# COMPUTER MODELS FOR SIMULATING PESTICIDE FATE AND TRANSPORT IN SOIL

by

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*Your file Votre référence*
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*Our file Notre référence*
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*This thesis is dedicated to my parents*

*Ibha and Nikhil Ranjan Bera*

*for their love, care, understanding and support*

*and to my uncle,*

*Manik Ranjan Bera*

## ABSTRACT

Two different modeling approaches to simulate pesticide fate and transport in soil were investigated in this study. First, a process-based mathematical model, DRAINMOD-P, was developed by combining the attractive features of DRAINMOD and PESTFADE. While DRAINMOD formed the main component to perform hydrological predictions, PESTFADE's pesticide sub-model was used to simulate pesticide fate. The new model was validated against three years of independently collected field data from southern Ontario. Several statistical parameters were calculated to evaluate model performance.

Results obtained from DRAINMOD showed acceptable model efficiencies, which ranged between 28-81%. The pesticide sub-model of PESTFADE accounts for intraparticle diffusion and both labile and non-labile sorption in a logical way. Calculations were performed using molar quantities to remain in accordance with standard stoichiometry. Results obtained from this study demonstrate that atrazine simulations were well within an order of magnitude of the observed data, which is in line with investigations done by other researchers. The root mean square error (RMSE) values were between 0.41 to 1.04 and 0.37 to 1.25 for the conventional and Gamble approach, respectively, which supports the acceptability of the model.

Second, an implicit model, Multivariate Adaptive Regression Splines, MARS, which is also a novel data mining tool, was used to assess pesticide transport. MARS was first validated against the field data on three herbicides, namely, atrazine, metribuzin and metolachlor. The MARS models yielded modeling efficiencies between 42 to 99% for all three herbicides at all depths. The execution time was less than DRAINMOD-P and MARS predictions were generally good in spite of the very small data size. A comparison drawn between the DRAINMOD-P and MARS models for atrazine also proved that MARS performed better than the process-based model. However, DRAINMOD-P and MARS simulations, though impressive, need further validations before they can be recommended for actual real-world use.

## RÉSUMÉ

Deux approches de modélisation ont été utilisées dans l'étude du devenir et du transport de pesticides dans les sols. En premier lieu, un modèle mathématique DRAINMOD-P a été développé en utilisant les points forts de DRAINMOD et de PESTFADE. Le module DRAINMOD composait la majeure partie des prédictions hydrologiques, alors que le sous module PESTFADE était utilisé pour la simulation du devenir des pesticides. Le nouveau modèle fut validé par trois années de données, recueillies dans le sud de l'Ontario. Plusieurs paramètres statistiques ont été calculés afin d'évaluer la performance du modèle.

Les résultats obtenus par DRAINMOD ont démontré une efficacité acceptable du modèle, variant entre 28 et 81%. Le sous-module PESTFADE prend en compte la diffusion des macropores et la sorption labile et non-labile. Les calculs ont été effectués en utilisant les quantités molaires en vertu de la stoéchiométrie standard. Les résultats obtenus lors de cette étude ont démontré que les simulations pour l'atrazine sont dans les limites des données observées, ce qui est le cas rapporté par d'autres chercheurs. Les valeurs d'erreur-type ont été entre 0.41 et 1.04 et 0.37 et 1.25 pour les méthodes traditionnelle et de Gamble respectivement, démontrant la validité du modèle.

En second lieu, un modèle implicite, de régressions multi-dimensionnelles adaptatives des splines (MARS), connu comme outil d'exploration de données, fut utilisé pour déterminer le transport des pesticides dans les sols. MARS fut premièrement validé grâce à des données recueillies pour trois herbicides, dont l'atrazine, la métribuzine et le métolachlore. Les modèles MARS ont obtenu une efficacité de simulation variant de 42 à 99%, pour les trois herbicides à toutes les profondeurs. Les temps d'exécution étaient considérablement réduits et les prédictions de MARS étaient généralement bonnes malgré la faible grosseur de l'échantillonnage. Une comparaison effectuée entre les modèles DRAINMOD-P et MARS pour les prédictions d'atrazine a démontré que MARS s'acquittait de la tâche avec plus de succès. Néanmoins, les simulations de DRAINMOD-

P et de MARS, bien qu'impressionnantes, nécessitent des validations plus approfondies avant que leur utilisation puisse être recommandée pour un usage réelle.

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## CONTRIBUTION OF AUTHORS

In line with the regulations of the faculty of Graduate Studies and Research of McGill University, the following statement from the Guidelines for Thesis Preparation is included.

*As an alternative to the traditional thesis format, the dissertation can consist of a collection of papers of which the student is an author or co-author. These papers must have a cohesive, unitary character making them a report of a single program of research. The structure for the manuscript-based thesis must conform to the following:*

*1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly-duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis.)*

*2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges preceeding and following each manuscript are mandatory.*

*3. The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts.*

*The thesis must include the following:*

*(a) a table of contents;*

*(b) a brief abstract in both English and French;*

*(c) an introduction which clearly states the rational and objectives of the research;*

*(d) a comprehensive review of the literature (in addition to that covered in the introduction to each paper);*

*(e) a final conclusion and summary;*

*(f) a thorough bibliography;*

*(g) Appendix containing an ethics certificate in the case of research involving human or animal subjects, microorganisms, living cells, other biohazards and/or radioactive material.*

*4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.*

*5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defence. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers.*

**Manuscripts based on the thesis:**

Bera, P., S. O. Prasher, A. Madani, J. D. Gaynor and C. S. Tan. Development and Validation of DRAINMOD-P for Southern Ontario Conditions. (Manuscript to be submitted to the Transactions of the ASAE journal).

Bera, P., S. O. Prasher, A. Madani, R. Lacroix, J. D. Gaynor, and C. S. Tan. Application of MARS in simulating pesticide movement in soil. (Manuscript to be submitted to the Transactions of the ASAE journal).

The development and validation of DRAINMOD-P and MARS, the performance of statistical analyses and the preparation of the manuscripts were completed by the candidate, P. Bera, under the supervision of Dr. Shiv Om Prasher. Dr. Shiv Om Prasher provided the funds required in carrying out this research. He provided his time and energy in assisting the candidate aptly from the inception of the project, dealing with

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## LIST OF SYMBOLS AND ACRONYMS

For the sake of brevity, the most commonly used symbols, abbreviations and acronyms are listed below. The notations pertaining to a particular equation are described wherever they appear in the text.

| | |
|---|---|
| $\theta$ | volumetric soil moisture, $cm^3\ cm^{-3}$ |
| $\rho$ | dry soil bulk density, $g\ cm^{-3}$ |
| $\varepsilon$ | air-filled porosity |
| $\phi$ | sink term for biochemical degradation, volatilization and root uptake, $g\ cm^{-3}\ h^{-1}$ |
| $\alpha$ | first-order degradation rate constant in the liquid phase |
| $\beta$ | first-order degradation rate constant in the solid phase |
| $\gamma$ | zero-order rate constant in the liquid phase |
| $\theta_c$ | labile sorption capacity, mol $g^{-1}$ of dry soil |
| $\theta_D$ | nonlabile uptake by intraparticle diffusion, moles $g^{-1}$ of dry soil |
| $\theta_L$ | Sorption sites occupied by pesticide |
| $\theta_o$ | Unoccupied sites |
| AAD | Average absolute deviation |
| AI | Artificial intelligence |
| ANN | Artificial neural networks |
| ANOVA | Analysis of variance |
| $b_1$ | empirical constants |
| $b_o$ | empirical constants |
| C | concentration of the chemical in the liquid phase, $mg\ L^{-1}$ |
| CADD | convection–adsorption-diffusion-degradation |
| Cairtem | Cumulative air temperature, °C |
| CBR | Case-based reasoning |
| CDE | convection-dispersion equation |

| | |
|---|---|
| $CO_2$ | Carbon dioxide |
| CP | Chisel plow |
| Cpet | Cumulative potential evapotranspiration, mm $day^{-1}$ |
| Crain | Cumulative rainfall, mm |
| CREAMS | Chemicals, runoff, erosion from agricultural management systems |
| Csoiltem | Cumulative soil temperature, °C |
| D | Free drainage |
| D | dispersion coefficient, $cm^2$ $h^{-1}$ |
| Dayafter | Days after pesticide application |
| $D_e$ | diffusion coefficient, $cm^2$ $s^{-1}$ |
| De | Diffusion coefficient |
| EF | Model efficiency |
| GA | Genetic algorithm |
| GCV | Generalized cross validation |
| GLEAMS | Groundwater loading effects of agricultural management systems |
| HPLC | High-performance liquid chromatography |
| i | Event |
| IMAC | Interim maximum acceptable concentration |
| IRRSCHM | Irrigation Scheduling Model |
| Jday | Julian day |
| $K_1$ | Weighted average sorption equilibrium constant |
| $k_{b1}$ | rate constants for adsorption, L $mol^{-1}$ $d^{-1}$ |
| $K_d$ | distribution coefficient, L of soil solution $g^{-1}$ of dry soil |
| $k_{d1}$ | first-order rate constant for inward intraparticle diffusion, $d^{-1}$ |
| $K_H$ | Henry's constant |
| Koc | Organic carbon sorption coefficient |
| $k_{ow}$ | Octanol –water partition coefficient |
| $k_{s2}$ | rate constants for desorption, $d^{-1}$ |
| l | mean particle radius, cm |
| LEACHM | Leaching estimation and chemistry model |
| LEACHP | Pesticide model of LEACHM |

| | |
|---|---|
| MAC | Maximum allowable concentrations |
| MARS | Multivariate adaptive regression splines |
| $M_{AT}$ | pesticide molarity in soil solution, mol $L^{-1}$ of soil solution |
| MB | Moldboard plow |
| MBD | moldboard plow with controlled drainage subirrigation |
| MBIC | Moldboard plow with intercropping |
| MBICD | moldboard plow with intercropping and free drainage |
| MBICW | moldboard plow with intercropping and controlled drainage subirrigation |
| MBW | moldboard plow with free drainage |
| MCL | Maximum contaminant level |
| MODFLOW | Modular three-dimensional finite difference ground-water flow model |
| MSE | Mean square error |
| MT3D | Three-dimensional numerical model |
| N | Nitrogen |
| n | Number of observations |
| O | Mean observed value |
| $O_i$ | Observed value |
| PE | Processing element |
| PESTFADE | Pesticide fate and dynamics in the environment |
| $P_i$ | Predicted values |
| PRZM2 | Pesticide root zone model release-2 |
| PRZM3 | Pesticide root zone model release 3 |
| q | water flux, cm $h^{-1}$ |
| Q | factor for converting time units, s $d^{-1}$ |
| R | retardation factor for the solute in the soil |
| RMSE | Root mean square error |
| RZWQM | Root zone water quality model |
| S | mass of solute adsorbed or desorbed per unit mass of soil, g $g^{-1}$ of soil |
| SD | Standard deviation |
| SE | Standard error |
| SS | Soil saver |

| | |
|---|---|
| SSD | soil saver with controlled drainage subirrigation |
| SSIC | Soil saver with intercropping |
| SSICD | soil saver with intercropping and free drainage |
| SSICW | soil saver with intercropping and controlled drainage and subirrigation |
| SSW | soil saver with free drainage |
| SWACROP | Soil Water Actual Transpiration and Crop Production Simulation Model |
| T | absolute temperature, K |
| TSNE | Two-site non-equilibrium |
| UNEP | United Nations Environment Program |
| USEPA | United States Environmental Protection Act |
| VADOFT | Vadoze zone flow and transport model |
| W | Controlled drainage and subirrigation |
| W/V | unit conversion factor, g $L^{-1}$ |
| WHO | World health organization |
| X | Variable to describe hockey stick function |
| X* | New variable to represent hockey stick function |
| $x_1$ | Mole fraction of occupied sites |
| $x_p$ | Predictor variable |

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# CHAPTER 1
# INTRODUCTION

Currently, farmers across the globe are applying pesticides extensively to achieve higher yields and to maintain the quality of agricultural products. It has been predicted that the global agrochemical market will grow by 1.9% a year between 1995 and 2005, to $36.8 billion US. It is reported that about 30 billion dollars (US) worth of chemical pesticides are sold annually (Marrone, 1999). Out of the 500,000 tons of pesticides used in the US, about 80% are used in agriculture. Herbicide sales accounted for 85% of total pesticide sales in 1997 in Canada and 70% in the USA (Shapir and Mandelbaum, 1997). There is a growing national and international concern about the environmental pollution caused by the extensive use of pesticides. About 25 million cases of acute occupational pesticide poisoning have been reported in developing countries and each year about one million people suffer from pesticide poisoning, leading to 20,000 deaths (WHO and UNEP, 1989). Usually with an increase in awareness, pesticides that are less harmful are chosen. Numerous studies have been conducted to assess the leaching potential of these pesticides (Cameira et al., 1998).

A thorough understanding of interdependent and dynamic natural processes is necessary to understand pesticide fate and transport in soils (Wagenet et al., 1985). The behavior of pesticides is governed by soil properties, chemical composition of the pesticide, site conditions and management practices, including the rate and method of pesticide application, and irrigation practices. After application, pesticides may be lost through vaporization/volatilization, plant uptake, runoff, and leaching. Depending on soil conditions, pesticides may undergo degradation by microorganisms. Pesticide transport is also affected by temperature, soil water content, pore size distribution in the soil, microbial populations, and organic matter content.

## 1.1 PROCESS-BASED MODELING

Various research efforts dealing with pesticide fate and transport have been carried out in the past, both in field and controlled laboratory conditions (Melancon et al., 1986; Gaynor et al., 1995; Azevedo et al., 1997; Li et al., 1999 and Gaynor et al., 2000). A field study can provide useful information for a given climate and soil type, whereas a soil column or lysimeter study permits isolation and detailed investigation of selected processes or parameters. However, both field and laboratory studies are costly and time-consuming (Malone et al., 1999; Li et al., 1999) and yield largely site-specific information. Modeling can eliminate the numerous shortcomings of the experimental procedures. It is fast, accurate, and efficient.

Process-based modeling is gaining wider acceptance as a tool for the evaluation of the environmental fate and transport of contaminants (Wagenet et al., 1997; Li et al., 1999; Chu et al., 2000; Celis et al., 1999 and Asare et al., 2001). Sorption, leaching, degradation and volatilization are some of the processes being integrated through the use of simulation modeling techniques (Wagenet et al., 1985). Some of the current pesticide models are the Leaching Estimation and Chemistry Model (LEACHM) (Wagenet and Hutson, 1989), Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) (Leonard et al., 1987), Pesticide Root Zone Model release-2 (PRZM2) (Mullins et al., 1993), and Pesticide Fate and Dynamics in the Environment (PESTFADE) (Clemente et al., 1993).

LEACHM can simulate the fate and transport of chemicals in transient-flow field situations and in laboratory columns that are subjected to steady-state or interrupted flow situations. It is comprised of components that differ in the way they describe chemical equilibrium, transformation, and degradation processes. LEACHM is a deterministic model that is popular among researchers, regulatory personnel, and management personnel (Wagenet et al., 1997). GLEAMS is a field scale model for analyzing the chemistry of pesticide movement and changes with respect to soil properties and different climatic conditions. The model assumes homogeneous land use, soils, and precipitation

in the field, and it predicts the effect of pesticides on water quality based on different farm level management practices. Pesticide Root Zone Model-release-2 (PRZM2) (Mullins et al., 1993) is a deterministic model which is partly mechanistic and partly functional. It deals with pesticide leaching, foliar interception, runoff losses, and plant uptake (Wagenet et al., 1997). Both GLEAMS and LEACHP do not consider macropore flow (Vanclooster et al., 2000), which might result in lower pesticide predictions (Malone et al., 1999). These models either consider linear or non-linear sorption. GLEAMS does not include volatilization losses (Vanclooster et al., 2000). PESTFADE (Clemente et al., 1993), a one-dimensional model, pays special attention to two-stage sorption kinetics, dispersion, volatilization, microbial degradation, and loss through runoff in its simulation; it can also handle macropore flow and has been tested and validated with field experiments (Clemente, 1991; Clemente et al., 1997; Kaluli et al., 1997; Li et al., 1999; Tafazoli, 2002).

Careful appraisal of these studies highlights issues that need wider attention. The inefficacy of current model predictions may be due to the inaccurate estimation of the sorption coefficient and the sorbed-phase degradation rate. Most of the studies overlook the differences that may exist in the degradation rates in the sorbed and dissolved phase (Gamble et al., 2000). The calculation of the partition coefficient is complex in itself (Schwarzenbach., 1993). Estimation of this transport parameter by means of simplification may yield incorrect results. The study by Seybold et al. (1996) of two Virginia soils, where the fate of atrazine and metolachlor and its metabolites were investigated, found that both adsorption and desorption isotherms need to be studied in order to be able to develop simulation models giving accurate results. The simulation of atrazine yielded better results when intraparticle diffusion and sorption capacity were included as soil functions (Li et al., 1999). Therefore, modeling contaminant transport must incorporate more realistic parameters to yield more realistic estimates. The emphasis that PESTFADE lays on sorption and its inclusion of microbial degradation and volatilization makes it an obvious choice for this study. The hydrology component of the model is based on Soil Water Actual Transpiration and Crop Production Simulation

Model (SWACROP), a Dutch water flow model, which is not very user-friendly or easy to use. Yet it is a comprehensive process-based water flow simulation model.

In this study, DRAINMOD (Skaggs, 1978), a water table management model, is used to simulate the water flow. This model is user-friendly and has been widely tested. It is renowned for its hydrological predictions in simulating water table depths, as well as surface and subsurface drainage discharges under different pedoclimatic zones in North America (Skaggs, 1982; Skaggs et al., 1981; Gayle et al., 1985; Fouss et al., 1987; Rogers, 1985; and Susanto et al., 1987). It allows the user to enter and edit input parameters with ease and portrays outputs graphically for easier interpretation. Simulations involving longer periods are executed within short periods of time. Therefore, it was decided to develop a new pesticide fate and transport model that employs DRAINMOD for hydrological simulations and subsequently use the water flow information with the pesticide simulation sub module of PESTFADE. In addition, the new model was tested against independently collected field data of pesticides to study the fate and transport of pesticides under field conditions.

## 1.2 MACHINE-LEARNING BASED MODELING

Process-based models involve too many input parameters and require long simulation periods. In addition, a thorough understanding of all the governing processes is a prerequisite in process-based modeling. Proper mathematical representation of the complex nature of these mechanisms is difficult without this knowledge. Most models are unable to account for the spatial variability, while many more are unable to account for macropore flow, which often results in underestimations. Uncertainties also arise due to incorrect estimations of vital input parameters. Implicit modeling, on the other hand, requires less execution time, does not demand prior process knowledge and still yields accurate results. This alternative approach was also attempted in this study because of these advantages.

Machine-based learning models, such as neural nets, rule induction, case-based reasoning and decision trees, are known for their speed and accuracy in simulating real-world phenomena. These algorithms perform well with limited inputs, need less computation time, and are user-friendly (Yang et al., 1996a; 1997f). Studies conducted by previous researchers provide evidence of the popularity of this approach (Ocerin et al., 1996; Altendorf et al., 1999; Yang et al., 1996a; 1997f; Lebron et al., 1999; Salehi et al., 2000; Abraham et al., 2001a,b; Sephton, 2001; Haas and Kubin, 1998). Artificial Neural Networks (ANNs) have been used extensively in agricultural studies in predicting soil moisture (Altendorf et al., 1999), soil temperature (Yang et al., 1997b,c), saturated hydraulic conductivity (Lebron et al., 1999), and annual nitrate-N losses in drain outflows (Salehi et al., 2000b). ANNs require a longer model development effort. . ANNs have been outperformed in their estimates of Mean Square Error (MSE) values by Multivariate Adaptive Regression Splines (MARS) in certain studies conducted by previous researchers (Abraham et al., 2001a,b).

MARS, a new regression model is able to carry out a rigorous search to identify relations amongst the input variables with the aid of basis functions (Abraham et al., 2001a,b; Sephton, 2001; Attoh-Okine et al., 2001). It assigns a significance factor to the input parameters thereby giving us an indication of those parameters which are essential to the performance of the model (Abraham et al., 2001a,b). The inclusion of Analysis of Variance (ANOVA) allows for the understanding of the interrelationships between variables (Attoh-Okine et al., 2001). Studies conducted by Abraham et al. (2001a,b) also concluded that MARS outperformed ANNs. ANNs have already been used for carrying out pesticide fate studies and have yielded good results (Yang et al., 1997f and Tafazoli, 2002). An attempt was made to simulate pesticide movement with MARS models in this exploratory study. This approach eliminates the shortcomings of process-based modeling, where approximations of parameters affect model performance.

## 1.3 OBJECTIVES

As a result of the above discussion, this research project addresses the following objectives:

a) to develop a new pesticide fate and transport model, DRAINMOD-P, for agricultural soils,
b) to validate the model in assessing the fate and transport of atrazine, a broadleaf herbicide, based on independently collected field data, and
c) to evaluate the use of MARS to simulate pesticide movement in soil for three commonly used herbicides: atrazine, metribuzin, and metolachlor.

## 1.4 THESIS ORGANIZATION

This thesis contains six chapters. In Chapter 1, an introduction is provided, while Chapter 2 deals with literature review. The focus of Chapter 3 is on the development and validation of the process-based model, DRAINMOD-P. In Chapter 4, the use of MARS, an automated regression model to predict pesticide concentrations, is highlighted. A discussion, summary and conclusions are presented in Chapter 5. Chapter 6 includes the references. The appendix includes the input-output files, program files, data files and the field layout.

## 1.5 SCOPE

This study mainly deals with the development and validation of a computer simulation model for atrazine transport with the help of independently collected data. However, the validation of the model is limited to atrazine measurements in one field in Southern Ontario. The performance of MARS is also restricted to data from three herbicides obtained over a period of three years. Further validations with larger databases using both models may increase the reliability of DRAINMOD-P and MARS.

# CHAPTER 2
# LITERATURE REVIEW

The use of simulation models to assess pesticide fate has become a common practice. Such assessments are useful to determine *a priori* the severity and future threat of contamination problems, and the models also provide an economical means to evaluate new management practices.

In this chapter, the environmental fate of three commonly used herbicides in eastern Canada are reviewed along with different modeling methods that can be used to follow their fate and transport in the environment. This chapter is divided into 4 sections. The first section reviews the fate of atrazine, metribuzin and metolachlor in the soil environment, the second reviews various pesticide transport processes, the third examines the role of water table management and pesticide movement, and the last section includes two subsections; the first subsection reviews a few existing process-based models, the second reviews the use of machine-learning methods.

## 2.1 ENVIRONMENTAL FATE OF ATRAZINE

Atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] is a pre-emergent herbicide, commonly used to control broadleaf weeds in corn fields. It is considered a possible human carcinogen, and a maximum contaminant level (MCL) of 3 $\mu gL^{-1}$ in drinking water has been assigned by the EPA in the US. The interim maximum allowable concentration for atrazine and its metabolites is 0.005 mg $L^{-1}$ in Canada (2001).

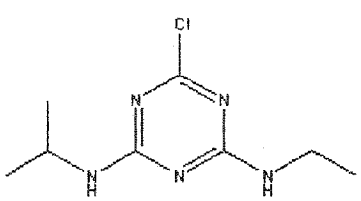


**Fig. 2.1 Structural formula of atrazine**

The structural formula of atrazine is shown in Fig. 2.1 and its physical and chemical properties are represented in Table 2.1.

**Table 2.1 Physical and chemical properties of atrazine**

| | |
|---|---|
| Chemical name | 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine |
| Molecular formula | $C_8H_{14}ClN_5$ |
| Molecular weight | 215.68 |
| CAS No. | 1912249 |
| Compound Class | Triazine |
| Form | White, crystalline powder |
| Density | 1.187 g $cm^{-3}$ at 20$^{O}$C |
| Melting point | 171-174 $^{O}$C |
| Odor | Odorless |
| Solubility | 33 mg $L^{-1}$ at 20$^{O}$C |
| Vapor pressure | 4 x $10^{-10}$ atm |
| Henry's law constant | 3 x $10^{-9}$ atm $m^3$ $mol^{-1}$ |
| Log $K_{ow}$ | 2.68 |

Atrazine is highly soluble in organic solvents, is sparingly soluble in water and possesses a high adsorption potential in organic matter. The products of microbial degradation are 2-chloro-4-ethyl-amino-6-amino-s-triazine, 2-chloro-4-amino-6-isopropylamino-s-triazine, 2-hydroxy-4-ethylamino-6-isopropyl-amino-s-triazine and 2-hydroxy-4-ethylamino-6-amino-s-triazine. Atrazine forms a protonated species, owing to its basicity, thus acting as a cation in the soil. It undergoes hydrolysis under acidic, neutral, or basic conditions. While the rate of hydrolysis is slow under neutral conditions, this increases with either increasing alkalinity or acidity (http://www.uky.edu/WaterResources/works22.html dt. 8/1/2002).

Movement of the sorbed atrazine molecules depends on the interactions between the atrazine molecules and the soil particles. These interactions may be compared to the

separation of components of an organic compound in a thin layer chromatography that depends on differential movements through the porous media. The three steps which chiefly constitute sorption are the movement of the atrazine molecules by diffusion from aqueous to soil particles, adsorption, and diffusion into the soil interiors.

Atrazine transport has been investigated by many researchers in the past (Clemente, 1991; Gamble et al., 1992a; 1992b; Gaynor et al., 1995; 2000; Seybold et al., 1996; Azevedo et al., 1997; Shapir et al., 1997; Jebellie, 1997; Liaghat, 1997; Ma et al., 1997; 2000; 2001; Levy et al., 1998; Li et al., 1999; Williams et al., 1999; Abdelhafid et al., 2000; Azevedo et al., 2000; Pham et al., 2000; Spongberg et al., 2000; Accinelli et al., 2001; Asare et al., 2001; Vinther et al., 2001). Atrazine degradation yielded metobolites from both dealkylation and hydroxylation (Abdelhafid et al., 2000). In a study conducted in Israel by Shapir et al. (1997), it was revealed that half of the atrazine degradation occurred in the upper layers of the soil to a depth of about 25 cm. They concluded that dealkylation was the major path in the degradation of atrazine. This was evident from the thin layer chromatography of the inoculated soil samples.

Vinther et al. (2001) concluded that N-dealkylation or dehalogenation are the two probable reactions for the degradation of atrazine. The triazine ring seems to undergo a rapid mineralization by providing N to the microbial community. Atrazine serves as a good carbon source thereby making microbial degradation possible to a great extent. Depending on the nature of N, atrazine decomposition may be hindered or enhanced. The application of organic-N increased the atrazine degradation rate when added to dairy manure while mineral N addition decreased the mineralization of atrazine in soil. Retentivity is responsible for the formation of bound sites; the microorganisms play a significant role in catering to the formation of sites available for the retention of pesticides.

It was further confirmed in a study conducted by Levy et al. (1998) that atrazine dealkylation increased with the addition of glucose and mineral N. Three chlorinated

atrazine metabolites formed primarily through desalkylation are desethylated atrazine, deisopropylated atrazine and 2-chloro-4, 6-diamino-s-triazine.

The major metabolite of atrazine, des-ethyl atrazine, was found at all depths in a study conducted by Gaynor et al. (1995, 2000). The concentration of this compound would be highest immediately after the application of atrazine. In a recent study by Ma et al. (2000), the predicted atrazine concentrations in runoff were within two orders of magnitude of the observed values.

## 2.2 ENVIRONMENTAL FATE OF METRIBUZIN

Metribuzin is used to control a large number of grass and broadleaf weeds infesting agricultural crops and is used as a pre- and post-emergence triazone herbicide. Metribuzin is a selective herbicide that inhibits photosynthesis, is highly soluble in water and has low solubility to adsorb in most soils. The maximum acceptable concentration (MAC) for metribuzin in drinking water is 80 $\mu gL^{-1}$. The structural formula of metribuzin is given in Fig. 2.2 and its physical and chemical properties are illustrated in Table 2.2.

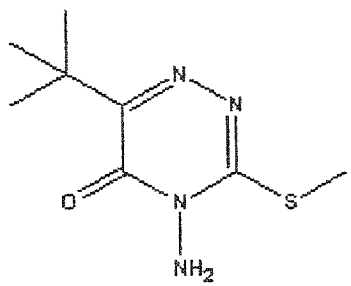


**Fig. 2.2 Structural formula of metribuzin**

Metribuzin is one of the herbicides that have the highest potential to leach into and contaminate ground water, according to the EPA in the USA. Metribuzin can be removed from air via rainfall, and particulate phase metribuzin may be removed from air via dry deposition. If released to soil, biodegradation will be the primary fate process. Metribuzin is moderately adsorbed ($K_{oc}$ of 95) on soils with high clay and/or organic

content by an H-bonding mechanism, and adsorption decreases with an increase in soil pH. Little leaching occurs on soils with high organic content, but metribuzin is readily leached in sandy soils. The soil half-life is in the range of 14-60 days.

**Table 2.2 Physical and chemical properties of metribuzin**

| | |
|---|---|
| Chemical name | 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one |
| Molecular formula | $C_8H_{14}N_4OS$ |
| Molecular weight | 214.3 |
| CAS No. | 21087649 |
| Compound Class | Triazine |
| Form | Colorless crystals, white crystalline solid |
| Density | 1.28 at $20^{O}C$ |
| Melting point | 125-126.5$^{O}C$ |
| Odour | Mild chemical odor |
| Solubility | 1050 mg $L^{-1}$ at $20^{O}C$ |
| Vapor pressure | 0.058 mPa at $20^{O}C$ |
| Henry's law constant | 3.55 x $10^{-6}$ Pa $m^3mol^{-1}$ |
| Log $K_{ow}$ | 1.7 |

The fate of metribuzin has not been studied extensively (Clemente et al., 1993; Jebellie, 1997; Liaghat, 1997; Jebellie et al., 1999; Gaynor et al., 2000). Metribuzin and its metabolites were found in 18 out of the 20 wells sampled in Wisconsin by the Wisconsin Department of Natural Resources. The highest concentration of metribuzin was 10.2 $mgL^{-1}$, while those of its metabolites were 1.56 $mgL^{-1}$ for deaminated metribuzin, 0.54 $mgL^{-1}$ for diketometribuzin, and 1.88 $mgL^{-1}$ for deaminated diketometribuzin (http://wri.wisc.edu/wgrmp/59dnr77.htm dt. 26/12/2001).

Field experiments conducted to ascertain the impact of moisture content on the rapidity with which degradation of metribuzin may occur revealed that the degradation of

metribuzin in sandy soils is faster in humid areas where the soil moisture is high due to appropriate water table management practices in these regions. It was also concluded by Jebellie et al. (1999) that the leaching of metribuzin could be controlled with adequate water management techniques. Metribuzin gets released into the environment primarily during agricultural spraying operations. If released into the atmosphere, there is significant degradation of the vapor phase metribuzin by reaction with photochemically produced hydroxyl radicals (estimated half-life of 11 h).

In a farm-level evaluation study by Alphen et al. (2002) carried out in the Netherlands, metribuzin was found to have a high risk of leaching. High risk areas were found in nine out of ten fields. The spatial variation of simulated leaching was substantial and concentrations in percolating water exceeded 0.1 $\mu gL^{-1}$ at the within-field, field, and farm-levels.

Conn et al. (1996) studied the leaching of metribuzin in two subarctic silt loam soils. They found that the initial degradation rate of metribuzin was similar in both soils while 5% of the applied metribuzin still remained after 468 days from the application date. Leaching was reduced due to its rapid degradation coupled with its sorption. Larger amounts of desaminometribuzin were found when compared to the diketometribuzin or desaminodiketoaminometribuzin in both soils.

## 2.3 ENVIRONMENTAL FATE OF METOLACHLOR

Metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(-2-methoxyl-1-methylethyl) acetamide] is a chloroacetamide compound. It is a pre-emergence herbicide belonging to the chloroacetanilide group used to impede the growth of weeds in the production of potatoes, sorghum, cassava, peanuts and corn. The high solubility of metolachlor makes it an easily leachable compound that can readily contaminate both groundwater and surface water. The interim maximum acceptable concentration (IMAC) for metolachlor is 50 $\mu gL^{-1}$ in drinking water.

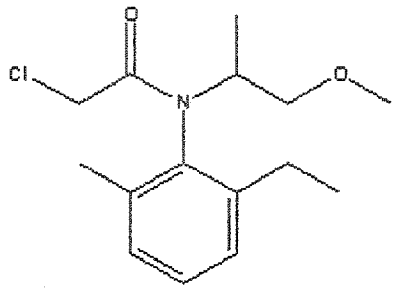

**Fig. 2.3 Structural formula of metolachlor**

The structural formula of metolachlor is given in Fig. 2.3 and its physical and chemical properties are shown in Table 2.3.

