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A LYSIMETER STUDY TO DETERMINE FATE AND TRANSPORT OF THREE AGRICULTURAL HERBICIDES UNDER DIFFERENT WATER TABLE MANAGEMENT SYSTEMS

by

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A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfilment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

Subirrigation systems are generally used in humid areas to provide suitable moisture conditions for plant growth. These systems can also be used to reduce pesticide loadings from agricultural lands, since they tend to keep the discharging waters within farm boundaries for extended periods of time. This allows for greater pesticide microbial and chemical degradation.

A three-year field lysimeter study was initiated to investigate the role of subirrigation systems in reducing the risk of water pollution from the three most commonly used herbicides in Quebec, 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-methlphenyl)-N-(2-methoxy-1-methylethyl)acetamide). Eighteen PVC lysimeters, 1 m tall x 0.45 m diameter, were packed with a sandy soil. Three water table management treatments, i.e. two subirrigation treatments with constant water table depths of 0.4 and 0.8 m, respectively, and a free drainage treatment in a completely randomized design with three replicates were used. Grain corn (*Zea mays* L.) and potatoes (*Solanum tuberosum* L.) were grown on lysimeters, and herbicides were applied each year at the locally recommended rates at the beginning of each summer. Soil and water samples were collected at different time intervals after each natural or simulated rainfall event. Herbicides were extracted from soil and water samples and were analyzed using Gas Chromatography.

From the three years results (1993-1995), it has been concluded that all three herbicides were quite mobile in this sandy soil, as they leached to the 0.85 m depth below the soil surface quite early in the growing season. This suggests that if the drainage effluent or seeping waters from sandy soils of agricultural lands in southern Quebec drain freely, they may be considered to be a serious non-point source of pollution to the water bodies. The results have also shown that herbicide concentration decreased with soil depth as well as with time, meaning that the higher herbicide residues were found at top layers, and soon after the herbicide application. The herbicide mass balance study revealed that when the drainage effluent was kept within the lysimeters under the subirrigation setup, there was a statistically significant reduction of atrazine and metribuzin residues (shorter half lives) in the adsorbed and liquid phases. However, the reduction in metolachlor concentration under the subirrigation system was not statistically significant. These findings suggest that subirrigation, combined with certain herbicides can significantly reduce the herbicide loadings from corn and potato farms in southwestern Quebec, and

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become environmentally beneficial.

A computer simulation model (PRZM2), was used to simulate atrazine, metribuzin, and metolachlor leaching in the lysimeters under subsurface drainage conditions. The simulated values for all three chemicals in most of the cases followed the leaching pattern of observed data. But the model either under- or over-estimated the herbicide concentrations in the soil. This could have been caused by simplistic instantaneous linear adsorption/desorption of herbicides, and inadequacy of conventional Darcian approach for the treatment of matrix flow.

RÉSUMÉ

Les systèmes d'irrigation par le sol sont généralement utilisés en région humide pour fournir un taux d'humidité favorable aux plantes. Ces systèmes peuvent aussi être utilisés pour réduire la quantité de pesticides dans les sol agricoles. En effet, en gardant les pesticides pendant une longue période dans le sol, la dégradation des pesticides devient plus importante suite à une activité micriobienne et chimique prolongée.

Une étude de trois ans en lysimètre a été effectué pour examiner le rôle des systèmes d'irrigation par le sol pour réduire la pollution des eaux de drainages par trois herbicides fréquement utilisés au Québec, soit l'atrazine (2-chloro-4[ethylamino]-6[isopropylamino]-1,3,5-triazine), le métrabuzin (4-amino-6(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one), et le métolachlor (2-chloro-N-(2-ethyl-6-methlphenyl)-N-(2-methoxy-1-methylethyl)acetamide). Dix-huit lysimètres de PVC (1m par 0.45m de diamètre), furent remplis d'un sol sablonneux. Trois traitements de niveau d'eau (0.4m, 0.8m, et drainage libre) organisés de façon aléatoire furent utilisés. Du maïs (*Zeas mays* L.) et des pommes de terre (*Solanum tuberosum* L.) furent cultivés sur les lysimètres. Les herbicides furent appliqués chaque année en début d'été. Des échantillons de sol et d'eau furent collectés à différents intervals de temps après chaque précipitation naturelle ou simulée. Le niveau d'herbicides dans les échantillons de sol et d'eau furent analysés par Gas Chromatographie.

Il a été conclu de ces trois années d'études (1993-1995) que les herbicides étaient relativement mobiles dans ce sol sablonneux étant donné qu'ils se retrouvaient rapidement à une profondeur de 0.85m en début de saison. Ceci indique que si les eaux de drainage provenant d'un sol sablonneux du sud du Québec draine librement, il pourrait en résulter en une sérieuse source de pollution des rivières. Les résultats ont aussi démontrés que la concentration en résidus d'herbicides diminuait avec la profondeur ainsi qu'avec le temps. Ceci implique que les résidus d'herbicides se trouvaient dans la couche supérieure du sol, et cela juste après l'application d'herbicides. Le bilan massique a révélé que lorsque l'effluent de drainage était conservé dans les lysimètres par le système d'irrigation par le sol, il y avait une réduction statistiquement significative du taux d'atrazine et de métrabuzine dans le sol et en phase liquide. Cependant, la réduction du métolachlore par le système d'irrigation par le sol n'était pas statistiquement significative. Ces résultats indiquent que les systèmes d'irrigation par le sol en combinaison avec l'utilisation de certains herbicides peut réduire le taux de pesticides dans les champs de maïs et de pommes de terre au Québec, et ainsi contribuer à une amélioration de la pollution agricole.

RESUME (CONT'D)

Un modèle de simulation par ordinateur (PRZM2) a été utilisé pour simuler le mouvement de l'atrazine, du métribuzine, et du métolachlore dans les lysimètres irrigués par le sol. Dans la plupart des cas, ces simulations étaient en accord avec les fluctuations mesurées. Cependant, le modèle sur-estimait ou sous-estimait les concentrations d'herbicides dans le sol. Ceci pourrait dû à des phénomènes d'adsorption/désorption instantannés et linéaires et à l'insuffisence de l'approche conventionelle de la loi de Darcy pour le traitement du flux matricielle.

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CONTRIBUTIONS TO KNOWLEDGE

Research in the field of non-point source (NPS) pollution control has increased since the 1980's, but our knowledge of the complex behaviour of agrochemicals in the soil is still rather limited. These limitations are due mainly to our lack of conceptual understanding of the fate and transport of chemicals in the soil, and to budgetary restrictions which limit the scope of many research projects. Because of diversity of the nature of NPS pollution problems, most experiments need to be carried out in the field for a specific chemical under certain climatological conditions, and for a given soil type, in order to be able to provide more realistic results. Few experimental studies on atrazine, metribuzin, and metolachlor fate in field plots have been carried out under Quebec climatological conditions, and several difficulties which affected the interpretation of results in one way or another were reported.

Difficulties in the interpretation of field results may be attributed to the spatial variability of soil physical and chemical properties, the field variability of pesticide applications, dependency of experimental results on weather patterns, minimal control on malfunction of buried experimental apparatus, difficulties in performing leaching and mass balance studies in the field plots, etc. Since these problems have not been adequately addressed in a single effort to this date, this research was designed and undertaken to minimize them and thus obtain a better understanding of the fate and transport of the three most commonly used herbicides in Quebec. Based on the results of this research, this dissertation offers the following major contributions to knowledge:

1. Lysimeter and laboratory results in this research have clarified the ambiguity regarding the environmental impact of water table management on the fate and transport of atrazine, one of the most commonly used herbicides in corn farms of southern Quebec. Results have shown that among the different water table managements, shallow subirrigation systems could significantly reduce the environmental pollution from atrazine in sandy soils under the southern Quebec climatological condition.

2. This research has answered some of the questions concerning the fate and transport of metribuzin under different water table management practices. Metribuzin is one of the most widely used herbicides in potato farms of southern Quebec, and result of this experiment clarified that shallow subirrigation systems could significantly reduce the load of metribuzin in sandy soils under the southern Quebec climatological condition.

3. This research has also addressed and clarified some of the ambiguity regarding the fate and transport of metolachlor under different water table management practices. Findings from this research showed that, although subirrigation systems could reduce the environmental impacts of metolachlor pollution to some extent, subirrigation systems may not be able to significantly reduce pollution from metolachlor in sandy soils of southern Quebec. Therefore, either alternative herbicides may be used (more degradable), or more attention should be given to other Best Management Practices (BMPs) to alleviate metolachlor pollution from agricultural lands.

4. The results of lysimeter and laboratory studies have contributed towards

building an empirical basis for understanding the transformation of atrazine, metribuzin, and metolachlor herbicides under subirrigation systems in sandy soil. This will help us to better understand the BMPs which can help minimize pollution from these herbicides.

5. The specific setup used in this lysimeter investigation has eliminated the possibility of errors which might occur in the collection of data in field plots and provided a reliable environment for leaching and mass balance studies. Based on the results of this research, it may now be concluded that subsurface irrigation systems can potentially be considered as effective BMP's for reducing herbicide pollution from farms of southern Quebec. Subirrigation systems may also be used as part of cheap, low-energy on farm pollution control systems to significantly reduce the non-point source pollution from other herbicides.

