

**Herbicides in Runoff From Agricultural Watersheds
in a High-Winter-Rainfall Zone**

by

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ABSTRACT

Relatively few studies have been made on the behavior of pesticides in relation to runoff from agricultural watersheds in the high-winter-rainfall zone of the northwestern United States. This study was designed to quantify runoff losses of two herbicides, diclofop-methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propanoate] and trifluralin [α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine], from small agricultural watersheds in the Willamette Valley, Oregon and identify factors and processes influencing herbicide transport in this region. Various diclofop-methyl soil interactions were also studied under conditions typically following a winter application of diclofop-methyl in western Oregon.

Diclofop-methyl hydrolysis, degradation, and leaching were studied in field and laboratory experiments. Greater than 75% of the applied diclofop-methyl hydrolyzed to diclofop in 2 days at 4°C, the prevailing soil temperature during western Oregon winters. Degradation beyond the diclofop molecule, also an active herbicide, was much slower with a half life of 42 days. Microbial activity was identified as the primary mechanism in both the hydrolysis and degradation processes. Diclofop residues were detected in the 1-5 and 5-10 cm depths, indicating that leaching had occurred.

Runoff losses of diclofop [2-(4-(2,4-dichlorophenoxy)phenoxy) propionic acid] were measured following January diclofop-methyl applications (1.12 kg/ha) to small (6.0 and 1.4 ha) agricultural watersheds in the Willamette Valley, Oregon. Diclofop runoff losses were higher in 1980 (7.1 and 3.9% of the applied herbicide at the 6.0 and 1.4 ha watersheds, respectively) than in 1981 (0.7 and <0.1%, respectively). In 1980, between 80 and 90% of the diclofop seasonal loss was partitioned into the aqueous phase of runoff. The maximum diclofop concentrations in runoff were 370 and 790 mg/m³ at the 6.0 and 1.4 ha watersheds, respectively. Larger diclofop losses in 1980 were attributed to (1) the close proximity of large runoff events to

the application date and (2) the high antecedent soil moisture status prior to the first runoff event which resulted in a high percentage runoff. The presence of a soil surface crust limited the depth to which overland flow extracted diclofop residues from the soil profile and resulted in very shallow calculated mixing depths (< 0.2 cm).

A subsurface drainage system installed at the 1.4 ha watershed effectively lowered antecedent soil moisture as compared to the 6.0 ha watershed. Consequently, percentage runoff and diclofop runoff losses were reduced at the 1.4 ha watershed. Diclofop losses in the subsurface drainage effluent accounted for 1.2 and $< 0.1\%$ of the applied herbicide in 1980 and 1981, respectively. Subsurface drainage and delaying the herbicide application date were recommended as potential management practices for reducing diclofop runoff losses.

Runoff losses of trifluralin were measured following a surface application (0.84 kg/ha) in late October, 1979. Trifluralin runoff losses were 0.9 and $< 0.1\%$ of the applied herbicide and maximum concentrations were 216 and 9.5 mg/m^3 at the 6.0 and 1.4 ha watersheds, respectively. A majority of the trifluralin lost in overland flow occurred in the first runoff event at the 6.0 ha watershed. The relatively large loss in this single event (0.6% of applied) was attributed to the close proximity of the runoff event (7 hours) to the application date and to the lack of herbicide incorporation. The low trifluralin seasonal loss at the 1.4 ha watershed reflected the effectiveness of the subsurface drainage system in reducing discharge, sediment loss, and percentage runoff at the 1.4 ha watershed as compared to the 6.0 ha watershed. Trifluralin was only detected (1.7 mg/m^3) in one of seven effluent samples collected from the effluent from the subsurface drainage system. Subsurface drainage was also recommended as a potential management practice to reduce trifluralin runoff losses.

FOREWORD

The Water Resources Research Institute, located on the Oregon State University campus, serves the State of Oregon. The Institute fosters, encourages, and facilitates water resources research and education involving all aspects of the quality and quantity of water available for beneficial use. The Institute administers and coordinates statewide and regional programs of multidisciplinary research in water and related land resources. The Institute provides a necessary communications and coordination link between the agencies of local, state, and federal government, as well as the private sector, and the broad research community at universities in the state on matters of water-related research. The Institute also coordinates the inter-disciplinary program of graduate education in water resources at Oregon State University.

It is Institute policy to make available the results of significant water-related research conducted in Oregon universities and colleges. The Institute neither endorses nor rejects the findings of the authors of such research. It does recommend careful consideration of the accumulated facts by those concerned with the solution of water-related problems.

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INTRODUCTION

Modern agriculture has become quite dependent on the use of pesticides. Their use has been dictated by the demand for greater production and by the utilization of relatively large areas for monoculture which is most favorable for the development of various pest problems. Although pesticides have permitted greater productivity, extensive use of these chemicals has elicited concern over possible environmental contamination resulting from their movement from treated areas. Much of this concern has been focused on the effect that pesticide use may have on water quality. In recognition of this problem, Congress passed an amendment to the Federal Water Pollution Control Act which requires states to identify nonpoint sources of pollution. One such source of water pollution is the transport of pesticides from agricultural lands (Stewart and Woolhiser, 1976).

Mechanisms by which off-site contamination of water occur from the agricultural use of pesticides include drift or non-target deposition, volatilization, percolation into ground water, and runoff from agricultural watersheds. Of these four mechanisms, the latter is potentially the greatest source of contamination. A number of studies have shown that pesticide residues are often runoff contaminants in drainage waters (Merkle and Bovey, 1974; Caro, 1976; Wauchope, 1978).

Forests dominate the major watersheds in the high-winter-rainfall zone of the Pacific Northwest. Consequently, most pesticide runoff studies have been concerned with chemicals used in forest regeneration programs. Small amounts of these chemicals have been found in streams emanating from treated watersheds. Pesticide residues in streams are usually associated with direct stream contamination during application, but low levels may persist over varying periods of time.

The potential for water contamination resulting from herbicide use may be greater on agricultural land than in forested areas. Results of forest watershed studies cannot be extrapolated to agricultural land for the following reasons:

1. Agricultural lands may receive one or more applications of herbicides per year, while a forested area will normally receive one or two applications during a regeneration cycle (40-80 years).
2. Surface runoff from agricultural lands is much greater than from forested areas which contain very porous soils. Soils on the forest floor also contain surface layers of organic matter which immobilize herbicide residues.
3. A wider range of chemicals are applied to agricultural land than are applied to forested areas.

Relatively few studies have been made on the behavior of herbicides in relation to runoff from agricultural lands in the high-winter-rainfall zone of the northwestern United States. Much of the northwestern region is characterized by a xeric moisture regime; it is the only region in the United States with this regime. This regime is associated with a mediterranean type climate which has warm-dry summers and cool-moist winters. Winter precipitation comes as frequent, low intensity frontal type-storms.

In addition to these unique climatic conditions, the northwestern United States also has a large number of soils developed on volcanic parent material. Many of these soils possess amorphous and poorly crystalline components which exhibit highly variable cation-anion exchange capacities in relation to the pH of the media. Thus, they are expected to influence the adsorption and movement of herbicides.

The greatest potential for degradation of water quality in surface runoff in the region is annual cropping on "hill soils" which surround the Willamette Valley. Crops are fall seeded so that cover is often minimal at the onset of the winter rainfall season and the potential for runoff is high. Herbicides can be applied in the fall, winter, or early spring. Lower temperatures in late fall and winter retard chemical and biological degradation of the herbicides. Consequently, herbicides applied in the late fall and winter may persist longer than for other management systems involving spring applications. The chemicals are also subject to loss by transport in runoff during the high-winter-rainfall season.

Objectives

This study was designed to determine the extent to which runoff of two herbicides, diclofop-methyl [methyl 2-(4-(2,4-dichlorophenoxy) phenoxy) propanoate] and trifluralin [α,α,α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine], contributed to water pollution in the high-winter-rainfall zone of the Pacific Northwest. The two herbicides chosen for study had different chemical characteristics and were applied at different times in the year. The two different application dates provided distinctive soil and climatic conditions for each herbicide runoff study.

Specific objectives of this study were:

1. To determine the degree to which diclofop-methyl and trifluralin residues were present in runoff waters from agricultural watersheds in the high-winter-rainfall zone of the Pacific Northwest.
2. To relate runoff losses of the herbicides to storm intensities and cycles, soil characteristics, herbicide chemical properties, and hydrologic processes.
3. To suggest improved management practices for the reduction of herbicide load in the event that significant degradation of water quality is found.

The study was coordinated with the STEEP (Solutions to Environmental and Economic Problems) runoff and erosion project at Oregon State University. The ongoing project provided background data to relate the runoff losses of herbicides to various soil properties and hydrologic processes. Coordination of these two studies avoided duplication of effort and maximized the return of scientific information per dollar of investment.

LITERATURE REVIEW

Pesticide Runoff Losses

Considerable information has been collected on pesticide residues in agricultural runoff from other regions of the United States. Pesticide losses vary with both the specific soil and hydrologic properties of the watershed as well as the chemical properties of the pesticide (Pionke and Chesters, 1973; Merkle and Bovey, 1974; Caro, 1976, Wauchope, 1978).

The magnitude of pesticide losses is controlled principally by the proximity of the runoff event to the application date and the availability of the chemical at the soil surface (Merkle and Bovey, 1974; Smith et al., 1978; Wauchope, 1978). Pesticide runoff losses are generally highest in the first runoff event after application (Merkle and Bovey, 1974; Caro, 1976). The effect of storm timing has more impact on seasonal losses of shorter lived pesticides than it has for persistent and incorporated pesticides (Caro, 1976).

Pesticides have been classified into three categories according to their seasonal runoff losses (Wauchope, 1978). Water soluble pesticides applied as aqueous solutions and incorporated pesticides had the lowest seasonal losses, usually less than 0.5 percent of the applied pesticide. Pesticides which were more water insoluble (often applied as emulsions) usually had losses less than one percent and comprised the next category. The highest long term or seasonal losses were found for pesticides formulated as wettable powders. Losses from 2-5 percent were common for pesticides in this category. Critical events often resulted in seasonal losses two or three times higher than the seasonal losses normally found for the three pesticide categories (Wauchope, 1978). Wauchope (1978) defines a critical runoff event as an event occurring within two weeks of application and having at least 50 percent runoff from 1 cm or more of precipitation.

Pesticide concentrations in runoff also decrease with time after application (Caro, 1976; Wauchope, 1978; Wauchope and Leonard, 1980). Factors which influence concentration levels in runoff include storm intensity and timing, rate of application, formulation, and field site

characteristics. Very high concentrations are often associated with low runoff volume events soon after application or for very soluble pesticides if runoff occurs before the chemical is leached into the soil. Pesticide concentrations are usually higher in the sediment phase than the aqueous phase of runoff (Merkle and Bovey, 1974; Wauchope, 1978). More pesticide, however, is generally lost in the aqueous phase because of the higher proportion of runoff water compared to sediment. Pesticides with solubilities greater than 1 ppm are lost primarily in the aqueous phase of runoff (Wauchope, 1978). The exceptions include very strongly adsorbed pesticides such as paraquat [1,1'-dimethyl-4,4'-bipyridinium ion] and soils with very high adsorptive capacities. The proportion of pesticide lost in the sediment phase of runoff usually increases in successive runoff events (Wauchope, 1978).

Pesticide removed in the sediment phase of runoff is generally associated with soil erosion. Quite often the sediment lost in the erosion process is enriched with clay, silt, and organic matter which have higher carrying capacities for pesticides and therefore higher concentrations of pesticide than the bulk soil material (Bailey et al., 1974; Bruce et al., 1975). Mechanisms by which a pesticide is lost in the aqueous phase of runoff include dissolution of the pesticide compound in the soil, desorption from soil particles, and diffusion or transport of dissolved pesticide in the soil solution (Bailey et al., 1974; Bruce et al., 1975). Sediment and aqueous pesticide routing processes have been incorporated in various pesticide runoff models (Crawford and Donigian, 1973; Bailey et al., 1974; Bruce et al., 1975; Frere et al., 1975; Donigian et al., 1977; Haith, 1980; Steenhuis and Walter, 1980).

Pesticides deposited on the soil and foliage surfaces are most subject to runoff losses (Wauchope, 1978). Steenhuis and Walter (1980) define the zone where overland flow extracts pesticide from the soil profile as the mixing depth. The depth of this zone can be calculated by regressing pesticide loss with cumulative precipitation. Bulk pesticide (aqueous and sediment) concentrations have been shown to decrease exponentially both during a storm event and over several events of similar precipitation characteristics (Baker et al., 1978;

Wauchope, 1978; Wauchope and Leonard, 1980). Pesticide concentrations decrease more rapidly in both runoff and the mixing depth than predicted from soil persistence data. Processes which decrease the concentration of available pesticide in the mixing depth occur both during and/or between storm events. Leaching and the routing of pesticide from the soil to overland flow occur during precipitation events. Pesticide concentrations in the soil are reduced between precipitation events or between the application date and the first precipitation event by biological and/or chemical pathways.

Pesticide losses in runoff may be reduced by several management practices. First of all, application rates may be reduced. This is often accomplished through improved management practices such as crop rotation, mechanical pest control methods, optimizing crop planting date, using resistant varieties, developing integrated pest control programs, and more precise applications only to the target species (Caro, 1976). The amount of pesticide available for runoff losses may also be reduced by using different formulations. More water soluble pesticides may be leached out of the mixing depth. Addition of certain surfactants to the pesticide formulation may also enhance leaching away from the surface or absorption into plant tissue (Caro, 1976). A pesticide application to very dry soil, as opposed to moist soil, may reduce the amount of available pesticide in the solution phase through non-reversible adsorption (Barnett et al., 1967; Baldwin et al., 1975).

Conservation practices may also reduce pesticide losses in overland flow by reducing runoff and/or the movement of sediments which may serve as carriers for the pesticide. Pesticides which are primarily lost in the sediment phase of runoff should be controlled by practices which reduce sediment loss. Runoff control practices are needed to control aqueous pesticide loss. Soil and water conservation practices include reduced tillage, contour tillage, strip cropping, ridge planting, sod-based rotations, cover crops, terraces, grass waterways, buffer strips, and subsurface drainage (Haith and Loehr, 1979). Since most pesticides are generally lost in the aqueous phase of runoff, practices which control erosion alone may not significantly reduce pesticide runoff losses (Wauchope, 1978). The implementation of conservation practices to control soil erosion did not reduce

atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide], cyanazine [2-((4-chloro-6-(ethylamino)-s-triazine-2-methylpropionitrile)], and diphenamid [N,N-dimethyl-2,2-diphenylacetamide] losses, but did reduce losses of less soluble pesticides such as fonofos [O-ethyl-S-phenylethylphosphonodithioate] and paraquat (Baker et al., 1978; Smith et al., 1978).

Leaching

Precipitation infiltrating into the soil may leach pesticides out of the mixing depth. The leaching potential of a pesticide is highly correlated with the adsorption-desorption of the chemical (Bailey and White, 1970; Helling, 1971; Bailey et al., 1974; Letey and Farmer, 1974; Tinsley, 1979). For nonionic pesticides, adsorption is highly correlated with the organic matter content (Bailey and White, 1964; Helling, 1971; Pionke and Chesters, 1973; Morrill et al., 1982) and the octanol/water partition coefficient (Tinsley, 1979). For compounds with acidic or basic groups, soil pH in relation to the pK value of the chemical is very important in the adsorption process (Helling, 1971; Pionke and Chesters, 1973; Tinsley, 1979; Morrill et al., 1982). When pesticides are weakly adsorbed, solubility is often the limiting factor in leaching. Other factors influencing leaching include the pesticide application rate, frequency and amount of precipitation, soil moisture, texture, type of clay mineral, porosity, and tortuosity (Bailey et al., 1974; Tinsley, 1979).

Pesticide Attenuation

Observed persistence of pesticides may be the net result of biological or chemical mechanisms depending on the nature of the chemical and the nature of the soil substrate. Processes included in pesticide attenuation include microbial, chemical, and photochemical degradation and volatilization (Bailey et al., 1974).

Hydrolysis reactions are important chemical reactions in the degradation process of many pesticides. The ability of soil colloids

to act as catalysts (Skipper et al., 1978) and availability of soil water help promote hydrolysis reactions in the soil media. Hydrolysis reactions are important in the degradation or detoxification of chloro-s-triazines, esters of carboxylic acids, amides, carbamates, organophosphates, and some halogenated compounds (Armstrong and Konrad, 1974; Tinsley, 1979). Hydrolysis reactions are very dependent on the pH of the medium. Chemical degradation can also involve oxidation, reduction, isomerization, polymerization, and free radical processes (Armstrong and Konrad, 1974; Bailey et al., 1974).

A wide range of pesticides are potentially susceptible to photochemical degradation. For photodegradation to occur in the field, the compound must first adsorb solar radiation. Only wavelengths greater than 290 nm actually reach the earth's surface. The pesticide must also contain the necessary chemical bonds which respond to the available energy by either breaking down or rearranging and be at the soil surface to be accessible to solar radiation (Tinsley, 1979). The first rainfall after application often moves the compound out of the zone of photolytic influence (Bailey et al., 1974). Photochemical reactions have been reported for chlorinated benzoic and phenylacetic acids, triazines, ureas, dinitroanilines, and picolinic pesticides (Armstrong and Konrad, 1974).

Pesticides lost by volatilization are characterized by high losses within 1 to 2 days of application followed by lower rates of volatilization (Guenzi and Beard, 1974). Initial high losses are the result of high pesticide concentrations on the soil surface. Surface concentrations can be replenished by simple diffusion or mass transfer from within the soil profile (Tinsley, 1979). Mass transfer is the result of water moving by capillary action to the surface (wick effect) because of the depletion or evaporation of soil water from the soil surface (Hartley, 1969; Spencer and Cliath, 1973). Volatilization of pesticides in soil is closely associated with the vapor density of the pesticide in the soil atmosphere. Vapor densities generally are higher for weakly adsorbed chemicals and with increased concentrations or application rate, higher temperatures, increased vapor pressure, and increased soil moisture content in very dry soils (Guenzi and Beard, 1974; Tinsley, 1979).

Among the different degradation mechanisms, microbial breakdown appears to be the most common pathway (Pionke and Chesters, 1973). Biological systems have an advantage over non-biological systems in that they can derive their energy through normal metabolic processes instead of solar radiation or thermal energy. The versatility in the populations of soil microorganisms enables a wide variety of reactions to be preformed (Tinsley, 1979). Microbial degradation rates can be altered by factors which either change the microbial population in the soil or how the chemical is distributed in the soil. Factors which can affect microbial degradation include organic matter content, soil texture, soil moisture, soil pH, nutrient availability, redox potential, pesticide formulation, and temperature (Bailey et al., 1974; Tinsley, 1979). Since there is a wide variety of microorganisms and pesticides, it is very difficult to assess how each factor will behave in degrading a specific pesticide. Generally, very dry soil moisture and extremes in pH are not conducive to high microbial activities (Pionke and Chesters, 1973).

Microorganisms degrade pesticides through many mechanisms. Microorganisms can decompose pesticides through enzymatic or non-enzymatic reactions by incorporating the pesticide molecule into a new substrate or breaking the pesticide molecule into smaller molecules (Tortensson, 1980). Enzymatic reactions include catabolism where the chemical is used as a carbon and energy source, co-metabolism or the breakdown of the pesticide as a non-growth substrate, and degradation by extracellular enzymes. Specific reactions possible include hydrolysis, dehalogenation, methylation, B-oxidation, cleavage of an ether linkage, N-dealkylation, ring hydroxylation, and ring cleavage (Bailey et al., 1974; Tinsley, 1979; Morrill et al., 1982). Pesticides may also be broken into smaller molecules by non-enzymatic processes resulting from microbial activities. Such processes include pH changes and/or the production of bi-products which can lead to photochemical or chemical reactions with the pesticide (Tortensson, 1980).

Oregon State University STEEP Erosion Project

The investigations of herbicides in runoff and the OSU STEEP erosion project were cooperating projects. A few comments on the erosion project therefore are in order.

STEPP is a multidisciplinary and regional research effort addressing soil erosion in the Pacific Northwest. Soil erosion leads to degradation of soil productivity as well as environmental damage to land and water resources. Increased awareness and concern by farmers working through various wheat producer organizations provided the stimulus to secure federal funding for the STEEP project. STEEP funding arises from a special U.S. Department of Agriculture (USDA) grant to Agricultural Experiment Stations in Oregon, Idaho, and Washington and to the USDA - Agricultural Research Service (Oldenstadt et al., 1982).

The STEEP program includes research in many areas which influence soil erosion. The five major areas include: 1) tillage and management, 2) plant design, 3) erosion and runoff prediction, 4) pest management, and 5) socioeconomics of erosion control. Responsibilities of the STEEP program in the Department of Soil Science at Oregon State University relate to objective 3 on erosion and runoff prediction. A watershed typical of the hill soils in the western margin of the Willamette Valley was chosen for study. The intent of the research was to relate soil detachment and sediment transport to physically based parameters and then to use soil properties to extend the information to other areas. The specific objectives of the STEEP erosion project are (Harward et al., 1980);

1. To determine the major factors which influence the erosion and transport of soil materials in the high winter rainfall climatic zone.
2. To apply the knowledge to soil management practices for minimizing yield of sediments while maintaining profitable agricultural enterprises.
3. To provide physically based predictive models for soil erosion hazard, soil loss, and sedimentation.

Measured annual amounts of gross erosion ranged between 0.5 and 9 Mg/ha·yr (0.2-4 T/acre·yr) over a three year period at the experimental watershed (Istok and Lowery, 1980). Average soil loss was less than 4.5 Mg/ha·yr. Soils in lower slope positions and/or less well drained soils with restrictive layers near the surface had the highest amounts of gross erosion as measured with erosion plots (Istok and Lowery, 1980). Long term erosion rates, estimated using ¹³⁷Cs activities, ranged between 3 and 27 Mg/ha·yr (Brown et al., 1981b). Cesium-137 activities were highest in depositional sites and lower in both sideslope and ridgetop sites (Brown et al., 1981a). Overland flow measured from flumes in small sub-watersheds (0.46-6.0 ha in size) indicated a very rapid response of discharge to changes in precipitation intensity and that suspended sediment load closely paralleled changes in discharge (Parsons et al., 1980). Highest amounts of runoff and erosion were found for storms following high antecedent moisture, extensive crusting, or frozen ground (Brown and Hickman, 1980). Most storms, however, produced runoff only from lower slope positions .

Antecedent soil moisture content and ephemeral perched water tables were major factors influencing erosion and runoff (Harward et al., 1980; Lowery et al., 1982). These factors are the result of the interaction between the soil and the climate in the region. Fall and winter precipitation in western Oregon is characterized by frequent low intensity frontal type storms. Early in the fall, the soil surface is very loose and porous because of recent tillage operations and the precipitation generally infiltrates into the soil and does not result in overland flow. Later in the season, with an increase in the frequency of precipitation events, the soil moisture increases and perched water tables develop above restrictive layers even on hill slopes (Lowery et al., 1982). Lowery et al. (1982) indicated an association between runoff and ephemeral perched water tables. Runoff was greatest following periods of high antecedent soil moisture. Runoff and erosion were also greater in soils with the restrictive layers closer to the soil surface which resulted in shallow depths to ephemeral perched water tables (Istok and Lowery, 1980; Lowery et al., 1982).

Runoff and erosion losses were also affected by landscape position. Runoff and erosion were greater in lower slope positions than upper slope positions (Harward et al., 1980; Brown et al., 1981a; Lowery et al., 1982). With the build up of ephemeral perched water tables on the hill soils there was a significant amount of downslope, lateral subsurface flow (Lowery et al., 1982). This water often surfaced in lower slope positions and served as source areas for storm runoff. Variation in ^{137}Cs activity across similar landscape units was also explained by landscape position (Brown et al., 1981a). Indistinguishable sideslope and ridgetop ^{137}Cs activities were attributed to widespread runoff over all landscape positions during large storms and the lack of major erosion events since 1954 which would preferentially deplete surface soil on sideslopes. Footslope positions were found to be very active landscape units (Brown et al., 1981a), serving as source areas for erosion and storage sites for sediment deposition.

