed off if the precipitation exceeds a preset threshold value. The partition of pesticides between the dissolved and adsorbed phases is determined by the Langmuir equation. The CREAMS pesticide submodel (Leonard and Wauchope, 1980) was verified against data from several experiments conducted with different pesticides under widely varying conditions. The authors found that, in general, the submodel predictions were reasonably close to those observed. In addition, the difference in pesticide behavior resulting from variations in pesticide solubility and application mode were adequately described. CREAMS uses the SCS Curve Number technique to predict runoff losses. Although this process is familiar to most modelers, it is a lumped parameter model and therefore is incapable of reflecting spatial variation of the simulation area. Since erosion and pesticide transport depend on runoff predictions, error resulting from use of the SCS Curve Number technique is reflected in soil and pesticide loss predictions.

HSPF

The Hydrologic Simulation Program — Fortran (HSPF) was developed by Johanson et al. (1984) to simulate the hydrologic and associated water quality processes which occur on pervious

and impervious land surfaces. Johanson et al. (1984) incorporated the pesticide transport algorithms developed for ARM (Crawford and Donigian, 1974) into HSPF. Although the simulation of hydrologic response is different in the two models, the similarity in pesticide transport components would lead to similar pesticide loss predictions. Weaknesses associated with the ARM also affect the HSPF model.

PRZM

PRZM, the Pesticide Root Zone Model (Carsel et al., 1984) was developed as a planning tool to assess potential contamination of groundwater by pesticides. PRZM simulates the vertical movement of pesticides in the unsaturated soil, within and below the plant root zone, and extending to the water table. The model consists of components which simulate runoff, erosion, plant uptake, leaching, degradation, foliar washoff and volatilization.

Runoff water losses are estimated using the SCS curve number technique and erosion is estimated using the USLE and an enrichment ratio. Pesticide degradation in the root zone is modeled with a first order rate equation (Equation 4). The degradation of foliarly applied pesticides is also estimated using a first order rate equation, however, the rate constant is modified to reflect the effects of pesticide volatilization. The washoff of foliarly applied pesticides is described using a linear relationship. Pesticide adsorption and desorption to and from soil particles is described with the Freundlich equation (Equation 7) assuming a value of 1.0 for n .

PRZM has been tested against data collected in New York, Wisconsin, Florida and Georgia. These tests indicate that PRZM can be used successfully to assess pesticide threats to groundwater. Although PRZM has been shown to be a tool for predicting subsurface movement of pesticides, it does not describe surface pesticide transport.

GLEAMS

Leonard et al. (1986) developed the Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) using the CREAMS model (Knisel, 1980) as a basis. The pesticide transport modeling components, such as degradation, adsorption/desorption, washoff, and transport in the dissolved and adsorbed phase described by Leonard and Wauchope (1980) for the CREAMS model are applied in GLEAMS. In addition, the effects of multiple and varying soil layers plus a vertical flux component are added in GLEAMS. Although these new modeling components have been added, they aid only in describing the downward movement of pesticides. Thus, surface transport estimates made by CREAMS and GLEAMS are essentially equivalent.

Summary

The models which have been previously described are adequate for describing pesticide movement under specific circumstances. However, these models either do not address all of the key processes which constitute pesticide transport or they rely on inadequate hydrologic models, such as the SCS Curve Number technique, to estimate runoff and erosion losses. In addition, none of the existing pesticide transport models are capable of predicting the movement of adsorbed pesticides as a function of the particle size distribution of eroded sediment. Finally, input parameters which are poorly defined or hard to obtain are used extensively by many of the existing pesticide transport models.

A need for a new pesticide transport model is therefore established. This new model should provide for the description of important pesticide movement processes using sound relationships. The model should have the capability to interface with a comprehensive distributed parameter watershed model to insure the reliability of hydrologic data used to estimate pesticide transport.

The model also should rely only on input parameters which can be easily obtained from available sources. The development and verification of such a model is described in the following chapters.

MODEL DEVELOPMENT

The Pesticide Losses In Erosion and Runoff Simulator (PLIERS), a field scale model for predicting the surface losses of pesticides, is described in this chapter. PLIERS accounts for pesticide losses by degradation and volatilization, the washoff of pesticide from crop canopy and surface residue, the adsorption of pesticides to and from soil particles and the movement of pesticides in the dissolved and adsorbed phases. Hydrologic data required by PLIERS are generated by a comprehensive watershed model. PLIERS is written in FORTRAN 77, and all equations are in the finite difference form. A block diagram of the PLIERS model is given in Figure 2.

The Hydrology Component

Distributed parameter models are better suited for pesticide transport modeling than are empirical or lumped parameter models since they reflect the spatial distribution of soil type and land use and are capable of analyzing the effects of different land management systems. Therefore, a distributed parameter model was selected to provide the hydrologic data required by PLIERS.

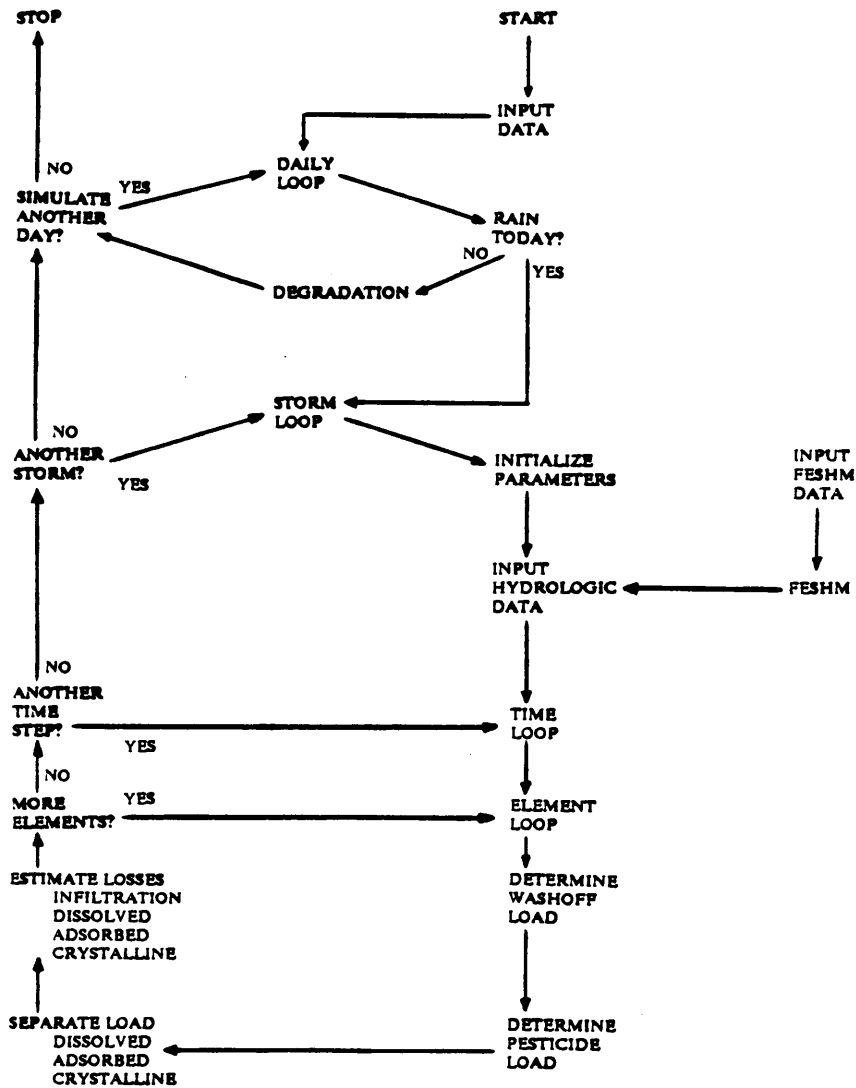


Figure 2. PLIERS block diagram.

FESHM (the Finite Element Storm Hydrograph Model) was adapted to provide the hydrologic data required by PLIERS. FESHM was developed at Virginia Tech and the runoff component has been tested throughout Virginia and also in Georgia, Illinois, Indiana, Mississippi, Ohio, and West Virginia (Ross et al., 1982). Since FESHM has been shown to be applicable to field conditions prevalent in Virginia, it was selected for use in this study. The distributed parameter structure of FESHM provides the flexibility required to simulate various management scenarios, and the required input parameters can be obtained from available watershed and climatic data. In addition, the extended sediment detachment and transport algorithm allows a better description of the movement of adsorbed pesticides.

The Degradation and Volatilization Component

Degradation and volatilization are lumped into one modeling component to simplify the modeling process and to limit the number of experimentally derived input parameters. In most circumstances, degradation rates are determined under conditions which allow volatilization losses. Volatilization losses are therefore frequently reflected in published pesticide degradation rates. Thus, these two components are easily combined. Researchers who have combined the degradation and volatilization components for modeling purposes include Leonard and Wauchope (1980), Carsel et al. (1984) and Leonard et al. (1986).

The first order rate equation (Equation 4) is used in PLIERS to estimate pesticide losses by degradation and volatilization. This equation is widely accepted and requires input parameters which are readily available in literature. Equation 4 can be rearranged and integrated to yield:

$$\ln (PT_{elem_i}) = -BC \times t_i + c \quad [10]$$

where PT_{elem_i} is the pesticide load on element i , t_i is time and c is the constant of integration. The pesticide half-life, the time required for one half of the initial pesticide mass to degrade, can be used to formulate boundary conditions to simplify Equation 10. These conditions take the form:

$$PT_{elem_i} = PT_{elem_0} \quad \text{at } t_i = 0$$

and

[11]

$$PT_{elem_i} = \frac{PT_{elem_0}}{2} \quad \text{at } t_i = t_{1/2}$$

where $t_{1/2}$ is the pesticide half life and PT_{elem_0} is the initial elemental pesticide loading. Incorporating these conditions into Equation 10 yields:

$$PT_{elem_i} = PT_{elem_0} \times \exp(-BC \times t_i) \quad [12]$$

where BC can be described as:

$$BC = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{t_{1/2}} \quad [13]$$

PLIERS estimates degradation and volatilization losses on a daily basis and assumes that degradation and volatilization are independent of soil pH, soil moisture content, tillage system, ambient conditions and the extent of pesticide adsorption. This assumption is quite significant since error in the degradation and volatilization rate would cause model over- or underestimation of the mass of pesticide in the system and subsequent errors in pesticide loss predictions. Several researchers have demonstrated the effects of ambient conditions such as temperature, moisture and pH on degradation (Kells et al., 1980; Moreale and van Bladel, 1980; Ou et al., 1982; and Parker and Duxtader, 1983). However, insufficient data exists for the development and verification of models which would incorporate these factors into the degradation and volatilization model. Pesticides on crop canopy and surface residue are subjected to higher temperatures and wind speeds than pesticides in the soil. However, these effects tend to be counterbalanced by the presence of

pesticide degrading micro-organisms in the soil. Therefore, the rate of pesticide degradation is assumed to be equal for pesticides in the soil and on crop canopy and surface residue. Pesticide metabolites, the compounds formed during degradation, are not considered by PLIERS.

The Washoff Component

A first order rate equation was developed to describe the washoff of pesticides from crop canopy and surface residue. The first order rate equation is used due to its ability to adequately predict observed washoff data reported by Martin et al. (1978), Baker and Shiers (1985), McDowell and Willis (1985) and Willis et al. (1986). The change in pesticide content in washoff water, PT_{wash_i} , with respect to the cumulative volume of intercepted rainfall, CIP, is described as:

$$\frac{\Delta PT_{wash_i}}{\Delta CIP} = -k \times PT_{wash_i} \quad [14]$$

where k is the washoff rate constant. Assuming that PT_{wash_i} is equal to PT_{wash_0} , the initial pesticide loading in washoff water, when CIP is equal to zero, and integrating yields:

$$\ln \left(\frac{PT_{wash_i}}{PT_{wash_0}} \right) = -k \times (CIP) \quad [15]$$

The boundary conditions required to solve for k in Equation 15 are obtained from Martin et al. (1978) who stated that as much pesticide washes off in the first 0.5 cm of intercepted rainfall as in the next 3.0 cm of intercepted rainfall. This gives the following boundary conditions:

$$PT_{wash_i} = PT_{wash_0} - x \quad \text{at } CIP = 0.5$$

$$\text{and} \quad [16]$$

$$PT_{wash_1} = PT_{wash_0} - 2x \quad \text{at CIP} = 3.5$$

where x is the mass of pesticide washed from crop canopy or surface residue. Incorporating these conditions into Equation 15 and solving for k results in a k value of 1.37. Rearranging yields:

$$PT_{wash_1} = PT_{wash_0} \times \exp(-1.37 \times CIP) \quad [17]$$

To simplify computations, the pesticide loading terms in Equation 17 were converted to pesticide concentrations by incorporating the rate of rainfall interception. This resulted in an equation relating pesticide concentrations in washoff water as a function of cumulative intercepted rainfall:

$$C_{wash_1} = C_{wash_0} \times \exp(-1.37 \times CIP) \quad [18]$$

where C_{wash_1} is the current pesticide concentration (g/L) and C_{wash_0} is the initial pesticide concentration in washoff water (g/L), respectively.

The initial pesticide concentration in washoff water is assumed to be equal to the "concentration" of the pesticide on surface residue and crop canopy. The initial pesticide load on crop residue or canopy at the start of PLIERS simulation is equal to the pesticide application rate multiplied by the fraction of soil covered by the crop residue. The initial concentration on soil cover is calculated as a function of the initial pesticide load on crop canopy and surface residue, PT_{res_0} , and the volume of soil cover, VOL_{res} :

$$C_{wash_0} = \frac{PT_{res_0}}{VOL_{res} \times A_{elem}} \quad [19]$$

where A_{elem} is the elemental area. The volume of crop canopy or surface residue, VOL_{res} , is determined from the residue level (mass/area), $RESLEV$, and the residue density (volume/mass), $RESDEN$:

$$VOL_{res} = \frac{RESDEN}{RESLEV} \quad [20]$$

PLIERS assumes that the rate of interception of both pesticides and rainfall is proportional to the percent soil cover (crop canopy or surface residue). Since, the effects of pesticide type, pesticide formulation and rainfall intensity on pesticide washoff are not generally quantified, these factors are ignored by PLIERS.

The Adsorption/Desorption Component

The adsorption of pesticides to soil particles is a reversible process. Generally, adsorption involves the formation of a monolayer of pesticides around a soil particle. This is followed by the accumulation of multilayers of pesticide (Haque and Freed, 1974). For the purposes of modeling, pesticide adsorption equilibrium is assumed to be instantaneous in well mixed soil-water slurries (Wauchope and Meyers, 1985), such as those which occur at the soil surface during a runoff event.

The Freundlich equation (Equation 7, Freundlich, 1926) is used in PLIERS to represent the separation of pesticides between the adsorbed and dissolved phase, because of its ability to adequately predict pesticide adsorption at low dissolved pesticide concentrations similar to those common in runoff water. In addition, the Freundlich equation accounts for the accumulation of pesticide multilayers during adsorption. The Freundlich equation is widely accepted for predicting pesticide adsorption and desorption, and the equation constants, K and n , are available for many pesticides in a wide variety of soil types (Rao et al., 1983). The assumptions implicit in using the Freundlich equation are:

1. Equilibrium between the dissolved and adsorbed phases is instantaneous,
2. Adsorption is single-valued reversible,
3. Adsorption and desorption are independent of soil pH and pesticide solubility, and

4. No competing ion effects occur.

Assumption 1 has been addressed by Wauchope and Meyers (1985). They concluded that in well mixed sediments, such as those occurring in runoff from agricultural lands, the adsorbed and dissolved concentrations of non-ionic pesticides reach equilibrium within minutes following a change in the sediment mixture. Assumption 2 concerns the ability of the Freundlich equation to predict desorption in addition to adsorption. This assumption states that not only is the adsorption process reversible, but that there are no hysteric differences between adsorption and desorption. This assumption is supported by findings reported by Rao and Davidson (1979), Wauchope and Meyers (1985) and Rao et al. (1984). Assumptions 3 and 4 are not substantiated by experimental findings, however, the assumptions must be made if the Freundlich equation is to be used. Crawford and Donigian (1973) predicted that the error caused by neglecting soil pH and competing ion effects is minimal. They based their prediction on the insignificant variation of pH during the growing season and the great availability of adsorption sites in sediment as compared to free pesticide molecules. Although pesticide solubility has been shown to be inversely correlated with adsorption (Karickhoff, 1981), the effects of pesticide solubility are not reflected in the adsorption/desorption algorithm in PLIERS. This assumption could lead to inaccurate separation of pesticides between the dissolved and the adsorbed phases, particularly for pesticides which are highly soluble.

The Freundlich exponent, n , is an indicator of the chemical nature of adsorption. The magnitude of n approaches unity for dilute solutions of non-ionic pesticides (Freed and Haque, 1973). The value of n has been found to be resistant to changes in soil type for dilute pesticide solutions (Moreale and van Bladel, 1980). Thus, it is assumed that n is constant for each pesticide. The Freundlich equilibrium constant, K , is related to the free energies of activation for adsorption and desorption (Davidson and McDougal, 1973; Wauchope and Koskinnen, 1983). In addition, the equilibrium constant is correlated with the organic matter content of the soil. This correlation has been demonstrated by several researchers (Sherburne and Freed, 1954; Haque and Sexton, 1968; Grover, 1977; Moreale and van Bladel, 1980; Nkedi-Kizza et al., 1983) and has led to the devel-

opment of the following equation where K is computed as a function of the equilibrium constant for adsorption to pure organic matter, K_{oc} , and the fractional organic matter content of the soil, F_{om} :

$$K = K_{oc} \times F_{om} \quad [21]$$

The K_{oc} value has been found to vary with soil particle size; being larger for soil fines than for larger particle size classes (Huang et al., 1984; Nkedi-Kizza et al., 1983). This correlation permits the description of pesticide adsorption onto separate particle size classes as a function of the mean diameter (MD) of that size class. Adsorption data reported by Grover (1977), Rao and Davidson (1979), Moreale and van Bladel (1980) and Wauchope and Meyers (1985) for atrazine and 2,4-D on various soil types were used to develop regression equations for predicting K_{oc} as a function of MD. The reported data for atrazine and 2,4-D are given in Tables 1 and 2, respectively. The soil mean diameter was calculated from the sand, silt and clay fractions as:

$$MD = \frac{(0.002 - 0.000)}{2}FCL + \frac{(0.050 - 0.002)}{2}FST + \frac{(2.000 - 0.050)}{2}FSD \quad [22]$$

where FCL, FST and FSD are the fraction of clay, silt and sand in the soil, respectively, with corresponding maximum diameters of 0.002, 0.050 and 2.000 mm. Simplification of this relationship yields:

$$MD = 0.001 \times FCL + 0.024 \times FST + 0.975 \times FSD \quad [23]$$

Plots of K_{oc} versus MD for atrazine and 2,4-D as computed from the data are given in Figures 3 and 4, respectively. The regression equations developed from this adsorption data take the general form:

$$K_{oc} = a_0 + a_1 \times MD + a_2 \times MD^{-0.5} \quad [24]$$

The coefficients of regression; a_0 , a_1 and a_2 ; and the R^2 values resulting from the regression analysis are given in Table 3.

Table 1. Data used for regression analysis for Equation 24 — atrazine.

Percent clay	Percent silt	Percent sand	K_{oc}	Reference
72.1	27.4	0.5	418	1
77.2	21.5	1.3	538	1
59.7	37.6	2.7	262	1
30.9	48.1	21.0	418	1
49.6	45.5	5.4	536	1
51.8	47.8	0.4	827	1
30.8	67.3	1.9	464	1
57.2	42.6	0.2	317	1
9.9	88.6	1.5	235	1
38.3	45.3	18.4	156	2
14.7	19.5	65.8	99	2
3.2	3.0	93.8	111	2
22.6	19.6	57.8	51	3
12.2	49.4	38.4	55	3
2.8	10.2	87.0	39	3

1. Wauchope and Myers, 1985
2. Rao and Davidson, 1979
3. Brukhard and Guth, 1981

Table 2. Data used for regression analysis for Equation 24 — 2,4-D.

Percent clay	Percent silt	Percent sand	K_{oc}	Ref.
38.3	45.3	18.4	119	1
14.7	19.5	65.8	72	1
20.3	33.2	47.5	12	2
19.2	27.5	53.3	7	2
18.5	12.3	69.3	8	2
8.0	10.4	81.6	5	2
9.8	18.9	71.2	34	3
15.1	69.9	15.0	39	3
12.2	55.2	32.6	38	3
6.3	59.8	23.8	34	3
33.8	59.7	6.5	357	3
27.4	61.7	10.9	316	3
22.2	69.7	8.1	174	3
8.5	73.0	18.5	114	3
0.5	68.5	31.0	190	3
6.9	17.1	76.0	34	3
7.8	72.9	19.3	31	3

1. Rao and Davidson, 1979
2. Grover, 1977
3. Moreale and van Bladel, 1980

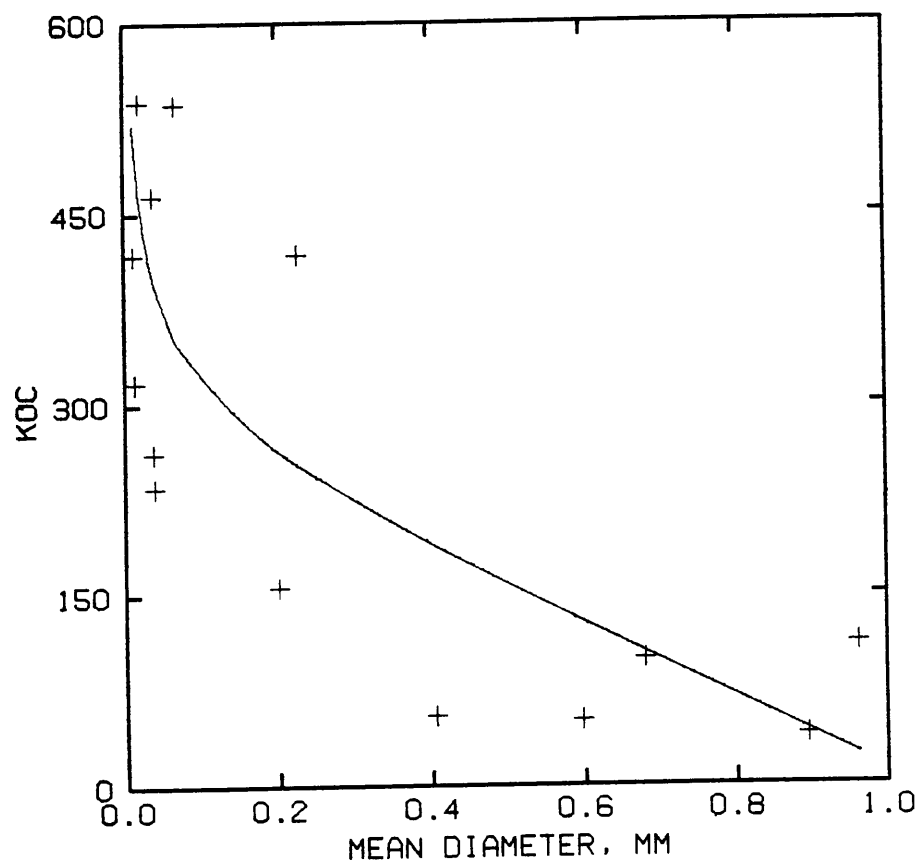


Figure 3. Plot of atrazine adsorption data for regression analysis.

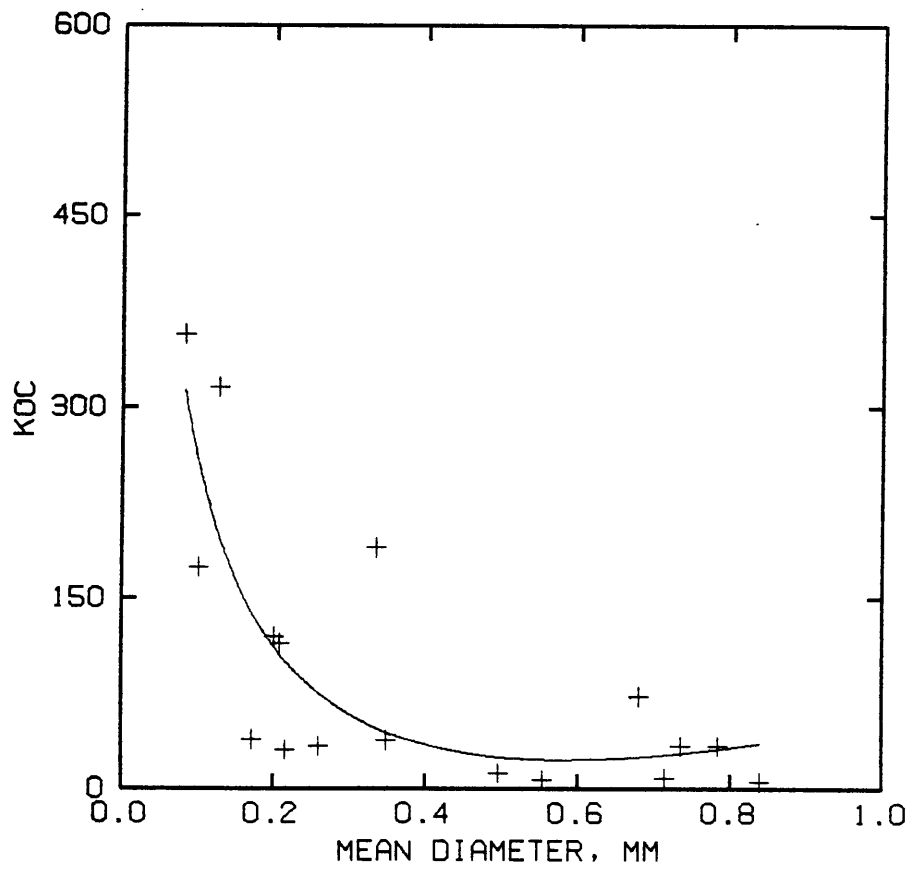


Figure 4. Plot of 2,4-D adsorption data for regression analysis.

Table 3. Regression coefficients for Equation 24.

Pesticide	N	a_0	a_1	a_2	R^2
Atrazine	15	245.87	-264.40	31.58	0.56
2,4-D	17	-333.96	205.00	181.08	0.66

Nonadsorbed pesticides are assumed dissolved until the pesticide concentration in the mixing zone water reaches the pesticide solubility limit. Nonadsorbed pesticides which are not dissolved after the solubility limit is reached are assumed to move with sediment in a crystalline (neither dissolved nor adsorbed) phase. The crystalline pesticide concentration (C_{crys}) is estimated as the mass of crystalline pesticide divided by the mass of soil in the mixing zone.

Pesticide Routing

A mass balance technique, based on the continuity equation, was used in PLIERS to route pesticides. A mass balance of water, sediment and pesticides was performed on each simulation element during each time step. The mass balance technique is used because it reflects the continuity of the water, sediment and pesticides within the elements, and because it is well adapted to the finite difference approximation techniques used in PLIERS. A schematic showing the mass balance inputs and outputs of pesticides for an element during each time step is shown in Figure 5. The elemental pesticide inputs include the pesticide load washed off of crop canopy and surface residue ($PT_{wash_i,t}$), as computed by Equation 19, and pesticides which enter the element from upslope sources in either the dissolved, adsorbed, or crystalline form ($PT_{dis_{i-1,t-1}}$, $PT_{ads_{i-1,t-1}}$, and $PT_{crys_{i-1,t-1}}$, respectively). The pesticide loads from these two sources are then combined with the pesticide load on the element remaining from the previous time step, $PT_{elem_{t-1}}$:

$$PT_{elem_t} = PT_{elem_{t-1}} + PT_{wash_i,t} + PT_{dis_{i-1,t-1}} + PT_{ads_{i-1,t-1}} + PT_{crys_{i-1,t-1}} \quad [25]$$

The elemental pesticide load is assumed to be evenly distributed throughout the "mixing zone", the immediate soil surface which is able to supply pesticides to runoff water and sediment. The mixing zone used in PLIERS was defined as the top 1 cm of the soil profile as suggested by other investigators (Knisel, 1980; Donigian et al., 1977; and Johanson et al., 1984). However, not

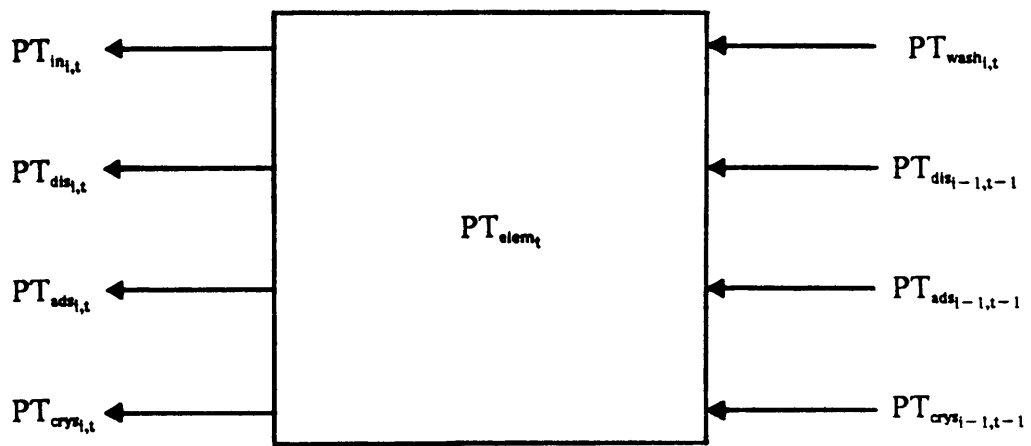


Figure 5. Element mass balance diagram.

all of the elemental pesticide load is available to runoff and sediment. Within the mixing zone, a portion of the soil is effective in supplying pesticides to runoff and sediment. This portion of the soil in the mixing zone is that which is most affected by surface flow and raindrop impact and is most thoroughly mixed with runoff water. Leonard and Wauchope (1980) described an extraction ratio parameter which represents the effective soil to water ratio at the soil surface. This extraction ratio parameter is defined as the ratio of the mass of the portion of soil which is thoroughly mixed with runoff water to the total volume of water and soil in the mixing zone plus the volume of water above the mixing zone. The value of the extraction ratio parameter cannot be measured directly, and is thought to be dependent on runoff characteristics. However, Leonard and Wauchope (1980) have found that values of the extraction ratio parameter vary from 0.05 to 0.20. The mass of pesticides available to runoff water and sediment, PT_{avail} , is determined as a function of the elemental pesticide loading and the extraction ratio parameter, ERP:

$$PT_{avail} = PT_{elem_t} \times ERP \quad [26]$$

Once the mass of available pesticide has been determined, the Freundlich equation (Equation 7) is used to separate the available load between the dissolved, adsorbed and crystalline phases.

Pesticides are transported out of the element in the dissolved phase by infiltrating water and runoff and in the adsorbed phase on sediment (Figure 5). Pesticide losses due to infiltration, PT_{in} , are estimated as a function of the dissolved pesticide concentration, C_{dis} , and the volume of infiltrating water, VOL_{in} :

$$PT_{in} = C_{dis} \times VOL_{in} \quad [27]$$

Dissolved pesticides lost in runoff, PT_{dis} , are similarly predicted as:

$$PT_{dis} = C_{dis} \times VOL_{run} \quad [28]$$

where VOL_{run} is the volume of runoff water. Adsorbed pesticide losses are determined for each particle size class of sediment using the following expression:

$$PT_{ads_k} = C_{ads_k} \times MASS_{sed_k} \quad [29]$$

where PT_{ads_k} is the mass of pesticide carried off the element by particles of size class k , C_{ads_k} is the concentration of pesticides adsorbed to that size class, and $MASS_{sed_k}$ is the mass of particle size class k transported from the element. Crystalline phase pesticide loss, PT_{crys} , is estimated as:

$$PT_{crys} = C_{crys} \times \sum_{k=1}^{k_{max}} MASS_{sed_k} \quad [30]$$

where C_{crys} is the crystalline pesticide concentration and $MASS_{sed_k}$ is as previously defined. The pesticide load remaining on the element at the end of the time step, PT_{rem} , is simply the elemental pesticide load minus the infiltrated pesticide losses and pesticide losses in the dissolved, adsorbed and crystalline phase:

$$PT_{rem} = PT_{elem_t} - PT_{in} - PT_{dis} - \sum_{k=1}^{k_{max}} PT_{ads_k} - PT_{crys} \quad [31]$$

where PT_{elem_t} , PT_{in} , PT_{dis} , PT_{ads_k} , and PT_{crys} are as described earlier.

