# STREAM TRANSPORT AND AGRICULTURAL RUNOFF OF PESTICIDES FOR EXPOSURE ASSESSMENT: A METHODOLOGY Part A--Text and Appendices A through F <br> by <br> A.S. Donigian, Jr., D.W. Meier, and P.P. Jowise Anderson-Nichols \& Co., Inc. Palo Alto, CA 94303 

Contract No. 68033116

Project Officer
Lee A. Mulkey Assessment Branch
Environmental Research Laboratory Athens, GA 30613

ENVIROEMENTAL RESEARCH LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY ATHENS, GA 30613

## DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68033116 to Anderson-Nichols \& Co., Inc. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient management tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Assessment Branch develops state-of-the-art decision tools for environmental and human risk assessments.

As part of the Federal Insecticide, Fungicide, and Rodenticide Act requirements, an exposure assessment is performed as part of the registration process for pesticides intended for use in the United States. This assessment seeks to estimate environmental concentrations and resulting exposures to humans and other organisms, including those from agricultural runoff into surface waters. This manual describes a technique for rapidly estimating these concentrations that is the latest product of more than a decade of research conduct at this Laboratory. Although there are some limitations and uncertainties that should be clearly understood by the user, the methodology should provide for accurate screening-level assessments for the many agricultural pesticides submitted for registration.

Rosemarie C. Russo, Ph.D. Director.
Environmental Research Laboratory Athens, Georgia

## ABSTRACT

To predict the potential environmental or human health risk posed by agricultural pesticides, exposure assessments require the estimation of chemical concentrations in field runoff and in associated water bodies. In this report a methodology is described for estimating the mean, maximum, frequency, and duration of pesticide concentrations, and the maximum daily pesticide runoff and its frequency for various agricultural crops and regions across the country. The Stream Transport and Agricultural Runoff of Pesticides for Exposure Assessment Methodology (called STREAM for convenience of reference) is designed for screening-level analyses to provide the order-of-magnitude accuracy appropriate for exposure assessment with minimal investment in time and resources.

The specific crops included in STREAM are corn, soybeans, cotton, wheat, and sorghum. Two major crops are considered in four agricultural regions--Southeast, Mississippi Delta, Eastern Cornbelt, and Western Cornbelt. STREAM has the potential for application to other crops and regions.

STREAM was developed by applying the Hydrological Simulation Program--FORTRAN to various test watersheds in each agricultural region, defining a "representative" watershed (based on regional conditions and the test watershed), and performing sensitivity analyses on key pesticide parameters to generate cumulative frequency distributions of pesticide concentrations and loadings in each region. HSPF is a comprehensive watershed hydrology and water quality model that was developed specifically for analyzing pesticide transport and transformation in agricultural watersheds. Thus, the user of STREAM is required to evaluate only the crops and regions of interest, the pesticide application rate, and three pesticide parameters--Koc, organic carbon partition coefficient; ks, soil/sediment decay rate; and kw, solution decay rate--in order to obtain pesticide loadings and concentrations. Included in the manual are detailed discussions of the STREAM application procedures, assumptions, limitations, and uncertainties, and methodology development.

This report is submitted in partial fulfillment of contract number 68033116 by Anderson-Nichols \& Co., Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 1983 to September 1985, and work was completed as of January 1986.

## CONTENTS

Page
Foreword ..... iii
Abstract ..... iv
Figures ..... vii
Tables ..... viii
Acknowledgments ..... x

1. Introduction ..... 1
1.1 Purpose and Scope ..... 2
1.2 Required User Background and Tranining ..... 4
1.3 Format of the Manual ..... 4
2. Development and Application of STREAM ..... 6
2.1 Methodology Development and Overview ..... 6
2.2 STREAM Application Procedures ..... 13
2.3 Interpretation and Use of Results ..... 27
2.4 STREAM Assumptions, Limitations, and Uncertainty. ..... 31
3. Example Applications ..... 36
3.1 Example No. 1: No Interpolation Required ..... 36
3.2 Example No. 2: Interpolation Required for All Parameters ..... 38
3.3 Example No. 3: Comparison of STREAM Predictions to HSPF Modeling of Alachlor in the Iowa River. ..... 40
4. Methodology Development ..... 44
4.1 Definition and Selection of Agricultural Regions. ..... 45
4.2 HSPF Application to Regional Watersheds ..... 51
4.3 Development of Regional "Representative" Watersheds ..... 62
4.4 Pesticide Parameters and Assumptions ..... 84
4.5 Simulation Runs and Production of Frequency Curves ..... 98
References ..... 102
Appendices
A. Pesticide Concentration and Runoff Frequency Curves for the Southeast Region ..... A-1
B. Pesticide Concentration and Runoff Frequency Curves for the Mississippi Delta Region ..... B-1
AppendicesC. Pesticide Concentration and Runoff FrequencyCurves for the Eastern Cornbelt$\mathrm{C}-1$
D. Pesticide Concentration and Runoff Frequency Curves for the Western Cornbelt ..... D-1
E. Pesticide Concentration and Runoff Frequency Curves for the Central Plains Region (incomplete) E-l
F. Analysis of Time Series Data ..... F-1
G. Little River, Georgia: Watershed Data, Segmenta- tion, and HSPF Calibration/Verification Report ..... G-I
H. Yazoo River, Mississippi: Watershed Data, Seg- mentation, and HSPF Calibration/Verification Report ..... H-1
I. Honey Creek, Ohio: Watershed Data, Segmentation, and HSPF Calibration/Verification Report ..... I-I
J. Iowa River, Iowa: Watershed Data, Segmentation, and HSPF Calibration/Verification Report ..... J-I
K. Turkey Creek, Nebraska: Watershed Data and Segmentation Report ..... K-1

## FIGURES

Page
2.1 Developmental pathways for STREAM ..... 7
2.2 Overview of pesticide exposure assessment with STREAM ..... 14
2.3 Explanation of figure matrices for locating pesticide concentration frequency curves ..... 19
2.4 Explanation of pesticide cumulative frequency concentration curves ..... 22
2.5 Explanation of pesticide cumulative frequency loading curves ..... 23
2.6 Time series of toxicant concentrations with moving average window of duration ..... 28
4.1 Locations of agricultural regions and HSPF applica- tion watersheds ..... 46
4.2 Average annual distribution of precipitation ..... 47
4.3 Generalized hydrologic soil groups for United States. ..... 48
4.4 Corn and soybean acreage in the United States ..... 49
4.5 Wheat, cotton, and sorghum acreage in the United States ..... 50
4.6 Little River research watershed, Georgia ..... 54
4.7 Yazoo Basin and study area location map ..... 56
4.8 Location of Honey Creek Basin ..... 58
4.9 Location of the Iowa River Basin ..... 59
4.10 Location of Turkey Creek Watershed ..... 61
4.ll Schematic of representative watershed drainage and reach confiquration ..... 77
4.12 Sample comparison of initial conditions with year-end pesticide bed concentrations and soil residues ..... 99
TABLES
Page
2.1 Values of key methodology parameters for sensitivity analysis ..... 13
2.2 Regression equations for the estimation of Koc ..... 17
2.3 Weighted Kd values for estimating suspended pesti- cide concentrations from solution concentrations ..... 30
4.1 Selected characteristics of HSPF application watersheds ..... 46
4.2 Key characteristics of the defined agricultural regions ..... 51
4.3 Land use/crop distribution for agricultural regions and representative watersheds ..... 65
4.4 Assumed sand/silt/clay percentages for sediment edge-of-stream loadings ..... 68
4.5 Assumed soil bulk densities for each agricultural region ..... 69
4.6 Assumed percent organic carbon for each soil layer. ..... 70
4.7 Assumed percent organic carbon for size fractions of suspended and bed sediments ..... 71
4.8 Summary of meteorologic data used in representative watershed l0-year simulations ..... 72
4.9 Summary of power functions for STREAM character- istics ..... 80
4.l0 Summary of computed channel characteristics for the downstream-most reach in each region ..... 80
4.ll Distinguishing characteristics of conservation tillage and conventional tillage ..... 82
4.12 Primary characteristics of "conventional" agricultural practices assumed in this study ..... 84
4.13 Annual target dates for agricultural activities ..... 85
4.14 HSPF pesticide parameters and methodology assumptions ..... 86
4.15 Calculation of partition coefficients from Koc and \% oc for the Southeast Region ..... 88
4.16 Calculation of partition coefficients from Koc and \% oc for the Mississippi Delta Region ..... 89
4.17 Calculation of partition coefficients from Koc and \% oc for the Eastern Cornbelt Region ..... 90
4.18 Calculation of partition coefficients from Koc and \% OC for the Western Cornbelt Region . . . . . . . . 91
4.19 Calculation of partition coefficients from K0c and \% oc for the Central Plains Region ..... 92
4.20 Values of key methodology parameters for sensi- tivity nalaysis ..... 101

This work represents the product of almost 15 years of model development, testing, and applications for analyzing pesticide runoff and stream concentrations, sponsored by the U.S. EPA, Environmental Research Laboratory in Athens, Georgia. Obviously, this manual would not have been possible without the body of research sponsored by the FPA Athens laboratory and the financial support for this project.

The personal involvement and technical guidance provided by Mr. Lee A. Mulkey, the EPA Project Officer, is gratefully acknowladged as a major ingredient in the successful completion of this work. In addition, various members of the Technology Development and Applications Branch of the Athens laboratory provided technical assistance, data, and recommendations throughout the project; their assistance is sincerely appreciated.

A variety of organizations and individuals provided data, information, and assistance related to the specific HSPF applications to the test watersheds in each region. Their contributions are acknowledged in the appropriate appendices ( $G$ through $K$ ) on each $H S P F$ watershed application. In addition, Dr. Lee A. Christensen, USDA-ERS, in Athens, Georgia provided data and review of the regional agricultural land use/crop distribution and agricultural practices based on his acknowleăged expertise in this area.

Among the authors, Mr. Anthony Donigian was the Project Director responsible for overall guidance, technical direction, and preparation of the final report. Mr. Dan Meier was Project Engineer, directing the meteorologic data preparation, performing $H S P F$ production runs and executing HSPF applications to the Jittle River and Honey Creek watersheds. Mr. Peter Jowise performed the HSPF applications to the Yazoo River and Turkey Creek, and assisted in the representative watershed development and preparation of the frequency diagrams.

Additional Anderson-Nichols staff participated in various aspects of the project. Mr. Douglas Beyerlein was involved initially as Project Manager directing HSPF applications and hydrologic calibration, and supervising meteorologic data preparation. Mr. J. David Dean participated in hydrologic and
sediment calibration, and analysis of statistical performance tests, and pesticide parameter relationships; Mr. Dean also prepared the initial draft of Appendix F., Analysis of Time Series Data. Dr. Benjamin Roberts developed procedures for estimating drainage area relationships and channel characteristics for the representative watersheds, and Mr. Mark Hersh assisted in developing meteorologic databases and frequency diagrams.

Word Processing was performed by Ms. Dorothy Inahara, Ms. Arinthia Jones and Ms. Carol McCullough, and report graphics were prepared by Ms. Marythomas Hutchins. All four individuals contributed to the successful completion of the project; their efforts are acknowledged and appreciated.

## INTRODUCTION

As part of its mandate under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the U.S. Environmental Protection Agency is required to register and approve pesticidal compounds for use in the U.S. An exposure assessment is performed as part of this registration process in order to estimate environmental concentrations and resulting chemical exposure to humans and other organisms resulting from applications for agricultural, silvicultural, and other purposes. Because of the toxicity and persistence of many pesticides and their ubiquitous use in modern agriculture, the runoff of pesticides from agricultural fields and the resulting concentrations in surface water bodies is a major environmental concern.

A complex interaction of natural events, chemical processes, and human intervention combine to produce pesticide concentrations in surface waters that are high enough to cause concern for potential human exposure and impact on aquatic organisms. In general, three conditions create the circumstances under which pesticide residues in surface water will occur: (l) applied pesticide persists on the land surface or in the soil profile long enough for subsequent transport in runoff, in subsurface flow, and on, eroded sediments; (2) rainfall, infiltration and storm runoff occurs during the time period when pesticides reside on or in the soil; and (3) the resulting pesticide runoff reaching surface waters persists long enough in the aquatic system to affect potential exposure to humans and aquatic organisms (Mulkey and Donigian, 1984).

Thus, the ultimate fate and migration of pesticides involves both a land/soil phase and a stream or aquatic phase. The land/soil phase produces pesticide loadings to water bodies and to ground water depending on the relative timing of applications and storm events; soil and chemical characteristics; topographic and geologic characteristics, and agronomic and engineering practices. After application, pesticides are subjected to numerous physical, chemical, and biological processes that transport, transform, ald degrade
the compound. The partitioning of the pesticide between the dissolved phase and the sorbed phase determines whether it will be transported with surface runoff or infiltration to ground water, or with eroded sediments from the land surface to the stream. For pesticides on the land surface, volatilization and photolysis can result in significant losses of the compound with less available to reach surface waters through runoff. Below the land surface, microbial degradation, hydrolysis, and plant uptake combine to control the persistence of the pesticide and thus its overall availability to reach surface water bodies through subsurface flow paths.

Pesticide loadings from the land/soil phase enter the stream system by either surface or subsurface pathways and then are transported, transformed, and degraded in the stream. Interactions with suspended and bed sediments will cause a redistribution of the pesticide between the dissolved and sorbed states; the dissolved pesticide will move with the streamflow whereas the sorbed pesticide may reside in the stream bed or move with the suspended sediments. The pesticide included in the stream bed sediments may subsequently desorb back into a dissolved phase and re-enter the streamflow days, months, or years after its initial attachment to the bed. Various transformation and degradation processes such as volatilization, hydrolysis, photolysis, oxidation, and microbial degradation, can occur at various rates in both the moving water and stream bed environments. These processes and their rates control the extent to which the pesticide loadings impact both the magnitude and variability of concentrations in the stream system throughout the watershed.

### 1.1 PURPOSE AND SCOPE

The objective of this work was to develop a procedure or methodology for rapidly estimating pesticide runoff and concentrations that are likely to occur in surface waters as a result of agricultural pesticide applications. This information is required as part of the exposure assessments performed by the EPA Office of Pesticide Programs when new pesticides are submitted for registration, when new uses are proposed for existing pesticides, and when existing pesticides are being re-evaluated because of concern for human health or environmental risk. The hundreds of exposure assessments to be performed annually underscores the need for simple procedures that can be completed rapidly (i.e. within a few days) and not require an extended investigation with an associated investment in time and resources. This need for speed and simplicity is acquired, by necessity, at the expense
of accuracy. For the screening-level assessments for which concentrations estimates are required, order-of-magnitude accuracy is the generally accepted criterion for environmental concentrations for exposure assessments (EPA, l982).

Inclusion of all crops and all agricultural regions was well beyond the scope and resources available for this study. Consequently, we limited our analysis to the primary crops of corn, soybeans, cotton, wheat, and sorghum. The specific agricultural regions included in the methodology are listed below with the specific crops analyzed:

## Region

Southeast Mississippi Delta Eastern Cornbelt Western Cornbelt Central Plains

## Crops

Corn, Soybeans
Cotton, Soybeans
Corn, Soybeans
Corn, Soybeans
Wheat, Sorghum (Incomplete)

The number of regions selected for analysis was primarily due to resource limitations. The selection of specific regions and associated crops was derived from information on the primary production crops and regions in the U.S., and the availability of detailed site-specific watershed meteorologic, hydrologic, and sediment data to support model calibration and verification, as described in Section 4. Although the STREAM procedures are currently limited to the five regions and crops listed above, the methodology is designed to be readily extended to include additional regions and crops as resources become available.

The scope of the methodology is further limited by a number of assumptions employed in the development of the procedures. Only non-irrigated agriculture is considered since irrigation is relatively minor in most of the regions studied. Conventional agricultural practices were defined for each region and used in the methodology. Only a single surface chemical application at or near the time of planting is considered, corresponding to preplanting, planting, or post-emergence type applications. The procedures are restricted to organic, hydrophobic compounds due to the methods of representing sorption and decay processes in the HSPF model (Johanson et al., 1984) used in the regional simulations. In spite of these limitations, the STREAM procedures provide a flexible means of quickly estimating pesticide loadings and concentrations for screening-level exposure assessments.

## 1. 2 REQUIRED USER BACKGROUND AND TRAINING

Normally, the development of environmental concentrations of pesticides for an exposure assessment would require expertise in a wide variety of disciplines, including hydrology, watershed modeling, sediment erosion, sediment transport, soil science, and environmental chemistry. Unfortunately this mix and breadth of experience is rarely available to the extent needed in a single organization. Consequently the STREAM procedures were specifically designed to minimize the expertise required by the user except in the areas of environmental chemistry and soil science. The approach of calibrating and verifying $H S \overline{P F}$ in each region, and then generating frequency-duration curves for selected combinations of key pesticide characteristics precludes the need for watershed modeling (and associated) expertise by the user. However, a firm background in soil science and environmental chemistry of pesticides is still required to properly evaluate the key methodology parameters and appreciate their variability and uncertainty.

Training in the use of the procedures described herein is required for proper application and interpretation of predicted pesticide loadings and concentrations. This training must result in a full comprehension of the assumptions, limitations, and potential uncertainty in both the modeling techniques and the methodology development, in addition to the specific calculational procedures of STREAM. Although the user need not be an expert in watershed modeling, he must appreciate the various assumptions and limitations in the HSPF representation of pesticide transport and fate in watershed systems to properly interpret the methodology results in light of the specific compound being analyzed.

### 1.3 FORMAT OF THE MANUAL

Following this Introductory Section, Section 2 describes the overall development of STREAM and discusses in detail the application procedures, interpretation and use of results, and primary assumptions, limitations, and uncertainty in the methodology. The user should carefully study section 2 for proper use of STREAM. Section 3 provides completed examples of using STREAM with step-by-step descriptions of the use of the frequency curves and of the required calculations. Section 4 presents the complete development of the methodology to provide the necessary background on how the frequency curves were developed.

Appendices A through $E$ include the frequency curves for pesticide solution and bed concentrations, and pesticide loading for each agricultural region in the following order:
A. Southeast
B. Mississippi Delta
C. Eastern Cornbelt
D. Western Cornbelt
E. Central Plains (Incomplete)

Each of these appendices include three tables which are the figure matrices, i.e., they show the specific figure number in the appendix for a specific combination of key methodology parameters. The three tables are for the pesticide solution concentration, bed concentration, and loading figures, respectively. These tables are followed by 150 frequency curves: 72 solution concentration frequency curves (i.e. 36 for each crop), 72 bed concentration frequency curves, and 6 pesticide loading frequency curves.

Appendix $F$ provides a general description of statistical analysis of time series data to provide the user with background on the development and interpretation of frequency-duration curves and various statistical goodness-of-fit tests used in model calibration and verification. Appendices $G$ through $K$ are the watershed data, segmentation, and HSPF calibration/verification reports for each application watershed, in the following order:
G. Little River, GA
H. Yazoo River, MS
I. Honey Creek, OH
J. Iowa River, IA
K. Turkey Creek, NB (Incomplete)

Note: Appendices $G$ through $K$ are presented in Part $B$ of this manual (EPA/600/3-86/001b), which is avaliable from the National Technical Information Service, 5285 Port Royal Road, Springfield VA 22161 (telephone: 703-487-4650).

## SECTION

DEVELOPMENT AND APPLICATION OF STREAM

In order to promote the intelligent use of the STREAM procedures, this section provides both an overview of the development process and a detailed description of the recommended application procedures. The overview is included here so that the potential user comprehends the various steps involved in the STREAM development before actually using the procedures; a complete detailed discussion of the methodology development is provided in Section 4. Each step in the application procedure is described, followed by a discussion on the interpretation and use of the pesticide concentration and loading frequency curves included in Appendices A through E. Finally, the assumptions, limitations, and uncertainty associated with both the model and methodology procedures are enumerated and discussed to allow a realistic appraisal of the specific concentration and loading values obtainable with STREAM.

### 2.1 METHODOLOGY DEVELOPMENT OVERVIEW

Development of the STREAM procedures involved the following sequence of activities:
a. Definition/selection of agricultural regions and model application watersheds.
b. HSPF applications to regional watersheds.
c. Development of regional "representative" watersheds.
d. Sensitivity analyses on key pesticide properties.
e. Development of pesticide frequency-duration information.

Figure 2.1 schematically shows the developmental pathway for STREAM demonstrating the interrelationships of these activities. Definition and selection of the specific agricultural regions and their approximate boundaries was governed by regional characteristics, such as climate, soils, topography, and cropping, and the existence of potential HSPF application sites. The criteria for selecting application


Figure 2.1 Developmental pathways for STREAM.
sites was the availability of sufficient meteorologic, hydrologic, and sediment data to support a valid HSPF calibration/verification for the chemical transport mechanisms of runoff, erosion, streamflow, and sediment transport. Although deficiencies existed primarily in the available sediment data, watersheds with the best overall data base were chosen and then regional information was analyzed to determine the extent to which the individual watershed was representative of a larger region.

Regional meteorologic, soils, topographic, and cropping characteristics on a national basis were overlayed to define approximate regional boundaries. These regions were then compared to the locations of the HSPF application watersheds and the boundaries were subsequently constricted in order not to imply that the selected watershed was able to represent a region larger than could be reasonably expected. Thus the regional meteorologic, soils, and topographic characteristics were considered constraints on the extent of area whose hydrologic response could be reasonably represented by a single watershed. Section 4.1 provides more detailed information on the region boundary definition process.

Since the STREAM procedures provide screening-level analyses, with an associated order-of-magnitude accuracy in the pesticide concentration and loading estimates, considerable latitude was possible in defining the region boundaries. Although the boundaries are clearly marked on Figure l.l, they are approximate boundaries and, by no means, definitive. They represent general regions within which the procedures described herein can be used to estimate instream pesticide concentrations and runoff loadings for screening-level analyses.

The Hydrologic Simulation Program-FORTRAN (HSPF) (Johanson et al., 1984) was selected to perform the model simulations on the regional watersheds because it is the only comprehensive model of watershed hydrology and water quality that allows the integrated simulation of land and soil pesticide runoff process with instream hydraulic and sediment-chemical interactions. In this way, the impacts of regional differences in climate, soils, topography, and cropping, that influence pesticide runoff, are directly considered in estimating pesticide stream concentrations likely to occur in different agricultural regions. HSPF and the earlier models from which it was developed have been extensively applied in a wide variety of hydrologic and water quality studies (Barnwell and Johanson, 1981; Barnwell and Kittle, 1984) including pesticide runoff model testing (Lorber and Mulkey, 1981), aquatic fate and transport model testing (Mulkey et at., 1982), analyses of agricultural best management practices in Iowa (Donigian et at., l983a; l983b; Imhoff et at., 1983) and
as part of a pesticide exposure assessment in surface waters (Mulkey and Donigian, 1984). Because of this prior experience with HSPF, its continued maintenance and sponsorship by the EPA Center for Water Quality Modeling (Barnwell, 1984) and existing model applications in different regions of the U.S., this project was specifically designed to take advantage of the capabilities of HSPF to simulate pesticide fate and migration in agricultural watersheds.

A key step in the development of STREAM was the definition and evolution of the concept of a regonal "representative" watershed. For the purposes of this study, the definition of a regional representative watershed can be stated as follows:

A regional representative watershed is a standarized watershed that demonstrates hydrologic, sediment, and water quality (primarily pesticide) behavior that is typical or representative of watersheds throughout the region, within the order-of-magnitude accuracy appropriate for a screening-level analysis.

Thus, the representative watershed will not exactly duplicate the behavior or response of all watersheds in the region, or any one specific watershed (except by pure chance), but it will demonstrate behavior that is typical of watersheds in the region within the latitude provided by the order-of-magnitude accuracy required.

The concept of regional "representative" watersheds was developed in this study and used as the basis for the sensitivity analyses and resulting pesticide frequency distributions. The primary need was a sound technical basis for stating that the frequency distributions can be reasonably applied and used for a broader geographical region than just the specific HSPF application watershed. In addition, since many exposure assessments conducted as part of the pesticide registration process will involve more than one region, some "normalization" is needed to allow comparisons between and among the various regions.

Thus, in place of the specific $H S P F$ regional application watershed, a regional representative watershed was developed with characteristics applicable to the broader agricultural region. In effect, we compared differences in characteristics between the HSPF application watersheds and regional values as a basis for transforming them into regional "representative" watersheds. Section 4.3 discusses the assumptions and adjustments made for the key characteristics of watershed area, land use/crop distribution, land and soil characteristics, meteorologic conditions, drainage
'characteristics' and agricultural practices.

As shown in Figure 2.l, both regional characteristics and the regional HSPF application provided the inputs for the development of the characteristics of the regional representative watershed. In brief, the representative watershed in each region has the following attributes:
a. an area of $1, \varnothing \varnothing \varnothing \mathrm{sq} . \mathrm{km}$ ( $386 \mathrm{sq} . \mathrm{mi}$.$) .$
b. land use/crop distribution typical of agricultural watersheds in the region, based on the 1978 Census of Agriculture (see Table 4.3).
c. land and soil characteristics derived from the HSPF application watershed, unless available information indicated an appropriate adjustment.
d. meteorologic conditions (primarily precipitation and potential evapotranspiration) representative of the region, developed by adjustments to the data used in the HSPF applications.
e. drainage and channel characteristics appropriate for a $1, \varnothing \varnothing \varnothing$ sq. km watershed derived from regional data and geomorphological relationships.
f. conventional cropland agricultural practices appropriate for the region.

Section 4.3 further elaborates on the concept and justification for the regional representative watershed, and describes in detail the transformation of each characteristic discussed above.

The timing and method of agricultural chemical applications can have a determining impact on the extent of chemical runoff and resulting stream concentrations. In fact, for relatively non-persistent pesticides, the first few runoff-producing storm events following a field application usually produce the greatest pesticide runoff and concentrations. In most agricultural watersheds, many different farmers will be applying chemicals at different times and at different rates. Since it would not be feasible to model each farmer's field individually in a complex multi-land use watershed of $1, \varnothing \varnothing \varnothing$ sq. km, and since a single simultaneous application by all farmers would be unrealistic (and possibly produce a worst-case scenario for pesticide runoff from the first storm event), procedures and assumptions for pesticide application were developed in order to provide a realistic compromise between the two extreme approaches described above.

The key assumptions used in this study for specifying pesticide applications are as follows:

1. A unit application rate of $1 . \varnothing \mathrm{kg} / \mathrm{ha}$ to all crops.
2. A single surface application at or near planting time.
3. Multiple farmer applications and timing approximated by three separate applications of $\varnothing .25, \varnothing .5 \varnothing$, and $0.25 \mathrm{~kg} / \mathrm{ha}$, respectively within a $10-15$ day planting "window".
4. No applications on the day of, or day after, a storm event.

A unit application rate of $1.0 \mathrm{~kg} / \mathrm{ha}$ was used in all simulations in order to provide the methodology user the flexibility of estimating concentrations and loadings for any application. All concentrations and loadings are linear functions of the application rate. Thus, for a $5.0 \mathrm{~kg} / \mathrm{ha}$ rate, the user simply multiplies the values from the frequency curves in Appendices A through E by 5.0 to obtain the correct concentrations and loadings. Section 4.4.2 fully discusses the pesticide application procedures and assumptions.

As shown in Figure 2.l, following development of the representative watershed characteristics and pesticide application procedures, sensitivity analyses were conducted. To maintain simplicity in application of STREAM for screening-level analyses, these sensitivity analyses were limited to the following key methodology parameters:

$$
\begin{aligned}
& \text { Koc - organic carbon partition coefficient } \\
& \text { ks - soil/sediment pesticide decay rate } \\
& \text { kw - solution pesticide decay rate }
\end{aligned}
$$

These three parameters are used in STREAM to represent, respectively, the sorption characteristics, the soil and instream/bed sediment persistence, and the solution persistence of the pesticide. All HSPF pesticide parameters were either based on the values of these three key methodology parameters, were derived from previous studies, or were amenable to the use of a default value. Section 4.4.1 discusses the selection of these methodology parameters and the assumptions used in specifying the values of the complete set of 35 HSPF pesticide-related parameters. However, the following key assumptions should be noted:
a. Koc was used to specify the partition coefficients for all layers of the soil profile and the suspended and bed sediments, based on estimated \% organic carbon values (presented in Section (4.4.1)) and the following equation:

$$
\begin{equation*}
\mathrm{Kd}=\operatorname{Koc} \frac{\star \mathrm{OC}}{1 \varnothing \emptyset} \tag{2.1}
\end{equation*}
$$

> where $\mathrm{Kd}=$ Soil-chemical partition coefficient, ml/g Koc $=$ Organic carbon partition coefficient, ml/g-organic carbon
> $O C=$ percent organic carbon

The specific Kd values resulting from this equation and the estimated \% organic carbon values for each region are shown in Tables 4.15 through 4.19 in section 4.4.1.
b. The soil/sediment decay rate, ks, represents a lumped first-order decay or attenuation process for all pesticide loss mechanisms. The value of ks was used to specify soil decay rates for all soil layers and all particle sizes (i.e. sand, silt, clay) for both the suspended and bed sediments.
c. The solution decay rate, kw , also represents a lumped first-order decay process for all pesticide loss mechanisms from the solution phase at a temperature of 20 deg. C. A standard temperature adjustment to this rate is performed based on estimated stream temperatures in each region. This adjustment allows for a two-fold change in decay rate for each $1 \varnothing$ deg. change in temperature.

Table 2.1 lists the specific values of the key methodology parameters used in the sensitivity analyses. The choice of these values is further elaborated on in Section 4.4.l. Performance of the sensitivity analyses involved the execution of lØ-year HSPF simulation runs for the 36 combinations of the key methodology parameters - Koc, ks, kw - shown in Table 2.l, for each of the five representative watersheds. Since it was necessary to simulate the results of pesticide applications to each crop separately, this required 72 pesticide simulations for each region resulting in a total of $3,6 \varnothing \emptyset$ pesticide simulation years i.e., 72 simulations x 5 regions x lø years.

The simulations were performed using a 2-hour time step, to be consistent with the modeling of the application watersheds, and produced a daily concentration time series by averaging the 2 -hour values during each day. Pesticide runoff was calculated as the total daily amount in $\mathrm{kg} / \mathrm{ha}$ for each day of the lø-year simulation period. Thus, time series consisting of about 3,652 daily values were generated for pesticide runoff and concentrations (i.e., solution and bed) from each simulation run.

TABLE 2.1 VALUES OF KEY METHODOLOGY PARAMETERS FOR SENSITIVITY ANALYSIS

| $\begin{gathered} \mathrm{KOC} \\ (\mathrm{ml} / \mathrm{g}) \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ (\text { per day) } \end{gathered}$ | $\begin{gathered} \mathrm{kw} \\ (\text { per day) } \end{gathered}$ |
| :---: | :---: | :---: |
| 50 | 0.1 | 1.0 |
| $5 ø \square$ | $\varnothing . \square 1$ | 0.5 |
| $150 \varnothing$ | Ø. $0 \emptyset 1$ | 0.05 |
| 5000 |  |  |

In the final step of the methodology development (shown in Figure 2.1) the time series were analyzed using the DURANL module of $H S P F$ to define the exceedance frequency, or percent of time specific values were exceeded, for durations of $1,2,4$, and 30 days. These durations were chosen to correspond to the standard 24-hour, 48-hour, 96-hour, and 30-day toxicity tests normally performed to establish LC5ø (i.e., concentration for 50\% mortality) and MATC (i.e., maximum allowable toxicant concentration) values for aquatic organisms. In addition to frequency-duration statistics on the time series, DURANL also provides the maximum and mean values.

The pesticide frequency-duration information, along with the maximum and mean values, was then plotted in a log-log format to place greater emphasis on the less frequent events and to accommodate the wide variation (i.e., up to five orders of magnitude) in pesticide concentrations and loadings.

### 2.2 STREAM APPLICATION PROCEDURES

Figure 2.2 provides a general overview of the various steps involved in performing a pesticide exposure assessment with STREAM. Intially, some event will occur or action will be taken to indicate a need for an exposure assessment. As noted in Section l.l, this could occur when a new pesticide is submitted for registration, when a new use is proposed for an existing pesticide, or when a current compound is being re-evaluated for any number of reasons. Based on the specific impetus for the exposure assessment, the pesticide(s) of interest will be identified and the next step in the assessment will be to determine the relevant use and chemical characteristics.


Figure 2.2 Overview of pesticide exposure assessment with STREAM.

The
usage characteristics such as the crops and regions where the pesticide is, or is to be, applied will determine whether or not the STREAM procedures are appropriate. The specific agricultural regions and crops included in this version of STREAM are listed below, and the region boundaries are shown in Figure l.l:

## Region

Southeast
Mississippi Delta
Eastern Cornbelt Western Cornbelt Central Plains

Crops
Corn, Soybeans
Cotton, Soybeans
Corn, Soybeans
Corn, Soybeans Wheat, Sorghum (Incomplete)

As noted above, the region boundaries are approximate and represent the generalized area where the STREAM procedures can be applied for screening-level analyses. Also, the procedures may be applicable to other crops with similar growth patterns, canopy development, planting and harvesting times, etc., but the accuracy and reliability of the procedures in such situations is uncertain.

Additional use characteristics including application rate, application method, potential use on multiple crops, and $\%$ of cropland to be treated will be needed later in the assessment to calculate estimated concentrations and loadings, and to assess the validity of the results. The chemical characteristics of interest are those related to estimation of the key methodology parameters - Koc, ks, kw. These are discussed further in subsequent steps.

Based on the pesticide use characteristics, the agricultural regions and crops of interest can be determined and the corresponding appendix or appendices can be located. As noted in Section l.3, the appendices $A$ through $E$ include the pesticide frequency-duration information for the five regions in the following order:
A. Southeast
B. Mississippi Delta
C. Eastern Cornbelt
D. Western Cornbelt
E. Central Plains (Incomplete)

### 2.2.1 Parameter Estimation

At this stage, the major effort in the exposure assessment begins - estimation of the key methodology parameters. For new compounds, data and information submitted by the chemical

manufacturer may be the only source of information on which to base the values of Koc, ks, and kw. Specific laboratory and/or field tests may be required in order to determine valid parameter values, and the chemical background and expertise of the user may be needed to estimate an appropriate value (or range of values) from the wide range of values often observed in such tests.

For existing pesticides, the current literature provides a variety of sources that may be helpful, in addition to data supplied by the manufacturer. Various parameter estimation techniques and sources of information are available and will be briefly mentioned here so that the user can study the procedures, data, and associated assumptions and limitations in the original documents. For Koc, values for a number of pesticides have been tabulated by Rao and Davidson (1980), Mabey et al. (1982), and Lyman et al. (1982), while Lyman has also summarized the major regression equations for estimation of Koc from solubility, the octanol-water partition coefficient (i.e., Kow) or, the bioconcentration factor (i.e., BCF). Table 2.2 from Lyman presents these equations, along with the number and classes of chemicals used in their development, and associated correlation coefficients for the equations. Many of the equations were developed specifically for pesticides. Users should review the discussion in Chapter 4 of Lyman et al. (1982) to fully comprehend the limitations, assumptions, and parameter ranges for these equations.

Lacking specific Koc values for the pesticide, information required to use the regression equations in Table:2.2 can be found in Rao and Davidson (1980), Mabey et al. (1982), and the Herbicide Handbook (Weed Science Society of America, 1983). Also, a very complete data base of Kow values is maintained by Dr. Corlan Hansch at Pomona College, Pomona, California (714-621-8øøø ext. 2225). Koc values should be used directly whenever available; otherwise estimation of Koc from the regression equations is appropriate when used with caution.

