Pesticide Environmental Fate

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Pesticide Environmental Fate

Bridging the Gap Between Laboratory and Field Studies

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Foreword

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Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

ACS Books Department

Preface

The study of the environmental fate of a pesticide covered in this book is focused primarily on the need to meet regulatory requirements for pesticide registration. The environmental fate study guidelines for many of these studies have been outdated as industry has strived to meet new regulatory requirements such as the Food Quality Protection Act (FQPA). The FQPA gives registration priority to low-use rate, safer pesticides. Other documents, such as the "Rejection Rate Analysis," though it is not a true guidance document, have also altered the way that classic environmental fate studies are conducted. One such example would be the need to apply the compound in the studies at the actual field-use rate. Many of the new pesticide chemistries are biologically effective at use rates of just grams per acre. These ultra-low use rates generate difficulties in the lab and field studies just to monitor the parent compound, not to mention the difficulties associated with identification of degradation products.

Another difficulty associated with studying the environmental fate of a pesticide is understanding the similarities and differences in laboratory and field studies. The objectives of the studies are quite different. The laboratories focus more on individual routes of degradation and on the development of a conceptual model for the pesticide degradation pathway, whereas the objective of the field study is to examine environmental fate of the pesticide under field conditions, where all routes of degradation and dissipation are occurring simultaneously. The identification of degradates (which typically occurs under laboratory conditions) is difficult with low-use rate compounds, but it is necessary to characterize the degradates before one can synthesize a residue method for analysis of field samples. Again, when the parent compound is only applied in the field at a few grams per acre, it is exceedingly difficult to detect degradates that may only represent 10% of the parent concentration, let alone be able to track them for 18 months in the field!

This book is a compilation of presentations from a Symposium held at the 1999 Fall American Chemical Society (ACS) Meeting. The

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symposium was entitled "Bridging the Gap between Laboratory and Field Environmental Fate Studies." The purpose of the symposium was to bring together personnel from state and federal regulatory agencies, industry, academia, and consulting firms that were interested in the study of pesticide environmental fate. The topics of the presentations focused on innovative methods, technologies, and study designs to enhance our knowledge of pesticide environmental fate, and to "Bridge the Gap" between the laboratory and field studies. The book includes chapters originally presented as posters, plenary presentations, and ideas shared during a panel discussion.

Anyone who is interested in the environmental fate of pesticides would benefit from reading this book. The book presents many novel ideas and spans studies that are confined to the laboratory, studies that introduce radiolabeled compounds to small plots, up to large studies that involve entire watersheds. Novel approaches to handling and presenting large quantities of data such as Geographic Information Systems and computer modeling techniques are also covered in a practical manner. As was mentioned earlier, the symposium and book encompassed work from many different arenas such as the regulatory, industrial, and academic perspectives, so the book presents the work from unbiased viewpoints. Also, every effort was made during the review process to ensure that the peer review process occurred from outside the author's venue (i.e. if the author was from industry, the reviewer was either from academia or a regulatory agency).

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Chapter 1

Integrating Laboratory and Field Environmental Fate Studies: An Introduction

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Agriculture, food production and environmental safety are of utmost concern for all of us. As the world population continues to increase to an anticipated 8 billion within the next 25 years, the challenge is for agronomists to produce more food on acreage that is already under cultivation. It is a challenge that we not only feed that population but to preserve natural resources as well. Crop protection compounds are an important aspect of the increased capacity for food production per acre. As environmental stewards, it is our global responsibility to ensure an adequate food supply and a safe environment in conjunction with preserving our natural resources through improved study designs, scientific methodology, cultural practices and methods of data interpretation.

Many groups examine and scientifically evaluate crop protection compounds. These groups include scientists at the U.S. Environmental Protection Agency as well as state regulatory agencies, and research scientists from public academic institutions and private agrochemical companies. Typically 8 to 10 years are required for scientific study and evaluation of a crop protection compound prior to its introduction to the market. These studies that support regulatory decisions frequently may cost upward of 10 to 15 million dollars before the compound is approved for registration and sold publicly. The studies evaluate both the efficacy as well as the human and environmental safety of the compound. The following chapters focus primarily on various aspects of laboratory- and field-based studies examining the environmental fate and transport of crop protection compounds.

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The data package that supports the environmental fate and transport components of a compound registration entails both laboratory and field studies. The environmental fate studies focus on degradation and dissipation. Degradation is considered to be the breakdown of the parent compound into various degrades, metabolites and volatile components. Dissipation is defined as an overall loss of the compound either by degradation, sorption to soil, transport via surface runoff or leaching to ground water, volatilization, loss with spray drift, or the general disappearance of the compound or degradates from the test system.

Environmental fate laboratory studies are primarily designed to evaluate a single route of degradation that might be encountered in the environment, such as hydrolysis at various pH's, photolysis (in water or on soil), volatilization, biologically mediated metabolism in soil and water, and mobility/sorption to soil. The laboratory studies help develop a "Conceptual Model" that describes the likely and principal degradation pathways, metabolites, and routes and rates of dissipation that would be predicted to occur in the environment. The laboratory studies typically use radiolabeled compounds to aid in the identification of unknown metabolites and to provide quantitative data for determining the mass balance of the test system. The laboratory studies serve as a guide to modes of degradation and the degradation products that should be examined in the residue studies. They also provide information on which matrices the parent and degradates may be associated.

Field studies are designed to focus on general types of dissipation pathways such as leaching, volatility and runoff. These studies include terrestrial field dissipation, ground-water leaching, surface water runoff, field volatility and aquatic dissipation, as well as dissipation through degradation and metabolism. The field studies, conducted outdoors under typical cultural practices, are designed to evaluate all routes of degradation and dissipation simultaneously under various natural environmental conditions. These studies usually do not employ radiolabeled compounds; therefore, researchers must know the degradates of interest, as well as have a well functioning analytical method prior to conducting the study. Despite the best study designs and expertise of the individual scientist, there are inherent "gaps" associated with each type of environmental study that make the comparison of field and laboratory studies very difficult.

Research in the area of environmental fate and transport involves many types of studies. In addition to the standard suite of laboratory and field studies, there is the need to evaluate the biological activity of the parent compound and degradates, the compound's availability in soil and aquatic systems, and the non-target effects associated with a compound. Bioassays, column and cubic lysimeters, radiolabeled field plots ("hot plots"), plant back studies and

computer modeling are current methods used to elucidate the environmental fate of a compound. Each type of study design has its strengths and weaknesses. The studies and designs described in this book are a compilation from many experts in the field of environmental fate and effects. The authors that contributed to the chapters were employed by state and federal pesticide regulatory agencies, academic institutions, and private agrochemical industries. The chapters were selected from platform presentations and posters presented at the American Chemical Society Annual Meetings in New Orleans, LA, Fall 1999. The symposium was entitled "Bridging the Gap Between Laboratory and Field Dissipation in Regulatory Process." The central theme of the symposium was to share ideas and methodologies that examine unique and creative ways to address the "gaps" that occur in our evaluation procedures and study designs for environmental fate research. Each chapter discusses specific strengths and weaknesses of specific study types and suggests creative ways to help bridge the "gap" for integrating information from laboratory and field studies.

Laboratory metabolism studies are designed to evaluate specifically one mode of degradation. The common laboratory studies that are conducted for the assessment of environmental fate are: hydrolysis, aqueous photolysis, soil photolysis, aerobic soil metabolism, anaerobic soil metabolism, anaerobic aquatic metabolism, anaerobic aquatic metabolism, laboratory volatility, parent column leaching, aged column leaching, and adsorption/desorption studies for parent and major degradates and fish bioaccumulation. These studies are conducted in the laboratory where environmental factors such as temperature, soil moisture, air flow speed, and pH can be controlled. The studies are often conducted according to standardized regulatory guidance, which allows for regulatory scientists to compare one compound to another. The laboratory studies are frequently conducted in a similar manner and under specified conditions (i.e., aerobic soil metabolism studies are typically conducted at 25 degrees Celsius with 75% moisture capacity at 1/3 bar). These studies are commonly dosed with radiolabeled parent compound. The radiolabel allows for measurement of mass balance of the test system. Quantifying the radiolabeled compounds associated with the parent compounds and degradates also demonstrates the extraction efficiency for the tested matrix, the amount of volatile components and the amount of bound material. The radiolabeled parent compound also is useful in the identification of unknown degradates.

One of the shortfalls of the laboratory studies is that while the studies are ideally designed to evaluate a single route of degradation, it is quite difficult to actually differentiate between various mechanisms in some studies. For example, in a photolysis on soil study, differentiation between soil metabolism and actual photolysis may be very difficult. In soil metabolism studies, it is likely that there are some populations of both aerobic and anaerobic soil microbes. The major drawback of the laboratory studies is that they do not

represent "real life." That is to say that while the laboratory studies help one to identify likely modes of degradation in the environment and help us to develop a "conceptual model" of the overall dissipation in the environment, the natural environment is very complex and has many interacting routes of dissipation and degradation occurring simultaneously.

The data derived from the laboratory studies are also used as inputs for computer modeling that predicts the fate of a compound in the environment based on the "conceptual model." The predictive computer modeling assists in estimating the movement and concentrations of parent compounds and metabolites in the environment based on empirical or mechanistic mathematical models and the environmental fate characteristics of the compound. The question frequently arises regarding the utility of using laboratory data to predict field results. The models serve to help us better understand the differences observed between laboratory and field studies. Once the model has been validated or "ground truthed," and the user is confident that the model will make accurate predictions, then the model results can provide an estimate of the environmental concentrations of the compound under many scenarios (i.e., varying soil types, different weather conditions, etc.). It is difficult to define when a model has been adequately "validated." When used correctly and with appropriate inputs, modeling is a powerful tool that allows an estimation of concentrations of the compound in the environment under a wide range of environmental conditions. It also provides inputs for probabilistic risk assessments. This is very important due to the associated costs and length of time required to conduct many field studies.

Field studies evaluate the compound under normal agricultural practices and in a natural environment. The study designs allow for replication, cropped and bare soil evaluations, various watering and application regimes, etc. Under field conditions, all routes of dissipation are occurring simultaneously. Not only are routes of degradation occurring in the field, but also dissipation such as volatilization, codistillation, off-site movement, leaching and runoff. The field studies provide the data with which one may validate the computer model. But the field study design is not without drawbacks. Field studies are subject to adverse conditions such as drought, floods and pestilence. They are also expensive and require a large amount of time. The particular location that was selected to conduct a study may have atypical weather for the year. Low use rate compounds are very difficult to track in the field for a long enough period of time to establish their environmental fate. The degradates must be known before developing an analytical method, and the method must be rugged enough to work on several types of soil that may be encountered at various depths and locations.

A real "gap" that occurs in the field study is due to the fact that when a residue method is used to quantitate the compound, a standard curve must be established to define the amount of compound in the sample. The standard curve is typically derived from a freshly dosed soil that is immediately extracted. This freshly dosed soil is used to determine the quantity of compound that is extracted from the soil that has been "aged" in the field for many months. For many compounds, their adsorption to soil increases with time; therefore, the comparison of freshly spiked soil for the standard curve to the "aged" field soil samples can lead to results that would indicate that the compound has dissipated when it may actually still be bound to the soil. Presently, there is no way to determine the amount of bound material using a residue method that does not employ a radiolabeled compound. It is typically assumed that if you cannot extract the compound chemically in the laboratory then it is not bioavailable, but that is another study in itself.

The soil column lysimeter study was designed to help bridge the gap described previously. These studies are sometimes referred to as "pipe studies". Intact soil columns that are often equipped with leachate collection devices and are dosed and maintained in the field. These studies combine the ^{14}C radiolabeled compound as used in the laboratory, but are conducted in a field setting. The ^{14}C-labeled compound allows for determination of mass balance, but due to the non-enclosed environment or "open" system design, adequate mass balance is frequently difficult to maintain. These studies are particularly useful because the chemical profile in both the soil and soil pore water can be determined. The study design also allows for an evaluation of the leaching potential of the compound. These studies are labor intensive, expensive and sometimes are difficult to establish due to regulations in each state that govern the use and cleanup of ^{14}C material outdoors. The study design is often criticized due to the potential for the compound to preferentially flow down the side of the lysimeter when certain soil types are encountered.

The cubic meter lysimeter design is similar to the column lysimeter but it generally entails one cubic meter of intact, relatively undisturbed soil that is enclosed in a steel container equipped with a leachate collection device. The evaluation of the leachate is the primary focus of these studies, and the soil is typically only collected at the end of the study, so no evaluation of the parent compound or degradates degradation rate are conducted. These studies often involve minimal or no replication and include the strengths and weakness of the pipe study described previously.

Another study design that also combines the utility of ^{14}C with the realism of the natural environment is "hot plots". Small outdoor plots are treated with the ^{14}C-radiolabeled compound. These studies are more realistic than pipe studies or cubic lysimeters because the potential wall or "edge" effect is not

present. The problems encountered with "hot plots" are those of disposal of soil when the study is completed, and no leachate is collected. There is also the possibility of contamination or off-site movement due to the lack of study containment.

All the aforementioned study designs help quantitate the environmental fate of a compound in the environment; however, the "effects" of the compounds have not been addressed. The studies described can quantitate how much of a compound is in the water or in the soil matrix and predict where and how quickly the compound is likely to move. But the only currently known way to evaluate what is bioavailable is to introduce plants or other organisms into the test system. A bioassay study employs a plant that is sensitive to the compound as an indicator of the amount of the compound that is bioavailable in the soil sample. This assay technique is typically a qualitative measure and compares a visual estimation of injury of a plant that is in treated soil to a "check" plant that is in untreated soil. The "gap" for bioassays results from the standard curve, where the standard curve is generated from freshly dosed soil and the impact of the bioavailability is needed on soils that have been aged in the field.

In summary, each type of study has its strengths, weaknesses and "gaps." It is frequently difficult to make comparisons from one study to another, not to mention understanding the complexities of the potential environmental impact associated with pesticide usage among widely varying environmental conditions. This book serves to compile the ideas of many scientists as they attempt to "bridge the gaps between the laboratory and field studies."

Chapter 2

GIS Decision Support System to Evaluate U.S. and Canada Field Study Areas for Pesticides

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A Geographic Information System (GIS) decision support system (DSS) was developed to help identify comparable field study areas for assessing pesticide dissipation under field conditions in the U.S. and Canada. The NAFTA GIS project is a collaborative effort of the United States Environmental Protection Agency (USEPA), U.S. Department of Agriculture Natural Resources Conservation Service (USDA/NRCS), Health Canada, and Agriculture and Agri-food Canada (AAFC). The GIS model utilizes North American ecological regions (CEC Ecoregions Level 2 Map), geospatial soil and agricultural crops databases, and climatic information. The soils information is based on the AAFC Soil Landscapes of Canada (SLC) and the USDA/NRCS State Soil Geographic (STATSGO) Data Base. Agricultural crops information was obtained from Canada's 1996 Census of Agriculture and the U.S. 1992 Census of Agriculture. Comparable field study areas in the U.S. and Canada can be investigated using geospatial environmental parameters in the GIS database,

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environmental fate and transport properties of pesticides and the conceptual pesticide dissipation model derived from laboratory fate studies. This chapter discusses the project's application for examining the geographic distribution of field study locations, and some of the limitations associated with spatial data resolution.

Introduction

Under the North American Free Trade Agreement (NAFTA), the Technical Working Group on Pesticides is working to reduce trade barriers through harmonization of environmental data requirements and test guidelines for pesticide registration in the United States, Canada and Mexico. Pesticide registrants conduct terrestrial field dissipation studies to collect field data because regulatory agencies need to assess the environmental fate and transport of pesticides under actual or planned use conditions for ecological and human health risk assessment. Terrestrial field dissipation studies examine various routes and rates of pesticide dissipation such as accumulation, degradation, transport by surface runoff and leaching, and potential pesticide residue carryover. The United States and Canadian pesticide regulatory agencies [USEPA Office of Pesticide Programs (OPP) and Health Canada's Pest Management Regulatory Agency (PMRA)] require these studies for registration and reregistration of pesticides applied under field conditions (AC, 1987; USEPA, 1975).

Field dissipation studies demonstrate the transformation, transport, and fate of pesticides at field locations that should be representative of actual use conditions (AC, 1987; USEPA, 1982). Laboratory studies provide data on physiochemical properties, abiotic and biotic transformation pathways that include the formation and decline of transformation products or degradates, leaching, sorption, and volatility that help conceptualize a model of the overall dissipation of the pesticide in the field. Pesticide dissipation is defined as the integration of the various environmental fate and transport processes under field conditions (Cheng, 1990). Field dissipation studies are designed to evaluate the validity of this conceptual model for assessing environmental exposure and to supplement the laboratory-derived results obtained under controlled environmental conditions.

Due to their experimental design, field studies typically require considerable resources to conduct, analyze and interpret (Fletcher et al., 1989). This resource commitment frequently limits the total number of field locations tested. The pesticide industry has expressed concerns regarding the economic burden of conducting terrestrial field dissipation studies in both the U.S. and Canada. Lack of field studies representative of U.S. or Canada conditions is also considered a potential impediment to joint review of pesticide registration submissions.

Under the NAFTA TWG for Pesticides, the U.S. and Canada agreed to develop a GIS-based tool that would help identify comparable field testing areas with common agricultural crops, similar soils and ecological regions. This tool would identify comparable field study areas in the U.S. northern tier states and the southern areas of Canadian provinces bordering the U.S. that might be suitable to support pesticide registration activities in both NAFTA countries. Hallett et al., 1995 described a GIS raster-based tool called *Spatial Environmental Information System for Modelling the Impact of Chemicals* or "SEISMIC" for assessing the environmental fate of pesticides applied to agricultural fields in Great Britain. The spatial data management system "SEISMIC" contains soil, climate, weather and land use data to model or assess the environmental fate and transport of environmental contaminants at regional to national scales for England and Wales.

This paper describes some preliminary results from the NAFTA GIS Project under development between the U.S. and Canada. A prototype model was developed in 1997 and presented to NAFTA stakeholders in Canada and the U.S. at two meetings in October and November, 1997, respectively. Kroetsch et al., 1998 discussed the methodology of the prototype GIS Decision Support System (DSS) and presented some revisions to the prototype model based on comments from the stakeholder presentations. Additional written and oral comments from these presentations were provided to the NAFTA GIS Project Team and a revised "beta" version was completed in June, 1999. Results from the beta version were described by Effland et al., 1999 at the ACS Annual Meeting Symposium on "Bridging the Gap Between Environmental Fate Laboratory and Field Dissipation Studies in the Pesticide Registration Process" during August, 1999 in New Orleans, LA.

We discuss the application of the DSS to examine the geographic distribution of various field study sites based on comparisons of the spatial extent and location of previously conducted terrestrial field dissipation studies. We studied the geographic distribution of field study locations through various queries using site-derived environmental conditions (crops and soil characteristics) and pesticide environmental fate and transport properties. This DSS application may identify the spatial location and extent where environmental conditions of terrestrial field dissipation studies apply to the U.S. and Canada to help improve our understanding of pesticide environmental fate and transport.

Methods

Kroetsch et al., 1998 described the methods used to develop the prototype NAFTA GIS project for the selection of areas that meet user-defined criteria for possible terrestrial field dissipation study sites in Canada and U.S. that could support pesticide registration in both countries. The DSS incorporates a

hierarchical query process with user-defined criteria based on crop growing area [or potential pesticide use area], ecological regions, and soil and climatic attributes. The DSS incorporates four basic steps to query the spatial data and identify potential field study areas or the geographic extent of currently studied research sites:

- Step 1: Select the crop(s) and delineate the crop growing area(s);

- Step 2: Divide the crop growing area into ecoregions and identify the ecoregion(s) for testing;

- Step 3: Select soil parameters (soil reaction or pH, organic carbon, textural class, etc.) that influence the environmental fate and transport based on pesticide physiochemical properties (e.g., solubility, octanol/water partition coefficient), laboratory-derived information (e.g., abiotic and biotic degradation, soil/water partitioning) or field-measured soil landscape characteristics (e.g., slope); and

- Step 4: Examine the selected polygons and identify the location(s) derived from the query process (see Table 1). Output is available in graphical and tabular formats.

Spatial data incorporated into the DSS varies in scale and complexity among the various GIS coverages. Scales of spatial data ranged from 1:250,000 to 1:1,000,000 [or smaller]. In the prototype model, the crop distribution data for Canada and United States were obtained from the 1996 Census of Agriculture, Statistics Canada and National Agricultural Statistics Service, United States Department of Agriculture, respectively. When the beta version was developed, the U.S. crop data (crop acres per county) were derived from the final release of the 1992 U.S. Census of Agriculture. The U.S. crop coverage was created by intersecting the STATSGO national coverage [clipped to conform with the limits of the 10 selected ecological regions] with the USGS 1:100,000 county boundary coverage resulting in 78,126 polygons. In the beta version, Canadian crop data were compiled from the SLC for the agricultural regions of Canada in a coverage described as the Agricultural Acumen of Canada. The Canadian crop information was compiled, processed and apportioned to the SLC polygon level from the 1996 Census of Agriculture (Huffman, 1997).

The Ecological Regions of North America - Level II Map delineates the ecological regions for the U.S., Canada and Mexico (CEC, 1997). Table 2 lists the 10 Ecological Regions (Level II) that were selected to represent common areas between the U.S. and Canada (see Figure 1). Ecological regions were

Table 1. Selected Examples of STATSGO Soils Identified by Querying the NAFTA GIS Project

MUID	Component	Percent of MUID	Soil Series or Taxonomic Class (U. S. Suborder or Great Group)
ND018	1	26	Borolls
ND017	6	11	Aquolls
MT055	1	31	Bonfri (Haplargids)
MT073	1	25	Busby (Ustochrepts)

Table 2. NAFTA GIS Project Level II Ecological Regions for the U.S. and Canada

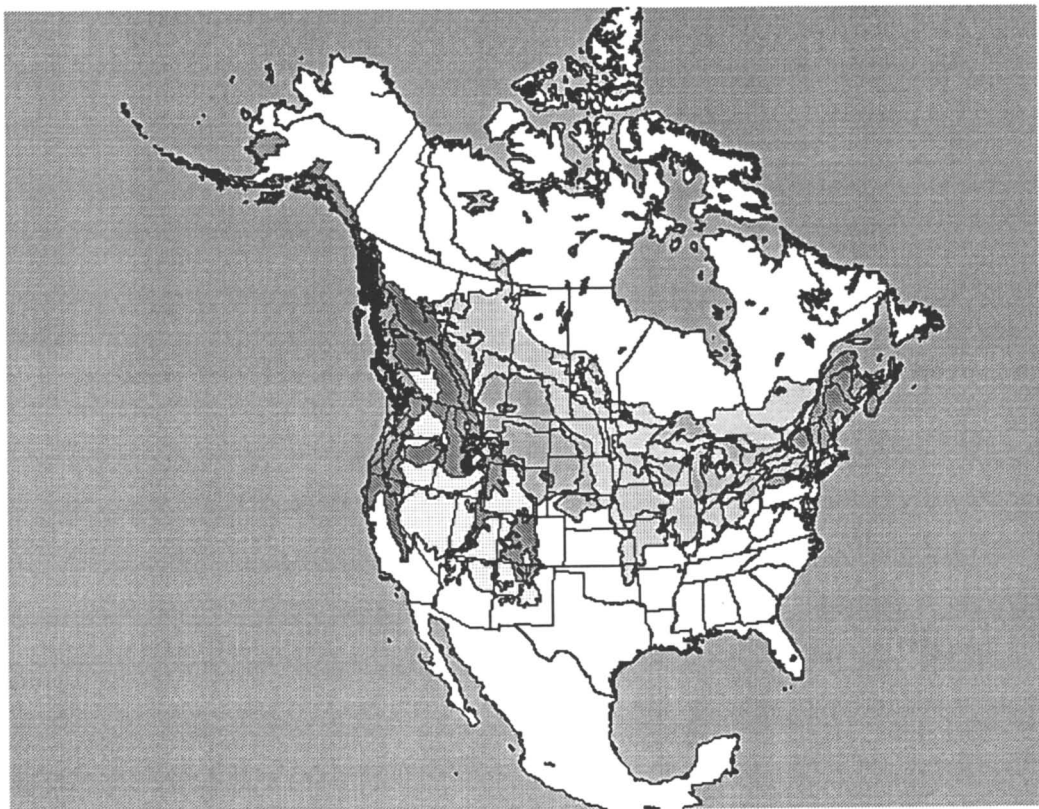| Ecological Region	Ecological Region Name – Level II
5.2	Mixed Wood Shield
5.3	Atlantic Highlands
6.2	Western Cordillera
7.1	Marine West Coast Forest
8.1	Mixed Wood Plains
8.2	Central U.S.A. Plains
9.1	Boreal Plain
9.2	Temperate Prairies
9.3	West-Central Semi-Arid Prairies
10.1	North American Deserts

Figure 1. CEC Ecological Regions Common to Canada and the United States

incorporated into the project to allow division of extensive crop growing regions (e.g., corn, wheat) based on broad geographic regions of varying soils, physiography and climate. The ecological region concept utilizes geographic regions to aid in planning and management of our natural environment.

The Soil Landscapes of Canada (SLC) and State Soil Geographic Database (STATSGO) digital maps provided the underlying soil polygon and associated attribute databases (AAFC, 1996; USDA/NRCS., 1991). Climate attribute data were compiled to the SLC polygon level from the Canadian Ecodistrict Climate Normals (http://res.agr.ca/CANSIS/NSDB/ECOSTRAT/DISTRICT/climate.html). For the SLC coverage, the map unit polygons may contain as many as 10 soil components while the STATSGO coverage displays polygons that may contain as many as 21 components. This inherent limitation does not allow the user to locate the exact location of the selected soils; however, the geographic area can be determined from the component percentage of a polygon and the area of the polygon. These soil data were chosen for this project because other research efforts between the U.S. and Canada resulted in correlation and matching of soil polygon lines along the U.S./Canadian border.

The NAFTA GIS Project was programmed using ArcView version 3.1 or 3.0a software which is IBM-PC compatible on the Windows 95 or NT operating system. Hardware requirements for the computer system include a Pentium processor with a minimum of 16 MB of RAM (preferably 32 MB RAM). The ArcView 3.0 [or newer] software package must be previously installed on the PC, and 300 MB of hard disk drive space is necessary to load the project and data files from the CD ROM storage media.

Results

Earlier presentations of the NAFTA GIS project focussed on describing a mapping tool that would help identify comparable field study locations in the U.S. and Canada with common agricultural crops, similar soils and ecological regions (Effland et al., 1998; Kroetsch et al., 1998). We now examine the application of the GIS project to mapping the spatial extent of crop, soil and environmental conditions from field dissipation studies that were completed and submitted to the U.S. EPA for registration or re-registration of three pesticides selected for various crop uses. We evaluated field studies for three pesticides with widely-varying uses: a wheat herbicide, a corn insecticide and a potato fungicide. From the study submissions to support registration or reregistration,

we extracted environmental conditions that characterized selected major crops, soil characteristics and ecological regions.

For the wheat herbicide example, soil properties' ranges were derived from three field study locations in North Dakota, Washington and Missouri. Soil reaction [pH] in the surface horizons ranged from 6.0 to 7.5. Organic carbon content varied from 0.5 to 1.5% and soil textures were loamy sand, sandy clay loam and silty clay loam. These environmental characteristics were applied as query inputs in the DSS and the graphical ouput is shown in Figure 2. Extensive wheat production areas in the midwest and western U.S. are displayed and several areas within the Canadian provinces of Alberta, Saskatchewan and Manitoba were selected by the query.

A query for the corn insecticide was developed from environmental conditions at a single [unspecified] location, a moderate leaching potential and label statements frequently applied as a groundwater advisory. Soil reaction in the surface horizons ranged from 5.5 to 7.0. Based on its moderate potential to leach, the organic carbon content in the surface horizons was characterized as greater than 0.5% and coarse soil textures (sands, loamy sands) were excluded from the query . Figure 3 illustrates the geographic extent of soils based on a DSS query with the above criteria. Large sections of the major corn production areas in the midwest U.S. were selected and comparable areas in several areas of Ontario were displayed.

The third example was developed for the potato fungicide studied at three field study locations in Europe. Soil reaction in the surface horizons varied for 4.5 to 6.0 with soil textures including sands, loamy sands and silt loams. Figure 4 displays the geographic extent of the soils from this relatively simple query. The geographic distribution of potato production areas in both the U.S. and Canada is less extensive in area than corn and wheat growing areas.

Discussion

The NAFTA GIS project was originally designed to help identify comparable field study areas in the northern tier states of the U.S. and the southern portions of the Canadian provinces where terrestrial field dissipation studies of pesticides could support registration requirements for both the U.S. and Canada. Following discussions with pesticide industry scientists and review by the FIFRA Science Advisory Panel, this project's information could be readily adapted to aid site
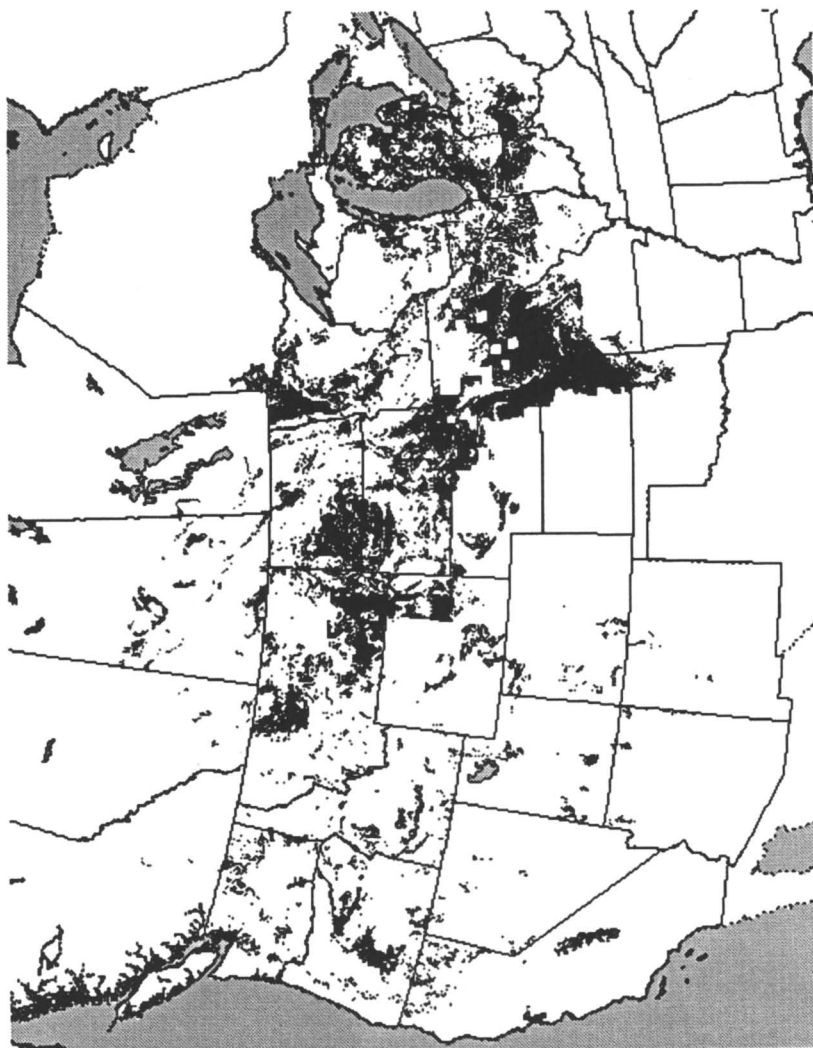
Figure 2. Canada and United States Areas Selected With the Wheat Herbicide Query
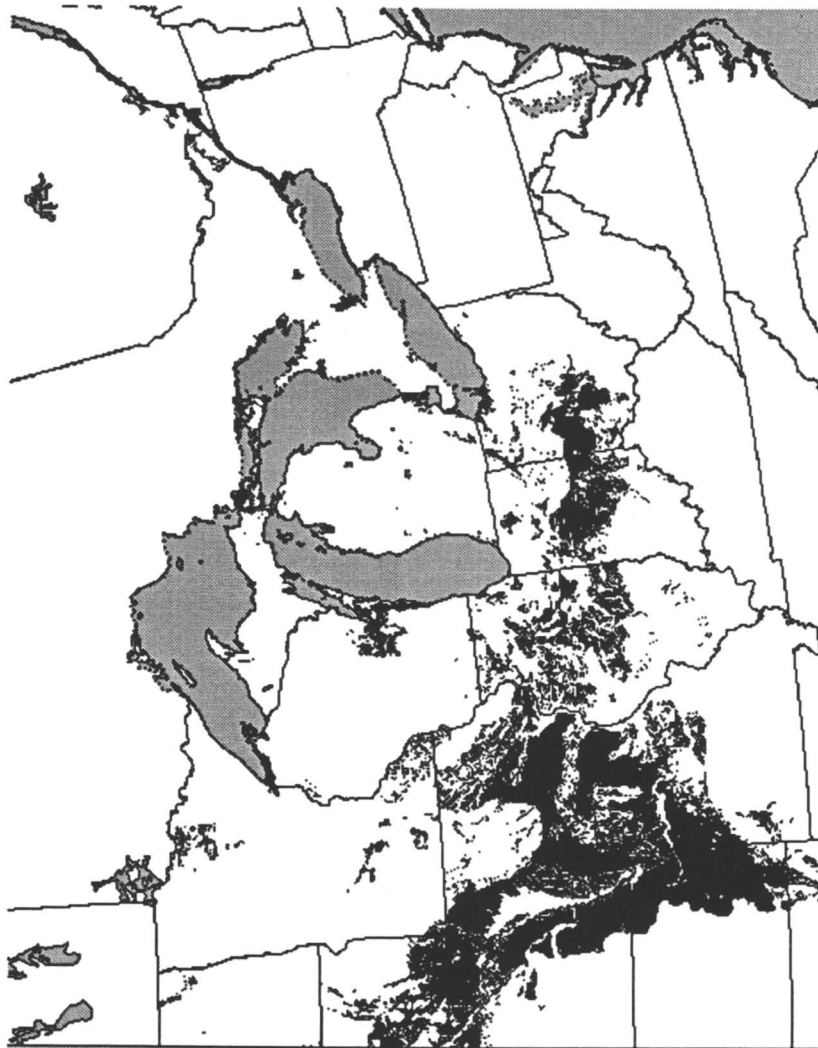
Figure 3. United States and Canada Areas Selected With the Corn Insecticide Query
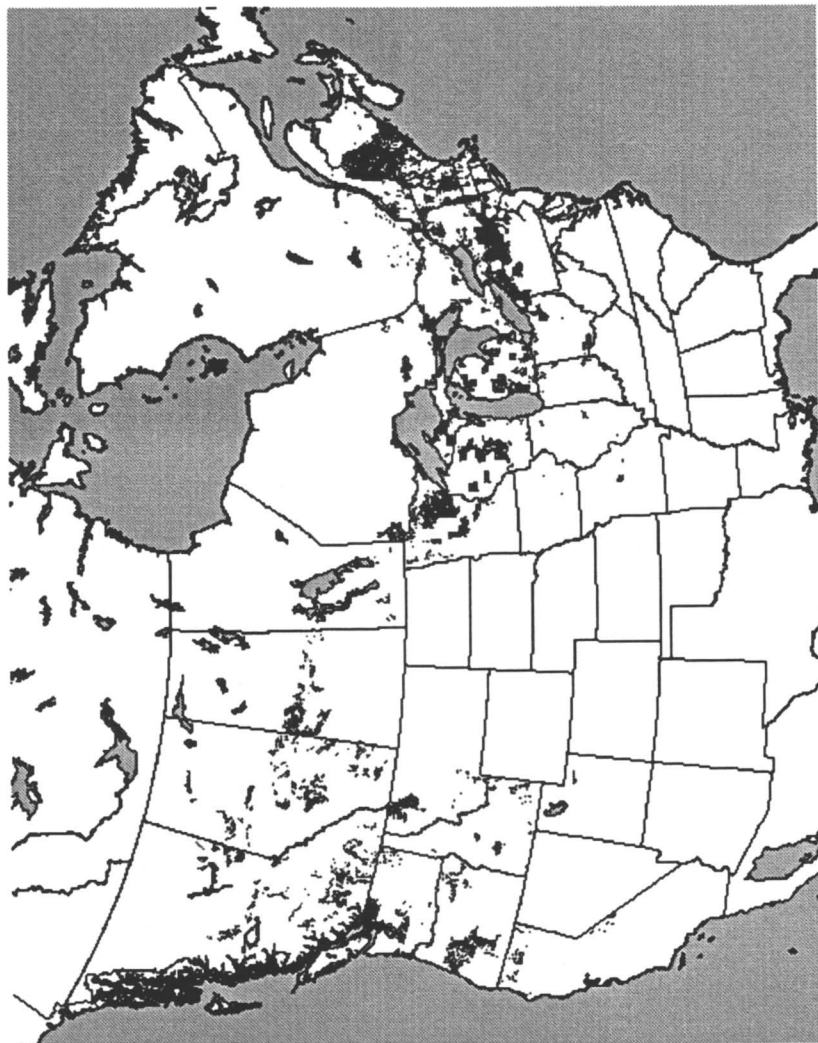
Figure 4. United States and Canada Areas Selected With the Potato Fungicide Query

selection and data interpretation from other types of field studies (e.g., prospective ground water monitoring studies, surface water monitoring) or vulnerability modeling (water resources, ecological conditions). The project output can be formatted to provide model inputs for environmental modeling, and improved characterization of ecological and human health risk assessments. Hallett et al., 1995, Carsel et al., 1991 and USEPA, 1990 previously described database management systems which were developed to improve access to spatial information and model parameter inputs for enviromental modeling. These potential applications would require additional spatial and tabular data (e.g., geographic distributions of watershed vulnerability or endangered species).

In consultation with the FIFRA Science Advisory Panel on revised guidance for conducting terrestrial field dissipation studies (http://www.epa.gov/scipoly/sap/1998/october/final.pdf), the NAFTA GIS Project was reviewed by a panel of scientists from several U.S. government agencies, academia and industry. Panelists commented that the NAFTA GIS project could be useful for evaluating the application of ecological regions to regional assessment of field study information. The SAP also commented on the applicability of this tool and indicated it was an example of a tool to help identify study regions. Other site-selection tools have been or are being developed and used by the pesticide industry for various applications such as precision agriculture and pesticide product marketing. The Panel suggested that the GIS Project might also help to extrapolate results and data from previously-studied locations to other field locations. Potential limitations were noted with respect to the scale variability and spatial resolution. The SAP recommended that the NAFTA GIS Project Team focus on the quality of the input data used in the DSS. Additional questions were discussed regarding the accuracy and reliability of the spatial data because they were derived from various government agency sources and probably collected for objectives that did not directly address the needs of the NAFTA GIS project. The SAP final report concluded that the GIS model and the reliability of its output should be evaluated by making comparisons among model-selected study locations and actual field observations.

Development of the DSS for both the U.S. and Canada was challenging because each country has unique intellectual property rights associated with products created by their respective federal governments. The NAFTA GIS Project Team discussed numerous issues involved with product distribution [development, maintenance, and revisions] and product ownership. The DSS is currently distributed by HealthCanada's PMRA or USEPA/OPP without cost to the user on the inexpensive CD–ROM media. Some discussion for distributing and maintaining this project as an Internet-accessible World Wide Web-based

application occurred; however, other factors were considered and the project team recommended continued distribution on CD media since CD drives are commonly available on PCs and the cost associated with CD media is very low. Databases for each country (e.g., soils, crops) are maintained as separate files within the project so that any revisions or corrections can be completed without impacting the other files.

Users of this GIS model should be aware of the limitations inherent to the spatial data contained within this DSS. The program user should exercise thoughtful judgement when selecting appropriate DSS input values to complete the GIS analysis. We recommend careful review and site-specific "ground truthing" for results derived from this data. The DSS is not intended to specify the exact field locations for conducting terrestrial field dissipation studies. Spatial data limitations and soil variability prevent the precise identification of field study locations. On-site evaluations of potential field study locations are the responsibility of investigators who conduct research on the terrestrial field dissipation of pesticides.

Conclusions

The NAFTA GIS project is a DSS that was developed to help identify comparable study locations for assessing pesticide dissipation under field conditions in the U.S. and Canada. The project is a collaborative effort of the USEPA, USDA/NRCS, Health Canada, and Agriculture and Agri-food Canada under NAFTA. The GIS model utilises North American ecological regions (CEC Ecoregions Level 2 Map), geospatial soil and agricultural crops databases, and climatic information. The soils information is based on the AAFC Soil Landscapes of Canada (map scale of 1:1,000,000) and from the USDA/NRCS STATSGO Data Base (map scale of 1:250,000). Agricultural crops information was obtained from Canada's 1996 Census of Agriculture and the U.S. 1992 Census of Agriculture.

Comparable field study areas in the U.S. and Canada can be investigated using geospatial environmental parameters in the GIS database, environmental fate and transport properties of pesticides and the conceptual pesticide dissipation model derived from laboratory and field environmental fate and transport studies. The project's applicability for examining the geographic distribution of field study locations provides graphical and tabular information on the spatial extent of environmental conditions associated with planned study locations or field locations that were previously studied. Some of the limitations associated with

spatial data resolution are discussed, and the project user is cautioned regarding application of this project's results for site-specific assessment.

Acknowledgements

The NAFTA GIS project and the DSS product are a collaborative effort under the NAFTA Technical Working Group for Pesticides. The cooperating agencies were the Pest Management Regulatory Agency, Environmental Assessment Division, Health Canada; Office of Pesticide Programs, Environmental Fate and Effects Division, U.S. Environmental Protection Agency; National Soil Survey Center, Natural Resources Conservation Service, U.S. Department of Agriculture; and the Land and Agronomy Program, Eastern Cereal and Oilseed Research Centre, Agriculture and Agri-Food Canada. We respectfully acknowledge the contributions of Deborah Pagurek, AAFC; Mike Ballard, Polestar Geomatics; Gail Thelin, U.S. Geological Survey; and Sharon W. Waltman, USDA/NRCS who directly contributed programming and spatial data to this project. We appreciate the comments and questions provided by numerous other scientists from the U.S. and Canada during various stages of project review.

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Chapter 3

Designing Effective Runoff Research Studies: A Review of Issues of Scale

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Concern over water quality in recent years has focused attention on the need for the development of efficient, cost-effective tools to investigate runoff as a component of overland flow. To do this effectively, tools are needed that permit efficient research within a variety of scales, from laboratory or field microplots to multi-state watersheds. Our own investigations have included the use of both rainfall simulators and natural rainfall to generate runoff from microplots such as the $2m^2$ "tilted" soil bed, the 0.1 hectare mesoplot or Small Scale Simulated Runoff (SSRO) field plot, and the conduct of large field and watershed scale aquatic monitoring programs. We have combined our field experiences with those recorded by other researchers to consolidate guidance for selecting the most appropriate technologies to answer specific research needs. One clear recommendation is that the SSRO or mesoplot study design probably offers the most reliable method for obtaining reproducible agricultural runoff data that will be extrapolable to field/watershed scale.

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Why Do We Do Runoff Studies?

The drivers for individual runoff studies are many. In the 1990s, the US Environmental Protection Agency, through the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) sometimes required pesticide registrants to demonstrate knowledge of the interactions between transported chemicals, soil and water in runoff. Concerns over potential impacts on aquatic ecosystems can result in local and federal requests for additional data regarding aquatic safety before a pesticide label or expanded use pattern is approved.

Confidence in the use of chemical transport models is improved through validation data provided by field runoff research programs. The development of agrochemical products which present minimal risk of transport in the environment can also be streamlined by early field runoff evaluation of potential analogues and formulation alternatives, benefiting both the manufacturer and the environment.

Proactive stewardship by the chemical industry, landowners, private organizations, and state or federal agencies also drives the need for continued runoff research. The effectiveness of Best Management Practices (BMPs) in reducing sediment erosion and contaminant transport in runoff flow (for example, modified tillage practices, vegetative filter strips, and structural impediments such as slotted board risers) can be measured through the conduct of runoff studies. Quantification of environmental risk mitigation provided by a label modification or recommended application practice is yet another use.

Runoff Processes

Simply put, runoff is generated when the infiltration capacity of a given soil is exceeded. Ponding, or depression storage, begins at the time the infiltration capacity of the soil equals the rate of rainfall. Mahoumad (1) reports that rainfall which occurs after the soil's depression storage capacity is filled, is partitioned into either detention storage or runoff. The rate of runoff increases until it equals the rate of excess (non-infiltrating) rainfall, at which point storage is at a maximum and runoff occurs at a steady rate.

A broad range of soil characteristics and hydrologic interactions influence the ability of a particular watershed to generate runoff. These can be loosely separated into "small" and "large" scale processes, and include:

"Large" Scale Processes	"Small" Scale Processes
• Soil Texture	• Soil Texture
• Tillage and Agronomic History	• Soil Aggregate Size
• Soil Aggregate Size	• Antecedent Soil Moisture

- Vegetative Cover
- Antecedent Soil Moisture
- Rainfall Intensity/Duration
- Soil Infiltration Capacity
- Soil Compaction
- Hydraulic Conductivity
- Depression Storage/Ponding
- Slope
- Scour
- Sheet Flow
- Rill Erosion
- Interrill Erosion
- Soil Detachment/Mixing
- Sediment Deposition
- Entrainment/Filtering

- Raindrop Impact/Kinetic Energy
- Rainfall Intensity/Duration
- Soil Infiltration Capacity
- Hydraulic Conductivity
- Depression Storage/Ponding
- Slope
- Sheet Flow
- Soil Detachment/Mixing
- Entrainment/Filtering
- Splash/Edge Effects

Agronomic practices such as tillage become particularly important when runoff is investigated for the purpose of extrapolation to "real world" exposure assessments. Tillage affects the soil surface, and thus directly impacts hydraulic conductivity, or the ability of the soil to conduct and store water (2). Mahoumad (3) considered hydraulic conductivity the single most important parameter in the infiltration process, as it mediated the partitioning of rainfall into runoff and infiltration.

Factors Impacting Chemical Transport in Runoff

The conceptual pesticide runoff model proposed by Leonard and Wauchope (4) describes runoff as a process whereby water flowing over a soil surface may extract pesticide residues from the arbitrarily-defined uppermost centimeter of the soil profile, as a result of dispersion and mixing processes influenced by rill erosion, interrill erosion and raindrop impact. Chemical extractants are exchanged in this "runoff-interaction zone" between the soil water and the flowing water, and together with entrained soil particles, are transported in overland flow. A process of soil filtering and "enrichment" also occurs during transport as coarser particles are deposited en route, with the result that the runoff sediment reaching edge of field is of smaller size and may therefore have a higher overall adsorptive capacity than whole soil.

In order to effectively select study designs to evaluate the potential runoff transport of agrochemicals, the researcher must consider both the agronomic scenario and the physicochemical characteristics of the pesticide. Since the

agrochemical product is comprised of one or more active ingredients (ais) associated with an inert "carrier" and, typically, surfactants or emulsifying agents, both the behavioral characteristics of the active ingredient and the formulation must be considered within the soil environment. For example:

Active Ingredient Factor
- water solubility of the ai
- K_{oc} (adsorption coefficient)
- soil aerobic/anaerobic half life
- volatility of the ai
- formulation type
- formulation adjuvants
- application rate

Agronomic Scenario Factor
- soil organic matter content
- soil moisture content
- soil permeability
- crop/residue cover
- tillage pre- and post-application
- time from application to runoff
- slope

Runoff Exposure Assessment

Depending upon the focus and desired endpoints of the study, a variety of runoff assessment tools are available to the researcher. Distinguishing features which enable separation of these tools into distinct categories are the elements of test system scale, and the use of either natural or simulated rainfall (or both) to generate runoff. Often, the selection of study type and rainfall delivery system will be interdependent, as requirements of test system scale may determine the ability to use one means of rainfall generation over another.

Rain - Simulated and Natural

The runoff erosion process involves the "expenditure of energy obtained from falling raindrops during a storm" (5). When a rain droplet impacts the soil surface, energy is imparted to that surface, resulting in the breakdown of soil aggregates and the movement of soil particles as splash, and, once a collective downslope momentum is established, as sediment entrained in runoff flow. Characteristics of natural rainfall which influence its erosivity include rainfall intensity, raindrop size distribution and raindrop-fall velocity (6). However, the temporal and spatial variabilities inherent in conducting research limited to runoff generation by natural rainfall make such a field study difficult to do. The rainfall simulator has become a well-respected alternative, providing a great measure of control, while still approximating "real world" erosive conditions. Effective simulators are now capable of providing uniform rainfall at a range of scales from less than $1m^2$ to more than 0.2 hectares.