Reduction in infiltration as the result of surface crusting also affected the runoff and erosion losses in western Oregon (Harward et al., 1980). Infiltration rates decreased as the winter season progressed from initially high rates in early fall (Lowery et al., 1980; Pronold and Harward, 1980). Fall and early winter rains which break down soil aggregates were responsible for the formation of the surface crust. Runoff from several storms on non-saturated soils was attributed to soil crust formation (Brown and Hickman, 1980; Lowery et al., 1982). Infiltration was also drastically reduced during frozen ground situations. The largest erosion events involved rain falling on frozen ground (Brown and Hickman, 1980). Drying and cracking of the soil crust and increased plant cover contributed to increases in infiltration rates in late winter or spring (Lowery, et al., 1980).

Gross erosion measured with erosion plots and estimated from ^{137}Cs activities were not as high as those reported in other regions of the United States (Istok and Lowery, 1980; Brown et al., 1981b). The rates were high enough, however, to warrant appropriate conservation measures. A subsurface drainage system installed on one of the small subwatersheds reduced runoff and erosion by lowering water tables and reducing seepage in lower slope positions (Harward et al.,

1980; Lowery et al., 1982; Istok and Kling, 1983). Watershed runoff and sediment yield were reduced 65 and 55%, respectively, following subsurface drainage installation (Istok and Kling, 1983). High intensity and/or long duration storms still produced overland flow in the subsurface drained watershed, but was of shorter duration and without base flow as compared to before drainage (Lowery et al., 1982; Istok and Kling, 1983). Subsurface drainage was recommended as a management practice for erosion control in western Oregon.

Properties of Selected Herbicides

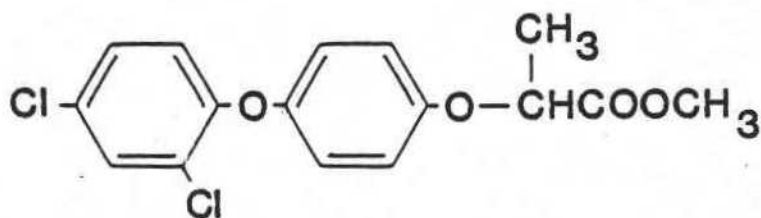
Diclofop-methyl

Diclofop-methyl (Hoelon) is formulated as an emulsifiable concentrate (35.5% W/W) containing 0.36 kg of active ingredient per liter (Marrese, 1980). Diclofop-methyl is a dichloro-diphenyl ether with a methyl propanoate side chain (Fig. 1). Diclofop-methyl rapidly hydrolyzes in either plants (Shimabukuro et al., 1979) or soil (Smith, 1977; Martens, 1978) to diclofop [2-(4-(2,4-dichlorophenoxy)phenoxy) propionic acid] (Fig. 1).

Diclofop-methyl is used for the control of wild oats (Avena fatua L.), various foxtails (Setaria spp.), and annual ryegrass (Lolium spp.) in wheat (Triticum) and barley (Hordium vulgare L.) and for control of foxtails, barnyardgrass (Echinochloa crusgalli L.), crabgrass (Digitaria spp.), and volunteer corn (Zea mays L.) in soybeans (Glycine max L.) (Andersen, 1974; Putman et al., 1974; Lee and Alley, 1975; Brewster et al., 1977). In western Oregon, diclofop-methyl is used for the control of wild oats and Italian ryegrass (Lolium multiflorum Lam.) in winter grains, especially winter wheat (Triticum aestivum L.) (Brewster et al., 1977). Brewster et al. (1977) found that diclofop-methyl (0.84-2.24 kg/ha) applied either early postemergence (wheat at two or three leaf stage) or late postemergence (wheat at early tillering) gave nearly complete control of both weed species, while preemergence applications were less consistent.

DICLOFOP-METHYL

Methyl 2-[4-(2,4-dichlorophenoxy)phenoxy] propanoate



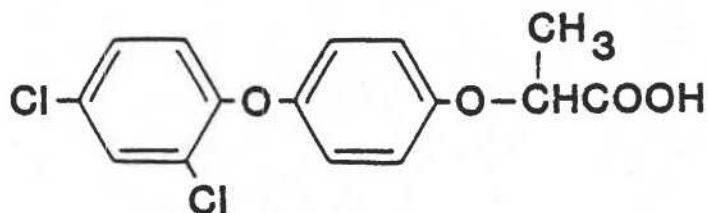
MW: 341 Melting point[†]: 39-41°C

Solubility in H₂O[†]: 3.0 mg/L @ 22°C

Volatility[†]: 2.58 x 10⁻⁷ torr @ 20°C

DICLOFOP

2-[4-(2,4-dichlorophenoxy)phenoxy] propionic acid



MW: 327 Melting point: 106°C

Solubility in H₂O: 33 mg/L @ 4°C

50 mg/L @ 22°C

pK_a: 4.5

[†] (Marrese, 1980)

Figure 1. Structure and chemical characteristics of diclofop-methyl and diclofop.

The herbicidal effect of diclofop-methyl may be the net result of both diclofop-methyl and diclofop (the propionic acid metabolite), each with a different mode of action and acting at different sites in the plant (Shimabukuro et al., 1978). In wild oats, diclofop-methyl is rapidly hydrolyzed to diclofop and then converted to an ester conjugate (Shimabukuro et al., 1979). Diclofop-methyl, diclofop, or its metabolites are not translocated in high concentrations within the plant (Brezeanu et al., 1976; Shimabukuro et al., 1979). Diclofop-methyl is a strong auxin antagonist and functions to inhibit growth in wild oat plants by reducing stem elongation (Shimabukuro et al., 1978). Diclofop, on the other hand, leads to reduced root growth and ultrastructural cell damage (Shimabukuro et al., 1978). Wheat, which is tolerant to diclofop-methyl and diclofop, absorbs similar amounts of the herbicide as wild oats, but detoxifies the compound by rapidly hydroxylating the 2,4-dichlorophenoxy ring in diclofop and forming a phenolic conjugate (Shimabukuro et al., 1979; Donald and Shimabukuro, 1980).

Several breakdown products beyond the diclofop molecule have been identified in soil incubation experiments utilizing ^{14}C ring-labelled material (Fig. 2). The metabolite 4-(2,4-dichlorophenoxy) phenol was identified in amounts as high as 10% of the applied radioactivity (Smith, 1977, 1979b; Martens, 1978). Traces of 4-(2,4-dichlorophenoxy) phenetole were also identified (Smith, 1977, 1979b). These breakdown products indicate a cleavage between the aromatic and aliphatic portions of the molecule. The cleavage may be a step-wise degradation of the side chain or a direct hydrolysis reaction liberating lactic acid. Generation of $^{14}\text{CO}_2$ from diclofop-methyl labelled on either the chlorinated or non-chlorinated ring supports a further mineralization of both aromatic rings (Martens, 1978). The degradation scheme beyond the 4-(2,4-dichlorophenoxy) phenol metabolite was not suggested because of a lack of intermediates in amounts high enough to be identified (Martens, 1978).

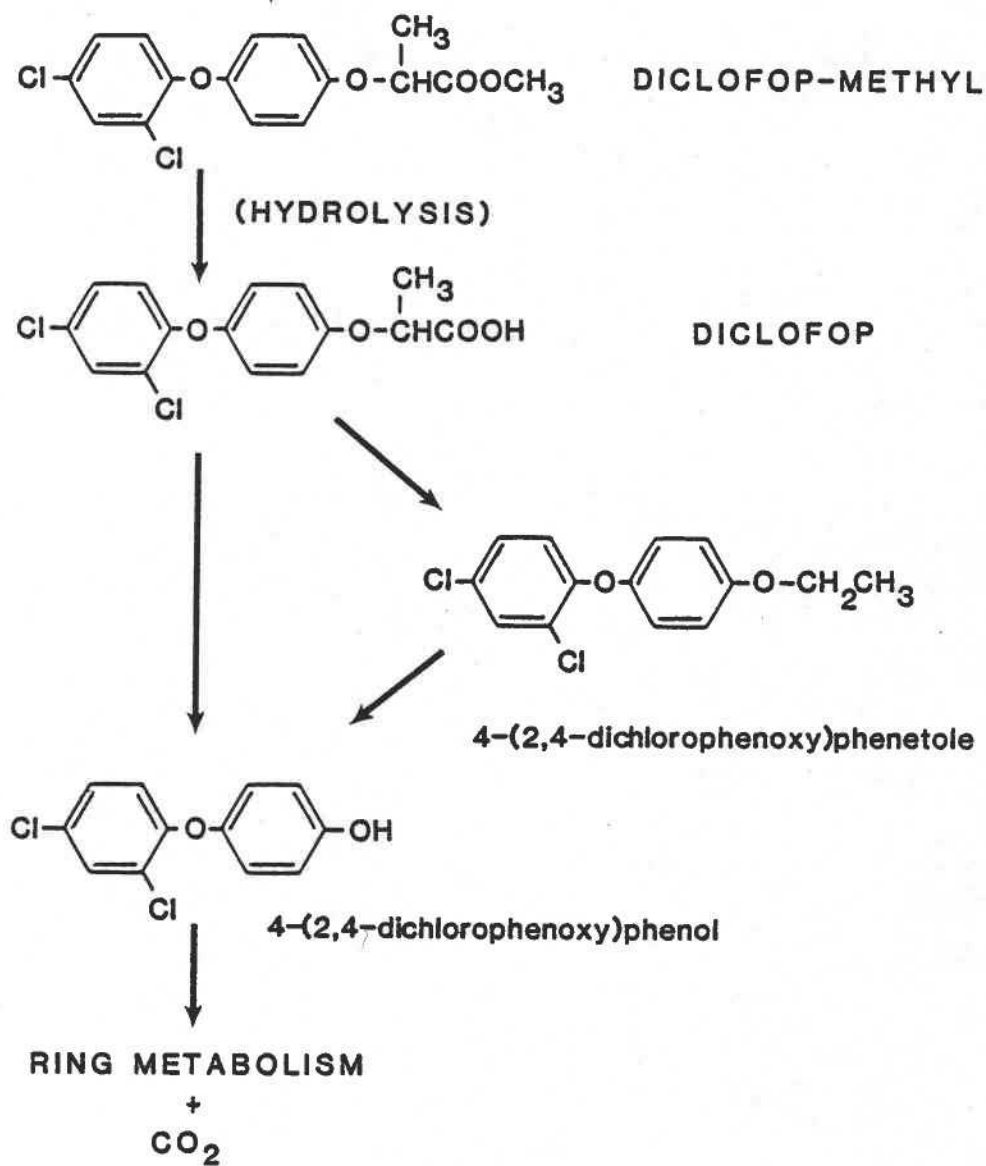


Figure 2. Degradation pathway for the breakdown of diclofop-methyl and diclofop (Smith, 1977).

Trifluralin

Trifluralin (Treflan) (Fig. 3) is used for the control of grasses and broadleaf weeds in a wide variety of tolerant crops (Weed Science and a 5% granule formulation (Probst et al., 1975). Trifluralin is commonly used as a pre-emergence herbicide and is recommended to be incorporated within 8 hours of application.

Trifluralin controls weeds by affecting seed germination (Weed Science Society of America, 1979) and inhibiting cell division in roots and germinating seedlings (Probst et al., 1975). Very little trifluralin is translocated from the treated roots to above ground plant portions. Trifluralin has very little contact activity when applied to plant foliage.

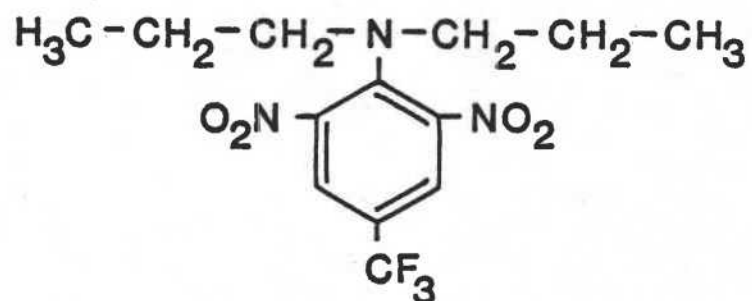
The observed persistence of trifluralin in soil is the net result of chemical and biological processes. Trifluralin generally dissipates to low levels (1-10% of applied) within a single growing season (Probst et al., 1967; Parka and Tepe, 1969; Savage and Barrentine, 1969; White et al., 1977) and does not accumulate in soil with repeated applications (Parka and Tepe, 1969). The rate of trifluralin breakdown in soil is a function of soil type, pH, temperature, moisture content, and incorporation method and depth (Probst et al., 1975; Morrill et al., 1982). Aerobic and anaerobic degradation (chemical and microbial), volatilization, and photodegradation are important processes in the overall disappearance of trifluralin in soil.

Trifluralin degradation is faster under anaerobic than aerobic conditions (Probst et al., 1967; Parr and Smith, 1973). Degradation followed the order of moist (1/3 bar) anaerobic > flooded anaerobic > moist aerobic with 99, 45, and 15% of the trifluralin being degraded in 20 days, respectively (Parr and Smith, 1973). Both non-biological (Probst et al., 1967; Messersmith et al., 1971) and microbial degradation (Parr and Smith, 1973; Weed Science Society of America, 1979) have been reported in the anaerobic and aerobic breakdown of trifluralin in soil. Degradation schemes for both the anaerobic and aerobic breakdown can be found in Probst et al. (1975).

Trifluralin is subject to volatilization losses as suggested by its relatively high vapor pressure (1.99×10^{-4} torr @ 29.5°C). White

TRIFLURALIN

α, α, α -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine



MW = 335

Melting point = 48.5-49C

Solubility in H_2O : 0.1-0.3 mg/L @ 27C

Vapor pressure: 1.99×10^{-4} torr @ 29.5C

Figure 3. Structure and chemical characteristics of trifluralin.

et al. (1977) reported a seasonal volatilization loss of 26% of the applied trifluralin following application to a sandy loam soil (0.55% organic carbon). Fifty percent of the volatilization loss occurred in the first 9 days after application (White et al., 1977).

Volatilization losses decrease when trifluralin is incorporated rather than surface applied (Spencer and Cliath, 1974) and with the increasing depth of incorporation (Savage and Barrentine, 1969). Trifluralin volatilization losses increase with increases in temperature, soil moisture content at low soil moisture, atmospheric turbulence, and application rate (until the concentration in the soil is such that the vapor pressure in the soil atmosphere is equivalent to the standard vapor pressure without soil) (Savage and Barrentine, 1969; Spencer and Cliath, 1974; Harper et al., 1976; White et al., 1977). Spencer and Cliath (1977) reported that trifluralin vapor density was inversely related to the organic matter content of the soil indicating the importance of increased adsorption in reducing volatilization losses.

Photodegradation of trifluralin has been found to occur under both artificial light and sunlight (Wright and Warren, 1965; Harrison and Anderson, 1970; Parr and Smith, 1973; Leitis and Crosby, 1974). Wright and Warren (1965) found a decrease in trifluralin absorption at 270 and 376 nm after exposure to sunlight and that light in the 360-380 nm range was sufficient to photodecompose trifluralin. Photodegradation of trifluralin after application to the soil surface has been reported, but at a slower rate than under artificial conditions (Wright and Warren, 1965). The pathways and bi-products involved in trifluralin photodegradation are discussed in Leitis and Crosby (1974) and Probst et al. (1975).

Trifluralin is strongly adsorbed to soil, especially organic soil colloids (Weber and Weed, 1974; Weed Science Society of America, 1979) and is relatively immobile in soils (Harris, 1967; Probst et al., 1967; Anderson et al., 1968; Mulder and Nalewaja, 1979).

HYDROLYSIS, DEGRADATION, AND LEACHING OF DICLOFOP-METHYL

Introduction

Diclofop-methyl is applied in the winter months to winter wheat in western Oregon. Cool moist soil conditions following application should retard chemical and biological degradation and enhance leaching as compared to other management systems which involve a spring/summer application. Several researchers have investigated the breakdown of diclofop-methyl in soil, but under warmer conditions than expected for this area. Diclofop-methyl rapidly hydrolyzes to diclofop, the corresponding propionic acid (Smith, 1977; Martens, 1978). Degradation beyond the diclofop molecule, also an active herbicide, proceeds much slower than the hydrolysis of diclofop-methyl (Wu and Santelmann, 1976; Smith, 1977; Martens, 1978; Smith, 1979b). Microbial activity has been suggested as the principle mechanism in diclofop degradation (Wu and Santelmann, 1976; Martens, 1978).

This study was designed to (1) measure the rate of diclofop-methyl hydrolysis, diclofop-methyl + diclofop degradation, and leaching under conditions typically following a winter application of diclofop-methyl in western Oregon, and (2) determine the influence of soil microbial activity in both the hydrolysis and degradation processes.

Materials and Methods

Laboratory Studies

Sample Incubation

Soil samples were collected from the plow layer of a Helmick variant silty clay loam (Brown et al., 1980) at the Elkins Road watershed experimental site in the western margin of the Willamette Valley. This soil is classified as a very fine, mixed, mesic, Aquic Xerochrept (Table 1).

Diclofop-methyl was incubated in sterile and non-sterile soils at 4 and 22°C. Soil for non-sterile incubations was sieved moist to pass a

Table 1. Chemical and physical characteristics[†] of soils used in the laboratory and field studies.

Sample	Sand (%)	Silt (%)	Clay (%)	CEC (mM/kg [§])	OM (%)	pH
Lab	25	52	23	154	4.7	5.1
Field Samples						
A	18	59	23	127	3.9	5.3
B	25	45	30	113	3.5	5.5
C	23	48	30	119	2.6	5.2
D	15	63	22	142	3.4	5.3
E	38	43	19	84	2.7	5.6

[†] Conducted by Oregon State University Soil Testing Laboratory. (Berg and Gardner, 1978).

[§] mM(ammonium acetate buffered at pH 7.0)/kg dry soil.

2 mm sieve. Soil for the sterile treatments was air-dried, sieved to pass a 2 mm sieve, and irradiated with 5 Mrad of cobalt-60. Twenty gram samples (105°C oven dry equivalent) of sterile or non-sterile soil were added to autoclaved 60 mm diameter glass petrie dishes. Reagent grade water was added to bring the samples to 80% of 33 kPa (0.33 bar) soil moisture. Samples were equilibrated at 22 or 4°C for 24 hours. Diclofop-methyl, as the emulsifiable concentrate, was then added (0.5 mL, 145 µg) to the surface of each sample bringing the moisture content to 90% of 33 kPa moisture (0.285 kg/kg gravimetric water content). The herbicide addition was equivalent to a 1.12 kg/ha application to the top 1 cm of the soil surface.

Sterile and non-sterile samples were incubated at 22 or 4°C. Lost moisture was replaced every 4-5 days with reagent grade water. A sufficient number of samples in petrie dishes were prepared to provide a complete sample for analysis at each sampling date. Soil samples were analyzed for diclofop-methyl and/or diclofop at 1, 2, 4, 6, 9, 14, 20, 30, and 47 days after diclofop-methyl application. The effectiveness of the irradiation treatment to sterilize the soil was measured using a bacterial count technique (Clark, 1965) at the initial stage of soil incubation. A bacterial count was not initiated at the termination of the study.

Diclofop-methyl and Diclofop Analysis

Diclofop-methyl and diclofop residues were analyzed immediately after sampling. Soils were extracted overnight in a soxhlet extractor with 350 mL acetone. The acetone extract was concentrated to 10 mL over steam, added to 150 mL of 0.05 M HCl and 1.3 M KCl, and extracted twice with 50 mL benzene. The benzene extracts were combined and then extracted twice with 20 mL of 0.14 M Na₂CO₃. This final extraction separated the diclofop residues into the Na₂CO₃ extract while the diclofop-methyl residues remained in the benzene fraction. The benzene fraction was concentrated and saved for gas chromatographic analysis of diclofop-methyl residues.

The Na₂CO₃ extracts were combined with the soil from the soxhlet extraction to isolate the remaining diclofop residues. The soil and the Na₂CO₃ extracts were added to a 250 mL centrifuge

bottle containing 200 mL of 0.2 M KOH and 1.3 M KCl. The mixture was heated on a steam bath for 1 hour, centrifuged, the supernatant decanted, and the process repeated with another 200 mL of the KOH-KCl solution. The supernatants were combined, acidified to pH 2 with 3 M H_2SO_4 , and extracted three times with 200 mL ether. The ether extracts were combined, concentrated to 20 mL, and added to a 400 x 20 mm chromatographic column containing 20 g basic alumina (Grade I). The column was washed with 100 mL chloroform, followed by 100 mL ether and then air-dried under a vacuum for 30 minutes. Diclofop residues were washed from the column with 125 mL of 0.09 M $NaHCO_3$. The $NaHCO_3$ column effluent was acidified to pH 2 and then extracted three times with 75 mL ether. The extracts were concentrated to 20 mL, methylated with diazomethane (Arndt, 1943), transferred to a benzene solvent, concentrated to 5 mL, and added to a 160 x 6 mm chromatographic column containing 8 grams of basic alumina (Grade IV). Diclofop was washed from the column with an additional 25 mL benzene. The benzene extract was concentrated and saved for gas chromatographic analysis of diclofop residues.

After a sufficient number of samples indicated that very little diclofop-methyl remained in the soil, the analytical procedure was altered to combine both diclofop-methyl and diclofop residues into a single analysis. Soil samples were added to a 250 mL centrifuge bottle containing 200 mL of 0.2 M KOH and 1.3 M KCl, and the procedure followed as if analyzing for diclofop alone (previous paragraph).

An Infotronics gas chromatograph equipped with a c-200 B microcoulometric detector was used to analyze diclofop-methyl and diclofop residues. The glass column (1.80 m x 2 mm i.d.) was packed with low level Carbowax 20 M on 80/100 mesh acid washed Chromosorb W (Aue et al., 1973). The flow rate of the nitrogen carrier gas was set at 45 mL/min. At a column temperature of 215°C, the retention time was 3.2 minutes.

The analytical procedure was sensitive to 0.5 μ g esterified diclofop or diclofop-methyl in the total sample extract. Recoveries of diclofop-methyl and diclofop were determined by adding standard solutions of one or both chemicals to the soil prior to chemical analysis. Fortification levels ranged from 0.5 to 10 μ g herbicide per

gram of soil. Recoveries were 95% and 90% for diclofop-methyl and diclofop, respectively. All results were based on the recovery of diclofop-methyl and diclofop in the fortified samples.

Hydrolysis of diclofop-methyl and degradation of diclofop-methyl + diclofop in the laboratory study were calculated from the following formulas:

$$\% \text{ hydrolysis} = [\text{diclofop}/(\text{diclofop-methyl} + \text{diclofop})] \times 100$$

$$\% \text{ degradation} = [(145 - (\text{diclofop} + \text{diclofop-methyl}))/145] \times 100$$

Field Studies

Sampling

Five field soil sampling stations were established within the boundaries of the Elkins Road watershed (Fig. 4). Chemical and physical properties of the soil at each site were determined (Table 1). The study area was planted to winter wheat in mid October, 1980 and diclofop-methyl was applied by a commercial operator to the soil surface on 7 Jan. 1981. The amount of diclofop-methyl applied at each sampling station was established by sampling the soil within 6 hours of application and analyzing for diclofop-methyl + diclofop residues.

Soil samples were taken from the 0-1, 1-5, and 5-10 cm depths at 0, 23, 54, and 87 days after application. Soil cores were taken with a 19 mm diameter stainless steel split tube sampler. Five soil cores were composited at each sampling site. Samples were frozen immediately after removal from the field.

Diclofop-methyl and Diclofop Analysis

Whole soil samples were analyzed for diclofop-methyl + diclofop residues as described in the laboratory study.

