USING A HYDROLOGICAL MODEL TO DETERMINE ENVIRONMENTALLY SAFER WINDOWS FOR HERBICIDE APPLICATION

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ABSTRACT

A modification of the GLEAMS model was used to determine application windows which would optimise efficacy and environmental safety for herbicide application to a forest site. Herbicide/soil partition coefficients were determined using soil samples collected from the study site for two herbicides (imazapyr, $K_{oc}=46$; triclopyr ester, $K_{oc}=1038$) and published values for two other herbicides (hexazinone, $K_{oc}=54$; triclopyr amine, $K_{oc}=20$) were used in the model. Other site-specific characteristics were taken from catchment topographic maps and soil data. Long-term climatic records for the region were then used to provide meteorological data for use in the hydrology component of the model. The model was run with herbicide application for each day of the manufacturers' recommended growing-season application windows. Average surface run-off losses, expressed as a percentage of applied, were low for all herbicides modelled (hexazinone, 0.37%; imazapyr, 0.34%; triclopyr amine, 0.21%; triclopyr ester, I .85%). Model predictions of herbicide loss for each application day were then summarised and the application days with the lowest predicted loss within the manufacturers' application

windows were identified as the environmentally safest days (environmental window) for application, This application of the GLEAMS model predicts an environmental window, for each herbicide for the site under consideration, during which the probability of adverse environmental impacts is at the lowest level achievable based upon long-term climatic records. The environmental window for pesticides other than herbicides can also be determined through modelling in a similar fashion. GLEAMS is the model chosen for this example, but other pesticide fate models may be equally applicable.

INTRODUCTION

Herbicides may have an adverse impact on aquatic ecosystems and water quality by leaving treated sites and entering surface or ground water. Studies of herbicides currently in use in forestry in the United States have not measured any adverse impacts on aquatic ecosystems when manufacturer's recommendations were followed (Michael & Neary 1993). However, the potential for adverse environmental impacts exists any time pesticides are used. Some sites, because of their topography, soil, climatic regime, location, and other site-specific factors (e.g., land use, intended use for run-off water, adjacent land and water use) are more susceptible to potential adverse impacts than others. Herbicide applications should always be made with the lowest acceptable application rate, and at a time when there is the least potential for off-site movement from large or intense storms.

Unlike annual applications for agricultural crops, one-time herbicide application for site preparation or release once in 20–30 years provides only short-term (single application with one weather pattern) information. Under these conditions, it is impossible to conduct enough long-term field research studies to cover all the permutations of weather which affect the amount of herbicide moving off any given site. Yet it is exactly this knowledge which would be most beneficial in determining which herbicide (where a choice exists) should be applied and when it should be applied to maximise environmental protection and water quality.

In the United States, the Clean Water Act amendments of 1972 specified that nonpoint source pollution from agricultural and forested areas would be evaluated, and alternative management practices (best management practices, BMPs) planned. Since most of the critical nonpoint sources were associated with sediment, fertilisers, and pesticides which arose from management practices, several mathematical models were developed to assess management systems. Models such as CREAMS (Chemical Runoff and Erosion from Agricultural Management Systems; Knisel 1980) represented physical processes and their interactions with climate and management. CREAMS was primarily a surface response model for field-size areas for comparison of alternative management systems.

Water quality is not restricted to surface or ground water, but is included in the continuum of the hydrosphere. The surface pesticide response of the CREAMS model was later expanded to include the capability of potential pesticide loading at the bottom of the root zone and developed into the GLEAMS (Groundwater Loading Effects of Agricultural Management &stems) model (Leonard et al. 1987; Knisel 1993). The CREAMS hydrology component was modified for forest sites and incorporated into the GLEAMS model, but the result was still primarily a mathematical model for agricultural sites until an option was added to the GLEAMS model to consider forest applications (Knisel 1993).