Evaluation of rainfall simulators on the basis of natural and simulated rainfall characteristics has been conducted internationally, and confirmed a range of drop diameters comparable to natural rainfall, comparable drop size distribution, drop velocities, water content, momentum and kinetic energy (5,7). Evaluation on the basis of field utility, time and cost has demonstrated that erosion research studies conducted using rainfall simulation are more efficient, more controlled and more adaptable than those that rely exclusively on natural storms (6).

Recommendations for the use of rainfall simulation in runoff research were proposed by Auerswald and Eicher (8) following a comparison of German and Swiss rainfall simulators. They included the application of simulated rain for at least 30 minutes after a constant runoff rate was achieved, in order to ensure a satisfactory measurement confidence interval. They also recommended using a minimum one hour rainfall when collecting infiltration and soil loss data for model parameterization, the application of rainfall to replicated plots on the same day, and the minimization of variability and error by the use of larger, rather than smaller sized test plots.

Nolan (9) investigated the relationship of soil loss generated using a rainfall simulator to that occurring on a field scale as the result of natural storm events. With appropriate scaling adjustments, he demonstrated an acceptable agreement between five year natural event erosion and that estimated using a rainfall simulator.

Some of the advantages and disadvantages of the use of natural and/or simulated rainfall to generate runoff include:

Natural Rainfall
• "natural" rainstorms/erosion
• wide area coverage
• limited area of coverage
• no water supply costs
• spatially variable
• temporally variable
• dangerous storm sampling
• uncontrollable timing

Simulated Rainfall
• rainfall characteristics near natural
• easily replicated storms
• portable
• uniform distribution
• planned storm generation
• water supply and equipment cost
• limited area of coverage

Laboratory and Field Microplots

Microplots have been described as small, artificially constructed boxes of soil, or small diked plots in a field where the variables of soil characteristics, slope and soil are controlled by the researcher (10). They typically encompass

an area of 3 m^2 or less and can be fairly easily replicated. Storm and runoff generation can be accomplished using either natural or simulated rainfall, and research can be conducted either indoors or in the field.

The issue of scale is of great importance in designing a microplot runoff study. The small size of the test area provides considerable experimental control, and the approach has been used effectively in targeted comparisons of specific interrill processes such as surface sealing, aggregate stability, raindrop detachment and splash transport (11). It is, however, difficult to extrapolate from microplot to field scale, because the microplot's small size precludes incorporation of transport processes such as rill erosion and sediment deposition into the runoff exposure assessment. The convenience of preparing many hand-packed soil bed replicates must be balanced against the lack of a field soil structure, and the difficulties of achieving hydrologic reproducibility between replicates. Additionally, the small experimental scale can exaggerate the effects of soil and climatological variables such as wind; runoff or erosion losses due to splash can become significant.

Laboratory quantification of runoff using hand-packed soil chambers has been used to provide information on the runoff and leaching of atrazine under hydrologic changes similar to those of a freshly tilled field after successive rain and drying cycles (12). Results indicated that the incorporation of at least one rainfall equilibration cycle was necessary to reduce variability between the test chambers to a level at which reliable agrochemical transport data could be generated. Data also suggested that transport replicability between individual test chambers could be greatly improved by selection of pre-determined hydrologic replicates prior to the application of test chemical (Isensee, personal communication).

Hand-packed or "Tilted" Soil Beds

We investigated the utility of a type of microplot, the "tilted" soil bed, as a potential research tool for evaluating the transport of agrochemical formulation types under simulated rainfall. Field research was conducted in cooperation with Virginia State University during 1998, using replicated 2m^2 stainless steel beds with hand-packed soils. A schematic of a single "tilted bed" is presented as Figure 1.

The soil in each bed was saturated from below during the packing process, and allowed to drain for approximately 24 hours. Test chemical was applied to the still-wet soil surface using field scale TeeJet® nozzles mounted on a custom-designed, motorized application unit at one day prior to rainfall initiation. Rain was delivered at the rate of 1 inch per hour for a duration of two hours to two or three bed replicates on a single day, using an oscillating head rainfall simulator

of the design of Meyer and Harmon (13). Runoff, leachate and interflow samples were collected from each bed for residue analysis and comparison of transport.

The distribution of simulated rainfall across the tilted bed soil surface was determined by placement of 12.5 cm diameter collection cups across the entire bed surface. Calibration data collected during the study confirmed both the relatively uniform and consistent volume of rain droplets delivered across each soil surface, and the replicability of rainfall intensity from test bed to test bed.

"Tilted Bed" Test Plot Design

Beds were handpacked to a depth of approximately 0.3 m with sieved soil, saturated prior to chemical application and subjected to simulated rainfall within 24 hours of treatment.

Direction of Slope

1.0 m   2.0 m

0.3 m

Runoff collection trough at downslope end

Slope adjustable by placement of 2.54 cm steel bars

Outlets for collection of runoff, leachate and interflow samples

Figure 1. "Tilted" Soil Bed Design

The transport data presented in Table I reflect the inconsistency of hydrology encountered in the study. The greater retention capacity of the clay loam than the sandy loam soil was apparent and expected. The very great variabilities between test beds within the same soil series were not anticipated,

however, and the lack of consistent hydrology ultimately precluded use of the beds for formulation comparison in these trials.

One possibly significant difference between our study and those of other researchers who have utilized the "tilted bed" for runoff research was the method of bed packing. Several authors (11, 14) have reported bed packing techniques based on achieving a target soil bulk density, ie, condensing a known mass of soil into a container of known volume. Our technique relied instead on layered distribution and saturation processes, which may have contributed to the variable transport results.

Soil sieving to a uniform 2-4 mm diameter and the initiation of simulated rainfall onto a saturated soil bed are two fairly typical but potentially confounding practices which have been used in the preparation of soil chambers and tilted beds for runoff research. Ambassa-Kiki and Lal (15) and Reichert and

Table I. "Tilted" Soil Bed Hydrology Results

Test Bed*	Total Rainfall (L)	Runoff (L)	Leachate (L)	Interflow (L)	Total Water (L)	Total Sediment (g)
SL 1	22.5	3.0	3.4	6.1	12.4	17.4
SL 2	22.5	9.6	3.0	0.0	13.5	37.5
SL 3	22.5	11.7	6.3	0.0	17.9	58.3
SL 4	23.1	13.7	2.6	0.0	16.3	58.9
SL 5	23.1	1.1	3.7	2.9	7.7	0.7
CL 6	22.9	1.8	0.1	0.0	1.9	1.0
CL 7	22.9	2.8	0.1	0.0	1.9	0.4
SL 8	23.2	10.1	1.0	0.2	11.3	54.7
SL 9	23.2	5.9	0.5	0.5	6.9	29.1
SL 10	23.2	1.8	0.1	1.0	2.9	2.0

*SL denotes Sandy Loam soil, CL denotes Clay Loam

Norton (16) compared the effects of surface soil aggregate size, and the pre-wetting and rapid-wetting of soil aggregates, respectively, and concluded that the presence and stability of aggregates of approximately 5 to 20 cm diameter significantly influenced erosion characteristics. The uniformly sieved fine soils used in our study may have further prejudiced already variable transport results.

A related process, surface sealing or crust formation, is a result of the breakdown of soil aggregates due to the action of raindrops and/or flowing water

across the soil surface. Rainfall impact moves clay particles downwards a short distance, leaving a proportionally higher concentration of sand and silt on the soil surface. As the pore space near the surface is filled, a seal is formed, infiltration is reduced, and runoff flow is increased The observed formation of soil seals early in the runoff process from our tilted beds was perhaps the direct result of the combined effects of minimizing aggregate size and the initiation of rainfall on an already saturated soil. In a discussion of splash and wash erosion rates, Moore and Singer (17) concluded that trends of increasing runoff towards equilibrated flow were "related to the decreasing size and degree of aggregation of surface material available for detachment, and the buildup of a layer of overland flow that appeared to enhance splash detachment while retarding splash transport".

Field Microplots

Other researchers have identified benefits and limitations afforded by the use of microplots in field runoff research. Wauchope (18) investigated the transport of sulfometuron-methyl and cyanazine from nested field microplots created by insertion of metal dikes into the soil profile to hydrologically isolate areas of approximately 3 m^2. He concluded that the erosion and runoff yields fell within the range of observations from full scale field experiments, but noted that the full scale range encompassed three orders of magnitude. Obi (19) also investigated the use of a rainfall simulations on *in situ* microplots of $0.036m^2$, but determined the technique to have apparently "serious limitations even for comparative studies... because of the high degree of variability in microenvironments".

The use of the "nested" microplot within a larger, monitored field environment is an appealing alternative to the larger watershed study for investigation of specific runoff parameters. An experimental design which enabled direct comparison of transport across replicated "nested" plot areas could provide the scaling factors necessary to extrapolate measured data to field dimension. The use of typical tillage practices upon an *in situ* soil structure is a strong advantage which may also facilitate "real world" interpretation of microplot-generated data relative to the assumptions inherent with hand-packed soil beds.

A summary of the benefits and limitations of packed bed and field microplots includes:

Benefits	Limitations
• use of real soils	• not generally representative of field scale
• use of rainfall simulation	• does not incorporate rill erosion
• less expensive	• problems with splash and edge effects
• easy to replicate	• sensitive to wind interferences
• control of some variables	• sensitive to small changes
• manual flow monitoring and sample collection	• not representative of field soil structure

"Meso" or Small Scale Simulated Runoff (SSRO) Plots

The development of the "small scale simulated runoff" (SSRO) or "meso plot" study design has provided researchers a "nearly field scale" tool that combines both the ease and replicability of the microplot with the realism of typical tillage and cropping practices. As pioneered by Miles, Inc. (presently Bayer Agricultural Division), a mesoplot is approximately 0.1 hectare in area, with a slope length sufficiently long to allow the movement of sediment through rill erosion as well as interrill processes. Although transport from "mesoplots" may be studied under conditions of natural rainfall, one of the principal advantages of the mesoplot design is the ability to utilize simulated rainfall to generate runoff. The portable runoff simulator designed by Coody (20) has been utilized in our mesoplot studies (Figure 2) because of its ability to replicate specific storms of a particular return frequency with a droplet spectrum and distribution approximating those of natural rainfall.

In 1992, we conducted an initial mesoplot study under typical agronomic conditions to investigate the effectiveness of a formulation change in reducing the amount of active ingredient transport in runoff. The study design was based on demonstrating hydrologic comparability between three 14 meter wide by 52 meter long test plots replicated within a field, each with the long dimension oriented parallel to the direction of overall slope, as determined by survey.

The entire field area was moldboard plowed, disked and harrowed to a good seedbed condition prior to the installation of the rainfall simulators and runoff collection flumes and samplers. Soil cores for determination of antecedent moisture and bulk density were collected prior to each simulated rainfall event from designated sampling areas.

Test chemicals were applied to each mesoplot using conventional farm equipment on the same day, and incorporated into the surface soil according to label specifications. Two-hour simulated rainstorms of approximately 1.1 inch per hour intensity were generated across each test plot in succession, at three and
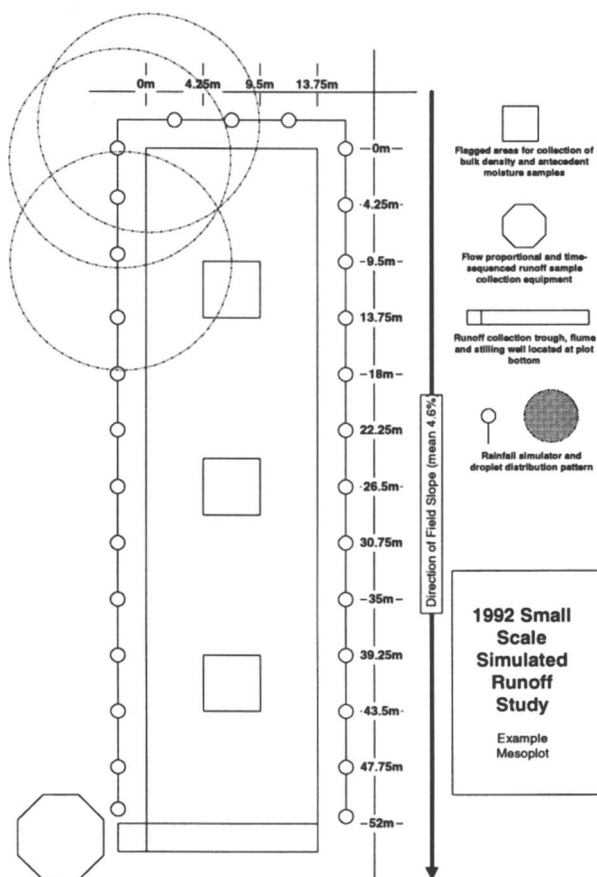
Figure 2. Example SSRO or Mesoplot Test System

ten days following application, and samples of runoff were collected on both time-sequenced and flow-proportional bases.

The data collected during the study are presented in Table II. The remarkably good hydrologic agreement between individual test plots was critical in enabling the valid comparison of transport variables related to chemical formulation. The test data were subsequently extrapolated to field scale via several erosion modeling algorithms, including the USLE soil loss equation and modifications proposed within the Onstad-Foster model and by Jimmy Williams (MUSLE). The modelled and transport data again showed strong agreement, particularly for the first runoff event from each test plot which occurred after planting (21).

Table II. Hydrology Summary of SSRO Test Plots

Study Plot	Overall Slope (%)	Runoff Event	Total Rainfall (mm)	Runoff Yield (L)	Sediment Yield (kg)	Runoff as % Total Rainfall
1	5.2	1	58.9	10818	161	28
2	4.6	1	58.9	11498	167	29
3	4.2	1	67.0	13990	229	31
1	5.2	2	64.0	24270	368	57
2	4.6	2	54.9	22486	459	62
3	4.2	2	59.4	27867	469	71

In addition to acknowledging the importance of slope length in the generation of rill erosion, researchers have addressed the importance of incorporating other field scale characteristics into the mesoplot design. In a discussion of the influence of plot dimensions, Auerswald (22) concluded that plot width might be nearly as important a variable as plot length in predicting erosion. He suggested that a representative test plot width should include a minimum of one tractor wheel track. Confirming research on the influence of wheel tracks in erosion and agrochemical transport assessments was reported by Baker and Laflen (23), who measured a nearly fourfold increase in atrazine from test plots with wheel tracks than from those where the herbicide had been incorporated by disking.

Another outcome of the development of the mesoplot test system is the ability to compare the effectiveness of tillage systems, vegetative buffer strips and BMPs in reducing erosion and sediment transport in a replicable, representative and cost effective manner. Sumner (24) concluded that the mesoplot simulator design met most of the characteristics of rainfall simulators recommended by Meyer, and effectively incorporated the dominant processes that controlled runoff and sediment yields from "field size" areas.

Benefits and limitations of the "mesoplots" include:

Benefits
•use of real soils
• uses rainfall simulation
• ideal for comparative studies
• useful for model validation
• reproducible
• control of some variables
• extrapolable due to real soil structure, agronomic practices

Limitations
• can be sensitive to wind effects
• scaling not fully validated yet
• replication can be costly
• requires flow monitoring and sampling instrumentation

Field Scale Runoff Studies

It has been postulated that "the ultimate measurement of the potential for a pesticide to be lost in runoff is a field test under natural conditions" (10). Nevertheless, the authors point out that although such a test is conceptually no more difficult than a smaller scale transport study, the results of its "laborious, time-consuming and expensive" conduct are ultimately not readily extrapolable to any other conditions.

We conducted a two-year, field scale aquatic monitoring study at the request of the US EPA during 1989-1990 in an attempt to obtain data that would establish a meaningful estimate of Expected Environmental Concentration for a soil insecticide. The concept behind studies at this scale is the investigation of runoff from a field or fields treated with the chemical in question. The catchment often has a pond into which the runoff drains.

In our study, ten watersheds, ranging in size from 4 to 57 acres, were engineered to maximize runoff transport from treated corn acreage to the receiving water body. The widely variable site characteristics of the fields agreed with EPA can be reviewed in Table III.

As with any field study of this magnitude, weather became a critical variable. Eighteen runoff events were recorded and sampled during the two year monitoring program, but were widely disproportionate in timing and scope. The length of time from test chemical application to runoff ranged from 3 to 37 days; the percentage of incident rainfall which ran off varied from 0 to 100 percent. One of the Iowa locations, in fact, never experienced a runoff event.

Table III. Aquatic Monitoring Field Site Characterisitics

Study Site	Land Area (A)	Pond Area (A)	Land:Water Ratio	Slope (%) (mean/range)	Soil Type[a]
IA (IA06)	5.9	0.25	24:1	8; (2-16)	Scl
IA (IA08)	4.3	0.28	16:1	8; (3-12)	Scl; Cl
MS (MS01)	8.6	1.13	8:1	8; (5-11)	Sl
MS (MS04)	8.2	0.83	10:1	8; (5-11)	Sl
MS (Swann)	23.8	3.86	7:1	5; (2-10)	Sl; Sc
OH (T'mas)	6.2	0.33	18:1	8; (3-9)	Scl
IA (Payton)	8.0	0.72	11:1	7; (2-14)	Cl; Scl
IA (Swack)	56.6	5.21	11:1	8; (2-14)	Cl; Scl
IA (Keller)	29.6	1.88	16:1	9; (2-12)	Cl; Scl
IA (Schwab)	9.2	0.84	11:1	7; (2-9)	Cl

[a]Scl = Silty Clay Loam; Cl = Clay Loam; Sc = Silty Clay; Sl = Silt Loam

In a discussion of the results of the study, Hendley (25) concluded that while field scale studies are potentially capable of measuring real environmental exposure for a given site in a given season, they are not cost-effective. The high degree of variability in time from application to first runoff, in rainfall duration and intensities, antecedent field moisture content and tillage effects combined to make the study data very difficult to interpret or extrapolate to other sites and weather conditions.

A summary of benefits and limitations of field scale monitoring includes:

Benefits	Limitations
• full scale assessments	• very expensive
• utilizes "natural" conditions	• very difficult to interpret
• can validate models	• no replicability
• integrates over a wide area	• cannot link findings to a specific variable
• actual use patterns	• extreme "worst case" exposure estimate

Watershed and Basin Scale Monitoring

Watershed or basin-scale monitoring programs introduce still more complexity and uncontrolled variability into the runoff experimental design because they require investigation of multiple fields and environments which may extend over hundreds of miles. The scale is so large, in fact, that the researcher is no longer able to relate outputs to individual processes influencing erosion, chemical or water flux, but must instead rely on non-point source assessments and alternative investigatory tools such as geographic information systems (GIS) and simulation models.

A watershed study is necessarily conducted over a period of years, in order to allow for trends to develop within the complexity of climatological, topographic and demographic variables. USGS researchers investigating the occurrence of triazinine and acetanilide herbicides in surface waters, however, recently proposed that the apparent increase in the use of these pesticides determined during the 1980s and 1990s was "more an indication of a trend towards more targeted monitoring than an actual trend in the occurrence of these compounds" (26). Current examples of watershed scale monitoring programs include both the Management Systems Evaluation Area (MSEA) studies, and the National Water Quality Assessment (NAWQA) project conducted under the auspices of the US Geological Survey (27). The NAWQA program design, because of scope and scale issues, is necessarily multi-tiered, and will be conducted over decades. Since inception in 1991, NAWQA has focused on "Occurrence and Distribution Assessment" of contaminants within the 60

hydrologic study units of interest. "Case Study" investigations intended to answer questions about contaminant sources, transport, fate and effects are not emphasized in present monitoring cycles because of significant resource demands (28). It has been our experience that programs of this type are best conducted within the community of government agencies.

Amongst the strengths of the watershed scale runoff program is the potential to integrate data across wide areas, and to reflect the impacts of landscape composition and flow dilution in the assessments. Additionally, monitoring data can be obtained for multiple analytes simultaneously under actual use conditions. Finally, work at this scale has the potential to be relevant to our understanding of the possible occurrence of agrochemical residues in drinking water supplies.

A summary of the benefits and limitations of watershed and basin-scale monitoring includes:

Benefits	Limitations
• integrates over a wide area	• difficult to simply findings
• reflects impact of diversity	• very expensive
• incorporates flow dilution	• time and resource intensive
• actual use patterns	• long delays in data availability
• allows regional averaging	• focus on occurrence rather than processes

Conclusions

Runoff and runoff measurement approaches are ultimately dependent upon spatial and temporal scale. Because the researcher has a plethora of options regarding study design and experimental format, it is critical to ensure that the tools selected are appropriate to the study objectives and will enable the researcher to achieve targeted endpoints.

Table IV summarizes five categories of runoff experimental design, and is intended as a guide for selecting a test system appropriate to the conditions, objectives and duration of the study. Accordingly, resource estimates of time and money are included for the benefit of the reader.

Ideally, the runoff researcher should strive to achieve a balance between "realism" and spatial scale, by taking care to match the study type to the process of interest. For example, laboratory and field microplot studies can be effective in investigating degradation processes, leaching potential and droplet/soil interactions. Mesoplot or SSRO studies are excellent tools for evaluating the same variables on a broader scale, and by incorporating "real world" agronomic and erosion processes, can provide an excellent basis for transport comparisons

Table IV. Guide to Plot Scale and Study Design

Test System	Rainfall	Benefits	Limitations	Cost	Example Study Types
Microplot, hand-packed soils	Simulated	•use of rainfall simulation •less expensive •easy to replicate •manual flow monitoring and sample collection	•not fully representative of field scale •no rill erosion •edge and splash effects •sensitive to small changes •artificial soil structure	•$K •days-weeks	•rainfall intensity •surface aggregate effects •effect of slope •comparison by soil type •surface sealing processes •interflow processes •soil detachment rate •sheet erosion processes
Microplot, *in situ* field soils	Simulated Natural	•field soil structure •use of rainfall simulation •less expensive •easy to replicate •manual flow monitoring and sample collection	•not representative of field scale •no rill erosion •edge and splash effects •sensitive to small changes •climatological impact/wind	•$$K •days - weeks	•effect of application rate •grass cover effects •dissolved chemical transport •nested comparison of scaling parameters •tire tracks/soil compaction •effects of tillage on soil loss •sheet erosion processes •formulation comparisons
Mesoplot	Simulated Natural	•generation of model input parameters	•can be sensitive to wind effects •scaling not fully validated	•$$$K •weeks-months	•chemical transport in water and sediment phases •tillage practices •effects of soil compaction

Test System	Rainfall	Benefits	Limitations	Cost*	Example Study Types
Mesoplot, continued	Simulated Natural	•control of key variables •extrapolable data •less expensive than field scale •field agronomic practice/equipment	•replication can becomes costly •requires flow monitoring and sampling instrumentation	•$$$K •weeks-months	•rill/interrill transport processes •estimates of soil loss •effect of crop cover •formulation comparison •buffer strip efficacy •erosion control efficacy •model parameterization
Farm Field	Natural	•full scale assessment •utilizes "natural" conditions •can validate models •spatial integration of variables	•very expensive •difficult to interpret •no replicability •cannot extrapolate between fields •extreme "worst case"	•$MK •1 to 2 years	•pesticide losses •BMP effectiveness •comparative cropping practices
Watershed/ Basin	Natural	•utilizes "natural" conditions •best managed through a government system •incorporates landscape factors reflects drinking water scale	•very expensive •difficult to interpret •cannot link findings to a specific cause •cannot extrapolate between fields •subject to weather variabilities	•$MMK •5 years+	•stewardship monitoring •impact of landscape scale factors •non-point source water pollution assessments •model correlation •integration of regional scale variability

and model parameterizations. The acquisition of data on the field and watershed or basin scale can provide an understanding of local or regional dynamics, and a synthesis of information from diverse environments. The task for the researcher is to make intelligent and responsible choices.

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Chapter 4

An Integrated Approach for Quantifying Pesticide Dissipation under Diverse Conditions I: Field Study Design

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Environmental fate studies for pesticide registration have traditionally focused on a single environmental media and over a single growing season (e.g., pesticide dissipation in the upper 90 centimeters of soil, residue levels in specific receiving waters, or residues leaching to ground water). Studies focusing on a single element of the hydrologic process, and under a narrow range of climatological conditions, can often generate more questions than answers in understanding and describing the environmental fate of a pesticide. These studies may not address the fundamental issue of mass balance closure for the pesticide and thus do not provide the necessary framework for predicting pesticide behavior under different environmental or climatological conditions. An alternative study documenting chlorpyrifos dissipation in soil, foliage, runoff, and receiving waters under a range of agronomic and climatological conditions is presented. This multi-year integrated field study consists of a 17.29 acre corn production watershed near Oskaloosa, IA which drains into a 0.6 acre pond. In addition, numerous

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0.16 acre meso-plot experiments are also subject to natural and/or simulated-rainfall and agricultural practices under a carefully controlled environment. Integrated studies quantifying runoff, dissipation, and scaling factors offer the advantage of a comprehensive, time- and cost-effective approach for evaluating the environmental fate of pesticides under field conditions. This rich data set is used for model validation and subsequent extrapolation to other environmental and climatological conditions to expand our understanding of the environmental impact resulting from the use of chlorpyrifos.

Introduction

This four part study details the results of an integrated field study design and modeling program used to monitor chlorpyrifos dissipation in soil, foliage, runoff, and receiving waters under a range of agronomic and climatological conditions. The integrated design incorporates a series of meso-plots (0.16 acres), in which simulated rainfall and agricultural practices under a carefully controlled environment can be varied to investigate pesticide transport over a short time frame (i.e., single precipitation event).

The integrated study design offers the advantages of a comprehensive, time- and cost-effective approach to evaluate the environmental fate of pesticides under field conditions. This is contrasted with the current USEPA FIFRA Subdivision N study requirements that include numerous distinct and unrelated media-specific studies. The integrated study was designed to generate data required to calibrate/validate simulation models in addition to providing site-specific behavior for chlorpyrifos formulations. Numerical models can subsequently be used to evaluate other environmental and climatological conditions to provide a decision support mechanism for environmentally-sound product use. This document discusses the field study design. Details of field observations, model validation, and extrapolation procedures are discussed in the companion documentation (1-3).

Methods And Materials

A 17.29 acre watershed located near Oskaloosa, Iowa was treated with chlorpyrifos during the 1992-1993 corn growing season and monitored for off-site movement of the pesticide. Much of the study design followed traditional practices as outlined by Wauchope et al. (4). The watershed consists predominantly of silt loam (Hydrologic Group C) as seen in Table I.

Table I. Watershed Soil Properties

Soil Series	Map Unit	Hydrologic Group	Approximate Area (%)
Ladoga silt loam	76C2	C	70
Downs silt loam	T162B	B	15
Fayette silt loam	163C2	B	15

The treatment of the watershed was typical of corn agronomic practices for the Midwestern U.S.A with corn planted on the contour. This particular watershed drained into a 0.60 acre farm pond. Both the watershed and pond (Figure 1) were surveyed and pond bathometric measurements made. Representative slopes within the watershed range between 2.6 - 5.1%, and the two primary drainage channels seen in Figure 1 have slopes of 2.6 and 3.2%, respectively. The pond had a single tile drain inflow (Station 6) and a primary drain outflow (Station 4), both of which were monitored for water flow and chlorpyrifos residues for mass balance closure.

Time-dependent samples of vegetation, soil, pond water and pond sediment were analyzed for chlorpyrifos residues to characterize chlorpyrifos leaching and dissipation patterns. In addition, spatial scaling issues between meso-plots (ca. 0.16-acre) and the watershed (17.29-acre) were addressed by two nested meso-plots within the watershed. These nested meso-plots received the same management practices and natural precipitation as the watershed (Figure 1) with the only major difference being in surface area and length scale.

In addition, four separate experiments consisting of 0.16-acre "meso-plots" were located within the same commercial cornfield as the main watershed, but part of a different drainage basin. These four artificially irrigated meso-plots each received different chlorpyrifos treatments at different times during the growing season to investigate both bare soil runoff and the effect of crop cover on hydrology, erosion, and chlorpyrifos edge-of-field transport.
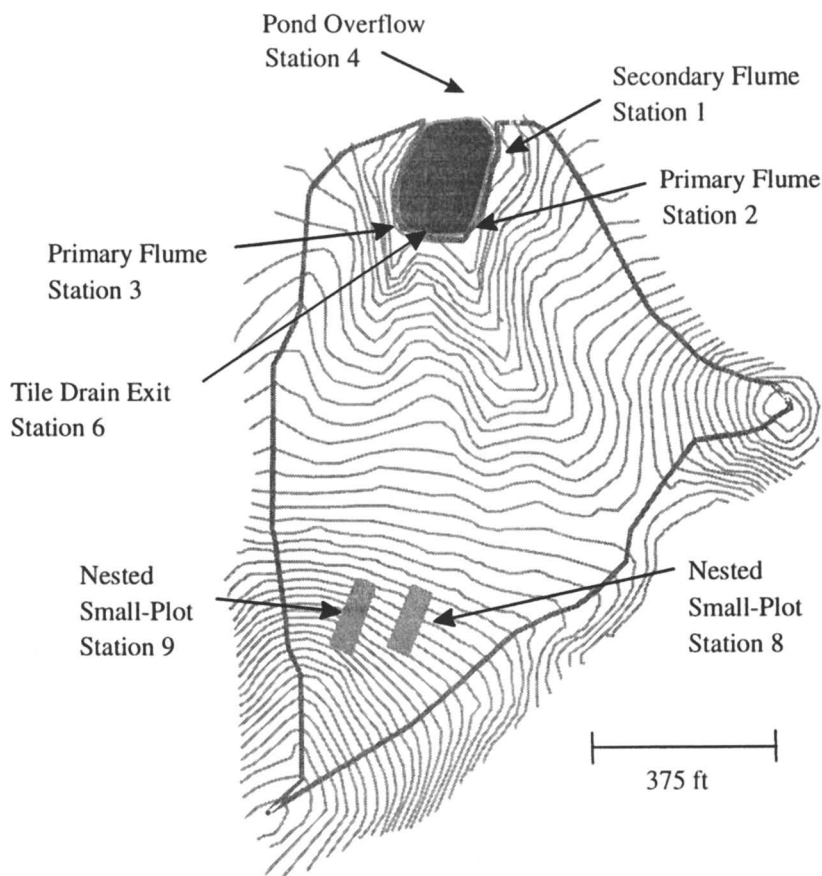
Figure 1. One foot topographic contour survey of watershed with locations for sampling equipment and nested meso-plots.

Instrumentation of the Main Watershed

Runoff Monitoring Stations

Primary runoff stations (Stations 2-3) were located immediately northwest and southwest of the pond and were placed where the two primary drainage

channels of the watershed enter the pond. These stations were equipped to monitor runoff flow rates through the flumes (Figure 2).
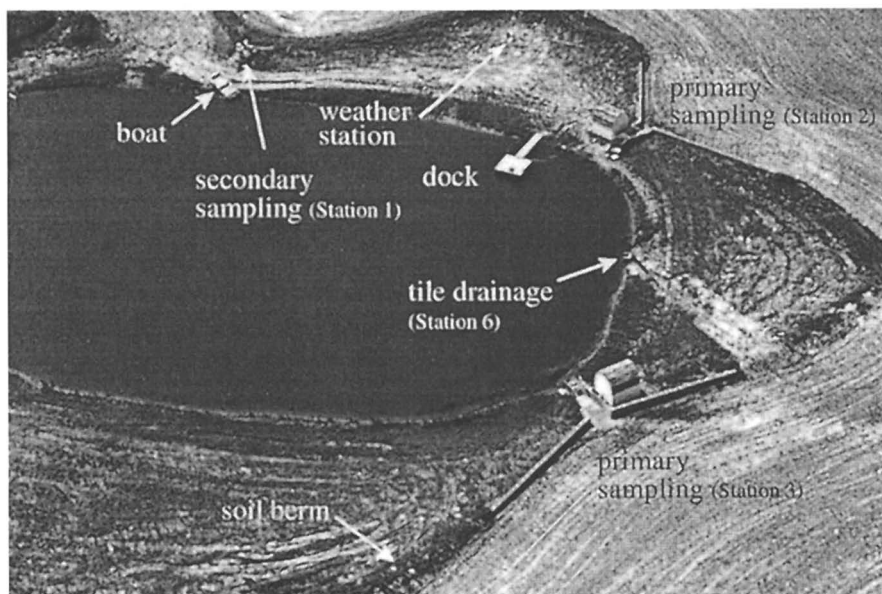
Figure 2. Location of runoff monitoring stations placed around the pond perimeter.

Sampling electronics in the primary runoff stations collected both a composited, flow-proportional sample of runoff where approximately 1 L of runoff water was collected for each 750 ft^3 of runoff passing through the Parshall flumes. Discrete runoff samples were also obtained according to a predetermined time sequence where the sampling frequency decreases as the runoff event continues. The discrete runoff-sampling scheme provided a capacity to sample long runoff events using the 24 sample containers supported by Isco model 2700 pump samplers. Flow-proportional samples were composited into stainless steel, 55-gallon drums while discrete samples were collected into l-quart (946 mL) glass or metal containers (Figure 3). The sampling scheme allowed for intensive sampling of short-duration runoff events or during the initial stages of longer storms until sample containers were replaced. All sampling equipment was housed in a temporary shed to avoid possible malfunctions due to inclimate weather.
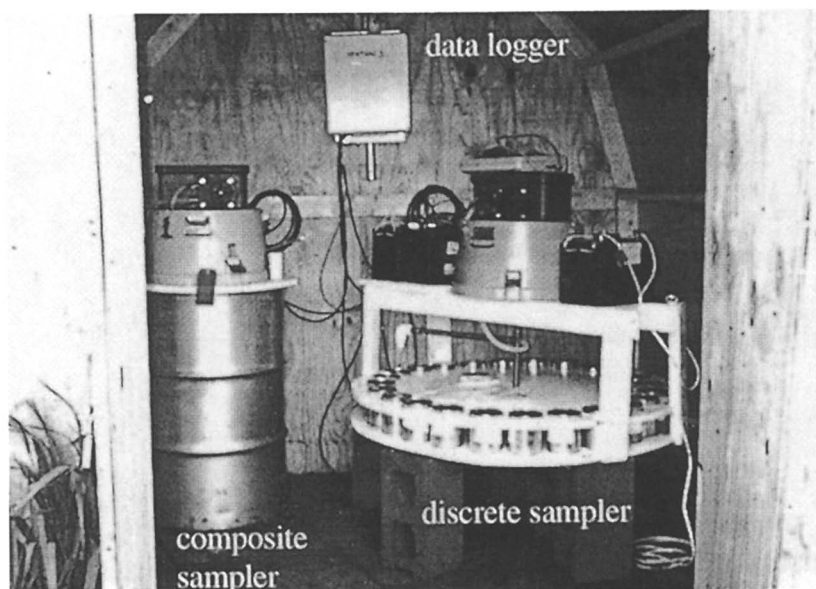
Figure 3. Primary flume sampling equipment comprised of Isco sampling pumps for both discrete and flow proportional composite sampling and a Campbell 21X data logger.

All watershed runoff with eroded sediment was forced through the sampling flumes. Concrete footings and block were used for each primary sampling flume to avoid possible washout from extremely large runoff events (Figure 4). The primary flumes were sized using predictions from the USDA model EPICWQ (5) for 1-in-10 year storm intensities for Southern Iowa.

A single secondary runoff station equipped to collect composite, flow-proportional samples from a relatively small drainage area within the watershed (identified as station 1) was located near the south shore of the pond (Figure 5). A Campbell Scientific 21X data logger was used at all sampling locations to control the sampling equipment and log water flow rates. The water level in each flume was monitored continuously using a Druck PDCR 950 submersible pressure transducer positioned in a stilling well connected to the flume.

Pond Overflow Monitoring

The pond was constructed with an overflow drainpipe. Flow-proportional samples from this overflow drain were collected into a stainless steel, 55-gallon

drum using equipment identical to that of the secondary flume station. Following the sample collection, the compositing barrel was emptied and prepared to receive additional samples.

Figure 4. Concrete block retaining walls and primary flume sampling stations for quantifying runoff hydrology, sediment yield, and chlorpyrifos transport.

Pond Water and Sediment Sampling

Pond water and sediment were sampled on both a predefined basis and defined time weighted intervals following any runoff event. Sample intervals were shorter immediately following a runoff event to properly capture chlorpyrifos dissipation patterns in pond matrices. The pond was sectioned into three zones for sampling purposes and samples from each zone were withdrawn on each sampling date (Figure 6). Water samples were obtained using a Sub-Surface Grab Sampler (Forestry Suppliers, Inc., Jackson, MS) with an aliquot collected just below the water surface, approximately half way to the pond bottom and near the pond bottom. The three aliquots were composited into glass or metal containers and were considered representative of a water sample from the entire water column for each specific section sampled.

Figure 5. Secondary flume sampling station. Nested meso-plots have similar sampling and electronic equipment (with smaller trapezoidal flumes).

Pond sediment samples were obtained using a Wildco 2410 sediment sampler with a 48 mm diameter cutting tip (Forestry Suppliers, Inc., Jackson, MS), which collects sediment cores into plastic sleeves. The sampler was forced into the pond floor to the maximum depth possible (~ 12 inches) by applying downward pressure. The core was then recovered from the sampler assembly and the plastic sleeve containing the sample was capped and maintained in a vertical position until frozen. Four sediment cores were generally collected from random locations within each of the three sampling zones to produce a total of 12 cores on each sampling day.

Instrumentation of Nested and Artificially Irrigated Meso-plots

Nested Meso-plots Within Watershed

Meso-plots of dimensions 41 ft x 170 ft (~ 0.16 acres) were nested within the main watershed and were instrumented immediately after the first

chlorpyrifos application was made. This allowed for the use of a commercial planter (John Deere 7200) without running the risk of interference by the scientific equipment necessary to quantitate runoff. A solid retaining wall was installed against the undisturbed soil with the upper edge approximately even with the soil surface. A metal gutter was then mounted to the retaining wall on a slight grade oriented perpendicular to the fall line of the plot. The gutter assembly attached directly to the inlet face of a large, 60° trapezoidal flume that was used to measure the flow from each meso-plot (Figure 7). Nested meso-plots were subjected to the same natural precipitation patterns as the watershed. Sprinkler irrigation was only added to those meso-plot experiments performed outside of the watershed.
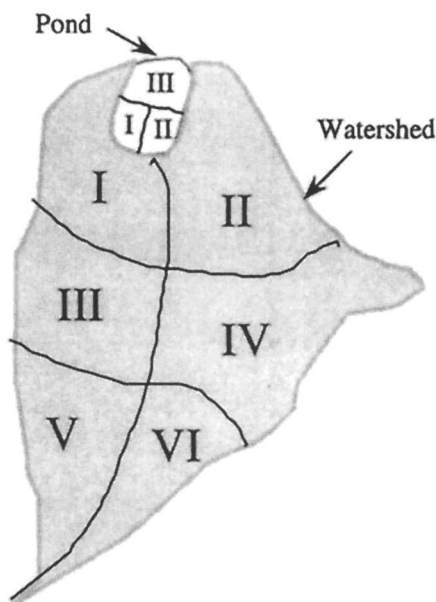
Figure 6. Schematic representation for pond and watershed sampling zones for pond water, pond sediment and surface soil transects.

Flow from the nested meso-plots was continuously monitored using calibrated Isco model 3230 bubble flow meters in conjunction with a 60° trapezoidal flume. Runoff water was sampled from behind the flume using Isco model 2700 or 3700 pump samplers. The flow-proportionally-sampled runoff (1-liter sample for each 3 ft^3 of runoff) was withdrawn through a Teflon-lined sampling tube (3/8" i.d.) and was delivered into stainless steel, 55-gallon

drums. Multiple aliquots for chlorpyrifos residue and sediment yield determination were withdrawn from the drum at the conclusion of each runoff event.
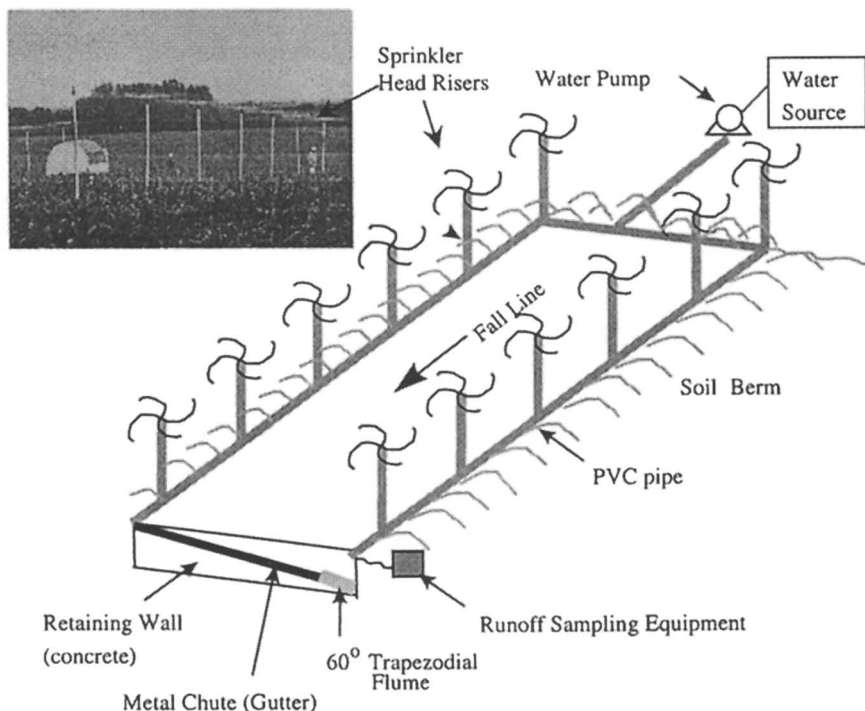
Figure 7. Schematic of Meso-plot and Drainage Area.

Meso-plots Outside Watershed Subjected to Artificial Precipitation

Four artificially irrigated meso-plots were located outside the watershed in 1992 and were identical in terms of size, construction, and sampling electronics to the nested meso-plots listed above with the exception of irrigation. Irrigation sprinkler heads were mounted on vertical risers to mimic typical raindrop energies upon impact with soil (Figure 7). Irrigated meso-plots 1 and 2 had discrete samplers, while irrigated meso-plots 3 and 4 consisted of both discrete and flow proportional composite sampling. Pre- and Post irrigation soil and vegetation samples (if appropriate) were taken for chlorpyrifos residue analysis

and Time Domain Reflectrometry was used to measure water infiltration rates into the soil.

The intensity of the synthetic storm was approximately 1.1 in/hr for two hours (i.e., an event having a 1-in-5 year return frequency for this section of Iowa). In addition, each plot was prewetted the day before an application was to be made to bring the surface soil moisture up to near field capacity. Lorsban* 15G insecticide T-band and Lorsban 4E insecticide broadcast-incorporated experiments were performed at corn planting at maximum labeled rates. Lorsban 15G banded over the corn whorl and Lorsban 4E surface broadcast experiments (with corn present) were also performed approximately 40 days after planting.

Application rates

The watershed was treated with chlorpyrifos at typical use rates (1992) and maximum labeled rates (1993). Chlorpyrifos applications for the watershed are given in Table II. Application rates for the external meso-plots are given in Table III.

Residue Analysis

Field samples were analyzed by Dow AgroSciences at the Midland Michigan, or Indianapolis, Indiana locations. Analyses were performed using gas chromatography (GC) with electron capture detection (ECD), flame photometric detection (FPD), or Mass Spectroscopy (MS). Limit of detection (LOD) and limit of quantitation (LOQ) are given in Table IV.

Soil Sampling Methodology

The surface soil was sampled and analyzed for chlorpyrifos at select time intervals throughout the study. The watershed was divided into six (1992) or four (1993) equal area subregions within the watershed (see Figure 6). Soil samples taken from each subregion were analyzed for chlorpyrifos residues. Variability in chlorpyrifos soil dissipation was characterized by keeping each subregion sample unique (i.e., no compositing).

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Table II. Application rates and dates for chlorpyrifos applications made to the watershed

Corn Stage	Method	Date	Formulation	Rate applied to watershed $[\frac{lb\,AI}{acre}]$
At Planting	T-Band	5/12/92 (Julian day 133)	Lorsban 15G	1.30
Mid-Late Whorl	Banded over whorls	6/9/92 (Julian day 161)	Lorsban 15G	1.35
Canopy near closure	Aerial Broadcast	7/14/92 (Julian day 196)	Lorsban 15G	0.94
At Planting	T-Band	5/19/93 (Julian day 139)	Lorsban 15G	2.12
Mid-Late Whorl	Foliar/ Surface Broadcast	6/29/93 (Julian day 180)	Lorsban 4E	1.01

Following the T-band application, either a 4"x4"x38" (1992) or 4"x4"x12" (1993) transect of surface soil (centered and placed perpendicular to the row) was taken for analytical determination of chlorpyrifos residues. The length of the transect was decreased in 1993 to avoid problems associated with working with such a large soil sample. The transect depth was 1" following all non T-band applications. Chlorpyrifos residue analysis of surface soil provides information about the mass of pesticide available prior to a precipitation/runoff event.

Deep soil core samples to thirty-six inches from the soil surface were taken and analyzed for chlorpyrifos residues at specific sampling intervals even though the physicochemical properties of chlorpyrifos indicate the molecule was relatively immobile in soil. Residue analysis of subsurface soil samples provided mass balance closure for chlorpyrifos fate. An acetate lined hydraulic sampler was used to obtain soil samples up to 36" in depth in a corner of the watershed from a randomized grid pattern. The first 0-4" of soil was removed by placing a metal sleeve directly into the soil and manually removing this soil layer. Once removed, the hydraulic probe was placed inside the metal sleeve and the remainder of the soil core to 36" (i.e., 4"-36") was taken.

Table III. Application rates for sprinkler irrigated meso-plots located outside the watershed boundaries (1992).

Plot	Formula-tion	Rate	Application Method	Planting Date	Treatment Date	Runoff Date
1	Lorsban 15G	2.07 lb AI acre	T-Band	May 16	May 16	May 17
2	Lorsban 4E	3 lb AI acre	Broadcast / Incorporate into soil	May 18	May 18	May 19
3	Lorsban 4E	1.5 lb AI acre	Broadcast over corn	May 15	June 25	June 26
4	Lorsban 15G	1.04 lb AI acre	Band over top of corn	May 12	June 24	June 25

Table IV. Level of Detection and Level of Quantification for chlorpyrifos in multiple environmental matrices.

Matrix	LOQ	LOD
Runoff Water	1.10 ng/mL	0.33 ng/mL
Runoff Sediment	0.040 µg/g	0.012 µg/g
Pond Water	62.9 pg/mL	18.9 pg/mL
Pond Sediment	1.18 ng/g	0.35 ng/g
Bulk soil Transects	0.011 µg/g	0.003 µg/g
Soil cores	0.012 µg/g	0.004 µg/g
Corn	0.016 µg/g	0.005 µg/g

CONCLUSIONS

A comprehensive nested field study has been designed and implemented to address many of the limitations found in current USEPA FIFRA Subdivision N guidelines. Hydrology, erosion, pesticide runoff, drift, degradation, and

leaching are measured.   Information on crop growth, heterogeneous soil properties,   and meteorological conditions are quantified.   Meso-plot experiments were designed and implemented to address length scale issues when extrapolating results to the watershed scale. The study design includes attributes to address mass balance closure and scaling effects, all while being performed under Good Laboratory Practices. Results from this study provide a comprehensive data set useful for site-specific model validation and subsequent extrapolation to predict pesticide behavior for other diverse watershed systems. Field observation results are found elsewhere (1).

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Chapter 5

An Integrated Approach for Quantifying Pesticide Dissipation under Diverse Conditions II: Field Study Observations

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An extensive multi-year runoff study was performed to quantify chlorpyrifos dissipation, leaching, and edge-of-field transport in a commercial corn production watershed. All runoff leaving the 17.29-acre watershed was quantified before entering a 0.6-acre farm. In addition, small scale runoff meso-plots (~0.16 acres) were both nested within the watershed and nearby to address scaling issues in extrapolating meso-plot results to watershed predictions. During 1992, the total chemical edge-of-field transport as quantified by flumes and pond monitoring corresponded to approximately 0.24 % of the seasonal chlorpyrifos applied. Chlorpyrifos edge-of-field transport during 1993, a year of intense precipitation and flooding, was approximately 0.38 % of applied. Even under the extreme precipitation conditions, limited amounts of chlorpyrifos were transported off-site.