The amount of herbicide measured at each sampling site or depth was expressed as a percentage of the applied herbicide at that site. Degradation in the field samples was calculated by the following formula:

$$\% \text{ Degradation} = [100 - (\text{diclofop-methyl} + \text{diclofop}(0-10 \text{ cm}))]$$

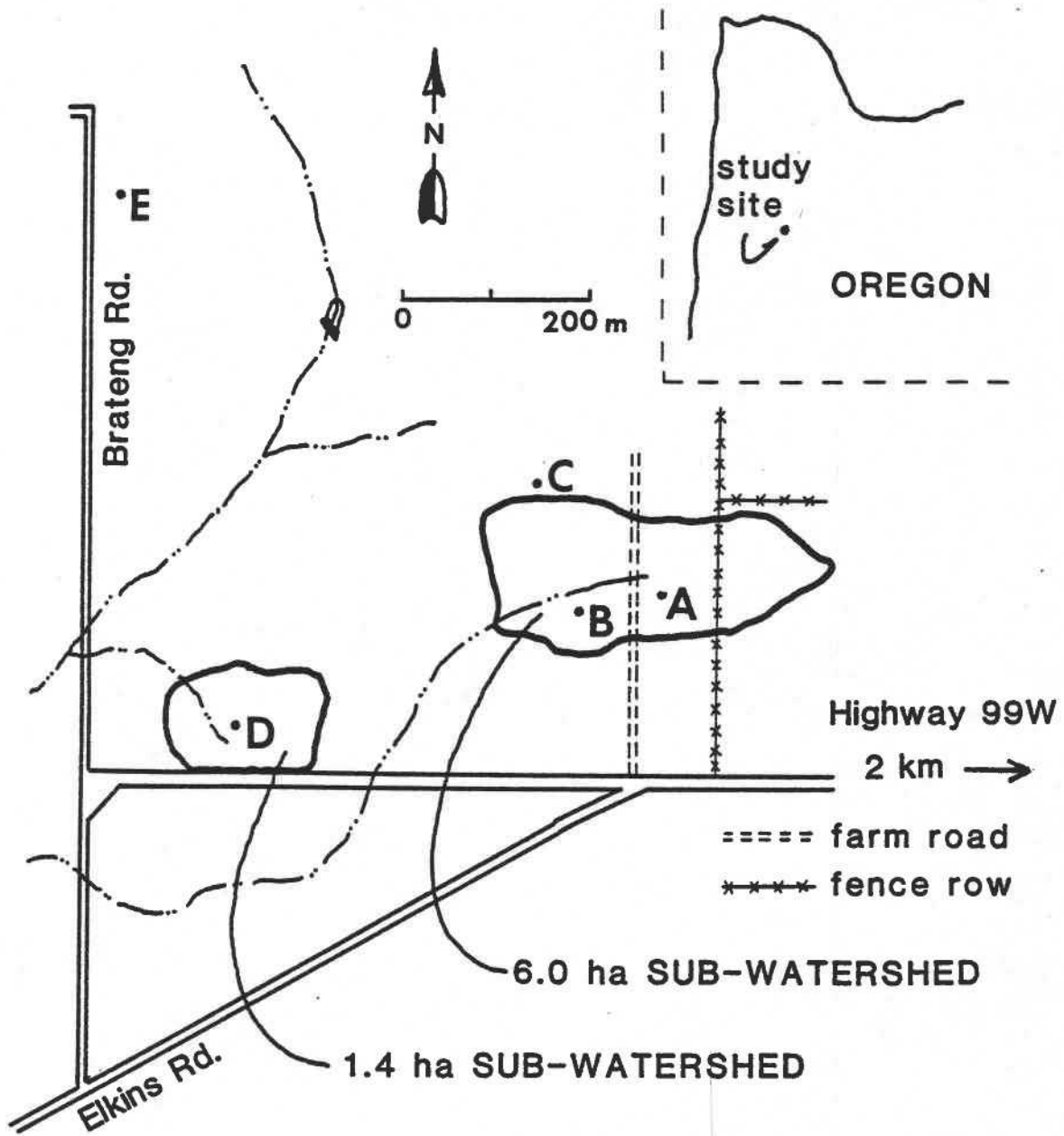


Figure 4. Location of field sampling sites within the Elkins Road watershed experimental system.

Statistical Analysis

The different treatments in the laboratory studies (Appendix Table 1) and sampling sites in the field studies (Appendix Table 2) were analyzed using curvilinear regression and comparing slopes of the regression lines. Exponential decay curves (Eq. [1]) were fit to the field and laboratory degradation data. Logarithmic curve fitting equations (Eq. [2]) were fit to the herbicide soil surface (0-1 cm) concentrations at each sampling site. Power curve fitting equations (Eq. [3]) were fit to the laboratory hydrolysis data.

$$\ln(Y) = \ln(a) + bX \quad [1]$$

$$Y = a + \ln(X) \quad [2]$$

$$\ln(Z) = \ln(a) + b\ln(X) \quad [3]$$

Where Y = percent of applied herbicide remaining at the sampling date,

Z = percent hydrolysis,

X = sampling date (days),

b = slope of regression equation,

a = regression coefficient.

When the slopes of the regression equations were not significantly different ($p=0.10$), the average of the samples at each site or treatment was reported.

Results and Discussion

Excellent recoveries were obtained from analysis of diclofop-methyl and diclofop residues. The procedure did not enhance hydrolysis of diclofop-methyl as evidenced by the sensitivity to high amounts of diclofop-methyl recovered in fortified samples. Cobalt-60 irradiation also gave complete sterilization at the start of the incubation period. Effectiveness of cobalt-60 irradiation as a sterilization technique has been previously reported (Hill and Arnold, 1978; Tortensson, 1980). Visible microbial colonies were observed on the surface of the sterilized samples at 16 days after application indicating subsequent microbial contamination.

Leaching

The concentration of herbicide at the soil surface is of particular interest in runoff studies. Only the diclofop-methyl + diclofop residues in the mixing depth will be available to overland flow for runoff losses. The amount of active herbicide remaining at the surface is the result of both leaching and herbicide breakdown. Leaching of diclofop is also important in controlling weed species which germinate after diclofop-methyl application. Diclofop effectively reduces root growth of wild oat plants at very low concentrations (Donald et al., 1982). Leaching of diclofop into the soil profile would move the herbicide closer to the roots and increase herbicidal action. Some mobility of the diclofop molecule in soils would be predicted from the chemical characteristics of the carboxylic acid functional group. Since the pH of the field soils (5.2-5.6, Table 1) is above the pK_a of diclofop (4.5), the compound would be predominantly negatively charged and some leaching would be expected (Bailey and White, 1970; Heller, 1971; Letey and Farmer, 1974).

Diclofop-methyl + diclofop residues were detected below the 0-1 cm depth indicating that leaching had occurred (Fig. 5). Most of the leached herbicide (below 0-1 cm) was detected in the 1-5 cm depth, with very little herbicide (< 5% of applied) detected in the 5-10 cm depth (Fig. 5). When averaged over all sampling sites, 20, 34, and 31% of the active herbicide remaining in the soil had leached out of the 0-1 cm depth at 23, 54, and 87 days (55, 150, and 230 mm of precipitation, respectively) after application. Total precipitation during the field study (230 mm) was far below normal (400 mm) for this period (Knezevich, 1975). More leaching would be expected with more precipitation.

Diclofop-methyl + diclofop leaching increased for five soil types when the volume of water added to soil columns increased (Mulder and Nalawaja, 1979). Herbicide movement was also greater in coarse textured soils than fine textured soils. When averaged over the different volumes of water added, herbicide movement out of the top 2 cm varied from 60% in a loamy sand to 34% in a clay soil. At the highest addition of water (100 mm), 94% of the herbicide remained in

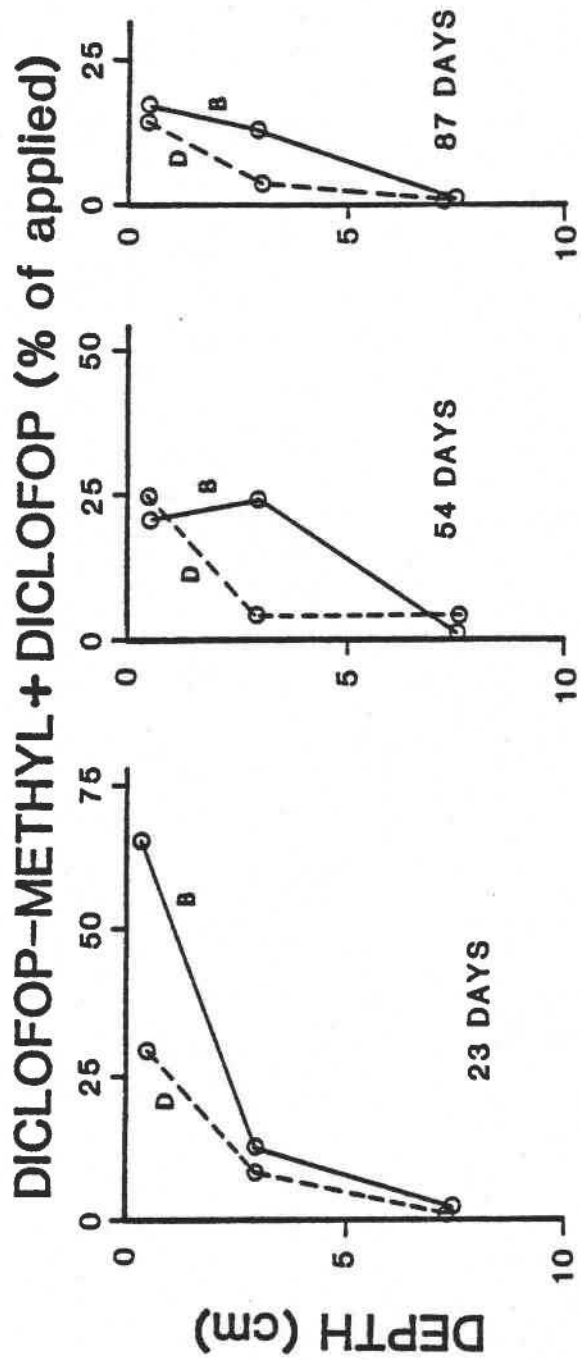


Figure 5. Amounts of diclofop-methyl + diclofop in 0-1, 1-5, 5-10 cm depths over the sampling period. Field sites B and D represent the extremes in leaching over the sampling period.

the top 10 cm when averaged over the five different soils. Smith (1979a) found no detectable diclofop or diclofop-methyl residues at depths greater than 5 cm in a Canadian prairie soil 5 months after a May herbicide application. Soil pH values in these studies (5.2-7.8) were also above the pKa of diclofop and some leaching would be expected. These studies were conducted, however, under drier conditions than would be expected following a winter application of diclofop-methyl in western Oregon. In a recent study conducted in the Willamette Valley, diclofop-methyl + diclofop residues were detected as deep as 20-30 cm and 60% of the chemical had leached out of the top 2.5 cm in 28 days (310 mm of precipitation) after application (Marvin Montgomery¹, unpublished data).

Hydrolysis

Hydrolysis of diclofop-methyl is the first step in the overall breakdown process. At 22°C, with a non-sterile soil, 84% of the diclofop-methyl hydrolyzed to diclofop in only 24 hours (Fig. 6). Other researchers also report rapid hydrolysis under similar conditions. Smith (1977) found 85, 68, and 40% hydrolysis in 24 hours for a moist (85% of field capacity) clay, loamy sand, and clay loam soil, respectively. Similar rates were also observed when the soil moisture was at 50% of field capacity (Smith, 1977) and under anaerobic conditions (Martens, 1978). When soils were air-dried, however, less than 5% of the diclofop-methyl hydrolyzed in a 24 hour period (Smith, 1977).

Hydrolysis of diclofop-methyl was faster ($p = 0.01$) at 22°C than at 4°C. However, even at lower temperatures, diclofop-methyl rapidly hydrolyzed to diclofop in the non-sterile soil (Fig. 6). Western Oregon winters are characterized by cool, moist conditions where soil surface temperatures are close to the 4°C incubation temperature used in the laboratory study. Most of the diclofop-methyl applied under field conditions should be converted to diclofop within 1 to 2 days after herbicide application.

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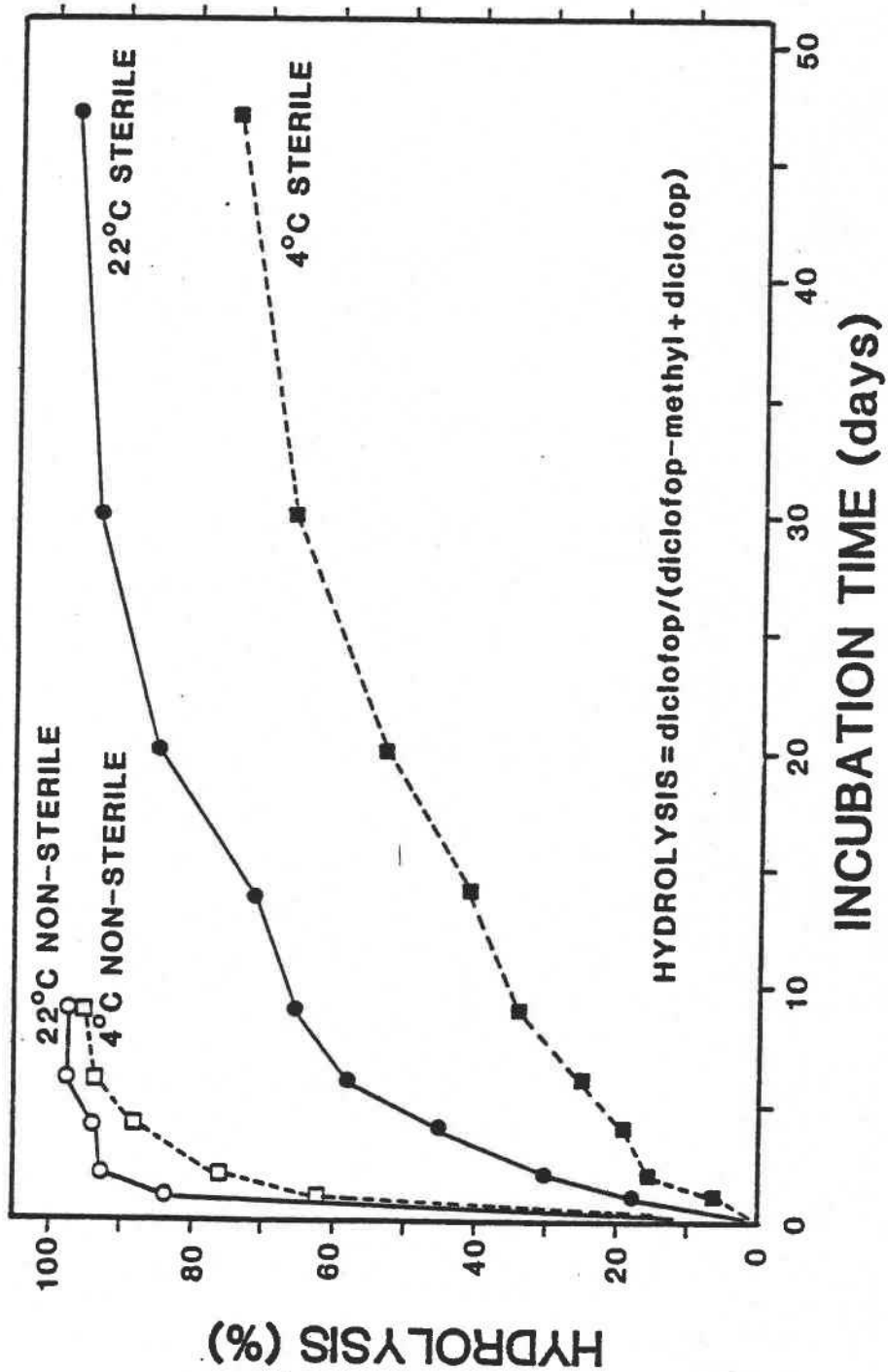


Figure 6. Hydrolysis of diclofop-methyl.

Hydrolysis was also significantly faster ($p = 0.01$) in non-sterile samples than sterile samples at both incubation temperatures. In sterile soil, 50% hydrolysis occurred in 5 and 18 days for samples incubated at 22°C and 4°C, respectively (Fig. 6). An equivalent amount of hydrolysis occurred in less than 24 hours in non-sterile soil. The large differences in the rate of hydrolysis between non-sterile and sterile soil indicates microbial action as the primary mechanism for hydrolysis. The soil microorganisms could either use the hydrolysis bi-product as a substrate or catalyze the hydrolysis reaction. The lack of hydrolysis in air-dried soil (Smith, 1977) also supports the importance of microorganisms in the hydrolysis process. Hydrolysis of the diclofop-methyl that did occur in the sterilized soil may also be the result of subsequent microbial contamination.

Degradation

Since both diclofop-methyl and diclofop are active herbicides (Shimabukuro et al., 1978), degradation beyond the diclofop molecule is very important. Degradation was defined as the difference between the total diclofop-methyl applied at the start of the experiment and the amount of active herbicide (diclofop-methyl + diclofop) remaining at the sampling date.

Degradation beyond the diclofop molecule in the laboratory study was much slower than the hydrolysis of diclofop-methyl and varied depending on the experimental conditions (Fig. 7). Degradation was most rapid in the 22°C non-sterile soil where over 40% of the active herbicide had degraded in 47 days. Degradation was significantly ($p = 0.01$) slower in sterile soils. The increase in degradation with time for the sterile samples may be microbial in nature from subsequent microbial contamination of the samples. Degradation was also slower at 4°C than 22°C for both non-sterile ($p = 0.05$) and sterile soil ($p = 0.10$).

Both degradation and leaching are major factors determining the residual active herbicide in the surface soil samples in the field. If very little herbicide is leached below 10 cm (Fig. 5), the amount of diclofop-methyl + diclofop in the 0-10 cm depth subtracted from the

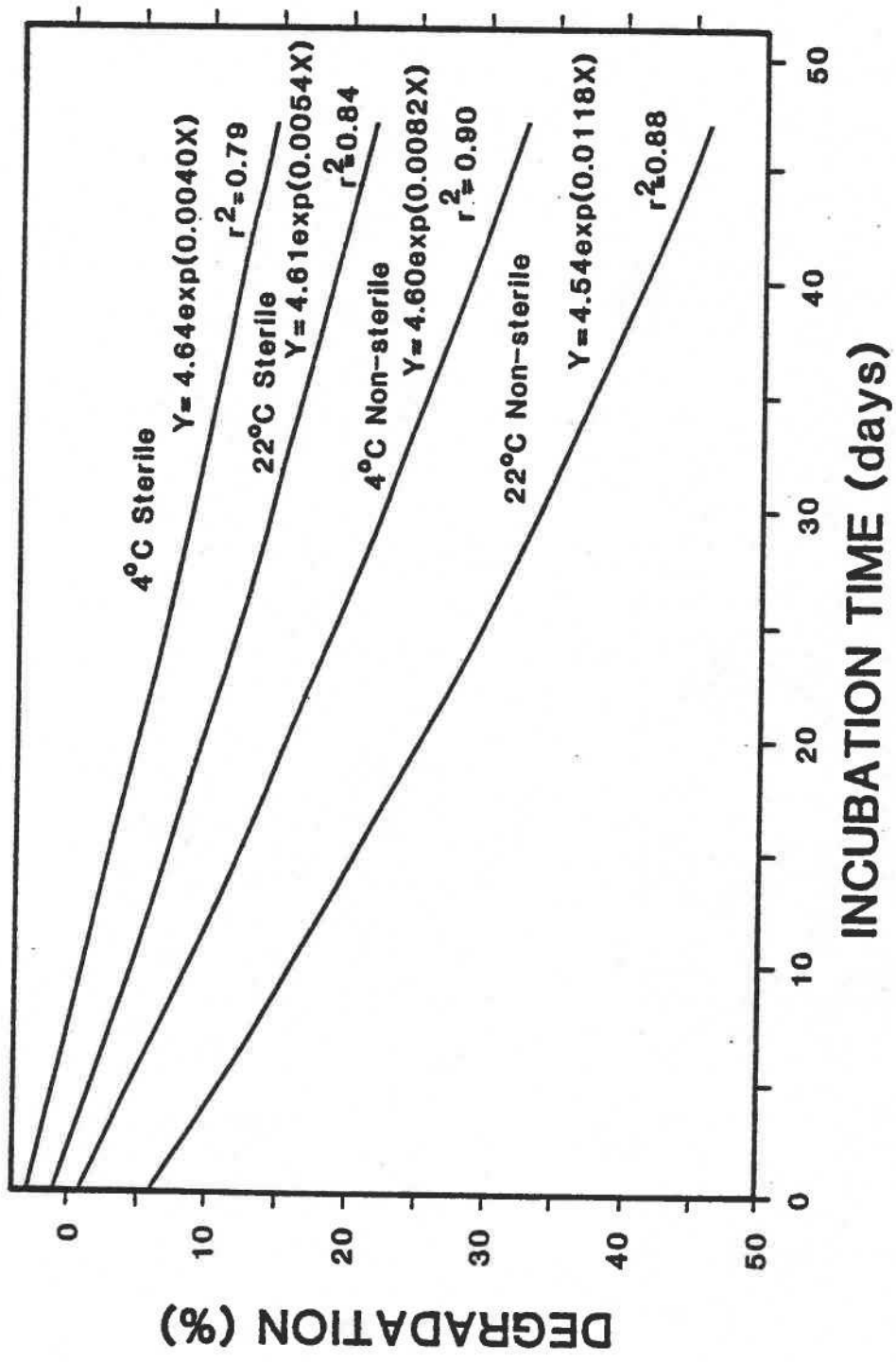


Figure 7. Degradation of diclofop-methyl + diclofop in the laboratory incubation study.

applied herbicide is an estimate of the degradation in the field. Degradation of the active herbicide in field soils (Fig. 8) was much faster than expected from the degradation rate measured in the laboratory experiment and from the environmental conditions following a winter herbicide application. Fifty percent of the active herbicide was degraded in 42 days in the field (Fig. 8), while less than 30% was degraded under similar conditions in the laboratory (Fig. 7). This discrepancy may be due to a higher microbial activity of soil in the field as compared to the laboratory study. Sieving soil, as was done in the laboratory study, often reduces the equilibrium level of microbial activity compared to non-disturbed soils (Gray and Williams, 1975).

Degradation rates measured in the field and laboratory study were in the range reported by other researchers. Degradation rates varied with both soil type and experimental conditions. Degradation half lives under moist, aerobic conditions at 22°C ranged between 10 and 54 days (Smith, 1977; Martens, 1978). Degradation of the active herbicide slowed considerably under anaerobic conditions (Martens, 1978), at very low soil moisture levels (Wu and Santelmann, 1976; Smith, 1979b), and at low soil temperatures (Wu and Santelmann, 1976).

Disappearance of the active herbicide from soil may result from microbial degradation, chemical degradation, photodegradation, and volatilization as well as herbicide runoff losses. The significant differences ($p = 0.01$) in degradation rates between non-sterile and sterile soil (Fig. 7) certainly suggest microbial degradation as the most likely means of diclofop degradation. Slower diclofop breakdown at very low soil moisture contents (Wu and Santelmann, 1976; Smith, 1979b) and under anaerobic conditions (Martens, 1978) also support this hypothesis. Photodegradation and volatilization were not measured in our studies, but losses from these processes were expected to be minimal under winter conditions in western Oregon. Cool temperatures, frequent precipitation, and low evapotranspiration would limit volatilization losses. Low inputs of solar radiation because of high amounts of winter cloud cover would also reduce photodegradation losses. Runoff losses of diclofop-methyl + diclofop accounted for less than 0.7% of the total applied herbicide during the study period.