6. The application of the PRZM2 model to the lysimeter study clarified the strength and weaknesses of the model in the simulation of atrazine, metribuzin and metolachlor leaching in sandy soil under the southern Quebec environment. It was established that PRZM2 still requires further improvement by incorporating more realistic approaches for the determination of fate and transport of pesticides.

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LIST OF SYMBOLS AND ABBREVIATIONS

AA	after application
a.i	active ingredient
avg	arithmetic average
BMP	best management practice
°C	degrees Celsius
cm	centimeter (10^{-2} meter)
cmol	centimole, unit for CEC (cation exchange capacity)
CP	coefficient of performance
CV	coefficient of variability (in percentage)
DAA	days after application
D.L.	detection limit
EPA	environmental protection agency (United States)
ET	evapotranspiration (millimeter)
g	gram
GC	gas chromatography
GG	Greenhouse-Geisser epsilon (term in statistics)
ha	hectare
HF	Huynh-Feldt epsilon (term in statistics)
i.d.	inside diameter
Kd	soil-water partitioning coefficient
kg	kilogram
kpa	kilopascal
Kow	octanol-water partition coefficient
L or l	liter
mg	milligram
min	minute
ml	milliliter
mm	millimeter
NA	not available
ND	not detectable
NPS	non-point source pollution
Pr	statistical probability
ppb	(μg/L) or (μg/kg), parts per billion
ppm	(mg/L) or (mg/kg), parts per million
sub	subirrigation treatment
(t/day)	ton per day
μg	microgram
μm	micrometer
WTM	water table management
WTL	water table level

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CHAPTER 1

INTRODUCTION

To sustain agriculture successfully, the soil and water resources should be exploited in such a manner that they are neither depleted nor degraded by their use. The agricultural activities must rely mainly on the utilization of soil and water resources without any significant waste for a continuously high level of crop production without disturbing the environmental equilibrium. It seems that man has not been very successful in this respect, since some of his agricultural efforts has caused ecosystem imbalances.

Most of the agricultural lands in the humid regions in Canada experience high rainfall/or snow pericipitation and poor natural drainage. Hence, in lands with no constructed drainage facilities, there are periods in which impeded percolation or high water table cause excess water in the soil profile or ponding on the land surface. This decreases root respiration and reduces soil workability. Therefore, some drainage measures are needed in order to remove excess soil moisture and improve the land for farming operations. With the expansion of agricultural activities in both arid and humid areas of North America since 1960's, land drainage, especially subsurface drainage, became essential and soon was accepted as one of the inherent elements of land development.

Although, subsurface drainage practices have proved to be quite efficient for agricultural crop production, it also seems to have caused greater leaching of soil nutrients and toxic materials to water bodies.

To maintain good water quality, drainage of polluted water to the surface and ground waters should be prevented. This may be only possible if the drainage outflow quality is improved. Since the 1980's the concept of water table management (subirrigation and controlled drainage) has been employed, by some researchers, to improve the quality of water leached from agricultural lands.

In this chapter, the agricultural and environmental benefits of water table management will be explained. The need for further experimental investigation and mathematical modelling will be also discussed. The justification for this research, and the scope of the study will be presented in the last section.

1.1. Agricultural Benefits of Water Table Management

One of the primary objectives of modern agriculture is to create and improve the soil and plant environment such that the highest possible crop yields may be obtained. However, in very rare cases the plant requirements with respect to soil and water are ideally met. In most circumstances, agricultural activities are faced with quantitative or qualitative limitations in soil and water resources.

Agricultural limitations may vary depending on the type of soil and the climatological conditions. In arid and semiarid areas, the major agricultural limitations are salinity and shortage of water in the growing season; whereas in humid regions, the dominant limitation is excess water. Efficient removal of excess water from agricultural lands, which causes less wastage of land, is mainly achieved by subsurface drainage installation.

There are about 2,100,000 ha of arable land in Quebec, most of which is located in the St. Lawrence lowlands. Jutras (1967) estimated that out of this area, 1,300,000 ha were in need of subsurface drainage. By 1986, subsurface drainage systems had been installed on over 609,000 ha of cultivated land in Quebec. This represents about 27% of 2,223,000 ha subsurface drained land in Canada (Anon., 1986).

There are about 748,000 ha of agricultural land in Canada which are under various types of irrigation (Anon., 1986). About 22,000 ha of land is under irrigation in Quebec (Anon., 1992). In 1986, the hand move sprinkler system was the most common in Quebec, followed by the giant raingun, wheelroll, and pivot systems. These systems usually provide only a supplementary irrigation in the fairly hot months of July and August. All of the above mentioned irrigation methods, involve the surface application of water to the lands. This again may cause soil erosion and chemical loading to the surface or groundwater bodies by producing low quality leaching water.

The installation of drainage systems is costly and time consuming; so is the installation and operation of irrigation systems. The need for drainage during wet periods and the need for irrigation during dry periods has led some researchers and farmers to use the same buried perforated drainage pipes to supply water to the root zone during the dry months of summer (Shirmohammadi, et al., 1995; Kalita and Kanwar, 1993; von Hoyningen Huene et al., 1985). Hence, the drainage pipes could function as a "subsurface irrigation" system, to supply water to the plant roots with no major additional expense, for the period that drainage functioning is not required. The only major additional cost would be that of pump and control chambers, to supply water and to control the water level in the soil.

The concept of using a dual-level water management system was also discussed and tested at Iowa State by Melvin and Kanwar (1995) to accomplish a simultaneous drainage and irrigation. This system allows drainage water recycling, and eliminates the need for switching between subirrigation and subsurface drainage.

A subirrigation system raises the water level in the field by either pumping the irrigation water into the subsurface drainage pipes or submerging the drainage outlets by head ditches. A control chamber at the drain outlet is set to keep water tables within a defined range. During periods of heavy rainfall, the outlet water level may be lowered by using the control chamber, to facilitate rapid drainage and to prevent crop damage due to excessive soil water (Skaggs, 1979).

If natural rainfall is high enough in summer to provide sufficient moisture at the root zone, the water level in the soil profile is managed by setting the control chamber at the desired level to avoid pumping water or using any supply ditches. This type of water level control, which could be practised in humid regions of North America, is called a controlled drainage scheme. Subirrigation has been used in Florida and North Carolina for over 30 years, but it is relatively new in Quebec (Broughton and Madramootoo, 1995). Subirrigation and controlled drainage systems, as water table management practices (WTM), are becoming more and more popular in Quebec.

Since a typical agricultural activity in southern Quebec involves both drainage and irrigation in the same season, therefore, installation of subirrigation systems will, combine the advantages of subsurface drainage practice with the benefits of low cost controlled drainage or subirrigation runs, to produce higher crop yields at a lower irrigation cost (Broughton, 1995; Camp et al., 1994; Kalita and Kanwar, 1993; von Hoyningen Huene et al., 1985).

1.2. Environmental Benefits of Water Table Management

Pesticides and fertilizers are the most frequent agrochemicals used to increase agricultural crop production. Data from the 1985 national pesticide registrant survey showed that (Table 1.1), about 36,025 metric tons of pesticide active ingredients were sold and sprayed on 27,539,000 ha in Canada (Anon., 1986). Over 30,180 metric tons (84%) of the pesticides sold were in the form of herbicides (Pierce and Wong, 1988).

Table 1.1. Pesticide Use

Chemicals	Sold (Metric Tons)(1)		Area Sprayed (ha)(2)	
	Canada	Quebec	Canada	Quebec
Pesticide	36,025	2,680	27,539,000	617,150
Herbicide	30,180	1,587	22,949,000	541,250

(1) Pierce and Wong (1988)

(2) Anon. (1986)

There were over 2,680 metric tons of pesticides sold and sprayed over 617,150 ha of agricultural lands in Quebec (Anon., 1986). The herbicide use accounted for about 1,587 metric tons of total weight. In herbicide sales in Canada, Saskatchewan and Alberta had the highest rank, and Quebec spotted fifth. In 1982 the pesticide use in the United States was about 300,000 metric tons (Kalita et al., 1992).

With the huge amount of pesticide used and large areas sprayed, a basic question may now be asked. Are the Canadian soils and groundwater bodies polluted with pesticide residues? This question may only be answered with the results of sample analysis, collected from surface and groundwater bodies, at different research sites in Canada. Most of the reported cases of groundwater sampling indicate that the Canadian soils and ground waters are polluted with different pesticide residues, and that they will be more and more polluted if the appropriate measures are not taken (Masse et al., 1994; Aubin et al., 1993; Southwick et al., 1988; Frank et al., 1987; Patni et al., 1987; Muir and Baker, 1978). Unfortunately, in many cases, pesticide concentration has exceeded the specified advisory limits (Frank et al., 1982; Patni et al., 1987).

Kanwar (1996) discussed three possible choices for reducing environmental related health risk due to agrochemical contamination. One radical approach which might have little chance for application, is to limit or ban the use of chemicals in agricultural watersheds. The second choice, which seems more reasonable, is the use of best management practices (BMPs) including water table management. The last approach is the application of precision farming using global positioning systems (GPS), which allow the distribution of chemicals according to land use and site specific needs. Among the various methods to alleviate the pollution from pesticide residues, that have been examined by researchers, enhancing the degradation of pesticides by managing the soil moisture content has introduced a new horizon in agricultural pollution control.