GLEAMS simulates the movement of pesticides in surface run-off and movement into, through, and below the effective rooting depth of the soil. Effective rooting depth is the maximum effective depth for water extraction. It is not necessarily the maximum rooting depth. On forest sites it may be much less than the maximum rooting depth. Rooting depth and run-off curve number are two of the more sensitive variables in the model (Leonard et al. 1987, 1990; Knisel 1993). Since curve number can vary slightly according to storm intensity (Park et al. 1994), GLEAMS cannot consistently predict the outputs from any single storm event. However, over longer simulation periods, the properly calibrated model adequately predicts yields for purposes of comparison.

GLEAMS has had minimal validation from a model user's viewpoint, but if there were enough data to properly validate a model, the model would not be needed (Leonard & Knisel 1990). GLEAMS is an extension of the CREAMS model (Knisel 1980), and is not a totally new replacement. Validation and sensitivity analyses of CREAMS serve for GLEAMS as well. Some validation of the hydrology and pesticide components has been presented by Leonard et al. (1987), and it was demonstrated that the model performs within the variability of field data. The metabolite component was validated by Leonard et al. (1990) to show that sequential metabolite generation and degradation operated properly. Knisel et al. (1991) made additional validation of the hydrology component. Shirmohammadi & Knisel (1994) used lysimeter data to validate the GLEAMS pesticide leaching component. The United States Environmental Protection Agency (USEPA) and several agrichemical companies have validated GLEAMS, but results have not been published because of the proprietary information of pesticide characteristics.

As a result of the validation, scientific merit, documentation, and usability of the model, GLEAMS is one of the two models recommended by the USEPA for use by agrichemical companies to supply supporting information for pesticide registration. A similar validation effort is going on in several European countries for GLEAMS to be used for supporting information for pesticide registration in the European Union. One of the authors of this paper is involved in a joint European Union project on validation of GLEAMS being completed in Germany, Italy, and Spain.

The GLEAMS model has been used in agricultural applications to predict year-to-year pesticide losses from corn fields based on the timing of application (Leonard et al. 1992). Smith et al. (1994), using herbicide run-off data from catchments in the south-eastern United States, proposed the use of GLEAMS to predict the environmentally safest application window for five forestry herbicides on a regional basis, but the results were up to several orders of magnitude greater than observed. The application described in this paper used measured hydrological responses on a study site on the Alum Creek Experimental Forest in the Ouachita Mountains near Hot Springs, Arkansas, to calibrate the model. Site-specific soil and herbicide characteristics and long-tan climatic data from the local area were used to predict environmental windows.

METHODS

The GLEAMS model Version 2.10 (Knisel 1993) was applied to site-specific data as an example of how a hydrological/pesticide fate model could be used as an aid to managers in selecting environmentally safer windows of pesticide application. For purposes of this example, environmental window is defined as the longest continuous period during which

loss is predicted to be one-half the average loss over the period of simulation. This definition is the most stringent that could be used with this dataset and may be too limiting for practical application. In the application of the GLEAMS model we assumed there was no herbicide residue in the soil at the beginning of each simulation. This is normally the situation because herbicides are applied to forest sites only once or twice in a rotation (20–30 years). For purposes of simplification, we did not consider metabolites in this example.

GLEAMS is composed primarily of a set of linked submodels which together yield an integrated estimate of stormflow, percolation, erosion, and movement of pesticides and nutrients. The hydrology component drives all the other submodels. The hydrology component uses daily precipitation totals with a modified United States Department of Agriculture, Natural Resource Conservation Service (NRCS, previously the Soil Conservation Service, SCS) run-off curve number method of predicting stormflow. Other inputs include soil data and long-term average temperature, and solar radiation data.

Long-term climatic data were required for the simulations in this study. A 50-year cycle was intended, but nearby weather stations did not include SO-year data records. Four nearby (12-37 km away) weather stations provided daily weather records which began in 1948. Temperature and precipitation recorded at the Alum Fork, Arkansas, weather station (12 km away) was nearly identical to observations on the study site for 1994 so we used the 46-year record available at Alum Fork for the long-term simulations.