**Table 2.3 Physical and chemical properties of metolachlor**

| | |
|---|---|
| Chemical name | 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(-2-methoxyl-1-methylethyl) acetamide |
| Molecular formula | $C_{15}H_{22}ClNO_2$ |
| Molecular weight | 283.8 |
| CAS No. | 51218-45-2 |
| Compound Class | Chloracetamide |
| Form | Off-white to colorless liquid at room temperature |
| Density | 1.12 g $cm^{-3}$ at 20 $^{O}C$ |
| Odor | Odorless |
| Solubility | 530 mg $L^{-1}$ at 20 $^{O}C$ |
| Vapor pressure | 1.7mPa at 20 $^{O}C$ |
| Henry's law constant | 9.2 x$10^{-9}$ atm $m^3$ $mol^{-1}$ at 20 $^{O}C$ |
| Log $K_{ow}$ | 3.45 |

Considerable efforts have been made to study the fate of metolachlor and its metabolites by several researchers (Clemente et al., 1993; Gaynor et al., 1995; 2000; Seybold et al., 1996; Jebellie, 1997; Liaghat, 1997; Singh et al., 1997; Sanyal et al., 1999; Ismail et al., 2000; Spongberg et al., 2000; Accinelli et al., 2001; Moore et al., 2001). The degradation

of metolachlor follows first order kinetics (Ma et al., 1997; Singh et al., 1997; Ismail et al., 2000).

An inverse positive relationship between adsorption and persistence of the herbicide was observed by Ismail et al. (2000) in Malaysia. The persistence of the herbicide also changed drastically with a change in the texture of the soil. Bioactivity and adsorption seemed to have a direct relationship with the organic matter content. In soils with less organic matter, metolachlor seemed to move downward at a faster pace. The dissipation of metolachlor occurs in two phases. It was concluded in a study by Singh et al. (1997) on potato tubers in India that the initial reaction takes place at a slower pace. This may be due to the two dispersion processes, namely adsorption and degradation. The aqueous solubility of metolachlor makes it a potential contaminant. It is also found to leach faster than atrazine and a part of it is lost as runoff, while some portion of it may find its way to the groundwater (Spongberg et al., 2000).

The persistence of metolachlor was also studied along with atrazine under both field and laboratory conditions by Dinelli et al. (2000). The degradation rates of the herbicides were calculated by using equations that were temperature and soil moisture dependent and were obtained from the laboratory experiments. These values were extrapolated for use under variable field conditions. It was found that laboratory studies conducted within a confined environment were representative of field mechanisms.

The fate of several pesticides including metolachlor and atrazine were investigated in a study conducted in Brazil (Laabs et al., 2002). High concentrations of metolachlor were detected 60 days after its application in the lysimeter at the 35 cm depth, indicating a progressive vertical movement of polar herbicides. The leaching of both atrazine and metolachlor at the 95 cm depth indicates the potential risk these two herbicides pose to the groundwater resources in tropical regions.

## 2.4 PESTICIDE FATE AND TRANSPORT

Properties of pesticide and soil site conditions, including rainfall and depth to groundwater, and management practices, including the method and the rate of application, are primary factors affecting pesticide movement (Werkheiser et al., 1996). The chief processes that determine its ultimate fate are sorption, degradation, volatilization, plant uptake, runoff, and leaching (Wagenet et al., 1985; 1997). Sorption is defined as the bonding of solute to adsorption sites of soil mineral and organic matter surfaces. It may be extractable or non-extractable. The extractable ones can be extracted with the conventional solvents whereas the non-extractable ones may only be studied by radio-labeling or super critical fluid extractions (Li et al., 1996). The sorption phenomenon has a dramatic effect on the fate and transport of an organic compound in the environment (Sabatini et al., 1990; Levy et al., 1998; Wagenet et al., 1997). In a column study performed by Shinde et al. (2001) in South Florida using Perrine and Krome soils, it was revealed that the two-site non-equilibrium (TSNE) model was able to simulate the atrazine movement, thus proving the existence of chemical non-equilibrium in atrazine sorption kinetics. They also concluded that independent estimation of kinetic parameters were necessary to better represent atrazine sorption in the Chekika soil columns.

In order to make realistic estimates of potential contaminants, studies distinguishing sorbed-phase degradation rates from those in the dissolved phase need to be conducted (Levy et al., 1998). Celis et al. (1999) modeled sorption of pesticides with the aid of an isotopic exchange method using $^{12}C$ and $^{14}C$-labeled triadimefon [(1-(4-chlorophenoxy)-3,3-dimethyl-1- (1H-1,2,4-triazol-1-yl)-1-butanone and imidacloprid-guanidine [1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-1 H-imidazol-2-amine] under two remarkably different soil conditions of sandy loam and silty clay loam soils. This experiment involved a direct *in situ* characterization of the irreversibility of the organic compounds. Results from the sandy loam soil revealed that 90% of the sorption occurred on reversible sites that underwent desorption with ease whereas 10% of the sorbed molecules were irreversibly sorbed on soil.

With the intention of differentiating labile surface sorption from total sorption, an online HPLC (high-performance liquid chromatography) extraction method was employed by Gamble et al. (2000a, 2000b) and Spongberg et al. (2000) to analyze the sorption behavior of chlorothalonil under quartz sandy soils. The labile sorption capacity of chlorothalonil was found to be high by several orders of magnitude. They reported that kinetic equilibrium values estimated during this process could be used in mathematical models to evaluate the degradation and leaching of pesticides. The phenomenon of intraparticle diffusion of pesticides has also been given due importance in this study.

An increase in carbon and clay content had a directly proportional impact on adsorption, as revealed by studies conducted by Ismail et al. (2000) and Gaynor et al. (2000). An ascending order pattern ranging from metribuzin to metolachlor was observed when the Freundlich constant was measured in both the $A_p$ and B horizons of the soil (Gaynor et al., 2000).

Biological decomposition of the sorbed form of metolachlor is slower in solids than solutions. In biological degradation, microorganisms within the soil profile act like scavengers by degrading the agrochemicals from their complex forms into simpler compounds. Temperature and soil moisture are crucial factors in this regard. Literature review reveals that the biological degradation of pesticides in soils follows first order kinetics (Singh et al., 1997; Gaynor et al., 2000; Gamble et al., 2000; Bending et al., 2001). Degradation of 2,4-D, lindane and paraquat were observed to follow first order kinetics under aerobic sand and anaerobic muck soils in a study carried out in Malaysian soils by Cheah et al. (1998). Repeated application of the pesticide in the same site may result in enhanced degradation (Cheah et al., 1998).

Degradation of pesticides may be either beneficial or inefficient. If degradation occurs, the pesticide residues that were formed would be transformed to inactive, less toxic, and harmless compounds. However, if the residues get degraded before serving their purpose, it would be a waste of resources. The extent to which a pesticide's persistence

in the environment is estimated rests on the microbial transformation it undergoes. The rate of microbial degradation is determined by the size of the microbial population and that section of the microbial community that will actively participate in the degradation process (Soulas et al., 2001). If the pesticide itself serves to be a carbon source, then the rate of degradation will be directly proportional to the rate of application of pesticides. The rate may be further enhanced by the presence of organic amendments. Energy liberated during this process will depend entirely on the pesticide that serves as a carbon and as an energy source. In microbial degradation, the factors determining the rate of degradation are moisture, temperature, aeration, pH and organic matter content. Whereas these factors are dependent on the soil conditions, the frequency of application may be another determinant factor that can affect the dissipation rate. The longevity of pesticides in the environment can be estimated with the help of degradation studies. Cheah et al. (1998) carried out research in Malaysian soils, showing that microbial degradation had a chief role to play in determining the fate of 2, 4-D. However, lindane, glyphosate and paraquat followed slow degradation, mainly due to their higher adsorptive capacity, as was observed in the same study.

Previous work by Ma and Spalding (1997) revealed that the decomposition of atrazine to hydroxyatrazine was the major pathway taken by atrazine in the Recharge Lake in York, Nebraska. Degradation half-lives of atrazine was 237 days in 1993 and 209 days in 1994 respectively. In an experiment conducted by Loiseau et al. (2002) with four agricultural soils, each possessing different capacities to effect degradation of atrazine, each having different pH levels and different organic matter content, a few factors deserved recognition. The presence of microflora, which can mineralize the triazine ring, helped in the formation of highly degraded products, which contributed to the formation of bound residue. The presence of humic acid in higher concentrations also enhanced the formation of bound residue. A soil pH of less than 6 promoted the formation and stabilization of hydroxylated derivatives of atrazine. Bound residue ranged from 10% to 40% of the initial atrazine.

The factors that determine the loss of pesticide through runoff are slope, soil texture, moisture content, precipitation, and the presence of vegetation or plant residues. Better water table management and tillage practices could be used to reduce loss through runoff. In a field study to investigate the loss of atrazine and metolachlor from three different tillage practices. Gaynor et al. (1995), the surface runoff was an increase to about 42% when conservation tillage was used, while the discharge through tiles lowered by about 15%. Maximum concentration and losses in the herbicides were attained after runoff events that immediately followed the application of herbicides.

Runoff events and herbicide application were found to be directly proportional to the concentrations found in the runoff. In 1993, the runoff losses and the concentrations of atrazine in the Recharge Lake were higher when compared to 1994 figures. The concentrations of atrazine lost were 0.28% and 0.19% in 1993 and 1994 respectively (Ma and Spalding, 1997).

Leaching and persistence of a herbicide is dependent upon its adsorption characteristics. An increase in soil carbon and clay content increases adsorption (Gaynor et al., 2000). The ability with which the pesticide moves into and through the groundwater is referred to as leachability. The factors that determine leachability are precipitation events, air and soil temperature, and evaporation rates. The leachability of a herbicide increases with an increase in its persistence (Conn et al., 1996). Heavy precipitation, especially following the application of pesticide, promotes leaching of the compound (Gaynor et al., 1995; Azevedo et al., 2000).

It was shown by Azevedo et al. (2000) that the physical properties of an alluvial soil did not promote the mobility of atrazine to deeper soil depths. However, it was observed that a large amount of rainfall led to the leaching of atrazine to deeper depths. In 1996, a similar scene was observed for a coarse sandy soil, resulting in an increase in leaching with an increase in irrigation. Atrazine residues were not found to accumulate under both alluvial and sandy soil conditions. The maximum distance to which the transfer of atrazine took place was within 10 cm of the soil profile under different soil conditions.

Most studies overlook the uptake of herbicides by plants. However, this affects leaching and should be taken into account while devising a method to assess the fate of a herbicide (Wagenet et al., 1985). The extent of plant uptake is somewhat governed by the solubility of the pesticide. The more soluble the pesticide, the higher the probability of its uptake by plants. Other factors that should be taken into consideration include rooting depth at different times of the year and root density distribution with respect to depth and time.

## 2.5 WATER TABLE MANAGEMENT AND PESTICIDE MOVEMENT

Water table management is the management, control, and regulation of soil-water conditions in agricultural soils. In order to provide better growing conditions for improved yields, the excess and/or deficit soil-water needs to be managed; this is the crux of water table management. It can be done with conventional drainage, controlled drainage, and sub-irrigation, depending on the soil and water conditions. In controlled drainage, water control structures are put up which permit the water in the outlet to attain a set level. Conventional drainage usually has equally spaced drains running parallel to each other with a free outlet. In sub-irrigation, water is pumped into the drainage outlet to maintain the outlet water level at a fixed point or at the weir level. Sub-irrigation is used in areas where the land is relatively flat. This provides a uniform water table depth that can be maintained with ease. Soil, adequate water supply, drainage, and topography all seem to govern sub-irrigation.

Jebellie (1997) concluded from a lysimeter study that subirrigation is an acceptable management technique to control pollution from atrazine and metribuzin. It was found that a shallow water table enhanced the dissipation of both herbicides. However, similar conclusions could not be drawn in the case of metolachlor.

Three different water table managements, namely, controlled drainage, subsurface irrigation, and subsurface drainage, were used to examine the transport of prometryn in an organic soil in southern Quebec by Arjoon et al. (1998). It was concluded that

pesticide fate was largely affected by the movement of water that led to high levels of contamination followed by high rainfall events. Subirrigation and controlled drainage were found to be helpful in minimizing herbicide transport and contributed in keeping the level of prometryn below drinking water quality.

In Harrow, Ontario, Canada a study was conducted by Gaynor et al. (2000) with four different tillage practices and two different water table management practices to analyze the impact of herbicides. The impact on herbicide decay in the 0 to 10 cm depth was insignificant under the tillage practices while the controlled-drainage coupled with sub-irrigation decreased the half-life in one of the two years of experimentation. Atrazine, des-ethyl atrazine and metolachlor were found to persist in the following year. It was concluded that rain, rather than management practices, had a more pronounced effect on the mobility of these organic chemicals.

The effect of tillage practices were examined by Kanwar and Bakhsh (2001) to assess herbicide movement under field conditions with respect to preferential flow. Higher atrazine concentrations were found under no-till and ridge till in tile flow when compared to chisel plow and moldboard plow. It was concluded that the no-till and ridge till had well-connected macropores which resulted in higher concentrations.

## 2.6 MATHEMATICAL MODELING

Computer models can be used to simulate pesticide fate and transport in agricultural soils. Both process-based and implicit models may be used for this purpose.

### 2.6.1 Process-based Models

To understand the basic transport mechanisms that pesticides undergo, several models have been developed (Wagenet et al., 1997). Among them only LEACHP, PRZM3, GLEAMS and PESTFADE are discussed in order to focus our attention on some of the

most widely used models. A summary of the modeling criteria used in these models is presented in Table 2.4.

**Table 2.4 A comparison in the modeling criteria of a few pesticide models***

| Subject | LEACHP | PRZM3 | GLEAMS-TC | RZWQM | PESTFADE |
|---|---|---|---|---|---|
| Reference | Wagenet and Hutson, 1989; Vanclooster et al., 2000 | Ma et al., 2000; Vanclooster et al., 2000 | Leonard et al., 1996; Vanclooster et al., 2000 | Azevedo et al., 1997; Cameira et al., 1998 | Clemente et al., 1993; 1997 |
| Governing equation for solute transport | Convection dispersion equation | Convection | Convection | Partial piston displacement; Darcy flux and evaporation | Convection dispersion equation |
| Sorption | Freundlich | Linear | Two-stage sorption kinetics | Two-stage sorption kinetics | Two-stage sorption kinetics |
| Macropore flow | No | No | Yes | Yes | Yes |
| Volatilization | Yes | No | No | No | Yes |
| Management practices | No | Yes | Yes | Yes | Yes |

* Adapted from Vanclooster et al. (2000)

### 2.6.1.1 The LEACHP Model

LEACHP assumes a spatially uniform and time-variable pesticide application over the land surface. Soil moisture in the root zone is calculated using Richard's equation, while pesticide movement is modeled using the convection-dispersion equation (CDE). LEACHP assumes that all flow paths are vertically downward so the pesticide molecules that survive degradation will confront the same environment. It has the ability to portray a range of subsurface activity in the vertical direction. This model is not able to analyze management practices (Clemente et al., 1993). In their review, Vanclooster et al. (2000) pointed out that LEACHP considers preferential flow and volatilization. It uses the Freundlich equation for nonlinear sorption. Plant uptake and first-order degradation are also taken into account in LEACHP.

Models, namely the pesticide module of the LEACHM Model (LEACHP) and Irrigation Scheduling Model (IRRSCHM), used to examine the leaching of atrazine with additional irrigation showed an increase in the rate of leaching. However, predictions using both the models were lower than the median. IRRSCHM predictions were closer to the observed data (Asare et al., 2001).

Both PRZM and LEACHMP models were used to determine the fate of atrazine in a soil column study conducted by Smith et al. (1991). The studies concluded that underestimation , in both models, was due to two factors. The first factor was the simplistic approach used in calculating the adsorption of the compound. The second factor was that the preferential flow was not considered.

### 2.6.1.2 The PRZM Model

PRZM is a well-known continuous simulation model, developed at the EPA Laboratory in Athens, Georgia, which has been tested using field data (Chu et al., 2000; Kaluli et al., 1997; Ma et al., 1999; 2000; Vischetti et al., 1995). It is a one-dimensional finite-difference model, which accounts for pesticide fate in the crop root zone. PRZM3 is a

culmination of two models, PRZM and the vadoze zone flow and transport model (VADOFT) (Mullins et al., 1993). PRZM uses the method of characteristic algorithms to nullify numerical dispersion. VADOFT uses Richard's equation for flow in the unsaturated zone. It assumes that the flow follows Darcy's law, is one-dimensional and is isothermal. It is able to simulate multiple zones, transport and transform the parent compound and as many as two daughter species within and immediately below the plant root zone. The advantage of PRZM is that it is able to handle more than one pesticide and make predictions. Soil temperature simulation, volatilization and vapor phase transport in soils, irrigation simulation and microbial transformation are some of the novel features in PRZM3 (Malone et al., 1999). For some of the processes like runoff, erosion, and evaporation, smaller time steps have been conceived to make realistic predictions. Diffusion of the solute is not dealt with in this model. Average and approximated data are used to represent spatially-heterogeneous soils which is another drawback of this model. An over-simplification made in this model is the assumption of a first-order rate constant as a fixed value. Flow of solute in fractured porous media is not considered. PRZM2 does not consider preferential flow, two-site sorption kinetics and volatilization as observed by Vanclooster et al. (2000) in their review.

The PRZM-2 model was used to predict the fate of napropamide and pendimethalin in soils in a tobacco field by Vischetti et al. (1995). The model simulations differed from the observed values. This may have been caused by the 40 cm deep plowing which allowed the displacement of the pesticide. Volatilization was another factor for the discrepancy in pendimethalin simulations. The mobility of aldicarb transport was compared using two models by Chu et al. (2000). While the first one comprised an analytical model to take care of the 1D transport of pesticide, the 2D model was used to assess the advection and dispersion processes. The other model used for this study is a culmination of PRZM2, MODFLOW (modular three-dimensional finite difference ground-water flow model) and MT3D (three-dimensional numerical model) numerical models. It was evident from this study that the results obtained from both the models were similar. Complete mixing, which was considered in the first model but not in the second model, may be the reason for the attainment of peak concentrations in the second

model. After the pesticide was applied, the amount of water that infiltrated seemed to have a marked effect on the leaching of aldicarb. It was concluded that both the models could be reliably used to make long-term predictions about pesticide contamination. However, the analytical model suffered from the drawback of not being able to handle the spatial variability of the flow and transport parameters and flow conditions in the soil and the aquifer.

In a study conducted by Ma et al. (2000) in a corn field on a Tifty loamy sand using conventional tillage practices, atrazine losses were predicted using GLEAMS, Opus, PRZM2β, and PRZM3. While both GLEAMS and PRZM3 were able to simulate atrazine amounts in the runoff within two orders of magnitude of the observed concentrations, PRZM2β overestimated the atrazine concentrations. This may have been due to an unrealistic mixing model.

Malone et al. (1999) studied the transport of metribuzin using both GLEAMS and PRZM-3 under three field conditions. Metribuzin was underestimated by both GLEAMS and PRZM-3 in runoff, sediment, pan lysimeter water at 75 cm and at the 15-75 cm soil depth. While the simulations from GLEAMS were closer to accuracy in the sediment runoff, PRZM-3 gave closer predictions in the subsurface soil regions. The pesticide simulations in the percolate and the runoff were similar with both models. Both models performed satisfactorily in assessing the runoff volume and herbicide concentration immediately after their application, when the concentrations are highest. Malone et al. (1999) also concluded that the addition of a macropore component in both models would have resulted in an improvement in the model efficiencies.

The movement of 2,4-D from small turf plots, were assessed by Ma et al. (1999) by using GLEAMS and PRZM-2. Both models underestimated the transport of 2,4-D in surface runoff although the predictions of surface water runoff were quite close to measured values. The low estimates were attributed to the inaccurate calculations involved in the partitioning of the compound.

### 2.6.1.3 The GLEAMS Model

GLEAMS is a one-dimensional field scale model (Knisel, 1993) which retains the ability of CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems) to simulate sophisticated management practice scenarios. It adds detail to the transmission of water and chemicals to the bottom of the root zone. In GLEAMS, the Soil Conservation Service Curve Number method is employed to simulate both runoff and the water available for infiltration. It consists of four components, one each for hydrology, erosion/sediment yield, pesticide transport, and nutrients. A lumped parameter approach is applied in order to simulate moisture movement in the soil profile. GLEAMS has been tested for pesticide transport by Zacharias et al. (1994), and in simulating the effects of tillage on nonpoint source pollution by Bakhsh et al. (2001).

In a recent study by Ma et al. (2000), the predicted atrazine concentrations in runoff were within two orders of magnitude of the observed values. The model, however, lacks a macropore flow component. Bakhsh et al. (2001) found GLEAMS (ver. 2.10) to perform well for chisel plow (CP) in simulating the subsurface drain water quality, while studying the non-point source pollution effects in a corn field over a three-year period for atrazine, nitrate-nitrogen and alachlor (1990-92). A substantial effect did not emerge when various management practices were tried, ranging from no-till, moldboard till and ridge till. The reasons were attributed to the absence of a macropore flow and lack of plowing in the fall of 1991 due to wet climatic conditions.

The GLEAMS model was used by Connolly et al. (2001), in an attempt to study the effect of different management scenarios on the transport of endosulfan. Out of the conventional, improved irrigation, dry land, stubble retained and reduced spray management practices, the stubble retained was declared the most effective management practice. They concluded that the transport of endosulfan in cotton farms was minimized due to an increase in infiltration, reduction in erosion, and neutralization of endosulfan in the stubble region. A high rainfall event could result in endosulfan exceeding the environmental regulations. Leonard et al. (1995) used GLEAMS to assess its ability in

selecting between effective management techniques that are environmentally safe under different pedo-climatic conditions.

Efforts have also been made by Leonard et al. (1996) to include a two-compartment pesticide transport model to GLEAMS, known as GLEAMS-TC, that links the labile and non-labile contributions of the pesticide with first-order chemical kinetics. This model performed better than the GLEAMS model in simulating pesticide sediment transport.

The effects of different herbicide and tillage practices were tested in a 50-year simulation carried out using GLEAMS by Gorneau et al. (2001) in south central Nebraska. It was found that pre-emergent banded application with ridge-till, early pre-emergent with no-till, incorporation application with disk till, and post-emergent application, were the best alternatives for minimizing atrazine losses over prolonged periods.

According to Bakhsh et al. (2001), the model considers a simple linear adsorption. In their review, Vanclooster et al. (2000) concluded that GLEAMS does not consider preferential flow, two-site sorption kinetics and volatilization, although plant uptake and first-order degradation are taken care of in this model.

#### 2.6.1.4 The RZWQM Model

The RZWQM, version 2.5, is a process-based model that simulates the water and chemical transport processes in the soil-crop-atmosphere system (Azevedo et al., 1997). It is a one-dimensional model developed by USDA-ARS scientists (Ahuja et al., 1996). RZWQM comprises six sub modules, one each for hydrology, crop growth, chemistry, nutrients, pesticide and management. RZWQM uses a simplistic approach for the transport of solutes. Instead of the commonly used conversion and dispersion equation (CDE), it considers a partial-piston displacement, partial mixing approach at every 1 cm in the soil profile during infiltration and varies the increments during the second phase of redistribution of the chemical. In the second phase, Darcy flux and evaporation are considered for the solute movement. Instantaneous equilibrium and kinetic pools are

taken into account while estimating the amounts of the chemical in the solution and the soil phases (Cameira et al., 1998). The RZWQM model considers the impact of different tillage practices, irrigation, pesticide applications and is thereby able to assess the effect of different management practices. It can also assess different crop combinations. In addition to daily rainfall amount, it also considers rainfall intensity (Azevedo et al., 1997).

Two tillage systems, namely no-till and moldboard plow, were evaluated by Azevedo et al. (1997) in a field study conducted in Iowa using the pesticide component of the RZWQM to simulate atrazine movement. Observed data and simulated data were found to have a significant difference as shown by the results of the statistical tests. Overestimates resulted at the end of the growing season, although the observed and simulated values were well within an order of magnitude. The prediction of the penetration of atrazine was very close to measured values. Impact of tillage practices was not pronounced. It emerged that there are three important factors that need to be considered while simulating pesticide fate, namely, macropore flow, variation in Koc and pesticide half-life with depth and interception of pesticide by surface residue during application.

In a study conducted by Ahuja et al. (1996) to assess the movement of metribuzin and cyanazine, it was concluded that the two-stage sorption of pesticide movement was able to predict the persistence of pesticides better in comparison to an equilibrium adsorption model. In this model, the equilibrium sorption was considered as an instantaneous process followed by a rate-limited kinetic sorption reaction. It was also concluded that overestimation may result due to the hysteresis of adsorption and desorption as is the case in RZWQM. Non-availability of adequate data and site-specificity were considered to be other hindrances pointed out from this study.

### 2.6.1.5 The PESTFADE Model

PESTFADE is a one-dimensional non-point source mathematical model to predict the fate and dynamics of pesticides. It was developed in Canada by Clemente et al. (1993). PESTFADE comprises five sub modules: RUNOFF, SWACROP, MOISTE, HEAT, and CADD (an acronym for convection–adsorption-diffusion-degradation). The US Soil Conservation Service Curve Number Method and Universal Soil Loss Equation are used in the RUNOFF model to estimate pesticide partitioning in runoff water (Haith, 1980). The Darcy and continuity equations are used in SWACROP (Wesseling et al., 1989) to determine the unsaturated water flow in heterogeneous soil-root systems. MOISTE estimates the soil moisture at each nodal point as obtained from SWACROP. The sub module HEAT calculates soil temperature distribution and thermal conductivity of the soil, which is used in the CADD sub module to estimate the microbial degradation. Both moisture and flux values obtained from SWACROP are used as inputs to the CADD sub module which ultimately determines the pesticide fate.

PESTFADE considers convection, adsorption, diffusion, degradation, volatilization, surface runoff and heat flow in simulating the fate and transport of pesticides. The uniqueness of PESTFADE lies in its consideration of macropore flow, a factor which is usually overlooked. It is able to operate under different boundary conditions, analyze the impact of different tillage and water table management practices and is able to predict the movement of salt (Clemente et al., 1993; 1997). PESTFADE is able to predict salt movement in soil with different salinity, irrigation water management and drainage conditions. This makes it a handy device in selecting a suitable water table management practice to minimize salinity problems in arid as well as semi-arid regions (Clemente et al., 1997). PESTFADE has been tested against analytical solutions and laboratory and field experiments (Clemente et al., 1993; Clemente et al., 1997; Kaluli et al., 1997; Li et al., 1999). However, it needs to be further validated with data from different climatic and terrestrial zones before it can be recommended.

In a study conducted by Kaluli et al. (1997), PRZM, GLEAMS and PESTFADE were used to assess atrazine movement in the top 20 cm of a clay loam corn field in southwestern Quebec. PRZM was able to make the most accurate predictions when all three models were used. However, a different scenario was observed when the macropore component and the two-stage sorption kinetics were incorporated in the PESTFADE model. PESTFADE results improved as judged by the lower standard errors obtained. This further confirms the need of a better and close-to-reality representation of sorption and the importance of a macropore component.

In conclusion, PESTFADE takes the macropore flow into account, which is unusual in almost all models except for RZWQM (Malone et al., 2001). It deals with the two-site kinetic sorption approach that also includes the intraparticle diffusivity of the pesticide, which is closer to the real world phenomenon. These advantages make PESTFADE an appropriate choice for pesticide simulations in the soil.

### 2.6.2 Machine Learning Models

Process based models usually require a large number of inputs, which, in many cases, may not be readily available. An understanding of the physical and chemical phenomena that govern the pesticide movement is essential in order to be able to make correct estimations. Simulation models are also limited in their scope by the inherent assumptions made and the availability and uncertainty of the required inputs. For instance, they are unable to account for preferential flow, which plays a vital role in determining the route of the pollutant. Process-based models also require longer execution periods. In contrast to these models, alternative modeling approaches have emerged based on artificial intelligence (AI). These demand very few input parameters, learn from the available data, and are robust in determining interrelationships between variables. Prior knowledge of the manner in which the processes and input parameters are inter-related is deemed unnecessary in this modeling approach.

AI can solve problems in the physical world with very high efficiency. Among the many artificial intelligence tools that have been developed, the most common are the Artificial

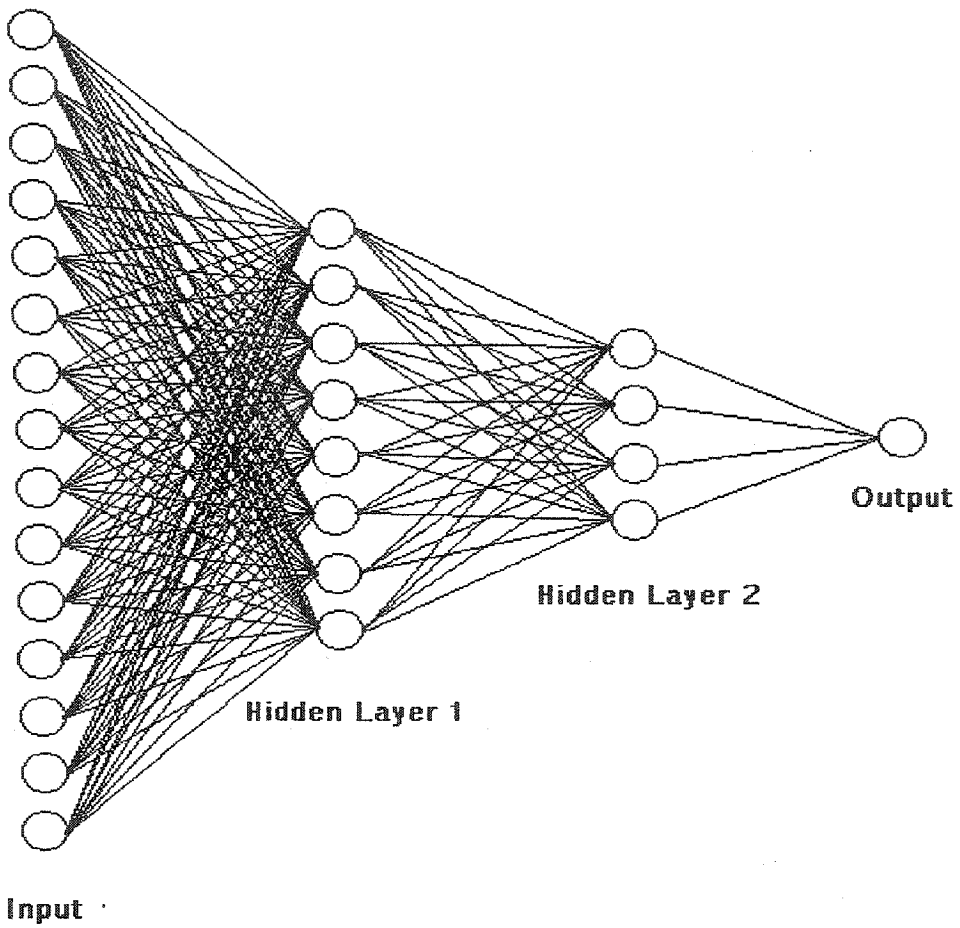


**Fig. 2.4 Structure of a Typical Artificial Neural Network**

Neural Networks (ANN), genetic algorithms (GA), case-based reasoning (CBR) and fuzzy logic. Artificial Neural Networks (ANNs) seem to work with greater accuracy when compared to Rule Induced methods or CBR. However, in the latter two, a better interaction with the user and higher transparency is observed. The diverse problems such as pattern recognition, prediction, or optimization that ANN can tackle by using either the static feedforward network or the dynamic recurrent network and its ability to learn from examples makes it a viable option. The structure of a typical ANN is given in Fig. 2.4.

Owing to its flexibility and utility, the back-propagation ANN has become the most popular (Haykin, 1994; Kartalopoulos, 1996; NeuralWare, 1993a, b, c, 1995). ANNs have been applied to simulate non-linear, implicit, complicated, and dynamic classification problems. They have also found application in areas in which mathematical and statistical algorithms conventionally fail, such as modelling, decision-making and recognition (Haykin, 1994; Kasabov, 1996; NeuralWare, 1993a; Skapura, 1996). ANNs emulate the function of a neuron in the human nervous system. The processing elements (PEs) are designed to simulate neurons, and transfer functions simulate the functions on biological neurons. The interconnections between PEs function similarly to those between dendrites and axons in the human nervous system. The learning rules simulate the learning procedure of a biological neural network (Caudill, 1987,1988a,b,c; Haykin, 1994; Kartalopoulos, 1996; MathWorks, 1998; Wasserman, 1993).

In agriculture, ANNs have been applied to a variety of problems. Predicting the soil moisture (Altendorf et al., 1999), soil temperature (Yang et al., 1997b,c), saturated hydraulic conductivity (Lebron et al., 1999), the interaction between soils and tools, and soil behaviour (Zhang and Kushwaha, 1999) have been some of the areas where neural nets have proven to be useful. ANN simulations have also been performed to simulate the fate and transport of pesticides in soils (Yang et al., 1997f) and predict the annual nitrate-N losses in drain outflows (Salehi et al., 2000b). McClendon et al. (1996) applied ANNs to control and optimize irrigation management for peanut fields, while Emaruchi et al. (1997) have used it in the simulation of runoff index. ANNs were used to estimate missing rainfall data (Kuligowski and Barros, 1998), to simulate peak stream discharge (Muttiah et al., 1997), to predict the occurrence of frost (Robinson and Mort, 1997), and to determine daily pan evaporation (Bruton et al., 2000). The capability of ANNs to simulate real-time control of water-table management systems under subsurface drainage and subirrigation (Yang et al., 1996a,b, 1997d,e, 1998, 2000b) or underground water management (Coulibaly et al., 2001) has also been demonstrated. In addition, ANNs have been used to predict watershed runoff (Zhang and Govindaraju, 2000). The

numerous examples listed above make it evident that neural nets are a powerful tool to apply when large data sets are handy and a quick assessment is required.