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Introduction

Details of an extensive field study design to quantify edge-of-field runoff has been documented elsewhere (1). All runoff leaving a 17.29-acre watershed was channeled through sampling flumes for quantification and directed into a neighboring farm pond. Observations of hydrology, erosion, chlorpyrifos transport, and dissipation in soil, pond water, pond sediment, and corn from this multi-year runoff study are presented. Data generated from this study is an ideal candidate for use in model validation procedures. Additional information regarding site-specific model validation and regional extrapolation of results can be found in the follow-up documentation for this work (2-3).

Observations

In 1992, no significant amount of precipitation occurred until late in the growing season around the time of the third application (Figure 1). Runoff from the relatively small events on days 184 and 187 were not properly sampled by the field equipment due to the position of the Teflon sampling tubes in the flume and the resulting cavitation. This problem was corrected for all later runoff events by installing a mixing chamber below the outflow of the flume from which samples were withdrawn. However, since the pond water and sediment were intensively sampled, the mass of chlorpyrifos leaving the field during these runoff events was estimated by differences in pond matrix concentrations.
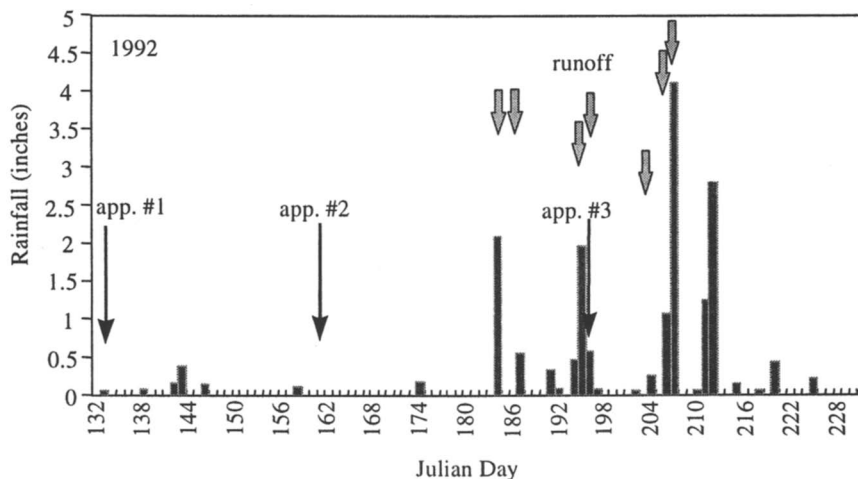
Figure 1. Precipitation and runoff events during the 1992 growing season.

Excessive precipitation during the 1993 growing season produced severe flooding in a nine-State area in the upper Mississippi River basin (4). Total rainfall in 1993 from planting (Day 139) up to the day before the second application (Day 179) was 7.69 inches. Precipitation within 12 days following the Lorsban* 4E insecticide application (Day 180-192) was 8.38 inches, with 5.46 inches falling on days 185-186. The rainfall received by the watershed for the runoff events on days 184-207 totaled 9.05 inches, or 681,603 ft^3. A large runoff event occurred on day 186, but the pond had inundated the sampling flumes at that time, and the flow-measuring portion of the study was terminated. Chlorpyrifos loadings from the Julian day 186 runoff event were estimated from residue measurements of the receiving pond.
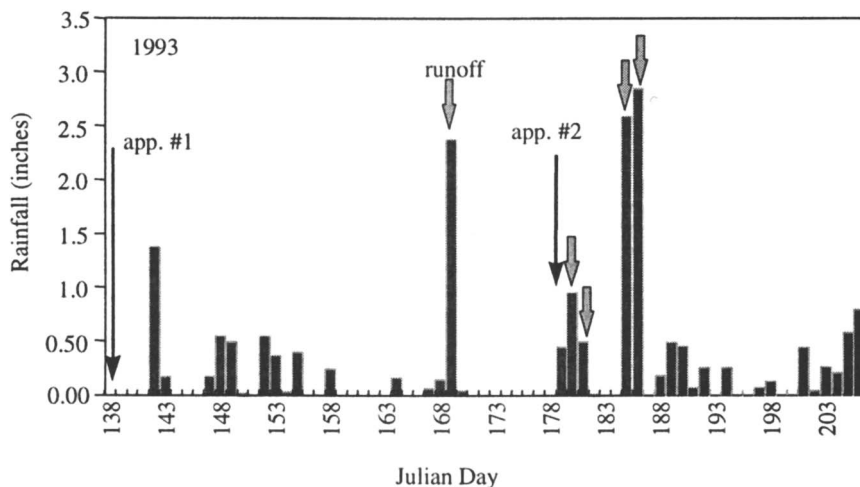
Figure 2. Precipitation and runoff events during the 1993 growing season.

Water and Eroded Sediment Transport

Near drought conditions early in 1992 were followed by massive precipitation amounts having almost a 100-year return frequency between day 184-207 during 1992. Based upon a 500-year weather simulation using the weather generator program CLIGEN (CLImate GENerator (5)) for Grinnell, Iowa, 9.05 inches between Days 184-207 would occur 1-in-71 years. A total of

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6 distinct periods of runoff into the pond were quantified in 1992, either by runoff sampling in the flume and/or by mass difference pre/post a runoff event between pond water and pond sediment[1]. Total runoff leaving the watershed through the flumes during the 1992 study interval measured 130,505 ft^3, or 19.2 % of the total rainfall.

The 1993 year had the largest monthly precipitation amounts in June and July ever recorded in the 121 years of records, with 16.55 inches falling at the study site from day 139 through day 199. Heavy rainfall between day 179 and 186 (7.38 inches) produced 4 discrete runoff events. Precipitation that occurred between Julian days 179-186 corresponds to a 1-in-500 to 1-in-833 year return frequency as determined by climatic modeling using the program CLIGEN. During the shorter monitoring interval in 1993, the quantified runoff from the watershed measured 131,152 ft^3, or 22.5 % of the total rainfall.

Chemical Transport

Chlorpyrifos transport ranged from 91 mg for small events to 37.5 g for the most significant runoff events captured late in 1993. Most of the chlorpyrifos was transported sorbed to the eroded sediment with values ranging from 63 to 99.5% for distinct runoff events. This distribution between soluble and sediment-bound pesticide is largely described by the soil/water partition coefficient (K_d) for the compound. Although a K_d determination (e.g. lab study) for the soil under study was not made, K_d values ranging from 16 to 397 mL/g have been reported for chlorpyrifos in silt loam soil (6). The tendency for significant binding to soil by chlorpyrifos described by the K_d values corroborate the strong binding to the eroded sediment observed in this experiment.

Water, sediment and chlorpyrifos yields in the aqueous and sediment phases of runoff, for both 1992 and 1993, are presented in Table I for quantified runoff events characterized in the main watershed during the study period. Not all stations logged runoff for a given runoff event. Transport measurements in Table I-II are derived from the composite sampling of the runoff events.

A representative example of a time-dependent "chemograph" for watershed runoff events is given in Figure 3. Time-dependent hydrology (water and sediment yield), along with chlorpyrifos transport are represented in this figure. Several storms produced chemographs consisting of multiple peak flow rates

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[1] Estimation of chlorpyrifos mass in runoff using pond matrix samples was performed when equipment failure and/or sampling flumes became inundated by the pond water.

within a 24-hr interval. This observation indicates numerical modeling based upon daily time steps can not capture the natural stochastic nature of unique storms that were observed in this study.

Table I. Watershed Runoff Events (Hydrology, Erosion, Pesticide - 1992)

Station	Julian Sample Date-Year	Runoff volume [cm^3]	Chlorp. transport in water phase [mg]	Chlorp. transport in eroded sediment [mg]	Total chlorp. transported (mg)	Eroded sediment %	Sed. Yield (kg)
Pond	184				5560		
1	195	1.56E+07	13.0	60.0	73	82%	67
2	195	1.63E+08	184	1010	1190	85%	1192
3	195	1.40E+08	133	308	440	70%	284
	Totals	3.19E+08	330	1379	1703	81%	1543
1	196	6.26E+06	11.0	33.0	44.0	76%	42
3	196	1.56E+07	18.2	29.0	47.0	62%	30
	Totals	2.19E+07	29.2	62.0	91.0	69%	73
2	206	3.19E+08	1236	4763	5999	80%	2442
3	206	4.35E+08	1668	4314	5982	73%	1438
	Totals	7.54E+08	2904	9076	1.20E+04	76%	3880
1	207	1.25E+08	195	451	646	71%	490
2	207	8.05E+08	1877	5418	7295	75%	3079
3	207	1.49E+09	4001	3988	7989	51%	2573
	Totals	2.42E+09	6073	9858	1.59E+04	63%	6142
Pond	212				1520		

Chlorpyrifos Soil Dissipation

Variability in soil concentrations associated with residue values using a granular formulation such as Lorsban 15G could not be avoided due to homogenization procedures during the sample preparation. It was assumed that chlorpyrifos from all applications degrades at the same rate once in soil to aid in fitting the superposition 1st order kinetic expressions to field observations. The chlorpyrifos soil dissipation half-life was estimated at 21 and 12 days for 1992 and 1993, respectively. Note that the degradation soil rate constant is a "pseudo" dissipation rate for the granular formulation that includes both the release rate of chlorpyrifos from the granule and the dissipation rate of chlorpyrifos once on the soil (7). Superposition of kinetic

Table II. Watershed Runoff Events (Hydrology, Erosion, Pesticide - 1993)

Station	Julian Sample Date	Runoff volume [cm^3]	Chlorp. transport in water phase [mg]	Chlorp. transport in eroded sediment [mg]	Total chlorp. transported (mg)	Eroded sediment %	Sed. Yield (kg)
1	169	2.91E+07	37.7	654.9	693	94.6	471
2	169	4.07E+08	426	10026	10452	95.9	12691
3	169	2.53E+08	328	5384	5712	94.3	3818
Totals		6.89E+08	7.92E+02	1.61E+04	1.69E+04	95.3	1.70E+04
1	180	1.20E+07	124.6	715.9	841	85.2	137
2	180	6.80E+07	2046	10834	12880	84.1	1414
3	180	1.06E+08	1097	14628	15725	93.0	1068
Totals		1.86E+08	3.27E+03	2.62E+04	2.94E+04	88.9	2.62E+03
2	181	1.18E+07	46.3	9551	9597	99.5	4208
Totals		1.18E+07	4.63E+01	9.55E+03	9.60E+03	99.5	4.21E+03
1	185	1.72E+07	1.2	112	113	98.9	88
2	185	4.05E+08	393	31419	31812	98.8	9880
3	185	1.18E+09	82.8	5466	5549	98.5	4304
Totals		1.60E+09	4.77E+02	3.70E+04	3.75E+04	98.7	1.43E+04
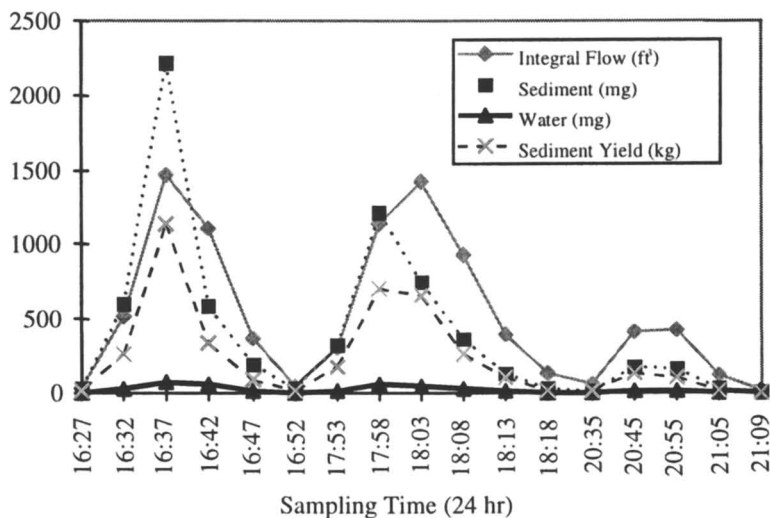
Figure 3. Chemograph for Station 3, Runoff event 1 (Julian Day 169) which occurred in 1993.

solutions for multiple applications provided an adequate fit to field observations (Figure 4).

Chlorpyrifos Soil Leaching

Soil cores to 36 inches were taken during the study interval to deduce the potential leaching behavior for chlorpyrifos. Cores were sectioned into 4-10", 10-16", 16-24" and 24-36" increments and each increment was analyzed for chlorpyrifos. No chlorpyrifos was found below 10 inches or beyond the first soil core section. This information is consistent with other studies which have demonstrated that chlorpyrifos does not leach (6). Thus, leaching was not a significant mode of dissipation for chlorpyrifos for this field study.
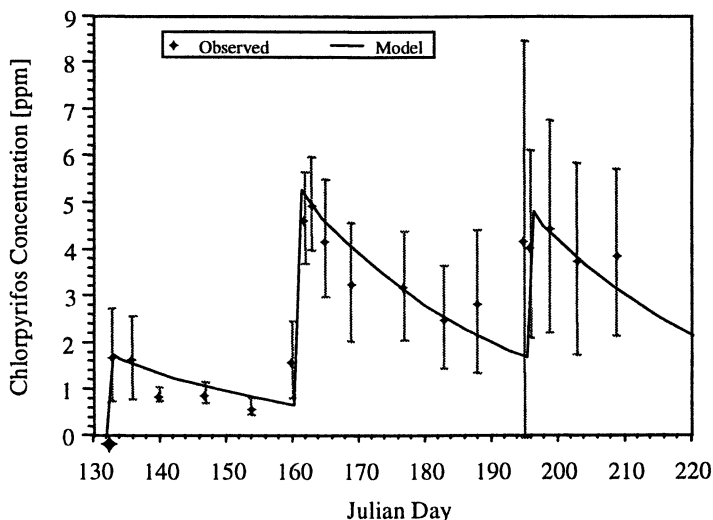
Figure 4. Chlorpyrifos dissipation patterns in surface soil transects taken from the watershed

Chlorpyrifos Corn Dissipation (1992-1993)

The dissipation pattern for chlorpyrifos residues (following the second Lorsban 15G insecticide application when corn was growing) was determined assuming a first order kinetic expression could capture the field behavior. A calculated foliage dissipation "pseudo" half-life of 17.7 days was observed.

This calculated half-life for Lorsban 15G granules was not for chlorpyrifos dissipation only, but rather for the combination of chlorpyrifos release from the formulated material and subsequent dissipation on foliage once released since only granulated material was used. For 1993, the calculated 1st order dissipation half-life for chlorpyrifos (Lorsban 4E) was 1.23 days. Differences between the dissipation rates between Lorsban 15G (1992) and Lorsban 4E (1993) on corn surfaces indicates the relative release rate of chlorpyrifos from the Lorsban 15G granules since the Lorsban 4E insecticide is an emulsifiable formulation.

Pond Residues

Runoff events from the watershed provide the chlorpyrifos loadings into the neighboring pond. Figure 5 represents observations for the chlorpyrifos concentrations in pond water. Large peaks in pond water concentrations correlate to large runoff events in the watershed. During 1992, chlorpyrifos runoff on day 184 was not quantified by runoff sampling due to sampling equipment failure. However, chlorpyrifos concentrations in pond water samples taken at that time (averaging 1103 ng/L, ppt) reveal that approximately 5.56 g of chlorpyrifos were present in the water column of the pond (day 184) following this runoff event. The other runoff event not quantified by the sampling flumes (day 187) in 1992 indicates no appreciable increase in chlorpyrifos mass within the pond occurred (based upon increases in water residues).
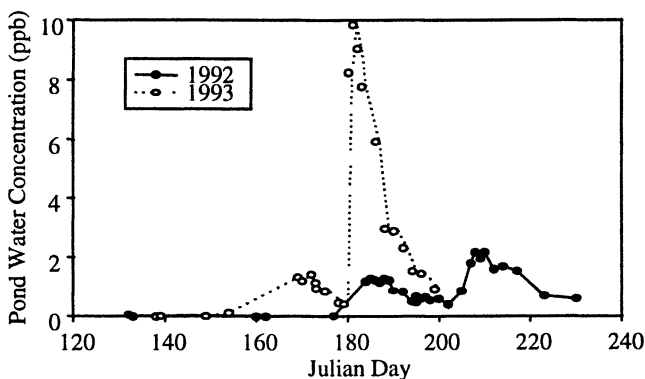
Figure 5. Average chlorpyrifos pond concentrations resulting from edge-of-field runoff loadings.

The most significant runoff activity in 1992 occurred on days 206-207. On these days a total of four distinct runoff events were quantified in terms of runoff water and these events were combined into two larger "daily" events based on when the flow-proportional samples were collected. The runoff results indicate that a total of 8.98 g of chlorpyrifos were dissolved in the runoff water from these events. The aqueous chlorpyrifos concentration in the pond increased from 783 ppt on day 205 to 2013 ppt on day 208, following the runoff activity. Total aqueous chlorpyrifos in the pond increased from 3.83 g to 15.95 g, suggesting that 12.1 g was added as runoff during the period. Once again, the calculated mass input to the pond based on pond water concentrations (12.1 g) showed good agreement to the input measured through the flumes as aqueous runoff (8.98 g) for the period. Runoff monitoring was terminated on day 208 during 1992. However, heavy rainfall on day 211 and 212, totaling 4.03 inches, did produce significant runoff on day 212, as indicated by a change in pond volume of 89,019 ft^3 between days 210 and 214. This runoff event increased chlorpyrifos mass within the pond from 10.65 to 12.17 g indicating that approximately 1.52 g chlorpyrifos were transported in the aqueous phase of runoff. First order kinetic degradation modeling for chlorpyrifos dissipation in pond water indicate a chlorpyrifos degradation half-life of 5.1 and 6.7 days for 1992 and 1993, respectively.

Chlorpyrifos residues found in the top two inches of pond sediment ranged from < 1.18 ng/g (LOQ = 1.18 ng/g) to a maximum of 1572 ng/g (1.572 ppm) during 1992, with the largest sediment concentration observed from pond zone II on Julian Day 207. For 1993, sediment residue concentrations ranged from 16 ng/g to a maximum of 2625 ng/g (2.625 ppm) from zone II on Julian Day 179. The highest area-weighted mean concentration from the three sampling zones in 1992 was 0.3697 ppm on Julian day 207. For 1993, the highest area weighted average concentration was 0.831 ppm occurring on Julian day 200. Average sediment concentrations for 1992-1993 are given in Figure 6.

Pond Inflow and Outflow

Chlorpyrifos residues were not found in tile drain samples entering the pond. No chlorpyrifos in tile drain water was expected given the high K_d of chlorpyrifos in silt loam soil. In addition, no chlorpyrifos was found in the soil horizon below 10 inches. This suggests that leaching of the test material to the subsurface tile drain in the field did not occur. Chlorpyrifos transport through the pond outflow drain (station 4) indicated a total of 8.68 g of chlorpyrifos passed through the pond outlet drain during 1992, and 36.3 g in 1993.
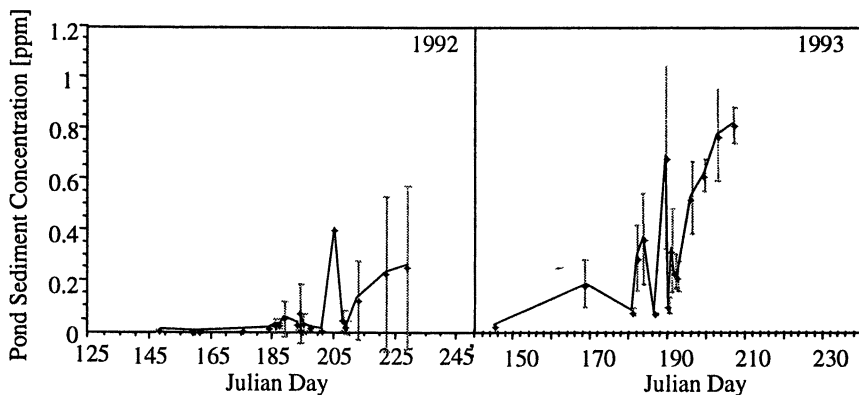
Figure 6. Average pond sediment concentrations of chlorpyrifos where the average pond sediment concentration is the weighted average between Sections I, II, and III of the pond.

Transport from Meso-plots Nested in the Watershed

In 1992, an electrical storm during the runoff event on day 184 damaged a flow meter on one of the plots that resulted in lost flow data. Also, one of the small plots [Station 8] flooded during runoff events in days 194-196 and 206-207. As a result, direct comparison of the runoff yields between the two meso-plots and a measure of transport scaling to the large watershed was difficult for 1992 observations. The transport values obtained from the nested meso-plots are presented in Table III. These data are limited to 1992 runoff events on days 185 and 187 for station 8 and days 196 and 208 for station 9. Sometime during Julian day 196, the sampling flume for Station 8 became flooded and thus the results on this day are unreliable. As reported in Table III, runoff volumes ranging from 15 to 979 ft³ were recorded with total chlorpyrifos transport ranging from 0.02 to 0.22 g. Transport between 15[2] - 98 % was determined to take place as sediment-bound material (mean = 52 %). Excluding the 15% value, the range and mean percent of chlorpyrifos transported in sediment bound material for the nested meso-plots was 50 - 98 % and 77 %, respectfully.

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[2] There was not enough sediment mass for analysis with this composite sample, and thus a value was approximated using a value of K_d characteristic of chlorpyrifos and the water concentration.

These values were similar to that observed for the watershed flumes in 1992 (63 to 81%, mean of 72.3 %).

In 1993, the meso-plot sampling equipment performed well at capturing natural precipitation induced runoff events. The transport results obtained from the nested meso-plots are also presented in Table III. A total of 3 runoff events were quantified between Julian Days 169 - 185. Runoff volumes ranging from 155 to 1100 ft^3 were recorded, with total chlorpyrifos transport ranging from 0.33 to 1.23 g. The majority of the chlorpyrifos transport was determined to take place as sediment-bound material, with a range between 63.9 - 80.5%.

Table III. Watershed Hydrology, Erosion, and Chlorpyrifos Runoff Events For Nested Meso-plots (1992-1993). Shaded cells represent flooded flumes and therefore results are not reliable.

Station	Julian Sample Date/Year	Runoff volume [cm^3]	Chlorp. transport in water phase [mg]	Chlorp. transport in eroded sediment [mg]	Total chlorp. transport (mg)	eroded sediment %	Sed. Yield (kg)
8	185 / 1992	3.85E+06	32	141	173	82%	30
8	187 / 1992	4.25E+05	3	105	108	98%	35
8	196 / 1992	2.64E+07	66	13	79	16%	21
8	208 / 1992	1.73E+08	1491	385	1880	21%	218
9	196 / 1992	9.03E+06	19	3	22	14%	6
9	208 / 1992	2.77E+07	114	109	223	49%	47
8	169 / 1993	2.21E+08	716	1594	2310	69%	561
8	180 / 1993	4.39E+06	218	388	606	64%	29
8	185 / 1993	3.12E+07	121	214	335	64%	77
9	169 / 1993	1.28E+07	41.7	172	213	81%	100
9	180 / 1993	6.26E+06	385	847	1232	69%	43
9	185 / 1993	3.06E+07	91.1	284	375	76%	148

The average percent of chlorpyrifos transported in sediment bound material was 65.7 and 75.0% for stations 8 and 9 (nested meso-plots), respectively. This distribution between aqueous and sediment-bound transport was lower then the range of 84.1 - 99.5 % (average = 95.6%) observed for the watershed flumes in 1993. This suggests a different distance length scale is appropriate to describe the erosion processes occurring within the meso-plot experiments as compared to the overall watershed (3).

Chemical Transport from Irrigated Meso-plots Outside the Watershed

Four 0.16 acre meso-plots were located within the same commercial corn field as the main watershed, but were part of a different drainage basin. Figure 7 represents Plot #1 where a Lorsban 15G application was made at planting. This figure illustrates the length scale for the plots was adequate to capture both overland, rill and inter-rill erosion. The irrigation source was the municipal water supply transported by tanker truck as no irrigation waters in the form of a pond or stream were nearby. Details are found in Table IV. A mean of 2.03 ± 0.42 inches was applied to each plot over approximately 120 minutes.
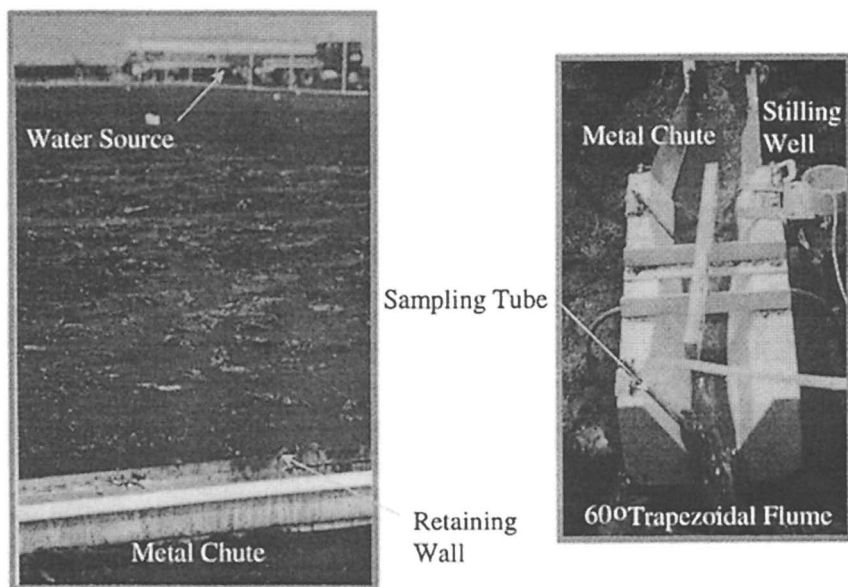
Figure 7. Meso-plot 1 illustrating irrigation and runoff setup, water source, and scale for bare soil experiments.

Table IV indicates that chlorpyrifos transport from the freshly tilled and disked bare soil meso-plots yielded the highest chlorpyrifos transport. Plots 1 and 2 yielded similar hydrology (i.e., 350 vs. 347 ft^3 of runoff) and chlorpyrifos transport (4395 vs. 4398 mg chlorpyrifos total). The sediment yield for plot 1 was lower than for plot 2 (382 vs. 901 kg). Plot 2 had the same tillage as plot 1, but was further perturbed due to the disking in of the Lorsban 4E insecticide. Therefore, differences were anticipated as the soil bulk density changes. Both plots 1 and 2 yielded similar chlorpyrifos transport within the sediment phase of runoff, (4378 vs. 4209 mg), but plot 1 had lower movement of chlorpyrifos

in the runoff water (17.3 vs. 189 mg). The overall chemical transport (4395 vs. 4398 mg) between these two plots was largely attributed to the large fraction of chlorpyrifos being transported in the sediment mass (99.6 and 95.7% for Plots 1 and 2, respectively). Soil incorporated Lorsban 4E and T-Banded Lorsban 15G insecticide have similar runoff potential for intense precipitation events, even though the formulations differ drastically (granule vs. emulsifiable). Total chlorpyrifos observed to leave the plot in surface runoff water and eroded sediment corresponded to 2.93 and 2.02% of the theoretical applied for Plots 1 and 2, respectively.

Table IV. Observations For Artificially Irrigated Meso-Plots Outside The Watershed Boundary.

Small-Plot #	Irrigation rate (in/hr)	Irrigation duration (hr)	Water Yield (cm³)	Chlorp. Water phase transport (mg)	Chlorp. sediment transport (mg)	Sediment Yield (kg)
1	0.95	2.00	9.90E+06	17.6± 0.068	4378	382
2	1.11	1.62	9.83E+06	193 ± 9.87	4209	900.6
3	1.00	1.83	8.63E+06	234 ± 15.8	513.8	62.3
4	1.33	2.00	6.26E+06	20.0 ± 0.128	335.2	223.1

Plots 3-4 had a stand of corn growing when the Lorsban applications were made. Vegetation should intercept the precipitation and subsequently reduce the kinetic energy of the rain droplets impacting the soil surface. Soil erosion should therefore be less than that observed for the bare soil experimental plots. The sediment yields for Plots 3-4 were 62.3 and 223 kg respectively. Plot 3 had a less intense storm than did Plot 4 [110-minute at 1.00 inch/hr vs. 120 minutes at 1.33 inch/hr]. As a result, the hydrology was different between these two plots. Plot 3 had an edge-of-plot flow of 305 ft³, vs. Plot 4's value of 221 ft³, even though plot 3 had a less intense storm. Plot 3 had a larger water yield but a smaller sediment yield than plot 4. This discrepancy between plots 3-4, which were performed 1-day apart, can possibly be attributed to normal field scale heterogeneity and/or perturbations to the meso-plot system due to the different application equipment being utilized. The latter seems unlikely due to similar antecedent soil moisture content and bulk density values immediately prior to the simulated precipitation. However, predicted curve numbers for Plots 3 and 4 differed widely with values of 81.7 and 63.9, respectively. In terms of chemical transport, Plot 3 yielded 744 mg of chlorpyrifos (0.68 % of applied), while Plot 4 yielded 355 mg (0.47 % of applied).

Conclusions

This multi-year comprehensive runoff study performed near Oskaloosa, Iowa provides a detailed data set for hydrology, erosion, and chlorpyrifos pesticide transport from field edge from a typical commercial corn production watershed. Hydrology, erosion, and chlorpyrifos transport were quantified by the use of sampling flumes, runoff samples, and chlorpyrifos analysis in water and eroded sediment making this data set an excellent choice for model validation exercises. Quantified runoff from the watershed provided the chlorpyrifos source terms for the neighboring farm pond at the field edge and chlorpyrifos dissipation patterns within the pond were quantified

During 1992 and 1993, significant runoff events occurred later in the growing season and results demonstrate the resolution with which runoff transport can be quantified. Chlorpyrifos runoff of less than 0.1 g were quantified by sampling and confirmed by monitoring residue levels in the pond. The percent of chlorpyrifos transport from the watershed into the pond on a per-storm basis ranged from 0.091 g to 37 g via the sampling flumes. A total of 28,118 g chlorpyrifos was applied to the 17.29-acre watershed as three applications of Lorsban 15G (T-Band, banded over the corn whorl, and broadcast) in 1992. Of this total applied to the watershed, 68.6 g was quantified as leaving the site in edge-of-field runoff through day 207 as measured by the three sampling flumes around the pond and pond residue monitoring (approximately 0.24 % of the total chlorpyrifos applied). Total chemical transport in 1993 measured from planting (Day 139) through Julian Day 185 (as quantified by flumes and sampling) was 93 g, corresponding to approximately 0.38 % of the seasonal chlorpyrifos application to the watershed of 24,579 g. Even under extreme precipitation conditions, limited amounts of chlorpyrifos were transported off of the field.

In 1992, four irrigated meso-plots (~0.16 acre) were planted with corn, treated with a single application of Lorsban 15G or 4E insecticide at the maximum labeled rate, and subsequently irrigated 1-day after application to simulate a natural precipitation event having a return frequency of 1-in-5 years for Southeast Iowa. The Lorsban 15G T-band and Lorsban 4E broadcast-incorporation applications yielded chlorpyrifos edge-of-field transport of 2.93 and 2.02 % of applied, respectively. Chlorpyrifos transported as eroded sediment ranged between 95.7 - 99.6 % of total edge-of-field transport. The two meso-plot experiments performed later in the growing season when a crop was present yielded edge-of-field transport of chlorpyrifos of 0.68% and 0.47 % of theoretical applied for Lorsban 4E broadcast and Lorsban 15G banded over the corn whorl, respectively.

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Chapter 6

An Integrated Approach for Quantifying Pesticide Dissipation under Diverse Conditions III: Site Specific Model Validation Using GLEAMS, EPICWQ, and EXAMS

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The USDA models EPICWQ and GLEAMS, and the USEPA model EXAMS II were used to predict edge-of-field and pond environmental concentrations of chlorpyrifos for an immense field study performed in Iowa. Comparison between field observation and uncalibrated modeling results showed tremendous variability between storms of different intensities and timings, with chlorpyrifos transport in the water phase overpredicted from 278-1133%, and transport in the sediment phase from 39.5-305%. However, when GLEAMS runoff predictions are used as loadings for an aquatic dissipation model (EXAMS II), estimated environmental concentrations in pond water and sediment followed the same trends and magnitudes as the observed field concentrations.

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INTRODUCTION

Figure 1 illustrates the dilemma associated with environmental predictions on a regional basis when only limited laboratory and/or field information is available. All experimental data should be distributed into a usable form for field and regional extrapolation. Laboratory soil column leaching studies, soil metabolism, equilibrium soil/water partitioning (K_d), formulation atomization trials, foliar dissipation, etc. can all be used for field study protocol development to address appropriate environmental matrix sampling schemes. Knowledge of agronomic practices coupled with pesticide properties measured in the lab can yield insight into plant wash-off, mass transfer from soil to runoff water, and the coupling of soil conditions such as moisture and temperature to the degradation of the pesticide. Ideally, variability associated with pesticide properties measured in the lab such as K_d, or the degradation half-life in a variety of matrices should be propagated in any assessment to address the likelihood of occurrence or the chance of being wrong with an assumption.

One way for extrapolation of laboratory results to field and regional conditions is through the use of numerical models. Numerical modeling provides a mechanism for extrapolation under a diverse set of conditions. One can often trace what physical descriptor(s) within a model are breaking down if validation against field observations is poor. There are a variety of environmental models to choose from for predicting the fate of pesticides. However, many models are based upon similar mathematical algorithms to describe physical phenomena. Often, government regulated industries such as agrochemical companies are required to use a specific model for pesticide exposure predictions. Thus, any model used for regulatory purposes should be capable of similar order of magnitude predictions as those observed in the field.

The USDA models GLEAMS (Groundwater Loading Effects of Agricultural Management Systems (1)), EPICWQ (Erosion-Productivity Impact Calculator-Water Quality (2)), and USEPA model EXAMS II (Exposure Analysis Modelin System (3)) are chosen to investigate the capabilities to accurately predict field observations of chlorpyrifos runoff and pond fate behavior. Both GLEAMS and EPICWQ are field-scale models used to predict daily runoff and leaching behavior of agricultural chemicals. Both have the ability to investigate managemnt practices. EXAMS II is an aquatic dissipation model for describing the fate of organic contaminants within surface bodies of water. GLEAMS was used to predict edge-of-field transport observations for both observation years (1992-1993), while EPICWQ was used for the 1993 season only. Edge-of-field runoff predictions of GLEAMS are used as loadings to the EXAMS model which was set up to simulate the dissipation of chlorpyrifos in the 0.6 acre pond found at the Oskaloosa, Iowa test site. Runoff

loadings in the water and sediment phase are placed directly into the pond water column and benthic sediment, respectively. The 2-compartment EXAMS II simulation (water column and benthic sediment) assumes an instantaneous completely mixed system when a loading is received.
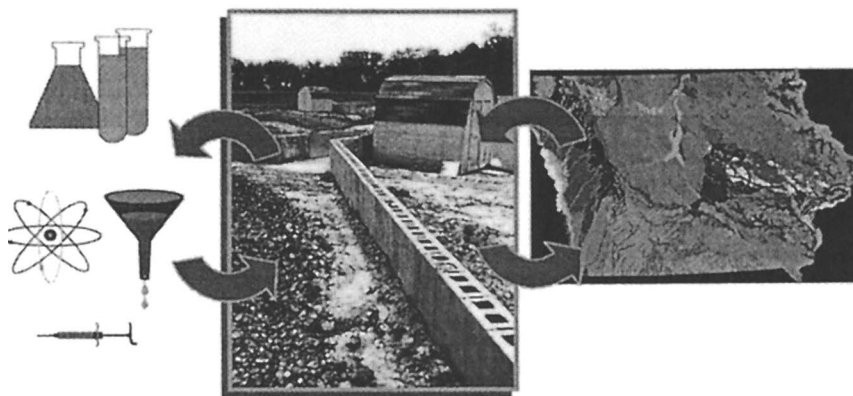
Figure 1. Dilemma in extrapolating finite laboratory and field observations to regional predictions having a semi-infinite parameter space.

Comparison between predicted water quality in the pond with field observations (4) are made. These types of comparisons give insight into the ability of these models to predict real-world observations (i.e., validation) without "calibration" or "curve-fitting" to field observations. Confidence is gained in model extrapolation once a model has been shown to adequately predict field observations for a specific parameter combination without intense calibration efforts. However, since the use of models is made without any validation, it is anticipated that comparison of predicted daily runoff events to field observations will be highly variable due to the stochastic nature of both precipitation patterns and the resulting physical mechanisms responsible for pesticide entrained in runoff.

Any representation of environmental behavior is an approximation with inherent error. Errors arise from attempting to describe the natural world through mathematical algorithms. This error can be attributed to the approximations/assumptions used to mathematically describe a physical process or parametric error associated with the proper choice of input parameters used in these mathematical expressions. Parametric error is being addressed by the American Crop Protection Association FIFRA Model Validation Task Force (5) and can often by quantified through stochastic techniques such as Monte Carlo, Latin Hypercube sampling methods, stochastic response surfaces, the Deterministic Equivalent Modeling Method, etc.

NUMERICAL MODELING

The work of Cryer and Laskowski (6) was used to estimate the chlorpyrifos release rate from the Lorsban* 15G insecticide granules into the surrounding soil since neither GLEAMS nor EPICWQ simulate granular or slow release pesticide formulations. The amount released into the soil is a function of the management practice and the daily climatic conditions. Chlorpyrifos must first be released from the granules before becoming available for runoff and degradation. The daily chlorpyrifos "bleed" rates from the granules are utilized by GLEAMS/EPICWQ as application rates such that the model source code did not require modification. It was assumed that the number of granules within the surface extraction zone (0-10mm) was 50 percent of applied. This is based on the work of Tollner and Cryer (7) for conventional tillage, where it was observed that 40-55 percent of the applied 15G granules are within the top 0-1 cm of soil. Daily GLEAMS predicted runoff outputs for chlorpyrifos transport are subsequently used as chemical loadings in an EXAMS II batch file for pond water quality estimates.

Input Parameters Selection

GLEAMS/EPICWQ input files are identical for the watershed and nested meso-plot simulations with the exception of the different length scales, field slopes, and geometry associated with the meso-plots/watershed. An attempt was made to generate GLEAMS and EPICWQ files which are identical concerning the soil properties, application dates and rates, runoff curve number, chemical properties, management practices, and field observed precipitation patterns. Therefore, direct comparison between model predictions can be made as each model was set up to mimic the same field and climatic conditions. Soil properties are obtained from site characterization samples but can equally be estimated using USDA soils databases such SSURGO or STATSGO (8). The watershed topography was complex in nature with regions of varying slope. The slope and slope length for the watershed was estimated using a topographic survey map (4). The EPICWQ model does not have the capability for modeling fields with complex topography and varying slope. The watershed slope for the EPICWQ model was assumed uniform and constant at a value of 4.3%. The slopes of the nested meso-plots (3.7% and 5.9%, respectively) are assumed constant for both EPICWQ and GLEAMS. Average soil properties (mean and standard deviation) for the watershed are given in

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Table I. Input parameters are not adjusted to produce the observed hydrology, erosion, or chemical observations. This is similar to what would be done if there were little or no *a priori* knowledge of the outcome. If any model is to be used to extrapolate beyond specific conditions of a few select field locations, it must be able to predict any field observation trends without calibration. The primary way to address regional extrapolation issues using a deterministic model is to develop confidence that the model(s) can at least explain the experimental observations that do exist.

Table I. Soil properties for watershed (mean and St. Deviation)

Attribute\Depth (cm)	0 - 10.2	10.2 – 30.5	30.5 - 61.0	61.0 - 91.4
pH	5.65 (0.23)	6.48 (0.23)	6.45 (0.48)	6.38 (0.60)
CEC (meq/100g)	14.48 (1.41)	14.87 (2.51)	16.36 (1.72)	18.14 (1.51)
O.M. (%)	3.16 (0.65)	2.33 (0.91)	1.6 (0.78)	0.99 (0.35)
WHC (%) at 1/3 Bar	23.85 (0.86)	25.53 (1.29)	27.57 (1.70)	29.61 (1.33)
WHC (%) at 15 Bar	9.59 (1.44)	10.22 (1.50)	11.2 (1.03)	12.39 (1.04)
Sand (%)	9.07 (1.84)	6.93 (3.68)	6.27 (3.31)	2.93 (2.36)
Silt (%)	65.33 (3.50)	63.67 (5.85)	60.67 (4.13)	64 (3.35)
Clay (%)	25.6 (3.76)	29.4 (4.19)	33.07 (2.61)	33.07 (3.68)
Bulk Density (g/cc)	1.16 (0.03)	1.13 (0.08)	1.18 (0.13)	1.19 (0.06)
Field Capacity	0.28 (0.011)	0.29 (0.014)	0.32 (0.021)	0.353 (0.03)
Wilting pt	0.11 (0.017)	0.12 (0.016)	0.13 (0.018)	0.15 (0.017)

Model Output Comparison

Watershed Observations

Tables II-III represent field observations and GLEAMS/EPICWQ predictions for watershed hydrology, erosion, and chlorpyrifos edge-of-field transport. Shaded rows indicate dates where problems existed in sampling such as when the sampling flumes were flooded, etc. The percent difference between model result and field observation is defined as

$$\text{\% Magnitude difference from field observation} = \frac{\text{model result}}{\text{watershed observation}} * 100. \tag{1}$$

Table II. Comparison of hydrology and sediment yield between watershed
model simulation and field observation.

Julian Day	Precip (cm)	GLEAMS Water Yield (m^3)	EPICWQ Water Yield (m^3)	Obs. Water Yield (m^3)	GLEAMS Runoff Sediment Yield (kg)	EPICWQ Sed. Yield (kg)	Obs. Runoff Sediment Yield (kg)
184 (1992)	5.3	362.2	NS[1]	176	647	NS	NR[2]
195 (1992)	5.0	490.7	NS	319.2	797	NS	1543
196 (1992)	1.4	NS	NS	21.9	NS	NS	73
206-207[3] (1992)	13.1	3031	NS	3171	8220	NS	10,022
211-212[4] (1992)	10.3	1678	NS	2304	3816	NS	NR
142 (1993)	3.51	62	376.9	NR	120	9400	NR
169 (1993)	6.05	816	1798	689	1515	24,700	16,980
180 (1993)	2.43	25	806.7	186	23.2	6500	2619
185 (1993)	6.59	1135	2783	1604[5]	2440	22,300	14,272
186 (1993)	7.25	1652	4869	NR	3731	26,200	NR
206 (1993)	2.01	3.51	976.7	NR	1.77	7500	NR

[1] NS = Not Simulated (current simulations predict no mass)

[2] NR = Not Recorded or calculable due to insufficient information or equipment malfunction.

[3] Several runoff events continued into the next day and are thus combined for model comparison.

[4] Quantified by chlorpyrifos mass increase in pond water or pond sediment as determined by pond monitoring and/or pond volume increase to deduce water yield

[5] Observed data unreliable as one of the primary sampling flumes on this date (day 185-186) was inundated by pond water.

It is apparent from Eq. 1 that values greater than (less than) 100% indicate model over (under) prediction. GLEAMS water and sediment yield comparisons ranged from 13-206 % [mean = 113%] and 1-52 % [mean = 21%], respectively. For EPIWQ simulations, the range was 261-434% (mean = 347%) and 146-248% (mean = 197%) for water and sediment yield, respectively. Since hydrological factors drive chemical transport, it would be expected that GLEAMS would under predict the sediment phase transport of chlorpyrifos. This was not observed experimentally, with percent differences between GLEAMS and field observations ranging from 28 - 3127% (mean = 873%) and 2 - 714 % (mean = 293%) for chlorpyrifos water and eroded sediment transport respectively. EPICWQ predictions for 1993 ranged from

676-2323% (mean=1500%) and 243-6036% (Mean = 423%) for chlorpyrifos transport in runoff water and sediment, respectively. Events where sampling flumes were flooded or inoperable are omitted from this analysis.

Table III. Comparison of chlorpyrifos edge-of-field transport between watershed simulation and field observation

Julian Day	Precip (cm)	GLEAMS Runoff water chlorp. mass (g)	EPICWQ Runoff water chlorp. mass (g)	Observed Runoff water chlorp. mass (g)	GLEAMS Runoff sediment chlorp. mass (g)	EPICWQ Runoff sediment chlorp. Mass (g)	Observed Runoff sediment chlorp. mass (g)
1992							
184	5.3	9.06	NS[6]	5.97	33.8	NS	5.3
195	5.0	10.32	NS	0.33	9.85	NS	1.379
196	1.4	NS	NS	2.90E-02	NS	NS	0.062
206-207	13.1	61.4	NS	8.70	63.0	NS	18.9
211-212	10.3	28.7	NS	5.37	9.10	NS	24.7
1993							
142	3.51	0.338	4.3	NR[7]	2.89	37.5	NR
169	6.05	4.16	18.4	0.792	12.45	97.0	16.07
180	2.43	0.908	22.1	3.27	0.415	63.5	26.18
185	6.59	36.7	69.7	0.477	29.5	219.2	36.97
186	7.25	49.0	110.1	NR	39.0	224.9	NR
206	2.01	0.041	7.9	NR	0.010	20.9	NR

[6] NS = Not Simulated (current simulations predict no mass)
[7] NR = Not Recorded or calculable due to insufficient information or equipment malfunction.

Large differences between field observations and model predictions are anticipated for uncalibrated model predictions since runoff events of different magnitudes, intensities, and timings are being simulated. Expectations for uncalibrated model predictions would be in the ability to predict similar order of magnitude predictions as that observed in the field. Differences between observations and predictions will decrease if the model is first calibrated for field observed water and sediment yield by varying the SCS curve number and erosion parameters found in the soil loss equation. Similarly, discrepancies between model predictions and observations can be reduced if a longer time window for averaging is used (i.e., monthly or quarterly runoff from the

watershed, etc.). Daily runoff loadings are used in this analysis because of the attempt to predict acute pesticide exposures within the neighboring farm pond.

GLEAMS/EPICWQ predicted considerably more chlorpyrifos mass being transported in runoff water and sediment than that observed. A likely explanation is that these models assume more chlorpyrifos mass is available for runoff on the days of runoff events than the actual amount present. The partition coefficient used in the modeling (K_{OC} = 6623) may have been higher than the actual partition coefficient occurring within the field to account for the differences between sediment yield and chlorpyrifos transport in sediment for both models. GLEAMS predicted (on average) 0.09 x lower sediment yield, but only 0.53 x lower chlorpyrifos transport in sediment. This indicates the modeled concentration of chlorpyrifos on the eroded sediment must be higher (i.e., explainable by higher K_{OC}) than in the actual field concentration. An additional explanation may be attributed to the total amount of chlorpyrifos available on the soil surface immediately prior to the runoff event.

Assumptions used in the modeling include chlorpyrifos rate of release from the 15G formulation, fraction of granules within the 0-1 cm surface soil layer, the fraction of the Lorsban 4E application broadcast onto the vegetation and soil, chlorpyrifos wash-off fraction from the corn crop, etc. All of these mechanisms can affect the amount of chlorpyrifos available for runoff on any given day. However, best estimates are chosen as model input in this cold validation exercise. Ideally, a model parameter sensitivity analysis should be performed to quantify which parameters create the largest variance in runoff outputs. This is indeed performed for regional extrapolations where researchers have shown that sensitive GLEAMS input parameters are functions of both the region and climatic conditions being simulated (*9*).

Nested Meso-plot Observations

Tables IV-V summarizes the comparison between GLEAMS predicted and observed runoff events for the nested meso-plots for the 1992-1993 growing season. For 1992 on days 195, and 206-207, Station 8 became flooded by runoff water that overflowed the pit that was dug to contain it. On Day 184 (1992), Station 9 was apparently struck by lightning and thus no measurements could be made. Values for runoff output parameters for Julian Days 206-207 (1992) have also been combined for comparative purposes, since precipitation and runoff overlapped on these two days.

The runoff water (m^3) and sediment yield (kg) are of similar magnitude when compared to field observations for most days when runoff events were observed. Percent differences of 51.5 - 103 % for the water yield and 20.4 - 297 % for the sediment yield are observed. Higher model predicted sediment

yield also contributed to higher sediment phase transport prediction of chlorpyrifos, with the largest percent difference of 1913 %. However, the water phase transport of chlorpyrifos was over predicted by GLEAMS from 285 - 546 %, even with an under-prediction of runoff volume (51.5 - 103 %).