FIELD INVESTIGATIONS OF PESTICIDE MOVEMENT

There are many factors which affect the transport of pesticides by runoff, as well as their movement through the soil profile. These factors include land use, soil type, time of application, application method, rainfall characteristics, and pesticide characteristics such as persistence, solubility, volatility, and adsorptivity. Another factor which may affect pesticide movement, is the amount of crop residue left on or incorporated into the soil. While crop residue improves infiltration and reduces erosion, pesticides may be intercepted by residue and thus be more susceptible to washoff. Presently, the effects of conservation tillage systems on losses of pesticides from agricultural lands are poorly defined. The importance of obtaining information regarding pesticide losses from cropland is evident from the large increase in pesticide usage, and from the emphasis on conservation tillage in land and water management. The objective of this portion of the study was, therefore, to investigate the effects of conservation practices, such as reduced tillage and crop residue levels, on losses of pesticides from agricultural lands. Since such field data is generally scarce, the data collected during this investigation was used to verify PLIERS.

Description of Field Plots

Field experiments were conducted in the spring of 1986 to assess the effects of two best management practices, no-till and crop residue management, on the losses of runoff, sediment and pesticides (atrazine and 2,4-D) from agricultural lands. Because of the unreliability of natural precipitation for such short time field research, a rainfall simulator was used to produce runoff from these plots.

Design and Location

Twelve experimental field plots located at the Virginia Polytechnic Institute and State University Price's Fork Research Farm, 10 km west of Blacksburg, Virginia, were used for the study. The plots were located on Groseclose silt loam soil (clayey, mixed, mesic Typic Hapludult). Groseclose soils occur on nearly level to very steep convex ridges and sideslopes in the Appalachian Valley, and are formed from materials weathered from interbedded limestone, shale, and sandstone. The soil is deep and well drained with slowly permeable subsoil. The Ap horizon is typically 0.25 m thick and has a loam texture with moderate fine granular structure. General characteristics of Groseclose silt loam soil are presented in Table 4.

Plots were prepared by installing metal borders to a depth of 15 cm along the boundaries, and a concrete gutter with a pipe outlet at the base of each plot. All border and gutter joints were sealed with caulking compounds to prevent leakage into or out of the plots. The gutters were installed so that their upper edge was level with the soil surface. The interface between the soil surface and the gutter was sealed with a cement grout and caulking to minimize leakage. The gutter was designed to collect and transport surface runoff without sedimentation to a 15 cm H-flume equipped with a FW-1 stage recorder for flow measurements. Each plot had a surface area of 0.01 ha (5.5 m by 18.3 m).

Table 4. Plot characteristics and treatments.

	QF1	QF2	QF3	QF4	QF5	QF6
Tillage treatment	NT ¹	CT ²	NT	CT	NT	CT
Residue level, kg/ha	0	1500	1500	0	750	750
Slope, %	9.2	9.0	9.9	14.1	15.1	14.0
	QFA	QFB	QFC	QFD	QFE	QFF
Tillage treatment	NT	CT	CT	NT	CT	NT
Residue level, kg/ha	1500	0	1500	750	750	0
Slope, %	9.7	8.9	9.1	9.4	8.6	8.3

Average slope for NT plots: 10.3 %

Average slope for CT plots: 10.6 %

Pesticide application rate: atrazine, 2.24 kg/ha
2,4-D, 0.56 kg/ha

Soil type: Groseclose silt loam
Bulk density: 1.39 g/cm³
Percent sand: 17.9
Percent silt: 58.9
Percent clay: 23.2
Percent organic matter: 3.7

Simulated rainfall intensity: 50 mm/hr
Simulated rainfall duration: Run 1 (R1), 60 min
Run 2 (R2), 30 min
Run 3 (R3), 30 min

¹ No-till

² Conventional till

Plot Preparation

The plots were divided between two tillage systems: a) no-till and b) conventional tillage. Within each tillage system, three crop residue amounts were studied: a) no residue, b) 750 kg/ha residue and c) 1500 kg/ha residue. Two replications of these six treatments required a total of twelve plots. All treatments were randomly assigned to the experimental plots.

All plots were planted in winter rye. In early summer, they were sprayed with paraquat to kill the rye cover. The rye was then cut leaving sufficient stubble to give residue amounts of 0, 750, or 1500 kg/ha. Six plots were randomly assigned to no-till and the remaining six were tilled to a depth of 20-30 cm with a tractor powered rototiller and then disked to represent conventional tillage treatments. Thus, for conventionally-tilled plots, the tillage operation incorporated the crop residue into the soil surface, whereas for no-till plots the residue was left standing on the plot surface.

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] and 2,4-D [(2,4-dichlorophenoxy) acetic acid], two commonly used herbicides in Virginia corn production, were applied at rates of 2.24 and 0.56 kg/ha (Hagood, 1986), respectively, to all treatments. The herbicides were applied using a pressure-regulated hand held sprayer about 24 hours before rainfall simulation.

Rainfall Simulator

The Department of Agricultural Engineering's rainfall simulator (Shanholtz et al., 1981; Dillaha et al., 1987) was used to apply approximately 100 mm of rainfall to each plot over a 2 day period. A 1 hour "dry" run (R1) was followed 24 hours later by a 30 minute "wet" run (R2) which was followed 30 minutes later by a 30 minute "very wet" run (R3). A rainfall intensity of 50 mm/hr was used for all simulations. A rainfall intensity of 50 mm/hr with a duration of 30 minutes has about a 2 year return period in southwest Virginia (Hershfield, 1961). This storm should create

critical conditions since pesticides had been applied during the previous 24 hours. The three run sequence of dry, wet and very wet was used because it is a common artificial rainfall sequence used for simulating different initial soil moisture conditions for erosion research.

The plots were protected from natural precipitation during the study period by covering them with plastic sheets when rain appeared imminent. The plots were left uncovered at all other times so that the soil would dry under normal conditions.

Rainfall simulator application rates and uniformity were measured for each simulation by locating 12 small raingages within each plot. The raingages were read after each simulation to determine the total amount of rain and the coefficient of uniformity for each run.

The rainfall simulator performed remarkably well for all simulations. The mean application rate during all simulations was 50.9 mm/hr and ranged from 46.8 to 54.4 mm/hr. Uniformity coefficients, which are a measure of the uniformity of rainfall application, were excellent averaging 92.3 %. Rainfall energy, however, was quite low averaging approximately 40% of the energy of natural rainfall (Neff, 1979).

Data Collection

Runoff water samples were collected during the first run (R1) from the outflow of each plot in 4 L glass bottles 3, 8, 13, 20, 30, 45 and 60 minutes after the start of runoff. Similarly, runoff water samples for storms two and three (R2 and R3) were collected 3, 10, 20, and 30 minutes after the start of each runoff event. A mark was made on the stage recorder charts whenever a water sample was collected to precisely record the time and flow rate at which each sample was taken. This procedure greatly simplified mass flow calculations and minimized timing errors. All water quality samples were refrigerated immediately after collection and stored for subsequent analysis. All samples were analyzed within 90 days of collection. Runoff rates were also checked gravimetrically by making time-weight measurements frequently during the simulations. Other data

collected from the plots included soil moisture samples, before and after each run, and soil bulk density.

A 900 mL subsample of water for pesticide analysis was decanted from each sample after sediment had settled. Sediment was separated from the remaining sample by filtering through a medium flow filter (#2 Whatman filter paper) under a vacuum. The atrazine in the water sample was extracted by shaking with 100 mL methylene chloride amended with 5 to 10 g sodium sulfate. The extraction process was repeated to improve extraction efficiency. The methylene chloride was drawn from the water subsample and prepared for gas liquid chromatography (GLC) analysis. 2,4-D was extracted by acidifying the remaining water sample and shaking with 100 mL ethyl ether. The ethyl ether was drawn from the water sample and was methylated for GLC analysis (U. S. Environmental Protection Agency, 1980a).

The atrazine was eluted from the sediment sample through a silica gel clean-up column with 250 mL methylene chloride. The collected methylene chloride was prepared for GLC analysis. Acidified acetone (250 mL) was added to the same column sample to extract 2,4-D (U. S. Environmental Protection Agency, 1980b).

All extracts were analyzed with a gas chromatograph with a Ni^{63} electron capture detector. The GLC column contained 1.5% OV-17, 1.95% QF-1, 100/120 mesh, and Chromasorb-WHP; and the operating conditions were: column temperature, 185 °C; inlet temperature, 215 °C; detector temperature, 350 °C; and N_2 carrier.

Pesticides losses from each simulated runoff event were calculated using pesticide concentrations of atrazine and 2,4-D for each sample and assuming that the average flow rate for the sample interval was equal to the average of the flow rates at the beginning and end of the interval.

Results and Discussion

Runoff and Sediment Losses

Average combined runoff and sediment losses for runs R1, R2 and R3 for each tillage system and residue level are given in Table 5. Both runoff and sediment losses decreased as crop residue levels increased, regardless of the tillage system. Runoff volumes from the conventional tillage plots were about 12 times greater than from the no-till plots. For the conventional tillage plots, increasing the residue level from 0 to 1500 kg/ha resulted in a 49 percent reduction in runoff (Table 5). The corresponding runoff reduction for the no-till plots at these residue levels was 96 percent. Comparing conventional plots with no residue to no-till with 1500 kg/ha residue, resulted in a 99 percent reduction in runoff, due to the combined effects of residue and no-till. The dramatic increase in runoff from the conventional plots reflects the lower infiltration rates due to poor structure and surface sealing.

Soil loss from the conventional tillage plots was much greater than that from no-till plots. The high soil loss from the conventional plots is the result of both higher runoff volumes and sediment concentrations. The high runoff rates increased the soil loss from these plots because of increased sediment detachment and transport capacity of the overland flow. Averaged over all residue levels, the no-till plots reduced runoff volume and soil loss by 92 and 98 percent, respectively, relative to the conventional tillage plots (Table 6).

Pesticide Concentrations in Runoff and Sediment

Concentrations of atrazine and 2,4-D in runoff for both tillage systems and all residue levels are presented in Table 7. Concentrations of atrazine ranged from 0.204 to 0.340 g/m³, while those

Table 5. Effects of residue level and tillage treatment on runoff and sediment losses.

Residue & Tillage treatment	Runoff volume (cm)	Runoff ¹ rate (cm/hr)	Time till runoff began (min)	Sediment losses (kg/ha)	Sediment concentration (g/m ³)
0 kg/ha					
NT	0.45	1.67	8	71.7	1593
CT	3.55	5.05	2	2812.3	7923
750 kg/ha					
NT	0.26	0.94	12	10.6	406
CT	3.27	3.35	5	1000.8	3061
1500 kg/ha					
NT	0.02	0.05	17	6.5	3250
CT	1.80	2.56	7	512.6	2848
Overall ²					
NT	0.24	1.67	16	29.6	1233
CT	2.87	5.05	5	1442.0	5024

¹ Maximum peak runoff rates

² Average over all residue levels and rainfall events

Table 6. Reductions in runoff and sediment losses due to no-till.

Residue level (kg/ha)	Runoff volume (%)	Peak runoff (%)	Sediment losses (%)	Sediment concentration (%)
0	87	67	97	80
750	92	72	99	87
1500	99	98	99	16
Overall ¹	92	67	98	75

¹ Averaged over all residue levels and rainfall events

Table 7. Effects of residue level and tillage system on concentrations of atrazine and 2,4-D in runoff and sediment.

Residue & tillage treatment	Water		Sediment	
	Atrazine (g/m ³)	2,4-D (g/m ³)	Atrazine (g/Mg)	2,4-D (g/Mg)
0 kg/ha				
NT	0.204	0.006	0.211	0.176
CT	0.204	0.001	0.089	0.082
750 kg/ha				
NT	0.340	0.002	0.146	0.283
CT	0.266	0.016	0.148	0.049
1500 kg/ha				
NT	0.308	0.002	0.371	0.153
CT	0.266	0.016	0.148	0.047
Overall ¹				
NT	0.284	0.003	0.243	0.204
CT	0.226	0.007	0.105	0.059
LSD ² _{0.05}	0.087	0.019	0.112	0.126

¹ Averaged over all residue levels and rainfall events

² Least Significant Difference at the 0.05 level

of 2,4-D varied from less than 0.001 to 0.019 g/m³. These concentrations are well below the LC50 (lethal chronic dose for 50% mortality) for aquatic vertebrates, such as rainbow trout (48 hours at 12.6 g/m³ atrazine and 24 hours at 250 g/m³ 2,4-D; Pimentel, 1971).

Health Guidance Levels (HGL's) or acceptable daily intake values for humans, adjusted to provide a safety factor for short term exposure, have been developed by the National Agricultural Chemicals Association (1985) for many pesticides. The HGL for 2,4-D is 1.25 g/m³, which is well above the concentrations found in runoff from the plots. However, the HGL for atrazine is 0.38 g/m³, which is close to the maximum average atrazine concentration observed.

The concentration of atrazine in runoff as a function of residue level and rainfall event for no-till and conventional tillage systems are given in Figures 6 and 7, respectively. Atrazine concentrations generally decreased with time and increased with higher residue levels. Studies conducted by Baker et al. (1978) and Baker and Johnson (1979) reported similar trends with alachlor, cyanazine, and fonofos. The direct relationship between atrazine concentration and residue level is probably the result of pesticide washoff from the residue.

Concentrations of atrazine in runoff were generally higher for no-till than for the conventional tillage plots. Although not quantified in this experiment, the soil surface of the conventionally tilled plots was rougher than the no-till plots because tillage broke up the soil surface and mixed residue with the soil, resulting in greater contact area between soil and the pesticides. The surface-applied atrazine, therefore, had better contact with soil and was better able to adsorb to soil particles; thus the losses of atrazine in surface runoff were reduced.

The concentrations of 2,4-D in runoff from the conventional tillage plots increased with residue level (Table 7). No general trend could be detected, however, for the concentrations of 2,4-D in runoff from the no-till treatments. When averaged over residue levels, the concentration of 2,4-D in runoff from the conventional plots was over twice as large as that from the no-till plots.

Atrazine and 2,4-D concentrations in sediment for each tillage system and residue levels also are given in Table 7. Concentrations of atrazine ranged from 0.08 g/Mg to 0.37 g/Mg, and 2,4-D concentrations varied from 0.05 g/Mg to 0.28 g/Mg. Although adsorbed pesticides are not

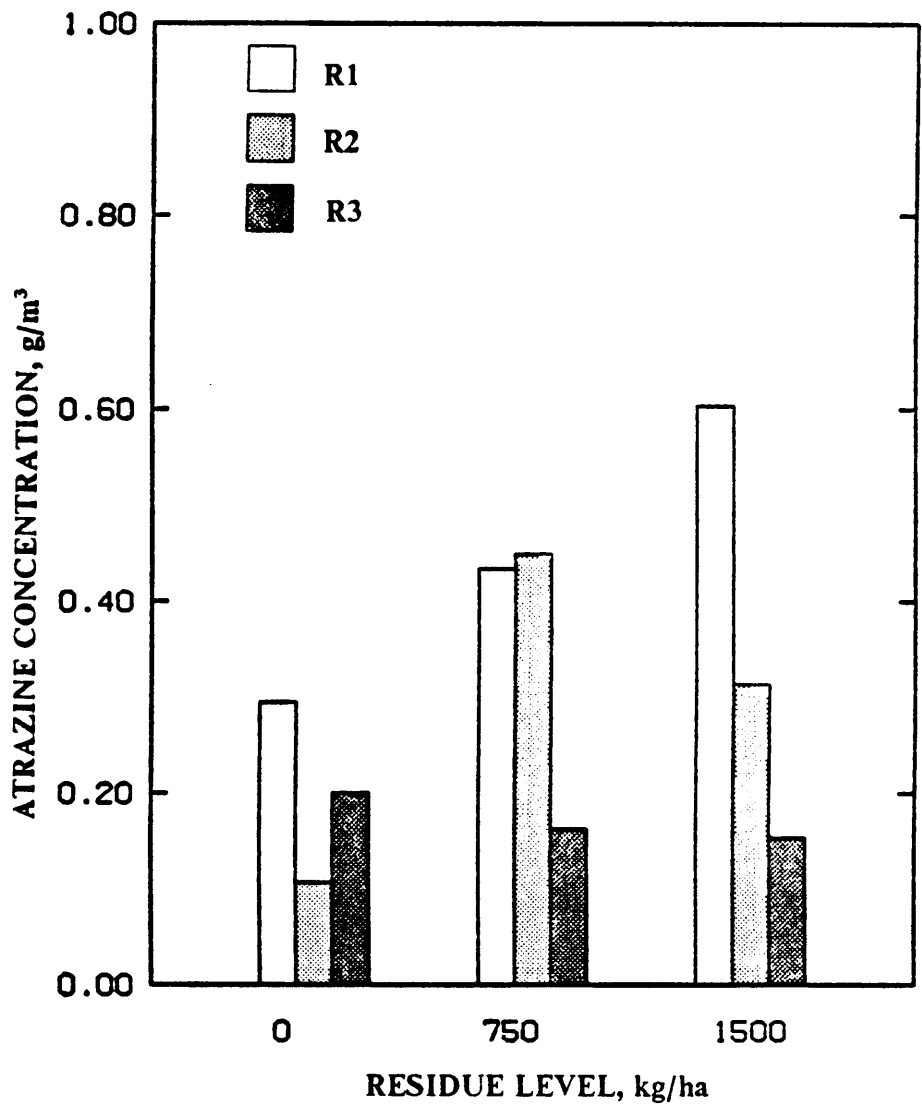


Figure 6. Atrazine concentrations in runoff water from no-till plots.

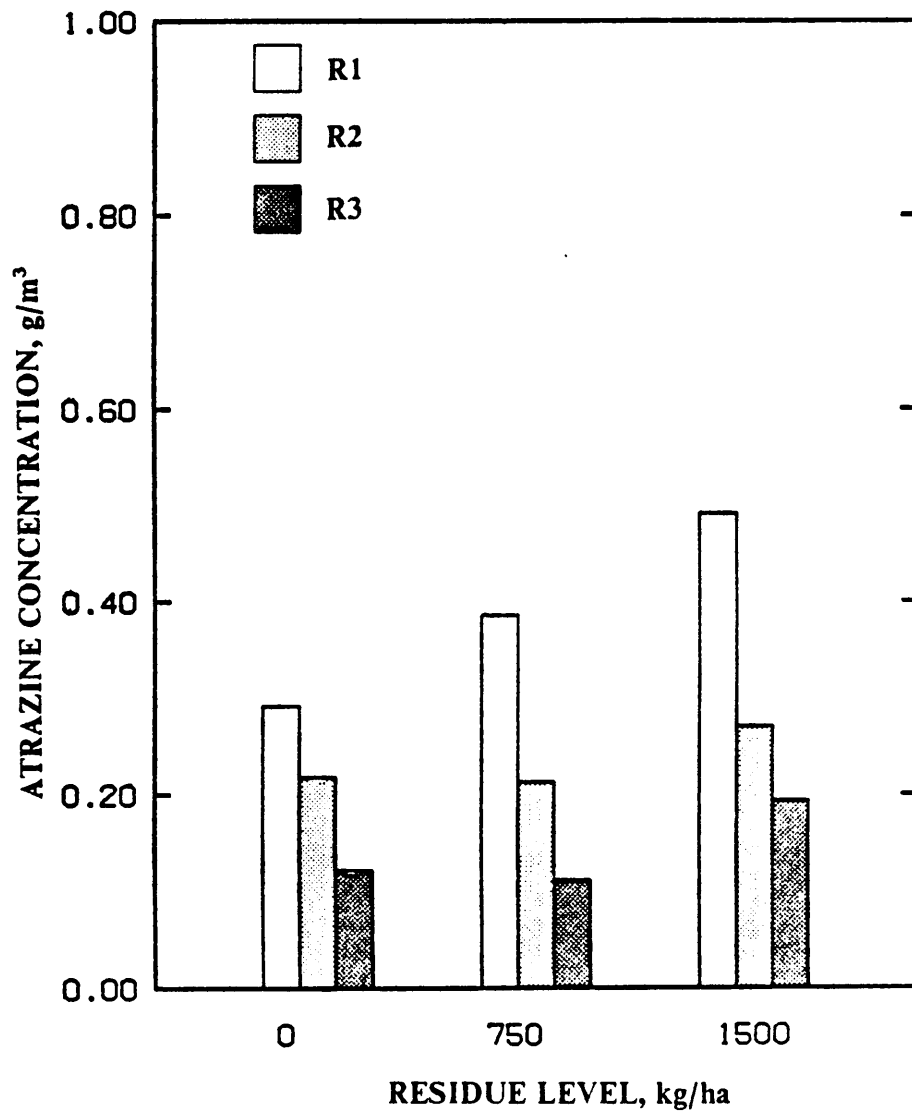


Figure 7. Atrazine concentrations in runoff water from conventional till plots.

as hazardous as soluble pesticides, the desorption process can release these chemicals into water where they may pose a health threat to humans and other organisms.

As shown in Table 7, atrazine concentrations in sediment were lowest at a residue level of 750 kg/ha, highest at 1500 kg/ha residue, and intermediate with no residue for both tillage systems. No general trends could be detected for the effect of residue level on the sediment losses of 2,4-D from the no-tillage plots; however, the 2,4-D concentration decreased with increased residue level on the conventional tillage plots. These results differ from those of Baker et al. (1982) who reported that atrazine concentrations in sediment were similar for all residue levels tested in their study. Variation in conditions under which the two studies were conducted, such as soil type, and rainfall amount and intensity, may partially explain these differences.

The concentrations of both atrazine and 2,4-D in sediment from the no-till plots were greater than those from conventional tillage treatments (Table 7, Figures 8 and 9). The increases in concentrations in no-till plots relative to the conventional tillage plots were 131 and 246 percent for atrazine and 2,4-D, respectively. Baker and Johnson (1979) reported similar results for atrazine and alachlor with the concentrations from conservation tillage plots averaging twice those from conventional tillage plots. The average 2,4-D concentrations in runoff were 1 and 12 percent of those in sediment from no-till and conventional tillage plots, respectively. The corresponding values for atrazine were 117 and 215 percent.

Pesticide Losses in Runoff and Sediment

Despite the higher concentration of atrazine and 2,4-D in the sediment from no-till plots, total pesticide losses were greater from the conventionally tilled plots. The greater losses from the conventional plots could be attributed to the increased sediment loss from these plots (Table 5). A graphical representation of the data for each tillage system and residue level is given in Figures 10 and 11. Concentrations of atrazine in sediment from the no-till plots ranged from 187 percent for 750 kg/ha residue to 251 percent for 1500 kg/ha residue — higher than those from the conven-

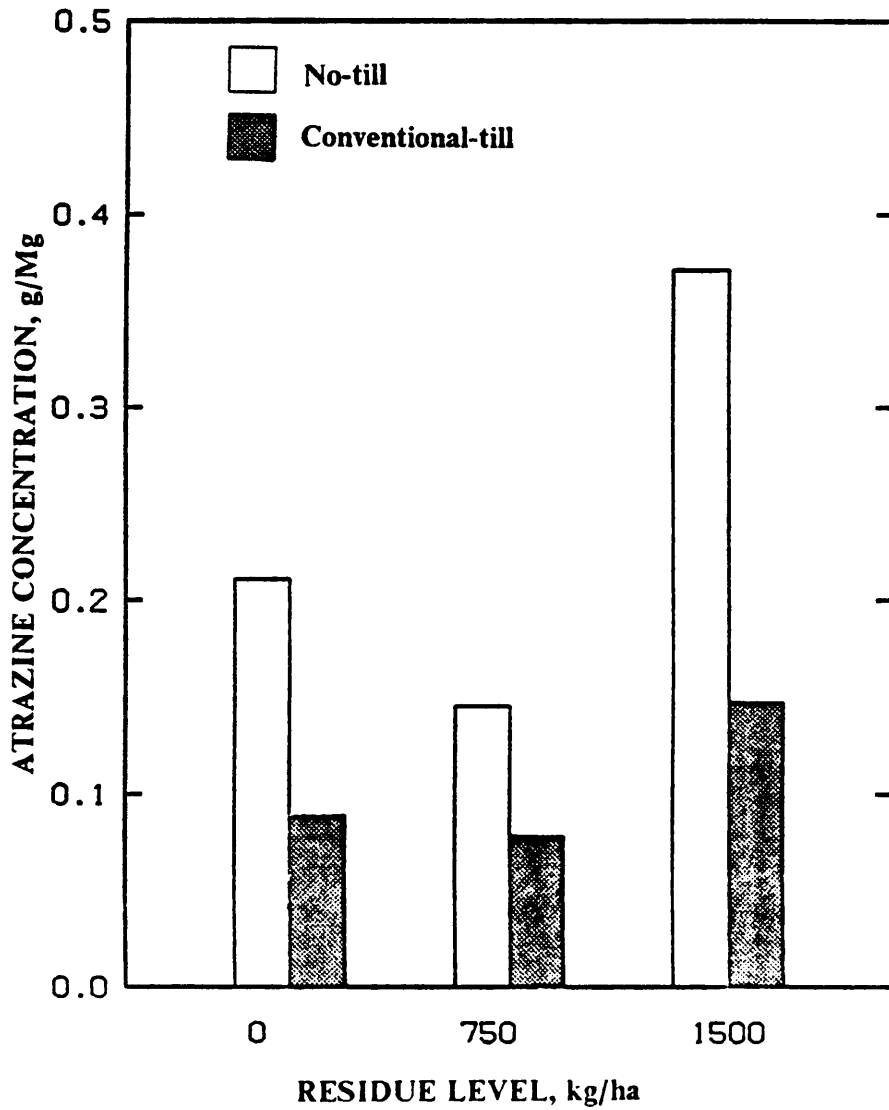


Figure 8. Concentrations of atrazine in sediment for different tillage systems and residue levels.

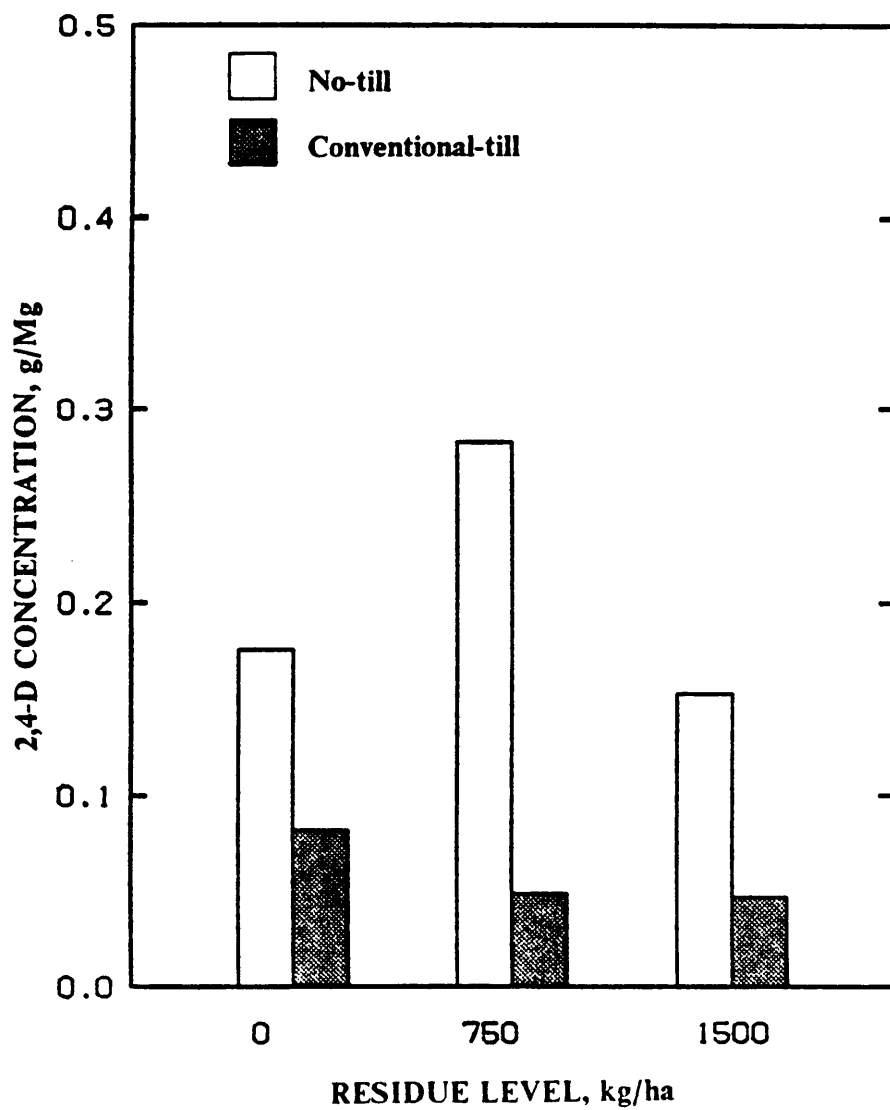


Figure 9. Concentrations of 2,4-D in sediment for different tillage systems and residue levels.

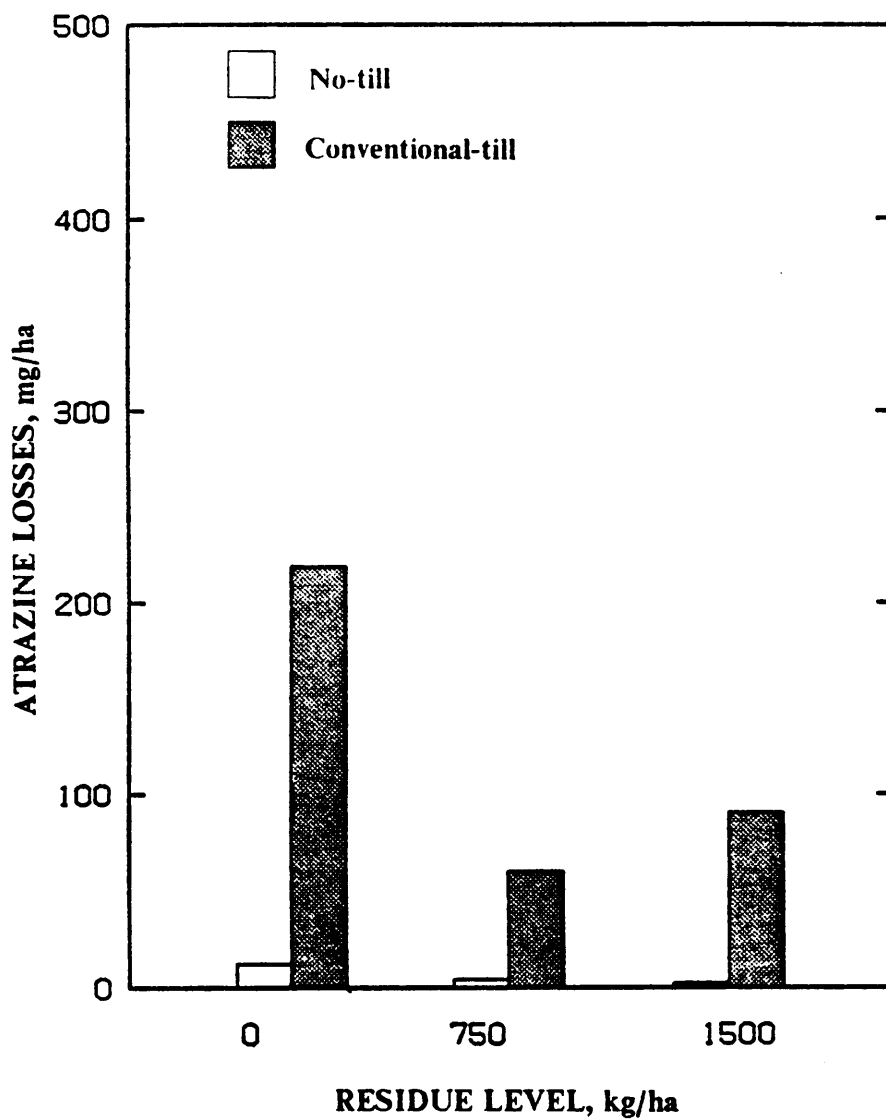


Figure 10. Sediment losses of atrazine for different tillage systems and residue levels.