It has been hypothesised that, in addition to the economical benefits that could be obtained from the water table management practices, it may also be possible to create a suitable moisture condition in the soil that includes many of the environmental benefits. The higher moisture provided to the soil during the warm months of summer by subirrigation, may maintain a soil-water micro environment at a favourable level. Thereby enhancement of some of the soil chemical, physical, and microbiological activities could be achieved.

The major results of this practice could be the rapid increase in the population of biomass (exponential growth stage). They will break down the contaminant molecules such as fertilizer and pesticide residues, in order to get their required energy growth. The degraded compounds thus produced, would generally be less toxic in most circumstances. They would carry less risk of pollution in the case of leaching to surface waters or aquifers. The loss of pesticides in drainage water, may be simply prevented by keeping the agricultural water within the farm boundaries (water table control) for extended periods of time.

Only about 10,000 ha of agricultural land in the entire province of Quebec, utilizes some form of water table control (Madramootoo et al., 1993). Further implementation of water table control practices will depend upon their environmental impacts (Skaggs and Breve, 1995; Shirmohammadi, et al., 1995). Broughton (1995) reported 20 to 40% increase in maize and soybean production, saving in water and energy, and less pesticide loading in subirrigated sandy soils in Quebec.

Installation of subsurface drainage systems in conjunction with any type of water table management systems in the existing 609,000 ha (Anon., 1986) drained lands, or in the total 1,300,000 ha future drained lands of Quebec, will be a win-win situation: higher crop yields due to good water table management during the growing season; with lower losses of fertilizers and pesticides from subsurface drained farmlands; and plants might be able to reuse some of the initially leached-out pesticides and fertilizer residues, thus increasing their use-efficiencies.

1.3. Need For Further Experimental Studies

Studies conducted under a wide range of conditions show that the environmental impacts of water table control are not clearly understood. They depend on soil type, crop, chemical, and climatological factors. It is known, however, that the route and the rate of draining waters from agricultural lands can be controlled by design and management (Skaggs and Breve, 1995). Most agricultural pesticides have a field half-life of about 4 to 8 weeks. Therefore, if drainage water containing the dissolved pesticides is kept within the farm boundaries for this period, the pesticides would have been subjected to microbial and chemical degradation over a longer period. They would be less toxic to the surface and groundwater resources at the time of release in late September.

Some field investigations have been carried out in Canada and the US to study the validity of the aforementioned hypothesis (Arjoon et al., 1994; Aubin et al., 1993; Kalita et al., 1992). Due to several problems and costs, the role of water table management systems in determining the fate and behaviour of pesticides has not been fully explored yet (Rambow and Lennartz, 1993). For instance, Thomas et al. (1991) reported unusual weather conditions during their three-year field study, which restricted their conclusions. The results of a field experiment by Arjoon et al. (1994) were difficult to explain due to the complex behaviour of metolachlor in a mineral soil. In general, the water table management experiments conducted in field plots in a number of cases did not give concrete results due to the following difficulties:

a. Spatial variability of soil physical and chemical properties from field to field could have caused different pesticide reactions, hence produced unreliable results.

b. Failure in the pumping system, control chamber or any other instruments had direct effects on the accuracy and the reliability of data.

c. The field variability of pesticide applications could have interfered with the results.

d. There were difficulties in collecting samples on certain events such as: after rainfalls etc., and the remote location of farmer-owned agricultural sites from research centres.

e. The researchers exercised minimal control of any possible malfunction of buried parts. This would include subsurface drain pipe clogging, pipe breaking etc.

f. There is always the possibility of interference due to water transport between adjacent plots.

g. The observations were completely dependent on the natural weather conditions. A wet or dry weather pattern during the period of experiments would give biased results.

To study the impact of water table management on the fate of pesticides, whilst avoiding the above mentioned difficulties, a field lysimeter study was proposed in a typical sandy soil under southern Quebec climatical conditions. Compared to the field plots, the proposed lysimeter setup of this experiment was expected to provide the following advantages:

1. A well controlled reliable environment eliminating the most of possible errors which could happen in the field plots.
2. Flexibility with respect to various study scenarios such as: rainfall simulation to study leaching, the pesticide mass balance, and the control of different water levels.
3. Simplicity and accessibility of the setup for close inspection, sample collection and observation of possible failures.
4. Elimination of mis-interpretation originating from spatial variability of

soil properties, by using a uniform soil.

5. Conducting the lysimeter studies in a fenced area eliminates the chance of interference of external sources such as human and animals.
6. Conducting a water table control study at minimum cost.

There are also some disadvantages of lysimeter studies. Since soil is generally packed into the large lysimeters, it is not possible to attain the soil structure that was existing in the field. In addition, there could be problems of preferential leakage around the sides of the lysimeter.

Investigators have conducted some water table management experiments at lysimeter and field scale in Quebec and elsewhere, (Masse et al., 1994; Arjoon et al., 1994; Aubin et al., 1993; Kalita et al., 1992), but present research will be different from the others since it studies a water table management in the exposed natural climate in combination with advantages of the controlled environment of the lysimeter setup.

1.4. Need For Mathematical Modelling

Mathematical models have been used to simulate the fate and transport of pesticides in soils. However, these simulations have not always been successful, due to the complexity of soil and pesticide behaviour, moisture distribution, and pesticide adsorption in the vadose zone. That is why usually contaminant transport models either under or over-estimate the results. With reference to the spatial variability of soil characteristics and pesticide properties, it is neither possible nor practical to carry out sufficient experiments, in order to study the fate of various pesticides for all soil types under different climatical conditions. The mathematical models, which possess the capability of expansion over time and space may be used to examine series of such alternative scenarios. Another positive aspects of using mathematical model is that they can handle large quantities of computations in a short period of time (Skaggs, 1992).

Mathematical models may be used to predict future conditions. Hence, based on the model response with the conditions imposed upon it, useful recommendations may be made to indicate best management practices. Mathematical models may also be employed to explore the sensitivity of the uncertain parameters involved in the transport processes.

Although, the existing mathematical models have been successful in simulating simple aspects of contaminant transport processes to a reasonable level, there are still difficulties in the simulation of realistic pesticide flux in the soil. Some mathematical models include the effects of subsurface drainage on the fate of pesticides (GLEAMS, Leonard et al., 1987; LEACH-P, Hutson and Wagenet, 1987; PRZM, Carsel et al., 1984), but rarely any model simulates the impacts of subirrigation systems.

A brief review of the most commonly used computer models will be presented in Chapter 2. Among the existing transport models, PRZM2 has the capability of simulating fate and transport of three pesticides simultaneously, and has already been tested and validated in various places in North America. This model will be used in the present study to simulate herbicide movement under subsurface drainage. In its current form, the model cannot be used for subirrigation due to its inability to simulate upward water movement.

1.5. Objectives

The main goal of this research is to investigate the feasibility of an on-farm pollution control system that would result in increased crop yields, provide agricultural pesticides in Quebec. This will be a low-energy water table management system satisfying both agricultural requirements and environmental concerns at the same time. Thus, it could serve as a best management practice for agricultural lands. More specifically, the objectives of this research are:

1. To study the fate and transport of the three most commonly-used herbicides in Quebec, namely, atrazine, metribuzin and metolachlor under different water table management practices at lysimeter scale.
2. To analyze the experimental results with a view to explore the possible use of subirrigation as a BMP for agricultural lands in Quebec.
3. To perform laboratory studies to support the results of lysimeter findings by studying the impact of soil moisture content on herbicide decay.
4. To use a mathematical model to simulate the fate and transport of the above mentioned herbicides.

In order to fulfil the objectives of this study, a three-year field lysimeter and a related laboratory investigation were started in 1993. The final results of this study in the rest of this thesis dissertation will be presented with the following organization:

1) The state of non-point source pollution from pesticides, is reviewed in chapter 2. The agricultural and environmental impacts of herbicides are discussed in this chapter. Since the present study is focused on environmental pollution from atrazine, metribuzin, and metolachlor, this chapter also contains a review of some of their physical and chemical properties.

2) The methodology and results of lysimeter studies will be presented in

2) The methodology and results of lysimeter studies will be presented in three consecutive chapters. Chapter 3 focuses on the fate and transport of atrazine. Whereas chapters 4 and 5 present metribuzin and metolachlor, respectively.

3) The results of laboratory degradation study are presented in chapter 6.

4) Chapter 7 contains results of PRZM2 simulation.

5) Chapter 8 contains the summary and overall conclusions, whereas chapter 9 includes the recommendations for future research.

6) Appendix A contains all raw data pertaining the experiment, and Appendix B contains PRZM2 input and output files.