Although ANNs have been popular, a new regression tool, Multivariate Adaptive Regression Splines (MARS) is gaining importance as of late and has been found to outperform ANNs in time applications (Abraham et al., 2001a,b; Sephton, 2001; Attoh-Okine et al., 2001). Unlike ANNs, MARS prevents over-fitting with the use of its backward deletion phase (Attoh-Okine et al., 2001). The power and flexibility of MARS lies in its intensive search mechanism with the aid of basis functions. It does a noteworthy job in fitting non-linear multivariate functions (Abraham et al., 2001a,b; Attoh-Okine et al., 2001). Its value also lies in the manner by which it prioritizes the occurrence of the various inputs fed into the model. This allows careful selection of parameters during model development (Attoh-Okine et al., 2001). Making assumptions at the beginning of the model creation is not essential, and MARS models are simple and easily comprehensible (Steinberg, 2001). Considering the many advantages MARS presents, an effort is made in this research project to assess its performance in predicting pesticide concentrations in the soil.

MARS, a non-parametric regression tool, is a very recent technique developed by Friedman, 1991. To understand how a MARS technique works, we need to understand a few definitions. A spline is a function defined on an interval. It is comprised of simple functions defined on subintervals and these are joined for smoothness. Splines are popular in the field of computer engineering and computer graphics. A knot is defined as the place where the behavior of the function changes. A large number of knots enables the approximation of any shape. For high-dimensional mathematics, basis functions are used to locate the knots (Abraham, 2001a,b). Salford Systems, San Deigo, CA has implemented the MARS procedure into a user-friendly computer software package, also called MARS. A special feature of this software lies in its dynamic selection of knots. The following segments decide the regions towards the right and left directions of the knot location, t which is identified by MARS:

$$b^{+}(x/t) = +(x-t)_{+}^{q} \qquad 2.1$$

$$b^{-}(x/t) = -(x-t)_{-}^{q} \qquad 2.2$$

where $b^{+}(x/t)$ and $b^{-}(x/t)$ represent the univariate spline basis functions for a variable x at knot location t. In equations (2.1) and (2.2), for $x \succ t, +(x-t)$ all points located on the right of t will be positive and for $x \prec t, -(x-t)$ all points located to the left of t will be positive (Attoh-Okine et al., 2001). The degree of smoothness is controlled with the index q. A linear estimate is calculated when q = 1 (Sekulic and Kowalski, 1992). MARS uses the following equation in model preparation:

$$\hat{f}(x) = a_o + \sum_{m=1}^{M} a_m \prod_{k=1}^{K_m} B_{km}(x_{v(k,m)}) \qquad 2.3$$

where $x_1, x_2, \ldots x_p$ are predictor variables and $(x_{v(k,m)})$ labels the predictor in the $k^{th}$ of the $m^{th}$ product. $K_m$ decides the order of interactions. An additive model is created when $K_m = 1$. Pairwise interactions are permitted when $K_m = 2$. The order of interactions is fixed arbitrarily when $K_m$ is equal to the number of compounds (n). Equations (2.1) and (2.2) describe the basis functions $B_{km}$ which represent first-order truncated power splines (Attoh-Okine et al., 2001). MARS uses basis functions that are added incrementally and the effect of addition of each of these basis functions is checked to determine whether they improve the model or deteriorate its performance. For this, MARS uses a forward step to over-fit the model and then prunes the unnecessary ones. The generalized cross validation (GCV), or the measure of goodness of fit adopted in MARS, is kept at the lowest possible limit. This is attained with the addition of basis functions and knots at every step. The process is repeated until the lowest GCV is attained. The GCV is expressed as follows:

$$GCV = Generalized\ cross\ validation = Ax\sum_{i}(y_i - \hat{f}(x))/N \qquad 2.4$$

where A = $(1\text{-}C(M)N)^{-2}$, and C(M)= 1+ trace$(B(B^{-}B)^{-1}B')$ is a complexity function (Friedman, 1991), with trace being the sum of the elements along the main diagonal of a square matrix. B is the M x N "data" matrix of the M (nonconstant) basis functions represented by $B_{ij} = B_i(X_j)$. The GCV criterion is the average residual error multiplied by a penalty to adjust for the variability associated with the estimation of more parameters in the model (Leblanc and Tibshirani, 1994).

Analysis of Variance (ANOVA) decomposition helps in understanding the underlying relationship amongst the variables. The basis functions that influence one predictor are clubbed into one group, while those that influence two predictors are put into a second group. This process goes on and is governed by the following equation:

$$\hat{f}(x) = a_0 + \sum_{k_m=1} f_i(x_i) + \sum_{k_m=2} f_{ij}(x_i, x_j) + \ldots \qquad 2.5$$

Attoh-Okine et al. (2001) studied the performance of MARS in pavement management under two different pavement types: asphalt concrete and surface treatment flexible pavements with three primary variables: pavement strength, annual traffic loading and environment. In the field of pavement performance modeling and management, it is difficult to ascertain the more influential factors. However, MARS was able to predict the most significant variable as the environmental factor in this study. It was concluded that MARS has the ability to capture strong relationships with its network of basis functions and knots aptly. This was reported as a boon to the field of pavement engineering wherein contributing factors can be rated and underlying relations can be well-understood, thus enabling engineers to focus only on those determining factors in their future endeavors.

MARS was employed along with ANNs and neuro-fuzzy systems to study their performance in predicting the concentration of $CO_2$ for a gas furnace by Abraham et al. (2001a,b). MARS excelled in its performance and proved better than ANNs (Abraham et al., 2001a,b). It required the lowest simulation period when compared to the other two

functional approximators. In another effort to assess both ANNs and MARS, Abraham et al. (2001a) studied its ability to predict rainfall a month in advance based on rainfall data from Kerala, India. Rainfall is known to be a highly unpredictable factor and this study was focused to aid in long-term predictions. MARS had two clear advantages over ANNs: the execution time and Root Mean Square Error (RMSE) value were both lower. The lower RMSE indicated its higher prediction accuracy (Abraham et al., 2001a,b).

Probit models are commonly used to model the probability of recessions by economists wherein the behavior of a model depends on two values taken by the dependent variable, zero for no recession or one for recession. Sephton (2001), in his efforts to predict recession in the financial world, applied MARS and found the MARS recession probability estimates to be more reliable than the probit model. For in-sample forecasts, the MARS RMSE was found to be the lowest for the three-month horizon and highest for the twelve-month horizon with a value of 24 %. However, MARS was not as good for out-of sample analyses (Sephton, 2001).

## 2.7 CONCLUDING REMARKS

Pesticides have found applications in agriculture for their contributions in increasing the crop yield, but their extensive use is also contributing to environmental pollution. Awareness has increased the demand for conducting environmental impact assessment studies on pesticide use. These studies include field experiments, column studies, and mathematical or implicit modeling. Mathematical modeling is the most economical method to assess environmental risks, and to study the impact of different tillage practices and water table management techniques for research purposes. This approach is also ideal for use by regulatory bodies before declaring a ban on a particular pesticide. These models are time-saving, provide a quick assessment of damage, and are accurate. Inaccuracy may, however, result if the governing processes are oversimplified or overlooked. Therefore, efforts are needed to study the pesticide fate, with special attention to the sorption phenomena that takes into account both labile and nonlabile contributions affecting contaminant transport. In addition, a reliable transport of

pesticides in soil cannot be achieved without accurate simulations of water flow in the unsaturated zones. DRAINMOD can be a good candidate for water flow modeling as it is fairly accurate.

Implicit modeling, an alternative approach to evaluate pesticide movement, which has added advantages over mathematical simulation models, is another area that needs further exploration. Implicit models are not only faster in their execution but also work well with fewer inputs and limited data. Although numerous researchers have evaluated ANN models for a variety of tasks, it appears that the MARS approach may prove to be simpler, at least as accurate as ANNs and easy-to-use. Therefore, this project will include both mathematical and machine-learning algorithms in tracking the ultimate fate of pesticides.

## PREFACE TO CHAPTER 3

Use of pesticide models is a prudent approach to minimizing environmental pollution, assess environmental risks, and choose between different management practices. After extensive literature review, it was found that the lumping of parameters to mathematically represent the complex network of reactions going on in the soil environment leads to inaccurate estimates. Therefore, it was decided to develop a new model, DRAINMOD-P, that incorporates the best features of two successful models, DRAINMOD and PESTFADE. This includes the former to perform water movement simulation and the latter to take care of pesticide fate and transport. A model that estimates hydrology correctly can accurately predict the movement of any solute since they follow almost the same route. The unparalled success of DRAINMOD over several climatic zones and soil conditions throughout North America, its user-friendliness and the advantage of shorter simulation periods made it an obvious choice to develop DRAINMOD-P. PESTFADE, on the other hand, simulates pesticide movement with special emphasis on the conventional and two-stage sorption phenomena, thereby accurately accounting for sorption, which is a predominant reaction affecting pesticide movement. Intraparticle diffusion is also considered in this model. Molar quantities are used keeping the conventional stoichiometry in mind. This chapter focuses on efforts that were made to analyze atrazine fate in an agricultural soil in southern Ontario against field data collected over a period of three years.

The role of the candidate, as the main author of the manuscript, was to develop and validate the mathematical model, DRAINMOD-P. The author was also responsible for performing statistical analyses to validate the model.

Right from the onset of this project, Dr. Shiv Om Prasher, Professor, Agricultural & Biosystems Engineering, McGill University, and supervisor of the candidate, has offered his competent supervision to the author. Advice was also readily available from Dr. A. Madani, Professor of Nova Scotia Agricultural College, Truro, Nova Scotia who was also the co-supervisor of the candidate. Drs. J. D. Gaynor and C. S. Tan, Agriculture Canada,

Ontario, provided the main author with the field data and have offered their valuable opinions from time to time to the author.

**Research paper based on the chapter:**

Bera, P., S. O. Prasher, A. Madani, J. D. Gaynor and C. S. Tan. Development and Validation of DRAINMOD-P for Southern Ontario Conditions. (Manusript to be submitted to the Transactions of the ASAE journal).

# CHAPTER 3

# DEVELOPMENT AND VALIDATION OF DRAINMOD-P

## 3.1 ABSTRACT

This study was conducted to develop DRAINMOD-P, a new pesticide fate and transport model by combining the best features of DRAINMOD, a well-known water table management model and the pesticide component of PESTFADE. The simulated hydrologic and pesticide concentrations were compared against independently collected data from a research site in Southern Ontario. The model performed well in predicting daily water table depths of the subsurface drained plots. The model efficiencies for 1992-94 were 28%, 81% and 63%, which shows a high degree of accuracy for the last two years. The average absolute deviation and standard error obtained from the water table depth simulations using DRAINMOD-P were within 6.71 to 13.61 cm and 6.72 to 8.59 cm, respectively, which are also in accordance with results obtained by previous researchers. The RMSE values for atrazine [2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine] concentrations, simulated by the conventional method, ranged from 0.41 to 1.28 at the 10 cm depth while the ones from the Gamble method based on newer sorption kinetics, lay between 0.77 to 0.88 for the three-year period. At the 15 cm depth, RMSE values were within 0.55 to 0.92 and 0.37 to 0.93 for the conventional and Gamble methods respectively. The RMSE values ranged from 0.65 to 1.04 and 0.91 to 1.25 for the conventional and Gamble methods at the 20 cm depth. Thus, the results of this study did not reveal any marked improvement in the model predictions using new sorption mechanisms. This does not fall in line with the work done by Kaluli et al. (1997) and Li et al. (1999) where a greater improvement was achieved in pesticide simulations with Gamble sorption kinetics using PESTFADE. However, the predictions for the movement of atrazine, were well within an order of magnitude of the measured values, which is in accordance with work done by previous researchers (Azevedo et al., 1997; Ma et al. 2000). In spite of model validation with the three-year data set, we feel that more field

testing of the model is needed before any concrete conclusions can be drawn about its performance.

## 3.2 INTRODUCTION

Atrazine, a member of the s-triazine group, is used extensively as a post- and pre-emergence herbicide in Canada. In North America, it is primarily used to control broadleaf weeds in cornfields. About 2 million kg active ingredient of atrazine were sold in 1988 in Canada. Out of this, about 70% was sold in Ontario (Environment Canada and Agriculture Canada, 1988). Approximately, 15.41 million kg of active ingredient of atrazine were applied on crops in 1988 in the United States (Nowell, 1999). Owing to its high efficiency and low cost, atrazine is the first choice of farmers for weed control in agriculture. According to the Ontario Ministry of Agriculture, atrazine application in 1993 was 585, 000 kg active ingredient.

Atrazine and its metabolites have been reported in soils, surface water and ground water (Koskinen et al., 1996: Solomon et al., 1996). It has also been detected in wells and tile drains (Masse et al., 1994). The Canadian Interim Maximum Acceptable Concentration (IMAC) for atrazine is 5 $\mu g\ L^{-1}$ in drinking water (Health Canada, 2001). Maximum admissible concentration of atrazine specified by the United States Environmental Protection Agency (USEPA) is 3 $\mu g\ L^{-1}$.

Numerous simulation models have been developed in the past two decades to assess pesticide fate (Wagenet et al., 1997). Among them, some noteworthy ones are LEACHM (Wagenet and Hutson, 1989), GLEAMS (Leonard et al., 1987), PRZM (Carsel et al., 1985), RZWQM (Ahuja et al., 1996) and PESTFADE (Clemente et al., 1993). Although these models have been widely used and they provide a fair estimate of the ultimate fate of a pollutant, they have certain deficiencies. Both GLEAMS and LEACHP do not consider macropore flow (Malone et al., 2001). An underestimation of pesticide losses may result if macropore flow is not considered (Malone et al., 1999). In certain models (GLEAMS), volatilization goes unaccounted (Vanclooster et al., 2000). In LEACHP and

GLEAMS, the sorption estimates are limited to either a linear or a nonlinear approach (Bakhsh et al., 2001). Sorption is one of the chief mechanisms that determine the fate of a pesticide. The two stages of sorption consist of a relatively fast labile adsorption process and a second stage, which is characterized by slow diffusion into the non-labile sites. However, very few models deal with two stages of sorption and usually lump the parameters based on best available literature values (Li et al., 1996; 1999). Some of these models are also incapable of predicting the effects of different tillage or water table management practices on herbicide carryover.

PESTFADE, a process-based model, was developed in Canada to simulate pesticide transport. It uses SWACROP (Soil Water Actual Transpiration and Crop Production Simulation Model), a soil and water flow model developed by Wesseling et al. (1989). Several processes that govern pesticide movement like convection, adsorption, diffusion, degradation, volatilization, surface runoff and soil heat flow are considered in the model. It can be applied to both undrained and subsurface-drained farmlands in arid, semi-arid, or humid regions. The model can consider the effect of different agricultural management practices and water table managements on pesticide fate and transport (Clemente et al., 1997).

PESTFADE has been verified against analytical solutions but has not been tested sufficiently against field data. Few field and column studies were conducted with PESTFADE (Clemente et al., 1993; 1997; Kaluli et al., 1997; Li et al., 1999; Tafazoli, 2002). The SWACROP model that it uses for hydrological predictions is not user-friendly and thus somewhat difficult to use. Moreover, it does not produce graphical output, which makes the interpretation of results rather difficult. Also, SWACROP has undergone limited testing in North America (Prasher et al., 1995; 1996).

A hydrologic model, called DRAINMOD, can be a good candidate for simulating soil hydrologic phenomenon. It is a Windows-based user-friendly software, allowing the user to view water transport phenomena graphically at any point of time after the simulations are performed. This provides a quick insight into the model performance. DRAINMOD

simulations require shorter time intervals and are equal or higher in their accuracy as compared to SWACROP (Prasher et al., 1995; 1996). DRAINMOD has been tested widely in North America (Skaggs, 1982), Ohio, USA (Skaggs et al., 1981), Louisiana, USA (Gayle et al., 1985; Fouss et al., 1987), Florida, USA (Rogers, 1985), Michigan, USA (Belcher et al., 1993), Virginia, USA (McMahon et al., 1988), Belgium, (Susanto et al., 1987), southern Ontario, Canada (Singh et al., 1994) and Altantic Canada (Prasher et al., 1996).

Therefore, it was decided in this study to develop a new pesticide fate and transport model, called DRAINMOD-P, which would use DRAINMOD for hydrologic simulations and employ the pesticide sub model of PESTFADE for solute transport. It was also decided that the sorption phenomena, one of the most important physico-chemical processes affecting pesticide movement, would be considered in the model in sufficient detail. More specifically, the objectives of this study were:

i. to develop a new mathematical model, DRAINMOD-P, to simulate the fate of atrazine in agricultural soil,
ii. to validate the model against independently collected field data over a three-year period.

## 3.3 MODEL DEVELOPMENT

As stated above, DRAINMOD-P utilizes DRAINMOD for its hydrological predictions since DRAINMOD has been tested and found accurate in many studies conducted in North America (Skaggs, 1982; Skaggs et al., 1981; Gayle et al., 1985; Fouss et al., 1987; Rogers, 1985; and Susanto et al., 1987). Its user-friendliness, ease of changing input parameters and visual presentation of outputs and short execution time make it very convenient for users. Hydrology transport forms the base of solute transport and therefore, a model that accurately estimates water movement will aid with pesticide fate. Pesticide fate is determined using the pesticide component of PESTFADE, which has also been tested and validated previously with field and laboratory experiments

(Clemente et al., 1993; 1997; Kaluli et al., 1997; Li et al., 1997). The novelty of DRAINMOD-P lies in its combining useful features within DRAINMOD and PESTFADE. This section is subdivided into two, the first dealing with the development of the model, DRAINMOD-P, and the second describing the experimental set up.

In the soil environment, pesticides undergo several transformations from the time of application. These include adsorption and desorption, biochemical degradation and volatilization. To account for the non-steady state of water and pollutant movement in an unsaturated porous medium, the following equation is used (Rao and Jessop, 1983):

$$\frac{\partial}{\partial t}(\theta C + \rho S + \varepsilon K_H C) = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x} - qC\right) - \phi \qquad (3.1)$$

where $\theta = \theta(x,t)$ = volumetric soil moisture ($cm^3\ cm^{-3}$), C is the concentration of the chemical in the liquid phase ($mg\ L^{-1}$), $\rho$ dry soil bulk density($g\ cm^{-3}$), S is mass of solute adsorbed or desorbed per unit mass of soil ($g\ g^{-1}$ of soil), $\varepsilon$ is air-filled porosity, $K_H$ is Henry's constant, $D = D(\theta, q)$ = moisture and flux dependent dispersion coefficient ($cm^2\ h^{-1}$), $q = \theta V$ = water flux ($cm\ h^{-1}$), and $\phi = \phi(x,t)$ sink term for biochemical degradation, volatilization and root uptake ($g\ cm^{-3}\ h^{-1}$).

By considering first-order degradation rate constants for the pesticide in the liquid and solid phases, equation 3.1 may be written as following (Nofziger et al., 1985):

$$\frac{\partial(\theta RC)}{\partial t} = \frac{\partial}{\partial Z}\left(\theta D\left(\frac{\partial C}{\partial Z} - qC\right)\right) - (\alpha\theta + \beta\rho K)C + \gamma\theta \qquad (3.2)$$

where $R = 1+\rho K/\theta$ is the retardation factor for the solute in the soil, C is the concentration of the chemical in the liquid phase ($mg\ L^{-1}$), D is the dispersion coefficient ($cm^2\ h^{-1}$), $\theta$ is the volumetric water content ($cm^3\ cm^{-3}$), q is flux of water ($cm\ h^{-1}$), $\rho$ is soil bulk density ($g\ cm^{-3}$), $\alpha$ is the first-order degradation rate constant in the liquid phase, $\beta$ is the first-order degradation rate constant in the solid phase and $\gamma$ is the zero-order rate constant in the liquid phase.

Most computer simulation models treat the sorption mechanism as a linear or a non-linear process. They are not able to distinguish between the labile, surface sorbed species and bound residues, which are chemically sorbed or are an outcome of intraparticle diffusion (Li et al., 1999). In this model, both the conventional and the Gamble kinetics sorption approach are adopted to assess pesticide movement. The conventional approach simply uses a constant value for the distribution coefficient, $K_d$ while the Gamble kinetics employs a two-stage sorption mechanism to calculate $K_d$. This mechanism considers the intraparticle diffusion of a pesticide, sorption capacity of a soil and a variable pesticide distribution coefficient, $K_d$. The partitioning coefficient depends on the pesticide characteristics, including water solubility and soil organic carbon among other factors, and it may vary from site to site (Bakhsh et al., 2001). It is one of the fundamental processes in the subsurface environment that governs contaminant transport (Li et al., 1996). Sorption is, however, dependent on factors like pesticide concentration in the solution phase, number of adsorption sites available and the texture of the soil. Atrazine, being neutral in nature (Schwarzenbach, 1993), the pH dependence of sorption has not been dealt with in this study.

Labile sorption is usually fast and can be represented by a first order reaction rate (Li et al., 1999). This is found to be in a pseudoequilibrium with respect to the nonlabile binding process. A second order rate law is generally used to account for the labile surface adsorption, and a first-order initial rate approximation is employed for the case of low coverage. The intraparticle diffusion process is treated with the labile sorbate coverage that serves as the driving force and can be described by first-order rate law.

The Gamble kinetics approach considers two processes: an instantaneous labile adsorption process followed by a slow diffusion into the nonlabile sites. Its novelty lies in assuming a complex formation model and another intraparticle diffusion model based on Crank's model (Crank, 1975).

**Labile surface adsorption**: The following equations are used in DRAINMOD-P to account for labile surface adsorption:

$$K_1 = k_{b1} / k_{s2} = \theta_L / \theta_O M_{AT} \quad (3.3)$$

$$\theta_c = \theta_L + \theta_O \quad (3.4)$$

$$X_1 = \theta_L / \theta_c \quad (3.5)$$

$$K_d = K_1 \theta_c (1 - X_1) \quad (3.6)$$

$$\frac{-dM_{AT}}{dt} = k_{b1} M_{AT} (W/V) \theta_O - k_{s_2} (W/V) \theta_L \quad (3.7)$$

where $K_1$ is the weighted average sorption equilibrium constant ($M^{-1}$), $\theta_L$ is the sorption sites occupied by pesticide (mol $g^{-1}$ of dry soil), $\theta_o$ is the unoccupied sites (moles $g^{-1}$ of dry soil), $M_{AT}$ is the pesticide molarity in soil solution (mol $L^{-1}$ of soil solution), $\theta_c$ is the labile sorption capacity (mol $g^{-1}$ of dry soil), $X_1$ is the mole fraction of occupied sites (dimensionless), and $K_d$ is the distribution coefficient (L of soil solution $g^{-1}$ of dry soil). Equation 3.7 is the chief expression for calculating adsorption/desorption rates, where $k_{b1}$ and $k_{s2}$ are the rate constants for adsorption (L $mol^{-1}$ $d^{-1}$) and desorption ($d^{-1}$), respectively, and the term (W/V) is a unit conversion factor (g $L^{-1}$).

The above equations indicate that the distribution coefficient, $K_d$, depends on site loading and will undergo changes depending on 1, $\theta_c$, and $X_1$ (Equation 3.6). This equation is used to determine the mass transfer of atrazine by adsorption, thereby making it possible to estimate the pesticide concentration in the solution phase.

To determine $K_d$ in the two-stage sorption mechanism, the final equation is derived from equations 3.3 to 3.6, after making the necessary substitutions and is represented as:

$$K_d = K_1 \theta_c / (1 + K_1 M_{AT}) \quad (3.8)$$

To calculate $K_d$, barring $M_{AT}$, the solution phase concentration, the other two factors that are significant are the labile sorption capacity $\theta_c$ and the sorption equilibrium constant $K_1$.

**Intraparticle diffusion**: The following equations can be used for calculating intraparticle diffusion of pesticides from the particle surface into its interior (Li et al., 1999):

$$d\theta_D / dt = k_{d1}\theta_L \qquad (3.9)$$

$$k_{d1} = Q(D_e / l^2) \qquad (3.10)$$

where $\theta_D$ represents the nonlabile uptake by intraparticle diffusion (moles $g^{-1}$ of dry soil), $k_{d1}$ is the first-order rate constant for inward intraparticle diffusion ($d^{-1}$), $D_e$ is the diffusion coefficient ($cm^2\ s^{-1}$), l is the mean particle radius (cm), and Q is a factor for converting time units (86,400 s $d^{-1}$).

Studies by Gamble et al. (1992) and Li et al. (1996a) have shown that intraparticle diffusion may be considered the rate-limiting process in comparison to labile surface adsorption for longer equilibration time scales. Therefore, a temperature-dependent expression is used to calculate $k_{d1}$ as per Gamble et al. (1992) and Li et al. (1996). The equations used in DRAINMOD-P are as follows:

$$u = b_0 + b_1 / T \qquad (3.11)$$

$$k_{d1} = e^u \qquad (3.12)$$

where $b_o$ and $b_1$ are empirical constants which may be determined with the help of kinetic experiments, and T is absolute temperature (K). The resulting $k_{d1}$ is used in the model to calculate mass transfer via the intraparticle diffusion process.

### 3.3.1 MODEL VALIDATION

The model was validated with field data collected at the Eugene F. Whelan Experimental Farm (Agriculture and Agri-Food Canada, Woodslee, Ontario). The experimental field consisted of 16 plots as illustrated in the Appendix. Each plot measured 15 m by 67 m.

Moldboard plow (MB), moldboard plow with rye grass (*Lolium multiflorum Lam.*) intercrop (MBIC), soil saver (SS) and soil saver with rye grass intercrop (SSIC) were the tillage practices applied to the research site. The water table techniques, namely, controlled drainage-subirrigation (W) and free drainage (D) were maintained during the entire experimental period. Plot numbers 1, 3, 7, 8, 10, 11, 13 and 15 were under controlled drainage-subirrigation while plot numbers 2, 4, 5, 6, 9, 12, 14, 16 had free drainage. While the distance between two drains was 7.5 m, the depth at which the drains were placed was 0.6 m. The soil is a poorly drained Brookston clay loam (fine-loamy mixed, superactive, mesic Typic Argiaquoll). The soil is characterized by an Ap horizon comprised of dark brown clay loam, 30 cm deep with 2.5% organic matter. The B horizon is a clay texture to a depth of 1.5 m. At the 0-10 cm depth in the Ap horizon, the soil contains 30% silt and 39% clay while at the 10-30 cm depth it contains 28% silt and 41% clay. In the B horizon, the silt content is 28% and the clay content is 48%.

Two 104 mm diameter (ID) plastic corrugated drains parallel to the length in each plot were laid out for tile drainage. The slope in this field was less than 1%. In order to prevent leakage and subsurface interaction between adjacent treatments, each plot was separated with a double layer 4 mm thick plastic sheet to a depth of 1.2 m. To avert cross contamination between plots, a 7.5 m wide and 67 m long buffer area was maintained. To store the surface runoff, surface ridges surrounding each plot were built. Risers were installed to control subsurface water levels at 30 cm below ground level during the growing season. When the water level dropped below 30 cm, subirrigation was initiated. Risers were reinstalled after harvest to control drainage at 30 cm in winter and spring and no subirrigation was practiced. Subirrigation began on days 161, 165 and 154 in 1992, 1993 and 1994, respectively and continued until days 259, 244 and 243 in 1992, 1993 and 1994, respectively. An overflow pipe removed excess rain when the water table was higher than the preset level (30 cm).

Corn (*Zea mays L.,* Pioneer 3573) was the only crop grown. The rate of application for atrazine was 1.1 kg $ha^{-1}$. The rate of application was the same for every year. Atrazine was applied on 14$^{th}$ May 1992, 17$^{th}$ May 1993 and 13$^{th}$ May 1994. For executing the

analyses on atrazine, sampling was done seven to nine times during the growing season. The herbicide was applied in a 38 cm band over the seeded row so that 550 g $ha^{-1}$ atrazine would be applied to the treatments, representing a 50% reduction in the amount of herbicide applied to the area compared to broadcast application.

Detailed weather data, comprising precipitation and potential evapotranspiration, was collected from an automated weather station in the vicinity for all three years. The data included maximum and minimum air temperature, solar radiation, rainfall intensity and amount, wind speed and direction, relative humidity and soil temperature. Measurements were taken in the months of June, July, August and September. The herbicide data for atrazine, metribuzin and metolachlor were taken at depths of 0-10 cm, 10-15 cm and 15-20 cm for all three years. For each plot, measurements were taken on 14th May, 20th May, 30th May, 11th June, 7th July, 20th August and 28th October in 1992. In 1993, measurements were taken on 17th May, 21st May, 26th May, 3rd June, 15th June, 13th July, 8th September, 6th October and 26th October. Sampling in 1994 was conducted on 13th May, 17th May, 25th May, 1st June, 23rd June, 28th July and 25th November. Thus, eight measurements were taken in 1992 and 1994 while ten were taken in 1993. Attention was focused on data from plots 8 and 11, which were under controlled drainage subirrigation with conventional tillage. Atrazine data from 1992-1994 are used for validating the model.

For each plot, sampling was carried out seven to nine times during the growing season for the herbicides. Soil residues at each sampling date were determined from analysis of 21 composited cores collected from each plot with a 2.5 cm diameter probe with an acetate sleeve. Since herbicide persistence is directly correlated to soil water content, which differs from over the tiles to that between the tile, two-thirds of the samples were collected over the drain tiles in the corn row and the remaining 7 samples were collected in the corn row midway between the two tiles.

Each sample was collected at 0 to 10 cm, 10 to 15 cm and 15 to 20 cm increments in the soil and stored at $-10°C$ for up to 2 months before further analysis. Gas chromatography

was used to determine the herbicide concentration at zero time using a thermionic sensitive detector operating in N mode by placing six petri dishes in each plot and then removing spray residue with methanol. Soil samples were prepared by mixing 132 g wet weight of soil with 100ml of methanol and water (95:5 v/v) for an hour. The samples were filtered through # 5 whatman filter paper and combined filtrates were reduced to 10 ml at 40°C. Herbicide residues were further dissolved in 100 ml distilled water and concentrated again on a preconditioned cyclohexyl extraction column. After loading the herbicide, the column was dried and the herbicides were eluted with 1.5 ml methanol for injection into the gas chromatography.

For a detailed description, the reader may refer to papers by Tan et al. (1993); Drury et al. (1996) and Gaynor et al. (1995; 2000; 2001).

#### 3.3.1.1 Statistical Analysis

A few statistical parameters were computed to ascertain the performance of the model. The standard error is a quantitative estimation of the dispersion that exists between the observed and predicted values. The equation used to calculate the standard error is given below (Singh et al., 1994; Prasher et al., 1995; Clemente et al., 1997; Kaluli et al., 1997):

$$SE = \sqrt{\frac{\sum (O_i - Pi)^2}{n}} \qquad (3.13)$$

where $O_i$ is the observed water table depth on any one day , $P_i$ is the predicted water table depth for the same day, n is the number of days. The value of the standard error is best when it is lowest.

The average absolute deviation (AAD) was also calculated to compare the dispersion in the observed and predicted values with the following equation (Singh et al., 1994; Prasher et al., 1995; Kaluli et al., 1997):

$$AAD = \frac{\sum |O_i - P_i|}{n} \tag{3.14}$$

where $O_i$ is the measured water table depth, $P_i$ is the predicted water table depth, n is the number of days. The value of average absolute deviation has an expectation of zero, which indicates that the model has done an excellent job in making predictions. The smaller the value of the average absolute deviation and standard error, the closer are the model predictions.

Another important statistic is the root mean square error, RMSE. This was calculated based on the equation below (El-Sadek et al., 2001):

$$RMSE = \sqrt{\frac{\frac{1}{n}\sum_{i=1}^{n}(P_i - O_i)^2}{\overline{O}}} \tag{3.15}$$

where $P_i$ is the predicted value, $O_i$ is the observed values, $\overline{O_i}$ is the mean observed value, i is the event and n is the number of observations. The value of RMSE varies between 0 and 1.

Modeling performance was also tested using the modeling efficiency equation as has been used by other researchers (Vanclooster et al., 2000 and El-Sadek et al., 2001):

$$EF = \frac{\left(\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2\right)}{\sum_{i=1}^{n}(O_i - \overline{O})^2} \tag{3.16}$$

where $O_i$ is the observed value, $P_i$ is the predicted value and $\overline{O_i}$ is the mean observed value. The efficiency evaluates the error relative to the natural variation in the observed values. An efficiency of 1.0 indicates a correct estimate, while a zero shows the inefficiency of the model. In other words, the higher the efficiency, the better the model. A negative sign indicates the inability of the model in making predictions.