Additional climatic data including solar radiation, wind movement, and dew point temperature are required for estimating potential evapotranspiration. The GLEAMS hydrology parameter editor contains a database with values for more than 1000 locations in the United States. One of these locations is Benton, Arkansas, which is 37 km from the study site. We used the radiation and mean daily temperature data available from the Benton location.

The soils on the study site are classified by the NRCS as the Carnasaw-Bengal complex (USDA, NRCS 1994), formerly Carnasaw-Townley-Pirum. They are strongly acid silt loam-silty clay loams (clayey, mixed, thermic Typic Hapludults). The study site is on a gently sloping hillside with a relatively constant gradient (11.1%). Permeability is low in these soils as they occur on the study site and ranges from 1.4×10^{-3} cm/sec in the upper horizons to 4.2×10^{-5} cm/sec in the lower horizons. Other characteristics of the soil were determined on field samples (Table 1).

TABLE 1–Characteristics of the silt loam-silty clay loam on the study site at Alum Creek Experimental Forest in Arkansas.

Sample depth (cm)	Bulk density (g/cm³)	Sand (%)	Silt (%)	Clay (%)	OM (%)	CEC (cmol/kg)
0–5	1.02	35	60	5	6.1	7.68
5–10	1.35	29	61	10	2.1	6.55
15–20	1.53	15	50	35	1.5	10.45

Effective rooting depth is an important variable in the GLEAMS hydrology submodel. Inspection of soil cores showed the mass of roots was in the upper 15 cm. When cores are not available, an estimation of effective rooting depth may be made from soil bulk density. Soil bulk density affects effective rooting depth. Tree mot distribution is affected by increasing bulk density above 1.2 g/cm³ for loam soils and is essentially inhibited at 1.8 g/

cm³ (Mitchell et al. 198 1; Wenger 1984). Therefore, according to the bulk densities in Table 1, effective rooting depth on the research site was between 10 and 20 cm. We chose the intermediate value of 15 cm as the effective rooting depth for modelling purposes.

Characteristics of the herbicides used in this simulation are presented in Table 2. Published values were used where appropriate, but some values were determined empirically. The organic carbon partition coefficient (K_{oc}) required by the model can be calculated from the soil partition coefficient, K_d (Knisel 1993):

$$K_{oc} = K_d / 0.0058 * \%OM$$

where OM is soil organic matter expressed as a percentage. K_d is readily determined for any soil fraction. We used the slurry method (Majka & Lavy 1977) as modified by Wehtje et al. (1987) to determine the K_d for imazapyr and triclopyr ester. Herbicide residues in solution after equilibration were quantified by Enzyme-Linked Immunosorbent Assay (ELISA) using kits obtained from Millipore Corporation and Obmicron Environmental Diagnostics, Inc. The ELISA kit for triclopyr ester from Millipore had a lower limit of detection (LLD) of 0.75 µg/ℓ while the kit from Obmicron had a LLD of 0.3 µg/ℓ. Millipore's ELISA kit for imazapyr had a LLD of 0.5 µg/ℓ.

TABLE 2-Herbicide input variables used in the GLEAMS model simulations.

| Herbicide | | K_{oc} | Water solubility (mg/ℓ) | Soil half-life (days)‡ | Application rate (kg a.i./ha) |
Trade name	Common name				
Arsenal	Imazapyr	46*	11 000†	30	1.12
Garlon 3	Triclopyr amine	20:	454‡	46	2.15
Garlon 4	Triclopyr ester	1038'	23†	46	1.12
Velpar L	Hexazinone	54†	33 000‡	30	1.12

* Calculated from K_d determined in this study by J.L.Michael at the George W. Andrews Forestry Science Laboratory, Auburn University, Alabama.
† Wauchope et a,. (1992)
‡ McCorquodale et al. (1990)