For ks, the soil decay rate, Nash (198ø) and Rao and Davidson (1980) tabulated rate values (in units of 'per day') for a wide variety of pesticides, while similar data on half-life and persistence have been reported by Menzie (1972), Stewart et al. (1975), Wauchope (1978), and Wauchope and Leonard (198ø). Half-life (i.e., t5ø) and persistence (i.e., t9ø) are generally defined as the time (in days) required for $50 \%$ and $90 \%$ degradation respectively, for the pesticide. Thus, the calculation of $k s$ from this type of data is as follows:

$$
\mathrm{ks}=\left\{\begin{array}{l}
0.693 / \mathrm{t} 50  \tag{2.2}\\
2.3 / \mathrm{t} 90
\end{array}\right.
$$

$$
\text { where } \begin{aligned}
\mathrm{ks} & =\text { soil decay rate, per day } \\
t 5 \emptyset & =\text { time required for } 50 \% \text { decay, days } \\
t 90 & =\text { time required for } 90 \% \text { decay, days }
\end{aligned}
$$

The open literature generally will include a number of field and/or laboratory studies for specific pesticides; users should make use of literature searches to help uncover compound-specific data for ks. However, Dean et al. (1984) have noted two potential problems in direct use of literature values. First, these rates usually have been measured under a wide range of environmental conditions, e.g., soils,soil pH, soil organic matter, soil moisture, soil temperature, etc.) which can have dramatic effects on reported values. The user should check the original references to determine if the reported conditions are applicable to his or her specified

TABLE 2. 2 REGRESSION EQUATIONS FOR THE ESTIMATION OF K

| Eq. Ho. | Equation ${ }^{\text {a }}$ | Ho. ${ }^{\text {B }}$ | $r^{2^{c}}$ | Chemical Classes Represented |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $108 K_{o c}=-0.55 \log S+3.64(S \mathrm{in} \mathrm{mg} / \mathrm{l})$ | 106 | 0.71 | Wide variety, mostly presticides |
| 2 | $\log K_{o c}=-0.54 \log s+0.44$ <br> (S in mole fraction) | 10 | 0.94 | Hostly aromatic or polynuclear aromatics; two chlorinated |
| $3^{\text {d }}$ | $\begin{aligned} & \log K_{O C}=-0.557 \text { log } S+4.277 \\ & (3 \mathrm{in} \text { nolos/L) } \end{aligned}$ | 15 | 0.99 | Chlorinated hydrocarbons |
| 4 | $\log K_{\text {oc }}=0.544108 \mathrm{~K}_{\text {Ow }}+1.377$ | 45 | 0.74 | Wide variety, mostly peaticides |
| 5 | $108 K_{\text {Oc }}=0.937 \mathrm{log} \mathrm{K}_{\text {Ow }}=0.006$ | 19 | 0.95 | Aromatics, polynuclear aromatics, triazines and dinstroanlline herbicides |
| 6 | $\log K_{o c}=1.00108 K_{o w}=0.21$ | 10 | 1.00 | Mostly aromatic or polynuclear aromatica; two chlorinatod |
| 7 | $\log \mathrm{Kac}_{\text {ac }}=0.94 \mathrm{log} \mathrm{K}_{\text {Ou }}+0.02$ | 9 | e | a-Trlazines and dinitroaniline herblcidea |
| 8 | $108 K_{\text {oc }}=1.029 \log K_{\text {Ow }}-0.18$ | 13 | 0.91 | Varlety of ineccticides, herbicides and. funglcides |
| 9. | $108 K_{\text {oc }}=0.524 \log K_{\text {Ow }}+0.855$ | 30 | 0.84 | Substituted phenyluraes and alkyl-H-phenylcarbamatea |
| 10d, 5 | $\log K_{\text {oc }}=0.0067(P-45 N) * 0.237$ | 29 | 0.69 | Aromatic compounds: ureas, 1,3,5-triazinet, carbamates, and uracilo |
| 11 | $108 \mathrm{~K}_{\text {OC }}=0.681 \mathrm{log} \operatorname{BCF}(\mathrm{f})+1.963$ | 13 | 0.76 | Wide variaty, mostly pesticidos |
| 12 | $\log K_{\text {oc }}=0.689 \log \operatorname{BCF}(t)+1.886$ | 22 | 0.83 | Wido varioty, mostly posticides |

a. $K_{o c}=$ soll (or aedigent) adeorption coefficient; $S$ water solubility, $K_{o u}$ z octanol-water partition coefPicient; $\operatorname{BCF}(\mathbb{C})=$ bloconcentration factor from flowing vater tests, $B C F(t)=$ biocancentration factor from model ecosyatema; $P$ - parachor; $H$ n numer of altes in molecule which can participate in the formation of a hydrogen bond.
b. Ho. number or chealcala used to obtaln regreasion equation.
c. $r^{2}=$ correlation coefficient for regrasaion equation.
d. Equation originaliy given in teras of $K_{o m}$. The rolationship $K_{o m}=K_{o c} / 1.724$ was used to rewrite the equation in teras of $K_{o c}$.

- Hot avallable.
f. Spacific chemicala used to obtain regreasion equation not apecified.
situation. Secondly, in this methodology, the decay rate is applied to both dissolved and adsorbed chemical. The user should be satisfied that this condition was met in the measurement of the decay rate or find another source of information about degradation of the compound.

An additional caution for the STREAM user is that the value of ks is also the decay rate of pesticide adsorbed to suspended and bed sediments. Little if any aquatic data on pesticide decay processes differentiate between rates for the solution and adsorbed phases, and stream bed decay processes have been identified as a significant research area for exposure assessment because of the general lack of information and understanding (EPA, 1982). Because of this lack of sediment-associated decay rates, the use of soil decay rates is a reasonable alternative.

For kw, the solution decay.rate, data and information provided in Mills et al. (l982), Callahan et al. (1979), Mabey et al. (1982) and Lyman et al. (1982) can help to identify the major fate processes for the pesticide of interest and the associated transformation or decay rates. Also, Lyman et al. (1982) and Mabey et al. (1984) provide methods of estimating process-specific rate constants based on available data. For the STREAM procedures, kw should be evaluated as the sum of the individual decay rates (in units of 'per day') or the maximum if one decay mechanism is predominant, since it represents an aggregate of all loss mechanisms.

### 2.2.2 Locating Frequency Curves

Once the methodology parameters have been estimated, the user then locates the proper figure or figures in the appendix for the selected region for the specific combination of parameter values. Each appendix includes three tables and 150 figures which are the pesticide frequency curves. The tables are matrices of figure numbers developed to assist the user in locating the needed figure(s) for any combination of parameter values; one table each is provided for the pesticide solution concentration curves, pesticide bed concentration curves, and the pesticide daily loading curves.

Figure 2.3 demonstrates how the figure matrices for the pesticide solution and bed concentrations curves are used to determine the needed figure number(s) for parameter combinations; the figures are located in numerical order following the tables in each appendix. For example, in figure 2.3, the table title indicates that the figure matrix is for pesticide solution concentrations for both corn and soybeans in the Southeast: a separate table is provided for bed


Figure 2.3 Explanation of figure matrices for locating pesticide concentration frequency curves.
concentrations in a similar format. The top half of the table is designated as corn in the Southeast, while the bottom half is for soybeans in the Southeast.

Thus, if the pesticide is applied to soybeans in the Southeast and the parameter values are estimated as Kor $=5 \emptyset \emptyset, \mathrm{ks}=$ Ø. Ø1, and $k w=\emptyset .5$, then Figure A. $5 \emptyset$ in Appendix $A$ is the needed frequency curve for pesticide solution concentrations, as demonstrated by the lines and boxes in the bottom half of Figure 2.3.

For the more difficult, and more likely, situation when the estimated parameter values are not exactly equal to the values used in our sensitivity analyses, a number of figures must be identified so that interpolation can be performed for the specific parameter set. The top half of Figure 2.3 demonstrates such an example for corn in the Southeast and Koc = løøØ, ks = Ø. Ø5, and $\mathrm{kw}=0.3$. Since none of the parameters are equal to our sensitivity values, eight separate figures are needed to perform the interpolation. If kw had been equal to Ø.5, then only four figures (i.e., A.11, A.l4, A.20, and A.23) would have been needed. A recommended interpolation procedure is discussed in section 2.2.3 below.

The figure matrices for the pesticide daily loading curves are considerably less complicated than those for the concentration curves, since only two parameters - Koc and ks - are involved and only a daily duration is considered. The kw value has no impact on pesticide loading to the stream, and durations other than one day are of no real interest or value for our purposes. Table A. 3 from Appendix A is reproduced below as an example of the loading figure matrix.

TABLE A. 3 FIGURE MATRIX FOR PESTICIDE LOADING CURVES FOR THE SOUTHEAST

Region: SOUTHEAST

|  | ks (per day) |  |  |
| :---: | :---: | :---: | :---: |
| Crop | 0.1 | . 01 | . .011 |
| Corn | A. 145 | A. 146 | A. 147 |
| Soybeans | A. 148 | A. 149 | A. 150 |

Only six figures are required since each figure includes four curves for each of the four Koc values. Thus, for soybeans in
the Southeast with ks = Ø. Øl, Figure A. 149 is needed. If ks $=$ Ø. Ø5, Figures A. 148 and A. 149 would be needed for interpolation.

### 2.2.3 Determine Unit Concentrations and Loads

Since we assumed a $1 . \varnothing \mathrm{kg} / \mathrm{ha}$ pesticide application in our methodology, all concentrations and loads estimated from the frequency curves in the appendices are unit values. Thus, determining the unit concentrations and loads simply involves proper interpretation of the frequency curves, and interpolation or extrapolation as required by the specific parameter values. Figures 2.4 and 2.5 provide explanations of the legends, terms, and information included in the pesticide concentration and loading curves, respectively, using figures from Appendix A as examples. Along the bottom of the figures, the figure number (keyed to the figure matrix), region, crop, and parameter values are indicated. Both the vertical and horizontal scales are logarithmic. The horizontal scale ranges from Ø.øl to løø. and indicates the '\% of time' that the concentration (solution or bed) or loading is exceeded. For the solution and bed concentration figures (Figure 2.4) the vertical scale is in units of parts per billion (ppb) and generally covers four to six orders of magnitude, ranging from
 2.5) have a vertical scale in units of $\mathrm{kg} / \mathrm{ha}$ generally ranging from $\emptyset . \emptyset \emptyset \emptyset 1$ to $1 . \varnothing \mathrm{kg} / \mathrm{ha}$.

Four curves are shown within each figure. For the concentration figures the four curves indicate the frequency for durations of $1,2,4$, and $3 \emptyset$ day time periods, while the curves in the loading figures are for the four different values of Koc. In order to read a concentration or loading value from the frequency curves the user must select an appropriate $\%$ of time or probability/risk level for the horizontal axis. The choice of an appropriate level is a user or policy decision, and will depend on the type of situation or exposure level being analyzed. If concentrations are high enough to indicate a concern for acute toxicity to aquatic organisms, values of $\emptyset .1$ to $1 \emptyset . \varnothing \%$ of time may be appropriate. If long or continuous exposure to low concentrations (i.e., chronic conditions) is the primary concern, higher values in the range of lø. 1 to 1 løø. $\%$ of time may be of interest. Also, the available toxicity data and the durations of potential exposure may be used to determine how often toxic conditions will exist by using the concentration (i.e., vertical) scale and the duration curves to locate a point on the horizontal scale. If average long-term exposure is the primary interest, such as in cancer risk assessments from drinking water sources, the user simply needs to read the 'Mean Daily'


Figure 2.4 Explanation of pesticide cumulative frequency concentration curves.


Figure 2.5 Explanation of pesticide cumulative frequency loading curves.
concentration value identified on the figure. Additional guidance in the interpretation and use of the frequency information is provided in Section 2.3.

Since most parameter estimates will not exactly equal the specific values of Koc, ks, and kw used in developing the frequency curves, interpolation or extrapolation may often be required. A number of detailed numerical techniques, such as the method of Lagrangian polynomials, are available in general references and texts (see Hornbeck, 1975). However, considering the screening-level analyses being performed with STREAM and the accuracy with which the user can read individual points from the frequency curves, simple linear and/or graphical interpolation/extrapolation is probably adequate in most circumstances. The user must decide if interpolation/extrapolation is required, based on the range and variability of unit values from the curves, and what methods are most appropriate for the specific analyses being performed.

However, if interpolation/extrapolation is needed, we recommend that the user observe the following step-wise, structured approach, because of the number of calculations that may be required:

1. Identify all frequency curves that are needed to bound the particular parameter combination; i.e., koc/ks/kw of interest.
2. Interpolate first for the desired values of kw using the frequency curves associated with the neighboring kw values.
3. Using the unit concentrations from step 2, interpolate next for the desired values of ks; step 2 will have provided the unit concentrations for the neighboring ks values.
4. Using the unit concentrations from step 3 for neighboring values of Koc, interpolate for the desired value of Koc.

This procedure is best shown by example. For the parameter combination of $\mathrm{Koc}=1 \varnothing \emptyset \emptyset, \mathrm{ks}=\emptyset . \emptyset 5$, and $\mathrm{kw}=0.3$, step l is completed in the top half of Figure 2.3 where Figures A.ll, A.12, A.14, and A.l5 are shown to bound the desired values of ks and kw , for $\mathrm{Koc}=5 \varnothing \varnothing$, and Figures A.20, A.21, A.23, and A. 24 bound the values for $K o c=1500$. If we reproduce and expand these sections of the figure matrix, as shown below, the step-wise interpolation is demonstrated:

| Koc | kw |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | ks | @. 5 | 0.3 | 0.05 |
| 5øø | 0.1 | $\begin{aligned} & \text { A. } 11 \longrightarrow \frac{x 1}{\frac{x}{4}} \\ & \text { A. } 14 \longrightarrow \frac{x 3}{4} \end{aligned}$ |  | A. 12 |
|  | 0.05 |  |  |  |
|  | $\varnothing .01$ |  |  | A. 15 |
| $1 \varnothing \varnothing \square$ | $\underline{\square .05}$ |  |  |  |
| 1500 | 0.1 | $\text { A. } 2 \varnothing \longrightarrow \frac{\mathrm{x} 4}{\downarrow}$ |  | A. 21 |
|  | 0.05 |  |  |  |
|  | 0.01 | A. 2 | - x 5 | A. 24 |

In this example, Step 2 involves reading unit values from Figures A.ll and A.l2 and then interpolating a value, shown as xl, for $k w=\emptyset .3$. Similarly, $x 2$ is interpolated from values obtained from figures A.l4 and A.15. The same procedures are then used to obtain values of $x 4$ and $x 5$. Then in step. 3, the value for x 3 (which corresponds to $\mathrm{Koc}=5 \emptyset \varnothing$, ks $=\varnothing . \emptyset 5$ and kw $=\varnothing .3 \varnothing$ ) is derived from interpolation between $x 1$ and $x 2$, and x 6 (for $\mathrm{Koc}=15 \emptyset \emptyset, \mathrm{ks}=\varnothing . \emptyset 5$, and $\mathrm{kw}=\varnothing .3$ ) is derived by interpolating between x 4 and x 5 . Finally, in step 4 , the unit concentration $x 7$ for our parameter set is calculated by interpolating between $x 3$ and $x 6$.

Extrapolation can be handled in an analogous step-wise manner. However, the user should review the interpretation guidelines in Section 2.3 in order to determine the need for, and uncertainties associated with extrapolation.

For the pesticide loading frequency curves, interpolation and extrapolation are relatively simple and straight-forward because only Koc and ks are involved and the four Koc curves are plotted on the same figure.

### 2.2.4 Adjustments to Unit Concentrations and Loads

As noted above, the values obtained from the frequency curves are unit values based on the following conditions:
a. unit application rate of $1.0 \mathrm{~kg} / \mathrm{ha}$
b. applications to each crop separately
c. application to 1 ø日\% of each cropland area (i.e., 1ø0\% treated)

To obtain concentrations and loadings under the user-specified conditions, adjustments to the unit values may be required. For pesticide concentration estimates (both solution and bed) adjustments for all three conditions can be made as follows:

$$
\begin{equation*}
C=U 1 * \frac{T 1}{100 .} * A 1+U 2 * \frac{T 2}{100 .} * A 2 \tag{2.3}
\end{equation*}
$$

$$
\text { where } \begin{aligned}
\mathrm{C}= & \text { predicted concentration for user } \\
& \text { conditions, ppb } \\
\mathrm{U} 1, \mathrm{U} 2= & \text { unit concentrations from frequency } \\
& \text { curves for crops } 1 \text { and } 2, \mathrm{ppb} \\
\mathrm{~A} 1, \mathrm{~A} 2= & \text { application rate for crops } 1 \text { and } 2, \\
& \mathrm{~kg} / \mathrm{ha} \\
\mathrm{~T}, \mathrm{~T} 2= & \% \text { of cropland for crops }(1 \text { and } 2) \\
& \text { receiving application }
\end{aligned}
$$

Equation 2.3 simply shows that the concentrations from each cropland are linearly related to the application rate and fraction of cropland treated, and that the total concentration is the sum of the concentration contributions from each cropland. These linear relationships have been confirmed in sensitivity trials with HSPF (Dean et al., 1984). The examples in Section 3 demonstrate the use of this equation.

For the unit pesticide loading values obtained from the frequency curves, the only required adjustment is for the application rate since the values are for a unit area of each crop type. Thus, for an application rate of $5.0 \mathrm{~kg} / \mathrm{ha}$ the user must multiply the values from the frequency curves by $5 . \emptyset$ to obtain the correct loading rate.

### 2.2.5 Evaluate Methodology Results

In the final steps of the STREAM methodology, the user must make a critical evaluation of the validity of the results with regard to the methodology assumptions and limitations, prior to their use in exposure/risk assessments or as input to other models or analyses. In this evaluation the user should consider the need to perform sensitivity analyses on the key methodology parameters, based on the degree of uncertainty and potential variability of their values, to determine the impact on the predicted concentrations and loadings. If sensitivity analyses are indicated, the user will need to reiterate many of the assessment steps as shown in Figure 2.2. If the
sensitivity analyses indicate a large variation in the methodology predictions resulting from uncertainty in the parameter values, the user may need to put more effort (and resources) into reducing parameter uncertainty. This is especially true if the variation in results, such as predicted concentrations, encroaches upon values where cancer risk or aquatic impact may be significant. However, this decision should be made in light of the methodology, assumptions, limitations, and uncertainty discussed in Section 2.4.

### 2.3 INTERPRETATION AND USE OF RESULTS

The curves presented in this methodology are actually cumulative frequency distributions although we have called them frequency distributions for the sake of simplicity and expediency. Strictly speaking, a frequency distribution indicates the $\%$ of time a given value occurs; whereas a cumulative frequency distribution indicates the $\%$ of time a given value is exceeded. The latter is derived from the former as the cumulative sum of the area under the frequency curve at any point. For our purposes, frequency and probability can be used interchangeably i.e., the '\% of time' is also the '\% chance' of a value being exceeded.

The concept of 'duration' of an event in conjunction with its frequency also requires some explanation in terms of its use in STREAM. All the statistical analyses were performed with the DURANL module of HSPF on 3652 daily values generated in the lø-year simulation runs. Thus the daily duration curves are simply the results of the statistical analysis on the individual daily values. For the other durations - 2,4, and $3 \varnothing$ day - the analysis results indicate the $\%$ of time a value is exceeded and this occurs during an event with the corresponding duration. Figure 2.6 schematically shows the concept of moving a 'window' of any specific duration, to, though time series of concentrations as a basis for determining how often such conditions occur. Appendix $F$ further discusses and clarifies these concepts of frequency, cumulative frequency, and duration in analyses of time series information.

With this brief background, we can provide some insight into the proper interpretation of the frequency curves. As shown in Figure 2.4, the concentration frequency curves intersect the $x$-axis generally in the region of lø.ø to lø0.\%, rise toward the y-axis on the left but never reach the y-axis. Also, each individual duration curve usually stops at different points; in Figure 2.4 the $3 \emptyset$-day duration curve ends at $2 \%$ while the daily curve ends at $0.08 \%$. We can calculate the minimum value of '\% of time' for each duration by dividing


Figure 2.6 Time series of toxicant concentrations with moving average window of duration $t_{c}$.
the duration by the total number of daily values, i.e., 3652. These minimum values are as follows:

Duration, days
1
2

4
$3 \varnothing$

Minimum '\% of time'
.027
.055
$.11 \varnothing$
. 821

The curves will not extend to the same minimum point because the duration represents a threshold that must be exceeded in order to register as an event. Thus, a single 29-day event over the lø-year period would exist $\varnothing .794 \%$ of time (i.e., 29/3652) for the daily duration analysis but would not even register as an event (i.e., $\varnothing \%$ ) for the $3 \varnothing$-day duration analysis. However, a single $3 \varnothing$-day event would exist $\quad 0.821 \%$ of the time for both durations.

In order to have the $3 \emptyset-d a y$ duration curve extend to the same minimum point as the daily curve (i.e., . $027 \%$ ), we would need to have a time series of lllll. daily values, i.e., 3ø/.øøø27, or 304 years of simulation!

The frequency curves do not normally reach even the minimum values noted above due to the computational procedures in DURANL. The program scans through the time series and compares the daily values to pre-specified levels to determine the exceedance percentages. Barring the use of an enormous number of incremental levels (HSPF allows up to $2 \emptyset$ levels), these procedures (and resulting curves) will generally come quite close to the minimum but not exactly equal it. Thus, in Figure 2.4 the daily curve ends at $0.08 \%$ whereas the minimum value is $\varnothing .0 \boxed{6} 7 \%$, quite acceptable for our purposes at these low exceedance percentages.

Related to this is the maximum daily value indicated on the frequency diagram. Since this value is the maximum l-day value in the lø-year time series, it occurs $0.027 \%$ of the time. Thus, the user can locate one additional point for the daily duration curve to extend it if necessary.

The mean daily value shown on the frequency figures represents the arithmetic mean of the time series i.e., the sum of all the daily values divided by 3652.

The user will notice occasionally a straight vertical rise in a frequency curve; this simply indicates that no additional events occurred between two pre-specified levels. This occurs usually at extremely low exceedance percentages.

The l-day, 2-day, and 4-day durations were selected to correspond to the standard 24-hour, 48-hour and 96-hour LC5ø tests performed to establish the aquatic toxicity of a compound i.e., the concentration level at which $50 \%$ of the test organisms die when exposed for the selected duration period. Thus if the user has this type of information for the pesticide, he can use the concentration value to enter the frequency diagram and determine the '\% of time' that such acute toxic conditions will exist.

The $3 \varnothing$-day duration was selected to correspond to the standard toxicity tests performed to establish the maximum allowable toxicant concentration (MATC) or the no observable effects. level (NOEL) for the pesticide. These threshold values. indicate the concentration level above which chronic toxicity effects may be important. Thus if the user has this type of information for the pesticide, he can determine how often lethal, or potentially lethal, conditions may exist under the proposed chemical and use conditions.

As noted earlier, frequency diagrams are provided in the appendices for pesticide solution concentration, pesticide bed concentration, and pesticide daily loading; the concentration values are in parts per billion ( ppb ) and the loading values are in kilograms per hectare ( $\mathrm{kg} / \mathrm{ha}$ ) of
cropland. The concentration values correspond to pesticide concentrations in the last stream segment of the watershed. Thus the solution concentrations represent the outflow from the representative watershed, while the bed concentrations pertain to the stream bed at the watershed outlet. Also, the user should note that all bed concentrations are based on an assumed 5.0 cm bed depth. The user can adjust the bed concentrations predicted by STREAM if information is available to indicate that a different bed depth is more appropriate. This adjustment is simply an inverse linear function of depth: a 1.0 cm depth would produce concentrations 5 times higher, and a $10 . \emptyset \mathrm{cm}$ depth would produce concentrations $1 / 2$ the value predicted by STREAM for the 5.0 cm depth. Note that this adjustment is in addition to adjustments for application rate, multiple crops, and \% of cropland treated.

Although STREAM does not explicitly provide pesticide concentrations on suspended sediments, the user can estimate these values by multiplying the estimated solution concentrations by the weighted $K d$ values for each region listed in Table 2.3. These values are derived from the instream Kd values shown in Tables 4.15 through 4.19 and weighted by the appropriate sand, silt, and clay fractions for edge-of-stream sediment loadings shown in Table 4.4. Because of the relatively stable simulation of bed scour and deposition processes experienced in our regional simulations, the size distribution of sediment edge-of-stream loadings essentially equals the distribution of the sediment yield from the representative watersheds. The yield is comprised primarily of silt and clay particles with a very minor percentage (i.e., less than 5 to $1 \not \equiv \%$ ) of sand.

TABLE 2.3 WEIGHTED Kd VALUES FOR ESTIMATING SUSPENDED PESTICIDE CONCENTRATIONS FROM SOLUTION CONCENTRATIONS

|  | Koc |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | 50 | 500 | 1590 | 5 ¢ø0 |
| Southeast | 1.0 | 9.2 | 27.8 | 92.5 |
| Mississippi Delta | 1.0 | 9.6 | 28.9 | 96.2 |
| Eastern Cornbelt | 1.2 | 12.ஏ | 36.0 | 120.0 |
| Western Cornbelt | 2.0 | 20.5 | 61.5 | $205 . \varnothing$ |
| Central Plains |  | ( Inco |  |  |

For the pesticide daily loading information available from STREAM there are no accepted standards for comparison analogous to the LC5 0 , MATC, and NOEL levels for concentration information. Since the loading values represent total daily pesticide load from a specific crop they can also be considered as storm loads because most pesticide runoff during a storm will likely occur during a one or two-day period, at most. Consequently, the time when the daily load occurs is only during or immediately after storm events when pesticide runoff is occurring. For this reason, the user will note that the maximum '\% of time' for the loading frequency curves is usually in the range of 10 to $20 \%$.

For a specific pesticide, the loading values can be used to determine what $\%$ of application runs off, to make loading comparisons between and among regions, and to provide loading information for other models (e.g., EXAMS (Burns et al., 1982), TOXIWASP (Ambrose et al., 1983)).

### 2.4 STREAM ASSUMPTIONS, LIMITATIONS, AND UNCERTAINTY

To fully appreciate and effectively utilize the information available from STREAM, the user must be aware of the primary assumptions, associated limitations, and resulting uncertainty in the methodology.

### 2.4.1 Assumptions and Limitations

In order to represent the complex processes governing the fate and migration of pesticides in agricultural watersheds and provide a screening methodology with general applicability, a wide variety of assumptions are required. For each assumption there may be an associated limitation related to conditions not represented by the methodology. For STREAM, the assumptions are divided into two categories: those assumptions inherent in HSPF in order to model pesticide fate and transport, and those assumptions required for development of a general screening methodology.

The HSPF, or model-related, assumptions are fully documented in the HSPF User Manual (Johanson et al., 1984) and Application Guide (Donigian et al., 1984) and cover the entire range of processes from evapotranspiration and infiltration to sediment-chemical interactions in the stream. Below are listed the primary pesticide-related assumptions that STREAM users should be aware of:
a. linear, reversible equilibrium sorption in the soil profile.
b. lumped, lst order pesticide decay in the soil and on sediments.
c. constant distribution of sorbed pesticide loading on sand, silt, and clay sediment fractions.
d. no impact of tillage practices on vertical pesticide distribution in the soil profile.

The first three assumptions are commonly used in pesticide modeling at the current state-of-the-art, and are entirely appropriate for screening-level analyses. The alternative to the third assumption would be to simulate soil erosion by separate size fractions, but this remains a research topic at the current time. The last assumption, i.e., no impact of tillage on the vertical pesticide soil distribution, will tend to provide higher pesticide runoff loadings, and resulting concentations, than if the re-distribution of the pesticide was explicitly considered. Pesticide parameters and assumptions are further discussed in Section 4.4.

The methodology-related assumptions are further divided into those required for development of the regional representative watersheds, and those needed for simulation of pesticide scenarios and sensitivity analyses. The primary assumptions used in developing the regional representative watersheds are discussed in Section 4.3 and are summarized below:
a. total watershed area of løøø sq. km.
b. land use/crop distribution based on regional data, emphasizing agricultural land (see Table 4.3 for distributions).
c. meteorologic conditions derived from the HSPF application sites and adjusted for regional conditions.
d. land and soil characteristics based primarily on the HSPF application watersheds and checked for consistency with available regional information.
e. drainage characteristics derived from general and regional. information, and compared/adjusted to be consistent with the HSPF application watershed.
f. conventional agricultural practices appropriate for each region.

As opposed to the pesticide assumptions inherent in the algorithms and equations of HSPF, the assumptions listed below
were necessary in order to provide a screening methodology with a reasonable scope within the resource limitations of the project:
a. single pesticide application to the land surface (i.e., top $1 . \emptyset \mathrm{cm}$ of soil).
b. application at planting time to approximate preplant, planting, or pre-emergence type applications.
c. pesticide behavior represented by three key parameters: Koc, ks, kw.
d. primarily organic, hydrophobic pesticides whose behavior can be represented by lumped decay and linear sorption as a function of $O C \%$.
e. lumped, lst order decay of dissolved pesticide instream.
f. uniform value for soil/sediment decay for pesticide in all soil layers, on suspended sediments, and on bed sediments.
g. constant bed-chemical exchange rate based on limited field experience.

The pesticide parameters and assumptions are further discusseत in Section 4.4. Some assumptions, such as the method and timing of pesticide applications can be alleviated as additional resources become available to evaluate the impacts of alternative procedures. However, expanding the number of Key parameters could make the procedures too cumbersome (and the number of frequency curves too voluminous) to be used effectively. At the other extreme, certain processes such as the bed-chemical exchange mechanism require more basic and applied (i.e., field) research to develop better qualitative understanding of the complex interactions.

In sum, conditions where the sTREAM procedures are not directly applicable due to the assumptions discussed above are as follows:
a. pesticides that are soil-incorporated.
b. foliar application.
c. multiple applications during the growing season.
d. applications with soil and water conservation practices and/or best management practices.
e. pesticides that undergo ion-exchange, or decay to toxic daughter products with different sorption and decay characteristics.

If users apply STREAM when these conditions exist, they will need either adjust the results or use them only as general guidance since the above factors are not explicitly considered.

### 2.4.2 Uncertainty

A complete treatise on all sources of potential uncertainty in the STREAM procedures, along with rigorous confidence limits on the resulting estimates is not possible at this time and at the current state-of-the art of pesticide modeling in agricultural watersheds. This section discusses some of the major sources of uncertainty and provides some justification for the order-of-magnitude accuracy possible with STREAM.

The uncertainty we are concerned with is the potential difference in pesticide concentrations and loadings obtained from STREAM compared to expected values from typical watersheds in the region under the pesticide application assumptions used in STREAM and listed above. The primary areas of uncertainty include the extent to which our 'representative' watershed is truly typical of the region, the uncertainty associated with watershed modeling of hydrology and sediment, and the uncertainty associated with pesticide modeling.

The first two areas are related and should have an uncertainty considerably less than the third area (i.e., pesticide modeling). Based on past (site-specific) experience in watershed modeling, and a general knowledge of the variability in watershed response as a function of meteorology, soils, land use, agricultural practices, etc. We estimate that our representative watershed would have a maximum uncertainty factor of less than 2 when compared to a typical watershed in the region. The model calibration/verification approach used, in part, to develop regional parameters should have a maximum uncertainty of 20 to $5 \varnothing \%$, based on site-specific studies such as the Iowa study (Donigian et al., 1983) and the HSPF application watersheds. This would produce maximum uncertainties in the range of 2.4 to 3.0 for the first two areas noted above.

For the pesticide simulation uncertainty, the only studies available on which to base uncertainty estimates (i.e., where observed data were compared to model results) are the Four Mile Creek Study in Iowa (Donigian, et al., l983), a modeling
study of alachlor residues (Mulkey et al., l984) and earlier studies of pesticide runoff model development and testing (Crawford and Donigian, 1973; Donigian and Crawford, 1976, Donigian et al., l977). Generally these studies show maximum uncertainty factors in the range of 2.0 to 4.0 when comparing observed and simulated concentrations and runoff loads. Combining this range of uncertainty with the factors noted above produces a range of 4.8 to $12 . \varnothing$ IF all of the uncertainty produces differences in the same direction. This brief analysis, based primarily on judgement and past experience, indicates that order-of-magnitude accuracy is a reasonable expectation from the STREAM procedures, and that a factor of 5 accuracy or less can occur in many situations. Section 3.3 discusses an example of where the STREAM predictions are compared to a site-specific HSPF application with only a $50 \%$ over-prediction by STREAM.

Two key areas where additional certainty exists are sediment transport and bed-chemical exchange, which have a direct impact on the accuracy of the estimated pesticide bed concentrations. Continuous simulation of stream bed processes including scour, deposition, and chemical exchange with the overlying water column is an extremely difficult environmental problem where more data, research, and model testing is needed. As is discussed in Section 4.3, chemical exchange rates for both suspended and bed sediments were derived from limited field experience in Iowa. The primary impact of this is that the bed chemical concentrations predicted by STREAM, which are based on an assumed 5.0 cm bed depth (see Section 2.3), are expected to have greater uncertainty than the runoff and solution concentration estimates. The bed concentrations should be used cautiously considering potential errors of one to two orders-of-magnitude.

## EXAMPLE APPLICATIONS

This section provides three example applications of STREAM to demonstrate the use and interpretation of the figure matrices and frequency diagrams in the appendices in estimating pesticide concentrations and runoff loadings. The first two examples demonstrate how information is extracted from the appendices, with and without the need for interpolation, while the third example demonstrates and discusses differences that may result between concentrations predicted by STREAM and those resulting from a site-specific HSPF application.

### 3.1 EXAMPLE NO. l: NO INTERPOLATION REQUIRED

PROBLEM STATEMENT: Compound $X$ has been submitted for registration for use on corn and soybeans in the Southeast, Eastern Cornbelt, and Western Cornbelt. The proposed label application rates are $2.5 \mathrm{~kg} / \mathrm{ha}$ on corn and $3 . \varnothing \mathrm{kg} / \mathrm{ha}$ on soybeans. Determine instream solution concentrations for the mean daily value, and daily concentrations exceeded $1 \%$ and $1 \emptyset \%$ of the time, for 25\%, 5ø\% and 100\% treatment levels. From information supplied by the registrant the key methodology parameters for compound $X$ are as follows:

$$
\begin{aligned}
& \mathrm{Koc}=5 \not 00 \mathrm{ml} / \mathrm{gm} \\
& \mathrm{ks}=0.01 \mathrm{per} \text { day } \\
& \mathrm{kw}=0.5 \text { per day }
\end{aligned}
$$

STREAM APPLICATION: Since Compound $X$ is to be applied in the Southeast, Eastern Cornbelt and Western Cornbelt, Tables A.l, C.l, and D.l are the appropriate figure matrices to use in locating the proper frequency diagrams. Based on the Koc, ks, and kw values noted above, the unit solution concentration values can be determined directly from the following figures, without interpolation:

Southeast Eastern Cornbelt Western Cornbelt
Corn
A. 14
C. 14
D. 14

Soybeans
A. $5 \emptyset$
C. $5 \emptyset$
D. $5 \emptyset$

The following unit concentrations (i.e., l. $\varnothing \mathrm{kg} / \mathrm{ha}$ application and $10 \varnothing \%$ treatment) are read directly from these figures.

## Unit Solution Concentrations (ppb)

Exceedance
Mean Max. $\quad \underline{1 \%}$
SOUTHEAST:

| Corn | 1.12 | 94.9 | $1 \emptyset . \emptyset$ | $2 . \emptyset$ | (From Figure A.14) |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| Soybeans | $2 . \emptyset 2$ | $461 . \emptyset$ | $22 . \emptyset$ | $3 . \emptyset$ | (From Figure A.5Ø) |

EASTERN CORNBELT

| Corn | 4.31 | $122 . \emptyset$ | $45 . \emptyset$ | $12 . \emptyset$ | (From Figure C.14) |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Soybeans | 5.98 | 237.0 | $70 . \emptyset$ | i5.ø | (From Figure C.5Ø) |

WESTERN CORNBELT:

| Corn | 0.96 | 78.5 | $20 . \emptyset$ | 1.1 | (From Figure D.14) |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Soybeans | $\emptyset .98$ | 82.5 | $20 . \emptyset$ | 1.1 | (From Figure D.5Ø) |

To obtain the predicted concentrations for the appropriate application rates and treatment levels, we use Equation 2.3 which simply multiplies the unit values for each crop by the corresponding application rate and fraction of area treated. Thus, the mean concentrations in the Southeast are 8.86 ppb , 4.43 ppb , and 2.22 ppb respectively for $100 \%$, $50 \%$, and $25 \%$ treatment. The resulting predicted solution concentrations for each regions are as follows:

## PREDICTED SOLUTION CONCENTRATIONS (ppb)



## WESTERN CORNBELT:

| $100 \%$ treatment | 5.34 | 444. | 110.0 | 3.96 |
| ---: | ---: | ---: | ---: | ---: |
| $50 \%$ treatment | 2.67 | 222. | 55.0 | 1.98 |
| $25 \%$ treatment | 1.34 | 111. | 27.5 | 0.99 |

Note that these calculations assume that the maximum, $1 \%$ exceedance, and $19 \%$ exceedance concentrations for each crop are coincident i.e., they occur at the same time. This produces higher values and greater uncertainty in the estimates, especially for the less frequent events such as the maximum and $1 \%$ exceedance values.
3.2 EXAMPLE NO. 2: INTERPOLATION REQUIRFD FOR ALL PARAMETERS

PROBLEM STATEMENT: Compound $Y$ has been submitted for registration for use on cotton in the Mississippi Delta with a proposed label application rate of $2.5 \mathrm{Kg} / \mathrm{ha}$. Determine the mean daily instream solution concentrations expected from this application, and the of time a MATC value of 0.25 ppb will be exceeded, under løø\% treatment levels. The key methodology parameters are as follows:

$$
\begin{aligned}
\mathrm{Koc} & =1 \varnothing \varnothing \emptyset \mathrm{ml} / \mathrm{gm} \\
\mathrm{ks} & =\emptyset . \emptyset 5 \mathrm{per} \text { day } \\
\mathrm{kw} & =\emptyset .1 \emptyset \text { per day }
\end{aligned}
$$

## STREAM APPLICATION:

Since none of the parameter values for compound $Y$ equal the levels included in STREAM, interpolation will be required for all parameter values. Following the step-wise interpolation procedures discussed in Section 2.2.3, the required frequency diagrams needed for cotton in the Mississippi Delta are determined from Table B.l in Appendix B. Simple linear interpolation will be used to determine the unit concentrations corresponding to values Xl through X7 from neighboring frequency diagrams as shown below:

| $\underline{\mathrm{KOC}}$ | ks | kw |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | 0.5 | 0.10 | $\underline{0.05}$ |
| $5 \emptyset \emptyset$ | 0.1 | B. 11 | X1 | B. 12 |
|  | 0.05 |  | $\overline{\mathrm{x} 3}$ |  |
|  | 0.01 | B. 14 | 区2 | B. 15 |
| 1000 | 0.05 |  | x7 |  |
| $150 \square$ | 0.1 | B. 20 | X4 | B. 21 |
|  | 0.05 |  | $\overline{\mathrm{X} 6}$ |  |
|  | 0.01 | B. 23 | X5 | B. 24 |

Thus, the value of XI is determined by interpolation between the mean values of 0.23 ppb and 0.35 ppb from Figures B.ll and B. 12, respectively, as follows:

$$
\begin{aligned}
& \mathrm{Xl}=0.23+\frac{(.5-.10)(.35-.23)}{(.5-.05)} \\
& \mathrm{XI}=0.23+0.11=0.34 \mathrm{ppb}
\end{aligned}
$$

Similarly, X 2 is calculated as 1.60 ppb , determined from interpolation between mean values read from Figures B. 14 and B.15. Then, X 3 is calculated as follows by interpolation between ks values of $\varnothing .1$ and $\varnothing . \varnothing 1:$

$$
\begin{aligned}
& \mathrm{x} 3=0.34+\frac{(.1-.05)(1.60-.34)}{(.1-.01)} \\
& \mathrm{x} 3=0.34+0.70=1.04 \mathrm{ppb}
\end{aligned}
$$

The same procedures are followed to evaluate $\mathrm{X} 4, \mathrm{X} 5$, and X 6 , producing values of $\varnothing .14, ~ \varnothing .88$, and 0.55 ppb , respectively.