1.6. Scope of Study

The present study is composed of three major parts, the experimental investigations, the laboratory study, and mathematical modelling. Attempts will be made to expand the results from this study and compare them with the findings of other researchers, however, the following limitations may still hold:

a. Only the three most commonly used herbicides atrazine, metolachlor, and metribuzin were selected for this study. Therefore, experimental observations will be restricted only to behaviour of these pesticides in a sandy soil under the southern Quebec climatological conditions.

b. The lysimeters were packed with a uniform sandy soil to eliminate any possible complexity in the interpretation of the breakthrough curves. Therefore, the experimental results in this study only represent observations in uniform sandy soil.

c. In the packing of the lysimeters, efforts were made to maintain a uniform compacted soil, but still it may vary from lysimeter to lysimeter.

d. The lysimeters have been kept above ground for ease of sampling and to facilitate inspection for any leakage. This has introduced 3 to 4 degrees of higher temperatures to the soil profile which might have further enhanced the degradation of herbicides.

e. In this research only the fate and transport of parent compounds was studied. Therefore, the study of fate of metabolites were not included in this research.

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CHAPTER 2

GENERAL REVIEW OF LITERATURE

Public awareness of the presence of toxic chemicals in the ground water is relatively recent. Since the early 1970's, public concern has focused on the incidence of pollution from agrochemical pollutants. Detection of pesticide and fertilizer residues in surface and subsurface waters has induced the monitoring of water quality as well as the study of the fate of pesticides, in regions of intensive agricultural practice.

From the mid 1970's, many research projects were initiated, in several countries, to study the fate of various pesticides under different soil and climatological conditions [in New Zealand, Rahman, (1975); Rahman et al., (1979); in Europe Brouwer et al., (1990); Giardini and Borin, (1995); in North America, Richard et al., (1975); Junk et al., (1980); Pye et al., (1983); Cohen et al., (1984); Ritter, (1987); Frank et al., (1987); Southwick et al., (1988); Aubin et al., (1993); Masse et al., (1994)].

This chapter reviews previous studies carried out by other researchers investigating the fate of pesticides under different water table management in two following areas: the experimental investigations and mathematical modelling.

2.1. Fate of Pesticides in Soils

Pesticides applied to the soils undergo physical, chemical and biological alterations. Since soils are composed of solid, liquid and gaseous phases, they interact with pesticides in a very complex manner. A fraction of the pesticide interacts with the gaseous phase and may eventually volatilize. Another part is adsorbed on the surface of the soil particles. This fraction accumulates in the soil with time and constitutes the pesticide residue which remains as a source of further environmental pollution. The remaining pesticide interacts with the liquid phase, and is either transmitted to the water courses or leaches down into the soil profile. This fraction is also considered as an environmental threat to the water bodies.

Although pesticides have received more attention than other toxic substances, toxicological and environmental data about them are still not readily available (Shirmohammadi et al., 1995; Pearse et al., 1985). It seems that the first public sensation occurred when chemical residues were found in Love Canal in New York (Logan, 1993). Then, detection of pesticides in other Canadian and American groundwater aquifers led scientists to study the fate of pesticides and to define the processes by which surface and groundwater body contamination occurs.

According to Donigian and Rao (1980) five processes that govern the fate and transport of pesticides are adsorption/desorption, transformation, transport, plant uptake and volatilization. The description of each of these processes is given below:

Adsorption/desorption: Adsorption/desorption is a surface attachment on or repulsion of pesticides from the surface of soil particles. In the process of adsorption, pesticide species are extracted from the liquid or gaseous phase and concentrated at the surface of soil solid phase. The ratio of adsorbed (*S*) to soluble species (*C*) at equilibrium is referred as the distribution coefficient K_d. Adsorption may appear as physical adsorption, involving mainly van der Waals forces and characterized by low energies of adsorption (about 5 kcal/mole), or a chemical adsorption involving the development of strong high energy permanent chemical bonds (20-100 kcal/mole). Pesticides may also penetrate into soil particle. Since it is usually impossible to separate the phenomenon of adsorption from that of absorption, the term absorption is sometimes used to cover both processes (Hillel, 1980).

The primary driving force for adsorption is the solvent-disliking (hydrophobic) character of a pesticide to a particular solvent, and the high affinity of the pesticide for the soil matrix (Abdel-warith, 1987). Conversely, desorption occurs as a result of the hydrophilic character of pesticide to a given solvent. The concentration of the pesticide species desorbed in the soil solution remains in dynamic equilibrium with that adsorbed at the soil surface (adsorption isotherm). The adsorption isotherm can be utilized to explain the equilibrium distribution between the adsorbed phase (*S*) and the liquid phase (*C*). The adsorption process ($\partial S/\partial t$) can be modeled as a kinetic equilibrium (time dependant) or as an instantaneous equilibrium (time independent).

The kinetic equilibrium can be expressed as (Sabatini and Al-Austin, 1990):

$$\frac{\partial S}{\partial t} = K_{ad}\, C - K_{de}\, S \qquad (2\text{-}1)$$

where

S = mass of solute adsorbed to the solid phase, g/g

t = time span, day

K_{ad} = first-order adsorption rate constant, day^{-1}

K_{de} = first-order desorption rate constant, day^{-1}

C = liquid phase solute concentration, g/cm^3

For instantaneous equilibrium, the left hand side of equation 2-1 will be zero and the expression simplifies to:

$$0 = K_{ad}\, C - K_{de}\, S \tag{2-2}$$

or

$$S = \frac{K_{ad}}{K_{de}}\, C \tag{2-3}$$

considering $K_{ad}/K_{de} = K_d$, the linear adsorption isotherm is derived:

$$S = K_d\, C \tag{2-4}$$

where

K_d = linear equilibrium partitioning coefficient, cm^3/g.

The parameter K_d can usually be measured in the laboratory by using a series of tests with varying ratios of soil mass to chemical concentration and shaking them until equilibrium adsorption is reached (about 24 hours). The pesticide concentration in the aqueous phase is determined for each chemical and the pesticide adsorbed to the soil matrix is calculated by mass balance. The slope of plotted values for adsorbed phase versus solution concentration, defines the K_d (partitioning coefficient) value.

Due to the time and expense required to determine the equilibrium partitioning coefficient for all possible combinations of soils and pesticides, relationships between partition coefficient and some easily obtainable soil parameters have been established. Because the organic matter of the soil has the highest combined cation exchange capacity and surface area which interacts with the chemical it qualifies for this relationship. Therefore, the partitioning coefficient can be normalized based on the soil organic carbon content which is essentially independent of soil type. The normalized partitioning coefficient, K_{OC} can be expressed as:

$$K_{oc} = \frac{K_d}{organic\ carbon\ content\ (\%)} * 100 \qquad (2-5)$$

Equation 2-4 assumes a linear relationship between adsorbed phase and liquid phase. Some researchers have found the assumption of linear equilibrium adsorption to be valid (Karickhoff et al., 1979), whereas others believe in a non-linear relationship (Rao and Davidson, 1980). In the case of non-linear behaviour, the adsorption equation may be expressed as a Freundlich isotherm:

$$S = K_d\ C^n \qquad (2-6)$$

where n is a constant value in the range of 0.7-1.2 (Rao and Davidson, 1980). In some cases even if nonlinearity is present, the isotherm still could be linear at low concentrations. In this case, the Langmuir adsorption model will be valid (Sabatini and Al-Austin, 1990). The Langmuir model can be expressed as:

$$S = \frac{QbC}{(1+bC)} \qquad (2-7)$$

where

Q = is the number of moles of contaminant adsorbed per unit weight of adsorbent to form a complete monolayer at the soil particle surface.

b = is a constant

This model assumes a finite number of adsorption sites in the soil, each with equal affinity for the pesticide. As more sites become occupied, the probability of the dissolved pesticide molecule finding one of the remaining adsorption sites becomes less favourable. This leads to non-linearity of the isotherm at higher concentrations, because most favourable sites with higher affinities are filled first (Sabatini and Al-Austin, 1990). Adsorption and desorption are the major mechanisms affecting the fate and transport of pesticides in soils when Darcian flow is considered. These mechanisms affect other processes such as biodegradation, hydrolysis, etc. by retarding the migration of pesticides in the soil profile.

Transformation: Transformation is any process in which a change takes place in the molecular structure of inorganic or organic compound. Nonphotosynthetic microorganisms such as microbes, obtain energy for growth by oxidation of organic compounds, hydrogen, or reduced inorganic elements such as iron, nitrogen and sulphur. Electron acceptors are needed for these oxidations (Bitton and Gerba, 1984). The most available electron acceptor used by microorganisms, is oxygen in air. That is why the highest biological activity is usually observed in aerobic environments. Nitrate, sulphate and carbon dioxide are the main electron acceptors in soil when anaerobic conditions prevail. The energy thus obtained from the oxidation/reduction reactions by microorganisms, is used for cell maintenance and growth (Coats, 1991).

Pesticides may be transformed by biological or nonbiological processes into transformation products. For most pesticides, transformation results in detoxification to innocuous products (Somasundram and Coats, 1991). Transformation of pesticides can start immediately after the application and may occur through chemical transformation and/or biological degradation. In chemical transformation, there will be a change in the structure of original compound through various chemical reactions such as hydrolysis or oxidation. Biological degradation takes place by soil biomass population and results in breakdown of pesticides into smaller fragments with final inorganic end products like CO_2 and H_2O. Biological agents such as bacteria and fungi are known to be the main degraders of pesticides.

