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MODELING PESTICIDE FATE AND TRANSPORT IN SOILS

BY
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ABSTRACT

The work presented in this thesis represents a contribution to the area of modeling of the transport and fate of herbicides applied to cropped fields, and was part of a larger research effort geared towards better management of herbicides. The main objective of this thesis was to develop a graphical user interface (GUI) for PESTFADE, a process-based mathematical model of pesticide transport and degradation, and to provide documentation for the execution of PESTFADE. The model simulates changes in pesticide concentration at different depths in the soil, based on relevant physical, chemical, biological and meteorological factors. PESTFADE is considered to be one of the most comprehensive models of its kind. However, it was, until now, difficult to implement due to absence of a user manual and graphical interface suitable for exploitation in a Windows environment. The author developed the GUI in Visual Basic, created macros to facilitate certain calculations, rewrote the original FORTRAN 77 code and then validated the updated version against field data obtained from an experimental site (Eugene Whelan Farm, Woodslea, Ontario). A preliminary development of an artificial neural network (ANN) to perform the same simulation implicitly, with fewer input parameters and less computational time, was also done.

The thesis describes PESTFADE and the GUI, gives guidelines for implementing the package, and presents the results of the field validation of the revised version. During this work, the author discovered that there were problems in the parts of the code dealing with sorption phenomena. This can be solved by conventional kinetics or by Gamble kinetics.

Using both methods, modifications made by this author significantly improved the correspondence between field measured and simulated pesticide concentrations. The field validation led to the conclusion that there is no clear advantage to using Gamble kinetics. These results cast some doubt on earlier conclusions that PESTFADE does not perform well in wet years. It is therefore suggested that the new version be further validated against earlier data from wet years.

The ANN development seemed to indicate that an adequate architecture for modeling pesticide concentration in the soil involves a back-propagation algorithm. The lowest RMS error was obtained with this architecture among 149 others tested. However, further work is needed to assess the generality of this architecture to other pesticides and on other sites.

Another suggestion for further work that arises from this study is to compare the ANN and PESTFADE simulations for several different sites.

RESUME

Le sujet de ce mémoire présente une contribution à la modélisation du transport et comportement des herbicides utilisés en agriculture. Cette contribution s'instaure au sein d'un projet de recherche sur le développement de meilleures pratiques de gestion des pesticides. L'objectif principal de ce mémoire était de développer une interface graphique pour PESTFADE, un outil de modélisation mathématique du transport et de la dégradation de pesticides et de fournir la documentation nécessaire à l'exécution de PESTFADE. Le modèle simule les changements dans les concentrations de pesticides à différentes profondeurs du profil de sol, considérant les composantes physiques, chimiques, biologiques et atmosphériques pertinentes. On considère PESTFADE comme étant l'un des outils les plus compréhensifs en son genre, bien qu'il fut jusqu'à maintenant difficile à implanter en raison de l'absence d'un guide d'utilisation et d'une interface graphique appropriée à l'exploitation du logiciel sur environnement Windows. L'auteur a développé l'interface graphique en Visual Basic, a créé des macro-commandes pour faciliter certains calculs et a réécrit le code FORTRAN 77 d'origine pour ensuite valider la mise à jour au moyen de données de terrain obtenues d'un site expérimental (Ferme Eugene Whelan, Woodslea, Ontario). L'auteur a de plus assuré le développement préliminaire d'un réseau de neurones artificiels permettant implicitement la même simulation tout en utilisant moins de paramètres cela en offrant un temps plus rapide de procédure de calcul.

Cet ouvrage décrit PESTFADE et l'interface graphique en exposant les directives nécessaires à l'implantation du logiciel. Au cours du développement, l'auteur a été

confronté à quelques problèmes présents au sein des codes exposant les propriétés de sorption qui peuvent être résolues grâce à la cinétique conventionnelle ou encore grâce à la cinétique de Gamble. Les modifications apportées par l'auteur ont sensiblement amélioré la correspondance entre les mesures de concentration de pesticides au champ et celles obtenues par l'une et l'autre des méthodes se basant sur les propriétés de sorption. La validation des résultats au champs permet d'affirmer qu'il ne semble pas y avoir d'avantages à utiliser la cinétique de Gamble. Ces résultats sèment le doute sur d'autres études affirmant que PESTFADE ne performe pas bien pour les analyses performées sur les années humides. On suggère donc de valider à nouveau la nouvelle version en utilisant des résultats préalablement obtenus lors d'années humides.

Le développement du réseau de neurones artificiels semble indiquer qu'une architecture appropriée à la modélisation de concentration de pesticides dans le sol implique un algorithme de rétropropagation. Il s'agit de l'architecture qui a permi de générer la plus basse erreur moyenne quadratique parmi les 149 autres testées. Par ailleurs, d'autres travaux sont nécessaires afin de d'évaluer la performance de cette architecture pour d'autres pesticides et pour d'autres sites. Une autre suggestion serait de comparer la performance de simulation du réseau de neurones et de PESTFADE pour plusieurs sites différents.

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I wish to dedicate this piece of work to my parents

Rahmatollah and Parvaneh

whose unique way of parental care and guidance

had left a Legacy of Righteousness,

closeness and Success to all

their Three Children,

and my husband

Hassan

for his understanding and support

with invigorating messages across the miles,

and my son

Kiarash.

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CHAPTER III

NOMENCLATURE

A Field or watershed area (ha)

C Solute solution concentration (mg/L)

CN Curve Number in the Runoff equation

$\mathbf{C_{At}}$ Sorption sites occupied by Atrazine (mole/L soil slurry)

$\mathbf{C_c}$ Sorption capacity (mole/L soil slurry)

$\mathbf{C_{OC}}$ Unoccupied site (mol/L)

$\mathbf{C_P}$ Sorption sites occupied by pesticide (mol/L)

$\mathbf{C_t}$ Soil cover factor in the Erosion equation

D Hydrodynamic dispersion coefficient (cm^2/day)

$\mathbf{D_A}$ Diffusion coefficient in air (cm^2/day)

$\mathbf{D_s}$ Effective diffusion coefficient (cm^2/day)

$\mathbf{H_L}$ Chemical soil half-life (days) at the corresponding soil temperature [ST(^oK)]

$\mathbf{H_T}$ Half-life at corresponding soil temperature (days)

k First order rate constant for degradation (per day)

$\mathbf{K_d}$ Soil distribution (sorption coefficient (cm^3/g)

$\mathbf{K_e}$ Soil erodibility factor in the Erosion equation (ton/ha-yr)

$\mathbf{K_H}$ Henry's Law constant in the Freundlich equation

$\mathbf{K_P}$ Pesticide sorption equilibrium function (L/mol)

$\mathbf{K_{r2}}$ First order rate constant for Atrazine (per day)

LS Length-slope (topographic) factor in the erosion equation

$\mathbf{M_P}$ Pesticide molarity (mol/L)

$\mathbf{P_r}$ Total pesticide remaining at the soil surface (g/ha)

$\mathbf{P_t}$ Pesticide level at the soil surface (g/ha)

$\mathbf{PQ_t}$ Dissolved phase pesticide loss in runoff (g/ha)

$\mathbf{PX_t}$ Solid phase pesticide loss in runoff (g/ha)

q Darcy flux (theta*v) (cm/day)

$\mathbf{q_t}$ Peak runoff rate (m^3/s)

$\mathbf{Q_t}$ Storm runoff (cm)

$\mathbf{Q_v}$ Diffusive flux for chemical volatilization (g/cm^2-day)

R	Retardation factor for the chemical in the soil
$\mathbf{R_t}$	Storm rainfall (cm)
S	Total mass of solute adsorbed (μg/g soil)
SP	Support factor in the Erosion equation
$\mathbf{S_t}$	Soil retention parameter (cm)
$\mathbf{S_l}$	Amount of chemical sorbed (g/g)
t	Time (days)
$\mathbf{t_{1/2}}$	Half-life (days)
V	Pore water velocity (cm/day)
$\mathbf{V_t}$	Runoff volume (m^3)
x	Distance along flow path (cm)
α	First-order degradation rate constant in the liquid phase
β	First-order degradation rate constant in the solid phase
δ_s	Surface soil film thickness (cm)
δ_a	Atmospheric film thickness (cm)
γ	Zero-order rate constant in the liquid phase
θ	Soil volumetric water content (cm^3/cm^3)
ρ	Soil dry bulk density (g/cm^3)
ϕ	Sink term for volatilization and degradation (μg/g)
ϕ_{chm}	Sink term for chemical degradation (μg/g)

CHAPTER I

INTRODUCTION

Pesticides are a group of chemically diverse control agents which are grouped together mainly on the basis of a common use. By their very nature, most pesticides create some risk of harm to humans, animals, or the environment because they are designed to kill or otherwise adversely affect living organisms. At the same time, pesticides are useful to society because of their ability to kill pathogens and to control insects, weeds, and other pests. The vital role these synthetic organic chemicals play in maintaining or increasing crop productivity and yields is well recognized. However, because of their varying persistence, leaching and dissipation characteristics in soils and ground water, there is an urgent need to assess, quantify and predict their toxicity levels and behavior in agro-ecosystems. Field investigations and extensive research during the past two decades have shown that the environment in general, and aquatic ecosystems in particular, have been affected by recalcitrant pesticides whose residual levels significantly exceeded tolerable limits (Cohen et al., 1986).

In the last two decades, there has been an unprecedented increase in the use of pesticides and fertilizers. Between 1970 and 1989, the global use of fertilizers has almost doubled (Brown, 1989). Fertilizers and pesticides have been detected in both shallow and deep groundwater aquifers (Warner, 1990). A 1990 study by the United States Environmental Protection Agency (USEPA) highlighted the presence of 74 pesticides in the ground water of 38 states. Atrazine, a herbicide that is heavily used on corn and soybeans,

suburban lawns and utility right-of-ways, shows up in alarming regularity in water supplies. Such levels of occurrence must be considered to be a serious hazard to human health, since over 50% of the US population relies on groundwater as a source of drinking water. There is also widespread occurrence of agricultural pesticides in surface and drainage water (Lal and Stewart, 1994). In Canada, federal and provincial government agencies have been mandated to assess the fate of pesticides in subsurface waters and to enact regulations designed to protect Canada's ground water from pesticide contamination. Since it would be extremely expensive, in terms of equipment, human resources and laboratory analysis, to set up a nationwide network to monitor the pesticide levels in groundwater, there has been substantial interest in developing models permitting the prediction of pesticide transport and fate in the environment, in Canada and elsewhere.

An effective pesticide modeling technology should contain validated algorithms for transport and transformation of pesticides, extensive databases of agro-ecosystem scenarios (crop and soil properties, meteorology, limnology, fish community ecology), and graphical user interfaces to maximize the ease of production and interpretation of complex, highly detailed probabilistic analyses. Models, once deemed sufficiently reliable, can be very cost-effective compared to extensive field and laboratory work. They can then also be used to generate data for implicit models, such as artificial neural networks or decision trees, which offer advantages in computer time and resources, for approximately the same level of reliability of prediction.

At least 15 simulation models, incorporating the major physical, chemical and biological processes involved in pesticide transportation and degradation, have been developed since 1975. They include, in chronological order: ACTMO (Frere et al., 1975), ARM (Donigian and Crawford, 1976; Donigian et al., 1977), CREAMS (Knisel, 1980), FEMWASTE (Yeh and Ward, 1981), SESOIL (Bonazountas and Wagner, 1984), PRZM (Carsel et al., 1984, 1985), PESTAN (Donigian and Rao, 1986),GLEAMS (Leonard et al., 1987), LEACHM (Wagenet and Hutson, 1987), VULPEST (Villenueve et al., 1987), RUSTIC (Dean et al., 1989), and PESTFADE (Clemente et al., 1991). However, none of these satisfy all the requirements of an effective pesticide modeling technology. In particular, none have graphical user interfaces, many are incomplete, and even the most complete to date, PESTFADE, has not been validated sufficiently.

Over the last twenty years, an alternative kind of computer model has gained recognition for its potential at solving complex problems implicitly, with far less input parameters and significantly lower computation time. These are artificial neural networks (ANNs). ANNs have been applied successfully to image recognition problems (Schmoldt et al., 1997, Yang et al., 2000, Timmermans et al., 1996) and agro-environmental applications (Wang et al., 1999). However, ANNs are most useful when the input parameters have been previously optimized prior to training and validation (Timmermans et al., 1996, Wang et al., 1999). Although one of the drawbacks of ANNs is that they are usually site-specific, it should be possible to extend the range of application by training it with data from diverse sources. Given that explicit models, such as PESTFADE, can generate data

for many different scenarios, they could be used to generate input/output data for training ANNs for this application.

PESTFADE is a modular pesticide transport model that was developed at McGill University by Clemente (1991). Li et al. (1999) modified the sorption component of this model based on laboratory data. The model is unique in terms of the following: unsaturated flow phenomena, sub-irrigation or controlled drainage systems, macropore flow, different agricultural management practices, new methods of predicting adsorption-desorption and chemical-microbial degradation, and predictions under both undrained and subsurface-drained farmlands in arid, semi-arid, or humid regions. However, the model was written in FORTRAN, has no proper user manual other than the thesis by Clemente(1991), and has no interactive user-interface. Thus, only those who were familiar with the code are able to run PESTFADE effectively. Given the importance of the impact of pesticides on the environment, as well as the need to provide an effective tool for research on pesticide transport and degradation, it was decided to make major modifications to the PESTFADE model.

1.1 Objectives

Thus, the main objective of this thesis was to develop a graphical user interface (GUI) for PESTFADE. This also involved revamping the original code (written in FORTRAN 77), improving the simulation grids for several modules, revalidating the modifications with field data. New macros were developed to facilitate the retrieval of output data from

generated files, as well as to improve the simulation by generating a tighter simulation grid. Efforts were also made to develop a back-propagation ANN model to predict pesticide concentrations at different depths and times.

1.2 Organization of the Thesis

The thesis has been organized into five chapters. Chapter 1 begins with an introduction to the importance of computer modeling in assessing pesticide pollution of groundwater and surface water resources. Chapter 2 is a literature review of studies conducted in this area and a description of the PESTFADE model, its structure, the phenomena simulated, and the equations behind the model, as well as the features that make it unique. Chapter 3 explains the development of the GUI for PESTFADE. Chapter 4 describes the field experimentation and measurements and details the steps taken for the field validation of PESTFADE. Chapter 5 describes the development of an ANN model to predict pesticide concentrations throughout the soil profile.

1.3 Scope

The model validation was done for only one specific site with one soil type. Further testing and validation must be done to fully ensure the model's reliability. The ANN model was developed with data from the same site and hence may not prove to be useful for other sites.

CHAPTER II

REVIEW OF LITERATURE

The use of pesticides in farming and other applications is associated with the risk of contamination of non-target sites or organisms, and more often than not, with the contamination of water resources. There are many processes involved in the transport of pesticides from the sites of application to non-target sites, as well as in the breakdown of these chemicals into non-toxic by-products. The reliability of models simulating pesticide transport and fate depends on how well these many processes have been described mathematically, on how well weather conditions may be predicted, and on how well the system at risk has been parameterized.

This literature review is therefore divided into 4 major sections. The first section reviews pesticide transport and the breakdown processes in the environment. The second section reviews simulation models for pesticide transport and fate, with particular emphasis on PESTFADE. The third section reviews the use of artificial neural networks (ANNs) and the final section is devoted to the importance of graphical user interfaces (GUI's).

The potential hazard from pesticides depends on the toxicity of the particular chemical and of its progressive breakdown products, on the method of application of the pesticide, and on the quantities applied in a given area, all relative to the conditions leading to the transport and breakdown of the active substance. The fate of a pesticide is affected by such factors as volatility and/or drift, method of application, type of formulation, soil and

plant characteristics, solubility of the pesticide, adsorption on soil or plant surfaces, persistence of the pesticide, and climatic conditions. Research suggests that the movement of pesticides in the environment is complex and that they are transferred between various media (air, soil, water, biota). However, this does not mean that all pesticides are mobile or threaten ground water (http://www.epa.gov/ . Date 24.05.2000).

Solutions to the water contamination problems caused by herbicide and nutrient use in agriculture are not simple and require an interdisciplinary and multifaceted approach (Gaynor et al., 2001). An understanding of these processes can help ensure that pesticide applications are not only effective, but also environmentally safe.

2.1 Pesticide Transfer

Pesticide transfer is sometimes essential for pest control. For example, to be effective, certain pre-emergence herbicides must move within the soil to reach the germinating weed seeds. However, excessive movement can move a pesticide away from the target plants. This can lead to reduced pest control, injury of non-target species including humans, and contamination of surface water and groundwater. Under field conditions, the variations in soil structure cause water transport to vary significantly both laterally and vertically (Beven and Germann, 1982; Jury and Sposito, 1985). The major transport mechanisms are: **volatilization**, **runoff, leaching**, **uptake**, **crop removal**, and **adsorption**.

2.1.1. Volatilization

Volatilization is the loss of chemical in vapor form from soil, plant and water surfaces into the atmosphere. Once volatilized, a pesticide can move in air currents away from the treated surface. Adsorption, water content, soil organic matter and soil chemical properties influence volatilization (Clemente, 1991). Environmental factors such as high temperature, low relative humidity and air movement tend to increase volatilization. A pesticide tightly adsorbed to soil particles is less likely to volatilize. Soil conditions, such as texture, organic matter content, and moisture content, can influence the volatilization of pesticides. Formulations can also help reduce volatilization. Granular and wettable powders are less susceptible to volatilization than emulsions and soluble powders (http://ohioline.osu.edu/b820/b820_3.html. Date: 08.05.2000).

The airborne movement of pesticides to non-target areas is commonly called "drift" and may damage other crops, livestock, humans and beneficial insects. The main factors responsible for drift are the wind velocity and the spraying equipment. Applying chemical pesticides on a windy day with poorly adjusted equipment (pump pressure, droplet size, spray height, choice of nozzles, etc.) can lead to an excessive amount of pesticide material not reaching the ground and being carried away to a non-intended location. Pesticides can also volatilize more rapidly into the atmosphere from the surface where they have been applied under high wind conditions. The accidental dumping or spillage of pesticides during mixing and filling operations or during transport, the emptying out of pesticides from application equipment and cleaning up after use, greatly

increase the chance of these materials ending up in ground or surface waters and into the atmosphere.

The diffusion-based form of volatilization loss can be expressed by the following equation (Wagenet and Hutson, 1989):

$$\mathbf{Q_V = - (K_H * D_A * D_S * C_{1L}) / (D_S * \delta_a + K_H * D_A * \delta_S)} \quad \mathbf{[2.1]}$$

where:

Q_V = diffusive flux (mg/mm^2-d)

C_{1L} = the aqueous concentrations of the chemical at the first soil compartment ($\mu g/mL$)

δ_S = thickness of the surface soil film of thickness (mm)

δ_a = thickness of the stagnant atmospheric film of thickness (mm)

D_S = effective diffusion coefficient in the surface soil segment (mm^2/d)

D_A = diffusion coefficient in air (mm^2/d)

K_H = Henry's constant

In this approach, the pesticide, present at a certain aqueous concentration at the first soil compartment (C_{1L}), is considered to diffuse through a surface soil film of thickness, δ_S, and a stagnant atmospheric film of thickness, δ_a, to the atmosphere whose concentration (C_A) is assumed to be zero. It is also assumed that steady state diffusion prevails, so that the diffusive flux (Q_V) can be considered equal through the soil and air films (Clemente et al., 1993).

2.1.2. Management Practices / Runoff

Runoff is the movement of water over a sloping surface. Runoff occurs when water is applied to the soil surface at a faster rate than it can enter the soil. Runoff water can carry pesticides in the water itself, as well as those bound to eroding soil particles (http://ohioline.osu.edu/b820/b820_3.html. Date: 08.05.2000).

Tillage systems, farming practices, crop rotation, and erosion control using diversions and terraces are some of the agricultural management practices that affect the movement of water and chemicals on the land surface, through the soil profile, and into the ground water (Clemente et al., 1993). Conservation tillage has been proven to reduce the surface loading of sediments and chemicals from agricultural lands (Bailey and Wadell, 1979). Similar conclusions have been drawn concerning the no-till strategy (Triplett et al., 1978; Shirmohammadi et al., 1988).

Gaynor et al. (1987, 1998) found that atrazine and metalochlor persist for a longer time in tillage ridges than in tillage valleys due to the lower moisture content of the ridges. Ghadiri et al. (1984), found that there was no difference in the half-life of atrazine in conventionally tilled and untilled plots of an acidic soil. Nevertheless, Bauman and Ross (1983) found there was a greater concentration of atrazine residue in surface soil of no-till plot than in the surface soils of conventional-tilled and chisel-plowed plots after five years of application.

No-till increases infiltration of rainfall because of greater crop residue on the surface, which reduces runoff velocity (Unger, 1990; Locke and Bryson, 1997). Higher water content in no-till may reduce soil temperatures (Stone et al., 1989). In consequence, chemical and microbial degradation rates are lower and the pesticide persists for a longer time. The increase in herbicide persistence in no-till may predispose this cultural practice to increased probability of surface and groundwater impairment (Gaynor et al., 2000). Herbicides with high water solubility and low affinity for soil will leach deeper into the profile in no-till than in conventional tillage systems (Isensee et al., 1990; Sadeghi and Isensee, 1992). Controlled drainage, coupled with conservation tillage and subirrigation, effectively reduces nitrate losses and increases crop yield (Drury et al. 1996). The greater herbicide residues associated with moldboard plowing are reflected by higher concentration in surface runoff and tile drainage (Gaynor et al., 2000).

Soil saver tillage combined with a ryegrass intercrop decreased total herbicide loss in runoff by 49% due to the associated reduction in runoff, compared to moldboard plowing Gaynor et al. (2001). Intercropping corn with ryegrass and banding the herbicides has been suggested as a best management strategy for optimizing runoff and tile drain water quality (Gaynor et al., 2001).

Runoff depth can be calculated using the U.S. Soil Conservation Service (US SCS) Curve Number Method (USDA, 1972).

$$Q_t = (R_t - 0.2S_t)^2 / (R_t + 0.8S_t), \quad R_t > 0.2S_t \qquad [2.2]$$

where:

Q_t = storm runoff (cm)

R_t = storm rainfall (cm)

S_t = a retention parameter (cm) related to soil moisture and Curve Number (CN)

= (25400 / CN) – 254

Soil Loss can be simulated using the Modified Universal Soil Loss Equation (Wischmeier and Smith, 1978).

$$\mathbf{X_t = (11.8 / A) * (V_t * q_t)^{0.56} * K_e * (LS) * C_t * SP} \qquad \mathbf{[2.3]}$$

where:

A = field area (ha)

V_t = runoff volume (m^3) given by 100 AQ_t

q_t = peak runoff rate (m^3/s)

K_e = standard soil erosion factor

LS = topographic factor

C_t = cover factor

SP = supporting factor

Pesticide partitioning in runoff can be estimated as follows (Clemente, 1991):

$$\mathbf{P_r = P_t - PX_t - PQ_t} \qquad \mathbf{[2.4]}$$

where:

P_r = total pesticide remaining in the top 10 mm soil layer after the rainstorm (g/ha)

P_t = pesticide level in the surface 10 mm (g/ha)

PX_t = solid phase pesticide loss in runoff (g/ha)

PQ_t = loss of dissolved pesticide in runoff (g/ha)

2.1.3. Leaching

Leaching refers to the lateral and/or vertical transport of chemicals to ground water that results from the movement and redistribution of water within the soil profile after irrigation or rainfall events. During the flow, however, the solute is subjected to a series of interactions, i.e., degradation, adsorption, volatilization and plant uptake that ultimately determine its fate (Clemente et al., 1993). The degree of adsorption depends on the interaction between the surface chemistry of the pesticide and that of the soil particles, the latter being due to soil texture, organic matter content, moisture content and pH of the soil water solution.

There are two modes of leaching: micropore and macropore flow. Micropore flow is associated with an ideal soil matrix where the bulk density may be considered to be homogeneous and devoid of macropores. Hillel (1980, 1982) defined macropores as inter-aggregate cavities and micropores as intraggregate capillaries. The demarcation between these two terms is often arbitrary and ambiguous (Dullien, 1992; Hillel, 1982; Skopp, 1981; Perret, 1998). Nevertheless, water percolation can be greatly accentuated by the presence of macropores in the soil (Bouma, 1981; Chen et al., 1993; Dipietro and Lafolie, 1991; Li and Ghodrati, 1994; Logsdon, 1995; Moore et al., 1986; Quinsenberry et al., 1994; Singh et al., 1991; Timlin et al., 1994; Li et al., 1994, Perret, 1998). The total

downward flux of water applied at the surface is the sum of micropore and macropore flows. Macropore flow has also been termed as finger or funnel flow (Gish et al., 1991; Kung, 1993; Rice et al., 1991; Edwards et al., 1993).

Pesticide leaching can also be influenced by the method and rate of application; the use of tillage systems that modify soil conditions; and the amount and timing of water an area receives after application. The closer the time of application is to a heavy or sustained rainfall, the greater the likelihood that some pesticide leaching will occur.

2.1.4. Uptake

Uptake is the movement of pesticides into plants and animals. Pesticide absorption by target and non-target organisms is influenced by environmental conditions and by the chemical and physical properties of both the pesticide and the soil. Once absorbed by plants, pesticides may be broken down or may remain inside the plant until non-harvested tissue decay, after which they are susceptible to transport and degradation processes. Pesticides that are translocated to edible tissues then represent a health hazard to the human consumer and to animals (http://ohioline.osu.edu/b820/b820_3.html. Date: 08.05.2000).

Detailed physical aspects of root water uptake studies by Philip (1957), Gardner (1960), Cowan (1965), and Newman (1969) are examples of a microscopic approach in which roots are viewed as discrete organs and consider radial flow of water into a single root.

Gardner (1960) considered a single root to be a hollow infinitively long cylinder of uniform radius with uniform water absorbing properties. This model can be extended to an entire (uniform) root system (Gardner, 1960; and Gardner and Ehlig, 1962).

2.1.5. Crop Removal

Crop removal transfers pesticides and their breakdown products from the treatment site. Most harvested food commodities are subjected to washing and processing procedures that remove or degrade much of the remaining pesticide residue. Although harvesting is more typically associated with food and feed products, it is easy to forget that pesticides can be transferred during such operations as pruning of trees and shrubs and mowing of turfgrass (http://ohioline.osu.edu/b820/b820_3.html. Date: 08.05.2000).

2.1.6. Pesticide Sorption

Retention, commonly known as adsorption, is the soil's ability to hold or retain the pesticide on its surface. Adsorptive bonding decreases the mobility of chemicals in the soil to an extent that depends on the solubility of the chemical, its adsorption/desorption characteristics and on the soil texture and chemical status (Walker, 1987, 1991). Several soil characteristics affect the adsorption rate of a pesticide. Adsorption of herbicides has been related to soil carbon content and soil texture (Chesters et al., 1989; LeBaron et al., 1988; Sharom and Stevenson 1976). Soil-pesticide interactions varies with soil properties such as clay, organic matter content, pH, moisture content, cation exchange capacity, and

temperature (Talbert and Fletchall, 1965). Adsorption often occurs because of the attraction between a chemical and soil or organic particles. Adsorption affects the pesticide's ability to be transported.

Soils high in organic matter or clay are more adsorptive than coarse sandy soils. This is in part due to their greater particle surface areas and partly due to surface charges on the particles. Soil moisture also influences adsorption. Wet soils tend to adsorb less pesticide than dry soils because water molecules compete with the pesticide for the binding sites on soil particles. Pesticides may adsorb onto plant materials such as litter in no-till or minimum-till fields, the bark of trees, or thatch in turf. These organic layers may prohibit pesticide movement to target areas deeper in the soil. Pesticides vary in their tendency to adsorb to soil particles according to their chemical structures and formulations. Some pesticides, such as paraquat and glyphosate, bind very tightly, while others bind weakly and are readily desorbed to the soil solution (http://www.nhq.nrcs.usda.gov/land/meta/m2084.html. Date: 23.04.2000).

The mobility of a particular herbicide in soil depends, in part, upon its adsorption-desorption characteristics and solubility (Walker, 1987, 1991). Herbicides with high water solubility and low affinity for soil move with the water front, increasing the risk of ground water contamination or transport through tile drainage (Gaynor et al., 2001).

There is a growing body of evidence that indicates that pesticide sorption involves two distinct processes: extractable and non-extractable sorption (Li et al., 1996). Extractable

pesticide residues are those that may be extracted using conventional organic solvents, such as methanol. Non-extractable or bound residues can only be desorbed by special techniques such as radio-labeling or supercritical fluid extractions (Li et al., 1996; Li et al., 1999). Non-extractibles are the result of chemical mechanisms such as covalent bonding, or physical mechanisms such as diffusion into dead-end pores, or structural collapse of mineral fractions around the sorbed species (Waters et al., 1998). The presence of non-extractable residues in the environment could be considered beneficial since they are neither leachable nor bio-available in the short term; however, since they may not have been detected at all by traditional analytical procedures or equipment they may be thought to have dissipated or been completely degraded (Smith et al., 1992), thus leading to a false sense of security.

Two adsorption models are presented below: a) equilibrium sorption and b) Gamble sorption kinetics in the presence of macropores.

a) Equilibrium adsorption can be simulated as (Clemente, 1991):

$$\partial S/\partial t = K_d * n * C^{n-1} * \partial C/\partial t \qquad [2.5]$$

where:

S = mass of solute adsorbed or desorbed per unit mass of soil (g/g soil)

K_d = sorption coefficient (cm^3/g)

C = solute concentration in solution (g/cm^3)

n = an empirical exponent (equal to 1 for linear, equilibrium sorption)

b) Gamble sorption kinetics can be simulated as (Gamble, 1990; Gamble and Khan, 1988, 1990):

$$\mathbf{K_P = C_P / C_{OC} * M_P} \qquad \textbf{[2.6]}$$

where:

K_P = Pesticide sorption equilibrium function (L/mol)

M_P = Pesticide molarity (mol/L)

C_P = sorption sites occupied by pesticide (mol/L)

C_{OC} = unoccupied site (mol/L)

While the numerical values of the unoccupied site variable, C_{OC}, depends on the sorption capacity, C_C (mol/L of slurry), which is related to C_{OC} as follows:

$$\mathbf{C_C = C_P + C_{OC}} \qquad \textbf{[2.7]}$$

The above equations were derived for atrazine but they are also applicable to a wide range of pesticides (Gamble and Khan, 1988, 1990).

2.1.7. Pesticide Degradation

Pesticide loss through microbial and chemical pathways of transformation are collectively known as degradation (Clemente, 1991; Bollag and Liu, 1990; Wu and Nofziger, 1999). The various form of degradation are defined in the following paragraphs.

Pesticide degradation, or the breakdown of pesticides, is usually beneficial. The reactions that destroy pesticides change most pesticide residues in the environment to inactive, less toxic, or harmless compounds. However, degradation is detrimental when a pesticide is destroyed before the target pest has been controlled. The degradation process is basically characterized by the transformation of the parent compound into various end-products or metabolites which are eventually decomposed into inorganic products such as CO_2, H_2O, and salts (Cheng and Lehman, 1985). Thus, the persistence of a pesticide in the soil depends entirely on how quickly it is metabolized or transformed into its derivatives (Smith, 1988). Three types of pesticide degradation occur: **microbial**, **chemical**, and **photodegradation**.

2.1.7.1. Microbial Degradation

Microbial degradation is the breakdown of pesticides by fungi, bacteria, and other microorganisms that use pesticides as a food source. Microbial degradation occurs mainly in the soil and to some extent in water courses. Soil conditions such as moisture, temperature, aeration, pH, and the amount of organic matter affect the rate of microbial degradation because of their direct influence on microbial growth and activity (http://www.nhq.nrcs.usda.gov/land/meta/m2084.html. Date: 23.04.2001).

The frequency of pesticide applications can also influence microbial degradation. Rapid microbial degradation is more likely when the same pesticide is used repeatedly in a

field. Repeated applications can actually stimulate the buildup of organisms effective in degrading the chemical. As the population of these organisms increases, degradation accelerates and the amount of pesticide available to control the pest is reduced (http://ohioline.osu.edu/b820/b820_4.html. Date: 08.05.2000).

Microbial degradation (dc/dt) can be estimated as follows (Clemente, 1991):

$$\mathbf{dc/dt = (0.693 / t_{1/2}) * C = (0.693/H_t) * C} \qquad \mathbf{[2.8]}$$

where:

C = solution concentration

$t_{1/2}$ = half-life

H_T = half-live at the corresponding soil temperature

2.1.7.2. Chemical Degradation

Chemical degradation is the breakdown of pesticides by processes that do not involve living organisms. Temperature, moisture, pH, and adsorption, in addition to the chemical and physical properties of the pesticide, determine which chemical reactions take place and how quickly they occur. Because of lack of light, heat and oxygen in the saturated layers of the soil profile, chemical breakdown is generally much slower there than at the surface (http://ohioline.osu.edu/b820/b820_4.html. Date: 08.05.2000).

One of the most common degradation reactions is hydrolysis, a breakdown process where the pesticide reacts with water. Depending on the pesticide, this may occur in both acid

and alkaline conditions. Many organophosphate and carbamate insecticides are particularly susceptible to hydrolysis under alkaline conditions. Some are actually broken down within a matter of hours when mixed with alkaline water (http://www.nhq.nrcs.usda.gov/land/meta/m2084.html. Date: 23.04.2000).

2.1.7.3. Governing Equations

Microbial and chemical degradation are generally treated separately in mathematical representations so that the reaction kinetcis may be better represented (Clemente, 1991).

a) The hydrolysis rate kinetics, developed by Gamble and Khan (1988), can be used to simulated chemical transformation.

Chemical transformation via hydrolysis can be simulated as (Clemente, 1991):

$$\mathbf{dM_P / dt = \phi_{CHM} = (Kr2 / K_P) * (S_l / A_c)} \qquad \mathbf{[2.9]}$$

where:

$dM_P / dt = \phi_{CHM}$ = the rate by which pesticide is hydrolyzed or the rate of disappearance from the solution (mol/L-d)]

Kr2 = the amount of chemical sorbed (g/g)

K_P = Pesticide equilibrium constant (L/mol)

S_l = the amount of chemical sorbed (g/g)

A_c = sorption capacity (mol/L) at any moisture content a soil bulk density

The above equations were derived for atrazine, but they are also applicable to a wide range of pesticides (Gamble and Khan, 1988, 1990).

b) The Arrhenius equation can be used to model microbial degradation (Walker, 1974). Microbial degradation can be simulated as (Clemente, 1991):

$$\mathbf{dC/dt = (0.693 / t_{1/2}) * C = (0.693 / H_L) * C} \qquad \mathbf{[2.10]}$$

where:

H_L = the chemical soil half-life (days) at the corresponding soil temperature [ST(^oK)]

C = solution concentration (g/cm^3)

$k = 0.693 / t_{1/2}$ = rate constant (per day)

2.2 Existing Models of Pesticide Transport and Fate

Computer models can be used to predict pesticide fate and behavior in the environment on a site-specific basis. They have become necessary tools for estimating the risk of water pollution by pesticides and fertilizers. Modeling, however, involves the understanding of complex chemical, physical, hydrological, and biological interactions which are difficult to incorporate into a mathematical scheme that includes all processes in full (Smith et al., 1991; Singh et al., 1994). These models are cost effective and less time consuming than field studies. They are convenient when planning a production system since the potentially adverse effects of applied chemicals can be calculated, thus enabling the implementation of necessary precautions (Kaluli et al., 1997).

2.2.1. Physical Models

Some of the well-known physical models developed since the early 1970's are LEACHM, PRZM, GLEAMS, CREAMS, ACTMO, ARM, FEMWASTE, PESTAN, SESOIL, VULPEST, RUSTIC, HSPF, PELMO, and MIKE-SHE. Among these, PRZM , LEACHM, GLEAMS, and PESTAN are the most popular for the simulation of pesticide movement in soil.

2.2.1.1. PRZM model

PRZM (Pesticide Root Zone Model) was developed at the EPA Environmental Research Laboratory in Athens, Georgia by Carsel et al. (1984, 1985). PRZM is a one-dimensional, finite-difference model that estimates the partition of pesticides between surface runoff, advection in percolation water, sorption to soil, dispersion, plant uptake and biochemical degradation.

The model uses a method of characteristics (MOC) algorithm to eliminate numerical dispersion. It calculates runoff and erosion based on the SCS (Soil Conservation Service) Curve Number technique and the USLE (Universal Soil Loss Equation), respectively. Water movement is simulated based on soil water parameters such as field capacity, wilting point, and saturation. The chemical transport subroutine in the model

calculates pesticide uptake by plants, surface runoff, erosion, decay/transformation, leaching, foliar loss, dispersion, and retardation (Nicholls et al., 1994).

The model divides the soil profile into a number of soil layers or compartments within a soil zone (i.e. surface, root, and below root zones). Advection, dispersion, adsorption, degradation, and plant uptake of the chemical are simulated for each compartment. However, its surface layer is relatively thick compared with other models, so PRZM is less responsive to rainfall for surface runoff and erosion (Leonard et al., 1987). Its treatment of the dynamic soil environment is also relatively simplistic (Carsel et al., 1986).

2.2.1.2. PRZM2 & PRZM3 models

PRZM2 is a one-dimensional model that tracks the mass balance of pesticide and recharge in the soil column over time. It consists of two main modules, PRZM and VADOFT. VADOFT permits extension of the analysis throughout the vadose zone (ie. from the surface to the water table, regardless of water table depth. PRZM2 incorporates simulation of soil temperature, volatilization and vapor phase transport in soils, irrigation, and microbial transformation. VADOFT is a one-dimensional finite-element code that solves Richards' equation for flow in the unsaturated zone. The user may build relationships between pressure, water content, and hydraulic conductivity to solve the flow equation. PRZM2 is capable of simulating multiple pesticides or parent-daughter relationships. PRZM2 is also capable of estimating probabilities of concentrations or

fluxes in or from various media for the purpose of performing exposure assessments. PRZM and VADOFT are linked together by a flexible execution supervisor that allows the user to build models that are tailored to site-specific situations. Monte Carlo pre- and post-processors are provided in order to perform probability-based exposure assessments.

PRZM3 is the most recent version of the PRZM series. PRZM-3 includes modeling capabilities for different phenomena such as soil temperature simulation, volatilization and vapor phase transport in soils, irrigation simulation, microbial transformation, and a method of characteristics (MOC) algorithm to eliminate numerical dispersion (http://www.epa.gov/ceampubl/przm3.htm. Date: 04.05.2002).

2.2.1.3. LEACHM model

LEACHM (Leaching Estimation And CHemistry model), is a process-based model of water and solute movement, physico-chemical transformations, plant uptake and chemical reactions, in the unsaturated zone (Wagenet and Hutson, 1986, 1987; Jemison et al., 1994). It consists of three parts, LEACHM-N to simulate nitrogen transport and transformation, LEACHM-P to determine pesticide displacement and degradation, and LEACH-S to describe transient movement of inorganic salts (i.e. SO_4^{2-}, Cl^-, CO_3^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and HCO_3^-) in the presence of soil chemical reactions.