### 3.3.2 MODEL EXECUTION

In its current form, DRAINMOD-P is executed in a few steps. At the onset, a runoff sub model, as per the PESTFADE model, is executed to calculate the pesticide remaining on the surface (Clemente et al., 1997). Following this, DRAINMOD is executed along with DRAINMOD-N. This is done in order to obtain the moisture and flux contents that enable assessment of pesticide transport. These values are then fed as input to the pesticide sub model of PESTFADE. It is necessary to run DRAINMOD-N at this point since DRAINMOD alone does not provide the temporal variation of soil moisture content and water flux for the soil profile. Efforts are being made by the developers of DRAINMOD to fix this step so that the required information for solute transport would be available directly from DRAINMOD.

The hydrology component within DRAINMOD is sub-divided into hydrology, soil, weather, crops, and nitrogen. Climatic data from 1992-1994 were first organized for use in DRAINMOD. The temperature data was first organized in a columnar format separated by year, day, maximum and minimum daily temperatures. A utility in DRAINMOD converted this data into an input file for temperature. For the rainfall file, a columnar input file with year, day, and rainfall in mm was prepared. In a similar manner, this file was processed with a utility tool of DRAINMOD to convert it into a suitable format. The rainfall data was thus converted to hourly amounts in hundredths of an inch. The soil component includes the soil water characteristics, drain volume-upflux and infiltration parameters. The soil water characteristic contains theta expressed in $cm^3$ $cm^{-3}$ and head in cm. The water table and volume drained are expressed in cm while the upward flux is expressed in cm $h^{-1}$. The infiltration parameters contain the water table (in cm), A coefficient and B coefficient.

The next step towards model development is calibration. The Harrow soil is known to crack considerably during hot and dry climatic conditions (Singh et al., 1994). Vertical seepage was used to calibrate DRAINMOD after discussions with the staff at the Research station (C. S. Tan, November, 2001). The parameters included the piezometric

head of aquifer, the thickness of the restrictive layer and the vertical conductivity of the restricting layer. The values that were used for calibrating the model were 500 cm, 1000 cm and 0.01 cm $h^{-1}$ respectively. DRAINMOD was calibrated for water table simulations with data from 1993. After calibrating the model, the parameters were not changed at all. The model was then tested with the data from 1992 and 1994.

In 1992, the pesticide simulation began from day 135 and went on to day 305. In 1993, the model runs covered the entire growing season from day 137 to 300 while for 1994 the simulation ran for days 133-330. These simulation periods were chosen with a view to obtaining maximum points for comparison between the measured and simulated concentrations of the pesticide during the growing season. The depth of the soil profile for all the simulations was 200 cm.

Two approaches were used for the simulation of pesticide fate. The first one was performed using the conventional method while the other one was performed using the Gamble kinetics that takes the sorption and intraparticle diffusion into account. The simulation results for both approaches were compared against the average of measured concentrations calculated from two samples at depths of 0-10 cm, 10-15 cm and 15-20 cm from plots 8 and 11.

## 3.4 RESULTS AND DISCUSSION

Before a model can be recommended for further use, it has to be validated against field data. PESTFADE has already been tested against field data and the model performed well in simulating pesticide movement in soil (Clemente et al., 1993; Clemente et al., 1997 and Kaluli et al., 1997; Tafazoli, 2002). A column study was also performed to test PESTFADE and the results obtained from Gamble kinetics were better when compared to the conventional approach (Li et al., 1999). In the present study, the ability of DRAINMOD-P was estimated quantitatively by comparing the simulated values against the observed ones. The hydrologic analysis is summarized first, followed by the pesticide transport. The results obtained from each year are dealt with separately.

Singh et al. (1994) used DRAINMOD with data for 1991 and 1992 from the same site in their study. However, they did not find a close agreement between the simulated and observed values in the case of subirrigation in plots 8 and 11. Efforts were made in this study to calibrate DRAINMOD to arrive at closer predictions since it would not have been prudent to explore pesticide simulations if water flow simulations were not satisfactory. The model was calibrated using 1993 as the base year. Fig 3.2 shows the uncalibrated model. Subsequently, DRAINMOD was executed for 1992 and 1994. This was performed without changing any of the parameters after calibration.

### 3.4.1 Hydrology Results

DRAINMOD was tested for predicting water table depth for the experimental plot 11 in the present study. Using the model, the predicted water table depths were evaluated and are presented in Figs. 3.1, 3.3 and 3.4 for 1992, 1993 and 1994. It is observed from these figures that the predicted values followed a similar trend as those of the measured water table depths under subsurface drained plots. With an increase in precipitation, there is a corresponding increase in the water table throughout the season in 1992. In 1993, water table depths seem to be governed by the rainfall intensity and periodicity up to day 195, after which the model seems to overestimate the water table depth. The soil at the experimental site is known to develop cracks during the hot season (Singh et al., 1994). DRAINMOD does not consider macropore flow and the disparity in the simulated water depths during the latter half of the growing season in 1993 may be attributed to this. The water table depth seems to respond well to the rainfall intensity and is governed by its periodicity in 1994.

The average absolute deviation (AAD), standard deviation (SD), standard error (SE), root mean square error (RMSE) and model efficiency were calculated and the results for 1992, 1993 and 1994 are presented in Table 3.1. The AAD, SD and SE for 1992 are 6.71, 6.23 and 6.72 cm, respectively. These low values, coupled with a low RMSE value of 0.15, indicate that the model has performed well. The EF value, on the other hand, is low at

28%. However, the EF is a stringent test to assess model efficiency. This ambiguity may also result from a small data size ranging from 15-32 data points. In 1993, the AAD, SD and SE for 1993 are 14.45, 15.47 and 7.73 cm, respectively, while the RMSE is 0.20. The low values obtained from these statistical tools indicate a reasonable model prediction. An EF of 81% further emphasizes the accuracy of hydrology simulations for 1993. The results from the statistical tools in 1994 were 13.61, 13.57 and 8.59 cm for the AAD, SE and SD, respectively. The similarity of the values of AAD, SD and SE indicate that there is not much of a variation compared to the mean value. A low RMSE of 0.18 is indicative of the high efficiency of the model. The EF obtained is 63%, which further supports the accuracy in model predictions.

These results are also in accordance with similar hydrology studies conducted in southern Ontario using SWACROP where the AAD ranged from 6.1 to 38 cm and the SE ranged from 10.1 to 43.7 cm respectively (Prasher et al., 1995).

### 3.4.2 Pesticide Simulation Results -1992

Fig 3.5 demonstrates that both simulated and measured values exhibit a similar concentration distribution pattern across the whole season of 1992 at all three depths. At the 0-10 cm depth, results obtained from the conventional approach were slightly higher than the measured values, but followed the same trend. The Gamble kinetics approach is similar, although the predictions were slightly lower than the observed. From day 150, the model predictions with both approaches are quite close to each other. Comparison of simulated and observed atrazine concentrations with 1:1 line also showed that atrazine concentrations were overpredicted using the conventional method at the 0-10 cm depth in 1992, as is evident from Fig 3.6. However, DRAINMOD-P seemed to underpredict atrazine concentrations when the Gamble kinetics was applied at the same depth. An underprediction, for the same degradation rate constant, means that more pesticide is getting sorbed onto the soil particles, while on the contrary, an overprediction implies less sorption. At the 10-15 cm depth, the conventional approach initially underpredicts the pesticide concentrations and then seems to overpredict the pesticide concentration

towards the end of the growing season. Both approaches seemed to underestimate atrazine concentrations, as is revealed from the 1:1 line shown in Fig 3.7 for the 15 cm depth. At the 15-20 cm depth, the two methods give lower predictions when compared to the measured pesticide concentrations. The conventional method seems to underestimate atrazine concentrations on all sampling dates while the Gamble approach overestimates slightly at the beginning of the season and underestimates at the 20 cm depth towards the end of the growing season as shown in Fig 3.8.

The results from the statistical tests are compiled in Table 3.2 for the 1992 simulations. SD is higher in the conventional method at the 10 cm depth when compared to the Gamble method. The AAD is very high in the Gamble approach at 152.47 $\mu g\ kg^{-1}$ when compared to 96.31 $\mu g\ kg^{-1}$ for the conventional way. Similarly, the SE in the Gamble approach is much more than that in the conventional method. Lower RMSE is obtained in the case of the conventional route at 0.64, showing a better performance over Gamble kinetics with an RMSE of 0.77. At the 15 cm depth, the AAD and SE from the Gamble approach are lower at 3.83 and 2.13 $\mu g\ kg^{-1}$ as compared to 14.13 and 17.07 $\mu g\ kg^{-1}$ for the conventional approach. The RMSE in both routes are almost equivalent to each other and are approaching 1.0, thereby signifying the low performance of both approaches. At the 20 cm depth, the three statistical tools return similar values with either of the approaches, except for SE which is very low at 0.41 $\mu g\ kg^{-1}$ with the Gamble approach.

### 3.4.3 Pesticide Simulation Results -1993

Fig 3.9 shows the simulated and measured concentration profiles of atrazine with respect to time at all depths. A similar concentration distribution pattern across the whole season is exhibited between the simulated and measured values. Conventional approach simulations were higher than the measured values, while the Gamble approach underestimated the measured values. Further comparisons with a 1:1 line to assess the performance of DRAINMOD-P for 1993 revealed similar results, as shown in Fig 3.10. Gamble kinetics overpredicts over a very small range and is observed to underpredict during most parts of the growing season at the 15 cm depth. At the 15 cm depth, both

methods do not seem to predict values closer to the measured ones on all sampling dates although a few lie closer to the 1:1 line as shown in Fig 3.11. In 1993, the conventional predictions are much closer than the Gamble ones, as illustrated in Fig 3.9. The Gamble approach seems to overpredict during most parts of the season and underpredicts towards the end of the season at the 20 cm depth. However, a closer look into Fig 3.12 reveals the closeness of conventional method predictions to the observed values. It is also clear that at this depth the trends are followed by both approaches.

The results from the statistical tests are compiled in Table 3.2. SD is higher in the conventional method at the 10 cm depth when compared to the Gamble method. The AAD is very high in the conventional approach at 292.58 $\mu g\ kg^{-1}$ when compared to 158.47 $\mu g\ kg^{-1}$ for the Gamble kinetics. However, the SE in the conventional approach is very close to that obtained from the Gamble method. Lower RMSE is obtained in the case of the Gamble route at 0.88, showing a significant performance over the conventional method for an RMSE of 1.28. A reverse situation is obtained in the 15 cm depth, where the RMSE is 0.55 from the conventional approach as compared to 0.72 for Gamble. The AAD, SE and SD in both routes are almost equal to each other. At the 20 cm depth, once again, the SE test returns similar values with either of the approaches. RMSE, AAD and SD values for the conventional model is lower at 0.65, 3.36 $\mu g\ kg^{-1}$ and 4.32 $\mu g\ kg^{-1}$, respectively, while it is higher at 1.25, 7.17 $\mu g\ kg^{-1}$ and 8.06 $\mu g\ kg^{-1}$ for the Gamble method, respectively. These values indicate that the Gamble kinetics gave closer predictions to the observed when compared to the conventional method at the 0-10 cm depth while the conventional better results than the Gamble method at both 10-15 and 15-20 cm depths.

### 3.4.4. Pesticide Simulation Results- 1994

Fig 3.13 shows the simulated and measured concentration profiles of atrazine with respect to time at the 0-10 cm for 1994. Both simulated and measured values exhibit a similar concentration distribution pattern across the whole season at all depths. At the 0-10 cm depth, the conventional approach overestimates slightly while the Gamble kinetics

approach underestimates the observed values. A comparison between the observed and simulated atrazine concentrations with a 1:1 line further supports the accuracy obtained with the conventional approach as shown in Fig 3.14. On the other hand, the Gamble predictions are further away from the 1:1 line and thus provide evidence of lower estimates. The comparison could not be made for the whole season as not enough measurements at the 15 cm depth were taken during the 1994 season. While the conventional approach seems closer at this depth, the Gamble approach also follows the same pattern. However, both approaches seem to underestimate the pesticide concentrations. As shown in Fig 3.15, the same situation is revealed when observed and simulated values are compared. In fact, the conventional predictions seem to be somewhat closer to the observed ones. In 1994, the simulated values are much lower than the measured ones irrespective of the approach used at the 15-20 cm depth. This is again supported when a comparison is drawn between the observed and the predicted values with a 1:1 line as shown in Fig 3.16.

The results from the statistical tests are compiled in Table 3.2. SD is higher in the conventional method at the 10 cm depth when compared to the Gamble method. The AAD is very high in the Gamble approach at 189.71 μg $kg^{-1}$ when compared to 58.33 μg $kg^{-1}$ for the conventional way. Similarly, the SE in the Gamble approach is much more than that in the conventional method. A lower RMSE is obtained in the case of the conventional route at 0.41, proving higher accuracy when compared to an RMSE of 0.77 for the Gamble kinetics. A reverse situation is obtained in the 15 cm depth, where the RMSE is 0.37 from the Gamble approach as compared to 0.81 for the conventional approach. The AAD, SE and SD in both routes are almost equal to each other. At the 20 cm depth, once again, the three statistical tools return similar values with either of the approaches. RMSE values for the conventional and Gamble approaches are also very close to each other at 0.99 and 0.91, respectively, for the two methods. These values highlight the inefficiency of the model predictions since they are closer to 1.00.

From the model performance assessments for all three years, no clear deduction can be made to state that the Gamble kinetics method is a better approach over the conventional

method. This varies from studies conducted by Kaluli et al. (1997) and Li et al. (1999) where a significant improvement was obtained using the two-stage sorption kinetics in PESTFADE. However, this non-conformity may be attributed to the swelling and shrinking nature of the soil in question, which might have led to a misrepresentation of the actual phenomena (Singh et al., 1994). Furthermore, no consistency was found in either of the approaches at a particular depth. However, the predicted values still satisfy the criterion for model acceptance as set by the Exposure Assessment Workshop (Hedden, 1986) which recommended that a model should be able to replicate observed data within an order of magnitude. Azevedo et al. (1997) in their study with RZWQM under no-till and moldboard plow also obtained similar results. This is also in conformity with results obtained by Ma et al. (2000). In a study performed with the same field data for the year 1993, Tafazoli et al. (2002) also concluded that the Gamble approach yielded better results at the 10 cm depth while the conventional method gave a good performance at both 15 and 20 cm depths. One problem with field data is the difficulty in obtaining representative values because of spatial variability (Kaluli et al., 1997). Since soil is known to be a highly variable medium, the measured chemical residues can also be expected to exhibit a higher degree of variability.

## 3.5 CONCLUSIONS

The DRAINMOD-P model has been developed in this study for simulating the fate and transport of pesticides in soils. The water flow in the model is simulated according to DRAINMOD, a popular model in the water table management field, and the pesticide movement is based on the mechanisms included in the PESTFADE model. The results show that hydrology simulations are commendable for all three years of simulation. The AAD and SE lie between 6.71 to 13.61 cm and 6.72 to 8.59 cm, respectively. These are comparable to past studies on DRAINMOD where the AAD values ranged from 6.1 to 38.1 cm and SE from 10.1 to 43.7 cm (Singh et al., 1994; Prasher et al., 1995). As far as the pesticide concentrations are concerned, the model results were within one order of magnitude, which is in accordance with work done by previous researchers (Azevedo et al., 1997; Ma et al. 2000; Tafazoli, 2002).

However, a clear deduction cannot be made from this study to state that the application of Gamble kinetics brought a significant improvement in simulating the movement of pesticides. The swelling and shrinking nature of the soil used in this study may be one of the reasons for overshadowing the real phenomena governing the sorption mechanism. A consistency in performance over the three-year period at any particular depth was also not evident with the application of either the conventional or the Gamble approach. Further validations with larger datasets should be carried out to make such an assessment. In this study, the model was not calibrated for simulating pesticide movement. Better results would have been obtained with model calibration.

**Table 3.1 Results of statistical tests for water table simulations for 1992-94**

| Statistical Parameters | 1992 | 1993 | 1994 |
|---|---|---|---|
| AAD* | 6.71 cm | 14.45 cm | 13.61 cm |
| SD | 6.23 cm | 15.47 cm | 13.57 cm |
| SE | 6.72 cm | 7.73 cm | 8.59 cm |
| RMSE | 0.15 | 0.20 | 0.18 |
| EF | 28% | 81% | 63% |

*AAD, Average absolute deviation; SD, Standard deviation; SE, Standard error; RMSE, Root mean square error; EF, Model efficiency

**Table 3.2 DRAINMOD-P Statistical Results for 1992-94**

| Statistical Parameters | Conventional 0-10cm | Gamble 0-10cm | Conventional 10-15 cm | Gamble 10-15 cm | Conventional 15-20 cm | Gamble 15-20 cm |
|---|---|---|---|---|---|---|
| SD* ($\mu g\ kg^{-1}$) | 120.23 | 98.44 | 15.98 | 17.62 | 7.88 | 8.31 |
| AAD ($\mu g\ kg^{-1}$) | 96.31 | 152.47 | 14.13 | 3.83 | 6.77 | 6.51 |
| SE ($\mu g\ kg^{-1}$) | 66.76 | 81.08 | 17.07 | 2.13 | 8.58 | 0.41 |
| RMSE | 0.64 | 0.77 | 0.92 | 0.93 | 1.04 | 0.95 |
| **For 1993** | | | | | | |
| SD ($\mu g\ kg^{-1}$) | 186.57 | 182.57 | 9.04 | 11.95 | 4.32 | 8.06 |
| AAD ($\mu g\ kg^{-1}$) | 292.58 | 158.47 | 8.10 | 8.92 | 3.36 | 7.17 |
| SE ($\mu g\ kg^{-1}$) | 111.43 | 109.91 | 8.45 | 8.42 | 3.88 | 3.84 |
| RMSE | 1.28 | 0.88 | 0.55 | 0.72 | 0.65 | 1.25 |
| **For 1994** | | | | | | |
| SD ($\mu g\ kg^{-1}$) | 102.47 | 88.15 | 8.29 | 8.90 | 5.57 | 4.90 |
| AAD ($\mu g\ kg^{-1}$) | 58.33 | 189.71 | 7.87 | 8.06 | 3.48 | 3.45 |
| SE ($\mu g\ kg^{-1}$) | 37.46 | 78.42 | 3.68 | 3.5 | 0.41 | 0.42 |
| RMSE | 0.41 | 0.77 | 0.81 | 0.37 | 0.99 | 0.91 |

* SD, Standard deviation; AAD, Average absolute deviation; SE, Standard error; RMSE, Root mean square error