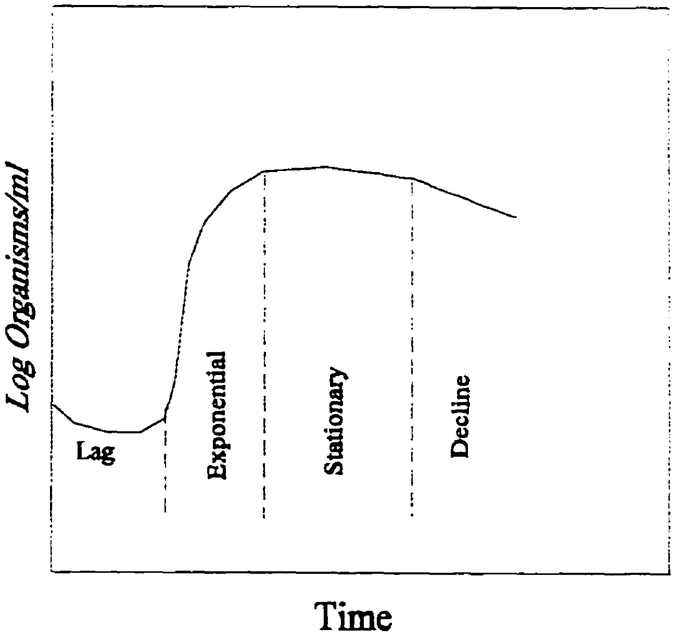

Figure 2.1. Idealized bacterial growth curve (Tate, 1995)

The microbial growth in soil is dependent upon the availability of carbon, nitrogen, other nutrients, aeration, pH, temperature, and soil moisture level. Each of these parameters may serve as stimulant, enhancing biological activities. Microbial growth in soil is usually divided into four phases: Lag Phase, Exponential Growth, Stationary, and Decline (Figure 2.1). Each of these phases can be observed in soil ecosystems depending on the status of nutrients and air in the soil (Tate, 1995).

A Lag Phase occurs when conditions for microbial growth are appropriate, but there is a delay before a measurable change in population density is detectable. Exponential Growth of a specific microbial population in soil may occur due to provision of growth stimulants such as nutrients, biodegradable organic substances, pH, soil moisture, etc. For many microbial species in soil, growth rate is limited to some extent by accompanying cell death. Some surface areas in soil may not be available to microbial colonies, therefore, colonial development is controlled by space available for expansion. The microorganisms which lack the capacity to migrate to new habitats soon become constrained by the accessible soil voids in which they are developing. Hence, replication of these bacteria will depend on production of space by death of companion cells. This situation leads the microbial colonies to a stage which is called a Stationary Phase (Tate, 1995).

Under relatively constant conditions, the long-term survival depends on maintaining balance in microbial population size. To maintain the stability of microbial community (carbon and energy supply in equilibrium with population size), the augmented population must return to its pre-existing density. Therefore, after the exhaustion of the available substrate, microbial colonies are forced to Decline Phase, and population increase are dampened by death and decay of the newly synthesized cell mass.

Among the various parameters, soil moisture is an important stimulant and essential contributor to the growth of soil microbes. The higher the soil moisture level, the greater the soil biological activities. Microbial population use soil moisture as a medium for growth as well as for cell metabolism. Water molecules serve as direct participants in the hydrolysis and hydroxylation reactions of biological compounds. Transport of microbial nutrients to the cells and waste materials away from them are accomplished by soil moisture. Soil water balances the temperature fluctuations of the soil system. The higher the soil moisture contents, the more resistant that soil ecosystem is to temperature fluctuations (Tate, 1995).

Among living entities, microbial communities have the greatest resistance to temperature extremes. Microbial growth in soil mainly occurs in the ranges 0 to 70 °C. Soil biological activity increases from a minimum at or near 0 °C to a maximum around 70 °C (Tate, 1995). In actual fields, climate controls the moisture and temperature levels which are the two important factors affecting soil microbial activities. By introducing these two stimulants, higher temperature and higher soil moisture contents to the soil profile (subirrigation), microorganism activity will increase, and those microorganisms which use the organic substrate (pesticides) generally win out in the food competition. Therefore, organic molecule oxidation usually proceeds first, followed by nitrification, provided that sufficient oxygen still remains (Bitton and Gerba, 1984). This may help boost the biomass growth rate (biological activity) to an exponential level, and increase biodegradation of organic materials such as pesticide residues (Figure 2.1).

There are many organic contaminants in the soil that are not readily transformed by biological processes. This may be due to absence of essential growth factors, structural characteristics of the organic molecule that prevent enzymatic attack, etc. Transformation rates under aerobic and anaerobic conditions will also be different. Some compounds appear to degrade only under aerobic conditions and others only in anaerobic environments. There are still compounds that transform under either condition, whereas some others are not transformed at all. Results of previous batch studies indicate that the aromatic compounds such as Chlorobenzene (C_6H_5Cl) and Naphthalene ($C_{10}H_8$) are susceptible to aerobic, but not anaerobic biodegradation. Halogenated aliphatic compounds like Chloroform ($CHCl_3$) and Trichloroethylene ($CHCl{:}CCl_2$) degraded only under anaerobic conditions (Bitton and Gerba, 1984). Herbicides such as atrazine and metribuzin degrade faster under aerobic conditions. Metolachlor degradation is not significant under anaerobic conditions (Jebellie et al., 1996).

The most acceptable model for the degradation of organic compounds is a first order kinetics (Wagenet and Rao, 1985). The mathematical model for first order degradation can be expressed as:

$$\frac{\partial C}{\partial t} = k(\rho * S + \theta * C) \qquad (2\text{-}8)$$

where

C = liquid phase solute concentration, g/cm^3
t = time span, day
k = decay rate constant for solid and liquid phase (day^{-1})
ρ = soil bulk density (g/cm^3)
S = mass of solute adsorbed to the solid phase, g/g
θ = soil volumetric moisture content (cm^3/cm^3).

This expression combines the total chemical and/or biological degradation occuring in the solid and liquid phases. The k value is dependent on the half-life of each compound, and can be determined empirically through laboratory experiments.

Transport: Solutes in the soil profile usually move under the influence of coupled flow processes. In coupled flow processes, solutes migrate not only in response to conventional advection-dispersion-diffusion flow, but also in response to gradients in chemico-osmosis, electro-osmosis, and thermal diffusion. Because coupled flow processes usually pertain only to very fine-grained soils, it is usually considered to be insignificant in the study of contaminant transport (Shackelford, 1993). Therefore, the transport of dissolved contaminants, such as pesticides, in the saturated and unsaturated soil profile can be simplified to the net effect of three main processes: advection, dispersion, and diffusion (Mackay et al., 1985).

Advection is a process by which solutes are transported with the bulk motion of flowing water in response to a total hydraulic head gradient. In addition to that, in traditional contaminant transport study, a mechanical dispersion term is also added to the total mass flux of the solute to account for the spreading of the contaminant due to different pore sizes. Random movement of molecules in a fluid produces an additional flux of contaminant which moves from regions of higher solute concentrations to those of lower ones. This phenomenon, which again takes place in the void space, is referred to as molecular diffusion. Because separation between these two processes is rather difficult, the term hydrodynamic dispersion is often used to denote solute spreading at the microscopic scale (Bear and Verruijt, 1994; Freeze and Cherry, 1979).

Considering all the three processes simultaneously, the convection-dispersion-diffusion for a reactive solute (pesticides) under a one-dimensional transient flow (vertical) in the unsaturated zone can be expressed as (Wagenet and Rao, 1985):

$$\frac{\partial(\theta C)}{\partial t} + \frac{\partial(\rho S)}{\partial t} = \frac{\partial}{\partial z}\left[\theta \cdot D(\theta,q)\,\frac{\partial C}{\partial z} - qC\right] \pm \phi(z,t) \qquad (2\text{-}9)$$

where

C = liquid phase solute concentration, g/cm^3
t = time span, h
ρ = soil bulk density (g/cm^3)
S = mass of solute adsorbed to the solid phase, g/g
z = soil depth, cm
θ = soil volumetric moisture content (cm^3/cm^3).
D = hydrodynamic dispersion coefficient, (cm^2/h)
q = water flux (cm/h)
Φ = sink term (g/cm^3/h).

Hydrodynamic dispersion is a function of soil moisture level (θ) and water flux (q). Because hydrodynamic dispersion is very difficult to measure, some empirical relationships between soil parameters and hydrodynamic dispersion have been established. These relationships take the measurable soil parameters as inputs, and estimate the soil hydrodynamic dispersion coefficient. The sink term in this equation includes all losses including degradation, plant uptake and volatilization.

Volatilization: Volatilization is characterized by the migration of molecules of chemicals in gaseous form from the surface of soil, water and plants to the atmosphere. The volatilization flux is influenced by the chemical aqueous solubility and sorption. A fraction of a chemical which adsorbs to the soil or dissolves in soil solution is still considered available for diffusion into the air. The distribution of a chemical between water and air is expressed by Henry's Law which can be written as :

$$K_w = \frac{C}{C_a} \tag{2-10}$$

where

K_w = Henry's Law constant

C_a = Concentration of chemical in air, g/g

This relationship describes how a chemical partitions itself between water and the atmosphere under equilibrium conditions (McCall et al., 1983). Henry's constant (K_w) is an empirical value which can be measured in the laboratory.