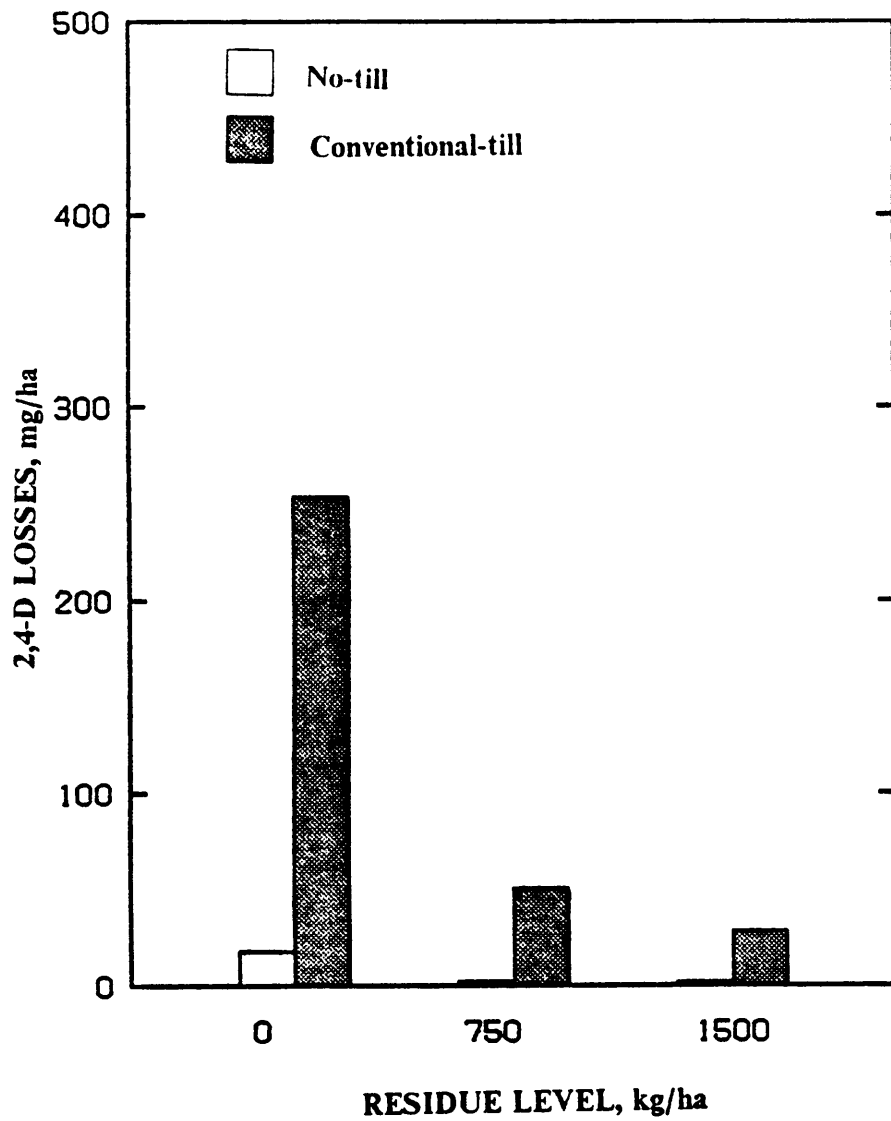


Figure 11. Sediment losses of 2,4-D for different tillage systems and residue levels.

tional plots. The corresponding values for 2,4-D ranged from 215 percent for 0 kg/ha residue to 578 percent for 750 kg/ha residue.

Atrazine and 2,4-D losses in runoff and sediment for each tillage system and residue level are presented in Table 8. Higher residue levels caused lower atrazine and 2,4-D losses in runoff and sediment for all cases except for 2,4-D in runoff water from the conventionally tilled plots. Although the concentration of 2,4-D in runoff water from conventionally tilled plots increased by 16 times (no residue compared to 1500 kg/ha residue), runoff losses were reduced by only 2 times. Apparently, the reduction in 2,4-D losses due to decreased runoff volume from the no-till plots was negated by higher pesticides concentrations in the water.

The losses of atrazine and 2,4-D in sediment were usually greatest during either the second or the third rainfall event (Figures 12 and 13). These results are comparable to those presented by Baker et al. (1978). Greater losses of herbicides were expected during the later rainfall events because higher soil moisture contents resulted in increased runoff and larger sediment losses. The fact that the differences between losses during the first and third runoff events were greater on plots with residue cover may indicate that atrazine was first washed off the residue and was then transported downslope by subsequent surface runoff.

Both atrazine and 2,4-D losses were greater in runoff than in sediment (Table 9). This result was anticipated since the volume of water lost was much greater than the volume of sediment. These results follow those reported by Baker and Johnson (1979) who concluded that from 80 to 90 percent of the average atrazine losses were soluble rather than sediment-bound. Data presented in Table 8 indicate that the fractions of atrazine lost in sediment were 0.2 percent of the total loss for both no-till and conventional tillage plots. The corresponding values for 2,4-D were 8.3 and 7.2 percent.

Also presented in Table 8 are the overall losses of atrazine and 2,4-D for each tillage system as a percentage of the amount applied. The percent losses were greater with conventional tillage for both atrazine and 2,4-D. No-till reduced total pesticide losses as a result of both decreased runoff and decreased erosion, even though the pesticide concentrations were generally higher for these treatments. For 2,4-D, the average losses were 0.02 and 0.3 percent of that applied to the

Table 8. Effects of residue and tillage system on losses of atrazine and 2,4-D losses in runoff water and sediment.

Residue & tillage treatment	Water		Sediment		Total	
	Atrazine (g/ha)	2,4-D (g/ha)	Atrazine (g/ha)	2,4-D (g/ha)	Atrazine (g/ha)	2,4-D (g/ha)
0 kg/ha						
NT	9.21	0.29	0.01	0.02	9.22	0.31
CT	73.59	0.25	0.22	0.25	73.81	0.50
750 kg/ha						
NT	8.84	0.05	0.00	0.00	8.84	0.05
CT	70.36	1.10	0.06	0.05	70.42	1.15
1500 kg/ha						
NT	0.71	0.00	0.00	0.00	0.71	0.01
CT	47.18	2.92	0.09	0.03	47.27	2.95
Overall ¹						
NT	6.25	0.11	0.01	0.01	6.26	0.12
CT	62.71	1.42	0.12	0.11	63.83	1.53
LSD ² _{0.05}	23.87	2.80	0.03	0.04	23.86	2.81
Overall as percent of applied load						
NT	0.28	0.02	NS ³	NS	0.28	0.02
CT	2.84	0.25	0.01	0.02	2.85	0.27

¹ Averaged over all residue levels and rainfall events

² Least Significant Difference at the 0.05 level

³ Not significant

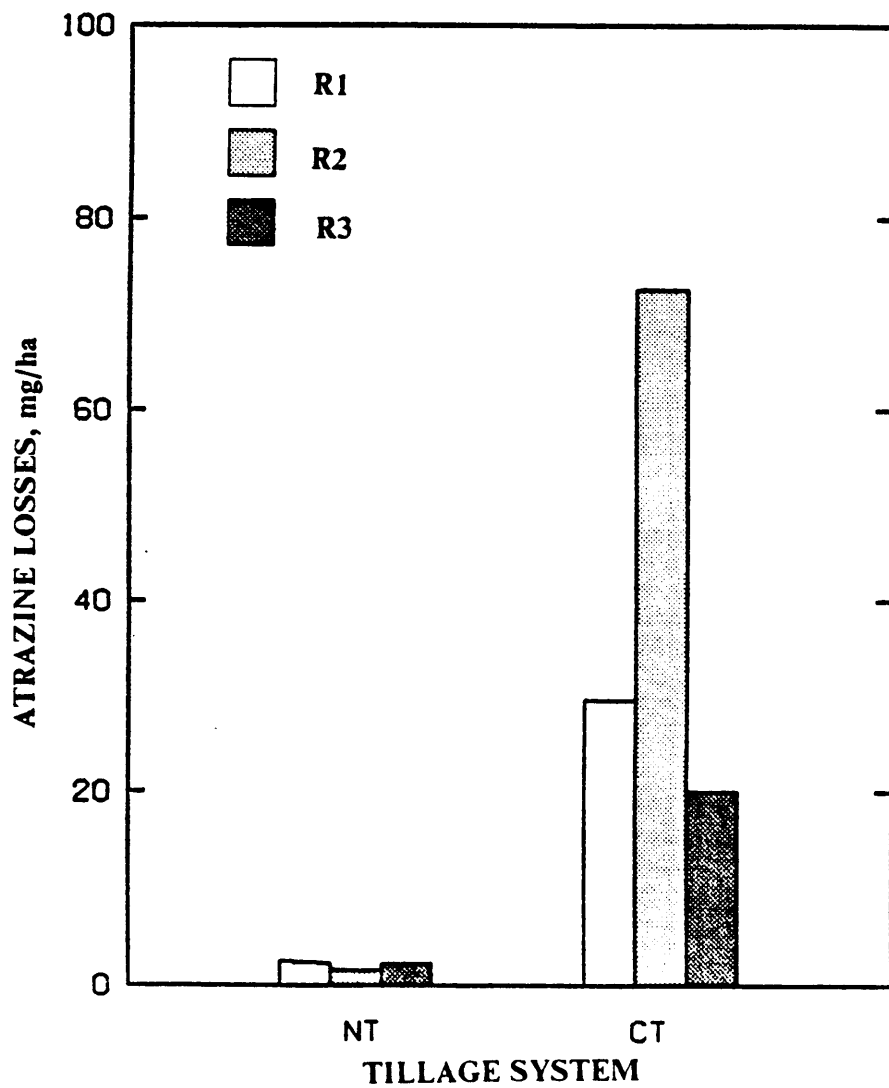


Figure 12. Sediment losses of atrazine for different tillage systems and rainfall events.

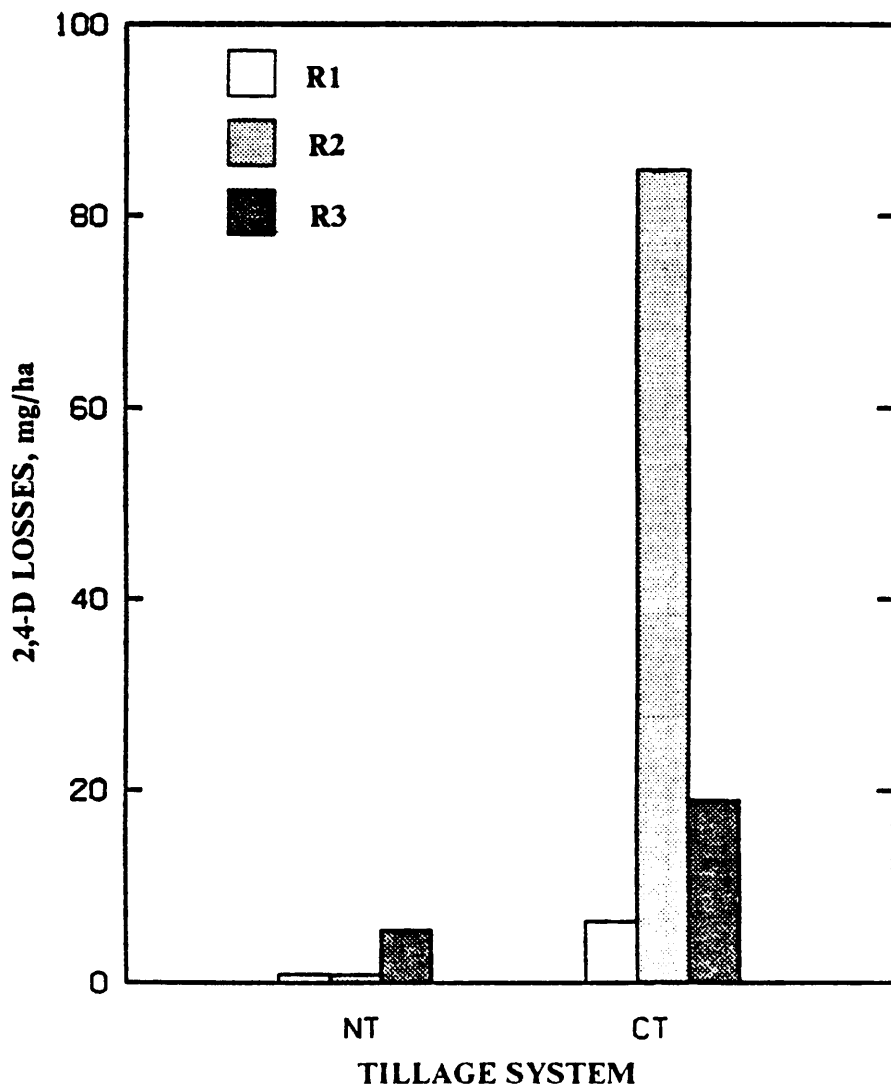


Figure 13. Sediment losses of 2,4-D for different tillage systems and rainfall events.

Table 9. Water to sediment ratios: concentrations and losses of atrazine and 2,4-D.

Residue & tillage treatment	Concentration		Loading	
	Atrazine	2,4-D	Atrazine	2,4-D
0 kg/ha				
NT	0.97	0.03	921.00	14.50
CT	2.29	0.01	334.50	1.00
750 kg/ha				
NT	2.33	0.01	0.00	0.00
CT	2.68	0.06	1172.70	22.00
1500 kg/ha				
NT	0.83	0.01	0.00	0.00
CT	1.80	0.34	524.20	97.30
Overall ¹				
NT	1.17	0.01	625.00	11.00
CT	2.15	0.12	564.20	12.90

¹ Averaged over all residue levels and rainfall events

no-till and conventional tillage plots, respectively. The corresponding values for atrazine were 0.3 and 2.9 percent. These values are similar in magnitude to those given by other researchers (Baker and Johnson, 1979 and Hall et al., 1972).

Percent reductions in pesticide losses due to no-till relative to conventional till are presented in Table 10. In all cases except one (2,4-D runoff losses for no residue), no-till resulted in significant reductions in pesticides losses. Averaged over the residue levels, no-till reduced atrazine and 2,4-D losses by 90 and 92 percent, respectively. As indicated in Table 10, there is a positive relationship between the percent reduction and residue level for total losses of both herbicides. Maximum reductions in losses of atrazine and 2,4-D (98 and 99 percent, respectively), were achieved with no-till and a crop residue level of 1500 kg/ha. These reductions are comparable to results achieved with no-till by Hall et al. (1983).

Percent losses are larger for atrazine than for 2,4-D in both the dissolved and adsorbed phase. Atrazine is much less soluble in water than 2,4-D, leading one to anticipate larger losses of 2,4-D in runoff. 2,4-D loss may have been reduced as a result of volatilization. A good indicator of volatilization is vapor pressure. Pesticides having large vapor pressures are more susceptible to volatilization than those with lower vapor pressures. The vapor pressure of 2,4-D is 4.0×10^{-1} mm Hg while that of atrazine is 1.4×10^{-6} mm Hg (WSSA, 1974). The surface application of these herbicides, coupled with the large amounts of residue cover, suggests that volatilization losses may have claimed a significant percentage of the non-adsorbed 2,4-D, which then would reduce the losses of 2,4-D in runoff.

Table 10. Reduction in pesticide losses due to no-till (negative value indicates percent increase).

Residue level (kg/ha)	Water		Sediment		Total	
	Atrazine (%)	2,4-D (%)	Atrazine (%)	2,4-D (%)	Atrazine (%)	2,4-D (%)
0	87	-17	94	93	88	38
750	87	95	93	98	87	96
1500	98	99	97	93	98	99
Overall ¹	90	92	95	93	90	93

¹ Averaged over all residue levels and rainfall events

MODEL VERIFICATION

The ability of PLIERS to adequately predict the movement of pesticides was evaluated by comparing PLIERS predictions with observed data collected during the rainfall simulator study discussed previously. Five of the twelve field plots used in the rainfall simulator study were used for PLIERS verification. These five plots represent both conventional and no-till systems and two different residue levels. The plots used for model verification were QFB, QF4, QF6, QFD and QFF. Plots QFB, QF4, and QFF, with 0 kg/ha residue, were selected because they represent the most extreme hydrologic conditions within each tillage treatment. Plots QF6 and QFD with 750 kg/ha were selected to show the effects of different residue levels on model predictions. Plots having 1500 kg/ha residue did not have sufficient runoff, sediment or pesticide losses to be useful for model verification, and were not used. A description of each of these plots can be found in Table 4. The procedures used to verify PLIERS, including the preparation of FESHM and PLIERS input data files, the calibration of FESHM and PLIERS input data files and an analysis of PLIERS' performance are presented in this chapter.

Calibration of FESHM

Before PLIERS was used to simulate the transport of pesticides on the field plots, the runoff and sediment loss predictions generated by FESHM were calibrated to closely approximate the observed field data. This calibration was performed to aid the evaluation of PLIERS by minimizing errors in the hydrologic data. This allowed a more accurate evaluation of PLIERS by reducing the effects of runoff and erosion on predicted pesticide losses. The main objective of the FESHM calibration was to match, as closely as possible, the cumulative runoff and sediment losses for each rainfall simulation (R1, R2 and R3) by adjusting FESHM input parameters. The calibration was conducted to insure that all input parameters were realistic and that the calibrated and observed runoff hydrographs were similar in shape.

Each field plot was divided into three elements having equal areas of 0.003 ha (5.5 m by 6.1 m). The input parameters required by FESHM for each of these elements were determined as follows. Estimates of the final infiltration rate (f_c), Manning's n , and Holtan's infiltration coefficient (a) were obtained from Haan et al. (1982). Soil parameters such as plant available water, gravitational water, the USLE erosivity factor (K) and the depth of the A horizon were obtained from the Soil Survey of Montgomery County, Virginia (USDA, 1985). Estimates of the USLE crop stage factor (C) and the hydrologic soil group classification were found in Schwab et al. (1981). A value of 1.0 was used for the USLE P factor for all plots. GINDEX, the growth index of crop maturity, has a minimum value of 0.1 for preplant conditions (Holtan et al., 1975). This minimum value was used for the 0 kg/ha residue plots. GINDEX for the plot having residue was estimated from data given by Ross et al. (1978). A particle size analyzer was used to determine the particle size distribution of composite soil samples taken from the top layer of each of the plots. The soil moisture content of the soil prior to the start of each rainfall simulation was determined experimentally. The particle size distributions for each of the plots is given in Table 11. A rainfall energy ratio was defined as the ratio of rainfall simulator drop impact energy to natural raindrop impact energy. This ratio was used to adjust the estimated sediment losses for the discrepancy between the

Table 11. Particle size distributions of soil from selected field plots.

Particle size (mm)	Percent of soil mass				
	QFB	QF4	QF6	QFD	QFF
0.000-0.075	16.38	13.20	9.71	12.37	17.08
0.075-0.125	20.76	17.35	14.30	18.75	23.02
0.125-0.250	18.18	17.56	16.10	18.63	20.21
0.250-0.500	14.06	14.83	14.84	13.26	13.54
0.500-1.000	11.15	11.99	13.40	10.91	9.54
1.000-2.000	19.47	25.08	31.65	26.08	16.61

energy of natural and simulated rainfall. A rainfall energy ratio of 0.4 was used for all plots (Neff, 1979).

FESHM input data was first calibrated to match the cumulative runoff predictions with the observed values. Agreement between the predicted and the observed runoff losses was obtained by varying the final infiltration rate (f_c), Manning's n and the cover coefficient (GINDEX). The calibrated input parameters along with the corresponding suggested input parameters for each of the field plots are listed in Table 12. The calibrated Manning's n values were generally higher than those suggested. This is attributed to additional roughness caused by the surface residue (roots and stems) on the no-till plots, and to surface roughness due to tillage on the conventional tillage plots. In order to obtain good agreement between the predicted and observed runoff losses, some of the Manning's n values were calibrated very high. These large values should be redefined for any future attempts to use or verify FESHM. The final infiltration rate, f_c , was occasionally calibrated to a higher value than suggested. High calibrated f_c values generally occurred during the second or third rainfall simulation (R2 or R3), and could be a result of infiltrating water moving through the soil profile through wetted fronts established during the first rainfall simulation (R1). In addition, f_c rates are higher for no-till plots than for conventional tillage plots, probably due to greater soil aggregation and a larger number of soil macropores often associated with no-till systems. After the runoff losses were calibrated, the FESHM input parameters were adjusted so that predicted sediment yields would closely approximate the observed. The USLE erosivity factor (K), the crop stage factor (C), and the rainfall energy ratio (RER) were varied to obtain agreement between the predicted and observed soil losses. Table 13 shows the predicted and observed runoff and sediment losses as well as the relative error of the predictions with respect to the observed values. The runoff hydrograph of a conventional tillage plot (QFB) and a no-till plot (QFF) are shown in Figures 14 and 15, respectively, to demonstrate the adequate fit between the observed and the predicted hydrographs.

Table 12. Suggested and calibrated FESHM input parameters.

Plot	GINDEX	Manning's			GW	f _c	Depth	K	C
		a	n	AW					
				(cm/cm)	(cm/cm)	(cm/hr)	(cm)		
QFB									
Suggested	0.10	0.30	0.20	0.15	0.25	1.42	40.7	0.35	0.40
Calibrated									
R1	0.40	0.15	0.45	0.11	0.25	1.331	40.7	0.308	0.546
R2	0.40	0.15	0.45	0.11	0.25	3.416	40.7	0.316	0.555
R3	0.40	0.15	0.45	0.11	0.25	3.408	40.7	0.336	0.598
QF4									
Suggested	0.10	0.30	0.20	0.15	0.25	1.42	40.7	0.35	0.40
Calibrated									
R1	0.46	0.15	0.45	0.11	0.25	1.641	40.7	0.247	0.482
R2	0.50	0.15	0.45	0.11	0.25	2.972	40.7	0.412	0.612
R3	0.50	0.15	0.45	0.11	0.25	2.159	40.7	0.387	0.587
QF6									
Suggested	0.10	0.30	0.20	0.15	0.25	1.42	40.7	0.35	0.40
Calibrated									
R1	0.28	0.30	0.35	0.11	0.246	1.389	40.7	0.299	0.131
R2	0.30	0.30	0.50	0.11	0.246	3.632	40.7	0.299	0.159
R3	0.30	0.30	0.43	0.11	0.246	1.321	40.7	0.299	0.320
QFD									
Suggested	0.60	0.80	0.40	0.15	0.25	1.42	40.7	0.35	0.03
Calibrated									
R1	0.40	0.30	0.35	0.11	0.246	1.389	40.7	0.296	0.020
R2	0.40	0.30	1.50	0.11	0.246	5.067	40.7	0.254	0.020
R3	0.40	0.30	0.90	0.11	0.246	4.775	40.7	0.254	0.020
QFF									
Suggested	0.10	0.80	0.40	0.15	0.25	1.42	40.7	0.35	0.03
Calibrated									
R1	0.40	0.30	0.35	0.11	0.25	1.389	40.7	0.300	0.020
R2	0.40	0.30	1.80	0.11	0.25	5.077	40.7	0.300	0.035
R3	0.40	0.30	0.90	0.11	0.25	4.699	40.7	0.350	0.087

Table 13. Predicted and observed runoff and sediment losses.

Plot: Treatment	Runoff (cm)	Sediment (kg)
QFB: Conventional till, 0 kg/ha		
Predicted	33.06	20.20
Observed	32.99	16.45
Relative error, %	0.21	22.79
QF4: Conventional till, 0 kg/ha		
Predicted	37.35	26.28
Observed	37.84	23.02
Relative error, %	-0.01	14.17
QF6: Conventional till, 750 kg/ha		
Predicted	38.50	10.49
Observed	38.30	7.79
Relative error, %	0.50	34.64
QFD: No-till, 750 kg/ha		
Predicted	4.74	0.02
Observed	4.78	0.01
Relative error, %	-0.1	100.00
QFF: No-till, 0 kg/ha		
Predicted	4.45	0.59
Observed	4.47	0.49
Relative error, %	-0.3	21.16

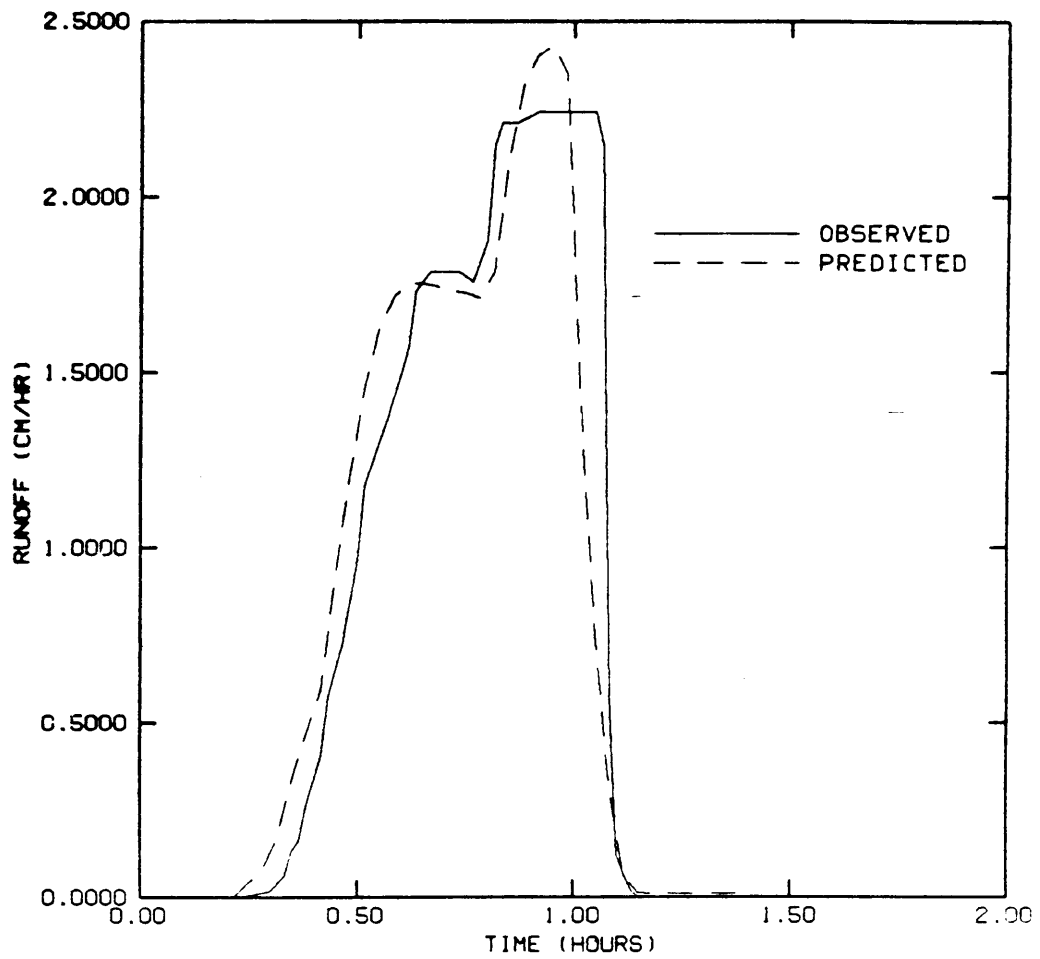


Figure 14. Calibrated and observed hydrographs from plot QFB (Conventional till, 0 kg/ha residue).

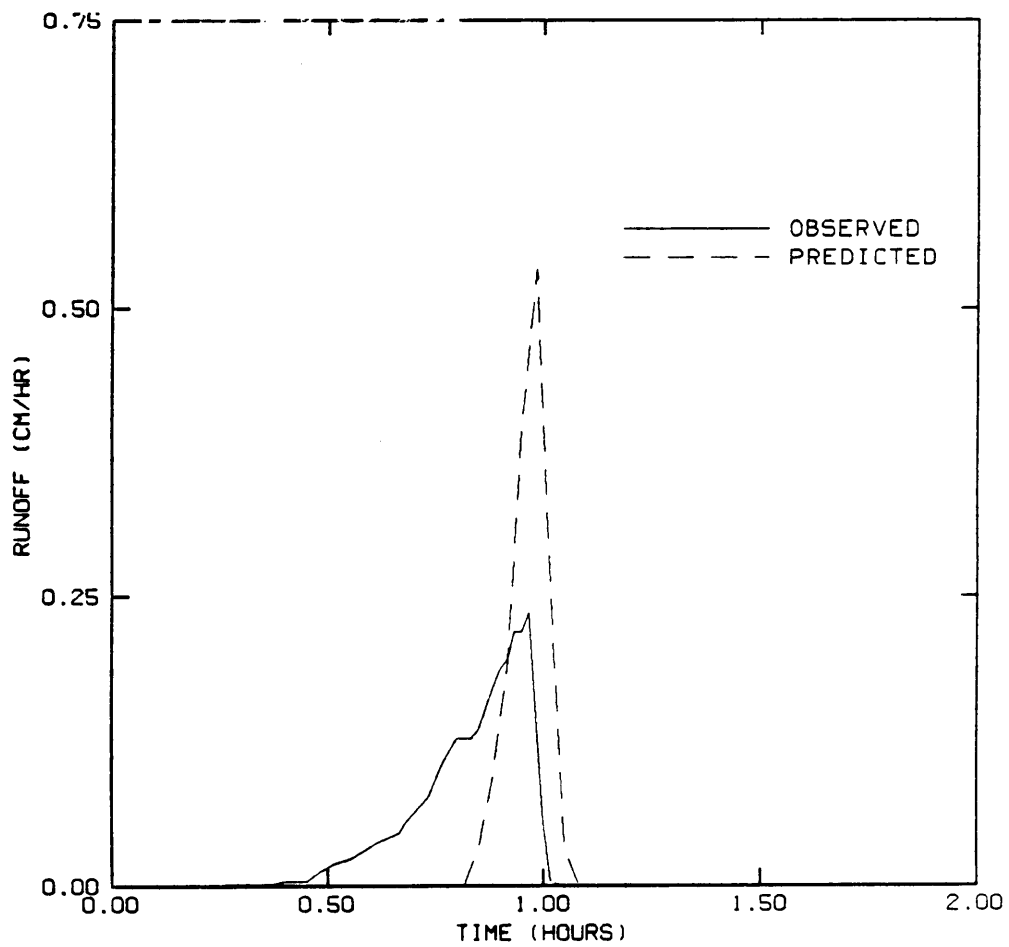


Figure 15. Calibrated and observed hydrographs from plot QFF (No-till, 0 kg/ha residue).