In the final step of the interpolation, the values of X3 and X6 (i.e., l. 04 ppb and 0.55 ppb ) are used to interpolate a value for $X 7$ between $K o c$ values of $5 \emptyset \emptyset$ and $150 \emptyset$, as follows:

$$
\begin{aligned}
& \mathrm{x} 7=1.04+\frac{(500-1000)(.55-1.04)}{(500-1500)} \\
& \mathrm{x} 7=1.04-0.24=0.80 \mathrm{ppb}
\end{aligned}
$$

Thus, for a unit solution concentration of $0.8 \emptyset \mathrm{ppb}$, the expected mean solution concentration for Compound $Y$ resulting from application to cotton at $2.5 \mathrm{Kg} / \mathrm{ha}$ and $1 \varnothing \varnothing \%$ treatment in the Mississippi Delta is 2. 0 ppb.

In order to determine the $\%$ of time a specific concentration is exceeded, such as the MATC value, the concentration must be converted to a unit concentration value (i.e., concentration resulting from $\bar{a} 1 . \varnothing \mathrm{Kg} / \mathrm{ha}$ application) and the frequency curves are used to determine \% exceedance for the unit concentration. Thus, for a MATC value of 0.25 ppb for Compound $Y$, the unit concentration is $\varnothing .10$ ppb (i.e., Ø. 25/2.5). With this unit concentration the interpolation procedure described above is performed again, interpolating \% exceedance values instead of concentrations. For a MATC value for Compound $Y$, the relevant intermediate values are determined from the $3 \emptyset$-day duration curves as follows:

$$
\left.\begin{array}{l}
\left.\begin{array}{l}
\mathrm{X} 1=10.8 \% \\
\mathrm{x} 2=78 \\
\%
\end{array}\right\} \\
\left.\begin{array}{l}
\mathrm{x} 4=9.5 \% \\
\mathrm{X} 5=67
\end{array}\right\} \quad \mathrm{x} 3=48.1 \% \\
\end{array}\right\} \quad \mathrm{x} 6=41.4 \% \text { x7 }=44.7 \%
$$

Thus, a MATC value of 0.25 ppb will be exceeded approximately $45 \%$ of the time if Compound $Y$ is applied to lø0\% of cotton cropland in the Mississippi Delta region at a label rate of $2.5 \mathrm{Kg} / \mathrm{ha}$.

### 3.3 EXAMPLE NO. 3: COMPARISON OF STREAM PREDICTIONS TO HSPF MODELING OF ALACHLOR IN THE IOWA RIVER

PROBLEM STATEMENT: Mulkey and Donigian (1984) report the results of using HSPF to predict alachlor solution concentrations in the Iowa River resulting from applications to corn and soybeans. How would the STREAM predictions compare with the alachlor concentrations reported by Mulkey and Donigian, and what assumptions or differences in the site-specific approach, as compared to the STREAM assumptions, would lead to the different predictions? Application rates of $2.58 \mathrm{Kg} / \mathrm{ha}$ and $3.58 \mathrm{Kg} /$ ha were used by Mulkey and Donigian (1984) for corn and soybeans, respectively, and produced a lø-year mean alachlor solution concentration of 5.83 ppb and $a$ maximan daily concentration of 722. ppb at Marengo, Lowa, assuming løø\% treatment of all corn and soybean cropland.

STREAM APPLICATION: To apply STREAM in this example, values of Koc, ks, and kw are required, in addition to the application rate and of treatment noted above. Mulkey and Donigian (1984) report that a variety of decay rates were used, as follows:
a. The solution decay rate was $\varnothing . \varnothing \emptyset 4$ per day
b. The suspended and bed sediment decay rate was $\varnothing .045$ per day
c. For the soil profile, the surface zone rate was 0.12 per day and changed to $\varnothing .06$ per day $1 \varnothing$ days after application; the upper zone rate was Ø. $\varnothing 45$ per day; and the lower and ground-water zone rates were Ø. $\varnothing 4$ per day.

Partition coefficients for alachlor were based on a Koc of 316 $\mathrm{ml} / \mathrm{gm}$ for the stream processes (L. Mulkey, personal communication), and the soil values were derived from field studies of alachlor in Iowa (Johnson and Baker, 1982). Thus, based on this information, the key STREAM methodology parameters can be estimated as follows:

$$
\begin{aligned}
\mathrm{Koc} & =316 \\
\mathrm{ks} & =\emptyset . \emptyset 5 \\
\mathrm{kw} & =9 . \emptyset \emptyset 4
\end{aligned}
$$

The primary uncertainty in these parameters is the value of k's since different values were used in each soil layer, and the surface layer values were changed $1 \varnothing$ days after application. The value of $\varnothing .05$ was selected as a conservative compromise; it is lower than the surface soil values and slightly higher then the value of $\varnothing .045$ per day used for the upper zone, suspended sediment, and bed sediment.

With the above values, the STREAM procedures can be applied as described in Examples No. 1, and No. 2. Since the value of kw is $\varnothing . \emptyset \emptyset 4$, corresponding to a half-life of 173 days, the lowest kw value in STREAM (i.e., Ø. Ø5) can be used because the normal flow times in the channel range from a few days to at most one to two weeks. Thus, an order of magnitude difference in kw (i.e., Ø. Øø4 to Ø. Ø5) will have a minor compact on the results (Mulkey and Donigian, 1984).

With a parameter combination of $316 / .05 / .05$, Figures D.3, D.6, D.12, and D. 15 are used to interpolate unit concentrations for corn, and Figures D.39, D.42, D.48, and D. 51 are used for soybeans. The resulting means and maximum unit concentrations and STREAM predictions based on the above application rates and løø\% treatment are as follows:

|  | $\begin{gathered} \text { Unit } \\ \text { Concentration (ppb) } \\ \hline \end{gathered}$ |  | STREAM Alachlor <br> Concentrations (ppb) |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Mean | Max | Mean | Max |
| Corn | 1.45 | 169 | 3.74 | 436 |
| Soybeans | 1.48 | 151 | 5.30 | 541 |
|  |  | STREAM | 9.04 | 977 |
|  | Mulk | Donigian | ults 5.83 | 722 |

Thus the STREAM procedures over-predict the alachlor concentration determined from this site-specific HSPF application by $55 \%$ for mean daily concentrations and $35 \%$ for the maximum daily concentration. These differences are in the proper direction (i.e., over-prediction) and are well within the order-of-magnitude accuracy needed for a screening-level analysis.

The major causes for the differences in the two predictions are directly related to the pesticide parameter and the representative watershed assumptions. The impacts of the pesticide parameters would likely be as follows, in decreasing order of significance:

1. The ks value of 0.05 was closer to the upper zone and stream sediment decay rates than the surface zones rates, and much of the alachlor decay may occur in the surface zone soon after application. Increasing the decay rate would have decreased the STREAM prediction to be closer to the site-specific predictions.
2. The Kd values of $4 . \varnothing$ used in the Iowa Study for the surface and upper soil zones were lower than the value of 6.2 which results from a $K o c$ of 316 and $2 \%$ OC, and used in STREAM. The pesticide loading frequency diagrams in Appendix $D$ show that the daily load generally tends to decrease as Koc (and thus Kd) increases for events occurring more than 1 to $2 \%$ of the time; however, for less frequent events this trend does not always hold. In any case, Kd values of 4 and 6.2 are close enough so that the impact on pesticide runoff loads would not be significant.
3. A kw value of Ø. Øø4 instead of $\varnothing . \varnothing 5$ would have increased the STREAM predictions slightly in the range of $5 \%$ or less for this specific parameter combination.

Similarly, the key representative watershed assumptions and their impacts would likely be as follows:

1. Meteorologic conditions, primarily precipitation were different between the representative watershed and the Iowa Basin. Three separate rain gages were used in the Alachlor study with rainfall adjustments ranging from $+5 \%$ to $-3 \%$, to better represent the spacial variation in rainfall in the basin. As shown in Table 4.8, the Western Cornbelt representative watershed used one rain gage increased by $15 \%$ to better represent the regional rainfall patterns. Thus, the greater rainfall produced greater runoff and associated pesticide runoff and instream concentrations compared to the Iowa River.
2. As shown in Table 4.3, the representative watershed for the Western Cornbelt was comprised of $75 \%$ cropland, whereas the Iowa River Basin included only 66\% cropland. Thus, if all other conditions and
parameter values were identical, the representative watershed would experience concentrations about 10\% higher than the Iowa River due to the greater cropland area contributing alachlor to the stream.
3. Differences in watershed area, drainage patterns, and channel characteristics between the representative watershed and the Iowa River Basin would likely produce some differences in individual daily concentration, but the differences in predicted mean concentrations would be small (see Section 4.3).

In summary, the primary causes for the differences in the STREAM predictions and the Iowa study results are the choice of the $k s$ value and the representative watershed meteorologic conditions. Both of these differences lead to higher concentration predictions by STREAM than from the site-specific HSPF application, indicating the conservative tendancy of the procedures which are appropriate for screening-level analyses.

## METHODOLOGY DEVELOPMENT

Development of the STREAM methodology for estimating instream pesticide concentrations and runoff loadings from agricultural watersheds involved the following steps:
a. Definition/selection of agricultural regions and model application watersheds
b. HSPF application to regional watersheds
c. Development of regional "representative" watersheds
d. Selection of key methodology parameters for sensitivity analyses
e. Development of pesticide frequency-duration information

Section 2.1 provided an overview of the methodology development shown schemcatically in Figure 2.1. Although the steps are listed separately, they are interrelated. Final selection of agricultural regions depended upon the existance of a regional watershed with an adequate database for a reasonable HSPF application. The HSPF application was guided by the mix of important crops in each region and the defined land use distribution for each "representative" watershed. The sensitivity analyses and production of frequency-duration information used the meteorologic database developed for the HSPF application and subsequently modified to be more generally representative of conditions in the entire agricultural region. Development of "representative" watershed characteristics for each region relied heavily on the HSPF application watersheds and their calibrated parameter values. This section discusses each of these steps to provide the user with the necessary background to use the STREAM procedures with a complete understanding of the required assumptions and associated limitations.

The specitic agricultural regions chosen for analysis in this study, and their approximate boundaries (Figure 4.l), were selected according to three major considerations: project resource limitations, existence of potential HSPF application sites, and regional characteristics. The first two considerations were primarily constraints on both the number and spacial extent or coverage of the selected regions. It was estimated initially that available project resources would be adequate for about five HSPF hydrology and sediment applications in addition to development of the overall methodology. A survey of agricultural watersheds with sufficient meteorologic, hydrologic, and sediment data to support an HSPE application was then conducted to enumerate potential sites. In conjunction with selected regional characteristics (discussed below), the tive HSPF application watersheds listed in Table 4.1 and whose locations are shown in Figure 4.1 were chosen to represent their respective regions. In eftect, watersheds with the best available data were chosen and then regional information was analyzed to determine the extent to which the individual watershed was representative of a larger region.

Regional meteorologic, soils, and cropping characteristics were used to detine approximate regional boundaries by overlaying national maps of each critical characteristic. For meteorologic conditions, a national isohyetal map (Figure 4.2) for precipitation and a national map of isopleths for potential evapotranspiration were used; greater emphasis was placed on precipitation patterns because of its greater spacial variability and its primary role in runoff generation. For soils conditions, the boundaries of the Land Resource Regions (US EPA, 1975) and a generalized mapping of hydrologic soil groups (figure 4.3) provided an overview of regional topographic and soils variability. The intensity and variation in cropping patterns tor the major crops of corn, soybeans, wheat, cotton, and sorghum was based on the 1978 Census of Agriculture (USDC, 1982); Figures 4.4 and 4.5 show the variation of these crops across the U.S. Superimposing these pieces of informationa allowed us to identity reyions with intensive agriculture and relatively unitorm meteorologic, soils and topographic conditions. The resulting regional boundaries, when considered on a state-wide basis, are generally consistent with regional definitions used by Unger (1979) in analyzing environmental implications of ayricultural trends, by Christensen and Magleby (1983) in regard to conservation tillage use, and by the USDA Crop Enterprise Buagets (USDA, 1981). Table 4.2 summarizes key characteristics of the detined agricultural regions.


Figure 4.1 Locations of agricultural regions and HSPF application watersheds.

TABLE 4.1 SELECTED CHARACTERISTICS OF HSPF APPLICATION WATERSHEDS

| Hatershed | Agricultural $\qquad$ | $\begin{gathered} \text { Precip } \\ \text { cm } \\ \hline \end{gathered}$ | itation (in.) | Potential ET cm (in.) |  | Predominant Soils |  | $\begin{array}{r} \quad \mathrm{Ar} \\ \mathrm{Sg} . \\ \hline \end{array}$ | $\begin{aligned} & \text { ea } \\ & \text { (sq. mi.) } \end{aligned}$ | $\begin{gathered} \text { Drainage } \\ \text { Basin } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Litela River, Georgia | Southeast | 127 | (50) | 114 | (45) | L.oamy | sands | 334 | (129) | Eastern Gulf/ South Atlantic |
| Upper Yazoo River, Hississippi | Mississippi Delta | 132 | (52) | 109 | (43) | Silty | clays | 5477 | (2115) | Lower Mississippi |
| Honey Creek, Ohio | Eastern Cornbelt | 89 | (35) | 81 | (32) | Silty | loams | 394 | (152) | Eastern Great Lakes/Ohio River |
| Iowa River, Iowa | Western Cornbelt | 81 | (32) | 89 | (35) | Silty <br> loams | clay | 7236 | (2794) | Upper Mississippi |
| Tuxkey Creek, Nebraska | Central Plains | 63 | (25) | 117 | (46) | Silty <br> loams | clay | 1191 | (460) | Upper Missouri |



Figure 4.2 Average annual distribution of precipitation in inches (Geraghty, et al., 1973).


Figure 4.3 Generalized hydrologic soil groups for the United States (Battelle, 1982).


Figure 4.4 Corn and soybean acerage in the United States,


Figure 4.5 Wheat, cotton, and sorghum acerage in the United States, 1978 (USDC, 1982).

TABLE 4.2 KEY CHARACTERISTICS OF THE DEFINED AGRICULTURAL REGIONS

| Region | Precipitation | Potential <br> Evapotranspiration | Predominent Soil Type | Hydrologic Soil Groups | $\begin{gathered} \hline \text { Primary } \\ \text { Crops } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \mathrm{cm} \\ \text { (inches) } \end{gathered}$ | $\begin{gathered} \mathrm{cm} \\ \text { (inches) } \end{gathered}$ |  |  |  |
| Southeast | $\begin{aligned} & 112-132 \\ & (44-52) \end{aligned}$ | $\begin{aligned} & 140-152 \\ & (55-60) \end{aligned}$ | Sandy loam Loamy sand | C , | Corn, Soybeans |
| Mississippi Delta | $\begin{aligned} & 132-163 \\ & (52-64) \end{aligned}$ | $\begin{aligned} & 127-165 \\ & (50-65) \end{aligned}$ | Silt clay | C-D | Cotton, Soybeans |
| Eastern <br> Cornbelt | $\begin{array}{r} 91-102 \\ (36-40) \end{array}$ | $\begin{aligned} & 102-114 \\ & (40-45) \end{aligned}$ | Silt loam <br> Silty clay <br> loam | B-C | Corn, Soybeans |
| Western Cornbelt | $\begin{gathered} 71-91 \\ (28-36) \end{gathered}$ | $\begin{aligned} & 102-165 \\ & (40-65) \end{aligned}$ | Silt loam | B-C | Corn, Soybeans |
| $\begin{aligned} & \text { Central } \\ & \text { Plains } \end{aligned}$ | $\begin{gathered} 41-81 \\ (16-32) \end{gathered}$ | $\begin{aligned} & 152-254 \\ & (60-100) \end{aligned}$ | Silt loam | A-D | Wheat, Sorghum |

These regions were then compared to the locations of the HSPF application watersheds and the region boundaries were subsequently constricted in order not to imply that the selected watershed was able to represent a region larger than could be reasonably expected. Thus the regional meteorologic, soils, and topographic characteristics were considered constraints on the extent of area whose hydrologic response could be reasonably represented by a single watershed. Since the STREAM procedures provide screening-level analyses, with an associated order-of-magnitude accuracy in the pesticide concentration and loading estimates, considerable latitude was possible in defining the region boundaries. Although the boundaries are clearly marked on Figure 4.1, they are approximate boundaries and, by no means, definitive. They represent general regions within which the procedures described herein can be used to estimate instream pesticide concentrations and runoff loadings for screening-level analyses.

### 4.2 HSPF APPLICATION TO REGIONAL WATERSHEDS

Prior to developing the "representative" watershed and generating pesticide frequency distributions, HSPF was applied to the selected application watersheds within each agricultural region. These applications involved simulation of hydrology, sediment erosion, stream hydraulics, and instream sediment transport.

Within the framework of this study, the objectives of these HSPF applications were as follows:
a. demonstrate and confirm the ability of HSPF to model the hydrologic, hydraulic, sediment erosion, and sediment transport behavior of agricultural watersheds characteristic of each region;
b. estimate selected model parameters, which are usually evaluated through calibration, as a basis for determining representative parameter values for the region.

Generally accepted "split-sample" model calibration and verification procedures were employed; half of the available data (i.e.,streamflow and sediment concentrations) were used in a model calibration exercise followed by a verification procedure with the remaining data. All model application procedures conformed to the guidelines and recommendations published in the HSPF Application Guide (Donigian et al., 1984).

Pesticide simulation was not performed as part of these applications due to the lack of observed pesticide data at most sites for comparison with model results, and lack of adequate project resources; however, previous studies with HSPF (Donigian et al., 1983; Mulkey and Donigian, 1984) and with predecessor models (Donigian et. al., l977) have sufficiently confirmed the pesticide simulation capabilities of HSPF for the purposes of this project.

Table 4.l summarizes selected characteristics of the HSPF application watersheds to demonstrate the range of watershed size, meteorologic conditions, and soils characteristics represented by these model applications. For each watershed listed in Table 4.l, Appendices $G$ through $K$ provide separate reports describing the data available for simulation, the segmentation plan for dividing each watershed into land and channel segments, and the results of the calibration and verification efforts.

Although each regional HSPF application was considered quite acceptable for the above-stated objectives of this study, the degree of agreement between simulated and observed values was variable. Runoff and streamflow simulation was consistently better than sediment simulation, and, with one exception, demonstrated good to very good agreement with observed streamflow data; a variety of statistical tests were used to quantify the comparisons. Also, hydrologic simulation of the southern watersheds (i.e., Little River and Yazoo River) was generally more accurate than in the northern watersheds due to the absence of the complicating effects of snow accumulation
and melt. However, in all watersheds, thunderstorms and their associated highly variable and erratic rainfall patterns presented significant problems for selected individual storm events. This is a common and well-documented problem in hydrologic modeling.

Sediment simulation suffered from the lack of adequate observed data such. as continuous (i.e., daily) instream concentrations, particle-size composition of suspended and bed sediments, stability of the stream bed, etc. With a few exceptions, sediment calibration relied upon a limited number of grab samples of sediment concentrations, primarily for non-storm periods, supplemented by generalized gross erosion and sediment delivery estimates and qualitative observations of bed composition and stability. Consequently, these data limitations precluded a rigorous sediment calibration/ verification exercise at most application sites. Within the limits of the observed data and available information, the sediment simulations did provide a reasonable representation of sediment behavior for agricultural watersheds.

This section has briefly discussed the HSPF applications to the regional watersheds to provide the user with a general appreciation of the basis for the development of the methodology. We recommend that interested users review the individual watershed reports in Appendices $G$ through $K$ to obtain a more indepth understanding of the problems, accuracy, and limitations of modeling agricultural watersheds with HSPF as used in this study.

### 4.2.1 Regional Watershed Descriptions

Each of the regional HSPF application watersheds are briefly described below to provide the user with a general overview of regional differences in meteorology, soils, topographic, and land use conditions. Detailed descriptions are included with the individual watershed reports in the Appendices.

## 4.2.l.l Little River Watershed--

The Little River Watershed is located in Tift, Turner, and Worth counties in south central Georgia (Figure 4.6). The Little River flows south to the Withlacoochee River, then to the Suwannee River which empties into the Gulf of Mexico west of Gainesville, Florida. The watershed used in this study has a drainage area of $334.3 \mathrm{sq} . \mathrm{km}$ (129.1 sq. mi.).

The climate of the Little River Watershed is characterized by long, hot, humid summers and short, mild winters. Mean annual
precipitation for the basin varies from approximately 112-122 cm (44-48 in.). The wettest months are March, June, July, and August; the driest months are October and November. Localized thunderstorm activity is common in the region.

The soils in the Little River Basin are predominantly sandy and can be divided into two basic groups in terms of their hydrologic properties. The upland areas are covered with well-drained loamy sands; the lowland areas and drainage ways are very swampy and are covered with poorly drained loamy sands which contain larger accumulations of organic matter than the upland soils (Jensen et al., 1959; Batten,1978; Calhoun, 1981).


Figure 4.6 Little River research watershed, Georgia

The Little River Basin is located in one of the important agricultural regions of the country. Approximately $36 \%$ of the study watershed is in crops, $18 \%$ in pasture, $40 \%$ in forest, and the remaining $6 \%$ in wetlands, lakes, roads, and residential and commercial areas (Asmussen, l982b).

The major agricultural crops grown in the basin are corn, soybeans, and peanuts, with smaller acreages in tobacco, cotton, and various vegetables. The various crops are uniformly distributed throughout the watershed with an average field size of 16 ha (4ø ac.) (Slack and Welch, 1980). Croplands are typically located on the well drained upland areas of the basin.

Normal planting and pesticide application times for corn and soybeans in the Little River Watershed are early to mid-March.

As an integral part of the drainage system, wetlands have a large attenuating effect on runoff and act as settling basins for suspended materials. There are over $2 \emptyset \emptyset$ small farm ponds Ø.1-1.2 ha (1/4-3 ac.) located throughout the watershed, some of which supply water to small irrigation systems for tobacco. These ponds have a negligible attenuating effect on runoff because the hydrologic response of the basin is very sluggish due to the large swampy areas (Asmussen, 1982b). However, these ponds will act as settling basins for eroded sediment from nearby fields.

## 4.2.l.2 Yazoo River Watershed--

A small portion of the $34,387 \mathrm{sq} . \mathrm{km}(13,277 \mathrm{sq} . \mathrm{mi}$.$) Yazoo$ River Basin (Figure 4.7) was chosen as the study area for this modeling effort. The Yazoo Basin study area comprises 5477 sq. km (2ll5 sq. mi.) and a major river channel 142 km ( 88.4 mi.) long. The river channel is known as the Coldwater and the Tallahatchie River as it flows through the study area, where it accepts water from the land immediately surrounding the channel, as well as from a series of reservoirs located on the eastern border of the study area. These large reservoirs contain water draining from the rolling hills located within the Yazoo River Basin to the east.

The climate of the Yazoo River Basin is humid and sub-tropical. Summers are hot and sultry, winters are wet and moderate. Although rainfall is well distributed throughout the year, pronounced local variations may occur due to summer thunderstorm activity. The average annual rainfall for the entire study area is close to 132 cm ( 52 in .). The greatest amount of rainfall occurs between December and April. The driest period of the year is September through October. The
most intense rainfall in terms of inches per hour occurs during local summer thunderstorm activity and can result in severe flooding (USDA, 1975).


Figure 4.7 Yazoo Basin and study area location map.

The Yazoo River Basin is located in one of the most intensively farmed areas of the United States. Approximately $44 \%$ of the study area is planted with crops, $18 \%$ is pasture, and $38 \%$ forested land. A very minor element is covered by urban land, wetlands, lakes, and roads.

### 4.2.1.3 Honey Creek--

The Honey Creek Basin (Figure 4.8) lies in the north-central section of Ohio. The study basin covers a drainage area of 392.1 sq. km (151.4 sq. mi.). It lies in the Till Plain area of the central lowlands physiographic region, which includes most of the glaciated part of Ohio. Relief in the watershed is mainly nearly level to undulating. The headwaters originate in a large swampy area and flow along the eastern and northern basin boundary.

The Honey Creek Basin experiences cold winters and uncomfortably warm summers. Average monthly temperatures range from 6 deg. $C$ in January to $3 \varnothing \mathrm{deg}$. $C$ in July. The average frost-free season is 160 days. Average annual precipitation is approximately 91 cm ( 36 in .). The wettest months are May and June, the driest are November and December.

The soils within the Honey Creek Watershed are relatively homogeneous across the basin. Typically, they consist of poorly drained silt loams on slopes of $\varnothing$ to $2 \%$. Movement of ground water north towards Lake Erie is an important factor in controlling the high water conditions in most of the Honey Creek Watershed. The flat high water table soils are very productive when drained.

The two rnajor crops grown are soybeans and corn. Their combined acreage covers approximately 60\% of the watershed. Seedbed preparation and planting usually occur in April and early May, with harvesting in October and November.

### 4.2.1.4 Iowa River Watershed--

The Iowa River Basin is located in central Iowa with its headwaters originating in Hancock County, of Northern Iowa (Figure 4.9). The river flows in a southeasterly direction to its confluence with the Mississippi River on the southeast border of the state. This study covers a drainage area of 7236 sq. km (2794 sq. mi.). The study basin is wholly contained in the state of Iowa, and 14 counties contribute to its drainage area. South of Marengo, the river drains into Coralville Reservoir, which is a major recreational area for central Iowa, and then flows past Iowa City, for which it serves as a water supply source.


Figure 4.8 Location of Honey Creek Basin

The growing season for warm weather crops extends from mid-May to early October. The dormant season, averaging 19 weeks, extends from mid-November to late March. The crop growing season is limited by both spring and fall freezes in Iowa.

Farmers in the southern portion of the Iowa River Basin typically plant and apply herbicides to corn cropland in early to mid-May and soybean cropland in late May to early June. This timetable generally precedes by up to two weeks these operations in the northern area of the watershed.

Mean annual precipitation for the basin varies from 77 cm ( $3 \varnothing$ in.) in the north to 84 cm ( 33 in.) in the southeast. Heaviest rainfalls occur in May and June, and diminish during July as the storms track across Canada. A secondary, but lesser, rainfall maximum is associated with the southward


Figure 4.9 Location of the Iowa River Basin.
movement of the prevailing storm track across Iowa in August or September.

The soil types of the Iowa River Basin may be generally grouped according to parent material into glacial drift soils and loess soils. Natural fertility is good, and the mineral and organic matter content is high. For the Iowa River Basin, between 65 and $85 \%$ of each county which contributes land to the basin is cropland, with the majority of the cropland being either corn or soybeans. Of all other land uses, only grassland comprises more than $1 \varnothing \%$ of the area's total usage.

### 4.2.1.5 Turkey Creek--

The Turkey Creek Watershed (Figure 4.l0) lies in the southeast section of the state of Nebraska and covers an area of 1191 sq. km ( $460 \mathrm{sq} . \mathrm{mi}$.$) . The main channel of the creek stretches$ $133.2 \mathrm{~km}(82.8 \mathrm{mi})$ through very level to gently roling farmland. The Turkey Creek drainage basin is long and narrow. The western half of the basin is extremely flat and the drainage channels, along with portions of the main-stem, flow intermittently throughout the summer and fall. In the middle of the watershed the land develops into a gently roling terrain, which becomes more pronounced to the east.

The climate of Turkey Creek is sub-humid continental and typical of the Central Plains region. It is characterized by wide variations in temperature between winter and summer. Cold winter systems travel from the north across the continent. Daily average winter temperatures remain below freezing. Summers are generally hot and humid. Average annual precipitation ranges from $68.6 \mathrm{~cm}(27 \mathrm{in}$.) in the west to 73.7 cm (29 in.) in the east. More than half of the annual rainfall is from thunderstorms during May, June, July, and August. Because of the large influence of thunderstorms on total annual precipitation, rainfall volumes from year to year vary dramaticaliy. Average seasonal snowfall ranges between 56 and 86 cm (22-34 in.). Snowpack does not remain on the ground all season long. The growing season ranges from between 17Ø-20ø days with the last frost date around April 15 and the first killing frost around October 23.

Turkey Creek is located in the Central Great Plains Winter Wheat and Range Region and lies on the eastern boundary of the Central Loess Plains (75) Land Resource Area. Soils in the drainage basin consist, for the most part, of silt loams. There are 3 major soil associations. Hastings soils are well drained throughout the profile and are classified under hydrologic group B. Crete and Butler soil associations have well drained surface layers and a restrictive silt clay sub-layer that blocks both water movement and root development. These soils are classified in hydrologic group D.


Figure 4.10 Location of Turkey Creek Watershed.

Approximately 95\% of the Turkey Creek Basin is devoted to agriculture. The major agricultural crops grown in the basin are corn, sorghum (milo), winter wheat, and soybeans. The mix of crops has changed drastically over the past 35 years, due in most part to the development of irrigation. Corn and soybeans are mostly irrigated. Sorghum and wheat are dryland farmed. With the development of irrigation, corn has replaced wheat as the major crop.

### 4.3 DEVELOPMENT OF REGIONAL "REPRESENTATIVE" WATERSHEDS

The concept of regional "representative" watersheds was developed in this study and used as the basis for the sensitivity analyses and resulting pesticide frequency distributions. The primary need was a sound technical basis for stating that the frequency distributions can be reasonably applied and used for a broader geographical region than just the specific HSPF application watershed. In addition, since many exposure assessments conducted as part of the pesticide registration process will involve more than one region, some "normalization" is needed to allow comparisons between and among the various regions.

With these needs in mind, the definition of a representative regional watershed can be stated as follows:

A regional representative watershed is a standarized watershed that will demonstrate hydrologic, sediment, and water quality (primarily pesticide) behavior that is typical or representative of watersheds throughout the region, within the order-of-magnitude accuracy appropriate for a screening-level analysis.

Thus, the representative watershed will not exactly duplicate the behavior or response of all watersheds in the region, or any one specific watershed (except by pure chance), but it will demonstrate behavior that is typical of watersheds in the region within the latitude provided by the order-of-magnitude accuracy required.

The underlying premises of the representative watershed concept are not new to the field of water resources. For example, a number of government agencies active in environmental research and monitoring often use point measurements or studies of a small area to help elucidate, analyze, and project behavior for a larger region. The Agricultural Research Service has established regional research watersheds and small experimental agricultural watersheds (see Burford et al., 1972) since the 1920's and 1930's in various locations across the country to study
watershed hydrologic processes and regional differences; the Little River Watershed in Georgia, which was an HSPF application site, is one such watershed. The U.S. Geological Survey has established "hydrologic benchmark" stations as general regional indicators of water quality conditions from natural watersheds across the country (Biesecker and Leifeste, 1975). The U.S. Forest Service has performed a survey of watershed databases suitable for nonpoint pollution model development and testing (USFS, l977); it classified watersheds as 'experimental' or 'representative', with representative referring to a watershed "that has been instrumented to be indicative of a broad, homogeneous area" (USFS, 1977, pg. 1ø1).

Thus, the approach of studying one small area as a basis for projecting environmental conditions and processes over a much larger region is well-established. To identify a watershed that is truly representative of a large region, we would ideally like to select a real watershed that has characteristics of size, land use/cropping distribution, soils, topography, climate/meteorology, and drainage that correspond to average or mean conditions throughout the region. However, lacking the resources to undertake such a data-intensive approach, in this study we compared differences in characteristics between the HSPF application watersheds and regional values as a basis for transforming them into regional "representative" watersheds. The remainder of this section describes this transformation process in terms of the assumptions and adjustments made for the key characteristics of watershed area, land use/crop distribution, land and soil characteristics, meteorologic conditions, drainage characteristics' and agricultural practices.

### 4.3.1 Watershed Area

Although the area of the representative watershed is a basic requirement for modeling, the specific value selected is less critical than the other watershed characteristics discussed in this section. For this study, a moderate size watershed of løø日 sq. km. ( 386 sq. mi.) was selected as the standard area for the representative watershed in all agricultural regions. Although this specific value is somewhat arbitrary, the selection was based on the following considerations:
a. The area must be large enough to support a perennial stream, i.e., continuous flow conditions in all agricultural regions to avoid the complications of no-flow conditions on pesticide concentrations. Generally, watersheds greater than 2.50 to $5 \emptyset \emptyset \mathrm{sq} . \mathrm{km}$. will support perennial streams although this range will vary significantly across the country.
b. The area should be comparable to the size of the HSPF application watersheds to avoid unnecessary extrapolation of the watershed conditions and characteristics developed from the calibration/ verification exercise. As shown in Table 4.l, the area of the application watersheds ranged from 334 to 7236 sq. km., with the larger watersheds including smaller subwatersheds that were modeled during the application.
c. The area should be large enough to provide a reasonable distribution between surface and sub-surface flow components, and to provide sufficient flow time in the stream channel to allow instream chemical fate processes to affect concentrations. The smaller HSPF application watersheds, with areas of $3 \varnothing \varnothing$ to $4 \varnothing \varnothing$ sq. km., were dominated by surface runoff, demonstrated zero-flow conditions during extreme dry periods, and experienced mean flow-through times of less than two to three days.

Based on these considerations, the $1 \varnothing \varnothing \emptyset \mathrm{sq} . \mathrm{km}$. watershed size was selected as a reasonable compromise that would provide continuous streamflow, with a more even distribution of surface and subsurface flow and longer instream flow times than the smaller application watersheds, but still remain within the size range of all the application watersheds.

### 4.3.2 Land Use/Crop Distribution for Representative Watersheds

A combination of data was used to derive land use/crop distribution values for the five agricultural regions. Table 4.3 lists the distribution values derived from the various sources, and the final values used for the representative watersheds. The 1978 Census of Agriculture, Summary and State Data (U.S. Dept. of Commerce, l981), provided a basis for calculating initial land use/crop distribution values. This source provides data, on a per state basis, such as total acreage in farmland, cropland, pastureland, as well as harvested acreage of specific crops. Using these data, percentages for major crops, pasture and/or other cropland, and forest were calculated for the regions in which the study watersheds are located. For example, the Delta States (i.e., Arkansas, Louisiana and Mississippi) were used for the Mississippi Delta Region.

Since these values are based on state boundaries, they do not accurately represent the land use solely within the agricultural region. Although the census provides

TABLE 4.3 LAND USE/CROP DISTRIBUTION FOR AGRICULTURAL REGIONS AND REPRESENTATIVE WATERSHEDS

| Region | Land Use/ Crop Category <br> ( 8 ) | HSPF <br> Application Watershed $\text { ( } 8 \text { ) }$ | $1978$ <br> Census Data (State-Basis) (8) | 1978 <br> Census Data <br> (Graphic Summary) <br> $(8)$ | Final Distribution for Representative Watersheds $(7)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Southeast | Corn | 10 | 11 | 15-20 | 20 |
|  | Soybeans | 10 | 15 | 25-30 | 30 |
|  | Pasture and/or other cropland | 40 | 46 | 10-15 | 10 |
|  | Forest . | 40 | 28 | 40 | 40 |
| Mississippi Delta | Cotton | 54 | 7 | 20-23 | 20 |
|  | Soybeans | 54 | 30 | 40-45 | 45 |
|  | Pasture and/or other cropland | 16 | 52 | $<10$ | 5 |
|  | Forest | 30 | 11 | 30 | 30 |
| EasternCornbelt | Corn | 25 | 36 | 30-40 | 40 |
|  | Soybeans | 34 | 29 | 30-35 | 35 |
|  | Pasture and/or other cropland, | 21 | 29 | 10-15 | 15 |
|  | Forest | 18 | 6 | 10 | 10 |
| Western | Corn | 44 | 29 | 35-40 | 40 |
| Cornbelt | Soybeans | 22 | 22 | 30-35 | 35 |
|  | pasture and/or other cropland, forest | 34 | 49 | 25-30 | 25 |
| Central | Wheat | 20 | 14 | 30-40 | 35 |
| Plains | Sorghum | 27 | 5 | 15-20 | 20 |
|  | Pasture and/or other cropland, forest | 53 | 81 | 40-45 | 45 |

county-level data for each state, the effort to aggregate the county data was not justified considering the approximate boundaries of our defined agricultural regions.

The 1978 Census of Agriculture, Graphic Summary (U.S. Dept. of Commerce, 1982) was used in correcting the state-based values: land use and crop distribution data is depicted on multicolor choropleth maps of the entire United States. A particular geographical location can easily be singled out from these maps, and estimates for land use/crop distribution in a particular region are, therefore, more accurate. In the case of the Delta States, for example, the calculations based on the 1978 Census of Agriculture, Summary and State Data indicate that $7 \%$ of cropland acreage was in cotton. In 1978, the majority $\overline{O f}$ the cotton grown in the Delta States was actually grown in the region of the Yazoo River watershed. According to the Graphic Summary, the percent acreage in cotton in the region near the Yazoo River was in the range of $20 \%$ to $23 \%$ or more. The disadavantages inherent in using the Graphic Summary is that the values tend to be rather approximate, since various color codes on the map represent different ranges of percentages, e.g., lø-19\%, 2ø-29\%, 3ø\% or more.