Table IV. Comparison of observed hydrology and sediment yield and GLEAMS simulation for watershed nested meso-plots (Stations 8-9)

Station	Julian Day	GLEAMS runoff (m^3)	Observed runoff (m^3)	GLEAMS sediment (kg)	Observed sediment (kg)
8	184 (1992)	3.42	3.9	6.1	29.9
8	187 (1992)	NS[8]	0.4	NS	24.6
8	169 (1993)	7.70	221.0	17.22	561
8	180 (1993)	0.23	4.4	0.58	29
8	185 (1993)	10.72	31.2	24.46	77
9	195 (1992)	4.6	9.0	15.2	5.9
9	207 (1992)	28.5	27.7	139.6	47.0
9	169 (1993)	7.7	12.8	31	100
9	180 (1993)	0.23	6.3	0.9	43
9	185 (1993)	10.7	30.6	44	148

[8] NS = Not Simulated (current simulations predict no mass).

Field Observations using watershed/pond monitoring

The ability of the uncalibrated GLEAMS/EXAMS modeling system to predict the observed peak and 96-hour maximum pond water concentrations was investigated. GLEAMS over-predicts the chemical transport of chlorpyrifos from the field edge (in runoff water and sediment) as seen in the previous analysis. Thus, it was anticipated predicted water concentrations would also be higher than observed values. Daily GLEAMS-predicted edge-of-field runoff loadings were input to the aquatic dissipation model EXAMS II as daily chemical loadings into the neighboring agricultural farm pond of dimensions 0.243 ha (0.6 acre). However, in addition to chemical loadings, the daily pond water volume was estimated based upon a simple water balance (*10*). This mechanistic approach is given in Figure 2. Daily pond volume updates are incorporated to account for runoff volume and precipitation inputs, along with seepage, pond overflow, and convection driven evaporation outputs.

Table V. Comparison of observed chlorpyrifos edge-of-plot transport and GLEAMS simulation for watershed nested meso-plots (Stations 8-9)

Station	Julian Day	GLEAMS Runoff water load (mg)	Observed Runoff water load (mg)	GLEAMS Runoff sed. load (mg)	Observed Runoff sed. load (mg)
8	184 (1992)	85.6	32.0	36.8	319.4
8	187 (1992)	NS[9]	3.0	NS	NR
8	211 (1992)	16.4	NR[10]	3.0	5.2
8	212 (1992)	255	NR	29.7	80.8
8	169 (1993)	130	716.4	540	1594
8	180 (1993)	25.7	217.5	131	388
8	185 (1993)	436	120.8	1160	214
9	195 (1992)	98.3	19.0	57.4	3.0
9	207 (1992)	581	114	344	109
9	169 (1993)	131.6	41.7	76	172
9	180 (1993)	12.2	384.5	17	847
9	185 (1993)	407.9	91.1	232	284

[9] NS = Not Simulated (current simulations predict no mass)
[10] NR = Not Recorded or calculable due to insufficient information or equipment malfunction.
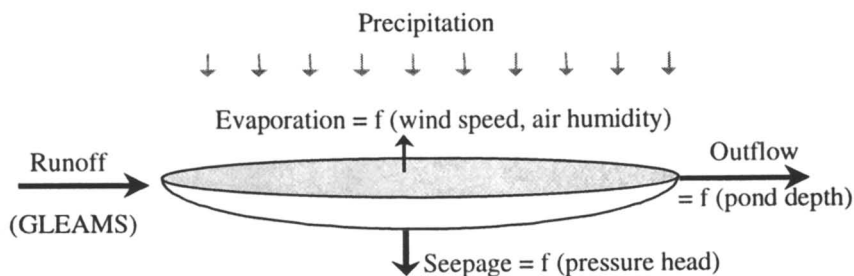
Figure 2. Mechanistic description used to estimate daily pond volume for Estimated Environmental Concentration (EEC) calculations.

Figure 3 illustrates the predicted and actual pond water volume observed for each year. Modeling efforts to describe dynamic pond volume changes captured the correct (observed) trends but are slightly off in overall magnitude. This may be due, in part, to lack of incorporation of subsurface flow. Figure 3 gives some indication of the increased uncertainty in Estimated Environmental

Concentration (EEC) prediction if the pond volume was assumed constant (as is often the case in simplistic exposure estimates) and not dynamic as observed (and modeled) in the field during the growing season. The sharp drop in pond volume occurring on Julian day 208 in 1992 was due to creating an emergency pond overflow spillway to quantify the pond water exits when intense precipitation/runoff from the watershed threatened to overwhelm the existing pond spillway.
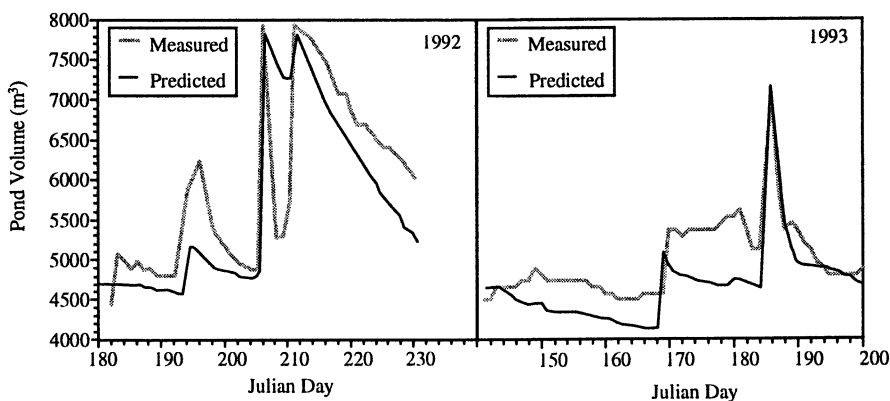
Figure 3. Pond volume changes over the course of the experiment. Modeled pond volume changes used in EEC predictions using EXAMS II.

Figures 4-5 include both observed and predicted (GLEAMS/EXAMS model) water column and benthic sediment concentrations for chlorpyrifos residues. Even though GLEAMS inputs more chlorpyrifos mass into the water and sediment phase than was observed, the calculated and measured EEC comparison still proved acceptable. The maximum pond water concentration observed for 1992 was 2013 ppt, while the largest pond water concentration predicted was 7729 ppt. The model over-predicted by 384 % (3.84 x) of the observed value. The observed 96-hr maximum water concentration was 1874 ppt while that predicted was 3047 ppt (163 % of observed). Although there was tremendous variability in pond sediment measurements (represented by the standard deviation error bars in Figure 5), the maximum sediment concentration observed in 1992 was 397 ppb while the maximum sediment concentration predicted was 203 ppb. In this case, the model predicted 51 % of observed for the maximum pond sediment concentration.
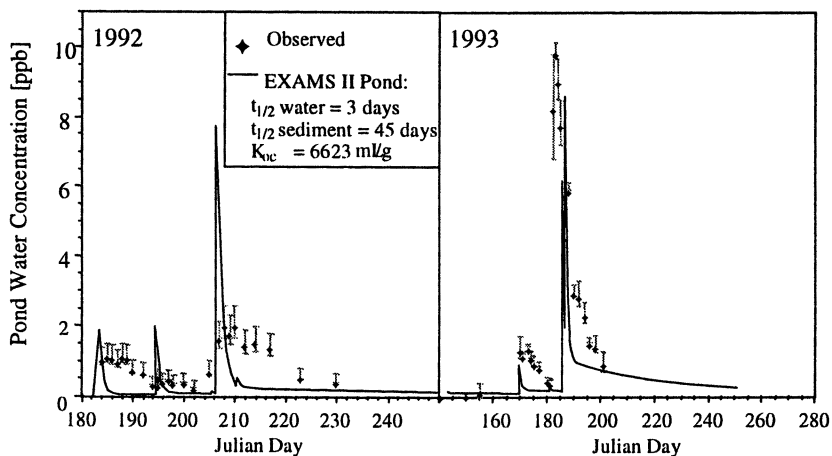
Figure 4. Pond water Dissipation Data with EXAMS II predictions. Loadings given by GLEAMS v. 2.10 simulation.
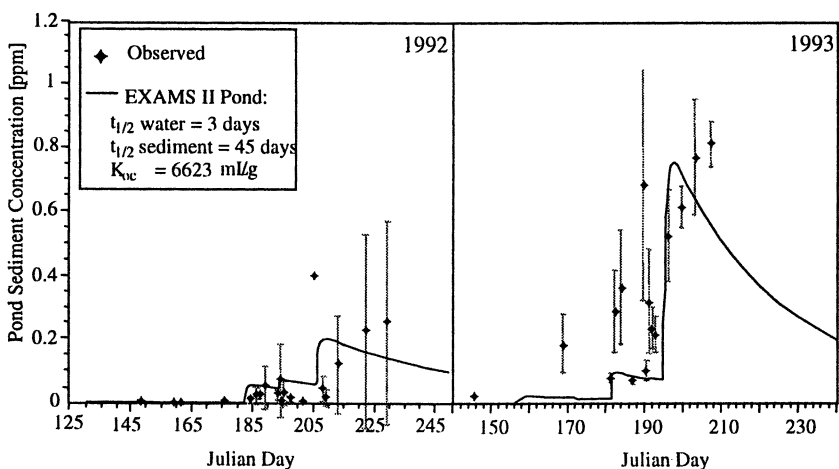
Figure 5. GLEAMS/EXAMS predictions for pond sediment concentrations of chlorpyrifos with field observations.

For 1993, the maximum pond water concentration observed was 9860 ppt, while the largest concentration predicted was 8540 ppt. Therefore, GLEAMS/EXAMS predicted 87% of the observed value. The maximum sediment concentration observed was 831 ppb while the maximum sediment concentration predicted was 756 ppb. In this case, the model predicted 0.91x of observed for the maximum pond sediment concentration. The coupling of GLEAMS (uncalibrated) with EXAMS provides excellent agreement with field

observations for the 1993-study year. This was a year of intense precipitation and runoff. Even though GLEAMS would over-predict chlorpyrifos mass leaving the field edge, the effect was somewhat mitigated by the dynamics/assumptions of the EXAMS II modeling. Chlorpyrifos fate predictions using GLEAMS are consistent with other researchers who have attempted to validate the GLEAMS model against field observations (*11-19*). Predictions of edge-of-field transport are typically within an order of magnitude for that observed experimentally and would be less if the model(s) were calibrated to the data set.

CONCLUSIONS

Significant runoff events occurred later in the growing season for both observation years (1992-1993). Modeling edge-of-field transport using GLEAMS and EPICWQ showed tremendous variability between storms of different intensities and timings. The models were set up and executed without any "calibration", much as a user would do without having any prior knowledge of the outcome. Both model over prediction and under prediction were encountered on an event-by-event basis. In terms of chlorpyrifos mass transport, the uncalibrated models typically over predicted chlorpyrifos transport in the water phase from 28-3127%, and in the sediment phase from 1.6-6036%. The GLEAMS model consistently under predicted sediment yield and chlorpyrifos in eroded sediment while EPICWQ over predicted chlorpyrifos transport under the same conditions. However, calibration of the field transport models can reduce the observed deviations from field observations.

Model calibration to multiple field observations (if available) would provide the most credible/optimal numerical predictions for environmental fate of agrochemicals. Nonetheless, favorable comparisons to field observations were obtained for pond water quality estimates when using GLEAMS loadings as input to EXAMS II simulations for a single multi-year field study, increasing the credibility of these numerical tools. Maximum water concentration predictions were within 15 percent of those observed in 1993. Predicted daily runoff amounts leaving the edge of the field compared favorably with observations both in timing and intensities. A numerical description of physical processes (i.e., model) which can accurately predict site-specific observations should be capable of extrapolation to other regions and climatic patterns. Uncalibrated EPICWQ simulations for the Iowa watershed provided better estimates for surface hydrology and edge-of-field chlorpyrifos transport than did GLEAMS on days when runoff events were observed. However, for 1993 EPICWQ predicted the occurrence of 13 runoff events to GLEAMS

predictions of 5 (actual number observed in the field was 4). Both models predicted runoff occurrences on the days observed in the field. In this respect, the uncalibrated GLEAMS model is superior in representing field observation and predicting quantifiable runoff events over EPICWQ. GLEAMS is a useful model for estimating EEC's since GLEAMS yielded, i) close approximation to the total number or runoff events observed, ii) excellent agreement between predictions and observations of pond environmental concentrations when GLEAMS is used to predict chlorpyrifos runoff loadings for EXAMS, and iii) wide acceptance by the academic community and regulatory organizations.

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Chapter 7

An Integrated Approach for Quantifying Pesticide Dissipation under Diverse Conditions IV: Scaling and Regional Extrapolation

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Various computer models have been developed to predict pesticide transport processes on a site-specific basis. Properties characterizing soil, climate, farm practices, application information, and so forth, are supplied as inputs for predicting pesticide transport characteristics through the use of these models. New approaches must be utilized to assign appropriate model input data sets for the these models that adequately captures the variability of the region at large and are capable of scaling field information to the watershed scale. A geographically based computer simulation has been developed that couples site-specific pesticide transport predictions to estimate regional behavior. An example is given using geo-spatial databases for soil, crop, and weather variability with the environmental fate models GLEAMS and EXAMS to predict Estimated Environmental Concentrations in surface water. Once a region of interest has been defined,

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a sensitivity analysis and grouping of similar scenarios allows for the construction of multiple simulation input data sets that represent the spectrum of environmental and weather properties for the region. These input sets, which number in the tens of thousands, are supplied to deterministic transport codes and are executed using parallel processing techniques. The GIS referenced results are automatically stored in a relational database and can be displayed as shaded maps or further processed to answer specific questions concerning the regional exposure characteristics for the pesticide in question.

INTRODUCTION

It has been illustrated that the GLEAMS/EXAMS numerical system is useful for predicting actual environmental concentrations in farm ponds immediately adjacent to a treated field (1). Attempts to document the ability of a cold validation numerical system to predict actual field observations increases the confidence of using models such as the GLEAMS\EXAMS system for extrapolations under different parameter combinations. There does exist the possibility of modeling system failure for different regions (i.e., GLEAMS/EXAMS may work for Iowa under intense precipitation patterns, but what about Kansas, etc.). However, keeping regional parameters close to those obtained for the Iowa field study location (i.e., Midwest) reduces the possibilities for these errors. A more comprehensive data set covering diverse regions and climatic conditions would have to be available to statistically deduce the latter concern. The focus now shifts to scaling issues when moving from meso-plot to the watershed scale, and in implementation of a regional assessment using numerical tools that incorporates soil variability, management practices, weather patterns, and so forth, found throughout a given region.

METHOD AND MATERIALS

Linear Scaling of Nested Meso-Plots

Figure 1 is an aerial photograph illustrating the scaling difference between the meso-plot and watershed length scales for a comprehensive field study described elsewhere (1-2). Meso-plot results indicate sediment yield, and
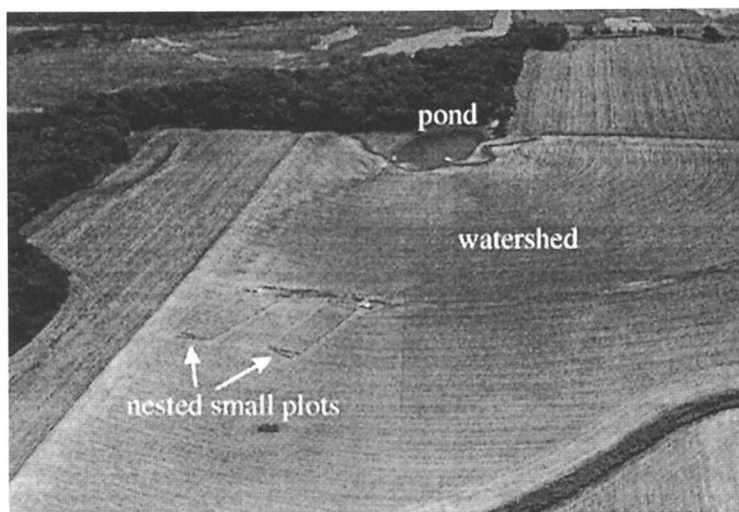
Figure 1. Photographic illustration of scaling between meso-plot and watershed length scales.

chlorpyrifos transport in runoff, cannot be scaled linearly based upon surface area. For example, the watershed has dimensions of 17.29 acres (7.02 ha), while the meso-plot has an area of 0.16 acres (0.065 ha). On Julian day 180, for station 9 (nested meso-plot), the chlorpyrifos in runoff water and sediment were 384.5 mg and 847 mg, respectively (2).

Assuming linear scaling, the observed watershed transport should be

$$384.5 \text{ mg} * \frac{17.29}{0.16} \frac{acre}{acre} = 41{,}550 \text{ mg} = 41.6 \text{ grams chlorpyrifos in water}$$

phase of runoff

$$847 \text{ mg} * \frac{17.29}{0.16} \frac{acre}{acre} = 91{,}529 \text{ mg} = 91.5 \text{ grams chlorpyrifos in sediment}$$

phase of runoff

The observed watershed transport observed on Julian day 180 was 7.03 and 26.2 g chlorpyrifos in the water and sediment phase of runoff, respectively. For this example, linear scaling of meso-plot runoff observations to watershed predictions would result in over prediction of 593 % and 349 % for the amount of chlorpyrifos transported from the watershed in the water and sediment phase of runoff, respectively.

Numerical Scaling of Meso-Plots using Models

GLEAMS model predictions and field observations for the watershed (17.29 acre) and nested and artificially irrigated meso-plots (0.16 acre) have been summarized elsewhere (3). A trend was observed when examining the percent deviation figures for the watershed and meso-plot experimentation for any given runoff day. If the meso-plot modeling over predicted the experimental observations, then the watershed modeling over predicted by the same order of magnitude (with converse also true). Figure 2 summarizes this information for the watershed and mesoplots for days when runoff was quantified from both experiments. Results in this figure are presented as a GLEAMS predicted percent deviation from field observations (Eq. 1).

$$\begin{array}{l} \% \text{ Magnitude difference} \\ \text{from field observation} \end{array} = \frac{\text{model result}}{\text{watershed observation}} * 100. \qquad (1)$$

The erosion algorithm of GLEAMS is fixed. EPICWQ addresses this oversight of GLEAMS by providing a modified soil loss equation specific for meso-plots that can be tailored to specific fields and/or observations. EPICWQ has the

capability of specifying various soil erosion sub-models over the normal Modified Universal Soil Loss Equation (MUSLE) employed in GLEAMS. All of the erosion equations are empirically based and are similar in function. However, only one equation (MUSS) is based on small field/plot experimentation, and as such should provide a more refined prediction for the meso-plot experiments. Comparisons of the erosion loss observations to model predictions for the irrigated meso-plot experiments are given in Figure 3. Here, USLE is the universal soil loss equation, and AOF represents erosion predictions using the Onstad-Foster modified USLE.
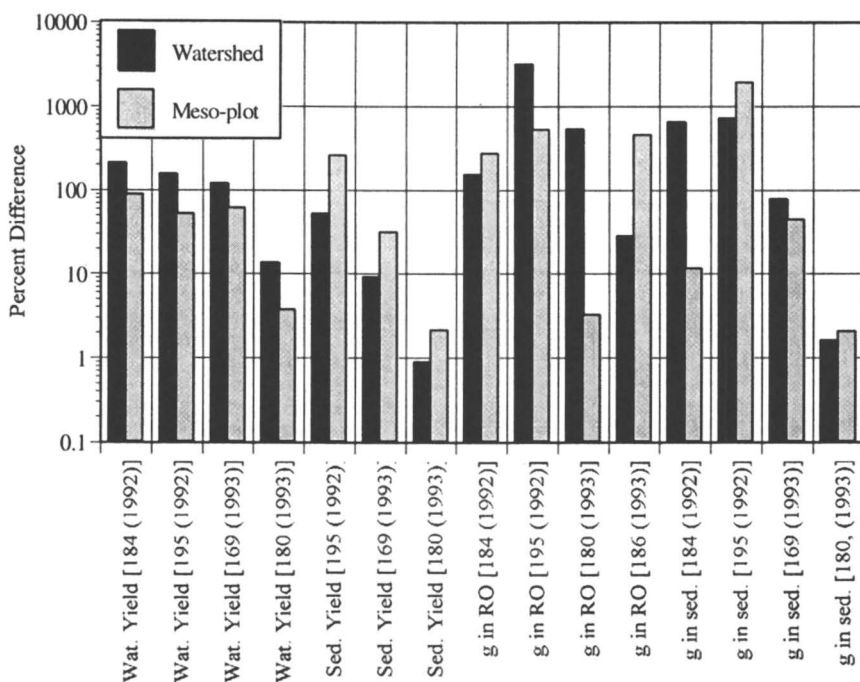
Figure 2. Percent difference between field observations and GLEAMS model predictions for where both watershed and nested meso-plot runoff events are quantified (attribute, Julian day, year).

Figure 3 represents the ability of the various erosion sub-models of EPICWQ to predict the observed sediment yield as the magnitude of the sediment yield increases (meso-plot observations), with results presented as a percent deviation. Thus, as this number increases/decreased from 100%, the worse the comparison becomes. A value greater than 100% indicates model over-prediction, while a value less than 100% indicates under-prediction with respect to field observations. In general, model predictions approached the field observations for the less severe sediment transporting runoff events, but in most every case over-predicted the field observations (although less than a

factor of ~2). Both USLE and AOF provide a better comparison to field observations than did MUSS or MUSLE. However, for runoff events transporting 200 kg or more of sediment, each of the 4 different erosion equations become indistinguishable in terms of measured uncertainty. This observation suggests that the MUSLE erosion equation (used by GLEAMS and EPICWQ) is adequate for storms of sufficient strength to transport large quantities of sediment. Small intensity storms may be better suited to the use of AOF or USLE, although the differences between the EPICWQ erosion equations and that employed in GLEAMS typically cannot account for the large variability witnessed in the irrigated meso-plot experiments (2).
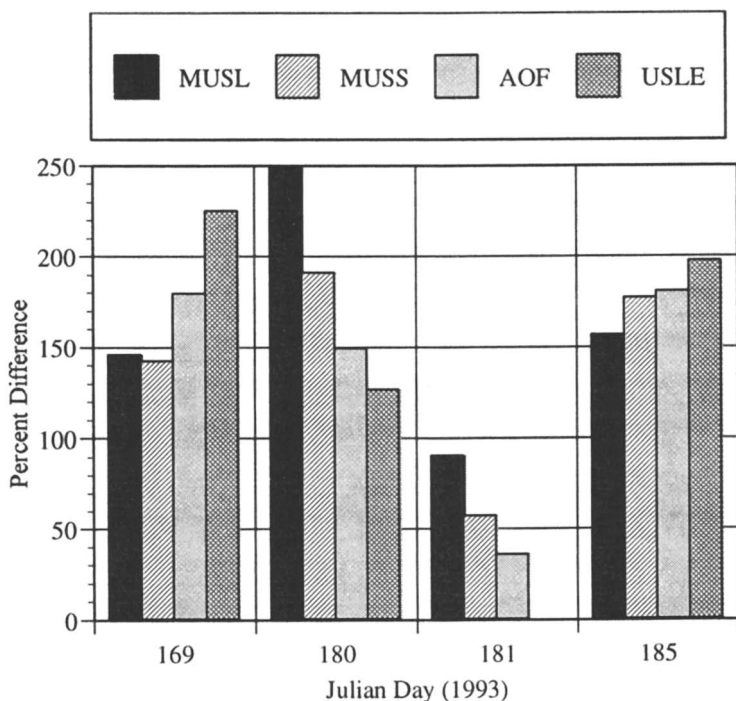
Figure 3. Percent difference between nested Meso-plot sediment yield observations for 1993 and EPICWQ predictions for various soil erosion algorithms.

This observation of scaling suggests that meso-plot experiments are acceptable in providing necessary input data for model predictions, although refinement of the models and/or calibration may be necessary to minimize discrepancies between model predictions and field observations. The computer model can then be used to "scale" up meso-plot observations to larger

field/watershed in a fashion superior to linear scaling. Assuming the models accurately and mechanistically account for the physical process involved in predicting edge-of-field runoff, then the ratio of meso-plot to watershed scaling is irrelevant, provided the user appropriately accounts for topography, slope length difference etc., between meso-plot and watershed simulations. Critiquing the methodology and algorithms used in GLEAMS and EPICWQ on a mechanistic basis is beyond the scope and intent of this work but can potentially be accomplished using the excellent field data set available for this study.

Using meso-plot experiments as a surrogate to larger watershed scale experiments is a valid approximation as long as a simulation model such as GLEAMS is used for scale-up predictions. The use of artificially irrigated meso-plot experiments overcomes many of the problems, resource constraints, and expense associated with watershed scale experimentation.

Regional Extrapolations

Difficulties in gathering appropriate input parameter values for all possible choices for a geographical assessment is a major limitation in the current group of mechanistically based environmental fate models. A model sensitivity analysis is therefore useful in determining which model-input parameter(s) create the largest variance in model output. A Plackett-Burman experimental design approach (4) was employed to rank the input parameters in terms of their effect on the model output variable of concern. The runoff models GLEAMS v. 2.10, and PRZM3 have been incorporated into a computer software system which employs the Plackett-Burman method, executes the various runoff models, and statistically summarizes the model output predictions (5). Results of the sensitivity analysis indicate approximately 2-10 input parameters have statistically significant effects on edge-of-field runoff. Sensitivities of these parameters are often coupled to both climatic and regional conditions. Thus, sensitivity analysis can be used as a tool to reduce the number of unique simulations required to describe a large geographic region since many model input parameters have little effect on model output.

Deterministic models require a combination of geographically referenced data and a appropriate methodology for obtaining input parameter combinations. Figure 4 is an example of defining the locations where corn is grown (and thus chlorpyrifos applications) in the United States based upon 1987 Department of Agriculture data. This map can be overlaid with multiple layers such as pesticide sales information, endangered species habitat, etc., to define a specific region of interest for simulation purposes.

Weather information has always been an area of debate. The model user can choose either historical or simulated weather patterns for a specific simulation. Weather station location is provided by the USDA climate generator program CLImate GENerator - CLIGEN (6). The developers of CLIGEN took weather station information from stations located as close as possible to equally spaced latitude and longitude grid locations. A weather station area of influence is defined by the grid locations where a unique weather station is centrally located within each grid (Figure 5). Any watershed/soil type within the confines of a weather station area of influence is simulated using the weather generated by the centrally located weather station.

Regional soil variability is partially avoided by keeping soil properties geographically referenced. Figure 6 is a false gray scale representation example of the USDA Natural Resource Conservation Service database STATSGO for the state of Iowa. All of the states within the United States have data at this detail and may have information down to the county level (http://www.itc.nl/~rossiter/research/rsrch_ss_digital.html). Each gray scale polygon represents a unique soil association map unit. There can be up to 21 similar soil phases within each map unit where each soil series can have different soil properties. Soil and weather information is combined into a single map (Figure 6). A soil map unit, which crosses boundaries between weather station regions of influence, is modeled as two distinct map units, each having different weather.

Pesticide properties are included into the GLEAMS/EXAMS regional simulation system based upon probability distributions generated from lab and field data. A value from the distribution can be chosen which represents a certain percentile of the distribution range. Pesticide properties are chosen for use in numerical simulation depending upon the level of likelihood the user would like to simulate (e.g., the 90th percentile for the half-life distribution).

RESULTS

An example of a regional exposure/risk assessment for chlorpyrifos (7) is given in Figure 7 which represents aquatic risk quotients[1] for organisms living in agricultural farm ponds immediately boarding chlorpyrifos treated fields. The field and pond sizes are geography specific as given by the USEPA pond

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[1] Ratio of estimated environmental concentration to a lethal concentration where 50% mortality occurs.
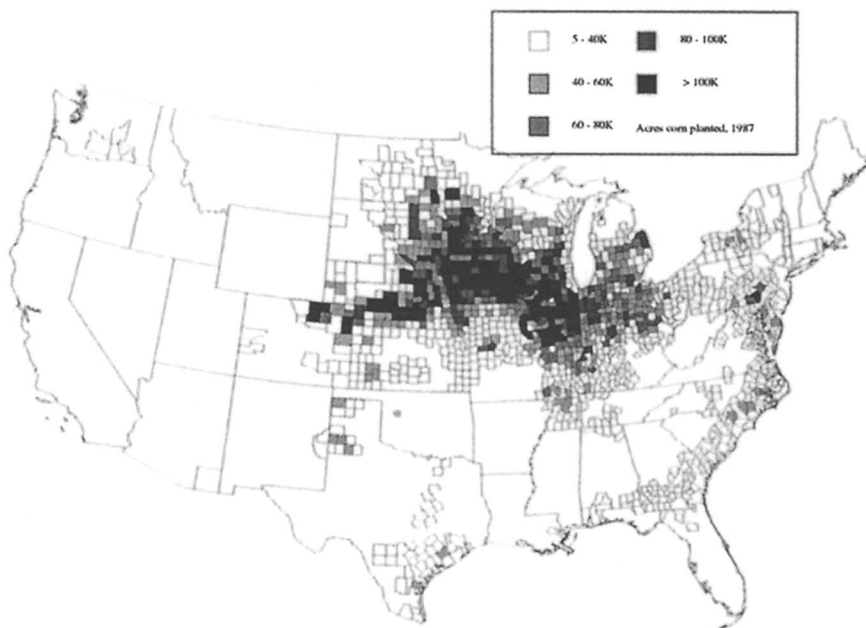
Figure 4. Definition of region of interest through 1987 Census cropping information.
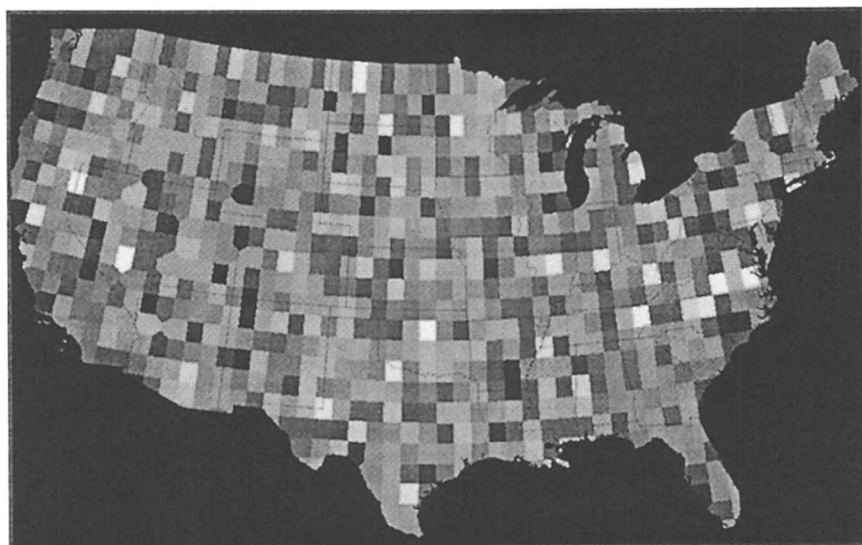
Figure 5. Accounting for Regional Weather Variability through discretization of the United States
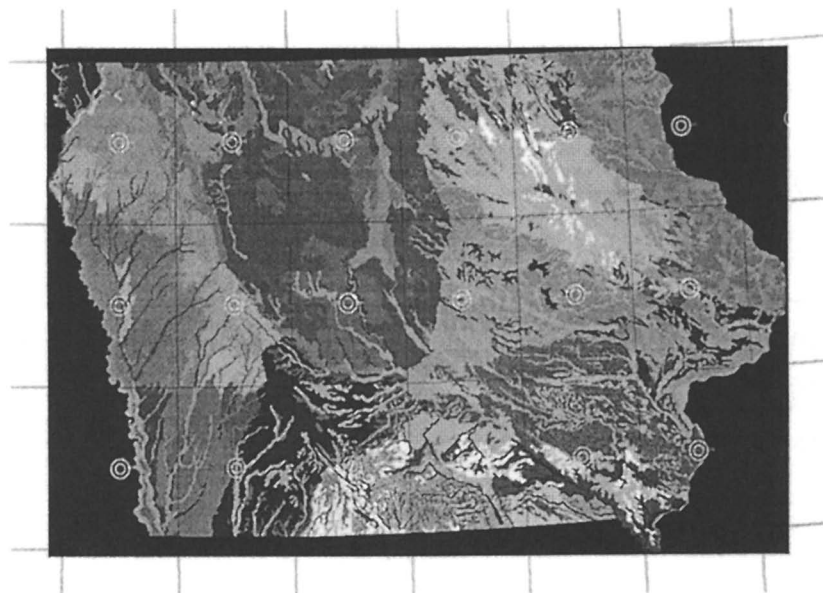
Figure 6. Combining Spatial Soil polygons from STATSGO and Weather Variability
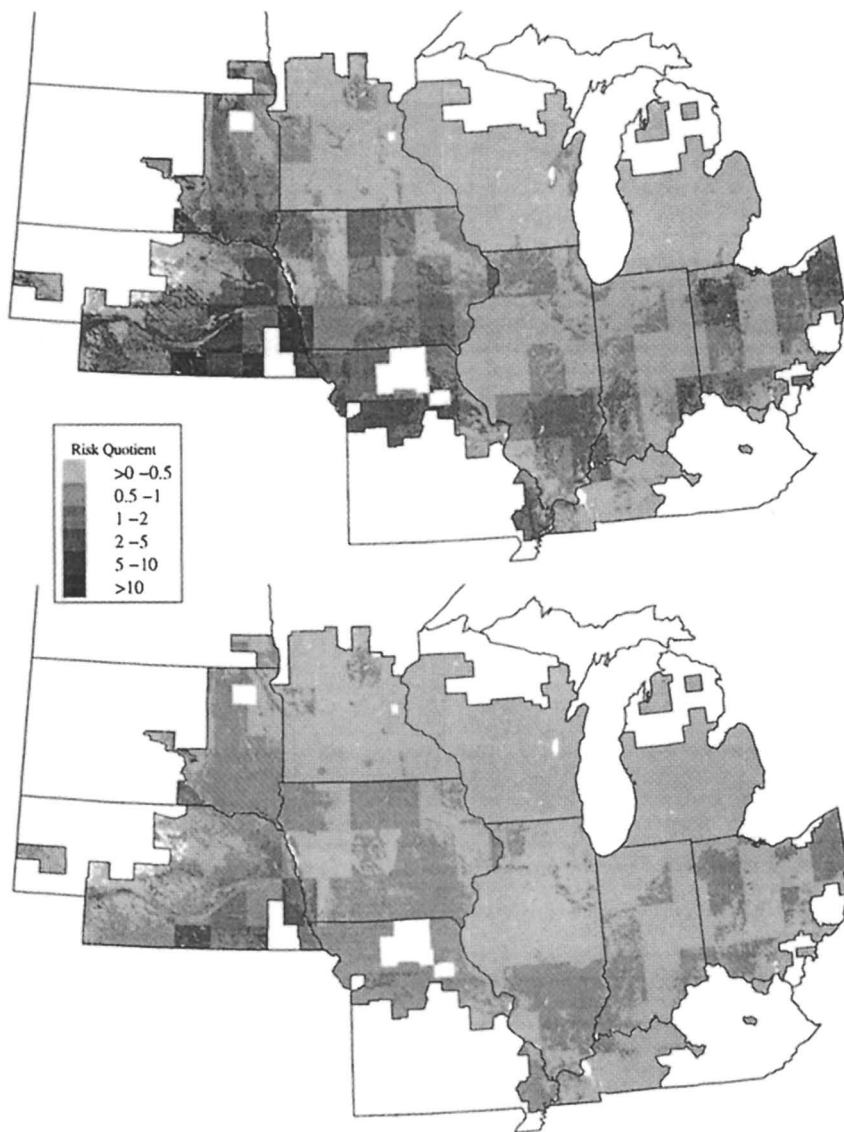
Figure 7. Example of Model Extrapolation for Chlorpyrifos Risk Quotient in Midwestern USA (5) [Reprinted with Permission from Environmental Toxicology and Chemistry, 1998, Tiered Aquatic Risk Refinement: Case Study-At Plant Applications of Granular Chlorpyrifos to Corn. Havens et al., Vol. 10, No. 7. Copyright Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, FL, 1998].

data base (8). Areas indicative of high risk can be further explored though field study placement and/or refined modeling procedures. An example for refined modeling is given by the lower graphic in Figure 7 where the effect of vegetated filter strips between field edge and pond has been simulated.

Numerical systems such as these are based upon no *a priori* knowledge of the output and are instrumental in defining where field studies should be placed, areas where vulnerability to runoff are high, etc, along with conservative estimates for environmental concentrations. Confidence is gained in the result of such extrapolations for the Midwest given the good agreement between the multi-year Iowa field runoff study and the GLEAMS/EXAMS modeling system.

CONCLUSIONS

Linear scaling between meso-plot result and watershed prediction is not adequate for realistic predictions. For the field study under investigation, overestimates for edge-of-field runoff for the watershed ensue. Field-scale numerical models were much better extrapolation tools to use when scaling results up from the meso-plot length scale. Similar trends are observed when simulating meso-plot and watershed behavior (i.e., if meso-plots overpredict, watershed simulations also overpredict).

A geographically based regional risk assessment system has been developed using the USDA model GLEAMS, and the USEPA models PRZM3 and EXAMS. This system allows site-specific pesticide transport simulations to be extrapolated to regional scales. The number of unique simulations for a region of interest is reduced using sensitivity analysis techniques and in grouping scenarios which are known a priori to yield similar numerical results. Simulation results are directly linked to the geographic information system for shaded map preparation. These maps are useful in visually understanding the numerical results and in the communication of results to the various stakeholders involved.

Regional extrapolations using numerical modeling tools provides insight into vulnerable areas, order of magnitude esitmated environmental concentrations (EEC), and exposure reduction resulting from implementation of various best management practices. The basis for such extrapolations resides on the ability of uncalibrated environmental fate models to accurately predict the limited number of field study observations that may be available. Simulating watershed and pond fate behavior using GLEAMS and EXAMS provides acceptable agreement with field observations and can be the basis for regional extrapolations for Estimated Environmental Concentraitons (EECs).

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Chapter 8

Modeling Pesticide Transformations in Soil and Aquatic Environments: Development of a Common Approach

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Understanding the kinetics of pesticide transformations is crucial to predicting the environmental fate of pesticides. Parameters describing transformation rates are required by regulatory agencies for use in models to predict environmental concentrations of pesticides. The predictions support ecological and human health risk assessments needed for registration. Equations representing transformation processes are used to derive rate parameters from laboratory or field data. Many equations and fitting methods are used; few are widely accepted by academic and industry researchers and regulatory agencies. ModelManager is an example of a flexible PC-based set of analysis tools offering a common approach that can be adapted to evolving scientific knowledge and regulatory needs.

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Introduction

The persistence of pesticides and their degradation products in soil and aquatic systems can largely determine the amounts of these compounds reaching groundwater and surface water. These levels affect the potential for acute and chronic chemical exposure (and the accompanying toxicological risks) of nontarget plants and wildlife, and of the human diet via drinking water. Estimation of degradation rates from laboratory and field studies is therefore a major concern of regulatory agencies that grant registrations for agricultural uses of pesticides.

In general, rates and related parameters are estimated by fitting mathematical representations of tranformation processes to experimental data. Levels of pesticides in soil and water are often much lower than those of many chemical species (*e.g.,* acids, bases and oxygen) that participate in degradative reactions. Enzymes and other microbial reagents, and some abiotic reagents, often have catalytic roles. Hence, the assumption that the transformation rate of a pesticide is dependent only on the level of the compound itself often provides a valid model. The resulting simple first-order (SFO) equation fits well with dissipation patterns of many compounds in both laboratory and field test systems. The associated concept of half-life is simple and widely understood. Many environmental models, including those used and accepted by regulatory agencies for exposure assessments, require estimated SFO rate constants as input values.

The accuracy of the SFO model depends on the validity of two assumptions: that the test system is homogeneous (with no functional compartments in which rates of transformation are significantly different) and that its behavior approximates a steady state (with no significant changes affecting rates of degradation, *e.g.,* in chemical properties, microbial population, or availability of nutrients). In reality, therefore, the SFO equation does not always fit decline patterns adequately, especially in soils and aquatic systems. The resulting estimated rate constants can lead to grossly underestimated or overestimated environmental concentrations in exposure-assessment models, especially at times greater than the estimated halflife. Many other equations, both mechanistic and empirical, have been developed to describe other patterns and more complex processes. These can add the flexibility needed for accurate kinetic analysis, but should be used in a systematic manner, along with appropriate fitting methods, to avoid vastly different interpretations of a single set of experimental data. No set of equations or fitting methods has met with universal acceptance among academic and industry researchers and regulatory authorities.

The present chaotic state of kinetic analysis reflects the lack of a common platform for testing and comparison of methods. Appropriate fitting routines

applied to a tiered set of equations, along with statistical techniques to minimize the number of parameters for an adequate fit, can facilitate quality assurance, comparison of rate estimates, and regulatory review. The features of ModelManager, a PC-based application developed by Cherwell Scientific in cooperation with Zeneca Agrochemicals (now Syngenta), support this approach. Built-in models represent dissipation schemes applicable to common study types. Widely used equations representing various dissipation patterns are fitted to the data, and the results are compared by means of statistical tests. The software also accepts entry of new study types and equations. Thus, ModelManager provides an example of a uniform set of procedures for estimating transformation rates, which can be modified in response to evolving scientific and regulatory needs.

Current Practices in Environmental Kinetic Analysis

The diverse array of dissipation studies required for pesticide registration demands a flexible set of methods for kinetic analysis. Decline patterns and data quality can be affected by properties of the test system. Aquatic hydrolysis and photolysis are studied under controlled conditions in homogeneous systems and usually follow SFO kinetics. Photolysis and evaporation on leaf surfaces and in soil can be affected by surface adsorption and biochemical transformations in the substrate. Laboratory studies of metabolism in soil are further complicated by spatial and temporal variations in microbial activity and availability of oxygen and nutrients. Flooded soil and water-sediment systems are the most complex laboratory systems with potential for volatilization from water, adsorption and desorption in soil or sediment, diffusion between compartments, and spatial variation in oxygen levels. Field dissipation studies are conducted under less-controlled conditions, leading to observations which are affected by chemical and physical heterogeneity of the soil, as well as spatial and temporal variations in environmental factors such as temperature, humidity, and rainfall.

Error Factors

Many sources of error, both random and systematic, can cause deviations from the "true" degradation pattern that reflects pesticide properties and the initial state of the test system. In heterogeneous systems, kinetic profiles may differ in distinct functional compartments. Diffusion between compartments may lead to significant variation in composite kinetic profiles. Study design also

influences variation. Laboratory soil and aquatic metabolism studies are often designed for incubation of discrete samples; inhomogeneities typically occur on a much smaller scale than the sample size. In contrast, field dissipation studies require analysis of small samples of a heterogeneous system; the expected variation of replicate samples is consequently higher. Other sources of error include pesticide application, sample preparation, and analytical methods. Analytical error generally declines with levels of analytes, in patterns related to study design. Errors in sample preparation and chemical analysis are proportional to the magnitude of the measurement. Errors in radiochemical analysis are proportional to the square root of the measurement, with additional error due to background radiation. System heterogeneity and environmental variation have dispersive effects which contribute to increased variation in measurements with time. Because of these diverse study-dependent effects, the weighting of experimental data can significantly affect the accuracy of fitting results.

Types of Information Needed

The purpose of kinetic analysis is to estimate transformation rate constants and related kinetic parameters for their predictive value in exposure and risk assessments. The first-order rate constant k and the corresponding half-life ($t_{1/2}$ = ln 2 / k) are of particular regulatory interest. Dissipation often follows other kinetic patterns; estimated DT_{50} and DT_{90} (dissipation times for 50% and 90%, respectively, of the initial mass) are useful when equations other than the SFO equation have been fitted to the data. In the case of first-order kinetics, DT_{50} = $t_{1/2}$ and the ratio $DT_{90}:DT_{50}$ = 3.32; observed ratios are often larger, indicating greater long-term persistence than the SFO equation predicts.

Regulatory interest has focused on the persistence of parent compounds, but metabolites have received increasing attention. Proposed additional studies on major metabolites may be unnecessary if kinetics of metabolite dissipation can be reliably estimated from data obtained in parent metabolism studies.

Approaches to Kinetic Analysis

Application of the SFO model is the most popular method of analysis. In this model, the pesticide enters a single conceptual compartment in which the dissipation rate is proportional to the mass of compound present (or its equivalent concentration). It is represented in integrated form by the equation M

$= M_0e^{-kt}$, where M is the mass of pesticide at time t, M_0 is the initial mass, and k is a rate constant. A logarithmic form, $\ln M = \ln M_0 - kt$, allows fitting to experimental data by linear regression. Because of the convenience of this linear equation, as well as the widely accepted concept of half-life, SFO rate constants are often preferred by investigators and regulatory agencies.

Because the SFO equation fits many degradation patterns inadequately, other equations have been applied. Occasionally, data fit well to zero-order (ZO) or constant-rate kinetics, with a linear decline of pesticide level with time $(M = M_0 - kt)$. Perhaps most frequently, data appear to follow equations of higher-than-first order, with nonlinear profiles in semilogarithmic plots. Many empirical equations have been developed. Perhaps the best-known are the Timme-Frehse set (1) which has been used in many regulatory studies. From this set of equations of different mathematical order, a best equation can be selected on the basis of quality of fit. Many researchers have used a biphasic model in which pesticide levels follow SFO kinetics, but the rate constant changes from k_1 to k_2 at a breakpoint time t_b; the two linear equations create a "hockey stick" (HS) shape. This allowance for temporal variation has achieved some regulatory acceptance: the new version of the EPA Pesticide Root Zone Model (PRZM) for assessment of groundwater and surface water exposure accepts biphasic SFO rate constants for degradation in soil (2). The first-order multi-compartment (FOMC) model accounts for spatial variability in dissipation rates (3). The pesticide enters a large number of conceptual compartments; degradation follows the SFO equation in each compartment, but at different rates. The FOMC model is represented by $M = M_0 (1 + \beta t)^{-\alpha}$, in which α and β are not rate constants but parameters describing the shape of a gamma distribution of SFO rate constants (3). A similar form, $M = M_0(1 + t/\beta)^{-\alpha}$, was developed independently in Zeneca by J. S. Dyson and has been applied to kinetic analyses in several regulatory reports. The flexibility of the FOMC equations creates a diversity of possible curve shapes.

A consensus set of approaches to kinetic analysis would ease the regulatory review process for researchers and regulators alike. Guidelines for their application should be flexible enough to address individual scientific requirements and adaptable to rapidly evolving science and regulatory needs.

ModelManager Environmental Kinetics, Version 1.1

ModelManager provides a platform for kinetic analysis of data from all types of dissipation studies. The simple fixed user interface is compliant with Good Laboratory Practice (GLP) regulations, ensuring reliable methodology and high-quality results. No special mathematical or programming knowledge is

necessary for full use of ModelManager's features. ModelManager provides a versatile built-in set of study types and transformation models but is also fully customizable by the system administrator. Study types, models, and report content can be added or deleted from the system; password-protected access to this feature prevents undocumented changes and facilitates GLP compliance.

ModelManager accepts multiple datasets of a single study type for simultaneous analysis. One or more models can be selected for fitting. Models are developed in ModelMaker, a widely used application which employs numerical approximation methods and an optimization routine for nonlinear curve-fitting (4). This approach is more versatile than linear regression because it does not require mathematical transformation of rate equations to linear forms, with the accompanying effects on data weighting. Equal or logarithmic weighting, as appropriate to the error structure of the data, can be selected. The curve-fitting routine offers the option of a floating or fixed intercept.

ModelManager interfaces with Microsoft Office software to store study information and experimental data in an Access database and generate reports as Excel worksheets. The standard report format displays study information, a summary of data entered, and equations selected. The report includes a graph for each equation showing experimental data points and the fitted dissipation curve. Results are expressed as a list of rate parameter values, dissipation times (DT_{50}, DT_{90} and a user-defined DT_x), a predicted value corresponding to each observed value, and correlation coefficients for the fitted equation. When multiple models are selected, an additional worksheet superimposes all dissipation curves on a single graph. It compares the fitting results by means of analysis-of-variance tables, and for each pair of models it reports the F-statistic and the associated probability that any improvement in fit from an added parameter is due to chance (p-value). This analysis safeguards against addition of parameters unnecessary for a best fit.