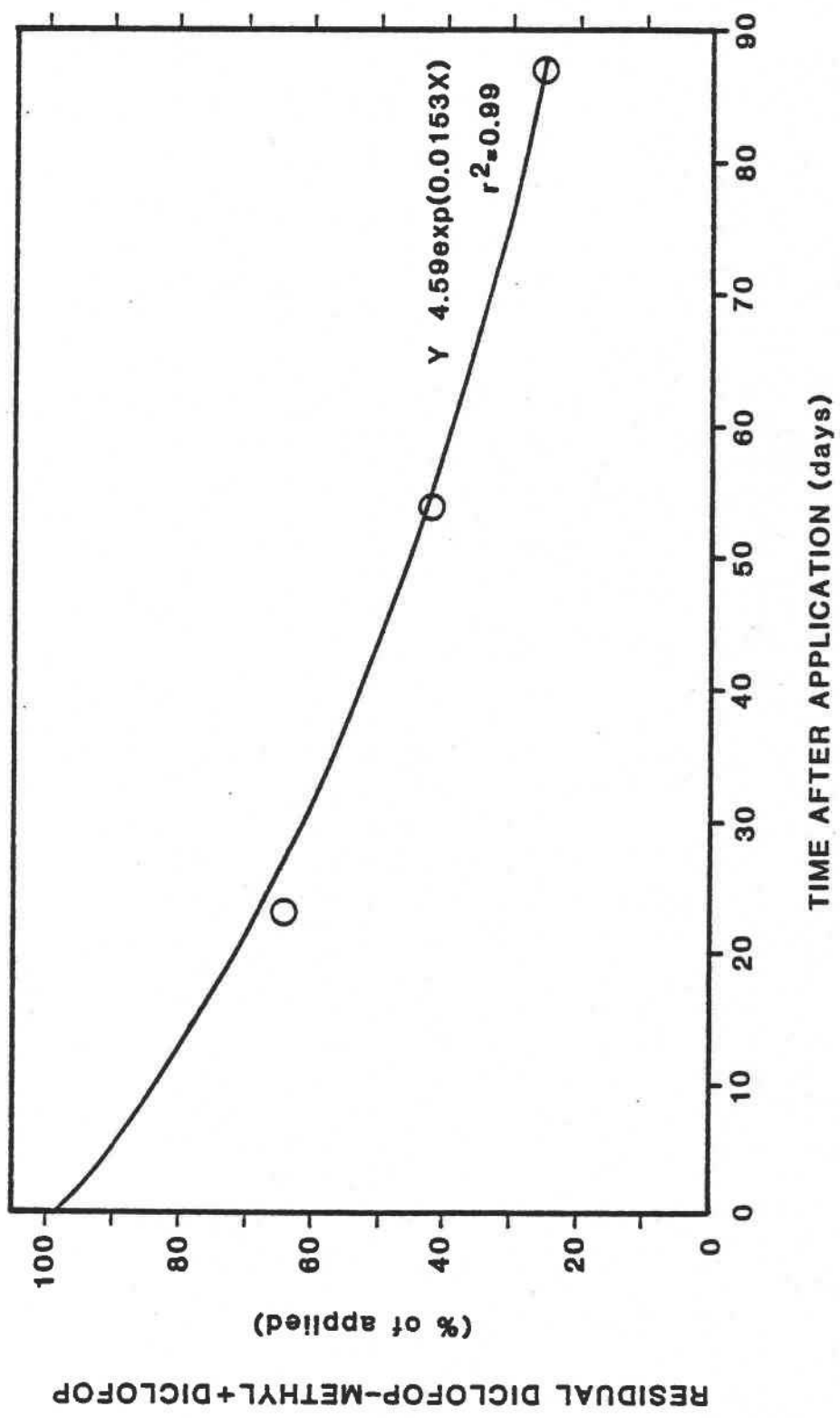


Figure 8. Degradation of diclofop-methyl + diclofop in the field.

DICLOFOP IN RUNOFF

Introduction

The behavior of herbicides in relation to runoff from agricultural lands in the high winter rainfall zone of the Pacific Northwest has not been studied extensively. A majority of the pesticide runoff studies have been conducted in the southeastern and central United States (Stewart, 1976; Wauchope, 1978). The vast difference in climate between these regions and western Oregon makes extrapolation of information from these regions difficult. Factors which affect diclofop runoff losses are expected to be closely associated with runoff and erosion losses. Highest amounts of erosion and runoff in the Willamette Valley were found for storms following high antecedent soil moisture, extensive crusting, or frozen ground (Harward et al., 1980).

Diclofop-methyl is a relatively new herbicide. In western Oregon, diclofop-methyl is applied in late fall or winter for the control of wild oats and Italian ryegrass in winter wheat (Brewster et al., 1977). Since the chemical is applied during the rainfall season, the potential for runoff is high.

Diclofop-methyl rapidly hydrolyzes to diclofop, even under the low soil temperatures prevailing in the late fall and winter in western Oregon; therefore, most of the active herbicide in the soil and in runoff should exist as diclofop and not diclofop-methyl. Lower soil temperatures did retard the degradation beyond the diclofop molecule.

The objectives of this study were to (1) quantify diclofop runoff losses from two small agricultural watersheds and (2) identify factors and processes which influenced diclofop transport under conditions typical of western Oregon following a winter herbicide application.

Materials and Methods

Study Site

The experiment was conducted at the Elkins Road Experimental watershed in cooperation with the STEEP erosion project at Oregon State University (Harward et al., 1980). The Elkins Road watershed is located in southern Polk County, Oregon (3 km south of Monmouth, Oregon), on soils representative of the terrain in the western margin of the Willamette Valley. Two small agricultural sub-watersheds (6.0 ha and 1.4 ha) within the the 285 ha Elkins Road watershed were chosen for study (Fig. 9).

Soils on the watersheds were classified as Ultic Haploxeralfs, Aquic Xerochrepts, and Fluventic Haplaquolls (Brown et al., 1980, Appendix Figure 1 and Appendix Table 3). Total relief in the watersheds is 15 m and 12 m in the 6.0 and 1.4 ha watersheds, respectively (Fig. 9), with slopes ranging from 0-15 percent.

All agronomic operations, except herbicide and fertilizer applications, were carried out by the farm operator before equipment installation in the field. This practice allowed diclofop runoff losses, erosion, and runoff to be studied under actual agricultural practices in the Willamette Valley.

The 6.0 ha and 1.4 ha watersheds were fall planted to winter wheat or grass, depending on soils and topographic position, in mid-October 1979 and 1980. Diclofop-methyl was applied only to areas planted to winter wheat. Only 3.1 ha and 5.0 ha of the 6.0 ha watershed (Fig. 10) were sprayed in 1980 and 1981, respectively, while the entire 1.4 ha watershed was sprayed in both years. Diclofop-methyl was applied by a commercial operator at a rate of 1.12 kg/ha on 5 Jan. 1980 and 7 Jan. 1981. Water was used as a carrier at 120 L/ha. The rate of diclofop-methyl application was not monitored.

Overland flow was obtained from H-flumes (U.S. Agricultural Research Service, 1962) equipped with ISCO Model 1700 flow meters and ISCO Model 1710 printers. Overland flow samples (500 mL) were taken with an ISCO Model 1680 wastewater sampler on a flow proportional

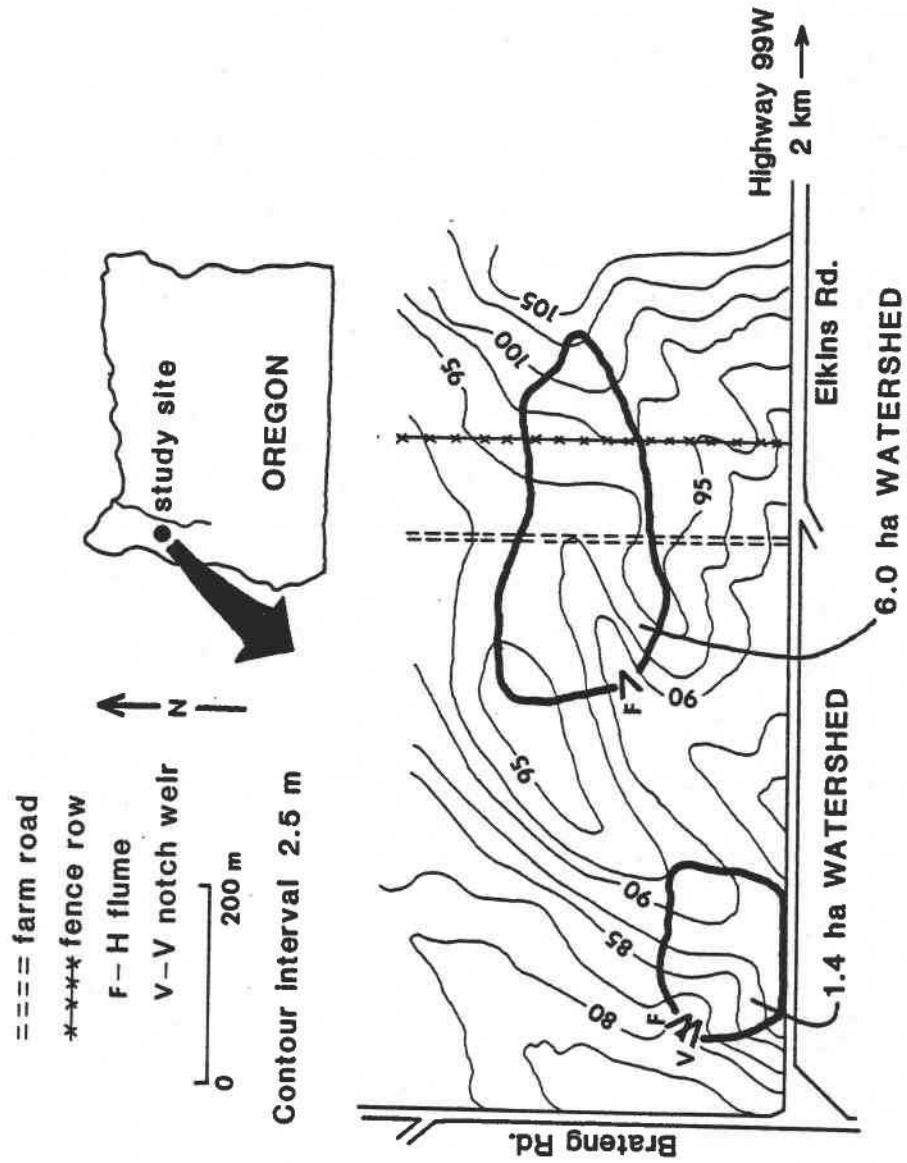


Figure 9. Locations and topographic map of the 6.0 ha and the 1.4 ha watersheds.

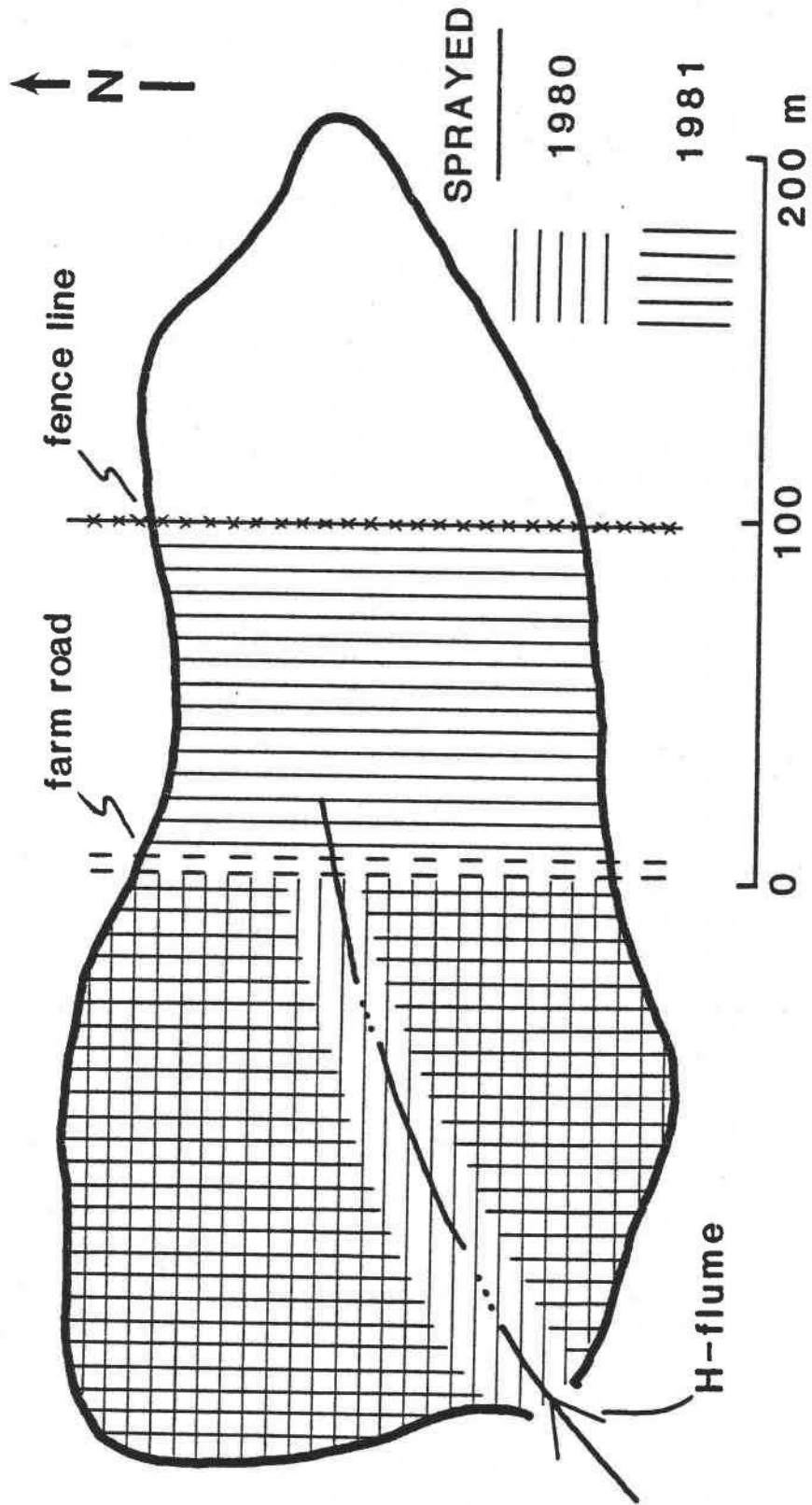


Figure 10. Portions of the 6.0 ha watershed sprayed with diclofop-methyl in 1980 and 1981.

basis. Samples were stored at 4°C and analyzed soon after removal from the field.

A subsurface drainage system was installed on the 1.4 ha watershed in August, 1979. The system drained the entire 1.4 ha watershed plus an additional 0.8 ha outside of the watershed. Plastic drain lines (10 cm in diameter) were installed in a patterned arrangement with a spacing of 12 m and at a depth of 0.9 to 1.2 m (Istok and Kling, 1983). A sampling station for the drain lines was located at the outlet of the 1.4 ha watershed (Fig. 9). Discharge measurements and effluent samples were taken with a v-notch weir and ISCO flow meter, printer, and sampler.

Precipitation amounts and intensities were measured using tipping bucket recording rain gauges sensitive to 0.25 mm of precipitation.

Laboratory Analysis

Sediment

Each overland flow and subsurface drainage effluent sample was analyzed for sediment concentration by oven drying an aliquot of the sample at 105°C.

Diclofop-methyl and Diclofop Analysis

Selected overland flow and subsurface drainage effluent samples (Appendix Tables 4 and 5) were analyzed for diclofop-methyl and diclofop residues. Approximately equal numbers of samples were taken from the rising and falling limbs of runoff hydrographs. Additional samples were taken at or near the peak of the runoff hydrographs. More samples were collected in the runoff events occurring closer to the herbicide application date anticipating the larger herbicide runoff losses in those early runoff events. Sampling was terminated when herbicide residues were no longer detected in the runoff samples.

The analytical procedure for herbicide analysis did not distinguish between diclofop-methyl and diclofop. Herbicide losses will be referred to as diclofop losses even though a small amount of diclofop-methyl may have been present in the overland flow samples.

In 1980, diclofop residues were analyzed in both the aqueous phase of runoff as well as the sediment phase of runoff. Runoff samples were

transferred to 250 mL centrifuge bottles and centrifuged to separate the aqueous and sediment phases. The supernatants were decanted and saved for analysis. The centrifuge bottles were rinsed with 400 mL of 0.2 M KOH and 1.3 M KCl to transfer the sediment back to the original sample bottles after which they were heated on a steam bath for 2 hours. These samples were centrifuged and saved for analysis.

Solutions containing either the aqueous or sediment phases were acidified to pH 2 with concentrated H_2SO_4 and extracted three times with 200 mL of ether. Ether extracts were concentrated to 20 mL and added to a 400 x 20 mm chromatographic column containing 20 g basic alumina (Grade I). The column was washed with 100 mL chloroform, 100 mL ether, and air-dried under a vacuum for 30 minutes. Diclofop residues were washed from the column with 125 mL of 0.09 M $NaHCO_3$. The $NaHCO_3$ solution was acidified to pH 2, extracted three times with 75 mL ether, the ether concentrated to 20 mL, and methylated with diazomethane (Arndt, 1943). The methylated extract was transferred to a benzene solvent, concentrated, and saved for gas chromatographic analysis of diclofop residues.

In 1981, the sediment and aqueous phases of runoff were not separated for diclofop analysis. Appropriate amounts of KOH were added to each sample to bring the sample-KOH concentration to 0.2 M. Samples were heated on a steam bath for 2 hours and the procedure repeated as described in the previous paragraph.

The procedure for gas chromatographic analysis of diclofop residues was identical to the procedure described previously (page 24). The analytical procedures were sensitive to 0.5 μg of esterified diclofop in the total sample extract. Recoveries were determined by fortifying water samples with diclofop-methyl or diclofop standard solutions at levels ranging from 1 to 1000 mg/m^3 . Recoveries ranged between 95 and 100 percent.

Data Management

Diclofop loss hydrographs in the aqueous and/or sediment phases of runoff were generated for each runoff event. Individual diclofop loads (g/h) were calculated from the diclofop concentrations, discharge, and

suspended sediment concentration at each diclofop sampling point (Appendix Tables 4 and 5). Diclofop losses were calculated on an hourly basis and added to an existing computer file containing hourly discharge and sediment loads (Jack Istok², unpublished data). Discharge, sediment loss, and diclofop loss characteristics for each event were calculated using the hourly data. Since the rate of diclofop-methyl application was not verified, diclofop losses were based on the rate of application, 1.12 kg/ha, calibrated by the commercial applicator.

Results and Discussion

Precipitation

Precipitation events in western Oregon are characterized by frequent, low-intensity frontal type storms. Average annual precipitation is 1030 mm of which 80% falls from 1 Oct. to 31 Mar. (Knezevich, 1975). Annual totals for the 1979-80 and 1980-81 seasons were 940 and 990 mm, respectively (Fig. 11).

Precipitation in the 75 days following diclofop-methyl application in 1980 and 1981 was 270 and 200 mm, respectively. The average precipitation for this time period is 340 mm (Knezevich, 1975). The largest storm after application in 1980 occurred just 6 days after application and resulted in 44 mm of precipitation (Table 2). This storm had a storm frequency of 4 (storms with this magnitude could be expected to occur four times in any given year) (Table 2). In 1981, the largest storm had a storm frequency of 12 and occurred 42 days after application (Table 2).

Diclofop Losses in Overland Flow

Diclofop seasonal losses resulting from overland flow in 1980 were 7.1% (80 g/ha) and 3.9% (44 g/ha) of the total herbicide applied at the 6.0 ha and 1.4 ha watersheds, respectively (Table 3). Of that which

²Jack Istok, Department of Soil Science, Oregon State University, Corvallis, Oregon, 97331.

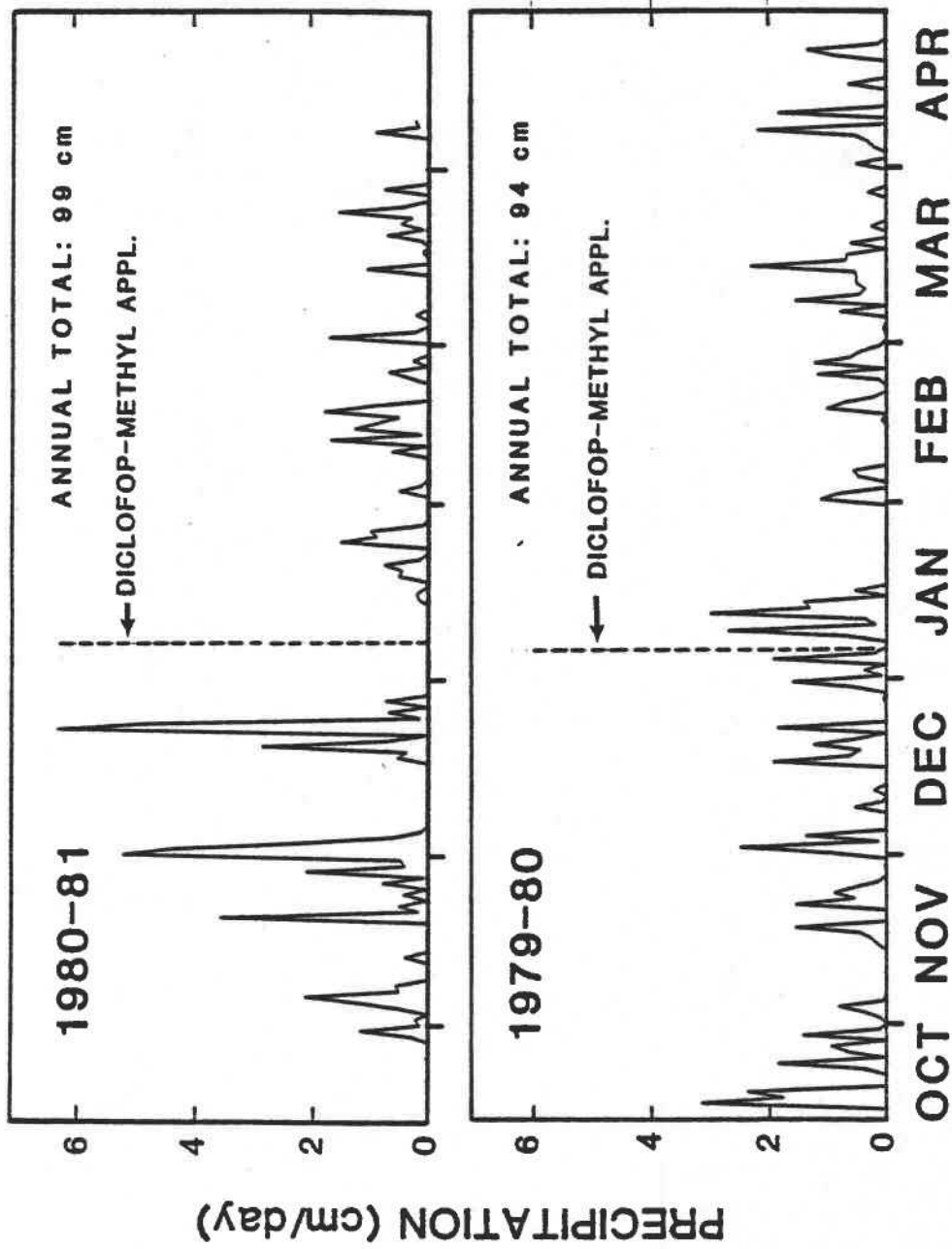


Figure 11. Daily precipitation at the study site during the 1979-80 and 1980-81 rainfall seasons.

Table 2. Precipitation characteristics for storm events occurring after diclofop-methyl application in 1980 and 1981.

STORM NO.	STORM DATE	DAYS AFTER APPLIC.	PRECIP TOTAL (mm)	STORM FREQUENCY [†]	PEAK INTENSITY (mm/hr)
(1980)					
1	10880	3	33	6	3.8
2	11180	6	44	4	5.6
3	11480	9	14	19	5.1
4	11680	11	4.8	46	1.3
5	20280	28	20	13	2.0
6	21780	43	17	16	1.8
7	22580	51	14	19	1.5
8	31280	67	5.3	43	3.0
9	31480	69	12	23	3.1
TOTALS			270		
(1981)					
1	12681	19	14	19	3.8
2	12781	20	7.4	34	2.5
3	12881	21	4.3	48	1.8
4	21381	37	10	41	4.6
5	21581	39	19	14	3.0
6	21881	42	21	12	3.6
7	21981	43	9	30	4.1
TOTALS			200		

[†] Storm frequency is defined as the number of precipitation events of the same or greater magnitude that would be expected to occur in any given year. Based on a 31½ year record.