Plot Simulations

PLIERS Parameter Estimation

Parameters describing soil properties, ambient conditions such as temperature and humidity, soil cover characteristics and pesticide characteristics must be supplied to PLIERS as input data. Soil properties such as organic matter content and bulk density determined from data presented by Kool et al. (1986). The moisture content of the soil at the start of each storm event was estimated by PLIERS to provide an initial value of water volume in the mixing zone at the start of rainfall. A first order rate equation was developed to predict soil water tension (TEN_i) as a function of the time following the last rainfall event (d_i). After integration and simplification, the first order rate equation for predicting soil water tension took the form:

$$TEN_i = TEN_0 \times \exp(k \times d_i) \quad [32]$$

where TEN_0 is the soil water tension when D_i is zero and k is the rate constant. Assuming that a soil originally near saturation will have a soil water tension of 0.333 atm. after 48 hours, a value of 1.55 was determined for k . A regression equation developed from data presented by Kool et al. (1986), as listed in Table 14, was used to estimate the soil moisture content (θ) as a function of the soil water tension (TEN_i):

$$\theta = c_0 + c_1 \times \log_{10}(TEN_i) \quad [33]$$

The regression coefficients, c_0 and c_1 , for Groseclose silt loam soil were found to be 0.2595 and -0.0897, respectively. The R^2 value for the regression analysis was 0.97. A plot of the moisture content versus the log of the soil water tension is given in Figure 16. Although the soil moisture content is estimated by PLIERS after the start of simulation, initial soil moisture is a model input. The soil moisture content at the start of PLIERS simulation used for model verification was as-

Table 14. Data used to develop moisture curve regression equation (Equation 33).

Soil water tension (atm.)	Soil moisture (m ³ /m ³)
0.1	0.348
0.3	0.315
1.0	0.263
3.0	0.194
15.0	0.166

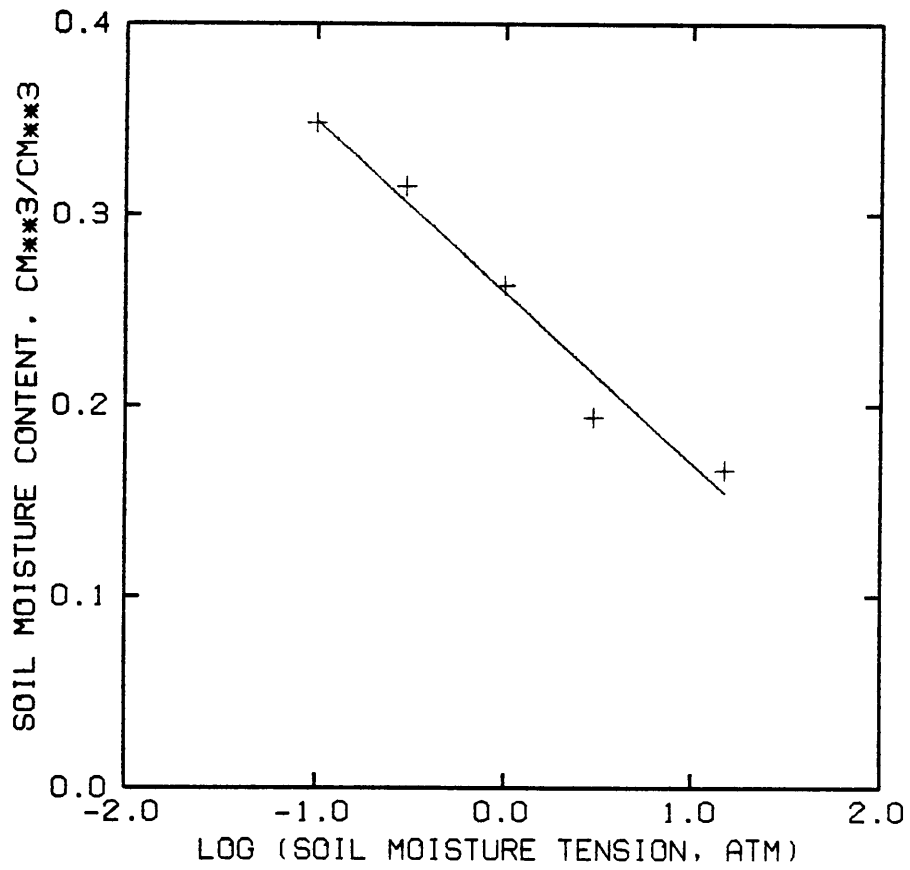


Figure 16. Plot of moisture curve data versus the log of soil water tension (data from Kool et al., 1986).

sumed to be equal to the soil moisture content measured just before the first rainfall simulator run (R1).

The residue level for each plot was measured prior to rainfall simulation, and the percent soil cover associated with these residue levels was determined from data presented by Carsel et al. (1984). The density of the residue (mass per unit volume) on the plots was estimated from data presented by Richey et al. (1961). It was assumed that residue which had been incorporated into the soil provided no surface cover.

The solubility and half-life data for atrazine and 2,4-D were obtained from the *Herbicide Handbook* (WSSA, 1974), and the pesticide breakdown coefficient was estimated using Equation 13. The coefficients used in the K_{oc} regression equation (Equation 24) were those determined during the previously described regression analysis. The Freundlich exponent, n , value for atrazine was obtained from Burkhard and Guth (1981) and for 2,4-D from Moreale and van Bladel (1980). An organic matter content of 0.037 and a soil bulk density of 1.39 g/cm^3 was used for each PLIERS simulation, other input parameters, obtained from the various sources listed above, used in PLIERS are presented in Table 15. The initial pesticide loading on the surface residue at the start of PLIERS simulation was estimated by multiplying the pesticide application rate by the percent of the soil covered by the residue. All remaining pesticides were assumed to be distributed evenly throughout the mixing zone.

The PLIERS input parameters were calibrated to aid the evaluation of model performance. Calibration benefits model verification by pinpointing problems which are intrinsic in the model as opposed to those which result from inaccurate input data. The calibration was conducted on plot QFB for both atrazine and 2,4-D simulations. The suggested input parameters for both atrazine and 2,4-D resulted in overprediction of the dissolved and adsorbed losses of both pesticides. The dissolved and adsorbed losses of both atrazine and 2,4-D were lowered by raising the breakdown coefficient estimate. Similar results were obtained by lowering the extraction ratio parameter. Increasing the value of the Freundlich exponent, n , caused the dissolved losses of both pesticides to reduce with a slight increase in the predicted adsorbed pesticide yield. The adsorbed losses of both pesticides could be lowered with a slight increase in the dissolved losses by lowering the K_{oc}

Table 15. Suggested PLIERS input parameters.

Parameter	QFB	QF4	QF6	QFD	QFF
Soil moisture coefficients					
atrazine, c_0	0.2595	0.2595	0.2595	0.2595	0.2595
c_1	-0.0897	-0.0897	-0.0897	-0.0897	-0.0897
2,4-D, c_0	0.2595	0.2595	0.2595	0.2595	0.2595
c_1	-0.0897	-0.0897	-0.0897	-0.0897	-0.0897
Initial soil moisture, cm^3/cm^3					
atrazine	0.68	0.80	0.80	0.57	0.61
2,4-D	0.68	0.80	0.80	0.57	0.61
Standing residue level, kg/ha					
atrazine	0.00	0.00	0.00	750.00	0.00
2,4-D	0.00	0.00	0.00	750.00	0.00
Residue density, kg/L					
atrazine	-----	-----	-----	0.016	-----
2,4-D	-----	-----	-----	0.016	-----
Percent soil cover					
atrazine	-----	-----	-----	80	-----
2,4-D	-----	-----	-----	80	-----
Breakdown coefficient, 1/day					
atrazine	0.0077	0.0077	0.0077	0.0077	0.0077
2,4-D	0.0693	0.0693	0.0693	0.0693	0.0693
Solubility, g/m^3					
atrazine	33.0	33.0	33.0	33.0	33.0
2,4-D	600.0	600.0	600.0	600.0	600.0
Extraction ratio parameter					
atrazine	0.10	0.10	0.10	0.10	0.10
2,4-D	0.07	0.07	0.07	0.07	0.07
Freundlich exponent					
atrazine	1.04	1.04	1.04	1.04	1.04
2,4-D	1.136	1.136	1.136	1.136	1.136
K_{oc} regression coefficients					
atrazine, a_0	245.87	245.87	245.87	245.87	245.87
a_1	-264.40	-264.40	-264.40	-264.40	-264.40
a_2	31.58	31.58	31.58	31.58	31.58
2,4-D, a_0	-333.96	-333.96	-333.96	-333.96	-333.96
a_1	205.00	205.00	205.00	205.00	205.00
a_2	181.08	181.08	181.08	181.08	181.08

regression coefficients. The calibrated input parameters and the corresponding suggested values are given in Table 16. The calibrated values were used for the atrazine and 2,4-D simulations of the four remaining plots.

While calibration was used in this study to refine PLIERS predictions for the purpose of model verification, calibration is not necessary to obtain adequate pesticide loss predictions. The sensitivity of PLIERS to variation of input parameters, which is discussed in the next chapter, shows that calibration is not crucial. However, if data is available, calibration should be used to minimize the differences between the predicted and observed values.

Results and Discussion

A summary of the predicted and observed pesticide losses (dissolved, adsorbed and total) are presented in Table 17. No pesticide losses in the crystalline form were observed in this study, and are, therefore, not presented. Results presented as a percent of the applied amount are shown in Table 18. Compared to the observed values, the predictions of the dissolved pesticide losses were very good and the adsorbed losses were satisfactory for both atrazine and 2,4-D. Averaged over the two residue levels, the total observed losses of atrazine and 2,4-D, as percent of the applied amounts, were 2.73 and 0.08, respectively, for conventional tillage; and 0.15 and 0.04, respectively, for no-till. Corresponding values for the predicted losses were 3.19 and 0.19 for atrazine and 2,4-D from conventional tillage plots, and 0.33 and less than 0.01 percent for atrazine and 2,4-D from no-till plots. As stated previously, the observed dissolved and adsorbed losses of atrazine and 2,4-D from no-till were less than those from conventional tillage plots. Likewise, the observed dissolved and adsorbed losses of atrazine and 2,4-D were generally lower from plots with 750 kg/ha residue as compared to plots having no residue (except for dissolved 2,4-D losses from conventional tillage plots). These reductions could be attributed to the reduced runoff and sediment losses associated with no-till and increased residue. No-till reduced runoff and sediment losses by 87.7 and 98.4 %, respectively.

Table 16. Suggested and calibrated PLIERS parameters.

Pesticide	BC	K _{oc} regression coefficients			n	E.R.P.
		a ₀	a ₁	a ₂		
Atrazine						
Suggested	0.0077	245.87	-264.40	31.58	1.04	0.10
Calibrated	0.0154	245.87	-264.40	31.58	1.00	0.10
2,4-D						
Suggested	0.0693	-333.96	205.00	181.08	1.136	0.07
Calibrated	0.1386	-250.47	153.75	135.81	1.400	0.05

Table 17. Predicted and observed pesticide losses.

Plot: Treatment	Atrazine		2,4-D	
	Pesticide loss, g/ha	Predicted	Observed	Predicted
QFB: Conventional till, 0 kg/ha				
Dissolved	54.77	58.40	0.25	0.23
Adsorbed	1.78	0.18	1.05	0.12
Total	56.55	58.58	1.30	0.35
QF4: Conventional till, 0 kg/ha				
Dissolved	69.66	88.03	0.75	0.13
Adsorbed	3.30	0.26	1.69	0.21
Total	72.96	88.29	2.94	0.34
QF6: Conventional till, 750 kg/ha				
Dissolved	83.62	37.01	1.28	0.56
Adsorbed	1.48	0.03	0.52	0.04
Total	85.10	37.04	1.80	0.60
QFD: No-till, 750 kg/ha				
Dissolved	2.08	0.42	0.00	0.01
Adsorbed	0.00	0.00	0.00	0.00
Total	2.08	0.42	0.00	0.01
QFF: No-till, 0 kg/ha				
Dissolved	6.51	6.20	0.01	0.45
Adsorbed	0.05	0.01	0.01	0.02
Total	6.56	6.21	0.02	0.47

Table 18. Predicted and observed pesticide losses as percent of applied.

Plot: Treatment	Atrazine		2,4-D	
	Pesticide loss, %	Predicted	Observed	Predicted
QFB: Conventional till, 0 kg/ha				
Dissolved	2.45	2.61	0.04	0.04
Adsorbed	0.08	0.01	0.19	0.02
Total	2.52	2.62	0.23	0.06
QF4: Conventional till, 0 kg/ha				
Dissolved	3.11	3.93	0.13	0.02
Adsorbed	0.15	0.01	0.30	0.04
Total	3.26	3.94	0.44	0.06
QF6: Conventional till, 750 kg/ha				
Dissolved	3.73	1.65	0.23	0.10
Adsorbed	0.07	0.001	0.09	0.01
Total	3.80	1.65	0.32	0.11
QFD: No-till, 750 kg/ha				
Dissolved	0.09	0.02	0.00	0.002
Adsorbed	0.00	0.00	0.00	0.00
Total	0.09	0.02	0.00	0.002
QFF: No-till, 0 kg/ha				
Dissolved	0.29	0.23	0.002	0.08
Adsorbed	0.002	0.00	0.002	0.004
Total	0.29	0.28	0.004	0.08

respectively, compared to conventional tillage. The effects of tillage treatment and residue level also were reflected in PLIERS predictions. The model response appeared to be due to the good agreement between the predicted and observed runoff and sediment yields.

Dissolved atrazine losses were underpredicted for plots QFB and QF4, and were overpredicted for plots QF6, QFD and QFF. Predictions of dissolved 2,4-D losses were underestimated for plots QFD and QFF, and overestimated for plots QF4 and QF6. Underestimation of dissolved pesticide losses are attributed to improper division of the available pesticide load between the adsorbed and dissolved phase. This miscalculation of adsorption is likely to be a result of the K_{oc} regression equations (Equation 24). The R^2 values for both the atrazine and the 2,4-D expressions were somewhat low. In addition, the regression equations were developed for the whole soil (soil samples which represent the average of all particle size classes) rather than for individual soil particle classes.

Overprediction of the dissolved losses of atrazine and 2,4-D has two possible explanations. First, the breakdown coefficient may have been underpredicted (the pesticide half life was overpredicted); thus, the breakdown coefficient did not adequately reflect the effects of pesticide volatilization and ambient conditions such as high temperature and humidity. Second, the extraction ratio parameter could have been overestimated, making too large a percentage of the pesticide mass available for transport. Overestimation of the extraction ratio parameter is considered to be a greater problem on no-till plots than on conventional tillage plots. The soil surface on the conventional tillage plots was loose such that the upper layer of soil could be easily mixed with runoff water. However, the soil in the no-till plots had not been disturbed, resulting in a smooth, compact soil surface where soil was less likely to be mixed with runoff water. Overprediction of the pesticide application rate would also cause overestimation of dissolved pesticide losses. The values of the pesticide application rate used in PLIERS for both atrazine and 2,4-D are likely to have been larger than the actual application rates due to pesticide losses by spray drift at the time of application.

Adsorbed pesticide loss predictions were approximately ten times larger than the observed values for all cases except 2,4-D losses from plot QFF. This overprediction is partially attributed

to the miscalculation of the division of available pesticides between the adsorbed and dissolved phase, as discussed earlier. In addition, it is possible that the increase in the adsorption amount with decreasing particle size is not as significant as indicated by the adsorption algorithm in PLIERS. The explanation provided by the misrepresentation of adsorption may be overshadowed by the likelihood that the measured adsorbed pesticide losses were simply too small for PLIERS to simulate accurately. The error associated with the assumptions, simplifications and regression expressions used in PLIERS may be equal to or larger than the adsorbed loss values. Although adsorbed pesticide losses were not accurately predicted by PLIERS, this does not significantly detract from the model's overall performance. Adsorbed losses, particularly adsorbed atrazine losses, are only a small portion of the total pesticide loss (observed dissolved to adsorbed loss ratios for atrazine were 625.0 and 564.2 for no-till and conventional tillage, respectively, and for 2,4-D were 11.0 and 12.9 for no-till and conventional tillage, respectively). The domination of dissolved pesticide losses over adsorbed are generally reflected in PLIERS predictions and total pesticide losses generally agree well with the observed data.

Since surface runoff is the major carrier of pesticides, the under- and overprediction of total losses of atrazine and 2,4-D generally follow the same trends as the dissolved atrazine and 2,4-D losses. However, the total losses of 2,4-D from plots QFB and QF4 were exaggerated by the overpredicted adsorbed losses.

It is evident from this model evaluation that more work is needed to better quantify the effects of soil particle size on pesticide adsorption and desorption. A greater knowledge of adsorption and its relationship with various soil properties such as particle size distribution, pH and CEC would greatly enhance the potential for modeling adsorption effectively. Research into defining the extraction ratio parameter also would prove beneficial, specifically the effects of soil type, tillage system and residue level on the extraction ratio parameter for various pesticides. Further verification of PLIERS for a pesticide which is predominately sediment bound, such as paraquat, would better identify possible problems in the prediction of adsorbed pesticide transport.

Although discrepancies exist between PLIERS predictions and the observed data, results suggest that PLIERS can adequately predict both dissolved and adsorbed pesticide losses. In ad-

dition, the ability of PLIERS to reflect changes in pesticide losses due to variations in runoff and sediment losses associated with different tillage types and residue levels indicate that PLIERS may be useful as a planning tool.

SENSITIVITY ANALYSIS

A sensitivity analysis was conducted on PLIERS to assess the sensitivity of the model to changes in the input parameters. This sensitivity analysis aids the identification of component processes and input parameter values which have the greatest impact on model predictions. The sensitivity analysis was performed on the input data for plot QF4. The selected parameters, their percent deviation and the resulting model predictions are presented in Tables 19 and 20. Table 19 shows the deviation of the PLIERS predictions, resulting from input parameter variation, from the original predicted values:

$$\text{DEV} = R_v - R_o \quad [34]$$

where DEV is the deviation, R_v is the prediction generated by the varied input and R_o is the prediction generated by the original data. The relative deviations presented in Table 20 are described as:

$$\text{RD} = \frac{R_v - R_o}{R_o} \times 100 \quad [35]$$

where RD is the relative deviation in percent.

Table 19. Deviation of PLIERS predictions due to changes in input parameters.

	Atrazine			2,4-D		
	Dissolved	Adsorbed	Total	Dissolved	Adsorbed	Total
Application rate						
+ 25	174.85	8.22	183.07	16.30	-10.24	6.06
+ 10	70.61	3.30	73.91	5.11	-0.39	4.72
-10	-69.28	-3.33	-72.61	-5.05	-0.08	-5.13
-25	-173.39	-8.22	-181.61	-7.41	-0.18	-7.59
Breakdown coefficient						
+ 25	-4.36	-0.24	-4.60	-2.20	-0.73	-2.93
+ 10	-1.61	-0.08	-1.69	-0.43	-1.05	-0.62
-10	2.08	-0.11	2.19	0.18	0.09	0.27
-25	4.88	0.25	5.13	0.97	0.00	0.97
Extraction ratio parameter						
+ 25	159.78	7.50	167.28	15.72	-10.11	5.61
+ 10	65.40	3.04	68.44	5.06	-0.42	6.64
-10	-64.79	-3.12	-67.91	-5.03	-0.06	-5.09
-25	-164.26	-7.80	-172.06	-7.41	-0.15	-7.56
Freundlich exponent						
+ 25	-179.70	2.97	-176.73	-7.46	2.88	-4.58
+ 10	-77.65	1.32	-76.33	-7.11	7.02	-0.09
-10	91.07	-1.53	89.54	26.32	-13.65	12.67
-25	251.88	-4.15	247.73	61.10	-13.92	47.18
Freundlich equilibrium constant						
+ 25	-105.93	1.77	-104.16	-4.59	6.61	2.02
+ 10	-46.72	0.73	-45.99	3.46	1.64	5.10
-10	55.49	-0.91	54.58	13.76	-7.55	6.21
-25	153.83	-2.68	151.15	24.42	-13.94	10.48
Organic matter content						
+ 25	-106.88	1.72	-105.16	-4.67	6.81	2.14
+ 10	-46.61	0.73	-45.88	3.46	1.64	5.10
-10	55.38	-0.92	54.46	13.77	-7.55	6.22
-25	153.09	-2.59	150.50	24.99	-14.18	10.81
Bulk density						
+ 25	-106.41	-5.22	-111.63	-4.54	1.83	-2.71
+ 10	-46.16	-2.32	-48.48	3.47	-0.04	3.43
-10	55.56	2.66	58.22	13.80	-6.53	7.27
-25	154.27	7.41	161.68	24.73	-12.90	11.83
Soil moisture						
+ 25	-13.46	-0.68	-14.14	4.13	-3.23	0.90
+ 10	-5.32	-0.27	-5.59	0.81	-2.46	-1.65
-10	5.72	0.20	5.87	2.16	1.41	3.57
-25	14.49	0.65	15.14	14.05	0.10	14.15

Table 20. Relative deviation of PLIERS predictions due to changes in input parameters.

	Atrazine			2,4-D		
	Dissolved	Adsorbed	Total	Dissolved	Adsorbed	Total
Application rate						
+ 25	25.10	24.91	25.09	218.50	-60.63	24.89
+ 10	10.14	10.00	10.13	68.00	-2.31	19.39
-10	-9.94	-10.09	-9.95	-67.69	-0.47	-21.07
25	-24.89	24.91	-24.89	-99.33	-1.07	-31.179
Breakdown coefficient						
+ 25	-0.63	-0.73	-0.63	-24.49	-4.32	-12.03
+ 10	-0.23	-0.24	-0.23	5.76	-6.22	-2.55
-10	0.30	0.33	0.30	2.41	0.53	1.11
-25	0.70	0.76	0.70	13.00	0.00	3.98
Extraction ratio parameter						
+ 25	22.94	22.73	22.93	210.72	-59.86	23.04
+ 10	9.39	9.21	9.38	67.83	-2.49	19.06
-10	-9.30	-9.45	-9.31	-67.43	-0.36	-20.90
-25	-23.58	-23.64	-23.58	-99.33	-0.89	-31.05
Freundlich exponent						
+ 25	-25.80	9.00	-24.22	-100.00	17.05	-18.81
+ 10	-11.15	4.00	-10.46	-95.31	41.56	-0.37
-10	13.07	-4.64	12.27	352.82	-80.82	52.03
-25	36.16	-12.58	33.95	819.03	-82.42	193.76
Freundlich equilibrium constant						
+ 25	-15.21	5.36	-14.28	-61.53	39.14	8.30
+ 10	-6.71	2.21	-6.30	46.38	9.71	20.94
-10	7.97	-2.76	7.48	184.45	-44.70	25.50
-25	22.08	-8.12	20.72	327.35	-82.53	43.04
Organic matter content						
+ 25	-15.34	5.21	-14.41	-62.60	40.32	8.79
+ 10	-6.69	2.21	-6.29	46.38	9.71	20.94
-10	7.95	-2.79	7.46	184.58	-44.70	25.54
-25	21.98	-7.85	20.63	334.99	-83.96	44.39
Bulk density						
+ 25	-15.28	-15.82	-15.30	-60.86	10.83	-11.13
+ 10	6.63	-7.03	-6.64	46.51	-0.24	14.09
-10	7.98	8.06	7.98	184.99	-38.66	29.86
-25	22.15	22.45	22.16	331.50	-76.38	48.58
Soil moisture						
+ 25	-1.93	-2.06	-1.94	55.36	-19.12	3.70
+ 10	-0.76	-0.82	-0.77	10.86	-14.56	-6.78
-10	0.82	0.61	0.80	28.95	8.35	14.66
-25	2.08	1.97	2.08	188.34	0.59	58.11

As shown in Tables 19 and 20, the dissolved losses of both atrazine and 2,4-D were moderately sensitive to the pesticide application rate, the extraction ratio parameter and the Freundlich exponent, n . Dissolved atrazine and 2,4-D losses were mildly sensitive to the breakdown coefficient, the Freundlich equilibrium coefficient, the organic matter content of the soil, the soil bulk density and soil moisture content. Adsorbed losses of both herbicides are moderately sensitive to changes in the pesticide application rate and the extraction ratio parameter, and slightly sensitive to variations in the breakdown coefficient, Freundlich exponent, organic matter content, bulk density and soil moisture content. The sensitivity of total atrazine and 2,4-D losses follow the same trends as the dissolved losses since the predicted dissolved losses were much greater than the adsorbed. Predicted 2,4-D losses were generally more sensitive to changes in input parameters than the atrazine predictions. This greater sensitivity is attributed to the small magnitude of the adsorbed, dissolved and total 2,4-D losses relative to atrazine loss predictions. Although not shown in either Table 19 or 20, PLIERS' estimates were found to be insensitive to changes in the pesticide solubility and the estimate of the initial soil moisture content. Since FESHM predictions were assumed correct, the impact of variation of FESHM input parameters and predictions on PLIERS predictions was not examined. However, variability in hydrologic predictions would be reflected in PLIERS results. Based on the results of this sensitivity analysis, efforts in defining model inputs should concentrate on accurately determining the extraction ratio parameter, methods for estimating K_{oc} for separate soil particle size classes and the effects of ambient conditions on pesticide breakdown.

SUMMARY AND CONCLUSIONS

The research presented in this thesis is composed of three major components: model development, field plot studies, and model verification. A summary of each of these components and the corresponding conclusions drawn from the study are presented in this chapter.

Model Development

PLIERS, the Pesticide Losses In Erosion and Runoff Simulator, was developed to simulate the transport of pesticides in the dissolved and adsorbed phases from field plots. Hydrologic data required by PLIERS were provided by the latest version of the comprehensive watershed model, FESHM. This version of FESHM contains an extended sediment algorithm which predicts the detachment and transport of individual size classes of sediment. PLIERS uses first order rate equations to describe pesticide degradation and volatilization and pesticide washoff from crop canopy and surface residue. The adsorption of pesticides to individual particle size classes is estimated using the Freundlich equation and a regression equation which was developed to determine the Freundlich K_{oc} value as a function of the mean diameter of a soil sediment class.

Basic assumptions of PLIERS are:

1. FESHM is appropriate for estimating the hydrologic input required by PLIERS.
2. The degradation and volatilization of pesticides is a function of the initial pesticide loading and time. In addition, pesticide degradation and volatilization are not affected by ambient temperature, soil moisture content, soil pH and tillage treatment.
3. Plant uptake of pesticides, compared to other pesticide losses, does not affect the loss of pesticides in surface runoff.
4. The washoff of pesticides from crop canopy and surface residue is a function of the cumulative intercepted rainfall, and is not affected by the pesticide type of formulation, nor the rainfall intensity.
5. Adsorption/desorption equilibrium is instantaneous. In addition, pesticide adsorption is single valued reversible and independent of soil pH and pesticide solubility.

Field Plot Studies

A rainfall simulator was used to study the effects of no-till and conventional tillage systems, with residue levels of 0, 750 and 1500 kg/ha, on the dissolved and adsorbed losses of atrazine and 2,4-D. Three simulated rainfall events were used to apply a total of 10.16 cm of rain with an intensity of 5.08 cm/hr to 12 field plots. The following conclusions were drawn from the field plot study:

1. Runoff and sediment losses increased as crop residue level decreased, regardless of the tillage system.
2. The no-till system reduced soil loss and runoff by up to 98 and 92 percent, respectively, relative to the conventional tillage plots.
3. Residue levels and no-till had a combined effect on runoff and soil losses. The highest reduction for both runoff and erosion occurred with no-till and 1500 kg/ha residue. Greater soil losses from the conventional tillage plots were attributed to higher runoff volumes and sediment concentrations.
4. Atrazine concentrations in runoff water increased with increasing residue level, regardless of the tillage treatment. Concentrations of atrazine in sediment were lowest at a 750 kg/ha residue level and highest with 1500 kg/ha of residue for both tillage systems. Concentrations of 2,4-D in runoff water increased with increasing residue levels for conventional tillage. However, no relationship between concentrations of atrazine, in either runoff or sediment, and residue level was observed for no-till.
5. Concentrations of both atrazine and 2,4-D in sediment and atrazine in runoff water were higher for no-till than for conventional tillage treatments.
6. Both herbicides moved predominately in the dissolved phase. Total atrazine losses, as percent applied, were 2.9 for conventional tillage and 0.3 for no-till. The corresponding values for 2,4-D were 0.3 and 0.02 percent for conventional and no-till, respectively.
7. Total losses of both atrazine and 2,4-D were lower from no-till than from conventional tillage plots. No-till reduced pesticide losses 90 percent for atrazine and 93 percent for 2,4-D relative to conventional till.

Model Verification

PLIERS was validated using atrazine and 2,4-D loss data from five of the field plots used in the rainfall simulator study. Agreement between the predicted and observed data was good for both pesticides. Although it is preferable to obtain the PLIERS input parameters experimentally, the parameters may be estimated from available literature. PLIERS shows great potential as a flexible planning tool. PLIERS may be used with any comprehensive watershed model since it is capable of directly reading in hydrologic data or using a comprehensive watershed model as a subroutine. The ability of a field scale version of PLIERS to predict the losses of pesticides from plots under different residue levels and tillage systems indicates that a watershed scale model, with appropriate verification, could be useful for the evaluation of agricultural BMPs.

POTENTIAL APPLICATIONS AND RECOMMENDATIONS

PLIERS has been designed to ultimately be used as a planning tool for agricultural applications. As shown earlier, PLIERS adequately predicts the movement of pesticides in both the dissolved and adsorbed phase from agricultural field plots. In addition, the effects of different tillage systems and residue levels are reflected in PLIERS' predictions. PLIERS is also a time efficient program, the time and effort spent in developing a PLIERS data set are small in relation to the value of the information generated during simulation. The ability of PLIERS to work with any comprehensive model enhances its flexibility, allowing the modeler to use the comprehensive watershed model of his choice. This flexibility also will allow PLIERS to be used when hydrologic model input data sets have already been formed. Since PLIERS is not a part of the watershed model, existing data sets need not be changed.

Although PLIERS shows great promise for becoming a reliable planning tool, the assumptions and simplifications made during model development may limit the model's potential applications. Therefore, the following recommendations for future investigations are given:

1. The effects of ambient conditions, such as temperature, soil moisture and soil pH, on pesticide degradation should be further investigated. Development of sound degradation relationships reflecting these ambient conditions would greatly enhance the modeling of degradation.
2. Further work aimed at quantifying and describing pesticide volatilization is needed. An expression for predicting pesticide volatilization which does not depend on unavailable and poorly defined coefficients would eliminate the adjustment of the degradation breakdown coefficient to include volatilization.
3. Investigations into the effects of pesticide type and formulation could lead to more detailed descriptions of pesticide washoff from crop canopy and surface residue. A larger base of pesticide washoff data, spanning many pesticides and surface covers, also would prove beneficial.
4. The impact of particle size distribution, soil pH and CEC on pesticide adsorption needs to be better defined. In addition, research aimed at describing pesticide desorption is needed. Currently, adsorption is assumed to be single value reversible. If this assumption is not valid, expressions describing pesticide desorption should be developed.
5. Procedures by which the extraction ratio parameter can be more accurately estimated must be developed. Should direct measurement of this parameter not be feasible, then the parameter should be defined for a wide variety of commonly used pesticides on several representative soil types. The effects of tillage system and residue level on the extraction ratio parameter also should be further examined.
6. The PLIERS model should be further tested using a variety of pesticides (including those which are either predominately soluble or sediment bound), various BMPs other than no-till and increased residue level, and different comprehensive watershed models.
7. Algorithms describing the subsurface movement of pesticides should be incorporated into PLIERS.

8. PLIERS should be expanded to simulate pesticide transport on a watershed scale. This watershed scale PLIERS must be verified using appropriate pesticide loss data collected from a wide variety of agricultural management practices.