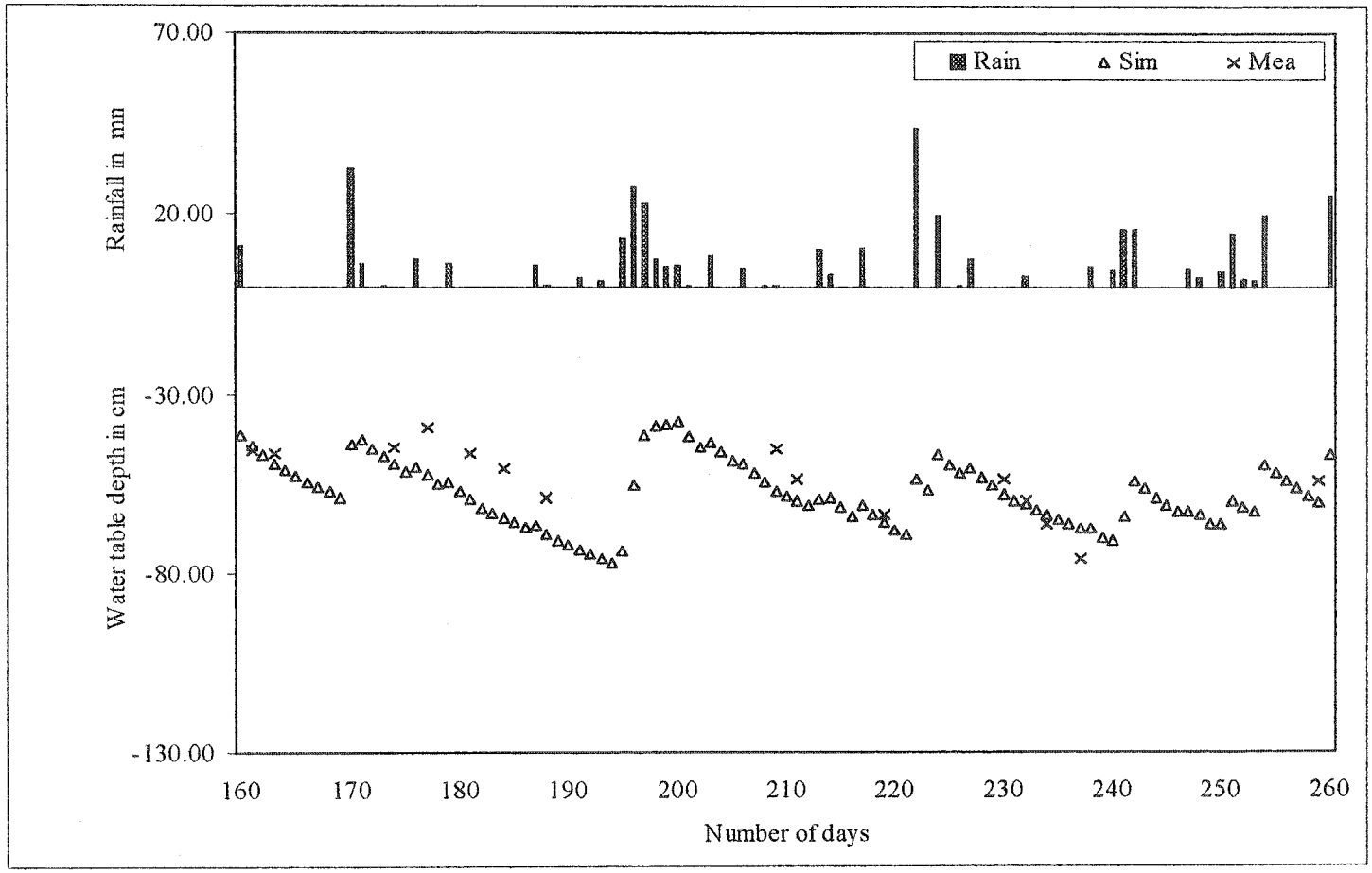


**Fig 3.1- Water table depth simulation by DRAINMOD-P for 1992**

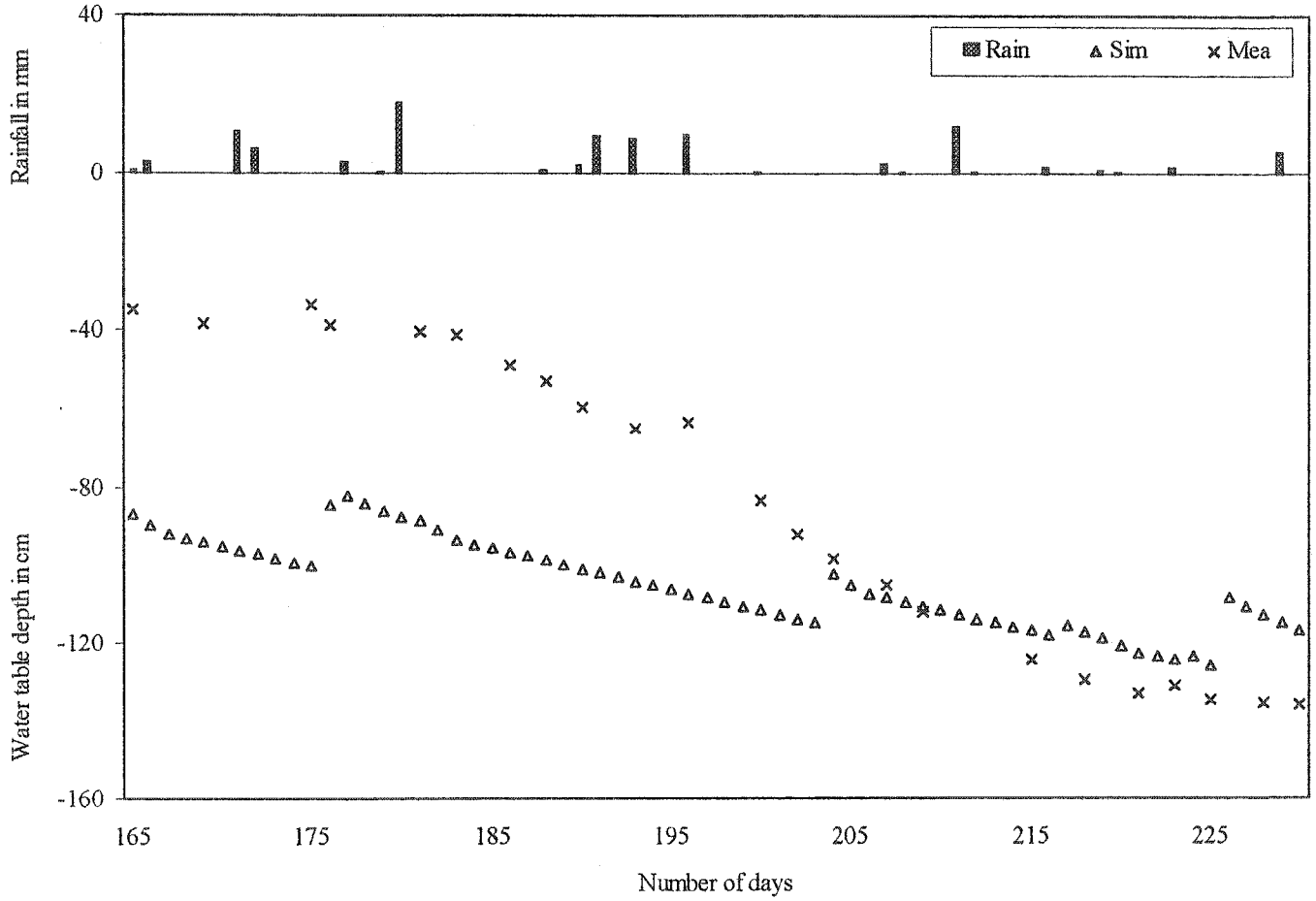


**Fig 3.2 Water table depth simulation by DRAINMOD-P for 1993 (uncalibrated)**

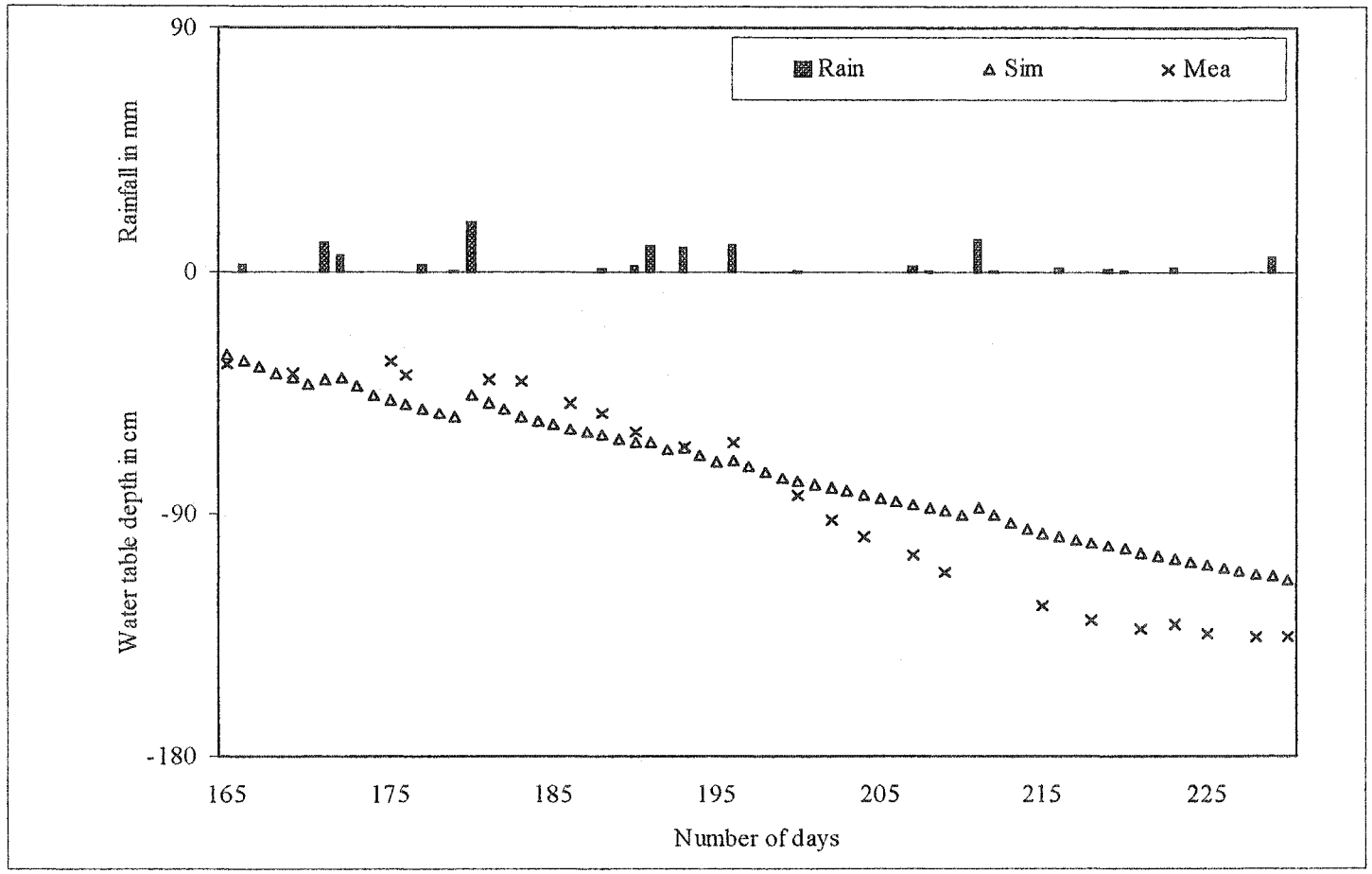


**Fig 3.3- Water table depth simulation by DRAINMOD-P for 1993**

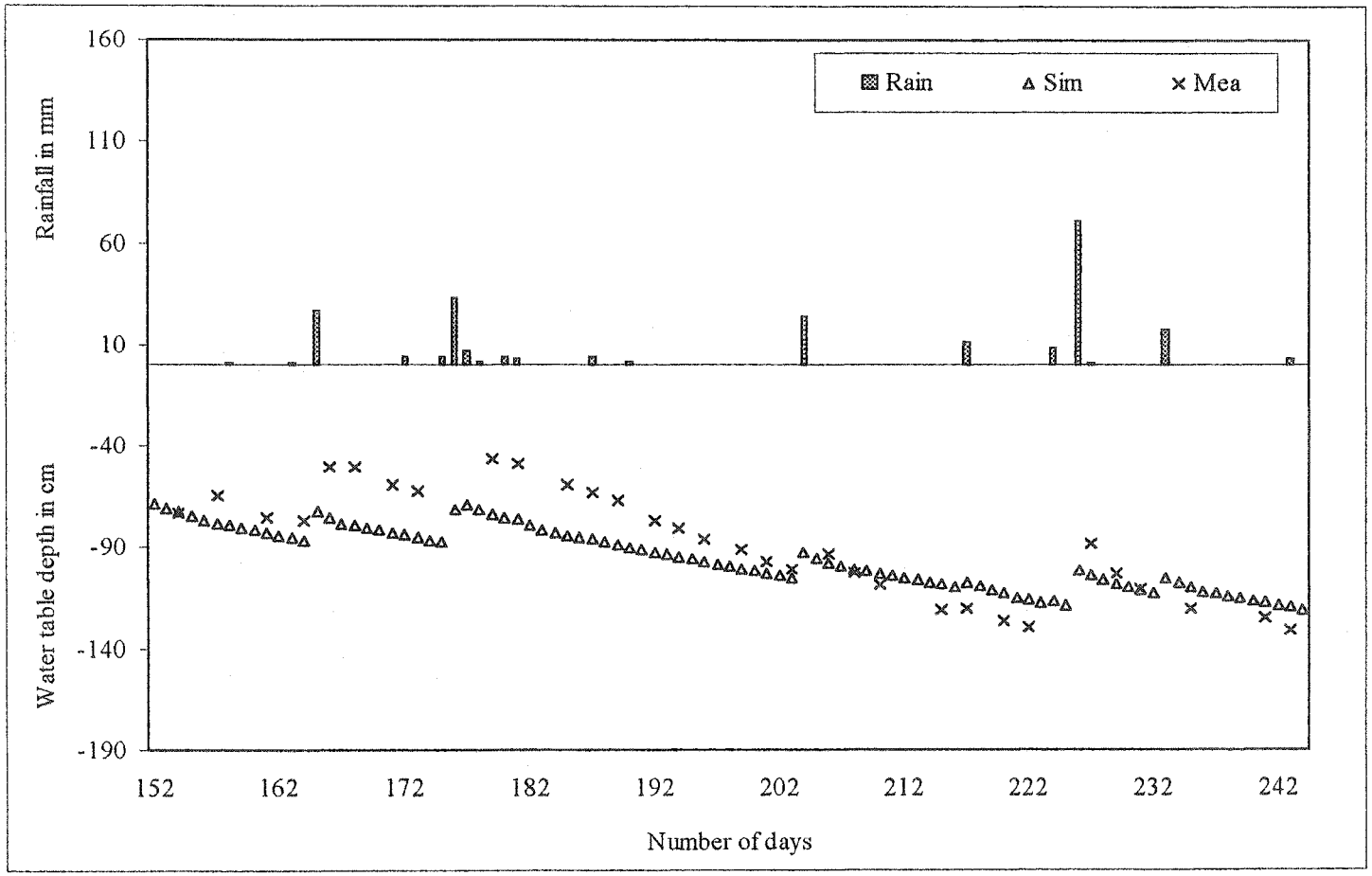


**Fig 3.4 - Water table depth simulation by DRAINMOD for 1994**

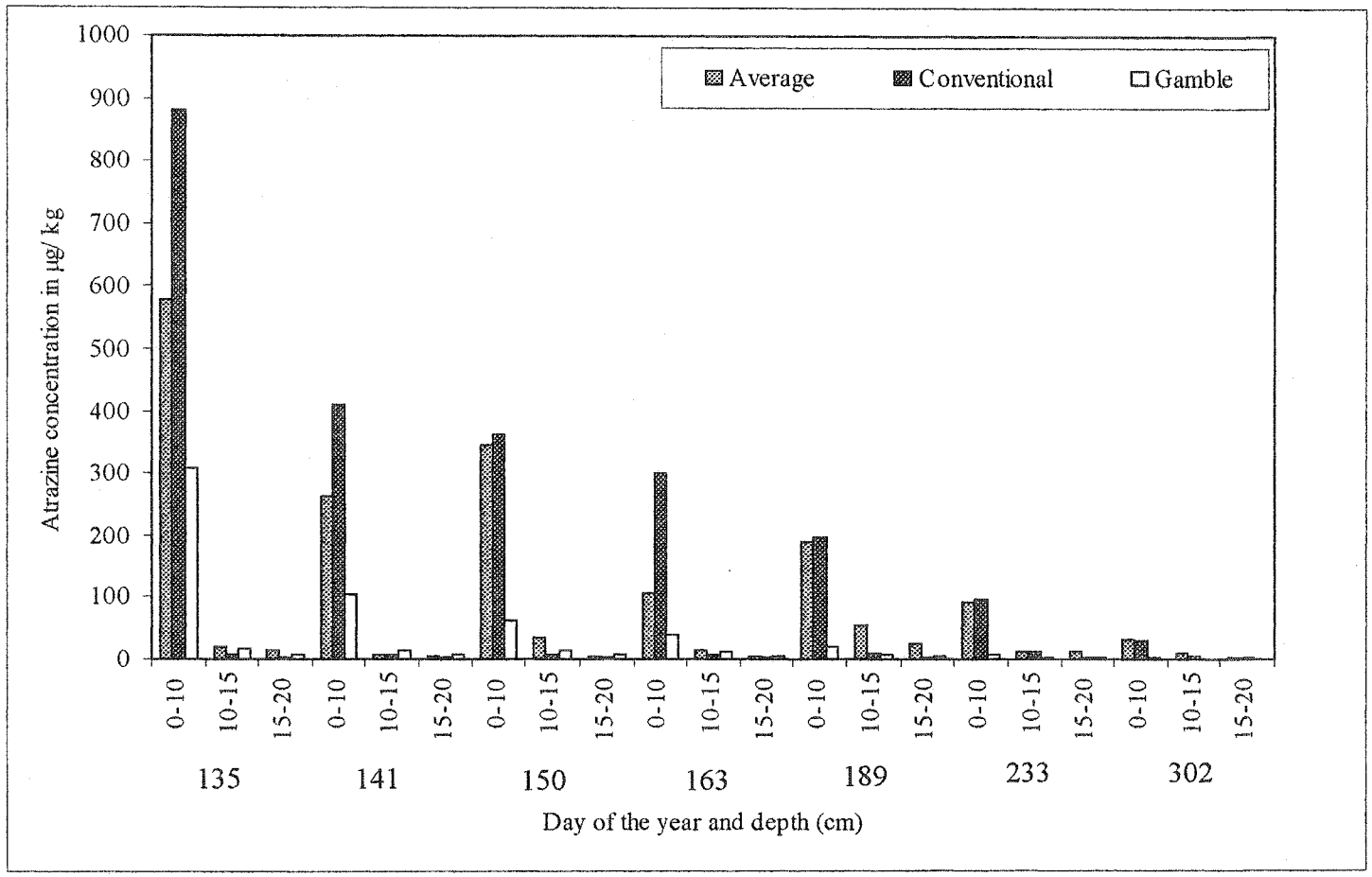


**Fig 3.5- Atrazine simulation by DRAINMOD-P for 1992**

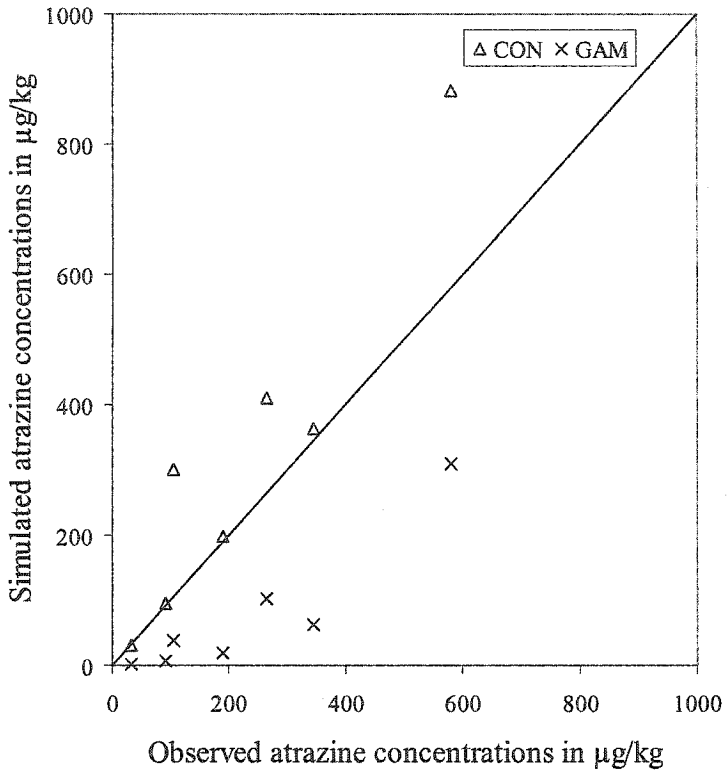


**Fig 3.6 Observed vs. simulated atrazine concentrations by DRAINMOD-P at 0-10 cm depth for 1992**

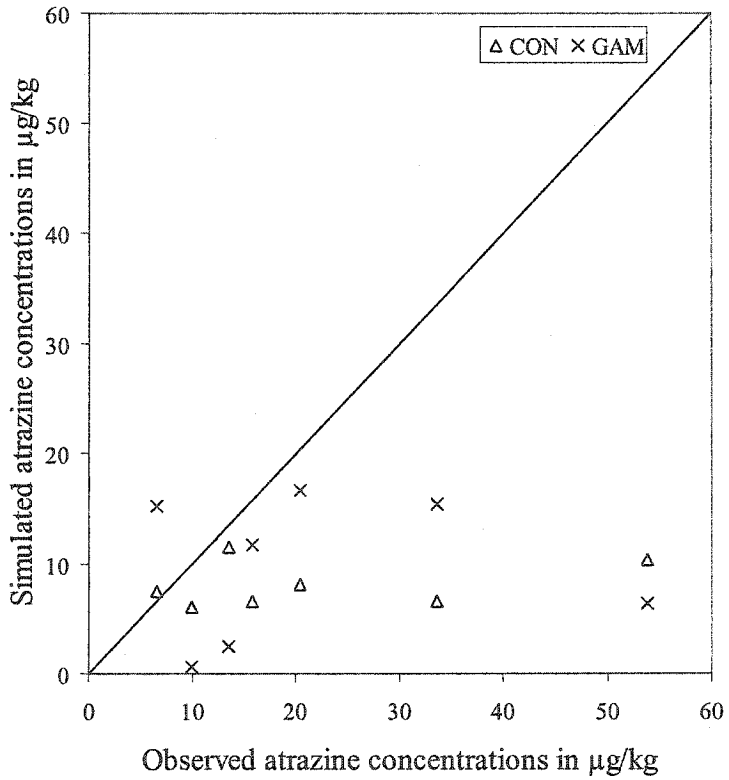


**Fig 3.7 Observed vs. simulated atrazine concentrationsby DRAINMOD-P at 10-15 cm depth for 1992**

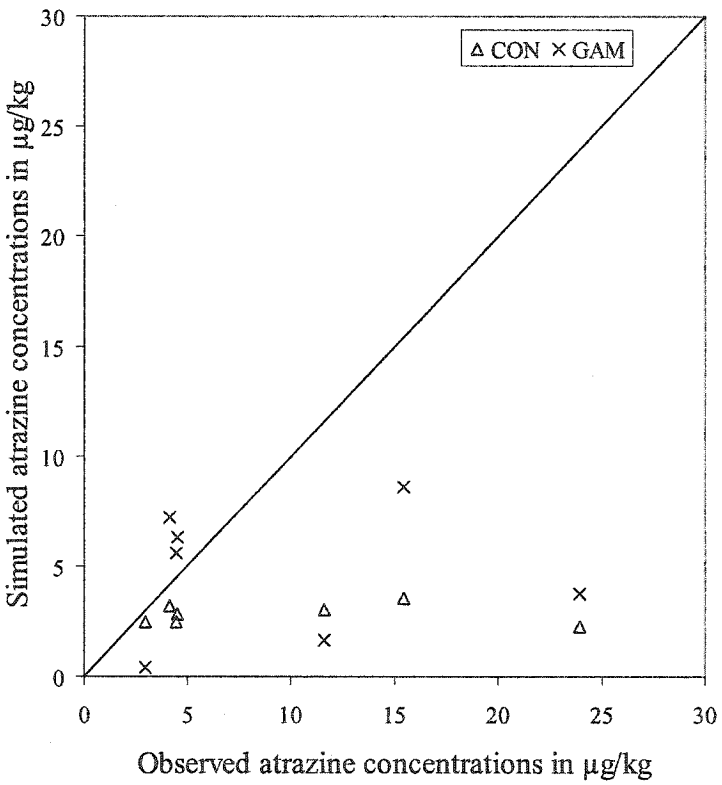


**Fig 3.8 Observed vs. simulated by DRAINMOD-P at 15-20 cm depth for 1992**

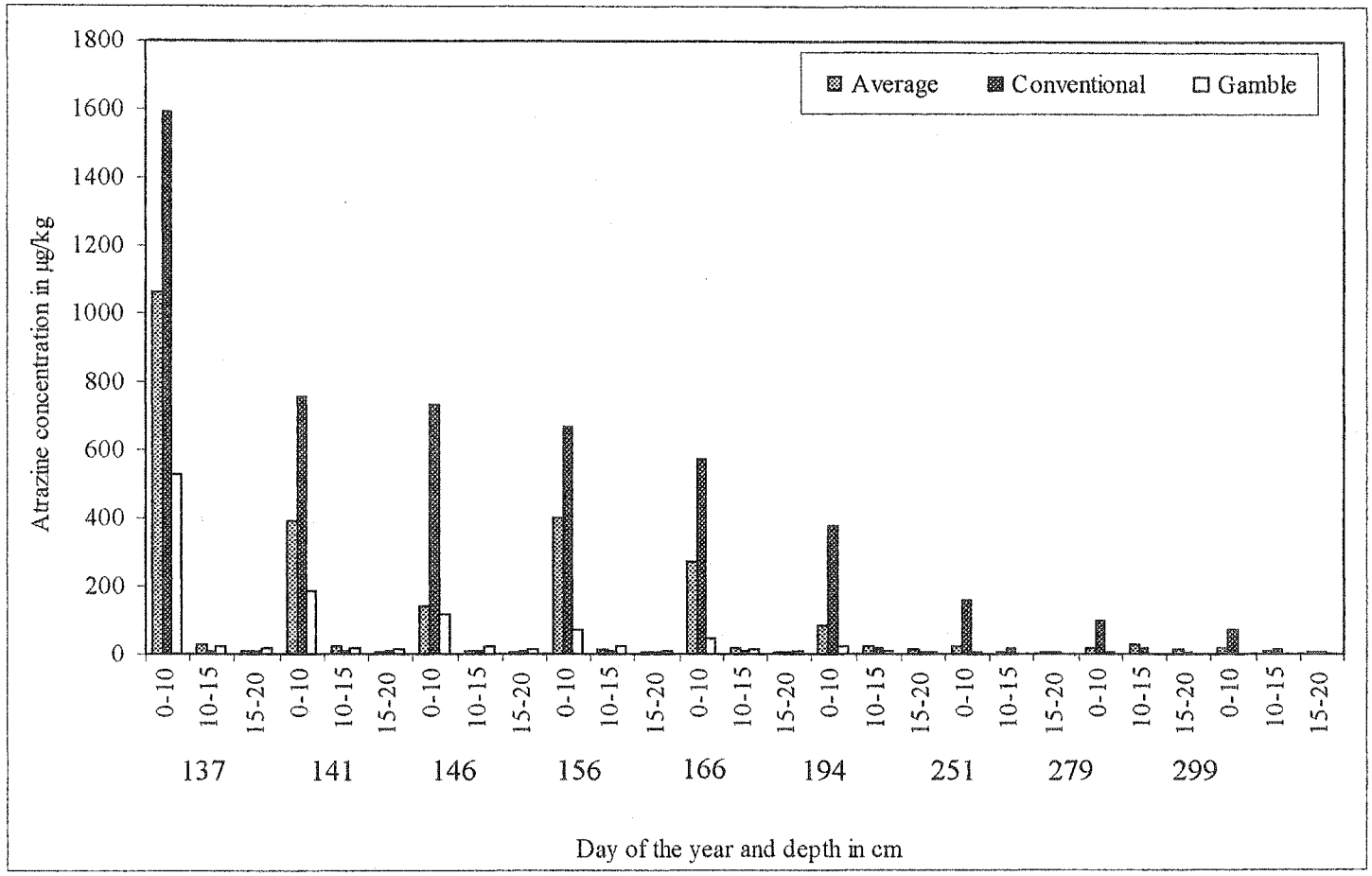


**Fig 3.9- Atrazine simulation by DRAINMOD-P for 1993**

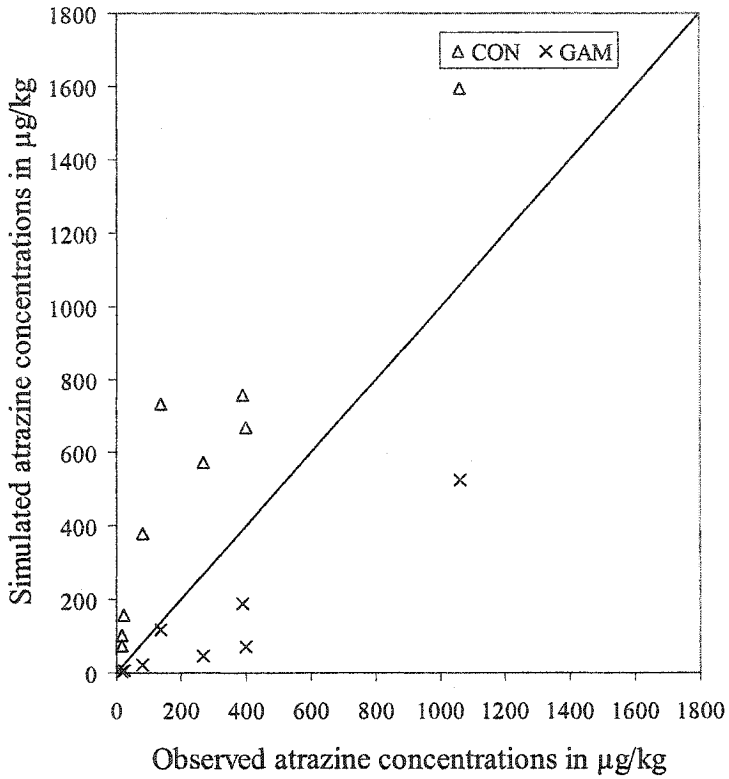


**Fig 3.10 Observed vs. simulated atrazine concentrations by DRAINMOD-P at 0-10 cm depth for 1993**

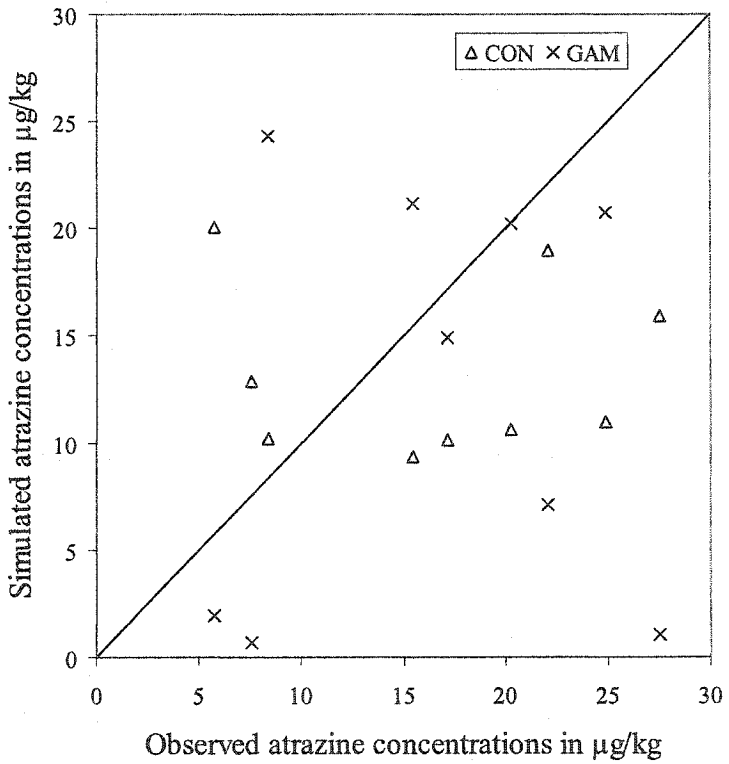


**Fig 3.11Observed vs. simulated atrazine concentrations by DRAINMOD-P at 10-15 cm depth for 1993**

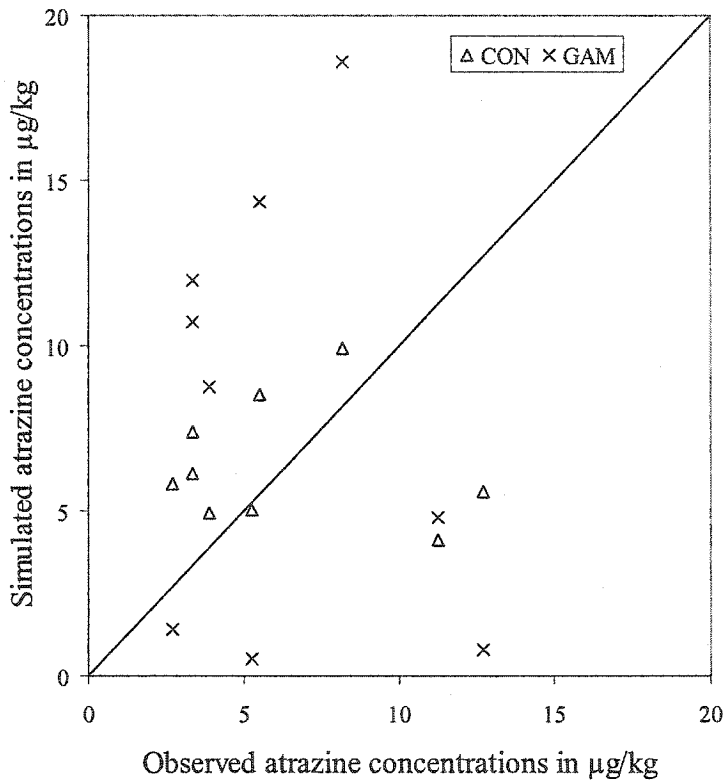


**Fig 3.12 Observed vs. simulated atrazine concentrations by DRAINMOD-P at 15-20 cm depth for 1993**

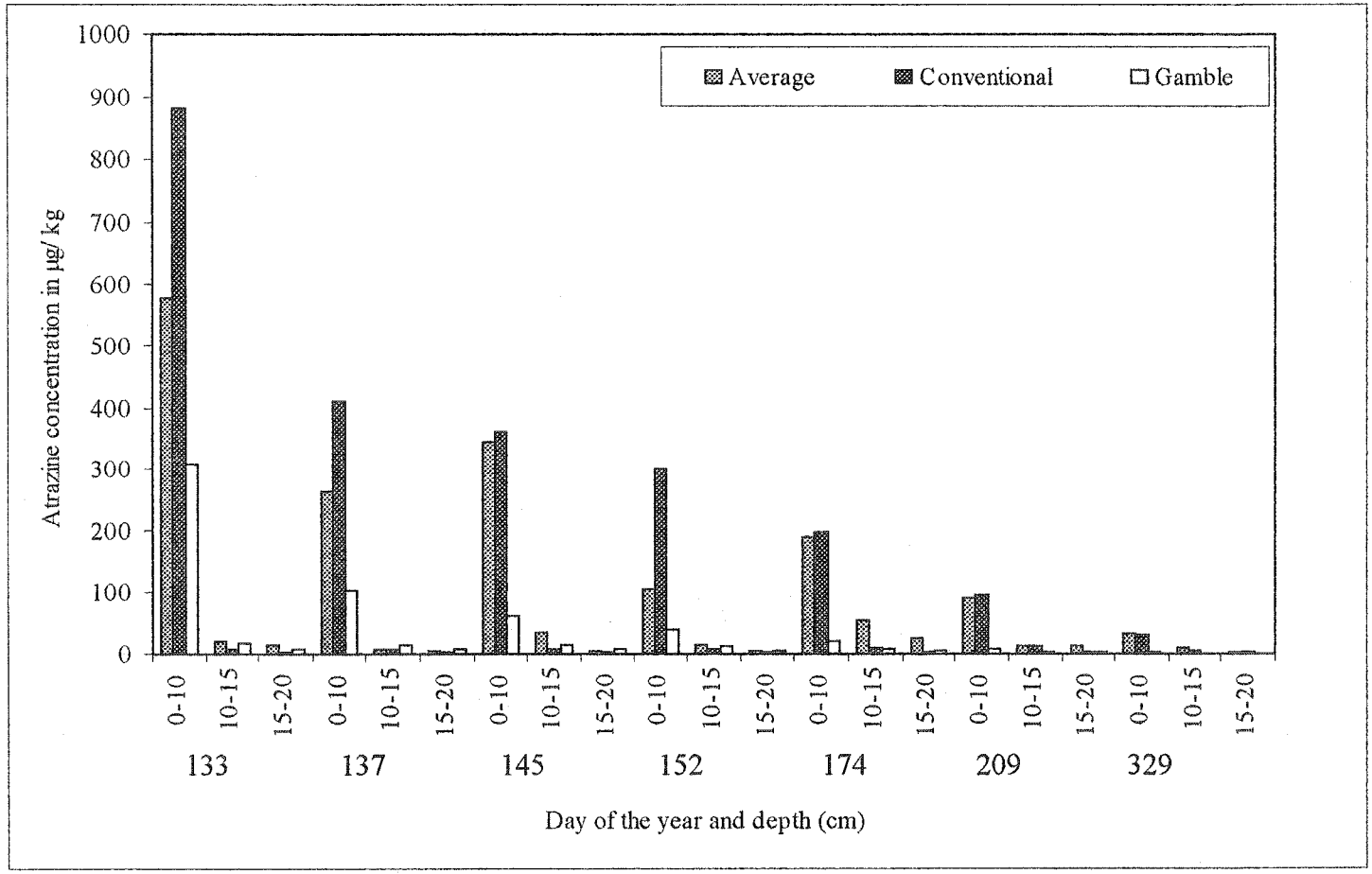


**Fig 3.13- Atrazine simulation by DRAINMOD-P for 1994**

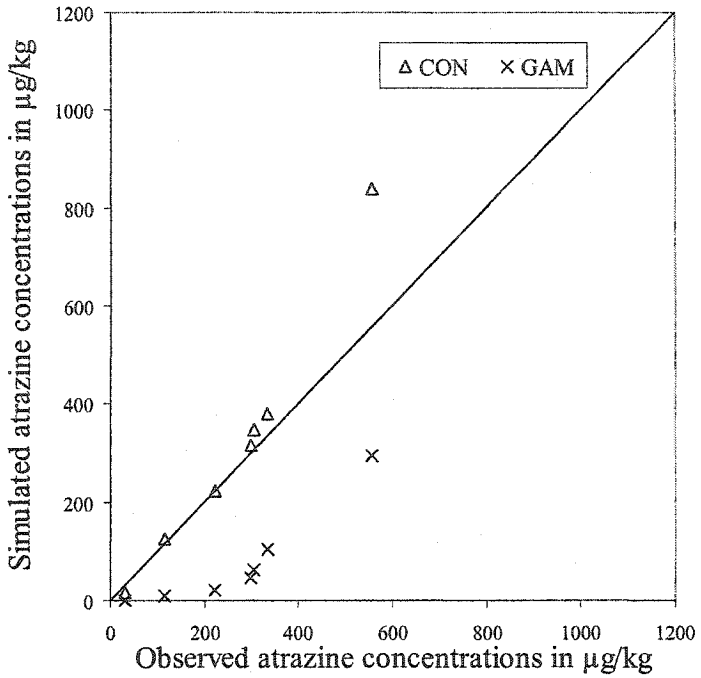


**Figure 3.14 Observed vs. simulated atrazine concentrations by DRAINMOD-P at 0-10 cm depth for 1994**

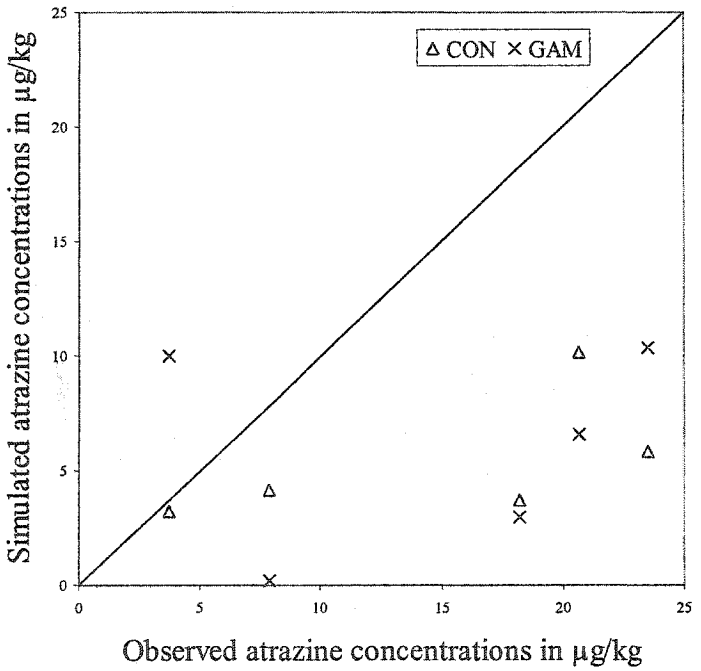


**Figure 3.15 Observed vs. simulated atrazine concentrations by DRAINMOD-P at 10-15 cm depth for 1994**

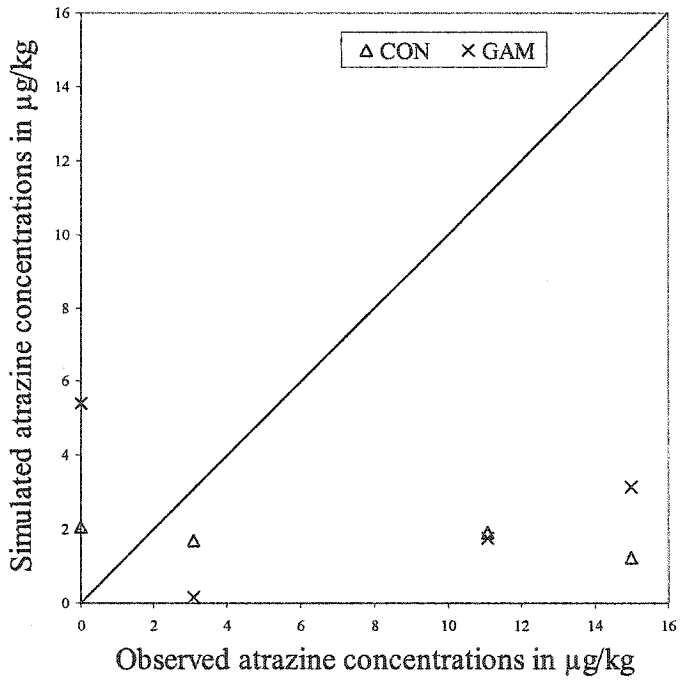


**Figure 3.16 Observed vs. simulated atrazine concentrations by DRAINMOD-P at 15-20 cm depth for 1994**

## PREFACE TO CHAPTER 4

DRAINMOD-P provided an insight into pesticide fate modeling, which is very complex as it encompasses many transformations that a pesticide undergoes in the soil environment. However, it requires too many input parameters and longer execution time. Out of the two approaches used in DRAINMOD-P, the conventional approach takes less than a minute for a single simulation and about eight hours for the Gamble method. Moreover, the accuracy is less than desirable. In this chapter, efforts were made to assess the success of an implicit modeling technique, MARS, to simulate pesticide transport of three herbicides from field data. Although ANNs have been used extensively for implicit modeling in the field of agriculture and are known to learn from examples, MARS was found to outperform ANNs (Abraham et al., 2001a,b). MARS is also faster in its execution, able to learn from very limited data, and has the ability to rank variables according to their significance. This study was organized to explore the possibilities of simulating pesticide concentrations in agricultural soil with very limited data in a short period of time without compromising the accuracy of the model output.

The candidate, being the main author of the manuscript, was responsible for carrying out the study, performing the statistical analyses to ascertain the efficiency of MARS and compare its performance with the mathematical model, DRAINMOD-P. Dr. Shiv Om Prasher, Professor of Agricultural & Biosystems Engineering and supervisor of the candidate, has rendered his able guidance and has encouraged the author from the inception of this project. Dr. A. Madani, Professor of Engineering, Nova Scotia Agricultural College, Truro, Nova Scotia, was the co-supervisor and advised the candidate on numerous occasions. Dr. R. Lacroix, Professor of Animal Science, McGill University offered his valuable time in initiating and improving the project. Dr. J. D. Gaynor and Dr. C. S. Tan have provided the main author with the field data and have been available for discussions with the author and her supervisors.

**Research paper based on the chapter:**

Bera, P., S. O. Prasher, A. Madani, R. Lacroix, J. D. Gaynor, and C. S. Tan. Application of MARS for simulating pesticide movement in soil. (Manuscript to be submitted to the Transactions of the ASAE journal).

# CHAPTER 4
# APPLICATION OF MARS FOR SIMULATING PESTICIDE CONCENTRATIONS IN SOIL

## 4.1 ABSTRACT

In this study, efforts were made to predict pesticide concentrations at three different depths in the soil profile, using models developed with Multivariate Adaptive Regression Splines (MARS), a regression analysis model. The models were developed with independently collected data from the Eugene F. Whelan Experimental Farm (Agriculture and Agri Food Canada, Woodslee, Ontario, Canada) from 1992 to 1994. Data from sixteen plots, subjected to four different tillage treatments and two different water table management practices, were used. The fate of three herbicides, namely atrazine, [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine], metribuzin, [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one], and metolachlor, [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(-2-methoxyl-1-methylethyl) acetamide], at three different soil depths were studied. The input variables for the models included Julian day, days after application of pesticide, measured herbicide concentrations and cumulative figures for rainfall depth, air temperature, soil temperature and potential evapotranspiration. Considering the limited size of the data set, a ten-fold cross validation was performed to test and validate the model. Model predictions at the 0-10 cm depth were very close to the measured values, with model efficiencies varying from 78 to 99%. The predictions at the 10-15 cm depth varied from 51 to 77%, while the ones at the 15-20 cm were within 42 to 95%. These results demonstrate that MARS was able to do a commendable job in simulating pesticide fate and transport in soil with limited data. A comparison between the performance of the mathematical model, DRAINMOD-P, and MARS in simulating atrazine at the same depths over the same period yielded better predictions with MARS as is evident from the higher efficiencies and lower RMSE values. Execution time with MARS models was significantly less than DRAINMOD-P simulations, lasting for a few seconds only. DRAINMOD-P simulations, on the other hand, require less than a minute using the conventional method and about eight hours using the Gamble kinetics

approach. Thus, MARS seems to outperform DRAINMOD-P, both in accuracy and execution time. However, the MARS modeling requires both input and output data *a priori*, like artificial neural networks, and generates site-specific models only.