Study Types Available

- *Parent Only* (PO): Dissipation of parent compound applied once to a single conceptual compartment
- *Parent with Multiple Applications:* Dissipation of parent compound applied more than once to a single conceptual compartment
- *Parent and Metabolite Dissipation* (PM): Dissipation of parent compound and a degradation product comprising a fraction C of total parent dissipation
- *Parent and Two-Metabolite Dissipation:* Dissipation of parent compound and two metabolites formed in sequence ($P \rightarrow M_1 \rightarrow M_2$)

- *Water-Sediment Dissipation:* Diffusion and dissipation of parent compound in a water-sediment system, using a model developed by Zeneca Agrochemicals (now Syngenta)

Kinetic Models Available

- ZO Kinetics - two parameters (M_0 and k)
- SFO Kinetics - two parameters (M_0 and k)
- FOMC Kinetics - three parameters (M_0, α and β)
- HS Kinetics - four parameters (M_0, k_1, k_2 and t_b)

Application of ModelManager

The useful features of ModelManager can be demonstrated with data from a laboratory study of the herbicide butylate [S-ethyl di-isobutylthiocarbamate] in soil under aerobic conditions (5). The compound, radiolabeled in an isobutyl group, was applied to weighed portions of soil which were incubated at 23°C. The initial level of butylate was 5.1 mg/kg. Levels of butylate and metabolites in mg/kg butylate equivalents were reported. The major route of dissipation is volatilization from the soil. Initial degradative reactions include oxidations to hydroxylated and dealkylated metabolites and butylate sulfoxide (Figure 1).

Results of PO modeling show that the SFO equation (Figure 2) fits only the first few data points well, and that the FOMC (Figure 3) and HS (Figure 4) equations fit all data points more closely. Both equations were significantly better than the SFO equation, as determined by the F-statistic and associated p-values (Figure 5). The FOMC fit, with only three parameters, has a higher level of significance (lower p-value) than the HS fit, with four parameters. PM modeling was also used to estimate the persistence of butylate sulfoxide in the test system. In this model, the numerical output of the parent equation is used as input for the metabolite equation. PM modeling with the FOMC-SFO (Figure 6) and FOMC-FOMC (Figure 7) models yielded significantly better results than the SFO-SFO model, as the PO fitting results would suggest. The FOMC-SFO and FOMC-FOMC models give similar estimates of DT_X, for butylate sulfoxide.

Butylate dissipates via two mechanisms with distinct kinetic profiles. Dissipation in soil water, largely by volatilization, is rapid; adsorbed to soil particles, butylate is more persistent as it is degraded by microbial action. Modeling of equally weighted data predicts DT50 of 19-22 days with all three models, but DT90 estimates differ substantially: 72, 102 and 103 days for SFO, FOMC and HS, respectively. Logarithmic weighting gives SFO estimates that follow the later dissipation phase more closely but inaccurately model the initial phase. This shows the advantages of the FOMC and HS models. With FOMC degradation of butylate, DT50 of butylate sulfoxide is estimated to be 103 days. The choice of metabolite dissipation model has little effect on this estimate, as the SFO equation is adequate to account for the dissipation pattern.
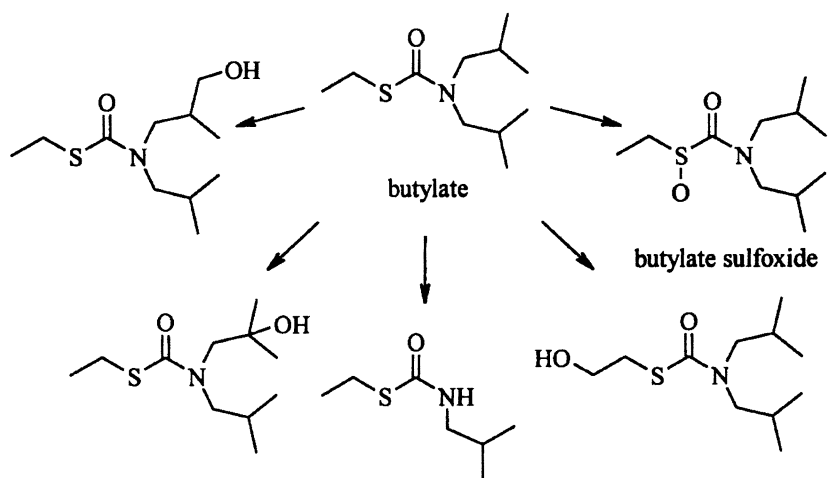
Figure 1. Initial steps in the degradation of butylate in soil under aerobic conditions.

Conclusions

The wide range of kinetics, fitting methods and statistical assessments that are now available should be used more fully to improve estimates of pesticide transformation rates in the environment. Such a full use will inevitably improve prediction of the environmental fate of pesticides. The use of ModelManager as an example of a flexible PC-based set of analysis tools demonstrated some of these improvements. Such tools must be exploited to lead to a common approach that can be adapted to evolving scientific knowledge and regulatory needs.

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ModelManager Report: Parent Only Study Type

Study Number: PMS-298
Study Name: Butylate Aerobic Soil Metabolism Study
Date of Analysis: 23-Apr-99
User Name: John Tarr

Dataset Name: Butylate

Simple First Order Model

$$M_p(t) = M_0 \exp(-kt)$$

Legend: Observed Data; Fitted SFO Model

X-axis: Time (days)
Y-axis: Residue (fraction of 14C applied)

Time (days)	Parent (fraction of 14C applied)	
	Observed	Fitted
0	0.9201	0.886
3	0.7928	0.805
7	0.7074	0.708
14	0.5528	0.566
20	0.4298	0.467
28	0.3589	0.362
59	0.1641	0.134
92	0.0959	0.047
150	0.0676	0.007
245	0.0437	0.000

Parameter	Estimate
m0 (fraction of 14C a	8.86E-01
k	3.20E-02
DT50 (days)	2.16E+01
DT90 (days)	7.19E+01
DT90 (days)	7.19E+01
R^2	9.87E-01
Adj R^2	9.86E-01
RMS	1.47E-03

Figure 2. ModelManager report showing the results of fitting the SFO equation to observed levels of butylate in soil.

ModelManager Report: Parent Only Study Type

Study Number: PMS-298
Study Name: Butylate Aerobic Soil Metabolism Study
Date of Analysis: 23-Apr-99
User Name: John Tarr

Dataset Name: Butylate

First Order Multi Compartment Model

$$M_p(t) = M_0 \left[\frac{t}{b} + 1 \right]^{-a}$$
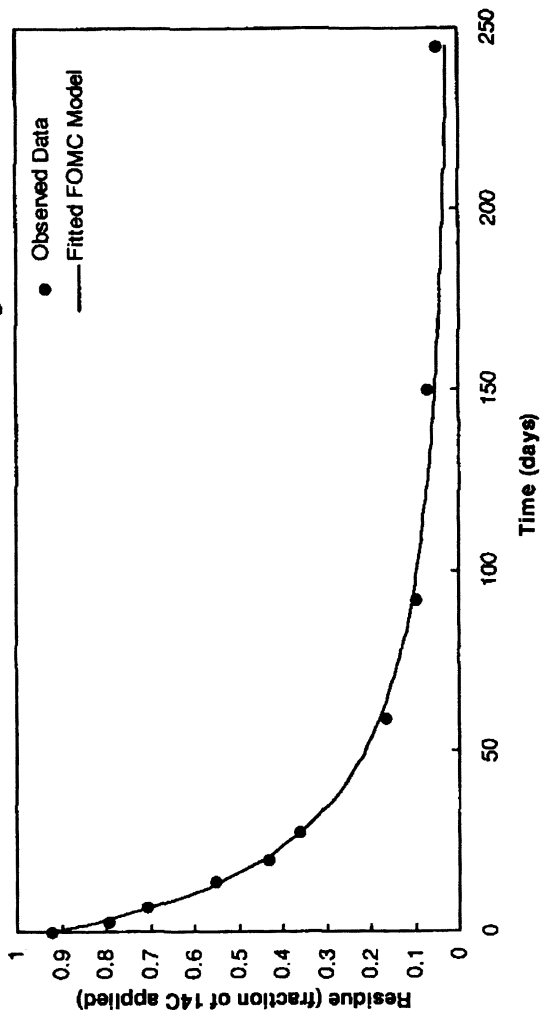
- ● Observed Data
- —— Fitted FOMC Model

Residue (fraction of 14C applied) vs Time (days)

Time (days)	Parent (fraction of 14C applied)	
	Observed	Fitted
0	0.9201	0.919
3	0.7928	0.809
7	0.7074	0.690
14	0.5528	0.538
20	0.4298	0.445
28	0.3589	0.355
59	0.1641	0.178
92	0.0959	0.105
150	0.0676	0.053
245	0.0437	0.025

Parameter	Estimate
m0 (fraction of 14C)	9.19E-01
a	1.90E+00
b	4.32E+01
DT50 (days)	1.90E+01
DT90 (days)	1.02E+02
DT90 (days)	1.02E+02
R^2	9.98E-01
Adj R^2	9.97E-01
RMS	2.65E-04

Figure 3. ModelManager report showing the results of fitting the FOMC equation to observed levels of butylate in soil.

ModelManager Report: Parent Only Study Type

Study Number: PMS-298
Study Name: Butylate Aerobic Soil Metabolism Study
Date of Analysis: 23-Apr-99
User Name: John Tarr

Dataset Name: Butylate

Hockey Stick Model

$$M_p(t) = \begin{cases} M_0 \exp(-k_1 t) & \text{for } t < t_b \\ M_0 \exp(-k_1 t_b - k_2(t - t_b)) & \text{for } t \geq t_b \end{cases}$$
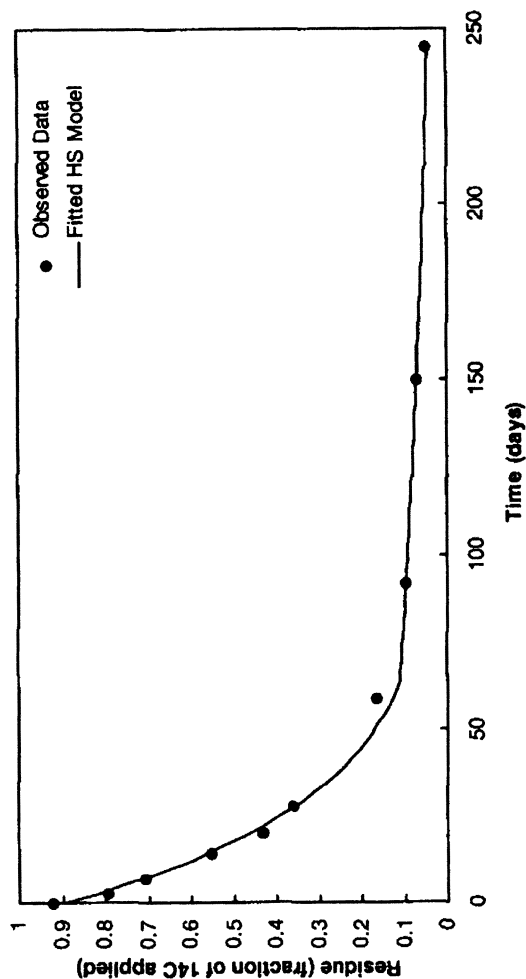
Time (days)	Parent (fraction of 14C applied)	
	Observed	Fitted
0	0.9201	0.894
3	0.7928	0.809
7	0.7074	0.708
14	0.5528	0.560
20	0.4298	0.459
28	0.3589	0.351
59	0.1641	0.125
92	0.0959	0.095
150	0.0676	0.070
245	0.0437	0.042

Parameter	Estimate
m0 (fraction of 14C)	8.94E-01
k1	3.34E-02
k2	5.28E-03
tb (days)	6.26E+01
DT50 (days)	2.08E+01
DT90 (days)	1.03E+02
DT90 (days)	1.03E+02
R^2	9.96E-01
Adj R^2	9.94E-01
RMS	5.73E-04

Figure 4. ModelManager report showing the results of fitting the HS equations to observed levels of butylate in soil.

ModelManager Report: Parent Only Study Type

Study Number: PMS-298
Study Name: Butylate Aerobic Soil Metabolism Study
Date of Analysis: 23-Apr-99
User Name: John Tarr

Dataset Name: Butylate

Comparison of Models
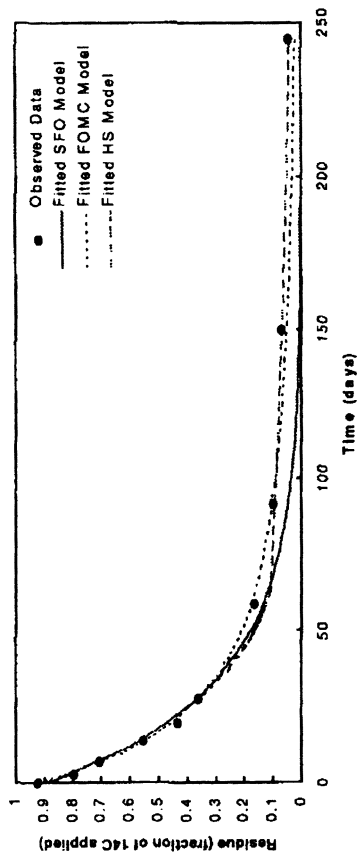
SFO Model

Parameter	Estimate	95% Confidence Limits
m0	0.8863	(0.824689 , 0.948)
k	0.032	(0.026115 , 0.03792)
DT50	21.65	(17.65961 , 25.6402)
DT90	71.919	(58.66396 , 85.175)
DT90	71.919	(58.66396 , 85.175)

HS Model

Parameter	Estimate	95% Confidence Limits
m0	0.8941	(0.852438 , 0.93584)
k1	0.0334	(0.029203 , 0.03755)
k2	0.0053	(-0.00416 , 0.01472)
tb	62.553	(33.83127 , 91.2749)
DT50	20.767	(18.16912 , 23.364)
DT90	103.22	(3.988948 , 202.449)
DT90	103.22	(3.988948 , 202.449)

SFO Model

Source	DF	Sum of Sq	Mean Sq
Model	2	2.625529	1.31276
Error	8	0.011731	0.00147
Uncorr. Total	10	2.637261	
(Corr. Total)	9	0.929009	

HS Model

Source	DF	Sum of Sq	Mean Sq

FOMC Model

Parameter	Estimate	95% Confidence Limits
m0	0.9189868	(0.88712 , 0.950855)
a	1.9047038	(1.18139 , 2.628009)
b	43.206299	(20.8724 , 65.54021)
DT50	18.965386	(16.9157 , 21.01503)
DT90	101.52521	(83.9721 , 119.0783)
DT90	101.52521	(83.9721 , 119.0783)

FOMC Model

Source	DF	Sum of Sq	Mean Sq
Model	3	2.63541	0.878469
Error	7	0.00185	0.000265
Uncorr. Total	10	2.63726	
(Corr. Total)	9	0.92901	

Figure 5. ModelManager report comparing the results of fitting SFO, FOMC and HS equations to observed levels of butylate in soil.

ModelManager Report: Parent and Metabolite Study

Study Number: Butylate Aerobic Soil Metabolism Study
Study Name: PMS-298
Date of Analysis: 23-Apr-99
User Name: John Tarr

Dataset Name: *Butylate sulfoxide*

FOMC with SFO Model

Sequential

$$M_p(t) = M_0 \left(\frac{t}{b_2} + 1 \right)^{-a_2}$$

$$M_n(t) = CM_0 \int_0^t \frac{a_2}{b_2} \left(\frac{t'}{b_2} + 1 \right)^{-(1+a_2)} \exp[-k_n(t-t')]dt'$$

Time (days)

Residue (fraction of 14C applied)

- ● Observed Parent
- ▲ Observed Metabolite
- —— Fitted Parent
- ·········· Fitted Metabolite

Time (days)	Parent (fraction of 14C) Observed	Fitted	Metabolite (fraction of 14C applied) Observed	Fitted	Parameter	Estimate
0	0.9201	0.918987	0.044	0	m0 (fraction of 14C applied)	9.19E-01
3	0.7928	0.808685	0.055	0.035024	C	3.21E-01
7	0.7074	0.690401	0.044	0.071521	kx	6.72E-03
14	0.5528	0.538433	0.126	0.115794	ap	1.90E+00
20	0.4298	0.445274	0.131	0.140485	bp	4.32E+01
28	0.3589	0.354849	0.132	0.161336		
59	0.1641	0.178272	0.224	0.181223		
92	0.0959	0.104622	0.168	0.16606	Parent	
150	0.0676	0.053009	0.112	0.125724	DT50 (days)	1.90E+01
245	0.0437	0.024748	0.07	0.072704	DT90 (days)	1.02E+02
					DT75 (days)	4.63E+01
					Metabolite	
					DT50 (days)	1.03E+02
					DT90 (days)	3.43E+02
					DT75 (days)	2.06E+02
					R²	9.94E-01
					Adj R²	9.93E-01
					RMS	5.35E-04

Figure 6. ModelManager report showing the results of fitting the FOMC equation for parent dissipation and the SFO equation for metabolite dissipation to observed levels of butylate and butylate sulfoxide in soil.

ModelManager Report: Parent and Metabolite Study

Study Number: Butylate Aerobic Soil Metabolism Study
Study Name: PMS-298
Date of Analysis: 23-Apr-99
User Name: John Tarr

Dataset Name: Butylate sulfoxide

FOMC with FOMC Model

Sequential

$$M_p(t) = M_0\left(\frac{t}{b_p}+1\right)^{-a_p}$$

$$M_x(t) = CM_0 \int_o^t \frac{a_p}{b_p}\left(\frac{t'}{b_p}+1\right)^{-(1+a_p)}\left[\frac{(t-t')}{b_x}+1\right]^{-a_x}dt'$$

Legend:
- ● Observed Parent
- ▲ Observed Metabolite
- —— Fitted Parent
- ······ Fitted Metabolite

y-axis: Residue (fraction of 14C applied)
x-axis: Time (days)

Time (days)	Parent (fraction of 14C) Observed	Fitted	Metabolite (fraction of 14C applied) Observed	Fitted	Parameter	Estimate
0	0.9201	0.918987	0.044	0	m0 (fraction of 14C applied)	9.19E-01
3	0.7928	0.808685	0.055	0.035027	C	3.21E-01
7	0.7074	0.690401	0.044	0.071526	ap	1.90E+00
14	0.5528	0.538433	0.126	0.1158	bp	4.32E+01
20	0.4298	0.445274	0.131	0.140491	ax	1.03E+03
28	0.3589	0.354849	0.132	0.161339	bx	1.53E+05
59	0.1641	0.178272	0.224	0.181217		
92	0.0959	0.104622	0.168	0.166048	Parent	
150	0.0676	0.053009	0.112	0.125717	DT50 (days)	1.90E+01
245	0.0437	0.024748	0.07	0.07272	DT90 (days)	1.02E+02
					DT75 (days)	4.63E+01
					Metabolite	
					DT50 (days)	1.03E+02
					DT90 (days)	3.43E+02
					DT75 (days)	2.06E+02
					R^2	9.94E-01
					Adj R^2	9.92E-01
					RMS	5.74E-04

Figure 7. ModelManager report showing the results of fitting FOMC equations for parent and metabolite dissipation to observed levels of butylate and butylate sulfoxide in soil.

Chapter 9

Laboratory, Greenhouse, and Field Lysimeter Studies of ^{14}C-Atrazine Volatilization

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Volatilization of ^{14}C-atrazine in laboratory and greenhouse studies was dependent on temperature, soil type and moisture content, air-flow rate, and exposure time. At an airflow rate of 2 L min^{-1} and temperature of 22 to 50°C, vapor losses of applied atrazine after a 6-h period were 0.4 to 7.8% from air-dry loamy sand and 0.6 to 15% from loamy sand at field capacity. Volatilization from three soils was inversely related to clay content and organic matter content and doubled as air-flow rate doubled. Atrazine volatilization from covered field lysimeters over a 30-d period was low and ranged from 6 to 8%. Volatilization from open lysimeters ranged from 21 to 37%, but vapor trapping systems were only partially effective.

Over the past twenty years pesticides, including atrazine, 6-chloro-*N*-ethyl-*N^1*-(1-methylethyl) - 1,3,5-triazine-2, 4-diamine, have been detected in rainwater (1, 2, 3), fog (4), air (5, 6, 7) and surface water (8, 9). The chemicals enter the atmosphere by physical drift of spray droplets during application, wind erosion of soil or plant particles

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Table I. Atrazine properties[a].

Parameter[b]	Description[b]
Chemical Family	Chloro-s-triazine
Molecular weight (g mol^{-1})	215.7
Physical state	White crystalline
Aqueous solubility (mg L^{-1})	33, pH 7, 22°C
K_{ow}	481, 25°C
Vapor pressure (mm Hg)	5.7×10^{-8}, 10°C
	3.0×10^{-7}, 20°C
	1.4×10^{-6}, 30°C
	6.0×10^{-6}, 40°C
	1.5×10^{-5}, 50°C
Henry's law constant (atm-m[3] mol^{-1})	2.48×10^{-9}
Melting point (°C)	173 to 175
pK_a	1.7, 21°C
Soil K_d (mL g^{-1})	0.20, sand, 0.9% OM, 2.2% CM, pH 6.5
	0.73, loam, 0.8% OM, 9% CM, pH 6.7
	0.79, sandy loam, 1.9% OM, 16.8% CM, pH 7.5
	2.46, clay, 4.8% OM, 42% CM, pH 5.9
Calc'd K_d^c (mL g^{-1})	0.5 ± 0.3, Dothan loamy sand, 1.1% OM
	1.2 ± 0.3, Rains sandy loam, 2.5% OM
	6.1 ± 0.3, Cape Fear loam, 12.1% OM

Calc'd K_d^d (mL g^{-1})	0.4 ± 0.2, Dothan loamy sand, 6% CM
	0.7± 0.2, Rains sandy loam, 12% CM
	1.0 ± 0.2, Cape Fear loam, 16% CM
$T_{1/2}$ - laboratory (d)	146 aerobic, loam, 25°C
	159 anaerobic, loam 25°C
$DT_{1/2}$ - field (d)	30, sandy loam, 1.7% OM, pH 6.8, GA
	119, sandy loam, 1.3% OM, pH 7.3, CA
	261, loam, 6.2% OM, pH 7.9, MN
	60, average

[a] Herbicide Handbook, (18).

[b] K_d = soil/solution distribution coefficient, OM = organic matter, CM = clay mineral, $T_{1/2}$ = half-life, $DT_{1/2}$ = half-dissipation time.

[c] Based on OM content (19).

[d] Based on CM content (19).

containing pesticides or wettable powder formulations, and/or volatilization during and after application.

Kearney et al. (10) studied volatilization losses of atrazine from metal planchets in the laboratory and reported losses ranging from 38 to 80%, at 25°C and 35°C, respectively, over a 6-h period. Loss from an air dry loamy sand was much lower and ranged from 5% at 35°C to 18% at 45°C over the same time period and appeared to be inversely related to soil organic matter and clay content. Loss was also greater from moist soil than from dry soil. In a similar study, Walker (11) reported a 57% loss of atrazine from metal planchets at room temperature (ca 20 to 25°C) over 24 h. Losses were reduced considerably when atrazine was present in co-extracted plant material.

Over a 48-h period and an air velocity of 2 L min^{-1} Burt (12) reported atrazine volatilization of 45 and 70% from glass surfaces at 20 and 40°C, respectively, and vapor losses of 18 to 27%, 50%, and 11%, were reported from dried plant material, living plant leaves, and soil surfaces, respectively, over the same time period at 40°C.

Direct measurement of atrazine vapor losses from soils in field studies were 2.5% in 21 d using air sampling and aerodynamic measurements (5), 4.5% in 26 d, as indicated by the difference between nominal application rates and residues measured on day 26 (13), and 9% in 35 d using acrylic chambers that sampled the atmosphere above the located field (6).

In undisturbed field lysimeter studies, Lee and Weber (14) reported ^{14}C vapor losses of 59% from ^{14}C-labeled atrazine treated Dothan loamy sand over a 90-d period. Keller and Weber (15) using the same system reported ^{14}C-atrazine volatilization of 63% in 1989 and 56% in 1990 over the same time period. Warren (16) and Taylor (17) reported ^{14}C vapor losses of 62 and 55%, respectively, from ^{14}C-atrazine-treated field lysimeters over a 130-d period.

Atrazine is a weakly basic, symmetrical, chloro-*s*-triazine herbicide that is used primarily as a soil-applied treatment for broadleaf and grass weed control in corn (18). Selected physicochemical properties of the compound are provided in Table 1. Atrazine is described as having low water solubility, low volatility, low soil reactivity, and moderate longevity in the soil environment (20).

The objectives of this paper were to compare ^{14}C losses of ^{14}C-atrazine in laboratory and greenhouse studies with losses in fallow field lysimeters. Parameters evaluated included temperature, soil type, soil moisture content and air-flow rate in the laboratory and greenhouse, and type of soil cover in the field.

Materials and Methods

Soil

Three soils were used in the laboratory studies and one soil was used in the greenhouse and field lysimeter studies. Laboratory and greenhouse soils were

Table II. Description and properties of 15 cm depth surface soils.

Parameter		Dothan	Rains	Cape Fear
Surface texture		loamy sand	sandy loam	loam
Taxonomic name		Plinthic Kandiudult	Typic Paleaquult	Typic Umbraquult
Textural class		fine-loamy	fine-loamy	clayey
Mineralogy class		siliceous	siliceous	mixed
Soil temperature range		thermic	thermic	thermic
Organic matter (OM)[a] (%)		1.1	2.5	12.1
Humic matter (HM)[b] (%)		0.3	1.1	6.0
Particle size[a]	sand (%)	84	56	52
	silt (%)	10	32	32
	clay (%)	6	12	16
Cation exchange capacity[a] (cmol kg^{-1})		3.5	5.5	11.1
1:1 water pH[a]		5.0	5.3	4.7
Weight/volume[b] (Mg m$^{-3)}$		1.35	1.23	0.93
Water content:	AD[c] (%, dry wt. basis)	0.3	2.2	4.5
	FC[d] (%, dry wt. basis)	24.4		

[a]Analysis by A & L Mid West Laboratories, Inc., Omaha, NE.

[b]Analysis by NC Department of Agriculture, Soil Test Laboratory, Raleigh, NC.

[c]AD=air-dry

[d]FC=field capacity.

screened to pass a 2-mm sieve. Descriptions and selected properties of the three soils are included in Table II. Additional details on the methodology are presented

elsewhere (21). The soils were all collected from the thermic region (15 to 22°C soil temperatures) of the U.S., also referred to as the cotton belt. Organic matter (OM) and humic matter (HM) contents ranged from 1.1 to 12.1%, and 0.3 to 6.0%, respectively. Clay mineral (CM) contents ranged from 6 to 16% and soil pH was in all cases strongly to very strongly acidic in reaction. Cation exchange capacities (CEC) ranged from 3.5 to 11.1 cmol kg^{-1}, and moisture contents of air dry samples ranged from 0.3 to 4.5%. Moisture content of Dothan loamy sand at field capacity (FC) was 24.4%.

Laboratory Studies

Studies 1, 2, and 3 were designed to evaluate ^{14}C-atrazine volatility as affected by soil system and temperature, soil type, and time of exposure (kinetics). Modified glass impingers, comprised of a bottom cylinder containing an 8-mL glass vessel, in which ^{14}C-atrazine treated soil was placed, and a top cylinder containing air-flow tubes and two polyurethane foam (PUF) traps were used in these studies. Regulated air entered the impinger from its top, passed over the contents of the vessel containing the treated soil and exited through the PUF plugs. The impingers were positioned inside of a forced-air oven at prescribed temperatures.

Greenhouse Study

In study 4, ^{14}C-atrazine volatilization, as influenced by air-flow rates was evaluated over a 7-d period in the greenhouse. A volatilization chamber consisted of a capped 250- mL Erlenmeyer flask equipped with an air intake tube centered and positioned approximately 75 mm over the soil surface. An outlet tube at the top of the flask expanded to contain two PUF plugs which were replaced daily. Regulated air was humidified and directed to each of 4 flasks via a pump and manifold. Chambers were positioned on a greenhouse bench and ambient air temperature was monitored with a temperature recorder.

Field Lysimeter Studies

Study 5 was designed to investigate ^{14}C-atrazine dissipation processes using fallow field lysimeters at the North Carolina State Unviersity Central Crops Research Station in Clayton, NC. Steel columns were driven into a conventionally-tilled Dothan loamy sand in the spring of 1993 and 1994 using a tractor-mounted post hole driver until 4 cm of the columns remained above the soil

surface (22). Soil was excavated from beneath each column and an aluminum foil-covered funnel and glass receptacle were installed to catch leachate. After study completion columns were extracted manually by use of a hoist, split and divided into 15-cm segments which were mixed, bagged and stored at 0°C. Treatments consisted of applying ^{14}C-atrazine to the soil surface in each column and equipping the columns to capture ^{14}C as dissipation occured as follows: Open (open)-column top open to the atmosphere, and surrounded by a 7.5-cm ID pan to catch splash erosion and Teflon tubing and catchment container to receive ponded water (runoff) deeper than 1 cm; Foil/plastic cover (F/P cover)- column top was covered by a double-layer of aluminum foil and a layer of polyethylene film held in place with plastic tape and hose clamps; Activated carbon cover (AC cover)- 50 g of Nuchar BX-MP40 4.0-mm OD pellets (Westvaco, Covington, VA) were layered evenly between two sheets of wire mesh and supported 2 cm above the soil surface; Bell jar cover (BJ cover)- an 18-L bell jar (23-cm ID) was placed on glass supports over the column top and connected by Teflon tubing to a vacuum pump manifold assembly equipped with PUF vapor trapping plugs and 1N NaOH CO_2-trapping solutions.

[14]C-Atrazine Applications and Analysis

[14]C-ring-labeled atrazine (specific activity = 0.54 TBq kg^{-1}) plus AAtrex Nine-0 formulation (Novartis Corporation, Greensboro, NC) in water/methanol solutions were applied to the surfaces of soils at 2.2 kg ha^{-1} atrazine in all studies (0.1g mist plus 0.5 mL ^{14}C-solution for air-dry treatment and 0.1 mL mist + 1.5 mL water + 0.5 mL ^{14}C-solution for FC treatment). Laboratory, greenhouse, and field studies received 8.7 to 9.6 kBq, 18.6 kBq; and 0.55 MBq of ^{14}C activity, respectively. Applied ^{14}C was quantified using 5-uL aliquots of solution and 0-d herbicide-fortified soil samples by liquid scintillation spectroscopy (LSS) (Packard TRI-CARB Model 2000cA, Packard Instruments Co., Downers Grove, IL). Volatile ^{14}C was removed from PUF traps with several 25-mL methanol rinse/squeeze extractions (100% recovery, CV=2.9%, n=8). All vessels were scrubbed with methanol solutions. One-mL aliquots were added to 15 mL of Scinteverse BD and analyzed by LSS. The proportion of ^{14}C-labeled atrazine was determined using normal phase thin-layer chromatographic (TLC) plates (Whatman Linear-K LK5F, Whatman USA, Hillsboro, OR) and primary (50:50 v/v toluene:ethyl acetate) and secondary (75:20:5 v/v/v toluene: acetone: acetic acid) solvent systems (23). R_f for parent atrazine in the primary solvent system was 0.67. Data were corrected for background radiation (0.47 Bq mL^{-1}). Extracts were stored at 1°C for further analysis. Volatile ^{14}C was extracted from activated carbon (sampled daily) with 750 mL of 1:1 v/v methanol:chloroform by sonication in a water bath at 25°C for 45 min. (80% recovery, CV = 2.0%, n = 12).

Leachate, splash out, runoff and trapped $^{14}CO_2$ (94% efficient, CV = 3.7%, n=12) were determined by LSS.

Soil samples from each treatment were thoroughly mixed and stored at -20°C for later analysis. After thawing, mixing, and weighing, four to twelve 1-g subsamples were combusted in a biological oxidizer (95% efficient) (Harvey OX 300, R.J. Harvey Instrument Co., Hillsdale, NJ) and the evolved $^{14}CO_2$ trapped in 15 mL of Harvey OX-161 Carbon-14 cocktail and quantified by LSS. Samples were corrected for background radiation of 0.59 Bq g^{-1} soil and moisture content determined by standard gravimetric methods.

All laboratory and greenhouse studies consisted of a randomized complete block design (RCBD) with two replications. Three replications of a RCBD were used in field lysimeter studies and all data were analyzed using PC SAS for Windows, version 6.08 (SAS Institute Inc., Cary, NC). The protected least significant difference (LSD) was used to separate means at the 5% level.

All ^{14}C wastes were disposed of by the North Carolina State University Life Safety Services following proper procedures (24). A weather station provided climatic data and a pan evaporator provided data on evaporative losses (25).

RESULTS AND DISCUSSION

Laboratory Studies

Volatility of ^{14}C-atrazine increased with increasing temperature from 1% at 22°C to 9% at 40°C and 27% at 50°C in the control (no soil) system (Table III) following the increase in vapor pressure with increasing temperature (Table I). Volatility of ^{14}C-atrazine from air-dry (AD) and FC soil systems was similar (4%) and less than half that of the control (9%) at 40°C. At 50°C volatility was 70 and 44% less in AD and FC soil, respectively, as compared to the control. The influence of temperature, soil, and moisture on atrazine volatility has been reported previously, but reported losses were considerably higher (10, 11, 12). Analysis of the soil phase confirmed that ^{14}C-atrazine was not lost from the system as noted by total recoveries ranging from 97 to 103% (Table III), an aspect not evaluated in previous studies.

^{14}C-atrazine volatilization from three AD soils at 50°C over a 6-h period ranged from 0.2% for Cape Fear loam, to 1.0% for Rains sandy loam and 10% for Dothan loamy sand (Table IV). As noted in Table II, volatility was inversely

related to OM, HM, CM, and water contents and CEC of the soils. Total ^{14}C recovery ranged from 96 to 97% (Table IV). ^{14}C-atrazine volatilization from AD Dothan loamy sand at 50°C and an air-flow of 2.0 L min^{-1} in Study 1 (Table III) amounted to 7.8% of applied, which was in agreement with a loss of 10% in Study 2 (Table IV) under similar conditions.

Table III. [14] **C-distribution from** [14]**C-atrazine-treated soil (Study 1).**[a]

Soil System	^{14}C-Distribution	Temperature (°C)		
		22	40	50
Control	Volatile phase	1.1a	9.2c	27e
(No soil)	Soil phase	101a	89a	75b
	Total	102a	98a	102a
AD soil	Volatile phase	0.4a	4.1b	7.8c
	Soil phase	99a	96a	89a
	Total	99a	100a	97a
FC soil	Volatile phase	0.6a	4.1b	15d
	Soil phase	98a	98a	88a
	Total	99a	102a	103a

[a]Units are percent of applied [14]C. Glass impinger chambers used with 10g Dothan loamy sand and 2.0 L min^{-1} air-flow rate over a 6-h period. Means within a given category followed by the same letter are not significantly different at the 0.05 level.

Table IV. [14]**C-volatilization from** [14]**C-atrazine-treated soils (Study 2)**[a]

[14]C-Distribution	Dothan loamy sand	Rains sandy loam	Cape Fear loam
Volatile phase	10a	1.0b	0.2c
Soil phase	87b	95a	96a
Total	97a	96ab	96.2 b

[a]Units are percent of applied [14]C. Glass impinger chambers used with 7 g of air-dry soil at 50°C and 2.0 L min^{-1} air-flow rate over a 6-h period. Means within a given category followed by the same letter are not significantly different at the 0.05 level.

Effects of OM and CM contents of soils on binding atrazine and reducing its volatilization have been reported previously (10). Reported soil/solution distribution coefficients (K_d) for atrazine range from 0.20 to 2.46 mL g^{-1} and are directly related to OM and CM contents of soils (Table I). Calculated K_d values (mL g^{-1}) using equations based on CM or OM contents of the three soils used in these studies were respectively, as follows: Dothan loamy sand 0.4 ± 0.2 and 0.5 ± 0.3; Rains sandy loam 0.7 ± 0.2 and 1.2 ± 0.3; and Cape Fear loam 1.0 ± 0.2 and 6.1 ± 0.3 (Table I).

A kinetic study (Study 3) of ^{14}C-atrazine volatilization from control (no soil) and AD and FC Dothan loamy sand at 50°C and an air-flow rate of 2 L min^{-1} showed that the vapor losses from the control treatment were much higher than those for the soils, as indicated by cumulative losses over the 16-h period of 76, 9.7, and 30%, respectively (Table V). Mean hourly losses decreased in a linear fashion for all treatments, with the exception of the 2-h measurement of the FC soil where losses were only 1.4%, probably because of reduced air flow through soil pores that contained 24% moisture. Overall mean volatilization of ^{14}C-atrazine from AD soil was less than one-eighth (0.6%) that of the control (4.8%), but increased by more than three times from the FC soil (1.9%). Volatilization losses of ^{14}C-atrazine from control, AD, and FC Dothan soil from Study 3 were in general agreement with losses from Study 1 under the same conditions (compare 36 vs 27%, 6.4 vs 7.8%, and 10 vs 15% for 4-h and 6-h periods, respectively) (Tables V and III, respectively).

Greenhouse Study

A second kinetic study (Study 4) of ^{14}C-atrazine volatilization over a 7-d period (12-h day^{-1} trapping) from Dothan loamy sand at FC in the greenhouse showed that air-flow rate had a substantial effect (Table VI). Highest losses occurred on the first day and amounted to 3.3% at an air-flow rate of 1 L min^{-1} and twice as much or 7.2% at an air-flow rate of 2 L min^{-1}. The 7.2% loss in 12 h at green-house temperatures of 22 to 36°C (Table VI) is comparable to the 4.1% loss in 6 h at 40°C (Table III), at similar air-flow rates from the Dothan loamy sand at FC. Daily volatility losses of ^{14}C-atrazine decreased with time in a curvilinear pattern at both 1 and 2 L min^{-1} air-flow rates and amounted to 8.8 and 18.3%, respectively, over the 7-d period (Table VI). No ^{14}C-atrazine volatilized in the static systems with 0 air-flow. Total ^{14}C recovered ranged from 98 to 101%.

Table V. [14]C volatilization from ^{14}C-atrazine treated soil (Study 3)[a].

Soil System	Measured parameter	Time (h)				Overall mean hourly loss
		2	4	8	16	
Control (No soil)	Loss	19	16	28	12	
	Cumulative loss	19c	36e	64f	76g	4.8
	Mean hourly loss	9.7f	8.2e	7.1e	1.5abc	
AD soil	Loss	3.4	2.7	2.7	0.6	
	Cumulative loss	3.4a	6.4ab	9.1b	9.7b	0.6
	Mean hourly loss	1.7bc	1.5abc	0.7ab	0.6a	
FC soil	Loss	2.7	7.0	11	9.0	
	Cumulative loss	3.0a	10b	21c	30d	1.9
	Mean hourly loss	1.4abc	3.7d	2.8cd	1.1ab	

[a]Units are percent of applied [14]C. Glass impinger chambers used with 10 g of Dothan loamy sand at 50°C and 2.0 L min^{-1} air-flow rate over a 16-h period. Means followed by the same letter are not significantly different at the 0.05 level for respective parameters.

Table VI. [14]C volatilization from ^{14}C-atrazine treated soil (Study 4)[a].

Air-Flow rate (L min^{-1})	Day (12 -h day^{-1} trapping)							Cumulative Volatile Phase	Residual Soil Phase	Total
	1	2	3	4	5	6	7			
0 (static)	0a	0a	0a	0a	0a	0a	0a	0a	101a	101a
1.0	3.3b	2.0b	1.0b	0.7b	0.5b	0.7b	0.7b	8.8b	89b	98a
2.0	7.2c	4.3c	2.0b	1.2b	0.9b	1.5b	1.2c	18.3c	80c	99a

[a]Units are in percent of applied [14]C. 250 mL Erlenmeyer flasks containing 100 g Dothan loamy sand with water content adjusted daily to field capacity (24%) and ambient temperature of 22 to 36°C in the greenhouse. Means within a column followed by the same letter are not significantly different at the 0.05 level.

Field Lysimeter Study

Daily air temperatures (°C) for study 5 are given in Table V11.

Total water inputs (rainfall and applied) and estimated evaporative losses (cm) using pan evaporator (25) for study 5 lysimeters over the 22 to 30-d period, except the F/P covered ones, were as follows: 1993A 10.1 and 6.7, 1993B 6.6 and 3.0, 1994 16.0 and 9.1. Water input and evaporative loss for the F/P covered lysimeters for the 1993 and 1994 studies were zero.

Mass balance of ^{14}C distribution in ^{14}C-atrazine treated lysimeters over the 21 to 30-d periods for each year is shown in Table VIII for Study 5. Soil and measured total recoveries of applied ^{14}C were highest in F/P covered treatments (92%), lower in AC covered treatments (88%) and similar between open (74%) and BJ covered (72%) treatments in 1993A. Highest amounts of ^{14}C were also recovered in the soil in 1993B and 1994, but in 1993B similar amounts (94 to 98%) were recovered from all of the covered lysimeters and only 79% was recovered from the open lysimeters. In 1994, 86% was recovered in the F/P covered treatments but only 63 to 75% recovered from open, AC, and BJ covered treatments, respectively. Soil and measured total recoveries were probably lower in 1994 than in 1993 due to higher temperatures, greater water input and a longer exposure time.

Less than 1% of applied ^{14}C-atrazine was recovered in splash out or runoff containers from the open lysimeters (Table VIII).

Measured volatile ^{14}C from AC and BJ lysimeters ranged from 0.76 to 0.85% in 1993A, 0.42 to 1.9% in 1993B, and 0.83 to 4.0% in 1994 (Table VIII). Trapped $^{14}CO_2$ was negligible except in BJ covered lysimeters in 1994, where it was 0.38% of applied ^{14}C.

Leachate volumes for the fallow open, AC covered, and BJ covered lysimeters approximated that for unaccounted-for losses when the estimated evaporative losses are subtracted from the input volumes (Table VIII). Unaccounted-for volumes amounted to 3.4 cm (10.1 cm input - 6.7 cm evaporative losses), 3.6 cm (6.6 cm input - 3.0 cm evaporative losses), and 6.9 cm (16.0 cm input - 9.1 cm evaporative losses), for 1993A, 1993B, and 1994, respectively. Leachate volumes for the three lysimeters for the three time periods were 2.8, 3.4, and 1.7 cm, 1.1, 2.1, and 1.7 cm, and 1.0, 0.7, and 1.3 cm, respectively. Leachate through the fallow lysimeters, with the exception of the F/P covered lysimeters which had zero water input, zero evaporative losses, and zero leachate, thus amounted to approximately 31% (10.1 cm/3.1 cm x 100), 34% (10.1 cm/3.4 cm x 100), and 25% (10.1 cm/2.5 cm x 100) of water input, respectively, for 1993A, 35% (6.6 cm/2.3cm x 100), 38%(6.6 cm/2.5 cm x 100), and 41% (6.6 cm/2.7cm x 100) of water input, respectively, for 1993B, and 40% (16.0 cm/6.4 cm x 100),

Table VII. Daily air temperatures (○C) for the field lysimeters (Study 5).

Year	Temperature	Open[a]	Foil/Plastic cover[b]	Activated Carbon[c] and Bell Jar cover[d]
1993A	Maximum	43	NM	53
	Mean maximum	37	NM	45
	Minimum	19	NM	22
	Mean minimum	22	NM	25
1993B	Maximum	33	NM	40
	Mean maximum	25	NM	33
	Minimum	0	NM	11
	Mean minimum	12	NM	18
1994	Maximum	34	NM	54
	Mean maximum	32	NM	45
	Minimum	14	NM	16
	Mean minimum	22	NM	22

[a]Lysimeter top open to the atmosphere.
[b]Lysimeter top covered with heavy foil and polyethylene film. NM = not measured, but probably higher than open lysimeters.
[c]Lysimeter top covered with activated carbon pellets layered in wire mesh.
[d]Lysimeter top covered with bell jar (1993) or Teflon cover (1994).

41% (16.0 cm/6.5 cm x 100), and 47% (16.0 cm/7.5 cm x 100) of water input, respectively, for 1994. High leachate for fallow lysimeters in this area of low groundwater recharge has been reported previously (14, 15, 20), but very low leachate has been reported to occur through lysimeters containing growing plants (soybean or turf) (25).

Recovered ^{14}C from equipment rinses was negligible except from the BJ covered treatments where amounts were 0.05% in 1993A and 1993B, and 0.04% in 1994 (Table VIII).

Assumed vapor losses calculated by subtracting measured total losses from 100% were very small from the F/P covered lysimeters and amounted to 7.2% in 1993A, 5.5% in 1993B, and 14.4% in 1994 (Table VIII). These unaccounted-for losses were higher in 1994 probably because of higher temperatures and longer exposure periods. Assumed ^{14}C vapor losses from open lysimeters were generally the highest of the treatments with 25.6% loss in 1993A and 20.6% loss in 1993B over the 21 and 22-d periods, respectively, and 37.1% loss in 1994 over a 30-d period. These values are lower than the 56% assumed vapor losses over 30-d periods in 1989 and 1990 from similar systems (15). The 1989 and 1990 studies were carried out under higher temperatures and water inputs.

Table VIII. ^{14}C-distribution from ^{14}C-atrazine treated Dothan loamy sand field lysimeters (Study 5).

Year[a]	Parameter[b]	Open[c]	Foil/Plastic Cover[d]	Activated Carbon Cover[e]	Bell Jar Cover[f]
1993A	Soil	73.6b	92.0a	87.6a	71.3b
	Splash Out	0.75	NA	NA	NA
	Runoff	0.04	NA	NA	NA
	Measured volatile	NA[g]	NA	0.85	0.76
	Measured CO_2	NA	NA	NA	NA
	Equipment rinses	NA	NA	NA	0.05
	Leachate	0.0	0.0	0.0	0.0
	Measured Total	74.4b	92.0a	88.5a	72.3b
	Assumed Vapor Loss[h]	25.6	7.2	11.5	27.7
	Leachate Volume	2.8b	0.2c	3.4a	1.7bc
1993B	Soil	78.8b	94.5a	96.5a	96.0a
	Splash Out	0.6	NA	NA	NA
	Runoff	0.05	NA	NA	NA
	Measured volatile	NA	NA	1.9	0.42
	Measured CO_2	NA	NA	NA	NA
	Equipment rinses	NA	NA	NA	0.05
	Leachate	0.0	0.0	0.0	0.0
	Measured Total	79.4b	94.5a	98.5a	96.5a
	Assumed Vapor Loss	20.6	5.5	1.5	3.5
	Leachate Volume	1.1a	0.0b	1.5a	1.9a

1994				
Soil	61.7b	85.6a	71.4b	70.3b
Splash Out	0.58	NA	NA	NA
Runoff	0.67	NA	NA	NA
Measured volatile	NA	NA	0.83	4.0
Measured CO_2	NA	NA	NA	0.38
Equipment rinses	NA	NA	NA	0.04
Leachate	0.0	0.0	0.0	0.4
Measured Total	62.9c	85.6a	72.3bc	74.7b
Assumed Vapor Loss	37.1	14.4	27.7	25.3
Leachate Volume	5.9a	0.0c	6.2b	8.2a

[a]1993A - 20-cm ID x 91-cm length steel column lysimeters used for 21-d; 1993B - 20-cm ID x 61-cm length lysimeters used for 22-d; 1994 - 20-cm ID x 61-cm length lysimeters used for 30-d; lysimeter top 4 cm above soil surface in all cases. Water input and evaporative losses for each year were 10.1 and 6.7, 6.6 and 3.0, and 16.0 and 9.1, respectively.

[b]Units are percent of applied ^{14}C, except leachate volumes which are in cm. For a given year within a row (across). means followed by the same letter are not significantly different at the 0.05 level.

[c]Lysimeter top open to the atmosphere and surrounded by a 7.5-cm ID pan, and Teflon tubing and catchment container to receive ponded water deeper than 1 cm.

[d]Lysimeter top covered with heavy foil and polyethylene film.

[e]Lysimeter top covered with activated carbon pellets layered in wire mesh.

[f]Lysimeter top covered with bell jar (1993) or Teflon cover (1994) attached to vapor traps and vacuum pump with Teflon tubing at a flow-rate of 5 L min^{-1}.

[g]NA = not applicable.

[h]Computed by subtracting total measured ^{14}C from 100 percent.

Comparison of Atrazine Volatilization Studies

Atrazine volatilization from metal planchets, glass, and dry and fresh plant matter was reported to be dependent on the following: surface to which it was applied, time, temperature, and air-flow rate. Reported losses from metal planchets ranged from 40 to 95% over time periods ranging from 6 to 48-h and temperatures ranging from 25 to 35°C (10,11). Calculated losses ranged from 1.67 to 13.33% h^{-1}.