Although LEACHM-P has been tested successfully and results show that it simulates nonvolatile pesticides in the unsaturated zone with great accuracy, there are some

limitations to this model (Clemente, 1991). It does not consider macropore flow of water, unequal depth increments, runoff, erosion, or the effects of management practices.

2.2.1.4. GLEAMS model

GLEAMS (Ground Water Loading Effects of Agricultural Management Systems) was developed for the United States Department of Agriculture (USDA) by Leonard et al. (1987) to simulate the movement of agricultural chemicals in and from the rootzone. It is a modified version of the Chemicals, Runoff, and Erosion from Agricultural Management Systems model (CREAMS), which adds details to the transmission of water and chemicals to the bottom of the rootzone. GLEAMS assumes that a field has homogeneous land use, soils, and precipitation (Knisel et al. 1993).

GLEAMS was developed to evaluate the impact of management practices on potential pesticide and nutrient leaching within, through, and below the root zone. It also estimates surface runoff and sediment losses from the field. GLEAMS was not developed as an absolute predictor of pollutant loading. It is a tool for comparative analysis of complex pesticide chemistry, soil properties, and climate. GLEAMS can be used to assess the effect of farm level management decisions on water quality. However, the transport of water and solute from the bottom of the rootzone to the water table is not calculated (Knisel et al., 1994a, 1994b; Leonard et al. 1987).

2.2.1.5. PESTAN model

PESTAN (PESTicide ANalytical Model) is a screening-level model developed by the U.S. EPA, R.S. Kerr Environmental Research Laboratory in Ada, Oklahoma to estimate the movement of organic chemicals through soils to ground water.

It uses an analytical solution to calculate organic movement based on a linear isotherm, first-order degradation and hydrodynamic dispersion. The model assumes steady water flow in a homogeneous soil profile with constant hydraulic, sorption and decay parameters. Thus, the temporal variability of soil processes such as leaching and the spatial variability of soil characteristics are largely ignored (Donigian and Rao, 1986).

2.2.1.6. Limitations

Some limitations of the available NPS models are:

- Preferential flow and non-equilibrium sorption through macropores have not been considered in GLEAMS, LEACHM, or PRZM.
- Plant uptake and vertical flux of pesticides are not included in CREAMS.
- Only partial representation of the vadose zone is provided in GLEAMS.
- Existing models do not simulate the combined effects of mass flow, chemical/microbial degradation, adsorption, dispersion, plant uptake, volatilization, and runoff.

- PRZM is limited to non-volatile pesticides since vapor phase partitioning is not considered.
- LEACHM does not consider erosion and runoff. It does not evaluate the effect of various agricultural management practices.
- The treatment of the dynamic soil environment is relatively simplistic in PRZM.
- LEACHM simulates pesticide transport in soils in the absence of agricultural drainage systems.

PESTFADE, developed by Clemente et al. (1993), was designed to improve the obove-mentioned limitations of the existing models.

2.2.1.7. PESTFADE model

Clemente et al. (1993) developed a one-dimensional transient mathematical model called PESTFADE (PESTicide Fate And Dynamics in the Environment). PESTFADE includes SWACROP (Soil Water Actual Transpiration and Crop Production) as a module. Swacrop was developed in the Netherlands by Wesseling et al. (1989) to evaluate one-dimensional (vertical), transient, unsaturated water flow in a heterogeneous soil-root system. It was incorporated into PESTFADE to take advantage of its state-of-the art methods for calculating evapotranspiration, as well as of the sophisticated water balance formulations that apply to both arid and humid regions.

PESTFADE accounts for simultaneous movement of water and reactive solutes through homogeneous soil systems under saturated and saturated conditions as affected by mass flow, heat flux, convection, runoff, leaching, dispersion, diffusion, volatilization, plant uptake, chemical and microbial degradation, sorption/desorption, and macropore flow. PESTFADE is a non-point source (NPS) mathematical model to predict the fate and transport of pesticides in soil and ground water (Clemente et al., 1991). The model is physically-based, and the initial-boundary value problem over-seeing pesticide fate and transport is solved by well-known and proven mathematical methods. It can be applied to evaluate different boundary conditions, tillage practices, and take into account accidental spills, salt movement, oxygen diffusion, and the presence or absence of drainage and/or sub-irrigation systems (Clement et al., 1991). The model was tested and validated by Clemente et al. (1991) using field data from experiments involving a post-emergence atrazine application on a cornfield on a loam soil. The field was located at the experimental farm of the Macdonald Campus of McGill University. Various published analytical solutions were also used to check the accuracy of the different components of PESTFADE (Clemente et al., 1991; Clemente et al., 1993). However, PESTFADE has undergone limited testing under field and laboratory conditions (Clemente, 1991; Clemente et al., 1997; Kaluli et al., 1997), and requires further validation before it can be used with confidence.

Li et al. (1999), modified PESTFADE by incorporating a new model of sorption kinetics. The kinetics now take into account intra-particle diffusion of pesticides into the soil matrix (also known as bound residues), the sorption capacity of soil, and a variable

pesticide distribution coefficient, K_d. A two-stage surface-adsorption/intra-particle-diffusion mechanism was proposed which accounts for pesticide-soil interactions based on the assumption that there are two kinetically-linked processes: relatively fast labile adsorption followed by highly retarded intra-particle diffusion (Gamble et al., 1992; Gilchrist et al., 1993; Li et al., 1996). A second-order rate law was used to account for the labile surface adsorption, and a first-order initial rate approximation was employed for the case of low coverage. The intra-particle diffusion process was treated with a particular solution of Crank's model (Crank 1975) and was described by a first-order rate law. The output from the modified model was in much better agreement with measured values than was that of the earlier version, which was based on a conventional adsorption approach (Li et al., 1999). However, they did not simulate total mass and did not compare the simulations by the modified version with field data. This component of PESTFADE also needs further validation and verification.

Both models, developed by Clemente et al. (1991) and Li et al. (1999) were implemented using FORTRAN. As a result, they are difficult to use and not user-friendly. A new revision of the model has therefore been developed and defined in this chapter. The entire code has been re-written. In this revision, a more accurate method of solving algebraic/ode (ordinary differential equation) systems has been used. The governing equation has been modified slightly according to the Chemflo model (Nofziger et al., 1985, 1994).

2.2.1.7.1. PESTFADE Structure

PESTFADE consists of five major submodels. They are: RUNOFF, SWACROP, MOISTE, HEAT, and CADD (Fig. 2.1).

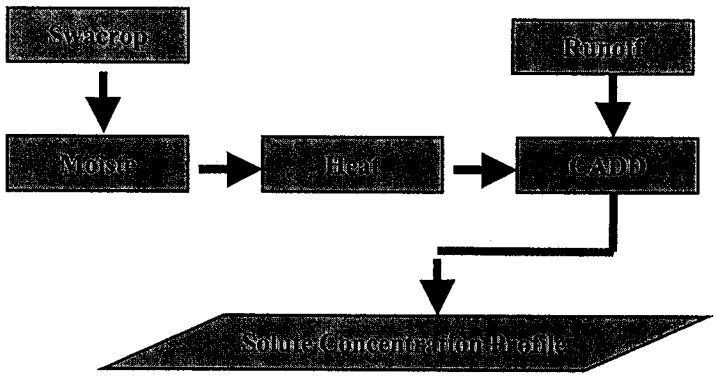

Figure 2.1 PESTFADE Structure

RUNOFF (Haith, 1980) analyzes pesticide partitioning in runoff water and sediment, as affected by climate and tillage practices based on the US Soil Conservation Service Curve Number Method and the Universal Soil Loss Equation to evaluate the runoff depth and soil loss, respectively.

SWACROP (Soil Water Actual transpiration and CROp Production) is a Dutch model which can evaluate one-dimensional (vertical) transient unsaturated water flow in heterogeneous soil-root systems in accordance with the Darcy and continuity equations (Wesseling et al., 1989). It uses the finite difference method to solve the Richard's Equation for soil moisture movement.

SWACROP is an updated version of the previous models SWATR, SWATRE, CROPR, and SWACRO, which were all developed at the Integrated Land, Soil, and Water Research Institute in the Netherlands. Feddes et al. (1978) developed the SWATR (Soil Water Actual Transpiration Rate) model to evaluate transient water flow in a heterogeneous soil-root system being under the influence of ground water. Belmans et al. (1983) modified it by applying a different numerical solution and extending the possible boundary conditions at the bottom of the soil profile. The modified version is called SWATRE (SWATR-Extended). The CROPR (Crop Production) model was developed by Feddes et al. (1978) to calculate the rate of dry matter growth of a crop having an optimal supply of nutrients. Feddes et al. (1984) linked SWATRE and CROPR into a single model (SWACRO). SWACRO is capable of simulating the development of a potato crop (Feddes et al., 1988). The model was later updated under the name SWACROP (Wesseling et al., 1989), a comprehensive model for simulating the water balance of a cropped soil, allowing different boundary conditions, the possibility of drainage and irrigation, and the calculation of crop yield.

SWACROP generates an output file of moisture and flux distribution in the soil profile that can be used by CADD to simulate solute transport. MOISTE obtains moisture distribution data on a nodal-point basis as the soil moisture profile generated by SWACROP is on a compartmental basis. The Darcy flux from SWACROP and the moisture content from MOISTE are stored in a file that is used by the CADD model to simulate solute transport as a function of the interacting processes of convection, adsorption, volatilization, and degradation (Clemente et al., 1991).

HEAT serves to analyze the conduction of heat in the soil profile, according to Walker (1981a, 1981b). Soil temperature distribution and soil thermal conductivity are calculated. The temperature profile from HEAT and the soil moisture content distribution from MOISTE, are required by CADD to simulate microbial degradation of the pesticide. CADD (Conduction Adsorption Diffusion Degradation) also evaluates pesticide transport by leaching, volatilization, and dispersion, adsorption and desorption and chemical degradation.

2.2.1.7.2. Unique Features of PESTFADE

The main feature of PESTFADE is that it considers most significant mechanisms affecting solute transport such as runoff, macropore flow, heat flow, and unsaturated moisture flow. Unlike other existing models, it considers different agricultural management practices, unsaturated flow phenomenon, sub-irrigation or controlled drainage systems, macropore flow, new methods of adsorption-desorption and chemical-microbial degradation, and is able to predict under both undrained and subsurface-drained farmlands in arid, semi-arid, or humid regions.

Although most mathematical models predict linear water flow through soil quite well (e.g., PRZM2, LEACHMP, RUSTIC, and PESTFADE), application to the sorption process seems somewhat compromised. One of their weaknesses is that the soil-water partitioning coefficient, K_d, is treated as a constant (Carsel et al., 1984; Wagenet and

Hutson, 1987), whereas PESTFADE adjusts K_d according to changes in soil PH, temperature, sorption capacity of the soil, and soil tortuosity (Li et al., 1999).

2.2.2. Artificial Neural Networks

ANNs (Artificial Neural Networks) are non-physical models that are designed to emulate the highly non-linear functions of human natural neural networks (NeuralWare 1993; Wasserman 1993; Haykin 1994; Yang et al., 2000). ANNs are trained by example data to build the input/output vector maps in an implicit way. Therefore, they can solve highly non-linear problems without the need to define the explicit relationship existing between inputs and outputs (Yang et al, 1997b). ANNs are composed of numerous processing elements (PEs) arranged in various layers, with interconnections between pairs of PEs (Haykin 1994; Kartalopoulos 1996; Kasabov 1996).

ANNs can often model various input/output relationships with less execution time than a procedural model (Haykin, 1994; NeuralWare, 1993; Shukla et al., 1996; Wasserman, 1993; Yang et al., 1997a, 1997b). ANN models can give a good prediction if they are defined properly and trained with reliable data.

Compared with conventional models, ANNs require significantly less input parameters to obtain equally appropriate results (Yang et al., 1996a). Therefore, the development of an ANN model can be considered a good alternative when a simple model with quick execution and accurate simulation is needed. The ANN technique has been applied

widely and successfully in many engineering and scientific fields with encouraging results (NeuralWare, 1993; Yang, 1996b).

2.3 Graphical User Interface

The User-interface design defines how an application will look and how it will interact with the user. This gives a very high importance to how the graphical user interface (GUI) is designed. It could be the cause of hours of frustration, "fighting" with the interface, or it can significantly increase the users' productivity. The difference in the two extremes is the quality of the design.

Considering the fact that users have much more freedom to do whatever they want in Windows-based interfaces, compared to old applications where the most common way to communicate with the user was through ASCII files, new concepts in computer programming come into play. Without this adaptation to the real world, it is burdensome to use old programs and take advantage of their features. Before diving into the design and development of the GUI for PESTFADE, some concepts need to be explained.

Windows is an event-driven operating system. It utilizes system events to react to the environment. Whenever the user clicks on a button, moves the mouse or resizes a form, Windows will generate a message that describes the action. This message then gets sent to the message queue. From here the message is sent to the appropriate control- for example a form. When the control receives this message, it then generates an appropriate

event. Code can be written in an event to force a control to react precisely the way we want it to (Brown, 1997).

One of the objectives of the present study was to design and develop a rich GUI for the PESTFADE model. Future work and study with a group of designers, programmers, and researchers with a good understanding of pesticide fate and transport can result in a well structured application with world-wide appeal.

Because of the author's background in using Visual Basic (ver. 3.1) as a tool to develop an application for greenhouse management, Visual Basic (ver. 6.0) was the programming language to develop the GUI for the PESTFADE model. Visual Basic is an object-oriented language with strong features.

2.3.1. Object-Oriented Definitions

As some concepts may be addressed in the following chapters, a brief definition of some of these is given below:

Object-oriented, or *OO:* means looking at a problem in terms of the objects involved with that problem. *Objects* are things. In object-oriented terms, the word *object* is used to describe one specific thing.

Objects have an identity and this identity is defined with *properties.* Objects also do things. The things an object can do are called its *behaviors*. Objects are bound together by their relationships.

2.3.2. Benefits of OO Systems

Some of the benefits of object-oriented systems are real-word modeling, reusability, reliability, and maintainability:

Real-World Modeling

Since people see the world in terms of objects, a program written in terms of objects should be more intuitive and understandable than a program structured in some other way.

Reusability

Objects have higher cohesion because they encapsulate code and data. Once they are modeled correctly, they can easily be lifted from one program context and used in another.

Reliability

When the number of classes is high, the development effort begins to shift from writing new code to assembling existing classes in new ways. It shortens development time and leads to more robust, error-free software systems.

Maintainability

Given that objects have greater modularity, the effects of program changes should be better localized, and therefore easier and cheaper to implement and maintain.

Object-oriented design involves organizing the software architecture into independent components called *objects*. Objects can be implementation-based components that are needed to construct an application. The object-oriented approach results in a design that resembles the real world rather than an artificial computer process.

2.4 Concluding Remarks

The most accurate approach to determine pesticide concentrations in soil would be direct measurements and field studies supported by laboratory analyses. This solution, although accurate, is expensive, slow, site-specific, and chemical-specific.

Mathematical models can substantially reduce the time involved in mapping pesticide concentrations with the limitation that non-measured grid points are estimates. Furthermore, a substantial number of input parameters for a given site are also required. Finally, existing models are difficult to run because the user environments are not "friendly", manuals are inadequate or do not exist, validation is limited to few sites and most models are incomplete.

In spite of all the advantages PESTFADE has over similar models, it has had limited validation. Each module used in PESTFADE was first tested analytically by Clemente et al., 1991. The model was then validated using field data collected at the college farm (Clemente et al., 1991). In order to improve the model, Li et al., 1999, made some modifications to it, including the consideration of macropore flow and new sorption kinetics, taking into account intraparticle diffusion of pesticide into the soil matrix (also known as bound residues), the sorption capacity of soil, and a variable pesticide distribution coefficient K_d (Li et al., 1999). The model needs to be validated more before being used world-wide.

The other limitation to using PESTFADE is its uncomfortable user interface. There are too many input parameters involved, making it difficult for the user to run the model. The other problem is its weak documentation for data entry. Chapter three will, therefore, detail the GUI development for PESTFADE and the model validation.

ANN models, on the other hand, are a faster less expensive type since they require fewer inputs to predict different phenomenon, if efficiently trained. The problem with ANN models is that they are site-specific and require accurate training data. Data can be obtained by field measurements or generated by well-validated reliable mathematical models. Interestingly enough, ANNs are more successfully validated when the training data inputs are first optimized by one of a number of statistical techniques that either reduce the number of inputs by reducing the dimensionality of the data set (eliminating redundant variables) and/or adjusting the predictor space to orthogonal axes of the

predictors (or linear combinations thereof) that explain most of the variability of the data set.

At this point in time it would be worthwhile to revamp the PESTFADE package, validate it and set it in a user-friendly environment, complete with user-manual. Investigations could also be made to see if an ANN could be developed (Chapter IV) to perform the same task as PESTFADE.

CHAPTER III

GUI FOR PESTFADE MODEL

This section describes the interface between the user and the various PESTFADE modules. It is essentially a user-manual.

The GUI for the PESTFADE model was developed using Microsoft Visual Basic 6.0. Visual Basic was chosen because of its superior features in creating Windows applications for PCs. It supports many useful tools that will help the model be more productive.

The relationships between the modules are presented schematically in Figure 2.1 (i.e. chapter 2) and described in more detail in section 3.1. This subsection describes the requirements for running PESTFADE, the design and development of different forms, and screen and keyboard functions.

3.1 Governing Equations

In the previous revisions, the governing partial differential equations in PESTFADE (i.e., CADD and HEAT programs) were solved using the Numerical Method of Lines (NMOL). This solution technique is part of the Differential Systems Simulator (DSS/2 package developed by Schiesser (1983), which contains three internal subroutines: INITIAL, DERV, and PRINT. These handle the initial conditions, the boundary conditions and differential equations, and the printing functions of the program, respectively.

In the new revision, the governing partial differential equation in the CADD module has been changed and solved using the LSODE (Livermore Solver for Ordinary Differential Equations) technique. This solution technique is used for algebraic/ode (ordinary differential equation) systems, developed by Alan Hindmarsh (1983), Lawrence Livermore National Laboratory. LSODE solves stiff and nonstiff systems of the form dy/dt = f(t,y). In the stiff case, it treats the Jacobian matrix df/dy as either a dense (full) or a banded matrix, and with user-supplied or internally approximated by difference quotients. It uses Adams methods (predictor-corrector) in the nonstiff case, and Backward Differentiation Formula (BDF) methods (the Gear methods) in the stiff case. The linear systems that arise are solved by direct methods (LU factor/solve). LSODE supersedes the GEAR and GEARB packages, and reflects a complete redesign of the user interface and internal organization, with some algorithmic improvements (Radhakrishnan, 1993, Byrne, 1992).

In this technique, LSODE1 is an interface program between DSS/2 applications and integrator LSODE. It calls a DSS/2 application, defined as the user-supplied subroutines INITIAL, DERV and PRINT, and DATA. The system of odes programmed in subroutine DERV is integrated by LSODEI. The model initial conditions are set in subroutine INITIAL, and the model derivatives are programmed in subroutine DERV. The numerical solution is printed and plotted in subroutine PRINT.

The governing equation for combined water flow and root uptake in SWACROP is solved numerically through the implicit finite difference method based on a number of boundary

conditions at the top and bottom of the soil profile. The upper and lower boundary conditions make it very flexible and applicable to a wide range of hydrologic problems in both humid and arid conditions. The model also considers various hydrologic, crop and climatic processes such as runoff, infiltration, evapotranspiration, root water uptake, etc. in the water balance calculation, which renders it capable of simulating water movement in soils.

3.1.1. Solute Concentration

The traditional approach for modeling pollutant transport in the soil environment is to evaluate the function C(x,t) which describes the solute concentration in space (x) and time (t) for appropriate initial and boundary conditions regarding the flow and concentration (C) of the pollutant (Clemente et al., 1993).

For convective-dispersive transport of a pollutant through a saturated porous medium, this function can be represented by the following one-dimensional governing equation:

$$\partial C/\partial t = D * \partial^2 C/\partial x^2 - V * \partial C/\partial x \qquad [3.1]$$

where:

C = solute concentration (g/cm^3)

D = hydrodynamic dispersion coefficient (cm^2/h)

V = pore-water velocity (cm/h)

x = distance along flow path (cm)

t = time (h)

Incorporating adsorption/desorption, biochemical degradation, and volatilization and considering the issue of field spatial variability, equation 3.2 was modified to describe the simultaneous interaction of these factors as well as the non-steady transport of water and solutes through unsaturated porous media (Rao and Jessup, 1983):

$$\partial/\partial t \left(\theta C + \rho S + \varepsilon K_H C \right) = \partial/\partial x \left(\theta * D * \partial C/\partial x - q * C \right) - \phi \qquad [3.2]$$

where:

C = solute concentration (g/cm^3)

$\theta = \theta(x , t)$ = volumetric moisture content (cm^3/cm^3)

$q = \theta * V$ = water flux (cm^2/h)

$D = D(\theta , q)$ = moisture and flux dependent dispersion coefficient (cm/h)

$\phi = \phi (x , t)$ = a sink term for degradation (chemical or microbial) and/or volatilization and/or root uptake (g/cm^3-h)

ρ = dry soil bulk density (g/cm^3)

S = mass of solute adsorbed or desorbed per unit mass of soil (g/g soil)

K_H = Henry's constant

PESTFADE uses the above function with additional features to better represent the complex behavior of solutes in soil systems.

3.1.2. New Governing Equation

A new governing equation (Eq. 3.3) has been used in this revision to better represent the solute concentration behavior in soil. This equation has been derived from the Chemflo application,

version 1.30, which simulates one-dimensional water and chemical movements in unsaturated soils. It was developed by the Department of Agronomy, Oklahoma State University, Stillwater, Oklahoma (Nofziger et al., 1985). The values for α and β have been hard-coded in the CADD program, however they can be easily modified if more accurate values are deemed necessary.

$$\partial (\theta RC)/\partial t = \partial (\theta D (\partial C/ \partial Z - qC) - (\alpha\theta + \beta\rho K) C + \gamma\theta) \quad [3.3]$$

where:

$R = 1 + \rho K / \theta$ is the retardation factor for the chemical in the soil

C = concentration of chemical in the liquid phase (mg/l)

D = dispersion coefficient (cm^2/h)

θ = volumetric water content (cm^3/cm^3)

q = flux of water (cm/h)

ρ = soil bulk density (g/cm^3)

α = first-order degradation rate constant in the liquid phase

β = first-order degradation rate constant in the solid phase

γ = zero-order rate constant in the liquid phase

3.2 Documentation & Standards

Lack of documentation made it too difficult to follow up work done for this model and to continue to improve it. The only available documentation was Clemente's thesis (Clemente

1991), publications by Clemente et al. (1993) and (1997), and papers by Li et al. (1996) and (1999). In order to facilitate future modifications, all the work done in exploring and executing the model was documented and the revised code was fully commented.

This documentation consists of a brief explanation of how to execute the model, and the steps of the GUI development.

3.2.1. Running PESTFADE

PESTFADE is usually executed in the following sequence: RUNOFF , SWACROP, MOISTE, HEAT, and CADD. Components should be executed, one after the other, to generate inputs for the next application. The input files required by each module and generated output files are given in Tables 3.1 to 3.5.

Module Name:	RUNOFF
Exe File:	Runoff.exe
Input Files:	Tyme.out Rain.dat Param5.dat
Output Files:	Rain.out Premain.out Pest.tot

Table 3.1 List of I/O Files for RUNOFF Model

Application:	SWACROP
Exe File:	Swap93.exe
Input Files:	Swap93.inp Meteo.dat Soil.dat drain.dat
Output Files:	Soilprof.prf

Table 3.2 List of I/O Files for SWACROP Model

The MOISTURE model requires the file Moisture.out. It is retrieved from the SWACROP output file Soilprof.prf by the macro Moisture Content, which is executed in Excel. After running the macro in Excel, the active sheet is saved in text format (i.e. space delimited) as Moisture.prn and then renamed as Moisture.out.

Module Name:	MOISTURE
Exe File:	Moiste.exe
Input Files:	Ttotal.out Moisture.out
Output Files:	Theta.out

Table 3.3 List of I/O Files for MOISTURE Model

Theta.out has 41 nodal points, however, HEAT and CADD require 201 nodal points. The macro Theta (composed of Theta1, Theta2, and Theta3) is executed to get the full set of nodal points. Columns A, B, and C are then stretched to have the same length as in the example file "Theta.xls". The active sheet is then saved in text format (space delimited) and named "Theta.prn" and renamed as "Theta.out". File theta.out is then ready to be used in the HEAT and CADD models.

Module Name:	HEAT
Exe File:	Heat.exe
Input Files:	Theta.out Param7.dat T.out T1.out DataHeat Temp.dat Heat.dat
Output Files:	Tflow.out

Table 3.4 List of I/O Files for HEAT Model

In order to execute CADD for 201 nodes it requires executing three macros, macro Flux, macro Theta, and macro Velocity.

CADD requires the file Velocity.out. It is obtained by running the macro Flux. This macro gets the flux values from Soilprof.prf generated by SWACROP. Macro Flux Fix should then be executed from the active sheet. This macro fixes the flux values in the required format. After running the macro, columns A, B, and C are stretched to have the same length as in the example file "Flux.xls". The active sheet is then saved in text format (i.e. space delimited) as Velocity.prn and renamed as Velocity.out. This file contains values for 40 compartments.

In order to get the 201 nodal points required by the CADD model, the macro Velocity is run. This macro has three different parts (i.e. Velocity1, Velocity2, and Velocity3). Columns A, B, and C are stretched to have the same length as in the example file "Velocity.xls". The active sheet is then saved in text format (space delimited), named "Velocity.prn" and renamed as "Velocity.out".

Module Name	CADD
Exe File	Cadd.exe
Input Files	Param1.dat Gamble.dat Micro.dat Steady.dat Volat.dat Tflow.out Theta.out Velocity.out DataCadd
Output Files	Output.dat

Table 3.5 List of I/O Files for CADD Model

The code for the macros introduced in this chapter is given on the enclosed CD.

In previous versions of PESTFADE, the user was required to prepare several input files in ASCII format in order to execute the model. Although the Output file generated by the CADD application within the PESTFADE model, was well documented, preparing the input files was tedious and difficult.

The new version of the model was designed based on the input/output files. Once the application is run, the PESTFADE form, which is the entry point to the model, will be displayed. Each sub-model (i.e. RUNOFF, MOISTE, HEAT, and CADD) can be executed individually from the menu bar available in the PESTFADE form. The model has been designed so as to permit the user to benefit from the final data generated by CADD, as well as to execute each sub-model and obtain outputs for each. The order of the list of the sub-models in the menu is the order in which they should be executed to obtain outputs from CADD.

It is optional to execute each single module before the next. The program can use the previously provided data in the default files located in the default directory to continue its processing.

As mentioned in the previous chapter, the RUNOFF program calculates runoff depth and soil loss. The output from this program consists of the values of rainfall excess (i.e. rain.out) which are required in the METEO file of SWACROP as well as the daily concentrations of the

chemical at the soil surface (i.e. premain.out) which are available for redistribution in the vadose zone. These surface concentrations are needed in CADD as the upper boundary conditions.

The HEAT program analyzes the conduction of heat in the soil profile. The temperature distribution profile generated by the model coupled with the moisture profile from SWACROP are used to simulate microbial degradation in CADD. The relation between different programs was illustrated previously in Figure 2.1.

3.2.2. GUI Development for PESTFADE

The design of the forms is based on the original input/output files. A tab strip is designed for each input/output with the name of the file along with the path being displayed at the bottom of each tab. The default path is hard-coded in the program to locate the required input files and output files produced.

3.2.2.1. VB Forms

Forms are designed to execute each sub-model. The PESTFADE form is the main form from which other programs (i.e RUNOFF, HEAT, MOISTE, SWACROP, and CADD) will be called. Once run, the forms, along with their contents, are loaded with data available by default to provide the user a better understanding of what the entries should look like.

3.2.2.2. Object & Variable Definition

There are some standards used in naming and defining different objects and variables, and they have been respected throughout the development process. This standard makes it much easier for future maintenance and gives a better impression of what each word stands for.

The form's names start with 'frm' as a prefix followed by the name of the program (e.g. the form used to execute the MOISTE program is called frmMoiste).

All frames used in each program start with 'fra' as a prefix followed by the name of the program (e.g. frames in the HEAT program are called fraHeat(0), fraHeat(1), etc.). Each tabstrip used in each program starts with 'tab' as a prefix followed by the name of the program (e.g. the tabstrip in the HEAT program is called tabHeat).

All textboxes used to show file names start with 'txt' as a prefix followed by the name of the file (e.g. txtPremain to show premain.out file).

Each form contains a tabstrip based on the input/output files necessary for that program. The tabstrips contain different tabs, one for each input/output file. Each tab is differentiated by its index. As an example frmCadd contains the input/output files for the CADD program using tabCadd.

This tabstrip contains different tabs for each file. The index used for each tab gives the flexibility to design each tab with different properties. Index 1 in this tabstrip represents file Param1. Each tab has a caption to display on the tabstrip with tooltips for the user to better understand what each tab contains. A tool tip is a little cream-color box that explains what the object function is. File Param1 contains different parameters used in the CADD program and therefore, the name Parameter has a tooltips "General parameters" being displayed once the mouse icon is placed on this tab. Index 3 in this tabstrip represents file Gamble.dat. This file contains different parameters for Gamble kinetics and is named Gamble Kinetics with a tooltips of "Gamble kinetics parameters" being displayed once the mouse icon is placed on it.

Any other object used in each form is named using the standards used for this application, which is the prefix followed by the filename being associated with it and a name to represent its functionality. For example, the label used on the frame which represents file t1.out and contains dispersivity is named lblT1Dispersivity.

Using this policy in naming the objects helps the reusability of each frame along with all its contents in other parts of the application where the same file will be used again (e.g. files used in both HEAT and CADD programs).

Object Naming:

Table 3.6 gives a list of all the objects used along with the prefix and an example for each.

Object	Prefix	Example
Frame	fra	fraRunoff
Label	lbl	lblGambleSorption
TextBox	txt	txtGambleSorption
CommandButton	cmd	cmdCalculate
Form	frm	frmCadd
List	lst	lstTflowTemperature
MSFlexGrid	grd	grdTflowTemperature
TabStrip	tab	tabCadd
CommonDialog	dlg	dlgFile
OptionButton	opt	optParam1Conventional
Module	mod	modGlobalVariables

Table 3.6 Object Naming

Variable Naming:

Table 3.7 gives a list of all variable types used along with their prefix and an example for each.

Variable Type	Prefix	Example
Boolean	b	bFileType
String	s	sFileName
Double	d	dReturnValue
Integer	n	nCount
Constant	cs	csDefaultPath

Table 3.7 Variable Naming

Some other examples of objects are given in Table 3.8. lblParam1Depth has been used to name a Label object, which has been used in the design of file Param1.dat and contains the Soil Depth, therefore, it has been called "lblParam1Depth". The same logic applies for grdThetaMoisture, which is a MSFlexGrid used in the design of file Theta.out and contains soil moisture content.

Object	Prefix	File (Tab)	Contents	Naming
Label	lbl	Param1.dat	Soil Depth	lblParam1Depth
Label	lbl	T1.out	Dispersivity	lblT1Dispersivity
TextBox	txt	Param1.dat	SoilDepth	txtParam1Depth
List	lst	Theta.out	Soil Moisture Content	lstThetaMoisture
MSFlexGrid	grd	Theta.out	Soil Moisture Content	grdThetaMoisture

Table 3.8 Examples for Object Naming, the Content, and Associated Files

The following objects are common for all forms (Table 3.9). cmdOpen is one of the command buttons used in all the forms to represent the Open button.

Object	Prefix	Contents	Naming
CommandButton	cmd	Open	cmdOpen
CommandButton	cmd	Save	cmdSave
Form	frm	HEAT	frmHeat
Form	frm	MOISTE	frmMoiste
TabStrip	tab	HEAT files	tabHeat
TabStrip	tab	CADD files	tTabCadd
CommonDialog	dlg	File	dlgFile

Table 3.9 Other Examples for Object Naming

3.2.2.3. Coding Standards

Each module, function, and subroutine has a heading to describe the main purpose of the code along with the date last modified.

3.2.2.4. Tool Tips

Tool tips have been added for each object (i.e. label, grid, list, tab, command button, etc.) to make the GUI self-explanatory. There is a ToolTipText associated with the objects to contain this explanation. This text is what will be shown as the tool tip for the object.

In the example below "Steady state water flow parameter" is the tool tip associated with "Steady" tabstrip and will appear when the mouse pointer is rested over an object for a moment (Fig. 3.1).

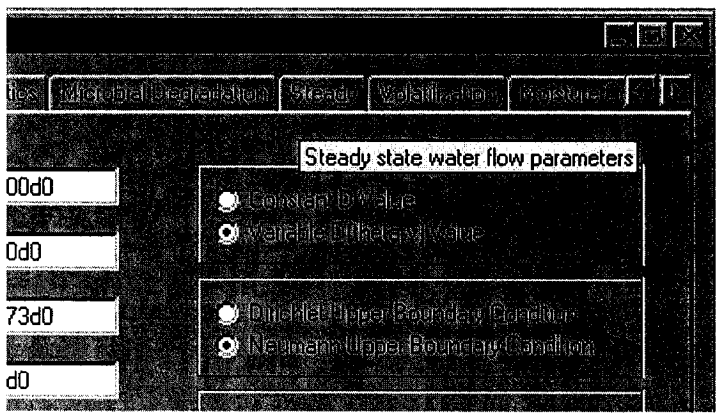

Figure 3.1 Example of a Tool Tip
(Some parts of the figure is purposely cut to highlight the tool tip option)

3.2.2.5. Right Click

Each textbox contains a default value obtained from the associated file and can be over-written. In cases where the user edits the value and wants to go back to the default value, right-clicking on the object will give the user this opportunity.

Right clicking on any textbox in the application (when enabled) will expose a pop-up menu. These menus will allow the user to quickly access tools to operate directly on the active object such as Undo, Cut, Copy, Paste, Delete, and Select All.

In the example below the pop-up menu is exposed after right clicking on the textbox associated with the "Constant B:" (Fig. 3.2).

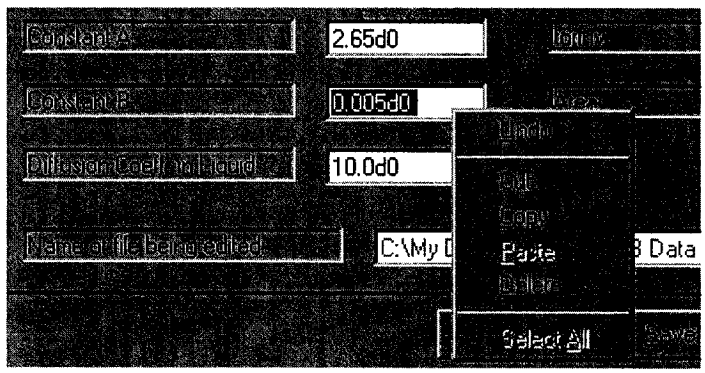

Figure 3.2 Example of a Right Click
(Some parts of the figure is purposely cut to highlight the tool tip option)

3.2.2.6. Other Features

The name of the file being processed is displayed in a disabled text box on the bottom of each tab to display the path and file name. Once each form is loaded, the data available in default files associated with that program will be loaded in appropriate objects and the file name will be displayed. The user is allowed to override data for input files where objects are enabled. Outputs files are for display purpose only and cannot be overridden. Once the Save button is pressed (if enabled), displayed data will be stored in the specified file.

Each object will become enabled/disabled when appropriate. This includes labels, textboxes, command buttons, and grids.

3.3 Sub-Models Design

As mentioned previously, each form represents a sub-program that contains a tabstrip to make it possible to launch through different input/output files associated with that sub-program. Different controls and objects are placed on each frame. There is one frame for each form. This frame is an array of sub-frames, differentiated with an index number, containing the controls. Clicking on each tab on the tabstrip loads the related sub-frame. The main properties of the controls and objects used in each form are described below.

3.3.1. Program RUNOFF

RUNOFF is used to analyze pesticide partitioning in runoff water and sediment as affected by climate and tillage practices. It consists of three input files (i.e. tyme.out, rain.dat, and param5.dat) and two output files (i.e. rain.out and premain.out).

3.3.1.1. Form Runoff

This form is loaded once the Runoff option is chosen from the menu option (Fig. 3.3). This event can be activated by clicking on the Runoff option or by pressing on the 'R' key on the keyboard. The GUI has been designed to allow a direct click on each enabled object or to go

from one object to the other using the tab key. Each object can also be enabled (displayed in its normal format) or disabled (displayed usually in gray). If an object is disabled the user does not have access to that object, as it is for display purposes only. A tool tip is associated with each object to explain the contents of that specific object. This explanation is obtained by holding the cursor on each enabled object for a while.

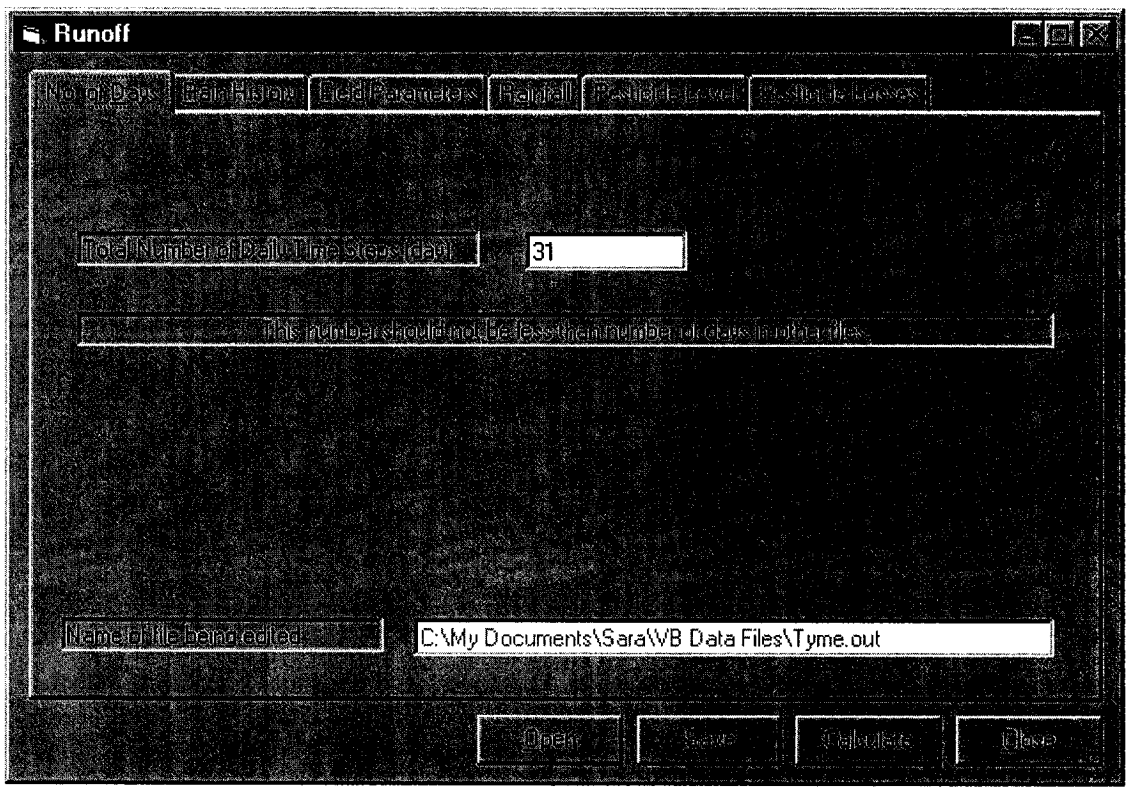

Figure 3.3 Form Runoff

3.3.1.1.1. Tab Runoff

This tab contains the information of five different input/output files involved with the RUNOFF program. One may click on a desired tab or press the underlined letter of that tab

along with the Alt key. The list of tabs used for RUNOFF which lead to five frames in the form of an array is shown in the Table 3.10.