In summary, the final values for land use/crop distributions of our representative watersheds are based on three sets of values derived from the 1978 Census of Agriculture Summary and State Data, the 1978 Census of Agriculture Graphic Summary and the actual land use distribution of the HSPF application watersheds. These values were also checked with other sources; a report titled "Major Land Uses in the United States: 1978" (Frey, l982), along with land use and crop season profiles (Unger, 1979), provided a means of checking the feasibility and consistency of the distribution values. The final land use/crop distribution shown in Table 4.3 were derived from the above sources, with the crop percentages usually set near the upper end of the range of values estimated. This was done to provide a degree of conservatism to the assessment procedures, since pesticide problems would likely occur in watersheds where cropland is predominant, while still maintaining a reasonable distribution of non-cropland for the region.

### 4.3.3 Topographic, Soils, and Sediment Characteristics

Whenever HSPF is applied to a new watershed, model parameters that reflect topographic, soils, and sediment characteristics must be evaluated. Most parameters, such as land slope, overland flow length, crop canopy and interception, etc. are determined from specific watershed and crop information, while
other parameters, such as effective infiltration rates, nominal soil moisture storages, recession rates, etc. are evaluated through the calibration process. Parameter values for the regional representative watersheds were developed primarily from the parameters evaluated for the HSPF application watersheds. Calibration parameters were assumed to be identical in both watersheds. For the remaining model parameters, selected county soil surveys, data on hydrologic soil groups, and other regional information was evaluated to determine if adjustments were needed to reflect any differences in characteristics between the application watershed and region-wide values.

In most all cases, little or no adjustment to the application watershed parameters was required. For the larger application watersheds, i.e., the Iowa River and Yazoo River, the entire watershed area was segmented into subregions with differing characteristics and parameter values providing a range of conditions from which the "representative" values could be selected. For example, the Iowa River was segmented into three groups representing the upper, middle, and lower regions of the basin; the parameters of the middle region were selected as most representative of the Western Cornbelt. In the Yazoo River, the study area was segmented into two regions representing the delta and bluff physiography; parameters for the delta region were selected as most representative of the agricultural land in the Mississippi Delta region (see Appendices $G$ through $K$ for the specific application watershed parameter values.)

If agricultural practices for the application watershed differed signicantly from the conventional agricultural practices assumed for each region, adjustments to land cover, crop interception, surface roughness, and soil moisture retention parameters were made to better reflect regional conditions. These adjustments were based on prior experience in evaluating the effects of agricultural practices on HSPF parameters (Donigian et al., 1983). Section 4.3.6 describes the nature and sequence of agricultural practices assumed in each region.

Selected sediment and soil characteristics that have a direct impact on pesticide processes are summarized in Tables 4.4 through 4.7 for each agricultural region. Table 4.4 shows the assumed sand/silt/clay percentage distribution of the edge-of-stream sediment loads from each crop and land use in each region. HSPF requires these distributions because instream processes of sediment transport (i.e., advection, scour, deposition) and sediment-chemical interactions are modeled separately for each size fraction, whereas the edge-of-stream sediment load is calculated as the total mass input. The range of distributions shown in Table 4.4 is based

TABLE 4.4 ASSUMED SAND/SILT/CLAY PERCENTAGES FOR SEDIMENT EDGE-OF-STREAM LOADINGS

| Region | Crop 1 | Crop 2 | Pasture | Forest |
| :--- | :---: | :---: | :---: | :---: |
| Southeast | Corn | Soybeans |  |  |
|  | $10 / 45 / 45$ | $10 / 45 / 45$ | $5 / 45 / 50$ | $0 / 50 / 50$ |
|  |  |  |  |  |
| Mississippi | Cotton | Soybeans |  |  |
| Delta | $5 / 50 / 45$ | $5 / 50 / 45$ | $2 / 53 / 45$ | $0 / 55 / 45$ |
| Eastern | Corn | Soybeans |  |  |
| Cornbelt | $5 / 55 / 40$ | $5 / 55 / 40$ | $0 / 55 / 45$ | $0 / 55 / 45$ |
|  |  | Corn | Soybeans |  |
| Western | $5 / 55 / 40$ | $5 / 55 / 40$ | $0 / 60 / 40$ |  |
| Cornbelt | Wheat | Sorghum | (Incomplete) |  |
| Central |  |  |  |  |
| Plains |  |  |  |  |

on limited particle-size data of eroded sediments from field-size areas in Iowa (Johnson and Baker, 1982) and Mississippi (Doty and Carter, 1965). Erosion from pasture and forest lands is assumed to produce little or no sand particle, while the analogous cropland percentage of sand is only 5 to $10 \%$. Thus, the edge-of-stream loadings are comprised primarily of fine silt and clay particles which are also the primary hosts for adsorbed chemicals.

Table 4.5 summarizes the soil bulk densities assumed for the various soil layers in each region. The values are based on some specific data in Iowa (Johnson and Baker, 1982) and correlations of bulk density with soil texture by Rawls (1983). They demonstrate the relatively small range of bulk density values commonly found for most agricultural soils.

Tables 4.6 and 4.7 respectively provide the percent organic carbon contents of the soil layers and instream suspended and bed sediments for each region. The soil organic carbon values shown in Table 4.6 are based primarily on data presented by Rao et al. (1984) for a group of selected soils from regions across the country; most of our defined agricultural regions were represented by Rao's data. In addition, Karickhoff et al. (1979) provided values for selected southeastern soils and Karickhoff (1981) reported percent organic carbon values for various sediment samples collected and analyzed by Hassett et al. (l98ø). These primary sources were supplemented by generalized information on percent nitrogen in surface soils
across the U.S. (Parker et al., 1946) and specific values for percent organic matter provided by Lyons et al. (1952). Site-specific values of percent organic matter for Iowa (Johnson and Baker, 1982) were used to confirm the appropriate values for the Western Cornbelt. The resulting surface values for percent organic carbon were assigned to the surface and upper zone soil layers (i.e., 15 cm depth); the variation with depth (i.e., lower and ground-water zones) was derived from regional soil profile data on organic matter from a computerized soils data base under development by. Carsel et al. (1983) and generalized information presented by Brady (1974) and Kilmer (1982). As shown in Table 4.6, we assumed the lower zone organic carbon values were one-half the surface and upper zone values, and the ground-water zone organic carbon values were a factor of 10 less than the lower zone values.

Very little data was available to define the percent organic carbon for each particle size fraction of the suspended and bed sediments shown in Table 4.7. We relied primarily on the data presented by Rao et al. (1984) for percent organic carbon on the sand fraction and fine fraction (i.e., silt and clay) for six soils across the country, similar data for southeastern soils by Karickhoff et al. (1979), and a detailed distribution for five size classifications for Webster soils from the Western Cornbelt (Rao et al., l984). Except for the

TABLE 4.5 ASSUMED SOIL BULK DENSITIES FOR EACH AGRICULTURAL REGION

| Region | Surface zone | Soil Bulk Density ( $\mathrm{g} / \mathrm{cc}$ ) |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Upper <br> Zone | Lower <br> Zone | Ground-water Zone |
| Southeast | 1.4 | 1.4 | 1.5 | 1.6 |
| Mississippi Delta | 1.35 | 1.35 | 1.5 | 1.6 |
| Eastern Cornbelt | 1.3 | 1.3 | 1.5 | 1.6 |
| Western Cornbelt | 1.2 | 1.2 | 1.5 | 1.6 |
| $\begin{aligned} & \text { Central } \\ & \text { Plains } \end{aligned}$ | 1.3 | 1.3 | 1.5 | 1.6 |

TABLE 4.6 ASSUMED PERCENT ORGANIC CARBON FOR EACH SOIL LAYER

| Region | \% Organic Carbon |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Surface Zone | Upper Zone | Lower Zone | Ground-water Zone |
| Southeast | 1.0 | 1.0 | 0.5 | 0.05 |
| Mississippi Delta | 1.5 | 1.5 | 0.75 | 0.075 |
| Eastern Cornbelt | 2.0 | 2.0 | 1.0 | 0.10 |
| Western Cornbelt | 2.5 | 2.5 | 1.25 | 0.125 |
| Central Plains | 2.0 | 2.0 | 1.0 | 0.10 |

Western Cornbelt, the carbon content of the silt and clay fractions were set equal due to the lack of data to justify different values.

### 4.3.4 Regional Meteorologic Conditions

In conjunction with the HSPF applications to the regional test watersheds, lo-year meteorologic data bases were developed in each region to provide the regional input data for running HSPF and producing frequency distributions of pesticide concentrations and loading. The lø-year data bases were an extension of the meteorologic time series used in simulating the actual application watershed in each region. The critical time series of precipitation and evaporation were subsequently adjusted, as described below, to better represent regional and long-term conditions for the representative watershed simulations.

Table 4.8 summarizes for each agricultural region the meteorologic data, station location, and period of record used in the representative watershed simulations. For the precipitation and evaporation, it also shows the long-term regional mean value, the lo-year station mean, and the adjustment factor. Only the precipitation and evaporation time series were adjusted. The remaining time series are used
exclusively in the snow calculations and thus only during the winter months. Because of the complexities of simulating snow accumulation and melt, the interactions between the calibrated parameters and the meteorologic data, and the relatively central location of the application watershed within the region, no adjustments were made to the snow-related meteorologic input data. Thus, we felt the snow simulation as performed on the application watershed would be reasonably representative of the region.

However, for both the precipitation and evaporation input data constant multipliers (i.e., adjustment factors in Table 4.8) were applied to each value in the lø-year time series. The objectives of the adjustment were to account for differences between the specific lø-year station time series and long-term region-wide values. Different procedures were required to determine the appropriate adjustment factor for each data type. For evaporation, the adjustment factor is the product of the ratio of the long-term regional mean to the lø-year station mean, and the appropriate pan coefficient. Values for long-term regional pan evaporation and pan coefficients were derived from the Climatic Atlas of the U.S. (USDC, l979).

Because of the critical impact of both precipitation intensity and volume on watershed runoff, the adjustment factor for precipitation was designed to consider both characteristics. The volume adjustment factor was calculated as the ratio of

TABLE 4.7 ASSUMED PERCENT ORGANIC CARBON FOR SIZE FRACTIONS OF SUSPENDED AND BED SEDIMENTS

|  |  |  |  |
| :--- | :--- | :---: | :---: |
| Sand | Silt Organic Carbon | Clay |  |
| Region | 0.5 | 2.0 | 2.0 |
| Southeast | 0.5 | 2.0 | 2.0 |
| Mississippi <br> Delta | 0.5 | 2.5 | 2.5 |
| Eastern <br> Cornbelt | 1.0 | 3.0 | 6.0 |
| Western <br> Cornbelt | 0.5 | 2.5 | 2.5 |
| Central <br> Plains |  |  |  |

## TABLE 4.8 SUMMARY OF METEOROLOGIC DATA USED IN REPRESENTATIVE WATERSHED 10-YEAR SIMULATIONS

| Region | Data Type | Station | Period of Record | Regio cm | $\begin{aligned} & \hline \text { nal Mean } \\ & \text { (in.) } \\ & \hline \end{aligned}$ |  | on Mean (in.) | Adjustment Factor |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Southeast | Precipitation | SEWRL Gage 27 | 1971-1980 | 122 | (48) | 126 | (49.8) | 1.00 |
|  | Evaporation | Tifton, GA | 1971-1980 | 146 | (57.5) | 145 | (57.2) | 0.75 |
| Mississippi Delta | Precipitation | Clarksdale, MS | 1970-1979 | 147 | (58) | 149 | (58.5) | 1.10 |
|  | Evaporation | Scott, MS | 1970-1979 | 147 | (58) | 143 | (56.4) | 0.78 |
| Eastern Cornbelt | Precipitation | Upper <br> Sandusky, OH | 1974-1983 | 91.4(36) |  | 91.7(36.1) |  | 1.00 |
|  | Evaporation | Hoytville, OH | 1974-1983 | 108 | (42.5) | 121 | (47.6) | 0.68 |
|  | Air Temperature | Tiffin, OH | 1974-1983 |  |  |  |  |  |
|  | Dew Point | Tiffin, OH | 1974-1983 |  |  |  |  |  |
|  | Wind | Hoytville, OH | $\begin{aligned} & 1974-1983 \\ & \text { (Apr-Oct) } \end{aligned}$ |  |  |  |  |  |
|  | Wind | Cleveland, OH | $\begin{aligned} & 1974-1976 \\ & \text { (Nov-Mar) } \end{aligned}$ |  |  |  |  |  |
|  | Wind | Mansfield, OH | $\begin{aligned} & \text { 1976-1983 } \\ & \text { (Nov-Mar) } \end{aligned}$ |  |  |  |  |  |
|  | Solar Radiation | Wooster, OH | 1974-1983 |  |  |  |  |  |

(continued)

TABLE 4.8 (continued)

| Region | Data Type | Station | Period of Record | Regional Mean cm (in.) | Station Mean cm (in.) | Adjustment Factor |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Western <br> Cornbelt | Precipitation | Traer, IA | 1969-1978 | 81.3(32) | 74.2(29.2) | 1.15 |
|  | Evaporation | Farmer's Coop WS | 1969-1978 | 127 (50) | 129.8(51.1) | 0.725 |
|  | Air Temperature | Marshalltown, IA | 1969-1978 |  |  |  |
|  | Dew Point | $\underset{\text { IA }}{\text { Marshalltown }}$ | 1969-1978 |  |  |  |
|  | Wind | Farmer's Coop WS | 1969-1978 |  |  |  |
|  | $\begin{gathered} \text { Solar } \\ \text { Radiation } \end{gathered}$ | Farmer's Coop WS | 1969-1978 |  |  |  |
| ```Central Plains``` | Precipitation | Crete, NB | 1972-1982 |  |  |  |
|  | Evaporation | $\begin{aligned} & \text { Clay Center, } \\ & \text { NB } \end{aligned}$ | 1972-1982. |  |  |  |
|  | Evaporation | Crete, NB | 1972-1982 |  |  |  |
|  | Air Temperature | Crete, NB | 1972-1982 |  |  |  |
|  | Dew Point | Crete, NB | 1972-1982 |  |  |  |
|  | Wind | Crete, NB | 1972-1982 |  |  |  |
|  | $\begin{aligned} & \text { Solar } \\ & \text { Radiation } \end{aligned}$ | FMC/Ames, IA | 1971-1983 |  |  |  |

the long-term regional mean annual precipitation to the lø-year station mean. To investigate any potential differences in precipitation intensity characteristics, the lo-year station record was analyzed for the frequency and duration of storm intensities, and this information was compared to long-term intensity-duration-frequency statistics for selected U.S. Weather Bureau Stations within each region (USDC, 1955). The l-hour, 3-hour, 6-hour, and 24-hour rainfall intensities for storms with return periods of 2-years, 5-years, and lø-years, were estimated from the U.S. Weather Bureau Technical Paper No. 25 (USDC, 1955) for available stations within each region and compared to the corresponding intensities derived from the lø-year station record. Intensity adjustment factors were then calculated as the ratio of the long-term intensity to the lø-year record value for each duration-frequency combination (e.g., 6-hour, 5-year storm). The average intensity adjustment factor was compared to the volume adjustment factor to produce the values shown in Table 4.8. In general, greater weight was given to the intensity adjustment factor because of the greater impact of rainfall intensity on storm runoff, as long as the resulting annual volumes were within the range of mean annual precipitation characteristic of the region.

A lø-year time period was chosen for simulating pesticide runoff and concentrations simulation as a compromise between the length of time required to establish a stable frequency distribution and computer cost considerations. Hydrologic modeling analyses to establish the frequency of extreme events, on the order of $5 \emptyset$ or 100 -year flood flows, often involve extrapolation of frequencies developed from 30 to 50 years of simulation. If stochastic procedures are used, many løø-year sequences of stream flow may be employed. However, frequency analyzes of water quality conditions often focus on 2-year, 5-year, or lø-year events since it is usually uneconomic to design facilities or base water quality management decisions on more extreme events. A study by Hydrocomp (1975) showed that for urban nonpoint pollution problems, a 5-year simulation period provides a stable frequency curve when compared to curves developed from both longer and shorter time periods. Because of the highly dynamic and seasonal nature of pesticide runoff, especially for short-lived or non-persistent chemicals, a lø-year simulation period was selected. In conjunction with the procedures discussed above for adjusting the lo-year meteorologic data base to better reflect average long-term conditions, the $1 \varnothing$-year simulation period producing 3650 daily values of concentration and runoff loading provides a valid population for developing exceedance frequency curves.

In addition to area, land use, soil characteristics, and meteorologic conditions, information on drainage and channel characteristics are required for any watershed modeling study. When a model is applied to a specific watershed, the required data can be readily obtained from detailed topographic maps or field surveys. However, since our application watersheds did not have the same drainage area as our løøø sq. km representative watershed, and since channel characteristics will change with drainage area and regional characteristics (e.g., climate, soils), procedures were needed to define channel length, slope, and geometry for each representative watershed. Standard hydrology references (e.g., Linsley et al., 1975; Chow, 1964) and geomorphology texts (e.g., Leopold et al., 1964) site the following relationship between channel length and drainage area first developed by Hack (1957):

$$
\begin{gather*}
\mathrm{L}=1.4 \mathrm{~A}^{0.6}  \tag{4.1}\\
\text { where } \mathrm{L}=\text { main stem channel length, mi. } \\
\mathrm{A}=\text { drainage area, sq. mi. }
\end{gather*}
$$

Hack initially developed the relationship from stream characteristics in the Shenandoah Valley of Virginia and Maryland, and later checked it with data from the northeastern U.S., Arizona, and South Dakota. Although the exponent was slighty higher for some western streams and the coefficient varied between $1 . \emptyset$ and 2.5 for individual watersheds, the average of all the data closely followed Equation 4.l.

Gray (1961) developed an almost identical relationship from data on more than $6 \emptyset$ watersheds in the northcentral and northeastern U.S. ranging in size from less than one square kilometer to more than $5 \emptyset \emptyset \emptyset \mathrm{sq}$. km. His coefficient was the same as the 1.4 value in Equation 4.1 but his exponent was Ø. 568 instead of Ø.6. Gray also developed 95\% confidence limits for his regression equation which provided a standard error of estimate of $25 \%$. Thus, for a løøø sq. km drainage area the channel length could vary between 54 and 131 km within these confidence limits and have an average length of $8 \emptyset \mathrm{~km}$. ,

Our own independent checks of Equation 4.1 using data on streams in Ohio (Langbein, 1947) and the drainage characteristics of the HSPF application watersheds further support the relationship. Although there appears to be some variation in the exponent and coefficient for different geographical regions, the available data was not sufficient to justify the use of different values in each agricultural region.

Consequently, Eguation 4.1 was used to define the drainage characteristics of the representative watersheds in each region because of its general applicability to a broad range of watershed sizes and locations. For our løøø sq. km (386 sq. mi) representative watershed, Equation 4.1 predicts an $8 \varnothing$ km ( $5 \emptyset$ mi.) channel length. This total length was divided into five separate channel reaches, to be consistent with the number of reaches used in our application watershed simulations, and Equation 4.1 was then used to back-calculate the area tributary to each reach. Figure 4.11 is a general schematic of the configuration of the representative watershed, with five equal channel reaches and associated tributary areas used for all agricultural regions.

In addition to tributary area and length, channel characteristics such as slope, geometry, and roughness are needed for modeling instream flow, sediment, and chemical processes. Travel time and chemical processes for pesticides in streams are dependent on these channel characteristics, since they determine the volume, surface area and velocity of flows. Thus, the design of representative watersheds must incorporate typical channel geometries and hydraulic conditions. Since such characteristics vary with distance from the basin headwaters due to increases in discharges, relationships between position in the watershed and channel characteristics must be developed.

Leopold and Maddock (1953) were one of the first investigators to suggest that power-law relationships can be defined between stream discharge and channel geometry. As discharge increases at a given point along a stream, depth, width and velocity of the flow increase as a power function of discharge, with width typically increasing most rapidly and velocity increasing most slowly. Leopold and Maddock differentiated between such relationships at a fixed point along a stream varying probability of occurrence and variations in geometry with distance downstream as discharge increases (constant probability of occurrence). Numerous investigators (Wolman and Leopold, 1957; Lumb, 1973; Osterkamp and Hedman, 1982; Williams, 1978; Osterkamp, et al., 1983) have used this approach to investigate stream morphology in various parts of the U.S. Consequently, it is an appropriate mechanism for defining stream channel geometries for our representative watersheds.

Since geometry is dependent on discharge, a controlling discharge must be specified at each point of interest in the channel system. It has been adequately demonstrated that, for a given frequency of occurrence, discharge is a power function of drainage area. Such functions can be defined for hydrologically homogeneous areas through regression analyses, as has been done by the U.S. Geological Survey, state


Figure 4.11 Schematic of representative watershed drainage and reach configuration.
geological surveys, and other agencies for most states and river basins. Hydraulic geometry in most streams changes abruptly at the top of channel banks. Flows in excess of the bankfull discharge begin to inundate the floodplain and occupy a much greater position of the floodplain. Consequently, the bankfull discharge is defined as the controlling discharge for the representative watersheds. While the hydrologic return period for bankfull discharges in streams is typically between 1 year and 4 years, a return period of 1.5 is a reasonable average (Leopold, et al., 1964). For convenience, a 2 year return period flood is used as the controlling discharge in this study without significant loss of accuracy.

Using the above concepts as a basis, the following procedure was used to calculate channel characteristics for each of the representative watersheds.

1. Determine the center point of each channel reach, defined as the mid-point of the channel reach length. Determine the drainage area (A ) at this point using Equation 4.l.
2. Compute the two year flood discharge from the regional equation for discharge versus drainage area:

$$
Q_{2}=a A_{d}{ }^{m}
$$

3. Compute channel geometry from bankfull discharge using the power functions for the region:

$$
\begin{array}{ll}
\text { top width } & W_{T}=b_{2} Q_{p}^{n} \\
\text { bottom width } & W_{B}=c_{2} Q_{q} \\
\text { depth } & D=d_{2} Q_{r} \\
\text { cross-sectional area } & A_{C}=e_{2} \tag{4.6}
\end{array}
$$

4. Compute average velocity in the reach from crosssectional area and discharge:

$$
\begin{equation*}
V=Q_{2} / A_{C}=\mathrm{f}_{2} \mathrm{Q}_{2}^{\mathrm{S}} \tag{4.7}
\end{equation*}
$$

5. Estimate Manning's $n$ (roughness) from photographs and field investigations in the application watersheds.
6. Calculate average channel slope by assuming normal depth and solving the Manning equation for slope.

The values for the coefficients (a-e) and exponents (m-r) were developed from regional regression analyses performed by others in each of the regions. Variations in geometry with
distance downstream for a given probability flood were used. The principle sources for these values are given along with the selected values in Table 4.9. Where no adequate definitions of particular exponents and coefficients for a region were available, channel geometries in the HSPF application watersheds were used as a basis for estimating reasonable values. The resulting power functions were tested by applying them to the application watershed in each region and comparing results with actual channel characteristics.

Comparisons were also made in each region with watersheds of comparable size to our representative watershed based on information/data obtained from the U.S. Geological Survey Streamflow/Basin Characteristics File (Dempster, 1983), which is part of the USGS WATSTORE System (USGS, 1981). Since channel sediment scour and deposition parameters were calibrated on each application watershed and since these processes are a function of channel slope, slope values calculated by the above procedures were adjusted, if necessary, to better reflect the range of channel slopes observed in the region and the application watersheds. Only the Eastern and Western Cornbelt regions required slight adjustments to the calculated slopes in order to agree with regional values and preclude excessive channel scour on the representative watershed.

The results of applying the regional power functions and subsequent adjustments are summarized in Table 4.10, which presents the channel characteristics of the most downstream reach in each region. The variations in channel characteristics with region is apparent.

### 4.3.6 Agricultural Practices for Representative Watersheds

In order to properly represent the complex interactions of climatic conditions and agricultural activities that produce and affect pesticide runoff, a detailed characterization of agricultural practices was developed for each agricultural production region. This required primarily a definition of the timing, type, and frequency of tillage practices and normal planting and harvesting periods for each crop and region. This information was then translated into model parameters in $H S P F$ for simulation of pesticide runoff from our representative watersheds.

Agricultural and tillage practices vary widely among different regions and within a region, based on local climate, soils, topography, and crops. Selection of a specific tillage practice or strategy by a farmer is a decision that considers many additional factors such as production costs, pesticide

TABLE 4.9 SUMMARY OF POWER FUNCTIONS FOR STREAM CHARACTERISTICS

| Region | a | m | b | n | c | P | d | q | e | $r$ | f | 5 | Source |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Southeast | 120 | 0.65 | 8.50 | 0.42 | 4.40 | 0.42 | 0.30 | 0.42 | 1.94 | 0.85 | 0.52 | 0.15 | Lumb (1973) |
| Mississippi Delta | 84.1 | 0.80 | 2.23 | 0.49 | 0.63 | 0.49 | 0.93 | 0.36 | 1.33 | 0.85 | 0.76 | 0.15 | Williams (1978) <br> Oster Kamp et al. (1983) |
| Eastern Cornbelt | 135 | 0.65 | 2.10 | 0.53 | 6.30 | 0.53 | 0.46 | 0.34 | 1.92 | 0.87 | 0.52 | 0.13 | Oster Kamp et al. (1983) |
| Western Cornbelt | 241 | 0.54 | 6.00 | 0.40 | 4.45 | 0.40 | 0.35 | 0.34 | 1.83 | 0.74 | 0.55 | 0.26 | Hedman et al. (1974) <br> Oster Kamp and Hedman 1982 |

TABLE 4.10 SUMMARY OF COMPUTED CHANNEL CHARACTERISTICS FOR THE DOWNSTREAM MOST REACH IN EACH REGION

|  | Top <br> Width | Bottom <br> Width | Depth | Channel <br> Channel <br> Slope | Channel <br> Region | Floodplain <br> "n" |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| Southeast | 316 | 164 | 11. | .0777 | .090 | .150 |
| Mississippi <br> Delta | 187 | 53 | 24. | .0208 | .042 | .200 |
| Eastern <br> Cornbelt | 189 | 82 | 8.8 | .0700 | .045 | .100 |
| Western <br> Cornbelt | 188 | 139 | 6.5 | .0436 | .035 | .060 |
| Central <br> Plains |  |  | (Incomplete) |  |  |  |

and fertilizer use, expected pest problems, crop rotations, available machinery, etc. (Duffy and Hanthorn, 1984). Available tillage methods cover a broad spectrum of practices, but they have been generally grouped in terms of "conservation" versus "conventional" tillage practices (Crosson, 1981). The Resource Conservation Glossary (Soil Conservation Society of America, 1982) defines conventional tillage as "the combined primary and secondary tillage operations performed in preparing a seedbed for a given crop grown in a given geographical area"; conservation tillage then is "any tillage system that reduces loss of soil or water relative to conventional tillage; often a form of noninversion tillage that retains protective amounts of residue mulch on the surface."

Using slightly different terminology, Duffy and Hanthorn (1984) describe available systems as no-till, reduced-till, and conventional-till. They further note that "delineation of tillage strategies can be thought of as a continuum based on the amount of plant residue left on the field and the extent of soil disturbance. No-till and conventional-till strategies comprise the extremes of the continuum, while reduced-till includes the range of practices in between." Reduced-till and no-till are forms of conservation tillage which is often functionally described as everything other than conventional tillage, with the primary differences of less soil disturbance and more plant residues left on the land surface. Table 4.11 from Crosson (1981) summarizes the key distinguishing characteristics of the two tillage systems.

After reviewing the agricultural literature on tillage systems in light of the objectives of this study, conventional tillage was selected as the standard agricultural practice included in each representative watershed simulation. This decision was based on the following:
a. Conventional tillage is still the predominant practice in most regions of the country, although its use has been steadily declining from 82.3\% of cropland areas in 1973 to $68.0 \%$ in 1981 (Christensen and Magleby, 1983).
b. For selected regions, the extent of conventional tillage use in 1981 was as follows (Christensen and Magleby, 1983).
Southeast 52\%
Delta States 82\%
Cornbelt 62\%
Northern Plains 67\%
Southern Plains 82\%

TABLE 4.11 DISTINGUISHING CHARACTERISTICS OF CONSERVATION TILLAGE AND CONVENTIONAL TILLAGE (Source: Crosson, 1981)

| Characteristic | Tillage system |  |
| :---: | :---: | :---: |
|  | Conservation | Conventional |
| Tillage instrument | Not the moldboard plow | Moldboard plow |
| Crop residue on soil and surface | Enough to reduce erosion significantly | Little or none |
| Weed control | Primarily herbicides, but may also cultivate | Mechanical cultivation more important than with conservation tillage, but herbicides typically used also |

c. Conventional tillage will generally result in higher runoff, erosion, and pesticide losses, and thus provide a reasonable 'worst-case' or conservative exposure assessment.
d. Many soils and regions are not well suited for conservation tillage; thus conventional tillage practices will continue to dominate in many if not most regions of the country.
e. Project resource and time constraints precluded simulation of more than one practice in each representative watershed; future studies could use the conventional practice results in this study as a 'base' condition against which the impact of best management practices, such as conservation tillage, could be compared.

Although a wealth of information exists on the practice, benefits, and economics of conservation tillage, there appears to be no central source of information to define the specific components and timing of conventional tillage practices in each region. Consequently, information from a variety of sources was integrated in order to develop appropriate regional definitions. A study of the impact of best management practices on HSPF parameters included a general definition of conventional practices for Iowa (Donigian et al., 1983). Moldenhauer et al. (1983) discuss conservation tillage practices on a regional basis and make comparisons to conventional methods. In discussing economic returns for corn and soybean tillage practices, Duffy and Hawthorn, (l984) note that the higher clay content of southern soils results in greater use of chisel or disc plows than in the Midwest, and that weed problems are usually more severe requiring more frequent cultivation.

In addition to these general references, site-specific information was available for each HSPF application watershed in each region. The USDA Crop Enterprise Budgets (USDA, l981), provided information on the usage of various farm implements for each major crop for multiple sub-regions within each state. For example, from these budgets we could determine how often and in which months farmers would likely use moldboard plows, chisel plows, row cultivators, planters, etc. throughout our agricultural regions. This detailed information helped to confirm and generalize the information developed from the other sources noted above.

Table 4.12 lists the primary characteristics of the conventional agricultural practices assumed for all crops on all our representative watersheds, except for winter wheat in the Central Plains which follows a different sequence and
timing of operations. The timing of activities for each crop in each region is keyed to the normal planting and harvesting dates as defined in USDA Agricultural Handbook No. 283, "Usual Planting and Harvesting Dates" (USDA, 1972). The USDA crop budgets were used to define plowing and cultivation times and to confirm the specific months for planting and harvesting. Table 4.13 list the target dates for the various activities for each crop and region; the actual dates were adjusted each year to preclude chemical applications and tillage on days when it rains and on the day after a major rainfall event (i.e. greater than 1.5 cm ) to allow soil drainage and farmer access to the fields.

### 4.4 PESTICIDE PARAMETERS AND ASSUMPTIONS

Modeling pesticide fate and transport in watersheds involves modeling two distinct phases - the land/soil phase and the channel phase - and then integrating these two phases to track the pesticide through the system and produce instream concentrations at the watershed outlet. This section discusses the key pesticide parameters and assumptions used in simulating both the land/soil and channel phases of pesticide fate on the representative watersheds with HSPF. Key aspects

TABLE 4.12 PRIMARY CHARACTERISTICS OF "CONVENTIONAL" AGRICULTURAL PRACTICES ASSUMED IN THIS STUDY*

Primary tillage in spring four to six weeks prior to planting.

Either moldboard plow and/or multiple discing used for primary tillage, resulting in all residue covered or buried.

Discing and seedbed preparation prior to planting.
Surface application of pesticide at planting time.
One to three mechanical cultivations for weed control beginning three to eight weeks after planting.

Discing in fall after harvesting, with plant residues removed or substantially reduced.

* Winter wheat in the Central Plains follows a different sequence and timing of operations.

TABLE 4.13 ANNUAL TARGET DATES FOR AGRICULTURAL ACTIVITIES

|  | Southeast |  | $\begin{gathered} \text { Missiasippi } \\ \text { Delta } \end{gathered}$ |  | Eastern Cornbelt |  | Western Cornbelt |  | Central Plains |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Corn | Beans | Cotton | Beans | Corn | Beans | Corn | Beans | Wheat | Sorghum |
| Primary Tillage | Mar 10 | Apr 14 | Mar 1 | Mar 30 | Apr 15 | Apr 25 | Apr 1 | Apr 15 | - | Apr 1 |
| Seedbed Preparation, Chemical Application, Planting | $\lambda \mathrm{pr} 10$ | May 14 | Apr 15 | May 10 | May 1 | May 15 | May 1 | May 21 | Sept 15 | May 10 |
| Cultivation | May 1 | Juna 7 | May 7 | June 7 |  | July 15 | June 1 | June 21 | - | June 15 |
| Cultivation | May 20 | June 30 | June 7 | July 15 |  |  | July 1 | July 21 | - | July 15 |
| Cultivation | - | - | July 15 | - |  |  | - | - | - |  |
| Harvest | Oct 20 | Nov 5 | Sept 20 | Oct 5 | Oct 10 | Sept 30 | Oct 15 | Oct 1 | June 15 | Sept 21 |
| Fall discing | Nov 1 | Nov 15 | Oct 15 | Oct 30 | Nov 10 | Nov 1 | Nov 15 | Nov 1 |  | Oct 15 |

of the pesticide simulation involve the specific HSPF pesticide parameters chosen for the methodology, sensitivity analyses, pesticide application procedures and assumptions, and specification of initial soil and stream conditions for persistent compounds. Each of these are discussed below.

### 4.4.1 HSPF Pesticide and Methodology Parameters

The HSPF PERLND (PEST) and RCHRES (GQUAL) modules were used in simulating the land/soil and channel phases, respectively, of pesticide fate and transport on the representative watersheds. Table 4.14 lists all the primary land and stream pesticide parameters used in HSPF, along with a short description and assumptions employed in our methodology. Thirty-five individual parameters are listed in Table 4.14; to perform sensitivity analyses on each parameter at three individual values for two crops and five representative watersheds would require $105 \bar{\emptyset}$ separate $H S P \overline{1 \emptyset}-y e a r$ simulation runs. This was well beyond available computing resources. Moreover, a methodology that requires the evaluation of 35 separate parameters would demand greater user effort than is appropriate for a screening-level analysis.

Consequently, considering the need for simple use procedures and taking advantage of the interrelationships between and among parameters, the methodology was designed to require only three key parameters - Koc, ks, kw - representing the soil/sediment adsorption characteristics, soil/sediment decay rate, and solution decay rate, respectively. All parameters were either based on the values of one of the three methodology parameters, were derived from past studies, or

## TABLE 4.14 HSPF PESTICIDE PARAMETERS AND METHODOLOGY ASSUMPTIONS

| HSPF Parameter Name | Description | Assumptions |
| :---: | :---: | :---: |
| Land (PERLND PEST) Parameters |  |  |
| CMAX: | maximum solubility in water | related to Kос |
| XFIX: | maximun permanently fixed soil concentration for each soil layer | equal to zero |
| *K1: | partition coefficient for each soil layer | related to Koc and 80C |
| NI: | adsorption exponent for each soil layer | equal to 1.0 |
| *SDGCON: | surface degradation rate | sensitivity test variable |
| UDGCON: | upper layer degradation rate | equal to SDGCON |
| LDGCON: | lower layer degradation rate | equal to SDGCON |
| ADGCON: | groundwater degradation rate | equal to SDGCON |
| Instream (RCHRES GQUAL) Parameters |  |  |
| *FSTDEC: | solution decay rate | sensitivity test variable |
| THFST: | temperature adjustment coefficient for solution decay rate | set to HSPF default value 1.072 |
| ADDCPM (1): | decay rate for chemical absorbed to | equal to SDGCON |
| ADDCPM (2): | temperature adjustment coefficient for <br> ADDCPM (1) | set to HSPF default value 1.072 |
| $\operatorname{ADDCPM}$ (3): | decay rate for chemical absorbed to bed sediment | equal to SDGCON |
| ADDCPM (4) | ```temperature adjustment coefficient for ADDCPM (3)``` | set to HSPF default value 1.072 |
| *ADPM (1-3, 1): | partition coef on suspended sand, silt, and clay | related to KOC and 80 C |
| *ADPM (4-6, 1) : | partition coef on bed sand, silt and clay | related to Koc and |
| ADPM (1-3, 2): | adsorption/desorption exchange rate on suspended sand, silt, and clay | equal to 36.0 to approximante equilibrium sorption |
| ADPM (4-6, 2) | adsorption/desorption exchange rate on bed sand, silt and clay | equal to .93 based on field study (Donigian et al. (1983)) |

were amenable to the use of a default value, such as the standard decay rate temperature correction coefficient of 1.072 .