BIBLIOGRAPHY

- Allen, J. D., D. E. Davis. 1979. The effects of fluometuron on a salt marsh ecosystem. *J. Environ. Qual.*, 8(4): 566-571.
- Anonymous. 1979. The Cornell Pesticide Model (CPM). In: *Effectiveness of Soil and Water Conservation Practices for Pollution Control*. D. A. Haith and R. C. Loehr, eds. U. S. Environmental Protection Agency, EPA-600/3-79-106, Athens, GA.
- Baier, J. H., S. F. Robbins. 1982. Report on the Occurrence and Movement of Agricultural Chemicals in Groundwater: South Fork of Suffolk County. Suffolk County Department of Health Services, Hauppauge, NY.
- Baily, G. W., R. R. Swank, Jr., H. P. Nicholson. 1974. Predicting pesticide runoff from agricultural land: a conceptual model. *J. Environ. Qual.*, 3(2): 95-102.
- Baker, J. L., H. P. Johnson. 1979. The effects of tillage systems on pesticides in runoff from small watersheds. *Transaction of the ASAE*, 22: 554-559.
- Baker, J. L., J. M. Laflen, R. O. Hartwig. 1982. Effects of corn residue and herbicide placement on herbicide runoff losses. *Transactions of the ASAE*, 25: 340-343.
- Baker, J. L., J. M. Laflen, H. P. Johnson. 1978. Effect of tillage systems on runoff losses of pesticides, a rainfall simulation study. *Transactions of the ASAE*, 21(5): 886-892.
- Baker, J. L., L. E. Shiers. 1985. Washoff characteristics of herbicides applied to corn residue. ASAE paper #85-1519, American Society of Agricultural Engineers, St. Joseph, MI.
- Beasley, D. B. 1977. ANSWERS: A mathematical model for simulating the effects of land use and management on water quality. Ph. D. Thesis. Purdue University, West Lafayette, IN.
- Beasley, D. B., L. F. Huggins. 1981. ANSWERS (Areal Nonpoint Source Watershed Environmental Response Simulation) Users Manual. Department of Agricultural Engineering, Purdue University, West Lafayette, IN.
- Beck, B. F. 1985. Relationships of geology, physiology, agricultural land use and groundwater quality in southwest Georgia. *Groundwater* 23: 627.

- Brewer, R. 1979. *Principles of Ecology*. Saunders College Publishing, Philadelphia, pg. 249, 258.
- Bruce, R. R., L. A. Harper, R. A. Leonard, W. M. Snyder, A. W. Thomas. 1975. A model for runoff of pesticides from small upland watersheds. *J. Environ. Qual.*, 4(4): 541-548.
- Burkhard, N., J. A. Guth. 1981. Chemical hydrolysis of 2-Chloro-4,6-bis(alkylamino)-1,3,5-triazine herbicides and their breakdown in soil under the influence of adsorption. *Pesticide Science*, 12(1): 45-52.
- Carsel, R. F., C. M. Smith, L. A. Mulkey, J. D. Dean, P. Jowise. 1984. Users manual for the Pesticide Root Zone Model (PRZM). U. S. Environmental Protection Agency, EPA-600/3-84-109, Athens, GA. ✓
- Cheng, H. H., R. G. Lehman. 1985. Characterization of herbicide degradation under field conditions. *Weed science*, 33(2): 7-10.
- Cohen, S. Z., S. M. Creeger, R. F. Carsel, C. G. Enfield. 1984. Potential pesticide contamination of groundwater from agricultural use. In: *Treatment and Disposal of Pesticide Wastes*. R. F. Kruger, J. N. Sieber, eds. ACS Sym. Series No. 259, American Chemical Society, Washington, D. C. ✓
- Crawford, N. H., A. S. Donigian. 1974. Pesticide Transport and Runoff Model for Agricultural Lands. U. S. Environmental Protection Agency, EPA-660/2-74-013, Athens, GA.
- Crosen, P. 1981. Conservation tillage and conventional tillage: a comparative assessment Soil Conservation Society of America, Akeny, Iowa.
- Dao, T. H., T. L. Lavy. 1978. Atrazine adsorption of soil as influenced by temperature, moisture content and electrolyte concentration. *Weed Science*, 26(3): 303-308.
- Davidson, J. M., J. R. McDougal. 1973. Experimental and predicted movement of three herbicides in a water saturated soil. *J. Environ. Qual.*, 2(4): 428-433.
- Dillaha, T. A. 1981. Modeling the particle size distribution of eroded sediment during shallow overland flow. Ph. D. Thesis. Purdue University, West Lafayette, IN.
- Dillaha, T. A., B. B. Ross, S. Mostaghimi, C. D. Heatwole, V. O. Shanholtz, F. B. Givens. 1987. Rainfall simulation/water quality monitoring for BMP effectiveness evaluation. Virginia Division of Soil and Water Conservation, Richmond, VA.
- Donigian, A. S., Jr., D. C. Beyerlein, H. H. Davis, Jr., N. H. Crawford. 1977. Agricultural Runoff Management (ARM) Model Version II: Refinement and Testing. U. S. Environmental Protection Agency, EPA-600/3-77-198, Athens, GA.
- Ehlers, W., J. Letley, W. F. Spencer, W. J. Farmer. 1969a. Lindane diffusion in soils: I. Theoretical considerations and mechanisms of movement. *Soil Sci. Soc. Am. Proc.*, 33: 501-504.
- Ehlers, W., J. Letley, W. F. Spencer, W. J. Farmer. 1969b. Lindane diffusion in soils: II. Water content, bulk density, and temperature effects. *Soil Sci. Soc. Am. Proc.*, 33: 505-508.
- EPA. 1980a. "Analysis of Soil, Dust, and Sediment". Section 11B. In: *Analysis of Pesticide Residues in Human and Environmental Samples*. U. S. Environmental Protection Agency Health Effects Research Lab, Environmental Toxicology Division, EPA-600/8-80-038, Research Triangle Park, NC.

- EPA. 1980b. "The Sampling and Analysis of Water for Pesticides". Section 10A. In: *Analysis of Pesticide Residues in Human and Environmental Samples*. U. S. Environmental Protection Agency Health Effects Research Lab, Environmental Toxicology Division, EPA-600/8-80-038, Research Triangle Park, NC.
- Farmer, W. J., J. Letley. 1974. Volatilization Losses of Pesticides from Soils. U. S. Environmental Protection Agency, EPA-660/2-74-054, Athens, GA.
- Finlayson, D. G., H. R. MacCarthy. 1973. Pesticide residues in plants. In: *Environmental Pollution by Pesticides*. C. E. Edwards, ed. Plenum Press, New York.
- Foster, G. R., L. J. Lane, J. D. Nowlin, J. M. Laflen, R. A. Young. 1980. A model to estimate sediment yield from field size areas: Development of model. In: *CREAMS: a Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems*, ed. W. G. Knisel. U. S. Department of Agriculture, Conservation Research Report No. 26.
- Foster, G. R., L. D. Meyer. 1972. Transport of soil particles by shallow flow. *Trans. of the ASAE* 15(1): 99-102.
- Frank, R., H. E. Brown, M. van Hove Holdrinet, G. J. Sirons, B. D. Ripley. 1982. Agriculture and water quality in the Canadian Great Lakes Basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-77. *J. Environ. Qual.*, 11(3): 497-505.
- Freed, V. H., R. Haque. 1973. Adsorption, movement, and distribution of pesticides in soils. In: *Pesticide Formulations*. W. van Valkenburg, ed. Marcel Dekker, Inc., NY.
- Frere, M. H. 1975. Integrating chemical factors with water and sediment transport from a watershed. *J. Environ. Qual.*, 11(3): 497-505.
- Freundlich, H. 1926. *Colloid and Capillary Chemistry*. Methven & Company, London.
- van Genuchten, M. Th., J. M. Davidson, P. J. Wierenga. 1974. An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media. *Soil Sci. Soc. Am. Proc.*, 38(1): 29-35.
- Gile, J. D. 1983a. 2,4-D — Its distribution and effects in a ryegrass ecosystem. *J. Environ. Qual.*, 12(3): 406-412.
- Gile, J. D. 1983b. Relative airborne losses of commercial 2,4-D formulations from a simulated wheat field. *Arch. Environ. Contam. Toxicol.*, 12(4): 465-469.
- Green, W. H., G. Ampt. 1911. Studies of soil physics, part I. — the flow of air and water through soils. *J. Agricultural Science* 4: 1-24.
- Grover, R. 1977. Mobility of dicamba, picloram, and 2,4-D in soil columns. *Weed Science* 25(2): 159-162.
- Grover, R., S. T. Shewchuk, A. J. Cessna, A. E. Smith, J. H. Hunter. 1985. Fate of 2,4-D Iso-octyl ester after application to a wheat field. *J. Environ. Qual.*, 14(2): 203-210.
- Haan, C. T. 1977. *Statistical Methods in Hydrology*. The Iowa State University Press, Ames, IA.
- Haan, C. T., H. P. Johnson, D. L. Brakensiek. 1982. *Hydrologic Modeling of Small Watersheds*. American Society of Agricultural Engineers, St. Joseph, MI.

- Hagood, E. S. 1986. Personal communications. Department of Plant Pathology, Physiology, and Weed Science, Virginia Polytechnic Institute and State University, Blacksburg, VA.
- Haith, D. A. 1980. A mathematical model for estimating pesticide losses in runoff. *J. Environ. Qual.* 9(3): 428-433.
- x Hall, J. K., N. L. Hartwig. 1972. Atrazine mobility in two soils under conventional tillage. *J. Environ. Qual.*, 7(1): 63-68.
- Hall, J. K., M. Pawlus, E. R. Higgins. 1972. Losses of atrazine in runoff water and soil sediment. *J. Environ. Qual.*, 1(2): 172-176.
- Hance, R. J. 1974. Soil organic matter and the adsorption and decomposition of the herbicides atrazine and linuron. *Soil Biology and Biochemistry*, 6(1): 39-42.
- Haque, R., V. H. Freed. 1974. Behavior of pesticides in the environment: Environmental chemodynamics. In: *Residue Reviews*. F. A. Gunther, ed. New York, 52: 89-116.
- Haque, R., R. Sexton. 1968. Kinetic and equilibrium study of the adsorption of 2,4-dichlorophenoxy acetic acid on some surfaces. *J. Colloid Interfac. Sci.*, 27: 818.
- Heatwole, C. D., V. O. Shanholtz, B. B. Ross. 1982. Finite element model to describe overland flow on an infiltrating watershed. *Trans. of the ASAE* 25(3): 630-637.
- Helling, C. S. 1971. Pesticide mobility in soils: III. Influence of soil properties. *Soil Sci. Soc. Am. Proc.*, 35(5): 743-748.
- Hershfield, D. N. 1961. "Rainfall Frequency Atlas of the United States". U. S. Weather Bureau, Technical Paper 40, Washington, D. C.
- Holtan, H. N. 1961. A concept for infiltration estimates in watershed engineering. U. S. Department of Agriculture, Agricultural Research Service, ARS-41-51.
- Holtan, H. N., G. J. Stiltner, W. H. Henson, N. C. Lopez. 1975. USDAHL-74 revised model of watershed hydrology. U. S. Department of Agriculture, Agricultural Research Service, Technical Bulletin No. 1518.
- Huang, P. M., R. Grover, R. B. McKercher. 1984. Components and particle size fractions involved in atrazine adsorption by soils. *Soil Science*, 138(1): 20-24.
- Huggins, L. F., E. J. Monke. 1966. The mathematical simulation of watersheds. Technical Report 1, Purdue University, West Lafayette, IN.
- Johanson, R. C., J. C. Imhoff, J. L. Kittle, Jr., A. S. Donigian, Jr. 1984. Hydrologic Simulation Program — FORTRAN (HSPF): Users Manual for Release 8.0. U. S. Environmental Protection Agency, EPA-600/3-84-066, Athens, GA.
- Judah, O. M., V. O. Shanholtz, D. N. Contractor. 1975. Finite element simulation of flood hydrographs. *Trans. of the ASAE* 18(3): 518-522.
- Karickhoff, S. W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10: 833-846.
- Kaufman, D. D. 1983. Fate of toxic organic compounds in land-applied wastes. In: *Land Treatment of Hazardous Wastes*. J. F. Parr, P. B. Marsh, J. M. Kila, eds. Noyes Data Corp., Park Ridge, NJ.

- Kells, J. J., C. E. Riek, R. L. Belvins, W. M. Muir. 1980. Atrazine dissipation as affected by surface pH and tillage. *Weed Science*, 28(1): 101-104.
- Knisel, W. G. 1980. CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems. U. S. Department of Agriculture, Conservation research Report No. 26.
- Kirkwood, R. C. 1983. The relationship of metabolism studies to the modes of action of herbicides. *Pesticide Science*, 14(4): 453-460.
- Kool, J. B., K. A. Albrecht, J. C. Parker, J. C. Baker. 1986. Physical and Chemical Characteristics of the Groseclose Soil Mapping Unit. Virginia agricultural Experiment Station, Bulletin 86-n, Blacksburg, VA.
- Leonard, R. A., G. W. Langdale, W. G. Fleming. 1979. Herbicide runoff from upland Piedmont watersheds — data and implications for modeling pesticide transport. *J. Environ. Qual.*, 8(2): 223-229.
- Leonard, R. A., A. Shirmohammadi, A. W. Johnson, L. P. Marti. 1986. Pesticide transport in shallow groundwater. ASAE paper no. 86-2508, Am. Soc. Ag. Engr., St. Joseph, MI. ✓
- Leonard, R. A., R. D. Wauchope. 1980. The pesticide submodel. In: CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems, ed. W. G. Knisel. U. S. Department of Agriculture, Conservation Research Report No. 26.
- Lindstrom, F. T., R. Haque, W. R. Coshov. 1970. Adsorption from solution: III. A new model for the kinetics of adsorption-desorption process. *J. Phys. Chem.*, 74(3): 495-502.
- Martin, C. D., J. L. Baker, D. C. Erbach, H. P. Johnson. 1978. Washoff of herbicides applied to corn residue. *Transactions of the ASAE*, 21(6): 1164-1168.
- McDowell, L. L., G. H. Willis. 1985. Insecticide washoff from cotton plants as a function of time between application and rainfall. ASAE paper #85-2525, American Society of Agricultural Engineers, St. Joseph, MI.
- Meyer, L. D., W. H. Wischmeier. 1969. Mathematical simulation of the processes of soil erosion by water. *Trans. of the ASAE* 12(6): 754.
- Montgomery, M. L., Y. L. Chang, V. H. Freed. 1971. comparative metabolism of 2,4-D by bean and corn plants. *J. Agr. Food Chem.*, 19(6): 1219-1221.
- Moreale, A., R. van Bladel. 1980. Behavior of 2,4-D in Belgian soils. *J. Environ. Qual.*, 9(4): 627-633.
- National Agricultural Chemicals Association. 1985. Health Guidance Levels for Agricultural Chemicals in Groundwater.
- Neff, E. L. 1979. Simulator activities — Sidney, Montana. In **proceedings: The Rainfall Simulator Workshop**. U. S. Department of Agriculture, Agricultural Research Service, ARS-W-10.
- Nkedi-Kizza, P., P. S. C. Rao, J. W. Johnson. 1983. Adsorption of diuron and 2,4,5-T on soil particle size separates. *J. Environ. Qual.*, 12(2): 195-197.
- O'Hare, M., D. Curry, S. Atkinson, S. B. Lee, L. Canter. 1985. Contamination of Ground Water in the Contiguous United States from Usage of Agricultural Chemicals. Volume 4: Pesticides

- and Fertilizers. Environmental and Ground Water Institute, University of Oklahoma, Norman, OK.
- Ou, L.-T., D. H. Gancarz, W. B. Wheeler, P. S. C. Rao, J. M. Davidson. 1982. Influence of soil temperature and soil moisture on degradation and metabolism of carbofuran in soils. *J. Environ. Qual.*, 11(2): 293-298.
- Overton, D. E. 1965. Mathematical refinement of an infiltration equation for watershed engineering. U. S. Department of Agriculture, Agricultural Research Service, ARS-41-99.
- Parker, L. W., K. G. Doxtader. 1982. Kinetics of microbial decomposition of 2,4-D in soil: effects of herbicide concentration. *J. Environ. Qual.*, 11(4): 679-684.
- Parker, L. W., K. G. Doxtader. 1983. Kinetics of the microbial degradation of 2,4-D in soil: effects of temperature and moisture. *J. Environ. Qual.*, 12(4): 553-558.
- Pimentel, D. 1971. Ecological Effects of Pesticides on Non-target Species. Executive Office of the President, Office of Science and Technology. Washington, D. C.
- Pimentel, D., L. Levitan. 1986. Pesticides: Amounts applied and amounts reaching pests. *Boisience*, 36: 86-91.
- Poinke, H. B., J. B. Urban. 1985. Effect of agricultural land use on groundwater quality in a small Pennsylvania watershed. *Groundwater* 23: 68. ✓
- Rao, P. S. C., J. M. Davidson. 1979. Adsorption and movement of selected pesticides at high concentrations in soils. *Water Research*, 13(4): 375-380.
- Rao, P. S. C., J. M. Davidson, R. E. Jessup, H. M. Selim. 1979. Evaluation of conceptual models for describing non-equilibrium adsorption/desorption of pesticides during steady flow in soils. *Soil Sci. Soc. Am. Proc.*, 43(1): 22-28.
- Rao, P. S. C., R. S. Mansell, L. B. Baldwin, M. F. Laurent. 1983. Pesticides and their behavior in soil and water. *Soil Science Fact Sheet*, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida.
- Rao, P. S. C., P. Nkedi-Kizza, J. M. Davidson, L.-T. Ou. 1983. Retention and transformations of pesticides in relation to nonpoint source pollution from croplands. In: *Agricultural Non-point Sources and Pollutant Processes*.
- Richey, C. B., P. Jacobson, C. W. Hall. 1961. *Agricultural Engineers Handbook*. McGraw-Hill Book Company, NY.
- Ritchie, J. T. 1972. A model for predicting evaporation from a row crop with incomplete cover. *Water Resources Research* 8(5): 1204-1213.
- Ritter, W. F., H. P. Johnson, W. G. Lovely, and M. Molnau. 1974. Atrazine, propachlor, and diazinon residues on small agricultural watersheds: runoff losses, persistence and movement. *Environ. Sci. and Technol.* 8(1): 38-42.
- Roeth, F. W., T. L. Lavy. 1971b. Atrazine uptake by sudangrass, sorghum, and corn. *Weed Science*, 19(1): 93-97.
- Rohde, W. A., L. E. Asmussen, E. W. Hauser, M. L. Hester, H. D. Allison. 1981. Atrazine persistence in soils and transport in surface runoff from plots in the coastal plain of the southern United States. *Agro-Ecosystems*, 7(3): 225-238.

- Ross, B. B., V. O. Shanholtz, D. N. Contractor, J. C. Carr. 1978. A model for evaluating the effect of land use on flood flows. Virginia Water Resources Research Center, Bulletin 85.
- Schwab, G. O., R. K. Frevert, T. W. Edminster, K. K. Barnes. 1981. *Soil and Water Conservation Engineering*. 3rd. edition, John Wiley & Sons, NY.
- Scott, H. D., R. E. Phillips. 1973. Movement of herbicides through soil to soybean roots. *Agronomy Journal*, 65(3): 386-390.
- Scott, H. D., R. E. Phillips, R. F. Paetzold. 1974. Diffusion of herbicides in the adsorbed phase. *Soil Sci. Soc. Am. Proc.*, 38: 558-562.
- Shanholtz, V. O., B. B. Ross, J. C. Carr. 1981. Effect of spatial variability on the simulation of overland and channel flow. *Trans. of the ASAE* 24(1): 124-133.
- Shanholtz, V. O., M. D. Smolen, D. F. Amos, J. B. Burger. 1981. Predicting the Soil Loss from Surface Mined Areas. State Mining and Mineral Research Institute, VPI & SU, Blacksburg, VA.
- Sherburne, H. R., V. H. Freed. 1954. Adsorption of 3(p-chlorophenyl)-1,1-dimethyl urea as a function of soil constituents. *J. Agr. Food Chem.* 2: 937.
- Smolen, M. D. 1983. Hydrologic/Water Quality Models for Agriculture and Forestry. Southern Cooperative Series Bulletin No. 291.
- Steenhuis, T. S., M. F. Walter. 1980. Closed form solution for pesticide loss in runoff water. *Transactions of the ASAE*, 23: 615-620, 628.
- Stewart, B. A., D. A. Woolhiser, W. H. Wischmeier, J. H. Caro, M. H. Frere. 1975. Control of Water Pollution from Cropland — Volume I — A manual for guideline development. Report ARS-H-5-1, U. S. Department of Agriculture, ARS, Washington, D. C.
- Swanson, R. A., G. R. Dutt. 1973. Chemical and physical processes that affect atrazine and its distribution in soil systems. *Soil Sci. Soc. Am. Proc.*, 37(6): 872-876.
- Thompson, D. G., G. R. Stephenson, M. K. Sears. 1984. Persistence, distribution and dislodgeable residues of 2,4-D following its application to turfgrass. *Pesticide Science*, 15(4): 353-360.
- U. S. Soil Conservation Service. 1973. A Method for Estimating Volume and Rate of Runoff in Small Watersheds. SCS-TP-149, Washington, D. C.
- Wauchope, R. D., W. C. Koskinen. 1983. Adsorption-desorption equilibria of herbicides in soil: a thermodynamic perspective. *Weed Science*, 31(4): 504-512.
- Wauchope, R. D., R. S. Myers. 1985. Adsorption-desorption kinetics of atrazine and linuron in freshwater-sediment aqueous slurries. *J. Environ. Qual.*, 14(1): 132-136.
- Wehtje, G. R., R. F. Spalding, O. G. Burnside, and S. R. Lowry. 1983. Biological significance and fate of atrazine under aquifer conditions. *Weed Science*, 31:610-618.
- Willis, G. H., L. L. McDowell, S. Smith, L. M. Southwick. 1986. Permethrin washoff from cotton plants by simulated rainfall. *J. Environ. Qual.*, 15(2): 116-120.
- Wischmeier, W. H., D. D. Smith. 1978. Predicting Rainfall Erosion Losses. Agricultural Handbook No. 537, U. S. Department of Agriculture, Science and Education Administration.

- Wolfe, M. L. 1982. Sediment detachment and transport functions to simulate soil loss from reclaimed mine soils. M. S. Thesis, Department of Agricultural Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA.
- WSSA. 1974. *Herbicide Handbook*. Weed Science Society of America, Champaign, IL. pg: 29-35, 116-122.
- Wu, T. L., D.L. Correll, H. E. Remenapp. 1983. Herbicide runoff from experimental watersheds. *J. Environ. Qual.*, 12(3): 330-336.
- Yalin, Y. S. 1963. An expression for bed-load transportation. *Hydraulics Division, Am Soc. Civil Engr.* 89(HY3): 221-250.

APPENDICES

Appendix A: PLIERS Variable Listing

Variable	Unit	Type	Description
APRATE	kg/ha	RV ¹	Pesticide application rate
AREA	ha	RV	Total simulation area
A0, A1, A2	---	RV	K _{oc} regression coefficients
BCT	1/day	RV	Pesticide breakdown coefficient
BD	g/cm ³	RV	Soil bulk density
CADS	g/kg	RA ²	Concentration of adsorbed pesticide
CDIS	g/L	RA	Concentration of dissolved pesticide
CIP	cm	RV	Cumulative intercepted precipitation
CLOW	g/L	RV	Lower limit of equilibrium dissolved pesticide concentration, used in method of bisection
COUT	g/L	RV	Equilibrium dissolved pesticide concentration

			resulting from entering CTRY in method of bisection
CTRY	g/L	RV	Trial equilibrium dissolved pesticide concentration, used in method of bisection
CVP	g/L	RV	Upper limit of equilibrium dissolved pesticide concentration, used for method of bisection
CWASH	g/L	RV	Concentration of pesticide in washoff water
CWASH0	g/L	RV	Initial concentration of pesticide in washoff water
C0, C1	--	RV	Moisture curve regression coefficients
DIAM	mm	RA	Upper diameter of particle size class k
DIAM50	mm	RA	Average diameter of particle size class k
DRAIN	cm	RV	Depth of rainfall during one time step
FCOV	--	RA	Fraction of soil covered by crop canopy or surface residue
FEXT	--	RV	Extraction ratio parameter
FOM	cm ³ /cm ³	RV	Fraction of soil organic matter
FSIZE	--	RA	Fraction of soil in particle size class k
HAREA	ha	RA	Element area
IDAY	day	IV ³	Number of days since start of simulation
IDTO	--	IV	Number of simulation time steps since start of storm
IELEM	--	IV	Ith element simulated during time step
IRAIN	--	IV	Ith storm during any day
ISIZE	--	IV	Ith soil particle size class
ITIME	sec	IV	Number of seconds since start of storm
JDAY	day	IV	Ith day since last storm
NDAY	day	IV	Total number of days of simulation
NELEM	--	IV	Total number of elements
NRAIN	--	IA ⁴	Number of storms during a day
NSIZE	--	IV	Number of soil particle size classes
NTIME	--	IV	Number of simulation steps in a storm

NTIMEM	min	IV	Total storm simulation time
NTIMES	sec	IV	Total storm simulation time
PELEM	g	RA	Current daily pesticide load on element
PELEMT	g	RA	Pesticide loading on total simulation area
PELEM0	g	RA	Pesticide load on element immediately following application or last storm event
PFCOV	%	RV	Percent of soil covered by crop canopy or surface residue
PNAME	--	CA ⁵	Pesticide name
PNOAD	g	RV	Nonadsorbed pesticide load
PRES	g	RA	Pesticide load on residue after degradation and volatilization
PRES0	g	RA	Pesticide load on residue at start of day
PTADNW	g	RV	Adsorbed pesticide load
PTDEG	g	RA	Daily pesticide losses due to degradation volatilization
PTDGNW	G	RV	PTDGOL minus PTDEG
PTDGOL	g	RV	Pesticide load at beginning of day
PTDIS	g	RA	Dissolved pesticide losses
PTDIST	g	RA	Cumulative dissolved pesticide losses
PTEFF	g	RV	Pesticide load available for transport
PTELEM	g	RA	current pesticide load during time step IDTO
PTIMF	g	RA	Infiltrated pesticide losses
PTSED	g	RA	Overall adsorbed pesticide losses
PTSEDK	g	RA	Adsorbed pesticide losses on particle size class k
PTSEDT	g	RA	Cumulative adsorbed pesticide losses
PTTOT	g	RA	Cumulative pesticide losses (all phases)
PTWASH	g	RV	Pesticide load washed from crop canopy or surface residue
RESDEN	kg/L	RA	Residue density

RESLEV	kg/ha	RA	Residue level
RESLOD	g	RA	Pesticide load on residue following washoff
RINT	cm/g	RA	Rainfall intensity
RN	--	RV	Freundlich exponent, n
SOLB	g/m ³	RV	Pesticide solubility
SOLMIN	kg	RA	Minimum mass of soil in mixing zone
TEN	atlm	RV	Current soil water tension
TEN0	atm	RV	Initial soil water tension
THETA	cm ³ /cm ³	RV	Current soil moisture content
THETA1	cm ³ /cm ³	RV	Initial soil moisture content
TITLE	--	CA	Simulation title
VOLCM	cm	RV	Runoff volume
VOLCMT	cm	RA	Cumulative runoff volume
VOLERS	kg	RA	Mass of sediment of particle size class k
VOLH20	L	RA	Volume of water on element
VOLINF	L	RA	Volume of infiltrating water
VOLRES	L	RA	Volume of residue
VOLRUN	L	RA	Total volume of runoff
VOLSED	kg	RA	Overall mass of sediment
VOLSOL	kg	RA	Mass of soil in mixing zone
XK	--	RA	Freundlich K for particle size class k
XKOC	--	RA	K _{oc} value for particle size class k
XMASS	kg	RA	Mass of soil particle size class k in mixing zone

¹ Real Variable

² Real Array

³ Integer Variable

⁴ Integer Array

⁵ Character Array

Appendix B: PLIERS Listing

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CX      P P P P P L      I I I I I E E E E E E R R R R R S S S S S      XX
CX      P   P L      I   E       R   R S   S      XX
CX      P   P L      I   E       R   R S      XX
CX      P P P P P L      I   E E E E E R R R R R S S S S S      XX
CX      P       L      I   E       R   R       S      XX
CX      P       L      I   E       R   R S   S      XX
CX      P       L L L L L I I I I I E E E E E R   R S S S S      XX
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CX
CX
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CX      THE PESTICIDE LOSSES IN EROSION AND RUNOFF SIMULATOR      XX
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CX      A LONG TERM MODEL FOR PREDICTING THE SURFACE LOSSES      XX
CX      OF PESTICIDES FROM AGRICULTURAL LANDS      XX
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CX      !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!      XX
CX      !!                                                    !!      XX
CX      !! NOTE! ALL ARRAYS IN THIS VERSION OF PLIERS !!      XX
CX      !! ARE DIMENSIONED WITH RESPECT TO THE !!      XX
CX      !! FOLLOWING SIMULATION CONDITIONS: !!      XX
CX      !! 3 ELEMENTS !!      XX
CX      !! 6 SOIL PARTICLE SIZE CLASSES !!      XX
CX      !! 30 DAYS SIMULATION, MAXIMUM !!      XX
CX      !! 900 TIME STEPS, MAXIMUM !!      XX
CX      !!                                                    !!      XX
CX      !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!      XX
CX
CX
CX
CX

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XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
C   PLIERS FORTRAN
C
C-----
C
C COMMON BLOCKS
C
C   COMMON /CHARA/ PNAME, TITLE
C
C   COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C
C   COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C
C   COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
&VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),
&VOLRT(30), VOLST(30), VOLRTI(30,5), VOLSTI(30,5)
C
C   COMMON /PEST/ APRATE, BC(30), BCT, DELG, FEXT, RN, SOLB
C
C   COMMON /PTCONC/ CADS(6), CCRYS, CDIS(30), CWASHO
C
C   COMMON /PTLOAD/ PELEM(30,4), PELEMO(4), PRES(30,4), PRESO(4),
&PTADNW, PTCRST(30), PTCRYS(2,4), PTDEG(30), PTDIS(2,4), PTDIST(30),
&PTEFF, PTELEM(2,4), PTINF(2,4), PTS(2,4), PTS(2,4,6), PTS(30),
&PTTOT(30), PTWASH, RESLOD(4)
C
C   COMMON /RESDUE/ FCOV(4), RESDEN(4), RESLEV(4), VOLRES(4)
C
C   COMMON /SOIL/ A0, A1, A2, BD, C0, C1, DIAM(6), DIAM50(6), FOM, FSIZE(6),
&ISIZE, NSIZE, SOLMIN(4), THETA, THETA1, XK(6), XMASS(2,4,6)
C
C   CHARACTER*70 PNAME, TITLE
C
C-----
C
C INITIALIZE PARAMETERS
C   JDAY = 0
C
C-----
C
C READ IN DATA AND PREPARE FOR SIMULATION
C   CALL SETUP
C
C-----
C
C BEGIN DAILY LOOP
C   DO 2000 IDAY = 1, NDAY

```