Index	Caption	ToolTipText
1	No. of Days	Total number of daily time steps
2	Rain History	Daily rainfall data
3	Field Parameters	Other field parameters
4	Output Files/Rainfall	Net rainfall
5	Output Files/Pesticide Level	Mass of pesticide remaining on soil surface

Table 3.10 Different Tabs in Runoff Form

3.3.1.1.2. Frame Runoff

The frames frmRunoff(0), frmRunoff(1), frmRunoff(2), frmRunoff(3), frmRunoff(4), and frmRunoff(5) are used as platforms to design the entries required for each input/output file associated with the RUNOFF model. Samples of the original files are shown in Figures 3.4, 3.6, 3.8, 3.10, 3.12, and 3.14 along with the GUI replacing the ASCII files (Figs. 3.5, 3.7, 3.9, 3.11, 3.13, and 3.15). The frames are designed to display default values for input files, providing the user with the possibility of changing or editing the values, reading them from the default path, or even re-saving the entered values in the default files. They are also used to display values for output files. In the case of input, the Save button is enabled in order to save the displayed values for each item. The user can press the Calculate button any time to execute the RUNOFF program with the values saved in the default input files. In order for the program to execute with the edited values, the user has to save the changes to each file by pressing the Save button prior to selecting the Calculate button. The Save button is disabled for output files. Wherever data is shown in a grid object, the user can view the data by scrolling up/down and

left/right the grid. The values shown in the grids are read from the default path. The program does not permit the user to edit these values. The data can be read from any existing file but should be saved to the default file by pressing the Save button prior to using them in the calculation. The objects and controls to create the GUI for this file are given in a tabular format on the enclosed CD.

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Figure 3.4 Original file Tyme.out

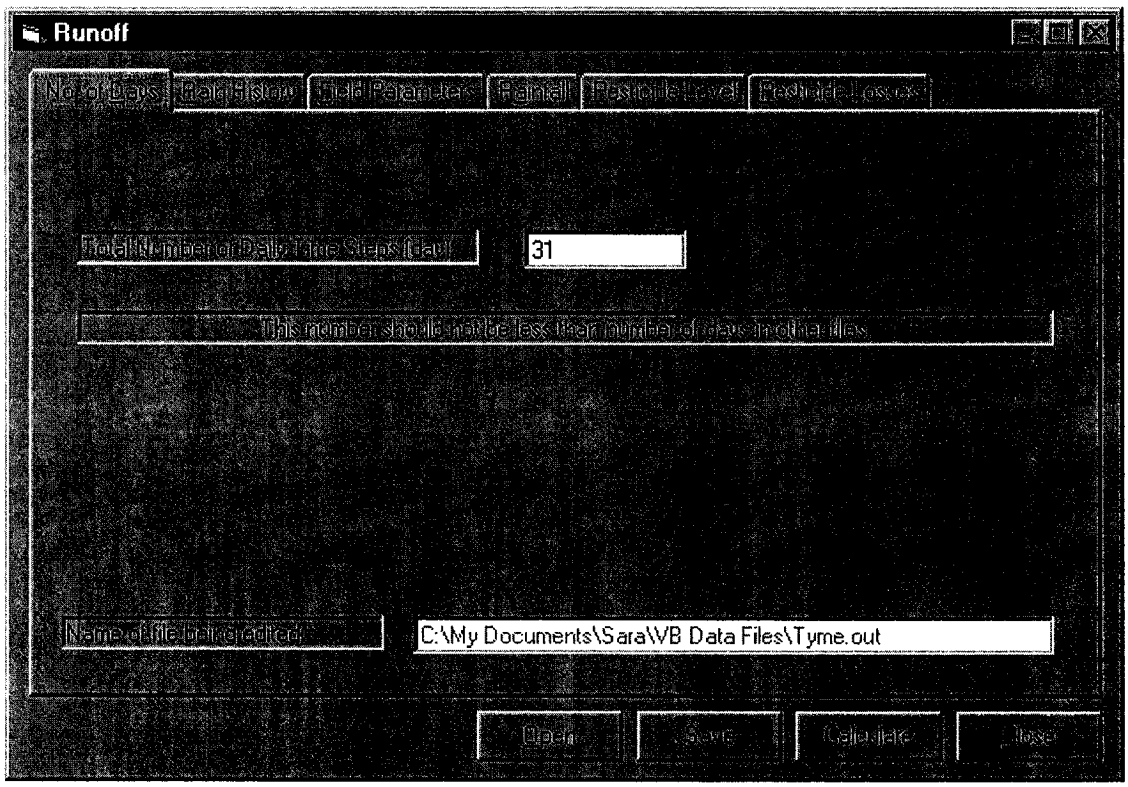


Figure 3.5 frmRunoff(0) - Final GUI for file Tyme.out

0.000D0	0.0
0.060D0	2.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.000D0	0.0
0.100D0	2.0
0.000D0	0.0
1.520D0	3.0
0.020D0	1.0
0.000D0	0.0
2.620D0	13.0
0.000D0	0.0
0.000D0	0.0

Figure 3.6 Original file Rain.dat

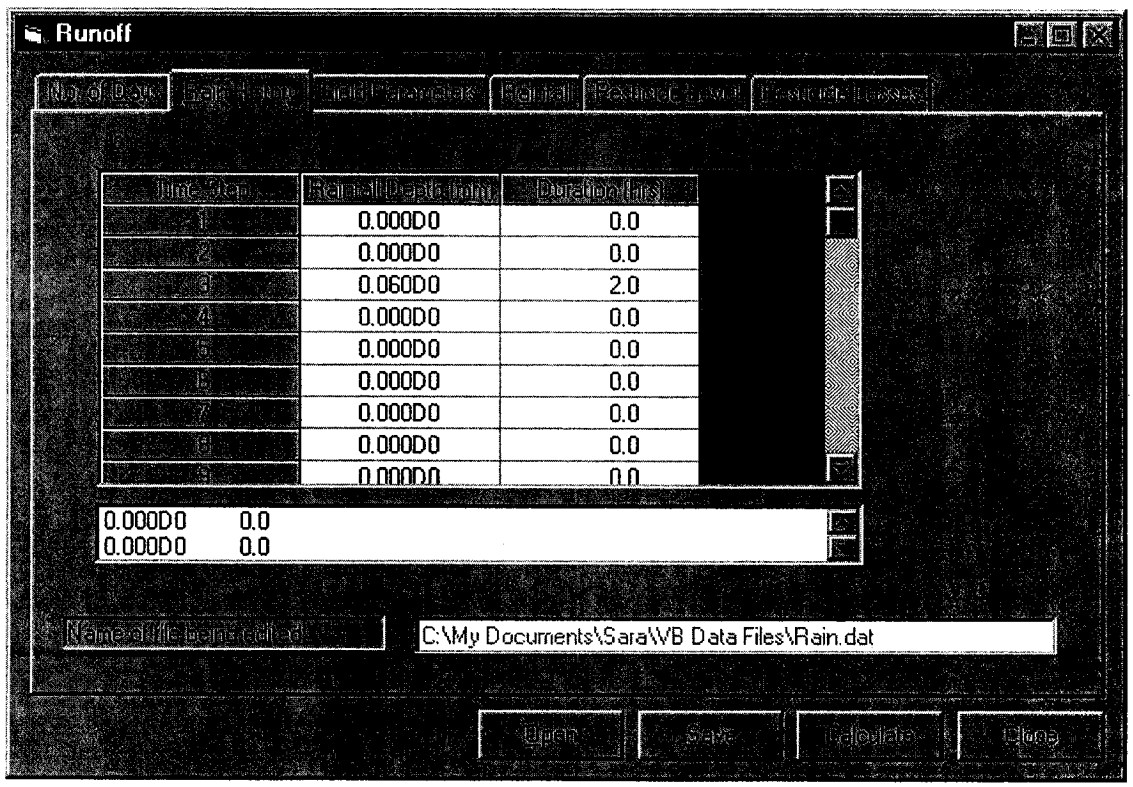


Figure 3.7 frmRunoff(1) - Final GUI for file Rain.dat

2350.0D0
0.01730D0
1.240D0
3.20D0
0.130D0
0.45D0
0.20d0
0.6640D0
0.40D0
1.0D0
80.0D0
□

Figure 3.8 Original file Param5.dat

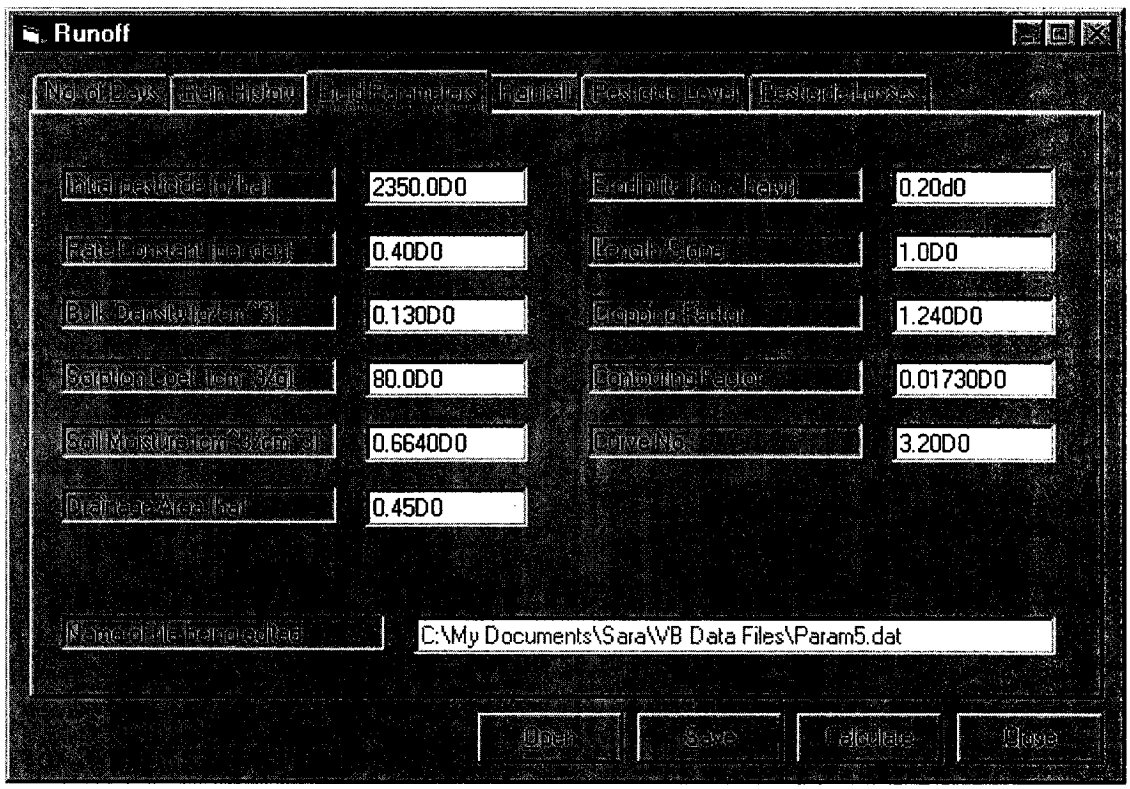


Figure 3.9 frmRunoff(2) - Final GUI for file Param5.dat

```
0.000000
  0.000000
  0.000000
  0.000000
  0.000000
  0.000000
  0.000000
  0.000000
  0.100000
  0.000000
   1.51053
  0.200000E-01
  0.000000
   2.38331
  0.000000
  0.000000
   1.43557
  0.200000E-01
   1.70761
```

Figure 3.10 Original file Rain.out

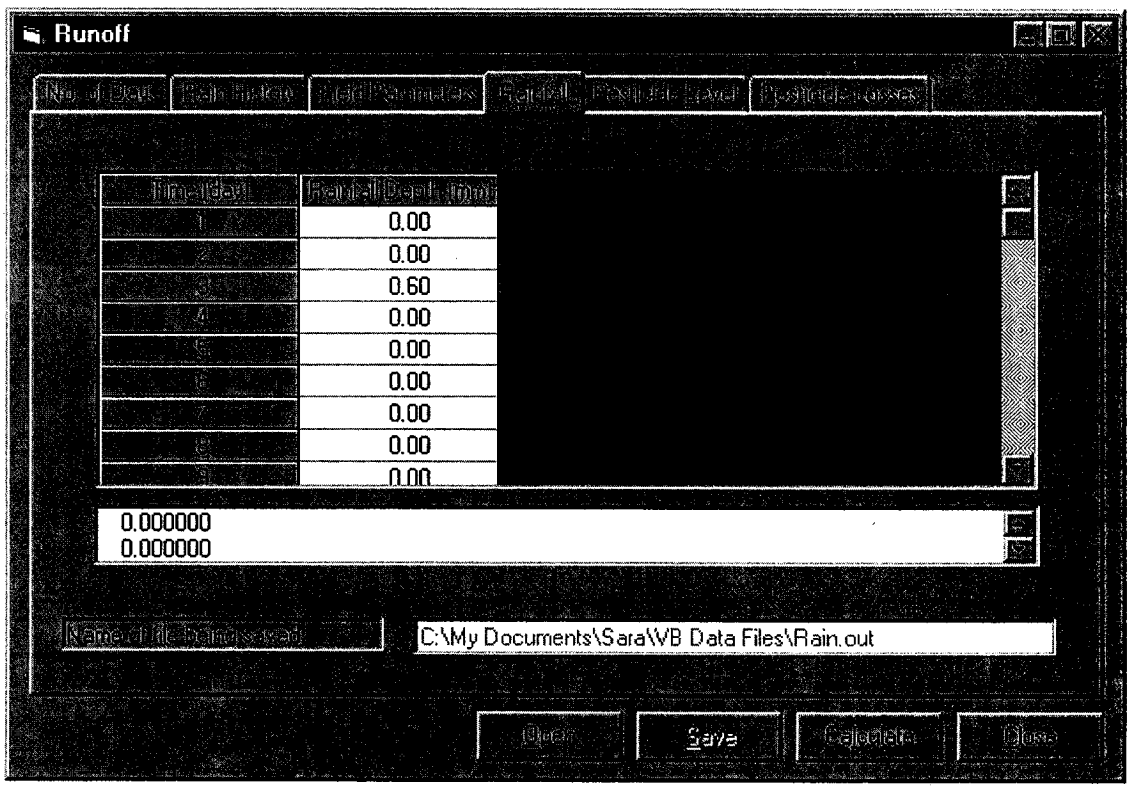


Figure 3.11 frmRunoff(3) - Final GUI for file Rain.out

17.0831
16.7901
16.5021
16.2191
15.9409
15.6675
15.3988
15.1347
14.8751
14.1949
13.9515
13.7122
13.0634
12.8393
12.6191
12.0444
11.8378
11.2923

Figure 3.12 Original file Premain.out

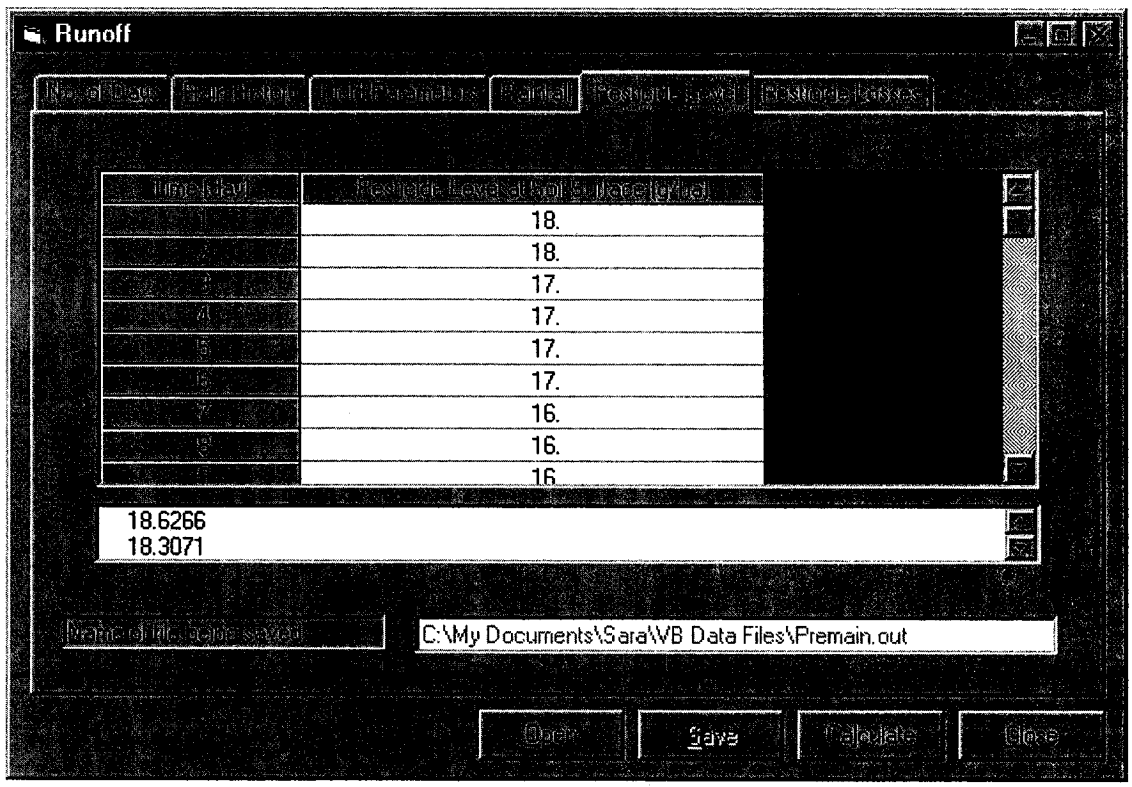


Figure 3.13 frmRunoff(4) - Final GUI for file Premain.out

1	0.000000E+00	0.000000E+00	0.000000E+00	7.391645
2	0.000000E+00	0.000000E+00	0.000000E+00	7.264870
3	0.000000E+00	0.000000E+00	0.000000E+00	7.140268
4	0.000000E+00	0.000000E+00	0.000000E+00	7.017804
5	0.000000E+00	0.000000E+00	0.000000E+00	6.897440
6	0.000000E+00	0.000000E+00	0.000000E+00	6.779141
7	0.000000E+00	0.000000E+00	0.000000E+00	6.662870
8	0.000000E+00	0.000000E+00	0.000000E+00	6.548594
9	0.000000E+00	0.000000E+00	0.000000E+00	6.436277
10	0.000000E+00	0.000000E+00	0.000000E+00	6.325888
11	0.000000E+00	0.000000E+00	0.000000E+00	6.217391
12	0.000000E+00	0.000000E+00	0.000000E+00	6.110755
13	0.000000E+00	0.000000E+00	0.000000E+00	6.005948
14	0.000000E+00	0.000000E+00	0.000000E+00	5.902939
15	0.000000E+00	0.000000E+00	0.000000E+00	5.801696
16	0.000000E+00	0.000000E+00	0.000000E+00	5.702190
17	0.000000E+00	0.000000E+00	0.000000E+00	5.604391
18	0.000000E+00	0.000000E+00	0.000000E+00	5.508269
19	0.000000E+00	0.000000E+00	0.000000E+00	5.413795
20	1.064119E-02	8.405185E-06	1.064960E-02	5.176280
21	0.000000E+00	0.000000E+00	0.000000E+00	5.087500
22	8.248705E-03	6.232781E-06	8.254939E-03	4.865901

Figure 3.14 Original file Pest.tot

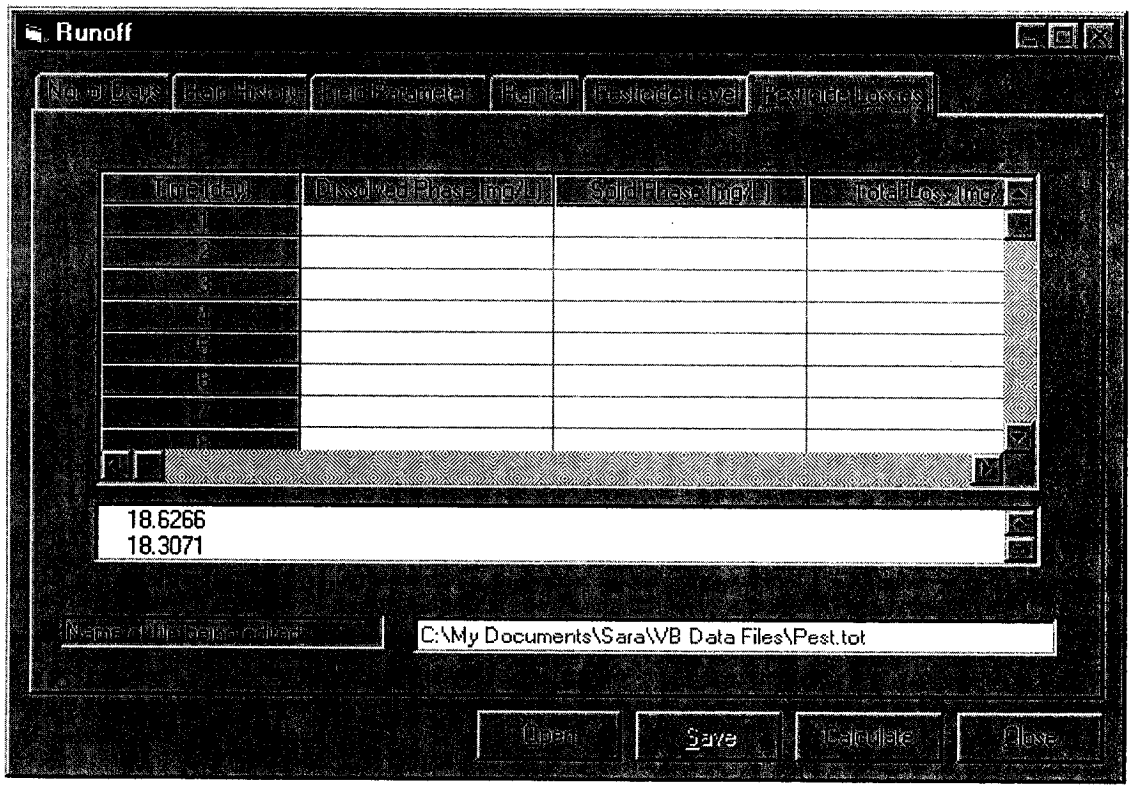


Figure 3.15 frmRunoff(5) - Final GUI for file Pest.tot

3.3.2. Program MOISTE

MOISTE is used to obtain moisture distribution on a nodal-point basis. The moisture profile generated by SWACROP is on a compartmental basis and should be generated before running MOISTE. MOISTE consists of two input files (i.e. ttotal.out and moisture.out) plus an output file (i.e. theta.out).

3.3.2.1. Form MOISTE

This form is loaded once the MOISTE option is chosen from the menu option (Fig. 3.16). This event can be the result of clicking on the MOISTE option or pressing on the 'M' key on the keyboard.

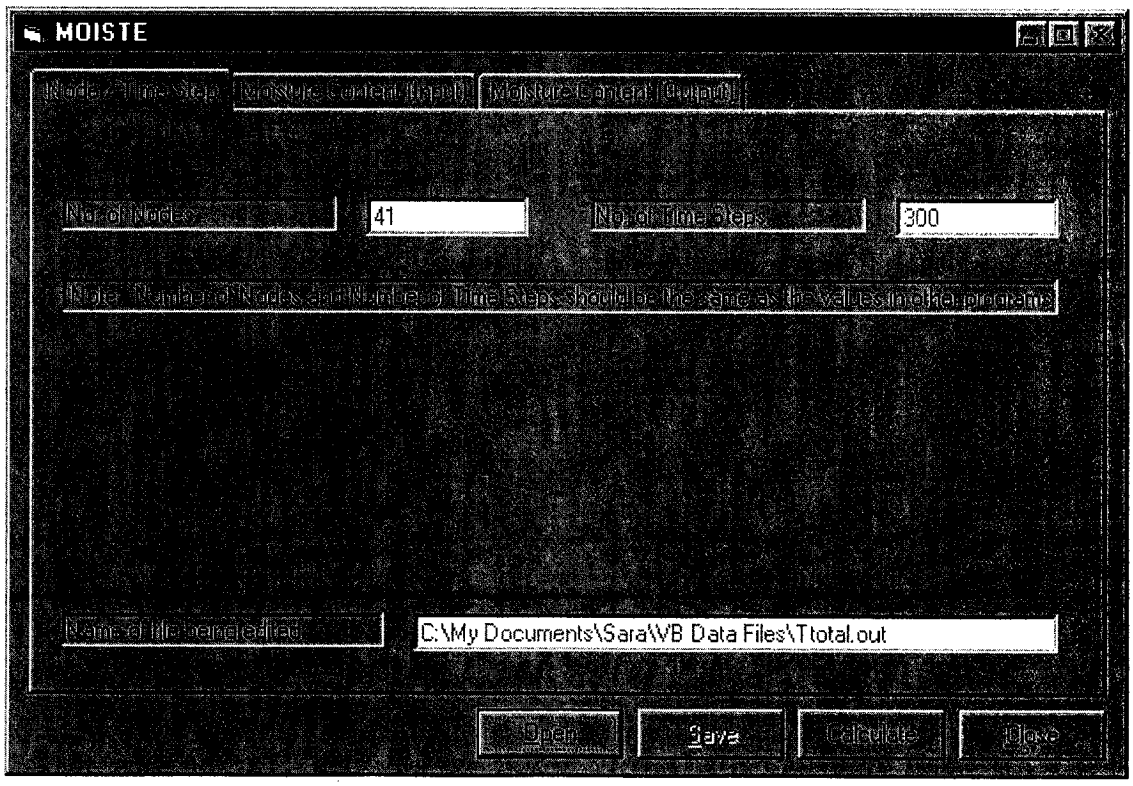


Figure 3.16 Form Moiste

3.3.2.1.1. Tab Moiste

This tab contains the information of three different input/output files involved with the MOISTE program. Below is the list of the tabs used which lead to three frames each in the form of an array (Table 3.11).

Index	Caption	ToolTipText
1	Node/Time Step	No. of Nodes / Time Steps
2	Moisture Content (Input)	Moisture content profile on a compartmental basis generated by SWACROP
3	Moisture Content (Output)	Moisture content profile on a nodal-point basis generated by MOISTE

Table 3.11 Different Tabs in Moiste Form

3.3.2.1.2. Frame Moiste

The frames frmMoiste(0), frmMoiste (1), and frmMoiste (2) are used as platforms to design the entries required for each input/output file associated with the MOISTE model. Samples of the original files are shown in Figures 3.17, 3.19, and 3.21 along with the GUI replacing the ASCII files (Figs. 3.18, 3.20, and 3.22). The user can press the Calculate button any time to execute the MOISTE program with the values saved in the default input files.

```
41      300
```

Figure 3.17 Original file Ttotal.out

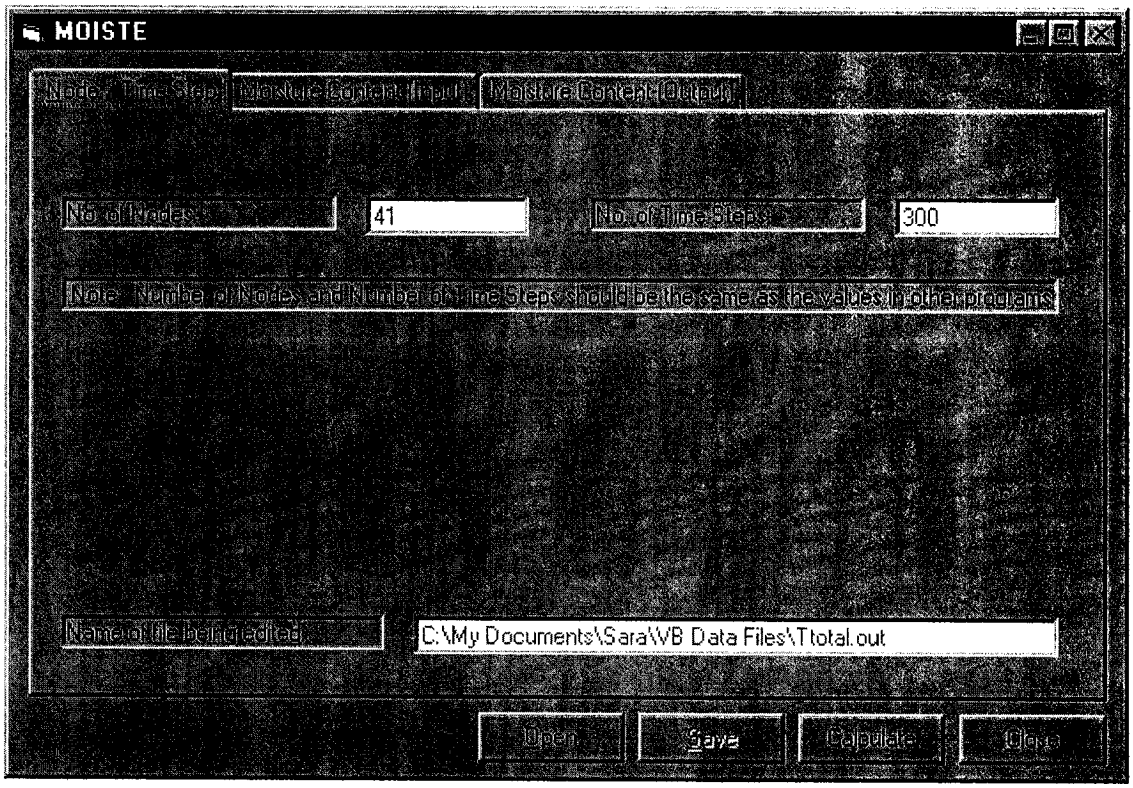


Figure 3.18 frmMoiste(0) - Final GUI for file Ttotal.out

0.269999964365042	0.271249993937078	0.272499993909150
0.273749993881211	0.274999993853271	0.276249993825331
0.277499993797392	0.278749993769452	0.279999993741512
0.281666660370926	0.283333327000340	0.284999993629754
0.286666660259167	0.288333326888581	0.289999993517995
0.291666660147409	0.293333326776822	0.294999993406236
0.296666660035650	0.298333326665064	0.299999993294477
0.302173906289365	0.304347819284252	0.306521732279140
0.308695645274028	0.311538454575034	0.315384608335220
0.319230762099274	0.324447579430169	0.499999988824129
0.499999988824129	0.499999988824129	0.499999988824129
0.499999988824129	0.499999988824129	0.499999988824129
0.499999988824129	0.499999988824129	0.499999988824129
0.499999988824129	152.000001000000	1

Figure 3.19 Original file Moisture.out

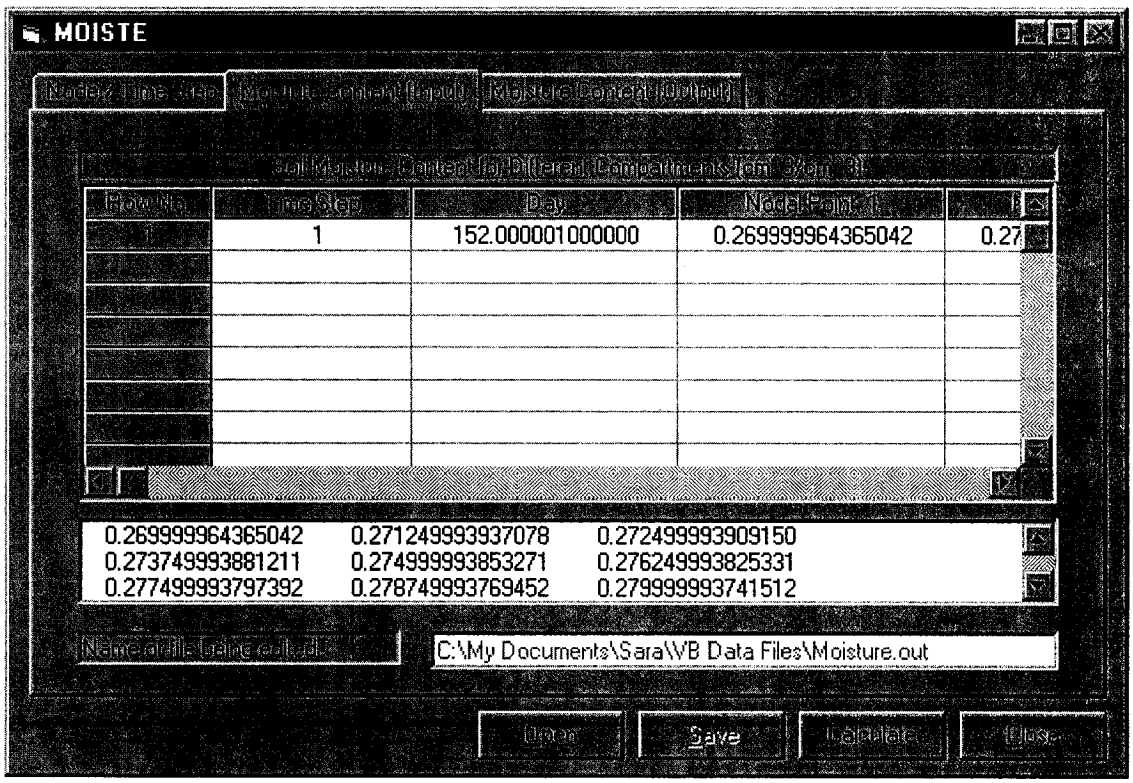


Figure 3.20 frmMoiste(1) - Final GUI for file Moisture.out

```
0.285000    0.285833    0.287500    0.289167    0.290833
0.292500    0.294167    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327222    0.332778
0.338492    0.345000    0.353286    0.363000    0.374000
0.386667    0.404167    0.427500    0.455001    0.485001
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000     152.000                1
0.278891    0.282446    0.287127    0.289122    0.290828
0.292499    0.294167    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327222    0.332778
0.338494    0.345011    0.353339    0.363164    0.374398
0.387422    0.405034    0.427509    0.452507    0.479939
0.497050    0.500000    0.500000    0.500000    0.500000
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000     152.196                2
0.272082    0.278074    0.285949    0.288869    0.290778
0.292490    0.294165    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327223    0.332782
0.338507    0.345040    0.353388    0.363176    0.374231
```

Figure 3.21 Original file Theta.out

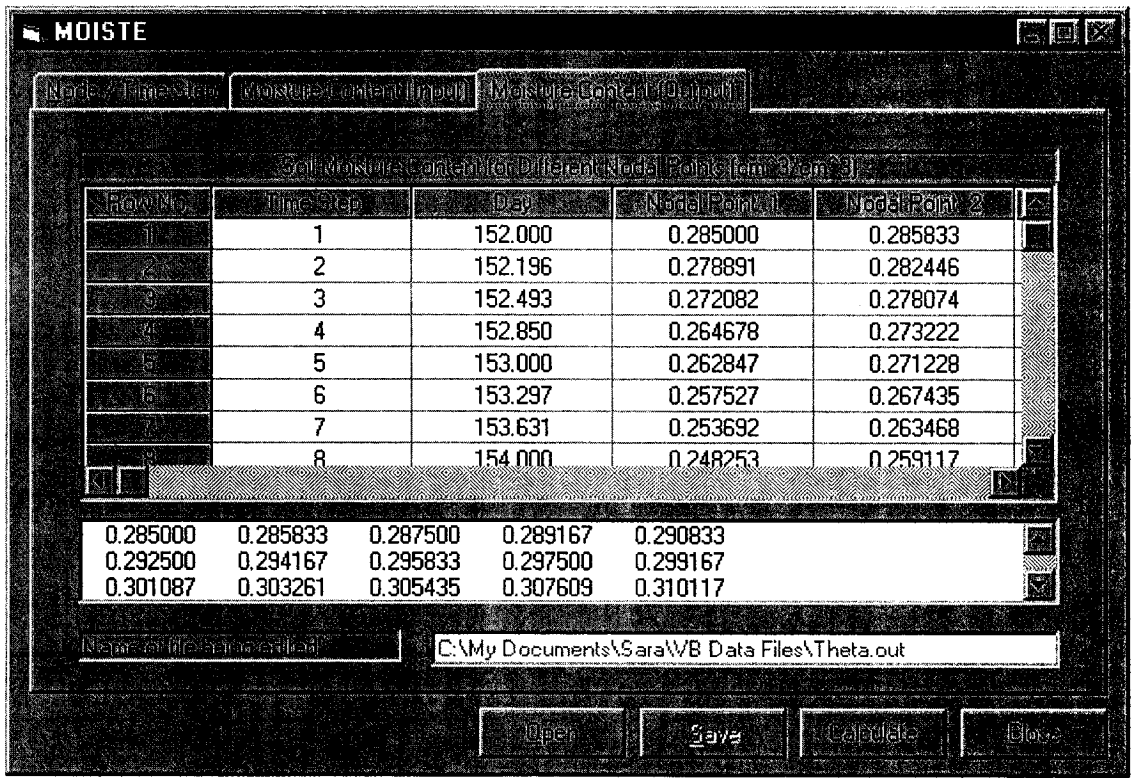


Figure 3.22 frmMoiste(2) - Final GUI for file Theta.out

3.3.3. Program HEAT

HEAT is used to analyze the conduction of heat in the soil profile. It consists of seven input files (i.e. theta.out, parm7.dat, t.out, t1.out, data, temp.dat and heat.dat) plus an output file (i.e. tflow.out).

3.3.3.1. Form Heat

This form is loaded once the Heat option is chosen from the menu option (Fig. 3.23). This event can occur by clicking on the Heat option or by pressing on the 'H' key on the keyboard.