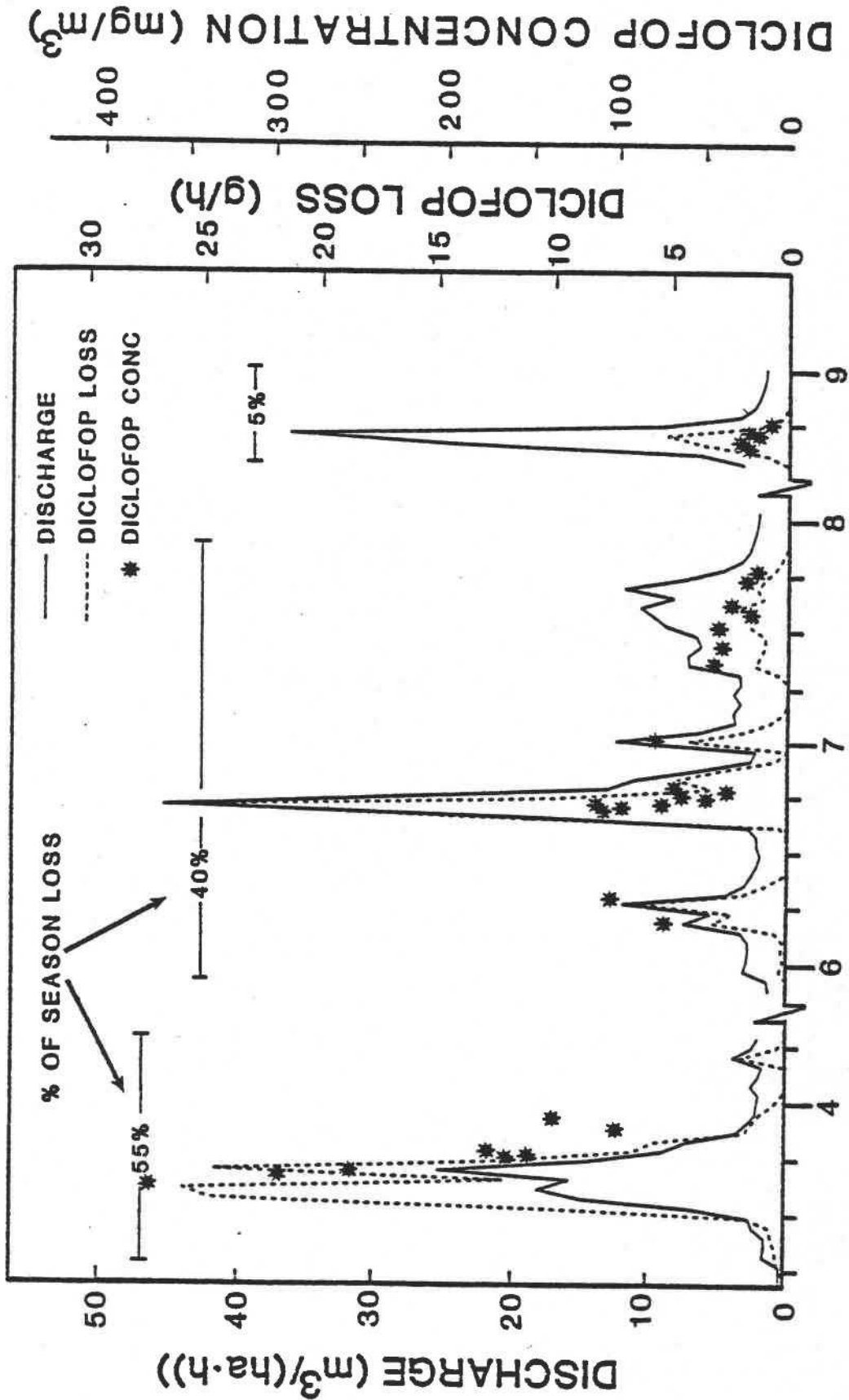
Table 3. Dicrofop runoff summary for 1980 storm events at both the 6.0 ha and 1.4 ha watersheds.

STORM NO.	STORM DATE	STORM CHARACTERISTICS				DICLOFOP LOSS			
		DAYS AFTER APPLIC.	DISCHARGE (m ³ /ha)	RUNOFF (%)	SEDIMENT (kg/ha)	LOSS (g/ha)	LOSS (% of APPLIED)	SEASONAL LOSS (%)	LOSS AQUEOUS (%)
6.0 ha WATERSHED									
1	10880	3	152	46	255	44	3.9	55	92
2	11180	6	342	78	489	32	2.9	40	88
3	11480	9	95	68	214	3.7	0.3	5	78
4	11680	11	33	69	6.5	0.2	<0.1	0.3	100
6	21880	44	6.4	9	3.5	<0.1	<0.1	<0.1	99
7	22580	51	9.4	7	2.6	<0.1	<0.1	<0.1	100
8	31280	67	2.6	5	1.6	<0.1	<0.1	<0.1	—
9	31480	69	21	18	4.4	<0.1	<0.1	<0.1	—
TOTALS			930		990	80	7.1		90
1.4 ha WATERSHED									
1	10980	3	59	18	596	20	1.8	47	87
2	11180	6	202	46	1160	21	1.9	49	74
3	11480	9	53	38	427	2.2	0.2	5	55
TOTALS			340		2200	44	3.9		79

was lost, more than 99% of the diclofop seasonal loss occurred in a series of early storm events within 9 days of diclofop-methyl application. At the 6.0 ha watershed, this series of storms which totaled 91 mm of precipitation (Table 2), resulted in 65% runoff. As a result of steady precipitation in late December 1979 and early January 1980 (Fig. 11), the soil profile was partially saturated at the time of diclofop-methyl application. Consequently, when 33 mm of precipitation fell in the first subsequent storm (3 days after application), 46% of the precipitation resulted in overland flow (Table 3). This storm accounted for more than 50% of the diclofop seasonal loss (Fig. 12). Another runoff event with a higher peak and total discharge occurred between 6 and 8 days after herbicide application and accounted for another 40% of the diclofop seasonal loss (Fig. 12). The soil profile was saturated during this storm as well as the storm at 9 days after application (Parsons et al., 1980), resulting in 78 and 68% runoff, respectively. The sharp runoff hydrograph occurring at 9 days after application resulted in only 5% of the diclofop seasonal loss (Fig. 12).

The diclofop concentrations in individual runoff samples over the storm period (Fig. 12) helped explain the proportion of diclofop seasonal loss occurring in each runoff event. Diclofop concentrations decreased very fast across the runoff hydrographs between 3 and 9 days after application, particularly in the first runoff event (Fig. 12). The maximum diclofop concentration of 370 mg/m^3 (370 ppb) occurred early in the first runoff event after application. Higher diclofop concentrations in the first runoff event (average storm concentration of 150 mg/m^3) resulted in greater amounts of diclofop lost in the first event as opposed to the runoff events between 6 and 8 days (average storm concentration of 48 mg/m^3) and 9 days (average storm concentration of 20 mg/m^3) after application. Since only 3.1 ha of the 6.0 ha watershed was sprayed with diclofop-methyl in 1980, runoff from the unsprayed areas of the watershed diluted diclofop concentrations in individual runoff samples as well as average storm concentrations.

Diclofop seasonal losses in overland flow from the 1.4 ha subsurface drained watershed (3.9% of applied) reflect the lower



TIME AFTER APPLICATION (days)

Figure 12. Discharge and diclofop loss hydrographs and diclofop concentrations at the 6.0 ha watershed for the storm events between 3 and 9 days after diclofop-methyl application in 1980.

discharge ($340 \text{ m}^3/\text{ha}$) at the 1.4 ha watershed as compared to the 6.0 ha watershed (7.1% of applied and $930 \text{ m}^3/\text{ha}$ discharge) (Table 3). Ninety six percent of the diclofop seasonal loss at the 1.4 ha watershed occurred in the two runoff events at 3-4 and 6-8 days after diclofop-methyl application (Fig. 13). Diclofop concentrations in runoff samples at the 1.4 ha watershed (Fig. 13) decreased very rapidly across the runoff hydrographs between 3 and 9 days after application just as at the 6.0 ha watershed (Fig. 12). A maximum concentration of $790 \text{ mg}/\text{m}^3$ was measured early in the first runoff event at the 1.4 ha watershed (Fig. 13).

Lower diclofop seasonal losses at the 1.4 ha watershed compared to the 6.0 ha watershed in 1980 resulted from the effectiveness of subsurface drainage in reducing watershed discharge. Runoff from the 1.4 ha watershed was only 35% of the total precipitation during the series of storms between 3 and 9 days after diclofop-methyl application compared to 65% at the 6.0 ha watershed. Subsurface drainage reduced runoff at the 1.4 ha watershed by lowering ephemeral perched water tables, particularly in lower slope positions (Lowery et al., 1982; Istok and Kling, 1983). The effect of subsurface drainage was most pronounced in the first runoff event as runoff was only 18% of precipitation in the 1.4 ha watershed as compared to 46% at the 6.0 ha watershed (Table 3). Consequently, the diclofop loss in the first storm was only 1.8% of applied at the 1.4 ha watershed as compared to 3.9% of applied at the 6.0 ha watershed (Table 3). In the storms occurring between 6 and 9 days after application, ephemeral perched water tables rose closer to the soil surface and the effectiveness of subsurface drainage in reducing runoff at the 1.4 ha watershed decreased (Lowery et al., 1982). Diclofop loss from the outlet of the subsurface drainage system accounted for an additional loss of 1.2% of the applied herbicide from the 1.4 ha watershed.

The decrease in diclofop concentrations in individual runoff samples across the runoff hydrographs at both the 6.0 ha and the 1.4 ha watersheds was much faster than the degradation of diclofop-methyl + diclofop in the soil profile (Fig. 8). Wauchope (1978) calculated runoff-available-pesticide half-lives by plotting the log of bulk pesticide concentration against the time after application.

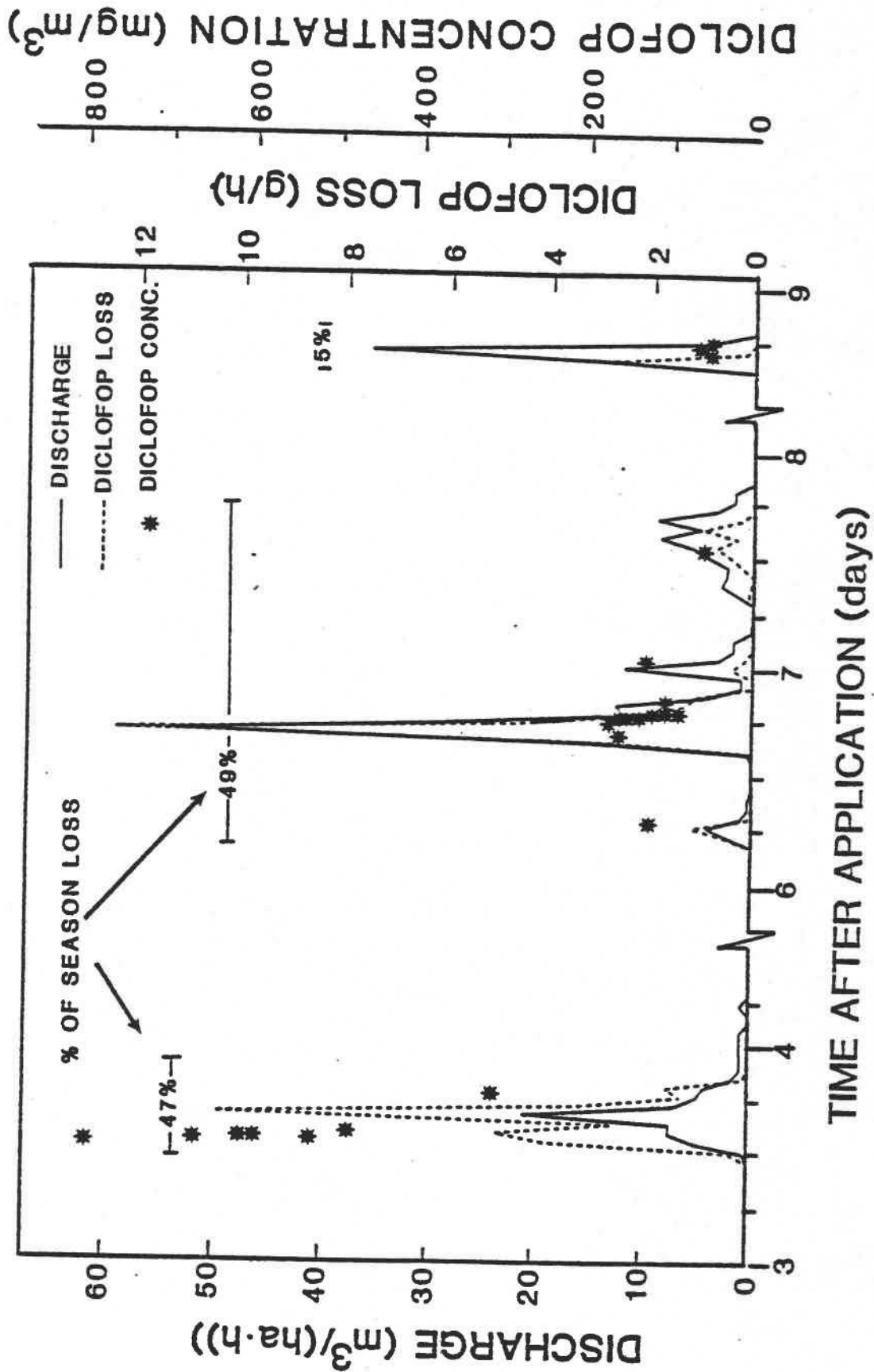


Figure 13. Discharge and diclofop loss hydrographs and diclofop concentrations at the 1.4 ha watershed for the storm events between 3 and 9 days after diclofop-methyl application in 1980.

Excellent linear plots were obtained in these studies when average diclofop storm concentrations during the storm events between 3 and 9 days after application were plotted in this manner (Fig. 14). Runoff-available-diclofop half-lives calculated from these plots were 2.0 days for both the 6.0 ha and the 1.4 ha watersheds in 1980 (Fig. 14). The difference between the runoff-available half-lives (Fig. 14) and the disappearance of diclofop-methyl + diclofop in the 0-1 cm depth in the soil (50% disappeared in 24 days, Appendix Fig. 2) indicate that the mixing depth or the depth to which overland flow extracts herbicide from the soil profile is shallower than 1 cm.

Steenhuis and Walter (1980) derived an empirical equation to calculate mixing depth "h_{mix}". The first step is to regress the natural logarithm of diclofop concentrations in overland flow with cumulative precipitation since runoff began. Mixing depth was calculated as:

$$h_{mix} = [-b \cdot (mcs + (p_s \cdot k))]^{-1}$$

where h_{mix} = mixing depth (cm),

b = slope of the regression line

$\ln(\text{concentration}) = a + b(\text{cumulative precipitation}),$

mcs = volumetric moisture content at saturation
(cm³/cm³),

p_s = bulk density of soil (g/cm³),

k = adsorption-partition coefficient.

Mixing depths were computed from diclofop concentrations in both the bulk (aqueous and sediment) and aqueous phases of runoff. The mixing depths calculated for the three storms between 3 and 9 days after application ranged between 0.13 and 0.16 cm (Table 4). The calculated mixing depths were essentially the same regardless of the phase (bulk or aqueous) or the watershed (Table 4). The similarity between the calculated mixing depths is surprising considering the wide variety of hydrologic conditions and precipitation intensities existing during this period. Mixing depths were not calculated from diclofop concentrations in the sediment phase of runoff because of the very poor correlation between the natural logarithm of diclofop concentrations in the sediment phase and cumulative precipitation.

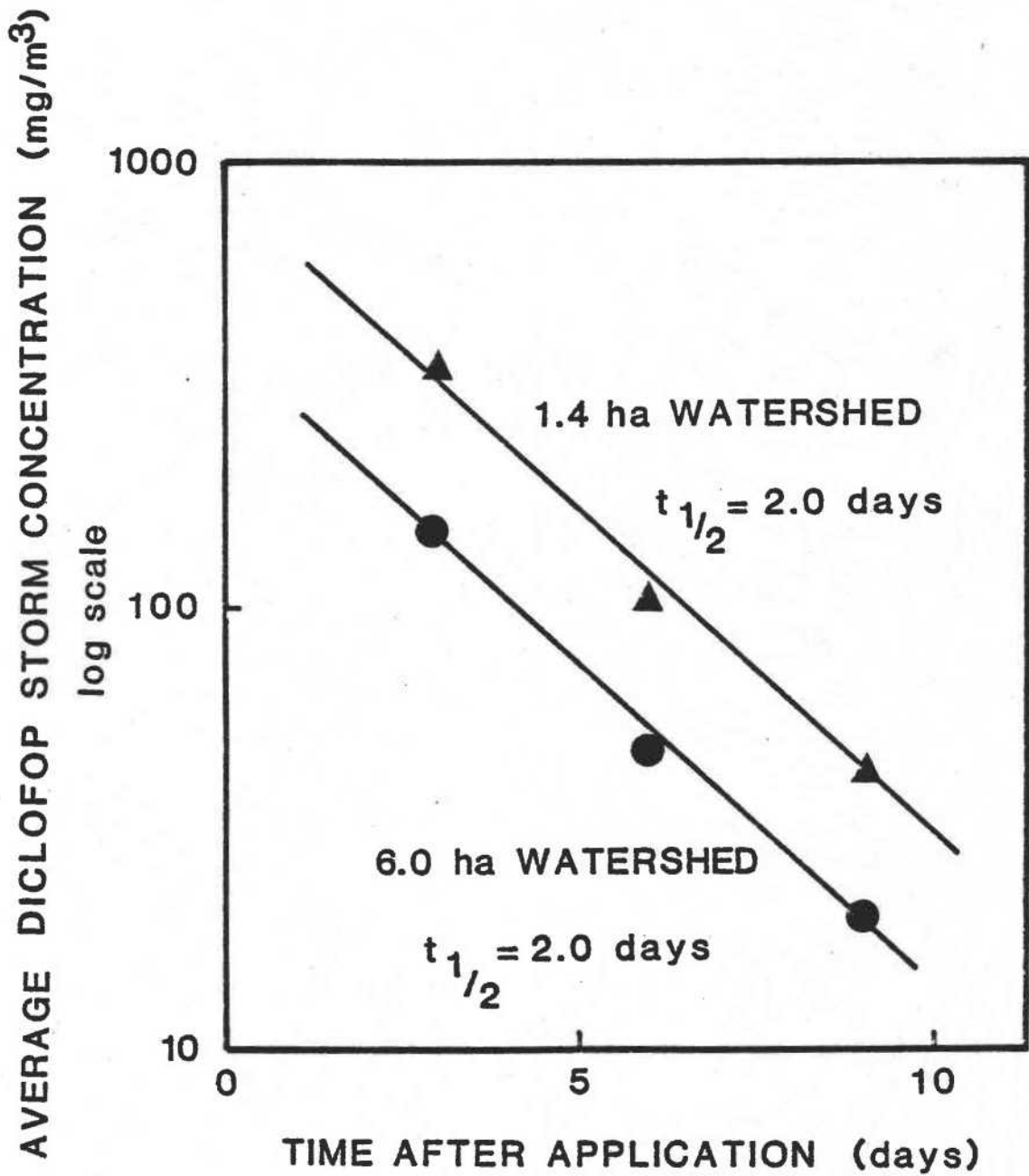


Figure 14. Relationship between the natural logarithm of the average diclofop storm concentrations in runoff and time after diclofop-methyl application.

Table 4. Mixing depth "h_{mix}" values and input parameters for the calculation of "h_{mix}" for the storms between 3 and 9 days after application in 1980.

WATERSHED	PHASE	a [†]	b	s(b)	r ²	ps (g/cm ³)	mcs (cm ³ /cm ³)	k	h _{mix} (cm)
6.0 ha	bulk [§]	-1.35	-0.30	0.022	0.87	1.37	0.40	15.3	0.16
	aqueous	-1.40	-0.32	0.022	0.89	1.37	0.40	15.3	0.15
1.4 ha	bulk	-0.44	-0.32	0.019	0.93	1.37	0.40	15.3	0.15
	aqueous	-0.50	-0.37	0.024	0.91	1.37	0.40	15.3	0.13

† a and b = regression coefficients for the regression line
(ln concentration) = a + b (cm cum precipitation)
s(b)₂ = standard error of b

r² = coefficient of determination of the regression line
ps = bulk density in g/cm³ (taken from Lowery, 1980)
mcs = volumetric moisture content at saturation in cm³/cm³ (taken from Lowery, 1980)
k = adsorption-partition coefficient (Appendix Fig. 3)

§ bulk phase includes the aqueous and sediment phases of runoff

Mixing depths calculated from the diclofop runoff data in this study were shallower than for reported mixing depths (Steenhuis and Walter, 1980). Steenhuis and Walter (1980) calculated a mixing depth of 0.9 cm using alachlor and cyanazine runoff data from Baker et al. (1978). Using the same mixing depth (0.9 cm), Steenhuis and Walter (1980) found reasonable agreement between observed pesticide runoff losses from Bailey et al. (1974) and predicted values using a closed form solution pesticide loss model. Smith et al. (1978) found that half lives estimated from soil-pesticide persistence data in the 0-1 cm surface zone agreed with the runoff-available-pesticide half-lives calculated from pesticide concentrations in runoff water. In each of the above cases, the pesticide was applied soon after tillage operations and/or planting.

In western Oregon, diclofop-methyl is usually applied several months after planting and seedbed preparation. Between the planting date and the 1980 diclofop-methyl application in this study, 370 mm of precipitation had fallen. The fall and early winter rains break down the soil aggregates which results in a surface crust (Harward et al., 1980). Subsequent thickening of the surface crust can be attributed to sedimentation from upslope erosion (Pronold and Harward, 1980). Timing of surface crust formation varies from year to year (Lowery et al., 1982). The shallow mixing depths reported from this study, 0.13-0.16 cm, indicate the formation of a surface crust which would limit the depth to which diclofop residues, soil solution, and overland flow intermix. Initially, high amounts of diclofop residues would be concentrated at the soil crust and available for overland flow losses. As the storm event progressed, precipitation infiltrating into the soil profile could leach diclofop out of the mixing zone, thus decreasing the diclofop concentrations in runoff, particularly, in the aqueous phase of runoff. This phenomenon seemingly explains the very rapid decrease of diclofop concentrations across runoff hydrographs in the series of storms between 3 and 9 days after diclofop-methyl application in 1980.

Diclofop, discharge, and sediment losses in the storms between 11 and 69 days after application in 1980 were very small at both watersheds (Table 3). Precipitation during this period totaled 160 mm.

Half of this precipitation fell in an 8 day period in early March (63-70 days after application), resulting in only 37 m³/ha of discharge (5% runoff) from the 6.0 ha watershed and zero discharge from the 1.4 ha watershed. Diclofop was not detected in any overland flow samples during this period. Discharge is reduced in late winter and/or early spring because of a reduction in the frequency of precipitation events, increasing evapotranspiration, and increasing infiltration due to surface cracking (Harward et al., 1980).

Most of the diclofop lost in overland flow in 1980 was lost in the aqueous phase of runoff. Ninety and 79% of the diclofop was partitioned into the aqueous phase of runoff at the 6.0 and 1.4 ha watersheds, respectively (Table 3). The percentage of diclofop partitioned into the aqueous phase of runoff was similar to that of other runoff studies conducted with pesticides of similar solubilities (Wauchope, 1978). More diclofop was lost in the aqueous phase of runoff than the suspended sediment phase of runoff even though diclofop concentrations (Appendix Table 4) were higher in the sediment phase. More diclofop was lost in the aqueous phase because the aqueous phase was a much larger proportion of the total runoff.

The fraction of diclofop lost in the sediment phase of runoff in each event increased with each successive storm during the series of storms between 3 and 9 days after application at both watersheds (Table 3). This phenomenon has been observed for other pesticides which are primarily lost in the aqueous phase of runoff and is attributed to the ease in which the "easily available pesticide" (dissolved pesticide) was lost in the earliest events (Wauchope, 1978). With each successive event, more dissolved pesticide leaches out of the mixing depth or has already been lost in the overland flow and therefore, the sediment phase diclofop comprises a larger fraction of the total pesticide loss. This phenomenon also explains the faster rate of decrease in diclofop concentrations in the aqueous phase compared to the sediment of runoff (Appendix Table 4) for the storms between 3 and 9 days after application in 1980. The larger fraction of diclofop lost in the sediment phase of runoff at the 1.4 ha watershed as compared to the 6.0 ha watershed (Table 3) may be due to the higher suspended sediment concentrations at the 1.4 ha watershed. A larger sediment loss (2200

vs. 990 kg/ha) and less total discharge (340 vs. 930 m³/ha) at the 1.4 ha watershed as compared to the 6.0 ha watershed (Table 3) explain the higher suspended sediment concentrations at the 1.4 ha watershed.

The 1980 diclofop seasonal losses were higher than the seasonal losses (<1% of applied) normally found for pesticides applied as emulsions (Wauchope, 1978). Wauchope (1978) lists some exceptions to this generalization such as DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane], where seasonal losses ranged as high as 2-3% of applied pesticide. DDT is an organochlorine insecticide that is very persistent and therefore is available for overland flow losses over a longer period of time than most pesticides. Other exceptions include cases where large losses were associated with a single runoff event such as alachlor under a simulated rainfall 2 days after application (Baker et al., 1978) and 2,4,5-T ester [(2,4,5-trichlorophenoxy)acetic acid] in a forested watershed (Lawson, 1976). Wauchope (1978) found that most large pesticide runoff losses, such as the 1980 seasonal losses in this study, occurred within a 2 week critical period after application. The events at 6 and 9 days after application at the 6.0 ha watershed in 1980 would be classified as critical events since they occurred within 2 weeks after application, had at least 1 cm of precipitation, and had greater than 50% runoff. The first two events at the 6.0 ha watershed in 1980 would even be classified as catastrophic (Wauchope, 1978) since they produced losses greater than 2% of the applied herbicide (Table 3).