Plant uptake: As plants transpire through the stomata, water is taken up by the roots to satisfy the plant water demand. The flux of water absorbed by the rooting system, transports dissolved chemical into the plant cells through the stem and leaves. Flow of organic chemicals such as pesticides to the plants is influenced by the plants transpiration, soil moisture retention curve characteristics, pesticide concentration etc.. Plant uptake of water is assumed to follow Ohm's law. The rate of water uptake is then assumed to be directly proportional to the difference in total head between the soil and the root density (Feddes et al., 1978). Therefore, plant uptake is usually quantified as a function of soil moisture pressure head and the rooting density.

In general, the fate and transport of pesticides in soils depend upon three main parameters. These include characteristics of pesticides themselves, the soil properties, and the weather conditions (Nicholls, 1988). The characteristics of the three herbicides selected for this study, atrazine, metribuzin, and metolachlor will be described in the following section. The soil properties and data on the climatic conditions will be presented in chapter 3.

2.1.1. Fate of Atrazine in Soil

Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, was first introduced in Canada about 1960 to control weeds in corn production. At present, atrazine is one of the most widely used pesticides in Canada (Trotter et al., 1990). Atrazine is a white crystalline compound with a molecular weight of 215.7, and melting point of 173-175 °C. The aqueous solubility of atrazine is only about 33 mg/L at 27 °C, but it is highly soluble in organic solvents such as methanol (18000 mg/L at 27 °C). Atrazine is a heterocyclic poorly polar selective herbicide with molecular formulation of $C_8H_{14}ClN_5$.

Atrazine is a selective pre-and post-emergence herbicide widely used in corn, sorghum, sugarcane, and pineapple farms for the control of annual broadleaf and grassy weeds. The principal mode of action of atrazine in plants appears to be the blockage of photosynthesis. It also has a high microbial decay rate. Except under dry and cold conditions, atrazine residues do not last longer than one year in the soil (Colby et al., 1989). The atrazine half-life is highly dependent upon soil pH, temperature, and organic matter. Half lives of 95-165, 145-350, and 3-5 years are estimated for pHs of 4, 7, and 8, respectively (Trotter et al., 1990).

Chemical hydrolysis of atrazine to hydroxyatrazine has been reported to be a major pathway of atrazine degradation. The rate of atrazine degradation by hydrolysis is positively correlated with soil adsorption. But as atrazine adsorption increases, its half life decreases. Higher soil temperatures and pH result in lower atrazine adsorption. Dealkylation of atrazine molecules through microbial activities is another primary mechanism for atrazine degradation. Biological dealkylation occurs simultaneously with chemical hydrolysis, which causes ring cleavage and results in total microbial degradation (Goswami and Green, 1971). In a field study in Quebec, Masse et al. (1994), found atrazine to be a persistent and leachable herbicide. Atrazine residues were reported to be one of the most commonly detected herbicides in Ohio (Baker, 1993). According to a risk assessment study that took into account the leaching potential, extent of usage, and toxicity of pesticides in the Nomini Creek watershed in Virginia, (Shukla et al., 1995), atrazine was ranked first as a frequent detected pesticide, and had the highest Relative Mobility Index (RMI).

According to literature, the significance of volatilization in atrazine dissipation is not fully understood. The available data indicate that volatilization can occur to some extent under conditions of high temperatures and prolonged light exposure (Ghassemi et al.,1981).

Atrazine residues are expected to be more persistent under saturated soil conditions due to the slower rate of chemical hydrolysis and lower microbial metabolism of atrazine under anaerobic conditions (Trotter et al., 1990).

2.1.2. Fate of Metribuzin in Soil

Broadleaf and grass weeds in potato, tomato, soybeans, sugarcane, and carrot farms are usually controlled by metribuzin (4-amino-6-(1,1-dimethylethyl)-3-methylthio)-1,2,4-triazin-5(4H)-one. Metribuzin was first synthesised and discovered more than two decades ago. The first patent application of metribuzin was made in former West Germany in 1966 (Hatzios and Penner, 1988). At present, metribuzin is one of the most active and most widely used herbicides in Canada, United States, and some other parts of the world.

Metribuzin can be applied as a pre-emergence or early post-emergence herbicide. Its mode of action in weeds consists of inhibiting photosynthesis by penetrating the leaf surface via the plant aqueous route.

Metribuzin is a white crystalline solid compound with a molecular weight of 214.3, and melting point of 125.5-126.5 °C. The density of metribuzin is about 1.28 g/cm^3. Metribuzin is a heterocyclic, basic organic molecule and its molecular formulation is $C_8H_{14}N_4OS$.

The solubility of metribuzin in water is about 1220 mg/L. It is highly soluble in most organic solvents including acetone (82000 mg/100g), and methanol (45000 mg/100g). Metribuzin adsorbs to the soil particles, and the rate of adsorption increases at lower soil pH. Under field conditions, adsorption of metribuzin to the soil matrix is very important since it influences the persistence and herbicidal activity of the herbicide (Hatzios and Penner, 1988). In any given soil, the adsorption/desorption rate of metribuzin will determine the availability of metribuzin for weed control, transport, and dissipation through leaching or degradation.

Microbial breakdown is the major mechanism by which metribuzin is lost from the soils. All environmental factors such as temperature, pH, and soil moisture, were also found to favour the degradation of metribuzin in soil. The heterocyclic ring of metribuzin could be cleaved by soil microorganisms (Hatzios and Penner, 1988). Degradation products are mostly formed by the action of soil micro-organisms. These products are usually less biologically active but more polar than the parent compounds, so they usually have a greater potential for leaching (Nicholls, 1988).

Metribuzin is relatively mobile in sandy soil but very immobile in soils with high organic matter. According to a risk assessment study in Nomini Creek watershed in Virginia, metribuzin was ranked as the second most frequent detected pesticide with a high Relative Mobility Index (RMI). The assessment was based on the leaching potential, extent of usage, and toxicity of pesticides

(Shukla et al., 1995). A study conducted at Louisiana Agricultural Experimental Station on a silty clay loam in a soybean field, found medium leachability of metribuzin (Orlino et al., 1994).

The mobility of metribuzin increases as the soil pH increases (Hatzios and Penner, 1988). Depending upon the soil type, soil pH, temperature, and soil moisture, the half-life of metribuzin in soil could range from a few days to more than four months. For instance, the half-life of metribuzin at normal usage rates is about 46 days at 20 °C, and 16 days at 35 °C (Hyzak and Zimdahl, 1974).

2.1.3. Fate of Metolachlor in Soil

Metolachlor, 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide, is another selective herbicide used to control grass weeds in corn, soybean, potatoes, snap beans, dry beans, sorghum, lima deans, sugar beets, and rutabagas fields. Metolachlor is not manufactured in Canada and was first registered in Canada in 1977 (Kent et al., 1991). Reported imports of metolachlor for Canada in 1987 were 4322 tons (Kent et al., 1991). Metolachlor is a colourless and odourless compound at 25 °C with a molecular weight of 283.8 and a molecular formula of $C_{15}H_{22}ClNO_2$. Metolachlor is a highly polar herbicide with an aromatic benzene ring in its chemical structure.

Metolachlor is very soluble in most organic solvents including benzene, dichloromethane, hexane, methanol. Its solubility in water is about 530 mg/L at 20 °C. It is a relatively non-persistent herbicide. Radio-labelled studies have shown a rapid decline of the parent compound. All biological evidence indicates that metolachlor does not persist from one season to the next (Colby et al., 1989). However, Masse et al. (1994) detected metolachlor in the groundwater samples after two years. The half-life dissipation rate for metolachlor has been determined from both laboratory and field studies, to be 30 to 50 days in northern areas and from 15 to 25 days in southern areas of North America.

Metolachlor is used as pre-emergence or pre-plant incorporation. The general mode of action for metolachlor appears to be the inhibition of protein synthesis in weeds. Volatilization and photodegradation losses of metolachlor from a soil surface are very small, but volatilization from glass or plant surfaces can approach 50 % (Kent et al., 1991).

Biodegradation is the primary cause of metolachlor dissipation from field soils. Factors such as temperature and higher organic matter that favour increases in microbial activity, will decease the persistence of metolachlor in soil. Shukla et al. (1995) ranked metolachlor as the fifth most frequent detected pesticide in Nomini Creek watershed in Virginia.

Major degradation of metolachlor occurs under anaerobic conditions, and its anaerobic metabolism is rather minimal (Kent et al., 1991). Table 2.1 provides the summary of the range of detected herbicides and their accepted limits in ground waters of Canada and USA.

2.1.4. Background of Water Table Management Practices

It is not quite clear from the published literature how and where the concept of water table management (WTM) was brought up. However, research on the environmental aspects of WTM began in the mid 1980's. Fausey et al. (1990) stated that primary WTM research was first started in the U.S., primarily in Indiana, Iowa, Louisiana, Ohio, North Carolina and Michigan. Research regarding WTM practice has recently expanded to other places in both Canada and the USA.