```

      JDAY = JDAY + 1
      IF(JDAY.EQ.1)THEN
        DO 998 IELEM = 2,NELEM+1
          PELEM(IDAY,IELEM) = PELEMO(IELEM)
998     PRES(IDAY,IELEM) = PRESO(IELEM)
        ELSE
          DO 999 IELEM = 2,NELEM+1
            PELEM(IDAY,IELEM) = PELEM(IDAY-1,IELEM)
999     PRES(IDAY,IELEM) = PRES(IDAY-1,IELEM)
        END IF
      C   WRITE(10,990)(PELEM(IDAY,IELEM),IELEM=2,NELEM+1)
      C
      C-----
      C
      C IF THERE IS RAIN ON IDAY, TRANSFER EXECUTION TO STORM
        IF(NRAIN(IDAY).GT.0)THEN
          DO 1000 IRAIN = 1,NRAIN(IDAY)
            CALL MOIST
      C   WRITE(10,990)(PELEM(IDAY,IELEM),IELEM=2,NELEM+1)
      C 990 FORMAT(3F10.4)
            CALL STORM
          1000 CONTINUE
            JDAY = 1
            DO 1100 IELEM = 2,NELEM+1
              PELEMO(IELEM) = PELEM(IDAY,IELEM)
          1100 PRESO(IELEM) = PRES(IDAY,IELEM)
            END IF
      C
      C-----
      C
      C DETERMINE DAILY DEGRADATION LOSSES
        CALL DEGRAD
      C
      C-----
      C
      C CONTINUE DAILY LOOP
        2000 CONTINUE
      C
      C-----
      C
      C WRITE OUT SUMMARIZING DAILY LOSSES
        CALL WRITE(3)
      C
      C-----
      C
      C TERMINATE EXECUTION
        STOP
        END
      C
      CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

```

XX

C
SUBROUTINE ADSORB

C
C-----

C
C THIS SUBROUTINE DIVIDES THE PESTICIDE LOAD BETWEEN THE ADSORBED AND
C NON-ADSORBED PHASES.

C
C-----

C
C COMMON BLOCKS

C
COMMON /ELEMNT/ HAREA(4), IELEM, NELEM

C
COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
&VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),
&VOLRT(30), VOLST(30), VOLRTI(30,5), VOLSTI(30,5)

C
COMMON /PEST/ APRATE, BC(30), BCT, DELG, FEXT, RN, SOLB

C
COMMON /PTCONC/ CADS(6), CCRYS, CDIS(30), CWASHO

C
COMMON /PTLOAD/ PELEM(30,4), PELEMO(4), PRES(30,4), PRESO(4),
&PTADNW, PTCRST(30), PTCRYS(2,4), PTDEG(30), PTDIS(2,4), PTDIST(30),
&PTEFF, PTELEM(2,4), PTINF(2,4), PTSED(2,4), PTSEDK(2,4,6), PTSEDT(30),
&PTTOT(30), PTWASH, RESLOD(4)

C
COMMON /SOIL/ AO, A1, A2, BD, CO, C1, DIAM(6), DIAM50(6), FOM, FSIZE(6),
&ISIZE, NSIZE, SOLMIN(4), THETA, THETA1, XK(6), XMASS(2,4,6)

C
DIMENSION PTAD(6)

C-----

C
C DETERMINE THE DISSOLVED PESTICIDE CONCENTRATION USING THE
C METHOD OF BISECTION

C
C SET LOWER AND UPPER CONCENTRATION LIMITS
CLOW = 0.0
CUP = PTEFF/VOLH2O(2, IELEM)

C
C ESTIMATE THE DISSOLVED PESTICIDE CONCENTRATION
C 50 CTRY = (CUP + CLOW)/2.0

C
C DETERMINE THE MASS OF ADSORBED PESTICIDE BASED ON CTRY
PTADNW = 0.0
DO 100 ISIZE=1, NSIZE
PTAD(ISIZE)=XMASS(2, IELEM, ISIZE)*XK(ISIZE)*CTRY**(.1./RN)

```

100 PTADNW = PTADNW + PTAD(ISIZE)
C
C DETERMINE THE DISSOLVED PESTICIDE CONCENTRATION BASED ON PTADNW
  COUT = (PTEFF-PTADNW)/VOLH2O(2, IELEM)
  IF (COUT.LT.0.0) THEN
    FACTOR = PTEFF/PTADNW
    PTADNW = PTEFF
    CCAL = PTEFF/VOLH2O(2, IELEM)
    COUT = 0.0
  ELSE
    CCAL = COUT
    FACTOR = 0.0
  END IF
C
C IF COUT AGREES WITH CTRY, EXIT ITERATION
  IF(ABS(COUT-CTRY).LE.0.01) GO TO 150
C
C RESET THE CUP OR CLOW BOUND, AND REITERATE
  IF(COUT.LE.CTRY)THEN
    CUP = CTRY
    GO TO 50
  ELSE
    CLOW = CTRY
    GO TO 50
  END IF
C
C-----
C
C DETERMINE CADS VALUES
150 DO 200 ISIZE = 1,NSIZE
  CADS(ISIZE) = XK(ISIZE)*CCAL**(.1./RN)
  IF (FACTOR.NE.0.0)CADS(ISIZE) = FACTOR*CADS(ISIZE)
200 CONTINUE
C
C-----
C
C RETURN PTADNW AND CADS VALUES CONC TO STORM
  RETURN
  END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
  SUBROUTINE DEGRAD
C
C-----
C
C THIS SUBROUTINE DETERMINES THE DAILY LOSS OF PESTICIDES BY
C DEGRADATION
C

```



```

C-----
C
C COMMON BLOCKS
C
C     COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C
C     COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C
C     COMMON /PEST/ APRATE, BC(30), BCT, DELG, FEXT, RN, SOLB
C
C     COMMON /PTLOAD/ PELEM(30,4), PELEMO(4), PRES(30,4), PRESO(4),
&PTADNW, PTCRST(30), PTCRYS(2,4), PTDEG(30), PTDIS(2,4), PTDIST(30),
&PTEFF, PTELEM(2,4), PTINF(2,4), PTSED(2,4), PTSEDK(2,4,6), PTSEDT(30),
&PTTOT(30), PTWASH, RESLOD(4)
C
C-----
C
C INITIALIZE PARAMETERS
C     PTDGNW = 0.0
C     PTDGOL = PTDGOL - PTTOT(IDAY)
C     IF (IDAY.EQ.1) THEN
C         DO 50 IELEM = 2, NELEM+1
50     PTDGOL = PTDGOL + PELEMO(IELEM) + PRESO(IELEM)
C     END IF
C
C-----
C
C DETERMINE THE BREAKDOWN COEFFICIENT BASED ON THE AVERAGE
C AMBIENT TEMPERATURE
C 2.0838E10 = BOLTZMAN'S CONSTANT/PLANCK'S CONSTANT
C 8.314 = IDEAL GAS CONSTANT
C 8.64E4 = CONVERSION BETWEEN BC(1/SEC) AND BC(1/DAY)
C     BC(IDAY) = 2.0838E10*TKEL(IDAY)*EXP(-DELG/8.314/TKEL(IDAY))*8.64E4
C     BC(IDAY) = BCT
C
C WRITE GENERAL INFO TO CHECK DATA
C     WRITE (10,55) BC(IDAY)
C     55 FORMAT(F10.4)
C
C-----
C
C DETERMINE THE DEGRADATION LOSSES
C     DO 100 IELEM = 1, NELEM+1
C     PELEM(IDAY, IELEM) = PELEMO(IELEM)*EXP(-BC(IDAY)*JDAY)
C     PRES(IDAY, IELEM) = PRESO(IELEM)*EXP(-BC(IDAY)*JDAY)
100 PTDGNW = PTDGNW + PELEM(IDAY, IELEM) + PRES(IDAY, IELEM)
C
C WRITE GENERAL INFO TO CHECK DATA
C     WRITE(10,57)PTDGOL,PTDGNW

```

```

C 57 FORMAT(2F10.4)
C
      PTDEG(IDAY) = PTDGOL - PTDGNW
      PTDGOL = PTDGNW
C
C-----
C
C RETURN PTDEG, PELEM, AND PRES VALUES BACK TO PLIERS
      RETURN
      END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
      SUBROUTINE DIAMTR
C
C-----
C
C THIS SUBROUTINE ESTIMATES THE MEAN DIAMETER OF EACH SOIL PARTICLE
C SIZE CLASS
C
C-----
C
C COMMON BLOCKS
C
      COMMON /SOIL/ A0,A1,A2,BD,C0,C1,DIAM(6),DIAM50(6),FOM,F SIZE(6),
      &ISIZE,NSIZE,SOLMIN(4),THETA,THETA1,XK(6),XMASS(2,4,6)
C
C-----
C
C DETERMINE THE MEAN DIAMETER OF EACH SOIL CLASS BASED ON THE SIZE
C LIMITS OF THAT SOIL SIZE CLASS
      DO 100 ISIZE = 1,NSIZE
      IF (ISIZE.EQ.1) THEN
          DIAM50(ISIZE) = DIAM(ISIZE)/2.0
      ELSE
          DIAM50(ISIZE) = (DIAM(ISIZE)-DIAM(ISIZE-1))/2.0 + DIAM(ISIZE-1)
      END IF
      100 CONTINUE
C
C-----
C
C WRITE DIAM50 VALUES TO CHECK DATA
C      WRITE(10,106) (DIAM50(ISIZE),ISIZE=1,NSIZE)
C 106 FORMAT(6F10.4)
C
C-----
C
C RETURN DIAM50 VALUES TO SUBROUTINE SETUP
      RETURN

```

END

C
CXX
CXX

C
SUBROUTINE GETDAT

C
C-----

C THIS SUBROUTINE READS IN THE DATA SPECIFICALLY REQUIRED BY PLIERS.
C ALL DATA ARE READ FROM FILE #4. DATA REQUIRED FOR HYDROLOGIC MODELING
C ARE READ IN BY FESHM.

C
C-----

C COMMON BLOCKS

C COMMON /CHARA/ PNAME, TITLE
C COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C COMMON /PEST/ APRATE, BC(30), BCT, DELG, FEXT, RN, SOLB
C COMMON /RESDUE/ FCOV(4), RESDEN(4), RESLEV(4), VOLRES(4)
C COMMON /SOIL/ A0, A1, A2, BD, C0, C1, DIAM(6), DIAM50(6), FOM, FSIZE(6),
C &ISIZE, NSIZE, SOLMIN(4), THETA, THETA1, XK(6), XMASS(2,4,6)
C CHARACTER*70 PNAME, TITLE

C
C-----

C READ IN THE TITLE OF THE SIMULATION, FORMAT(A70)
READ(4,700)TITLE
700 FORMAT(A70)

C
C-----

C READ IN THE NUMBER OF DAYS OF SIMULATION AND THE NUMBER OF ELEMENTS.
C IF USING FESHM, THE MINIMUM NUMBER OF ELEMENTS IS 3. FORMAT(2I10)
READ(4,705)NDAY, NELEM
705 FORMAT(2I10)

C
C-----

C READ IN THE MOISTURE CONTENT OF THE FIRST DAY OF SIMULATION
READ(4,706)THETA1

```

706 FORMAT(F10.4)
C
C-----
C
C READ IN THE ELEMENT INFORMATION (1 LINE PER ELEMENT)
C ELEMENT AREA (HA), RESIDUE LEVEL (KG/HA), FRACTION OF SOIL COVER,
C AND RESIDUE DENSITY (KG/L); FORMAT(4F10.4)
      DO 709 IELEM = 2,NELEM+1
709 READ(4,710)HAREA(IELEM),RESLEV(IELEM),FCOV(IELEM),RESDEN(IELEM)
710 FORMAT(4F10.4)
C
C-----
C
C READ IN PESTICIDE DATA
C PESTICIDE NAME, FORMAT(A20)
      READ(4,712)PNAME
712 FORMAT(A20)
C APPLICATION RATE (KG/HA), FORMAT(F10.4)
      READ(4,714)APRATE
714 FORMAT(F10.4)
C SOLUBILITY (MG/L), FREE ENERGY OF ACTIVATION, FREUNDLICH N;
C FORMAT(3F10.4)
      READ(4,716)SOLB,DELG,RN
716 FORMAT(3F10.4)
C BREAKDOWN COEFFICIENT, FRACTION OF EXTRACTION; FORMAT(2F10.4)
      READ (4,717) BCT,FEXT
717 FORMAT (2F10.4)
C COEFFICIENTS FOR KOC REGRESSION EQUATION:  A0, A1, A2; FORMAT(3F10.4)
      READ (4,718) A0,A1,A2
718 FORMAT(3F10.4)
C
C-----
C
C READ IN SOILS DATA:
C FRACTION ORGANIC MATTER AND NUMBER OF PARTICLE SIZE CLASSES,
C FORMAT(F10.4,I10)
      READ(4,722)FOM,NSIZE
722 FORMAT(F10.4,I10)
C BULK DENSITY AND SPECIFIC GRAVITY, FORMAT(2F10.4)
      READ(4,724)BD,SG
724 FORMAT(2F10.4)
C COEFFICIENTS FOR THE DRYING MOISTURE CURVE, FORMAT(2F10.4)
      READ(4,726)C0,C1
726 FORMAT(2F10.4)
C PARTICLE SIZE INFORMATION:  DIAMETER OF PARTICLE AND FRACTION OF
C SOIL IN THAT PARTICLE SIZE CLASS; FORMAT(2F10.4)
      DO 727 ISIZE = 1,NSIZE
727 READ(4,728)DIAM(ISIZE),FSIZE(ISIZE)
728 FORMAT(2F10.4)
C

```

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C-----
C
C READ IN DAILY INFORMATION (ONE LINE PER DAY):
C NUMBER OF STORMS, AVERAGE AMBIENT TEMPERATURE; FORMAT(I10,F10.4)
  DO 730 IDAY = 1,NDAY
  730 READ(4,731)NRAIN(IDAY),TCEL(IDAY)
  731 FORMAT(I10,F10.4)
C
C-----
C
C RETURN DATA TO SUBROUTINE SETUP
  RETURN
  END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
  SUBROUTINE GETK
C
C-----
C
C THIS SUBROUTINE DETERMINES THE ADSORPTION CONSTANT, K, FOR EACH
C PARTICLE SIZE CLASS
C
C-----
C
C COMMON BLOCKS
C
  COMMON /SOIL/ A0,A1,A2,BD,CO,C1,DIAM(6),DIAM50(6),FOM,FSIZE(6),
  &ISIZE,NSIZE,SOLMIN(4),THETA,THETA1,XK(6),XMASS(2,4,6)
C
  DIMENSION XKOC(6)
C-----
C
C ESTIMATE KOC FOR EACH SIZE CLASS
  DO 20 ISIZE = 1,NSIZE
    XKOC(ISIZE) = A0 + A1*DIAM50(ISIZE) + A2/SQRT(DIAM50(ISIZE))
  20 XK(ISIZE) = XKOC(ISIZE)*FOM
C
C WRITE GENERAL INFO TO CHECK DATA
C   WRITE(10,25) (XKOC(ISIZE), ISIZE=1,NSIZE)
C  25 FORMAT(6F10.4)
C
C-----
C
C RETURN XK VALUES TO SUBROUTINE SETUP
  RETURN
  END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

```

```

CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
C      SUBROUTINE MOIST
C
C-----
C
C THIS SUBROUTINE DETERMINES THE SOIL MOISTURE CONTENT OF THE MIXING
C ZONE J DAYS FOLLOWING THE LAST RAINFALL EVENT
C-----
C
C COMMON BLOCKS
C
C      COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C
C      COMMON /SOIL/ AO, A1, A2, BD, CO, C1, DIAM(6), DIAM50(6), FOM, FSIZE(6),
C      &ISIZE, NSIZE, SOLMIN(4), THETA, THETA1, XK(6), XMASS(2,4,6)
C-----
C
C DETERMINE THE INITIAL SOIL WATER TENSION, TENO
C      IF (IDAY.EQ.1) THEN
C          TENO = 10.0**((THETA1-CO)/C1)
C      ELSE
C          TENO = 0.01
C      END IF
C-----
C
C DETERMINE THE SOIL WATER TENSION
C      TEN = TENO * EXP(1.55*JDAY)
C-----
C
C DETERMINE THE SOIL MOISTURE CONTENT AS A FUNCTION OF TENSION
C      THETA = CO + C1*ALOG10(TEN)
C-----
C
C RETURN THETA TO PLIERS
C      RETURN
C      END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
C      SUBROUTINE NONADS
C
C-----
C

```

```

C THIS SUBROUTINE DIVIDES THE NON-ADSORBED PESTICIDE LOAD INTO THE
C DISSOLVED AND CRYSTALLINE PHASES
C
C-----
C
C COMMON BLOCKS
C
COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C
COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C
COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
&VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),
&VOLRT(30), VOLST(30), VOLRTI(30,5), VOLSTI(30,5)
C
COMMON /PEST/ APRATE, BC(30), BCT, DELG, FEXT, RN, SOLB
C
COMMON /PTCONC/ CADS(6), CCRYS, CDIS(30), CWASHO
C
COMMON /PTLOAD/ PELEM(30,4), PELEM0(4), PRES(30,4), PRES0(4),
&PTADNW, PTCRST(30), PTCRYS(2,4), PTDEG(30), PTDIS(2,4), PTDIST(30),
&PTEFF, PTELEM(2,4), PTINF(2,4), PTSED(2,4), PTSEDK(2,4,6), PTSEDT(30),
&PTIOT(30), PTWASH, RESLOD(4)
C
C-----
C
C INITIALIZE PARAMETERS
PCRYIS = 0.0
CCRYIS = 0.0
C
C-----
C
C WRITE GENERAL INFO TO CHECK DATA
C WRITE(10,10)VOLH2O(2, IELEM)
C 10 FORMAT(F10.4)
C
C-----
C
C DETERMINE MASS OF NON-ADSORBED PESTICIDE
PNOAD = PTEFF - PTADNW
C WRITE(10,12)PTEFF, PTADNW
C 12 FORMAT(F10.4)
C
C-----
C
C DETERMINE MASS OF DISSOLVED AND CRYSTALLINE PESTICIDES
PDIS = PNOAD
IF ((PDIS/VOLH2O(2, IELEM)).GT.SOLB) THEN
PDIS = SOLB * VOLH2O(2, IELEM)
PCRYIS = PNOAD - PDIS

```

```

      END IF
C
C-----
C
C WRITE GENERAL INFO TO CHECK DATA
C   WRITE(10,13) IDAY, PDIS, PCRY, PTADNW, PTELEM(2, IELEM),
C   $VOLH2O(2, IELEM), VOLSOL(2, IELEM)
C 13 FORMAT(I10,6F10.4)
C
C-----
C
C DETERMINE CONCENTRATION OF DISSOLVED AND CRYSTALLINE PESTICIDES
C   CDIS(IDAY) = PDIS/VOLH2O(2, IELEM)
C   CCRY = PCRY/VOLSOL(2, IELEM)
C
C-----
C
C WRITE CONCENTRATIONS TO CHECK DATA
C   WRITE(10,15) CDIS(IDAY), CCRY
C 15 FORMAT(2F10.4)
C
C-----
C
C RETURN CDIS AND CCRY TO SUBROUTINE STORM
C   RETURN
C   END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
C   SUBROUTINE SETUP
C
C-----
C
C THIS SUBROUTINE INITIALIZES PARAMETERS AND PREPARES DATA FOR PLIERS
C
C-----
C
C COMMON BLOCKS
C
C   COMMON /CHARA/ PNAME, TITLE
C
C   COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C
C   COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C
C   COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
C   &VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),
C   &VOLRT(30), VOLST(30), VOLRTI(30,5), VOLSTI(30,5)
C