Atrazine vapor losses from glass surfaces were relatively low at temperatures <22°C (0.18 to 0.50% h^{-1}) (12, Table III) but increased greatly with temperature, and amounts lost at 50°C ranged from 19 to 76% with calculated hourly losses of 4.50 to 9.50% h^{-1} (Table III and V). Volatilization of atrazine from dry plant matter was lower than losses from glass at the same temperature (40°C) and air-flow rate (2 L min^{-1}) and amounted to 30 and 22%, respectively, and hourly loss rates of 0.62 and 0.47% h^{-1}, respectively (12). Atrazine losses from fresh plant leaves was more than twice that volatilizing from dry plant matter with losses of 22 and 50%, respectively, and hourly losses of 0.47 and 1.04% h^{-1}, respectively (12).

Vapor losses of atrazine from a variety of soils under field and laboratory conditions have been reported to be dependent on soil texture, OM and moisture content, time, temperature, and air-flow rate (5, 6, 13, 14, 15, 16, 17, and Table VIII). Atrazine volatilization from field soils at ambient temperatures ranged from 0.3 to 63% of applied, depending on time of exposure, method of measurement and probably climatic conditions. Calculated hourly losses ranged from 0.005 to 0.051 % h^{-1}.

Atrazine volatilization from soils in laboratory studies was dependent on texture and OM content and increased as texture became coarser and OM content decreased (compare losses of 10, 1.0, and 0.2% from loamy sand (1.1% OM), sandy loam (2.5% OM), and loam (12.1% OM), respectively, under similar conditions (Table IV). Volatilization of atrazine (% of applied lost) from moist soils has been reported to be twice as high as from air-dry soils (6, 10, 12). In our studies losses were two to three times as high from soils at FC as from air-dry soils under comparative conditions (Tables III, IV, V, VI).

Vapor loss rates (% h^{-1}) of atrazine were reported to decrease with time in linear or curvilinear fashion in comparative systems (10).

Volatilization of atrazine (% of applied loss) increased logarithmically with temperature from air-dry soils and from the same soils at FC over the same time period and respective temperatures (Table III).

Atrazine volatilization (% of applied lost) from loamy sand at FC was twice as high at an air-flow rate of 2 L min^{-1} as it was at 1 L min^{-1} (Table VI).

Acknowledgment

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Chapter 10

S, S, S-Tributyl Phosphorotrithioate Washoff and Dissipation of Foliar Residues

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Individual mature cotton leaves were treated with [^{14}C]tribufos and subjected to intense rainfall during a 15-day post-treatment interval. Ten centimeters of washoff from each leaf was collected as 1-cm fractions. Radioactivity in each fraction and the amount remaining on each washed leaf was quantified at each of six time intervals. Washoff decreased over time and was found to be negligible after 3 days post-treatment compared to the amount of tribufos which was applied. The first 1-cm fraction of rainfall was found to be the most effective at washing foliar residues of tribufos from treated leaves at all time intervals. Unwashed treated leaves were also analyzed to determine the foliar dissipation of tribufos over the course of the study. Tribufos dissipated with a foliar half-life of 20.0 days ($R^2 = 0.70$). The greenhouse test procedure was shown to be a useful method to quantify foliar washoff potential.

Tribufos (S,S,S-tributyl phosphorotrithioate) is an organophosphate herbicide which is applied to mature cotton plants as a defoliant to aid mechanical harvesting. This unique use pattern dictates that the compound be applied to a closed, or nearly closed, plant canopy approximately 7 to 15 days before harvesting. Since the

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chemical is applied only to mature plants, the majority of the spray application is intercepted by the plant canopy, with little deposition on the soil surface. Relevant physicochemical properties of tribufos are provided in Table I. Tribufos has a low water solubility (2.3 mg L^{-1}) and relatively high soil Koc (4,870 - 12,684 mL g^{-1}).

A primary consideration of the environmental fate and transport for tribufos, the active ingredient (a.i.) of DEF®, is the potential for rainfall to wash the compound from cotton leaves. Clearly for a foliar applied pesticide such as tribufos, the contamination of local water resources in an agricultural setting is dependent upon the compound washing off treated leaves and moving from the field in runoff. Upon treatment with tribufos, cotton plants undergo significant physiological changes. This laboratory/greenhouse study was performed to measure tribufos washoff from cotton leaves up to 15-days post-treatment. Treated leaves were subjected to simulated rainfall having a statistically-significant (approximately 1-in-10 years) return frequency in Mississippi. Therefore, the study provides data for extreme storm events.

The study was performed using radiolabeled tribufos to allow convenient measurement of tribufos present on individual cotton leaves prior to rainfall, a.i. present in washoff fractions, and a.i. retained on the treated leaves after significant rainfall (i.e., bound residues). The goal was to generate data which define the foliar dissipation and potential for runoff losses as influenced by rainfall amount and post-treatment timing.

Table I. Physical and Chemical Properties of Tribufos

Parameter	Units	Value[a]	Study Date
Molecular weight	g mol^{-1}	314.5	
Physical state		liquid	
Water Solubility 20°C	mg L^{-1}	2.3	1980
K_{ow} 20°C		1,700	1987
Vapor pressure 20°C	torr	1.7E-06	1987
Melting point	°C	< -25	
Boiling point	°C	Decomposes > 210	
Henry's law constant	Pa m^3 mol^{-1}	0.029	1986
Aerobic soil half-life	days	10 - 173	2001
Soil K_{oc}	mL g^{-1}	4,870 - 12,684	1987

[a] Bayer Corporation, Agriculture Division, Kansas City, MO.

Materials and Methods

Cotton plants were grown under greenhouse conditions in individual containers with approximately five gallons of soil. Plants received water daily until application of the test material. The mature cotton plants were approximately 2.5 feet in height when treated. Following treatment, the plants were maintained in a greenhouse for 15 days with only minimal water added after the defoliation process was initiated. A collection tray was placed at the bottom of each plant to contain any water that leached through the soil. No leachate was recovered during the study.

Preparation and Application of Tribufos

The experiment was designed to simulate agricultural use conditions of tribufos. Therefore, cotton plants were treated with the commercially-available DEF® 6 EC formulation while following all safety precautions on the product label. This application initiated defoliation of the cotton plants. A secondary treatment solution of [14C]tribufos in blank EC formulation was prepared to treat selected leaves. A nominal amount of radiolabeled test material applied to individual leaves allowed the use of radiometric procedures for sample analysis. Storage, handling, analyses and disposal of radioactive material during the conduct of this study was conducted in accordance with all appropriate licensing and Standard Operating Procedures of Bayer Corporation, Kansas City, Missouri.

The commercial DEF® 6 (6 lb a.i. gallon^{-1} or 720 g a.i. L^{-1}) treatment solution was prepared by transferring 1 mL of commercial DEF® 6 into a 500-mL graduated cylinder and diluting it to 425 mL with water. The application solution was prepared to deliver a total of 17 mg tribufos per plant, or 0.85 mg/leaf. This rate is equivalent to a nominal 2 pints of DEF® 6 per acre, assuming 40,000 plants/acre and 20 leaves per plant.

The [14C]tribufos treatment solution was prepared by first transferring approximately 221 µCi of [14C]tribufos (219 µCi/mL in acetonitrile) into a 13-mL centrifuge tube. Acetonitrile was evaporated and the [14C]residue was dissolved with 100 µL blank DEF® 6 formulation and sonicated. The solution was then diluted to 13 mL with HPLC-grade water and vortexed. The treatment solution was radioassayed by Liquid Scintillation Counting (LSC) for quantitation of [14C]tribufos residues and analyzed by HPLC to verify the radiochemical purity of the treatment solution.

Before application of the DEF® treatment solutions, all bolls were removed from the cotton plants and discarded in order to avoid complication of radioactive

uptake by this part of the plant. Twenty plants were treated with the commercial DEF® 6 solution. Approximately 10 mL of the application solution was sprayed evenly on each plant using a spray bottle. Four leaves from each of sixteen plants were then treated with 100 µL/leaf of radiolabeled DEF® solution to provide a nominal 29.6 µg/leaf of radiolabeled tribufos. The radiolabeled DEF® treatment solution was applied drop-wise using a syringe while making sure none of the test material dripped off the leaves. The stem of each leaf treated with [¹⁴C]tribufos was tagged with a small piece of tape. Four plants were used as study control, and none of their leaves were treated with radiolabeled material. Following treatment, all plants were maintained in a greenhouse until being used for washoff testing or otherwise sampled during the study.

Experimental Design and Sampling

Rainfall Simulator and Washoff Collection

Rainfall was simulated using an agricultural spray boom fitted with two (TeeJet FL-5VS) spray nozzles spaced on 140-cm centers. The spray boom was positioned approximately 1.5 meters above the cotton leaves to achieve a uniform spray pattern. A pressure gauge was placed in-line between the spray boom and a tap water source. During each washoff test, water pressure from the supply was maintained at 15 ± 5 psi. A single spray boom regulated to deliver approximately 4.5 cm/hr was used for all washoff tests. This precipitation rate is approximately equal to a rainstorm with a one-in-ten-year return frequency in central Mississippi(1). On each sampling day, four collection systems were placed under the spray boom to collect washoff. A washoff collection system consisted of a 4-mm wire mesh disc seated inside a 30.5-cm diameter plastic funnel which directed water into a 1-quart glass jar. A calibration mark was added to each jar to allow the collection of 1-cm of simulated rainfall intercepted by the funnel (730 mL). A series of ten jars was used for each washoff test to capture 10, 1-cm increments of washoff from each leaf.

At each of six post-treatment intervals, three plants were selected at random (2 treated with [¹⁴C]tribufos; and 1 control at specified intervals). Two of four leaves previously treated with radiolabeled test material were removed from each of the two treated cotton plants and subjected to simulated rainfall. Leaf washoff was collected in 1-quart glass jars. As washoff in the jar reached the 1-cm washoff mark, the time was documented and the jar was replaced, thereby obtaining data to confirm the rainfall intensity and allowing washoff to be quantified as ten, 1-cm rainfall/washoff intervals. Duplicate control leaves were subjected to the simulated

rainfall for comparison to the treated replicates. A separate runoff collection apparatus was used for the control leaves to avoid possible radiochemical contamination. The two treated leaves on each plant that were not subjected to simulated rainfall were removed and analyzed for [^{14}C] content.

Following washoff testing, samples were transported from the greenhouse to an analytical laboratory at the test site. A magnetic stir bar was added to the washoff jars, and the samples were mixed on a stir plate. The radioactive content of each washoff jar was determined by LSC using three, 4 - 5 mL aliquots.

Cotton Leaves, Plants, and Soil

At each time interval, two washed and two unwashed leaves from each of two treated plants (and one control plant at designated intervals), were cut into small segments and oxidized to $^{14}CO_2$. $^{14}CO_2$ was captured in a trapping solution and radioassayed by LSC to quantify the amount of [^{14}C]tribufos present on replicate leaves before and after washoff by rainfall.

Following the removal of its [^{14}C]-treated leaves, each cotton plant was removed from its container and homogenized with dry ice to determine if radioactive residues were translocated from the treated leaves to the remainder of the plant. The homogenized samples were placed in a walk-in freezer (-25 °C) to allow sublimation of the dry ice. Aliquots ranging from 200-250-mg of the homogenized residues were then radioassayed.

The soil used to grow the cotton plants was sampled at 1, 3 and 15 days after treatment. Soil was radioassayed to determine if any translocation of radioactive residues had occurred. The soil in each 5-gallon bucket was mixed thoroughly and air-dried. Triplicate aliquots were oxidized to $^{14}CO_2$ and radioassayed.

Results and Discussion

Elapsed times were recorded during each rainfall simulation and washoff test at 0, 1, 3, 6, 10, and 15 days post-treatment. These data, along with nominal volumes of the individual washoff fractions, allowed the calculation of simulated rainfall rates. The average rate of simulated rainfall over the course of the study was 1.71 in/h (4.34 cm/h). The target rainfall rate for the study was 1.75 in/h (4.45 cm/h). A storm of this intensity has a one-in-ten year return frequency in Mississippi (1). Thus, the study was successful in simulating an intense, Mississippi rainfall of environmental and regulatory significance.

Dissipation of Tribufos from Treated Leaves

Residues of [^{14}C]tribufos on unwashed treated leaves declined over the course of the study. The decline of these residues followed first-order decay. Average residues of tribufos on unwashed treated leaves are presented in Table II and are expressed in terms of percentage of applied radioactivity. Foliar residues from unwashed leaves declined from 86.8 % of the nominal dose at Day 0 to 42.1 % at Day 15. It is important to note that the analysis of treated leaf tissues involved the oxidation of entire leaves to recover total radioactivity as $^{14}CO_2$. This facilitated recovery of the applied radiocarbon without concern for leaf uptake or strong binding. This determination method provides a level of confidence that all radioactivity from the treated leaves was recovered. A first-order half-life was calculated based on these results. The foliar half-life over the course of the study was 20.0 days (R^2=0.70). No radioactive residues were found on any untreated leaves from control plants over the course of the study.

Table II. Tribufos Residues on Treated Leaves and Cumulative Washoff

Days After Treatment	Residual % of Dose	Cumulative Washoff (% of Dose) at Rainfall Amount (cm)					
		1	2	3	4	5	10
0	86.8	55.7	61.5	63.5	64.5	65.1	66.8
1	66.9	11.6	13.2	13.8	14.3	14.7	15.8
3	55.7	3.2	3.5	3.6	3.7	3.8	4.0
6	55.0	0.9	1.0	1.2	1.3	1.3	1.5
10	59.3	0.4	0.6	0.7	0.7	0.7	0.9
15	42.1	0.5	0.5	0.6	0.6	0.7	0.8

The potential for translocation of the test material within the plant was quantified by radiochemical analysis of the entire plants after the ^{14}C-treated leaves were removed for use in the experiment. Less than 1% of the radioactivity from the treated leaves was recovered in remaining plant tissues at each time interval. Translocation of the test material away from the treated leaves did not contribute to the observed foliar dissipation of radiolabeled tribufos.

Soil used to grow the cotton plants was mixed and sampled 1, 3 and 15 days post-treatment. Samples were radioassayed to determine if the test material moved into the soil during the dessication period. Radioactivity in the soil was not above background for the majority of samples and the highest total recovery for a single

plant was only 1.8% of the dose. The highest average value was 1.5% of applied at 15 days post-treatment. The levels of radioactivity observed in the plants and soil do not account for the overall dissipation observed from the treated leaves.

Washoff of Tribufos from Treated Leaves

Summarized results of washoff testing are shown in Table II. These results provide the average washoff per cm rainfall among the four replicate leaves on each testing day. The results in Table II illustrate the rapid washoff of the test material from treated leaves with the first 2-3 cm of rainfall. These results are also presented in Figure 1 and clearly show the decrease in tribufos washoff from the treated leaves with time post-application.
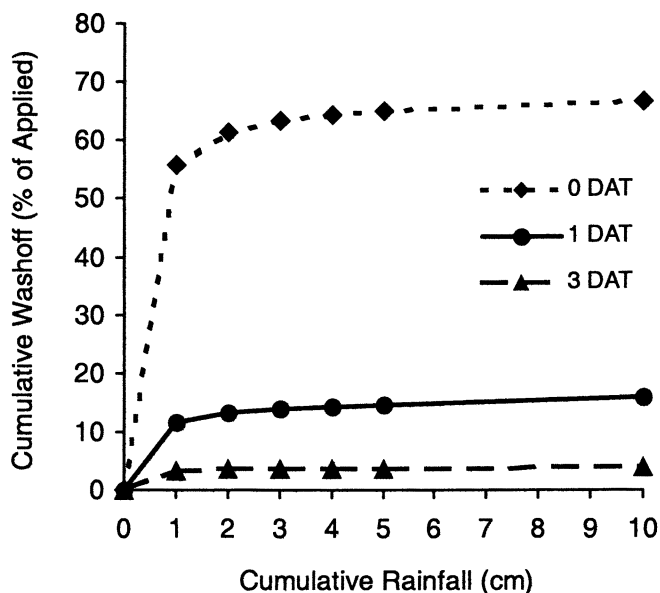
Figure 1. Cumulative Washoff % at 0, 1, and 3-Days After Treatment (DAT)

Examination of the results demonstrates that time post-treatment is the driving factor for total washoff of tribufos under the experimental conditions tested in this

study. These results for tribufos are similar to those previously reported for other pesticides by McDowell et al in 1985 (2), Sundaram in 1994 (3), and Willis et al in 1992 and 1994 (4,5,6). Except for the day of treatment, increasing cumulative rainfall did not significantly influence total tribufos washed from the treated leaves after the first centimeter of rainfall at each time interval. On day 0, about 83% of the total washoff was recovered from the first centimeter of rainfall. At each time interval, the first 1-2 cm of rainfall removed the majority of the total residue recovered in washoff fractions. Although for other pesticides, comparable findings have been reported in numerous studies where washoff fractions were also collected individually during each washoff event (3,4,5,6,7). Under the conditions tested in this study, total tribufos washoff was found to be minimal after 3 days post-treatment. No radioactivity was found in the washoff fractions from any of the untreated control leaves at any time interval.

Overall Recovery of Radioactive Residues

As discussed previously, a distinct decline in the radioactive residues on individually treated cotton leaves was observed during the study. This trend was also observed for the test system as a whole. On the day of treatment, the average total recovery of radioactive residues per plant was 89.6%. Total recovery of radioactivity steadily declined at each sampling interval, reaching 39.2% at Day 15. Dissipation studies performed by Bayer Corporation have consistently shown that tribufos undergoes significant degradation under field conditions. Likewise, recent laboratory studies performed by Bayer resulted in half-life values for tribufos ranging from 10 - 173 days in microbially active soils.

Conclusions

This study suggests that the most important factor influencing washoff potential of tribufos from cotton leaves is post-application timing of rainfall. The results indicate that tribufos is available to be washed from cotton leaves for only a short period of time after application. Although the majority of [14C]tribufos washoff occurred during the first 1-cm of simulated rainfall over the course of the study, the magnitude of this effect was diminished over time due to foliar dissipation and possibly by binding of radioactive residues through 15 days post-treatment.

This study demonstrates that under greenhouse conditions designed to simulate field conditions, tribufos is susceptible to foliar extraction by rainfall, immediately after application to cotton. However, substantial foliar dissipation coupled with some increased binding of aged foliar residues, strictly limits the potential transport via runoff that can be expected from tribufos applications. The results of this study

indicate that by the third day following an application of tribufos, only about 4% of the tribufos applied to the leaves would be expected to be washed off by 10 cm (about 4 inches) of rain falling at 4.35 cm per hour (1.71 in/h).

Acknowledgment

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Chapter 11

Evaluation of Laboratory and Field Extraction Methods: Extraction of [Phenyl-U-^{14}C] Flufenacet from Aged Soils

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A study was conducted to compare the extraction efficiency of [phenyl-U-^{14}C] flufenacet from aged soil using both laboratory and field extraction methods. Soil (sandy loam) was obtained from Howe, Indiana and treated with [phenyl-U-^{14}C] flufenacet at the application rate of 0.9 ppm (equivalent to 0.8 lb. a.i./acre). After treatment, soils were aged aerobically in an environmental chamber at 21 ± 1 °C for 32 days. Extraction methods were compared. The laboratory extraction method employs a more aggressive procedure which involves three extraction steps while the field extraction method involves a single extraction step. At day 0, the laboratory method extracted 97.8% of applied radioactivity while the field method extracted 86%. At day 32, laboratory and field methods extracted 81.9% and 73.1% of applied radioactivity, respectively. The results demonstrated that the field extraction method could extract around 90% of the residues when compared with the laboratory extraction method. Degradates detected using both extraction methods were identical. The distribution of degradates in the extract when calculated based on the percent of analytes from the high-

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performance liquid chromatography (HPLC) instead of the percent of applied radioactivity were comparable with approximately 61% flufenacet, 27% flufenacet oxalate, and 5% flufenacet sulfonic acid.

During the course of studies conducted in environmental fate for the registration of a new pesticide, laboratory metabolism studies are usually conducted first. The goal is to determine, under a variety of conditions, how a compound is metabolized (i.e. breaks down) in soil and water, and to specifically identify the various breakdown products. Once the major metabolites (greater than 10% of applied material) are known, analytical residue methods are developed to measure the parent and metabolites after application of the formulated product in the field.

Most of the laboratory metabolism studies are conducted with radiolabelled compound, which makes it much easier to identify various breakdown products. The extraction procedures usually involve tedious, multiple extraction steps. This is especially important for aged residues since the extractability of residues from soil usually decrease over time. Additionally, the regulatory guideline requires that radioactivity material balance must be in the range of 90 to 110% (1). Sample clean-up steps are usually not needed since radioactive detectors on high-performance liquid chromatography are selective for only radioactive compounds.

Field studies are usually conducted with formulated non-radiolabelled compound so as to mimic the actual field conditions. Since non-radiolabelled compound is used, quantitation is done by a calibration curve with either external or internal standards (2). Extensive sample clean-up steps such as liquid-liquid partition or solid phase extraction (SPE) are usually needed to eliminate interference peaks from analytes, especially using conventional UV detectors. Since there are a large number of field samples (about 300 soil samples per site), extraction methods for field studies are often a modified and refined version of those developed in the laboratory metabolism studies.

When different extraction methods are used for laboratory and field studies, there is always a concern about whether both methods can extract the same amount of parent and degradation products especially from aged soil. If the absolute amount of recoveries are different for both methods, will the relative degradation profile (based on the HPLC chromatograms) be the same? This non-guideline

Good Laboratory Practice (GLP) study was conducted in order to bridge our understanding on the extraction methods used in laboratory and field studies.

Fluenacet   (N-(4-fluorophenyl)-N-(1-methylethyl)-2-[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]acet-amide) is an acetanilide herbicide developed by Bayer Corporation. Flufenacet, marketed as AXIOM®, is a selective herbicide which is targeted to control annual grasses and certain small-seeded dicot weeds.

Experimental Methods

Chemicals. Radiolabelled [phenyl-U-^{14}C] flufenacet was obtained from Bayer Corporation , and the structure of flufenacet and its potential metabolites are shown in Figure 1. The radiochemical purity was determined to be > 98.5% by both thin-layer chromatography (TLC) and HPLC. All solvents used were of HPLC-grade purity or equivalent.

Soil. The soil (Table I) used was the same as in the aerobic soil metabolism study (*3*) which was obtained from the Bayer Research Farm in Howe, Indiana. The soil series were classified as sandy loam with 75% sand, 16% silt and 9% clay. The soil had a bulk density of 1.35, organic matter of 1.6% and water holding capacity of 14% at 1/3 bar. The soil was sieved with a 2-mm mesh sieve prior to use. Immediately prior to starting the study, approximately 500 g of soil was sent to ABC Laboratories for microbial analysis.

Test Systems. The test systems were set up as shown in Figure 2. Twenty flasks were prepared, and each flask contained 100 g of soil (dry weight). Six of the flasks were used for the laboratory extraction method, and six flasks were used for the field extraction method. The remaining flasks were retained as spares. Using a microwave oven, the amount of moisture in the soil was determined to be 7.3%. Application solution and water (~3.2 mL) were added to the soil (100-g dry weight) to attain a chemical concentration of [phenyl-U-^{14}C] flufenacet of 0.9 ppm (equivalent to 0.8 lb a.i./acre), and a soil moisture level of 10.5% (i.e. 75% of 1/3 bar). All flasks were stoppered with towers filled with soda lime (~10 g) to trap CO_2, and glass wool (~1 g) moistened with 2% mineral oil in hexane to trap potential volatile metabolites (Figure 2) . Aerobic conditions were maintained by statically allowing air to pass through the towers. Treated soils were aged aerobically in an environmental chamber at 21 ± 1 °C. Soils were extracted on day 0 and day 32 using either the extraction method developed for the aerobic

Flufenacet

Flufenacet Oxalate

Flufenacet Sulfonic Acid
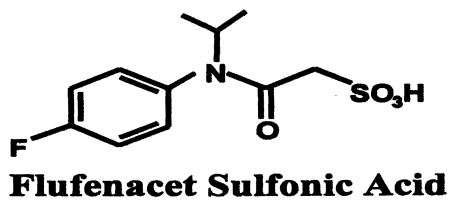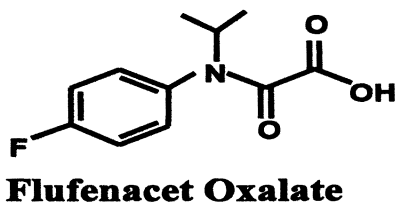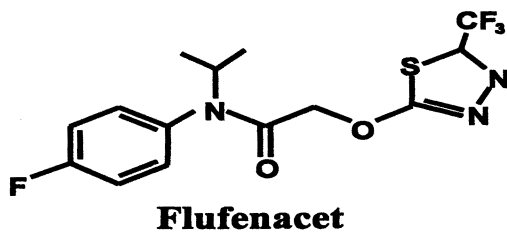
Figure 1. Structure of Flufenacet and its degradation products.

Table I. Soil Characterization Data

Howe, Indiana Soil	
SCS Classification	
Soil Series	Sandy Loam
Taxanomy Class	Sandy-Skeletal, Mixed, Mesic Typic ARGIUDOLL
Sand (%)	75
Silt (%)	16
Clay (%)	9
pH	6.2
Cation Exchange Capacity (meq/100g)	12.1
Organic Matter (%)	1.6
Water Holding Capacity (%) @ 1/3 Bar	14.0
Water Holding Capacity (%) @ 15 Bar	6.2
Bulk Density (g/cc)	1.35
Total Nitrogen (%)	0.094
Soluble Salts (mmhos/cm)	1.03
Percent Base Saturation	
% Calcium	51.8
% Magnesium	16.6
% Sodium	4.6
% Potassium	5.1
% Hydrogen	21.9
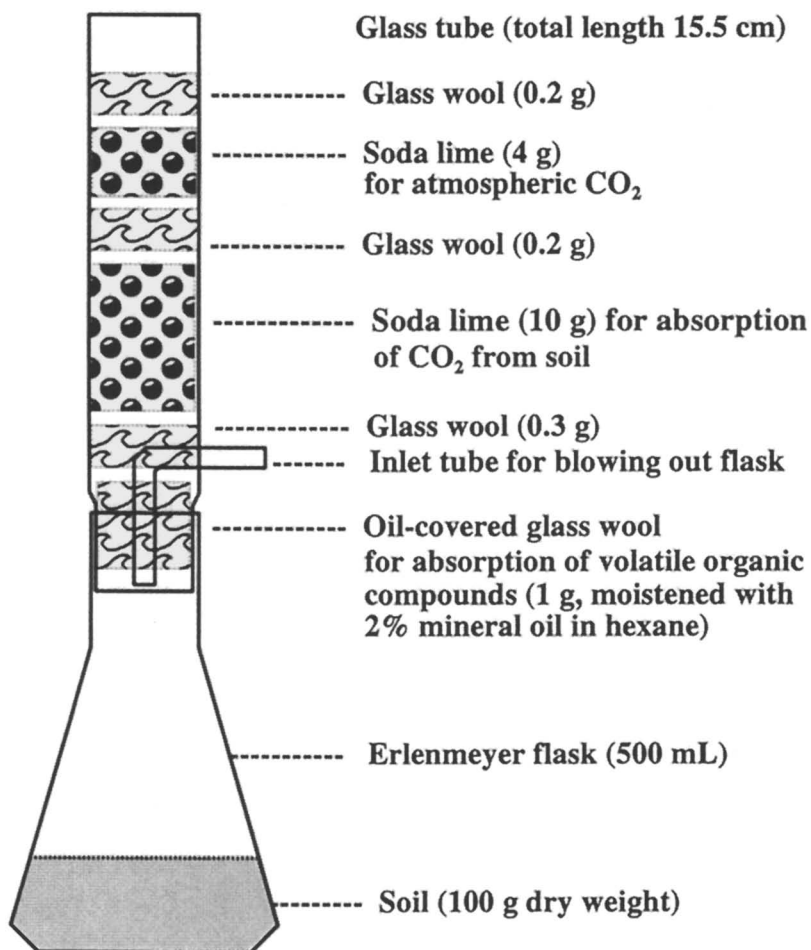
Figure 2. Schematic representation of the test system used to incubate soils.

soil metabolism study (*3*) or the soil residue method developed for the field studies (*4*).

Laboratory Extraction Method (*3*). Each soil sample (100 g dry weight) was extracted in sequence, using a magnetic stirrer, for one hour with the following solvents : (a) Acetonitrile (ACN, 150 mL), (b) ACN:H_2O (7:3, 150 mL) and (c) 0.2 N HCl:ACN (1:1, 150 mL). Each extract was filtered through #1 Whatman filter paper, and triplicate aliquots (0.5 mL) were radioassayed by a liquid scintillation counter (LSC). Each extract was concentrated to approximately 5-10 mL using a rotary evaporator. Triplicate aliquots (50 μL) of the extracts after concentration were radioassayed by LSC to ensure radioactive recovery after the filtration and evaporation steps. The concentrated extracts (from ACN extraction solvent) were filtered through 0.45-μm nylon acrodisc filters prior to HPLC analysis. The extracted soils were air dried, weighed, homogenized, oxidized, and analyzed by LSC for [^{14}C]residues.

Field Extraction Method The original field extraction method used a 10-g soil sample (*4*) and this quantity was modified to 100-g soil sample so that it could be compared directly with the laboratory extraction method. Radiolabelled compound was used, and the amount of residues was quantified by means of HPLC with radioactive detector instead of liquid chromatography electrospray tandem mass spectrometry (LC-ESI/MS/MS) as described in the original method (*4*). An internal standard was not needed due to the use of the radiolabelled compound. Each soil sample was extracted with 200 mL of 0.1 N hydrochloric acid : acetonitrile (1:1) for 1 hour using a magnetic stirrer. This less aggressive, one-solvent system was done so that it would simplify subsequent clean-up steps. The extract was vacuum filtered, and an aliquot (100 mL) of the extract was transferred to a graduated cylinder. Triplicate aliquots (500 μL) of the extract were radioassayed by LSC. Methanol (10 mL) was added to the graduated cylinder and concentrated to approximately 5-10 mL using a rotary evaporator (Büchi). Triplicate aliquots (50 μL) of the extract after concentration were radioassayed by LSC to ensure radioactive recovery after the filtration and evaporation steps. The concentrated extracts were filtered through 0.45-μm nylon acrodisc filters prior to HPLC analysis. The extracted soils were air dried, weighed, homogenized, oxidized, and analyzed by LSC for [^{14}C]residues.

Volatile Metabolite Analysis. Volatile metabolites trapped in the mineral-oil-coated glass wool (Figure 2) were quantitated at day 32. The flask headspace was purged with compressed air at approximately 400 mL/min for 15 min just prior to the removal of the trapping tower from the test set-up. The mineral-oil-coated glass wool and ethyl acetate (50 mL) were added to a 250-mL Erlenmeyer flask. The

sample was sonicated for 30 min. The ethyl acetate was decanted from the glass wool and triplicate aliquots (1 mL) of the solution were radioassayed using LSC.

The $^{14}CO_2$ trapped by the soda lime was quantitated at day 32 using the set-up shown in Figure 3. The soda lime (10 g) was transferred into a 125-mL Erlenmeyer flask. Water (10 mL) was added to the soda lime. While the system was under a constant flow of nitrogen gas ($\sim$ 20 mL/min), 12 N HCl (30 mL) was added dropwise. The $^{14}CO_2$ resulting from the reaction was trapped using a mixture of Carbo-Sorb E : Permafluor-E$^+$ (3:5, $\sim$ 12-15 mL, Packard Instrument, Connecticut) in three scintillation vials which were connected in series. To minimize the loss of $^{14}CO_2$, all scintillation vials were placed in an ice bath. The trapping solutions were radioassayed for [^{14}C]content by LSC.

Radiometric Analysis. LSC analyses were performed using a Packard Tri-Carb Model 4640 liquid scintillation counter equipped with automatic external standardization. Triplicate aliquots of liquid samples (100 µL to 1000 µL, depending on the radioactivity of the sample) were analyzed by adding 15 mL of scintillation cocktail (Ultima Gold, Packard). Quench curves were measured weekly to monitor equipment performance.

Oxidation Analysis. After extraction (laboratory or field methods), soil samples were air-dried, and homogenized, and triplicate aliquots (150 - 200 mg) were oxidized to $^{14}CO_2$ using a Packard 307 sample oxidizer equipped with Oximate 80 robotics system. To aid in combustion, 200 µL of combustaid was automatically added to each sample prior to oxidation. The $^{14}CO_2$ produced was quantitatively dissolved in 6 mL of Carbosorb E (Packard) and mixed with 15 mL of Permaflour E$^+$ (Packard). All values obtained were corrected for instrument efficiency by spiking a known quantity of radioactivity of ^{14}C-standard (Spec-Chec^{TM}) onto the combustion cone and comparing results of oxidation with the same quantity spiked into the scintillation vial. An oxidizer efficiency > 95% was required prior to combustion of the samples.

HPLC Analysis. All extracts were analyzed using a Hewlett Packard Model 1090 HPLC equipped with auto-sampler and coupled to a Raytest Ramona 5-LS radioactivity monitor ($\sim$400 µL flow cell). The column was a Hamilton semi-preparative PRP-1 (305 x 7mm, 10-µm). Mobile phase conditions were A: 0.4% acetic acid in water and B: 0.4% acetic acid in ACN at flow rate of 2 mL/min. The solvent gradient began at 0% B and was increased to 25% B in 25 min. It was held at 25% B for 15 min and was increased to 70% B at 75 min. It was finally increased to 90% B at 85 min and held at 90% B for 10 min.
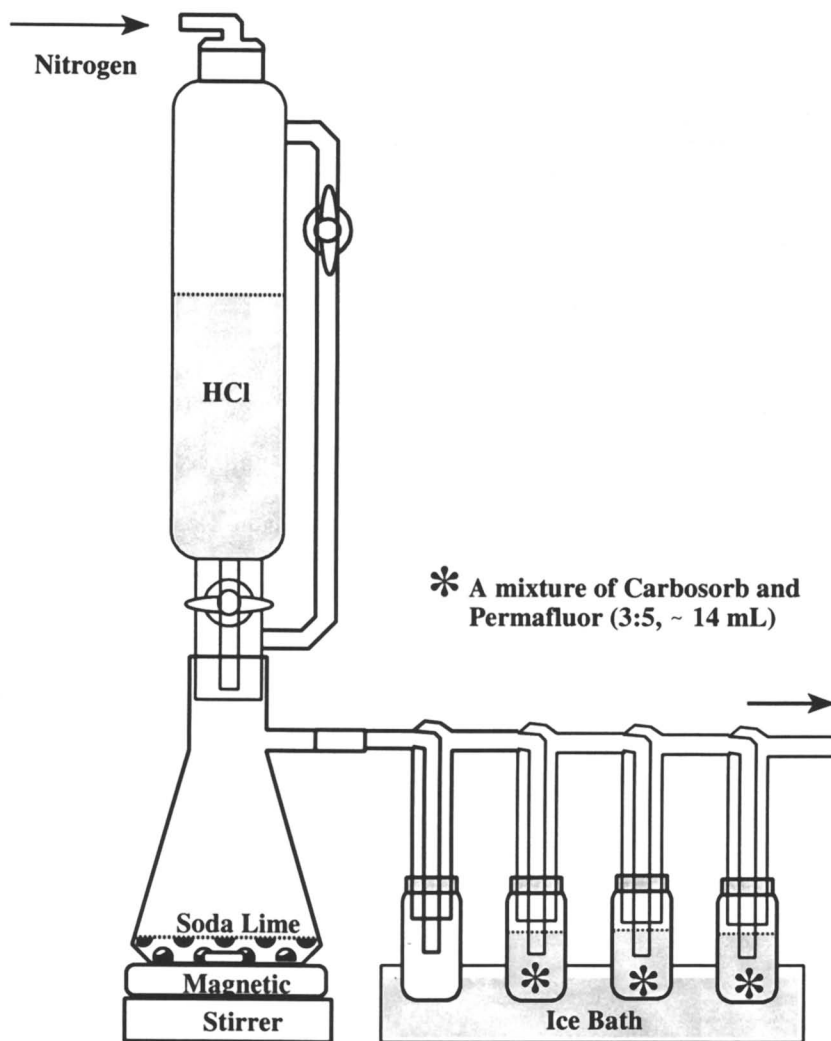
Figure 3. Apparatus for releasing and trapping $^{14}CO_2$ from soda lime.

Results and Discussion

Total Recoveries. The total radioactivity recovered throughout the study ranged from 97.9% (day 0) to 92.9% (day 32) for the laboratory extraction method and from 97.4% (day 0) to 101.6% (day 32) for the field extraction method (Table II). Residues extracted from the soil ranged from 97.8% (day 0) to 81.9% (day 32) for the laboratory extraction method and from 86.0% (day 0) to 73.1% (day 32) for the field extraction method. The bound residues that remained in the soil ranged from 0.1% (day 0) to 10.5% (day 32) for the laboratory extraction method and from 11.4% (day 0) to 28.0% (day 32) for the field extraction method. The level of volatile organic carbons (VOCs) and carbon dioxide evolved throughout the study for both methods were insignificant.

The laboratory extraction method was more rigorous, as would be expected from the series of three solvent extractions. However, the one step extraction solvent (0.1 N HCl : ACN [1:1]) employed in field extraction method was the combination of three solvents used in laboratory extraction method (ACN, ACN : H_2O [7:3] and 0.2 N HCl : ACN [1:1]). As shown in Table III, the extraction efficiency for the field method even in aged soil when compared with the laboratory extraction method was about 90%. The one-step extraction procedure for the field method is much faster and consumes less solvents when compared with the laboratory method. These are very important factors especially in the analysis of soil dissipation studies which involves hundreds of samples.

Quantitation of Flufenacet and its Metabolites. The parent compound, flufenacet and its metabolites, flufenacet oxalate and flufenacet sulfonic acid, were identified by comparison of HPLC retention times with known standards (Table IV). In the laboratory extraction method, the parent compound accounted for 97.8% of the residues at day 0 and decreased to 51.4% at day 32 (Table IV). In the field extraction method, flufenacet accounted for 86.0% of the residues at day 0 and decreased to 44.8% at day 32. The flufenacet oxalate and flufenacet sulfonic acid increased to 22.7% and 4.0% of the applied radioactivity at day 32 in the laboratory extraction method compared to 19.5% and 4.3% in the field extraction method, respectively. Since the extraction efficiency of the field method is less than the laboratory method, a relative comparison of both extraction methods was obtained by assessing the distribution in terms of the percent of analytes in the extracts instead of the percent of applied radioactivity (Table IV). Using this approach, both laboratory and field extraction methods were very comparable. For both extraction methods, flufenacet sulfonic acid made up ~5% of the region of interest, whereas flufenacet oxalate made up ~27% (Table IV).

Table II. Radioactive residues recovered from the soil sample expressed as percent of applied radioactivity

	Percent of Applied Radioactivity (Laboratory Extraction Method)	
	Day 0	Day 32
ACN	90.2	45.8
ACN : H$_2$O (7:3)	6.4	25.6
ACN : 0.2 N HCl (1:1)	1.2	10.5
Solvent Extracted	**97.8**	**81.9**
Volatile Organic	NA	ND
Carbon Dioxide	NA	0.5
Bound Residues	**0.1**	**10.5**
Total	**97.9**	**92.9**

	Percent of Applied Radioactivity (Field Extraction Method)	
	Day 0	Day 32
ACN : 0.1 N HCl (1:1)	86	73.1
Solvent Extracted	**86**	**73.1**
Volatile Organic	NA	ND
Carbon Dioxide	NA	0.5
Bound Residues	**11.4**	**28.0**
Total	**97.4**	**101.6**

Table III. Comparison of radioactive residues recovered from the soil sample expressed as percent of applied radioactivity for both field and laboratory extraction methods at (Top) Day 0; (Bottom) Day 32.

	Percent of Applied Radioactivity Extracted at Day 0		
	Laboratory Method	*Field Method*	*Field vs Laboratory[A]*
Solvent Extracts	97.8	86.0	87.9
Bound Residues	0.1	11.4	-
Total	**97.9**	**97.4**	-

	Percent of Applied Radioactivity Extracted at Day 32		
	Laboratory Method	*Field Method*	*Field vs Laboratory[A]*
Solvent Extracts	81.9	73.1	89.3
Bound Residues	10.5	28.0	-
Volatile Organics	ND	ND	-
Carbon Dioxide	0.5	0.5	-
Total	**92.9**	**101.6**	-

[A] Calculated by : (% from laboratory method / % from field method) x 100%

Table IV. Distribution of [phenyl-U-^{14}C]flufenacet and its metabolites in soil using both laboratory and field extraction methods.

| | HPLC R_t (min) | Percent of Applied Radioactivity | | | |
| | | Day 0 | | Day 32 | |
		Laboratory Method	Field Method	Laboratory Method	Field Method
Flufenacet	78	97.8	86.0	51.4	44.8
Flufenacet Oxalate	29	-	-	22.7	19.5
Flufenacet Sulfonic Acid	31	-	-	4.0	4.3
Unknowns	33 + 36 + 52	-	-	3.8	4.5
Total		97.8	86.0	81.9	73.1

| | HPLC R_t (min) | Percent of Analytes in the HPLC analysis | | | |
| | | Day 0 | | Day 32 | |
		Laboratory Method	Field Method	Laboratory Method	Field Method
Flufenacet	78	100	100	62.8	61.2
Flufenacet Oxalate	29	-	-	27.7	26.7
Flufenacet Sulfonic Acid	31	-	-	4.9	5.8
Unknowns	33 + 36 + 52	-	-	4.6	6.2
Total		100	100	100	99

Conclusion

The extraction efficiency of [phenyl-U-^{14}C]flufenacet from aged soil using both laboratory and field extraction methods were compared. Extraction efficiency was greater with the use of the more rigorous laboratory method; however, the efficiency for the field method even in aged soil was about 90% when compared with the laboratory extraction method. The field extraction method which employed one extraction solvent (0.1 N HCl : ACN [1:1]) was much faster and consumed less solvent. In addition, degradates detected using both extraction methods were identical, and the distribution of degradates in the extracts were very similar. In this laboratory, however, the need for comparison of both methods has been eliminated by the use of an Accelerated Solvent Extractor (ASE, 5) developed by Dionex Corporation (Sunnyvale, CA). In environmental fate studies currently the extraction method for laboratory studies is developed by using the ASE, and the same vigorous extraction conditions are transferred to the soil residue methods. The use of multiple solvent extraction steps is not of big concern since the extraction is done automatically by the ASE.

Acknowledgments

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Chapter 12

Outdoor Soil Metabolism of [Phenyl-U-^{14}C] Flufenacet on California Soils

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An outdoor soil metabolism study with [phenyl-U-^{14}C] flufenacet was conducted on two sandy loams collected from Chualar and Fresno sites in California. This study involved more natural environmental conditions than a laboratory study and was conducted to obtain information on flufenacet residue identification and leaching potential. Vessels filled with approximately 13 cm of each soil were placed in an outdoor plot at Pan-Agricultural Laboratories in Madera, California, and treated with radioactive flufenacet at an equivalent rate of 0.89 lb a.i. per acre. Samples were collected in duplicate immediately after application and at 1, 4, 7, 11, 15, 19, 27, 35, 46, and 88 days after treatment. At each sampling interval, the top 3 cm (approximately) of soil was removed, extracted, and analyzed by high-pressure liquid chromatography for parent compound and metabolites. The total [^{14}C]residues recovered from the vessels remained above 85.9% in the Fresno soil and 92.8% in the Chualar soil throughout the 88-day study with the greatest percentage of the radioactivity remaining in the top 0- to 3-cm layers. The extracted [^{14}C]residues in the top layer decreased to

44.3% of the applied radioactivity in the Fresno soil and 62.6% in the Chualar soil at the 88-day interval, with 19.5% and 25.3% remaining bound to the soil, respectively. Residues of parent compound decreased to 17.8% and 29.0% at the 88-day interval in the Fresno and Chualar soils, respectively. The flufenacet alcohol and oxalate were the two major metabolites detected in this study. The flufenacet alcohol reached a maximum level of 21.2% in the Chualar 88-day sample, whereas the flufenacet oxalate reached a maximum of 13.0% in the Fresno 46-day sample. The half-lives for flufenacet in the Fresno and Chualar soil were calculated to be 36.1 days ($k = 0.0192$ days^{-1}) and 49.9 days ($k = 0.0139$ days^{-1}), respectively.

During the course of studies conducted for the registration of a new pesticide, laboratory metabolism studies are usually conducted first, with the intent of determining a conceptual model for breakdown of the compound in the environment. In doing so, major degradates are determined and consist typically of those products that occur at approximately 10% or greater of the applied pesticide in a given study. These major degradates are incorporated into a soil residue method that is used when analyzing samples that come from the later field dissipation studies.

This outdoor metabolism study was used to bridge the laboratory and field studies in several ways. It incorporated the use of radiolabelled pesticide, making it easier to monitor degradation of the compound. This is in contrast to field dissipation studies that use formulated (non-radioactive) pesticide. Even though this study was carried out in a partially closed system, in order to contain radioactivity, it did give some indication of leaching potential. Finally, the study was carried out under more real-world environmental conditions. This contrasts with laboratory studies that are usually carried out under as much control as possible (darkness, controlled temperature and soil moisture). Information obtained from this study accelerated the development of the soil residue method that was used for the subsequent field dissipation studies. This study was conducted in order to bridge our understanding of laboratory and field studies and to confirm that the laboratory results do represent the results seen in field dissipation studies.

Flufenacet (N-(4-fluorophenyl)-N-(1-methylethyl)-2-[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy] acetamide; CAS# 142459-58-3) is an acetanilide herbicide developed by Bayer Corporation, Agriculture Division, Kansas City, Missouri. Flufenacet, which is marketed as AXIOM®, was developed by Bayer

under the name FOE 5043. This compound is noted for its excellent activity against the main grasses in soybeans such as *Digitaria sanguinalis*, *Echinochloa crus-galli* and *Sorghum halepense*, and it also has good herbicidal efficacy against a number of dictoyledonous weeds *(1)*. Flufenacet belongs to the chemical group of oxy-acetamides and is taken up mainly through the root system *(2)*. This outdoor soil metabolism study was conducted to evaluate the degradation and dissipation of [^{14}C]flufenacet under field conditions. The main objectives of this non-GLP supplemental study were to (a) determine the half-life and first-order degradation rate constant (k) for flufenacet in each soil, (b) identify the flufenacet metabolites, and (c) evaluate the leaching potential of flufenacet and its metabolites under field conditions.

Experimental Methods

Field Procedures

The field portion of the study was conducted at Pan-Agricultural Laboratories, Inc. in Madera, California, from July 16, 1992, to October 12, 1992. The extraction and analysis portions of the study were conducted at Bayer Corporation, Agriculture Division, Environmental Research Section, Stilwell, Kansas.

The soils used in this study were collected from the same fields where earlier soil dissipation studies were conducted, but were from untreated areas. The soil series name for the Fresno soil is Hesperia fine sandy loam as classified by the USDA Soil Conservation Service Survey of the Eastern Fresno Area in California. The taxonomy class is a course-loamy, mixed, nonacid, thermic Typic Xerorthents. The clay mineralogy is mixed. The soil series name for the Chualar soil is Salinas loam as classified by the USDA Soil Conservation Service Survey of Monterey County, California. The taxonomy class is a fine-loamy, mixed, thermic Pachic Haploxerolls. The clay mineralogy is mixed. The soil characteristics and biological activity of the Chualar and Fresno soils are summarized in Table 1. Prior to the study initiation, the soils were sieved through a 2-mm wire mesh.

The small outdoor test plot consisted of 44 vessels (one-gallon jars, 6 inches in diameter cut off to 6 inches in depth) placed in the ground and filled with approximately 5 to 5½ inches of soil. The bottom of each vessel was closed, preventing radioactivity from moving into surrounding soil. Twenty-two of the vessels were filled with Fresno soil and the other twenty-two vessels contained Chualar soil (Figure 1). Two vessels, placed in the middle of the plot between the

Table 1. Pertinent characteristics of soils used in the ^{14}C-flufenacet outdoor metabolism study.