Table 2.1. Herbicides Found in Groundwater

Herbicides	Detected (µg/L) Canada	Detected (µg/L) USA	Accepted Limits (µg/L) Canada(1)	Accepted Limits (µg/L) USA (2)
Atrazine	0.1 - 74	0.01 - 88	60	3
Metolachlor	0.2 - 29	0.1 - 55	50	10
Metribuzin	7.8 - 29.4	1.0 - 4.3	80	175 (for whole life)

(1) Anon. (1987a)

(2) Anon. (1987b)

The concept of water table management and its impacts on the fate of pesticides was initiated by the development of subsurface drainage. Subsurface drainage, as a dominant drainage practice in humid regions of North America, provided several agricultural benefits. These included optimal crop growth and better soil workability.

Schwab and Frevert (1985) discussed several benefits of subsurface drainage for both soil and plant environments. Smedema and Rycroft (1983) summarized all drainage benefits as "better yields at lower costs"; however, they also warned drainage planners about some harmful impacts of subsurface drainage.

Since similar warnings had also been expressed by other researchers, further investigations were initiated to determine the impact of subsurface drainage on the environment. It has been found that compared to undrained soils, the subsurface drained soils can reduce pesticide loading by reducing the amount of surface runoff from agricultural lands (Schwab et al., 1973; Baker and Johnson, 1977; Bengtson et al., 1984; Southwick et al., 1990; Bengtson et al., 1990).

However, findings from several other investigations revealed that the drain outflows containing nutrients and pesticide residues, could themselves become a source of pollution for the water bodies (Muir and Baker, 1976; Patni et al., 1987; Gilliam, 1987; Hall et al., 1989). Therefore, subsurface drainage systems, which proved to be beneficial from an agricultural point of view, turned out to have some negative as well as positive environmental impacts.

Most of the pollution risks from the subsurface drained fields, come from the fertilizers and pesticides applied to the soils rather than the mere installed drain pipes. If pesticide concentration in soil or water bodies exceeds the advisory limits, this may cause health problems for humans and disturb the aquatic life of ecosystems. Unfortunately the considerable amount of pesticides sold and sprayed each year (Table 2.1) have polluted Canadian and American soils and water resources. The following evidences demonstrate the continued increase of pesticide pollution from agricultural lands.

Cohen et al. (1986) reported that metolachlor levels in Pennsylvania ground water ranged from 0.1 to 0.5 µg/L (ppb). Atrazine has been detected in Nebraska ground waters in large concentrations (Helling and Gish, 1986). In Maryland, the maximum level of atrazine detected was 6 µg/L (Isensee et al., 1988).

Atrazine and metolachlor concentrations in subsurface drain outflows, in southern Louisiana, were reported to vary from 0.015 to 3.53 µg/L and 0.4 to 29.3 µg/L, respectively (Southwick et al., 1988). Frank et al. (1982) reported detection of atrazine in surface waters in southern Ontario, with a maximum concentration of 32.8 µg/L; whereas the USEPA safe limit for atrazine is about 3 µg/L.

In a survey of 91 wells in southern Ontario atrazine residues ranged from 0.1 to 74 µg/L (Frank et al., 1987). Muir and Baker (1976) reported atrazine concentration in a subsurface drain outflow in Quebec, ranging from 0.3 to 1.5 µg/L. Muir and Baker (1978) reported atrazine concentrations of 0.01 to 26.9 µg/L in the surface waters of the Yamaska River basin, Quebec. Patni et al. (1987) reported a maximum concentration of metolachlor of 12 µg/L in the drainage water of a field near Ottawa. It should be noted that the maximum recommended level of this herbicide in drinking water, is 10 µg/L in the US.

Aubin et al. (1993) conducted a field study in sandy soil in Quebec, and reported metribuzin in ground waters in concentrations up to 279 µg/L. Studies conducted by Masse et al. (1994) in St-Amable sandy soil at Macdonald Campus Farm, Quebec, showed atrazine and metolachlor concentrations in ground waters to be 14 and 5 µg/L, respectively .

After each rainfall or irrigation, the dissolved pesticides tend to find their way to the water bodies by surface runoff, subsurface drain outflows or direct leaching through the soil profile. Therefore, drainage and related water management systems should be designed to satisfy both agricultural and environmental goals (Skaggs, 1992). Pesticides usually have a field half life of less than two months. A tentative hypothesis maintains that if herbicides are prevented from being leached to the water bodies for this period of time, the micro-organisms may tend to break them down, and hence reduce the residues to safe levels. In areas, such as southern Quebec, where the installation of subsurface drainage is essential and supplementary irrigation is also provided, subirrigation or controlled drainage could help achieve these goals. Kanwar

(1996) reported that from previous investigations conducted in USA, water table management practices (subirrigation) can be recommended with other sound agricultural practices to reduce the environmental pollution.

2.1.5. Fate of Herbicides Under WTM

Field studies have been carried out in both organic and mineral soils to study the fate of herbicides under subirrigation, controlled drainage and subsurface drainage systems (Fausey, 1995; Arjoon et al., 1994; Aubin et al., 1993). Using subirrigation in the subsurface drained fields as a means of water table management could provide optimal moisture condition for plant growth, and the environmental benefits by reducing the possibility of pollution of water bodies (Kanwar, 1996; Broughton, 1995).

A three-year field experiment by Chieng (1987) revealed that subirrigation can be practised successfully through existing subsurface drainage systems; however, there were also some adverse effects on the hydraulic properties of the soil. The drainable porosity of subirrigated soils may be reduced by the transportation and deposition of fine soil particles, or by compaction of soil.

Belcher (1989) conducted a field experiment to study the effects of subirrigation on the fate of agricultural chemicals. In a three-year field experiment in the Georgia flatwoods, Thomas et al. (1991) used controlled drainage-subirrigation systems to study the WTM impact on the water quality in loamy soil. In their monitoring studies, controlled drainage-subirrigation plots showed less chemical concentrations in the outflow water. They concluded that controlled drainage and subirrigation systems can improve the water quality of shallow ground water. However, they maintained that "not enough information is available to quantify the environmental effects of this practice." This finding agrees with the experimental results of some other researchers, such as Kalita et al. (1992) and Aubin et al. (1993).

A field experiment was conducted on lysimeters by Kalita and Kanwar (1990) in Iowa to investigate the effects of different WTM practices on the movement of pesticides in a loamy soil. They tried to maintain three water levels, i.e. 0.3, 0.6, and 0.9 m below the soil surface, in order to represent different subirrigation treatments. However, they had difficulty maintaining constant water levels in the plots. Water samples were collected from 1.2, 1.8, and 2.4 m depths from subirrigation treatments.

The lowest concentration in this experiment was found in the 0.9 m water table treatment. In most cases, the concentration at 1.2 m depth decreased with time, but showed different trends at other sampling depths. The influence of water table management practices on pesticide mobility was not clear with one year of data, since the relationship between the water table depth and pesticide leaching was not properly established.

In another experiment using a dual pipe subirrigation-drainage system, Kalita et al. (1992) in Iowa, reported results similar to those of Belcher (1989), and Aubin et al. (1993). Five water table depths were maintained at 0.20, 0.3, 0.6, 0.9, and 1.1m below the soil surface. In the groundwater samples taken from different water table depths, they found that atrazine concentration decreased under shallow water-table conditions. Atrazine concentrations showed a considerable decreasing trend with respect to soil depth and time (Kalita et al., 1992).

A three-year field experiment was undertaken by Arjoon et al. (1994) to study the effects of subirrigation, controlled drainage, and subsurface drainage systems on water quality, in organic soil in southern Quebec. Results of this experiment showed that less pesticide leaching occurred in controlled drainage and subirrigation treatments. It was postulated that the shallow water table in the "managed" treatments kept the pesticide closer to the soil surface, providing a greater probability of pesticide degradation. This, in turn, decreased the amount of pesticide available for leaching. However, based on this experiment, the distinction between leaching and degradation of pesticide was not clear.

Arjoon et al. (1994), also studied the influence of water table management on the reduction of pollution by metolachlor from a typical loamy sand soil of Quebec. This field experiment supported the results obtained by other researchers regarding the limited movement of metolachlor in soil. However, they found that under water table management, in some cases the higher water table could induce the movement of pesticides into lower soil levels and consequently into the ground water. Metolachlor showed higher concentrations in subirrigation treatments. This was possibly due to desorption and higher solubility, which left more pesticide for leaching. This study, which investigated the influence of water table management in the fate of metolachlor, did not confirm findings by other researchers regarding the reduction of pesticide concentration at shallower depths.

Aubin et al. (1993) conducted a field experiment in Quebec to investigate the role of water table management on the leaching of metribuzin in a sandy soil in Quebec. They reported longer persistence for metribuzin under drainage vs. subirrigation plots. In their experiment, higher adsorption and higher microbial degradation was observed at higher soil moisture content. Their findings agreed with the results of other researchers, who found that the herbicides dissipate faster in subirrigation plots compared to drainage plots. However, the authors pointed out the necessity for further investigation.

Referring to the preceding review of literature, it seems that the water table management experiments conducted in field plots were not always successful in producing reliable results. As was discussed in chapter 1, the field variability of soil properties and pesticide application as well as the inflexibility of field setups to the research scenarios were among the major reported problems.