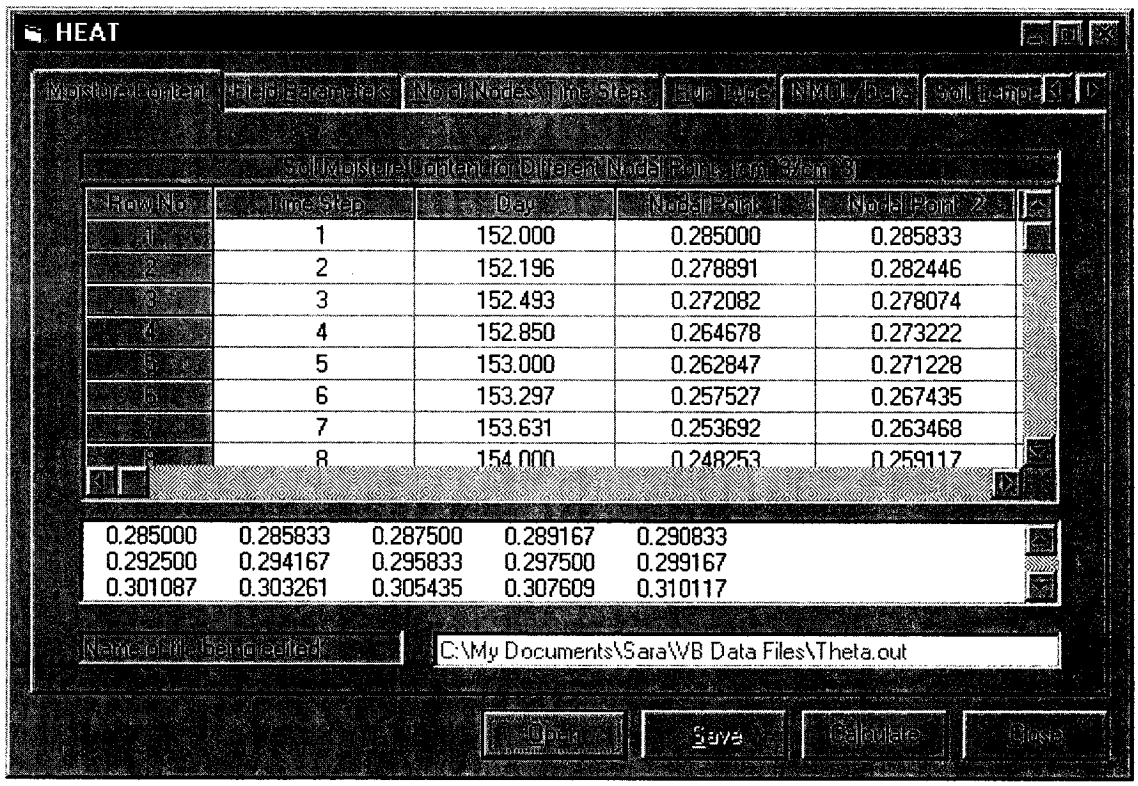


Figure 3.23 Form Heat

3.3.3.1.1. Tab Heat

This tab contains the information of eight different input/output files involved in the HEAT program. One can either click on a desired tab or press the underlined letter of that tab plus the Alt key. Below is the list of the tabs used which lead to five frames in the form of an array (Table 3.12).

Index	Caption	ToolTipText
1	Moisture Content	Moisture content profile
2	Field Parameters	
3	No. of Nodes/Time Steps	Total number of nodes and time steps
4	Run Type	Input data and codes which control the type of model run
5	NMOL/Data	Standard data format for NMOL
6	Soil Temperature	Inputs for simulating soil temperature
7	Soil Constituent	Soil constituent characteristics
8	Output File/Temperature	Soil temperature

Table 3.12 Different Tabs in Heat Form

3.4.1.1.2. Frame Heat

The frames frmHeat(0), frmHeat(1), frmHeat(2), frmHeat(3), frmHeat(4), frmHeat(5), frmHeat(6), and frmHeat(7) are used as platforms to design the entries required for each input/output file associated with the HEAT model. Samples of the original files are shown in Figures 3.24, 3.26, 3.28, 3.30, 3.32, 3.34, 3.36, and 3.38 along with the GUI replacing the ASCII files (Figs. 3.25, 3.27, 3.29, 3.31, 3.33, 3.35, 3.37, and 3.39). The user can press the

Calculate button any time to execute the HEAT program with the values saved in the default input files.

```
0.285000    0.285833    0.287500    0.289167    0.290833
0.292500    0.294167    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327222    0.332778
0.338492    0.345000    0.353286    0.363000    0.374000
0.386667    0.404167    0.427500    0.455001    0.485001
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000     152.000           1
0.278891    0.282446    0.287127    0.289122    0.290828
0.292499    0.294167    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327222    0.332778
0.338494    0.345011    0.353339    0.363164    0.374398
0.387422    0.405034    0.427509    0.452507    0.479939
0.497050    0.500000    0.500000    0.500000    0.500000
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000     152.196           2
0.272082    0.278074    0.285949    0.288869    0.290778
0.292490    0.294165    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327223    0.332782
0.338507    0.345040    0.353388    0.363176    0.374231
```

Figure 3.24 Original file Theta.out

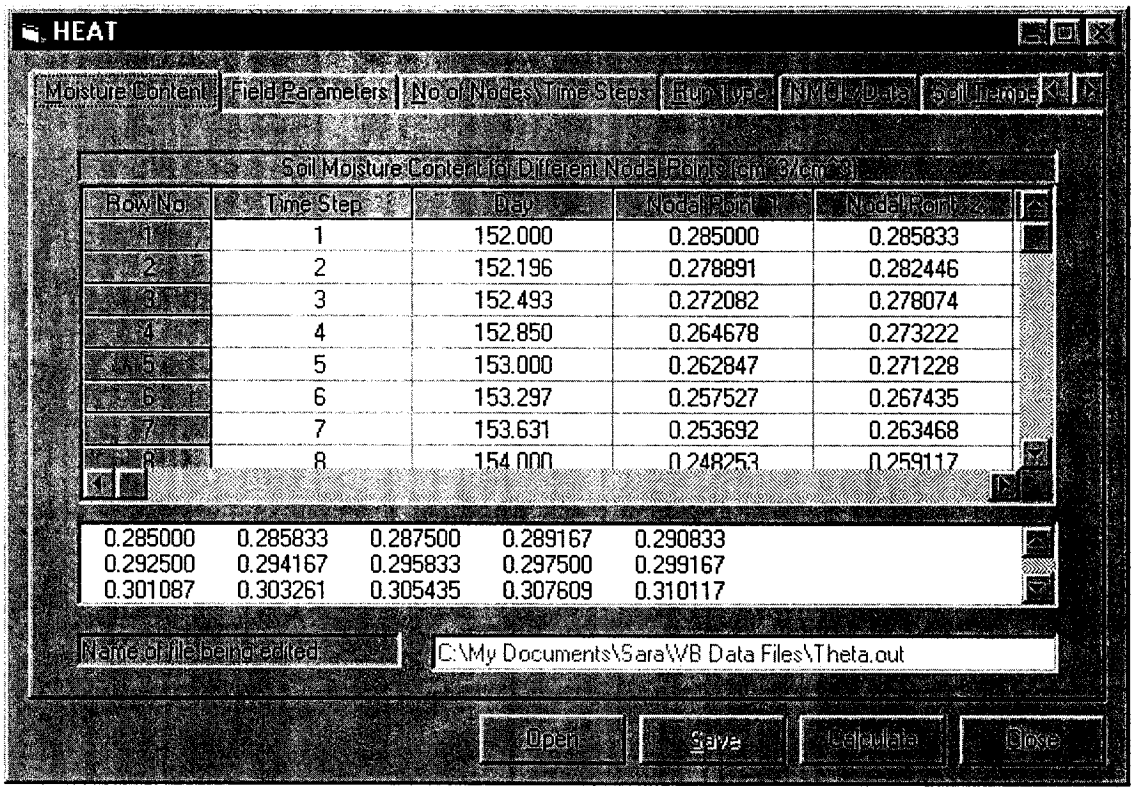


Figure 3.25 frmHeat(0) - Final GUI for file Theta.out

```
180.77d0
200.00d0
3.200d0
0.0173d0
1.30d0
2.650d0
0.005d0
10.0d0
1.200d0
4.0d0
4300.d0
2.50d-07
0.70d0
0.150d0
```

Figure 3.26 Original file Param7.dat

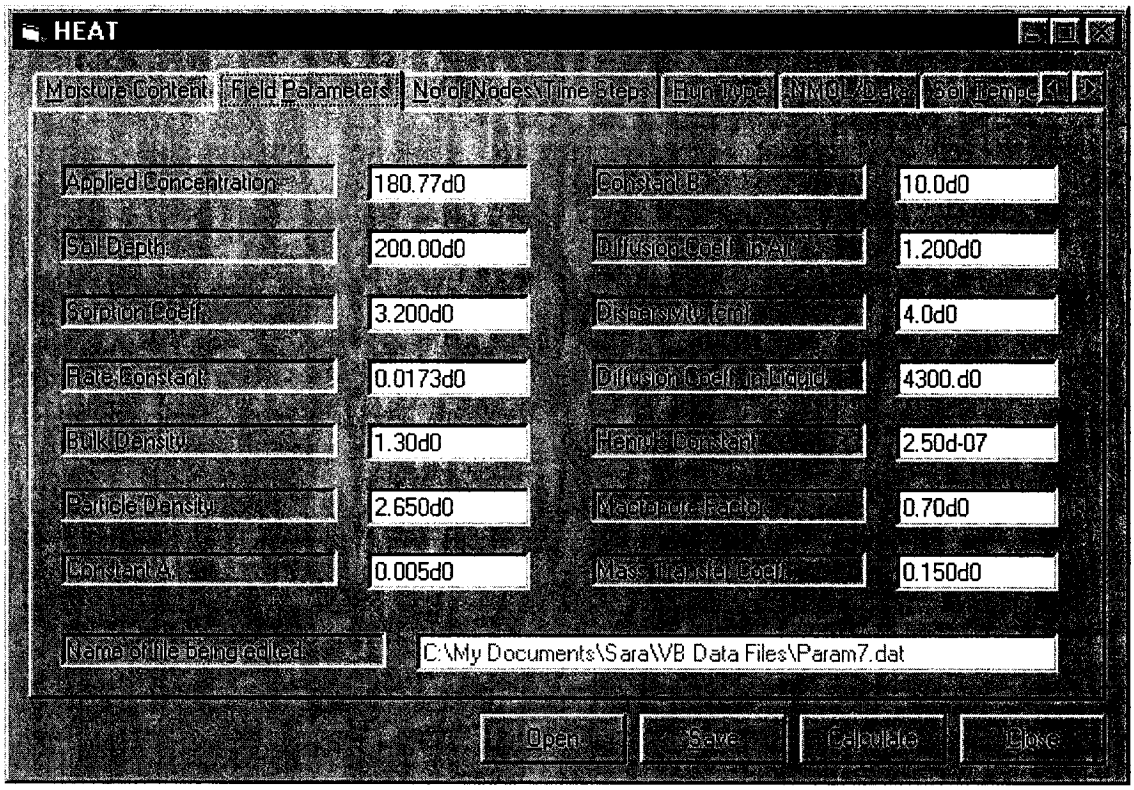


Figure 3.27 frmHeat(1) - Final GUI for file Param7.dat

```
66      1
□
```

Figure 3.28 Original file T.out

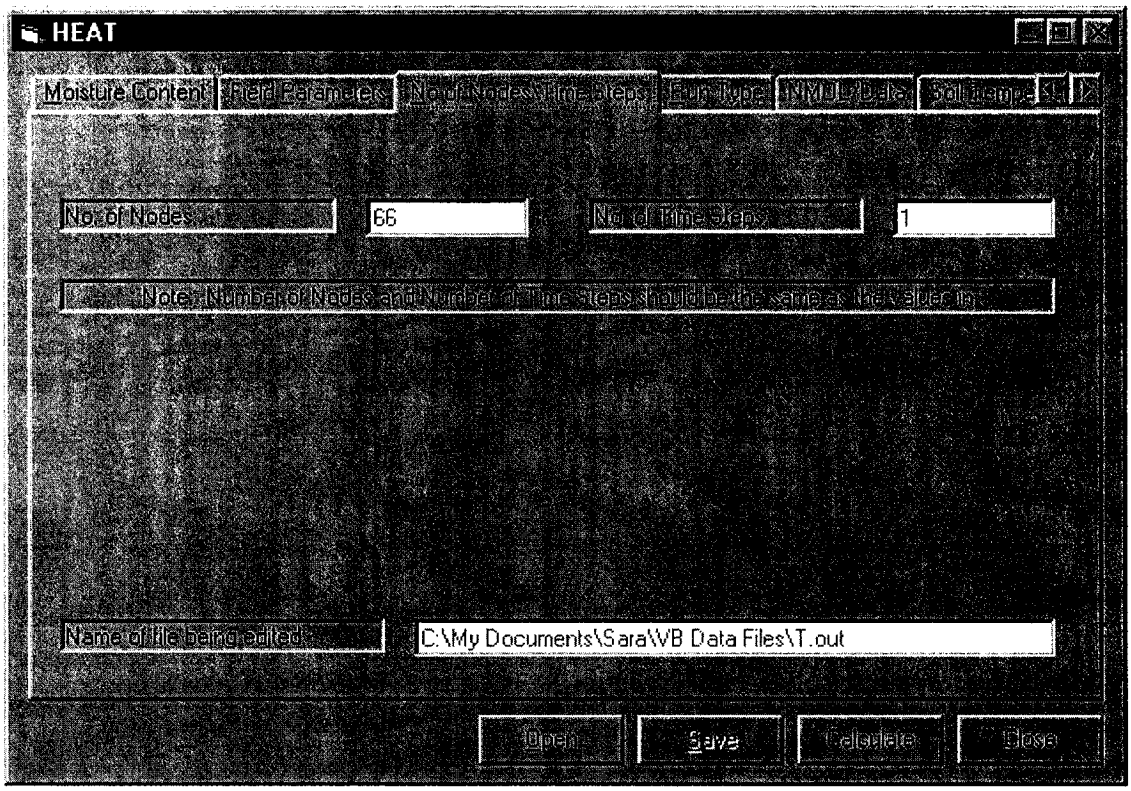


Figure 3.29 frmHeat(2) - Final GUI for file T.out

```
64  1   0   1   1   1   1   1   1   1
1.0d0 0.0d0
□
```

Figure 3.30 Original file T1.out

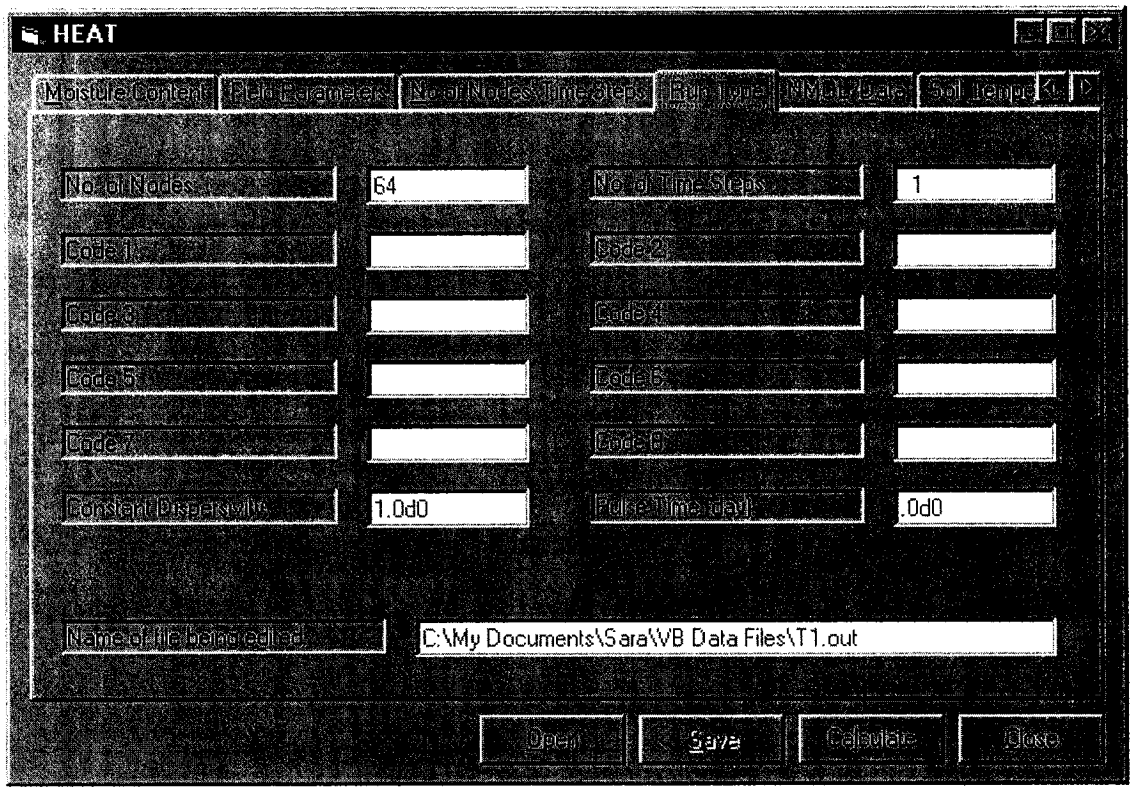


Figure 3.31 frmHeat(3) - Final GUI for file T1.out

```
salt program
152      182.0     1.0
 101   500    1    1 rel   0.0001
END OF RUNS
```

Figure 3.32 Original file DataHeat

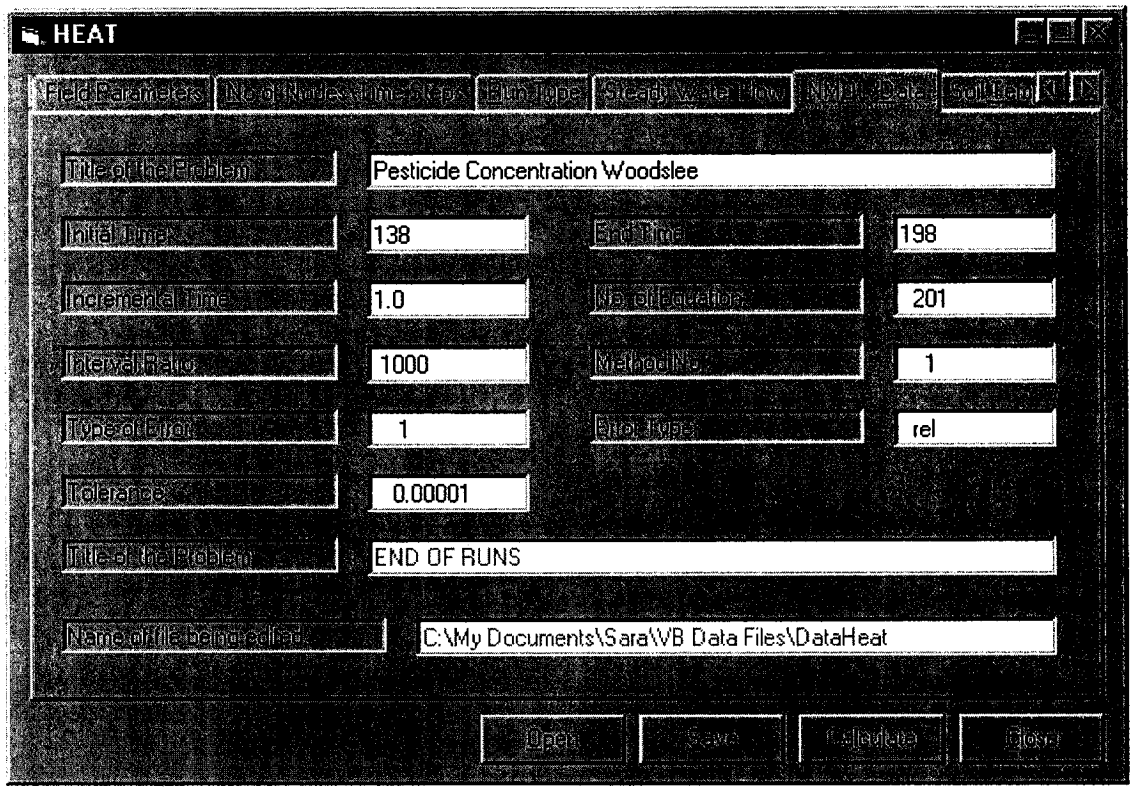


Figure 3.33 frmHeat(4) - Final GUI for file DataHeat

```
152.0d0  182.0d0  5.50d0
19.00d0
16.50d0
12.75d0
13.00d0
15.25d0
20.75d0
18.75d0
16.25d0
13.50d0
11.25d0
14.00d0
18.50d0
21.25d0
21.75d0
24.75d0
27.25d0
26.75d0
18.75d0
18.25d0
22.50d0
25.75d0
```

Figure 3.34 Original file Temp.dat

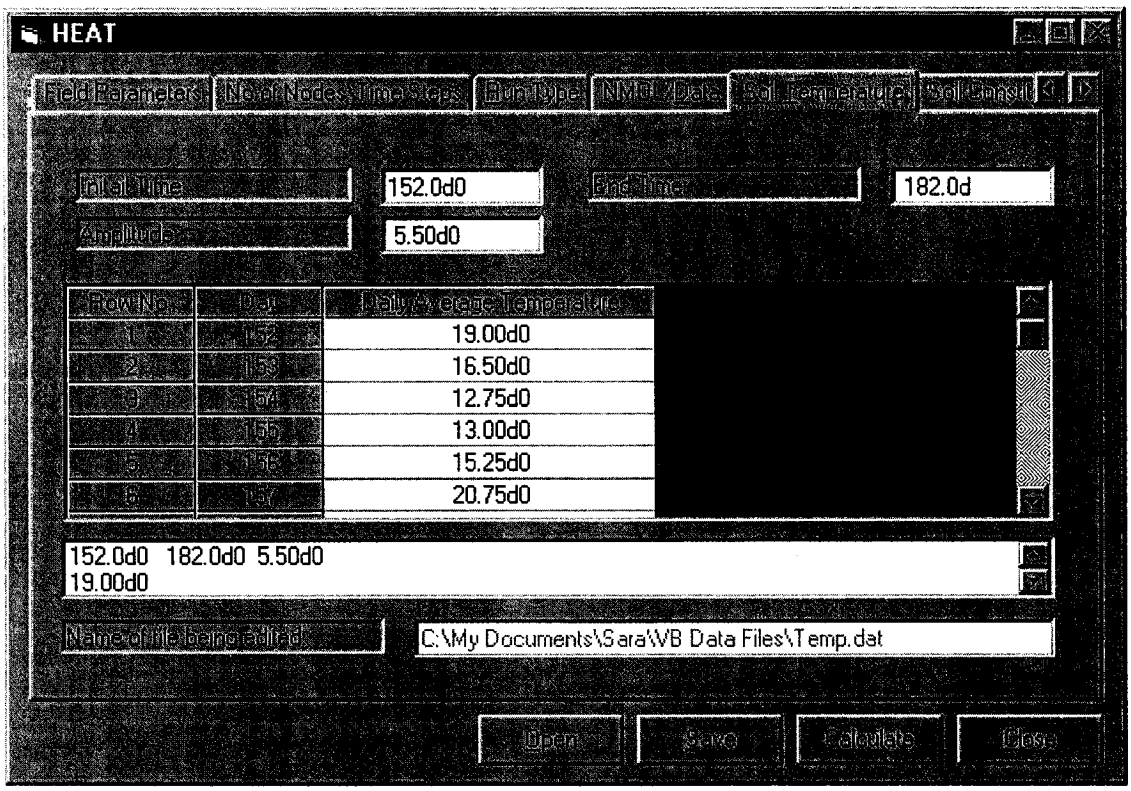


Figure 3.35 frmHeat(5) - Final GUI for file Temp.dat

```
0.45
0.32
0.23
0.04
2.65
0.125
0.125
0.750
0.125
0.125
0.750
0.125
0.125
0.750
0.500
0.500
0.00
0.333
0.105
0.015
7.00D-03
7.00D-03
```

Figure 3.36 Original file Heat.dat

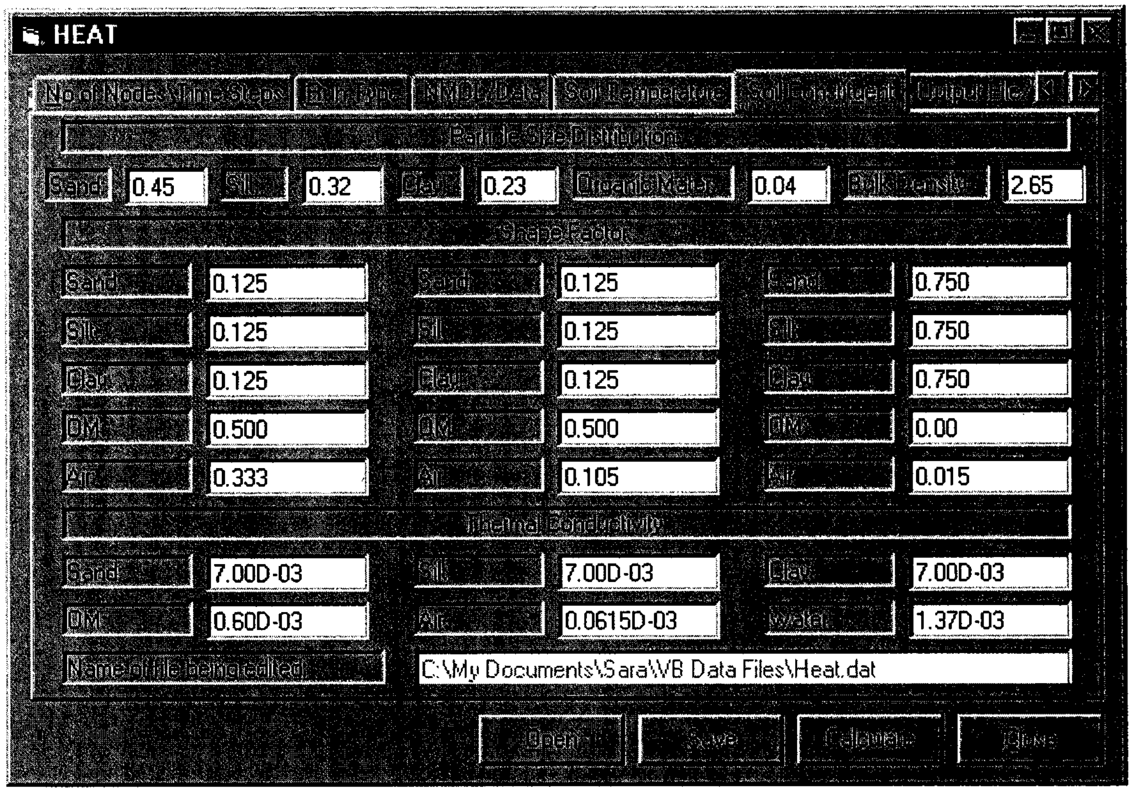


Figure 3.37 frmHeat(6) - Final GUI for file Heat.dat

25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	10.0000000000000	
25.0000000000000	25.0000000000000	25.0000000000000

Figure 3.38 Original file Tflow.out

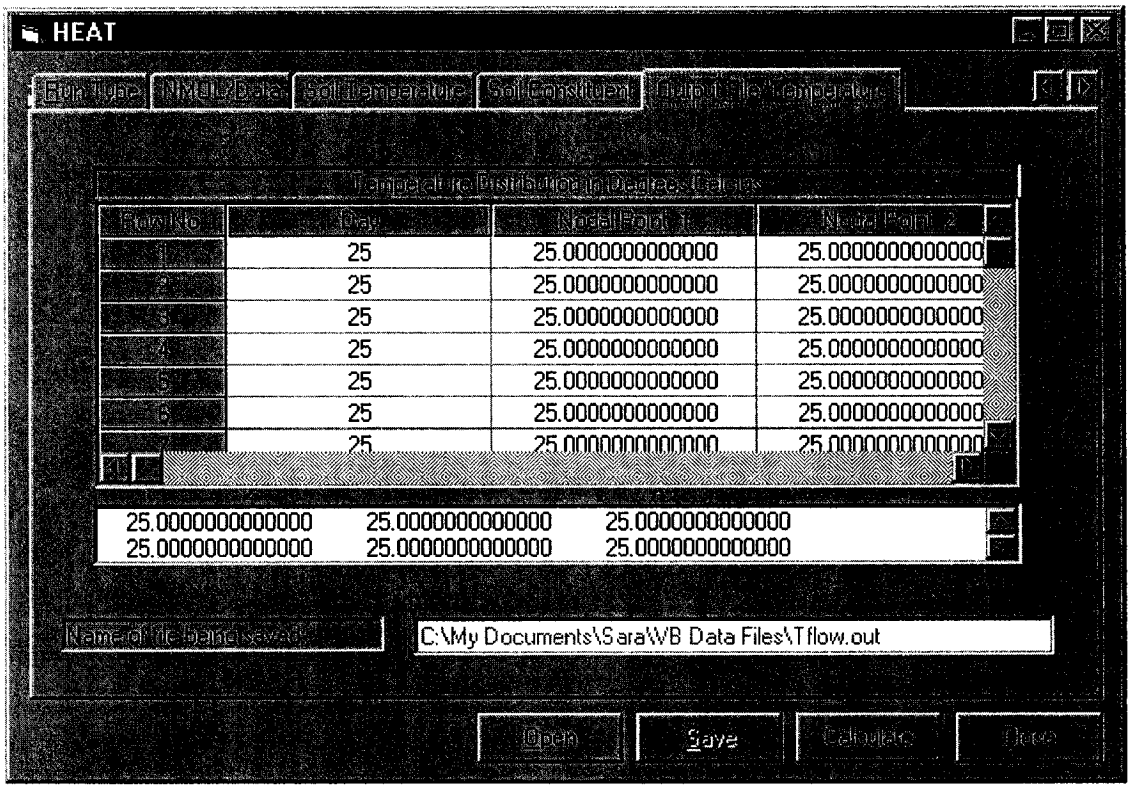


Figure 3.39 frmHeat(7) - Final GUI for file Tflow.out

3.3.4. Program CADD

CADD is used to analyze pesticide partitioning in runoff water and sediment affected by climate and tillage practices. It consists of nine input files (i.e. param1.dat, gamble.dat, micro.dat, steady.dat, volat.dat, tflow.out, theta.out, velocity.out, and data) plus an output file (i.e. output.dat). The old revision provided three other output files (i.e. diffused.out, decayed.out, and kd.out).

3.3.4.1. Form Cadd

This form is loaded once the Cadd option is chosen from the menu option (Fig. 3.40). This event can be activated by clicking on the Cadd option or by pressing on the 'C' key on the keyboard. The GUI has been designed to allow a direct click on each enabled object or to go from one object to the other using the tab key. Each object can be enabled (displayed in its normal format) or disabled (displayed usually gray). If an object is disabled the user does not have access to that object, as it is for display purposes only. A tool tip is associated with each object to explain the contents of that specific object. This explanation is obtained by holding the cursor on each enabled object for a while.

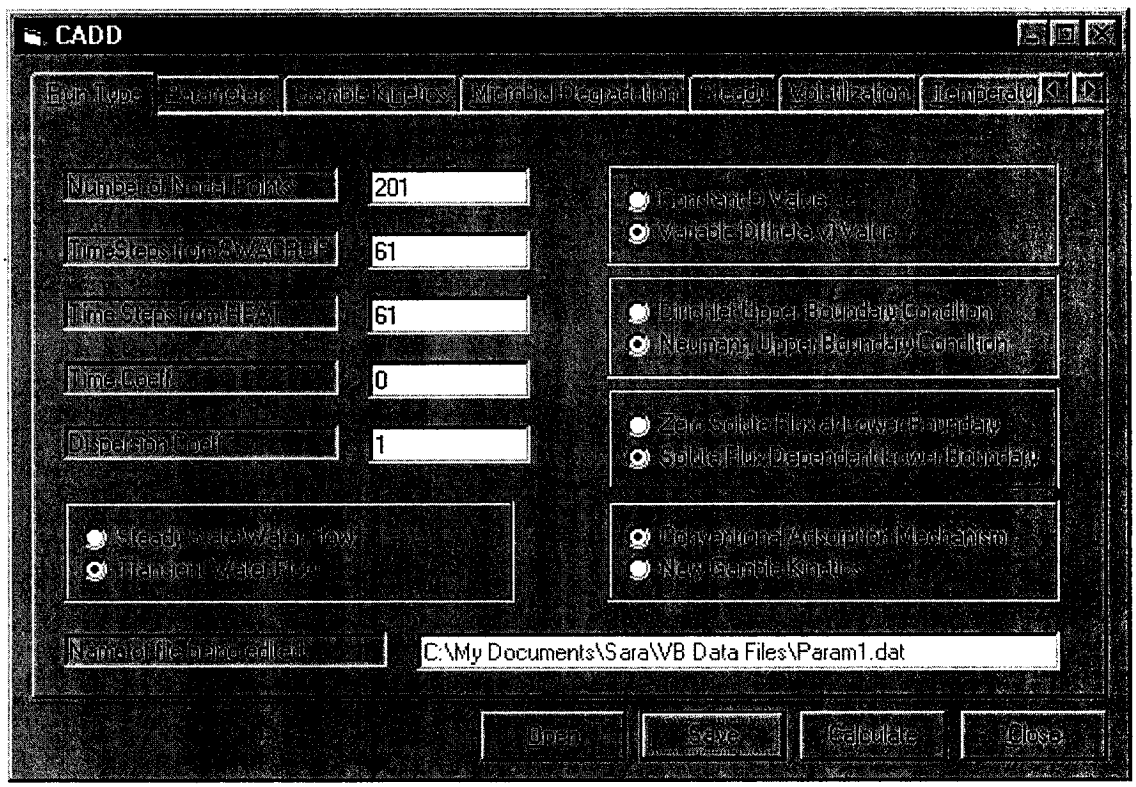


Figure 3.40 Form Cadd

3.3.4.1.1. Tab Cadd

This tab contains the information of sixteen different input/output files involved with the CADD program. One can either click on a desired tab or press the underlined letter of that tab plus the Alt key. Below is the list of the tabs used which lead to five frames in the form of an array (Table 3.13).

Index	Caption	ToolTipText
1	Parameters	Field parameters
2	Run Type	Flags specifying run type
3	Gamble Kinetics	Gamble kinetics parameters
4	Microbial Degradation	Microbial degradation parameters
5	Steady	Steady state water flow parameters
6	Volatilization	Volatilization parameters
7	Moisture Content	Moisture content as a function of depth and time
8	Theta	Moisture content profile
9	Velocity	Flux values
10	Data	Standard data format for NMOL
11	Total Output	Total concentration in the whole profile for each day
12	Solution Phase	Detailed output of pesticide concentration in solution phase
13	Adsorbed Phase	Detailed output of pesticide concentration in adsorbed phase
14	Diffused Phase	Pesticide diffused intrapartically
15	Decayed Phase	Pesticide diffused microbially
16	Kd	Soil-water partitioning coefficient
17	Summary Output	Total concentration in different particular depths of the soil

Table 3.13 Different Tabs in Cadd Form

3.3.4.1.2. Frame Cadd

The frames frmCadd(0), frmCadd(1), frmCadd(2), frmCadd(3), frmCadd(4), frmCadd(5), frmCadd(6), frmCadd(7), frmCadd(8), frmCadd(9), frmCadd(10), frmCadd(11), frmCadd(12), frmCadd(13), frmCadd(14), frmCadd(16), and frmCadd (16) are used as platforms to design the entries required for each input/output file associated with the CADD model. Samples of the original files are shown in Figures 3.41, 3.43, 3.45, 3.47, 3.49, 3.51, 3.53, 3.55, 3.57, 3.59, 3.61, 3.63, 3.65, 3.67, 3.69, 3.71, and 3.73 along with the GUI replacing the ASCII files (Figs. 3.42, 3.44, 3.46, 3.48, 3.50, 3.52, 3.54, 3.56, 3.58, 3.60, 3.62, 3.64, 3.66, 3.68, 3.70, 3.72, and 3.74). The user can press the Calculate button any time to execute the CADD program with the values saved in the default input files.

```
200.00d0
3.200d0
0.0173d0
1.30d0
2.65d0
0.005d0
10.0d0
1.200d0
4.0d0
4300.d0
2.50d-07
0.70d0
0.150d0
```

Figure 3.41 Original file Param1.dat

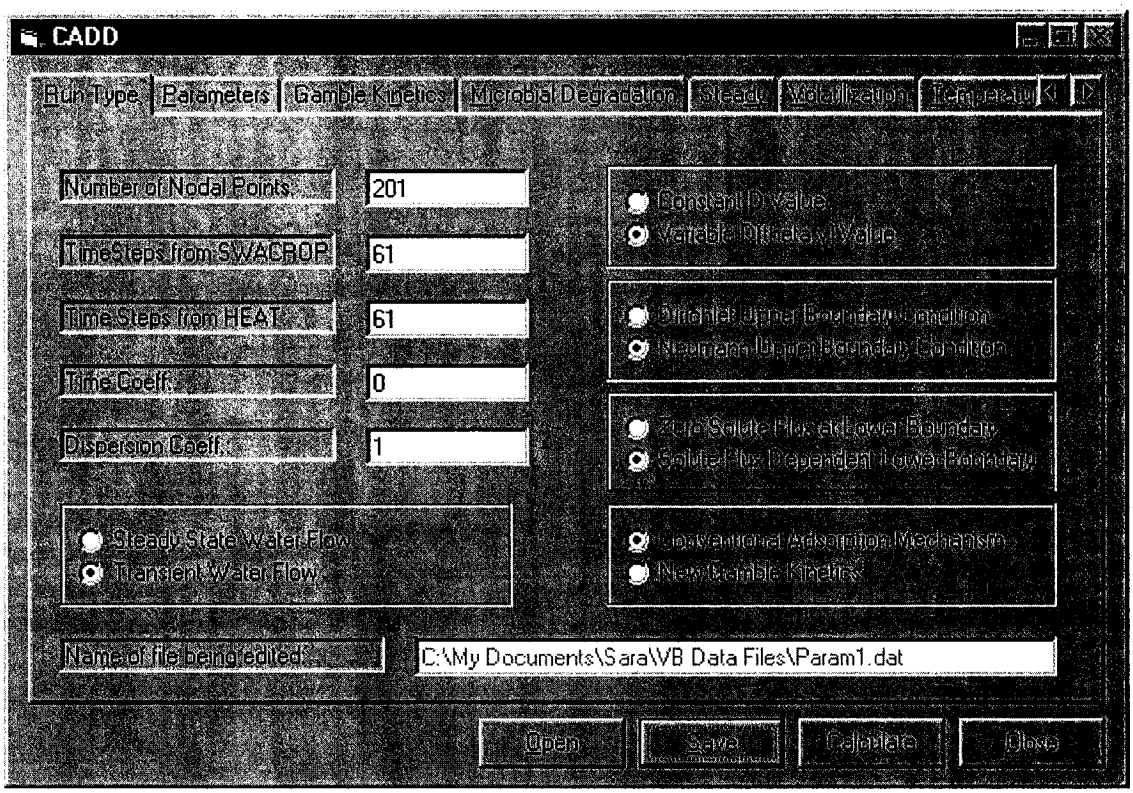


Figure 3.42 frmCadd(0) - Final GUI for file Param1.dat

This frame is used as a platform to design the entries required for file param1.dat. There are various codes used in this file as described below:

code1 = 0 for steady state water flow

= 1 for transient water flow

code2 = 0 for inputting a constant D value

= 1 for variable D(theta,v) value - calculated by the program

code3 = 0 for dirichlet upper b.c.