Koc, the organic carbon partition coefficient, is used to calculate the soil-chemical partition coefficient, Kd, based on the $\%$ organic carbon as follows:

$$
\begin{equation*}
\mathrm{Kd}=\operatorname{Koc} \frac{* \mathrm{OC}}{1 \emptyset \emptyset} \tag{4.8}
\end{equation*}
$$

$$
\text { where } \begin{aligned}
K d= & \text { Soil-chemical partition coefficient, } \\
& \mathrm{ml} / \mathrm{g} \\
\text { Koc }= & \text { Organic carbon partition coefficient, } \\
& \text { ml/g-organic carbon } \\
O C= & \text { percent organic carbon }
\end{aligned}
$$

A variety of investigations have shown that $K o c$ and OC can be used to characterize the sorption process for hydrophobic organic compounds in both soil and aqueous systems (Hamaker and Thompson, (l972), Rao and Davidson, 1980; Karickhoff et al., 1979; Karickhoff, l981; Rao et al., l984). Consequently, Koc is used in this study with the OC values shown in Tables 4.6 and 4.7 to calculate partition coefficients for the various soil layers and the sand, silt, and clay fractions of the stream suspended and bed sediments. Thus, each value of Koc specifies $1 \varnothing$ partition coefficients: four for the soil profile, three for the suspended sediments (i.e. sand, silt, clay) and three for the bed sediments. Four values of Koc 50, 500, 1500, and 50ø0 - were used in the sensitivity analyses to cover the primary range of values for pesticides where concentrations in surface water may be problematic. Tables 4.15 through 4.19 show the specific partition coefficients used in the sensitivity analyses from each Koc value for each agricultural region.

Koc was also used to determine the appropriate water solubility (i.e. CMAX in Table 4.16) for each sensitivity run based on the following relationship developed by Kenaga and Goring (1980):

$$
\begin{equation*}
\log \mathrm{Koc}=-.55 \log s+3.64 \tag{4.9}
\end{equation*}
$$

where $\mathrm{S}=$ water solubility, mg/l
Pesticide runoff and stream concentrations are generally insensitive to specific compound solubility limits since under normal agricultural usage concentrations rarely, if ever, approach the solubility of the compound. Equation 4.9 was used to insure consistent Koc and solubility limits in our

TABLE 4.15 CALCULATION OF PARTITION COEFFICIENTS (Kd) FROM Koc and \% OC FOR THE SOUTHEAST REGION

| Soil | 80C/100. | Koc |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 50 | 500 | 1500 | $59 \square 0$ |
| Surface Layer | . 01 | 0.5 | $5 . \varnothing$ | 15. | 50. |
| Upper Layer | . 01 | $\emptyset .5$ | 5.0 | 15. | 50. |
| Lower Layer | . $0 \square 5$ | 0.25 | 2.5 | 7.5 | 25. |
| Ground-water Layer | . øøø 5 | $\emptyset .025$ | $\emptyset .25$ | Ø. 75 | 2.5 |
| Stream <br> (Suspended and Bed Sediment) |  |  |  |  |  |
| Sand | . 005 | 0.25 | 2.5 | 7.5 | 25. |
| silt | . $\varnothing 2 \emptyset$ | 1.0 | 10.0 | 30.0 | 100. |
| Clay | . $\varnothing 20$ | 1.0 | 10.0 | 30.0 | $1 \varnothing \emptyset$. |

simulations. Thus for the four Koc values, solubilities of 3382., 51., 6.97 , and $\varnothing .87 \mathrm{mg} / \mathrm{l}$ were defined by Equation 4.9 .

The soil and sediment decay rate, ks is the second key methodology parameter. Although HS $\overline{\mathrm{PF}}$ allows the use of different chemical decay rates for each soil layer, suspended sediment, and bed sediment, we used the value of ks for decay rates in all soil layers and stream sediments. For the soil environment, decay rates for many compounds would likely decrease with depth since surface decay processes, such as volatilization and photolysis, would become less significant at lower soil depths. However, if subsurface processes, such as microbial degradation and hydrolysis, are the primary attenuation mechanisms for a compound, the rates would initially increase with depth. Relating soil pesticide rates to stream suspended and bed sediment pesticide decay rates would also depend on the primary attenuation mechanisms of a pesticide and the relative occurrence of these mechanisms in
each environment. Thus, defining a specific change in decay rates with soil layers, or between soil and stream sediments, would be highly compound specific. To maintain the simplicity of using the methodology, to minimize the required simulation runs, and lacking any evidence of a general, well-accepted relationship, the ks value was used to define all six soil/sediment decay rates (i.e. four soil layers, suspended sediment, bed sediment). The three ks values of $\varnothing .1, \emptyset . \emptyset 1$, and Ø. Øøl per day, with associated half lives of 6.9, 69., and 693. days, were selected for the sensitivity analysis to cover the range of decay rates demonstrated by most agricultural pesticides.

The pesticide solution decay rate, $k w$, is the final methodology parameter representing the net effect of all instream attenuation mechanisms on the solution phase. Although HSPF allows the simulation of the individual stream decay processes of hydrolysis, oxidation, photolysis,

TABLE 4.16 CALCULATION OF PARTITION COEFFICIENTS (Kd) FROM Koc and \% OC FOR THE MISSISSIPPI DELTA REGION

| Soil | \%OC/100. | Koc |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 50 | 500 | 1500 | $50 \square 0$ |
| Surface Layer | . 015 | . 75 | 7.5 | 22.5 | 75. |
| Upper Layer | . 015 | . 75 | 7.5 | 22.5 | 75. |
| Lower Layer | . 0075 | . 375 | 3.75 | 11.25 | 37.5 |
| Ground-water Layer. | . $0 \boxed{1075}$ | . 0375 | . 375 | 1.125 | 3.75 |
| Stream <br> (Suspended and Bed Sediment) |  |  |  |  |  |
| Sand | . $\varnothing 05$ | . 25 | 2.5 | 7. 5 | 25. |
| Silt | . $\varnothing 2 \varnothing$ | 1.0 | 10.0 | 30.0 | $1 \varnothing \varnothing$. |
| Clay | . $02 \varnothing$ | 1.0 | 10.0 | 30.0 | 100. |

TABLE 4.17 CALCULATION OF PARTITION COEPFICIENTS (Kd) EROM KOC and \% OC FOR THE EASTERN CORNBELT REGION

| Soil | \%OC/100 | Koc |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 50 | $50 \emptyset$ | $150 \emptyset$ | 5 5øøワ |
| Surface Layer | .02 | $1 . \emptyset$ | 10.0 | 30.0 | $1 \emptyset \emptyset$. |
| Upper Layer | - 02 | 1.0 | 10.0 | 30.0 | $1 \varnothing \emptyset$. |
| Lower Layer | . $\varnothing 1$ | 0.5 | 5.0 | 15.0 | 50. |
| Ground-water Layer | . Øロ1 | .05 | $\emptyset .5$ | 1.5 | 5.0 |
| Stream (Suspended and Bed Sediment) |  |  |  |  |  |
| Sand | . $\emptyset 05$ | . 25 | 2.5 | 7.5 | 25. |
| Silt | . 025 | 1.25 | 12.5 | 37.5 | 125. |
| Clay | .025 | 1. 25 | 12.5 | 37.5 | 125. |

volatilization, and biodegradation, a lumped first-order decay mechanism was used to provide a more generally applicable approach. The importance of any specific combination of processes would be highly compound specific, and rate constants for individual processes may not be generally available to the methodology user. As for the ks values, the three kw values of $1 . \varnothing, \varnothing .5$, and $\varnothing . \emptyset 5$ per day were selected to cover the primary range of decay rates of concern. Also, the compound half lives associated with each rate - 0.7 , 1.4, and 14 days.respectively - were designed with respect to the mean flow-through times of two to four days on our representative watersheds to span the range of non-persistent to persistent chemicals experiencing solution decay. Thus, a solution decay rate of Ø.ø5, with a half life of 14 days, would not undergo significant instream decay because the flow time instream is so short. Slower solution decay rates would produce concentration frequency curves similar to the curves with the 0.05 kw rate.

A few remaining parameters in Table 4.14 are not directly calculated from Koc, ks, or kw. Two soil adsorption parameters, XFIX and Nl, are respectively the amount of pesticide permanently adsorbed to the soil and the adsorption exponent in the Freundlich equation used in HSPF. Values other than $\varnothing . \emptyset$ and $1 . \emptyset$ for $X F I X$ and $N 1$, respectively, would violate the assumption of reversible linear sorption, and would be compound specific. Also, the linear relationship between pesticide loading and concentrations, and pesticide application rate would not exist for other values of XFIX and Nl. In any case, there is little evidence to justify using other values of these parameters, and Rao and Davidson (1980) have shown that the use of a linear isotherm (i.e. Nl=l. 0 ) is quite reasonable for agricultural systems.

The temperature adjustment coefficient for the instream decay rates (i.e. solution, suspended, bed) adjusts for stream temperatures other than $2 \varnothing$ degrees $C$. The value of 1.072

TABLE 4.l8 CALCULATION OF PARTITION COEFFICIENTS (Kd) FROM Koc AND \% OC FOR THE WESTERN CORNBELT REGION

| Soil \% | \%OC/100. | KOC |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 50 | 500 | 1500 | 50ロロ |
| Surface Layer | .025 | 1. 25 | 12.5 | 37.5 | 125.0 |
| Upper Layer | . 025 | 1.25 | 12.5 | 37.5 | 125.0 |
| Lower Layer | .0125 | . 625 | 6.25 | 18.75 | 62.5 |
| Ground-water Layer | . 00125 | .0625 | . 625 | 1.875 | 6.25 |
| Stream (Suspended and Bed Sediment) |  |  |  |  |  |
| Sand | .01 | 0.5 | 5.0 | 15.9 | $50 . \emptyset$ |
| Silt | .03 | 1.5 | 15.0 | 45.0 | 150.0 |
| Clay | .06 | 3.0 | 30.0 | 90.0 | $3 \varnothing \square . \emptyset$ |

TABLE 4.19 CALCULATION OF PARTITION COEFFICIENTS (Kd) FROM KOC AND \% OC FOR THE CENTRAL PLAINS REGION

| Soil | \%OC/100. | KOC |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 50 | $50 \square$ | 1500 | 5000 |
| Surface Layer | . 82 | 1.0 | 10.0 | 30.0 | 100.0 |
| Upper Layer | . 82 | 1.0 | $1 \varnothing .0$ | 30.0 | $1 \varnothing \varnothing . \varnothing$ |
| Jower Layer | . 01 | 0.5 | 5.0 | 15.0 | 50.0 |
| Ground-water <br> Layer | . $0 \square 1$ | .05 | Ø. 5 | 1.5 | 5.0 |
| Stream (Suspended and Bed Sediment) |  |  |  |  |  |
| Sand | . 005 | 0.25 | 2.5 | 7.5 | 25.0 |
| Silt | . 025 | 1.25 | 12.5 | 37.5 | 125.0 |
| Clay | . $\quad 025$ | 1.25 | 12.5 | 37.5 | 125.0 |

allows for a two-fold change in the decay rate for each 10 degree change in temperature. This value is the default value in HSPF and has also been recommended for screening analyses by Mills et al. (1982).

The final parameters in Table 4.14 not directly calculated from Koc, ks or $k w$ are the exchange (or transfer) rates between the solution (dissolved) chemical and the suspended and bed sediments. These rates are essentially first-order mass transfer coefficients between the solution chemical mass and the mass of chemical sorbed to the suspended sediments and the bed sediments in each reach of the channel system. As such they represent a lumped parameter approach to very complex and poorly understood processes involving the integrated effects of sorption, turbulence, sediment scour/deposition, and bed chemical diffusion/exchange. The value of 36.0 per day for the solution/suspended exchange rate
is based on HSPF application guidelines (Donigian et al., 1984) and limited field experience for a small watershed in Iowa (Donigian et al., 1983). The value is set to approximate instantaneous equilibrium in each simulation time interval between the dissolved chemical and the chemical sorbed to the suspended sediments. The assumption of instantaneous equilibrium is reasonable for this exchange process since it occurs primarily during and immediately following storm events when significant chemical and suspended sediment concentrations exist in the stream channel. Also, turbulent exchange and mixing processes are at their peak during these periods.

However, the solution-bed exchange process is a much slower mechanism and instantaneous equilibrium is not likely to occur. The value of 0.03 per day for the bed exchange rate was determined by calibration in the Iowa field study mentioned above. Theoretical considerations suggest that this value is near the maximum estimated rate based on our understanding of the various chemical and physical exchange processes it attempts to represent. Sensitivity analyses where this rate was decreased from Ø. Ø3 to $\varnothing . \emptyset \emptyset \emptyset \emptyset 1 ~ p e r ~ d a y ~$ (i.e. more than three orders of magnitude) show no significant impact on solution or suspended chemical concentrations for mean annual (Mulkey et al., 1984) or peak daily values; bed concentrations generally decreased, however, by one to two orders of magnitude. Also, the value of $0 . \varnothing 3$ was used in successfully simulating alachlor concentrations in the lowa River when compared to limited field data (Mulkey and Donigian, 1984). Because of the complexity of the bed-chemical exchange process, the lack of testing and field data, and the lack of a defensible theory for adjusting the exchange rate as a function of chemical properties, the field calibrated value of $\varnothing .03$ was used for all simulations in this study. This value is most valid for the Western Cornbelt region, and its extrapolation to other regions is largely unknown. However, any uncertainty in this parameter will have a significant impact only on the predicted bed chemical concentrations resulting in a conservative (or high) estimate. As a result, the bed chemical concentrations predicted by the STREAM procedures should be used cautiously considering potential errors of one to two orders of magnitude.
4.4.2 Pesticide Application Procedures and Assumptions

The timing and method of agricultural chemical applications can have a determining impact on the extent of chemical runoff and resulting stream concentrations. In fact, for relatively non-persistent pesticides, various studies have shown that the first few runoff-producing storm events following a field
application consistently produce the greatest pesticide runoff and concentrations (Johnson and Baker, 1982; Smith et al., 1978; Ellis et al., 1977; Baker, 1983). Consequently the highest pesticide concentrations occur during the first two to three months after application, and for most parts of the country this occurs in the spring and early sumner for conventional spring-planted crops. In most agricultural watersheds, many different farmers will be applying chemicals at different times and at different rates. Since it would not be feasible to model each farmer's field individually in a complex multi-land use watershed of løøø sq. km, and since a single simultaneous application by all farmers would be unrealistic (and possibly produce a worst-case scenario for pesticide runoff from the first storm event), procedures and assumptions for pesticide application were developed in order to provide a realistic compromise between the two extreme approaches described above.

The key assumptions used in this study for specifying pesticide applications are as follows:

1. A unit application rate of $1 . \varnothing \mathrm{kg} / \mathrm{ha}$ to all crops
2. A single surface application at or near planting time
3. Multiple farmer applications and timing approximated by three separate applications of $\varnothing .25$, 9.50 , and Ø. $25 \mathrm{~kg} / \mathrm{ha}$, respectively within a $1 \not \equiv-15$ day planting "wịndow"
4. No applications on the day of, or day after, a storm event

A unit application rate of $1 . \varnothing \mathrm{kg} / \mathrm{ha}$ was used in all simulations in order to provide the methodology user the flexibility of estimating concentrations and loadings for any application. All concentrations and loadings are linear functions of the application rate, as established in a previous study (Dean et al., l984a). Thus, for a $5.0 \mathrm{~kg} / \mathrm{ha}$ rate, the user simply multiplies the values from the frequency curves in Appendices A through E by 5.0 to obtain the correct concentrations and loadings.

A single surface application at or near planting time was assumed for two reasons: (l) project resource limitations precluded the evaluation of more than one application method, and (2) surface applications will usually produce the highest pesticide runoff and concentrations and thus provide a conservative approach for screening purposes. Since the application occurs at or near planting time, the methodology is appropriate for pre-plant, planting, and pre-emergence chemicals. Although these application procedures (i.e.,
timing and method) are most common for herbicides, there are no specific assumptions that limit the methodology to only herbicidal compounds.

The procedures for selecting specific application dates are based on pesticide modeling studies using HSPF on both a small watershed (Donigian et al., 1983) and a large river basin in Iowa (Imhoff et al., 1983; Mulkey and Donigian, 1984). The single application of l. $0 \mathrm{~kg} / \mathrm{ha}$ is actually represented by three separate applications of $\varnothing .25, \varnothing .5 \varnothing$, and $\varnothing .25 \mathrm{~kg} / \mathrm{ha}$ to approximate the variable timing of chemical applications by many individual farmers within a watershed. The three applications represent an approximate normal distribution about the "target" planting date, as defined by IJSDA Agricultural Handbook No. 283, "Usual Planting and Harvesting Dates" (USDA, 1972) for each crop in each agricultural region. The $0.5 \emptyset \mathrm{~kg} / \mathrm{ha}$ application was defined to occur on the planting day, with the $0.25 \mathrm{~kg} / \mathrm{ha}$ applications occuring about five days before and after. The final choice of each application date was made by analyzing this target window for each year of the 10 -year precipitation record and adjusting the selected dates to preclude applications during, or the day following, a significant storm event (i.e. greater than l. $\quad$ to 2. 0 cm ). These adjustments reflect the assumptions that (1) most farmers will not apply pesticides during a storm or if a storm is predicted for that day, and (2) traction and/or access to the field may be difficult or impossible on the day after a major storm. No attempt was made to prevent an application on the day before an event because many compounds require moisture for efficacy, and farmers may not disrupt their planned applications based on a future rainfall forecast.

In summary, the assumptions regarding chemical application rate, timing, and method were designed to be as realistic as possible within the limitations of the model and project resources. Since HSPF can be used to represent a variety of application methods (e.g., foliar application, soil incorporation) additional simulation runs with chemicalspecific parameters can be made for compounds for which the above application assumptions are inappropriate.

### 4.4.3 Estimation of Initial Conditions for Persistent Pesticides

For agricultural chemicals that are persistent in the environment and thus demonstrate soil or sediment decay rates (i.e., ks) of about $\varnothing . \emptyset l$ per day or less (i.e., half lives of 69 days or greater) annual applications will lead to a build-up of chemical residues in the soil. The compound
decays at such a slow rate that a significant amount is still present in the soil at the time of application the following year. If the farmer continues to apply the pesticides each year, after many years the residue in the soil prior to each application will vary about a steady-state value that depends primarily on the chemical decay rate. The year-to-year variations will depend on climatic conditions and the resulting variation in pesticide runoff. After the pesticide runoff enters the stream system, it interacts with the stream bed through sorption onto bed sediments, scour and deposition of sediments with adsorbed pesticide, and other exchange processes. Similar to the soil system, persistent chemicals will begin to accumulate in the bed sediments and, with annual pesticide applications and runoff, bed concentrations will increase and demonstrate a great deal of variation about a mean steady-state value. The relative variation in bed concentrations will be significantly larger than the variation in soil residues because the bed concentrations depend on both a variable annual loading from pesticide runoff and highly variable flow rates affecting the bed exchange processes.

In order to represent pesticide runoff and stream concentrations as a function of chemical characteristics, it was necessary to estimate mean steady-state pesticide soil residues and bed concentrations for the ks rates of $\emptyset .01$ and Ø. Øøl per day used in our methodology. These mean values were then used as the initial conditions at the beginning of our lø-year simulation runs in order to provide a stable representation of pesticide behavior without the distorting impact of a 'build-up' period. For a ks value of $\quad 0.1$ per day, this procedure was not necessary because the pesticide decays to negligible values in both the soil and bed sediments prior to the next annual application.

For the soil residues, the specific initial conditions required are the mass of pesticide per unit area (i.e., kg/ha) in each of the surface, upper, lower, and ground-water soil. layers on January'l, resulting from annual applications of l.ø $\mathrm{kg} / \mathrm{ha}$ at planting time. The following equation was used to estimate the total steady-state residue in the soil prior to each annual application:

$$
\operatorname{Pss}=A(1-R) \cdot \frac{e^{-365 k s}}{1-e^{-365 k s}}
$$

where Pss = Steady-state pesticide residue, $\mathrm{kg} / \mathrm{ha}$

$$
A=\text { Annual application, } \mathrm{kg} / \mathrm{ha}
$$

```
R = Annual pesticide runoff loss as fraction of application
ks = Soil decay rate, per day
```

Since annual runoff losses are usually in the range of 1.0 to $5.0 \%$ of the application, an average of $2.5 \%$ was assumed for initial estimates. In any case, the amount lost by runoff is small compared to degradation and attenuation processes and could be ignored without significant impact. The exponential term in Equation $4.1 \varnothing$ is the sum of a geometrical progression with the annual variation defined by the first-order (i.e., exponential) decay (C.R.C., 1959). This approach has been used in a number of studies and investigations to represent the build-up of pesticide residues in soils (Hydrocomp, 1979; Hamaker, 1966; Hill et al., 1955).

The residue values calculated by Equation $4.1 \varnothing$ were increased to account for the decay occuring between planting and January l, by using the ks value and the appropriate time span for each crop in each region. This was necessary because all lø-year simulation runs began in January while planting was usually in April or May.

The distribution of the total pesticide residue among the various soil layers was initially defined by using the LEACH Manual (Dean et al., 1984a) to estimate the \% of application reaching the lower and ground-water zones as a function of Koc and ks. Remaining residues for the surface and upper zones were estimated from past experience with the leaching functions in HSPF. Both the total year-end residue and the distribution among soil layers predicted by the model was checked and compared with initial estimates to insure consistency and a stable representation.

Unfortunately, for initial bed concentrations simple analytical methods could not be found or developed that would reliably predict mean steady-state concentrations of pesticide on the sand, silt, and clay particles in the stream bed. These concentrations depend not only on the pesticide runoff from each crop, but also the specific Koc and ks values, the bed sediment composition, the organic carbon content of the bed sediment size fractions, and the land area in each crop which specifies the total pesticide load to the stream channel. Consequently an iterative trial-and-error procedure was adopted whereby the year-end values of both soil residues and stream bed concentrations were compared with the initial condition estimates and the simulation run was re-executed if a significant difference existed. The key criterion for determining whether or not a run would be re-executed was that the initial conditions would need to be far enough outside the range of year-end values so as to affect a measurable shift in
the frequency curve developed from 10 years of daily loading and concentration values. If there was no detectable shift in the frequency curve, then the value determined by the user from the curve would not be affected by the initial condition.

This criterion provided sufficient latitude so that only a handful of lof-year model runs were re-done due to inaccurate estimates of initial conditions. The year-end values of soil residues and bed concentrations were tabulated and analyzed to determine if there existed a significant increasing or decreasing pattern over the l l-year simulation period or if the initial conditions were sufficiently outside the range of values to have an impact on the frequency curve. For example, in one run, the initial bed concentrations were the peak values observed for the entire period; consequently the run was re-executed with initial conditions reset to the average of the year-end values.

Figure 4.12 shows an example of the variation in soil residues and bed concentrations for a Western Cornbelt run, as compared to initial conditions. The year-to-year variation is sufficient, especially for the bed concentrations, to show that the initial conditions are reasonable and would not impact the resulting frequency curves. In general, total mean soil residues for a ks value of $\varnothing . \emptyset 1$ per day were in the range of 0.05 to $\varnothing .1 \varnothing \mathrm{~kg} / \mathrm{ha}$ for all sites, crops, and Koc values, and $1 . \varnothing$ to $2 . \emptyset \mathrm{kg} / \mathrm{ha}$ for a ks value of $\varnothing . \emptyset \emptyset l$ per day. The amount of residue in the surface zone showed a much greater variation, but the impact of initial conditions for the surface zone was generally restricted to the first few months of the lø-year simulation period until the first annual chemical application.

Bed concentrations demonstrated a much greater range of variation in year-end values, up to an order-of-magnitude in many instances. Thus, greater latitude was possible in estimating initial values. The relative concentrations on sand, silt, and clay are a direct function of the organic carbon contents of each fraction (Table 4.7), further simplifying the estimation procedures. After completing simulation runs on the first two representative watersheds, patterns in the variation of bed and soil residue values with changes in Koc and ks were analyzed and used in estimating initial conditions for subsequent watersheds.

### 4.5 SIMULATION RUNS AND PRODUCTION OF FREQUENCY CURVES

The final step in the development of the STREAM procedures was the execution of the lø-year HSPF simulation runs for the 36 combinations of the key methodology parameters - Koc, ks, kw -


Figure 4.12 Sample comparison of initial conditions with yearend pesticide bed concentrations and soil residues (Western Cornbelt, $\mathrm{Koc}=500$, $\mathrm{ks}=0.001$, $\mathrm{kw}=\mathrm{l} .0$ ).
shown in Table 4.20, for each of the five representative watersheds. Since it was necessary to simulate the results of pesticide applications to each crop separately, this required 72 pesticide simulations for each region resulting in a total of $36 \varnothing \varnothing$ pesticide simulation years i.e., 72 simulations $x$ regions $x$ lø years. Using the capability of HSPF to simulate three different chemicals, or parameter combinations, for each separate hydrology/sediment/hydraulics run, resulted in $12 \emptyset$ individual HSPF, lø-year simulation runs. The computer runs were performed on the EPA National Computer Center IBM 3081 Computer, by remote jow entry (RJE) from Anderson-Nichols' offices in Palo Alto, California. Each individual run required approximately 22 minutes of CPU time, and two to five hours of elapsed time, depending on system loading.

The simulations were performed using a 2 -hour time step, to be consistent with the modeling of the application watersheds, and produced a daily concentration time series by averaging the 2-hour values during each day. Pesticide runoff was calculated as the total daily amount in $\mathrm{kg} / \mathrm{ha}$ for each day of the lø-year simulation period. Thus, time series consisting of about 3652 daily values were generated for pesticide runoff and concentrations (i.e., solution and bed) from each simulation run, and analyzed using the DURANL module of HSPF to define the exceedance frequency, or percent of time specific values were exceeded, for durations of $1,2,4$, and 30 days. These durations were chosen to correspond to the standard 24-hour, 48-hour, 96-hour, and 3ø-day toxicity tests normally performed to establish LC5ø (i.e., concentration for 5ø\% mortality) and MATC (i.e., maximum allowable toxicant concentration) values for aquatic organisms. In addition to frequency-duration statistics on the time series, DURANL also provides the maximum and mean values. All frequency-duration analyses were also executed on the EPA NCC computer with the results returned to Palo Alto by remote job retrieval for development of the curves. The resulting frequency curves in Appendices A through E were prepared with a Hewlett-Packard Model 150 Personal Computer with an attached HP $7 \emptyset 74$ graphics plotter using the Picture Perfect Software package developed by Computer Software Corporation of Dallas, Texas. Each appendix includes $15 \emptyset$ frequency-duration curves, comprised of 36 pesticide solution concentration curves, 36 pesticide bed concentrations curves, and three pesticide loading curves (includes a curve for each Koc value on one figure) for each crop.

TABLE 4.2ø VALUES OF KEY METHODOLOGY PARAMETERS FOR SENSITIVITY ANALYSIS

| $\begin{gathered} \mathrm{KOC} \\ (\mathrm{ml} / \mathrm{g}) \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ \text { (per day) } \end{gathered}$ | $\begin{gathered} \text { kw } \\ \text { (per day) } \\ \hline \end{gathered}$ |
| :---: | :---: | :---: |
| 50 | 0.1 | 1. $\quad \square$ |
| 500 | $\emptyset .01$ | $\emptyset .5$ |
| 1500 | 0.001 | 0.05 |
| 5000 |  |  |

## REFERENCES

Ambrose, R.B. Jr., S.I. Hill, and L.A. Mulkey. 1983. User's Manual for the Chemical Transport and Fate Model (TOXIWASP), Version 1. EPA-6ØØ/3-83-Øø5. U.S. EPA, Environmental Research Laboratory, Athens, GA.

Baker, D.B. 1983. Studies of Sediment, Nutrient and Pesticide Loading in Selected Lake Erie and Lake Ontario Tributaries. Draft Final Report, EPA Grant No. Rø05708-Ø1.

Barnwell, T.O. and R. Johanson. 1981. HSPF: A Comprehensive Package for Simulation of Watershed Hydrology and Water Quality, In: Nonpoint Pollution Control-Tools and Techniques for the Future. Tech. Pub. 8l-1, Interstate Comm. on the Potomac River Basin. Rockville, MD. pp. l35-l53.

Barnwell, T.O. 1984. EPA's Center for Water Quality Modeling. In: Proceedings of the Third International Conference on Urban Storm Drainage. In press, Chalmers Institute of Technology, Goteborg, Sweden.

Barnwell, T.O. Jr. and J.L. Kittle. 1984. Hydrologic Simulation Program - FORTRAN: Development, Maintenance and Applications. In: Modeling of Storm Sewer Systems Proc. Third International Conference on Urban Storm Drainage, Goteberg, Sweden. June 4-8, 1984. pp. 493-502.

Biesecker, J.E. and D.K. Leifeste. 1975. Water Quality of Hydrologic Bench Marks - An Indicator of Water Quality in the Natural Environment. Geological Survey Circular 460-E. U.S. Geological Survey, Reston, Va.

Brady, N.C. 1974. The Nature and Properties of Soils. Bth Edition, McMillan Publishing Co., Inc. NY.

Burford, J.B., J.L. DeLashmutt, and R.T. Roberts. 1972. Hydrologic Data for Experimental Agricultural Watersheds in the United States, 1972. U.S. Department of Agriculture. Miscellaneous Publication no. 1412. Beltsville, MD.

Burns, L.A., D.M. Cline, and R.R. Lassiter. 1982. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. EPA-6øø/3-82-ø23. U.S. EPA Environmental Research Laboratory, Athens, GA.

Callahan, M.A., M.W. Slimak, N.W. Gable, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Whitmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. Volumes I and II. Prepared for EPA Office of Water Planning and Standards, Washington, D.C. by Versar, Inc., Springfield, VA. Available from NTIS. PB80-2ø4373.

Carsel, R.F., C. Smith and W. Bellamy. 1983. Computerized Soils Data Base (unpublished). U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Chemical Rubber Company. 1959. Standard Mathematical Tables. l2th Edition. Chemical Rubber Publishing Company, Cleveland, OH .

Christensen, L.A. and R.S. Magleby. 1983. Conservation Tillage Use. I. Soil and Water Conservation. May-June. pp. 156-157.

Crosson, P.R. 1981. Conservation Tillage and Conventional Tillage: A Comparative Assessment. Soil Conservation Society of America, Ankeny, IA.

Dean, J.D., P.P. Jowise and A.S. Donigian, Jr. 1984a. Leaching Evaluation of Agricultural Chemicals (LEACH) Handbook. EPA-6øØ/3-84-øø68. U.S. Environmental Protection Agency, Environmental Research Laboratory. Athens, GA.

Dean, J.D., D.W. Meier, B.R. Bicknell, and A.S. Donigian, Jr. 1984b. Simulation of DDT Transport and Fate in the Arroyo Colorado Watershed, TX. EPA Contract No. 68-ø3-3116, Work Assignment No. 14.

Dempster, G.R. Jr. 1983. Instructions for Streamflow/Basin Characteristics File. (Program E796). Chap. II in WATSTORE User's Guide, U.S. Geological Survey, Reston, VA

Donigian, A.S. Jr., D.C. Beyerlein, H.H. Davis and N.H. Crawford. 1977. Agricultural Runoff Management (ARM) Model - Version II: Testing and Refinement. EPA-6ØØ/3-77-Ø98. U.S. Environmental Protection Agency, Athens, GA.

Donigian, A.S. Jr., J.C. Imhoff and B.R. Bicknell. 1983. Modeling Water Quality and the Effects of Agricultural Best Management Practices in Four Mile Creek, Iowa. EPA Contract No. 68-Ø3-2895. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Donigian, A.S. Jr., J.C. Imhoff, and B.R. Bicknell and J.L. Kittle, Jr. 1984. Guide to the Application of the Hydrological Simulation Program - FORTRAN (HSPF). EPA 600/3-84-ø65, U.S. Environmental Protection Agency, Athens, GA.

Doty, C.W. and C.E. Carter. 1965. Rates and Particle-Size Distributions of Soil Erosion from Unit Source Areas. Trans. ASAE p. 369-3ll.

Duffy, M. and M. Hanthorn. 1984. Returns to Corn and Soybean Tillage Practices. Agricultural Economic Report No. 508. Economic Research Service, U.S. Department of Agriculture. Washington, D.C.

Ellis, B.G., A.E. Erickson, A.R. Wolcott, M. Zabik, and R. Leavitt. l977. Pesticide Runoff Losses From Small Watersheds in Great Lakes Basin. EPA-6øø/3-77-112. U.S. EPA, Environmental Research Laboratory, Athens, GA.

Frey, H.T. 1982. Major Uses of Land in the United States: 1978. Natural Resource Economics Division, Economic Research Service, U.S. Dept. of Agriculture. Agricultural Economic Report No. 487.

Gray, D.M. 1962. Interrelationships of Watershed Characteristics, Journal of Geophysical Research, \#66, p. 1215.

Hack, J.T. 1957. Studies of Longitudinal Stream Profiles in Virginia and Maryland. USGS Prof. Paper \#294-B.

Hamaker, J.W. 1966. Mathematical Prediction of Cumulative Levels of Pesticides in Soil. In: Organic Pesticides in the Environment. (A.A. Rosen and H.F. Kraybill, Eds.) pp. 122-131. Advances in Chemistry Series No. 6ø, American Chemical Society, Washington, D.C.

Hamaker, J.W., and J.M. Thompson. 1972. Adsorption. In: (eds. C.A.I. Goring and J.W. Hamaker) Organic Chemicals in the Environment, Mercel Dekker Inc., N.Y. P. 5l-139.

Hassett, J.J., J.C. Means, W.L. Banwart and S.G. Wood. $198 \emptyset$. Sorption Properties of Sediments and Energy Related Pollutants. EPA-6øø/3-8ø-ø41. U.S. EPA, Environmental Research Laboratory, Athens, GA.

Hedman, E.R., W.M. Kastner and H.R. Hejl. 1974. Selected Streamflow Characteristics as Related to Active Channel Geometry of Streams in Kansas. Kansas Water Resources Board, Topeka, Ks.

Hill, G.D., McGahen, J.W., Baker, H.M., Finnerty, D.U. and Bingeman, C. W. 1955. The Fate of Substituted Area Herbicides in Agricultural Soils. Agron. J., 47, 93-1ø4.

Hornbeck, R.W. 1975. Numerical Methods. Quantum Publishers, Inc. New York, NY.

Hydrocomp, Inc. 1975. EvaJuation of the Effects of Urbanization on Aquatic Ecology and Hydrologic Regimes. Office of Water Research and Technology, Department of the Interior. Washington, D.C. Contract No. 14-31-øøøl-42ø3.

Hydrocomp, Inc. 1979. Estimation of Toxaphene Concentrations in the Mouth of the Yazoo River, MS. Resulting from Basin-Wide Application of Toxaphene to Cotton and Soybeans. U.S. EPA, Environmental Research Laboratory, Athens, GA.

Johnson, H.P. and J.L. Baker. 1982. Field-to-Stream Transport of Agricultural Chemicals and Sediment in an Iowa Watershed: Part I. Data Base for Model Testing (1976-1978). EPA-6ø0/3-82-ø32. U.S. EPA, Environmental Research laboratory, Athens, GA.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Research, Vol. 13, pp. 241-248.

Karickhoff, S.W. 1981. Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. Chemosphere, Vol. lø(8): 833-846.

Kenaga, E.E. and C.A.I. Goring. 1989. Relationship Between Water Solubility, Soil Sorption, Octanol-Water Partitioning, and Concentration of Chemicals in Biota. In: Aquatic Toxicology, J.G. Eaton, P.R. Parrish, and A.C. Hendricks (Editors), Amer. Soc. Testing \& Materials, Special Technical Publication No. 7ø7, pp. 78-lly.

Kilmer, J.K. ed. 1982. Handbook of Soils and Climate in Agriculture. CRC Press, Inc., Boca Raton, FL.

Langbein, W.B. and others. 1947. Topographic Characteristics of Drainage Basins. USGS Water Supply Paper \#968-C.

Leopold, L.B. and T. Maddock, Jr. 1953. The Hydraulic Geometry of Stream Channels and Some Physiographic Implications, U.S. Geological Survey, Professional Paper \#252, Washington, D.C.

Leopold, L.B., M.G. Wolman and J.P. Miller. 1964. Fluvial Processes in Geomorphology. Freeman \& Co., San Francisco, CA.

Linsley, R.K., M.A. Kohler, and J.L.H. Paulus. 1975. Hydrology for Engineers. 2nd Edition McGraw-Hill Book Co. New York, N.Y.

Lorber, M.N. and L.A. Mulkey. 1982. An Evaluation of Three Pesticide Runoff Loadings Models. J.Environ. Qual., Vol. ll, pp. 519-529.

Lumb, A. M. 1973. Travel Time of Georgia Streams, Report ERC-1273, School of Civil Engineering, Georgia Inst. of Tech., Atlanta, GA.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw Hill Co., NY.

Mabey, W.R., J.H. Smith, R.T. Podoll, H.L. Johnson, T. Mill, T.W. Chou, J. Gates, I. Waight Partridge, and D. Vandenberg. 1982. Aquatic Fate Process Data for Organic Priority Pollutants. Prepared by SRI International, Menlo Park, CA for U.S. EPA Office of Water Regulations and Standards. Washington, D.C.

Mabey, W.R., T. Mill, and R.T. Podoll. 1984. Estimation Methods for Process Constants and Properties Used in Fate Assessments. EPA-6øø/3-84-035. U.S. EPA Environmental Research Laboratory, Athens, GA.

Mannering, J.V. and C.R. Fenster. 1983. What is Conservation Tillage? J. Soil and Water Conservation, May-June. pp. 141-143.