Herbicides are frequently formulated in a variety of ways including quaternary ammonium salts (usually referred to as amines), and butoxyethyl esters (usually referred to as esters) to name two. Solubilities of these formulated products, however, may be unavailable or very misleading. Two examples are triclopyr and imazapyr. Triclopyr amine has a water solubility of approximately 2 100 000 mg/ℓ (Wauchope et al. 1992). Imazapyr amine has a water solubility of approximately 500 000 mg/ℓ (Wauchope et al. 1992). Both of these compounds, however, exist only in the formulated product as the amine, hydrolysing almost instantaneously when mixed with water (i.e., in the batching process preparatory to spraying) to the free acid. Solubility of the triclopyr free acid is 454 mg/ℓ (Table 2). Similarly, imazapyr is soluble in water at 1–1.5%, i.e., 10 000–15 000 mg/ℓ. The intermediate value of 11 000 mg/ℓ is frequently used for imazapyr in modelling (Smith et al. 1994). We have used the solubility of the free acid of both of these amines for modelling in this study. The converse situation exists for triclopyr ester. Triclopyr ester has a water solubility of 23 mg/ℓ (Table 2) and is moderately stable in water with a hydrolytic half-life of 84 days at pH5 (McCall & Gavit 1986). Photolysis occurs when the ester is exposed to light in aqueous solution with a photolytic half-life of 26.8 hours at pH5.2 (McCall & Gavit 1986). When broadcast applied,

the water carrier can be observed to evaporate in sunlight in less than 1 hour. Thus the more appropriate solubility to use when triclopyr is applied as the ester to these acid soils is that of the ester, i.e., 23 mg/ℓ. In more basic soils it may be more appropriate to use the solubility of the acid form.

The application rate selected for this simulation was 1.12 kg active ingredient (a.i.)/ha except for triclopyr amine where the actual application rate of 2.15 kg a.i./ha was used. The 1.12 kg a.i./ha rate is commonly used for all of the herbicides except imazapyr. The more common rate for imazapyr is 0.56 kg a.i./ha. Results of all simulations are reported as "percentage of applied" to normalise results. In determining the safest environmental window for a given herbicide, the shape of the curve reveals the longest periods of minimum run-off so actual application rate is not important. It would be imperative to use the actual rates to be applied if an attempt were being made to discriminate among herbicides since the positions of the curves relative to each other would also be important.

All model simulations were run on desktop or laptop personal computers. A modification of the model allows the simultaneous consideration of application of a single herbicide on as many as 366 successive days by assigning different names to the herbicide with the same properties on each day of application. By using separate identification for each daily application as a different herbicide, the results of an application are not affected by any previous or subsequent application. The advantage of this modification is that the antecedent weather conditions can be simulated for every day of the year for any given herbicide as a single application and within a single simulation. Therefore the long-term probability of a problem can be predicted for any day of the year. Model output includes annual losses and the final total losses in surface run-off, adsorbed on to sediment, and in percolate below 15 cm.

The model was calibrated using site-specific data and observations from the study site. Weather conditions and hydrological response were observed for 1994 during a subsurface flow study on the site (Michael *et* al. 1994). A detailed description of measurements of surface flow from the litter, and flow from horizons A, B, and C, have been given elsewhere (Williams 1990). Site-specific soil parameters were included in the GLEAMS hydrology model, the 1994 weather observations were included in the temperature and precipitation data input tiles, and solar radiation values for use with the Priestly-Taylor method of simulating potential evapotranspiration were taken from the model's climate database site in nearby Benton, Arkansas. The model was then run to simulate the hydrological response for the year 1994. Observed and simulated hydrological responses were close. Sensitive parameters were tine-toned to give the best comparison with observed run-offvolume. After tine-toning the sensitive hydrology parameters, 0.30 cm of surface run-off was simulated in May 1994 compared with 0.30 cm observed on the study site. This was the only observed or simulated surface run-off during the field study. GLEAMS simulated 7.13 cm of percolation loss for April and May compared with 6.54 cm subsurface flow observed during the same period. The calibrated model correctly simulated only a trace of sediment loss from the site during 1994. Thus the adjusted parameter values give a very good comparison with water balance components during the field study.