= 1 for neumann upper b.c.

code4 = 0 for zero solute flux at lower boundary

= 1 for solute flux dependent lower boundary

code5 = 0 for conventional adsorption mechanism

= 1 for new Gamble kinetics

code6 = 0 for zero initial concentration with depth

= 1 for variable initial concentration with depth

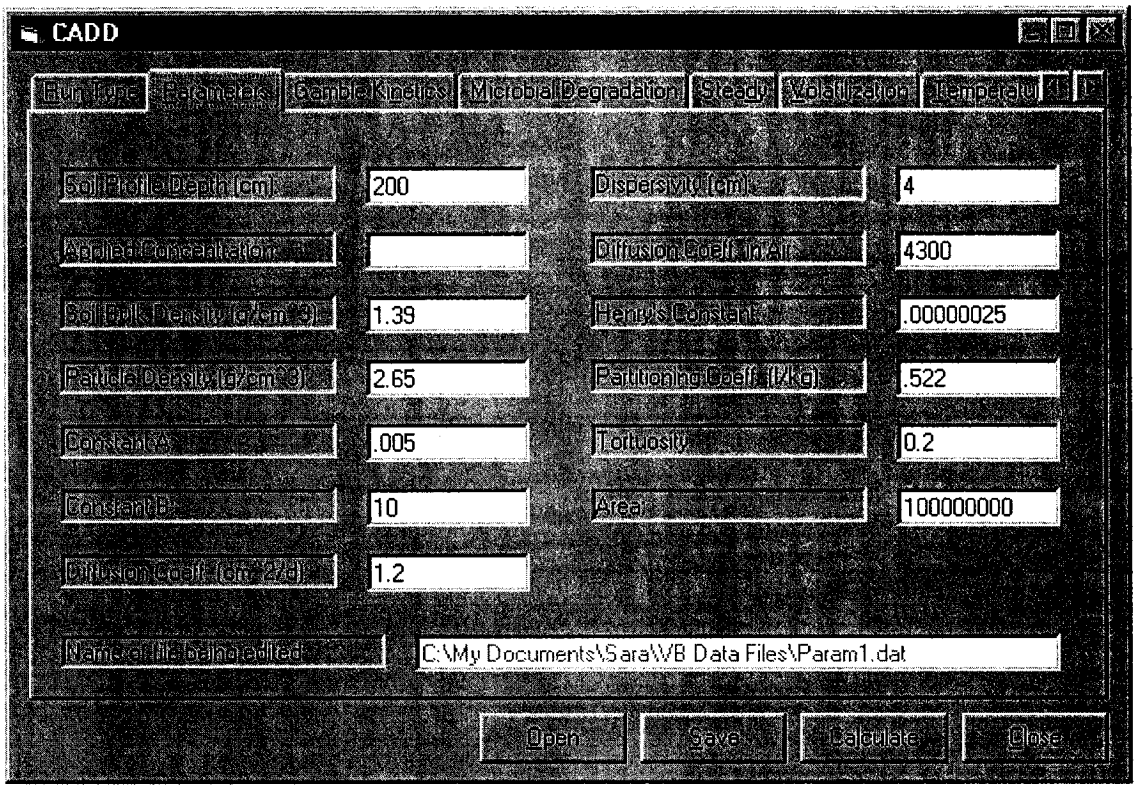


Figure 3.43 frmCadd(1) - Final GUI for file Param1.dat

```
1
2
3
4
```

Figure 3.44 Original file Gamble.dat

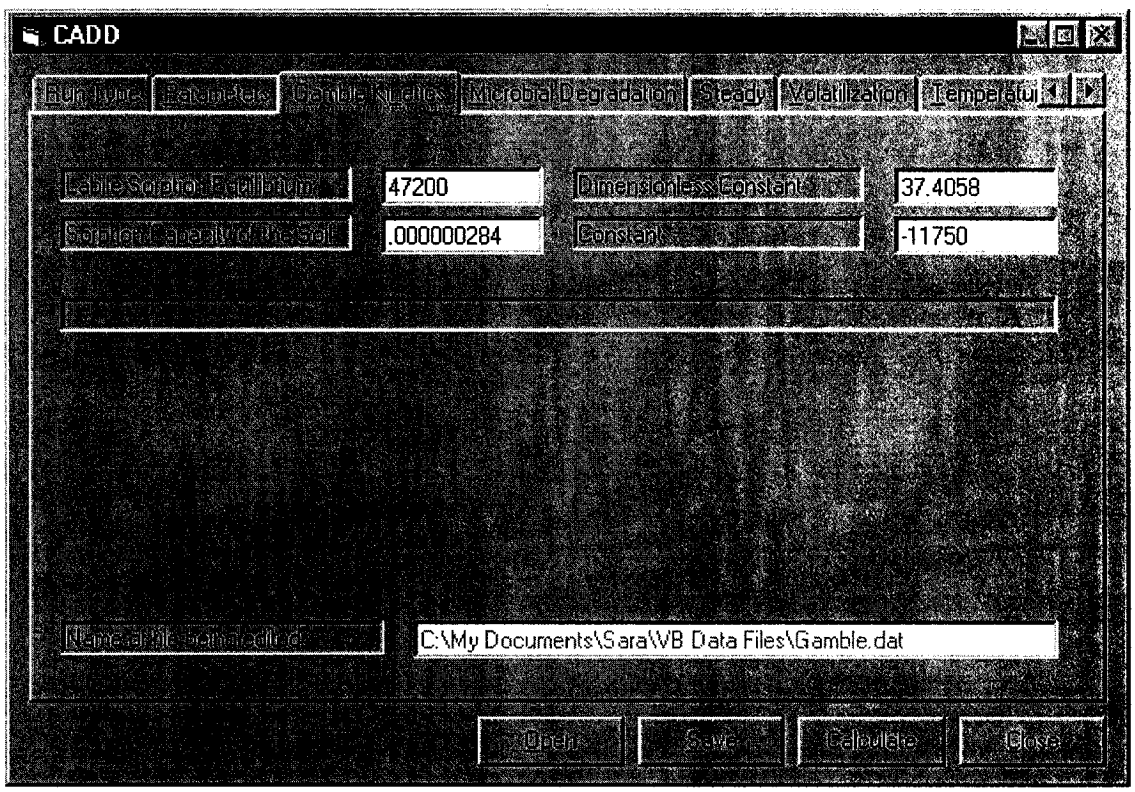


Figure 3.45 frmCadd(2) - Final GUI for file Gamble.dat

1
2
3
4

Figure 3.46 Original file Micro.dat

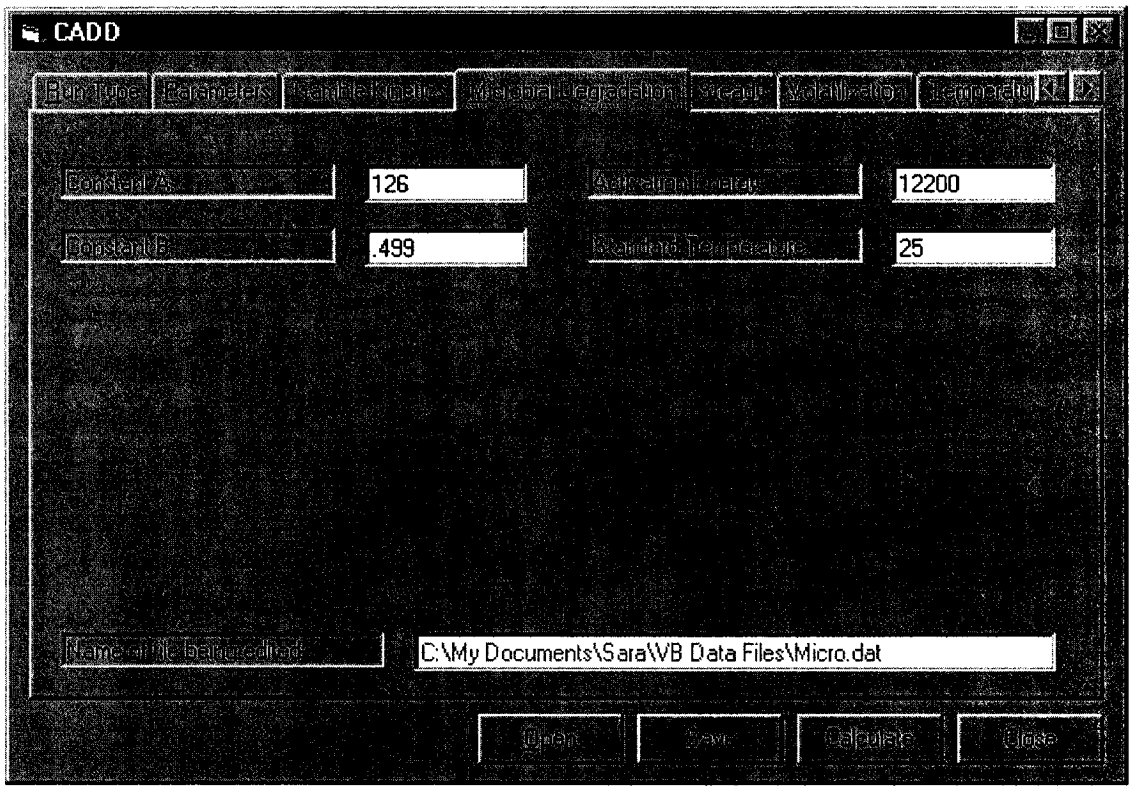


Figure 3.47 frmCadd(3) - Final GUI for file Micro.dat

1
2
3
4

Figure 3.48 Original file Steady.dat

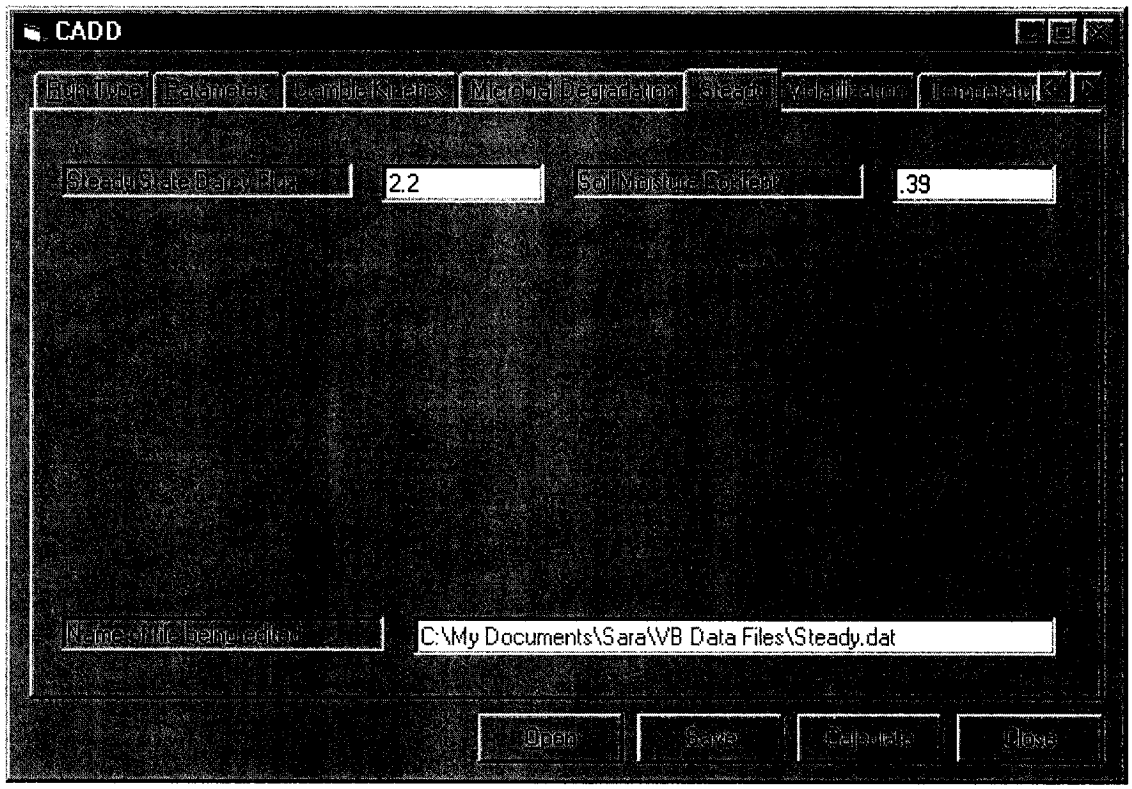


Figure 3.49 frmCadd(4) - Final GUI for file Steady.dat

```
1
2
3
4
```

Figure 3.50 Original file Volat.dat

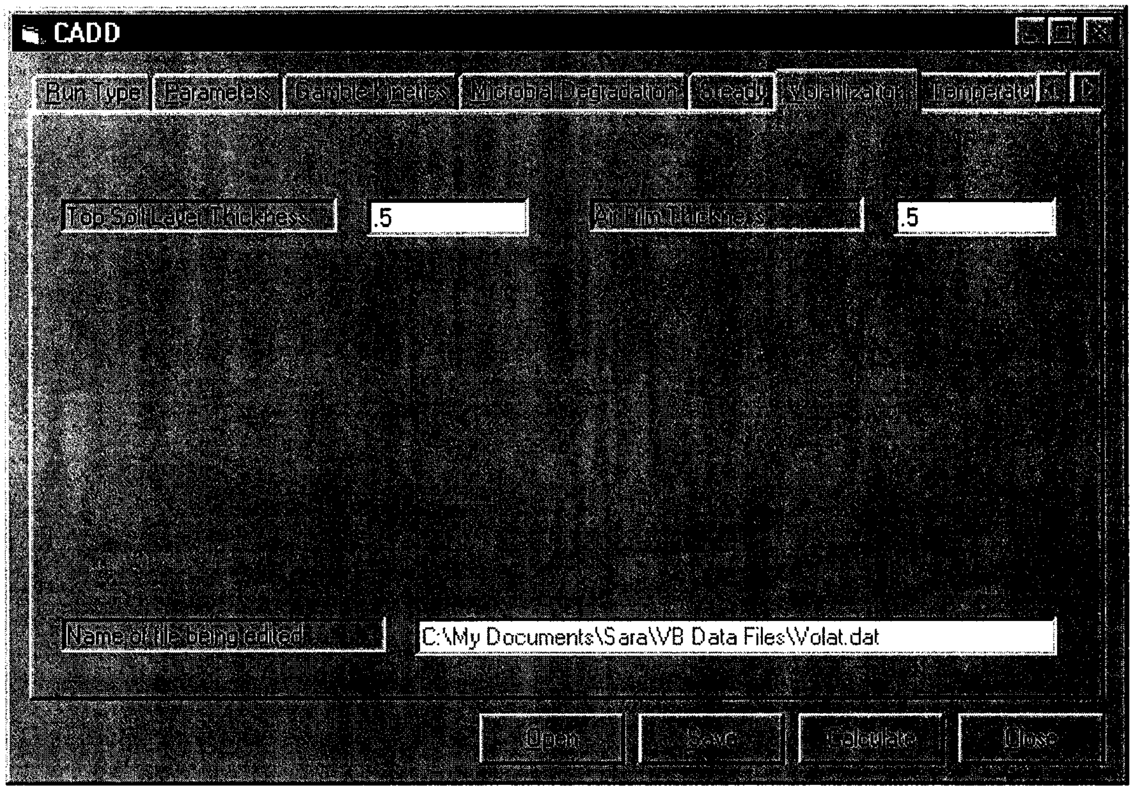


Figure 3.51 frmCadd(5) - Final GUI for file Volat.dat

25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	25.0000000000000	25.0000000000000
25.0000000000000	10.0000000000000	

Figure 3.52 Original file Tflow.out

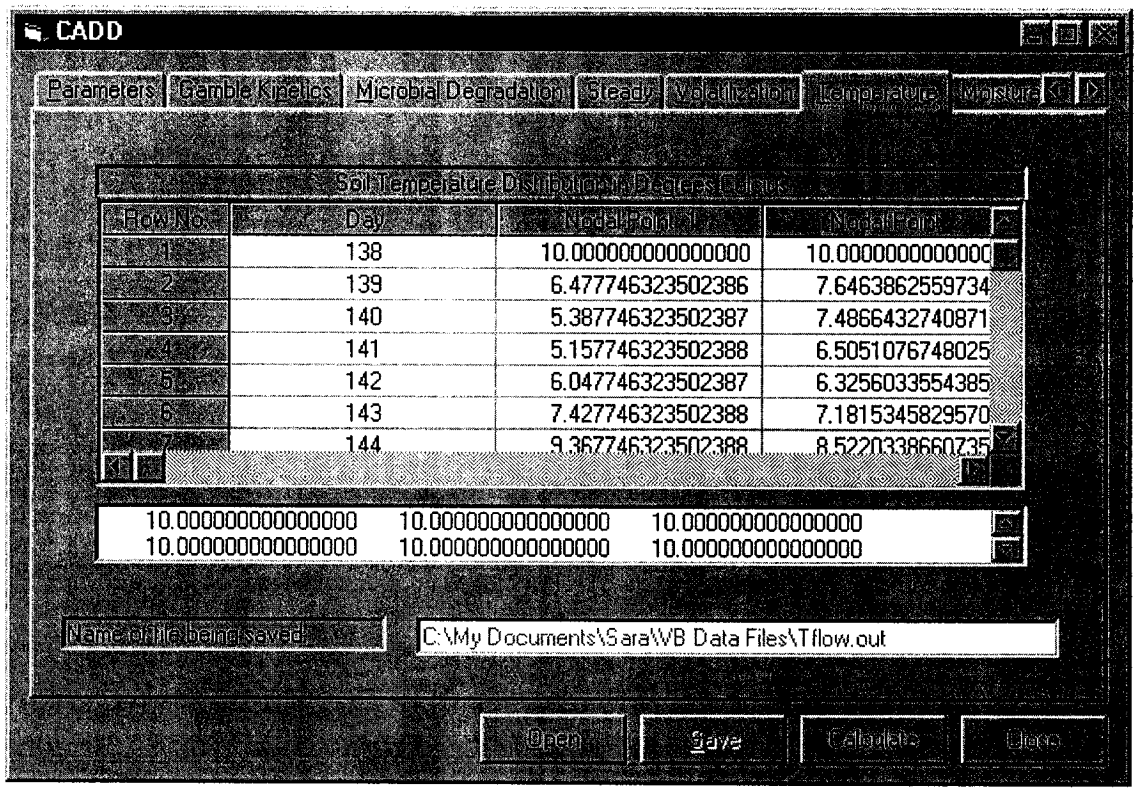


Figure 3.53 Final GUI for file Tflow.out

```
0.285000    0.285833    0.287500    0.289167    0.290833
0.292500    0.294167    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327222    0.332778
0.338492    0.345000    0.353286    0.363000    0.374000
0.386667    0.404167    0.427500    0.455001    0.485001
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000     152.000           1
0.278891    0.282446    0.287127    0.289122    0.290828
0.292499    0.294167    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327222    0.332778
0.338494    0.345011    0.353339    0.363164    0.374398
0.387422    0.405034    0.427509    0.452507    0.479939
0.497050    0.500000    0.500000    0.500000    0.500000
0.500000    0.500000    0.500000    0.500000    0.500000
0.500000     152.196           2
0.272082    0.278074    0.285949    0.288869    0.290778
0.292490    0.294165    0.295833    0.297500    0.299167
0.301087    0.303261    0.305435    0.307609    0.310117
0.313462    0.317308    0.321838    0.327223    0.332782
```

Figure 3.54 Original file Theta.out

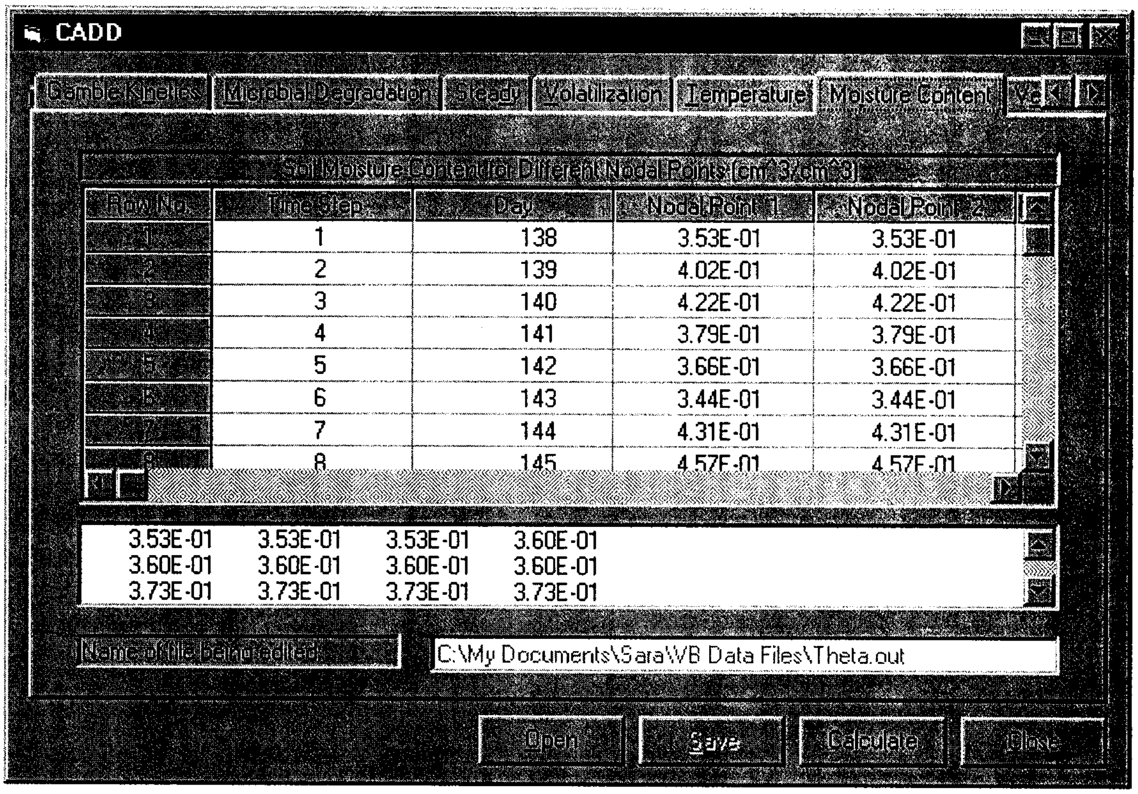


Figure 3.55 frmCadd(7) - Final GUI for file Theta.out

0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	0.000000000000000
0.000000000000000	0.000000000000000	152.000001000000
1		

Figure 3.56 Original file Velocity.out

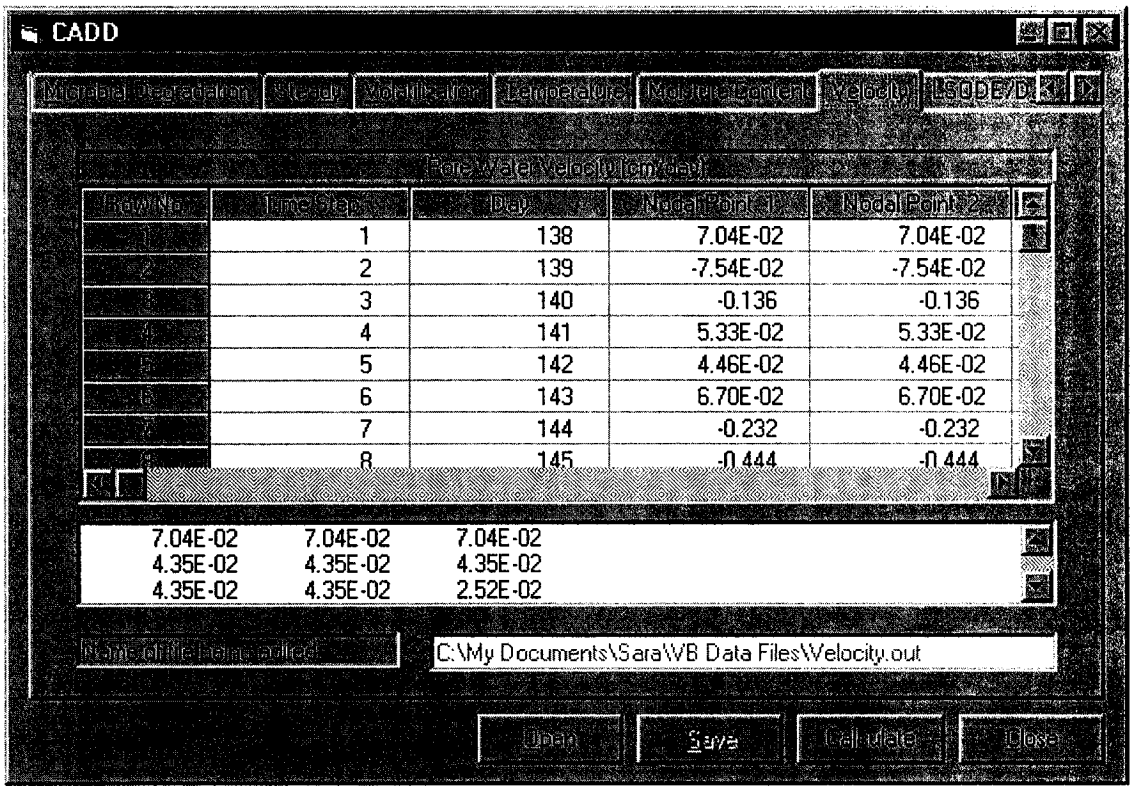


Figure 3.57 frmCadd(8) - Final GUI for file Velocity.out

```
salt program
152      182.0     1.0
 101   500   1    1 rel   0.0001
END OF RUNS
```

Figure 3.58 Original file DataCadd

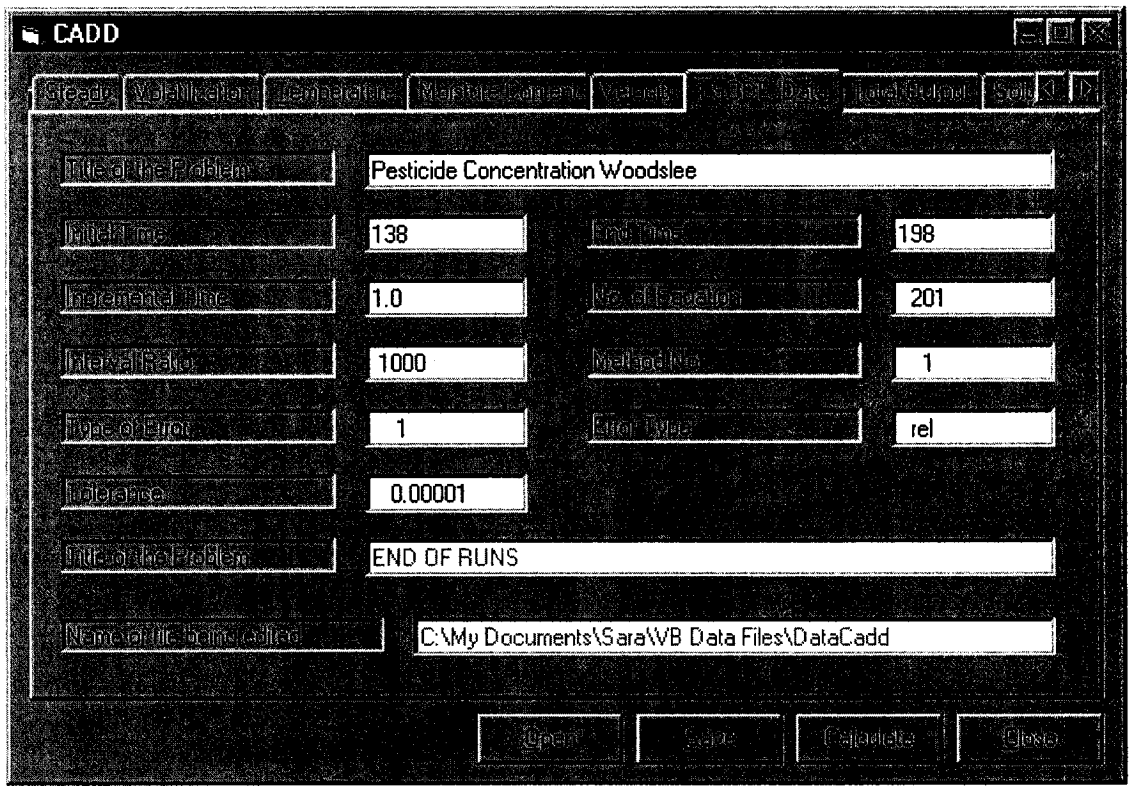


Figure 3.59 frmCadd(9) - Final GUI for file DataCadd

```
1 RUN NO. -    7  Pesticide Concentration Woodslee

 INITIAL T -   0.138D+03

   FINAL T -   0.198D+03

   PRINT T -   0.100D+01

 NUMBER OF DIFFERENTIAL EQUATIONS - 201

 PRINT INTERVAL/MINIMUM INTEGRATION INTERVAL -  1000

 INTEGRATION ALGORITHM -  1 - LSODE

 INTEGRATION ERROR MESSAGES - 1

 ERROR CRITERION - rel

 MAXIMUM INTEGRATION ERROR -  0.100D-06

1

  Solution concentration in mg/L of water
   4920.00000000000        5.81000000000000        5.81000000000000
```

Figure 3.60 Original file Output.dat

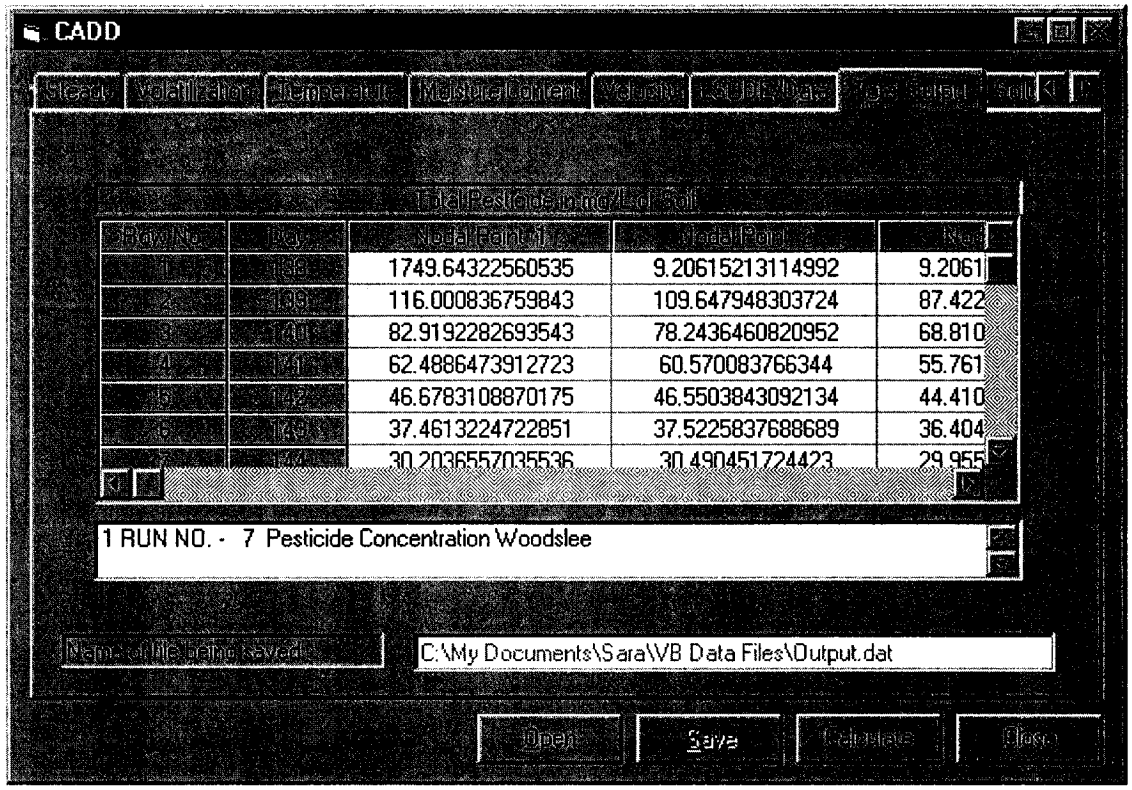


Figure 3.61 frmCadd(10) - Final GUI for file Output.dat

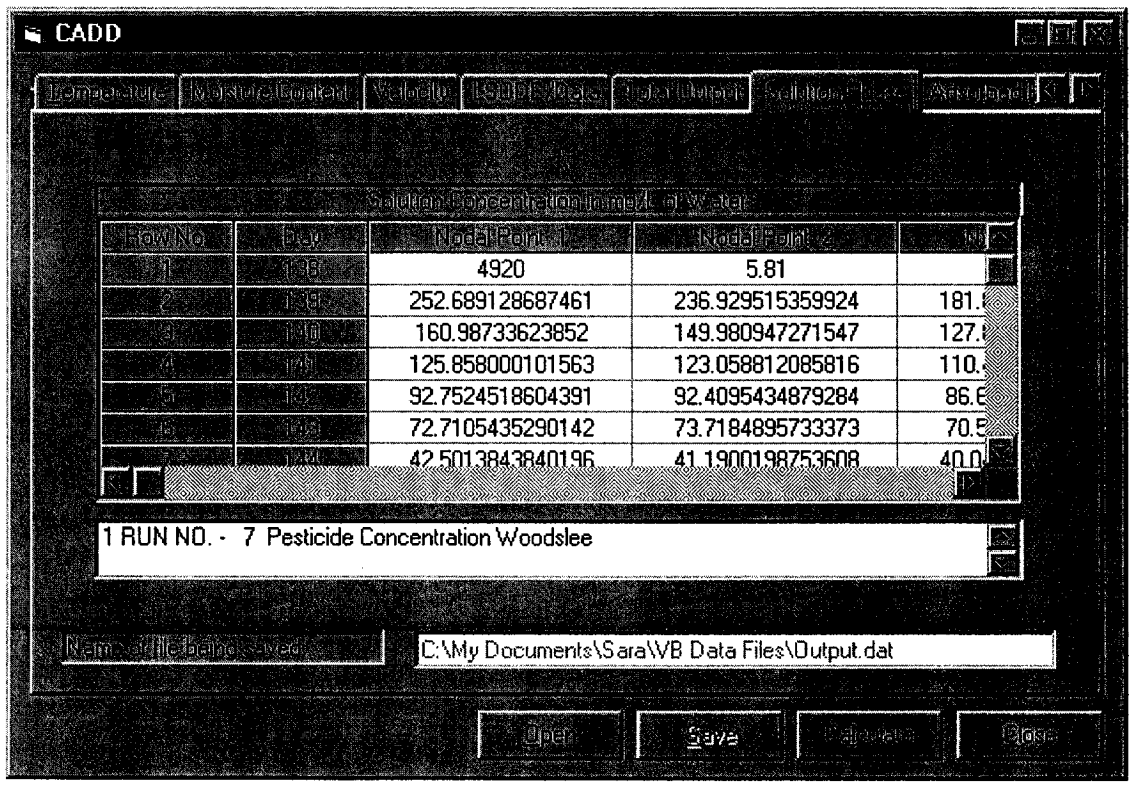


Figure 3.62 frmCadd(11) - Final GUI for file Output.dat

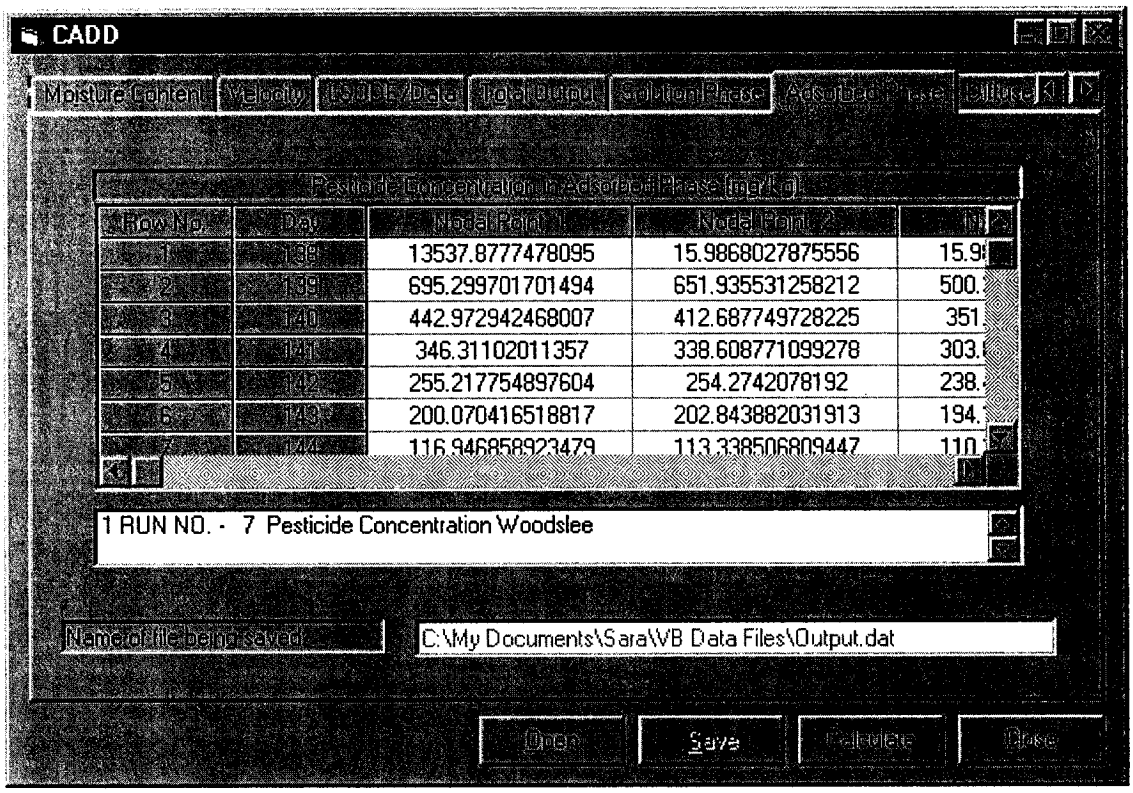


Figure 3.63 frmCadd(12) - Final GUI for file Output.dat

The original PESTFADE model created outputs for pesticide diffused intrapartically. The new revision of the code does not provide this feature, the GUI has been designed based on the previous output. The code can later be advanced to provide the user with these values as well.

```
Number of Nodes        201
  Intraparticle diffusion in ug/g
   2.632527067894802E-001   2.645503402365312E-001   2.669140807732209E-001
   2.725389721425561E-001   2.696122144744742E-001   2.708334908235491E-001
   2.702366783891250E-001   2.713633862184836E-001   2.758283362072049E-001
   2.728421513709272E-001   1.859592083582573E-001   1.848677623262278E-001
   1.711833134256471E-001   1.850683502782671E-001   1.822243944417704E-001
   2.180465561438942E-001   2.160284364342965E-001   2.223686033205791E-001
   2.149123048835732E-001   2.060427614505980E-001   1.880890733389444E-002
   2.539913637857437E-002  -6.269486251493662E-003   2.080803528290344E-003
  -4.717007981205024E-004   7.224212039794842E-004   3.560005177116055E-004
   4.814709195913862E-004   4.500335164792084E-004   4.558452916785638E-004
```