Menzie, C.M. 1972. Fate of Pesticides in the Environment. Annual Review of Entomology. 17:199-122.

Mills, W.B. et al. 1982. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants-Part I. EPA-6øø/6-82-øø4a. U.S. EPA, Environmental Research Laboratory, Athens, GA.
Mi.lls, W.B., J.D. Dean, D.B. Porcella, S.A. Gherini, R.J.M. Hudson, W.E. Frick G.L. Rupp, and G.L. Bowie. 1982. Water Quality Assesment: A Screening Procedure for Toxic
and Conventional Pollutants. U.S. EPA Environmental Research Laboratory, Athens, GA. EPA/600/6-85/002a\&b.

Moldenhauer, W.C. et al. 1983. Conservation Tillage for Erosion Control. J. Soil and Water Conservation. May-June. pp. 144-15l.

Mulkey, L.A., R.B. Ambrose and T.O. Barnwell. 1982. Aquatic Fate and Transport Modeling Techniques for Predicting Environmental Exposure to Organic Pesticides and Other Toxicants. In: Proceedings of International Workshop on the Comparison and Application of Mathematical Models for the Assessment of Changes in Water Quality in River Basins, Both Surface and Groundwater, In: press, UNESCO, Paris, France.

Mulkey, L.A. and A.S. Donigian, Jr. 1984. Modeling Alachlor Behavior in Three Agricultural River Basins. U.S. EPA, Environmental Research Laboratory, Athens, GA.

Nash, R.G. 1980. Dissipation Rate of Pesticides from Soils. Chapter l7 In: CREAMS, A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems. Vol. III. U.S. Department of Agriculture. Conservation Research Report No. 26.

Osterkamp, W.R. and E.R. Hedman. 1982. Perennial Streamflow Characteristics Related to Channel Geometry and Sediment in Missouri River Basin, U.S. Geological Survey Professional Paper \#l242. Washington, D.C.

Osterkamp, W.R., L.J. Lane and G.R. Foster. 1983. An Analytical Treatment of Channel Morphology Relations, U.S. Geological Survey Professional Paper \#l288, Washington, D.C.

Parker, C.A., et al. 1946. Fertilizers and Lime in the United States. USDA Misc. Pub. No. 586.

Rao, P.S.C. and J.M. Davidson. 198ø. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models. In: Environmental Impact of Nonpoint Source Pollution, M.R. Overcash and J.M. Davidson (Editors), Ann Arbor Sci. Publishers, Inc., pp. 23-67.

Rao, P.S.C., V.E. Berkheiser, L.T. Ou. 1984. Estimation of Parameters for Modeling the Behavior of Selected Pesticides and Orthophosphate. EPA-6ØØ/3-84-Ø19. U.S. EPA, Environmental Research Laboratory, Athens, GA.

Rawls, W. 1983. Soil Science l35(2): l23-125.

Smith, C.N., R.A. Leonard, G.W. Langdale, and G.W. Bailey. 1978. Transport of Agricultural Chemicals from Small Upland Piedmont Watersheds. EPA-6øØ/3-78-Ø56. IA G No. IA G-D6-Ø381. U.S. EPA, Athens, GA. and USDA, Watkinsville, GA.

Soil Conservation Society of America. 1982. Resource Conservation Glossary. Ankeny, IA.

Stewart, B.A., D.A. Woolhiser, W.H. Wischmeier, J.H. Caro, and M.H. Frere. 1975. Control of Water Pollution from Cropland. U.S. EPA-ORD and USDA-ARS. EPA-6ø0/2-75-ø26a, ARS-4-5-1. pp.188.

Unger, S.G. 1979. Environmental Implications of Trends in Agriculture and Silviculture, Volume III: Regional Crop Production Trends. EPA-6øø/3-79-Ø47, U.S. Environmental Protection Agency, Athens, GA.
U.S. Dept. of Agriculture. 1972. Usual Planting and Harvesting Dates. Agricultural Handbook No. 283. Statistical Reporting Service, U.S. Department of Agriculture, Washington, D.C.
U.S. Dept. of Agriculture. 1981. Crop Enterprise Budgets for 1981. FIRM Enterprise Data System, Economic Research Service, U.S. Department of Agriculture, Stillwater, OK.
U.S. Dept. of Agriculture. 1981. Land Resource Regions and Major Land Resource Areas of the United States. Agricultural Handbook No. 296. Soil Conservation Service, Washington, D.C.
U.S. Dept. of Commerce. 1955. Rainfall Intensity-Duration-Frequency Curves For Selected Stations in the United States, Alaska, Hawaiian Islands, and Puerto Rico. U.S. Weather Bureau, Technical Paper No. 25. Washington, D.C.
U.S. Dept. of Commerce. 1979. Climatic Atlas of the U.S. Environmental Sciences Administration Environmental Data Service. Washington, D.C.
U.S. Dept. of Commerce. 1981. 1978 Census of Agriculture, Sumnary and State Data - United States. Bureau of Census, Washington, D.C.
U.S. Dept. of Commerce. 1982. 1978 Census of Agriculture, Graphic Summary. Vol 5, Part l. Bureau of Census, Washington, D.C.
U.S. Environmental Protection Agency. 1975. Control of Water Pollution from Cropland: Volume l, A Manual for Guideline Development. EPA-600/2-75-026a. U.S. Environmental Protection Agency, Athens, GA.
U.S. Environmental Protection Agency. 1982. Predictive Exposure Assessment Workshop Summary: Level $I$ and Level II. Environmental Research Laboratory, Athens, GA.
U.S. Environmental Protection Agency. 1982. Testing for the Field Applicability of Chemical Exposure Models. Proc. Workshop on Field Applicability Testing. Exposure Modeling Committee Report. U.S. EPA, Athens, GA.
U.S. Forest Service. 1977. Non-Point Water Quality of Hydrologic Bench Marks - An Indicator of Water Quality in the Natural Environment. Geological Survey Circular 460-E. U.S. Geological Survey, Reston, VA.
U.S. Geological Survey. l981. WATSTORE: A WATer Data STOrage and Retrieval System. U.S. Department of the Interior, washington, D.C.

Wauchope, R.D. 1978. The Pesticide Content of Surface Water Draining from Agricultural Fields - A Review. J. Environmental Quality, 7(4): pp.459-47l.

Wauchope, R.D. and R.A. Leonard. 1980. Maximum Pesticide Concentrations in Agricultural Runoff: A Semiempirical Prediction Formula. J. Environmental Quality, 9(4): pp. 665-672.

Weed Science Society of America. 1983. Herbicide Handbook. 5th Edition. Weed Society of America, Champaign, IL.

Williams, G.P. 1978. Hydraulic Geometry of River Cross Sections - Theory of Minimum Variance, U.S. Geological Survey Professional Paper \#1ø29, Washington, D.C.

Wolman, M.G. and L.B. Leopold. 1957. River Flood Plains: Some Observations on Their Formation, U.S. Geological Survey Professional Paper \#282-C, Washington, D.C.
table a. 1 figure matrix for pesticide solution concentration CURVES FOR CORN AND SOYBEANS IN THE SOUTHEAST

| Region: Crop: | SOUTHEAST CORN |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | kw (per day) |  |  |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{mI} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ \text { (per day) } \end{gathered}$ | 1.0 | $\underline{0.5}$ | $\underline{0.05}$ |
| 50 | $ø .1$ | A. 1 | A. 2 | A. 3 |
|  | 0.01 | A. 4 | A. 5 | A. 6 |
|  | 0.001 | A. 7 | A. 8 | A. 9 |
| 500 | 0.1 | A. $1 \varnothing$ | A. 11 | A. 12 |
|  | 0.01 | A. 13 | A. 14 | A. 15 |
|  | 0.001 | A. 16 | A. 17 | A. 18 |
| 1500 | 0.1 | A. 19 | A. 20 | A. 21 |
|  | Ø.ø1 | A. 22 | A. 23 | A. 24 |
|  | ø.ø01 | A. 25 | A. 26 | A. 27 |
| 5000 | 0.1 | A. 28 | A. 29 | A. 30 |
|  | 0.01 | A.31 | A. 32 | A. 33 |
|  | $\varnothing .001$ | A. 34 | A. 35 | A. 36 |


| Region: Crop: | SOUTHEAST |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | kw (per day) |  |  |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ (\mathrm{per} \text { day }) \end{gathered}$ | 1.0 | 0.5 | 0.05 |
| $5 \varnothing$ | $\emptyset .1$ | A. 37 | A. 38 | A. 39 |
|  | 0.01 | A. 40 | A. 41 | A. 42 |
|  | 0.001 | A. 43 | A. 44 | A. 45 |
| $5 \varnothing 0$ | 0.1 | A. 46 | A. 47 | A. 48 |
|  | 0.01 | A. 49 | A. 50 | A. 51 |
|  | ø.øø1 | A. 52 | A. 53 | A. 54 |
| 1500 | 0.1 | A. 55 | A. 56 | A. 57 |
|  | 0.01 | A. 58 | A. 59 | A. $6 \square$ |
|  | 0.001 | A. 61 | A. 62 | A. 63 |
| $5 \varnothing \varnothing \varnothing$ | 0.1 | A. 64 | A. 65 | A. 66 |
|  | 0.01 | A. 67 | A. 68 | A. 69 |
|  | 0.001 | A. $7 \varnothing$ | A. 71 | A. 72 |

A-1

TABLE A. 2 FIGURE MATRIX FOR PESTICIDE BED CONCENTRATION CURVES FOR CORN AND SOYBEANS IN THE SOUTHEAST


Region: SOUTHEAST
Crop: SOYBEANS

| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | ks |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | 0.5 | 0.05 |
| 50 | 0.1 | A. 109 | A.110 | A. 111 |
|  | 0.01 | A. 112 | A. 113 | A. 114 |
|  | Ø.øø1 | A.ll5 | A. 116 | A. 117 |
| $50 \emptyset$ | 0.1 | A. 118 | A. 119 | A. 120 |
|  | 0.01 | A. 121 | A. 122 | A. 123 |
|  | 0.001 | A. 124 | A. 125 | A. 126 |
| 1500 | $\emptyset .1$ | A. 127 | A. 128 | A. 129 |
|  | 0.01 | A. 130 | A. 131 | A. 132 |
|  | $0.0 \emptyset 1$ | A. 133 | A. 134 | A. 135 |
| $50 \square \varnothing$ | 0.1 | A. 136 | A. 137 | A. 138 |
|  | 0.01 | A. 139 | A. 140 | A. 141 |
|  | Ø.øØ1 | A. 142 | A. 143 | A. 144 |

## TABLE A. 3 FIGURE MATRIX FOR PESTICIDE LOADING CURVES FOR THE SOUTHEAST

Region: SOUTHEAST






FIGURE A. 4
Region:
SOUTHEAST

Crop:
CORN
Koc:
ks:
0.01
kw:
1.0




FIGURE A. 7
Region:
SOUTHEAST
Crop:
Koc:
50
ks:
kw:
1.0


[^0]Region: SOUTHEAST

Crop:
CORN
Koc:
Ks:
0.001
kw:
50
0.001
0.5


FIGURE A. 9
Region:
SOUTHEAST
Crop:
CORN
Koc:
ks:
kw:
0.05















FIGURE A. 23
Region:
SOUTHEAST
Crop:
CORN
Koc:
ks:
kw: 1500
0.01
0. 5


FIGURE A. 24
Region: SOUTHEAST
Crop:
CORN

Koc:
ks:
kw: $1500 \quad 0.01$ 0.05











FIGURE A. 34
Region: SOUTHEAST
Crop:
CORN

Koc:
ks:
kw:
5000
0.001
1.0







FIGURE A. 40
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
ks:
0.01
kw:
1.0





| FIGURE | A. 44 | Region: | Crop: | Koc: | ks: | kw: |
| :--- | :--- | :---: | :--- | :--- | :--- | :--- |
|  |  | SOUTHEAST | SOYBEANS | 50 | 0.001 | 0.5 |







FIGURE A. 49
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
500
ks:
kw:
1.0


FIGURE A. 50
Region:
SOUTHEAST

Crop:
SOYBEANS
Koc:
ks:
kw:
0.5




FIGURE A. 53
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
ks:
$500 \quad 0.001$
kw:
0. 5


FIGURE A. 55
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
1500
ks:
kw:
1.0




FIGURE A. 58
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
1500
ks:
kw:
1.0




FIGURE A. 61
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
ks:
0.001
kw:
1.0









FIGURE A. 69
Reqion: SOUTHEAST
Crop: SOYBEANS

Koc:
5000
ks:
0.01
kw:



FIGURE A. 71
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
5000
ks:
kw:
0.5

















FIGURE A. 87
Region:
SOUTHEAST
Crop:
CORN
Koc:
Ks:
kw:
0.05








FIGURE A. 94

Region:
SOUTHEAST
Crop:
CORN
Koc:
ks:
kw:
1.0








FIGURE A. 101
Region: SOUTHEAST

Crop:
CORN
Koc: 5000
ks:
Kw:
0.5





[^1]Region: SOUTHEAST

Crop:
CORN

Koc: 5000
ks:
0.01
kw:
0.05


FIGURE A. 106
Region:
SOUTHEAST

Crop:
CORN
Koc:
5000
ks:
0.001
kw:
1.0



FIGURE A. 108

Region: SOUTHEAST

Crop:
CORN
Koc:
5000
ks:
0.001
kw:
0. 05


FIGURE A. 109
Region:
SOUTHEAST
Crop:
Koc:
ks:
kw:
50
0.1
1.0









[^2]Region: SOUTHEAST
Crop: SOYBEANS

Koc:
50
ks:
kw:
0.05


FIGURE A. 118
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc: 500
ks:
kw:
1.0


[^3]Region: SOUTHEAST
Crop: SOYBEANS

Koc:
500
ks:
kw:
0.5




FIGURE A. 122
Region:
SOUTHEAST
Crop:
Koc:
ks:
kw:
SOYBEANS
500
0.01
0.5



FIGURE A. 124
Region:
SOUTHEAST
Crop:
SOYBEANS
Koc:
500
ks:
0.001
kw:
1.0





FIGURE A. 128

## Region: SOUTHEAST

Crop:
SOYBEANS
Koc:
ks:
kw:
$1500 \quad 0.1$
0.5







FIGURE A. 134
Region:
SOUTHEAST

Crop:
SOYBEANS

| Koc: | Ks: |
| :--- | :--- |
| 1500 | 0.001 |

kw:
0.5











[^4]Region: SOUTHEAST
Crop:
SOYBEANS

Koc:
ks:
0.001
kw:
0. 05




FIGURE A. 147
Region: SOUTHEAST
Crop:
CORN
ks:
0.001




FIGURE A. 150
Region:
SOUTHEAST
Crop:
SOYBEANS
ks:

TABLE B. 1 FIGURE MATRIX FOR PESTICIDE SOLUTION CONCENTRATION CURVES FOR COTTON AND SOYBEANS IN THE MISSISSIPPI DELTA

Region: MISSISSIPPI DELTA
Crop: SOYBEANS

|  | - |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \text { ks } \\ \text { (per day) } \\ \hline \end{gathered}$ | 1.0 | 0.5 | $\boxed{\square} .05$ |
| 50 | 0.1 | B. 37 | B. 38 | B. 39 |
|  | 0.01 | B. 40 | B. 41 | B. 42 |
|  | 0.001 | B. 43 | B. 44 | B. 45 |
| 500 | 0.1 | B. 46 | B. 47 | B. 48 |
|  | 0.01 | B. 49 | B. 5 ø | B. 51 |
|  | 0.001 | B. 52 | B. 53 | B. 54 |
| 1500 | 0.1 | B. 55 | B. 56 | B. 57 |
|  | 0.01 | B. 58 | B. 59 | B. 60 |
|  | 0.001 | B. 61 | B. 62 | B. 63 |
| 5000 | 0.1 | B. 64 | B. 65 | B. 66 |
|  | 0.01 | B. 67 | B. 68 | B. 69 |
|  | 0.001 | B. 70 | B. 71 | B. 72 |

TABLE B. 2 FIGURE MATRIX FOR PESTICIDE BED CONCENTRATION CURVES FOR COTTON AND SOYBEANS IN THE MISSISSIPPI DELTA
Region: MISSISSIPPI DELTA
Crop: COTTON

|  |  |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \text { ks } \\ \text { (per day) } \\ \hline \end{gathered}$ | 1.0 | 0.5 | 0.05 |
| $5 \emptyset$ | $\emptyset .1$ | B. 73 | B. 74 | B. 75 |
|  | 0.01 | B. 76 | B. 77 | B. 78 |
|  | Ø.øø1 | B. 79 | B. 80 | B. 81 |
| 5øø | 0.1 | B. 82 | B. 83 | B. 84 |
|  | 0.01 | B. 85 | B. 86 | B. 87 |
|  | 0.001 | B. 88 | B. 89 | B. $9 \varnothing$ |
| 1500 | $\varnothing .1$ | B. 91 | B. 92 | B. 93 |
|  | 0.01 | B. 94 | B. 95 | B. 96 |
|  | 0.001 | B. 97 | B. 98 | B. 99 |
| $50 \varnothing \square$ | $\emptyset .1$ | B. $10 \varnothing$ | B. 101 | B. $1 \varnothing 2$ |
|  | $\emptyset . \emptyset 1$ | B. 103 | B. 104 | B. 105 |
|  | Ø.øø1 | B. 106 | B. 107 | B. 1 ¢8 |

Region: MISSISSIPPI DELTA
Crop: SOYBEANS

| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | ks |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | 0.5 | 0.05 |
| $5 \emptyset$ | 0.1 | B. 109 | B.110 | B. 111 |
|  | $\emptyset .01$ | B. 112 | B. 113 | B. 114 |
|  | ¢.0ø1 | B. 115 | B. 116 | B. 117 |
| 5்øø | 0.1 | B. 118 | B. 119 | B. 120 |
|  | 0.01 | B. 121 | B. 122 | B. 123 |
|  | $\varnothing .0 \emptyset 1$ | B. 124 | B. 125 | B. 126 |
| 15øø | 0.1 | B. 127 | B. 128 | B. 129 |
|  | $\varnothing .01$ | B. 130 | B. 131 | B. 132 |
|  | 0.001 | B. 133 | B. 134 | B. 135 |
| $5 \varnothing \square \varnothing$ | 0.1 | B. 136 | B. 137 | B. 138 |
|  | Ø.ø1 | B. 139 | B. 140 | B. 141 |
|  | Ø.øø1 | B. 142 | B. 143 | B. 144 |

# TABLE B. 3 FIGURE MATRIX FOR PESTICIDE LOADING CURVES FOR THE MISSISSIPPI DELTA 

Region: MISSISSIPPI DELTA

|  | 0.1 | ks (per day) |  |
| :---: | :---: | :---: | :---: |
| Crop |  | .01 | .001 |
| Cotton | B. 145 | B. 146 | B. 147 |
| Soybeans | B. 148 | B. 149 | B. 150 |



FIGURE B. 2
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
0.1
kw:
50
0.5

$\begin{array}{cccclll}\text { FIGURE B. } 3 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { MISSISSIPPI DELTA } & \text { COTTON } & 50 & 0.1 & 0.05\end{array}$


| FIGURE B. 4 | Region: | Crop: | Koc: | ks: | kw: |  |
| :--- | :--- | :---: | :--- | :--- | :--- | :--- |
|  |  | MISSISSIPPI DELTA | COTTON | 50 | 0.01 | 1.0 |



FIGIRE B. 5
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
kw:
0.01
0.5



$\begin{array}{lllllll}\text { FIGURE B. } 8 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { Kw: } \\ & \text { MISSISSIPPI DELTA } & \text { COTTON } & 50 & 0.001 & 0.5\end{array}$




FIGURE B. 11
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
0.1
kw:
500
0.5


FIGURE B. 12
Region:
MISSISSIPPI DELTA
Crop:

Koc:
ks:
kw:
.05

$\begin{array}{lllllll}\text { FIGURE B. } 13 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { Kw: } \\ & \text { MISSISSIPPI DELTA } & \text { COTTON } & 500 & 0.01 & 1.0\end{array}$

$\begin{array}{llllll}\text { FIGURE B. } 14 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { MISSISSIPPI DELTA } & \text { COTTON } & 500 & 0.01 & 0.5\end{array}$



| FIGURE B. 16 | Region: | Crop: | Koc: | ks: | kw: |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  | MISSISSIPPI DELTA | COTTON | 500 | 0.001 | 1.0 |




FIGURE B. 18

$$
\begin{gathered}
\text { Region: } \\
\text { MISSISSIPPI DELTA }
\end{gathered}
$$

Crop:
Koc:
500
ks:
kw:
0. 05


FIGURE B. 19
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
0.1
kw:
1.0


FIGURE B. 20
Region:
MISSISSIPPI DELTA
Crop:
COTTON

Koc:
1500
Ks:
0.1
Kw:
MISSISSIPPI DELTA 1500
0.5








FIGURE B. 27
Region:
MISSISSIPPI DELTA
Crop:
COTfON
Koc:
1500
0.001
kw:
0. 05


FIGURE B. 28
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc: 5000
ks:
0.1
kw:
1.0


FIGURE B. 29


Crop:
COTTON
Koc:
ks:
0.1
kw:
0.5





$\begin{array}{cccccc}\text { FIGURE B. } 34 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & & \text { MISSISSIPPI DELTA } & \text { COTTON } & 5000 & 0.001\end{array}$


FIGURE B. 35
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc: ks:
kw:
5000 0.001
0.5



FIGURE B. 37
Region:
MISSISSIPPI DELTA Crop:
SOYBEANS

Koc:
ks:
kw:
50
0.1
1.0


FIGURE B. 38

| Region: | Crop: |
| :---: | :---: |
| MISSISSIPPI DELTA SOYBEANS |  |

Koc:
50
ks:
kw:
MISSISSIPPI DELTA SOYBEANS
0.1
0.5


| Region: | Crop: |
| :---: | :---: |
| MISSISSIPPI DELTA | SOYBEANS |

Koc:
ks:
kw:
MISSISSIPPI DELTA SOYBEANS
50
0.1
0.05






FIGURE B. 44

$$
\begin{gathered}
\text { Region: } \\
\text { MISSISSIPPI DELTA }
\end{gathered}
$$

Crop:
SOYBEANS

| Koc: | ks: |
| :--- | :--- |
| 50 | 0.001. |

kw:
0.5



FIGURE B. 46
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { SOYBEANS }\end{array}$
Koc:
ks:
$500 \quad 0.1$
kw:
1.0


FIGURE B. 47
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { SOYBEANS }\end{array}$
Koc:
ks:
0.1
kw:
0.5



FIGURE B. 49
Region: $\quad$ Crop:
MISSISSIPFI DELTA SOYBEANS
Koc:
ks:
0.01

Kw:



FIGURE B. 51
Region:
MISSISSIPPI DELTA
Crop:
SOYBEANS
Koc:
Ks:
kw:



FIGURE B. 53
Region:
MISSISSIPPI DELTA Crop:

Koc:
ks:
kw:
$500 \quad 0.001$
0.5

$\begin{array}{llccccc}\text { FIGURE B. } 54 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { kw: } \\ & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 500 & 0.001 & 0.05\end{array}$



FIGURE B. 56
Region:
MISSISSIPPI DELTA
Crop:
SOYBEANS
Koc:
1500
Ks:
kw:
0.5

$\begin{array}{ccccccc}\text { FIGURE B. } 57 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 1500 & 0.1 & 0.05\end{array}$





| FIGURE B. 60 | Region: | Crop: | Koc: | ks: | kw: |
| :---: | :---: | :---: | :---: | :--- | :--- |
|  | MISSISSIPPI DELTA | SOYBEANS | 1500 | 0.01 | .05 |






Crop:
SOYBEANS
Koc:
1500.001
kw:
.05





FIGURE B. 67
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { SOYBEANS }\end{array}$
Koc:
ks :
kw:
1.0

$\begin{array}{llllll}\text { FIGURE B. } 68 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { Kw: } \\ & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 5000 & .01 & 0.5\end{array}$



FIGURE B. 70
Region:
MISSISSIPPI DELTA SOPO:
$\begin{array}{ll}\text { Koc: } & \text { Ks: } \\ 5000 & 0.001\end{array}$
kw:
1.0


FIGURE B. 71
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { SOYBEANS }\end{array}$
Koc:
5000
ks:
kw:
0.001
0.5




FIGURE B. 74
Region:
MISSISSIPPI DELTA
Crop: COTTON

Koc:
50
ks:
kw:


FIGURE B. 75
Region:
MISSISSIPPI DELTA
Crop:
COTYON
Koc:
50
ks:
kw:
0.05




FIGURE B. 78
Region:
MISSISSIPPI DELTA
Crop:
COTYON
Koc:
50
ks:
kw:
Mississip







FIGURE B. 84
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { COTTON }\end{array}$
Koc:
500
ks:
0.1
kw:
.05



$$
\begin{array}{llllll}
\text { FIGURE B. } 86 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\
& & \text { MISSISSIPPI DELTA } & \text { COTTON } & 500 & 0.01 \\
& 0.5
\end{array}
$$






FIGURE B. 90

$$
\begin{gathered}
\text { Region: } \\
\text { MISSISSIPPI DELTA }
\end{gathered}
$$

Crop:
COTTON
Koc:
Ks:
0.001
kw:
0.05

$\begin{array}{cccccc}\text { FIGURE B. } 91 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { MISSISSIPPI DELTA } & \text { COTTON } & 1500 & 0.1 & 1.0\end{array}$



$\begin{array}{lllllll}\text { FIGURE } & \text { B. } 94 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { kw: } \\ & & \text { MISSISSIPPI DELTA } & \text { COTTON } & 1500 & 0.01 & 1.0\end{array}$

$\begin{array}{lllllll}\text { FIGURE } & \text { B. } 95 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { Kw: } \\ & \text { MISSISSIPPI DELTA } & \text { COTTON } & 1500 & 0.01 & 0.5\end{array}$

$\begin{array}{lllllll}\text { FIGURE B. } 96 & \text { Regions } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { mississipl } \\ & & \text { delta } & \text { COTTON } & 1500 & 0.01 & .05\end{array}$


| FIGURE B. 97 | Region: | Crop: | Koc: | ks: | kw: |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | SSIPPI DELTA | COTTON | 1500 | 0.001 | 1. |



FIGURE B. 98
Region:
MISSISSIPPI DELTA $\quad$ Crop:
COTTON
Koc:
1500
ks:
kw:
0.5


FIGURE B. 99
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc: 1500
ks: 0.001
kw:
0.05



| FIGURE | B. 101 | Region: | Crop: | Koc: | ks: | kw: |
| :--- | :--- | :---: | :--- | :--- | :--- | :--- |
|  | MISSISSIPPI DELTA | COTPON | 5000 | 0.1 | 0.5 |  |



FIGURE B. 102
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
kw:
5000
0.1
0.05


FIGURE B. 103
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
0.01
kw:
1.0


FIGURE B. 104
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
0.01
kw:
0.5


FIGURE B. 105
Region:
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
ks:
kw: 5000
0.01
. 05



FIGURE B. 107
Region:
MISSISSIPPI DELTA
Crop:
COTPON

Koc: 5000
ks:
0.001
kw:
0.5


FIGURE B. 108
MISSISSIPPI DELTA
Crop:
COTTON
Koc:
5000
$\mathrm{ks}:$
0.001
kw:
0.05



FIGURE B. 110
Region:
MISSISSIPPI DELTA
Crop:
SOYBEANS
Koc:
50
ks:
kw:
0.5






FIGURE B. 115
Region:
MISSISSIPPI DELTA $\quad$ COP:
Koc:
ks:
0.001
kw:
50
1.0

$\begin{array}{lllllll}\text { FIGURE B. } 116 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { Kw: } \\ & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 50 & 0.001 & 0.5\end{array}$


FIGURE B. 117
Region:
MISSISSIPPI DELTA
Crop:
SOYBEANS
Koc:
50
0.001
kw:
0.05


$\begin{array}{cccccc}\text { FIGURE B. } 119 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kws } \\ & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 500 & 0.1 & 0.5\end{array}$


FIGURE B. 120

MISSISSIPPI DELTA SOYBEANS

Koc:
ks:
0.1
kw:
500
.05



FIGURE B. 122
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { SOYBEANS }\end{array}$
Koc:
ks:
0.01
kw:
0.5




FIGURE B. 125
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI } & \text { DELTA }\end{array}$
Koc:
ks:
kw:
$500 \quad 0.001$
0. 5



FIGURE B. 127
Region:
MISSISSIPPI DELTA Crop:
Koc: 1500
0.1
kw:
1.0


FIGURE B. 128
Region:
MISSISSIPPI DELTA Crop:
Koc:
ks:
kw:
Mississled delta soybens
1500
0.1
0.5



FIGURE B. 130
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { MISSISSIPPI DELTA } & \text { SOYBEANS }\end{array}$
Koc:
ks:
kw:
$1500 \quad 0.01$
1.0



FIGURE B. 132

## Region: Crop: MISSISSIPPI DELTA SOYBEANS

Koc: ks:
kw: 1500
0.01
.05


$\begin{array}{llcccll}\text { F IGURE } & \text { B. } 134 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 1500 & 0.001 & 0.5\end{array}$


FIGURE B. 135

## MISSISSIIPPI DELTA

Crop:
SOYBEANS
$\begin{array}{ll}\text { Koc: } & \text { Ks: } \\ 1500 & 0.001\end{array}$
kw:
.05



FIGURE B. 137

| Region: | Crop: |
| :---: | :---: |
| MISSISSIPPI DELTA SOYBEANS |  |

Koc:
ks:
kw:
5000 0.1
0.5


| FIGURE B. 138 | Region: | Crop: | Koc: | ks: | kw: |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | MISSISSIPPI DELTA | SOYBEANS | 5000 | 0.1 | 0.05 |



FIGURE B. 139
Region:
MISSISSIPPI DELTA

Crop:
SOYBEANS
Koc:
ks:
kw: $5000 \quad 0.01$
1.0




FIGURE B. 142

> Region: MISSISSIPPI DELTA Crop: SOYBEANS

Koc:
5000
ks:
0.001
kw:
1.0

$\begin{array}{lllllll}\text { FIGURE B. } 143 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { MISSISSIPPI DELTA } & \text { SOYBEANS } & 5000 & 0.001 & 0.5\end{array}$


| FIGURE | B. 144 | Region: | Crop: | Koc: | ks: | kw: |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | MISSISSIPPI DELTA | SOYBEANS | 5000 | 0.001 | 0.05 |  |





FIGURE B. 147
Reqion: MISSISSIPPI DELTA
Crop: COTTON
ks:
0.001




FIGURE B. 150

Region:
MISSISSIPPI DELTA
Crop:
SOYBEANS
ks:
0.001

Region: EASTERN CORNBELT
Crop: SOYBEANS

| - |  |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ (\mathrm{per} \text { day }) \\ \hline \end{gathered}$ | 1.0 | 0.5 | 0.05 |
| 50 | 0.1 | C. 37 | C. 38 | C. 39 |
|  | 0.01 | C. 49 | C. 41 | C. 42 |
|  | 0.001 | C. 43 | C. 44 | C. 45 |
| $50 \square$ | 0.1 | C. 46 | C. 47 | C. 48 |
|  | 0.01 | C. 49 | C. 50 | C. 51 |
|  | 0.001 | C. 52 | C. 53 | C. 54 |
| 1500 | 0.1 | C. 55 | C. 56 | C. 57 |
|  | 0.01 | C. 58 | C. 59 | C. 60 |
|  | 0.001 | C. 61 | C. 62 | C. 63 |
| 5000 | 0.1 | C. 64 | C. 65 | C. 66 |
|  | 0.01 | C. 67 | C. 68 | C. 69 |
|  | 0.001 | C. 70 | C. 71 | C. 72 |

TABLE C. 2 FIGURE MATRIX FOR PESTICIDE BED CONCENTRATION CURVES FOR CORN AND SOYBEANS IN THE EASTERN CORNBELT

| Region: <br> Crop: | EASTERN CORNBELT CORN |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | per d |  |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ (\mathrm{per} \text { day }) \\ \hline \end{gathered}$ | 1.0 | 0.5 | 0.05 |
| $5 \varnothing$ | $ø .1$ | C. 73 | C. 74 | C. 75 |
|  | Ø.ø1 | C. 76 | C. 77 | C. 78 |
|  | Ø.øø1 | C. 79 | C. $8 \varnothing$ | C. 81 |
| $5 \emptyset \varnothing$ | 0.1 | C. 82 | C. 83 | C. 84 |
|  | ¢. 01 | C. 85 | C. 86 | C. 87 |
|  | Ø.øø1 | C. 88 | C. 89 | C. 90 |
| $150 \varnothing$ | $\emptyset .1$ | C. 91 | C. 92 | C. 93 |
|  | Ø.ø1 | C. 94 | C. 95 | C. 96 |
|  | ø.øø1 | C. 97 | C. 98 | C. 99 |
| $50 \varnothing \square$ | 0.1 | C. 100 | C. 101 | C. 102 |
|  | 0.01 | C. 103 | C. 104 | C. 105 |
|  | Ø.0ø1 | C. 106 | C. 107 | C. 108 |

Region: EASTERN CORNBELT
Crop: $\quad$ SOYBEANS

| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \text { ks } \\ \text { (per day) } \end{gathered}$ | 1.0 | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | 0.5 | 0.05 |
| $5 \emptyset$ | 0.1 | C. 109 | C. 110 | C. 111 |
|  | Ø.ø1 | C. 112 | C. 113 | C. 114 |
|  | Ø.øø1 | C. 115 | C. 116 | C. 117 |
| $5 \square \varnothing$ | $\emptyset .1$ | C. 118 | C. 119 | C. $12 \varnothing$ |
|  | 0.01 | C. 121 | C. 122 | C. 123 |
|  | ø.øø1 | C. 124 | C. 125 | C. 126 |
| 1500 | $\emptyset .1$ | C. 127 | C. 128 | C. 129 |
|  | 0.01 | C. 130 | C. 131 | C. 132 |
|  | Ø.øø1 | C. 133 | C. 134 | C. 135 |
| $5 \varnothing \varnothing \square$ | 0.1 | C. 136 | C. 137 | C. 138 |
|  | Ø. 01 | C. 139 | C. 140 | C. 141 |
|  | Ø.øø1 | C. 142 | C. 143 | C. 144 |

## TABLE C. 3 FIGURE MATRIX FOR PESTICIDE LOADING CURVES FOR THE EASTERN CORNBELT

## Region: EASTERN CORNBELT

|  | ks (per day) |  |  |
| :---: | :---: | :---: | :---: |
| Crop | 0.1 | .01 | .001 |
| Corn | C. 145 | C. 146 | C. 147 |
| Soybeans | C. 148 | C. 149 | C. 150 |



FIGURE C. 1
Region:
EASTERN CORNBELT
Crop:
CORN
Koc: 50
ks:
kw:
1.0






FIGURE C. 6
Region:
EASTERN CORNBELT
Crop: CORN

Koc:
ks:
0.01
kw:
0.05



FIGURE C. 8

$$
\begin{gathered}
\text { Region: } \\
\text { EASTERN CORNBELT }
\end{gathered}
$$

Crop:
CORN
Koc:
ks:
0.001
kw:
0.5




FIGURE C. 11
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
kw:
500
0.1
0.5


FIGURE C. 12
Region:
EASTERN CORNBELT
Crop:
Koc:
ks:
kw:
CORN
500
0.1
0.05



| FIGURE C. 14 | Region: | Crop: | Koc: | Ks: | Kw: |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  | EASTERN CORNBELT | CORN | 500 | 0.01 | 0.5 |



FIGURE C. 15
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.01
kw:
0.05






FIGURE C. 20
Region:
EASTERN CORNBELT
Crop:
Koc: 1500
ks:
kw:
0.5






FIGURE C. 25
Region:
EASTERN CORNBELT
Crop:
Koc:
1500
ks:
kw:
1.0


FIGURE C. 27
Region:
EASTERN CORNBELT
Crop:
Koc:
ks:
kw:
0.001
0.05






FIGURE C. 32
Region:
EASTERN CORNBELT
Crop:
Koc:
ks:
Kw:
5000
0.01
0.5



FIGURE C. 34
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.001
kw:
1.0




FIGURE C. 37
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
50
ks:
kw:
1.0







FIGURE C. 43
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
50
ks:
kw:
1.0


FIGURE C. 45
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
$\begin{array}{ll}\text { Koc: } & \text { ks: } \\ 50 & 0.001\end{array}$
KW:


FIGURE C. 46
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
0.1

Kw:
1.0






FIGURE C. 51
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
500
ks:
kw:
0.05


| FIGURE C. 52 | Region: | Crop: | Koc: | ks: | kw: |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | EASTERN CORNBELT | SOYBEANS | 500 | 0.001 | 1.0 |




FIGURE C. 54
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
Ks:
kw:
0. 05





$$
\text { FIGURE C. } 58
$$

Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
0.01
kw:
1.0


FIGURE C. 59
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
1500
ks:
kw:
0.5



FIGURE C. 61
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
1500
ks:
0.001
kw:



FIGURE C. 63
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
1500
ks:
kw:
0.001
0.05


FIGURE C. 64

$$
\begin{array}{cc}
\text { Region: } & \text { Crop: } \\
\text { EASTERN CORNBELT } & \text { SOYBEANS }
\end{array}
$$

Koc:
ks:
kw:
1.0


| FIGURE C. 65 | Region: | Crop: | Koc: | ks: | kw: |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | EASTERN CORNBELT | SOYBEANS | 5000 | 0.1 | 0.5 |