## 4.2 INTRODUCTION

Judicious and timely application of pesticides can not only increase food/agricultural productivity but also improves the quality of the produce (Gaynor et al., 1995). Perceived benefits from the use of pesticides have resulted in their extensive use across the world. Herbicide sales alone accounted for 85% of the total pesticide sales in Canada in 1997 (Gorse, 2000). However, the threat of increasing soil and water pollution has made the public very skeptical about their continued use on the farm. In a recent study, atrazine and metolachlor were detected in the St. Lawrence River, with most of the contamination coming from the Great Lakes (Cossa et al., 1998). The harmful effects of pesticide use are now well known and this awareness has resulted in a decrease in its consumption. Herbicide usage for corn in the United States has also dropped from 84,811 thousands kilograms, applied in 1996, to 68,433 thousands kilograms in 1999 (Anonymous, 2001).

The fate and transport of pesticides can be investigated by column studies, field experiments and mathematical simulations (Melancon et al., 1986; Gaynor et al., 1995; Azevedo et al., 1997; Li et al., 1999 and Gaynor et al., 2000). Column studies and field experiments both involve vast expenditures and are time-consuming. Since column studies are conducted in isolated environments, they cannot provide an actual representation of the complexities involved in the field. Mathematical modeling, on the other hand, is fast and accurate. However, most process-based models fail to account for spatial variability and preferential flow that might result in inaccurate estimations. Uncertainties may also arise due to approximations involved in calculating certain key parameters or while attempting to simulate the complex processes that govern the movement of the solute in the soil environment. Some of the shortcomings of process-based models are taken care of by machine learning models. Machine learning

algorithms, work efficiently with limited inputs. They are user-friendly and require less computation time. These artificial intelligent tools are capable of mimicking nature without compromising its complexities.

Among the popular artificial intelligence tools are case-based reasoning, artificial neural networks (ANN), genetic algorithms, rule induced systems and fuzzy logic. These tools have been used in agriculture extensively (Ocerin et al., 1996). Fuzzy logic has been employed to estimate evapotranspiration successfully (Odhiambo et al., 2001). ANNs have been widely used to make predictions about the soil moisture (Altendorf et al., 1999), soil temperature (Yang et al., 1996; 1997), saturated hydraulic conductivity (Lebron et al., 1999), and annual nitrate-N losses in drain outflows (Salehi et al., 2000b). ANNs have also been used to simulate pesticide movement in soil by researchers (Yang et al., 1997; Tafazoli, 2002). ANNs are known for their ability to learn from examples, work efficiently with few input parameters, and are very popular. MARS, a novel data-mining regression tool, is also gaining popularity of late due to its simple, easily comprehensible models and its extensive search mechanism, which makes it possible to identify interrelationships between parameters. Previous studies have shown MARS to have an edge over ANNs with respect to speed and RMSE values (Abraham et al., 2001a,b).

MARS segregates the training data into separate sectors with regression lines. The rapidity with which MARS captures the complexity involved in the relations between the parameters makes it a novel method. Previous studies reveal that MARS is a reliable software to use because of its strong regression capabilities (Abraham et al., 2001a,b). In another review, the significance of the MARS model was highlighted in making close predictions for in-sample studies while making predictions for recessions in the financial world (Sephton, 2001). However, its predictions for out-of sample forecasts for recession were less than desirable. These studies highlight the fact that MARS is a robust tool to detect patterns from training datasets. Therefore, an attempt was made, in this exploratory study to test the efficiency of MARS to predict pesticide concentrations. To

the best of our knowledge, MARS has so far not been used to simulate pesticide movement in the soil environment. The objectives of this study were:

i. to apply MARS to simulate the concentrations of three herbicides, namely atrazine, metribuzin and metolachlor, in an agricultural soil at three specified depths, and
ii. to compare atrazine simulations obtained from DRAINMOD-P, a physically-based mathematical model, with MARS.

## 4.3 THEORY

MARS is a non-parametric adaptive regression technique (Friedman, 1991). It builds flexible regression models by fitting separate splines to distinct intervals of the predictor variables. A spline is a function that is defined on an interval and may be used to approximate another function. It consists of simple functions, defined on subintervals, and these are joined at their endpoints with a suitable degree of smoothness. A spline is built by dividing regions on the X-axis. The point where the behavior of the function changes is called a knot. In the case of a classical spline, the knots are determined beforehand and are spaced at regular intervals. However, in MARS, basis functions explore the possibility of a knot location. By employing basis functions to hunt for knots, certain regions of a particular variable are blocked, which enables MARS to highlight on the subsets of data. This mechanism allows MARS to identify strong relations amongst the variables. MARS can be employed without making any assumptions beforehand. The famous "hockey stick" function explains the way the basis functions work. The hockey stick basis function projects variable X to a new variable X* as under:

max (0, X-c), or
max (0, c-X)

where X* is set to zero for all values of X up to some threshold value c, and X* is equal to X for all values of X greater than c. X* is equal to the amount by which X exceeds threshold c. This kind of rigorous search takes place incrementally to arrive at an

optimum generalized cross validation (GCV). The GCV criterion, introduced by Craven and Wahba (1979) is represented by the following equation:

$$GCV(M) = \frac{1}{N}\sum_{i=1}^{N}\frac{[y_i - f_M(x_i)]^2}{[1-\frac{C(M)}{N}]^2} \qquad 4.1$$

where C(M) is the cost-complexity measure of a model, containing M basis functions. In a linear regression model, C(M) = M. The measure of mean squared error, MSE, is calculated by dividing the sum of squared errors by N-M instead of by N. The GCV formula enables C(M) > M; which enables "charging" each basis function with more than one degree of freedom. The basis functions are similar in nature to the variable combinations, which are utilized in principal component analyses. After the selection of the number of basis functions and knots that best fit the model, a final regression equation is given based on the basis functions.

The process of selecting significant factors is a two-stage process. The least important factors are removed from the initial model, created by a forward knot selection phase, in the second phase of model development. MARS detects the basis function, which affects the accuracy of the model with the residual sum of squares criterion. After the model is pruned, a second process begins in order to remove the redundant basis functions. Several iterations are conducted until all unimportant basis functions are eliminated from the model. Mean squared error (MSE) values are observed for the different models that may be prepared. With the addition of each basis function, the MSE value decreases. The upper limit of the number of knots may be 3-4 times the number of basis functions of an optimal model (Abraham et al., 2001a). The degree of freedom has an impact on the final model performance. The higher the degrees of freedom, the smaller the final model, and vice versa. There are three possible ways in which an optimal number of degrees of freedom may be determined. It can be done manually, or automatically, by selecting a portion of the data set, or by using a 10-fold cross validation.

MARS detects variable impact with analysis of variance (ANOVA), thereby allowing us to choose the variables that affect model performance (Friedman, 1991; Sephton, 2001). Setting a higher limit for the number of knots is a standard practice. This enables the development of the best model. Rigorous search through basis functions helps identify transformations of the data that affect model performance (Abraham et al., 2001a). Irregular functions can be fitted automatically with the aid of regression splines (Courtois et al., 2000). These studies bring to light that MARS is a robust data-mining tool that can help identify patterns if provided with sufficient training data. In this exploratory study, the ability of MARS was examined to estimate pesticide concentrations at three depths in the soil profile.

## 4.4 MATERIALS AND METHOD

The reader is referred to the third chapter of this thesis on DRAINMOD-P for details on this section. Only those portions, typical to this paper, have been included in this section to avoid repetition.

### 4.4.1 Data Acquisition

The inputs to the model were selected based on the work done by previous researchers (Yang et al., 1997f and Tafazoli, 2002). The input variables for the model included Julian day of the year, days after application of the pesticide, measured herbicide concentrations, cumulative figures for rainfall depth, air temperature, soil temperature and potential evapotranspiration. The weather data were taken every day for all three years, which included the precipitation and potential evapotranspiration. The data comprised 416 records, out of which 128 records were from 1992; 160 from 1993 and 128 from 1994.

### 4.4.2 Herbicide Analysis

The reader is referred to the third chapter on DRAINMOD-P for details on herbicide analysis. Metribuzin and metolachlor were sampled on the same dates as atrazine. For further details, the reader is referred to papers by Tan et al. (1993); Drury et al.(1996) and Gaynor et al. (1995; 2000;2001).

### 4.4.3 Development of the MARS Model

In this study, MARS $^{TM}$ version 2.0 for Windows (Salford Systems, San Deigo, CA) was used in order to implement the multivariate adaptive regression splines to estimate the pesticide concentrations in the soil. Building the model commenced with the selection of the predictor and target variables. Julian day, days after pesticide application, cumulative rainfall (mm), cumulative soil temperature ($^{O}$C), cumulative air temperature ($^{O}$C), cumulative potential evapotranspiration (mm day$^{-1}$) and pesticide concentration (μg kg$^{-1}$) were selected as input variables, while pesticide concentration (μg kg$^{-1}$) was the only output variable. MARS assigns a significance factor to the various input parameters used in model development. This provides a guideline for choosing more appropriate variables for modeling. Total interaction amongst the variables was allowed during model development. Separate analyses were performed for the different water table management and tillage practices for all the sixteen plots. To begin with, the default parameters such as testing up to three degrees of freedom, speed accuracy of four, etc., were used to develop the MARS models. This is in line with suggestions made by previous researchers while conducting similar implicit modeling studies (Salehi et al., 1998 and Lacroix et al., 1997). Model refinement was accomplished using some of the options provided by the MARS software. The number of basis functions was changed to two to four times the number of predictor variables, and the different options were checked to ensure that they were in accordance with the recommendations in the MARS manual (Salford Systems, San Deigo, CA). Some of the criteria employed in model refining was changing the number of basis functions, specifying a minimum distance between the knots, allowing select interactions, and reducing the speed factor. The speed

factor was lowered to allow more accuracy in model development. Maximum interactions were increased from one to six, to allow all six predictor variables to interact. Interim results were observed while making changes to each of the parameters. No limit was attached while processing the number of records. The minimum observation between knots was increased from zero to three, to study their impact on the model. While testing, the default parameter for degree of freedom was kept at three. However, one can further explore by forbidding transformations between the selected variables or using a penalty on the number of distinct variables to achieve better results. Model testing during development was performed by using the in-built ten-fold cross validation because of limited data size. This was in accordance to the CART suggestions (Salford Systems, San Deigo, CA; Salehi et al., 2000b).

Another uniqueness of MARS is its power to assign a degree of importance to all the variables being used in the development of the model. For instance, in the moldboard plow with drainage and sub-irrigation and controlled drainage, the order of importance of the variables, for the 0 to 10 cm depth for atrazine, was found to be as shown in Table 4.1. The cumulative soil temperature was found to be the most important variable, whereas the cumulative potential evapotranspiration was the least effective one. Each model input is assigned a degree of importance and hence it is easier to determine the factors that had a major impact on the predictor variable. A typical MARS model, developed in this study, is given in Table 4.2. This represents the equation based on the basis functions and can be modeled with ease. MARS models are simplistic in their approach, highly comprehensible and easy to execute in a personal computer.

In order to compare the results obtained from MARS with those obtained from DRAINMOD-P, a process-based model, independently collected atrazine data over a period of three years was used. The next section briefly explains DRAINMOD-P. For additional details, the reader is referred to Chapter 3 on DRAINMOD-P.

### 4.4.4 DRAINMOD-P

DRAINMOD-P was developed by using DRAINMOD (Skaggs, 1978) for hydrology and the pesticide component of PESTFADE (Clemente, 1991) for pesticide simulations. The details of DRAINMOD-P are given in the chapter on DRAINMOD-P. DRAINMOD is a well-known program used for the design and evaluation of water table management systems in North America and has been widely used in several regions in the United States and Canada. DRAINMOD was developed at North Carolina State University in the mid 1970's (Skaggs, 1978, 1980). DRAINMOD was chosen for its user-friendliness, fast execution times, and accuracy in hydrological estimations. The pesticide component of PESTFADE is capable of dealing with sorption, a significant phenomenon in determining the ultimate fate of a solute, by taking into consideration both the conventional and Gamble kinetics (Gamble et al., 1992; Li et al., 1996) approaches. While the conventional approach adopts a fixed sorption coefficient, the Gamble approach actually calculates it, taking into consideration the labile and nonlabile contributions (Gamble et al., 1992; Li et al., 1996). Since the Gamble kinetics has only been developed for atrazine, the results obtained from DRAINMOD-P were compared with those from MARS for atrazine. This provides a further insight into the performance of both models.

### 4.4.5 Statistical Analysis

The performance of the model was checked by calculating three statistical parameters.
The standard error is a quantitative estimation of the dispersion that exists between the observed and predicted values. The equation used to calculate the standard error is given by the following equation (Singh et al., 1994):

$$SE = \sqrt{\frac{\sum (O_i - P_i)^2}{n}} \qquad 4.2$$

where $O_i$ is the measured water table depth, $P_i$ is the predicted water table depth, n is the number of days. The value of standard error is best when it is lowest.

The root mean square error, RMSE, a good indicator for model performance, was calculated as per El Sadek et al. (2001):

$$RMSE = \sqrt{\frac{\frac{1}{n}\sum_{i=1}^{n}(P_i - O_i)^2}{\overline{O}}} \qquad 4.3$$

where $P_i$ is the predicted value, $O_i$ is the observed values, i is the event and n is the number of observations. The value of RMSE varies between 0 and 1 signifying a better fit.

The model efficiency evaluates the error relative to the natural variation in the observed values (Vanclooster et al., 2000 and El-Sadek et al., 2001). It can be calculated as:

$$EF = \frac{\left(\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2\right)}{\sum_{i=1}^{n}(O_i - \overline{O})^2} \qquad 4.4$$

An efficiency of 1.0 indicates a correct estimate, while a zero shows the inefficiency of the model. In other words, the higher the efficiency the better the model. A negative sign indicates the inability of the model in making predictions.

## 4.5 RESULTS AND DISCUSSION

The estimated concentrations of the three herbicides, viz. atrazine, metribuzin and metolachlor, using the MARS model at three different depths were plotted against the measured field data. Figs. 4.1 to 4.8 represent the success of MARS in predicting the herbicide concentrations. MARS predictions were not very acceptable as is seen in Fig. 4.9. To illustrate the capabilities of the MARS model, out of all the four different tillage practices and two different water table treatments, only the case of moldboard plow with controlled drainage and sub-irrigation is discussed in more detail. The results obtained from the statistical tools are displayed in Table 4.3 for all the other treatments. However, the results are not discussed at length for these treatments for the sake of brevity. Moldboard plow with controlled drainage and subirrigation was also chosen in order make comparisons with the results obtained from DRAINMOD-P. Moreover, previous studies (Tafazoli, 2002) performed with ANN have been validated with the same field data and the performance of MARS over ANN could be easily adjudged. The predictability of the MARS model in simulating atrazine, metribuzin and metolachlor at three different soil depths is discussed in this chapter, followed by a comparison between the implicit model, MARS, and the process-based model, DRAINMOD-P, in simulating atrazine concentrations.

### 4.5.1 Results at the 0-10 cm depth

Figs. 4.1 to 4.3 contain the graphical representations of results obtained for the conventional tillage treatment with controlled drainage and sub-irrigation for 0-10 cm soil depth. It is observed from Fig. 4.1 that there is close agreement between the observed and predicted atrazine concentrations with sporadic minor variations. A standard error (SE), root mean square error (RMSE) and model efficiency (EF) of 28.79 $\mu g\ kg^{-1}$, 0.13, and 99% were obtained, respectively, which shows the closeness of the simulated values to the measured data. It is also reflected in Fig. 4.2 that there is no significant difference between the predicted and observed concentrations of metribuzin. The simulated data follow the trend of the observed values throughout the period. A SE,

a RMSE, and EF of 46.18 μg $kg^{-1}$, 0.50 and 85% were obtained, respectively. Moreover, it is also seen from Fig. 4.3 that the MARS model predicted well for metolachlor applications with prediction efficiency of 96%, RMSE of 0.15 and SE of 64.40 μg $kg^{-1}$.

For the rest of the treatments, the SE and the RMSE were calculated, as shown in Table 4.3. The treatments are abbreviated as "MB" for moldboard plow, MBIC for moldboard plow with intercropping, "SS" for soil saver technique and "SSIC" for soil saver with intercropping. The letters "W" and "D" denote the free drainage and controlled drainage with sub-irrigation conditions. The SE, RMSE, and EF values for atrazine varied from 32.43 to 89.16 μg $kg^{-1}$, 0.15 to 0.32, and 89 to 99%, respectively. The SE and RMSE values for metribuzin varied from 19.85 to 49.13 μg $kg^{-1}$ and 0.25 to 0.50, while the model efficiencies varied from 78 to 99%. The SE and RMSE values for metolachlor varied from 64.40 to 171.12 μg $kg^{-1}$ and 0.11 to 0.28, while the EF varied from 83% to 96%.

The high model efficiencies indicate the excellent performance of MARS at the 0-10 cm depth in predicting pesticide concentrations. Similarly, the low values of SE and RMSE indicate less variation over the magnitudes of the observed and predicted datasets. These results are also in close coordination with the results obtained by Tafazoli et al. (2002) with ANNs where the pesticide simulations were also very good. Higher values of SE and RMSE and lower efficiencies indicate the inability of MARS to learn from the measured data, as seen in Table 4.3 in a few cases. A close look at Table 4.5 also reveals that these are the instances where the standard deviation values for the measured data are high, indicating difficulty for the MARS model to learn well from the measured data.

### 4.5.2 Results at the 10-15 cm depth

As for the 10-15 cm depth, the results in Figs. 4.4 to 4.6 indicate the closeness in the pattern between the observed and predicted concentrations for atrazine, metribuzin and metolachlor for the moldboard plow and controlled drainage and sub-irrigation conditions. However, sporadic minor variations are also apparent on certain events,

while the SE was 8.33, 1.34, and 21.17 μg $kg^{-1}$, the RMSE was 0.48, 0.59, and 0.51 for atrazine, metribuzin and metolachlor, respectively. The model efficiency was 71% for atrazine and 77% for both metribuzin and metolachlor.

While the SE ranged from 3.52 to 10.19 μg $kg^{-1}$, the RMSE values for atrazine varied between 0.36 to 0.63, and the model efficiencies ranged from 62 to 77%. For metribuzin, the SE and RMSE values for metribuzin varied from 0.61 to 2.15 μg $kg^{-1}$ and from 0.45 to 1.04 respectively. The efficiencies varied from 51 to 77% indicating high model efficiencies. Only three cases were identified with zero and low efficiency in the case of metribuzin. There were three cases where the model efficiencies were either low or zero in the case of both atrazine and metribuzin. RMSE and SE in all these cases are high, which also explains the lower efficiency. These also happened to be the cases where the MARS model was not able to simulate at all. It appears that too much noise in the data made it very difficult for MARS to learn from it. The RMSE values for metolachlor varied from 0.33 to 1.03. The efficiencies varied from 49% to 83%, except for two occasions where the efficiency was either very low or zero. A high SE and RMSE indicates the reason for lower efficiency, as is seen from Table 4.3. From Table 4.5, it is also observed that the SD from the observed mean is also high in these two cases.

The low SE and RMSE values certify the high dexterity with which MARS has succeeded in its simulations. High model efficiencies further ascertain the robustness of MARS, especially keeping in mind the stringency involved in this test. Similar results were also observed by Tafazoli et al. (2002) for ANNs.

### 4.5.3 Results at the 15-20 cm depth

Figs. 4.7 to 4.9 display the results for atrazine, metribuzin and metolachlor at the 15-20 cm depth for the conventional tillage and controlled drainage with subirrigation treatment. The simulated values follow the same trend as the observed values, barring a few instances where the concentrations may be slightly underestimated. SE of 3.44 μg $kg^{-1}$, 0.0 and 5.92 and RMSE of 0.45, 1.76 and 0.37 were obtained for atrazine,

metribuzin and metolachlor, respectively. The model efficiencies were 73, 86 and 0%, respectively. Fig. 4.9 shows the results for metolachlor at the 15-20 cm depth. The simulated values do not seem to follow the pattern of the observed values. The SE is as high as 5.92 $\mu g\ kg^{-1}$, and the RMSE value obtained was 0.37. However, a closer look into the measured values of metolachlor brings to light the fact that the observed values also differed over a modest range of approximately 0-12 $\mu g\ kg^{-1}$. Higher variations in the observed concentrations may be one of the causes for discrepancy. This is further confirmed by the standard deviation, which is also high, as is seen in Table 4.5.

For atrazine, the RMSE values varied from 0.45-1.15, while the SE ranged in between 2.82 to 10.78 $\mu g\ kg^{-1}$, and the model efficiencies varied from 41 to 73%. In the case of metribuzin, the SE and RMSE model efficiencies varied between 0.61 to 1.24 $\mu g\ kg^{-1}$, 0.27 to 1.81 and 53 to 88% for all the other treatments. The SE, RMSE and EF for metolachlor lay in the range of 0.37 to 1.39 $\mu g\ kg^{-1}$, 0.40-1.39 and 42 to 95% respectively. There were one, two and three cases where MARS did not seem to learn from the measured concentrations in the case of atrazine, metribuzin and metolachlor, respectively. These also appear to be the ones with high variations in the observed data, as is seen in Table 4.5.

It can be concluded that MARS models have largely been able to capture the movement of all three herbicides for the three measurement depths. Results obtained with ANNs to simulate pesticide transport by Tafazoli et al. (2002) reveal that ANNs were not able to perform efficiently at the 20 cm depth. On the contrary, this study indicates that MARS can perform well, even at lower depths with very limited data.

### 4.5.4 Comparison with DRAINMOD-P

Both visual comparison and statistical methods were used to compare the MARS results with those of DRAINMOD-P. First, a visual comparison was drawn with the results obtained from MARS with those of DRAINMOD-P. Since DRAINMOD-P includes two mechanisms to simulate the sorption mechanism, MARS results are discussed for both

approaches. While the conventional approach assumes a constant partition coefficient for atrazine, the Gamble approach calculates it based on other parameters. Since the Gamble kinetics was developed for atrazine only, the discussion is confined to this herbicide.

Fig. 4.10 shows a comparison between the predictions made by the MARS and DRAINMOD-P models for atrazine at the 0-10 cm depth for 1992-94. In these graphs "con" refers to the conventional approach while "gam" refers to the Gamble approach, used in DRAINMOD-P, and "mea" represents the average of the measured values from plot numbers 8 and 11, which were the moldboard plow with controlled drainage sub-irrigation treatment. The simulated concentration values by the process-based model and the implicit model seem to follow the path taken by the measured values, as is evident from the graph. The conventional approach seems to overestimate whilst the Gamble approach appears to underestimate the measured concentrations. MARS appeared to predict measured concentrations more accurately than either the conventional or the Gamble kinetics methods.

The statistical analysis between DRAINMOD-P and MARS was performed using the SE, RMSE and EF tests (Table 4.4). SE at the 10 cm depth varied between 37.46 to 111.43 $\mu g\ kg^{-1}$ in the conventional approach using DRAINMOD-P, and 78.42 to 109.91 for the Gamble kinetics approach. The SE from the MARS simulations lies between 32.43 to 89.16 $\mu g\ kg^{-1}$. The RMSE values at the 10 cm depth for the period 1992 to 1994 ranged between 0.15 to 0.32 when MARS was used, as against the high RMSE values from 0.41-1.28 for the same period from DRAINMOD-P which used the conventional approach. The results from 1992 and 1994 better compare with lower RMSE values of 0.64 and 0.41, respectively. With the Gamble kinetics approach, the RMSE values are within a lower range, between 0.77-0.88 when compared to the conventional approach and can therefore be said to perform closer to the MARS simulations and the observed values. EF from DRAINMOD-P at the 0-10 cm depth yielded positive values for the conventional approach in 1992 and the Gamble approach in 1993 with EF equal to 29% and 45% respectively. All other instances yielded negative results for EF. MARS on the other

hand, has EF in the range of 89 to 99%, which signifies the accuracy with which MARS was able to simulate the pesticide fate, even with very limited data.

Fig. 4.11 depicts the atrazine simulations results at the 10-15 cm depth for 1992-94. The simulations made by DRAINMOD-P and MARS follow the same trend as the observed values. The conventional and Gamble approaches are often observed to underestimate. MARS results are in closer agreement with those of the observed concentrations.

At the 10-15 cm depth, the SE ranged between 3.5-17.07 $\mu g\ kg^{-1}$ for DRAINMOD-P when compared to 3.52-10.19 for MARS. The SE in the case of the Gamble approach is lower than the conventional one. The RMSE values ranged between 0.37 to 0.93, while the RMSE values for MARS lie in the range 0.36-0.63. The RMSE values for both approaches yielded similar results for 1992, and the conventional approach appears to perform better in 1993, while the Gamble method appears to do better in 1994 at this depth. EF for the conventional method in 1993 is the only commendable value obtained from this test. All the others are indications that DRAINMOD-P has not yielded satisfactory results at the 10-15 cm depth. On the contrary, EF figures from MARS lie between 62% to 77%, which shows greater predictability with MARS.

The SE and RMSE values are in good agreement with each other when DRAINMOD-P and MARS results are compared. However, a stringent test, like the EF test, signifies the higher success rate of MARS in simulating pesticide concentrations at the 10-15 cm depth.

Fig. 4.12 shows the results for atrazine obtained at the 15-20 cm depth for 1992-94. All the simulations follow the track of the observed pesticide concentrations. While the Gamble predictions are much lower in 1992 and 1994, they seem to be higher in 1993. The conventional simulated values are slightly lower in 1992 and 1994, while they are higher in 1993. Once again, MARS is seen to make the closest predictions.

A comparison is once again drawn with the statistical tests. The SE ranges from 0.41 to 8.58 $\mu g\ kg^{-1}$, when compared to the SE values of 2.82 to 10.78 $\mu g\ kg^{-1}$ for MARS. The SE values are lower in the case of the Gamble kinetics approach when compared to the conventional ones. RMSE lies in between 0.65 to 1.25 for DRAINMOD-P simulations while the ones from MARS are in between 0.45 to 1.15. The conventional approach in 1993 is the best performer from DRAINMOD-P results since it has the lowest RMSE of 0.65. EF in DRAINMOD-P simulations are either negative or are highly positive thereby indicating that the model has not performed successfully. However, EF from MARS lies in the range of 43% to 73% with only one instance of failure.

In conclusion, MARS has accomplished better results when compared to DRAINMOD-P simulations at the 20 cm depth as is evident from the statistical analysis. It is even more impressive when one considers the limited amount of data that was used to develop the model and also a rather simplistic set of inputs was used with the MARS modeling. The execution times required for the MARS models were invariably less than one second, which provides good evidence of its fast operational speed.

## 4.6 CONCLUSIONS

Pesticide concentrations were modeled in this study through a new data-mining tool, called Multivariate Adaptive Regression Splines, MARS. The data consisted of pesticide concentrations during 1992-94, collected at the Eugene F. Whelan Experimental Farm (Agriculture Canada, Woodslee, Ontario, Canada). The experiments consisted of four tillage and two water table management practices. The MARS model developed in this study simulated the pesticide concentrations with high accuracy. The prioritization of input parameters made the selection of inputs to the model an easy task. MARS models needed very few input parameters in comparison to the large number of parameters required in DRAINMOD. While DRAINMOD-P for the Gamble approach took about eight hours for a single simulation, the same simulation took less than a minute with the conventional approach. It can be safely declared that the execution time is admirably less in the case of MARS models since a one-year simulation lasted for a few seconds only.

MARS also yielded superior results when compared to the DRAINMOD-P simulations for atrazine. The results were closer to the observed values at the 0-10 cm and the 10-15 cm depths for 1992-94 when compared to those obtained from DRAINMOD-P. At the 15-20 cm depth, MARS outperformed the mathematical model. In a study, Tafazoli (2002) had concluded that ANNs estimated pesticide concentrations very well at the 10 cm and 15 cm depths but were not able to simulate pesticide movement at the 20 cm depth. The RMSE was less than 0.1 at the 0-10 cm and 10-15 cm depths (Tafazoli, 2002). These results compare well with those obtained in this study where, under the same field conditions, the RMSE was 0.15 at the 0-10 cm depth and 0.51 at the 10-15 cm depth. At the 15-20 cm depth, the RMSE obtained was 0.37. In fact, MARS has outperformed ANNs, even at the 20 cm depth. MARS can thus be regarded as an effective tool in modeling solute transport and it is likely that better predictions may be possible with larger data sets. However, like artificial neural networks, MARS models require both input and output data *a priori*, and generates site-specific models only.

**Table 4.1 Variable importance**

Significance attached to the variables in predicting the pesticide concentrations in the moldboard plow with drainage and sub-irrigation and controlled drainage, were as under for the 0 to 10 cm depth for atrazine:

| | | |
|---|---|---|
| *Cumulative soil temperature | : | 100.000 |
| Days after pesticide application | : | 91.954 |
| Cumulative air temperature | : | 76.782 |
| Julian day | : | 41.624 |
| Cumulative rainfall | : | 29.327 |
| Cumulative potential evapotranspiration | : | 15.027 |

* Units are in percentage.