Figure 3.64 Original file Diffused.out

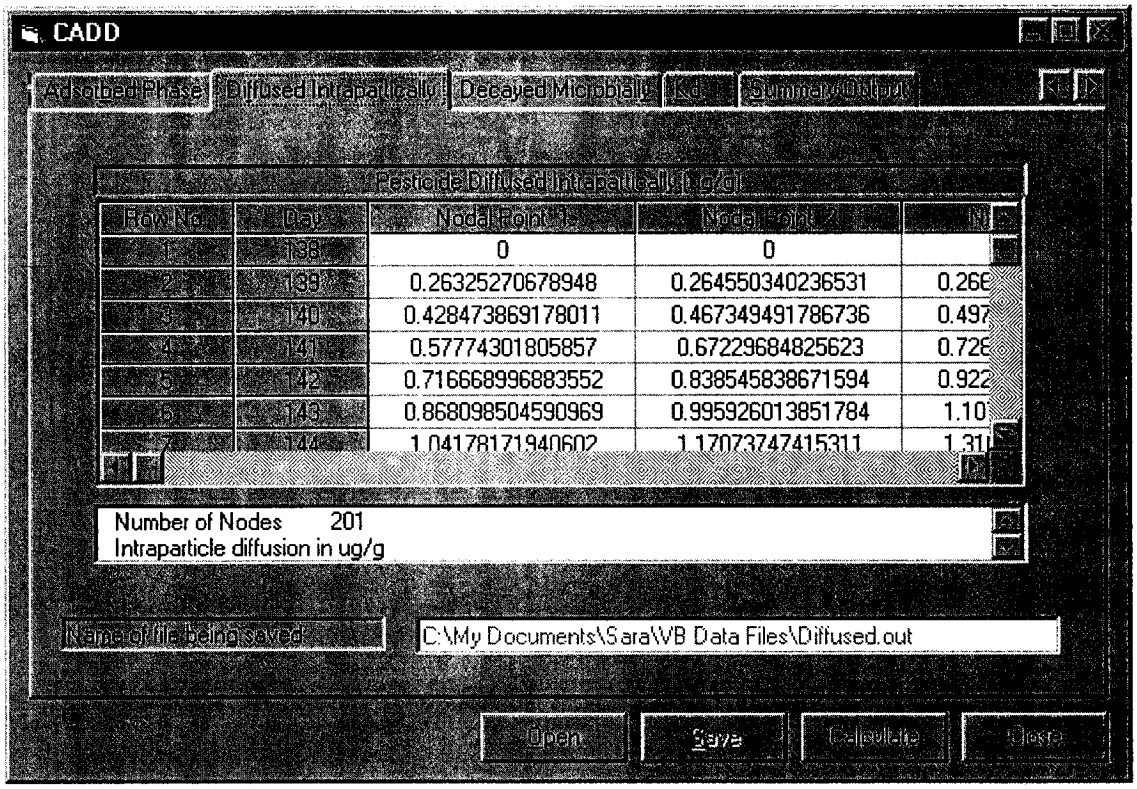


Figure 3.65 frmCadd(13) - Final GUI for file Diffused.out

The original PESTFADE model created outputs for pesticide decayed microbially. The new revision of the code does not provide this feature, the GUI has been designed based on the previous output. The code can later be advanced to provide the user with these values as well.

```
Number of Nodes          201
  Microbial decay in mg herbicide/L of B.S.
  -3.871893476570058E-002   -3.916871460339073E-002   -4.004521952614984E-002
  -4.150266220100339E-002   -4.035719077387980E-002   -4.080871997616984E-002
  -4.057534960786749E-002   -4.100236907408832E-002   -4.147247612602510E-002
  -4.044188310007535E-002   -2.224415567211192E-002   -2.207847986304655E-002
  -2.008440103278429E-002   -2.225231220109585E-002   -2.183231173767045E-002
  -2.747378684089725E-002   -2.712643833694763E-002   -2.825013612354116E-002
  -2.705148750746401E-002   -2.561066317965331E-002   -2.061501463781023E-003
  -2.792451177844041E-003    6.796234383551716E-004   -2.280644723649841E-004
   5.162119096917752E-005   -7.912985875293695E-005   -3.898953109432287E-005
  -5.273266677859901E-005   -4.959477411254224E-005   -5.023538785639864E-005
  -5.006828490769232E-005   -5.008511988117672E-005   -5.008261456870489E-005
  -5.079414643401110E-005   -5.084140476004405E-005   -5.082193164200828E-005
  -5.082664803543372E-005   -5.081841070165116E-005   -5.153443221850281E-005
  -5.158811132186775E-005   -5.156618483538402E-005   -5.157136959896421E-005
  -5.156181228100561E-005   -5.227623357263154E-005   -5.233928585336158E-005
  -5.231362128236470E-005   -5.232082646629745E-005   -5.231158435139095E-005
```

Figure 3.66 Original file Decayed.out

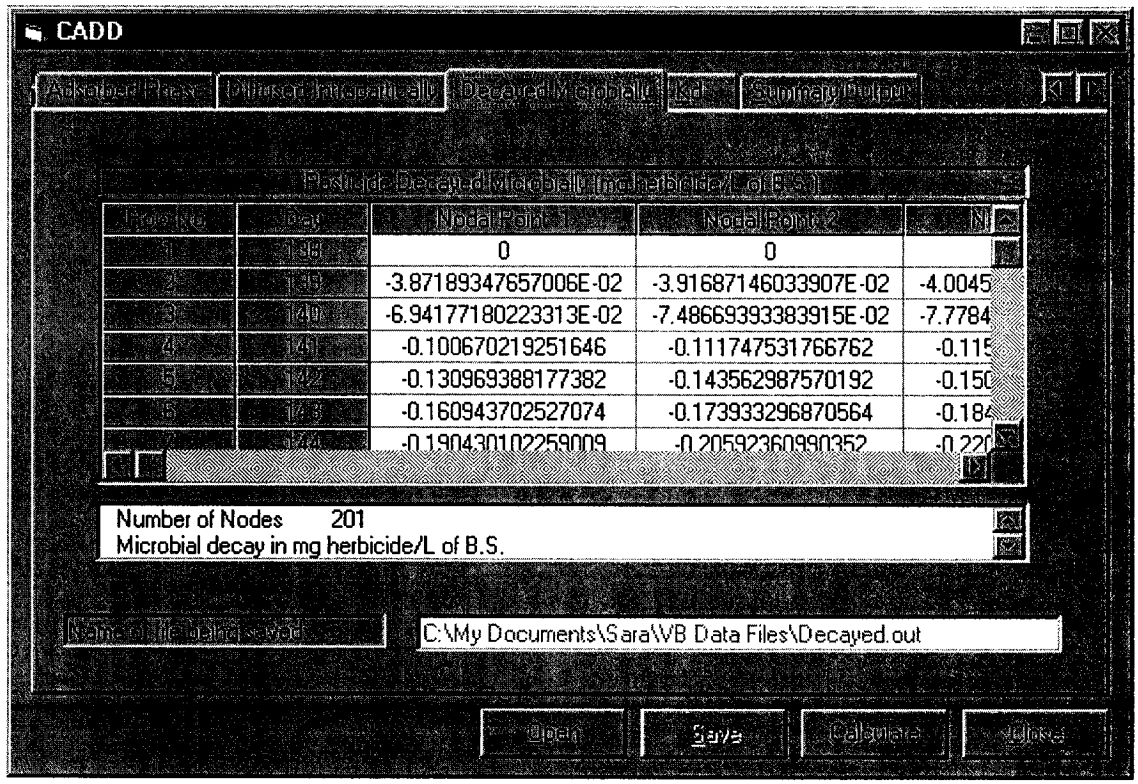


Figure 3.67 frmCadd(14) - Final GUI for file Decayed.out

The original PESTFADE model created outputs for soil-water partitioning coefficients. The new revision of the code does not provide this feature however the GUI has been designed based on the previous output. The code can later be advanced to provide the user with these values as well.

```
Number of Nodes        201
  kd values
   4.119029691694399E-001   4.119029691694399E-001   4.119029691694399E-001
   4.188063708873636E-001   4.188063708873636E-001   4.188063708873636E-001
   4.188063708873636E-001   4.188063708873636E-001   4.314626073702234E-001
   4.314626073702234E-001        1.062926895466577        1.062926895466577
        1.062926895466577        1.091271612679019        1.091271612679019
   8.423472037810222E-001   8.423472037810222E-001   8.423472037810222E-001
   8.642263519311786E-001   8.642263519311786E-001        2.224545468465501
        2.224545468465501        2.224545468465501        2.258336032543458
        2.258336032543458        2.258336032543458        2.258336032543458
        2.258336032543458        2.286494835941756        2.286494835941756
        2.286494835941756        2.286494835941756        2.286494835941756
        2.309021878660392        2.309021878660392        2.309021878660392
        2.309021878660392        2.309021878660392        2.331548921379031
        2.331548921379031        2.331548921379031        2.331548921379031
        2.331548921379031        2.354075964097669        2.354075964097669
        2.354075964097669        2.354075964097669        2.354075964097669
```

Figure 3.68 Original file Kd.out

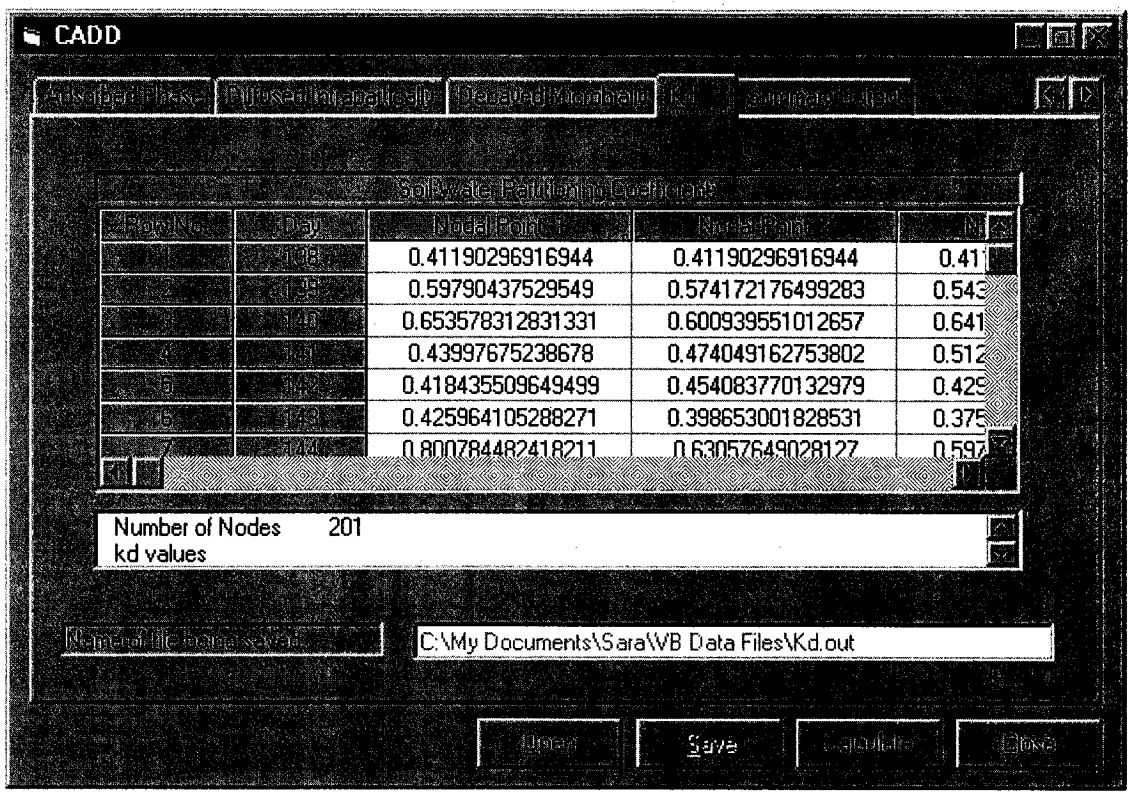


Figure 3.69 frmCadd(15) - Final GUI for file Kd.out

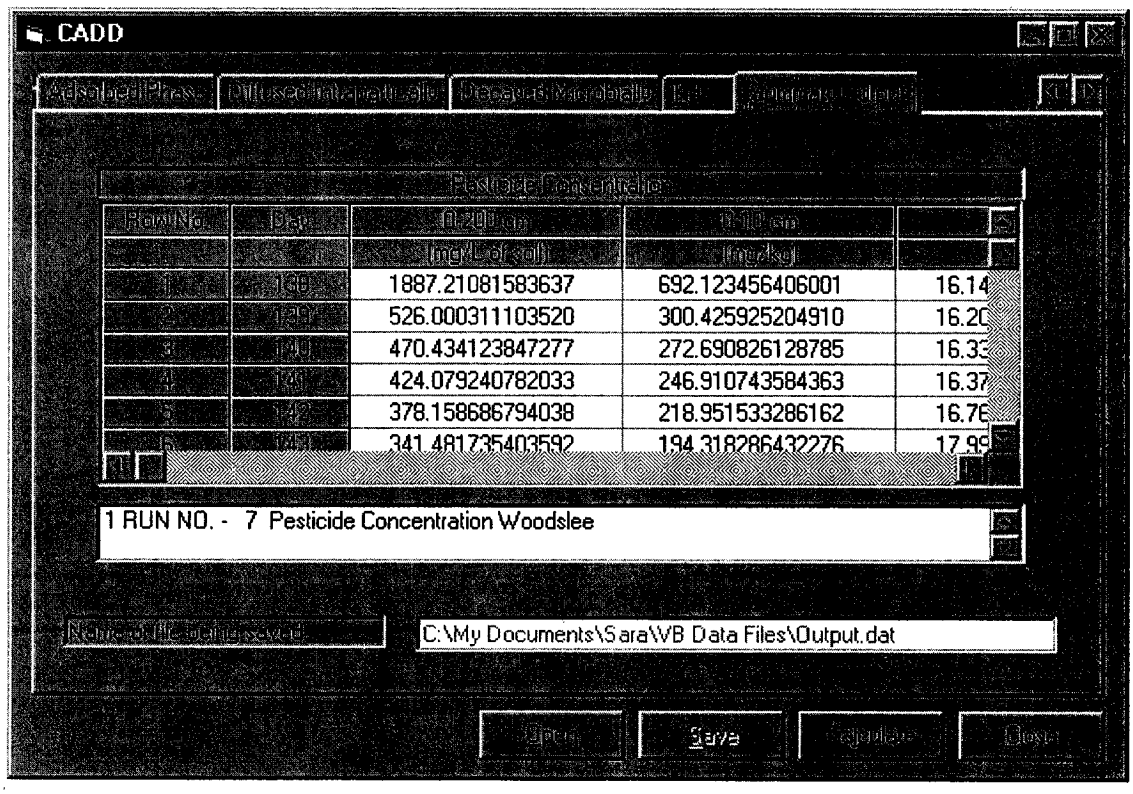


Figure 3.70 frmCadd(16) - Final GUI for file Output.dat

3.4 Objects Used

Many objects were used in the development of the GUI. Every form in an application is an *object*. Each and every *control* (a command button, for example) that appears on a form is also an object. In Visual Basic, objects have *properties* that define the appearance and behavior characteristics of the object. Thus, a form has properties, and any controls placed on a form have properties, too. The most common objects used in this application are described below along with tables outlining their properties.

3.4.1. Label

A label is a graphical control to display a read-only text in order to provide information to the user. Table 3.14 gives examples of the properties used in the GUI development.

Properties	Description	Value
Alignment	Sets the alignment of the control's text to be in left, right, or center justified	0 – Left Justify
Appearance	The appearance of the object to be in 3-D form or flat	1 – 3D
BorderStyle	To have a border around the object or display in without border	1 – Opaque
BackStyle	Indicates the background to be transparent or opaque	1 – Fixed Single
Enabled	If enabled the object can respond to user-generated events	False or True
Visible	To indicate whether the object be visible or hidden	True
MousePointer	Sets the type of mouse pointer displayed when over part of the object	0 – Default
ToolTipText	Sets the text displayed when the mouse is paused over the control	Proper text

Table 3.14 Label Properties

3.4.2. Text Box

A text box, sometimes called an edit field or edit control, is commonly used for accepting user input or for entering data. It displays information entered at design time, entered by the user, or assigned to the control in code at run time (Table 3.15).

Properties	Description	Value
Alignment	Sets the alignment of the control's text to be in left, right, or center justified	0 – Left Justify
Appearance	The appearance of the object to be in 3-D form or flat	1 – 3D
BorderStyle	To have a border around the object or display in without border	1 – Fixed Single
Enabled	If enabled the object can respond to user-generated events	True or False
Visible	To indicate whether the object be visible or hidden	True
TabStop	Indicates whether the user can use the TAB key to give the focus to the object	True
TabIndex	Sets the tab order of the object within its parent form	An integer number starting from 0
MousePointer	Sets the type of mouse pointer displayed when over part of the object	0 – Default
ToolTipText	Sets the text displayed when the mouse is paused over the control	Proper text

Table 3.15 Text Box Properties

3.4.3. Frame

Frames are used as a container for other controls in order to group them together. They can be used to subdivide form functionality (Table 3.16).

Properties	Value
Appearance	1 – 3D
BorderStyle	1 – Fixed Single
Enabled	True
Visible	True
MousePointer	0 – Default
ToolTipText	Proper text

Table 3.16 Frame Properties

3.4.4. Command Button

Command button is one of the most common controls found in Windows applications. It serves to elicit simple responses from the user or to invoke special functions on forms. In other words it is used to begin, interrupt, or end a process. When chosen, a command button appears pushed in and so is therefore also referred to as a push button (Table 3.17).

Properties	Value
Appearance	1 – 3D
Enabled	True or False
Visible	True
TabStop	True
TabIndex	An integer number starting from 0
MousePointer	0 – Default
ToolTipText	Proper text

Table 3.17 Command Button Properties

The command buttons used are Open, Save, Calculate, and Close, described in Table 3.18.

Name	Function
Open	Opens a file using a dialog box Load the controls with data available in the file (Note: Displayed data can be saved in the default file using Save button)
Save	Accepts modifications entered Overrides default file with displayed data (Enabled for inputs files only)
Calculate	Runs the appropriate executable file for each program with data saved in default files Generates new output files in the default directory Re-loads the output displaying objects and controls to view the generated output
Close	Reject modifications entered Closes the form

Table 3.18 Command Button Functions

3.4.5. Form

Forms are the most basic objects used and are the visual foundations of the application. They are basically windows or dialog boxes making up part of an application's user interface and can contain different elements to create a GUI (Table 3.19).

Properties	Value
Appearance	1 – 3D
BorderStyle	2 – Sizable
Caption	Name of the form
Enabled	True or False
MaxButton	True
MDIChild	False
MinButton	True
Moveable	True
Visible	True
MousePointer	0 – Default
WindowState	2 - Maximized

Table 3.19 Form Properties

3.4.6. Tab

A Tab object represents an individual tab in the Tabs collection of a TabStrip control. A TabStrip control is like the dividers in a notebook or the labels on a group of file folders. Tab

Strip controls are useful since they permit the definition of multiple pages for the same area of a window or dialog box in an application.

With this control one can effectively present several screens' worth of data in the space of one screen, extending a metaphor that is familiar to users. With labeled tabs neatly presented, the user can see at a glance what options are available and easily navigate between them by pointing and clicking on the desired tab (Table 3.20).

Properties	**Value**
Style	0 - tabTabs
TabWidthStyle	0 - tabJustified
Placement	0 - tabPlacementTop
TabStyle	0 - tabTabStandard
Separators	ticked
ShowTips	ticked
Enabled	True
MultiRow	False
MultiSelect	False
MousePointer	0 – ccDefault
TabStop	True
Visible	True

Table 3.20 Tab Properties

3.4.7. Events

Events are initiated by pushing command buttons. This section describes the various operations that are involved in initiating the four commands described in section 3.7.4.4.

3.4.7.1. "Open" Button Pressed

When the "Open" button is pressed, the cmdOpenClick command will be performed. In this subroutine an existing file name will be read by calling the GetFile function. The general purpose of this function is to get a file name. A dialog box will open, and depending on which module it is called from, different information will be displayed by default. The information includes the title, the default files and extensions to be displayed, and the different filters available for the particular module. Two examples of the dialog box are displayed below, one for the MOISTE routine and the other for the HEAT routine (Figs. 3.71 and 3.72).

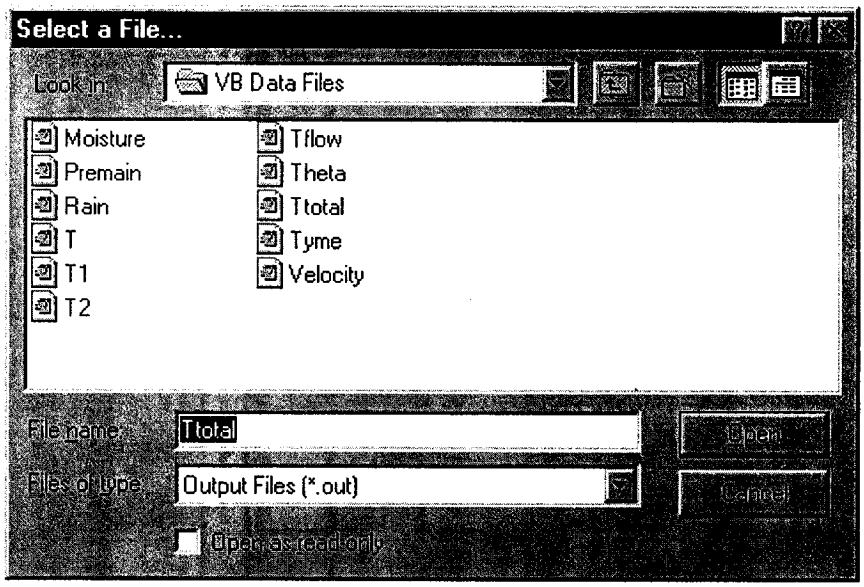


Figure 3.71 Dialog Box for *.out Files

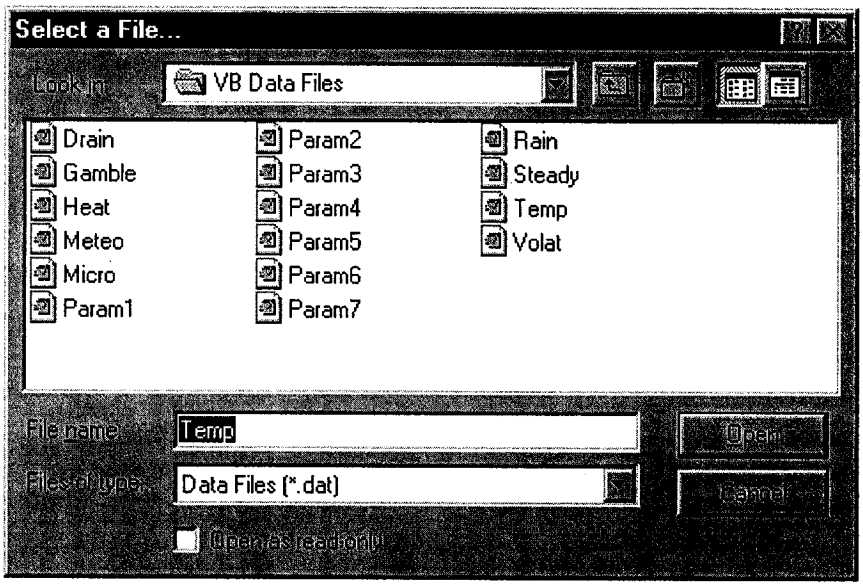


Figure 3.72 Dialog Box for *.dat Files

3.4.7.2. "Save" Button Pressed

When the "Save" button is pressed the displayed data will be saved in the default file.

3.4.7.3. "Calculate" Button Pressed

Pressing this button will lead to execution of the module's .exe file, which retrieves the appropriate input files and performs the calculations involved in that particular part of the overall simulation.

3.4.7.4. "Close" Button Pressed

This process will lead to closing the open form.

CHAPTER IV

FIELD VALIDATION OF PESTFADE

As mentioned earlier, PESTFADE has not been sufficiently validated, and has not been validated with field data after Li et al. (1996) modified the sorption kinetics component. This chapter, therefore, revisits the experimental site and methods used in the field validation, previously published by Tan et al. (1993a, 1993b). It describes the comparison between simulated pesticide concentration with the model, as revised during the course of this thesis and data obtained in 1993. It also gives a comparison between the simulations on the same data that based on the old versions of PESTFADE by Clemente (1991) and the version that included Gamble sorption kinetics by Li et al. (1999).

4.1 Field Experimentation and Measurements

For details on field experimentation and measurements, the reader is referred to the paper by Tan et al. (1993a, 1993b).

4.1.1. Experimental Site Characteristics

The experiment was initiated in 1991 at the Eugene F. Whelan Experimental Farm (Agriculture Canada, Woodslee, Ontario). The dominant soil series is a Brookston clay loam, a poorly drained lacustrine soil (Typic Argiaquoll). The soil at the experimental site had a 0.30 m deep dark brown, clay loam A_p horizon with an organic matter content

of 2.5%. The B horizon has a clay texture extending to a depth of 1.5 m. The B horizon is underlain by an interrupted layer of sand with a thickness ranging from 1 mm to 1 m to a depth of approximately 2.6 m. Below this layer, the profile consists of clay and clay loam.

4.1.2. Experimental Design

This project is a small component of an extensive study undertaken to evaluate and quantify surface and subsurface transport and dissipation of pesticide and nitrogen under four cropping/soil management systems, with and without water table control. The experiment was initiated in spring 1991 and consisted of a corn crop in four intercrop/tillage regimes and two water table management schemes. The experiment was laid out as a randomized complete block design with two replicates. The intercrop/tillage treatments were moldboard plow tillage (MP), moldboard plow tillage with annual ryegrass (Lolium multiflorum Lam) intercrop (MP-IC), soil saver (SS) and soil saver with annual ryegrass intercrop (SS-IC). Water table management treatments were subsurface drainage and controlled drainage/subirrigation. All experimental plots received the same pesticide and nutrient applications. Two plots with conventional tillage management were also used in this study.

4.1.3. Field Layout and Installation

The field consisted of sixteen plots, each 15 m wide by 67 m long with an area of about 0.1 ha. Each plot contained two 104 mm diameter subsurface drains. Drains were

installed at 7.5 m spacing and 0.6 m depth in a west-east direction. Experimental plots were isolated by: (1) a double layer of 4 mil thick plastic barrier from the surface to a depth of 1.2 m to prevent leakage and subsurface interaction between adjacent treatments; (2) a 7.5 m wide by 67 m long buffer area with a single drain to prevent cross-contamination between plots; and (3) a 20 cm high berm surrounding each plot to retain the surface runoff (Tan et al., 1993a, 1993b, Gaynor et al., 2000, 2001).

The water table in the irrigated plots was controlled with water level control structures. These structures were built such that when the bottom drain plug was closed the water rose to the desired level in the structure creating a pressure head which forced the water into the subsurface drains for subirrigation. When the bottom plug was opened, water drained freely from the plots. During irrigation, the water level in these structures was maintained at a given height by means of a float valve. An overflow pipe allowed drainage to proceed when water tables in the center of the plots rose above the pre-set levels. These structures are used for subirrigation during the growing season and controlled drainage during fall, winter and spring.

The source of water was an irrigation pond located at the north-west corner of the experimental field. Irrigation water was pumped and conveyed to the water table control structures via an underground 50 mm diameter polyethylene pipe. Water meters located at the control structures recorded the total volume of irrigation water delivered to each plot (Tan et al., 1993a, 1993b).

Subsurface runoff and tile drain outflow from each individual plot was collected in a 0.5 m diameter catch basins connected, via 104 mm corrugated non-perforated drain pipes, to the central instrumentation building at the North-East corner of the experimental field.

4.1.4. Surface and Tile Flow Measurements

Samples of surface runoff and tile drainage water for herbicide and nitrate analyses were collected automatically in 32 polyethylene auto-samplers (500 mm diameter by 750 mm deep) (CALYPSO 2000S, Buhler Gmbh & Co.) in the instrumentation building. Each auto-sampler contained 24 one-liter bottles. The auto-sampler was activated by digital signals from the water meter. Each auto-sampler was equipped with an electrical, float-activated effluent pump. Surface runoff and subsurface drainage from each individual plot flowing into the respective sumps was pumped through water meters to an outlet drain. Each water meter records drainage volumes mechanically and sends and digital pulse signals. A multi-channel data logger used the analog signal of the water meters to record the drainage volumes on a continuous basis (Soultani et al., 1993). Sample collection was based on flow volume with collections at 500 to 3000 L depending upon the time of year and expected runoff volumes. The more frequent sampling was done after herbicide application, where herbicide concentration would be most dynamic. Water samples were stored in glass bottles at 4°C prior to analysis. The data stored in the data logger were automatically transmitted every 24h via modem to an IBM PC computer at the Harrow Research Station (HRS), 32 km from the field site.

4.1.5. Herbicide and Nitrate Analyses

Water samples were analyzed for herbicide and nitrate concentrations within two months of collection. A 500 ml aliquot was filtered under suction through a 0.45 μm filter (Gelman Cat Gn-6). Herbicides were concentrated from the water on a preconditioned cyclo-hexyl Sep Pak cartridge (Baker Cat No. 7212-03). After herbicide loading, the cartridge was dried and the herbicide eluted with 1.5 ml methanol. Volumes were adjusted for analysis by gas chromatography. Analytes were separated on a 15 m DB-5 capillary column with a temperature programmed from 70 to 210° C. A thermionic sensitive detector operating in N mode was used to detect and quantify the herbicides.

Surface and tile water samples filtered through a 0.45 μm filter were analyzed on a TRAACS 800 autoanalyzer (Bran & Leubbe, Buffalo Grove, IL) for nitrates using the cadmium reduction method (Tel and Heseltine, 1990). Flow-weighted nitrate concentrations were calculated by taking the sum of the nitrate loss over the period divided by the sum of the total flow volume (Baker and Johnson, 1981).

4.1.6. Water Table Depth Measurements

Water table elevations in each plot are monitored using eleven 25.4 mm diameter perforated PVC pipes, wrapped in filter material. Three pipes were installed between the tiles, three adjacent to the tiles, and two between the tiles and the plastic barrier on each

side of the plot. Water table depth was monitored every second day during the growing season and on a weekly basis during the off-season.

The other two pipes were installed at the center of the plot midway between the drains and the plastic barrier on each side. Water table depths were monitored eight and fifteen times during the growing seasons according to considerable fluctuations in water table due to the occurrence of rainfall events and dry periods.

4.1.7. Crop Parameters

Corn (Zea mays L., Pioneer 3573) was seeded, with a Kinze 4 row planter, at a rate of 65,000 seeds ha^{-1} in 75 cm wide rows. Fertilizer (8-32-16) was banded beside the seed at a rate of 132 kg ha^{-1}. Urea (46-0-0) was applied with a brush applicator (307 kg ha^{-1}) on June 29. An annual ryegrass intercrop was seeded between the rows of corn with a Brillion seeder.

Herbicide was applied to the treatments on May 14, 1992 with a Chelsea sprayer fitted with 8004 EVS flat fan nozzles. The herbicides were applied in 270 L water ha^{-1} at 210 kPa. Atrazine was applied at 1.1 kg ha^{-1}, metribuzin at 0.5 kg ha^{-1}, and metolachlor at 1.68 kg ha^{-1}. The herbicide was applied in a 38 cm band over the seeded row so that 550 g ha^{-1} atrazine, 250 g ha^{-1} metribuzin, and 840 g ha^{-1} metolachlor were applied to the treatments, representing a 50% reduction in the amount of herbicide applied to the area compared to broadcast application.

Grain was harvested by a 3-row Gleaner combine for yield determination. The corn was shelled in the field, and the yields were adjusted to 15.5% moisture content.

4.1.8. Climatological Data

Detailed weather data was collected from a nearby automated weather station and transferred the HRS via modem. The data included maximum and minimum air temperature, solar radiation, rainfall intensity and amount, wind speed and direction, relative humidity and soil temperature.

4.2 Field Validation

PESTFADE was executed using measured inputs from the study site, and simulated outputs were compared with actual field-measured values obtained in 1993. However, the water flow submodel (SWACROP), which had already been verified against field data by various researchers (de Jong and Kabat, 1990; Workman and Skaggs, 1989; Prasher et al., 1987a, 1987b; Brandyk and Wesseling, 1987; Dierichx et al., 1986; Feddes et al., 1978, 1984), was not tested in this study. The simulation was performed only for atrazine.

4.2.1. Model Predictions vs Measured Values for Atrazine

The initial concentration of the chemical at the soil surface is based on the amount of pesticide applied. Unlike some NPS models, this initial concentration is not treated as a

constant value. This was done keeping in mind the fact that chemical applied to the surface could disappear via various loss mechanisms or remain there for some time. The chemical could undergo degradation, volatilization or leaching depending on the prevailing climatic, soil, hydrologic conditions and management practices. The RUNOFF model is therefore executed first to calculate the amount of pesticide remaining at the soil surface for any given day from the time of application.

At the start of the simulation, it was assumed that the concentration at the surface was that of the first value of concentration generated by the RUNOFF model and the lower nodes have a zero concentration. The simulation of contaminant transport is done for each day starting from Julian day 138 until day 198. The depth of the soil profile was considered to be 2 m (200 cm). The number of compartments used in the water flow model (SWACROP) was limited to 40, therefore the distance between adjacent nodes was 5 cm. However, in the CADD model this number was extended to 201 giving an inter-nodal distance of 1 cm.

In this simulation, the code specifications (CODE1 to CODE7) is given below:

CODE1 = 1 for transient water and solute flow

CODE2 = 1 for variable dispersivity to be calculated by the program

CODE3 = 1 for Neumann upper boundary condition

CODE4 = 1 for solute flux dependent lower boundary

CODE5 = 0 for conventional adsorption mechanism

= 1 for new Gamble kinetics

CODE6 = 1 for variable initial concentration with depth

The applied rate used in the program has been calculated as follows:

The average of pesticide concentration for plots 5 & 9 on day 138, 1993 was measured 1249.48 (mg/kg).

C (mg/kg) * BD (g/cm^3) / Theta (cm^3/cm^3) => C (mg/L)

Bulk density = 1.39 (g/cm^3)

Theta = 0.353 (cm^3/cm^3)

C = 1249.48 * BD / Theta = 4920.05 (mg/L)

The sorption coefficient, Kd was calculated as follows.

Koc = 163 (ml/g or cm^3/g) for Atrazine

O.M. = %2.2 = 0.022

%O.C = 2.2 / 1.724 = %1.27 = 0.0127

Kd = Koc * O.C = 163 * 0.0127 = 2.07 (cm^3/g)

This Kd value is just used when conventional sorption kinetics have been specified. If Gamble kinetics are desired, Kd is calculated by the program.

In this simulation, the initial pesticide concentration was based on the average concentration in plots 5 & 9 on day 132 (day before application) for the top ten cm of the soil. That average was 18.18 (mg/kg).

Theta = 0.35 (cm^3/cm^3)

BD = 1.39 (g/cm^3)

Kd = 2 (cm^3/g)

Total = C * Theta + Kd * C * BD

C = Total / (Theta + Kd*BD)

C = 18.18 / (0.35 + 2*1.39)

C = 5.81 (mg/L)

The same calculation applies to other depths.

The values for α and β, the first-order degradation rate constants in the liquid and solid phases, respectively (Eq.3.3) were:

α = 0.0149

β = 0.0149

The results of the simulation with conventional and Gamble sorption kinetics (i.e. tab Summary Output, depths 0-10 cm, 10-15 cm, and 15-20 cm) were compared with the average measured concentrations at soil depths of 10, 15, and 20 cm from two different plots (i.e. plots 5 and 9) (Figs. 4.1 to 4.3).

4.2.2. Model Accuracy and Performance

In previous studies Clemente et al. (1991) validated the original PESTFADE model using data measured over a period of several days. They used the statistical technique of Nash and Sutcliffe (1970) to evaluate the performance of PESTFADE. Clemente et al. (1991) found a close correspondence between the numerical and analytical solutions and

suggested that the model satisfied the first requirement of model accuracy and applicability. Li et al. (1999) later concluded that Gamble kinetics were more appropriate for modeling sorption of pesticides and modified the package to provide this method as an option in PESTFADE. As mentioned earlier, Li et al. (1999) did not validate the Gamble kinetics against field data. Furthermore, during the work involved in understanding PESTFADE and developing its GUI, the original computer code was reworked, and various changes were deemed necessary. In consequence, the results will first compare the simulations performed by the original code with those performed by the latest version (ie. those done by the author) for both methods of calculating the sorption kinetics (conventional and Gamble). The comparison between the simulations performed with the new code and the observed data is discussed in the subsequent section.

4.2.2.1 Comparison of new version of PESTFADE with previous version

The three graphs comprising Figure 4.1 clearly indicate that the old version of the PESTFADE package was adequate at following the trends in concentration at all three soil depths (10, 15 and 20 cm). Insofar as absolute values are concerned, the conventional method of computing sorption kinetics with the earlier version led to far more significant overestimations of the observed values than did the new version (Fig. 4.1).