FIGURE C. 67
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
$5000 \quad 0.01$
kw:
1.0





FIGURE C. 71
Region:
Crop:
EASTERN CORNBELT
SOYBEANS
Koc: ks:
$5000 \quad 0.001$
kw:
0.5




FIGURE C. 74
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
kw:
50
0.1
0.5



FIGURE C. 76


Crop:
Koc:
ks:
kw:
EASTERN CORNBELT
CORN
50
0. 01
1.0







$\begin{array}{lcccll}\text { FIGURE C. } 83 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { EASTERN CORNBELT } & \text { CORN } & 500 & 0.1 & 0.5\end{array}$





FIGURE C. 87
Region:
EASTERN CORNBELT
Crop:
Koc:
ks:
kw: 500
0.01
0.05


FIGURE C. 88
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.001
kw:
500
1.0


FIGURE C. 89
Region:
EASTERN CORNBEL.T
Crop:
CORN
Koc:
ks:
0.001
kw:
500
0.5


FIGURE C. 90
Region:
EASTERN CORNBELT

Crop:
CORN
Koc: 500
ks:
kw:
0.05










FIGURE C. 99
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
1500
ks:
kw:
0.001
0.05



FIGURE C. 101
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
kw:
5000
0.1
0.5


$\begin{array}{lccccc}\text { FIGURE } C .103 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { kw: } \\ & \text { EASTERN CORNBELT } & \text { CORN } & 5000 & 0.01 & 1.0\end{array}$


FIGURE C. 104
Region:
EASTERN CORNBELT
Crop:
CORN
Koc: 5000
ks:
kw:
0.5


FIGURE C. 105
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
5000
ks:
kw:
-


FIGURE C. 106
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.001
kw:
5000
1.0


FIGURE C. 107
Region:
EASTERN CORNBELT
Crop:
CORN
Koc:
5000
ks:
kw:
0.001
0.5




FIGURE C. 110

$$
\begin{gathered}
\text { Region: } \\
\text { EASTERN CORNBELT }
\end{gathered}
$$

Crop:
SOYBEANS
Koc:
ks:
kw:
0.5


FIGURE C. 112
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT SOYBEANS }\end{array}$
Koc:
50
ks:
0.01
kw:
1.0


FIGURE C. 113
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
kw: 50
0.01
0.5




FIGURE C. 116

## $\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$

Koc:
ks:
0. 001

Kw:



FIGURE C. 118
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
kw:
1.0





FIGURE C. 122

## Region: <br> EASTERN CORNBELT <br> Crop: SOYBEANS

Koc:
ks:
$500 \quad 0.01$
kw:
0.5



FIGURE C. 124
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
500
ks:
kw:
1.0





FIGURE C. 128

## $\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$

Koc:
1500
ks:
kw:



FIGURE C. 130

Region: EASTERN CORNBELT

Crop:
SOYBEANS
Koc:
1500
ks:
kw:
01
1.0


FIGURE C. 131
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
1500
ks:
kw:
0.5


FIGURE C. 132
Region:
EASTERN CORNBELT
Crop:
SOYBEANS
Koc:
1500
ks:
kw:
0.05




FIGURE C. 135

## Region: EASTERN CORNBELT

Crop:
Koc: $1500 \quad 0.001$
kw:
0. 05



FIGURE C. 137
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { EASTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
5000
ks:
0.1
kw:
0.5







$\begin{array}{cccccc}\text { FIGURE C. } 144 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & & \text { EASTERN CORNBELT } & \text { SOYBEANS } & 5000 & 0.001\end{array}$


FIGURE C. 145
Region:
EASTERN CORNBELT
Crop:
CORN
ks:
0.1




FIGURE C. 148

Region:
EASTERN CORNBELT
Crop:
SOYBEANS
ks:
0.1




Region: WESTERN CORNBELT

| Crop: SOYBEA |  |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \text { ks } \\ \text { (per day) } \end{gathered}$ | 1.6 | 0.5 | 0.05 |
| 50 | 0.1 | D. 37 | D. 38 | D. 39 |
|  | 0.01 | D. 40 | D. 41 | D. 42 |
|  | 0.001 | D. 43 | D. 44 | D. 45 |
| 500 | 0.1 | D. 46 | D. 47 | D. 48 |
|  | 0.01 | D. 49 | D. 50 | D. 51 |
|  | 0.001 | D. 52 | D. 53 | D. 54 |
| 1500 | 0.1 | D. 55 | D. 56 | D. 57 |
|  | 0.01 | D. 58 | D. 59 | D. 60 |
|  | Ø. 0.1 | D. 61 | D. 62 | D. 63 |
| $5 \varnothing \square \varnothing$ | 0.1 | D. 64 | D. 65 | D. 66 |
|  | 0.01 | D. 67 | D. 68 | D. 69 |
|  | 0.001 | D. 70 | D. 71 | D. 72 |

TABLE D. 2 FIGURE MATRIX FOR PESTICIDE BED CONCENTRATION CURVES FOR CORN AND SOYBEANS IN THE WESTERN CORNBELT

## Region: WESTERN CORNBELT <br> Crop: CORN

| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ |  |  | kw (per day) |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \text { ks } \\ \text { (per day) } \end{gathered}$ | 1.6 | 0.5 | 0.05 |
| 50 | $\emptyset .1$ | D. 73 | D. 74 | D. 75 |
|  | Ø.01 | D. 76 | D. 77 | D. 78 |
|  | $\varnothing .0 \varnothing 1$ | D. 79 | D. 80 | D. 81 |
| $5 \varnothing \square$ | $\emptyset .1$ | D. 82 | D. 83 | D. 84 |
|  | 0.01 | D. 85 | D. 86 | D. 87 |
|  | Ø.øø1 | D. 88 | D. 89 | D. 90 |
| $150 \varnothing$ | $\emptyset .1$ | D. 91 | D. 92 | D. 93 |
|  | 0.01 | D. 94 | D. 95 | D. 96 |
|  | 0.001 | D. 97 | D. 98 | D. 99 |
| $50 \emptyset \square$ | 0.1 | D. 100 | D. 101 | D. 102 |
|  | 0.01 | D. 103 | D. 104 | D. 105 |
|  | Ø.øø1 | D. 106 | D. 167 | D. 108 |

## Region: WESTERN CORNBELT Crop: SOYBEANS

| $\begin{gathered} \mathrm{Koc} \\ (\mathrm{ml} / \mathrm{gm}) \\ \hline \end{gathered}$ | $\begin{gathered} \mathrm{ks} \\ \text { (per day) } \end{gathered}$ | 1.0 | 0.5 | 0.05 |
| :---: | :---: | :---: | :---: | :---: |
| $5 \varnothing$ | 0.1 | D. 109 | D.110 | D. 111 |
|  | 0.01 | D. 112 | D.113 | D. 114 |
|  | Ø.001 | D. 115 | D. 116 | D. 117 |
| $50 \square$ | $\emptyset .1$ | D. 118 | D. 119 | D. 120 |
|  | 0.01 | D. 121 | D. 122 | D. 123 |
|  | Ø.øØ1 | D. 124 | D. 125 | D. 126 |
| 1500 | $\emptyset .1$ | D. 127 | D. 128 | D. 129 |
|  | 0.01 | D. 130 | D. 131 | D. 132 |
|  | 0.001 | D. 133 | D. 134 | D. 135 |
| 5 5øø | 0.1 | D. 136 | D. 137 | D. 138 |
|  | 0.01 | D. 139 | D. 140 | D. 141 |
|  | Ø.øø1 | D. 142 | D. 143 | D. 144 |

# TABLE D. 3 FIGURE MATRIX FOR PESTICIDE LOADING CURVES FOR THE WESTERN CORNBELT 

Region: WESTERN CORNBELT

|  | ks (per day) |  |  |
| :---: | :---: | :---: | :---: |
| Crop | 0.1 | .01 | .001 |
| Corn | D. 145 | D. 146 | D. 147 |
| Soybeans | D. 148 | D. 149 | D. 150 |




| FIGURE D. | Region: | Crop: | Koc: | Ks: | Kw: |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | WESTERN CORNBELT | CORN | 50 | 0.1 | 0.5 |


FIGURE D. 3
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
$\mathrm{Ks}:$
0.1
kw:
0.05


FIGURE D. 5
WESTERN CORNBELT
Crop:
CORN
Koc: 50
ks:
0.01
kw:
0.5


FIGURE D. 6

## Region:

Crop:
Koc:
ks:
$50 \quad 0.01$
kw:
.05



FIGURE D. 8

## Region: <br> WESTERN CORNBELT <br> Crop:

Koc:
ks:
0.001
kw:
0.5

$\begin{array}{ccccccc}\text { FIGURE } & \text { R. } 9 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { WESTERN CORNBELT } & \text { CORN } & 50 & 0.001 & 0.05\end{array}$



| FIGURE | R. 11 | Region: | Crop: | Koc: | ks: |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | WESTERN CORNBELT | CORN | 500 | 0.1 |



| FIGURE | D. 12 | Region: | Crop: | Koc: | ks: |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | WESTERN CORNBELT | CORN | 500 | 0.1 | .05 |



| FIGURE D. 13 | Region: | Crop: | Koc: | Ks: | Kw: |
| :---: | :---: | :---: | :---: | :--- | :--- |
|  | WESTERN CORNBELT | CORN | 500 | 0.01 | 1.0 |



FIGURE D. 14
Region:
WESTERN CORNBELT
Crop:
CORN
Koc: 500
ks:
kw:
0.5







FIGURE D. 20
Region:
WESTERN CORNBELT
Crop:
CORN
Koc: 1500
ks:
Kw:
0.5




FIGURE D. 23
Region:
WESTERN CORNBELT
Crop:
Koc:
1500
ks:
kw:
0.5


FIGURE D. 24

## Region: WESTERN CORNBELT

Crop:
CORN
Koc:
ks:
kw:
0.05



FIGURE D. 26
Region:
WESTERN CORNBELT
Crop:
Koc:
1500
ks:
kw:
0.5


FIGURE D. 27
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks: 0.001
kw:
0.05


FIGURE D. 28
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.1
kw:
1.0







FIGURE D. 34
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.001
kw:
1.0


| FIGURE D. 35 | Region: | Crop: | Koc: | ks: | Kw: |
| :--- | :--- | :---: | :--- | :--- | :--- | :--- |
|  | WESTERN CORNBELT | CORN | 5000 | 0.001 | 0.5 |






FIGURE D. 39

## Region: <br> WESTERN CORNBELT SOYBEANS

Koc:
ks:
0.1
kw: 50
.05

$\begin{array}{cccccll}\text { FIGURE } & \text { D. } 40 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { ks: } & \text { kw: } \\ & \text { WESTERN CORNBELT } & \text { SOYBEANS } & 50 & 0.01 & 1.0\end{array}$


FIGURE D. 41
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
0.01
kw:


| FIGURE | D. 42 | Region: | Crop: | Koc: | ks: | kw: |
| :---: | :---: | :---: | :---: | :--- | :--- | :--- |
|  | WESTERN CORNBELT | SOYBEANS | 50 | 0.01 | .05 |  |






FIGURE D. 46
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$

| Koc: | ks: |
| :--- | :--- |
| 500 | 0.1 |

kw:
1.0





FIGURE D. 50
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
500
ks:
kw:
0.5


FIGURE D. 51
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT SOYBEANS }\end{array}$
Koc:
500
ks:
kw:
0.05



FIGURE D. 53
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
500
ks:
kw:
0.5


FIGURE D. 54
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
Ks:
0.001
kw:
0.05




| FIGURE | D. 57 | Region: | Crop: | Koc: | ks: | kw: |
| :---: | :---: | :---: | :---: | :---: | :---: | :--- |
|  | WESTERN CORNBELT | SOYBEANS | 1500 | 0.1 | .05 |  |





$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT }\end{array}$
Koc: 1500
ks: 0.001

Kw:
1.0


FIGURE D. 63
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
Kw:
CBEANS
1500
0.001
0.05




FIGURE D. 66
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
kw:
0.1
0.05



FIGURE D. 68

$$
\begin{array}{cc}
\text { Region: } & \text { Crop: } \\
\text { WESTERN CORNBELT } & \text { SOYBEANS }
\end{array}
$$

Koc:
ks:
kw:
5000
0.01
0.5


FIGURE D. 69
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
5000
ks:
kw:
0.05


FIGURE D. 70
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
kw:
5000
0.001
1.0




FIGURE D. 73
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
50
ks:
kw:
1.0



| FIGURE $\square_{0} 75$ | Region: | Crop: | Koc: ks: | Kw: |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | WESTERN CORNBELT | CORN | 50 | 0.1 | 0.05 |



FIGURE D. 76
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.01
kw:
而
50
-

$$
1.0
$$




FIGURE D. 78
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.01
kw: .05



FIGURE D. 80
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.001
kw:
50
0.5


FIGURE D. 81
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
kw:
0.05


FIGURE D. 82
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0. 1
kw:
500
1.0



| FIGURE | D. 84 | Region: | Crop: | Koc: | ks: |
| :---: | :---: | :---: | :---: | :---: | :---: |








FIGURE D. 90
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
Ks:
kw:
0.05


FIGURE D. 91
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
kw:
1500
0.1
1.0


FIGURE D. 92
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
kw:
0.5






| FIGURE | R. 97 | Region: | Crop: | Koc: |
| :---: | :---: | :---: | :---: | :--- |
|  | WESTERN CORNBELT | CORN | 1500 | 0.001 |



FIGURE D. 98
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.001
kw:
0.5







FIGURE D. 104
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
ks:
0.01
kw:
0.5




FIGURE D. 107
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
5000
ks: 0.001
kw:
0.5


FIGURE D. 108
Region:
WESTERN CORNBELT
Crop:
CORN
Koc:
Ks:
0.001
kw:
0.05


FIGURE D. 109

| Region: | Crop: |
| :---: | :---: |
| WESTERN CORNBELT | SOYBEANS |

Koc:
ks:
kw:
50
0.1
1.0



FIGURE D. 111
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
50
0.1
kw:
05




$\begin{array}{llllll}\text { FIGURE D. } 115 & \text { Region: } & \text { Crop: } & \text { Koc: } & \text { Ks: } & \text { Kw: } \\ & & \text { WESTERN CORNBELT } & \text { SOYBEANS } & 50 & 0.001\end{array}$


FIGURE D. 116
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
kw:
50
0.001
0.5




FIGURE D. 119
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
ks:
kw:
500
0.1
0.5





FIGURE D. 124
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
0.001
kw:
500
1.0







FIGURE D. 130
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
1500
ks:
0.01
kw:
1.0




FIGURE D. 133
$\begin{array}{cc}\text { Region: } & \text { Crop: } \\ \text { WESTERN CORNBELT } & \text { SOYBEANS }\end{array}$
Koc:
ks:
kw: 1500
0.001
1.0



FIGURE D. 135
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
1500
Ks:
0.001
kw:
0.05





| FIGURE D. 139 | Region: | Crop: | Koc: | ks: | Kw: |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: |
|  | WESTERN CORNBELT | SOYBEANS | 5000 | 0.01 | 1.0 |




FIGURE D. 141
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
5000
ks:
kw: 0.05


FIGURE D. 142
WESTERN CORNBELT
Crop:
Koc:
5000
ks:
kw:
1.0


FIGURE D. 143
WESTERN CORNBELT
Crop:
SOYBEANS
Koc:
5000
ks:
kw:
0.5








FIGURE D. 150
Region:
WESTERN CORNBELT
Crop:
SOYBEANS
ks:
0.001

APPENDIX E

# PESTICIDE CONCENTRATION AND RUNOFF FREQUENCY CURVES FOR THE CENTRAL PLAINS REGION 

 (INCOMPLETE)Frequency curves and pesticide loading data were not completed for the Central Plains agricultural region.

$$
\mathrm{E}-1
$$

APPENDIX F<br>STATISTICAL ANALYSIS OF TIME SERIES DATA

## F. 1 INTRODUCTION

The objective of environmental modeling is to mathematically represent real-world environmental systems so that we can then use the model to learn more about system behavior under both existing and alternative conditions.

However, when we simulate environmental systems we rarely match exactly what is observed. There are several possibilities for explaining these discrepancies (Young and Alward, 1983):

- There may be errors in the mathematical description of the real-world process (i.e., the model algorithms)
- There may be ercors in the observed measurements that have been made
- There may be errors in the input parameters or time series required to use the model

Figure F.l schematically shows where errors, or differences, can occur whenever model results are compared to field measurements from a natural system, such as a watershed. Similar to the categories listed above, Donigian (1982) has discussed the various types of errors that can occur in a model application, in terms of input errors. Whenever a measurement or observation is made, a potential source of error is introduced. Although these errors may be difficult to detect, users of the data should be informed of the potential uncertainty involved and consider these uncertainties during model application.

$$
\mathrm{F}-1
$$

In spite of these errors or differences, in the discussions which follow the observed phenomena are assumed to be perfectly measured and the sources of error rest with the model and its various inputs above. We will concern ourselves mainly with the analysis of simulated and observed time series to determine how well these two agree (i.e., goodness-of-fit) discounting any potential errors in the observed measurements. Goodness-of-fit tests can be used for a variety of purposes, including: to ascertain when our model calibration effort is good enough, and to ascertain if, given a good calibration, we can expect the model to perform well during another time period (verification).


Figure F.I Model versus natural systems: inputs, outputs, and errors (Donigian, 1982).

$$
\mathrm{F}-2
$$

## F.l.l Exposure Assessment and Time Series Analysis

In addition to providing a means of evaluating model performance, time series information is also used in this report as an integral part of an exposure assessment for toxic chemicals. An exposure assessment is a determination of the magnitude (concentration) of a toxicant to which an organism will be exposed over a given period of time (duration). The model produces a time series of toxicant concentrations in a specific medium (e.g., water, air, soil) such as appears in Figure F.2. The time series can be compared to a critical value of the concentration $y$ (this might be, for instance, the LC5ø value, i.e., concentration for 5 Ø\% mortality). This type of analysis easily shows if the criterion is exceeded and gives a qualitative feel for the severity of the exceedance state. If we determine how often it is at a particular level or within a specified range we can create a frequency distribution of the values of " $Y$ " (Figure F.2a). If, in addition, we choose any value of $y$ in figure $F .2 a$ and determine the area under the curve to the right of that value, we can plot Figure $F .2 b$, which is a cumulative frequency distribution of the toxicant concentration. In other words, it shows the chance that any given value "y" that we select will be exceeded. If our example time series is long enough, then the "chance" approaches the true "probability" that "y" will be exceeded.

Thus far, only the concentration to which the organism will be exposed has been discussed and nothing has been said concerning the duration of the event. If we take the same time series and impose a window of length $t_{c}$ on it at level $Y_{C}$ Figure $F .3$ ), and move it incrementally forward in time, we can make a statement concerning the toxicant concentration within the duration window. Normally, the average concentration


Time ( t )
Figure F. 2 Time series plot of toxicant concentration.


Figure F.2a Frequency distribution of toxicant concentrations.

$\begin{array}{ll}\text { Figure F.2b } & \begin{array}{l}\text { Cumulative fre- } \\ \text { quency distri- } \\ \text { bution of toxi- } \\ \text { cant concentra- } \\ \text { tions. }\end{array}\end{array}$


Figure F. 3 Time series of toxicant concentrations with moving average window of duration $t_{c}$.
within the window is used. The resulting cumulative frequency distribution shows the chance that the moving average of duration $t_{c}$ will exceed the critical value of " $y$ ", $y_{C}$. The moving average window should be the same length as that specified for $Y_{C}$. For instance, if the 48 -hour LC5ø is the criterion, a 48-hour moving window should be used to average the data in the simulated time series. The use of the moving window or averaging the time series allows us to compare both the concentration and duration against the standard.

The chance or probability that the moving average concentration exceeds the survival standard of a given species is the essence of the exposure assessment. This type of information provides an estimate of the risk taken in using this chemical under the conditions of the model simulation. .

In this manual we are discussing exposure from instream pesticide concentrations produced by pesticide runoff from fields. How, then, does this fit within the general framework
of an exposure assessment? Figure F. 4 demonstrates the relationship. The pesticide is introduced to the watershed system at the top of the figure. Precipitation events produce runoff and sediment transport events, which, at the field scale, are intermittent. That is, runoff and transport only occur during or immediately following rainfall (or snowmelt) events. The pesticide, either dissolved in water or attached to sediments, moves off the field into adjacent streams. In these streams, the dissolved pesticide may be diluted by uncontaminated water and pesticide attached to sediments may be deposit to the stream bed. In general, because of these mixing processes, the stream system produces a more continuous time series of concentrations, especially if the pesticide is not subject to. rapid degradation. It is these concentrations in the stream to which aquatic species or humans may be exposed, and therefore are used in the exposure assessment. Thus, pesticide runoff information must be linked with instream conditions in order to perform a complete exposure assessment.
F.I. 2 Choice of Method of Analysis

Goodness-of-fit techniques can be applied to a number of statistics derived from the observed and simulated time series. Aitken (1973) demonstrated several techniques of model analysis including mean, standard deviation, coefficient of determination ( $r^{2}$ ), coefficient of efficiency, serial correlation coefficients, sign tests and residual mass curve coefficients. Young and Alward (1983) used the coefficient of variation and the Kolmogorov-Smirnov test in determining goodness-of-fit of $A R M$ and NPS model calibrations. Chen et al. (1984) used student's $t$ and $F$ tests to test mean and variance, and the sign test, Kolmogorov-Smirnov (K-S test),


Figure F. 4 Schematic of natural systems which produce environmental time series of pesticide concentrations.

Pearson product-moment correlation coefficient, and the McCuen-Snyder index (McCuen and Snyder, 1975) to indicate goodness-of-fit.

The fact is that there are a number of tests which can be used to test differences in various aspects of two time series. No single test will be best for all circumstances; multiple tests statistics should be generated and analyzed. Goodness-of-fit tests should also be tailored to those aspects of the time series important to the problem at hand. For instance, if one is concerned with flooding, the tests should concentrate on peak flows; whereas if one is interested in dissolved oxygen, correct simulation of low flows would be most important.

Thus we are guided to the question, "Which variables and corresponding statistical tests should be used to evaluate the calibration of models for simulation of pesticide runoff?". Obviously volume of water is important purely from a dilution standpoint. Since pesticides are transported in runoff events from the watershed, peak storm flows are important. Because pesticides are partitioned between sediment and water, the simulation of sediment movement is also important. The simulation of peak flow, then, becomes increasingly important for strongly adsorbed pesticides since sediment transport, either from the land surface or instream, can be described as power functions of flow with exponents >l.ø. Proper simulation of velocity (or flow) is important for strongly adsorbed chemicals when the velocities are above the scour and deposition shear velocities of particles to which they are attached. For weakly adsorbed pesticides, sediment and hence peak flows should probably be deemphasized with proper simulation of runoff volumes given more attention. The key concept here is that the emphasis for analysis may shift depending upon pesticide properties. If we are interested in calibrating the hydrology and sediment transport model to

$$
F-8
$$

enable us to simulate pesticides with wide ranges of adsorption properties, it is important to simulate both flow rate (as well as velocity) and volumes properly, over the full range of watershed response.

In addition, models can be calibrated in the frequency or real time domains. That is, we can use tests to tell us if the frequency responses of the simulated and observed data are not different or if the point-to-point (real time) simulated and observed results are not statistically different.

Many times it is useful to compare the frequency with which events of certain magnitudes occur in both the observed and simulated model outputs. This is accomplished by grouping the data to intervals and counting the number of occurrences in each interval in the observed and simulated data sets.

The construction of frequency histograms is a relatively straight-forward procedure. Consider the flow data in Table F.l. Twenty-one intervals of 25 cfs each were established (Table F.2) and the number of flows in each of the intervals was counted. These counts appear in columns (3) and (4). The collective of these interval counts is called a frequency histogram. When the count in each interval is divided by the total number of occurrences in the histogram (cols. (7) and (8)) a relative frequency histogram results (i.e., the area under the histogram is unity). When these relative counts are summed over each interval a cumulative relative frequency histogram results. This cumulative histogram can be used in statistical testing of model simulation results. As the intervals become smaller, the cumulative histogram becomes a cumulative frequency distribution as shown in Figure F.2.

The Kolmogorov-Smirnov two-sample test is one that represents a more or less "holistic" comparison technique for observed
F-9

TABLE F.l INDEPENDENT OBSERVED AND SIMULATED FLOW TIME SERIES FOR THE ARROYO COLORADO AT WESLACO, TEXAS

| $S$ | 0 | $S$ | 0 | $S$ | 0 |
| ---: | :---: | :---: | :---: | :---: | :---: |
| 124.95 | 126. | 86.33 | 113. | 151.45 | 304. |
| 133.79 | 114. | 82.96 | 149. | 237.98 | 266. |
| 192.50 | 113. | 80.51 | 98.5 | 144.17 | 137. |
| 130.98 | 102. | 78.72 | 121. | 134.76 | 156. |
| 140.75 | 92.5 | 107.33 | 111. | 135.26 | 161. |
| 114.95 | 95.7 | 81.31 | 114. | 125.33 | 168. |
| 119.38 | 141. | 87.85 | 107. | 119.13 | 139. |
| 172.73 | 155. | 267.97 | 121. | 113.86 | 136. |
| 162.89 | 106. | 104.67 | 92.90 | 108.86 | 127. |
| 117.13 | 108. | 99.2 | 89.0 | 104.64 | 114. |
| 138.81 | 140. | 96.28 | 92.5 | 177.07 | 129. |
| 138.17 | 111. | 93.52 | 101. | 112.92 | 111. |
| 160.38 | 168. | 136.07 | 94.3 | 107.71 | 135. |
| 359.02 | 307. | 223.16 | 188. | 439.09 | 123. |
| 104.71 | 119. | 123.13 | 82.3 | 132.14 | 143. |
| 88.97 | 149. | 120.19 | 117. | 123.83 | 168. |
| 92.15 | 171. | 119.05 | 105. | 207.73 | 142. |
| 116.61 | 174. | 117.02 | 152. | 132.62 | 129. |
| 105.28 | 157. | 171.82 | 138. | 142.56 | 149. |
| 91.82 | 139. | 124.32 | 136. | 128.76 | 106. |
| 80.14 | 122. | 126.95 | 150. | 162.97 | 94.6 |
| 72.80 | 112. | 138.16 | 148. | 145.48 | 87.6 |
| 219.67 | 325. | 146.92 | 144. | 138.00 | 106. |
| 78.48 | 132. | 2465.2 | 1410. |  |  |
| 90.69 | 133. | 222.22 | 131. |  |  |

$\mathrm{s}=$ Simulated
0 O Observed

and simulated data (whereas the $t$-test, for instance, specifically tests the mean). It keys on the maximum difference between the cumulative frequency distributions of two data sets. Thus it considers mass of the distributions (i.e., volume) as well as the closeness of frequency response of the two distributions. Because of its generality, however, it tends to be an easy test to pass (Haan, 1977). That is, the probability of accepting the hypothesis that the two samples are drawn from the same population, when in fact it is false, is high. Thus the test should not be used by itself, but in conjunction with other statistics to derive conclusions in goodness-of-fit.
F-1l

If point-to-point simulation of observed values is important (e.g., timing of peaks and valleys), then a "real-time" approach, rather that one based purely on frequencies, must be taken. Regression analysis is a suitable tool for this for two reasons:

- It measures the point-to-point correlation between observed and simulated data, and
- tests are available for inference concerning the slope and intercept of the regression line.

It can also be used to give us information about the relative masses of the two samples since the mean of both enter into the calculations of the least squares method.

These two methods have been chosen for discussion as ways to test observed and simulated flow and sediment concentrations for model calibration purposes. However, there are some pitfalls in using these methods on time series data which should be avoided. These caveats are discussed in the following sections which also discuss the analysis of data and application of the tests.

While the value of statistics in calibration and verification is enormous, rigorous comparisons of time series data for these purposes have been largely neglected. Typically, the judgement of the modeler has been the key criteria in judging goodness-of-fit. What is advocated here is intelligent use of the tools available to us for making the judgement of "how-good-is-good." Certainly, the simulated and observed data should in every case be plotted and inspected visually. We can usually tell an "excellent" fit from an "atrocious" one. In the "atrocious" case, statistical measures may be of little value. However, when observed and simulated values are

$$
\mathrm{F}-12
$$

closer, statistical measures can be valuable in making the determination if changes in model parameters are actually "improving" the fit. Valuable time and effort can be wasted by trying to "perfect" the calibration.
F. 2 THE KOLMOGOROV-SMIRNOV TWO-SAMPLE TEST

The Kolmogorov-Smirnov two-sample test (K-S test) requires that cumulative frequency distributions be developed from the data. In our applications this data is almost always a time series, and is nearly always serially correlated to some extent. This fact requires some special preprocessing of the data before the $K-s$ test can be applied. This will be discussed later.

First, let us show how the $K-S$ two-sample test is used. The following discussion is taken from Siegel (1954).
"The Kolmogorov-Smirnov two-sample test is a test of whether two independent samples have been drawn from the same population (or from populations with the same distribution). The two-tailed test is sensitive to any kind of difference in the distributions from which the two samples were drawn - differences in location (central tendency), in dispersion, in skewness, etc. The one-tailed test is used to decide whether or not the values of the population from which one of the samples was drawn are stochastically larger than the values of the population from which the other sample was drawn.

This two-sample test is concerned with the agreement between two-cumulative distributions.

If the two samples have in fact been drawn from the same population distribution, then the cumulative distributions of both samples may be expected to be fairly close to each other, inasmuch as they both should show only random deviations from the population distribution. If the two-sample cumulative distributions are "too far apart" at any point, this suggests that the samples come from different populations. Thus a large enough deviation between the two-sample cumulative distributions is evidence for rejecting $H$ (i.e., the hypothesis of same distributions).

## Method

To apply the Kolmogorov-Smirnov two-sample test, we make a cumulative frequency distribution for each sample of observations, using the same intervals for both distributions. For each interval, then, we subtract one step function from the other. The test focuses on the largest of these observed deviations.

Let $S_{n_{1}}(X)=$ the observed cumulative step function of one ${ }^{l}$ of the samples, that is, $S_{n_{1}}(x)=K / n_{l}$, where $K=$ the number of scores equal to or less than $X$. And let $S_{n_{2}}(X)=K / n_{2}$. Now the Kolmogorov-Smirnov two-sample test focuses on:

$$
\begin{equation*}
D=\operatorname{maximum}\left[S_{n_{1}}(x)-s_{n_{2}}(x)\right] \tag{F.1}
\end{equation*}
$$

for a one-tailed test, and on:

$$
\begin{equation*}
D=\operatorname{maximum}\left|s_{n_{1}}(X)-s_{n_{2}}(X)\right| \tag{F.2}
\end{equation*}
$$

for a two-tailed test. The sampling distribution of $D$ is known and the probabilities associated with the occurrence of values as large as an observed $D$ under the null hypothesis (that the two samples have come from the same distribution) have been tabled.

Notice that for a one-tailed test, we find the maximum value of $D$ in the predicted direction [by equation $F$.l] and that for a two-tailed test we find the maximum absolute value of $D$ [by equation F.2], i.e., we find the maximum deviation irrespective of direction. This is because in the one-tailed test, $H_{1}$ is that the population values from which one of the samples was drawn are stochastically larger than the population values from which the other sample was drawn, whereas in the two-tailed test, $H_{l}$ is simply that the two samples are from different populations."

The analysis of data to produce a cumulative frequency distribution was discussed earlier.

One of the assumptions of the $K-S$ test is that observations within a sample are independent. The problem with applying the $K-S$ test to time series data is that, more often than not, this assumption is not met. This is due to the fact that most natural time series (e.g., flow, sediment concentrations, etc.) are serially correlated. This is especially true for larger watersheds where streamflow, sediment transport, etc. are continuous. Less serial correlation will be evident in data from smaller areas. In order to use a $K-S$ test, any serial correlation in the data must be removed from the sample.

$$
F-15
$$

## F.2.1 Tests for Serial Correlation

The way to detect serial correlation in a data set is to compute the Pearson product-moment correlation coefficient of each data point with its preceeding value, which is called the lag 1 serial- (or auto-) correlation coefficent and is denoted r(l). If the data sets are lagged again so that each data point is correlated with the second preceeding point then the lag 2 coefficient, $r(2)$, results. This process can be continued and serial correlation coefficients $r(k)$ can be computed (see Yevjevich, 1972, for a complete discussion). A plot of $r(k)$ versus $k$ is called a serial correlogram. An example is shown in Figure F.5.

Notice that generally the $r(k)$ decreases as $k$ increases until they hover close to or cycle around zero. Confidence limits (dashed lines) can be computed around zero. Once the correlation coefficients consistently fall inside these bands, we can say that they are statistically not different from zero for this sample size and confidence level (for computation limits see Anderson, l942, or Jenkins and Watts, 1969). In the example correlogram of Figure F.5, then, we can say that approximately every løth point (streamflow value for every 1øth day, in this case), is uncorrelated (i.e., independent). To apply the K-S test, then, these two time series could be sampled by taking every løth point and using this new series to form the cumulative distribution histograms.

While this method will virtually guarantee independence, others might also be tried. Another method would be to randomly sample each time series, in hopes of coming up with an independent subset of values. Another method would be to aggregate data and perform the test on monthly as opposed to daily data, for instance. While more aggregated series generally have less serial correlation, this method does not guarantee independence.

$$
F-16
$$

Maln Floodway at Weslaco


Figure F. 5 Serial correlogram of observed and simulated mean daily flow for the Main Floodway at Weslaco.

## F.2.2 Example Application

Data from the HSPF calibration of the Arroyo Colorado watershed in Texas (Dean et al., 1984) were used to construct the following example of the application of the $K-S$ test to serially correlated daily streamflow data.

From the serial correlogram in Figure F.5 it was noted that every løth point (or day) in both the simulated and observed time series is independent. Therefore the original two time series of $73 \varnothing$ values were sampled by selecting every løth value in each. The resulting independent subsets were shown in Table F.l.

Table F. 2 showed the frequency and cumulative frequency distributions of the observed and simulated independent series. The final column, |D\|, is the absolute difference between the observed and simulated cumulative frequency distributions. The maximum of these occurred in interval 4, therefore $D_{\max }=\varnothing .0822$. The value of $D$ at a 0.05 (5\%) probability level is calculated from:

$$
\begin{equation*}
\mathrm{D}_{0.05}=1.36 \sqrt{\frac{\mathrm{n}_{1}+\mathrm{n}_{2}}{\mathrm{n}_{1} \mathrm{n}_{2}}} \tag{F.3}
\end{equation*}
$$

where $n_{1}$ and $n_{2}$ are the respective sample sizes. In this case $n_{1}=n_{2}=73$, and the value of $D_{0.05}$ is calculated to be 0.225 . Thus, $D_{\max }>D_{0.05}$ and the distributions cannot be said to be drawn from different populations. This calculation of $D$ in the Kolmagorov-Smirnov two-sample test was obtained from Siegel (1954).

## F. 3 LINEAR REGRESSION ANALYSIS

Regression analysis involves the point-to-point comparison of an independent and dependent variable. This is accomplished by fitting a line through the $x, y$ pairs of data. The line is fit by minimizing the sums of squares of the deviations in the $y$-direction of each point from the best fit line. The line can be described by two parameters; a slope and a y-intercept. The model, of course, is:

$$
\begin{equation*}
y=\alpha+\beta x+\epsilon \tag{F.4}
\end{equation*}
$$

```
where \(y=\) dependent variable
    \(\alpha \quad=\quad y\)-intercept
    \(\beta=\) slope of the linear relationship
    \(\mathrm{x}=\) independent variable
    \(\epsilon=\) error
```

The method for determining the coefficients in equation $F .4$ can be found in a number of texts (Bhattacharyya and Johnson, 1977; Haan, 1977; Fischer, 1981) and are not presented here.

The major interest in applying regression analysis for the comparison of simulated and observed time series is to test the slope and intercept ( $\alpha$ and $\beta$ ) of the regression equation. The aim is to obtain an $\alpha$ not statistically different from zero and a $\beta$ not statistically different from l. Confidence in our inference about $\alpha$ and $\beta$ is enhanced, however, by knowing that the linear model is a good one and that the good fit is not just fortuitous. This can be done simply by visual inspection of the line plotted on a scattergram of the points. A more objective method is by computing the coefficient of determination from the data. This coefficient is computed by:

$$
\mathrm{F}-19
$$

$$
\begin{equation*}
r^{2}=1-\frac{s}{n s^{2} y} \tag{F.5}
\end{equation*}
$$

where $x^{2}=$ coefficient of determination $S \quad=$ sums of squares of the residuals (deviations in the $y$-direction from the best fit line) $n_{2}=$ total number of $x, y$ points $S_{y}=$ variance of the dependent $y$ variables

The coefficient of determination, $r^{2}$, can take on values between $\varnothing$ and $1 . \quad V a l u e s$ closer to $l$ indicate that the points are closer to the best fit line. In fact, the value of $r^{2}$ may be thought of as the fraction of the total variability in $y$ that is explained by the linear relationship. It should be noted that for simple bivariate ( $x, y$ ) regression, $r^{2}$ is identically the square of the pearson product moment correlation coefficient. However, for multiple regression (more than one independent variable) this is not the case (Fischer, 1981).

There are some special considerations for applying regression techniques to the problem of comparing two time series. Yevjevich (1972) states that the method of least squares only gives reliable estimates of $\alpha$ and $\beta$ if two conditions are met. First, the residuals must be independent and second, the variance of the residuals must not be a function of the independent variable $x$.