Diclofop seasonal losses in overland flow were considerably lower in 1981 (Table 5) than in 1980 (Table 3). Diclofop seasonal losses were 0.7% (7.4 g/ha) of that applied at the 6.0 ha watershed and less than 0.1% (0.3 g/ha) of that applied at the 1.4 ha watershed (Table 5). Diclofop concentrations were also lower at the 6.0 ha watershed in 1981 (Fig. 15) than in 1980 (Fig. 12). Diclofop seasonal losses in 1981 were in the range classified by Wauchope (1978) for pesticides applied as emulsions. The largest precipitation event in 1981 had a storm frequency of 12 (storms with this magnitude could be expected to occur four times in any given year) as compared to the two largest events in 1980 which had storm frequencies of 4 and 6 (Table 2). The first runoff event did not occur until 19 days after the diclofop-methyl

Table 5. Diclofop runoff summary for 1981 storm events at both the 6.0 ha and 1.4 ha watersheds.

STORM NO.	STORM DATE	STORM CHARACTERISTICS				DICLOFOP LOSS		
		DAYS AFTER APPLIC.	DISCHARGE (m ³ /ha)	RUNOFF (%)	SEDIMENT (kg/ha)	LOSS (g/ha)	LOSS (% of applied)	SEASONAL LOSS (%)
					6.0 ha WATERSHED			
1	12681	19	17	12	29	1.0	0.1	13
2	12781	20	27	36	40	1.7	0.2	23
3	12881	21	28	65	22	1.4	0.1	19
4	21381	37	21	21	82	0.6	0.1	8
5	21581	39	44	23	221	0.8	0.1	10
6	21781	41	77	37	125	1.1	0.1	15
7	21981	43	55	61	221	0.9	0.1	13
TOTALS			450		1000	7.4	0.7	
					1.4 ha WATERSHED			
2	12781	20	2.5	3	19	<0.1	<0.1	15
4	21381	37	0.3	0.3	5.8	<0.1	<0.1	2
6	21881	42	2.8	1	52	<0.1	<0.1	15
7	21981	43	15.8	18	210	0.2	<0.1	68
TOTALS			21		270	0.3	<0.1	

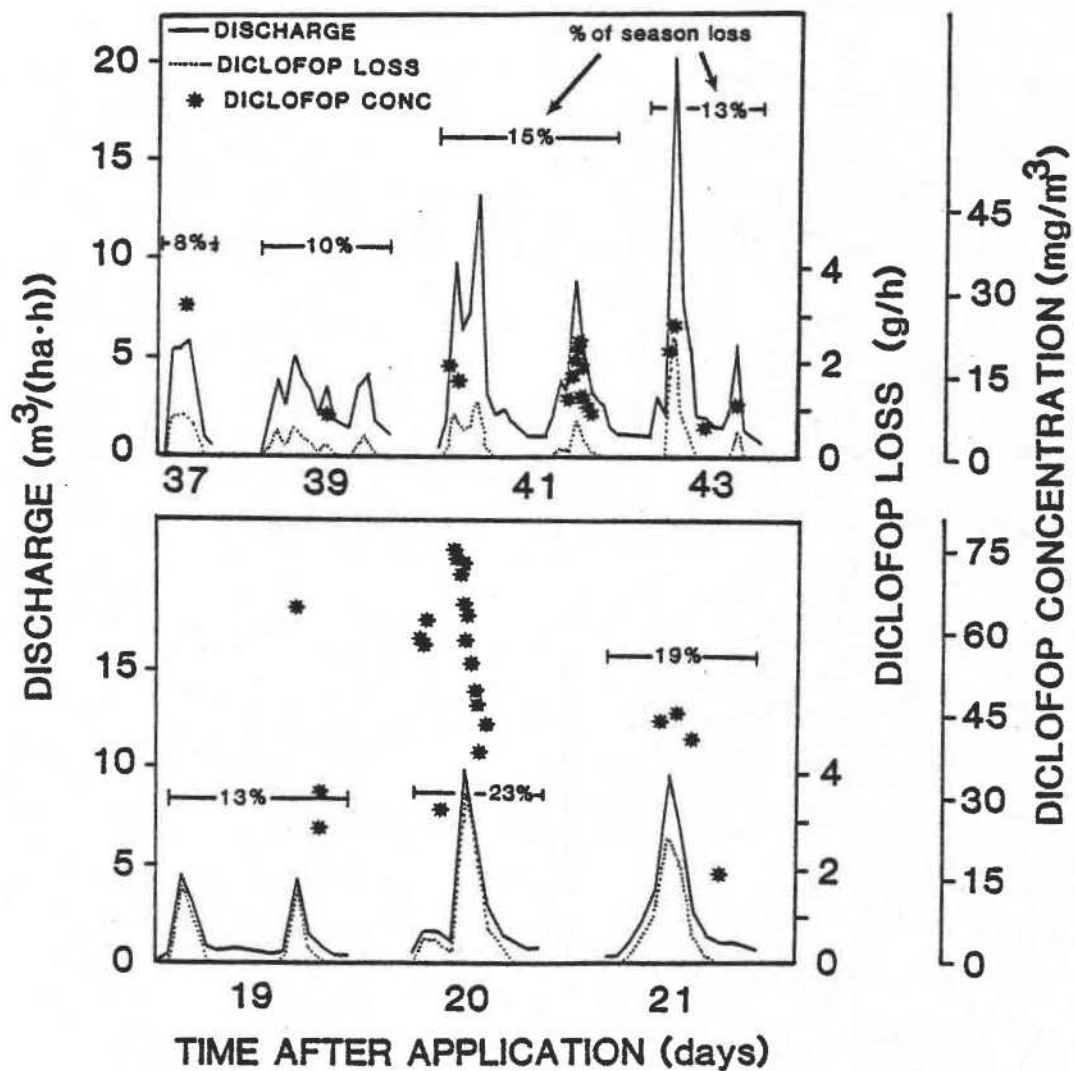


Figure 15. Discharge and diclofop loss hydrographs and diclofop concentrations at the 6.0 ha watershed for the storm events between 19 and 43 days after diclofop-methyl application in 1981.

application (Table 5), giving the diclofop a chance to degrade before the first runoff event. The half life of diclofop-methyl + diclofop in the soil (0-10 cm) was 42 days (Fig. 8). Using the degradation curve depicted in Fig. 8, only 68% of the herbicide applied would be remaining in the soil profile at the time of the first runoff event. Some precipitation (2.1 cm) between 10 and 19 days after application, but before the first runoff event, may have also resulted in leaching of diclofop out of the mixing depth before runoff began.

At the 6.0 ha watershed, percentage runoff for both the January (19-21 days after application) and the February (37-43 days after application) series of storms averaged between 30-35%. The first runoff event, 19 days after application, resulted in only 12% runoff (Table 5) and 13% (Fig. 15) of the diclofop seasonal loss. The low percentage runoff was due to the low antecedent soil moisture at the time of this storm. Low percentage runoff storms at the Elkins Road watershed generally produced runoff only from lower slope positions (Harward et al., 1980). At the 6.0 ha watershed in 1981, the lower slope positions (waterways) were planted to annual ryegrass and were not sprayed with diclofop-methyl (Fig. 9), therefore little diclofop loss would be expected in the first storm. In the later runoff events in the January storm period, percentage runoff increased (Table 5) and diclofop seasonal loss also increased (Fig. 15) as overland flow originated from a larger proportion of the 6.0 ha watershed including the areas sprayed with diclofop-methyl. The January series of storms accounted for 55% of the diclofop seasonal loss.

Percentage runoff in the February series of storms showed the same trends as the January storms by starting low (21%) in the first storm and increasing with successive storms (Table 5). The February storms accounted for a higher discharge ($200 \text{ m}^3/\text{ha}$) than the January storms ($72 \text{ m}^3/\text{ha}$) (Table 5), but accounted for only 45% of the diclofop seasonal loss. Lower diclofop losses in the February series of storms as compared to the January series may be the result of both additional diclofop degradation and leaching out of the mixing depth in the time period (16 days) between the January and February storms.

Runoff from the 1.4 ha watershed after diclofop-methyl application was less than 2% of the precipitation in 1981. Diclofop seasonal loss

was only 0.3 g/ha (<0.1% of applied) at this watershed in 1981 (Table 5). Most of the diclofop seasonal loss (68%) occurred in the storm 43 days after application (Table 5). This storm also had the highest percentage runoff (18%) of any of the 1981 events at the 1.4 ha watershed and accounted for 75% of the seasonal watershed discharge (Table 5). The very low percentage runoff and low diclofop losses at the 1.4 ha watershed as compared to the 6.0 ha watershed (Table 5) can be attributed to the effect of subsurface drainage in reducing antecedent soil moisture and hence watershed runoff (Harward et al., 1980; Lowery et al., 1982; Istok and Kling, 1983).

Diclofop Losses in Subsurface Drainage Effluent

Diclofop seasonal loss from the subsurface drainage system installed at the 1.4 ha watershed was 1.2% and <0.1% of the diclofop-methyl applied in 1980 and 1981, respectively (Table 6). As was the case for diclofop losses in overland flow in 1980, a high percentage of the seasonal loss (97%) in the subsurface drainage system occurred in the series of storms within 9 days of herbicide application (Table 6). Discharge in the drain lines during these storms accounted for 55% of the precipitation during this period. Overland flow from the 1.4 ha watershed accounted for only 35% of the precipitation in the same period. Forty five percent of the diclofop seasonal loss was accounted for in the first runoff event which occurred between 3 and 5 days after application (Fig. 16). The runoff event between 5.5 and 8 days after application resulted in an additional 50% of the diclofop seasonal loss (Fig. 16). Ninety eight percent of the diclofop lost in the subsurface drainage effluent in 1980 was partitioned into the aqueous phase of discharge (Table 6). Only in the first event after application was any diclofop detected in the sediment phase of discharge (Table 6). In 1981, diclofop was detected only in 10 of 22 effluent samples (Appendix Table 5).

In 1980, diclofop residues were detected in most effluent samples taken at the outlet of the subsurface drainage system (Fig. 17). Diclofop concentrations decreased very quickly across the seasonal hydrograph (Fig. 17) after reaching a maximum concentration of 74

Table 6. Dicrolofop discharge summary for 1980 and 1981 storm events in the subsurface drainage system.

STORM NO.	STORM CHARACTERISTICS					DICLOFOP LOSS				
	STORM DATE	DAYS AFTER APPLIC.	DISCHARGE (m ³ /ha)	SEDIMENT (kg/ha)	LOSS (g/ha)	LOSS (% of applied)	SEASONAL LOSS (%)	LOSS AQUEOUS (%)		
(1980)										
1	10880	3	107	19	6.2	0.6	45	95		
2	11180	6	286	40	7.0	0.6	50	100		
3	11480	9	108	6.0	0.3	<0.1	2	100		
4	11680	11	32	2.2	<0.1	<0.1	<0.1	—		
5	20280	28	55	3.8	0.2	<0.1	1	100		
6	21780	43	42	5.8	0.1	<0.1	0.9	100		
7	22580	51	41	3.9	<0.1	<0.1	0.3	100		
9	31380	68	125	6.0	<0.1	<0.1	<0.1	100		
TOTALS			1300	140	14	1.2		98		
(1981)										
1	12681	19	24	3.8	<0.1	<0.1	—	—		
2	12781	20	8.9	1.7	<0.1	<0.1	—	—		
3	12881	21	14	2.6	<0.1	<0.1	—	—		
5	21581	39	71	7.9	<0.1	<0.1	—	—		
6	21781	41	105	9.8	<0.1	<0.1	—	—		
7	21981	43	96	8.9	<0.1	<0.1	—	—		
TOTALS			580	80	<0.1	<0.1				

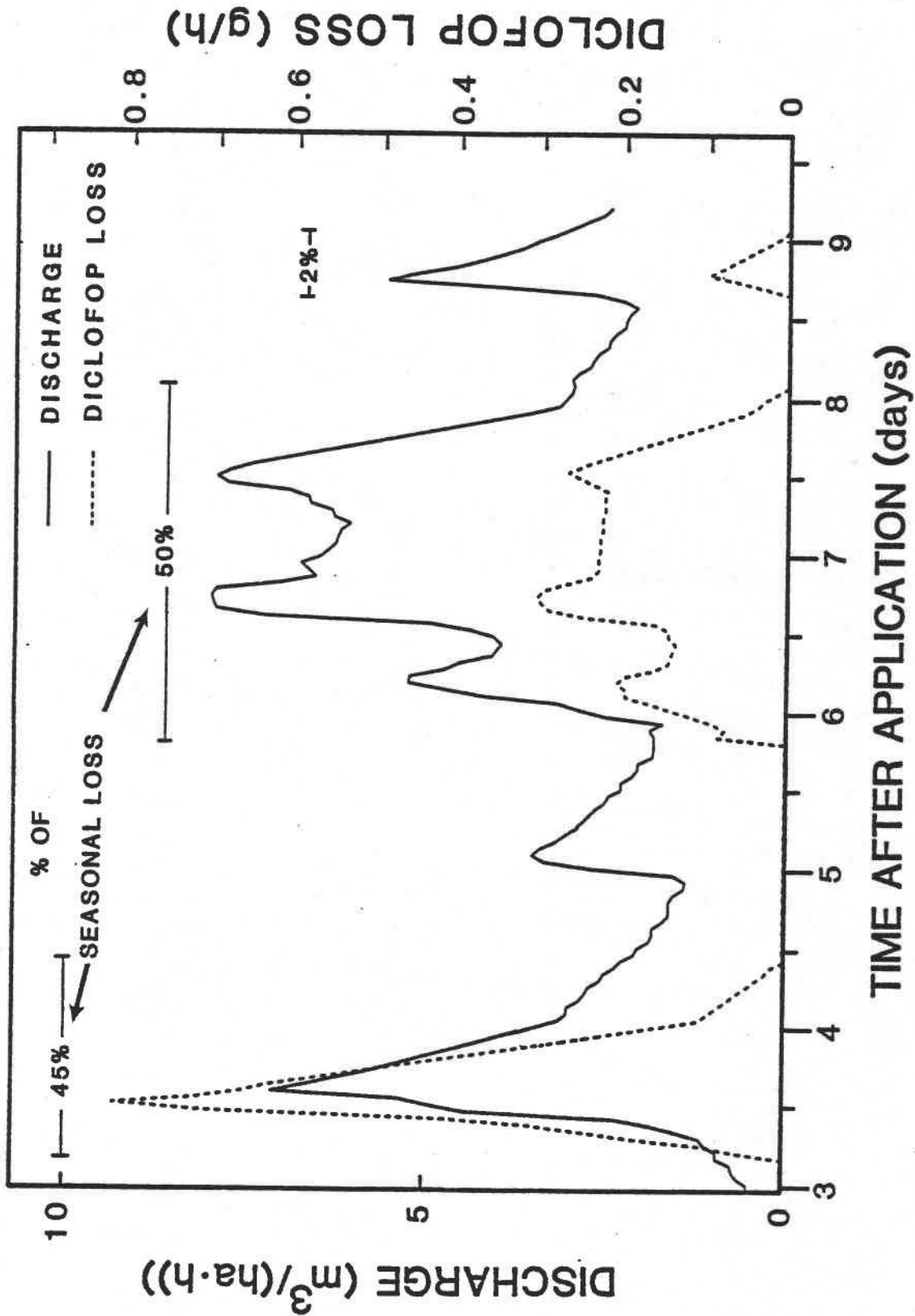


Figure 16. Discharge and diclofop loss hydrographs from the subsurface drainage system for the storm events between 3 and 9 days after diclofop-methyl application in 1980.

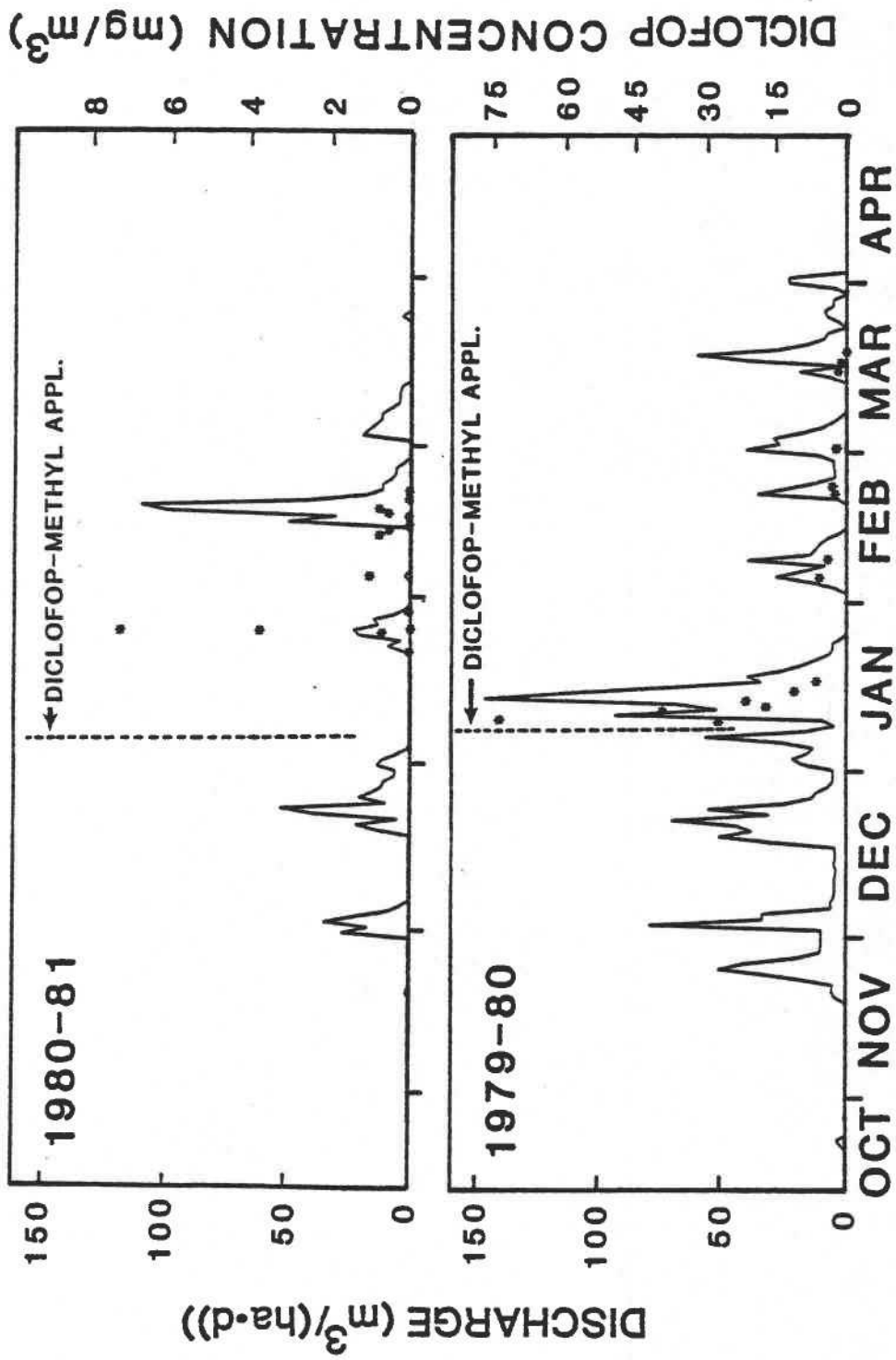


Figure 17. Subsurface drainage system discharge and diclofop concentrations for 1979-80 and 1980-81.

mg/m³ on the rising limb of the first hydrograph, only 3 days after diclofop-methyl application. The maximum concentration in 1981 (7 mg/m³) occurred in the event at 21 days after application. All diclofop concentrations were diluted somewhat because only 1.4 ha of the 2.2 ha drained by the subsurface drainage system was sprayed with diclofop-methyl in either year.

One might not expect diclofop to move in appreciable concentrations through the soil and into the drain line effluent. Very little diclofop or diclofop-methyl (<5% of applied) was leached into the 5-10 cm depth in the soils at the Elkins Road watershed (Fig. 5). Another study conducted in the Willamette Valley found small amounts of diclofop residues as deep as 20-30 cm (Marvin Montgomery¹, unpublished data), but neither study would indicate that diclofop would leach 90 to 120 cm to the drain lines and be detected in the subsurface drainage system. Passage of surface overland flow to the drain lines through large cracks and pores created from the recent drain line installation and settling of backfill material above the drain lines provides a pathway for diclofop to enter into the subsurface drainage system.

Passage of surface water to drain lines through large pores was evidenced by the rapid response of discharge in the subsurface drainage system to the precipitation events. The sharp peaks and steep rising limbs on the discharge hydrographs (Figs. 16 and 17) indicated that subsurface drainage discharge increased within one hour of increased precipitation. Settling of the backfill material above the recently installed drain lines was observed in 1979-80 after 1 to 2 months of precipitation. Overland flow on the surface could collect in these depressed areas and move rapidly through large cracks and pores to the drain lines. The depressions above the drain lines were not observed in 1980-81, but the rapid response of the drain line discharge hydrographs (Fig. 17) to increases in precipitation still suggests the rapid movement of surface water through large pores and cracks to the drain lines.

The passage of surface overland water to the subsurface drainage system would explain the high diclofop concentrations (Fig. 17) and losses (Table 6) in the drainage effluent, particularly during the

events between 3 and 9 days after application in 1980. Higher losses in 1980 compared to 1981 were the result of high surface diclofop concentrations in the surface overland flow, the close proximity of the first event to the application date, and settling of backfill material above the drain lines. Bottcher et al. (1981) reported seasonal losses of 0.1% and maximum concentrations of 210 and 40 mg/m³ for carbofuran [2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate] and alachlor, respectively, from a tile system installed on a silty clay soil. The fact that the drainage system studied by Bottcher et al. (1981) was over 25 years old indicates that the passage of surface water to drain lines is not limited to newly installed systems.

Management Implications

Most of the diclofop lost in overland flow was lost in the aqueous phase of runoff (Tables 3 and 4). Large diclofop losses were associated with large runoff events which occurred soon after herbicide application. In western Oregon, high amounts of runoff occur during storms following periods of high moisture, frozen ground, or extensive crusting (Harward et al., 1980). Effective management practices, therefore, must reduce overland flow in potentially large runoff events which occur soon after the herbicide application in order to reduce diclofop runoff losses.

Two potential management practices should be considered; (i) the use of subsurface drainage to reduce antecedent soil moisture and hence overland flow and (ii) moving the application date from early January to early February to decrease the probability of large precipitation events occurring soon after application.

The installation of a subsurface drainage system would not be a cost effective management practice if the only benefit was in reducing diclofop runoff losses. However, subsurface drainage has other benefits for agriculture in this area. Subsurface drainage allows the production of higher valued crops in poorly drained soils by improving the soil trafficability and protecting the crop from high water tables. Perched water tables tend to develop even on the hill soils in the margins of the Willamette Valley because of the frequent, low intensity

precipitation and the presence of a restrictive layer close to the soil surface. Subsurface drainage has also been recommended as a management practice for erosion control in western Oregon (Istok and Kling, 1983).

Subsurface drainage was found to reduce runoff losses by reducing antecedent soil moisture and reducing seepage in lower slope positions (Harward et al., 1980; Lowery et al., 1982; Istok and Kling, 1983). At the 1.4 ha watershed, overland flow was reduced by 65% following subsurface drainage installation compared to before drainage (Istok and Kling, 1983). The reduction in overland flow allows more precipitation to infiltrate into the soil profile leaching diclofop out of the mixing depth. Comparisons of diclofop runoff losses from the 6.0 ha watershed and the 1.4 ha watershed (subsurface drained) help evaluate the effectiveness of subsurface drainage in reducing diclofop runoff losses. The largest diclofop losses in this study occurred in the series of storms within 9 days of application in 1980, when the 1.4 ha watershed had a lower percentage runoff and discharge than the 6.0 ha watershed (Table 3). Since the highest seasonal losses are generally associated with the first runoff event after application (Merkle and Bovey, 1974; Caro, 1976), reducing percentage runoff in the first event is of particular importance in reducing diclofop runoff losses. Percentage runoff and diclofop loss in the first event were only 20% and 1.9% of applied, respectively, at the 1.4 ha watershed compared to 45% and 3.9% of applied, respectively, at the 6.0 ha watershed. Diclofop losses in the subsurface drainage effluent were much lower than in the surface overland flow.