**Table 4.2 Basis function of a typical MARS model**

A set of basis functions (BFs) to predict pesticide concentrations in the soil at a depth of 10 cm by a MARS model using the soil saver and controlled drainage with subirrigation are shown below:

BF1 = max (0, CSOILTEM - 82.800)
BF3 = max (0, DAYAFTER - 4.000)
BF4 = max (0, 4.000 - DAYAFTER )
BF5 = max (0, CRAIN - 0.750) * BF4
BF6 = max (0, 0.750 - CRAIN ) * BF4
BF7 = max (0, JDAY - 194.000)
BF8 = max (0, 194.000 - JDAY )
BF10 = max (0, 38.500 - CRAIN )
BF11 = max (0, DAYAFTER - 6.000) * BF10
BF12 = max (0, 6.000 - DAYAFTER ) * BF10
BF13 = max (0, JDAY - 141.000) * BF10
BF15 = max (0, DAYAFTER - .372417E-06) * BF8
BF16 = max (0, CSOILTEM - 15.610) * BF6

Y = 473.453 - 0.218 * BF1 - 1.911 * BF3 + 2.666 * BF5
- 182.478 * BF6 + 4.537 * BF7 - 6.592 * BF10
+ 2.154 * BF11 + 1.499 * BF12 - 1.739 * BF13
- 0.128 * BF15 + 5.152 * BF16;

JDAY, Julian day
DAYAFTER, days after pesticide application
CRAIN, cumulative rainfall
CAIRTEM, cumulative air temperature
CSOILTEM, cumulative soil temperature
CPET, cumulative potential evapotranspiration

**Table 4.3 Statistical parameters for 1992-1994 as obtained from MARS**

| | Atrazine | | | Metribuzin | | | Metolachlor | | |
|---|---|---|---|---|---|---|---|---|---|
| Treatment | SE | RMSE | EF | SE | RMSE | EF | SE | RMSE | EF |
| **0-10 cm** | ($\mu g\ kg^{-1}$) | | | ($\mu g\ kg^{-1}$) | | | ($\mu g\ kg^{-1}$) | | |
| MBD* | 28.79 | 0.13 | 99.00 | 46.18 | 0.50 | 85.00 | 64.40 | 0.15 | 96.00 |
| MBW | 40.44 | 0.18 | 99.00 | 46.23 | 0.49 | 78.00 | 93.55 | 0.22 | 92.00 |
| MBICD | 89.16 | 0.32 | 89.00 | 44.13 | 0.41 | 88.00 | 171.12 | 0.11 | 83.00 |
| MBICW | 83.69 | 0.31 | 94.00 | 35.58 | 0.32 | 92.00 | 134.00 | 0.28 | 89.00 |
| SSD | 32.43 | 0.15 | 98.00 | 19.85 | 0.25 | 99.00 | 92.78 | 0.26 | 91.00 |
| SSW | 32.80 | 0.15 | 98.00 | 22.89 | 0.27 | 96.00 | 73.32 | 0.20 | 95.00 |
| SSICD | 37.63 | 0.16 | 97.00 | 35.74 | 0.37 | 90.00 | 80.16 | 0.19 | 95.00 |
| SSICW | 47.73 | 0.19 | 96.00 | 49.13 | 0.50 | 84.00 | 99.06 | 0.23 | 93.00 |
| **10-15 cm** | | | | | | | | | |
| MBD | 8.33 | 0.48 | 71.00 | 1.34 | 0.59 | 77.00 | 21.17 | 0.51 | 63.00 |
| MBW | 10.19 | 0.63 | 33.00 | 1.02 | 0.45 | 73.00 | 21.33 | 0.55 | 83.00 |
| MBICD | 0.00 | 0.80 | 0.00 | 2.15 | 0.77 | 51.00 | 19.63 | 0.55 | 49.00 |
| MBICW | 4.88 | 0.36 | 69.00 | 1.02 | 0.45 | 76.00 | 10.35 | 0.33 | 83.00 |
| SSD | 5.06 | 0.43 | 62.00 | 1.85 | 1.04 | 0.00 | 0.00 | 1.03 | 22.00 |
| SSW | 3.52 | 0.36 | 77.00 | 0.61 | 0.55 | 0.00 | 0.00 | 0.87 | 79.00 |
| SSICD | 5.22 | 0.49 | 68.00 | 1.30 | 0.76 | 69.00 | 9.17 | 0.45 | 73.00 |
| SSICW | 0.00 | 0.90 | 0.00 | 0.00 | | 35.00 | 18.81 | 0.88 | 0.00 |
| **15-20 cm** | | | | | | | | | |
| MBD | 3.44 | 0.45 | 73.00 | 0.00 | 1.76 | 86.00 | 5.92 | 0.37 | 0.00 |
| MBW | 3.56 | 0.45 | 70.00 | | 0.27 | 77.00 | 8.61 | 0.55 | 95.00 |
| MBICD | 5.97 | 0.77 | 41.00 | 1.24 | 1.31 | 74.00 | 10.34 | 0.75 | 58.00 |
| MBICW | 3.24 | 0.44 | 70.00 | 0.00 | 1.28 | 0.00 | 0.00 | 1.39 | 0.00 |
| SSD | 10.78 | 1.15 | 43.00 | 0.96 | 1.08 | 88.00 | 4.67 | 0.40 | 58.00 |
| SSW | 2.82 | 0.49 | 59.00 | 0.00 | 1.81 | 61.00 | 3.83 | 0.42 | 0.00 |
| SSICD | 0.00 | 1.00 | 0.00 | 0.64 | 0.98 | 53.00 | 5.65 | 0.68 | 42.00 |
| SSICW | 3.62 | 0.58 | 61.00 | 0.61 | 0.95 | 0.00 | 0.00 | 1.11 | 46.00 |

*MBD, moldboard plow with controlled drainage subirrigation; MBW, moldboard plow with free drainage; MBICD, moldboard plow with intercropping and free drainage; MBICW, moldboard plow with intercropping and controlled drainage subirrigation; SSD, soil saver with controlled drainage subirrigation; SSW, soil saver with free drainage; SSICD, soil saver with intercropping and free drainage; SSICW, soil saver with intercropping and controlled drainage and subirrigation; RMSE, Root mean square error; SE, Standard error; EF, Model efficiency

**Table 4.4 DRAINMOD-P results for 1992-94**

| **0-10 cm depth** | | | | | | |
|---|---|---|---|---|---|---|
| | Conventional | | | Gamble kinetics | | |
| | SE* | RMSE | EF | SE | RMSE | EF |
| 1992 | 66.76 | 0.64 | 0.29 | 81.08 | 0.77 | -0.04 |
| 1993 | 111.43 | 1.28 | -0.17 | 109.91 | 0.88 | 0.45 |
| 1994 | 34.46 | 0.41 | nil | 78.42 | 0.77 | nil |
| **10-15 cm depth** | | | | | | |
| | Conventional | | | Gamble kinetics | | |
| | SE | RMSE | EF | SE | RMSE | EF |
| 1992 | 17.07 | 0.92 | -0.75 | 2.13 | 0.93 | -0.76 |
| 1993 | 8.45 | 0.55 | 0.51 | 8.42 | 0.72 | -1.59 |
| 1994 | 3.68 | 0.81 | 52.71 | 3.5 | 0.37 | 51.78 |
| **15-20 cm depth** | | | | | | |
| | Conventional | | | Gamble kinetics | | |
| | SE | RMSE | EF | SE | RMSE | EF |
| 1992 | 8.58 | 1.04 | -0.88 | 0.41 | 0.95 | -0.56 |
| 1993 | 3.88 | 0.65 | -0.39 | 3.84 | 1.25 | -4.1 |
| 1994 | 0.41 | 0.99 | 1.81 | 0.42 | 0.91 | 1.7 |

*SE, Standard error; RMSE, Root mean square error; EF, Model efficiency

**Table 4.5 Mean and standard deviation in observed values from 1992-1994**

| | Atrazine | | Metribuzin | | Metolachlor | |
|---|---|---|---|---|---|---|
| **Treatment** | **Mean** | **SD** | **Mean** | **SD** | **Mean** | **SD** |
| **0-10 cm** | ($\mu g\ kg^{-1}$) | ($\mu g\ kg^{-1}$) | ($\mu g\ kg^{-1}$) | ($\mu g\ kg^{-1}$) | ($\mu g\ kg^{-1}$) | ($\mu g\ kg^{-1}$) |
| MBD* | 222.66 | 28.50 | 89.94 | 45.73 | 408.30 | 63.79 |
| MBW | 225.26 | 40.04 | 93.11 | 45.78 | 413.09 | 92.62 |
| MBICD | 271.07 | 88.28 | 105.54 | 43.70 | 482.87 | 169.43 |
| MBICW | 267.11 | 82.86 | 109.96 | 35.23 | 476.70 | 132.68 |
| SSD | 208.29 | 32.11 | 79.19 | 19.66 | 353.12 | 91.86 |
| SSW | 215.25 | 32.48 | 83.87 | 22.66 | 366.63 | 72.60 |
| SSICD | 239.22 | 37.74 | 95.64 | 35.39 | 421.49 | 79.37 |
| SSICW | 241.47 | 47.26 | 96.56 | 48.64 | 418.81 | 98.09 |
| **10-15 cm** | | | | | | |
| MBD | 17.03 | 8.23 | 40.61 | 20.93 | 2.23 | 1.32 |
| MBW | 17.27 | 10.99 | 37.84 | 21.10 | 2.23 | 1.01 |
| MBICD | 19.16 | 15.47 | 34.81 | 19.41 | 2.74 | 2.13 |
| MBICW | 16.12 | 5.81 | 30.64 | 10.23 | 2.23 | 1.01 |
| SSD | 11.41 | 5.00 | 23.61 | 24.51 | 1.74 | 1.83 |
| SSW | 9.68 | 3.48 | 20.22 | 17.88 | 1.08 | 0.60 |
| SSICD | 10.43 | 5.16 | 19.76 | 9.07 | 1.68 | 1.29 |
| SSICW | 10.96 | 9.96 | 20.96 | 18.60 | nil | nil |
| **15-20 cm** | | | | | | |
| MBD | 7.41 | 3.40 | 15.83 | 5.85 | 1.21 | 2.16 |
| MBW | 7.69 | 3.52 | 15.21 | 8.51 | 0.88 | 0.24 |
| MBICD | 7.58 | 5.90 | 13.39 | 10.22 | 0.92 | 1.22 |
| MBICW | 7.16 | 3.21 | 14.87 | 20.97 | 0.92 | 1.19 |
| SSD | 9.20 | 10.66 | 11.38 | 4.62 | 0.86 | 0.95 |
| SSW | 5.59 | 2.78 | 8.83 | 3.78 | 0.78 | 1.42 |
| SSICD | 5.71 | 5.76 | 8.07 | 5.59 | 0.63 | 0.63 |
| SSICW | 6.12 | 3.58 | 10.32 | 11.56 | 0.63 | 0.61 |

*MBD, moldboard plow with controlled drainage subirrigation; MBW, moldboard plow with free drainage; MBICD, moldboard plow with intercropping and free drainage; MBICW, moldboard plow with intercropping and controlled drainage subirrigation; SSD, soil saver with controlled drainage subirrigation; SSW, soil saver with free drainage; SSICD, soil saver with intercropping and free drainage; SSICW, soil saver with intercropping and controlled drainage and subirrigation; SD, Standard deviation