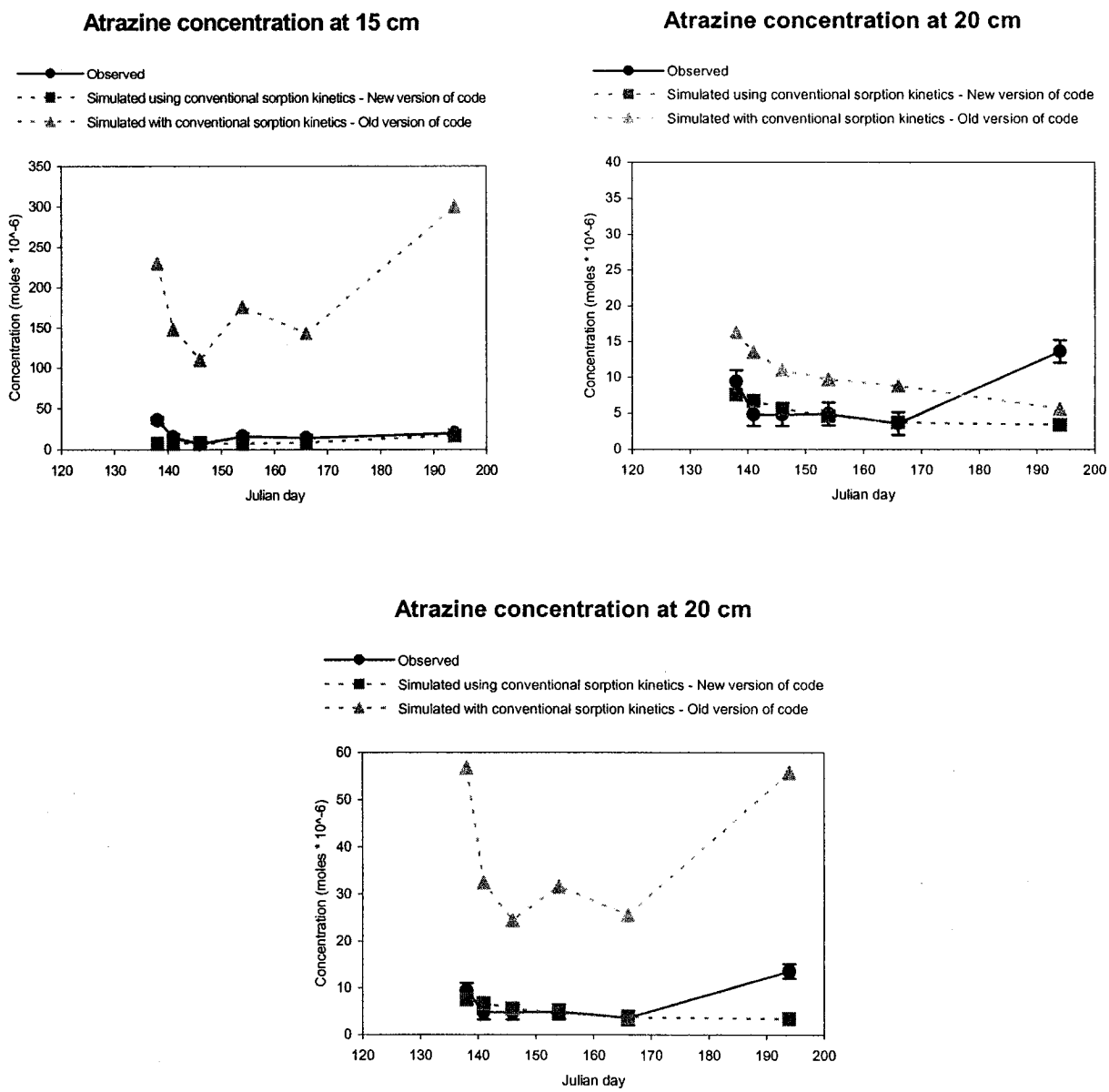


Figure 4.1. Comparative simulations of atrazine concentration in the upper profile by previous and new versions of PESTFADE: conventional sorption kinetics

The simulations using Gamble kinetics (Fig. 4.2) seem to have more trouble following the trends in the observed values (first line segment from the left, in particular), but the absolute values were generally closer than those simulated by the conventional sorption model, except at 10 cm where both methods led to very similar predicted values.

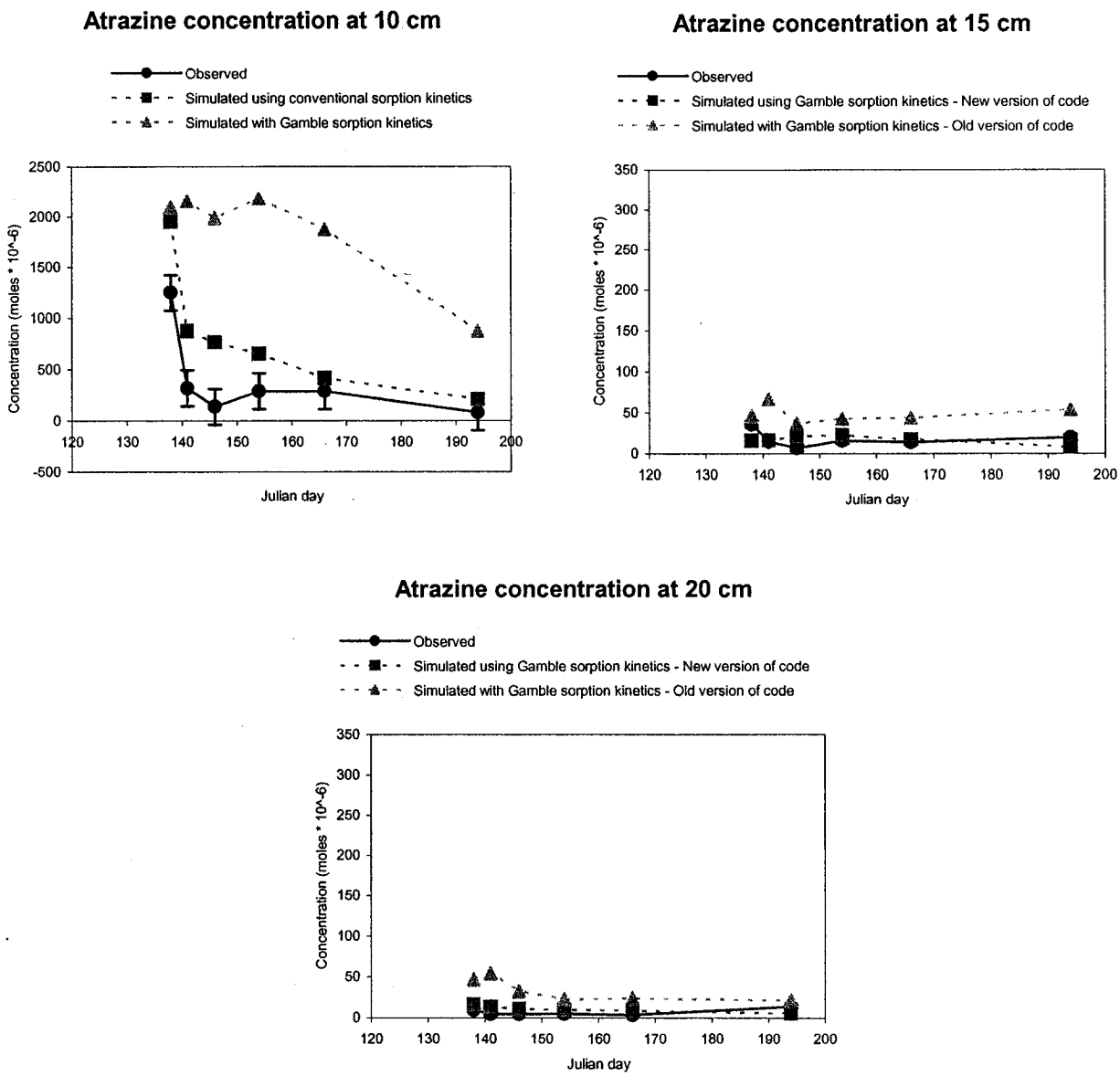
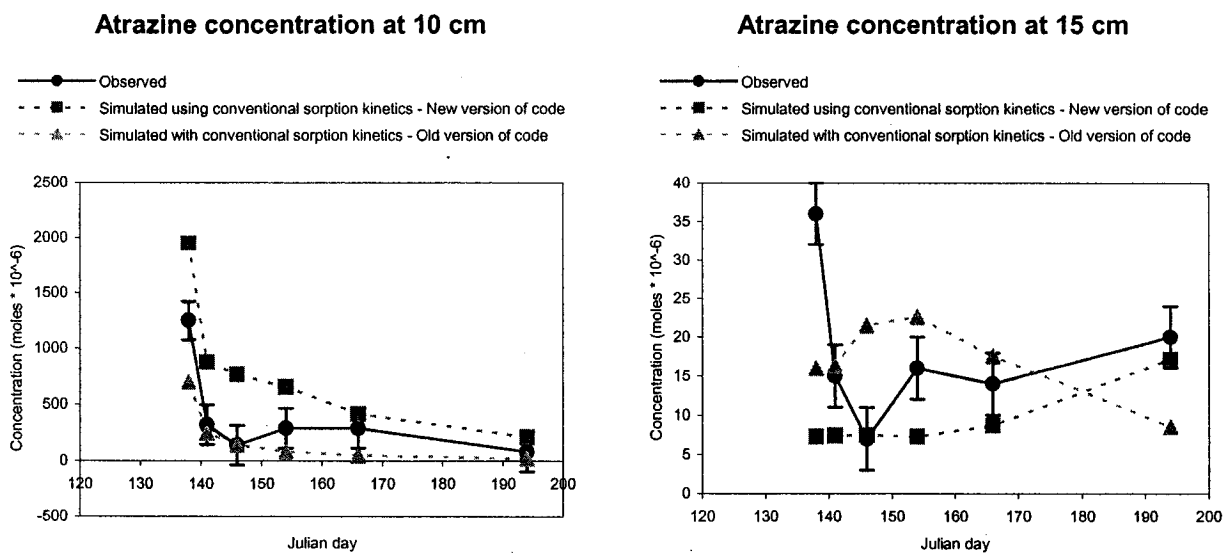


Figure 4.2. Comparative simulations of atrazine concentration in the upper profile by previous and new versions of PESTFADE: Gamble sorption kinetics

In summary, the above figures clearly show that the modifications made to PESTFADE have improved the relationships between predicted and observed absolute values.

4.2.2.2 Evaluation of simulated atrazine concentrations by new version of PESTFADE

Figure 4.3 provides a comparison of the two methods of calculating the sorption kinetics in the new version of PESTFADE. There does not appear to be a clear overall advantage in using either sorption model at the depths considered. At 10 cm, the conventional method clearly follows the observed trend more accurately but overestimates absolute values significantly. At15 cm, neither method leads to a particularly satisfying simulation (although both are far better than in the original code (Figs. 4.1 and 4.2). At 20 cm, the conventional kinetics simulations are more accurate except for the last point, for which neither method was able to follow the change in trend.



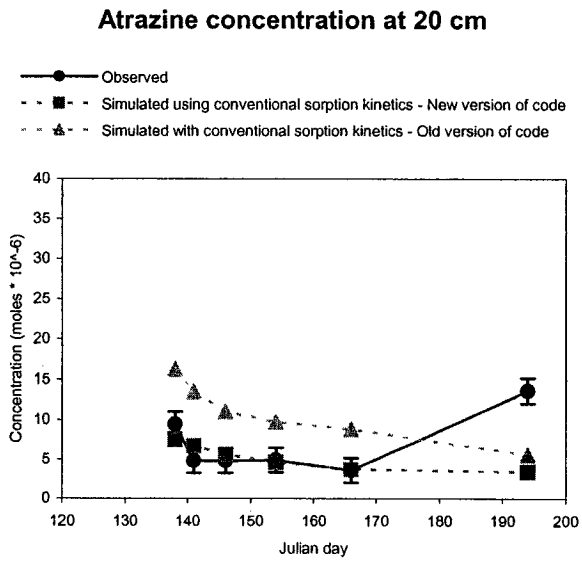


Figure 4.3 Comparison of simulations of atrazine concentration in the upper profile based on conventional and Gamble sorption kinetics

Li et al. (1999) validated the sorption behavior of atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) on intact soil columns by incorporating the two-stage sorption mechanism (Gamble kinetics) into the PESTFADE model. This mechanism takes into account intraparticle diffusion of a pesticide into the soil matrix, the sorption capacity of soil, and a variable pesticide distribution coefficient, K_d. They validated the modified model by comparing simulated values with data obtained from an intact column study in the laboratory. The two-stage mechanism was also compared with the conventional adsorption approach based on a constant K_d and showed a closer agreement with measured values compared to the conventional adsorption approach for intact soil columns. Nevertheless, when compared to field data, one cannot conclude that this was an improvement.

While one might be tempted to compare the performance of the conventional and two-stage mechanism by plotting the observed and simulated values for each method of simulation and then computing coefficients of determination (R^2) for the resulting regressions, there is little to be gained given that each plot consists of only 6 points and confidence intervals on the regression parameters are likely to be so wide as to be useless for practical purposes. The plots with R^2 values are nevertheless presented for completeness (Figs. 4.4 and 4.5). Suffice it to say that the modifications made to PESTFADE by the present author resulted in a clear improvement in terms of absolute values for both methods of treating the sorption kinetics. Finally, there is an obvious problem in matching the initial measured concentration to the initial simulated value, which may be responsible for some of the odd behaviors noticeable in the above figures.

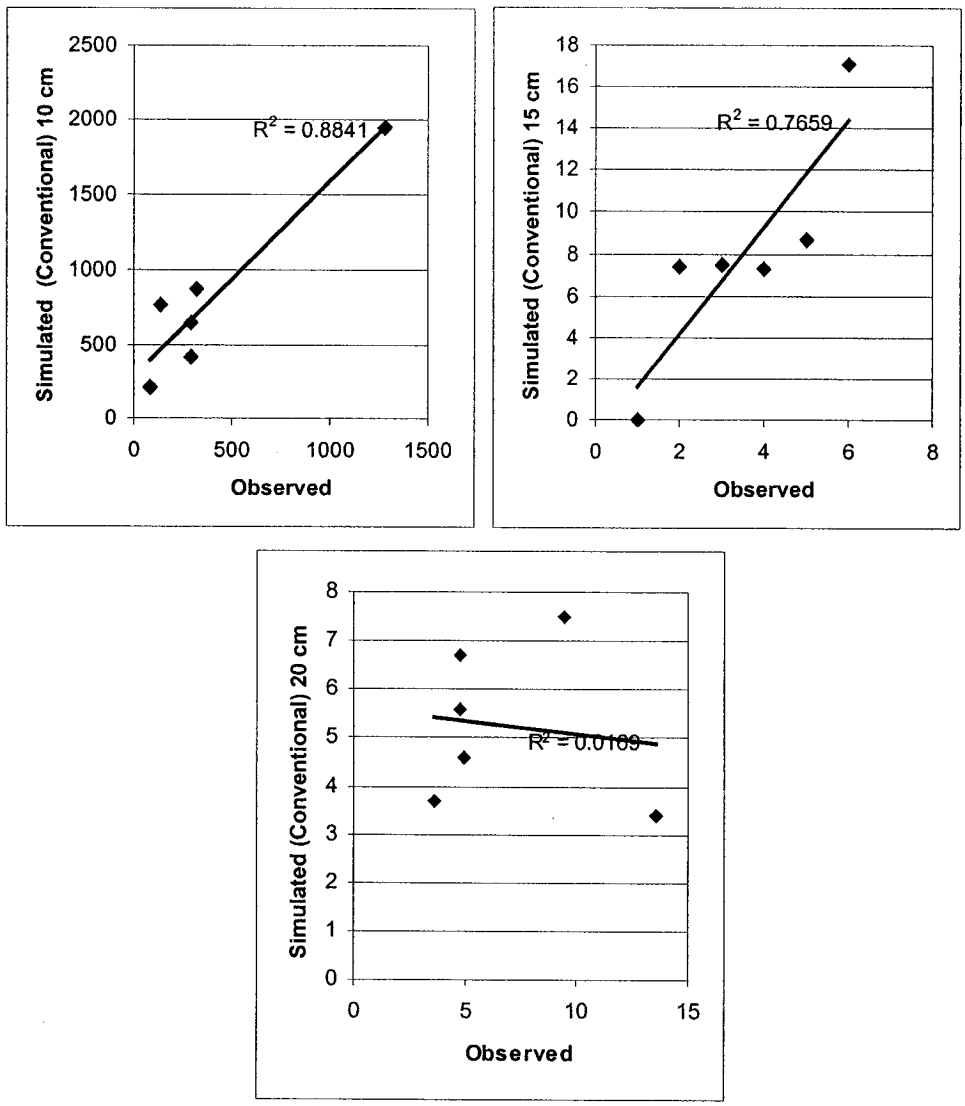


Figure 4.4 R-Squared values for Conventional Sorption Kinetics at different depths

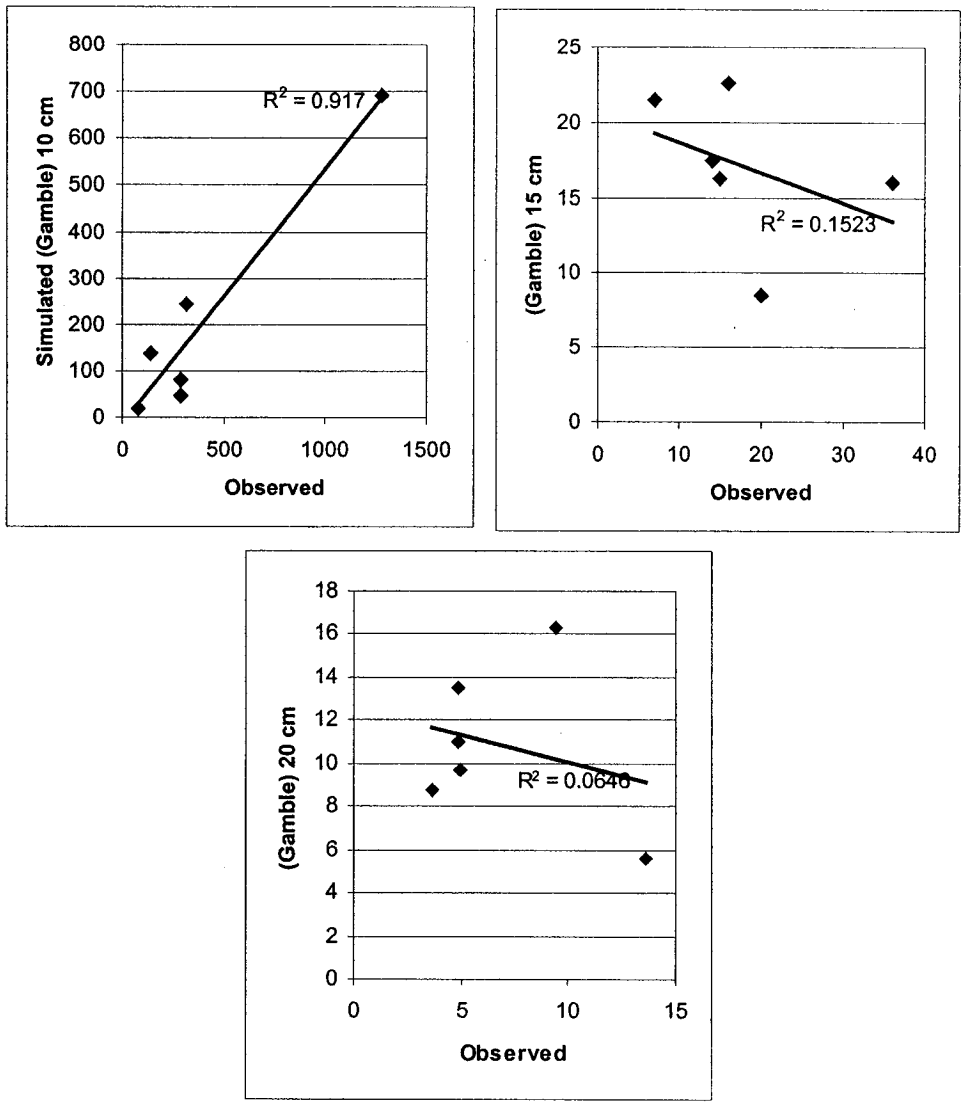


Figure 4.5 R-Squared values for Gamble Sorption Kinetics at different depths

4.2.3. Summary and Conclusions

In this study, a user-friendly and graphical input/output (GUI) was presented for PESTFADE model which makes it very easy to use. The present package is easy to use and well documented.

A new revision of the code with a new governing equation has been developed to better simulate the pesticide fate and transport throughout the soil profile. The new PESTFADE model was tested against actual field data. The model gives better predictions than the previous version, however, there are several points that need to be considered. Since all measured data are subject to some error, it would be useful to perform a sensitivity analysis of the new version of PESTFADE in order to find solutions to specific problems, one of which is the non-concordance of the initial value from the simulation with the initial measured value.

This revision only provides the output values for pesticide in solution and adsorbed phase described in section 3.7.3.1.1. The GUI for the other three frames (i.e. frmCadd(13), frmCadd(14), and frmCadd(15)) has been developed based on the old revision of PESTFADE. The new revision does not provide the values for pesticide diffused intrapartically, pesticide decayed microbially, and soil-water partitioning coefficient required for these frames. Future work can be done on the model to re-provide the user with these outputs.

CHAPTER V

ARTIFICIAL NEURAL NETWORK MODEL

The use of herbicides, fungicides and pesticides has led to significant improvements in the production and protection of food, feed, and fiber (McRae, 1989). However, these chemicals and their residues can accumulate in the food chain, causing damage to birds, fish, and other forms of animal life (Balogh and Walker, 1992). They have been found in lower soil profiles and can leach into ground water after each application in the field (Masse et al., 1996; Peralta et al., 1994; Mannion, 1995; Smith et al., 1995). It is through a better understanding of the processes involved in pesticide transport and degradation that models can be developed and then used to elucidate better strategies of application and control, leading to reduced health risks and environmental impact (Mutch et al., 1993). However, mathematical/physical modeling of complex natural systems usually requires simplifying assumptions that affect the accuracy of predictions. This has led to interest in developing implicit models based on the concepts of artificial intelligence, such as artificial neural networks (ANNs). One of the underlying principles of ANNs is that they mimic the cognitive capabilities of the human brain, and can therefore be trained to evaluate situations much more rapidly than can a process-based model, and with far fewer inputs (Shukla et al., 1994).

The main objective of this study was to exploit the capability of ANNs to simulate pesticide concentrations in soil under different tillage and water management conditions.

In addition, the possibility of developing a better ANN model by changing some of the default parameters of the ANN model was explored.

5.1 Data Description and Agronomic Practices

This study sought to develop an artificial neural network (ANN) model to simulate pesticide fate and transport in an agricultural soil. The input data to train and test the ANN model were collected in 1992 and 1993 at the Eugene F. Whelan experimental farm of Agriculture and Agri-Food Canada, located in Woodslee, Ontario (Tan et al., 1993a, 1993b). For further information on the site description refer to Chapter IV. These values included information on different tillage and water management practices, rainfall and temperature data, and variations in soil moisture content with depth and time. The output from the ANN model consisted of daily pesticide concentration at three soil depths: 0-10 cm, 10-15 cm, and 15-20 cm.

5.2 Neural Network Development

NeuralWorks Professional II/PLUS version 5.23 (NeuralWare, 1996) software was used for the development of the ANN model. Backpropagation was used in this study as it is one of the most popular methods for developing ANN models and has been used in solving non-linear problems in many field situations (NeuralWare, 1993; Yang et al., 1997c, 1997e, 1997f).

Neural networks learn the input-output relationships from sample data. The data presented to a network should, therefore, be correct and cover the whole range of different combinations that could occur, including extreme cases (Salehi et al., 1998). Various architectures, learning rates and momentum values, and learning rules may be used. Decisions must also be made about many other factors such as the method of presenting input data and data preprocessing.

In this study, available data (768 records) for 1992 and 1993 were used for the learning and testing processes of the ANN model. Additional data were considered to represent soil and weather conditions.

The ANN model was trained with the following input data: year of simulation, day of year, intervals between measurements (days), tillage treatment (moldboard plow - converted to a binary code of 0001; soil saver - converted to a binary code of 0010; moldboard plow inter cropping - converted to a binary code of 0100; and soil saver inter cropping - converted to a binary code of 1000, water table control: controlled drainage - converted to a binary code of 0; and drainage - converted to a binary code of 1, soil depth: 0-10 cm - converted to a binary code of 001; 10-15 cm - converted to a binary code of 010; and 15-20 cm - converted to a binary code of 100, soil moisture content (%), bulk density (g/cm^3), average temperature for each interval between measurements (^oC), cumulative potential evapotranspiration, and accumulated rainfall for each interval between measurements (mm/day). The output from the ANN model was pesticide concentration at the three soil depths (Fig. 5.1).

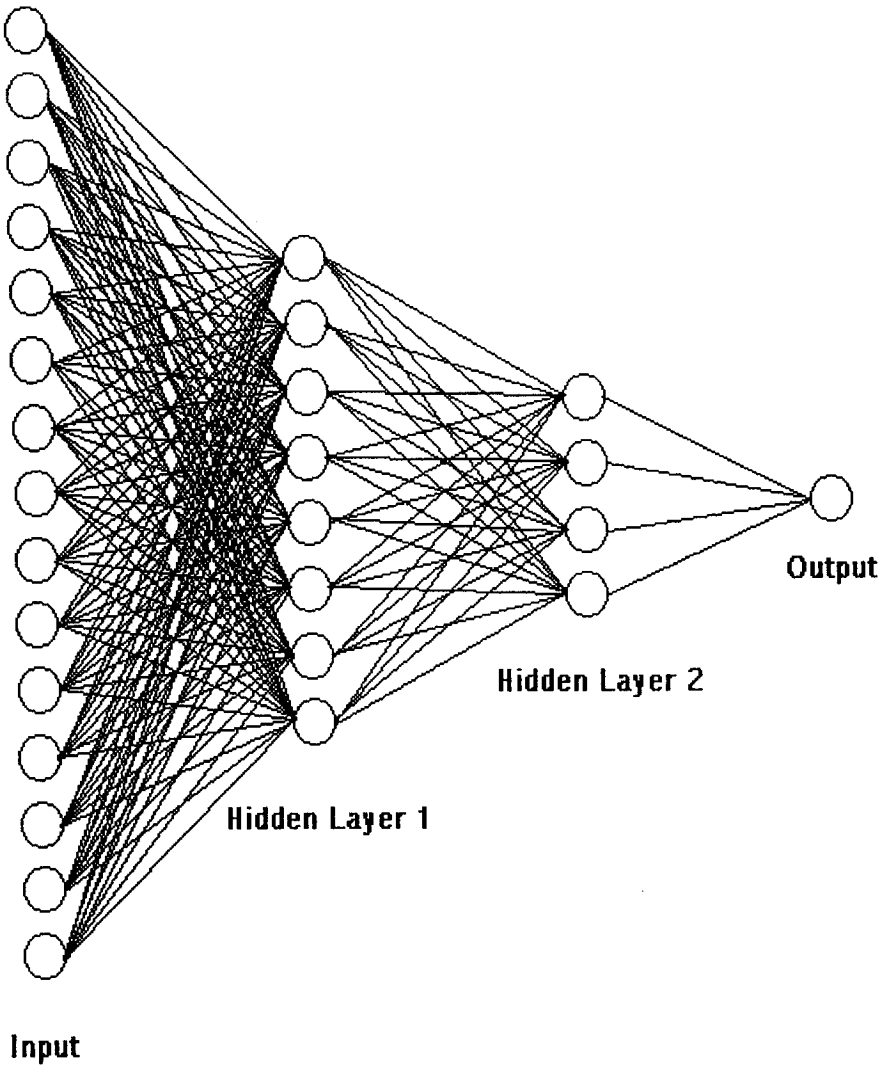


Figure 5.1 ANN Structure

Tillage treatments, water table control method, and soil depths, were used as binary codes in the model since they do not have any numeric meaning. The data were shuffled to obtain a good unbiased distribution for choosing the training and testing files. The model was first trained with 80% of the data (615 records) and then tested with the remaining 20% (153) records. Previous studies show this method of constructing the training and

testing subsets results in a good learning process (Salehi et al. 1998, Lacroix et al., 1997). Different ANN models were designed for the 15 inputs and 1 output, with different number of hidden layers and different number of PEs.

Training is the stage at which data records are introduced to a pre-configured network for it to detect the relationships between the input and output variables. In other words, learning is the self-adaptation at the processing element level, where weighted connections between processing elements are adjusted to achieve specific results, eliminating the need for writing a specific algorithm for each problem. During this stage, data records are randomly selected and entered in the network and weights are constantly updated for the network outputs to match the observed values, thus producing smaller errors at each iteration. This process is repeated until the network has converged and the global error has reached its minimum. At this point, the network is said to be trained and weights are fixed.

Testing is the stage where the trained network is tested against data records that did not participate in the training. Network performance during this stage indicates whether or not the network is reliable in producing acceptable outputs.

In this study, the normalized-cumulative-delta learning rule was chosen with the tangent hyperbolic function in the PEs. This learning rule is a variant of the delta rule that attempts to alleviate the problem of structured presentation of the training set. It accumulates the weight changes and updates weights at the end of an epoch. It is

normalized so that the learning rate is independent of the epoch size. This learning rule automatically adjusts the learning rate as a function of the epoch size.

The random seed for the learning procedure was set to 257. The "Run/SaveBest" option (Neural-Ware, 1996) was chosen to run the ANN models, allowing one to run Train/Test cycles and save the network with the best test results during the run. The networks repeated the recall cycle 100,000 times, the number of the learn iterations between each test run, was set to 10,000, with 10 retries, the number of test runs Professional II/PLUS attempts before giving up on finding a better result. If the error value exceeds the absolute error, error tolerance triggers a category reset by sufficiently increasing vigilance. The tolerance was set to 0.001 in this experiment.

It is a common practice to use the default configurations values for the learning parameters, as proposed by the available softwares (NeuralWare, 1993; Salehi et al., 1998; Lacroix et al., 1997). In this study, different parameters were changed from their default values to improve the network's performance and to obtain a better predictive ability.

Different networks were designed with different initial learning coefficients (Lcoef) for each hidden layer and for the output layer to obtain the best network. These values set the learning/recall schedules and directly relate to the learning rule in this experiment, the normalized-cumulative-delta. The initial momentum, along with the transition point and lcoef ratio determines the learning coefficient decay rate. The transition point is the learn

count at which the lcoef is reduced from the initial lcoef by an amount corresponding to the lcoef ratio. F'offset is the value added to the derivative of the transfer function prior to calculating the value to back propagate from each PE. In back-propagation networks, this allows a saturated processing element to continue learning. Epoch is the number of sets of training data presented to the network (learning cycles) between weight updates. In order to obtain the optimal network, 154 different networks were designed keeping all parameters constant and changing one at a time over a wide range.

Since a network's performance must be independent of the values set for different parameters, this independency was investigated by repeating the network training several times, each time with a differently randomized file. RMS values were compared for seven different runs with seven training and testing files randomized separately. The comparison was between the RMS value obtained by keeping the default values for the parameters in each training process and the RMS value obtained after changing the parameters from their defaults. During this experiment, the parameters were kept unchanged for the seven different runs.

The objective of the last part of the experiment was to determine how accurately the model could predict values at different depths (0-5, 5-10, and 10-20 cm) each containing a narrower range of data. In order to do so, the model was tested with files containing data for a single depth range at a time.

Some negative values were observed among the predicted values. These values occurred when the measured values were small and close to zero. Considering the fact, that the negative concentrations cannot physically exist, these values were replaced with zero.

5.3 Results and Discussion

In order to find the optimum network, various network architectures and learning parameter values were examined. The network was tested with seven different testing files in order to judge the performance of the final network.

The best network (RMS = 0.0633) was determined to have 15 PEs in the input layer, 8 PEs for hidden layer 1 with a learning coefficient of 1.5, 4 PEs for hidden layer 2 with a learning coefficient of 0.2, an output learning coefficient of 0.2, a momentum of 0.4, 19000 transition points, a learning ratio of 0.508, an F' offset of 0.1, and 35 epochs. The default values were 1 hidden layer with 1 PE, a learning coefficient of 0.3, an output learning coefficient of 0.150, a momentum of 0.4, a Trans. Pt. of 10000, a learning ratio of 0.5, an F' Offset of 0.1, and 16 Epochs. There was a significant difference between the RMS values for the best trained network and the network trained with the default values, as changing the parameters from their default values helped in the training process of the ANN model.

The learning coefficient had a very important role in decreasing the RMS value. Figure 5.2 shows the effect of the learning coefficient on the RMS value. Learning coefficient

values between 0.40 and 1.50 gave acceptable RMS values (below 0.10). However, the best learning coefficient for this problem was found to be 1.5. By increasing the learning coefficient, the RMS error decreases until the best learning coefficient (of 1.5) is reached (Fig. 5.2). Changing the transition point had a great effect on the RMS value as well as the other parameters (Fig. 5.3). Transition point values between 10,000 and 21,007, yielded lower RMS values than transition points greater than 21,000.

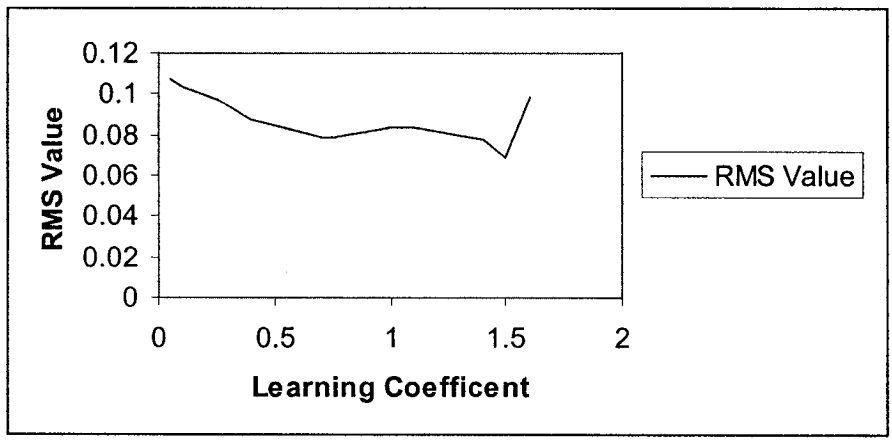


Figure 5.2 Effect of Learning Coefficient on RMS Values

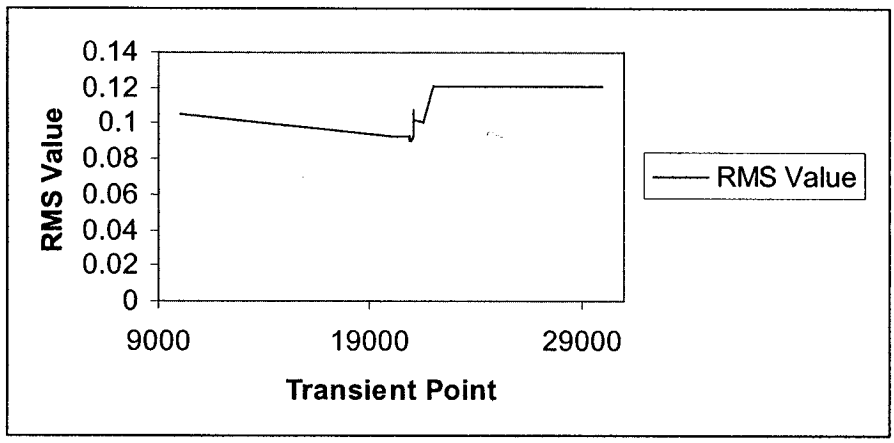


Figure 5.3 Effect of Transition Point on RMS Values

Another important factor in the training process was found to be the epoch number. In this study, larger epoch sizes were chosen because the data was found to contain some noise (NeuralWorks, 1993). An experiment was done, changing the epoch while other parameters remained the same (Fig. 5.4). Various epoch numbers between 8 and 40 were used as parameters for the ANN model. Of these values, the lowest RMS values were obtained for epochs of 12, 30, 35, and 36, the lowest being for an epoch of 35.

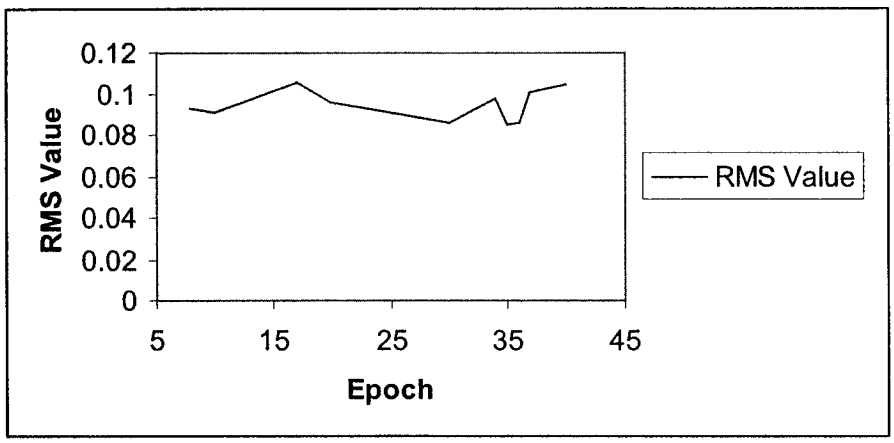


Figure 5.4 Effect of Number of Epochs on RMS Values

The number of processing elements (PEs) had an effect on the performance of the ANN. Previous studies have demonstrated that ANNs can produce satisfactory output with various numbers of PEs (Yang et al., 1997e, 1997f, 1996a, b, c). At the beginning of the experiment, various numbers of PEs between 8 and 16 were used to build the ANNs. Higher values were not used because previous studies have shown that it is not necessary to build ANNs with more PEs. (Yang et al., 1997a, 1997b, 1997c; Salehi et al., 1998). Since the ANN model was complicated and required many inputs to obtain the results, two hidden layers were used to increase training efficiency.

The next part of the experiment was to analyze model performance at different soil depths. To do so, the model was tested with files containing data for a single depth. The model predicted very well for depths of 0-10 and 10-15 cm (Figs. 5.5 and 5.6); however, the predicted values for the 15-20 cm depth did not give good results (Fig. 5.7).