The calibrated model parameters were used for all subsequent simulations. Weather data were included for the years from 1948 using the Alum Fork temperature and precipitation data records. Individual herbicide characteristics were input through the pesticide parameter

editor for hexazinone, imazapyr, triclopyr amine, and triclopyr ester. The GLEAMS model was used to simulate the application of each herbicide on each of 245 days following 1 March for each of 46 years. The annual herbicide losses were averaged for each day of application over the 46-year period to provide an average annual loss which would occur for each day of application. Losses were partitioned into surface run-off loss, loss on sediment, and loss by percolation below 15 cm. Sediment losses were negligible over the entire period of simulation. Surface run-off losses include herbicide carried in Hortonian surface flow (surface flow resulting from an infiltration excess mechanism), while percolation loss includes all herbicide carried below 15 cm depth.

RESULTS AND DISCUSSION

Forty-six-year simulations were made for each herbicide listed in Table 2. Average surface run-off losses of each herbicide are given in Fig. 1. The largest post-application concentrations of herbicides observed in streams generally occur in the first three storm events as a function of run-off (Michael & Neary 1993). Over the 46-year period of simulation, surface run-off losses by day of application for hexazinone, imazapyr, and triclopyr amine were similar. Surface run-off losses averaged less than 0.4% of the total applied for hexazinone (0.37%), imazapyr (0.34%), and triclopyr amine (0.21%). Surface run-off losses for triclopyr ester were considerably higher for each of the 245 days of simulated application (average 1.85% of applied). The reason for the higher surface run-off loss of triclopyr ester is that the K_{oc} is higher, thus the ester is less mobile than the other three herbicides. It does not leach out of the soil surface as rapidly, and is available for extraction into surface run-off for a longer period of time. Environmental windows are listed for all four herbicides in Table 3. Where surface run-off may pose a potential problem, application may be restricted to these windows.
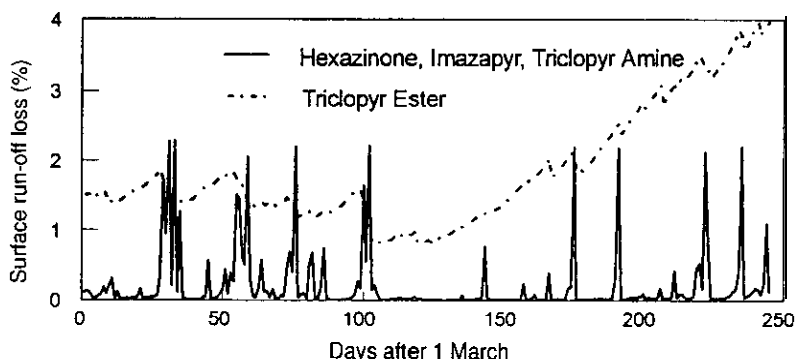

FIG. 1—Comparison of GLEAMS model simulated surface run-off losses (percentage of applied) from a catchment in Alum Creek Experimental Forest in Arkansas as a function of day of application for four herbicides over a 46-year period. The shape of the curves for hexazinone, imazapyr, and triclopyr amine are too similar to distinguish graphically. Minor differences occur in their respective maximum and minimum values. Therefore, they are represented here as a single line.