Characteristic	Chualar	Fresno
Texture	sandy loam	fine sandy loam
Organic Matter %	1.3	0.5
Sand %	70.0	64.7
Silt %	18.0	31.3
Clay %	12.0	4.0
pH	6.4	7.5
Colony Forming Units[1]	1.08×10^6	1.03×10^6

[1] Microbial colonies per gram soil (dry weight) quantified on plate count agar; analysis performed by ABC Laboratories, Columbia, Missouri.
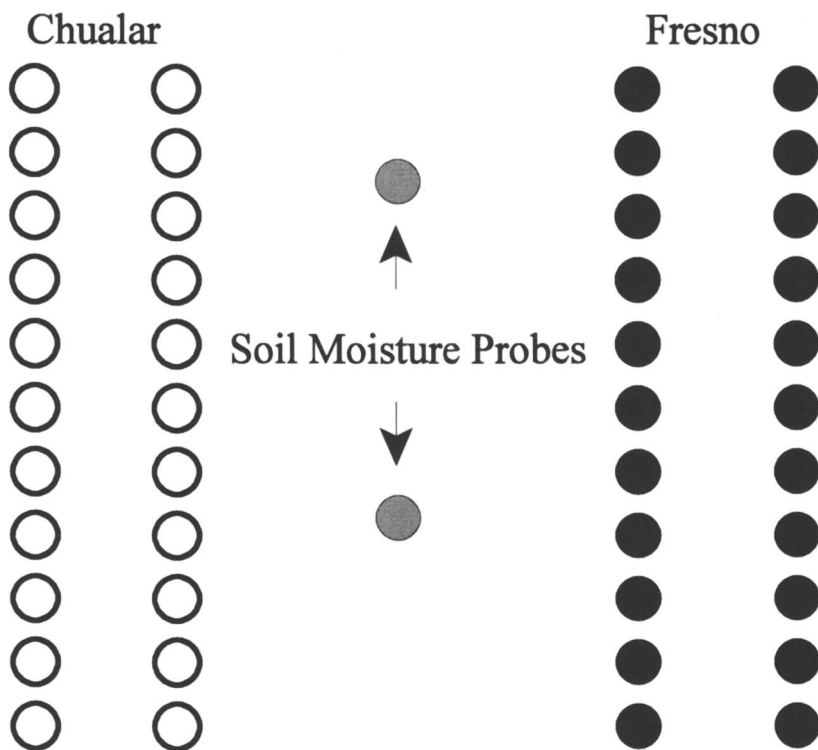
Figure 1. Test plot diagram for ^{14}C-flufenacet outdoor metabolism study.

two soil types, contained a mixture of Fresno and Chualar soils and three moisture sensors (Model 200 Watermark sensor) which were monitored with a 30 KCT meter (Irrometer). The plot was irrigated daily to maintain the soil at 50 to 90 percent moisture holding capacity. Overflow from excessive rainfall was prevented by covering the plot with a tarp when inclement weather was anticipated. The plot was weeded around the vessels at the 29-day (post-treatment) interval.

Cumulative irrigation and rainfall totaled 11.19 inches during the test period. Climate conditions (i.e. air temperature, relative humidity, precipitation, ground temperature, and wind speed) were monitored with an on-site weather station located 300 feet from the test site.

Chemicals and Application

[Phenyl-U-^{14}C]flufenacet was synthesized by Koch (3) and the structure is shown in Figure 2. The treatment solution was prepared on the day of application by dissolving an appropriate quantity of [^{14}C]flufenacet in acetonitrile (ACN). Unlabeled flufenacet was added to the flask to adjust the specific activity to 231,231 dpm/μg. The test material was then diluted to 100 mL with distilled water. Prior to shipment to Pan-Ag Labs for treatment of plots, the radiochemical purity of the stock solution was determined by thin-layer chromatography (TLC) to be 99.0%.

Each vessel was treated with [^{14}C]flufenacet at a rate of 0.89 lb a.i. per acre. The test solution was applied to the surface of the soil using a 2-mL syringe equipped with a thin-gauged needle. The percent of applied radioactivity referenced in this chapter is based on the radioactivity determined from the dosing solution, not the 0-day recovery values.

Sampling Intervals

Duplicate samples from each soil type were collected immediately after application of [^{14}C]flufenacet to the Fresno and Chualar soils and at 1, 4, 7, 11, 15, 19, 27, 35, 46, and 88 days after treatment. The top layers (0 to 3 cm) of soil were removed from each vessel, placed in one-gallon jars and flooded immediately with 700 mL of ethyl acetate. Within one-half hour, samples were transported in a cooler containing substitute ice (blue ice) to a freezer and then shipped on dry ice in insulated boxes to Bayer Corporation where they were extracted and analyzed.

Soil Extractions

The sample processing scheme for this study is shown in Figure 3. The one-gallon jars containing the 0- to 3-cm soil layers and 700 mL of ethyl acetate were mechanically shaken for 30 minutes. The mixture was vacuum filtered through Whatman #541 filter paper, and the extracted soil was allowed to air dry. Extracted soil samples were then homogenized in a General Electric food processor and rolled in a tumbler (Model A-R2 Rock Polisher) for 20 min prior to aliquoting for oxidation analysis. The soils collected at the 27 through 88-day intervals were further extracted at reflux for 4 h with ACN/water (7:3). These extracts were vacuum filtered through Whatman #541 filter paper. Each filtered extract was radioassayed by LSC (liquid scintillation counting) and concentrated under nitrogen. A subsample of each extract sample was filtered using a Nylon Acrodisc® syringe filter (0.45 μm) and concentrated to 1 mL by evaporating under a stream of nitrogen before analysis by HPLC. Aliquots of each subsample were radioassayed by LSC to ensure radioactive recovery after the filtering and evaporating steps. The average recoveries for the ethyl acetate and ACN/water extracts were 104% and 99%, respectively. Samples were extracted and analyzed soon after sampling, therefore stability data was not required.

Radiometric Analysis

Radiometric measurements were determined using a Packard Tricarb Liquid Scintillation Counter Model 4640, equipped with automatic external standardization. Liquid samples (100-μL aliquots) were radioassayed in triplicate using 15 mL of Ultima Gold liquid scintillation cocktail (Packard, Illinois) with 4 mL of water and counted for 5 minutes.

Oxidation Analysis

The radioactive residues in the extracted soils and 3- to 13-cm layer soils from the 15- to 46-day intervals were air-dried and oxidized in a Packard sample oxidizer (Model 306). The 3- to 13-cm layers of soil from the 88-day interval were subsectioned into layers of approximately 2 cm, and each subsection was oxidized separately. The $^{14}CO_2$ produced from complete combustion of the sample was quantitatively dissolved in 6 mL of Carbosorb E (Packard) and mixed with 15 mL of Permafluor E$^+$ (Packard). The samples were radioassayed by LSC and corrected for oxidizer efficiency. Oxidizer recoveries were checked before and after analysis by combusting a known amount of [^{14}C]standard (Spec-Chec, Packard).
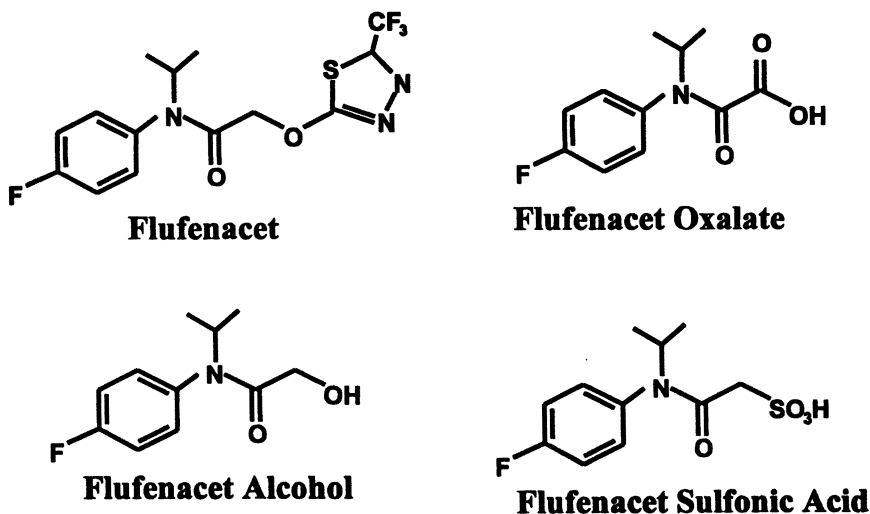
Figure 2. Chemical structures of flufenacet and degradates formed in the ^{14}C-outdoor metabolism study.
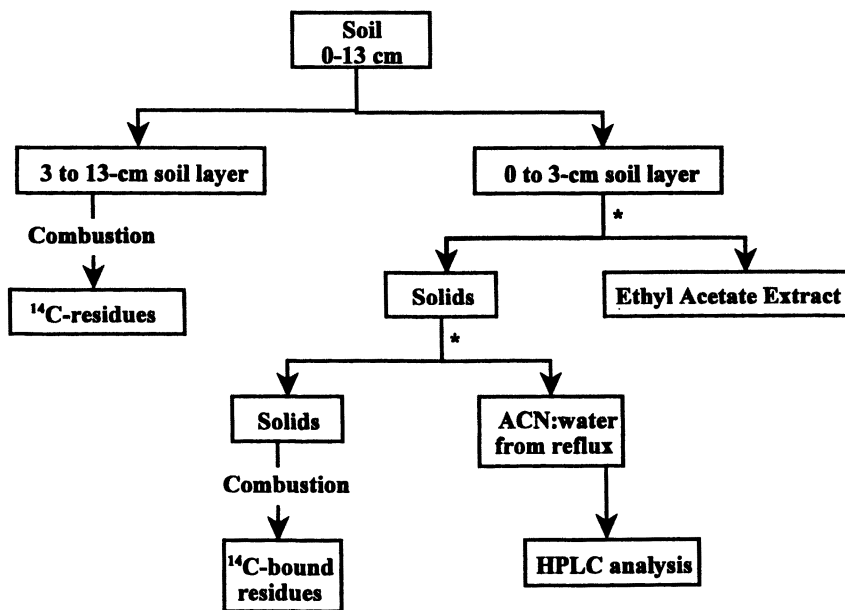
Figure 3. Analytical scheme for samples from the ^{14}C-flufenacet outdoor metabolism study (denotes soil extraction occuring at this step).*

Thin-Layer Chromatography (TLC)

The purity of the dosing solution was determined by thin-layer chromatography with Merck silica gel 60 F_{254} plates (0.25 mm) and developed in a chloroform/methanol solvent system (9:1). Radioactive zones were detected using a radioactive (Raytest Rita 6800) TLC scanner.

High-Performance Liquid Chromatography (HPLC)

Analyses of sample extracts were conducted using a Shimadzu SCL-6A Liquid Chromatograph and a Hewlett-Packard 1090 Liquid Chromatograph. Both instruments were equipped with a variable UV detector and a Raytest Ramona 90 radioactive monitor (400 μL flow cell). Sufficient sample volumes were injected to detect radioactive residue levels down to approximately 7.5 ppb for each sample. The HPLC method used for this study is shown in Table 2.

Thermospray LC/MS Analysis

Thermospray LC/MS was performed using a Finnigan MAT 90 mass spectrometer equipped with a thermospray interface. A Varian 5040 HPLC coupled with a Berthold LB 505 radioactivity monitor was used to resolve analytes prior to the introduction into the thermospray interface. The HPLC was equipped with a Hamilton PRP-1 (150 x 4.1 mm) column. The analyses were performed using a linear gradient from 100% water to 100% methanol over 30 min at a flow rate of 0.8 mL/min. A 0.2 M solution of ammonium acetate was added post-column at a rate of 0.2 mL/min. The mass spectrometer was operated in the positive and negative-ion mode at aerosol and source temperatures of 210 °C

Results and Discussion

Material Balance and Residue Distribution

The total radioactive residues recovered from the vessels remained above 85.9% in the Fresno soil (Table 3) and 92.8% in the Chualar soil (Table 4) throughout the 88-day study. A preliminary laboratory study showed minimal volatility of [phenyl-U-^{14}C] flufenacet, thus volatiles were not trapped in the

Table 2. HPLC Method of Analysis

Column	Hamilton PRP-1, 305 x 7 mm		
Guard Column	Hamilton PRP-1		
Injector	Rheodyne 7161		
Detector	Variable UV detector, 230 and 254 nm		
	Raytest Ramona 90 radioactive monitor (400 μL flow cell)		
Flow	2 mL/min		
Solvents	A = Water with 0.4% acetic acid		
	B = Acetonitrile with 0.4% acetic acid		
Gradient	Time(min)	%A	%B
	0	100	0
	15	70	30
	65	40	60
	70	0	100
	80	0	100
	90	100	0

Table 3. Distribution of radioactive residues from Fresno soil.[1]

Days	0	1	4	7	11	15	19	27[2]	35[2]	46[2]	88[2]
					Expressed as % of Applied Radioactivity						
Topsoil (0-3 cm)	99.1	102	105	90.7	93.0	87.2	87.3	84.9	80.1	80.5	63.8
Extractable Residues	99.1	95.8	93.2	79.9	77.2	67.1	62.9	68.5	65.1	63.1	44.3
Flufenacet[3]	98.2	94.3	91.4	78.3	74.3	64.6	59.9	50.9	52.7	35.9	17.8
Alcohol	0.3	0.7	1.5	1.4	2.5	2.0	2.7	5.2	6.1	7.8	8.1
Oxalate	-[3]	-	-	-	-	-	-	9.1	4.6	13.0	11.7
Sulfonic Acid	-	-	-	-	-	-	-	1.4	0.4	1.9	2.4
Other Degradates	0.2	0.8	0.3	0.2	0.4	0.5	0.3	1.9	1.3	4.5	4.3
Bound Residues	-	6.0	11.5	10.8	15.8	20.1	24.4	16.4	15.0	17.4	19.5
Subsoil (3-13 cm)											
Bound Residues	*[4]	*	*	*	*	8.9	6.6	11.6	15.6	6.9	22.1
Total Recovery	99.1	102	105	90.7	93.0	96.1	93.9	96.5	95.7	87.4	85.9

[1]Results are the mean of two samples per interval and are determined by HPLC analysis of sample extracts
[2]Soil samples were extracted with ethyl acetate and then refluxed with acetonitrile/water (7:3)
[3]Not detected
[4]Not analyzed

Table 4. Distribution of radioactive residues from Chualar soil.[1]

Days	0	1[2]	4	7	11	15	19	27[3]	35[3]	46[3]	88[3]
					Expressed as % of Applied Radioactivity						
Topsoil (0-3 cm)	**98.0**	**98.6**	**97.5**	**101**	**97.7**	**84.1**	**82.7**	**86.8**	**97.8**	**90.1**	**87.9**
Extractable Residues	98.0	94.4	86.4	87.1	84.8	65.1	59.0	64.5	73.6	67.8	62.6
Flufenacet[3]	97.0	92.9	84.5	84.5	79.8	62.6	56.8	51.5	51.3	42.3	29.0
Alcohol	0.4	0.8	1.5	2.1	4.3	2.2	1.9	9.5	14.2	16.3	21.2
Oxalate	-[4]	-	-	-	0.1	-	-	1.7	5.2	6.1	7.6
Sulfonic Acid	-	0.1	-	-	-	-	-	0.5	0.8	0.9	1.3
Other Degradates	0.6	0.6	0.4	0.5	0.6	0.3	0.3	1.3	2.1	2.2	3.5
Bound Residues	-	4.2	11.1	13.7	12.9	19.0	23.7	22.3	24.2	22.3	25.3
Subsoil (3-13 cm)											
Bound Residues	*[5]	*	*	*	*	11.1	12.7	6.0	1.0	5.1	6.3
Total Recovery	**98.0**	**98.6**	**97.5**	**101**	**97.7**	**95.2**	**95.4**	**92.8**	**98.8**	**95.2**	**94.2**

[1]Results are the mean of two samples per interval and are determined by HPLC analysis of sample extracts
[2]Results from this interval are from one sample.
[3]Soil samples were extracted with ethyl acetate and then refluxed with acetonitrile/water (7:3)
[4]Not detected
[5]Not analyzed

current study. The majority of the residues stayed in the top 0- to 3-cm layer. The total radioactive residues extracted from the top 0- to 3-cm layer decreased to 44.3% of the applied radioactivity in the Fresno soil and 62.6% in the Chualar soil after 88 days. Bound residues remaining in the 0- to 3-cm layer after the ethyl acetate and ACN/water extractions ranged from 6.0 to 24.4% in the Fresno soil and from 4.2 to 25.3% in the Chualar soil. Bound radioactivity detected in the 3- to 13-cm layers ranged from 6.6 to 22.1% of the applied radioactivity in the Fresno soil and 1.0 to 12.7% in the Chualar soil. The 3- to 13-cm layer samples were not extracted since >90% of the applied radioactivity remained in the top 0- to 3-cm layer.

Residues of the parent compound decreased to 17.8% of the applied radioactivity in the Fresno soil (Table 3) and 29.0% in the Chualar soil after 88 days (Table 4, Figure 4). Flufenacet alcohol was detected at each interval and reached a maximum value of 8.1% and 21.2% at the 88-day interval in both the Fresno and Chualar soils, respectively. When the 27 through 88 day soil samples were further extracted with ACN/water, the flufenacet oxalate and flufenacet sulfonic acid were detected. The flufenacet oxalate reached a maximum level of 13.0% in the Fresno soil at the 46-day interval and 7.6% in the Chualar soil at the 88-day interval. The flufenacet sulfonic acid reached maximum levels of 2.4% and 1.3% in the Fresno and Chualar soils, respectively, at the 88-day interval (Tables 3 and 4). Structures of flufenacet and degradates are shown in Figure 2. In plant metabolism studies, flufenacet oxalate and flufenacet sulfonic acid were major metabolites found in mature crop matrices *(4)*.

Leaching Potential of Flufenacet Residues in Sandy Loam

In order to evaluate the leaching potential of flufenacet residues in sandy loam, the 3- to 13-cm layer of the Fresno and Chualar 88-day samples were further divided into four 2-cm subsections and analyzed for [^{14}C]residues (Figure 5). In the Fresno soil, 63.8% of the residues remained in the top 0-3 cm layer with 17%, 3.7%, 1.1%, and 0.3% detected in the 3- to 5-cm, 5- to 7-cm, 7- to 9-cm and 9-to 13-cm layers, respectively. The 0-to 3-cm top layer of the Chualar soil contained 87.9% of the radioactivity with 4.4% detected in the 3- to 5-cm, 0.7% in the 5- to 7-cm, 0.5% in the 7-to 9-cm, and 0.7% in the 9-to 13-cm layers. Based on these results, minimal leaching of the flufenacet residues through sandy loam was observed.
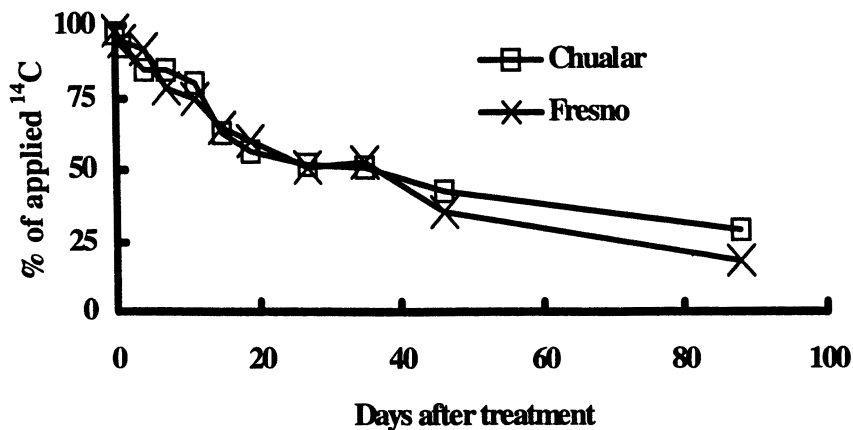
Figure 4. Degradation of ^{14}C-flufenacet in Chualar and Fresno soil in the outdoor metabolism study.
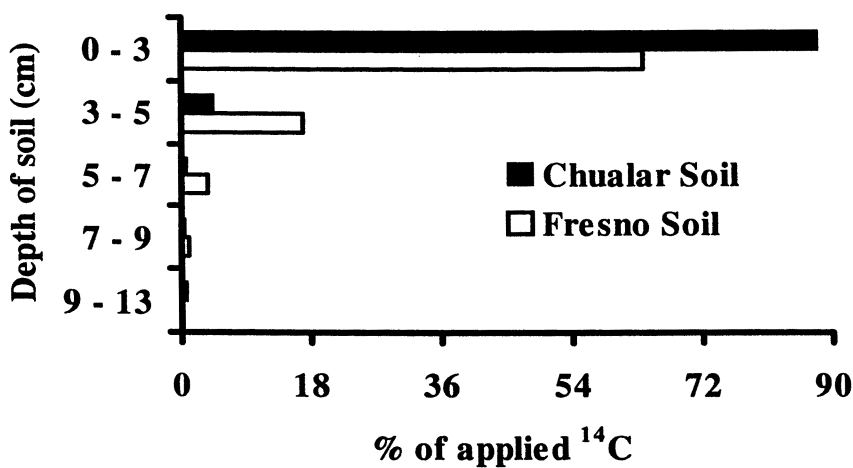
Figure 5. Leaching potential of ^{14}C-flufenacet determined in the outdoor metabolism study.

Half-Life Determination

First-order reaction kinetics calculations were used to determine half-lives for flufenacet in the two soils. A good linear fit was seen for both soils with r^2 at 0.96 and 0.99 for Chualar and Fresno, respectively. The half-life calculated for Chualar was 49.9 days ($k = 0.0139$ days^{-1}), while for Fresno it was 36.1 days ($k = 0.0192$ days^{-1}). Half-lives observed in the outdoor metabolism study fell within the ranges seen in both the laboratory metabolism studies and in field dissipation studies for this compound.

Metabolite Identification

Parent flufenacet and the flufenacet metabolites were initially identified by comparison with HPLC retention times of authentic standards. Identification of these compounds was further substantiated by comparison of the LC/MS of each isolated sample with the LC/MS of an authentic standard.

Conclusions

Bridging studies for flufenacet were useful in determining, early in the series of environmental fate studies, important degradates that occur in the environment. The outdoor metabolism study provided an opportunity to study the fate of flufenacet under confined field conditions, presenting a more controlled environment than traditional field studies. The study also provided more real-world natural conditions than controlled laboratory metabolism studies. Under these conditions, the study also evaluated other possible routes of degradation such as photolysis and hydrolysis. The confined conditions and use of radiolabeled pesticide provided an opportunity to obtain a material balance, identify with relative ease unknown degradates, and quantify radioactive bound residues by soil combustion. Determination of bound residues in field dissipation studies where non-radiolabeled compound is used is not possible. The results from this study indicated a low leaching potential of flufenacet residues. Similar results were obtained in subsequent field dissipation studies.

Additionally, metabolites seen in this outdoor metabolism study were also observed in laboratory metabolism studies and field dissipation studies. Major degradates identified in the outdoor metabolism study were incorporated into the soil residue method and used in the analysis of subsequent field dissipation studies.

From this outdoor soil metabolism study with [^{14}C]flufenacet the major findings were:

1. The half-lives of flufenacet in the Fresno and Chualar soils were calculated to be 36.1 days and 49.9 days, respectively. These half-lives were comparable to values obtained in laboratory and field studies. Half-lives were not calculated for the metabolites due to low rates of formation and no observable decline in the metabolite concentration.

2. The major metabolites identified in this study were the flufenacet alcohol, oxalate, and sulfonic acid.

3. Results from this study indicated a low leaching potential of flufenacet residues, with similar results seen in subsequent field dissipation studies.

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Chapter 13

Use of ^{14}C-Flupyrsulfuron-methyl in Small Plot Field Soil Dissipation Testing to Validate Laboratory Soil Degradation Rate Measurements

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The environmental fate of flupyrsulfuron-methyl in soil was studied under laboratory and field conditions. Laboratory degradation rate studies indicate that flupyrsulfuron methyl will degrade via hydrolysis and intramolecular rearrangement with a DT_{50} of 8 to 26 days. Bare-soil field dissipation studies using radiolabeled test substance were conducted using small plots (91 x 335 cm or 225 x 335 cm) at sites in the US and Europe. The rate of degradation and degradate profile confirmed expectations of environmental fate of flupyrsulfuron-methyl formed from the laboratory study results. Flupyrsulfuron-methyl dissipated in the small plot field soil dissipation studies with a DT_{50} of 6 to 11 days, and the major degradate was the same pyrimidinedione found in laboratory studies. In the laboratory studies, decreases in temperature reduced the rate of degradation in soil. However, in the small plot field studies, the DT_{50} value of flupyrsulfuron-methyl was not influenced by the season of

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application (autumn versus spring), but did seem to influence the DT_{90} measurements. Flupyrsulfuron-methyl exhibited limited mobility under field conditions, which was corroborated by computer simulations using PRZM-2. The small plot field dissipation studies gave good overall agreement with lab data and verified the predicted behavior of flupyrsulfuron-methyl in the field.

Introduction

Flupyrsulfuron-methyl is the active ingredient in the Lexus® brand of sulfonylurea herbicides and is used to control grasses and broad-leaved weeds in cereals. Extensive overviews of the environmental fate of flupyrsulfuron-methyl and its metabolic fate in animals and plants have been published elsewhere (*1, 2*). This publication will focus on the comparison of the environmental fate data generated in laboratory studies and the behavior of flupyrsulfuron methyl in small plot field dissipation studies.

Degradation Pathway

The route and rate of degradation of flupyrsulfuron-methyl in soil and water is influenced by pH (*1, 2*). At neutral and basic pH, an intramolecular rearrangement occurs leading to formation of the pyrimidinedione (Figure 1). The sulfonylurea bridge is cleaved at acidic pH. Microbial degradation is a minor pathway, leading to 0-demethylation of the pyrimidinedione.

Laboratory Studies

Rate of degradation and adsorption/desorption studies were performed using soils obtained from the proposed use areas of flupyrsulfuron methyl. These studies were performed using flupyrsulfuron-methyl that was uniformly labeled on either the pyridine or pyrimidine ring.
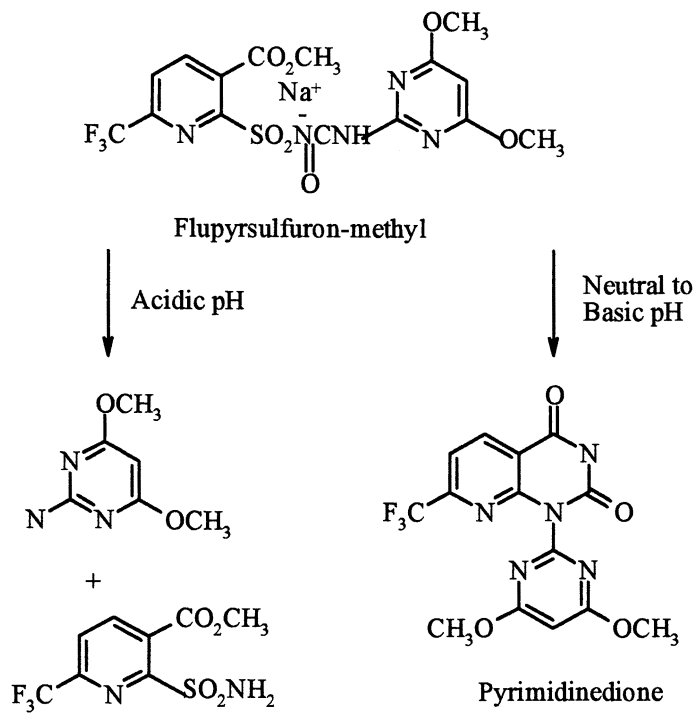
Figure 1. Major degradation products of flupyrsulfuron-methyl.

Rate of Degradation

The rate of degradation of ^{14}C-flupyrsulfuron-methyl was studied in 5 different soils under laboratory conditions, as shown in Table I (*1*). All soils were used within 3 months of collection to preserve microbial viability. The soils were incubated at 20°C and 50% of the maximum water-holding capacity. Soils were extracted with acetonitrile:0.1 M phosphate buffer (pH 6.5, 3:1, v:v). Analyses were performed using reversed-phase HPLC with fraction-collection of the eluate followed by liquid scintillation counting (HPLC-LSC) to determine the amount of radioactivity associated with each chromatographic peak. Limit of detection for radiochemical methods was 0.3 ng flupyrsulfuron

methyl/g of soil. Recoveries were >95% of the applied radioactivity in all of the studies. The rate of degradation was first-order and linear regression analysis was used to calculate the half-lives of flupyrsulfuron-methyl in the various soils.

Flupyrsulfuron methyl degraded rapidly in laboratory soils. The rate of degradation generally was dependent upon soil pH, with shorter half-lives at alkaline pH. Soil pH did affect the route of degradation, with cleavage of the sulfonylurea bridge occurring at soil pH ≤ 6.4. As expected, lowering the incubation temperature reduces the rate of degradation.

Table I. Rate of degradation of flupyrsulfuron-methyl under laboratory conditions

Soil Texture (source)	Soil pH	Incubation Temperature (°C)	$t_{1/2}$ (days)
Sandy loam (UK)[a]	7.4	10	58
Sandy loam[a]	7.4	20	26
Sandy loam (France)	7.6	20	8
Clay loam (UK)	7.1	20	10
Silt loam (France)	6.4	20	16
Loam (Germany)	6.1	20	16

[a]Same soil was used for both incubation temperatures.

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Adsorption to Soil

Adsorption of flupyrsulfuron-methyl was measured in 5 soils with a range of pH and organic matter contents (1). Adsorption studies were carried out with a 1:2 ratio of soil to 0.1M calcium chloride solution and were shaken for 8 hr at 25 co to equilibrate. The test vessels were centrifuged and the supernatants were analyzed by reversed-phase HPLC-LSC. The soils were extracted with ACN: 0.1M ammonium carbonate or sodium phosphate (3:1, v:v) and the extracts analyzed by reversed-phase HPLC-LSC. After extraction the soil solids were combusted and analyzed by LSC to determine total recovery of radioactivity.

Flupyrsulfuron-methyl is weakly sorbed to soil with an average Koc of 20 µg (Table II). Freundlich adsorption constants (Kd) had a linear correlation with the organic carbon content of the soils.

Table II. Koc values for flupyrsulfuron-methyl on soil.

Soil Texture (source)	Soil Organic Carbon (%)	Soil pH	Koc
Sandy loam (France)	0.7	8.8	19
Silt loam (France)	1.3	7.4	22
Sandy loam (UK)	1.5	7.4	15
Clay loam (UK)	1.9	8.1	23
Loamy sand (Germany)	2.3	5.8	22

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Field Studies

Small plot (91 x 335 cm in the US and 225 x 335 cm in Europe) field dissipation trials were performed with flupyrsulfuron methyl. Bare ground plots were divided into approximately 100 cm^2 subplots and numbers were assigned to 56 subplots throughout the test plot; the remaining subplots were not numbered. Figure 2 shows a representation of a portion of the plot layout. Radiolabeled flupyrsulfuron-methyl was mixed with appropriate inert ingredients to simulate a 50DF formulation, diluted with water and applied as a soil directed spray using hand-held plant misters. Each radiolabel was applied to a separate plot. Field dissipation studies were conducted at 4 sites in the US and Europe with a single application of approximately 15 g ai/ha, at either a spring or an autumn application time. Soil sampling was performed using a Concord multistage soil probe (Concord Researcher's Special, S & G Soil Services, Bedfordshire, UK or Concord Environmental Equipment, Hawley, MN, USA), which allows sampling of 0-15 cm core (10 cm diameter), followed by a 15 –90 cm soil core (2.5 cm diameter). This multi-stage coring approach minimizes the potential of contaminating the lower soil segment with material from the soil surface. Three soil cores were harvested randomly across each plot at each time point. Plots were sampled for approximately 300 days.
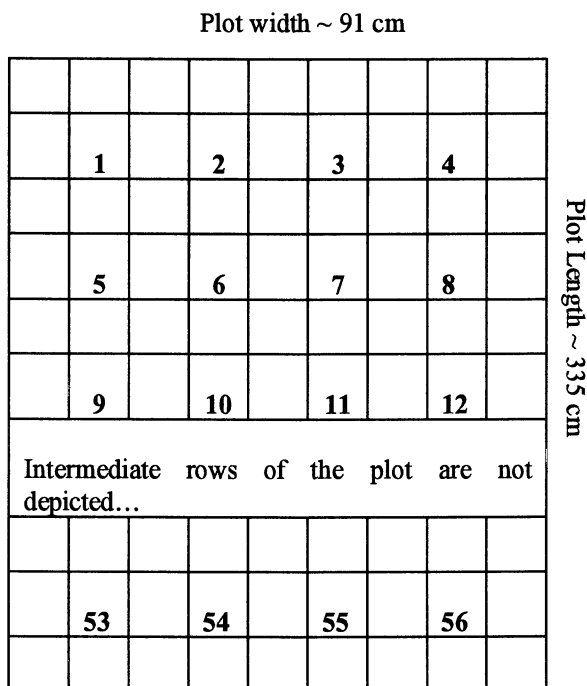
Plot width ~ 91 cm

Figure 2. Graphical representation of a portion of the plot layout of a small plot field dissipation study.

Rate of Degradation

Dissipation of flupyrsulfuron-methyl was measured in the top 0-15 cm soil core. At each sample point, soil cores were composited and homogenized. A subsample of the homogenized sample was exhaustively extracted, concentrated and analyzed by reversed-phase HPLC-LSC (*1*). The limit of detection for radiochemical HPLC was 0.3 ng flupyrsulfuron methyl/g of soil. Dissipation of flupyrsulfuron-methyl under field conditions was biphasic and non-linear regression analysis was used to calculate the DT_{50} and DT_{90} values (*3*). The regression analysis was performed on the data using the following function: ln $C = \ln C_0 - A*\ln(1+B*t)$. The dissipation times, DT_{50} (half-life) and DT_{90}, were calculated from the following equations: where $DT_{50} = [(0.5)^{-1/A}-1]/B$

and $DT_{90} = [(0.1)^{-1/A} - 1]/B$. The term DT_{50} is used to differentiate these values from half-lives calculated using pseudo-first order equations.

Dissipation of flupyrsulfuron-methyl under field conditions was very rapid (Table III). There was no significant difference in DT_{50} based on soil type, soil pH or season of application. The season of application may have affected the DT_{90}, but only one site allows direct comparison. The DT_{90} at the UK site autumn application being longer than the DT_{90} after a spring application. More alkaline soils generally had a shorter DT_{90}.

Table III. Rate of degradation of flupyrsulfuron-methyl under field conditions

Site/ Season	Soil Texture	Soil pH	Organic Carbon (%)	DT_{50}	DT_{90}
US/Spring	Silt loam	6.1	1.9	6	123
UK/Autumn	Clay loam*	7.3	1.9	10	104
UK/Spring	Clay loam*	7.3	1.9	11	77
France/Spring	Sandy silt loam*	7.8	1.1	6	35

*Classified according to the Soil Survey of England and Wales texture classification system, otherwise the USDA classification system was used.

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Mobility in Soil

The lower soil segments from the field soil dissipation trials were segmented into three sections: 15-30, 30-60 and 60-90 cm cores. At each sampling point, soil cores from the same depth and treatment were composited and homogenized. Soil segments were combusted and analyzed by LSC to determine total radioactive residue. The limit of detection for combustion analysis was 0.1 ng flupyrsulfuron-methyl/g soil.

There was little consistent movement of radioactivity in the lower cores and the radioactivity did not move below 60 cm at any site. Figures 3 and 4 show the distribution of radioactivity throughout the soil horizons at the UK site after autumn and spring applications of flupyrsulfuron-methyl at 10g ai/ha.
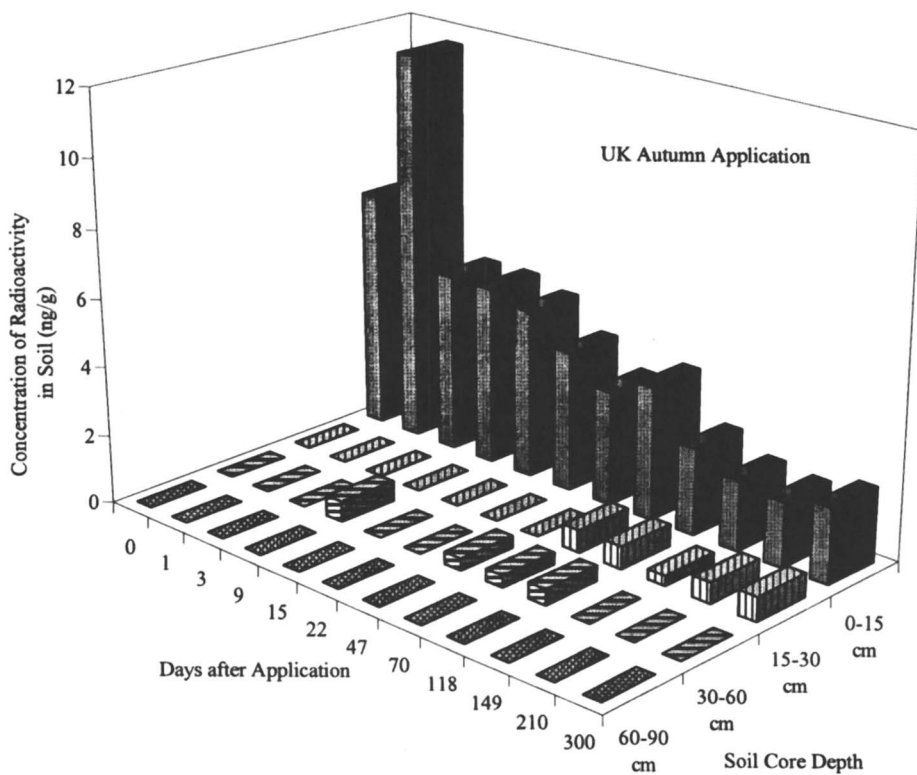
Figure 3. Distribution of radioactivity in soil horizons at UK site after autumn application of flupyrsulfuron-methyl.
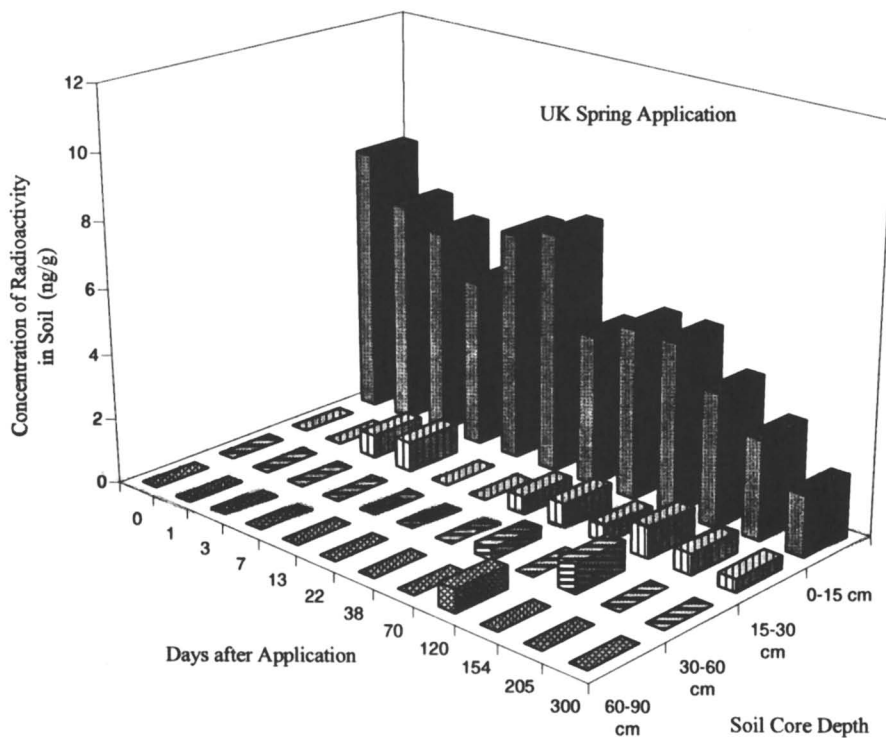
Figure 4. Distribution of radioactivity in soil horizons at UK site after spring application of flupyrsulfuron-methyl.

Computer Modeling of Mobility in Soil

The US Environmental Protection Agency "Pesticide Root Zone Model" (PRZM-2) was used to further assess the leaching potential of flupyrsulfuron-methyl under field conditions (4). A sandy loam soil was used in combination with a weather scenario modeled as an above average rainfall year in Hamburg, Germany repeated over ten years (5). The model simulates 10 consecutive years, 8 years at the maximum use rate (12 g ai/ha) for flupyrsulfuron-methyl on winter cereal crops, followed by 2 years of no application (Table IV). Soil and meterologic parameters are sufficient to allow movement of applied substances into the groundwater. The model then calculates the concentration of flupyrsulfuron-methyl in soil pore water at a one-meter depth. The estimated concentration of flupyrsulfuron-methyl at one meter never exceeded 1×10^{-3} µg/L during the entire 10-year simulation, which is the trigger value for the European Union drinking water directive.

Comparison of Laboratory to Field Data

Rate of Degradation

In laboratory soils, half-lives ranged from 8 to 26 days, at 20°C. The rate of degradation under laboratory conditions was influenced by temperature (reduced at 10°C) and soil pH (generally increased at basic pH). In the field, DT_{50} values ranged from 6 to 11 days, with DT_{90} values ranging from 35 to 123 days. The half-life in the field studies was not affected by the season of application, but the DT_{90} may have increased after an autumn application, but only the UK site was available for direct comparison. The DT_{90} values of flupyrsulfuron-methyl in the field studies were pH-dependent, with longer DT_{90} values in the more acidic soils.

Mobility in Soil

Freundlich adsorption constants showed a linear correlation to the organic matter content of soils. Koc values ranged from 15 to 22, suggesting that flupyrsulfuron-methyl would be highly mobile in soils. In the field soil dissipation studies, there was no significant movement of radioactivity below 60 cm (limit of detection = 0.1 ng/g) in field soils at three locations in the US and Europe. Under field conditions, the mobility of flupyrsulfuron-methyl was mitigated by the rapid degradation in soil. Computer modeling (PRZM-2)

Table IV. Model inputs for PRZM-2 calculation of flupyrsulfuron-methyl concentration in soil pore water at a one-meter depth

Input Variable Name	Input Variable Value
Soil (Top Layer, 0-30 cm)	Sandy Loam (68% sand)
	1.5% organic carbon
	Density = 1.5 g/cm^3
	Slope <0.5%
Climatic Conditions	Hamburg, Germany (year: 1961)
	875 mm cumulative rainfall
	Average air temperature: 9.1 °C
Groundwater Recharge (1-m depth)	~57% of the precipiation
Aqueous Solubility	1.23 moles/L
Vapor Pressure	<1 x 10^{-11} torr
Soil DT$_{50}$	8 days
Koc	15 mL/g
Maximum Annual Use Rate	12 g ai/ha

showed that the concentration of flupyrsulfuron-methyl in soil pore water at a 1-meter depth was negligible (<0.001 µg/L) which supports the limited mobility seen in the field soil dissipation studies.

Conclusions

For flupyrsulfuron methyl, there was good agreement between half-lives measured under laboratory conditions and those measured in the field. The variables affecting half-life in the laboratory soils (temperature and soil pH) correlated better with the DT_{90} values measured in the small plot field soil dissipation studies, than with the DT_{50} values from the field studies. While Koc values indicate that flupyrsulfuron-methyl was weakly sorbed by soil, movement of flupyrsulfuron-methyl to lower soil horizons in the field was mitigated by the rapid degradation of flupyrsulfuron-methyl under field conditions. The minimal movement of flupyrsulfuron-methyl under field conditions was corroborated by the results of PRZM-2 computer modeling. The small plot field dissipation studies gave good overall agreement with lab data and verified the predicted behavior of flupyrsulfuron-methyl in the field.

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Chapter 14

Changes in Soil Biomass and Microbial Community Structure as Affected by Storage Temperature and Duration: Effect on the Degradation of Metsulfuron Methyl

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The persistence of crop protection products (CPP) in field studies is often less than that observed in laboratory studies conducted on the same soils. In this study, the effects of prior soil storage on microbial biomass and community structure were measured in conjunction with the disappearance and mineralization of [phenyl (U)-^{14}C] metsulfuron methyl herbicide. Laboratory soils in this study were collected and used fresh (stored less than 3 weeks) or stored at 4 and 20 °C for 3 and 6 months prior to use. The phospholipid fatty acid technique was used to monitor changes in the microbial biomass. Results indicate that both the storage duration and temperature significantly impacted the soil biomass, while the degradation and mineralization of metsulfuron methyl were only significantly impacted by the duration of storage.

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Introduction

Currently, US EPA regulatory guidelines require an aerobic soil metabolism study and at least two terrestrial field dissipation studies completed for the registration of crop protection products (CPP). Often the half-lives generated in the laboratory are generally longer than those generated in the field (1,2). The longer laboratory half-lives for some CPP may in part be attributed to a decline in the viability of the soil biomass during storage. This is especially true if biotic degradation plays a significant role in the CPP degradation. Studies on the effect of storage to soil have reported declines in soil biomass (3,4,5), community structure (6,7), and genetic diversity (8) during storage. For CPP in which microorganisms are the predominate agent involved in their transformation, differences between the degradation rates in laboratory compared to field may ultimately be linked to changes that occur during a soil's storage. Thus a better understanding of how storage affects a soil's microbial community may improve the design and interpretation of laboratory soil metabolism studies of CPP.

This laboratory study was designed to investigate the effect storage duration and storage temperature have on a soil's microbial community and, in turn, how these changes affect its capacity to degrade metsulfuron methyl. Metsulfuron methyl was chosen as the probe compound since it has a moderate half-life of 10-30 days (9,10), and has a large microbial component to its degradation (10). Abiotic degradation (hydrolysis) of metsulfuron methyl was minimized in this study through the use of an alkaline (pH 8.0) soil.

Materials and Methods

Soil

Selected soil properties are listed in Table I. Soil samples were collected from a potato field in American Falls, Idaho, on October 8, 1998 and sieved through a 2-mm sieve prior to storage. Soils were stored in the dark at field moisture levels (57% of 1/3 bar). The storage conditions investigated in this study were the following: 1) fresh soil stored for <3 weeks at 4 °C; 2) soil stored for 3 months at 4 °C; 3) soil stored for 3 months at 20 °C; 4) soil stored for 6 months at 4 °C; and 5) soil stored for 6 months at 20 °C.

Table I. Selected properties of Trevino soil

Texture	pH	Organic Carbon	Soil Water Content	Particle Size Analysis		
			1/3 bar	Sand	Silt	Clay
			$g\ kg^{-1}$			
Silt loam	8.0	22	200	210	650	140

Soil Biomass Analysis

Soil microbial biomass and community structure were determined by phospholipid fatty acid (PLFA) analysis (11). Triplicate 10 g sub-samples of soil were extracted in a solution containing methanol:chloroform:phosphate buffer (2:1:0.8; v:v:v). Lipid extracts were separated into neutral, glyco-, and phospholipids using silica gel solid-phase extraction columns. The phospholipid fraction was subject to a mild alkaline methanolysis with the resulting fatty acid methyl esters (FAME) being extracted and purified on a C_{18} solid phase extraction column. The FAMEs were separated on a GC system using a 30 m X 0.25 mm DB-5ms (J&W Scientific) column and a programmed temperature increase from 110 to 300 °C at 15 °C min^{-1} held for 15 min at 300 °C. Total microbial biomass was related to total extractable PLFA while changes in individual PLFA were used to reflect changes in bacterial, actinomycete or fungal communities. Identification of individual FAMEs were based on retention times from standards and quantitation of individual FAMEs were based on an internal standard (20:0 ethyl ester) by GC/FID (11). Table II list signatures PLFA and their relationships with the bacterial, actinomycete or fungal communities.

Soil Application, Extraction, and Analysis

The aerobic soil metabolism of [phenyl-(u)-^{14}C] metsulfuron methyl was conducted in a flow-through tests system consisting of ten 250-mL centrifuge bottles containing 50 g of soil (oven dry weight) each, and connected to KOH traps and incubated in the dark at 20 ± 2°C. Two replications per treatment were prepared. Each test vessel was treated with 10 µg of ^{14}C -metsulfuron methyl (radiochemical purity ≥ 95%) for a total of 14.3 KBq per vessel, which corresponds to a final concentration of 0.2 µg ^{14}C -metsulfuron methyl g^{-1} of dry soil. Metsulfuron methyl was applied drop-wise by pipette in an aqueous solution in order to bring the soil moisture contents to 75% of 1/3 bar. Soils

were mixed by hand for 2 minutes following the application of the test compound.