Diclofop runoff losses may also be reduced by changing the date that diclofop-methyl is applied. Brewster et al. (1977) found nearly complete control of wild oats and Italian ryegrass when diclofop-methyl was applied either early or late postemergence. The late postemergence treatment was applied when the wheat was at the early tillering stage. This application date varied from 31 Dec. to 9 Feb. depending on the experimental site (Brewster et al., 1977). A survey of the 100 largest precipitation events (sorted by magnitude) in a 31½ year period from 1948-1979, indicated that 22 and 25 of the events occurred in the months of December and January, respectively, while only 13 events occurred in the month of February (Brown et al., 1983). Moving the

application date from early January to early February would reduce the probability of a large storm occurring soon after the application date.

Leaching of diclofop into the root zone is necessary to control root growth of weed species which germinate after the herbicide application. One question with a later application date would be if there is enough precipitation to leach diclofop into the root zone. Average precipitation in February is 130 mm (Knezevich, 1975). In this study, after 55 mm of precipitation (23 days after application), 25 ng/g of active herbicide was detected in the 5-10 cm depth. Marvin Montgomery¹ (unpublished data) found 100 ng/g of active herbicide in the 5-10 cm after 7.5 cm of precipitation (14 days after application). Assuming a diclofop adsorption partition coefficient of 15 (Appendix Fig. 3) and a gravimetric moisture content of 0.3 kg/kg, these diclofop concentrations in the 5-10 cm depth would correspond to concentrations of 0.02-0.07 μM in the soil solution. Donald et al. (1982) found that diclofop severely reduced seminal root growth of wild oats at concentrations of 0.01-0.05 μg . Our leaching data would indicate that diclofop concentrations in the soil solution may be in the lethal concentration range for seminal roots. Additional research on the weed control of surface-applied diclofop-methyl at later application dates is suggested.

TRIFLURALIN IN RUNOFF

Introduction

In western Oregon, trifluralin is applied in early fall for the control of annual grasses and broadleaf weeds in winter wheat. Soil moisture contents are generally low in early fall following the dry summer season. The soil surface is also very loose and porous because of the recent tillage operations. Consequently, the precipitation during this period generally infiltrates into the soil and percentage runoff is low. Soil temperatures are also warmer following a fall herbicide application than would be expected after a late fall or winter herbicide application. Warmer soil temperatures would accelerate herbicide breakdown in the soil and leave less herbicide available for runoff losses.

The runoff losses of trifluralin are expected to reflect the environmental conditions at the time of trifluralin application. The objectives of this study were to (1) quantify trifluralin runoff losses from two small agricultural watersheds and (2) identify factors and processes which influenced trifluralin transport following a fall herbicide application in western Oregon.

Materials and Methods

Study Site

The experimental watershed location, soils, relief, agronomic practices, and instrumentation were described previously (pages 38-41).

The 1.4 ha watershed and the lower 3.1 ha of the 6.0 ha watershed (Figs. 9 and 10) were sprayed with trifluralin (emulsifiable concentrate) on 24 Oct. 1979. Trifluralin was applied by a commercial operator at a rate of 0.84 kg/ha. Precipitation occurring soon after the application prevented the commercial operator from incorporating the trifluralin. No attempt was made to incorporate the herbicide at a later date.

Laboratory Analysis

Sediment analysis and selection of overland flow and subsurface drainage effluent samples for herbicide analysis were described previously (page 41).

Selected discharge samples for trifluralin analysis (Appendix Table 6) were transferred to 250 mL centrifuge bottles and centrifuged. The supernatants were decanted and saved for analysis. The centrifuge bottles were then rinsed with 400 mL of acetone, the acetone transferred back to the original sample bottle and heated on a steam bath for 30 minutes. The acetone mixture was evaporated to 20 mL, combined with the aqueous solution (supernatant), and extracted 3 times with 100 mL of hexane. The hexane extract was concentrated and saved for analysis of trifluralin by gas chromatography.

A Varian model 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector was used for trifluralin detection. The glass column (0.9 m x 2 mm I.D.) was packed with low level Carbowax 20 M on 80/100 mesh acid washed Chromosorb W (Aue et al., 1973). The flow rate of the nitrogen carrier gas was 20-30 mL per minute. At a column temperature of 130C and an oven temperature of 300C, the retention time was 2.3 minutes.

The analytical procedure was sensitive to 0.2 μg of trifluralin in the total sample extract. Recoveries were determined by fortifying water samples with a trifluralin standard at levels ranging from 1 to 1000 mg/m^3 . Recoveries were greater than 90%.

Data Management

Discharge, sediment loss, and trifluralin loss calculations for each storm event were similar to those described previously (pages 42-43). Trifluralin losses were based on an application rate of 0.84 kg/ha.

Results and Discussion

Precipitation

Precipitation in the 75 days following trifluralin application was 300 mm. The average precipitation in this time period is 390 mm (Knezevich, 1975). The first precipitation event following trifluralin application occurred only 7 hours after the application and resulted in 17 mm of precipitation (Table 7). The two largest precipitation events occurred 38 and 54 days after trifluralin application (Table 7). The precipitation event at 38 days after application also had the largest peak (1 hour) precipitation intensity (5.3 mm/hour) of any precipitation event occurring during the study period. In general, the precipitation events occurring later in the study period (December) had smaller storm frequencies (larger magnitude) and occurred more frequently than the precipitation events in the first 30 days (October - November) after application (Table 7).

Trifluralin Losses in Overland Flow

Trifluralin seasonal loss resulting from overland flow at the 6.0 ha watershed was 0.9% (7.4 g/ha) of the total trifluralin applied (Table 8). A majority of this loss (65%) occurred in the first storm event, only 7 hours after application (Fig. 18). Two storms occurring at 30 and 38 days after application accounted for an additional 23% of the seasonal loss. The storms occurring between 41 and 72 days after application accounted for only 5% of the trifluralin seasonal loss even though the event resulted in 50% of the discharge during the study period.

A high percentage of trifluralin was lost in the first runoff event even though total discharge ($17 \text{ m}^3/\text{ha}$) and percentage runoff (10%) was lower than in many of the later runoff events (Table 8). The relatively high sediment loss in first event (232 kg/ha) (Table 8) may have contributed to the large trifluralin runoff loss by transporting trifluralin adsorbed on suspended sediment particles. Such would be the case if a large proportion of trifluralin was partitioned into the

Table 7. Precipitation characteristics for storm events occurring after trifluralin application in 1979.

STORM NO.	STORM DATE	DAYS AFTER APPLIC.	PRECIP TOTAL (mm)	STORM FREQUENCY [†]	PEAK INTENSITY (mm/hr)
1	102579	0.3	17	16	4.6
2	102879	4	9.4	28	4.6
3	103079	7	15	18	4.3
4	111879	25	8.6	31	2.5
5	112279	29	15	18	2.8
6	112379	30	4.6	47	2.0
7	112379	30	9.1	29	2.8
8	120179	38	28	8	5.3
9	120479	41	14	19	2.5
10	121779	54	26	9	3.3
11	121979	56	3.1	58	1.0
12	122079	57	18	15	2.3
13	122379	60	18	15	3.1
14	123179	68	18	15	1.5
15	10480	72	21	12	2.5

[†] Storm frequency is defined as the number of precipitation events of the same or greater magnitude that would be expected to occur in any given year. Based on a 31½ year record.

Table 8. Trifluralin runoff summary for 1979 storm events at both the 6.0 ha and 1.4 ha watersheds.

STORM NO.	STORM DATE	STORM CHARACTERISTICS				TRIFLURALIN LOSS		
		DAYS AFTER APPLIC.	DISCHARGE (m ³ /ha)	RUNOFF (%)	SEDIMENT (kg/ha)	LOSS (g/ha)	LOSS (% of applied)	SEASONAL LOSS (%)
6.0 ha WATERSHED								
1	102579	0.3	17	10	232	4.7	0.5	65
2	102879	4	11	12	18	0.2	<0.1	2
3	103079	7	3.9	3	7.4	<0.1	<0.1	0.4
4	111879	25	19	22	49	0.2	<0.1	2
5	112279	29	25	17	44	0.1	<0.1	2
6	112379	30	15	33	16	0.1	<0.1	1
7	112379	30	51	56	31	0.6	0.1	9
8	120179	38	112	40	597	1.0	0.1	14
9	120479	41	49	35	120	0.2	<0.1	2
10	121779	54	93	36	72	<0.1	<0.1	1
11	121979	56	7.8	25	5.7	<0.1	<0.1	<0.1
12	122079	57	72	40	111	<0.1	<0.1	1
13	122379	60	79	44	20	<0.1	<0.1	<0.1
14	123179	68	52	29	45	<0.1	<0.1	<0.1
15	10479	72	79	38	38	<0.1	<0.1	<0.1
TOTALS			860		1500	7.4	0.9	
1.4 ha WATERSHED								
1	102579	0.3	4.6	3	14	<0.1	<0.1	32
8	120279	38	15	5	83	0.1	<0.1	58
12	122079	57	4.4	2	18	<0.1	<0.1	10
TOTALS			29		125	0.1	<0.1	

sediment phase of runoff. Sediment and aqueous phases of runoff were not separated for the trifluralin analysis. Data from other trifluralin runoff studies concerning the partitioning of trifluralin into the aqueous and sediment phases of runoff are conflicting. Sheets et al. (1972) reported that 84% of the trifluralin was lost in the sediment phase of runoff, while Leonard et al. (1979) found that 89-95% of the trifluralin was lost in the aqueous phase of runoff.

High pesticide runoff losses in the first runoff event after application are well documented for a wide variety of pesticides (Merkle and Bovey, 1974; Caro, 1976; Wauchope, 1978). Rhode et al. (1980) found that trifluralin runoff losses were highest in the first of several simulated precipitation events following trifluralin application. Trifluralin loss in the first event was even greater in precipitation events occurring closer to the application date (Rhode et al., 1980).

The trifluralin seasonal loss from the 6.0 ha watershed (0.9% of applied) was higher than the seasonal losses found in other trifluralin runoff studies under natural rainfall conditions (0 - 0.8% of applied) (Sheets et al., 1972; Willis et al., 1975; Willis et al., 1976; Wauchope et al., 1977; Smith et al., 1978; Rhode et al., 1980). The high seasonal loss at the 6.0 ha watershed may be attributed to the lack of incorporation of the herbicide after application. In the other trifluralin runoff studies, trifluralin was incorporated immediately after application. Trifluralin is usually incorporated to place the herbicide in close contact with germinating weed seeds as well as reducing volatilization and photodegradation losses (Wright and Warren, 1964; Savage and Barrentine, 1969; Spencer and Cliath, 1974; Weed Science Society of America, 1979). Since the first runoff event in this study occurred only 7 hours after application and at midnight, volatilization and/or photodegradation losses should not have greatly reduced the trifluralin concentration in the soil. Therefore, when the first runoff event did occur, trifluralin residues were concentrated at the soil surface and were readily available for overland flow losses.

The maximum trifluralin concentration measured in an individual water sample taken at the 6.0 ha watershed was 216 mg/m^3 (216 ppb) which occurred in the first runoff event (Fig. 18). All trifluralin

concentrations measured in subsequent runoff events were less than 20 mg/m³ (Fig. 18). The rapid decrease in trifluralin concentrations between the first event and later events was similar to that found in the diclofop runoff study. Trifluralin was not detected (<0.2 mg/m³) in the 9 samples taken between 60 and 72 days after application (Appendix Table 6). Since only 3.1 ha of the 6.0 ha watershed was sprayed with trifluralin, reported trifluralin concentrations are lower than would be expected had the entire watershed been sprayed.

The maximum trifluralin concentration found at the 6.0 ha watershed was higher than the maximum concentrations (1.9 - 38 mg/m³) reported in other trifluralin runoff studies (Sheets et al., 1972; Willis et al., 1975; Wauchope et al., 1977; Smith et al., 1978; Rhode et al., 1980). The high trifluralin concentrations may be the result of not incorporating the herbicide as well as the close proximity of the first runoff event to the application date. The maximum trifluralin concentration was above the static water LC₅₀ found for bluegills (58 mg/m³) and fathead minnows (94 mg/m³), but below the static water LC₅₀ of goldfish (585 mg/m³) and well below the static-soil water LC₅₀ (2800 - 32,000 mg/m³) of all three species (Parka and Worth, 1965). All trifluralin concentrations were below the EC₅₀ immobilization values found for two species of daphids (240 - 450 mg/m³) (Sanders and Cope, 1966).

Trifluralin seasonal loss at the 1.4 ha watershed was <0.1% (0.1 g/ha) of applied (Table 8). The lower trifluralin runoff losses at the 1.4 ha watershed as compared to the 6.0 ha watershed (0.9% of applied) reflect the lower discharge (29 m³/ha) and sediment loss (125 kg/ha) at the 1.4 ha watershed as compared to the 6.0 ha watershed (860 m³/ha discharge and 1500 kg/ha sediment loss) (Table 8). The very low percentage runoff (Table 8) at the 1.4 ha watershed can be attributed to the effect of subsurface drainage in reducing antecedent soil moisture and hence watershed runoff. The maximum trifluralin concentration at the 1.4 ha watershed was 9.5 mg/m³ and occurred at the event at 38 days after application (Appendix Table 6). The event at 38 days after application also resulted in 58% of the trifluralin seasonal loss. The first runoff event after application accounted for an additional 32% of the trifluralin seasonal loss (Table 8).

The trifluralin seasonal losses (0.9% and <0.1% of applied at the 6.0 and 1.4 ha watersheds, respectively) were in the range of seasonal losses (<1% of applied) normally found for pesticides applied as emulsions (Wauchope, 1978).

Trifluralin Losses in Subsurface Drainage Effluent

Trifluralin was detected in only one of seven effluent samples taken from the discharge of the subsurface drainage system (Fig. 19). Only 1.7 mg/m³ trifluralin was measured in the runoff event 7 hours after trifluralin application (Fig. 19). Trifluralin was not detected (<0.2 mg/m³) in any effluent sample taken between 29 and 75 days after application when discharge in the subsurface drainage system had increased (Fig. 19). Rhode et al. (1980) also detected small amounts of trifluralin (concentrations ranging from 0.06 to 0.25 mg/m³) in the discharge from a tile drain installed in a loamy sand soil in Georgia. Trifluralin was only detected in one year of the two year study in which the trifluralin seasonal loss was only 0.00011 kg/ha or 0.01% of the trifluralin applied (Rhode et al., 1980).

Trifluralin is strongly adsorbed to soil and thus relatively immobile in soil (Harris, 1967; Probst et al., 1967; Anderson et al., 1968; Weber and Weed, 1974; Mulder and Nalewaja, 1979; Weed Science Society of America, 1979). Consequently, trifluralin would not be expected to leach through the soil profile and into the drain line effluent. Passage of surface overland flow containing trifluralin residues to the drain lines through large cracks and pores created from the recent drain line installation may provide a pathway for trifluralin to enter into the subsurface drainage system. The same phenomenon was suggested as the mechanism in which diclofop residues entered into the subsurface drainage system.

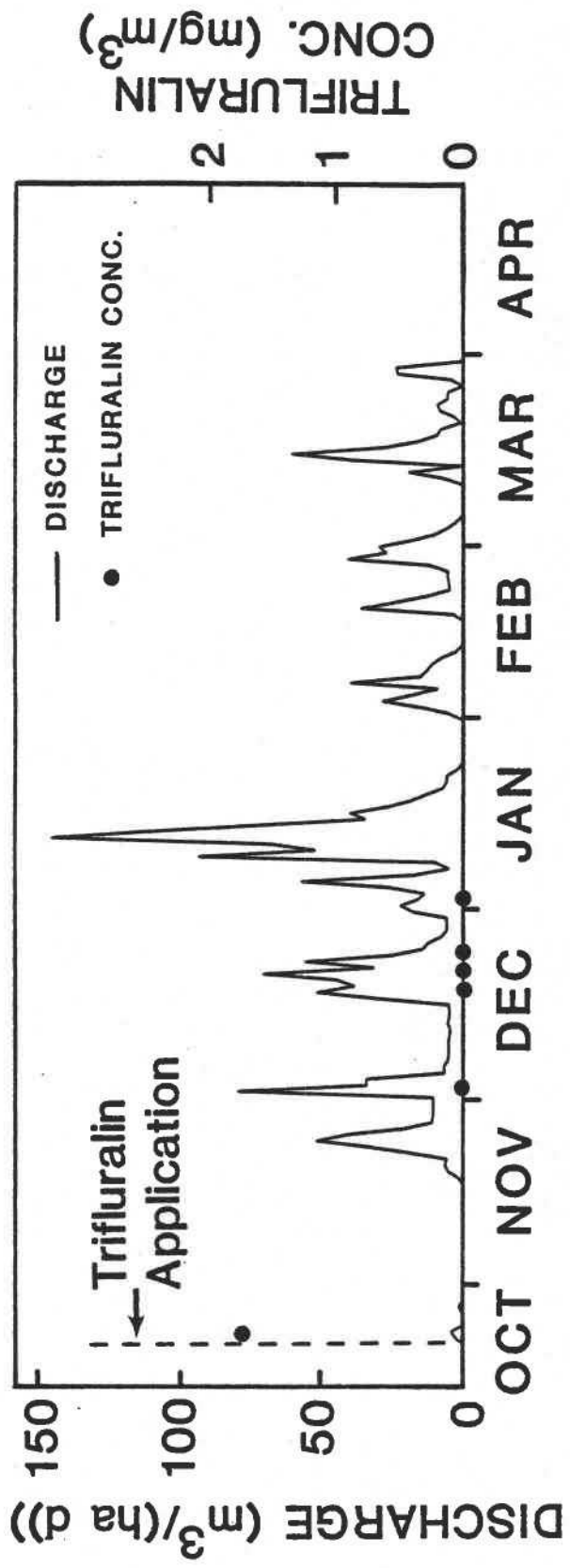


Figure 19. Subsurface drainage system discharge and trifluralin concentrations after trifluralin application in 1979.

Management Implications

A majority of the trifluralin lost in overland flow in this study occurred in the first runoff event at the 6.0 ha watershed. The relatively large magnitude of trifluralin lost in this single event (0.6% of applied) was attributed to the close proximity of the runoff event (7 hours) to the application date and the lack of herbicide incorporation. Trifluralin was not incorporated as a result of a precipitation event which began immediately after trifluralin application. Incorporation of the herbicide is an obvious management practice which would have reduced trifluralin runoff losses.

Conservation practices, which reduce runoff and/or the movement of sediments, may also serve as potential management practices for the reduction of trifluralin losses in overland flow. Subsurface drainage has been found to reduce both sediment loss and runoff from agricultural watersheds in western Oregon (Harward et al., 1980; Istok and Kling, 1983) and could be considered as a potential management practice to reduce trifluralin runoff losses. The large differences in trifluralin runoff losses between the 1.4 ha watershed (subsurface drained) and the 6.0 ha watershed were attributed to the effectiveness of subsurface drainage in reducing watershed discharge and sediment loss.

SUMMARY OF RESULTS

The differences between diclofop runoff losses in 1980 and 1981 helped illustrate the major factors affecting diclofop runoff losses in western Oregon. The major factors were (1) timing or the proximity of the first runoff event to the herbicide application date, (2) the soil moisture status before and during storm events, (3) magnitude or storm frequency of the precipitation event, and (4) soil crust formation which can lead to high amounts of overland flow by reducing the infiltration capacity of the soil as well as limiting the mixing depth or the depth to which overland flow can extract herbicide from the soil profile.

Diclofop seasonal losses were high in 1980 (7.1 and 3.9% from the 6.0 ha and the 1.4 ha watersheds, respectively) even though the largest precipitation event (6 days after application) would be expected to occur four times in any given year. Certainly one of the reasons for the high diclofop runoff losses in 1980 was the close proximity of the first three runoff events to the application date. The first three events occurred only 3, 6, and 9 days after application and resulted in greater than 99% of the diclofop seasonal loss at both watersheds. The high antecedent soil moisture status at the time of diclofop-methyl application also contributed to the large diclofop runoff losses, especially at the 6.0 ha watershed. Precipitation in late December and early January before the herbicide was applied raised the soil moisture status prior to the first event. Consequently, at the 6.0 ha watershed, percentage runoff for the events within 9 days of application in 1980 was high. At the 1.4 ha watershed, subsurface drainage reduced antecedent soil moisture, thereby reducing overland flow and diclofop runoff losses. The condition of the soil surface was also important in the diclofop runoff study. The herbicide was initially concentrated in a zone very close to the soil surface because of soil surface crust that had formed by the application date. Since percentage runoff was high, less precipitation infiltrated into the soil leaching diclofop below the shallow mixing depth (< 0.2 cm), therefore large amounts of diclofop were available for overland flow losses.

Diclofop seasonal losses in 1981 (0.7% and <0.1 % for the 6.0 ha and the 1.4 ha watersheds, respectively) were much less than the diclofop runoff losses in 1980. In 1981, the precipitation events had larger storm frequencies (smaller magnitude) than in 1980. Also in 1981, no runoff events occurred within the 2 week critical period; in fact the first runoff did not occur until 19 days after diclofop-methyl application. Using the degradation data, 68% of the active herbicide that was applied would still be remaining in the soil profile. Degradation alone would not explain the reduction in diclofop losses between 1980 and 1981. In 1981, some precipitation (2.1 cm) fell between 10-19 days after application, but before the first runoff event. This precipitation may very well have leached some diclofop out of the very shallow mixing depth, thereby reducing the amount of diclofop available for overland flow losses. Also antecedent soil moisture and ephemeral perched water tables were much lower at the time of the first runoff event in 1981 than 1980. Low antecedent soil moisture resulted in low percentage runoff in the first storm after application as well as the later storms.

The major factor affecting trifluralin runoff losses was the close proximity of the first runoff event to the application date. The first runoff event occurred only 7 hours after application and accounted for 65% of the trifluralin seasonal loss at the 6.0 ha watershed. Trifluralin losses and concentrations at the 6.0 ha watershed were much lower in later events despite most of the events having smaller storm frequencies, larger amounts of discharge, and a higher percentage runoff. Trifluralin losses at the 1.4 ha watershed were very low reflecting the effectiveness of the subsurface drainage system in reducing discharge, sediment loss, and percentage runoff at the 1.4 ha watershed as compared to the 6.0 ha watershed. The lack of trifluralin incorporation also contributed to higher runoff losses by leaving trifluralin residues concentrated at the surface and readily available for overland flow losses.

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APPENDICES

Appendix Table 1. Degradation of diclofop-methyl + diclofop and hydrolysis of diclofop-methyl in the laboratory incubation study.

DAYS AFTER APPLIC.	TREATMENT	DICLOFOP-	DICLOFOP	DEGRADATION	HYDROLYSIS
		METHYL ————— (µg) —————	—————	(%)	(%)
1	22°C N [†]	24	123	0	84
	22°C S [§]	121	26	0	18
	4°C N	53	87	3	62
	4°C S	135	8	1	6
2	22°C N	10	135	0	93
	22°C S	99	42	3	30
	4°C N	34	107	3	76
	4°C S	127	24	0	16
4	22°C N	10	125	7	93
	22°C S	79	64	1	45
	4°C N	17	130	0	88
	4°C S	118	28	0	19
6	22°C ZN	3	120	15	98
	22°C S	60	84	1	58
	4°C N	9	136	0	94
	4°C S	115	38	0	25
9	22°C N	3	110	22	97
	22°C S	48	91	4	65
	4°C N	6	126	9	95
	4°C S	95	50	0	34
14	22°C N	—	110	24	—
	22°C S	41	102	1	71
	4°C N	—	124	14	—
	4°C S	84	58	2	41
20	22°C N	—	100	31	—
	22°C S	20	110	10	85
	4°C N	—	117	19	—
	4°C S	65	72	6	53
30	22°C N	—	96	34	—
	22°C S	8	109	20	93
	4°C N	—	109	20	93
	4°C S	43	83	13	66
47	22°C N	—	84	42	—
	22°C S	4	113	19	97
	4°C N	—	103	29	—
	4°C S	33	94	12	74

[†] Sample incubated in non-sterile soil at 22°C.

[§] Sample incubated in sterile soil at 22°C.

Appendix Table 2. Amount of diclofop-methyl and diclofop remaining in field soils after an early January diclofop-methyl application.