```



```

COMMON /PEST/ APRATE,BC(30),BCT,DELG,FEXT,RN,SOLB
C
COMMON /PTCONC/ CADS(6),CCRY,CDIS(30),CWASHO
C
COMMON /PTLOAD/ PELEM(30,4),PELEMO(4),PRES(30,4),PRESO(4),
&PTADNW,PTCRST(30),PTCRYS(2,4),PTDEG(30),PTDIS(2,4),PTDIST(30),
&PTEFF,PTELEM(2,4),PTINF(2,4),PTSED(2,4),PTSEDK(2,4,6),PTSEDT(30),
&PTTOT(30),PTWASH,RESLOD(4)
C
COMMON /RESDUE/ FCOV(4),RESDEN(4),RESLEV(4),VOLRES(4)
C
COMMON /SOIL/ A0,A1,A2,BD,C0,C1,DIAM(6),DIAM50(6),FOM,FSIZE(6),
&ISIZE,NSIZE,SOLMIN(4),THETA,THETA1,XK(6),XMASS(2,4,6)
C
CHARACTER*70 PNAME,TITLE
C
C-----
C
C INITIALIZE PARAMETERS
C
C-----
C
C INPUT REQUIRED DATA
CALL GETDAT
C
C-----
C
C DETERMINE RESIDUE VOLUME, THE MINIMUM SOIL MASS PER ELEMENT,
C AND THE INITIAL PESTICIDE LOADING ON THE SOIL COVER AND IN THE
C MIXING ZONE
DO 810 IELEM = 2,NELEM+1
IF(RESDEN(IELEM).EQ.0.0)THEN
VOLRES(IELEM) = 0.0
GO TO 809
END IF
VOLRES(IELEM) = RESLEV(IELEM)*HAREA(IELEM)/RESDEN(IELEM)
809 SOLMIN(IELEM) = HAREA(IELEM)*1.*BD*100000.
PELEMO(IELEM) = APRATE*HAREA(IELEM)*(1.-FCOV(IELEM))*1.0E6
PRESO(IELEM) = APRATE*HAREA(IELEM)*FCOV(IELEM)*1.0E6
C WRITE(10,808)PELEMO(IELEM)
C 808 FORMAT(F10.4)
810 CONTINUE
C
C-----
C
C DETERMINE THE MWD AND FREUNDLICH K VALUE FOR EACH PARTICLE SIZE
C CLASS OF SOIL
CALL DIAMTR
CALL GETK
C

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C-----
C
C DETERMINE THE AVERAGE AMBIENT TEMPERATURE IN KELVIN
  DO 820 IDAY = 1,NDAY
  820 TKEL(IDAY) = TCEL(IDAY) + 273.
C
C-----
C
C WRITE GENERAL INFORMATION INTO A CHECK FILE
C   WRITE(10,830)TITLE,NELEM,NDAY,PNAME,APRATE,THETA1
C 830 FORMAT(1X,A70,/,1X,2I10,/,A20,F10.4,/,1X,F10.4)
C   DO 832 IELEM = 1,NELEM+1
C 832 WRITE(10,834)IELEM,HAREA(IELEM),RESLEV(IELEM),VOLRES(IELEM),
C   &FCOV(IELEM),PRESO(IELEM),PELEMO(IELEM)
C 834 FORMAT(1X,I9,6F10.4)
C
C-----
C
C OUTPUT GENERAL PLIERS INFORMATION
  CALL WRITE(1)
C
C-----
C
C RETURN DATA TO PLIERS
  RETURN
  END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
C   SUBROUTINE STORM
C
C-----
C
C THIS SUBROUTINE ESTIMATES PESTICIDE MOVEMENT OCCURING DURING A
C RAINFALL/RUNOFF EVENT
C
C-----
C
C COMMON BLOCKS
C
C   COMMON /CHARA/ PNAME,TITLE
C
C   COMMON /DAILY/ IDAY,IRAIN,JDAY,NDAY,NRAIN(30),TCEL(30),TKEL(30)
C
C   COMMON /ELEMNT/ HAREA(4),IELEM,NELEM
C
C   COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
&VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),

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```

&VOLRT(30),VOLST(30),VOLRTI(30,5),VOLSTI(30,5)
C
COMMON /PEST/ APRATE,BC(30),BCT,DELG,FEXT,RN,SOLB
C
COMMON /PTCONC/ CADS(6),CCRY,CDIS(30),CWASHO
C
COMMON /PTLOAD/ PELEM(30,4),PELEMO(4),PRES(30,4),PRESO(4),
&PTADNW,PTCRST(30),PTCRYS(2,4),PTDEG(30),PTDIS(2,4),PTDIST(30),
&PTEFF,PTELEM(2,4),PTINF(2,4),PTSED(2,4),PTSEDK(2,4,6),PTSEDT(30),
&PTTOT(30),PTWASH,RESLOD(4)
C
COMMON /RESLUE/ FCOV(4),RESDEN(4),RESLEV(4),VOLRES(4)
C
COMMON /SOIL/ A0,A1,A2,BD,CO,C1,DIAM(6),DIAM50(6),FOM,FSIZE(6),
&ISIZE,NSIZE,SOLMIN(4),THETA,THETA1,XK(6),XMASS(2,4,6)
C
CHARACTER*70 PNAME,TITLE
C
C-----
C
C CALL THE COMPREHENSIVE WATERSHED MODEL, FESHM, TO OBTAIN THE
C NECESSARY HYDROLOGIC INFORMATION
C CALL FESHM
C
C READ IN THE HYDROLOGIC DATA FROM THE INPUT FILE
C IF DESIRED, ECHO HYDROLOGIC INPUT INTO CHECK DATA
READ(4,70)NTIME,IDTO
C WRITE(10,70)NTIME,IDTO
70 FORMAT(2I10)
DO 75 ITIME = 2,NTIME+1
DO 74 IELEM = 2,NELEM+1
READ(4,72) RINT(ITIME,IELEM),VOLINF(ITIME,IELEM),VOLRUN(ITIME,
& IELEM),(VOLERS(ITIME,IELEM,ISIZE),ISIZE=1,NSIZE)
C WRITE(10,72)RINT(ITIME,IELEM),VOLINF(ITIME,IELEM),VOLRUN(ITIME,
C & IELEM),(VOLERS(ITIME,IELEM,ISIZE),ISIZE=1,NSIZE)
72 FORMAT(3F10.4,/,6F10.4)
74 CONTINUE
75 CONTINUE
C
C-----
C
C INITIALIZE PARAMETERS
C
C SET ALL INITIAL PESTICIDE MASSES IN THE ADSORBED, DISSOLVED,
C AND CRYSTALLINE PHASES TO ZERO
DO 100 IELEM = 1,NELEM+1
PTDIS(1,IELEM) = 0.0
PTCRYS(1,IELEM) = 0.0

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100 PTSED(1, IELEM) = 0.0
C
C OBTAIN INITIAL LOADINGS FROM PLIERS FOR THE FIRST STORM
  IF (IRAIN.EQ.1) THEN
    DO 110 IELEM = 1, NELEM+1
      RESLOD(IELEM) = PRES(IDAY, IELEM)
      VOLH2O(1, IELEM) = THETA * 1000.
      VOLSOL(1, IELEM) = SOLMIN(IELEM)
      DO 109 ISIZE = 1, NSIZE
109    XMASS(1, IELEM, ISIZE) = VOLSOL(1, IELEM)*FSIZE(ISIZE)
110    PTELEM(1, IELEM) = PELEM(IDAY, IELEM)
      END IF
C
  PTSEDT(IDAY) = 0.0
  PTCRST(IDAY) = 0.0
  PTDIST(IDAY) = 0.0
  PTTOT(IDAY) = 0.0
C
C-----
C
C BEGIN TIME LOOP
  DO 200 ITIME = 2, NTIME+1
C
C-----
C
C BEGIN ELEMENT LOOP
  DO 300 IELEM = 2, NELEM+1
C
C-----
C
C WRITE GENERAL INFO TO CHECK DATA
C   WRITE (10, 305) PTELEM(1, IELEM)
C 305 FORMAT(F10.4)
C
C DETERMINE CUMULATIVE INTERCEPTED PRECIPITATION
  CIP = RINT(ITIME, IELEM)*IDTO*FCOV(IELEM)
C
C-----
C
C DETERMINE WASHOFF LOAD
  PTWASH = 0.0
  IF (RESLOD(IELEM).LE.0.0) GO TO 310
  CWASHO = RESLOD(IELEM)/VOLRES(IELEM)
  CALL WASH
  310 CONTINUE
C
C-----
C
C WRITE GENERAL MASS BALANCE INFO TO CHECK DATA
C   WRITE(10, 315) VOLH2O(1, IELEM), VOLSOL(1, IELEM), (XMASS(1, IELEM, ISIZE)

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C      &, ISIZE=1, NSIZE)
C 315 FORMAT(8F10.4)
C
C-----
C
C DETERMINE THE LOADS OF PESTICIDE, SEDIMENT, AND WATER ON THE ELEMENT
      VOLH2O(2, IELEM) = VOLH2O(1, IELEM) + VOLRUN(ITIME-1, IELEM-1) +
      &RINT(ITIME, IELEM)*IDTO*HAREA(IELEM)*100000.
      VOLSOL(2, IELEM) = VOLSOL(1, IELEM) + VOLSED(1, IELEM-1)
      DO 320 ISIZE = 1, NSIZE
      VOLSED(2, IELEM) = VOLSED(2, IELEM) + VOLERS(ITIME, IELEM, ISIZE)
320 XMASS(2, IELEM, ISIZE) = XMASS(1, IELEM, ISIZE) + VOLERS(ITIME-1,
      &IELEM-1, ISIZE)
      PTELEM(2, IELEM) = PTELEM(1, IELEM) + PTDIS(1, IELEM-1) + PTCRYS(1,
      &IELEM-1) + PTS(1, IELEM-1) + PTWASH
C
C DETERMINE AVAILABLE PESTICIDE LOAD
      PTEFF = PTELEM(2, IELEM) * FEXT
C
C-----
C
C WRITE GENERAL INFO TO CHECK DATA
C      WRITE(10, 330) VOLSOL(2, IELEM), (XMASS(2, IELEM, ISIZE), ISIZE=1, NSIZE)
C 330 FORMAT(1X, 7F10.4)
C
C-----
C
C DETERMINE THE SEPARATION OF PESTICIDES BETWEEN THE ADSORBED AND
C NON-ADSORBED PHASES
      CALL ADSORB
C
C-----
C
C WRITE GENERAL INFO TO CHECK DATA
C      WRITE(10, 332) PTELEM(2, IELEM)
C 332 FORMAT(F10.4)
C
C-----
C
C DETERMINE THE SEPARATION OF NON-ADSORBED PESTICIDES BETWEEN THE
C DISSOLVED AND CRYSTALLINE PHASES
      CALL NONADS
C
C-----
C
C WRITE PESTICIDE CONCENTRATION VALUES TO CHECK DATA
C      WRITE(10, 328) CDIS(IDAY), CCRYS, (CADS(ISIZE), ISIZE=1, NSIZE)
C 328 FORMAT(8F10.4)
C
C-----

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C
C DETERMINE THE MASS OF PESTICIDES LEAVING THE ELEMENT IN THE
C DISSOLVED, CRYSTALLINE, AND ADSORBED PHASES
C
C DISSOLVED SURFACE LOSSES
      PTDIS(2,IELEM) = CDIS(IDAY)*VOLRUN(ETIME,IELEM)
C
C INFILTRATION LOSSES
      PTINF(2,IELEM) = CDIS(IDAY)*VOLINF(ETIME,IELEM)
C
C CRYSTALLINE LOSSES
      PTCRYS(2,IELEM) = CCRYS*VOLSED(2,IELEM)
C
C ADSORBED LOSSES
      DO 350 ISIZE = 1,NSIZE
      PTSSEDK(2,IELEM,ISIZE) = CADS(ISIZE)*VOLERS(ETIME,IELEM,ISIZE)
      350 PTSSE(2,IELEM) = PTSSE(2,IELEM)+PTSSEDK(2,IELEM,ISIZE)
C
C WRITE GENERAL INFO TO CHECK DATA
C   WRITE(10,352) PTDIS(2,IELEM),PTINF(2,IELEM),
C   &(PTSSEDK(2,IELEM,ISIZE),ISIZE=1,NSIZE)
C 352 FORMAT(8F10.4)
C
C-----
C
C IF THE ELEMENT CURRENTLY UNDER SIMULATION IS THE LAST ELEMENT, WE
C TALLY THE SURFACE LOSSES OF PESTICIDES FROM THE PLOT AND OUTPUT
C PERTINENT INFORMATION
      IF (IELEM.EQ.NELEM+1) THEN
          VOLRT(IDAY) = VOLRT(IDAY) + VOLRUN(ETIME,IELEM)
          VOLRTI(IDAY,IRAIN) = VOLRTI(IDAY,IRAIN) + VOLRUN(ETIME,IELEM)
          VOLST(IDAY) = VOLST(IDAY) + VOLSED(2,IELEM)
          VOLSTI(IDAY,IRAIN) = VOLSTI(IDAY,IRAIN) + VOLSED(2,IELEM)
          PTSSEDT(IDAY) = PTSSEDT(IDAY) + PTSSE(2,IELEM)
          PTCRST(IDAY) = PTCRST(IDAY) + PTCRYS(2,IELEM)
          PTDIST(IDAY) = PTDIST(IDAY) + PTDIS(2,IELEM)
          PTTOT(IDAY) = PTTOT(IDAY) + PTSSE(2,IELEM) +
          & PTCRYS(2,IELEM) + PTDIS(2,IELEM)
          CALL WRITE(2)
      END IF
C
C-----
C
C WRITE LOSS INFO TO CHECK DATA
C   WRITE(10,280)VOLH2O(2,IELEM),VOLRUN(ETIME,IELEM),VOLINF(ETIME,
C   &IELEM)
C 280 FORMAT(3F10.4)
C
C RECALCULATE THE LOADING OF PESTICIDES, SEDIMENT, AND WATER
      PTELEM(1,IELEM) = PTELEM(2,IELEM) - PTDIS(2,IELEM) - PTCRYS(2,

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&IELEM) - PTSED(2,IELEM) - PTINF(2,IELEM)
C
C   WRITE(10,289)PTELEM(2,IELEM),PTDIS(2,IELEM),PTCRYS(2,IELEM),
C   &PTSED(2,IELEM),PTINF(2,IELEM)
C 289 FORMAT(5F10.4)
      PTSED(2,IELEM) = 0.0
      VOLH2O(1,IELEM) = VOLH2O(2,IELEM) - VOLRUN(ITIME,IELEM) -
&VOLINF(ITIME,IELEM)
      VOLSOL(1,IELEM) = VOLSOL(2,IELEM) - VOLSED(2,IELEM)
      IF(VOLSOL(1,IELEM).LT.SOLMIN(IELEM))VOLSOL(1,IELEM)=SOLMIN(IELEM)
      VOLSED(2,IELEM) = 0.0
      DO 290 ISIZE = 1,NSIZE
290 XMASS(1,IELEM,ISIZE) = XMASS(2,IELEM,ISIZE) - VOLERS(ITIME,IELEM,
&ISIZE)
C-----
C
C CONTINUE ELEMENT LOOP
300 CONTINUE
C
C-----
C
C CONTINUE TIME LOOP
200 CONTINUE
C
C-----
C
C RESET VALUES OF ELEMENTAL PESTICIDE LOAD AND PESTICIDE LOAD ON
C RESIDUE AND RETURN TO PLIERS
      DO 400 IELEM = 2,NELEM+1
          PELEM(IDAY,IELEM) = PTELEM(2,NELEM+1)
400 PRES(IDAY,IELEM) = RESLOD(NELEM+1)
C
C-----
C
      RETURN
      END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
      SUBROUTINE WASH
C
C-----
C
C THIS SUBROUTINE DETERMINES THE MASS OF PESTICIDE WASHED FROM THE
C SOIL COVER TO THE MIXING ZONE
C
C-----
C

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```

C COMMON BLOCKS
C
C     COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C
C     COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
&VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),
&VOLRT(30), VOLST(30), VOLRTI(30,5), VOLSTI(30,5)
C
C     COMMON /PTCONC/ CADS(6), CCRYS, CDIS(30), CWASHO
C
C     COMMON /PTLOAD/ PELEM(30,4), PELEMO(4), PRES(30,4), PRESO(4),
&PTADNW, PTCRST(30), PTCRYS(2,4), PTDEG(30), PTDIS(2,4), PTDIST(30),
&PTEFF, PTELEM(2,4), PTINF(2,4), PTS(2,4), PTS(2,4,6), PTS(30),
&PTTOT(30), PTWASH, RESLOD(4)
C
C-----
C
C DETERMINE PESTICIDE CONCENTRATION IN WASHOFF WATER
CWASH = CWASHO * EXP(-1.37*CIP)
C
C-----
C
C DETERMINE PESTICIDE LOADING FROM WASHOFF
DRAIN = RINT(ITIME, IELEM) * IDTO
PTWASH = CWASH * DRAIN
C
C-----
C
C DETERMINE THE REMAINING PESTICIDE LOAD ON SOIL COVER
RESLOD(IELEM) = RESLOD(IELEM) - PTWASH
IF (RESLOD(IELEM).LT.0.0) RESLOD(IELEM) = 0.0
C
C-----
C
C RETURN PTWASH VALUE BACK TO SUBROUTINE STORM
RETURN
END
C
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
CXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
C
C     SUBROUTINE WRITE(N)
C
C-----
C
C THIS SUBROUTINE WRITES PLIERS OUTPUT TO FILE NUMBER 7
C
C-----
C

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C COMMON BLOCKS
C
C   COMMON /CHARA/ PNAME, TITLE
C
C   COMMON /DAILY/ IDAY, IRAIN, JDAY, NDAY, NRAIN(30), TCEL(30), TKEL(30)
C
C   COMMON /ELEMNT/ HAREA(4), IELEM, NELEM
C
C   COMMON /HYDRO/ CIP, IDTO, ITIME, NTIME, RINT(900,4), VOLERS(900,4,6),
&VOLH2O(2,4), VOLINF(900,4), VOLRUN(900,4), VOLSED(2,4), VOLSOL(2,4),
&VOLRT(30), VOLST(30), VOLRTI(30,5), VOLSTI(30,5)
C
C   COMMON /PEST/ APRATE, BC(30), BCT, DELG, FEXT, RN, SOLB
C
C   COMMON /PTCONC/ CADS(6), CCRYS, CDIS(30), CWASHO
C
C   COMMON /PTLOAD/ PELEM(30,4), PELEMO(4), PRES(30,4), PRESO(4),
&PTADNW, PTCRST(30), PTCRYS(2,4), PTDEG(30), PTDIS(2,4), PTDIST(30),
&PTEFF, PTELEM(2,4), PTINF(2,4), PTSED(2,4), PTSEDK(2,4,6), PTSEDT(30),
&PTTOT(30), PTWASH, RESLOD(4)
C
C   COMMON /RESDUE/ FCOV(4), RESDEN(4), RESLEV(4), VOLRES(4)
C
C   COMMON /SOIL/ A0, A1, A2, BD, C0, C1, DIAM(6), DIAM50(6), FOM, FSIZE(6),
&ISIZE, NSIZE, SOLMIN(4), THETA, THETA1, XK(6), XMASS(2,4,6)
C
C   CHARACTER*70 PNAME, TITLE
C
C   DIMENSION PFCOV(4), PELEMT(30), VOLCMT(30)
C
C-----
C
C WRITE OUT GENERAL INFO TO CHECK DATA
C   WRITE(10,10)TITLE, N, NELEM, NDAY, PNAME, APRATE, THETA1
C 10 FORMAT(1X, A70, /, 1X, 3I10, /, A20, F10.4, /, 1X, F10.4)
C   DO 12 IELEM = 1, NELEM+1
C 12 WRITE(10,14)HAREA(IELEM), RESLEV(IELEM), VOLRES(IELEM), FCOV(IELEM),
C   &PRESO(IELEM), PELEMO(IELEM)
C 14 FORMAT(1X, 6F10.4)
C
C SEND EXECUTION TO APPROPRIATE LOCATION
C   920:  RESTATE INPUT
C   940:  STORM GENERATED OUTPUT
C   960:  SUMMARIZE DAILY PESTICIDE LOSSES
C   GO TO (920,940,960), N
C
C-----
C
C   920 CONTINUE
C   WRITE(7,921)

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921 FORMAT(2(1X,71('X'),/))
C OUTPUT GENERAL INFORMATION:
C
C SIMULATION TITLE
  WRITE(7,922) TITLE
922 FORMAT(/,1X,A70,/)
C
C NUMBER OF DAYS OF SIMULATION, NUMBER OF ELEMENTS
  WRITE(7,924)NELEM,NDAY
924 FORMAT(10X,I2,' ELEMENTS WERE SIMULATED FOR ',I2,' DAYS'//)
C
C PESTICIDE TYPE AND APPLICATION RATE
  WRITE(7,926) PNAME,APRATE
926 FORMAT(10X,A20,' WAS APPLIED AT ',F5.2,' KG/HA'//)
C
C INITIAL SOIL MOISTURE CONTENT
  WRITE(7,927)THETA1
927 FORMAT(10X,'INITIAL MOISTURE CONTENT = ',F5.3,////)
C
C SUMMARIZE ELEMENTAL INPUT
  WRITE(7,928)
928 FORMAT(1X,71('-'),/,1X,5(' ',9X),' | PEST | PEST |',/,
  @1X,' | ELEMENT | ELEMENT |',3(1X,'RESIDUE |'),2(' APPLIED |'),/,
  #1X,' | NUMBER | AREA | LEVEL | VOLUME | COVER |TO COVER |
  $TO SOIL |',/,
  %1X,' | ',9X,' | (HA) | (KG/HA) | (L) | (%) | (MG) | (M
  G) |',/,1X,71('-'))
  DO 929 IELEM = 2,NELEM+1
  JELEM = IELEM-1
  PFCOV(IELEM) = FCOV(IELEM)*100.
929 WRITE(7,930) JELEM,HAREA(IELEM),RESLEV(IELEM),VOLRES(IELEM),
  &PFCOV(IELEM),PRESO(IELEM),PELEMO(IELEM)
930 FORMAT(1X,' | ',3X,I2,4X,' | ',F8.4,1X,' | ',5(F8.2,1X,' | '))
  WRITE(7,931)
931 FORMAT(1X,71('-'))
  GO TO 999
C
C-----
C
940 CONTINUE
C OUTPUT DATA GENERATED DURING RAINFALL/RUNOFF EVENTS
C
C BYPASS HEADING FORMATION AFTER THE FIRST SIMULATION TIME STEP
  IF(ITIME.GT.2) GO TO 950
C GENERATE HEADINGS FOR THE STORM SIMULATION OUTPUT
  WRITE(7,942)
942 FORMAT(////,2(1X,71('X'),/))
C OUTPUT GENERAL INFORMATION CONCERNING THE RAINFALL/RUNOFF EVENT
  NTIMES = NTIME*IDTO
  NTIMEM = NTIMES/60.

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WRITE(7,944) IRAIN, IDAY, NTIMEM, NTIMES, IDTO
944 FORMAT(////, 10X, 'STORM ', I2, ', DAY ', I3, /,
@      10X, 'TOTAL SIMULATION TIME = ', I5, ' MIN = ', I7, ' SEC', /,
#      10X, 'SIMULATION TIME INCREMENT = ', I3, ' SEC', /)
C OUTPUT LOSSES OCCURRING DURING THE RAINFALL/RUNOFF EVENT
WRITE(7,946)
946 FORMAT(T24, 'LOSSES FROM OUTLET ELEMENT', /, 1X, 71('-'), /,
@1X, '|', 3(9X, '|'), 2(' DISS |'), ' CRYST | ADSORB |', /,
#1X, '|', 9X, '| RUNOFF | SEDIMENT |', 4(' PEST |'), /,
$1X, '| TIME |', 2(' LOSSES |'), ' CONC |', 3(' LOSSES |'), /,
%1X, '| (SEC) | (CM) | (KG) | (MG/L) |', 3(' (MG) |'), /,
1X, 71('-'))
950 JTIME = (ITIME-1)*IDTO
VOLCM = VOLRUN(ITIME, IELEM)/HAREA(IELEM)/100000.
WRITE(7,952) JTIME, VOLCM, VOLSED(2, IELEM), CDIS(IDAY),
&PTDIS(2, IELEM), PTCRYS(2, IELEM), PTS(2, IELEM)
952 FORMAT(1X, '|', 1X, I6, 2X, '|', 3(F8.3, 1X, '|'), 3(F8.4, 1X, '|'))
C
C IF THIS IS THE LAST TIME STEP OF SIMULATION, SUMMARIZE THE
C RAINFALL/RUNOFF EVENT LOSSES
IF(ITIME.GE.NTIME+1)THEN
AREA = 0.0
DO 953 IELEM = 1, NELEM
953 AREA = AREA+HAREA(IELEM)
VOLCM = VOLRTI(IDAY, IRAIN)/AREA/100000.
WRITE(7,954) VOLCM, VOLRTI(IDAY, IRAIN), VOLSTI(IDAY, IRAIN),
& PTDIST(IDAY), PTCRST(IDAY), PTS(2, IELEM), PTTOT(IDAY)
954 FORMAT(1X, 71('-'), //,
@      10X, 'TOTAL RUNOFF LOSSES = ', F12.4, ' CM', ' = ', F12.4, ' L',
#      /, 10X, 'TOTAL SEDIMENT LOSSES = ', F12.4, ' KG', /,
$      10X, 'PESTICIDE LOSSES:', /,
15X, 'DISSOLVED = ', F12.4, ' MG', /,
&      15X, 'CRYSTALLINE = ', F12.4, ' MG', /,
*      15X, 'ADSORBED = ', F12.4, ' MG', /,
+      15X, 'TOTAL = ', F12.4, ' MG')
END IF
GO TO 999
C
C-----
C
960 CONTINUE
C OUTPUT DATA SUMMARIZING DAILY PESTICIDE LOSSES
C
DO 995 IDAY = 1, NDAY
C BYPASS HEADINGS AFTER THE FIRST DAY
IF(IDAY.GT.1)GO TO 970
C GENERATE HEADINGS
WRITE(7,962)
962 FORMAT(////, 2(1X, 71('X'), /), ////,
@T24, 'SUMMARY OF DAILY LOSSES', /, 1X, 71('-'), /,

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#1X,'|',3X,'|',4X,'|',9X,'|',6X,'|',7X,'|',7X,'| DISS | ADS |
$ TOT '|',/,
%1X,'| |AVE | DEGRAD |NO OF | RUNOFF| SED | PEST | PEST |
SURFACE '|',/,
@1X,'|DAY|TEMP| LOSSES |STORMS| LOSSES| LOSSES| LOSSES | LOSSES |
#LOSSES '|',/,
&1X,'| |(C) | (MG) | | (CM) | (KG) | (MG) | (MG) |
* (MG) '|',/,1X,71('-'))
970 CONTINUE
DO 974 IELEM = 2,NELEM+1
VOLCMT(IDAY) = VOLRT(IDAY)/AREA/100000.
974 PELEMT(IDAY) = PELEMT(IDAY) + PELEM(IDAY,IELEM)
WRITE(7,976)IDAY,TCEL(IDAY),PTDEG(IDAY),NRAIN(IDAY),VOLCMT(IDAY),
&VOLST(IDAY),PTDIST(IDAY),PTS EDT(IDAY),PTTOT(IDAY)
976 FORMAT(1X,'|',I3,'|',F4.1,'|',F9.2,'|',2X,I2,2X,'|',F7.2,'|',
@F7.2,'|',F8.3,'|',F8.3,'|',F9.3,'|')
IF(IDAY.GE.NDAY)THEN
WRITE(7,980)
980 FORMAT(1X,71('-'),//,2(1X,71('X'),/))
END IF
995 CONTINUE
C
999 CONTINUE
RETURN
END

```

Appendix C: Sample PLIERS Input Data

SIMULATION OF ATRAZINE ON PLOT QF6, JUNE 12 AND 13, 1986

	3	3		
0.80				
0.0033	0.00	0.00	0.00	0.00
0.0033	0.00	0.00	0.00	0.00
0.0033	0.00	0.00	0.00	0.00
ATRAZINE				
2.24				
33.00	100640.000	1.000		
0.0154	0.10			
245.8700	-264.4000	31.5800		
0.037	6			
1.39	2.65			
0.2595	-0.0897			
0.075	0.0970			
0.125	0.1430			
0.250	0.1610			
0.500	0.1480			
1.000	0.1340			
2.000	0.3170			

Appendix D: Sample PLIERS Output

XX
XX

SIMULATION OF ATRAZINE ON PLOT QF6, JUNE 12 AND 13, 1986

3 ELEMENTS WERE SIMULATED FOR 3 DAYS

ATRAZINE WAS APPLIED AT 2.24 KG/HA

INITIAL MOISTURE CONTENT = 0.800

ELEMENT NUMBER	ELEMENT AREA (HA)	RESIDUE LEVEL (KG/HA)	RESIDUE VOLUME (L)	RESIDUE COVER (%)	PEST APPLIED TO COVER (MG)	PEST APPLIED TO SOIL (MG)
1	0.0033	0.00	0.00	0.00	0.00	7392.00
2	0.0033	0.00	0.00	0.00	0.00	7392.00
3	0.0033	0.00	0.00	0.00	0.00	7392.00

XX
XX

STORM 1, DAY 2
TOTAL SIMULATION TIME = 120 MIN = 7200 SEC
SIMULATION TIME INCREMENT = 30 SEC

LOSSES FROM OUTLET ELEMENT

TIME (SEC)	RUNOFF LOSSES (CM)	SEDIMENT LOSSES (KG)	DISS PEST CONC (MG/L)	DISS PEST LOSSES (MG)	CRYST PEST LOSSES (MG)	ADSORB PEST LOSSES (MG)
30	0.000	0.000	0.291	0.0000	0.0000	0.0000
60	0.000	0.000	0.289	0.0000	0.0000	0.0000
90	0.000	0.000	0.286	0.0000	0.0000	0.0000
120	0.000	0.000	0.284	0.0000	0.0000	0.0000
150	0.000	0.000	0.293	0.0000	0.0000	0.0000
180	0.000	0.000	0.279	0.0000	0.0000	0.0000
210	0.000	0.000	0.287	0.0000	0.0000	0.0000
240	0.000	0.000	0.274	0.0000	0.0000	0.0000
270	0.000	0.000	0.281	0.0000	0.0000	0.0000
300	0.000	0.000	0.287	0.0000	0.0000	0.0000
330	0.000	0.000	0.275	0.0000	0.0000	0.0000
360	0.000	0.000	0.281	0.0000	0.0000	0.0000
390	0.000	0.000	0.285	0.0000	0.0000	0.0000
420	0.000	0.000	0.274	0.0000	0.0000	0.0000
450	0.000	0.000	0.278	0.0000	0.0000	0.0000
480	0.000	0.000	0.282	0.0000	0.0000	0.0000
510	0.000	0.000	0.272	0.0000	0.0000	0.0000
540	0.000	0.000	0.275	0.0000	0.0000	0.0000
570	0.000	0.000	0.278	0.0000	0.0000	0.0000
600	0.000	0.000	0.268	0.0000	0.0000	0.0000
630	0.000	0.000	0.271	0.0000	0.0000	0.0000
660	0.000	0.000	0.274	0.0000	0.0000	0.0000
690	0.000	0.000	0.264	0.0000	0.0000	0.0000
720	0.000	0.000	0.266	0.0000	0.0000	0.0000
750	0.000	0.000	0.269	0.0000	0.0000	0.0000
780	0.000	0.000	0.260	0.0000	0.0000	0.0000
810	0.000	0.000	0.272	0.0000	0.0000	0.0000
840	0.000	0.000	0.263	0.0000	0.0000	0.0000
870	0.000	0.000	0.265	0.0000	0.0000	0.0000
900	0.000	0.000	0.266	0.0000	0.0000	0.0000
930	0.000	0.000	0.258	0.0000	0.0000	0.0000
960	0.000	0.000	0.268	0.0000	0.0000	0.0000
990	0.000	0.000	0.260	0.0000	0.0000	0.0000
1020	0.000	0.000	0.252	0.0000	0.0000	0.0000
1050	0.000	0.000	0.261	0.0000	0.0000	0.0000
1080	0.000	0.000	0.254	0.0000	0.0000	0.0000
1110	0.000	0.000	0.262	0.0000	0.0000	0.0000
1140	0.000	0.000	0.255	0.0000	0.0000	0.0000
1170	0.000	0.000	0.248	0.0000	0.0000	0.0000
1200	0.000	0.000	0.256	0.0000	0.0000	0.0000
1230	0.000	0.000	0.249	0.0000	0.0000	0.0000
1260	0.000	0.000	0.256	0.0000	0.0000	0.0000
1290	0.000	0.000	0.250	0.0021	0.0000	0.0000

1320	0.000	0.026	0.244	0.0297	0.0000	0.0211
1350	0.001	0.037	0.252	0.0793	0.0000	0.0419
1380	0.002	0.046	0.247	0.1282	0.0000	0.0698
1410	0.002	0.046	0.242	0.1710	0.0000	0.0684
1440	0.003	0.046	0.249	0.2165	0.0000	0.0702
1470	0.003	0.046	0.244	0.2464	0.0000	0.0687
1500	0.003	0.046	0.239	0.2695	0.0000	0.0673
1530	0.004	0.046	0.244	0.2994	0.0000	0.0689
1560	0.004	0.046	0.249	0.3255	0.0000	0.0703
1590	0.005	0.053	0.244	0.4331	0.0000	0.0908
1620	0.007	0.064	0.240	0.5697	0.0000	0.1269
1650	0.009	0.067	0.246	0.7395	0.0000	0.1434
1680	0.011	0.068	0.242	0.8791	0.0000	0.1467
1710	0.013	0.054	0.238	1.0045	0.0000	0.1126
1740	0.014	0.022	0.242	1.1584	0.0000	0.0466
1770	0.016	0.023	0.238	1.2577	0.0000	0.0498
1800	0.017	0.024	0.233	1.3422	0.0000	0.0507
1830	0.019	0.024	0.237	1.4640	0.0000	0.0516
1860	0.020	0.019	0.241	1.5774	0.0000	0.0420
1890	0.021	0.019	0.229	1.5705	0.0000	0.0398
1920	0.022	0.019	0.232	1.6626	0.0000	0.0404
1950	0.022	0.019	0.235	1.7455	0.0000	0.0409
1980	0.023	0.019	0.238	1.8210	0.0000	0.0414
2010	0.025	0.019	0.226	1.8698	0.0000	0.0394
2040	0.029	0.019	0.229	2.2133	0.0000	0.0399
2070	0.033	0.019	0.233	2.5254	0.0000	0.0405
2100	0.036	0.019	0.235	2.7928	0.0000	0.0409
2130	0.038	0.023	0.224	2.8384	0.0000	0.0455
2160	0.040	0.024	0.225	3.0053	0.0000	0.0490
2190	0.042	0.024	0.227	3.1326	0.0000	0.0494
2220	0.043	0.024	0.229	3.2244	0.0000	0.0497
2250	0.043	0.024	0.230	3.2864	0.0000	0.0499
2280	0.044	0.024	0.231	3.3273	0.0000	0.0502
2310	0.044	0.024	0.232	3.3486	0.0000	0.0504
2340	0.044	0.024	0.220	3.1757	0.0000	0.0478
2370	0.044	0.024	0.221	3.1796	0.0000	0.0481
2400	0.043	0.024	0.222	3.1790	0.0000	0.0483
2430	0.043	0.024	0.223	3.1766	0.0000	0.0485
2460	0.043	0.024	0.224	3.1724	0.0000	0.0487
2490	0.043	0.024	0.225	3.1679	0.0000	0.0489
2520	0.042	0.024	0.226	3.1644	0.0000	0.0491
2550	0.042	0.024	0.227	3.1638	0.0000	0.0492
2580	0.042	0.023	0.228	3.1378	0.0000	0.0463
2610	0.041	0.019	0.228	3.0923	0.0000	0.0398
2640	0.041	0.019	0.218	2.9402	0.0000	0.0379
2670	0.041	0.019	0.219	2.9864	0.0000	0.0381
2700	0.042	0.019	0.221	3.0633	0.0000	0.0384
2730	0.043	0.019	0.222	3.1628	0.0000	0.0386
2760	0.044	0.019	0.224	3.2795	0.0000	0.0389
2790	0.046	0.019	0.214	3.2410	0.0000	0.0372

2820	0.047	0.019	0.215	3.3678	0.0000	0.0375
2850	0.049	0.019	0.217	3.4934	0.0000	0.0377
2880	0.050	0.019	0.218	3.6126	0.0000	0.0380
2910	0.051	0.019	0.219	3.7219	0.0000	0.0382
2940	0.052	0.019	0.220	3.8193	0.0000	0.0384
2970	0.053	0.019	0.221	3.9033	0.0000	0.0385
3000	0.054	0.019	0.212	3.7933	0.0000	0.0370
3030	0.055	0.019	0.213	3.8497	0.0000	0.0371
3060	0.055	0.019	0.214	3.8935	0.0000	0.0373
3090	0.055	0.019	0.215	3.9267	0.0000	0.0374
3120	0.055	0.019	0.216	3.9504	0.0000	0.0376
3150	0.055	0.019	0.207	3.7907	0.0000	0.0360
3180	0.055	0.019	0.208	3.8030	0.0000	0.0362
3210	0.055	0.019	0.208	3.8100	0.0000	0.0363
3240	0.055	0.019	0.209	3.8140	0.0000	0.0364
3270	0.055	0.019	0.210	3.8168	0.0000	0.0365
3300	0.055	0.019	0.211	3.8168	0.0000	0.0366
3330	0.055	0.019	0.211	3.8169	0.0000	0.0367
3360	0.055	0.019	0.212	3.8173	0.0000	0.0369
3390	0.054	0.019	0.212	3.8190	0.0000	0.0370
3420	0.054	0.019	0.213	3.8198	0.0000	0.0371
3450	0.054	0.019	0.214	3.8227	0.0000	0.0372
3480	0.054	0.019	0.214	3.8258	0.0000	0.0372
3510	0.054	0.019	0.206	3.6770	0.0000	0.0359
3540	0.054	0.019	0.207	3.6842	0.0000	0.0360
3570	0.054	0.019	0.207	3.6933	0.0000	0.0361
3600	0.054	0.019	0.208	3.7080	0.0000	0.0362
3630	0.049	0.001	0.206	3.3241	0.0000	0.0024
3660	0.042	0.000	0.205	2.8326	0.0000	0.0000
3690	0.035	0.006	0.212	2.4793	0.0000	0.0117
3720	0.029	0.002	0.211	2.0012	0.0000	0.0075
3750	0.022	0.000	0.210	1.5244	0.0000	0.0000
3780	0.017	0.000	0.208	1.1682	0.0000	0.0000
3810	0.013	0.002	0.207	0.9043	0.0000	0.0073
3840	0.010	0.001	0.206	0.6622	0.0000	0.0024
3870	0.006	0.000	0.205	0.4188	0.0000	0.0000
3900	0.004	0.000	0.205	0.2578	0.0000	0.0000
3930	0.002	0.000	0.204	0.1201	0.0000	0.0000
3960	0.001	0.000	0.213	0.0621	0.0000	0.0000
3990	0.001	0.000	0.212	0.0379	0.0000	0.0000
4020	0.000	0.000	0.212	0.0259	0.0000	0.0000
4050	0.000	0.000	0.212	0.0198	0.0000	0.0000
4080	0.000	0.000	0.212	0.0168	0.0000	0.0000
4110	0.000	0.000	0.212	0.0144	0.0000	0.0000
4140	0.000	0.000	0.212	0.0132	0.0000	0.0000
4170	0.000	0.000	0.212	0.0126	0.0000	0.0000
4200	0.000	0.000	0.212	0.0126	0.0000	0.0000
4230	0.000	0.000	0.212	0.0126	0.0000	0.0000
4260	0.000	0.000	0.212	0.0126	0.0000	0.0000
4290	0.000	0.000	0.212	0.0108	0.0000	0.0000

5820	0.000	0.000	0.212	0.0054	0.0000	0.0000
5850	0.000	0.000	0.212	0.0042	0.0000	0.0000
5880	0.000	0.000	0.212	0.0036	0.0000	0.0000
5910	0.000	0.000	0.212	0.0036	0.0000	0.0000
5940	0.000	0.000	0.212	0.0036	0.0000	0.0000
5970	0.000	0.000	0.212	0.0036	0.0000	0.0000
6000	0.000	0.000	0.212	0.0036	0.0000	0.0000
6030	0.000	0.000	0.212	0.0036	0.0000	0.0000
6060	0.000	0.000	0.212	0.0036	0.0000	0.0000
6090	0.000	0.000	0.212	0.0036	0.0000	0.0000
6120	0.000	0.000	0.212	0.0036	0.0000	0.0000
6150	0.000	0.000	0.212	0.0036	0.0000	0.0000
6180	0.000	0.000	0.212	0.0036	0.0000	0.0000
6210	0.000	0.000	0.212	0.0036	0.0000	0.0000
6240	0.000	0.000	0.212	0.0036	0.0000	0.0000
6270	0.000	0.000	0.212	0.0036	0.0000	0.0000
6300	0.000	0.000	0.212	0.0036	0.0000	0.0000
6330	0.000	0.000	0.212	0.0036	0.0000	0.0000
6360	0.000	0.000	0.212	0.0036	0.0000	0.0000
6390	0.000	0.000	0.212	0.0036	0.0000	0.0000
6420	0.000	0.000	0.212	0.0036	0.0000	0.0000
6450	0.000	0.000	0.212	0.0036	0.0000	0.0000
6480	0.000	0.000	0.212	0.0036	0.0000	0.0000
6510	0.000	0.000	0.212	0.0036	0.0000	0.0000
6540	0.000	0.000	0.212	0.0036	0.0000	0.0000
6570	0.000	0.000	0.211	0.0036	0.0000	0.0000
6600	0.000	0.000	0.211	0.0036	0.0000	0.0000
6630	0.000	0.000	0.211	0.0036	0.0000	0.0000
6660	0.000	0.000	0.211	0.0036	0.0000	0.0000
6690	0.000	0.000	0.211	0.0036	0.0000	0.0000
6720	0.000	0.000	0.211	0.0036	0.0000	0.0000
6750	0.000	0.000	0.211	0.0036	0.0000	0.0000
6780	0.000	0.000	0.211	0.0036	0.0000	0.0000
6810	0.000	0.000	0.211	0.0036	0.0000	0.0000
6840	0.000	0.000	0.211	0.0036	0.0000	0.0000
6870	0.000	0.000	0.211	0.0036	0.0000	0.0000
6900	0.000	0.000	0.211	0.0036	0.0000	0.0000
6930	0.000	0.000	0.211	0.0036	0.0000	0.0000
6960	0.000	0.000	0.211	0.0030	0.0000	0.0000
6990	0.000	0.000	0.211	0.0018	0.0000	0.0000
7020	0.000	0.000	0.211	0.0018	0.0000	0.0000
7050	0.000	0.000	0.211	0.0018	0.0000	0.0000
7080	0.000	0.000	0.211	0.0018	0.0000	0.0000
7110	0.000	0.000	0.211	0.0018	0.0000	0.0000
7140	0.000	0.000	0.211	0.0018	0.0000	0.0000
7170	0.000	0.000	0.211	0.0018	0.0000	0.0000
7200	0.000	0.000	0.211	0.0018	0.0000	0.0000

TOTAL RUNOFF LOSSES = 1.5182 CM = 1002.0239L

TOTAL SEDIMENT LOSSES = 2.0162 KG

PESTICIDE LOSSES:

DISSOLVED = 219.1730 MG

CRYSTALLINE = 0.0000 MG

ADSORBED = 3.8087 MG

TOTAL = 222.9812 MG

XX
XX

STORM 1, DAY 3

TOTAL SIMULATION TIME = 120 MIN = 7200 SEC

SIMULATION TIME INCREMENT = 30 SEC

LOSSES FROM OUTLET ELEMENT

TIME (SEC)	RUNOFF LOSSES (CM)	SEDIMENT LOSSES (KG)	DISS PEST CONC (MG/L)	DISS PEST LOSSES (MG)	CRYST PEST LOSSES (MG)	ADSORB PEST LOSSES (MG)
30	0.000	0.015	0.272	0.0131	0.0000	0.0107
60	0.001	0.044	0.269	0.0464	0.0000	0.0578
90	0.001	0.050	0.275	0.0934	0.0000	0.0803
120	0.002	0.054	0.270	0.1856	0.0000	0.0893
150	0.003	0.050	0.268	0.2976	0.0000	0.0863
180	0.005	0.081	0.265	0.4097	0.0000	0.1930
210	0.006	0.081	0.261	0.5189	0.0000	0.1925
240	0.007	0.083	0.256	0.6192	0.0000	0.1939
270	0.009	0.073	0.268	0.7575	0.0000	0.1787
300	0.010	0.032	0.261	0.8596	0.0000	0.0762
330	0.012	0.027	0.256	1.0523	0.0000	0.0577
360	0.015	0.027	0.254	1.2635	0.0000	0.0571
390	0.018	0.027	0.251	1.4766	0.0000	0.0565
420	0.021	0.027	0.248	1.6938	0.0000	0.0557
450	0.024	0.027	0.256	1.9928	0.0000	0.0577
480	0.026	0.027	0.251	2.1856	0.0000	0.0566
510	0.029	0.027	0.257	2.4664	0.0000	0.0579
540	0.032	0.027	0.251	2.6202	0.0000	0.0566
570	0.034	0.027	0.245	2.7493	0.0000	0.0552
600	0.036	0.027	0.249	2.9748	0.0000	0.0560
630	0.038	0.027	0.251	3.1796	0.0000	0.0566
660	0.040	0.027	0.244	3.2388	0.0000	0.0549