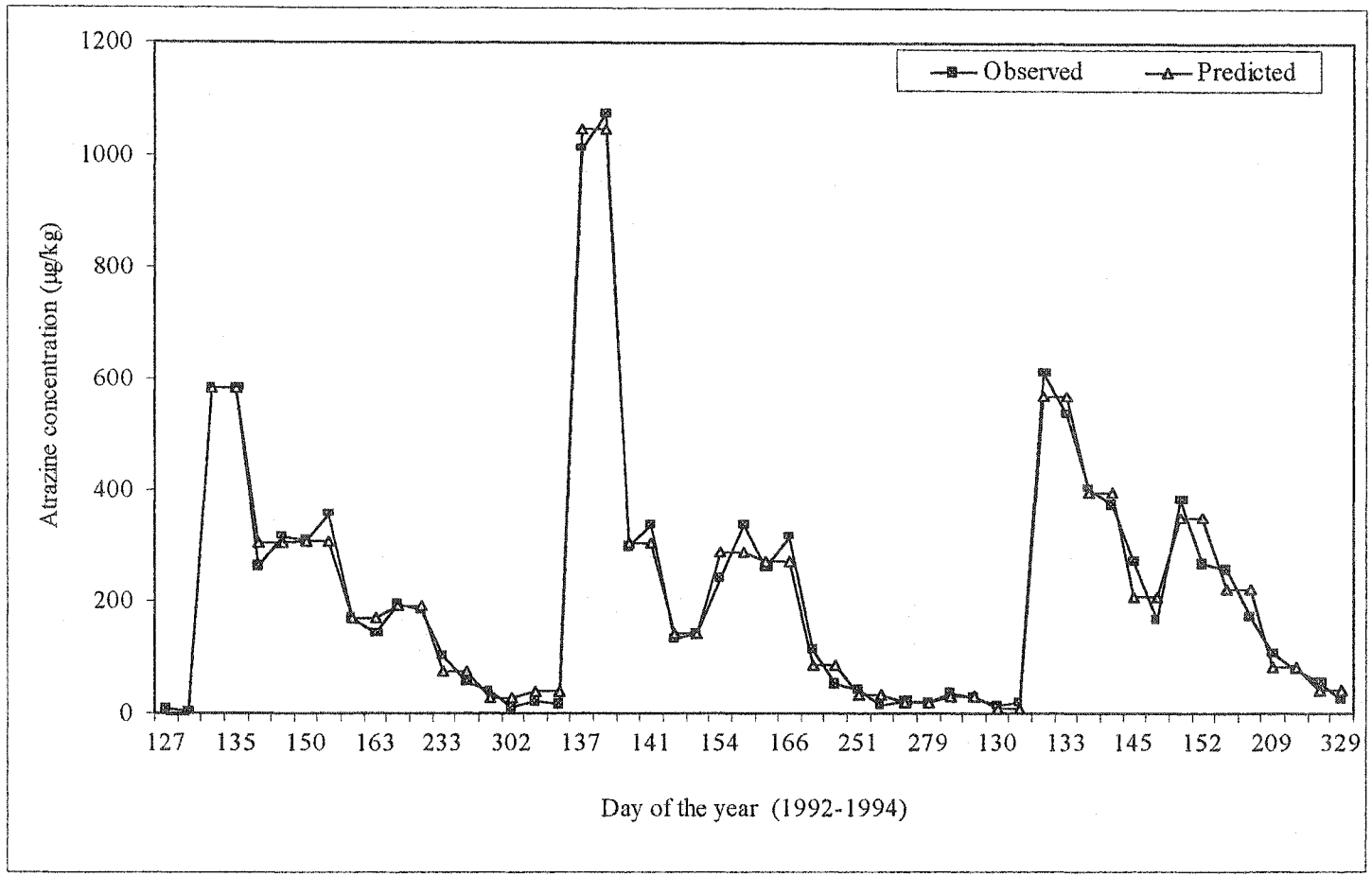


**Fig 4.1 Atrazine simulation by MARS at 0-10 cm depth**

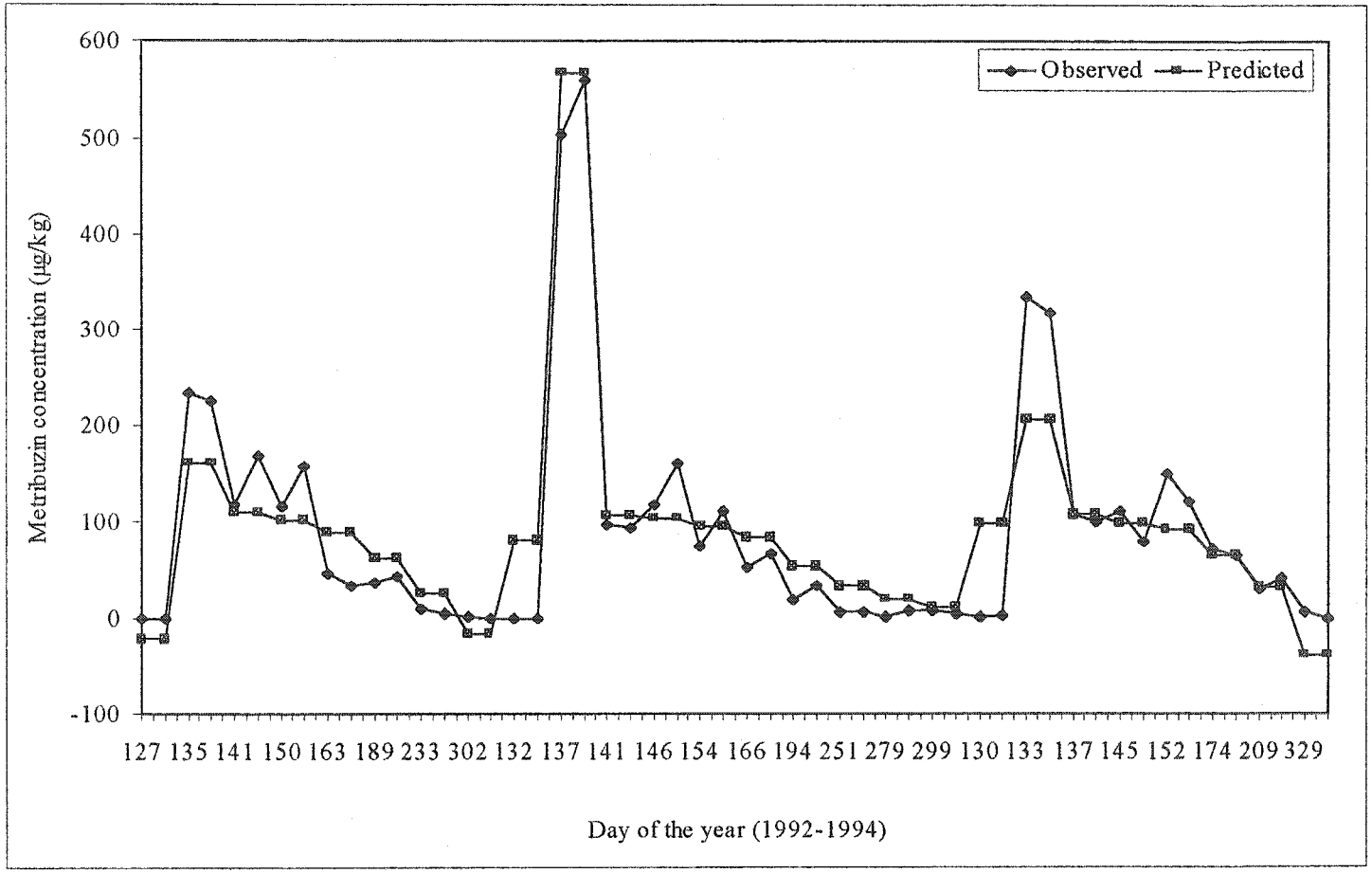


**Fig 4.2 Metribuzin simulation by MARS at 0-10 cm depth**

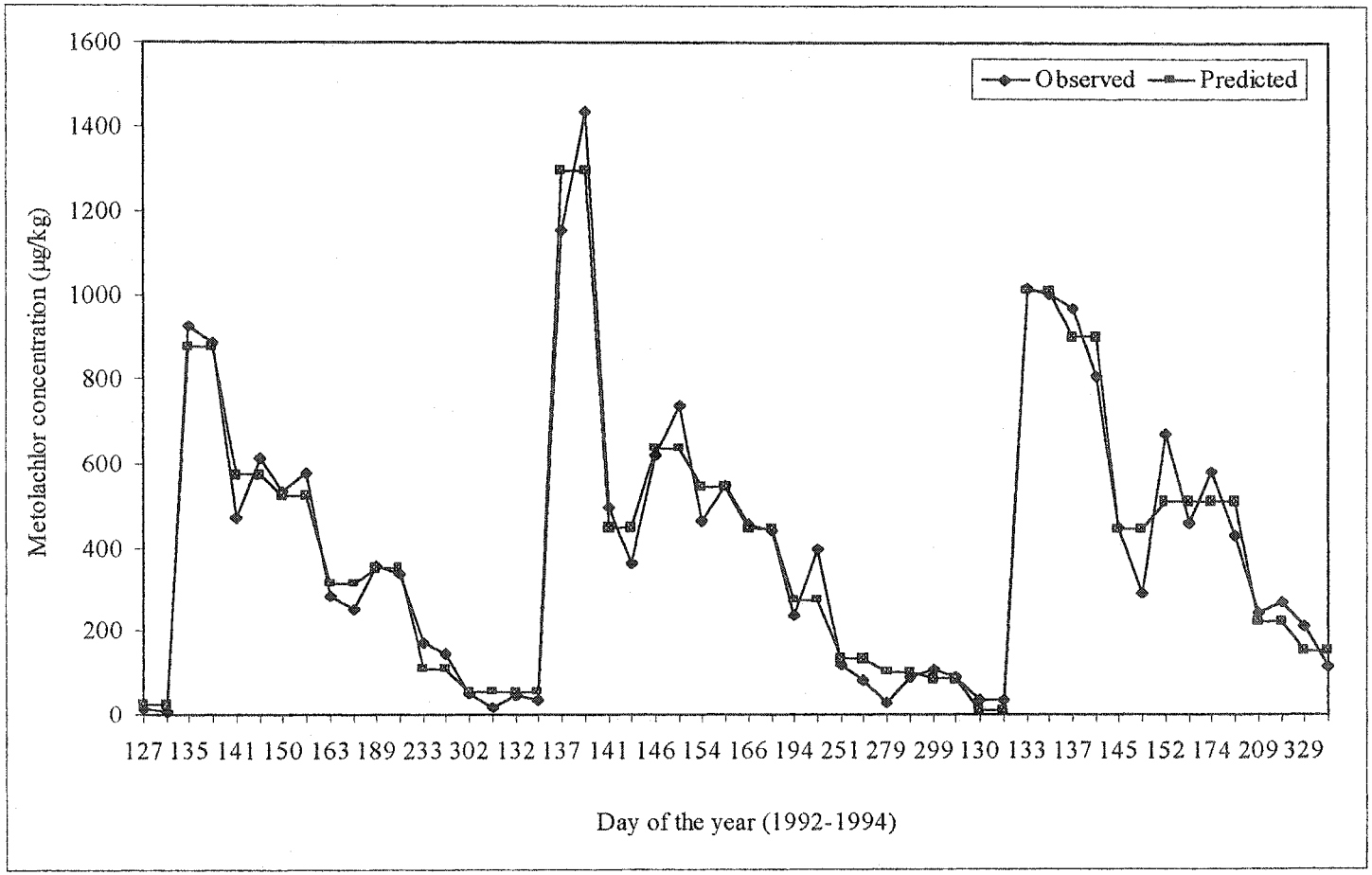


**Fig 4.3 Metolachlor simulation by MARS at 0-10 cm depth**

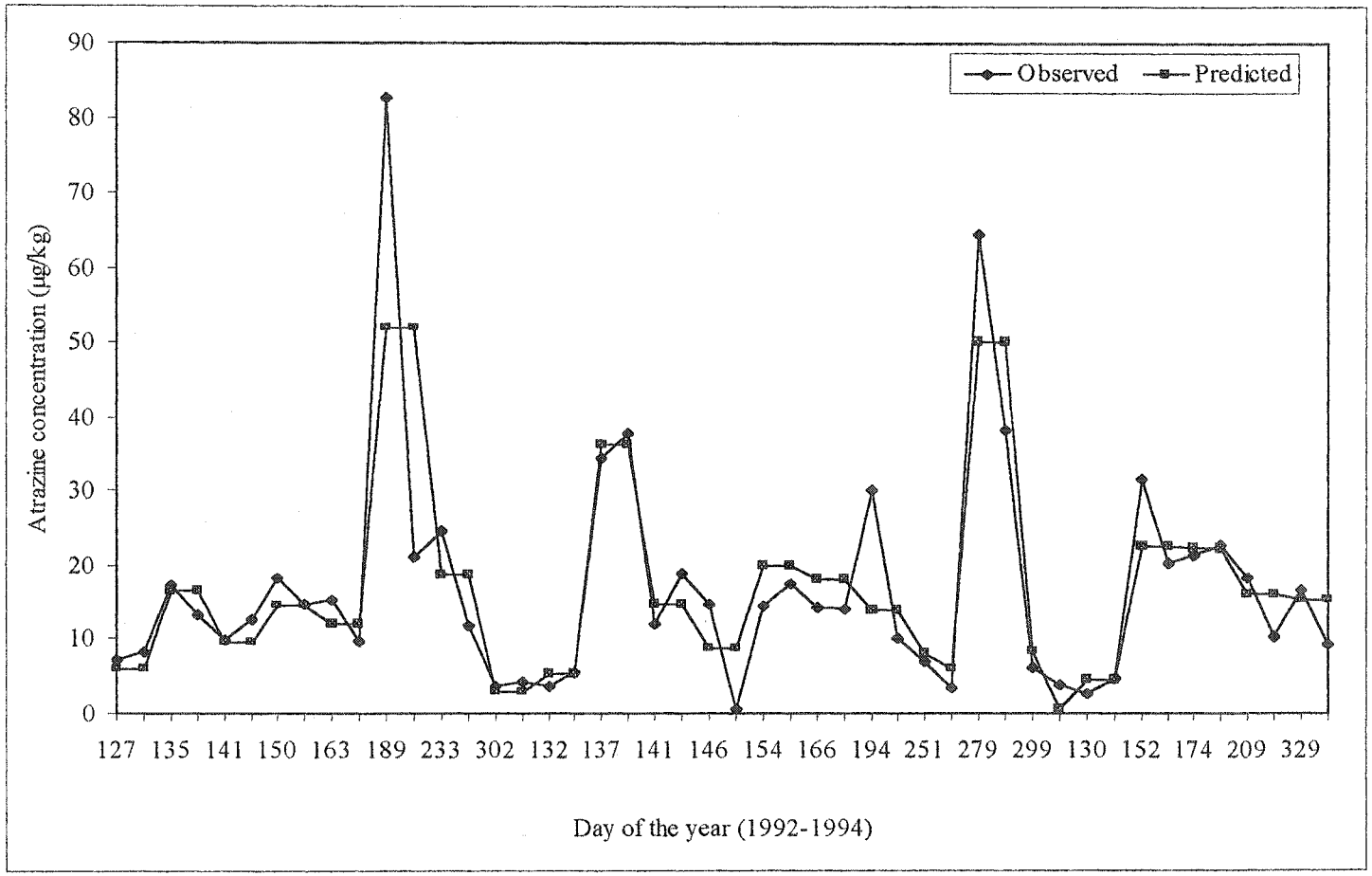


**Fig 4.4 Atrazine simulation by MARS at 10-15 cm depth**

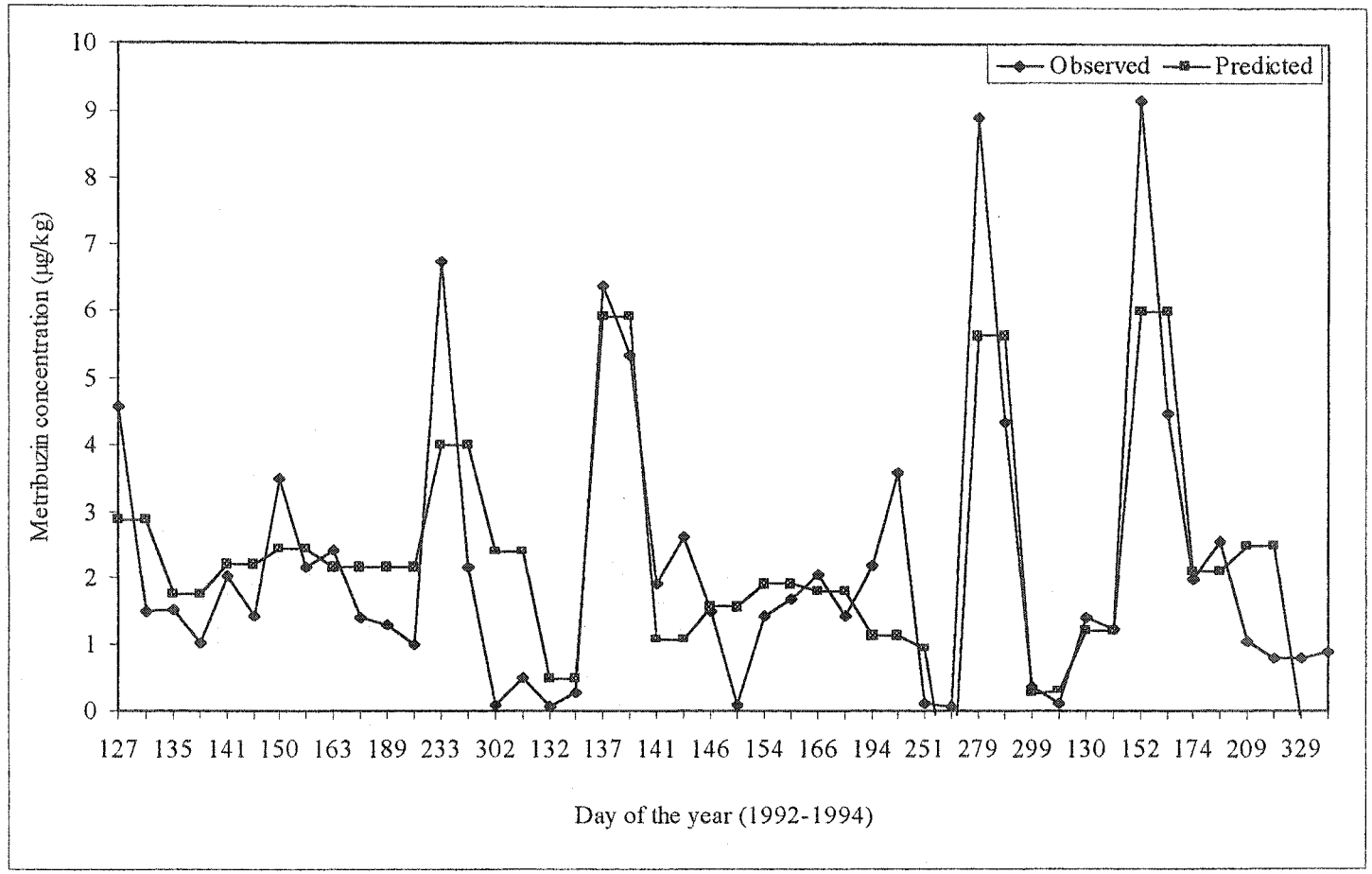


**Fig 4.5 Metribuzin simulation by MARS at 10-15 cm depth**

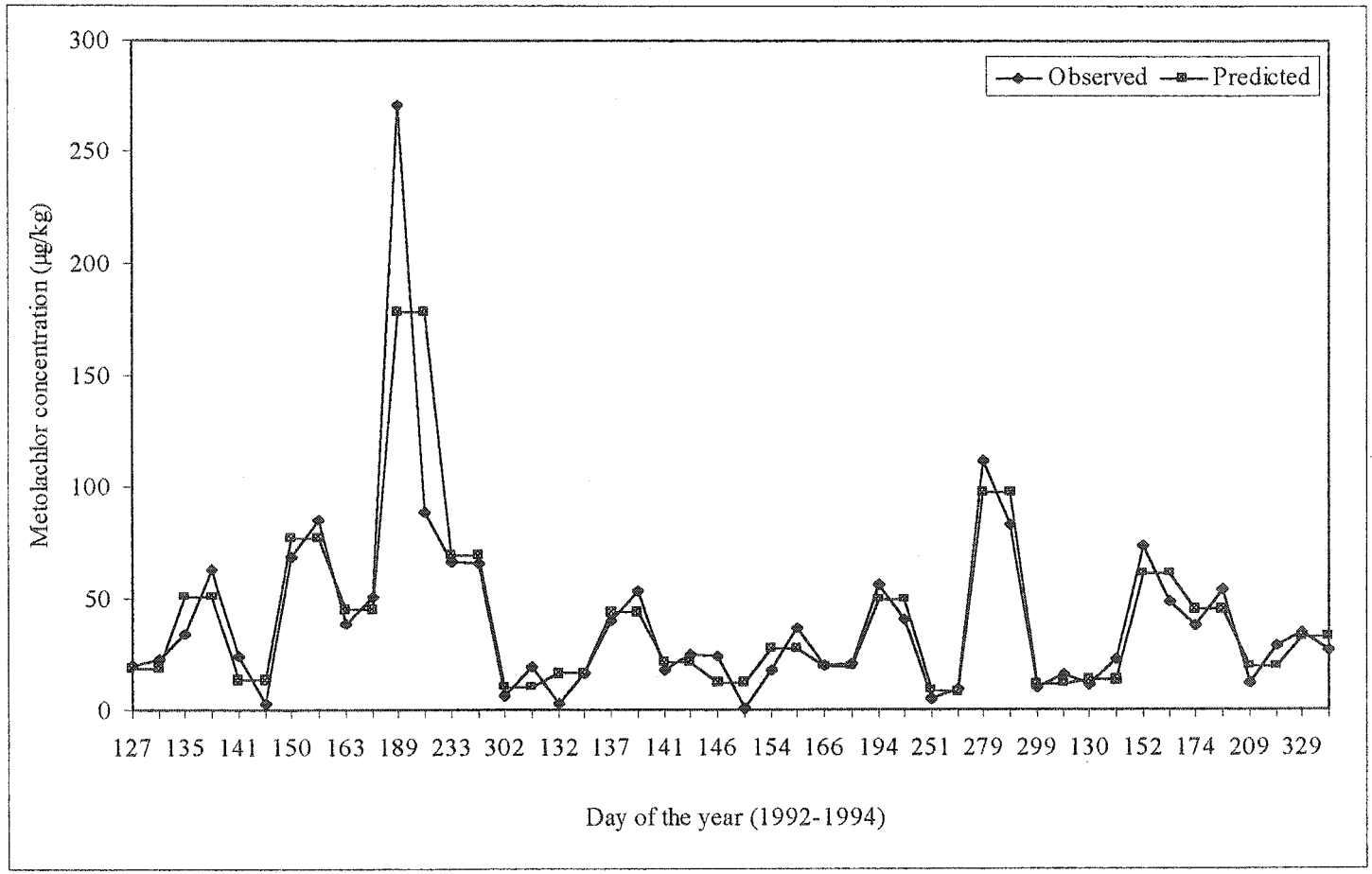


**Fig 4.6 Metolachlor simulation by MARS at 10-15 cm depth**

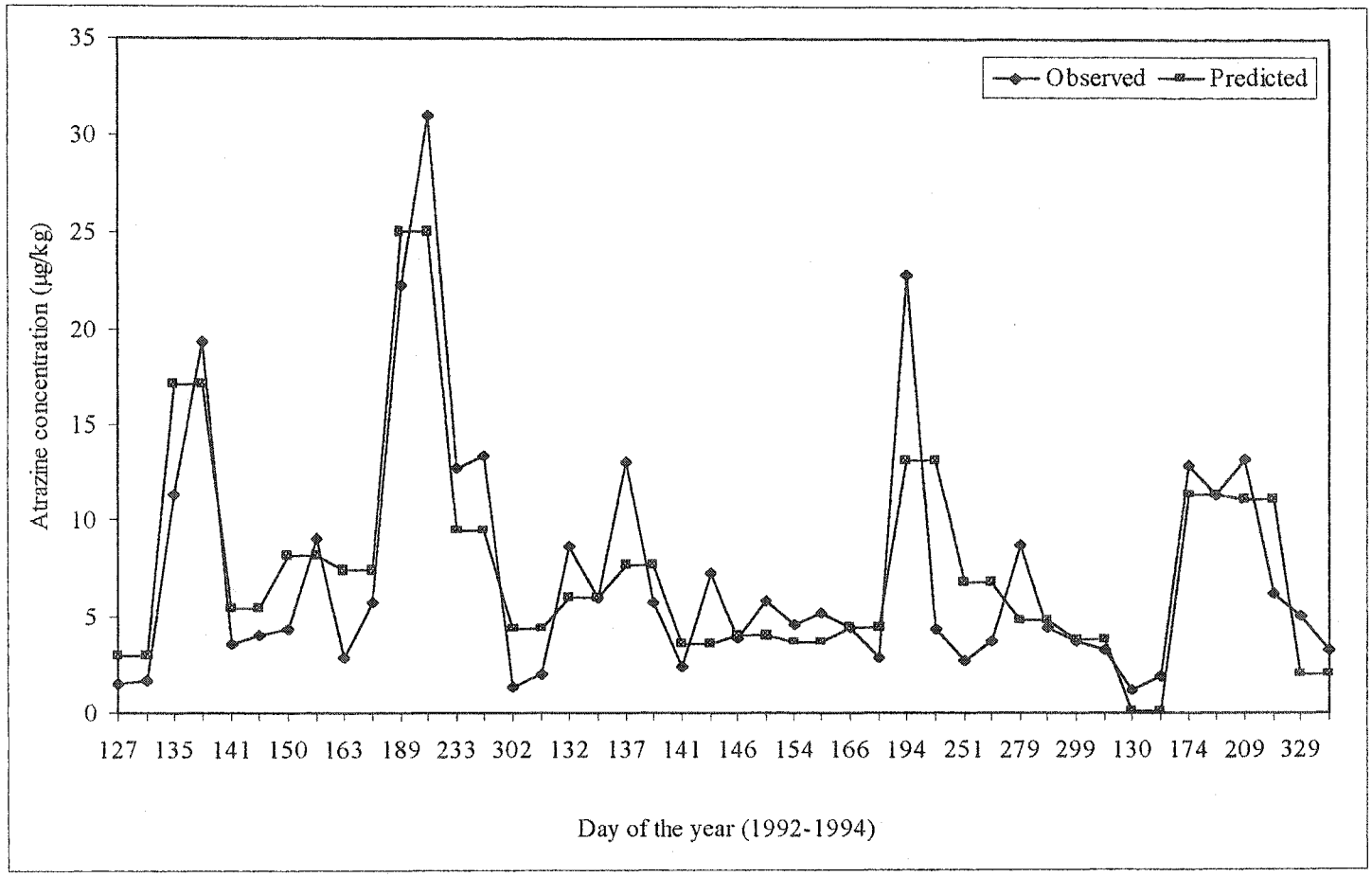


**Fig 4.7 Atrazine simulation by MARS at 15-20 cm depth**

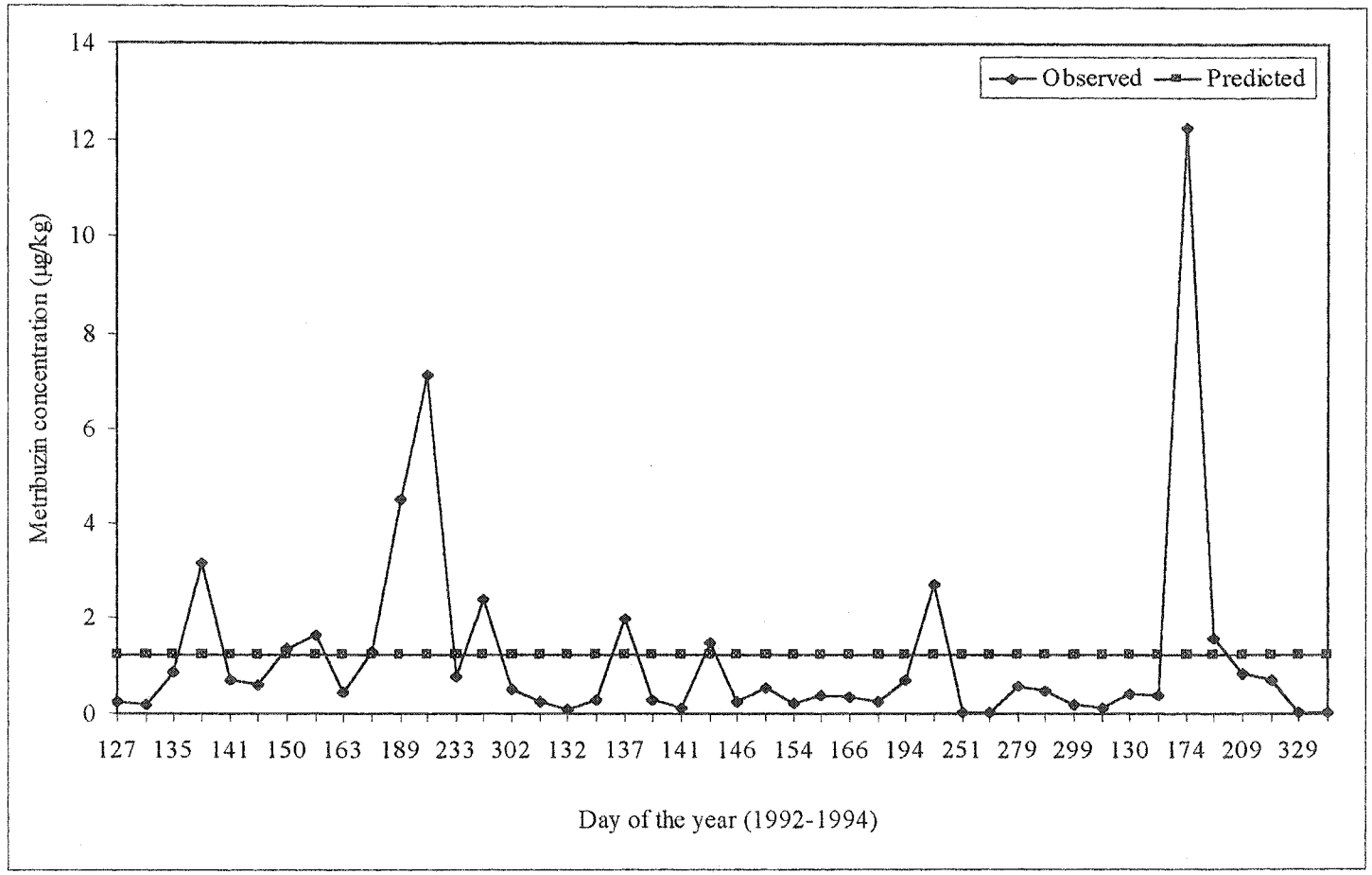


**Fig 4.8 Metribuzin simulation by MARS at 15-20 cm depth**

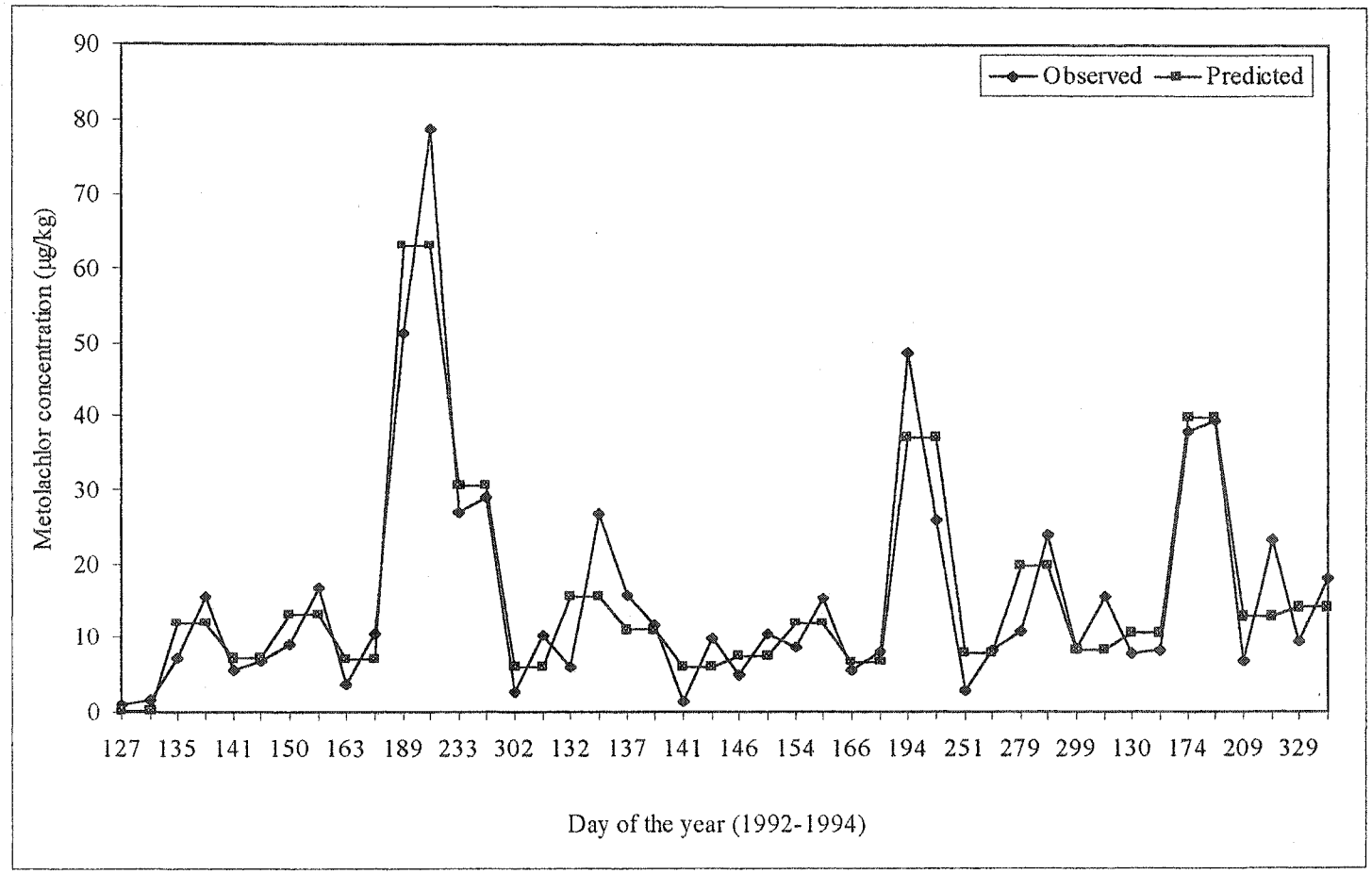


**Fig 4.9 Metolachlor simulation by MARS at 15-20 cm depth**

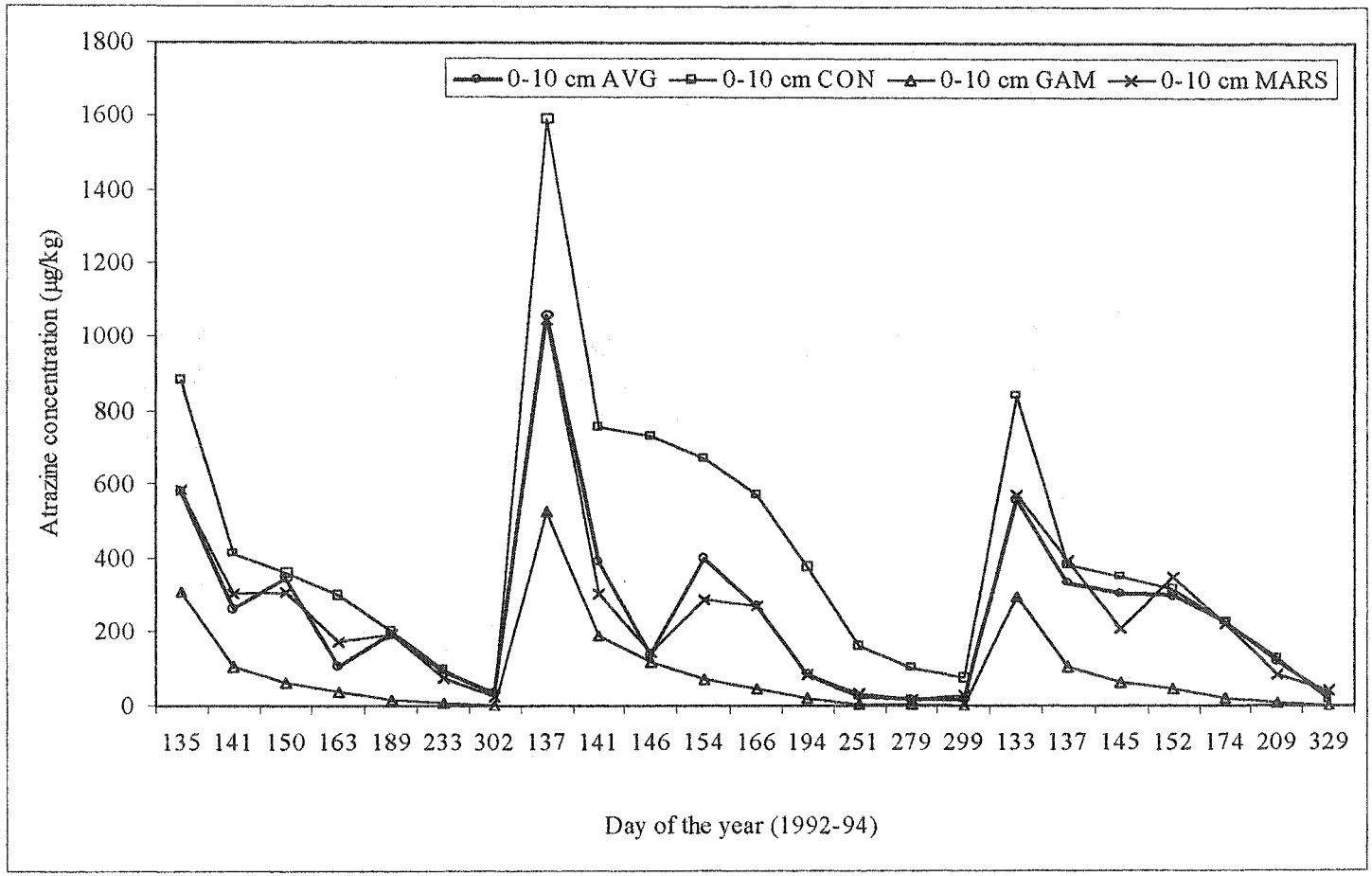


**Fig 4.10 Comparison of MARS and DRAINMOD-P for atrazine at 0-10 cm depth**

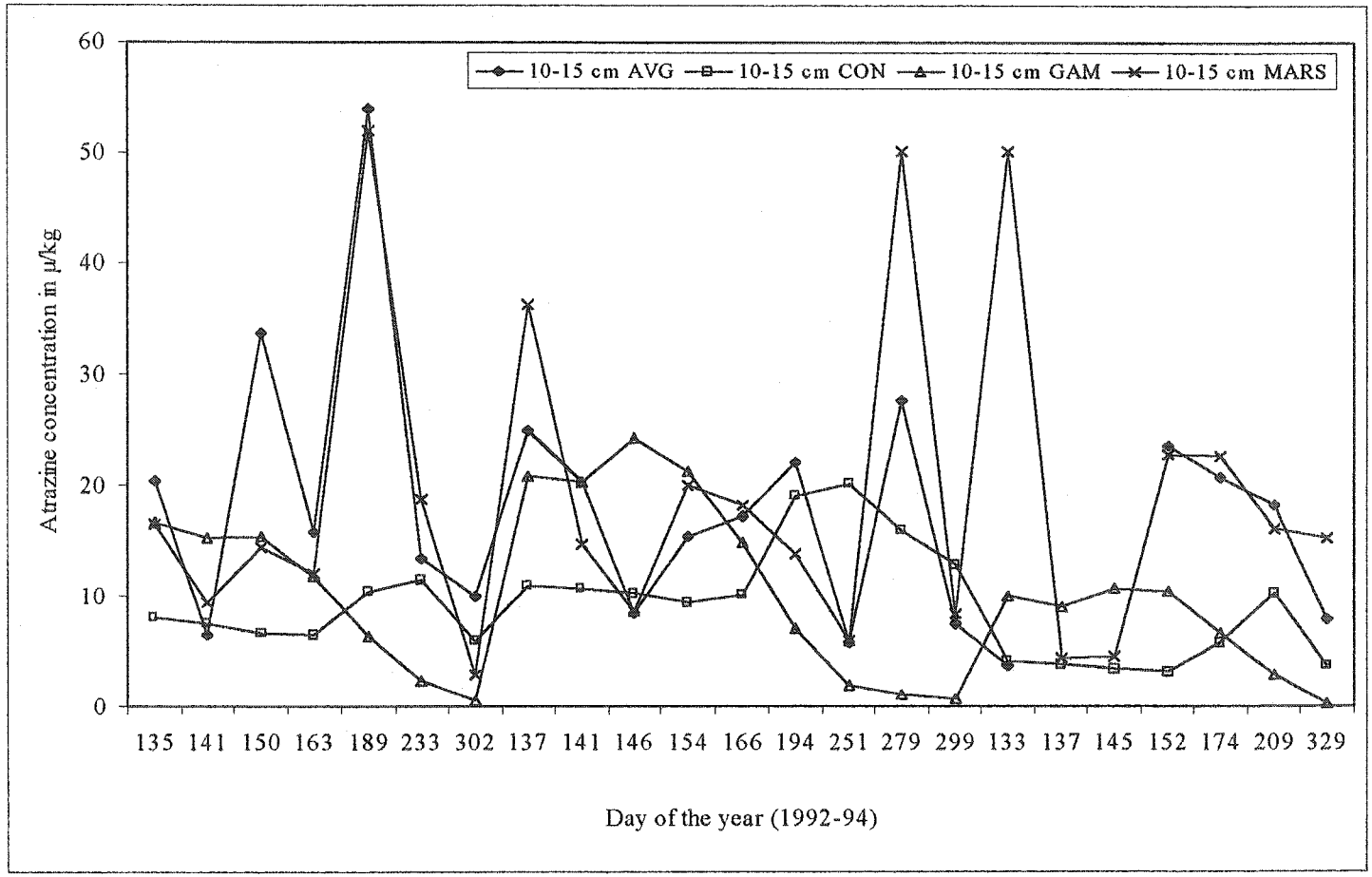


**Fig 4.11 Comparison of MARS and DRAINMOD-P for atrazine at 10-15 cm depth**

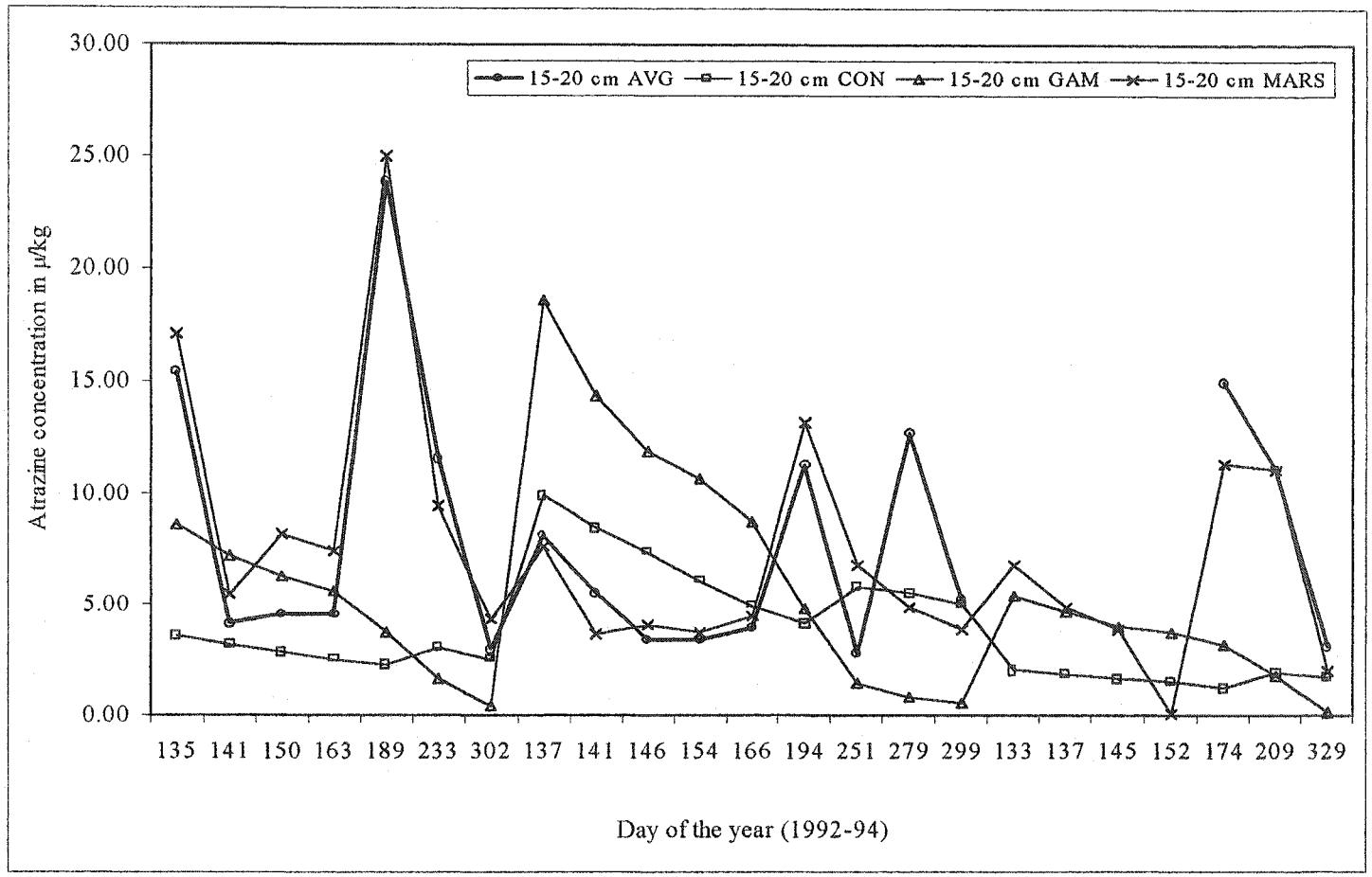


**Fig 4.12 Comparison of MARS and DRAINMOD-P for atrazine at 15-20 cm depth**

# CHAPTER 5
# SUMMARY AND CONCLUSIONS

In this study, models for the simulation of pesticide fate and transport in agricultural soils were developed. The first was a process-based model, DRAINMOD-P, that was developed and validated against independently collected data for simulating pesticide leaching from an agricultural field for herbicide atrazine at three different depths in the soil profile over a three-year period. The second was an implicit model, MARS, that was tested against data obtained from the same field for three herbicides, viz. atrazine, metribuzin and metolachlor, at three different soil depths over a three-year period.

An extensive literature review was carried out to analyze the advantages and disadvantages of various pesticide fate and transport models. The models that performed best for each of the two essential components of pesticide modeling namely, water and solute transport, were chosen to formulate a new model, called DRAINMOD-P. DRAINMOD was selected for hydrologic modeling, while the pesticide component of PESTFADE was chosen for solute transport. DRAINMOD has excelled in predicting hydrology under different pedo-climatic conditions throughout North America, is well-suited to the Windows environment, and is easy to use. The fact that it runs fast on a personal computer and provides outputs graphically makes it more appealing. PESTFADE, on the other hand, handles sorption of pesticides well. It was developed to incorporate both conventional and two-stage sorption kinetics (Gamble kinetics), which also include intraparticular diffusivity of pesticides. Thus, DRAINMOD-P allows better representation of the sorption mechanism affecting the pesticide fate. Accurate simulations of the water transport also contribute towards higher probability of success in pesticide simulations. Field validation was performed with independently collected field data from an agricultural field in southern Ontario that included a three-year period. DRAINMOD-P was validated for atrazine by employing various statistical tools to assess the model performance. As reported by previous researchers, atrazine concentrations were found to be within an order of magnitude of measured values. It cannot be

concluded from this study that one of the two approaches performed better than the other, at any particular depth. The results obtained from all three years, however, do not support the Gamble kinetics to be a better approach. This is not in agreement with the work done by previous researchers (Kaluli et al., 1997 and Li et al., 1999). The non-conformance in model predictions resulting in its inability to model the preferential flow may be attributed to the nature of the soil which is known to crack. In 1993, however, Gamble kinetics yielded better results at the 10 cm depth, which is in accordance with results from previous studies performed using the same field data (Tafazoli, 2002). Also, conventional predictions by DRAINMOD-P were better than the Gamble simulations at the 15 and 20 cm depths, which is in line with previous work done by Tafazoli (2002). Further studies may be performed using larger datasets in order to make assessments between the two sorption methods. Also, the model should be tested at different locations to assess the accuracy of its simulation.

As an alternative approach to mathematical modeling, implicit modeling was attempted with the aid of MARS. MARS is a data mining tool that distinguishes itself by its ability to detect the impact of one variable on the other by a rigorous search mechanism. It prioritizes the variables based on their impact, which aids in model development and pesticide predictions. MARS simulations require minimum execution time when compared to other artificial intelligence tools like ANNs. Lower root mean square values were obtained for the same set of data from MARS when compared to ANNs. Statistical analyses proved that MARS could successfully predict pesticide concentrations at 10, 15 and 20 cm depths with very limited data for all three herbicides. Lower RMSE values and higher efficiencies obtained at these depths provided evidence to this effect. Very few instances were detected where higher deviations in the observed values yielded lower efficiencies. MARS models were also found to be faster than DRAINMOD-P models. The execution time was eight hours for DRAINMOD-P simulations using the Gamble kinetics while computations lasted less than a minute using the conventional method. MARS models, on the other hand, took only a few seconds for a single simulation. MARS has proven itself to be a valuable tool in environmental risk assessments because

it is quick, economical, and reliable. The final conclusions that were drawn are as follows:

i. DRAINMOD-P is robust in its hydrology predictions, which also forms the basis of pesticide fate. The predictions from DRAINMOD-P for atrazine were well within one order of magnitude of the observed data. This is considered to be acceptable as concluded by previous researchers. Gamble kinetics did not bring about a significant improvement in the model performance. Out of the two approaches, neither conventional nor Gamble performed consistently at any particular depth. Simulations carried out over a larger period with a larger dataset may be conducted to make a better assessment. The model should also be tested at different locations to estimate its performance. This inconsistency also lays emphasis on the fact that the transformations that a pesticide undergoes from its time of application is very complex in nature and is, difficult to model accurately with process-based models. This is the case despite the large number of input parameters that are needed to run this model and the long model execution times.

ii. MARS models performed well, even though the data was very limited. The simulations at all depths yielded good results, as was evident from the high model efficiencies. There were very few cases where the noise in the data hindered its predictive abilities. MARS had a clear advantage over the mathematical model, DRAINMOD-P. MARS models provided a significance factor to all input parameters that affected model performance. This enabled the correct selection of inputs. The execution time was also much less when compared to the mathematical model.

## 5.1 RECOMMENDATIONS FOR FURTHER RESEARCH

Future research work may be done by using a larger data set, comprising more than one pesticide from different climatic zones. A sensitivity analysis of DRAINMOD-P may be performed to determine the important inputs of the model. DRAINMOD-P may further

be expanded by incorporating sub-modules for volatilization, degradation and macropore flow. A larger database may also lead to closer predictions in pesticide leaching studies.

Also, the performance of the MARS model can be further substantiated with data involving a longer time period. Both models, whether mathematical or implicit, may prove to be handy in assessments of pollution through different solutes in the soil environment.

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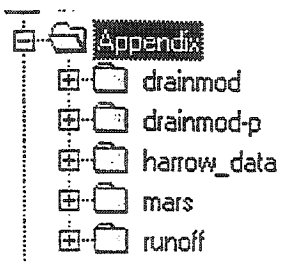
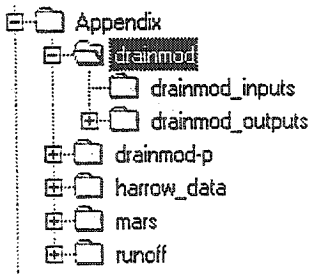
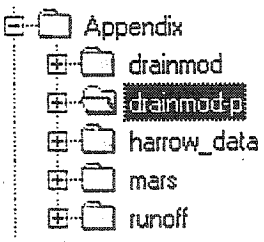
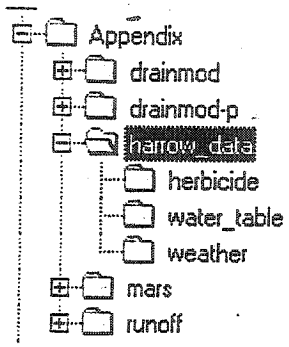
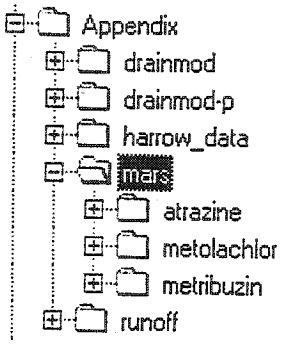
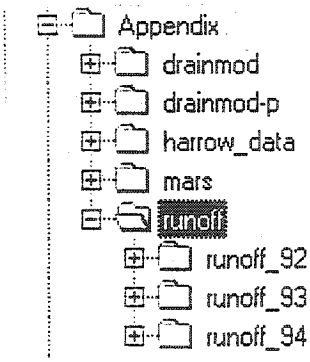
## APPENDIX –A

The details of the content of the CD-ROM are briefly given in the table below:

| Directory/Subdirectory | Content |
|---|---|
|  | The root directory contains three files called read_me.txt, file_description and field_layout.pdf which are self-explanatory.<br>The root directory *appendix*, is divided into five directories, *drainmod*, *drainmod-p*, *harrow_data*, *mars*, and *runoff*. |
|  | *Drainmod* directory is divided into two directories, *drainmod_inputs* and *drainmod_outputs*. The second directory contains three sub-folders, *1992*, *1993*, *1994*, which contain the DRAINMOD outputs required for DRAINMOD-P. |
|  | *Drainmod-p* directory contains six sub-directories, *conventional_92*, *conventional_93*, *conventional_94*, *gamble_92*, *gamble_93*, and *gamble_94*. Each of these sub-directories are further divided into three sub-directories, *input*, *output*, *programfiles*, which are self-explanatory. |
| | *Harrow_data* directory contains three subdirectories, *herbicide*, *water_table*, and weather. The *herbicide* subdirectory contains the measured herbicide |

| | |
|---|---|
|  | concentrations for 1992-94 for atrazine, metribuzin and metolachlor. The sub-directory, *water_table* contains three files for the water table measurements for 1992-94, while the sub-directory, *weather* contains three subdirectories *weather_XX*, where "XX" stands for '92, '93, '94, respectively. |
|  | The directory *mars*, contains three sub-directories for *atrazine*, *metolachlor* and *metribuzin*, respectively. Each of these sub-directories are further divided into *0-10*, *10-15* and *15-20* to denote the levels. These subdirectories are further sub-divided into two sub-directories called *input* and *output*. The names themselves suggest the contents of these sub-directories. |
|  | *Runoff* directory contains three sub-directories, *runoff_XX*, where "XX" stands for '92, '93, '94, respectively. These sub-directories are further divided into input, output and program files. The titles of these sub-directories are self-explanatory. |

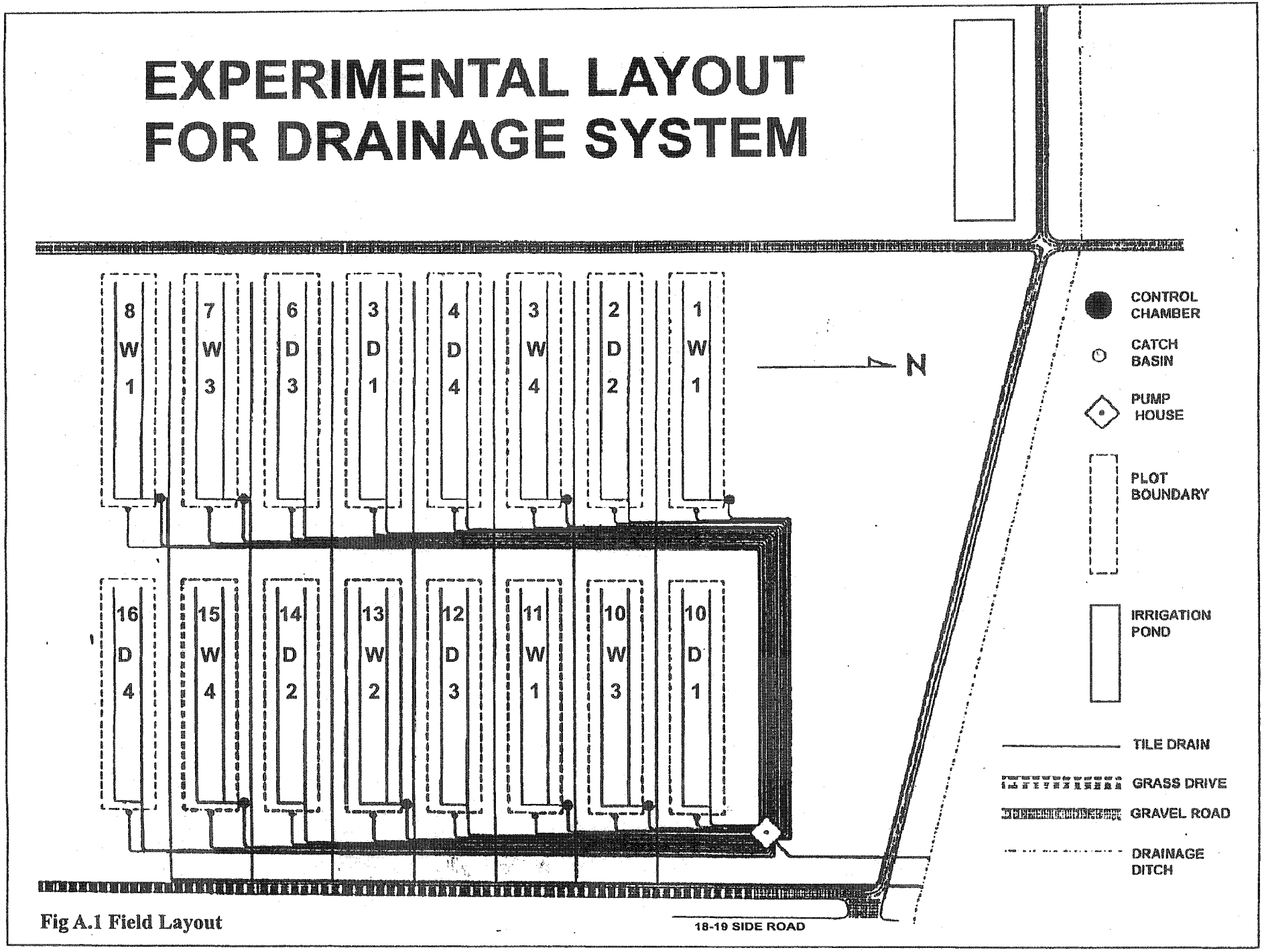



Fig A.1 Field Layout