The first assumption is equivalent to saying that no time dependent or serial correlation exists among the residuals. This can easily be checked by the method of constructing a serial correlogram using the residuals.

The second assumption is referred to as homoscedasticity. If the scatter of the $x, y$ points around the regression line
tends to increase as the values of $x$ increase, then the assumption is violated. The easiest way of dealing with this problem is to transform the data so that the variance is approximately equal along the regression line. The regression analysis is then performed on the transformed data.

No further assumptions are required for assuming that the estimates of $\alpha$ and $\beta$ are unbiased. However, for the purposes of making inferences about the regression coefficients the distribution of the residuals around the regression line should be normal. Bhattacharyya and Johnson (1977) state that a moderate deviation from normality does not impair inference especially when the data set is large.

Given that these conditions are met, we can test $\alpha$ and $\beta$ to see if they meet the requirements for a good fit of the simulated to observed data.

## F.3.1 Significance Tests for $\alpha$ anci $\beta$

To test if $\beta$ is not significantly different from unity the $t$ statistic is computed:

$$
t=\frac{s_{x}(\beta-1)}{s}
$$

$$
\begin{equation*}
s_{x}=\sqrt{\Sigma x^{2}-n \bar{x}^{2}} \tag{F.7}
\end{equation*}
$$

where $\beta=$ least squares estimate of the scope

$$
\mathrm{F}-21
$$

$$
\begin{equation*}
s \quad=\sqrt{\left(s_{y}^{2}-\frac{s_{y}^{2}}{s_{x}^{2}}\right) /(n-2)} \tag{F.8}
\end{equation*}
$$

The value of $t$ can be compared to values of critical $t$ at some probability level with $\mathrm{n}-2$ degrees of freedom.

The parameter $\alpha=\emptyset$ can be tested by:

$$
\begin{equation*}
t=\frac{\alpha}{s \sqrt{\frac{1}{n}+\frac{x^{2}}{s_{x}^{2}}}} \tag{F.9}
\end{equation*}
$$

with n-2 degrees of freedom.
F.3.2 Example Regression Analysis

An example of the above procedures is provided below using the data from the Arroyo Colorado (Table F.l). The plotted data are shown in Figure F.6. From the plot it does not appear that there is necessarily an increasing variance with the level of the observed values. However, the grouping of most of the data at the $90-16 \emptyset$ cfs level, with only a few points at higher flows, may lead to some problems which will be discussed later. Notice that there is one point ( $x=141 \varnothing$, $y=2465.2$ ) that does not appear on the graph. From the least squares we derive the parameters:

$$
\begin{aligned}
& \alpha=94.06 \\
& \beta=1.71
\end{aligned}
$$

The $r^{2}$ value is $\varnothing .92$ indicating that the linear fit is good. It should be pointed out here that spurious (inflated

$$
\mathrm{F}-22
$$

estimates of correlation as evidenced by high values of 'r') correlation can arise out of the type of situation represented in Figure F.6, where most of the data is clustered except for a few outlying points. In fact, the reason that the slope is


Figure F. 6 Regression analysis of observed and simulated flows for the Arroyo Colorado.

$$
F-23
$$

so large is due to the influence of the ( $x, y$ ) pair (141ø, 2465). If this point were eliminated, the $r^{2}$ value would drop drastically but the slope may or may not be closer to unity. Haan (1977) provides a more in-depth discussion of spurious correlation.

Once the least squares line is defined it can be plotted on the scattergram and visually compared to the line of perfect agreement. These are also plotted in Figure F.6.

The residuals are tabulated in Table F.3. An autocorrelogram of the residuals is plotted in Figure F.7. The correlogram indicates that while one or two of the coefficients lie outside the $95 \%$ confidence band, on the whole the correlogram is well contained indicating an independent series.

The test for normality of the residuals is done as follows. We compute the frequency histogram of the residuals as shown in Table F.4. We then compute the mean and variance of the residuals and compute the standard normal deviate value of the upper end of the frequency class. The standard normal deviate is computed by:

$$
\begin{equation*}
z=\frac{e_{Y}-\bar{e}_{Y}}{s_{e}} \tag{F.10}
\end{equation*}
$$

where $\quad e_{y}=$ value of the upper limit of a frequency class

$$
\bar{e}_{\mathrm{Y}}=\text { mean of the residuals }
$$

$$
s_{e}=\text { standard deviation of the residuals }
$$

In this case $\bar{e}_{y}=-\emptyset .0111$ and $s_{e}=79.296$. Once the standard normal deviates are found, the cumulative area under the normal curve lying to the left of the SND can be found in

$$
\mathrm{F}-24
$$

TABLE F. 3 RESIDUAL OF REGRESSION OF ARROYO COLORADO SIMULATED AND OBSERVED STREAMFLOW ( $s-(\alpha+\beta \mathrm{O})$

| Data <br> Point \# | Residual | Data <br> Point \# | Residual | Data <br> point \# | Residual |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 3.26 | 26 | -13.10 | 51 | -275.02 |
| 2 | 32.65 | 27 | -78.11 | 52 | -123.43 |
| 3 | 93.07 | 28 | 5.09 | 53 | 3.65 |
| 4 | 50.39 | 29 | -34.41 | 54 | -38.30 |
| 5 | 76.42 | 30 | 11.33 | 55 | -46.36 |
| 6 | 45.14 | 31 | -19.83 | 56 | -68.27 |
| 7 | -27.99 | 32 | -1.30 | 57 | -24.82 |
| 8 | 1.39 | 33 | 154.84 | 58 | -24.45 |
| 9 | 75.45 | 34 | 39.66 | 59 | -14.54 |
| 10 | 26.26 | 35 | 40.87 | 60 | 3.50 |
| 11 | -6.85 | 36 | 31.95 | 61 | 50.24 |
| 12 | 42.17 | 37 | 14.64 | 62 | 16.92 |
| 13 | -33.22 | 38 | 68.66 | 63 | -29.39 |
| 14 | -72.59 | 39 | -4.69 | 64 | 322.54 |
| 15 | -4.99 | 40 | 76.27 | 65 | -18.66 |
| 16 | -72.10 | 41 | 13.91 | 66 | -69.77 |
| 17 | -106.59 | 42 | 33.32 | 67 | 58.65 |
| 18 | -87.27 | 43 | -49.19 | 68 | 5.80 |
| 19 | -69.49 | 44 | 29.58 | 69 | -18.51 |
| 20 | -52.13 | 45 | -14.49 | 70 | 41.32 |
| 21 | -34.70 | 46 | -35.83 | 71 | 45.05 |
| 22 | -24.92 | 47 | -21.20 | 72 | 89.54 |
| 23 | -242.76 | 48 | -5.59 | 73 | 50.56 |
| 24 | -33.48 | 49 | 144.95 |  |  |
| 25 | -42.98 | 50 | 91.97 |  |  |

Table F.5. Subtracting the cumulative probabilities, one can find the individual cell probabilities (column 4). Multiplication by the number of observations (73) gives the expected cell frequency.

The test for goodness-of-fit is Pearson's $\chi^{2}$. By using the formula below, the $\chi^{2}$ statistic can be found:

$$
\mathrm{F}-25
$$



TABLE F. 4 COMPUTATION OF THE $\chi^{2}$ STATISTIC FOR THE TEST OF NORMALITY OF RESIDUALS

|  | Cell No. | Range | Observed Frequency | standard Normal Deviate | Cumulative Normal Prob. | $\underset{\text { Probability }}{\text { Cell }}$ | Expected Frequency | $\frac{(0-E)^{2}}{E}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 | - $\infty$ to -100. | 4 | -1.261 | . 1038 | 0.1038 | 7.577 | 1.689 |
|  | 2 | -100 to -75. | 2 | -. 9458 | . 1736 | 0.0698 | 5.095 | 1.883 |
| N | 3 | -75 to -50. | 6 | -. 6305 | . 2643 | 0.0907 | 6.621 | 0.058 |
| $\checkmark$ | 4 | -50 to -25. | 11 | -. 3154 | . 3783 | 0.1140 | 8.322 | 0.861 |
|  | 5 | -25 to 0 | 15 | 0 | . 5 | 0.1217 | 8.88 | 4.497 |
|  | 6 | 0 to 25 | 10 | . 3154 | . 6217 | 0.1217 | 8.88 | 0.138 |
|  | 7 | 25 to 50 | 10 | . 6305 | . 7357 | 0.1140 | 8.322 | 0.336 |
|  | 8 | 50 to 75 | 5 | . 9458 | . 8264 | 0.0907 | 6.621 | 0.394 |
|  | 9 | 75 to 100 | 7 | 1.261 | . 8962 | 0.0698 | 5.095 | 0.715 |
|  | 10 | 100 | 3 |  | 1.000 | 0.1038 | 7.577 | $\underline{2.744}$ |

$$
\begin{equation*}
\chi^{2}=\sum_{i}^{k} \frac{\left(0_{i}-E_{i}\right)^{2}}{E_{i}} \tag{F.ll}
\end{equation*}
$$

where $\quad \begin{aligned} & O_{i}=\text { observed cell frequency } \\ & E_{i}=\text { expected cell frequency } \\ & k=\text { number of cells }\end{aligned}$
The $\chi^{2}$ statistic is shown in the table also. From Table F.6, which shows the percentage points of the $\chi^{2}$ distribution for $k-1$ degrees of freedom and $\varnothing . \emptyset 5$ probability, the $\chi^{2}$ value is 16.919. Therefore we cannot reject the hypothesis that the distribution of residuals is non-normal since our $\chi^{2}$ of 13.3 does not exceed the $\chi^{2}{ }_{9,0.05}$ value of 16.9 .

Since we have established that the residuals are independent and normally distributed we can perform the t-test to infer whether $\beta$ differs from unity and $\alpha$ differs from zero. From the computations we find that the t for $\beta$ is 11.14 and the $t$ for $\alpha$ is -6.75. From the $t$ tables (Table F.7) we can find critical values of $t$ at the $\varnothing .05$ probability level with $n-2$ (73) degrees of freedom. Since this value should be <l.6, we can conclude that the $\beta$ is different from unity and the $\alpha$ is different from zero. Thus the point-to-point correlation between our model and the observed data is imperfect.

## F. 4 FREQUENCY ANALYSIS FOR EXPOSURE ASSESSMENT

Frequency analysis for the performance of an exposure assessment is performed generally in the same way as in the example for flow frequency. However, for exposure assessment, duration, as well as the frequency of events, is important, as discussed in Section F.l.2. These concepts are clarified in the following example.

$$
F-28
$$

|  |  |  |  |  |  |  |  | $P[\%<2]$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | . 00 | . 01 | . 02 | . 03 | . 04 | . 05 | . 06 | . 07 | . 08 | . 09 |
| -3.5 | . 0002 | . 0002 | . 0002 | . 0002 | . 0002 | . 0002 | . 0002 | . 0002 | . 0002 | . 0002 |
| -3.4 | . 0003 | . 0003 | . 0003 | . 0003 | . 0003 | . 0003 | . 0003 | . 0003 | . 0003 | . 0002 |
| -3.3 | . 0005 | . 0005 | . 0005 | . 0004 | . 0004 | . 0004 | . 0004 | . 0004 | . 0004 | . 0003 |
| -3.2 | . 0007 | . 0007 | . 0006 | . 0006 | . 0006 | . 0006 | . 0006 | . 0005 | . 0005 | . 0005 |
| -3.1 | . 0010 | . 0009 | . 00009 | . 0009 | . 0008 | . 0008 | . 0008 | . 0008 | . 0007 | . 0007 |
| -3.0 | . 0013 | . 0013 | . 0013 | . 0012 | . 0012 | . 0011 | . 0011 | . 0011 | . 0010 | . 0010 |
| -2.91 | . 0019 | . 0018 | . 0018 | . 0017 | . 0016 | . 0016 | . 0015 | . 0015 | . 0014 | . 0014 |
| -2.8 | . 0026 | .0025 | . 0024 | . 0023 | . 0023 | . 0022 | . 0021 | . 0021 | . 0020 | . 0019 |
| -2.7 | . 0035 | . 0034 | . 0033 | . 0032 | . 0031 | . 0030 | . 0029 | . 0028 | . 0027 | . 0026 |
| -2.6 | . 0047 | . 0045 | . 0044 | . 0043 | . 0041 | . 0040 | . 0039 | . 0038 | . 0037 | . 0036 |
| -2.5 | . 0062 | . 0060 | . 0059 | . 0057 | . 0055 | . 0054 | . 0052 | . 0051 | . 0049 | . 0048 |
| -2.4 | . 0082 | . 0080 | . 0078 | . 0075 | . 0073 | . 0071 | . 0069 | . 0068 | . 0066 | . 0064 |
| -2.3 | . 0107 | . 0104 | . 0102 | . 0099 | . 0096 | . 0094 | . 0091 | . 0089 | . 0087 | . 0084 |
| -2.2 | . 0139 | . 0136 | . 0132 | . 0129 | . 0125 | . 0122 | . 0119 | . 0116 | . 0113 | . 0110 |
| -2.1 | . 0179 | . 0174 | . 0170 | . 0166 | . 0162 | . 0158 | . 0154 | . 0150 | . 0146 | . 0143 |
| -2.0 | . 0228 | . 0222 | . 0217 | . 0212 | . 0207 | . 0202 | . 0197 | . 0192 | . 0188 | . 0183 |
| -1.9 | \|. 0287 | . 0281 | . 0274 | . 0268 | . 0262 | . 0256 | . 0250 | . 0244 | . 0239 | . 0233 |
| -1.8 | . 0359 | . 0351 | . 0344 | . 0336 | . 0329 | . 0322 | . 0314 | . 0307 | . 0301 | . 0294 |
| -1.7 | . 0446 | . 0436 | . 0427 | . 0418 | . 0409 | . 0401 | . 0392 | . 0384 | . 0375 | . 0367 |
| -1.6 | . 0548 | . 0537 | . 0526 | . 0516 | . 0505 | . 0495 | . 0485 | . 0475 | . 0465 | . 0455 |
| -1.5 | . 0668 | . 0655 | . 0643 | . 0630 | . 0618 | . 0606 | . 0594 | . 0582 | . 0571 | . 0559 |
| -1.4 | . 0808 | . 0793 | . 0778 | . 0764 | . 0749 | . 0735 | . 0721 | . 0708 | . 0694 | . 0681 |
| -1.3 | . 0968 | . 0951 | . 0934 | . 0918 | . 0901 | . 0885 | . 0869 | . 0853 | . 0838 | . 0823 |
| -1.2 | . 1151 | . 1131 | . 1112 | . 1093 | . 1075 | . 1056 | . 1038 | . 1020 | . 1003 | . 0985 |
| -1.1 | . 1357 | . 1335 | . 1314 | . 1292 | . 1271 | . 1251 | . 1230 | . 1210 | . 1190 | . 1170 |
| -1.0 | . 1587 | . 1562 | . 1539 | . 1515 | . 1492 | . 1469 | . 1446 | . 1423 | . 1401 | . 1379 |
| -. 9 | \| 1841 | . 1814 | . 1788 | . 1762 | . 1736 | . 1711 | . 1685 | . 1660 | . 1635 | . 1611 |
| -. 8 | 2119 | . 2090 | . 2061 | . 2033 | . 2005 | . 1977 | . 1949 | . 1922 | . 1894 | . 1867 |
| -. 7 | . 2420 | . 2389 | . 2358 | 2327 | 2297 | . 2266 | 2236 | 2206 | 2177 | 2148 |
| -. 6 | . 2743 | 2709 | . 2676 | 2643 | 2611 | 2578 | . 2546 | 2514 | . 2483 | 2451 |
| -5 | 3085 | . 3050 | . 3015 | . 2981 | . 2946 | . 2912 | . 2877 | . 2843 | . 2810 | . 2776 |
| -. 4 | . 3446 | . 3409 | . 3372 | 3336 | . 3300 | . 3264 | 3228 | 3192 | 3156 | 3121 |
| -. 3 | . 3821 | . 3783 | 3745 | . 3707 | . 3669 | . 3632 | . 3594 | . 3557 | . 3520 | . 3483 |
| -. 2 | . 4207 | . 4168 | . 4129 | . 4090 | . 4052 | . 4013 | 3974 | . 3936 | 3897 | . 3859 |
| -. 1 | . 4602 | . 4562 | . 4522 | . 4483 | . 4443 | . 4404 | . 4364 | . 4325 | . 4286 | . 4247 |
| -. 0 | . 5000 | . 4960 | . 4920 | . 4880 | . 4840 | . 4801 | . 4761 | . 4721 | . 4681 | . 4641 |

(continued)

$$
F-29
$$

| 2 | . 00 | . 01 | . 02 | . 03 | . 04 | . 05 | . 06 | . 07 | . 08 | . 09 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| . 0 | . 5090 | . 5040 | . 5080 | 5120 | . 5160 | . 5199 | . 5239 | . 527 | . 5319 | . 535 |
| . 1 | . 5398 | . 5438 | . 5478 | . 5517 | . 5557 | . 5596 | . 5636 | . 5675 | . 5714 | . 5753 |
| 2 | . 5793 | . 5832 | . 5871 | . 5910 | . 5948 | 5987 | . 6026 | . 6064 | . 6103 | 41 |
| 3 | . 6179 | . 6217 | . 6255 | . 6293 | . 6331 | . 6368 | . 6406 | . 6443 | . 6480 | . 6517 |
| . 4 | . 6554 | . 6591 | . 6628 | . 6664 | . 6700 | . 6736 | . 6772 | . 6808 | . 6844 | . 6879 |
| 5 | . 6915 | . 6950 | . 6985 | . 7019 | . 7054 | . 7088 | . 7123 | . 7157 | 7190 | . 7224 |
| . 6 | . 7257 | . 7291 | . 7324 | . 7357 | . 7389 | . 7422 | . 7454 | . 7486 | 7517 | 7549 |
| . 7 | . 7580 | 7611 | . 7642 | . 7673 | . 7703 | . 7734 | . 7764 | . 7794 | . 7823 | . 7852 |
| . 8 | .7881 | 7910 | . 7939 | . 7967 | . 7995 | . 8023 | .8051 | . 8078 | . 8106 | 8133 |
| . 9 | . 8159 | . 8186 | . 8212 | . 8238 | . 8264 | . 8289 | . 8315 | . 8340 | . 8365 | 9 |
| 1.0 | . 8413 | . 8438 | . 8461 | . 8485 | . 8508 | . 8531 | . 85 | . | . 8 | 8621 |
| 1.1 | . 8643 | . 8665 | . 8686 | . 8708 | . 8729 | . 8749 | . 8770 | . 8790 | . 8810 | 8830 |
| 1.2 | . 8849 | . 8869 | . 8888 | . 8907 | . 8925 | . 8944 | . 8962 | . 8980 | . 8997 | . 9015 |
| 1.3 | . 9032 | . 9049 | . 9066 | . 9082 | . 9099 | . 9115 | . 9131 | . 9147 | . 9162 | . 9177 |
| 1.4 | . 9192 | . 9207 | . 9222 | . 9236 | . 9251 | . 9265 | . 9279 | . 9292 | . 9306 | . 9319 |
| 1.5 | . 9332 | . 9345 | . 9357 | . 9370 | . 9382 | . 9394 | . 9406 | . 9418 | . 9429 | . 9441 |
| 1.6 | . 9452 | . 9463 | . 9474 | . 9484 | . 9495 | . 9505 | . 9515 | . 9525 | 953 | 9545 |
| 1.7 | . 9554 | . 9564 | . 9573 | . 9582 | . 9591 | . 9599 | . 9608 | . 9616 | . 9625 | . 9633 |
| 1.8 | . 9641 | . 9649 | . 9656 | . 9664 | . 9671 | . 9678 | . 9686 | . 9693 | . 9699 | . 9706 |
| 1.9 | . 9713 | . 9719 | . 9726 | . 973 | . 9738 | . 9744 | . 9750 | . 9756 | . 9761 | . 9767 |
| 2.0 | . 9772 | . 9778 | . 9783 | . 9788 | . 9793 | . 9798 | . 9803 | . 9808 | . 9812 | . 9817 |
| 2.1 | . 9821 | . 9826 | . 9830 | . 9834 | . 9838 | . 9842 | . 9846 | . 9850 | . 9854 | . 9857 |
| 2.2 | . 9861 | . 9864 | . 9868 | . 9871 | . 9875 | . 9878 | . 9881 | . 9884 | . 9887 | 9890 |
| 2.3 | . 9893 | . 9896 | . 9898 | . 9901 | . 9904 | . 9906 | . 9909 | . 9911 | . 9913 | . 9916 |
| 2.4 | . 9918 | . 9920 | . 9922 | . 9925 | . 9927 | . 9929 | . 9931 | . 9932 | . 9934 | . 9936 |
| 2.5 | . 9938 | . 9940 | . 9941 | . 9943 | . 9945 | . 9946 | . 9948 | . 9949 | . 9951 | . 9952 |
| 2.6 | . 9953 | . 9955 | . 9956 | . 9957 | . 9959 | . 9960 | . 9961 | . 9962 | . 9963 | . 9964 |
| 2.7 | . 9965 | . 9966 | . 9967 | . 9968 | . 9969 | . 9970 | . 9971 | . 9972 | . 9973 | . 9974 |
| 2.8 | . 9974 | . 9975 | . 9976 | . 9977 | . 9977 | . 9978 | . 9979 | . 997 | . 9980 | . 9981 |
| 2.9 | . 9981 | . 9982 | . 9982 | . 9983 | . 9984 | . 998 | . 9985 | . 9985 | . 9986 | . 9986 |
| 3.0 | . 9987 | . 9987 | . 9987 | . 9988 | . 9988 | . 9989 | . 9989 | . 9989 | . 9990 | . 9990 |
| 3.1 | . 9990 | . 9991 | . 9991 | . 9991 | . 9992 | . 9992 | . 9992 | . 9992 | . 9993 | . 9993 |
| 3.2 | . 9993 | . 9993 | . 9994 | . 9994 | . 9994 | . 9994 | . 9994 | . 9995 | . 999 | . 9995 |
| 3.3 | . 9995 | . 9995 | . 9995 | . 9996 | 6.9996 | . 9996 | . 9996 | . 9996 | . 9996 | . 9997 |
| 3.4 | . 9997 | . 9997 | . 9997 | . 9997 | . 9997 | . 9997 | . 9997 | . 9997 | 7. 9997 | . 9998 |
| 3.5 | . 9998 | . 9998 | . 9998 | . 9998 | . 9998 | . 9998 | . 9998 | . 9998 | . 9998 | . 9998 |

$$
F-30
$$

TABLE F. 6 PERCENTAGE POINTS OF $\mathrm{X}^{2}$ DISTRIBUTIONS

| $\text { d.f. }{ }^{\alpha}$ | . 995 | . 990 | . 975 | . 950 | . 050 | . 025 | . 010 | . 005 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $392704 \times 10^{-10}$ | $157088 \times 10^{-9}$ | $982069 \times 10^{-9}$ | $393214 \times 10^{-8}$ | 3.84146 | 5.02389 | 6.63490 | 7.87944 |
| 2 | . 0100251 | . 0201007 | . 0506356 | . 102587 | 5.99147 | 7.37776 | 9.21034 | 10.5966 |
| 3 | . 0717212 | . 114832 | . 215795 | . 351846 | 7.81473 | 9.34840 | 11.3449 | 12.8381 |
| 4 | 206990 | . 297110 | . 484419 | . 710721 | 9.48773 | 11.1433 | 13.2767 | 14.8602 |
| 5 | . 411740 | . 554300 | . 831211 | 1.145476 | 11.0705 | 12.8325 | 15.0863 | 16.7496 |
| 6 | . 675727 | . 872085 | 1.237347 | 1.63539 | 12.5916 | 14.4494 | 16.8119 | 18.5476 |
| 7 | . 989265 | 1.239043 | 1.68987 | 2.16735 | 14.0671 | 16.0128 | 18.4753 | 20.2777 |
| 8 | 1.344419 | 1.646482 | 2.17973 | 2.73264 | 15.5073 | 17.5346 | 20.0902 | 21.9550 |
| 9 | 1.734926 | 2.087912 | 2.70039 | 3.32511 | 16.9190 | 19.0228 | 21.6660 | 23.5893 |
| 10 | 2.15585 | 2.55821 | 3.24697 | 3.94030 | 18.3070 | 20.4831 | 23.2093 | 25.1882 |
| 11 | 2.60321 | 3.05347 | 3.81575 | 4.57481 | 19.6751 | 21.9200 | 24.7250 | 26.7569 |
| 12 | 3.07382 | 3.57056 | 4.40379 | 5.22603 | 21.0261 | 23.3367 | 26.2170 | 28.2995 |
| 13 | 3.56503 | 4.10691 | 5.00874 | 5.89186 | 22.3621 | 24.7356 | 27.6883 | 29.8194 |
| 14 | 4.07468 | 4.66043 | 5.62872 | 6.57063 | 23.6848 | 26.1190 | 29.1413 | 31.3193 |
| 15 | 4.60094 | 5.22935 | 6.26214 | 7.26094 | 24.9958 | 27.4884 | 30.5779 | 32.8013 |
| 16 | 5.14224 | 5.81221 | 6.90766 | 7.96164 | 26.2962 | 28.8454 | 31.9999 | 34.2672 |
| 17 | 5.69724 | 6.40776 | 7.56418 | 8.67176 | 27.5871 | 30.1910 | 33.4087 | 35.7185 |
| 18 | 6.26481 | 7.01491 | 8.23075 | 9.39046 | 28.8693 | 31.5264 | 34.8053 | 37.1564 |
| 19 | 6.84398 | 7.63273 | 8.90655 | 10.1170 | 30.1435 | 32.8523 | 36.1908 | 38.5822 |
| 20 | 7.43386 | 8.26040 | 9.59083 | 10.8508 | 31.4104 | 34.1696 | 37.5662 | 39.9968 |
| 21 | 8.03366 | 8.89720 | 10.28293 | 11.5913 | 32.6705 | 35.4789 | 38.9321 | 41.4010 |
| 22 | 8.64272 | 9.54249 | 10.9823 | 12.3380 | 33.9244 | 36.7807 | 40.2894 | 42.7956 |
| 23 | 9.26042 | 10.19567 | 11.6885 | 13.0905 | 35.1725 | 38.0757 | 41.6384 | 44.1813 |
| 24 | 9.88623 | 10.8564 | 12.4011 | 13.8484 | 36.4151 | 39.3641 | 42.9798 | 45.5585 |
| 25 | 10.5197 | 11.5240 | 13.1197 | 14.6114 | 37.6525 | 40.6465 | 44.3141 | 46.9278 |
| 26 | 11.1603 | 12.1981 | 13.8439 | 15.3791 | 38.8852 | 41.9232 | 45.6417 | 48.2899 |
| 27 | 11.8076 | 12.8786 | 14.5733 | 16.1513 | 40.1133 | 43.1944 | 46.9630 | 49.6449 |
| 28 | 12.4613 | 13.5648 | 15.3079 | 16.9279 | 41.3372 | 44.4607 | 48.2782 | 50.9933 |
| 29 | 13.1211 | 14.2565 | 16.0471 | 17.7083 | 42.5569 | 45.7222 | 49.5879 | 52.3356 |
| 30 | 13.7867 | 14.9535 | 16.7908 | 18.4926 | 43.7729 | 46.9792 | 50.8922 | 53.6720 |
| 40 | 20.7065 | 22.1643 | 24.4331 | 26.5093 | 55.7585 | 59.3417 | 63.6907 | 66.7659 |
| 50 | 27.9907 | 29.7067 | 32.3574 | 34.7642 | 67.5048 | 71.4202 | 76.1539 | 79.4900 |
| 60 | 35.5346 | 37.4848 | 40.4817 | 43.1879 | 79.0819 | 83.2976 | 88.3794 | 91.9517 |
| 70 | 43.2752 | 45.4418 | 48.7576 | 51.7393 | 90.5312 | 95.0231 | 100.425 | 104.215 |
| 80 | 51.1720 | 53.5400 | 57.1532 | 60.3915 | 101.879 | 106.629 | 112.329 | 116.321 |
| 90 | 59.1963 | 61.7541 | 65.6466 | 69.1260 | 113.145 | 118.136 | 124.116 | 128.299 |
| 100 | 67.3276 | 70.0648 | 74.2219 | 77.9295 | 124.342 | 129.561 | 135.807 | 140.169 |

From "Biometrika Tables for Statisticians," Vol. 1, (3rd Edition) Cambridge University Press (1966); Edited by E. S. Pearson and H. O. Hartley.

$$
\mathrm{F}-31
$$



$$
F-32
$$

Consider the time series of chemical concentrations in Table F.8. A plot of this data is shown in Figure F.8. We want to compute a 24 -hour duration frequency distribution to compare to the 24 hour LC5 for a certain species.

First, we want to compute the 24 -hour moving average concentration time series, from the original series. The formula is:

$$
\overline{\mathrm{X}}(\mathrm{~m})=\sum_{\mathrm{m}+\mathrm{i}-1}^{\mathrm{m}+\mathrm{n}-1}\left(\mathrm{X}_{\mathrm{i}} / \mathrm{n}\right) \quad, \mathrm{m}=1, \ldots \mathrm{~N}-\mathrm{n}+1
$$

where $\bar{X}(m)=$ moving average of the variable $X_{i}$ in the $m$ th interval
$\mathrm{n}=$ length of the moving average window
$\mathrm{N}=$ total number of observations

Table F.9 is constructed by taking the averages of values 1through 24, then 2 through 25,3 through 26 , etc. in Table F.8. Once these moving averages have been determined, a frequency histogram can be constructed. This is done by selecting a number of intervals of equal concentration ranges and counting the occurrence of values within each interval. To be sure to include all the data, the highest or lowest values are found. From Table F.9 these values are found to be $10 \varnothing .57$ and 190.21.

We will round our highest and lowest values to $2 ø \varnothing$ and $1 \varnothing \varnothing$ for the purpose of constructing the histogram. We then divide this range into $1 \varnothing$ intervals, or any other suitable integer, giving us ranges for each interval of $1 \varnothing \varnothing$ to $11 \varnothing, 11 \varnothing+$ to $12 \emptyset$, $120+$ to $13 \varnothing$, etc. Counting the occurrences of the 24 -hour moving average values in each interval gives the histogram of Table F.l0. The relative frequency is found by dividing the

$$
F-33
$$

TABLE F. 8 HYPOTHETICAL VALUES OF CHEMICAL VERSUS TIME (hrs)

| Time | Concentration | Time | Concentra |
| ---: | ---: | ---: | ---: |
|  |  |  |  |
| 1 | 0.0 | 23 | 289.0 |
| 2 | 0.1 | 24 | 240.0 |
| 3 | 0.2 | 25 | 198.0 |
| 4 | 0.2 | 26 | 120.0 |
| 5 | 0.6 | 27 | 110.0 |
| 6 | 0.8 | 28 | 95.0 |
| 7 | 1.5 | 29 | 86.0 |
| 8 | 16.0 | 30 | 40.0 |
| 9 | 21.0 | 31 | 38.0 |
| 10 | 20.0 | 32 | 60.0 |
| 11 | 26.0 | 33 | 120.0 |
| 12 | 28.0 | 34 | 94.0 |
| 13 | 140.0 | 35 | 30.0 |
| 14 | 160.0 | 36 | 28.0 |
| 15 | 171.0 | 37 | 25.0 |
| 16 | 420.0 | 38 | 13.0 |
| 17 | 431.0 | 39 | 4.0 |
| 18 | 430.0 | 40 | 2.0 |
| 19 | 410.0 | 41 | 1.0 |
| 20 | 409.0 | 42 | 0.6 |
| 21 | 411.0 | 43 | 0.0 |
| 22 |  | 44 | 0.0 |

number of occurrences in each category by the total number of occurrences. The cumulative relative frequency is then determined by summing the relative frequency incrementally for each interval.

A plot of the cumulative frequency is shown in Figure F.9. It is interpreted as follows:

$$
F-34
$$

The ordinate for interval 7, for instance, is the accumulation of the frequencies of all values less than or equal to $17 \varnothing$. Therefore, we can say that, in this sample, there is a 33\% chance that the 24 -hour moving average concentration is less than or equal to 179 . Conversely, there is a 67\% chance that the 24 -hour moving average concentration exceeds 170 . Since the data are taken on equal time intervals, it can also be said that $67 \%$ of the time the 24 -hour average concentration exceeds l7ø. This statement cannot be made if the data are unequally spaced.

If we further suppose that the 24 -hour LC5Ø for this chemical is $18 \emptyset$ then we can make a statement concerning the exceedence of this criteria. In this case, the chance is about 38\%.


Figure F. 8 Time series of chemical concentrations in Table F.8.

$$
F-35
$$

TABLE F. 9 24-HOUR MOVING AVERAGES OF THE DATA IN TABLE F. 8

| Interval | Average |
| :---: | ---: |
| 1 | 152.52 |
| 2 | 160.76 |
| 3 | 165.76 |
| 4 | 170.34 |
| 5 | 174.29 |
| 6 | 177.85 |
| 7 | 179.48 |
| 8 | 181.00 |
| 9 | 182.83 |
| 10 | 186.96 |
| 11 | 190.04 |
| 12 | 190.21 |
| 13 | 190.21 |
| 14 | 189.79 |
| 15 | 184.50 |
| 16 | 178.00 |
| 17 | 170.96 |
| 18 | 153.50 |
| 19 | 135.57 |
| 20 | 117.65 |
| 21 | 100.57 |

F. 5 REFERENCES FOR APPENDIX F

Aitken, A.P. 1973. Assessing Systematic Errors in RainfallRunoff Models. Journal of Hydrology. 20:121-136.

$$
F-36
$$

TABLE F. 10 FREQUENCY HISTOGRAM OF 24 -HOUR MOVING AVERAGE CONCENTRATIONS INCLUDING RELATIVE AND CUMULATIVE FREQUENCY HISTOGRAMS

| Interval | Range | Number of Occurences | Relative Frequency | Cumulative <br> Relative <br> Frequency |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 100. to 110. | 1 | 0.0476 | 0.0476 |
| 2 | 110.+ to 120. | 1 | 0.0476 | 0.0952 |
| 3 | 120.t to 130. | 0 | 0.0 | 0.0952 |
| 4 | $130 .+$ to 140. | 1 | 0.0476 | 0.1428 |
| 5 | $140 .+$ to 150. | 0 | 0.0 | 0.1428 |
| 6 | 150.+ to 160. | 2 | 0.0952 | 0.2380 |
| 7 | $160 .+$ to 170. | 2 | 0.0952 | 0.3332 |
| 8 | 170.+ to 180. | 6 | 0.2857 | 0.6189 |
| 9 | 180.+ to 190. | 5 | 0.2381 | 0.8570 |
| 10 | 190.+ to 200. | 3 | 0.1429 | 0.9999 |

Anderson, R.L. 1942. Distribution of the Serial Correlation Coefficients. Annals of Mathematical Statistics. 8(1): 1-13.

Bhattacharyya, G.K. and R.A. Johnson. 1977. Statistical Concepts and Methods. John L. Wiley and Sons, N.Y.

Chen, C.W., S.A. Ghereni, J.D. Dean, R.J.M. Hudson and R.A. Goldstein. 1984. Development and Calibration of the Integrated Lake-Watershed Acidification Study Model. In: Modeling of Total Acid Precipitation Impacts. J.L. Schnoor, ed. Acid Precipitation Series, Vol. 9. J.I. Teasley, ed. Butterworth Publishers.


$$
\begin{aligned}
\text { Figure F.9 } & \text { Plot of cumulative relative frequency of } \\
& \text { 24-hour moving averages of the concentra- } \\
& \text { tion data in Table F.8. }
\end{aligned}
$$

Dean, J.D., D.W. Meier, B.R. Bicknell, and A.S. Donigian. 1984. Simulation of DDT Transport and Fate in the Arroyo Colorado Watershed, Texas. Draft Report. Prepared for U.S. EPA, Athens, GA.

Donigian, A.S. Jr. 1982. Field Validation and Error Analysis of Chemical Fate Models. In: Modeling the Fate of Chemicals in the Aquatic Environment. K.L. Dickson, A.W. Maki, and J. Cairns Ed. Ann Arbor Science, Ann Arbor, MI. pp. 3ø3-323.

Fischer, W.D. 1981. Statistics Economized. University Press of America. Washington, D.C.

Haan C.T. 1977. Statistical Methods in Hydrology. Iowa State University Press, Ames, IA.

Jenkins, G.M. and D.G. Watts. 1969. Spectral Analysis and Its Applications. Holden Day Co., San Fransisco, CA.

MCCuen, R.H. and W.M. Snyder. 1975. A Proposed Index for Computing Hydrographs. Water Resources Research. 11(6): 1ø21-1ø24.

Seigel, S. 1954. Nonparametric Statistics for the Behavioral Sciences. McGraw-Hill Book Co., NY.

Yevjevich, V. 1972. Probability and Statistics in Hydrology Water Resources Publications. Fort Collins, CO.

[^5]$$
\mathrm{F}-39
$$


[^0]:    FIGURE A. 8

[^1]:    FIGURE A. 105

[^2]:    FIGURE A. 117

[^3]:    FIGURE A. 119

[^4]:    FIGURE A. 144

[^5]:    Young, G.K. and C.L. Alward. 1983. Calibration and Testing of Nutrient and Pesticide Transport Models. In: Agricultural Management and Water Quality. F.W. Schaller and G.W. Bailey, eds. Iowa State University Press, Ames, IA. du.S. Government PRinting office: 1986/646-116/20790