690	0.042	0.027	0.246	3.3997	0.0000	0.0553
720	0.043	0.027	0.247	3.5393	0.0000	0.0555
750	0.045	0.027	0.238	3.5301	0.0000	0.0537
780	0.046	0.027	0.247	3.7557	0.0000	0.0556
810	0.047	0.027	0.239	3.7092	0.0000	0.0537
840	0.048	0.027	0.246	3.8975	0.0000	0.0554
870	0.049	0.027	0.238	3.8185	0.0000	0.0534
900	0.049	0.027	0.244	3.9756	0.0000	0.0549
930	0.050	0.027	0.235	3.8720	0.0000	0.0530
960	0.050	0.027	0.241	4.0037	0.0000	0.0543
990	0.052	0.027	0.233	3.9725	0.0000	0.0524
1020	0.055	0.027	0.239	4.3552	0.0000	0.0538
1050	0.058	0.027	0.232	4.4389	0.0000	0.0521
1080	0.061	0.027	0.237	4.7289	0.0000	0.0533
1110	0.062	0.027	0.241	4.9703	0.0000	0.0542
1140	0.064	0.027	0.232	4.8933	0.0000	0.0521
1170	0.065	0.027	0.235	5.0482	0.0000	0.0529
1200	0.066	0.027	0.238	5.1675	0.0000	0.0535
1230	0.066	0.027	0.240	5.2582	0.0000	0.0540
1260	0.067	0.027	0.230	5.0523	0.0000	0.0517
1290	0.067	0.027	0.232	5.1025	0.0000	0.0522
1320	0.067	0.027	0.234	5.1384	0.0000	0.0526
1350	0.066	0.027	0.235	5.1643	0.0000	0.0530
1380	0.066	0.027	0.225	4.9223	0.0000	0.0507
1410	0.066	0.027	0.227	4.9393	0.0000	0.0511
1440	0.066	0.027	0.229	4.9553	0.0000	0.0514
1470	0.065	0.027	0.230	4.9698	0.0000	0.0518
1500	0.065	0.027	0.232	4.9859	0.0000	0.0522
1530	0.065	0.027	0.233	5.0028	0.0000	0.0525
1560	0.065	0.027	0.235	5.0222	0.0000	0.0529
1590	0.065	0.027	0.225	4.8045	0.0000	0.0507
1620	0.064	0.027	0.227	4.8302	0.0000	0.0511
1650	0.064	0.027	0.229	4.8588	0.0000	0.0515
1680	0.064	0.027	0.231	4.8898	0.0000	0.0519
1710	0.064	0.027	0.221	4.6930	0.0000	0.0498
1740	0.064	0.027	0.223	4.7300	0.0000	0.0502
1770	0.064	0.027	0.225	4.7672	0.0000	0.0506
1800	0.064	0.027	0.227	4.8064	0.0000	0.0510
1830	0.057	0.003	0.220	4.1357	0.0000	0.0091
1860	0.048	0.002	0.234	3.6924	0.0000	0.0083
1890	0.041	0.001	0.228	3.0439	0.0000	0.0027
1920	0.035	0.000	0.221	2.5437	0.0000	0.0000
1950	0.030	0.000	0.227	2.2322	0.0000	0.0000
1980	0.025	0.002	0.234	1.9301	0.0000	0.0055
2010	0.019	0.001	0.228	1.4649	0.0000	0.0027
2040	0.015	0.000	0.235	1.1885	0.0000	0.0000
2070	0.012	0.001	0.230	0.9120	0.0000	0.0027
2100	0.010	0.002	0.239	0.7631	0.0000	0.0056
2130	0.007	0.000	0.235	0.5298	0.0000	0.0000
2160	0.004	0.000	0.230	0.3406	0.0000	0.0000

2190	0.003	0.000	0.226	0.1987	0.0000	0.0000
2220	0.001	0.000	0.237	0.0979	0.0000	0.0000
2250	0.001	0.000	0.234	0.0564	0.0000	0.0000
2280	0.000	0.000	0.233	0.0362	0.0000	0.0000
2310	0.000	0.000	0.232	0.0276	0.0000	0.0000
2340	0.000	0.000	0.231	0.0216	0.0000	0.0000
2370	0.000	0.000	0.231	0.0183	0.0000	0.0000
2400	0.000	0.000	0.231	0.0170	0.0000	0.0000
2430	0.000	0.000	0.231	0.0157	0.0000	0.0000
2460	0.000	0.000	0.230	0.0157	0.0000	0.0000
2490	0.000	0.000	0.230	0.0157	0.0000	0.0000
2520	0.000	0.000	0.230	0.0157	0.0000	0.0000
2550	0.000	0.000	0.230	0.0137	0.0000	0.0000
2580	0.000	0.000	0.230	0.0137	0.0000	0.0000
2610	0.000	0.000	0.230	0.0137	0.0000	0.0000
2640	0.000	0.000	0.230	0.0137	0.0000	0.0000
2670	0.000	0.000	0.230	0.0137	0.0000	0.0000
2700	0.000	0.000	0.230	0.0137	0.0000	0.0000
2730	0.000	0.000	0.230	0.0137	0.0000	0.0000
2760	0.000	0.000	0.230	0.0130	0.0000	0.0000
2790	0.000	0.000	0.230	0.0117	0.0000	0.0000
2820	0.000	0.000	0.230	0.0117	0.0000	0.0000
2850	0.000	0.000	0.230	0.0117	0.0000	0.0000
2880	0.000	0.000	0.230	0.0117	0.0000	0.0000
2910	0.000	0.000	0.230	0.0117	0.0000	0.0000
2940	0.000	0.000	0.230	0.0117	0.0000	0.0000
2970	0.000	0.000	0.229	0.0117	0.0000	0.0000
3000	0.000	0.000	0.229	0.0117	0.0000	0.0000
3030	0.000	0.000	0.229	0.0117	0.0000	0.0000
3060	0.000	0.000	0.229	0.0104	0.0000	0.0000
3090	0.000	0.000	0.229	0.0097	0.0000	0.0000
3120	0.000	0.000	0.229	0.0097	0.0000	0.0000
3150	0.000	0.000	0.229	0.0097	0.0000	0.0000
3180	0.000	0.000	0.229	0.0097	0.0000	0.0000
3210	0.000	0.000	0.229	0.0097	0.0000	0.0000
3240	0.000	0.000	0.229	0.0097	0.0000	0.0000
3270	0.000	0.000	0.229	0.0097	0.0000	0.0000
3300	0.000	0.000	0.229	0.0097	0.0000	0.0000
3330	0.000	0.000	0.229	0.0097	0.0000	0.0000
3360	0.000	0.000	0.229	0.0097	0.0000	0.0000
3390	0.000	0.000	0.229	0.0097	0.0000	0.0000
3420	0.000	0.000	0.229	0.0091	0.0000	0.0000
3450	0.000	0.000	0.229	0.0078	0.0000	0.0000
3480	0.000	0.000	0.229	0.0078	0.0000	0.0000
3510	0.000	0.000	0.229	0.0078	0.0000	0.0000
3540	0.000	0.000	0.229	0.0078	0.0000	0.0000
3570	0.000	0.000	0.229	0.0078	0.0000	0.0000
3600	0.000	0.000	0.229	0.0078	0.0000	0.0000
3630	0.000	0.000	0.229	0.0078	0.0000	0.0000
3660	0.000	0.000	0.229	0.0078	0.0000	0.0000

6690	0.000	0.000	0.227	0.0019	0.0000	0.0000
6720	0.000	0.000	0.227	0.0019	0.0000	0.0000
6750	0.000	0.000	0.227	0.0019	0.0000	0.0000
6780	0.000	0.000	0.227	0.0019	0.0000	0.0000
6810	0.000	0.000	0.227	0.0019	0.0000	0.0000
6840	0.000	0.000	0.227	0.0019	0.0000	0.0000
6870	0.000	0.000	0.227	0.0019	0.0000	0.0000
6900	0.000	0.000	0.227	0.0019	0.0000	0.0000
6930	0.000	0.000	0.227	0.0019	0.0000	0.0000
6960	0.000	0.000	0.227	0.0019	0.0000	0.0000
6990	0.000	0.000	0.227	0.0019	0.0000	0.0000
7020	0.000	0.000	0.227	0.0019	0.0000	0.0000
7050	0.000	0.000	0.227	0.0019	0.0000	0.0000
7080	0.000	0.000	0.227	0.0019	0.0000	0.0000
7110	0.000	0.000	0.227	0.0019	0.0000	0.0000
7140	0.000	0.000	0.227	0.0019	0.0000	0.0000
7170	0.000	0.000	0.227	0.0019	0.0000	0.0000
7200	0.000	0.000	0.227	0.0019	0.0000	0.0000

TOTAL RUNOFF LOSSES = 1.4742 CM = 972.9868L
 TOTAL SEDIMENT LOSSES = 1.9146 KG
 PESTICIDE LOSSES:
 DISSOLVED = 228.8456 MG
 CRYSTALLINE = 0.0000 MG
 ADSORBED = 3.8759 MG
 TOTAL = 232.7212 MG

XX
 XXX

STORM 2, DAY 3
 TOTAL SIMULATION TIME = 120 MIN = 7200 SEC
 SIMULATION TIME INCREMENT = 30 SEC

LOSSES FROM OUTLET ELEMENT

TIME (SEC)	RUNOFF LOSSES (CM)	SEDIMENT LOSSES (KG)	DISS PEST CONC (MG/L)	DISS PEST LOSSES (MG)	CRYST PEST LOSSES (MG)	ADSORB PEST LOSSES (MG)
30	0.000	0.060	0.225	0.0313	0.0000	0.0656

60	0.002	0.110	0.237	0.1407	0.0000	0.1661
90	0.004	0.100	0.234	0.2956	0.0000	0.1546
120	0.007	0.167	0.231	0.5003	0.0000	0.3401
150	0.010	0.169	0.229	0.7517	0.0000	0.3422
180	0.014	0.095	0.227	1.0310	0.0000	0.1913
210	0.018	0.054	0.224	1.3309	0.0000	0.1084
240	0.023	0.054	0.222	1.6490	0.0000	0.1072
270	0.028	0.054	0.229	2.0833	0.0000	0.1109
300	0.034	0.054	0.216	2.3975	0.0000	0.1046
330	0.040	0.054	0.224	2.9420	0.0000	0.1081
360	0.046	0.054	0.221	3.3870	0.0000	0.1067
390	0.053	0.054	0.218	3.8313	0.0000	0.1052
420	0.060	0.054	0.223	4.4325	0.0000	0.1078
450	0.067	0.054	0.211	4.6560	0.0000	0.1019
480	0.073	0.054	0.215	5.2100	0.0000	0.1040
510	0.079	0.054	0.219	5.7283	0.0000	0.1058
540	0.085	0.054	0.222	6.1968	0.0000	0.1073
570	0.089	0.054	0.209	6.1477	0.0000	0.1009
600	0.093	0.054	0.211	6.4795	0.0000	0.1020
630	0.096	0.054	0.213	6.7479	0.0000	0.1028
660	0.098	0.054	0.214	6.9550	0.0000	0.1034
690	0.100	0.054	0.215	7.1062	0.0000	0.1039
720	0.101	0.054	0.216	7.2092	0.0000	0.1042
750	0.102	0.054	0.216	7.2710	0.0000	0.1045
780	0.102	0.054	0.217	7.3019	0.0000	0.1047
810	0.102	0.054	0.217	7.3072	0.0000	0.1048
840	0.102	0.054	0.217	7.2960	0.0000	0.1048
870	0.102	0.054	0.217	7.2740	0.0000	0.1049
900	0.101	0.054	0.203	6.7657	0.0000	0.0980
930	0.101	0.054	0.203	6.7419	0.0000	0.0981
960	0.100	0.054	0.203	6.7172	0.0000	0.0981
990	0.100	0.054	0.203	6.6962	0.0000	0.0982
1020	0.099	0.054	0.203	6.6806	0.0000	0.0984
1050	0.099	0.054	0.204	6.6699	0.0000	0.0985
1080	0.099	0.054	0.204	6.6643	0.0000	0.0986
1110	0.099	0.054	0.204	6.6658	0.0000	0.0988
1140	0.099	0.054	0.205	6.6739	0.0000	0.0989
1170	0.099	0.054	0.205	6.6857	0.0000	0.0991
1200	0.099	0.054	0.205	6.6951	0.0000	0.0993
1230	0.099	0.054	0.206	6.7074	0.0000	0.0994
1260	0.099	0.054	0.206	6.7244	0.0000	0.0996
1290	0.099	0.054	0.206	6.7444	0.0000	0.0998
1320	0.099	0.054	0.207	6.7722	0.0000	0.1000
1350	0.099	0.054	0.207	6.8042	0.0000	0.1002
1380	0.100	0.054	0.208	6.8427	0.0000	0.1004
1410	0.100	0.054	0.208	6.8844	0.0000	0.1007
1440	0.101	0.054	0.209	6.9298	0.0000	0.1009
1470	0.101	0.054	0.196	6.5405	0.0000	0.0948
1500	0.102	0.054	0.197	6.5897	0.0000	0.0950
1530	0.102	0.054	0.197	6.6386	0.0000	0.0953

1560	0.103	0.054	0.198	6.6875	0.0000	0.0955
1590	0.103	0.054	0.198	6.7329	0.0000	0.0958
1620	0.103	0.054	0.199	6.7764	0.0000	0.0960
1650	0.104	0.054	0.199	6.8157	0.0000	0.0962
1680	0.104	0.054	0.199	6.8519	0.0000	0.0964
1710	0.104	0.054	0.200	6.8839	0.0000	0.0966
1740	0.105	0.054	0.200	6.9121	0.0000	0.0967
1770	0.105	0.054	0.200	6.9367	0.0000	0.0969
1800	0.105	0.054	0.201	6.9571	0.0000	0.0970
1830	0.098	0.032	0.197	6.3718	0.0000	0.0574
1860	0.088	0.022	0.206	6.0021	0.0000	0.0402
1890	0.080	0.017	0.202	5.3191	0.0000	0.0280
1920	0.072	0.016	0.199	4.6942	0.0000	0.0282
1950	0.064	0.010	0.209	4.4108	0.0000	0.0210
1980	0.057	0.003	0.205	3.8627	0.0000	0.0085
2010	0.050	0.002	0.201	3.3480	0.0000	0.0071
2040	0.044	0.001	0.198	2.8478	0.0000	0.0023
2070	0.038	0.000	0.209	2.6182	0.0000	0.0000
2100	0.033	0.011	0.206	2.2557	0.0000	0.0192
2130	0.029	0.015	0.203	1.9402	0.0000	0.0265
2160	0.025	0.011	0.200	1.6705	0.0000	0.0207
2190	0.022	0.003	0.206	1.4974	0.0000	0.0085
2220	0.019	0.002	0.212	1.3451	0.0000	0.0075
2250	0.016	0.001	0.209	1.1334	0.0000	0.0025
2280	0.014	0.006	0.207	0.9427	0.0000	0.0095
2310	0.012	0.014	0.205	0.7853	0.0000	0.0251
2340	0.010	0.010	0.203	0.6556	0.0000	0.0205
2370	0.008	0.003	0.202	0.5555	0.0000	0.0083
2400	0.007	0.002	0.200	0.4691	0.0000	0.0071
2430	0.006	0.001	0.207	0.3929	0.0000	0.0024
2460	0.004	0.000	0.215	0.3186	0.0000	0.0000
2490	0.004	0.000	0.213	0.2472	0.0000	0.0000
2520	0.003	0.000	0.212	0.1925	0.0000	0.0000
2550	0.002	0.000	0.212	0.1432	0.0000	0.0000
2580	0.001	0.000	0.211	0.0955	0.0000	0.0000
2610	0.001	0.000	0.210	0.0684	0.0000	0.0000
2640	0.001	0.000	0.209	0.0456	0.0000	0.0000
2670	0.000	0.000	0.209	0.0301	0.0000	0.0000
2700	0.000	0.000	0.208	0.0230	0.0000	0.0000
2730	0.000	0.000	0.208	0.0183	0.0000	0.0000
2760	0.000	0.000	0.208	0.0165	0.0000	0.0000
2790	0.000	0.000	0.208	0.0147	0.0000	0.0000
2820	0.000	0.000	0.208	0.0141	0.0000	0.0000
2850	0.000	0.000	0.208	0.0141	0.0000	0.0000
2880	0.000	0.000	0.208	0.0141	0.0000	0.0000
2910	0.000	0.000	0.208	0.0129	0.0000	0.0000
2940	0.000	0.000	0.207	0.0123	0.0000	0.0000
2970	0.000	0.000	0.207	0.0123	0.0000	0.0000
3000	0.000	0.000	0.207	0.0123	0.0000	0.0000
3030	0.000	0.000	0.207	0.0123	0.0000	0.0000

3060	0.000	0.000	0.207	0.0123	0.0000	0.0000
3090	0.000	0.000	0.207	0.0123	0.0000	0.0000
3120	0.000	0.000	0.207	0.0112	0.0000	0.0000
3150	0.000	0.000	0.207	0.0106	0.0000	0.0000
3180	0.000	0.000	0.207	0.0106	0.0000	0.0000
3210	0.000	0.000	0.207	0.0106	0.0000	0.0000
3240	0.000	0.000	0.207	0.0106	0.0000	0.0000
3270	0.000	0.000	0.207	0.0106	0.0000	0.0000
3300	0.000	0.000	0.207	0.0106	0.0000	0.0000
3330	0.000	0.000	0.207	0.0106	0.0000	0.0000
3360	0.000	0.000	0.207	0.0106	0.0000	0.0000
3390	0.000	0.000	0.207	0.0088	0.0000	0.0000
3420	0.000	0.000	0.207	0.0088	0.0000	0.0000
3450	0.000	0.000	0.207	0.0088	0.0000	0.0000
3480	0.000	0.000	0.207	0.0088	0.0000	0.0000
3510	0.000	0.000	0.207	0.0088	0.0000	0.0000
3540	0.000	0.000	0.207	0.0088	0.0000	0.0000
3570	0.000	0.000	0.207	0.0088	0.0000	0.0000
3600	0.000	0.000	0.207	0.0088	0.0000	0.0000
3630	0.000	0.000	0.207	0.0088	0.0000	0.0000
3660	0.000	0.000	0.207	0.0088	0.0000	0.0000
3690	0.000	0.000	0.207	0.0088	0.0000	0.0000
3720	0.000	0.000	0.207	0.0076	0.0000	0.0000
3750	0.000	0.000	0.207	0.0070	0.0000	0.0000
3780	0.000	0.000	0.207	0.0070	0.0000	0.0000
3810	0.000	0.000	0.207	0.0070	0.0000	0.0000
3840	0.000	0.000	0.207	0.0070	0.0000	0.0000
3870	0.000	0.000	0.207	0.0070	0.0000	0.0000
3900	0.000	0.000	0.207	0.0070	0.0000	0.0000
3930	0.000	0.000	0.207	0.0070	0.0000	0.0000
3960	0.000	0.000	0.207	0.0070	0.0000	0.0000
3990	0.000	0.000	0.207	0.0070	0.0000	0.0000
4020	0.000	0.000	0.207	0.0070	0.0000	0.0000
4050	0.000	0.000	0.207	0.0070	0.0000	0.0000
4080	0.000	0.000	0.207	0.0070	0.0000	0.0000
4110	0.000	0.000	0.207	0.0070	0.0000	0.0000
4140	0.000	0.000	0.207	0.0070	0.0000	0.0000
4170	0.000	0.000	0.207	0.0070	0.0000	0.0000
4200	0.000	0.000	0.206	0.0053	0.0000	0.0000
4230	0.000	0.000	0.206	0.0053	0.0000	0.0000
4260	0.000	0.000	0.206	0.0053	0.0000	0.0000
4290	0.000	0.000	0.206	0.0053	0.0000	0.0000
4320	0.000	0.000	0.206	0.0053	0.0000	0.0000
4350	0.000	0.000	0.206	0.0053	0.0000	0.0000
4380	0.000	0.000	0.206	0.0053	0.0000	0.0000
4410	0.000	0.000	0.206	0.0053	0.0000	0.0000
4440	0.000	0.000	0.206	0.0053	0.0000	0.0000
4470	0.000	0.000	0.206	0.0053	0.0000	0.0000
4500	0.000	0.000	0.206	0.0053	0.0000	0.0000
4530	0.000	0.000	0.206	0.0053	0.0000	0.0000

6060	0.000	0.000	0.206	0.0035	0.0000	0.0000
6090	0.000	0.000	0.206	0.0035	0.0000	0.0000
6120	0.000	0.000	0.206	0.0035	0.0000	0.0000
6150	0.000	0.000	0.206	0.0029	0.0000	0.0000
6180	0.000	0.000	0.206	0.0017	0.0000	0.0000
6210	0.000	0.000	0.206	0.0017	0.0000	0.0000
6240	0.000	0.000	0.206	0.0017	0.0000	0.0000
6270	0.000	0.000	0.206	0.0017	0.0000	0.0000
6300	0.000	0.000	0.206	0.0017	0.0000	0.0000
6330	0.000	0.000	0.206	0.0017	0.0000	0.0000
6360	0.000	0.000	0.206	0.0017	0.0000	0.0000
6390	0.000	0.000	0.206	0.0017	0.0000	0.0000
6420	0.000	0.000	0.206	0.0017	0.0000	0.0000
6450	0.000	0.000	0.206	0.0017	0.0000	0.0000
6480	0.000	0.000	0.206	0.0017	0.0000	0.0000
6510	0.000	0.000	0.206	0.0017	0.0000	0.0000
6540	0.000	0.000	0.206	0.0017	0.0000	0.0000
6570	0.000	0.000	0.206	0.0017	0.0000	0.0000
6600	0.000	0.000	0.206	0.0017	0.0000	0.0000
6630	0.000	0.000	0.206	0.0017	0.0000	0.0000
6660	0.000	0.000	0.206	0.0017	0.0000	0.0000
6690	0.000	0.000	0.206	0.0017	0.0000	0.0000
6720	0.000	0.000	0.206	0.0017	0.0000	0.0000
6750	0.000	0.000	0.206	0.0017	0.0000	0.0000
6780	0.000	0.000	0.206	0.0017	0.0000	0.0000
6810	0.000	0.000	0.206	0.0017	0.0000	0.0000
6840	0.000	0.000	0.206	0.0017	0.0000	0.0000
6870	0.000	0.000	0.206	0.0017	0.0000	0.0000
6900	0.000	0.000	0.206	0.0017	0.0000	0.0000
6930	0.000	0.000	0.206	0.0017	0.0000	0.0000
6960	0.000	0.000	0.206	0.0017	0.0000	0.0000
6990	0.000	0.000	0.206	0.0017	0.0000	0.0000
7020	0.000	0.000	0.206	0.0017	0.0000	0.0000
7050	0.000	0.000	0.206	0.0017	0.0000	0.0000
7080	0.000	0.000	0.206	0.0017	0.0000	0.0000
7110	0.000	0.000	0.206	0.0017	0.0000	0.0000
7140	0.000	0.000	0.206	0.0017	0.0000	0.0000
7170	0.000	0.000	0.206	0.0017	0.0000	0.0000
7200	0.000	0.000	0.206	0.0017	0.0000	0.0000

TOTAL RUNOFF LOSSES = 2.8410 CM = 1875.0928L

TOTAL SEDIMENT LOSSES = 3.7846 KG

PESTICIDE LOSSES:

DISSOLVED = 388.1604 MG

CRYSTALLINE = 0.0000 MG

ADSORBED = 7.0669 MG

TOTAL = 395.2231 MG

XX
XX

SUMMARY OF DAILY LOSSES

	AVE	DEGRAD	NO OF	RUNOFF	SED	DISS	ADS	TOT
DAY	TEMP	LOSSES	STORMS	LOSSES	LOSSES	LOSSES	LOSSES	SURFACE
	(C)	(MG)		(CM)	(KG)	(MG)	(MG)	(MG)
1	27.5	338.89	0	0.00	0.00	0.000	0.000	0.000
2	26.3	1158.89	1	1.52	2.02	219.173	3.809	222.981
3	25.4	1988.43	2	4.32	5.70	388.160	7.067	395.223

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Appendix E: Data from Field Plot Studies

Atrazine concentrations in runoff water (g/m³).

Run Sample	QF1	QF2	QF3	QF4	QF5	QF6
R1						
3	0.140	0.524	0.377	0.848	---	0.910
8	0.195	0.539	0.299	0.523	---	0.875
13	0.260	0.819	0.317	0.383	---	0.579
20	0.286	0.387	0.244	0.236	---	0.482
30	0.409	0.440	0.255	0.344	---	0.248
45	---	0.527	---	0.189	---	0.133
R2						
3	0.294	0.384	0.518	0.560	---	0.367
10	0.138	0.337	0.271	0.135	---	0.250
20	---	0.287	0.265	0.174	---	0.265
30	---	---	---	0.159	---	---
R3						
3	0.233	0.349	0.197	0.183	0.303	0.247
10	0.232	0.259	0.159	---	0.197	0.148
20	0.207	0.185	---	0.076	0.153	0.168
30	0.246	0.320	---	0.101	0.194	0.153
	QFA	QFB	QFC	QFD	QFE	QFF
R1						
3	---	0.934	0.690	0.916	0.754	0.355
8	0.869	0.454	0.543	0.649	0.568	0.554
13	0.613	0.666	0.707	0.459	0.831	0.584
20	0.477	0.501	0.674	0.470	0.483	0.453
30	0.516	0.075	0.525	0.377	0.281	0.335
45	---	0.031	0.482	0.612	0.574	0.418
R2						
3	0.431	0.442	0.428	0.442	0.162	0.526
10	0.346	0.196	0.223	0.196	0.204	0.002
20	0.216	0.146	0.191	0.165	0.132	0.210
30	---	0.107	0.370	---	0.126	---
R3						
3	0.234	0.124	0.214	0.202	0.073	0.115
10	0.176	0.065	0.115	0.119	0.032	0.110
20	0.150	0.061	---	0.152	0.078	0.113
30	---	0.061	0.197	---	0.086	0.113

2,4-D concentrations in runoff water (g/m³).

Run Sample	QF1	QF2	QF3	QF4	QF5	QF6
R1						
3	0.009	ND	0.001	0.001	---	0.024
8	0.003	ND	0.002	---	---	0.048
13	0.010	ND	0.001	ND	---	0.022
20	0.000	0.000	0.005	ND	---	0.000
30	ND	ND	0.011	0.000	---	0.001
45	---	0.003	---	---	---	0.009
R2						
3	ND	0.067	---	0.002	---	ND
10	0.055	0.057	0.005	ND	---	0.006
20	---	0.032	0.002	ND	---	0.005
30	---	---	---	0.002	---	---
R3						
3	---	0.001	0.000	ND	0.005	0.004
10	0.006	0.000	0.000	0.002	0.000	0.003
20	ND	0.001	---	0.003	ND	0.000
30	ND	---	---	0.000	0.001	---
	QFA	QFB	QFC	QFD	QFE	QFF
R1						
3	0.012	ND	0.360	0.012	ND	0.124
8	0.001	ND	0.059	ND	ND	0.172
13	0.005	0.000	0.236	0.018	0.001	0.133
20	ND	ND	0.289	0.013	---	0.058
30	0.000	ND	0.124	0.015	0.007	0.063
45	---	0.000	0.121	0.000	---	0.000
R2						
3	ND	0.003	0.011	0.003	0.001	0.002
10	ND	ND	ND	ND	ND	0.010
20	0.000	ND	0.000	---	0.001	0.004
30	---	0.004	0.001	---	ND	---
R3						
3	0.001	0.002	ND	0.020	ND	0.010
10	0.002	0.002	ND	0.001	0.007	0.001
20	0.001	0.001	---	ND	0.003	0.001
30	---	0.002	ND	---	0.001	0.002

Atrazine concentrations in sediment (g/Mg).

Run Sample	QF1	QF2	QF3	QF4	QF5	QF6
R1						
3	0.460	0.520	0.000	0.140	---	0.050
8	---	0.130	0.000	0.090	---	0.100
13	0.000	0.220	0.000	0.050	---	0.060
20	0.490	0.030	0.130	0.020	---	0.060
30	0.310	0.050	0.000	0.010	---	0.020
45	---	0.080	---	0.020	---	0.000
R2						
3	0.000	0.030	---	0.000	---	0.050
10	0.000	0.000	0.150	0.340	---	---
20	---	---	1.440	0.040	---	0.080
30	---	---	---	---	---	---
R3						
3	---	0.400	0.770	0.000	0.380	0.040
10	---	0.190	0.000	0.010	0.000	0.000
20	0.210	---	---	0.000	0.000	0.030
30	0.170	---	---	0.010	0.380	0.370
<hr/>						
	QFA	QFB	QFC	QFD	QFE	QFF
R1						
3	0.120	0.470	---	0.160	0.250	---
8	0.210	0.190	---	0.240	0.120	---
13	0.140	0.070	---	---	0.380	---
20	0.330	0.070	---	0.200	---	---
30	0.580	0.140	---	0.260	0.060	---
45	---	0.030	---	---	---	.0200
R2						
3	0.290	0.240	0.120	0.120	0.240	0.090
10	0.540	0.200	0.080	0.200	0.170	0.090
20	0.480	0.250	0.140	0.250	0.030	0.110
30	---	0.050	0.260	---	0.060	---
R3						
3	0.240	0.020	0.000	0.370	0.030	0.090
10	0.320	0.050	0.040	0.350	---	0.110
20	0.410	0.000	---	0.340	0.040	0.180
30	---	0.100	0.000	---	0.070	0.140

2,4-D concentrations in sediment (g/Mg).

Run Sample	QF1	QF2	QF3	QF4	QF5	QF6
R1						
3	0.340	0.000	0.000	0.030	---	0.000
8	---	0.000	0.160	0.010	---	0.090
13	0.000	0.010	0.250	0.000	---	0.000
20	0.070	0.000	0.000	0.000	---	0.020
30	0.000	0.000	0.000	0.010	---	0.030
45	---	0.000	---	0.000	---	0.110
R2						
3	0.160	0.000	---	0.020	---	0.000
10	---	---	0.050	0.520	---	---
20	---	---	0.110	0.000	---	0.020
30	---	---	---	---	---	---
R3						
3	---	0.000	0.340	0.050	0.400	0.010
10	---	0.020	0.000	0.010	0.470	0.150
20	0.200	---	---	0.020	0.340	0.020
30	0.110	---	---	0.020	0.210	0.260
	QFA	QFB	QFC	QFD	QFE	QFF
R1						
3	0.000	0.010	---	0.000	0.000	---
8	0.040	0.020	---	0.000	0.000	---
13	0.120	0.000	---	---	0.020	---
20	---	0.020	---	---	---	---
30	0.050	0.010	---	0.170	0.080	---
45	---	0.000	---	---	---	0.030
R2						
3	0.170	0.200	0.030	0.200	0.130	0.380
10	---	0.340	0.140	0.340	0.160	0.090
20	0.240	0.110	0.140	0.110	0.030	0.050
30	---	0.040	0.090	---	0.040	---
R3						
3	0.410	0.010	0.040	0.110	0.010	0.180
10	0.410	0.030	0.000	0.090	---	0.200
20	0.280	0.020	---	0.380	0.020	0.650
30	---	0.080	0.060	---	---	0.310

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