Percolation losses may account for more loss from the site than surface run-off. Whether percolation losses are a potential problem depends on the degree of degradation that occurs

in the soil as a function of biological and chemical processes. Average losses due to percolation below 15 cm are presented in Fig. 2. Percolation losses of triclopyr ester were predicted to be negligible with an average of only 0.10% of applied moving below 15 cm. Average percolation loss below 15 cm was higher for hexazinone (6.52%), imazapyr (7.33%), and triclopyr amine (I 5.4%). Environmental windows for percolation loss are listed in Table 3. Percolation loss for triclopyr ester was continuous and at a low level so that there is not a window during which the percolation loss is one-halfthe average for the period of simulation. Under these conditions any day of application would be assumed to be acceptable. However, over time this ester would be converted to the free acid, so use of the same window as recommended for the amine would provide the safest choice.
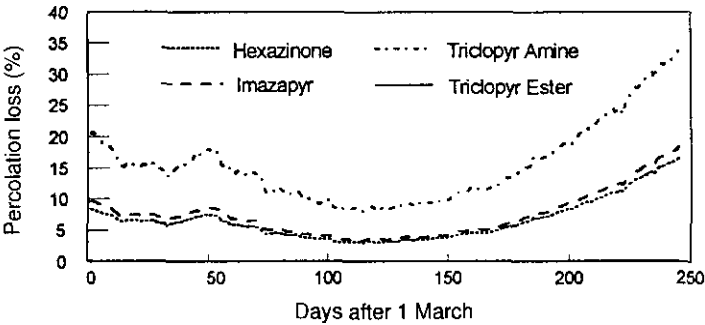

FIG. 2–Comparison of GLEAMS model simulated percolation losses (percentage of applied) from a catchment in Alum Creek Experimental Forest in Arkansas as a function of day of application for four herbicides over a 46-year period.

TABLE 3-Herbicide application windows suggested by the manufacturer compared with the growing season window of least potential for loss via the simulated routes from the treated site.

Herbicide common name	Manufacturer recommended window	Best environmental window*		
		Surface run-off	Percolation	Total
Imazapyr	May–Oct.	17/6–19/7	16/6–1817	17/6–18/7
Triclopyr amine	Jan.-Dec.	17/6–20/7	13/6–31/7	17/6–20/7
Triclopyr ester	Jan.–Oct.	11/6–24/6	None	11/6–24/6
Hexazinone	Mar.-June	17/6–20/7	16/6–8/7	17/6–8/7

* Longest continuous period during which loss is predicted to be one-half or less than the average loss over the period of simulation.

The fate of those herbicides which move below 15 cm is not indicated in this model. However, fate studies have been conducted with some of the herbicides. Imazapyr was not detected below 50 cm in sandy loam soils and not below 40 cm in loam soils treated with 2.24 kg a.i./ha and monitored for a period of 1 year (Michael 1986). Similarly, hexazinone was rarely detected below 60 cm in loam soils treated with 6.72 kg a.i./ha and monitored for a period of 1 year. Five metabolites of hexazinone were detected in these soil samples at depths to 75 cm with most of the metabolites occurring in the region of 0–45 cm depth (Michael 1992).

CONCLUSIONS

This application of the GLEAMS model demonstrates it to be a valuable tool for forest managers. Safer environmental windows can be determined within the manufacturer's suggested application windows based upon potential loss in surface run-off and/or percolation (Table 3). While the definition of an environmental window will change depending on the site sensitivity or management objective, some decision point must be defined for determination of environmental windows. For our example (Table 3) we chose a very limiting definition of environmental window which may be impractical for application. Here it provides an example of how the model simulations can be used.

Use of the GLEAMS model simulations demonstrates how management alternatives can be evaluated prior to finalisation of management decisions. Clearly there are opportunities for use in highly sensitive areas, but on such sites some options might be eliminated. For example, on a site where there is concern about surface run-off loss of triclopyr amine, dormant season stem injection in early March may be eliminated as an option in favor of growing season injection. In Table 3 is provided some information for the manager to consider in selecting management options with the lowest probability of adverse environmental impacts, and some additional information for use in areas which are especially sensitive.

Results presented here are site and herbicide specific. Blanket recommendations cannot be made for all soils, climatic regions, and herbicides. This study demonstrates how a model such as GLEAMS can be used with local data to help make management decisions.

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