TIME (days)	DEPTH (cm)	FIELD SAMPLING SITE				
		A	B	C	D	E
		(% of applied diclofop-methyl)				
0	0-1	100	100	100	100	100
7	0-1	96	—	65	74	—
16	0-1	84	88	63	44	66
23	0-1	74	65	45	29	48
	1-5	6.8	13	16	8.8	13
	5-10	<0.5	2.3	4.7	1.8	0.5
30	0-1	37	47	30	33	40
54	0-1	38	21	31	25	24
	1-5	8.7	24	6.7	4.0	21
	5-10	0.6	0.6	0.8	4.3	0.5
87	0-1	28	16	13	14	17
	1-5	8.3	13	2.0	4.5	9.4
	5-10	0.6	0.6	<0.5	1.7	<0.5

Appendix Table 3. Soil map legend (taken from Brown et al., 1980).

MAP SYMBOL	SOIL [†]	SLOPE (%)	RANGE IN CHARACTERISTICS
DvB	Dupee Variant, Fine-silty ^S (Aquultic Haploxeralfs, fine-silty, mixed, mesic)	3-7	Somewhat poorly drained, except moderately well drained in higher elevations of some delineations; greater than 100 cm over bedrock; 50 to about 95 cm of surface silts over paleosol, although usually 70 to about 95 cm; this soil found in wide swales along ephemeral drainageways, in fan-like positions, and in footslopes; moderate to severe flood hazard.
HdB	Helmiçk Variant, Moderately Deep (Aquic Xerochrepts, very-fine, mixed, mesic)	3-7	Somewhat poorly or moderately well drained; 50 to 100 cm over clayey bedrock; this unit difficult to map because occurrence of fine-textured layers in bedrock is difficult to predict; these clayey layers usually 4 m or more thick with 35 to 50% clay, but occasionally thinner, and occasionally having 50 to 70% clay.
HdC	Helmiçk Variant, Moderately Deep (Aquic Xerochrepts, very-fine, mixed, mesic)	7-12	Same as for HdB.
WdB	Willakenzie Variant, Deep [#] (Ultic Haploxeralfs, fine-silty, mixed mesic)	3-7	Well or moderately well drained; 100 to 150 cm over bedrock; 25 to 90 cm of surface silts over paleosol.
WdC	Willakenzie Variant, Deep [#] (Ultic Haploxeralfs, fine-silty, mixed, mesic)	7-12	Well or moderately well drained; 100 to 150 cm over bedrock; 50 to 90 cm of surface silts over paleosol; silts commonly reworked and in some cases overthickened by slope wash, the latter particularly apparent in footslope positions.

Appendix Table 3. Continued.

MAP SYMBOL	SOIL	SLOPE (%)	RANGE IN CHARACTERISTICS
WkA	Willakenzie (Ultic Haploxeralfs, fine-silty, mixed, mesic)	0-3	Moderately well or well drained; 50 to 100 cm over mainly silty bedrock; 50 to 75 cm of surface silts over paleosol.
WkB	Willakenzie (Ultic Haploxeralfs, fine-silty, mixed, mesic)	3-7	Well or moderately well drained; 50 to 100 cm over mainly silty bedrock; 25 to 90 cm of surface silts over paleosol
WkC	Willakenzie (Ultic Haploxeralfs, fine-silty, mixed, mesic)	7-12	Same as for WkB.
WkD	Willakenzie (Ultic Haploxeralfs, fine-silty, mixed, mesic)	12-20	Same as for WkB.
WnB	Woodburn (Aquiltic Argixerolls, fine-silty, mixed, mesic)	3-7	Moderately well drained; greater than 150 cm over bedrock

Appendix Table 3. Continued.

MAP SYMBOL	SOIL	SLOPE (%)	RANGE IN CHARACTERISTICS
WoA	Waldo (Fluventic Haploaquolls fine, mixed, mesic)	0-3	Poorly drained; greater than 150 cm over bedrock; greater than 100 cm of alluvium over an argillic horizon, with silt coatings common on prism faces above this depth; stratified; texture variable within fine-silty textural family; channel scars apparent in least disturbed parts of landscape; severe flood hazard.
WvB	Waldo Variant, Gently Sloping†† (Fluventic Haploaquolls fine, mixed, mesic)	3-7	Somewhat poorly or poorly drained; greater than 150 cm over bedrock; greater than 150 cm alluvium over an argillic horizon; this unit similar to WoA but found on higher, gently sloping areas along ephemeral drainageways; severe flood hazard.

† All surface textures are silty clay loam except that of Woodburn which has a silt loam surface.

§ True Dupee soils are in a fine family and have a loam or silt loam surface texture.

¶ The Helmick series consists of deep soils that formed in "mixed alluvium and colluvium over residuum weathered from sandstone and siltstone" (Official Series Description, National Cooperative Soil Survey, USDA<1/77). This variant differs in that it is moderately deep to clayey bedrock. Also the depth of solum in this variant is often greater than the 50 cm allowed for Helmick soils.

True Willakenzie soils are moderately deep (50 to 100 cm) to bedrock.

†† True Waldo soils are nearly level and poorly drained. This variant is gently sloping and often somewhat poorly drained.

Appendix Table 4. Diclofop concentrations in individual overland flow and subsurface drainage effluent samples and calculated loads in 1980.

Date	Time	Diclofop Concentration			Diclofop Load		
		Sediment (mg/kg)	Aqueous (mg/m ³)	Total	Sediment	Aqueous	Total
					(mg/(ha·h))		
6.0 ha WATERSHED							
10880	2244	54.1	63.7	66.1	3	90	93
10980	217	10.4	330.0	366.0	349	3224	3574
10980	311	7.6	254.5	289.1	702	5189	5891
10980	342	6.2	227.9	255.4	640	5331	5971
10980	402	6.2	171.0	189.5	304	2833	3137
10980	441	7.7	149.0	162.9	180	1949	2130
10980	502	9.3	138.0	146.2	88	1512	1601
10980	517	6.1	160.0	177.6	433	3960	4394
10980	748	8.4	90.0	94.6	32	645	677
10980	822	7.3	127.0	134.5	93	1583	1675
10980	919	9.8	61.4	64.0	13	306	319
10980	1323	nd [†]	18.4	18.4	nd	39	39
11180	1746	5.3	67.1	69.8	24	589	613
11180	1953	3.9	89.3	100.5	235	1884	2119
11180	2233	nd	19.5	19.5	nd	55	55
11280	453	4.1	103.0	112.5	198	2173	2372
11280	532	2.3	78.8	95.2	861	4162	5023
11280	547	2.2	82.5	102.3	1373	5750	7123
11280	557	1.8	58.5	67.0	479	3313	3793
11280	614	2.2	38.0	43.5	149	1031	1180
11280	644	2.8	50.7	58.2	294	1997	2291
11280	724	4.8	28.3	32.0	50	386	436
11280	818	3.2	57.8	61.3	64	1056	1120
11280	1307	3.6	72.7	76.8	55	1001	1056
11280	1452	8.9	21.6	22.7	4	83	87
11280	2048	14.8	37.6	39.7	18	314	332
11280	2221	3.3	35.1	36.9	18	356	374
11380	48	8.1	31.4	34.2	29	326	355
11380	205	6.0	12.7	19.0	92	186	278
11380	256	3.4	27.2	28.5	19	385	404
11380	515	4.8	18.0	19.5	23	277	300
11380	645	nd	15.9	15.9	nd	86	86
11480	730	2.7	23.7	25.6	21	268	290
11480	816	2.9	15.5	26.8	413	566	979
11480	838	1.3	19.4	25.6	308	961	1269
11480	903	1.9	16.5	21.0	138	512	650
11480	1020	nd	9.5	9.5	nd	50	50

Appendix Table 4. (Continued)

Date	Time	Diclofop Concentration			Diclofop Load		
		Sediment (mg/kg)	Aqueous — (mg/m ³) —	Total	Sediment	Aqueous (mg/(ha·h))	Total
6.0 ha WATERSHED							
20280	1515	.8	3.0	6.3	50	46	96
20280	1944	1.0	3.3	5.1	9	17	26
20680	128	1.8	2.0	3.4	2	3	5
21880	1130	1.0	2.8	4.9	9	11	20
22580	2324	nd	2.0	2.0	nd	5	5
31480	1301	nd	nd	nd	nd	nd	nd
31480	1750	nd	nd	nd	nd	nd	nd
31580	415	nd	nd	nd	nd	nd	nd
31580	847	nd	nd	nd	nd	nd	nd
31580	1759	nd	nd	nd	nd	nd	nd
31680	1843	nd	nd	nd	nd	nd	nd
1.4 ha WATERSHED							
10980	218	5.9	720.0	791.2	180	1835	2015
10980	248	6.7	625.0	671.6	118	1593	1711
10980	307	4.2	528.0	589.0	566	4934	5500
10980	314	4.7	468.0	530.8	849	6362	7211
10980	327	6.8	548.0	603.2	481	4811	5292
10980	337	7.4	405.0	483.1	1145	5964	7109
10980	811	5.8	279.0	302.7	253	3002	3256
11180	1939	80.2	93.7	121.8	71	239	310
11280	445	4.3	146.0	158.0	30	372	402
11280	504	2.3	150.0	165.5	492	4800	5292
11280	526	2.5	159.0	176.9	614	5494	6107
11280	537	1.6	132.0	163.7	2748	11476	14224
11280	543	5.1	90.7	173.3	9112	10018	19130
11280	550	7.9	64.0	149.8	7738	5782	13520
11280	603	1.8	141.0	157.6	1082	9264	10346
11280	628	10.2	55.4	119.3	1988	1726	3714
11280	642	1.8	72.9	88.1	986	4748	5735
11280	708	2.3	97.3	104.9	170	2204	2375
11280	812	2.6	92.0	102.1	246	2267	2513
11280	918	9.8	43.7	94.1	1639	1423	3062
11280	1246	2.7	114.0	125.6	234	2325	2558
11380	56	2.8	54.0	58.0	28	382	410
11480	808	.3	27.3	47.3	440	603	1043
11480	839	.5	31.0	64.4	2047	1905	3952
11480	900	3.5	31.3	53.4	838	1188	2026

Appendix Table 4. (Continued)

Date	Time	Diclofop Concentration			Diclofop Load		
		Sediment (mg/kg)	Aqueous (mg/m ³)	Total ---	Sediment -----	Aqueous (mg/(ha·h))	Total -----
SUBSURFACE DRAINAGE EFFLUENT							
10580	1348	nd	nd	nd	nd	nd	nd
10580	2148	nd	nd	nd	nd	nd	nd
10780	548	nd	nd	nd	nd	nd	nd
10880	2055	11.0	25.8	27.6	3	44	47
10980	320	13.5	67.5	73.8	60	650	710
10980	527	7.3	41.9	44.8	35	522	558
10980	823	12.9	38.3	39.8	16	423	439
11080	1836	nd	17.4	17.4	nd	108	108
11180	1557	nd	22.7	22.7	nd	122	122
11380	339	nd	16.0	16.0	nd	233	233
11380	600	nd	12.7	12.7	nd	191	191
11480	1108	nd	7.6	7.6	nd	63	63
20380	1659	20.5	4.3	5.6	4	13	17
20680	747	nd	3.3	3.3	nd	15	15
21780	2133	nd	1.8	1.8	nd	3	3
21880	1443	nd	2.19	2.1	nd	7	7
22680	38	nd	1.5	1.5	nd	7	7
22680	1118	nd	nd	nd	nd	nd	nd
31180	1022	nd	1.7	1.7	nd	2	2
31380	2046	nd	1.4	1.4	nd	8	8
31380	2227	nd	nd	nd	nd	nd	nd
31380	2346	nd	nd	nd	nd	nd	nd

† non-detectable

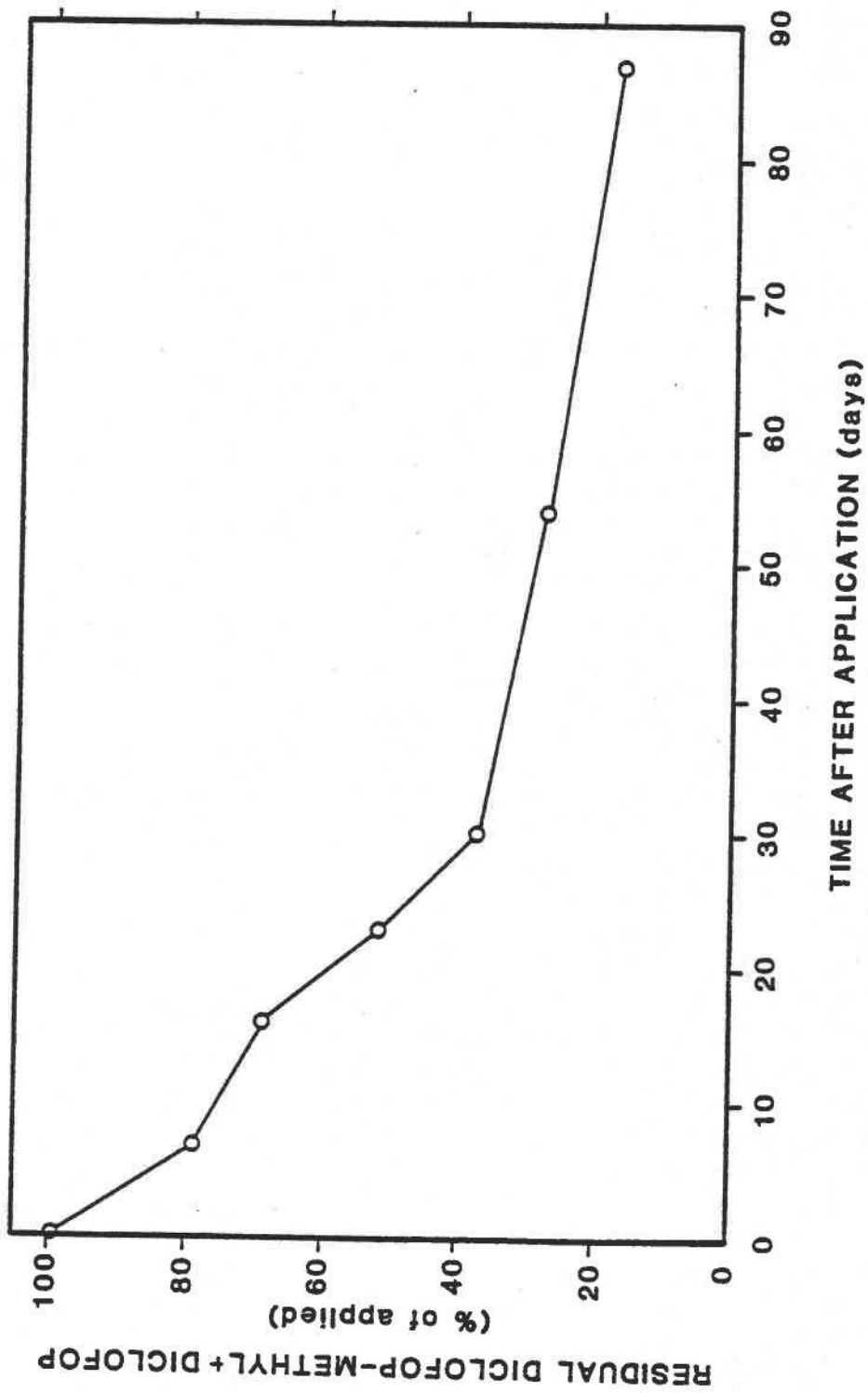
Appendix Table 5. Diclofop concentrations in individual overland flow and subsurface drainage effluent samples and calculated loads in 1981.

Date	Time	Diclofop Conc (mg/m ³)	Diclofop Load (mg/(ha·h))
6.0 ha WATERSHED			
12381	1340	1.8	1
12681	1011	64.8	440
12681	1143	30.3	57
12681	1151	24.4	35
12781	928	59.3	84
12781	933	58.7	100
12781	948	62.3	164
12781	1028	27.1	46
12781	1151	75.2	128
12781	1200	74.0	231
12781	1211	71.0	396
12781	1225	71.2	686
12781	1235	59.1	770
12781	1240	71.4	965
12781	1245	66.7	926
12781	1255	63.9	832
12781	1305	53.3	619
12781	1317	50.9	468
12781	1330	39.8	241
12781	1334	47.3	261
12781	1345	43.7	173
12781	1414	40.2	93
12881	1411	44.0	112
12881	1541	46.0	547
12881	1653	39.2	193
12881	1849	16.0	20
21381	2247	28.3	260
21681	313	8.4	15
21781	2315	18.8	154
21881	8	14.2	121
21881	224	14.9	285
21881	348	6.8	15
21881	908	4.9	6
21881	1434	12.6	141
21881	1435	16.8	202
21881	1438	18.0	273
21881	1441	20.4	364
21881	1445	22.4	444
21881	1450	17.2	268
21881	1451	16.8	260

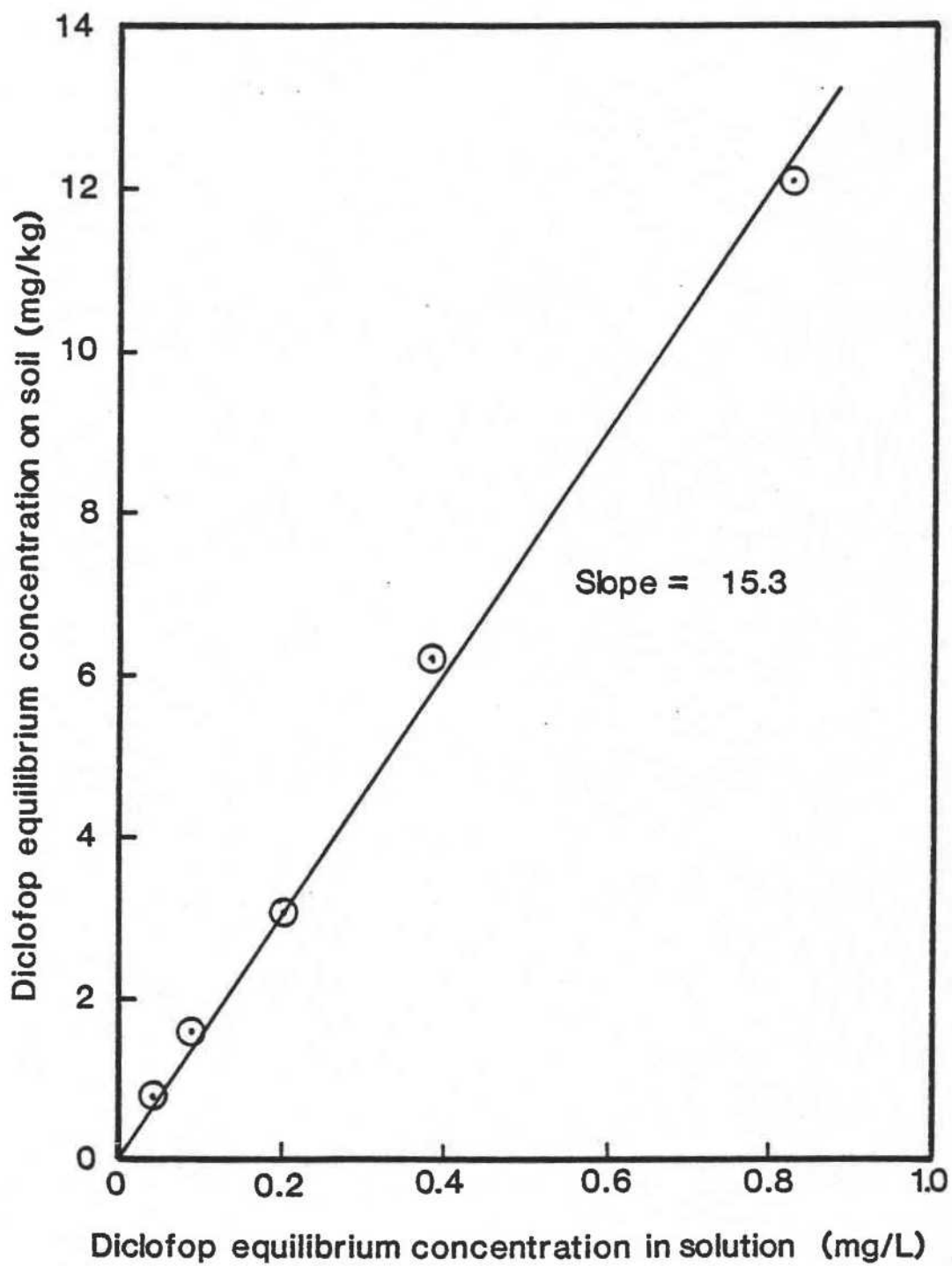
Appendix Table 5. (Continued)

Date	Time	Diclofop Conc (mg/kg)	Diclofop Load (mg/(ha·h))
6.0 ha WATERSHED			
21881	1459	15.3	169
21881	1506	12.0	95
21881	1510	10.3	69
21881	1520	9.8	42
21881	1526	8.0	27
21981	241	24.6	982
21981	258	19.2	391
21981	653	5.3	9
21981	1021	10.3	79
22481	332	3.4	1
1.4 ha WATERSHED			
21881	1431	38.5	164
21981	246	39.3	211
21981	953	28.5	444
SUBSURFACE DRAINAGE EFFLUENT			
12381	1315	nd [†]	nd
12681	1430	.8	4
12781	1429	3.8	13
12781	1601	nd	nd
12881	1551	7.4	22
12881	2045	nd	nd
13081	1300	nd	nd
20681	845	1.2	nd
21581	2310	.9	2
21681	524	.6	1
21681	1043	nd	nd
21681	1320	nd	nd
21681	1535	.9	5
21681	1914	nd	nd
21881	257	.7	6
21881	659	nd	nd
21881	1402	nd	nd
21881	1754	nd	nd
21881	2230	.6	5
21981	319	.7	8
21981	835	nd	nd
21981	1145	nd	nd

[†] non-detectable



Appendix Figure 2. Disappearance of diclofop-methyl + diclofop in the 0-1 cm zone in the field.



Appendix Figure 3. Partitioning of diclofop between soil and water at 4°C.

Appendix Table 6. Trifluralin concentrations in individual overland flow and subsurface drainage effluent samples and calculated loads in 1979.

Date	Time	Trifluralin Conc (mg/m ³)	Trifluralin Load (mg/(ha·h))
6.0 ha WATERSHED			
102579	40	216.0	5383
102579	44	164.3	6840
102579	49	114.8	3089
102579	101	57.5	489
102879	45	13.8	107
102879	56	11.5	118
102879	111	8.5	60
102879	256	6.0	45
102879	307	5.5	14
103079	2045	4.2	30
103079	2055	3.6	23
111879	1758	6.7	81
111879	1805	5.0	96
111879	1832	4.8	48
112279	1142	3.4	19
112279	1218	5.5	60
112279	1240	5.5	24
112279	1441	5.2	48
112379	719	4.5	32
112379	736	5.9	75
112379	751	3.9	33
112379	2343	2.8	33
112479	36	18.8	379
112479	127	4.5	39
120179	2259	2.8	31
120279	9	6.2	281
120279	15	14.1	1112
120279	21	11.3	820
120279	32	4.3	225
120279	122	nd [†]	nd
120279	351	3.1	38
120279	644	1.1	4
120279	1712	0.8	2
120279	2247	nd	nd
121779	616	1.4	47
121779	701	2.0	18
121779	1435	nd	nd
121779	1458	nd	nd
121779	1640	.7	3
121779	2207	.7	3
121879	630	1.2	10
121979	1046	nd	nd

Appendix Table 6. Continued.

Date	Time	Trifluralin Conc. (mg/m ³)	Trifluralin Load (mg/(ha·h))
6.0 ha WATERSHED			
122079	1625	1.4	21
122079	1645	nd	nd
122079	1743	1.5	30
122079	1840	nd	nd
122079	1917	2.3	79
122079	1937	nd	nd
122179	617	1.4	18
122379	509	nd	nd
122379	728	nd	nd
122379	859	nd	nd
122379	1103	nd	nd
123179	834	nd	nd
123179	1934	nd	nd
10480	1757	nd	nd
10480	2112	nd	nd
1.4 ha WATERSHED			
102579	35	9.3	4
120279	15	9.5	188
120279	26	5.5	138
120279	38	4.5	32
120279	414	3.1	14
122079	1859	1.0	4
122079	1914	3.1	32
122079	1936	nd	nd
SUBSURFACE DRAINAGE EFFLUENT			
102579	310	1.7	0
120379	1144	nd	nd
121779	751	nd	nd
122079	1946	nd	nd
122379	818	nd	nd
123179	2147	nd	nd

† non-detectable