At predetermined time intervals, soils were extracted 3 times with 100 ml of a saturated acetonitrile: 2M ammonium carbonate solution and radioactivity determined in each extract by liquid scintillation analysis (LSA). Soil extracts were concentrated and analyzed for radiolabled compounds using an HPLC system equipped with a radiochemical detector and fraction collector. The HPLC system separated radiolabeled compounds using a 4.6 mm X 250 mm RX-C8 Zorbax ODS HPLC column, a solvent flow rate of 1.5 ml min^{-1}, and a column temperature set at 40 °C. A non-linear mobile phase gradient consisting of acetonitrile and 0.1% formic acid buffer were previously described (10). Unextractable radioactivity was determined by combustion of triplicate 1.0-g soil samples. At each sampling interval, the KOH trapping solutions were removed and replaced with fresh solution. Radioactivity in the trapping solutions was quantified by LSA. The material balances for applied ^{14}C material ranged from 91 to 110 % and averaged 102% of the applied radioactivity.

Statistical Analysis

Total Biomass:

Analysis of variance and mean separation (LSD) techniques were used to test for significant differences ($\alpha = 0.05$) of the total PLFA contents, as well as of the signature PLFA representing either fungal, bacterial, or actinomycete populations.

Metsulfuron-Methyl Degradation and Mineralization Comparisons:

The natural log-transformed data for metsulfuron methyl degradation (loss of parent compound) versus time and the data for the mineralization of metsulfuron methyl versus time were fitted to a linear regression line. The half-lives and rates of mineralization were calculated from the fitted equations

All statistical calculations were performed using JMP statistical software (SAS Institute, Cary, NC).

Results and Discussion

Soil biomass

Storage duration and temperature did have a significant ($p<0.05$) impact on the total microbial biomass for stored soils. Biomass levels in soils stored for 3 and 6 months at 4 °C were found not to be significantly different from fresh soil

(p<0.05) while soils stored at 20 °C for 3 and 6 months did have a significantly smaller biomass when compared to fresh soils (Figure 1A). Compared to fresh soil loss of total biomass for soil stored at 20 °C ranged from 47% (3 months) to 58% (6 months). These results are in agreement with previous studies that reported biomass stability was maintained in soils stored cold compared to soils stored at elevated temperatures (i.e., > 20°C) (2,4). The Trevino soil stored for 6 months at 4 °C maintained its biomass just as well as the soil stored for 3 months at 4 °C even though previous studies have generally shown a rapid decline in the soil biomass for soils stored longer than 3 months at 4 °C (4). However, other studies have shown that in isolated cases some soils do retain a significant portion of their biomass following storage at 4 °C and some as long as 14 months (2,11). A possible reason for the ability of this soil to maintain its biomass may be related to the soil's microbial community ability to adapt to cold environments since the average temperature in the geographic region where this soil was sampled ranged between 10 and -1 °C.

The PLFA profiles also provide information on changes within the microbial community during storage (6). Soil fungal lipid levels, as indicated by lipid biomarkers, were reduced by longer soil storage (p<0.05), whereas storage temperature did not have an effect (Figure 1B). Fungal lipid biomarkers decreased 37% (3 month) and 68% (6 month) during storage compared to fresh soil. Since fungi typically make-up the single largest fraction of the soil biomass and produce extracellular enzymes that enable them to metabolize recalcitrant compounds, it might be expected that changes in the fungal population reflect changes in degradation kinetics of metsulfuron methyl. Thus storage duration would have more of an influence on metsulfuron methyl degradation in alkaline soil than storage temperature.

Both storage duration and storage temperature significantly (p <0.05) affected bacterial PLFAs (Figure 1C). Fresh soils contained a larger amount of bacterial PLFA than soils stored for 3 or 6 months at 20 °C and for 6 months of

Table II. Signature phospholipid fatty acids and their interpretations.

Fatty acid	Interpretation
i15:0, a15:0, 15:0, i16:0, 16:1ω9c, i17:0, a17:0, 17:0, cy17, cy19	Predominately bacterial
18:2 ω 9, 18:3 ω 6	Fungi
10 Me18:0	Actinomycete

Note: Fatty acids are designated as total number of carbon atoms: number of double bonds, with the position closest to the carboxyl (ω) end indicated and using a c for cis or t for trans. The prefixes 'i," "a,", "cy," and "Me" refer to iso, anteiso, cyclopropyl and methyl branching, respectively.
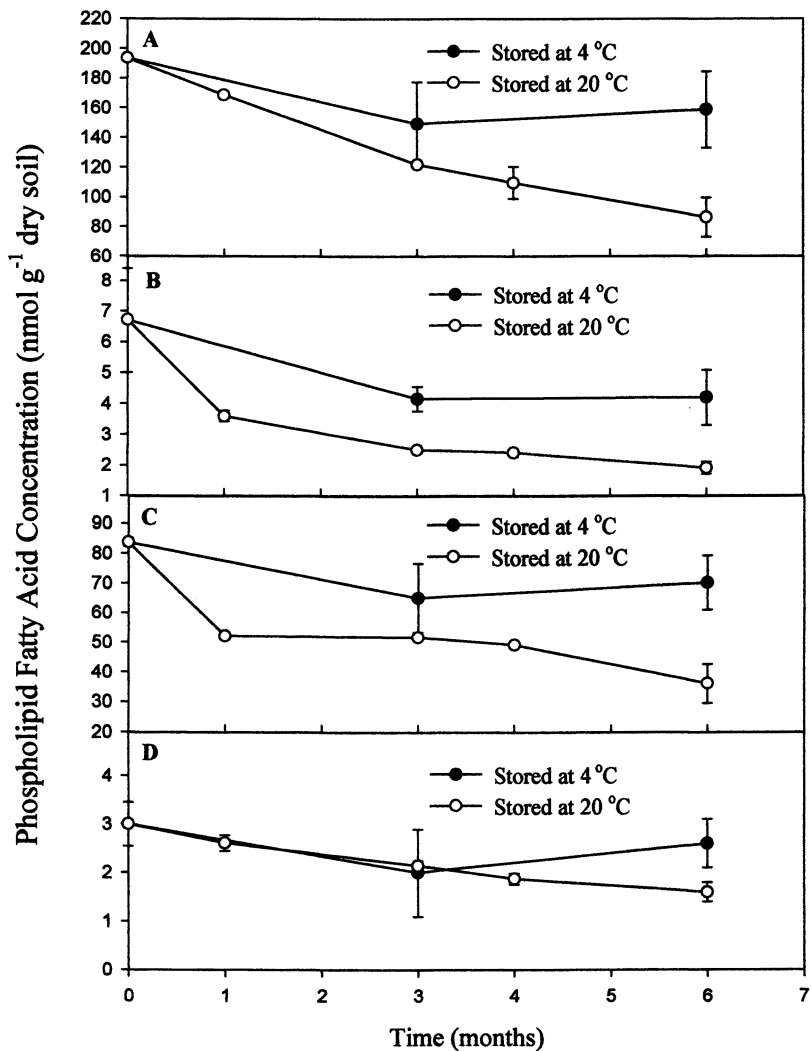
Figure 1. Changes in extractable PLFA content of samples throughout 6 months of storage at 4 °C and 20 °C. (A) Total extractable phospholipid; (B) Fungi PLFA biomarkers, (C) Bacterial PLFA biomarkers; (D) Actinomycete PLFA biomarkers. Error bars represent the standard deviation of the mean.

storage at 4 °C (p<0.05). Soils stored for 3 months had more bacterial PLFAs than soils stored for 6 months (p<0.05). There was no significant effect of storage temperature (p<0.05) on bacterial lipid content after storage for either 3 or 6 months. As with fungi, storage duration is more detrimental to bacterial survival than storage temperature.

Actinomycete PLFA content was significantly different (p<0.05) only for storage duration (Figure 1D). Compared to fresh soil, actinomycete PLFAs decreased by 44% after 6 months storage at 20 °C (p<0.05). In previous studies, the lipid biomarkers for gram positive organisms which include actinomycete were not affected by storage and in fact proportionately tended to dominate PLFA profiles with storage (5,6). Based on PFLA biomarkers, actinomycete were the least affected by soil storage than either fungi or bacteria, and this is in agreement with other studies (5,6).

Overall, the duration of storage rather than storage temperature control soil microbial PLFA contents with decreasing microbial biomass being associated with increasing storage duration. Consequently, if soil microorganisms are the dominant agents involved in the degradation of metsulfuron methyl in alkaline soil, it would stand to reason that storage duration would have a more significant impact in altering the degradation kinetics of metsulfuron methyl than storage temperature.

Degradation and mineralization of metsulfuron-methyl

Degradation of metsulfuron methyl in fresh soil was significantly faster than in stored samples (Table III). There were no significant differences in the degradation rates for soils stored for 3 or 6 months regardless of the temperature of storage (Figure 2). The half-lives of metsulfuron methyl were between 30%

Table III. First order degradation rates for metsulfuron-methyl in fresh and stored soil

Length of storage months	Storage temperature °C	K_1 10^{-2} days^{-1}	$t_{1/2}$ days	r^2
0	4/20	1.56	45	0.985
3	4	1.15	60	0.966
3	20	0.98	71	0.967
6	4	1.11	62	0.928
6	20	1.19	58	0.957

$t_{1/2}$, half-life based on first order degradation model; r^2, regression coefficient for first order fit
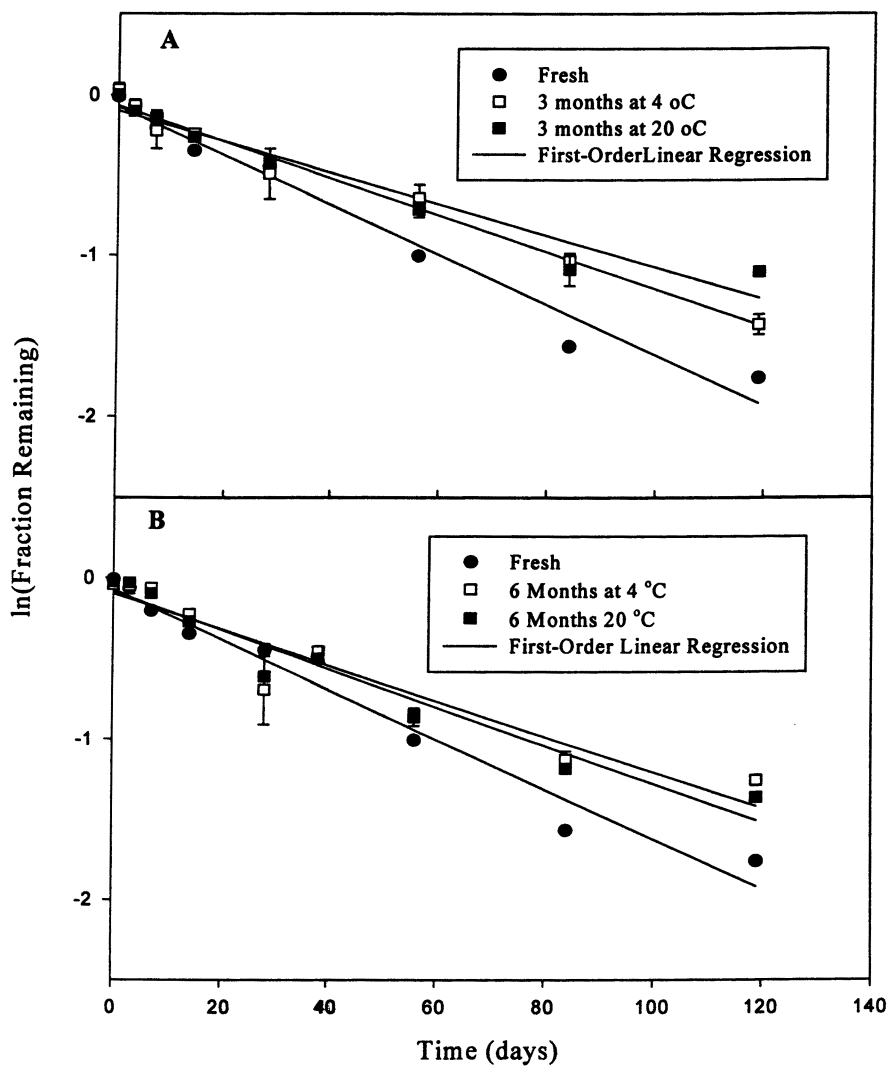
Figure 2. Changes in dissipation rate of 0.2 μg g-1 of [14C]-metsulfuron methyl in stored Trevino soil at different temperatures based on first-order degradation kinetics: (A) Soils stored for 3 months; (B) Soils stored for 6 months. Error bars represent the standard deviation of the mean.

and 59% longer in stored soil versus fresh soil. Similarly, mineralization of the phenyl ring of metsulfuron methyl was also significantly impacted by storage duration. Mineralization of metsulfuron methyl in stored soils was reduced between 20% and 30% when compared to that of fresh soil (Figure 3).

The decline in the degradation rate and mineralization of metsulfuron-methyl did not correspond to the decline in soil biomass or the decline of any specific microbial subgroup. This may signify that no specific subset of the soil biomass was involved in the degradation of metsulfuron-methyl, but rather a mixture of soil microorganisms (i.e., fungi, actinomycete, etc) mediates degradation of metsulfuron-methyl.

Functional redundancy in the soil microbial community may have limited significant changes to metsulfuron-methyl degradation during storage. Functional redundancy in the soil biomass may help explain why linuron degradation was only moderately affected in 12 different soils stored cold or frozen (-20 °C) for 13 months (12) even though there were significant reductions in the soil biomass.

It is possible that chemical hydrolysis of metsulfuron-methyl may have obscured changes in the degradation rate that otherwise would be attributed to soil microorganisms. However, given that mineralization rate of the phenyl moiety of metsufluron methyl is due to biological transformation any changes in the microbial community should also be reflected in changes in mineralization rate of metsulfuron methyl (e.g., $^{14}CO_2$ evolution). Thus if the microbial community's role in the degradation of metsulfuron methyl was obscured by chemical hydrolysis then changes in the mineralization rate of metsulfuron methyl should be observed while changes in the degradation rate of parent would not be observed. Yet no such observation was made between the mineralization rate and the degradation rate of metsulfuron methyl. In fact the mineralization rate and degradation rate of metsulfuron methyl followed similar patterns of change (i.e., as the rate of parent loss declined so did the rate of mineralization). Consequently it would appear that chemical hydrolysis did not obscure changes to the biological degradation rate of metsulfuron methyl since changes in the mineralization and degradation rate of metsulfuron methyl were similar.

Conclusion

Long-term storage (≥3 mo.) of soil prior to use in a laboratory degradation study reduced total soil biomass, caused changes in the microbial community and reduced degradation and mineralization rates of metsulfuron methyl when compared to fresh soil. Such changes in microbial biomass and community structure may explain, in part, differences commonly observed between laboratory- and field-generated soil persistence data. The duration of a soil
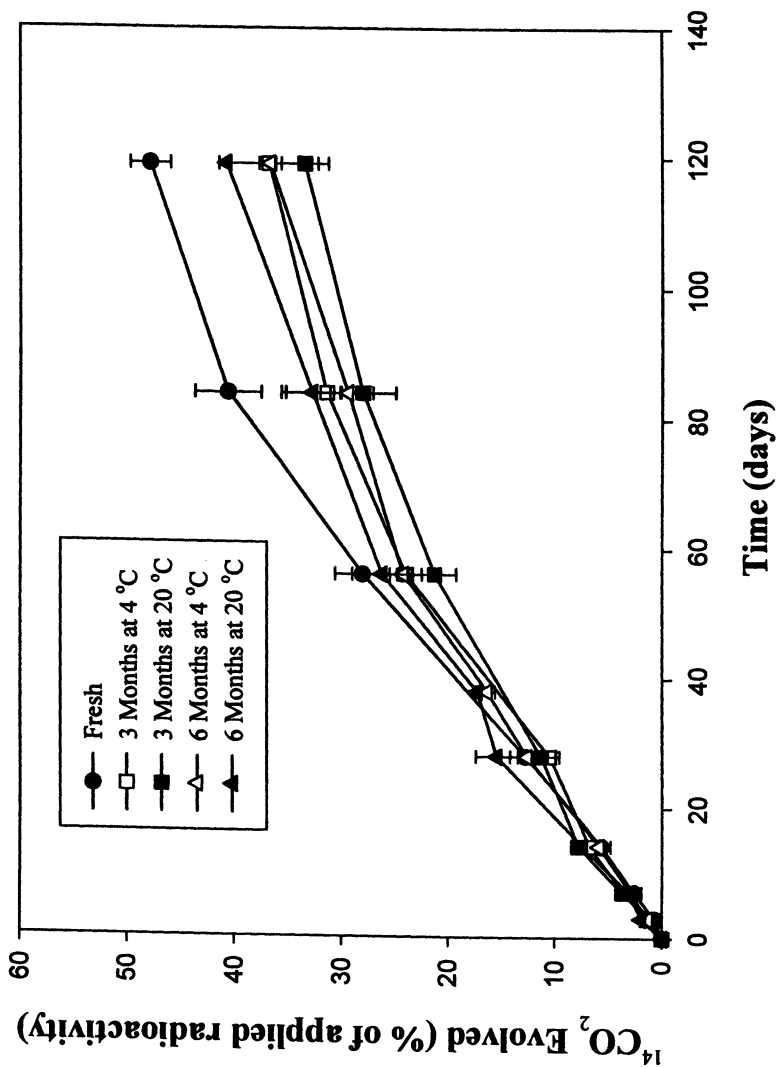
Figure 3. Mineralization of [^{14}C]-metsulfuron methyl in fresh Trevino soils or Trevino soils stored for 3 and 6 months at 4 °C and 20 °C. Error bars represent the standard deviation of the mean.

storage more negatively impacted soil biomass and community structure than did storage temperature. Declines in the soil biomass during storage may result in the loss or reduction of certain functional properties. It is thus recommended that soils used in aerobic soil metabolism studies be fresh soil. If the use of fresh soils is not feasible soils stored at 4 °C for less than 3 months would be acceptable.

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Chapter 15

Degradation of Pyrithiobac Sodium in Soil in the Laboratory and Field

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Pyrithiobac sodium is an acetolactate synthase inhibiting herbicide with both preemergence and postemergence activity. Pyrithiobac sodium is used in cotton for control of broadleaf weeds and grasses. In the laboratory, ^{14}C-pyrithiobac sodium was used to determine the degradation rate and degradation pathway in soil. Bare-soil field dissipation studies using ^{14}C-pyrithiobac sodium were conducted in Mississippi and California using small plots (91 x 335 cm) and soil columns (9.5 x 96.5 cm columns inserted ~ 90 cm into soil). Full-scale field dissipation studies (4 x 15 m and 4 x 18-m plots) with non-labeled pyrithiobac sodium were conducted in Texas and Mississippi. In the laboratory, pyrithiobac sodium was degraded microbially (60-73% mineralized) with a half-life of 60 days. Adsorption studies suggested pyrithiobac sodium would be mobile in soil, with linear Koc values ranging from 14.7 to 26.9. In the field, pyrithiobac sodium degradation was more rapid with half-lives ranging from 11 to 46 days. Small plot and full-scale field dissipation studies gave comparable degradation rates from the same site. In addition, the field studies showed limited mobility of pyrithiobac sodium under field conditions. This was corroborated by the results of a small-scale prospective groundwater monitoring study. The

three designs for the field soil dissipation studies gave similar results for the dissipation and mobility of pyrithiobac sodium under field conditions.

Introduction

Pyrithiobac sodium (sodium 2-chloro-6-[(4,6-dimethoxypyrimidin-2-yl)thio]benzoate) is the active ingredient in DuPont's Staple® herbicide that inhibits acetolactate synthase in sensitive weeds (*1*). Pyrithiobac sodium is a low use-rate herbicide for pre- and postemergence control of annual and perennial broad-leaved weeds in cotton. This publication will focus on the comparison of the environmental fate data generated in laboratory studies and the behavior of pyrithiobac sodium in field soil dissipation studies. Further, the results from three types of field soil dissipation studies will be discussed: small plot studies using radiolabeled material, full-scale field studies using unlabelled material and soil cylinder studies using radiolabeled material.

Degradation Pathway

Pyrithiobac sodium was hydrolytically stable. Pyrithiobac sodium degraded rapidly in aqueous photodegradation studies, with cleavage of the sulfur bridge to yield 2-chloro-6-sulfobenzoic acid and 4,6-dimethoxy-2-pyrimindinol (Figure 1). The pyrimidine ring was further degraded under irradiated conditions to urea. In soil photolysis studies, carbon dioxide and urea were the major degradates formed. In soil incubated under darkness, microbial degradation to carbon dioxide (60 to 73% of the applied radioactivity at 1 year) and unextractable residues (14 to 24% of the applied radioactivity) was the major degradative pathway.

Laboratory Studies

Rate of degradation and adsorption/desorption studies were performed using soils obtained from the proposed use areas of pyrithiobac sodium. These studies were performed using pyrithiobac sodium that was either uniformly labeled on the phenyl or in the 2 –position of the pyrimidine ring.

Rate of Degradation

The rate of degradation of pyrithiobac sodium was measured in a silt loam soil obtained from Mississippi (USA), under both non-irradiated and irradiated
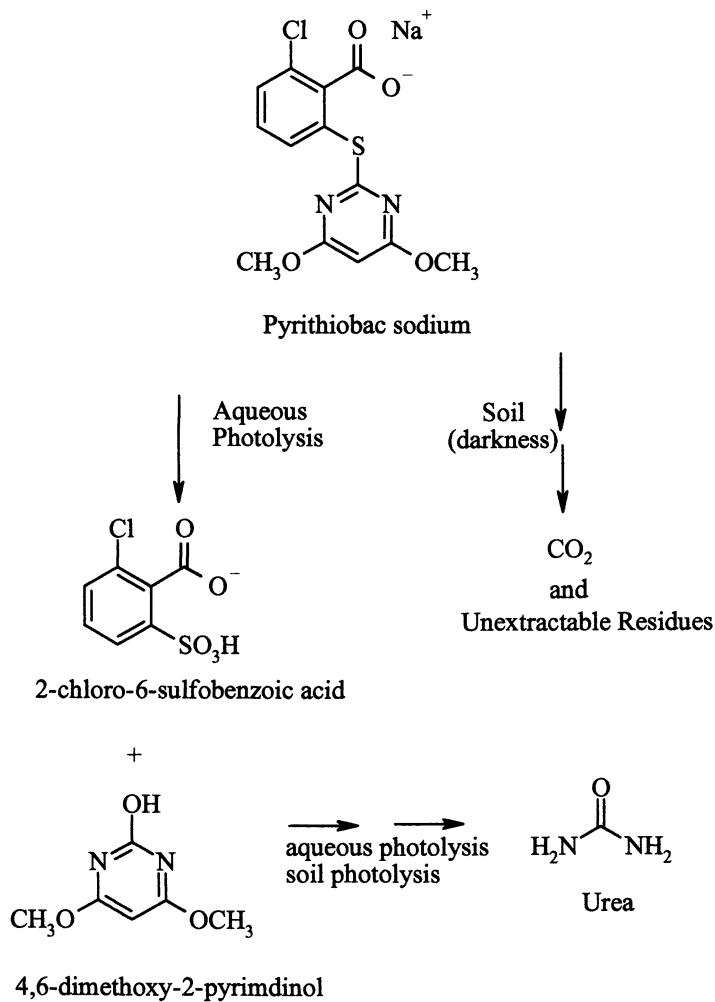
Figure 1. Major degradation products of Pyrithiobac sodium.

conditions. For the non-irradiated study, soils were incubated under aerobic conditions in darkness at 25 °C and 75% of 0.33 bar soil moisture-holding capacity. Pyrithiobac sodium was applied to soil at a nominal concentration of 0.1 mg/kg soil. Volatile radioactivity (carbon dioxide) was trapped in 1 N NaOH and confirmed by precipitation as barium carbonate. For the irradiated study, air-dried silt loam soil (Mississippi) was placed in soil trays. Pyrithiobac sodium was applied to the soil surface at a rate equivalent to 140 g ai/ha. Soil samples were irradiated under xenon arc lamps inside a Suntest® accelerated exposure unit for 15 days, at a temperature of approximately 25°C. Volatile radioactivity (carbon dioxide) was trapped in 1 N NaOH and confirmed by precipitation as barium carbonate. A second set of soil trays were incubated in the dark.

Soils were extracted with acetone: 0.05 M ammonium carbonate (9:1, v:v), followed by 0.5 M ammonium carbonate. For the irradiated studies, additional extractions with acetone:water (50:50, v:v) were performed. Analyses were performed using reversed-phase HPLC with fraction-collection of the eluate followed by liquid scintillation counting (HPLC-LSC), to determine the amount of radioactivity associated with each chromatographic peak. Limit of detection for radiochemical methods was 0.4% of the applied radioactivity. Recoveries were >98% of the applied radioactivity (%AR). The rate of degradation was first-order and linear regression analysis was used to calculate the half-life of pyrithiobac sodium.

Under non-irradiated conditions, pyrithiobac sodium degraded with a half-life of 60 days, with extensive mineralization. The only other significant degradation product occurring at > 10 %AR was unextractable residue. In irradiated soil, degradation was clearly accelerated relative to similar samples protected from light.

Adsorption to Soil

Adsorption of pyrithiobac sodium was measured in 4 soils with a range of pH and soil textures. Adsorption studies were carried out with a 1:1 ratio of soil to 0.01 M calcium chloride solution and were shaken for 24 hr at 25 °C to equilibrate. The test vessels were centrifuged and the supernatants were analyzed by reversed-phase HPLC-LSC. The soils were extracted with acetone:0.05 M ammonium carbonate (9:1, v:v) and the extracts analyzed by reversed-phase HPLC-LSC. After extraction the soil solids were combusted and analyzed by LSC to determine total recovery of radioactivity.

Pyrithiobac sodium is weakly sorbed to soil (Table I). Freundlich adsorption constants (Kd) for all 4 soils were less than one, ranging from 0.06 to 0.61, with some general correlation to the percent organic carbon content.

Table I. Koc values for pyrithiobac sodium on soil.

Soil Texture (source)	Soil Organic Carbon (%)	Soil pH	Koc[a]
Silt loam (Delaware)	3.0	5.9	14.7
Silt loam (Mississippi)	0.64	6.5	15.1
Sandy loam (California)	0.64	7.2	18.0
Clay loam (North Dakota)	2.9	7.7	26.9

a. Linear adsorption data

Field Studies

Field soil dissipation studies were performed at 3 sites in the United States. Three study designs were used: small plot studies with radiolabeled material, large-scale studies with unlabelled material and soil cylinder studies with radiolabeled material. For the small plot and large-scale studies, soil sampling was performed using a Concord multistage soil probe (Concord Environmental Equipment, Hawley, MN, USA), which allows sampling of 0-15 cm core (~6 cm diameter), followed by a 15 –90 cm soil core (2.5 cm diameter). This multistage coring approach minimizes the potential of contaminating the lower soil segment with material from the soil surface. In the soil cylinder study, the entire cylinder as sampled. In all studies, pyrithiobac sodium was applied to the bare soil surface at a rate of approximately 140 g ai/ha (2 oz/A).

At the Mississippi test site, both a small-plot radiolabeled test and a more standard full-scale test with non-radiolabeled material were conducted. For the small-plot field soil dissipation study (91-x 335 cm), bare ground plots were divided into approximately 100 cm^2 subplots and numbers were assigned to 56 subplots throughout the test plot; the remaining subplots were not numbered. Figure 2 shows a representation of a portion of the plot layout. Radiolabeled pyrithiobac sodium was mixed with appropriate inert ingredients, diluted with water and applied as a soil directed spray a CO_2 plot-sprayer with a hand-held boom. Each radiolabel was applied to a separate plot. Triplicate soil cores were taken randomly across the plot at each sampling point. The plots were sampled for 534 days after treatment. The 15-90 cm core was cut into 5 segments: 15-30, 30-45, 45-60, 60-75 and 75-90 cm. For each sampling point, soil segments from the same depth and treatment were composited and homogenized.

Full-scale field dissipation studies were performed at two sites (dimensions either 4 x 18 m or 4 x 15 m), one of which was the same as the small-plot field dissipation site. Each plot was divided into 3 replicate plots, each consisting of 10 equal subplots measuring 0.18 m^2. A treated buffer zone was around the

replicate plots, no soil samples were taken in the buffer zone. Figure 3 shows a graphical representation of the plot design. Formulated pyrithiobac sodium (water-soluble powder containing 85% active ingredient) was mixed with water and applied with a CO_2 plot sprayer with hand-held booms as a soil directed spray. The sprayers were equipped with standard flat fan nozzles. At each sampling point, one soil core was taken from either every even- or every odd-numbered subplot in each replicate plot (5 cores/replicate or 15 cores total). The plots were sampled for 210 days after application of pyrithiobac sodium. The lower soil core (15-90 cm) was cut into 2 segments: 15-45 and 45-90 cm. At each sampling point, soil segments from the same depth and replicate plot were homogenized (3 samples/depth/sampling time).

A field soil dissipation study using soil cylinders was conducted at one site. In two separate plots (210 x 750 cm) , twenty-three stainless steel cylinders with plastic sleeves inserted (95 cm long, 9 cm i.d.) were driven into the ground, leaving 2.5 to 5 cm above the soil surface. At least 60 cm was left between the cylinders to allow for ease of removal. Figure 4 shows a graphical representation of the plot layout. Radiolabeled pyrithiobac sodium was mixed with appropriate inert ingredients, diluted with water and pipetted evenly across the soil surface within each cylinder. Each radiolabel was applied to the cylinders within a separate plot. At each sampling point, one cylinder was harvested from each of the two plots (one cylinder per radiolabel per sampling point). The plots were sampled for 540 days after application. The soil cylinders were cut into 6 segments: 0-15, 15-30, 30-45, 45-60, 60-75 and 75-90 cm. Each segment was homogenized prior to analysis.
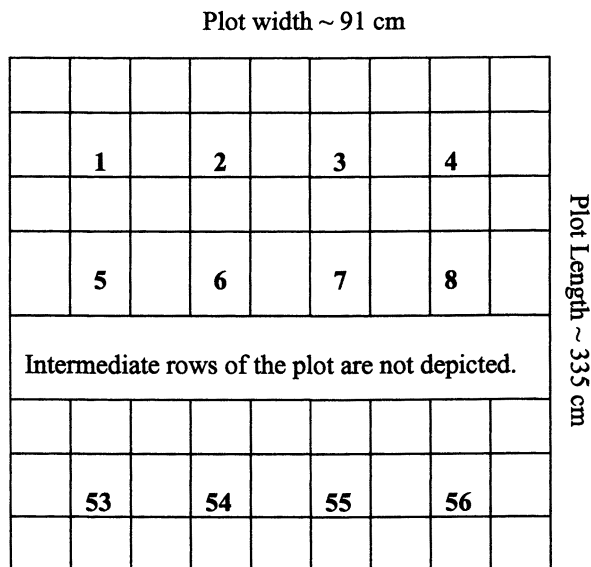
Plot width ~ 91 cm

Figure 2. Graphical representation of a portion of the plot layout of a small plot field dissipation study

Approximately 4 m, including buffer zone

1	2	1	2	1	2
3	4	3	4	3	4
5	6	5	6	5	6
7	8	7	8	7	8
9	10	9	10	9	10

Approximately 18 m including buffer zone
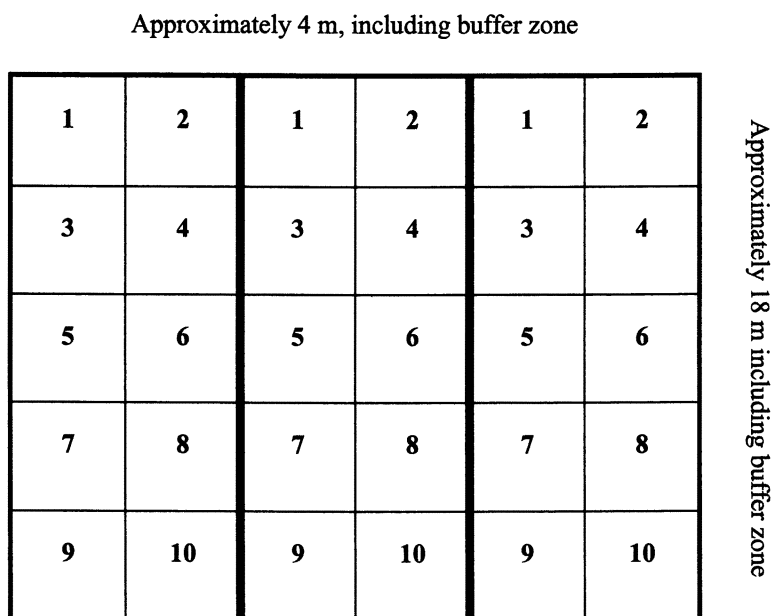
Figure 3. Graphical representation of the full-scale field soil dissipation plot layout

Plot 1   Plot 2
210 cm

Approximately 750 cm

Cylinders are at least 60 cm apart
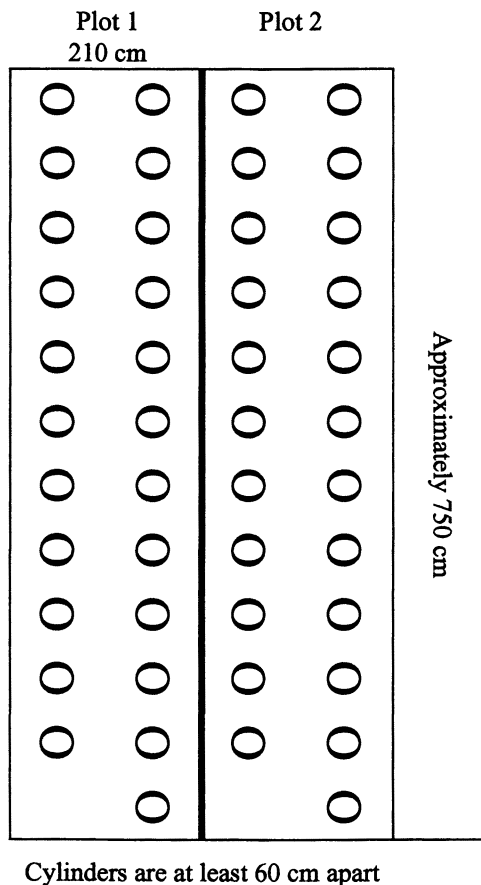
Figure 4. Graphical representation of plot layout of soil cylinder study

Rate of Degradation

Dissipation of pyrithiobac sodium was measured in the top 0-15 cm soil core.
For the studies performed with radiolabeled material, a subsample of the
homogenized soil sample was exhaustively extracted as described above,
concentrated and analyzed by reversed-phase HPLC-LSC. The limit of detection
for radiochemical HPLC was 1 ng/g of soil. For studies using unlabeled
material, a subsample of the homogenized soil was mixed with acetone: 1N

sulfuric acid (4:1) and was extracted in a soxhlet apparatus and then the mixture was centrifuged. The supernatant was partitioned with dichloromethane (DCM), the DCM layer was concentrated, derivatized with diazomethane and eluted through a florisil column. The derivatized samples were analyzed by gas chromatography with mass selective detection (GC/MSD) using a DB 1701 column. The limit of detection for the GC/MSD method was 4 ng/g soil. Dissipation of pyrithiobac sodium under field conditions was biphasic and non-linear regression analysis was used to calculate the DT_{50} and DT_{90} values (2). The regression analysis was performed on the data using the following function: $\ln C = \ln C_0 - A*\ln(1+B*t)$. The dissipation times, DT_{50} (half-life) and DT_{90}, were calculated from the following equations: $DT_{50} = [(0.5)^{-1/A}-1]/B$ and $DT_{90} = [(0.1)^{-1/A}-1]/B$. The term DT_{50} is used to differentiate these values from half-lives calculated using pseudo-first order equations.

Pyrithiobac sodium dissipated relatively quickly under field conditions (Table II). In the small plot study, the concentration of degradation products was not significant (<8% applied radioactivity). In the soil cylinder study, two significant degradation products were seen: O-desmethyl pyrithiobac and 2-chloro-6-sulfobenzoate, both of which reached a peak concentration 92 days after application (0.01-0.02 µg/g), but had decline to undetectable levels by Day 181. In the full-scale field studies only the concentration of pyrithiobac sodium in the soil was measured. There was no clear correlation between the rate of degradation and soil characteristics.

Table II. Rate of degradation of pyrithiobac sodium under field conditions

Site	Soil Texture	Soil pH	Organic Carbon (%)	Plot Type	DT_{50} (days)	DT_{90} (days)
Mississippi	Silt loam	6.6	0.64	Small plot	19	179
Mississippi	Silt loam	6.1	1.0	Full-scale	14	86
Texas	loam	8.2	0.81	Full-scale	11	49
California	loam sand	5.6	0.41	Soil cylinder	46	208

Mobility in Soil

For the studies using radiolabeled pyrithiobac sodium, total radioactivity in the lower soil horizons was measured by combustion followed by LSC analysis. The limit of detection for soil combustion analysis was 6 ng/g soil, allowing for detection of approximately 1% of the initial application. For the studies using

unlabeled material, the concentration of pyrithiobac sodium was determined using the GC/MSD method described above (limit of detection was 4 ng/g soil).

The four field dissipation studies showed that pyrithiobac sodium and its related degradation products were basically immobile under field conditions. Figures 5 through 7 show the concentrations of pyrithiobac sodium or total radioactivity measured in the soil horizons. The three different plot designs used for the field soil dissipation studies gave essentially the same results.

Small-scale Prospective Groundwater Study

A small-scale prospective groundwater monitoring study was conducted in North Carolina with a worst-case vulnerable soil (>90% sand). Pyrithiobac sodium was applied at the maximum use rate of 140 g ai/ha postemergent to a cotton crop following normal agronomic practices. Potassium bromide was applied (167 kg/ha) as a reference compound to evaluate water movement to the water table. Three well clusters were placed within the treatment area, with each cluster consisting of a shallow well (upper 150 cm of the water table) and a deep well (150 to 300 cm below the water table. The well clusters were used to sample groundwater. In addition, three suction lysimeter clusters were installed adjacent to the well clusters. The lysimeter clusters consisted of duplicate sets of 90, 180, 270 and 360 cm deep lysimeters. The lysimeters were used to sample soil pore water. Soil samples were collected using a Concord Model SS4804, two stage soil probe. Soil samples were collected in 0-60 cm (5.6 cm diameter) and 60- to 120 cm (5 cm diameter) segments.

Water samples were filtered through a graphitized carbon solid phase extraction cartridge and analyzed by reversed-phase HPLC with UV detection. The limit of detection for water methods was 0.05 ng pyrithiobac sodium/g water. The soil samples were extracted using Milli-Q® water at subcritical conditions (100 °C and 2000 psi) using a DIONEX ASE™ 200 extractor. The extract was passed through a graphitized carbon column and analyzed by column-switching HPLC with UV detection. The limit of detection for the soil method was 0.3 ng pyrithiobac sodium/g soil. Ion chromatography analysis was used to measure bromide concentrations in the water samples.

Bromide was detected in lysimeters at all four soil depths, with the first detection at the 90 cm depth at 28 days after application (DAT). Bromide was found in soil, soil-pore water and groundwater samples throughout the study, indicating that the test site was hydrogeologically vulnerable for movement of compounds into groundwater. Pyrithiobac sodium was detected in 90 cm depth lysimeters (soil-pore water) at 63 DAT and was last detected in two 98 DAT soil pore water samples. There were no other detections of pyrithiobac sodium in soil pore water at any depths throughout the course of the study, except for a
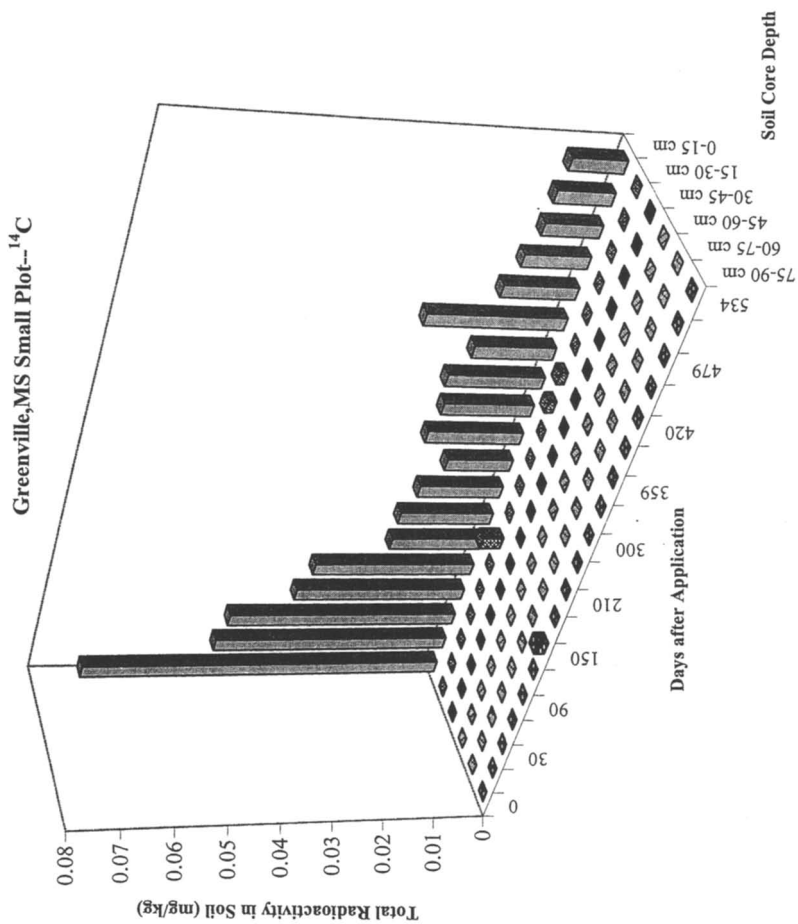
Figure 5. Distribution of radioactivity in soil horizons at Mississippi site with a small plot design
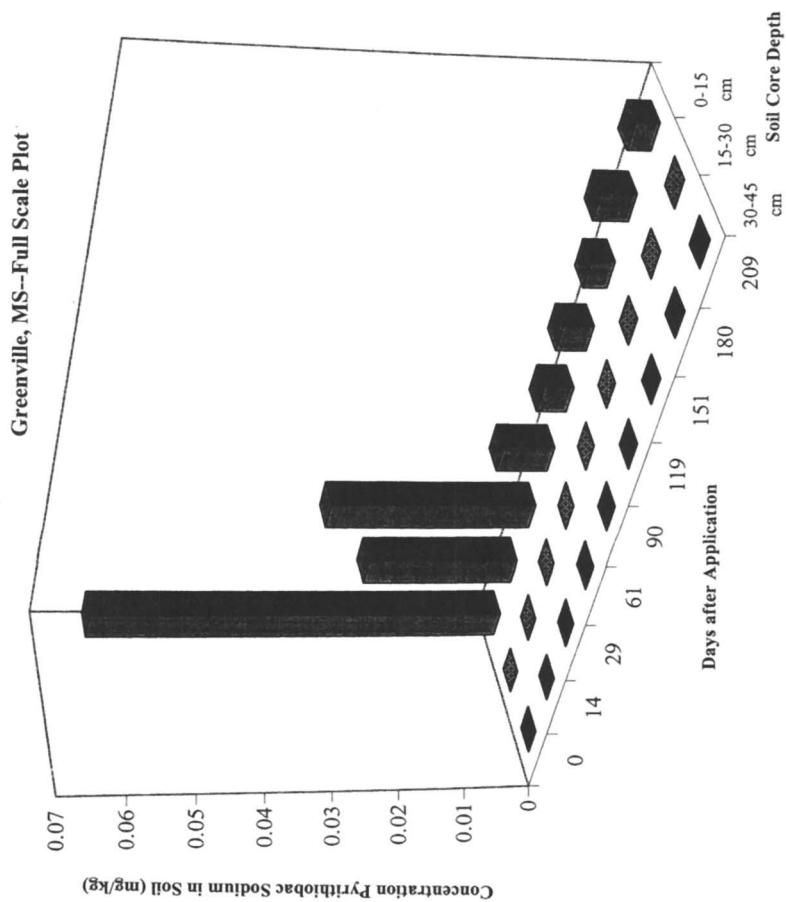
Figure 6. Distribution of pyrithiobac sodium in soil horizons at Mississippi site with a full-scale plot design.
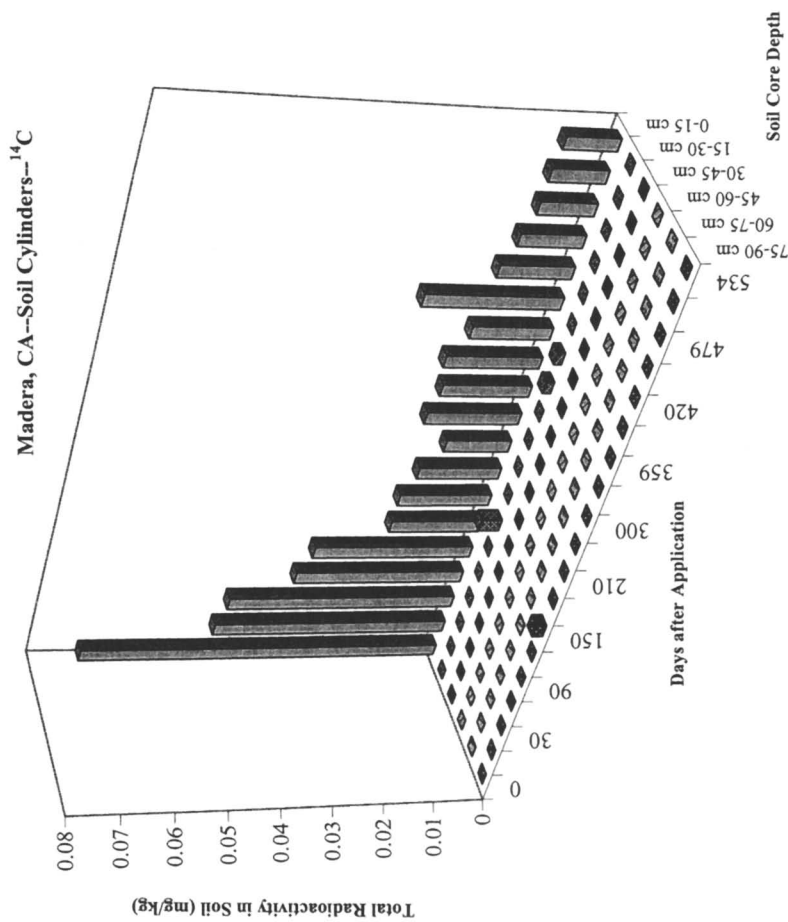
Figure 7. Distribution of radioactivity in soil horizons at California site with a soil cylinder plot design

single detection in a 270 cm depth on 63 DAT, which was suspected to be cross contamination. There were no detections of pyrithiobac sodium in groundwater (monitoring wells) through the course of the study, except for one sample on the day of treatment, which was likely to be contaminated.

Comparison of Laboratory to Field Data

Rate of Degradation

The half-life of pyrithiobac sodium was measured in a silt loam soil under nonirradiated and irradiated conditions. Under nonirradiated conditions, the half-life was 60 days. Under irradiated conditions, pyrithiobac sodium degradation was clearly accelerated relative to similar samples protected from light. Under field conditions, DT_{50} values ranged from 11 to 46 days. The enhanced degradation under field conditions could be due to the differences in microbial biomass in the field soils and the presence of UV light. The three different field soil dissipation designs gave similar results for the dissipation of pyrithiobac sodium from soil.

Mobility in Soil

Adsorption studies indicated that pyrithiobac sodium was weakly sorbed to soil (Koc = 14.7 to 26.9). Pyrithiobac sodium and its degradation products were essentially immobile in the four field dissipation studies. In addition, a small-scale prospective groundwater study, in a vulnerable sandy soil, confirmed the minimal potential for movement of pyrithiobac sodium to groundwater. Dissipation of pyrithiobac sodium and its degradation products in soil mitigate the potential for movement into groundwater.

Conclusions

For pyrithiobac sodium, the results from the laboratory soil studies provided more conservative estimates of the rate of degradation. Pyrithiobac sodium and its degradation products degraded rapidly under field conditions, most likely due to variations in the microbial biomass and contributions from UV-enhanced degradation. While Koc values indicate that pyrithiobac sodium was weakly sorbed by soil, movement of pyrithiobac sodium to lower soil horizons in the

field was mitigated by the degradation of pyrithiobac sodium under field conditions. A small-scale prospective groundwater monitoring study confirmed the limited mobility of pyrithiobac sodium under actual use conditions. In addition to the groundwater study, three different field soil dissipation designs were used measure the dissipation and mobility of pyrithiobac sodium: small plot with radiolabeled material, full-scale with unlabeled material and soil cylinders with radiolabeled material. The field soil dissipation studies gave similar results for the degradation and movement of pyrithiobac sodium under field conditions. These data show comparability of the smaller scale designs with that of the more traditional large-scale field soil dissipation study.

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