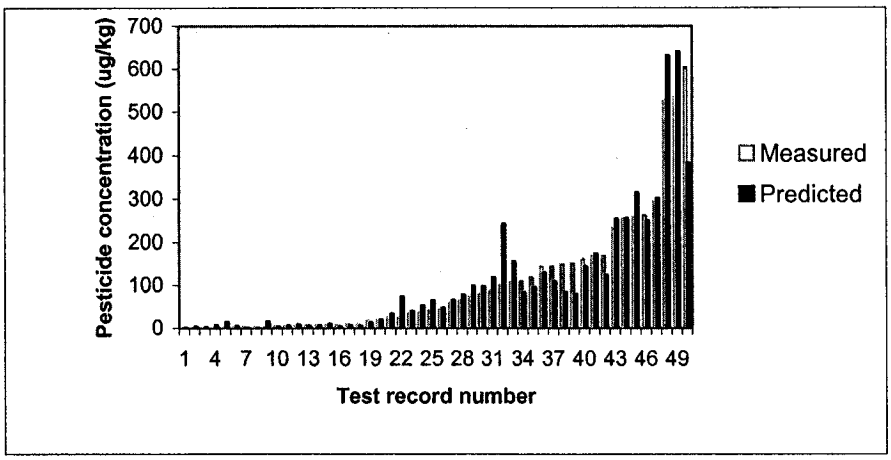


Figure 5.5 Measured Values vs Predicted Values for 0-10 cm

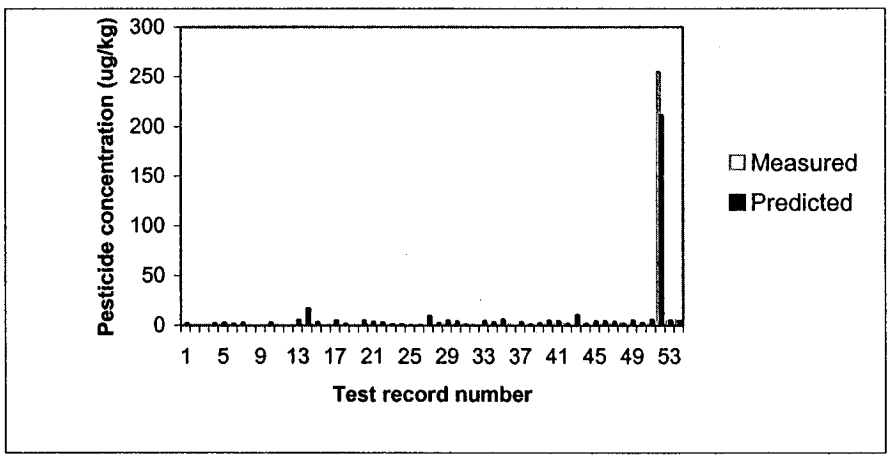


Figure 5.6 Measured Values vs Predicted Values for 10-15 cm

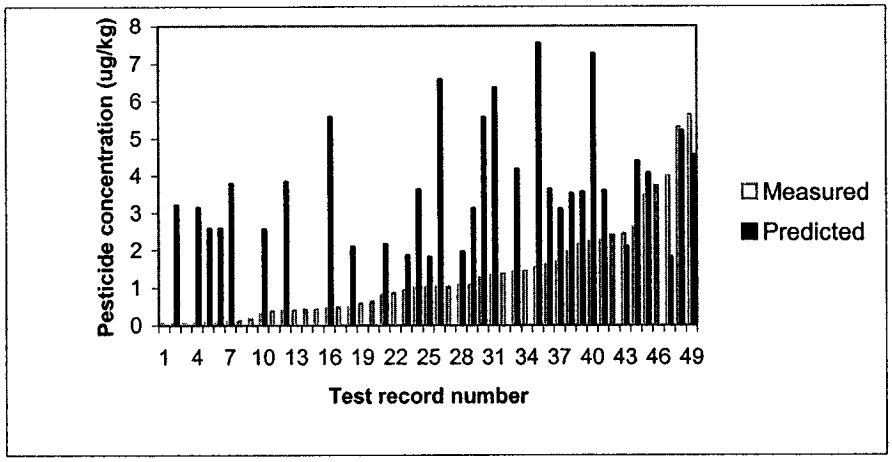


Figure 5.7 Measured Values vs Predicted Values for 15-20 cm

The values predicted by the ANN model for the 0-10 cm (Fig. 5.5) and 10-15 cm (Fig. 5.6) profiles agreed closely with the measured values. For depths between 15 and 20 cm, the level of precision was poor in comparison. This could be because measured values for pesticide concentration at these depths were low (from 0 to 6 μg/kg), whereas those measured at depths of 0-10 cm and 10-15 cm ranged from 0 to 250 μg/kg and 0 to 650 μg/kg respectively. With a narrower range of values, it was more difficult for the ANN model to make accurate predictions because it was trained to predict values over a wider range for the three depths.

To test the accuracy of the ANN model with different sets of data, two networks were set up to compare the RMS values for seven different runs. One network was set up using the default parameters, while the second network was established using the best network parameters. The original data was shuffled seven times to make seven different training and testing files. The networks were, then run seven times using these files. When the second network was run using the new parameters, the RMS values were much lower than those for the network that was using the default values (Fig. 5.8). This observation is analogous to those of studies where it has been shown that an adjustment of input parameters can optimize the predictive ability of an ANN model (Salehi et al., 1998).

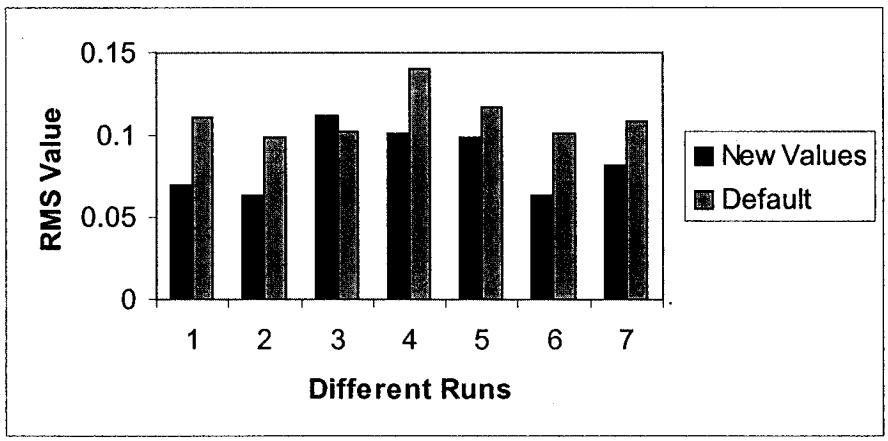


Figure 5.8 RMS Values for 7 Different Runs

5.4 Summary

The major focus of this study was to develop models based on artificial neural networks for the simulation of pesticide concentration through the soil profile. One of the potential benefits of these models is the fast running speed of the simulation. On the other hand,

the disadvantages of such models are that they are site-specific and need to be re-trained for another site.

Efforts were also made to use non-default values for the various ANN-model building parameters in order to optimize the model and compare the results with the default set of parameters. The ANN model simulated pesticide concentrations quite well at 0-10 and 10-15 cm depths; the root mean square (RMS) error between the simulated and observed values was always less than 0.1, which is a good indicator of model performance. However, the model did not perform as well for the 15-20 cm depth. Also, lower RMS values were obtained with the optimized set of ANN-model parameters than with the default set.

Predictions were very good and the ANN model was able to learn the cases the experimental field conditions sufficiently (Fig. 5.9). The root mean square (RMS) error can vary from zero to one, with values close to zero signifying a better fit. The RMS errors in this experiment were less than 0.1, which are an acceptable value. The best network gave a mean RMS value of 0.084 for seven different runs. The average RMS value for the initial network with default values was 0.111. Therefore, changing different parameters helped the ANN model in the learning process, which results, in a better prediction with a lower RMS value.

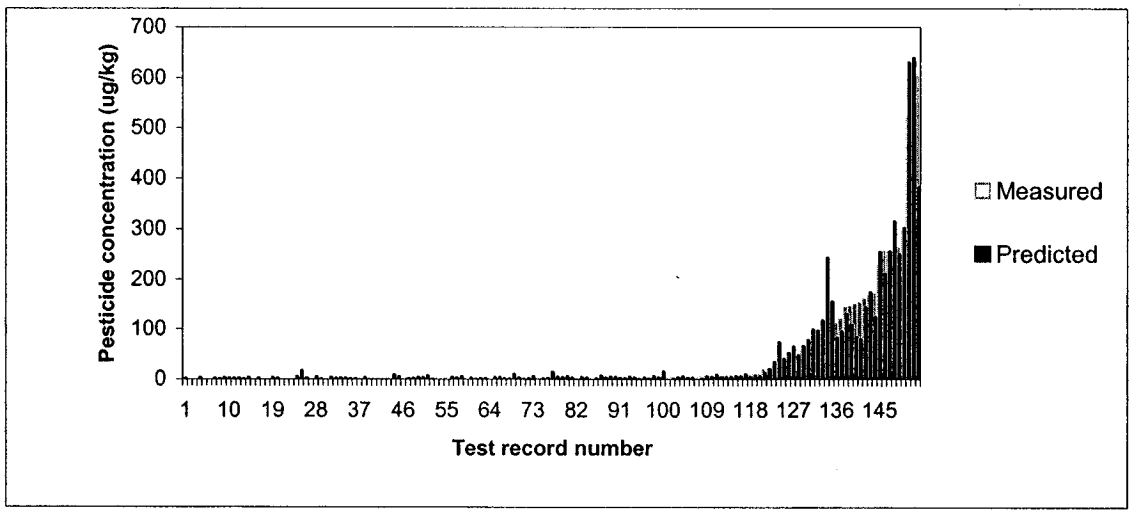


Figure 5.9 Measured Values vs Predicted Values

Data preprocessing and the modification of learning parameters have a considerable effect on the performance of artificial neural networks. In order to identify the best model under the given circumstances and to optimize learning and predicting ability, it is necessary to adjust the parameters involved in the network structure. Different networks were designed with different initial learning coefficients for each hidden layer and for the output layer to determine the best network.

However, the model was unable to predict the small concentrations found in deep soil (i.e. 10-20 cm). Since the ANN model was developed to simulate the concentration of pesticides throughout the soil profile, more long-term information may be helpful for an ANN simulation to better understand the input/output relationship.

CHAPTER VI

REFERENCES

Bailey, G.W. and T.E. Wadell. 1979. Best management practices for agriculture and silviculture: An integrated overview. P 350-546, In: Best management practices for agriculture and silviculture, Loech, R.C., D.A. Haith, M.F. Walter, and C.S. Morton (Eds.) Ann Arbor Science Publishers Inc. Ann Arbor, MI.

Balogh, J.C., and W.J. Walker. 1992. Golf course management & construction environmental issues. Chelsea, Michigan: Lewis Pub.

Baker, J. L., H.P. Johnson. 1981. Nitrate-nitrogen in tile drainage as affected by fertilization. J. Environ. Q. 10:519-522.

Bauman, T.T., and M.A. Ross. 1983. Effect of three tillage systems on the persistence of atrazine. Weed Sci. 31:423-426.

Belmans, C., J.G. Wesseling, and R.A. Feddes. 1983. Simulation model of the water balance of a cropped soil: SWATRE. Journal of Hydrology 63 p 271-286.

Beven, K. and P. Germann. 1982. Macropores and water flow in soils. Water Resour. Res. 18(5), 1311-1325.

Bollag, J. -M. and S. -Y. Liu. 1990. Biological transformation processes of pesticides. P. 169-211. *In* H.H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA Book Ser. 2. SSSA, Madison, WI.

Bonazountas, M. and J. Wagner. 1984. SESOIL: A Seasonal Soil Compartment Model. Cambridge, MA: Arthur D. Little, Inc.

Bouma, J. 1981. Comments on "Micro-, meso-, and macroporosity of soil". Soil Sci. Soc. Am. J. 45:1244-1245.

Brandyk, T. and J.G. Wesseling. 1987. Soil moisture flow in drainage-subirrigation system. J. Hydrology 113(1):86-97

Brown, S. 1997. Visual Basic. Sybex Inc., Alameda, CA.

Brown, L.R. 1989. Reexamining the World Food Prospect. P. 1-58. In: State of the world. W.W. Norton and Company, New York, USA.

Byrne, G.D. 1992. Pragmatic Experiments with Krylov Methods in the Stiff ODE Setting, Computational Ordinary Differential Equations. Oxford Univ. Press, Oxford. pp. 323-356.

Carsel, R.F., C.N. Smith, L.A. Mulkey, J.D. Dean, and P. Jowise. 1984. User's Manual for the Pesticide Root Zone Model (PRZM): Release 1 EPA-600/3-84-109, U.S. EPA,

Athens GA.

Carsel, R.F., L.A. Mulkey, M.N. Lorber, and L.B. Baskin. 1985. The Pesticide rootzone model (PRZM): A procedure for evaluating pesticide leaching threats to groundwater. Ecological Modelling 30(1985) 49-69.

Carsel, R.F., W.B. Nixon, and L.G. Balentine. 1986. Comparison of Pesticide Root Zone Model predictions with observed concentrations for the tobacco pesticide metalaxyl in unsaturated zone soils. Environ. Toxicol. Chem. 5:345-353.

Chen, C., D.M. Thomas, R.E. Green and R.J. Wagenet. 1993. Two-domain estimation of hydraulic properties in macropore soils. Soil Sci. Soc. Am. J., 57:680-686.

Cheng, H.H. and R.G. Lehman. 1985. Characterization of herbicide degradation under field conditions. Weed Sci. Vol 33(2) pp 7-10.

Chesters, G., G.V. Simsiman, J.Levy, B.J. Alhajjar, R.N. Fathulla, and J.M. Harkin. 1989. Environmental fate of alachlor and metolachlor. Rev. Environ. Contam. Toxicol. 110:1-74.

Clemente, R. S. 1991. A mathematical model for simulating pesticide fate and dynamics in the environment (PESTFADE), PhD thesis, Macdonald Campus of McGill University, Ste-Anne de Bellevue, PQ, Canada.

Clemente, R.S. and S.O. Prahser. 1991. PESTFADE Model User's Guide and Documentation. Dept. of Agricultural Engineering, Macdonald Campus of McGill University, Ste Anne de Bellevue P.Q. Canada.

Clemente, R. S., S. O. Prasher and S. F. Barrington. 1993. PESTFADE, A new pesticide fate and transport model: Model development and verification. Transactions of the ASAE 36(2):357-367.

Clemente, R. S., S. O. Prasher, C. A. Madramotoo, R. Bonnell, and I. N. Mathur. 1997. Application of PESTFADE to simulate salt movement I soils. Can. Water Resour. J., 22(2): 63-80.

Cohen, S.Z., C. Eiden, and M.N. Lorber. 1986. Monitoring groundwater for pesticides. In: Evaluation of Pesticides in Groundwater. Garner, W.Y., R.C. Honeycutt, and H.N. Niggs (Eds.) ACS Symposium Series No. 315, American Chemical Society, Washington D.C.

Cowan, I.R. 1965. Transport of water in the soil-plant-atmosphere system. J Appl. Ecol. 2:221-239.

Crank, C. 1975. The mathematics of diffusion, 2nd Ed., Oxford University Press, London.

Dean, J. D., P. S. Huyakorn, A. S. Jr. Donigian, K. A. Voos, R. W. Schanz, Y. J. Meeks, and R.F. Carsel. 1989. Risk of unsaturated transport and transformation of chemical concentration (RUSTIC) model." U.S. EPA, Athens, Ga.

De Jong, R. and P. Kabat. 1990. Modeling water balance and grass production. Soil Sci. Soc. Am. J. 54:1725-732.

Dierichx, J., C. Belmans and P. Pauwels. 1986. SWATRER: a computer package for modeling the field water balance (reference manual). Laboratory of soil and Water Engineering, Faculty of Agricultural Sciences, KU Leuven, Belgium.

Dipietro, L. and F. Lafolie. 1991. Water flow characterization and test of a kinetic-wave model for macropore flow in a highly contrasted and irregular double-porosity medium. J. Soil Sci. 42:551-563.

Donigian, A. S. Jr. and N. H. Crawford. 1976. Modeling pesticides and nutrients on agricultural lands. EPA 600/2-76-043. Environmental Research Laboratory, US EPA, Athens, GA 317 p.

Donigian, A. S. Jr., D. C. Beyerlein, H. H. Davis, and N. H. Crawford. 1977. Agricultural Runoff Management (ARM) model version II: refinement and testing. EPA 600/3-77-098. Environmental Research Laboratory, US EPA, Athens, GA. 293 p.

Donigian, A.S. Jr. and P.S.C. Rao. 1986. Overview of terrestial processed and modeling. In: Vadose Zone Modeling of Organic Pollutants. Hern, S.C. and S.M. Melancon (Eds.) Lewis Publishers Inc. MI pp 3-35.

Drury, C.F., C.S. Tan, J.D. Gaynor, T.O. Oloya, and T.W. Welacky. 1996. Influence of controlled drainage-subirrigation on surface and tile drainage nitrate loss. J. Environ. Qual. 25:317-324.

Dullien, F.A.L. 1992. Porous media – Fluid transport and pore structure. 2nd Ed. Academic Press, New York, USA.

Edwards, W.M., M.J. Shipitalo, L.B. Owens, and W.A. Dick. 1993. Factors affecting preferential flow of water and atrazine through earthworm burrows under continuous no-till corn. J. Environ. Qual. 22:453-457.

EPA Newsroom. http://www.epa.gov/ . Date 24.05.2000.

Feddes, R.A., P.J. Kowalik, and H. Zaradny. 1978. Simulation of field water use and crop yield. Simulation Monograph. PUDOC, Wageningen, Netherlands. pp 189.

Feddes, R.A., J.G. Wesseling, and R. Wiebing. 1984. Simulation of transpiration and yield of potatoes with the SWACRO-model. 9th Tri-annual conference of the European Aassoc. of Potato Res. (EAPR), Interlaken, Switzerland, July 2-6.

Feddes, R.A., P. Kabat, P.J.T. Van Bakel, J.J.B. Bronswijk and J. Hlbertsma. 1988. Modeling soil water dynamics in the unsaturated zone-state of art. Journal of Hydrology, 100: 69-111.

Frere, M. H., C. A. Onstad, and H. N. Holtan. 1975. ACTMO: AN Agricultural Chemical Transport Model. U.S. Dep. of Agric. Res. Serv. ARS-H-3. U.S. Gov. Print. Off., Washington DC.

Gamble, D.S. and S.U. Khan. 1988. Atrazine in organic soil: chemcal speciation during heterogeneous catalysis. Paper presented in part at the third Chemical Conference of North America 31 p.

Gamble, D. S. 1990. Personal communication. Land Resource Research Institute, Agriculture Canada, Ottawa, Canada.

Gamble, D.S. and S. U. Khan. 1990. Atrazine in mineral soil: Chemical species and catalysed hydrolysis. Land Resource Research Center, Agriculture Canada, Ottawa, Canada.

Gamble, D.S., J. Li, G.F.R. Gilchrist, and C.H. Langford. 1992. Atrazine in a mineral soil: Chemical species and sorption processes. Proc., 75th Can. Chemical Conf.

Gardner, W.R. 1960. Soil water relations in arid and semi-arid conditions. In: Plant-water relationships in arid and semi-arid conditions. UNESCO, Paris Rev. of Res. Pp 37.

Gardner, W.R. and C.F. Ehlig. 1962. Some observations on the movement of water to plant roots. Agron. J. 54:453-456.

Gaynor, J.D., J.A. Stone, and T.J. Vyn. 1987. Tillage systems and atrazine and alachlor residues on a poorly drained soil. Can. J. Soil Sci. 67:959-963.

Gaynor, J.D., D.C. MacTavish, and A.B. Labaj. 1998. Atrazine and metolachlor residues in Brookston cl following conventional and conservation tillage culture. Chemosphere 36:3199-3210.

Gaynor, J.D., C.S. Tan, C.F. Drury, H.Y.F. Ng, T.W. Welacky, and I.J. van Wesenbeeck. 2000. Tillage and controlled drainage-subirrigated management effects on soil persistence of Atrazine, Metribuzin, and Metolachlor in corn. J. Environ. Qual. 29:936-947.

Gaynor, J.D., C.S. Tan, C.F. Drury, H.Y.F. Ng, T.W. Welacky, and I.J. van Wesenbeeck. 2001. Tillage, intercrop, and controlled drainage-subirrigation influence Atrazine, Metribuzin, and Metolachlor Loss. J. Environ. Qual. 30:561-572.

Ghadiri, H., P.J. Shea, G.A. Wicks, and L.C. Haderlie. 1984. Atrazine dissipation in conventional-till and no-till sorghum. J. Environ. fQual. 13:549-552.

Gilchrist, G.F.R., D.S. Gamble, H. Kodama, and S.U. Khan. 1993. Atrazine interactions with clay minerals: Kinetics and equilibria of sorption. J. Agric. Food Chem., 41, 1748-1755.

Gish, T.J., C.S. Helling, and M. Mojasevic. 1991. Preferential movement of atrazine and cyanazine under field conditions. Trans. ASAE 34:1699-1705.

Haith, D.A. 1980. A mathematical model for estimating pesticide losses in runoff. J. Environ. Qual. 9:428-433.

Haykin, S. 1994. Neural Networks: A Comprehensive Foundation. New York, NY: Macmillan College Publishing Company, Inc.

Hillel, D. 1980. Fundamental of Soil Physics. Academic press pp 287-317.

Hillel, D. 1982. Introduction to soil physics. Academic Press, Inc. New York, USA.

Hindmarsh, A.C. 1983. ODEPACK, A Systematized Collection of ODE Solvers in Scientific Computing. IMACS Transactions on Scientific Computation. Vol(1):55-64.

Isensee, A.R., R.G. Nash, and C.S. Helling. 1990. Effect of conventional vs. no-tillage on pesticide leaching to shallow groundwater. J. Environ. Qual. 19:434-440.

Jemison Jr., J. M., J. D. Jabro and R. H. Fox. 1994. Evaluation of LEACHM: I. Simulation of drainage, bromide leaching, and corn bromide uptake. Agron. J. 86(5):843-851.

Jury, W.A. and G. Sposito. 1985. Field calibration and validation of solute transport models for unsaturated zone. Soil Sci. Soc. Am. J., 45:671-672.

Kaluli, W. J., S. O. Prasher, R. S. Clemente, and F. Salehi. 1997. Performance evaluation and comparison of three pesticide transport models. Can. Water Resour. J., 22(1): 23-39.

Kartalopoulos, S.V. 1996. Understanding Neural Networks and Fuzzy Logic. Basic Concepts and Applications. New York, NY: the Institute of Electrical and Electronics Engineers, Inc.

Kasabov, N.K. 1996. Foundations of Neural Networks, Fuzzy Systems, and Knowledge Engineering. Cambridge, MA: The MIT Press.

Knisel, W. G. 1980. CREAMS: A field scale model for chemicals, runoff, and erosion from agricultural management systems. Sci. and Educ. Admin. Conservation Res. Rep. No. 26, U.S. Department of Agriculture.

Knisel, W.G., R.A. Leonard, and F.M. Davis. 1993. GLEAMS Version 2.1 Part I:Model Documentation. UGA-CPES-BAED.

Knisel, W.G.,F.M.Davis, and R.A.Leornard. 1994a. GLEAMS VERSION 2.0 PartIII:User Manual.USDA-ARS,Coastel Plain Experiment Station.Southeast Watershed Research Laboratory.Tifton, Georgia, 31793.200pp.

Knisel,W.G.,R.A.Leornard,and F.M.Davis. 1994b. The GLEAMS MODEL PLANT NUTRIENT COMPONENTPart I:MODEL DOCUMENTATION.USDA.ARS,Coastal Plain Experiment Station.Southeast WatershedResearch Laboratory. Tifton, Georgia, 31793.57pp.

Kung, K.-J.S. 1993. Laboratory observation of funnel flow mechanisms and its influence on solute transport. J. Environ. Qual. 22:91-102.

Lal, R. and B.A. Stewart. 1994. Soil processes and water quality. Lewis Publishers, Boca Raton, Florida, USA.

Lacroix, R., F. Salehi, X. Z. Yang, and K. M. Wade. 1997. Effects of data preprocessing on the performance of artificial neural networks for dairy yield prediction and cow culling classification. Transactions of the ASAE 40(3):839-846.

LeBaron, H.M., J.E. McFarland, B.J. Simoneaux, and E. Ebert. 1988. Metolachlor. p. 335-382. In P.C. Kearney and D.D. Kaufman (ed.) Herbicides: Chemistry, degradation and mode of action. Vol. 3. Marcel Dekker, New York.

Leonard, R.A., W.G. Knisel, and D.A. Still. 1987. GLEAMS: Groundwater Loading Effects of Agricultural Management Systems. Transactions of the ASAE 30(5):1403-1418.

Li, Y. and M. Ghodrati. 1994. Preferential transport of Nitrate through soil columns containing root channels. Soil Sci. Soc. of Am. J., 58:653-659.

Li, J., C.H. Langford, and D.S. Gamble. 1996. Atrazine sorption by a mineral soil: Processes of labile and nonlabile uptake. J. Agric. Food Chem., 44(11), 3672-3679.

Li, J., S.O. Prasher, R.S. Clemente, W.D. Reynolds, W.N. Smith, D.S. Gamble, E. Topp, C.H. Langford, and F. Salehi. 1999. Modeling sorption behavior of Atrazine on intact soil columns. Journal of Irrigation and Drainage Engineering. 125(4): 212-222.

Liaghat, A., S.O. Prasher, R.S. Broughton. 1996. Evaluation of an On-Farm Pollution Control System for Reducing Pesticide Pollution. Transactions of ASAE. 39(4): 1329-1335.

Locke, M.A. and C.T. Bryson. 1997. Herbicide-soil interactions in reduced tillage and plant residue management systems. Weed Sci. 45:307-320.

Logsdon, S.D. 1995. Flow mechanisms through continuous and buried macropores. Soil Sci., 160:237-242.

Mannion, A. M. 1995. Agriculture and Environmental Change. New York, N.Y.: John Wiley & Sons.

Masse, L., N. K. Patni, P. Y. Jui and B. S. Clegg. 1996. Tile effluent quality and chemical losses under conventional and no tillage – Part I: Atrazine and metolachlor, Transactions of the ASAE 39(5):1673-1679.

McRae, B. 1989. The characterization and identification of potentially leachable pesticides and areas vulnerable to groundwater contamination by pesticides in Canada. Agriculture Canada. Pesticide Directorate, Ottawa, Canada.

Moore, I.D., G.J. Burch and P.J. Wallbrink. 1986. Preferential flow and hydraulic conductivity of forest soils. Soil Sci. Soc. Am. J., 50:876-881.

Mutch, J.P., A.S. Crowe and O. Resler. 1993. EXPRES: An Expert System for Assessing the Fate of Pesticides in the Subsurface. Users' Manual. Scientific Series No. 201. Burlington, Ont.: Environment Canada.

Nash, J.W. and J.V.Sutcliffe. 1970. River flow forecasting through conceptual models, 1. A discussion of principles. J. Hydrol. 10:282:290.

Natural Resources Conservation Service. Pesticide Runoff Potential for 13 Crops. http://www.nhq.nrcs.usda.gov/land/meta/m2084.html. Date: 23.04.2000.

NeuralWare. 1993. Neural Computing: A Technology Handbook for Professional II/Plus and NeuralWorks Explorer. NeuralWare Inc., Pittsburgh, PA, USA.

NeuralWare. 1996. NeuralWorks Professional II/Plus: System Guide for Windows. NeuralWare Inc., Pittsburgh, PA, USA.

Newman, E.I. 1969. Resistance to water flow in soil and plant. I. Soil resistance in relation to amounts of root: theoretical estimates. J. Appl. Ecol. 16:1-12.

Nicholls, P.H. 1994. Simulation of the movement of bentazon in soils using the CALF and PRZM models. J. Environ. Sci. and health A29(6):1157-1166.

Nofziger, D.L. and A.G. Hornsby. 1985. Chemical movement in soil (CMIS). User's guide. University of Florida. Gainesville, FL.

Nofziger, D.L., J. –S. Chen and C.T. Haan. 1994. Evaluating the chemical movement in layered soil model as a tool for assessing risk of pesticide leaching to froundwater. J. Environ. Sci. and Health A29(6):1133-1155.

Peralta, R.C., M.A. Hegazy and G.R. Musharrafieh. 1994. Preventing pesticide contamination of groundwater while maximizing irrigated crop yield. Water Resour. Res. 30(11):3183-3193.

Pesticide Runoff Potential for 13 Crops, Natural Resources Conservation Service. http://www.nrcs.usda.gov/technical/land/meta/m2084.html. Date: 23.04.2000.

Perret, J.S. 1998. Characterization, visualization and quantification of soil macropores and preferential flow using spect and x-ray cat scanning, PhD thesis, Macdonald Campus of McGill University, Ste-Anne de Bellevue, PQ, Canada.

Philip, J.R. 1957. The physical principles of soil water movement during the irrigation cycle. Trans. 3rd Cong. Intern. Comm. Irr. Drain., Question 8 125-154.

Prasher, S.O., R.P. Rudra, S.F. Barrington, C.A. Madramootoo, and K.C. Khatri. 1987a. Design of water management systems in layered soils. Paper presented at the 1987 North Atlantic Region Annual Meeting of the ASAE, Rutgers University, New Jersey.

Prasher, S.O. and C.A. Madramootoo. 1987b. Applications of the Numerical Method of Lines (NMOL) in Soil Hydrology. Transactions of the ASAE.

Quisenberry, V.L., R.E. Philips and J.M. Zeleznik. 1994. Spatial distribution of water and chloride macropore flow in a well structured soil. Soil Sci. Soc. Am. J., 58:1294-1300.

Radhakrishnan, K., A.C. Hindmarsh. 1993. Description and Use of LSODE, the Livermore Solver for Ordinary Differential Equations. LLNL report UCRL-ID-113855.

Rao, P.S.C. and R.F. Jessup. 1983. Sorption and movement of pesticides and other toxic substances in soils. In: Chemical Mobility and Reactivity in Soil Systems. Soil Sci. Soc. Amer., Madison pp 183-201.

Rice, R.C., D.B. Jaynes, and R.S. Bowman. 1991. Preferential flow of solutes and herbicide under irrigated fields. Trans. ASAE 34:914-918.

Sadeghi, A.M., and A.R. Isensee. 1992. Effect of tillage systems and rainfall patterns on atrazine distribution in soil. J. Environ. Qual. 21:464-469.

Salehi, F., R. Lacroix, K. M. Wade. 1998. Effects of learning parameters and data presentation on the performance of backpropagation networks for milk yield prediction. Transactions of the ASAE, Vol. 41(1):253-259.

Schiesser, W.E. 1983. DSS/2, An introduction to the use of mathematical software for ordinary and partial differential equations. Guidelines for the programming of a numerical method of lines code. Lehigh University, Bethlehem, PA, p 316.

Schmoldt, D.L., P. Li and A.L. Abbott. 1997. Machine vision using artificial neural networks with local 3D neighbourhoods. Computers and Electronics in Agriculture 16: 255-271.

Sharom, M.S., and G.R. Stephenson. 1976. Behavior and fate of metribuzin in eight Ontario soils. Weed. Sci. 24:153-160.

Shirmohammadi, A., W.L. Magette, and L.L. Shoemaker. 1988. Agricultural management practices and water quality. Paper No. 88-2035 presented at the ASAE Conference at St Joseph, MI.

Shukla, M.B., S.O. Prasher, A. Madani, and G.P. Gupta. 1994. Field validation of DRAINMOD in Atlantic Canada. Can. Agric. Eng. 36(4):205-213.

Shukla, M.B., R. Kok, S.O. Prasher, G. Clark, and R. Lacroix. 1996. Use of artificial neural networks in transient drainage design. Transactions of the ASAE 39(1):119-124.

Singh, P., and R.S. Kanwar. 1991. Preferential solute transport through macropores in large undisturbed saturated soil columns. J. Environ. Qual., 20:295-300.

Singh, M., S. O. Prasher, C. S. Tan and C. M. Tejawat. 1994. Evaluation of DRAINMOD for Southern Ontario Conditions. Canadian Water Resources Journal. 19(4).

Skopp, J. 1981. Comments on "Micro-, meso-, and macroporosity of soil". Soil Sci. Soc. Am. J., 45:1246.

Smith, A.E. 1988. Transformations in soil. In Environmental Chemistry of Herbicides. Grover, R. (Ed.) CRC Press Inc. Florida. Pp 171-200.

Smith, W.N., S.O. Prasher, S. Barrington. 1991. Evaluation of PRZM and LEACHMP on intact soil columns. Trans. ASAE 34(6), 2413-2420.

Smith, W.N., S.O. Prasher, S.U. Khan, and N.N. Barthakur. 1992. Leaching of C-labelled atrazine in long, intact soil columns. Trans. ASAE, 35(4), 1213-1220.

Smith Jr.,S., J.D. Schreiber and R.F. Cullum. 1995. Upland soybean production: Surface and shallow groundwater quality as affected by tillage and herbicide use. Transactions of the ASAE 38(4):1061-1068.

Soultani, M.,C. S. Tan, J.D. Gaynor, R. Neveu and C.F. Drury. 1993. "A Simple Automated System to Sample and Measure Volume of Surface Runoff and Subsurface Drainage." Applied Engineering in Agriculture. 9(5): 447-450.

Stone, J.A., T.J. Vyn, H.D. Martin, and P.H. Groenevelt. 1989. Ridge-tillage and early-season soil moisture and temperature on a poorly drained soil. Can. J. Soil Sci. 69:181-186.

Talbert, R.E. and H.O. Fletchall. 1965. The adsorption of some s-triazines in soils. Weeds 13:653-656.

Tan, C.S., J.D. Gaynor, C.F. Drury and T.W. Welacky. 1993a. "Tillage and Water Table Management to Abate Herbicide and Nitrate Loss in Surface Runoff and Tile Drainage Water". ASAE Paper No. 932081.

Tan, C.S., C.F. Drury, J. D. Gaynor and T.W. Welacky. 1993b. "Integrated Soil, Crop and Water Management System to Abate Herbicide and Nitrate Contamination of the Great Lakes." Wat. Sci. Tech 28(3-5): 497-507.

Tel, D.A. and C. Heseltine. 1990. The analyses of KCI soil extracts for nitrate, nitrite and ammonium using a TRAACS 800 analyzer. Commun. In Soil Sci. Plant Anal., 21: 1681-1688.

The Ohio State University. Pesticides and groundwater contamination, bulletin 820. http://ohioline.osu.edu/b820/b820_3.html. Date: 08.05.2000.

Timlin, D.J., L.R. Ahuja and M.D. Ankeny. 1994. Comparison of three field methods to characterize apparent macropore conductivity. Soil Sci. Soc. Am. J., 58:278-284.

Timmermans, A.J.M. and A.A. Hulzebosch. 1996. Computer vision system for on-line sorting of pot plants using an artificial neural network classifier. Computers and Electronics in Agriculture 15: 41-55.

Triplett, G.B.Jr., B.J. Conner, and W.M. Edwards. 1978. Transport of atrazine and simazine in runoff from conventional and no-tillage corn. J. Environ. Qual. 7:77-84.

Unger, P.W. 1990. Conservation tillage systems. Adv. Soil Sci. 13:27-68.

United States Environmental Protection Agency. Center for exposure assessment modeling PRZM3. http://www.epa.gov/ceampubl/przm3.htm. Date: 04.05.2002.

U. S. Department of Agriculture (USDA) Soil Conservation Service. 1972. National Engineering Handbook, Section 4, Hydrology.

Villenvueve, J.P., O. Banton, P. Lafrance, and P.G.C. Cambell. 1987. A new model for the evaluation of groundwater vulnerability to non-point contamination by pesticides. Proceedings and Information No. 38 of the International Conference on Vulnerability of Soil and Groundwater to Pollutants. The Hague, The Netherlands.

Wagenet, R.J. and J.L. Hutson. 1986. Predicting the fate of nonvolatile pesticides in the unsaturated zone. J. Environ. Qual. 15:315-322.

Wagenet, R.J. and J.L. Hutson. 1987. LEACHM: Leaching Estimation and Chemistry Model. Center for Environmental Research, Cornell University, Ithca, NY.

Wagenet, R. J. and J. L. Hutson. 1989. LEACHM: Leaching Estimation and Chemistry Model. Version 2. Center for Environmental Research, Cornell University, Ithaca, NY.

Walker, A. 1974. A simulation model for prediction of herbicide persistence. J. Environ. Quality. Vol. 3 396-401.

Walker, A., and R.L. Zimdahl. 1981a. Simulation of the persistence of atrazine, linuron, and metolachlor in soils at different sites in the U.S.A. Weed Res. 21:255-265.

Walker, A. and A. Barnes. 1981b. Simulation of herbicide persistence in soil; a revise computer model. Pesticide Science. 12:123:132.

Walker, A. 1987. Herbicide persistence in soil. Rev. Weed Sci. 3:1-17.

Walker, A. 1991. Influence of soil and weather factors on the persistence of soil-applied herbicides. Appl. Plant Sci. 5:94-98.

Wang, D., F.E. Dowell and R.E. Lacey. 1999. Single wheat kernel color classification using neural networks. Transactions of the ASAE 42: 233-240.

Warner, G.S. 1990. Characterization of soil macropores by computed tomography. Ph.D. Thesis. Universit of Minnesota. Michigan, USA.

Wasserman, P.D. 1993. Advanced methods in neural computing. Van Nostrand Reinhold, New York, NY. 235 pp.

Waters, R.D., P.V. Brady, D.J. Borns. 1998. Natural attenuation of metals and radionuclides-An overview of the Sandia/DOE approach. Sandia National Laboratories, <http:..www.sandia.gov/eesector/gs/wm98rna.htm>.

Wesseling, J.G., P. Kabat, B.J. van den Broek, and R.A. Feddes. 1989. Simulation model of the water balance of a cropped soil with different types of boundary conditions including the possibility of drainage and irrigation and the calculation of crop yield (SWACROP). Wageningen, the Netherlands.

Wischmeier, W.H. and D.D. Smith. 1978. Predicting rainfall erosion losses from cropland – A guide to conservation planning. Agriculture Handbook 537, U.S. Dept. of Agriculture.

Workman, S.R. and R.W. Skaggs. 1989. Comparison of two drainage simulation models using field data. Transactions of the ASAE Vol 32(6): 1933-1938.

Wu, J. and D.L. Nofziger 1999. Incorporating temperature effects on pesticide degradation into a management model. J. Environ. Qual. 28:92-100.

Yang, C.–C., S.O. Prasher, R. Lacroix. 1996a. Application of artificial neural networks to simulate water-table depths under subirrigation.. Can. Water Resour. J. 21(1):27-44.

Yang, C.–C., S.O. Prasher, R. Lacroix. 1996b. Applications of artificial neural networks to land drainage engineering. Transactions of the ASAE, Vol. 39(2):525-533.

Yang, C.–C., S.O. Prasher, S. Sreekanth. 1996c. An artificial neural network model for pesticide fate and transport. ASAE paper No. 962025. St. Joseph, Mich.: ASAE.

Yang, C.-C., S.O. Prasher, R. Lacroix, S. Sreekanth, A. Madani and L. Masse. 1997a. Artificial neural network model for subsurface-drained farmlands. Journal of Irrigation and Drainage Engineering 123: 285-292.

Yang, C.-C., S.O. Prasher and G.R. Mehuys. 1997b. An artificial neural network to estimate soil temperature. Canadian Journal of Soil Science 77: 421-429.

Yang, C.-C., S.O. Prasher, R. Lacroix, A. Madani. 1997c. Application of artificial neural networks in subsurface drainage system design. Canadian Water Resources Journal, Vol. 22, No. 1, 1997.

Yang, C.–C., S.O. Prasher, J. A. Landry. 1997d. "Application of Machine Vision and Artificial Neural Networks in Precision Farming". ASAE Annual International Meeting Presentation, paper no. 973107.

Yang, C.–C., S.O. Prasher, G. R. Mehuys, N. K. Patni. 1997e. Application of neural networks for simulation of soil temperature. Transactions of the ASAE, Vol. 40(3):649-656.

Yang, C.-C., S.O. Prasher, S. Sreekanth, N. K. Patni, L. Masse. 1997f. An artificial neural network model for simulating pesticide concentration in soil. Transactions of the ASAE 40(5):1285-1294.

Yang, C.-C, S.O. Prasher, and C. S. Tan. 1999. An Artificial Neural Network Model for Water Table Management Systems. Canadian Water Resources Journal 24(1): 25-34.

Yang, C.-C., S.O. Prasher, J.-A. Landry, H.S.Ramaswamy and A. Ditommaso. 2000. Application of artificial neural networks in image recognition and classification of crop and weeds. Canadian Agricultural Engineering 42(3): 147-152.

Yeh, G.T. and D.S. Ward. 1981. REMWASTE: A Finite Element Model of Waste Transport through Porous Saturated-Unsaturated Media. ORNL-5567. Oak Ridge National Laboratory, Oak Ridge TN.