2.2. Mathematical modelling

Contaminant transport modelling efforts started almost two decades ago, coinciding with a rapid increase in the use of agrochemicals. Several mathematical models have been developed since that time. Mathematical models may not always give a complete picture of the various aspects of the complex processes occurring in the soil. Over-simplification of the complex processes, which is usually necessary in mathematical modelling, often leads to unrealistic response of the models. However, the efforts to develop new models or improve the performance of existing ones should not be stopped, since the dynamic nature of environmental problems cannot otherwise be easily understood. Mathematical models are also useful in quantifying various processes because they allow us to handle large numbers of computations over long periods of time (Skaggs, 1992).

There are many contaminant transport models which simulate the non-point source pollution (NPS) in soils. The most commonly used models in chronological order may be listed as follows:

1. CREAMS (Knisel, 1980);
2. PRZM (Carsel et al., 1984);
3. CMIS (Nofziger and Hornsby, 1986);
4. MOUSE (Steenhuis et al., 1987);
5. GLEAMS (Leonard et al., 1987);

6. LEACH-P (Hutson and Wagenet, 1987);
7. RUSTIC (Dean et al., 1989);
8. PREFLO (Workman and Skaggs, 1990);
9. MACRO (Jarvis et al., 1991);
10. PRZM2 (Mullins, 1992);
11. ARS-RZWQM (Ahuja et al., 1993);
12. PESTFADE (Clemente et al., 1993).

A brief review of the performance of selected mathematical models will be carried out here. It was not intended to include all existing models in this review. Therefore, according to a preliminary judgment, the most commonly used and the more closely related pesticide transport models were selected for this purpose.

1. CREAMS, or Chemical Runoff and Erosion from Agricultural Management Systems, is a physically-based continuous simulation computer model which can analyze up to 10 chemical compounds and several years of records (Knisel, 1980). The model is composed of three major components that simulate hydrologic processes, erosion, and non-point source contaminants. The Green-Ampt infiltration equation or Soil Conservation Service (SCS) Curve Number method may be selected to calculate the runoff depth.

The CREAMS model has been tested against observations from several research watersheds, and can be used to study the management practices (Rudra et al., 1985; Matthew and Mulkey, 1982). However, further improvement may be needed to evaluate vertical flux and plant uptake by pesticides. The model assumes uniform porosity and moisture retention characteristics for the entire soil, which is an over simplification. The model can handle neither the water table management practices such as subsurface drainage systems, nor the macropore flow in the soil profile.

2. **PRZM,** which stands for Pesticide Root Zone Model, is a continuous simulation model. It includes surface runoff, erosion, leaching, and the related pesticide transport compartments (Carsel et al., 1984). The SCS curve number is used along with the daily rainfall to compute daily runoff. The water balance equation is coupled to a modified version of the advection-dispersion equation in order to estimate solute movement. The model allows multi-layer or multi-compartment treatment of pesticide transport.

PRZM has been used to simulate the pesticide movement to ground waters (Smith, 1991; Smith et al., 1989). However , but further evaluation of the performance of this model may be required before its application to sophisticated cases of solute transport in different soils. There are also inadequacy of some elementary soil hydraulic assumptions (i.e., drainage of entire soil column in one day, no particular treatment of preferential flow, etc.).

3. **CMIS,** is known as Chemical Movement In Soil. This is a simple continuous simulation model which deals with linear and reversible equilibrium adsorption (Nofziger and Hornsby, 1986) . The infiltration and evaporation are inputs and can be varied to simulate different leaching potentials. The model does not include the runoff and erosion losses. The chemical transport in this model is based on the traditional convective-dispersive equation and no provision of macropore flow has been provided. This model is mainly used for instructional purposes.

4. **MOUSE,** stands for Method Of Underground Solute Evaluation. This model deals with the movement of soluble chemicals in saturated and unsaturated zones (Steenhuis et al., 1987). The model includes several processes such as

linear adsorption/desorption isotherms, first order degradation, dispersion, diffusion and mass movement.

This model has been mainly oriented for teaching purposes and has the limitation of simulating highly soluble chemicals. The model does not include plant uptake and volatilization. The transport of chemicals is based on the conventional convective-dispersive equation, and preferential flows are not included in the model.

5. GLEAMS, is the Groundwater Loading Effects of Agricultural Management Systems model (Leonard et al., 1987). This model is a new streamlined version of CREAMS with the added capability of simulating sophisticated management practices, together with better treatment of the bottom of the root zone. The basic components of pesticide transport are the same, except that the important advantages over the CREAMS model are the inclusion of vertical flux and uptake of pesticides.

The soil porosity, moisture retention characteristics, and organic matter content are inputs to the hydrology component of the model. The storage routing technique is used to calculate the percolation. The model uses the Soil Conservation Service curve number method to simulate runoff. The upward movement of pesticides due to plant uptake and evaporation is included.

The GLEAMS model is a field scale model, and has been tested against several field observations (Kumar and Kanwar, 1996; Masse and Prasher, 1989; Shoemaker et al., 1988; Leonard et at., 1987). It seems that the model is not yet complete, and further development of the vadose zone from the bottom of the root zone to the ground water is necessary (Leonard et al., 1987). However, the transport process in the root zone area is based on the Darcian-based equation of convection and dispersion. This only deals with matrix flow in the unsaturated zone. This model has been equipped to study the impacts of subsurface drainage.

6. **LEACH-P,** stands for Leaching Estimation and Chemistry Model (Hutson and Wagenet, 1987). LEACHM-P is one of the five versions of LEACHM model, which simulates nonvolatile pesticides in the unsaturated zone. The model has considerable sophistication and flexibility so that water and solute movement can be calculated with great accuracy (Hutson and Wagenet, 1993).

LEACH-P is primarily a research model which can answer research questions. The model has three different versions with capabilities for calculating instantaneous and reversible pesticide sorption. The pesticide movement is based on the convective-dispersive equation. The model does not include the runoff, the effects of management practices, crop yield, unequal increment of soil depth, macropore flow, and fate of degradation products.

7. **RUSTIC,** is the abbreviation for Risk of Unsaturated Saturated Transport and Transformation of Chemical Concentrations (Dean et al., 1989). The fate and transport of pesticides are predicted via three linked submodels PRZM-II, VADOFT, and SAFTMOD. PRZM-II is a new version of PRZM with additional features such as: irrigation simulation, volatilization, and vapour phase transport in soils.

VADOFT carries a finite element code to solve the one-dimensional form of Richard's equation, in a single domain approach. The pressure head, water content, and hydraulic conductivity can all be input to this submodel. In saturated flow, SAFTMOD uses a two-dimensional finite element model to simulate the solute transport.

The RUSTIC model has the flexibility to handle various cases of hydrological conditions, soil types, climates and pesticides. However, there are certain limitations such as the incompatibility of coupling between the submodels.

8. PREFLO, is a Preferential Flow model, which uses a one-dimensional finite difference solution to the Richard's equation with a nonuniform grid spacing (Workman and Skaggs, 1990). The PREFLO model studies unsaturated and saturated movement of water in a soil profile. Vertical movement of water in large pores is computed based on the equation for flow in capillary tubes. In this model, large pores are assumed to represent some measurable percentage of the soil surface area.

In an evaluation with field data, PREFLO tended to show some inaccuracy in the simulated water table depth and evapotranspiration (Workman and Skaggs, 1991). It seems that further model validation efforts are required before the model could be used as a flow simulator in any existing solute transport models.

9. MACRO, is a transient field scale model which uses a two-domain flow model of convective-dispersive transport. It also separates the micropores from macropores by their water content or water potential (Jarvis et al., 1991). Each domain is characterised by a degree of saturation, conductivity and a flux, while interaction terms account for convective and diffusive exchange between flow domains. In the MACRO, as in the van Genuchten and Wagenet (1989) approach, the sorption sites are assumed to be partitioned into a fraction *f* that equilibrates with the macropore fluid and another fraction (1-*f*) that equilibrates with the micropore liquid.

This model has been applied and tested against a lysimeter study in a well-structured clay soil and showed good agreement with the experimental results.

However, some researchers (Gupte et al., 1991) suggested that the simple concept of dividing total flow into macropore and matrix flow may not be sufficient to explain the very high velocities involved in macropores. Therefore, the model may not be able to simulate all possible cases of pesticide transport in all soils.

10. PRZM-2, the next generation of PRZM model, has two major computational components PRZM and VADOFT (Mullins et al., 1992). The PRZM-2 code has been designed to provide state-of-the-art deterministic simulation of fate of pesticides, applied for agricultural purposes, both in the crop root zone and the underlying vadose zone. The model is capable of simulating multiple pesticides or parent/metabolite relationships. The model is also capable of estimating probabilities of concentrations or fluxes from various media for the purpose of performing exposure assessments.

Due to its comprehensive treatment of important processes, its dynamic nature, and its widespread use, PRZM (Carsel et al., 1984), was selected to simulate the crop root zone depth in PRZM-2. Next, the enhanced version of PRZM was linked to a one-dimensional vadose zone flow and transport model (VADOFT). Both the VADOFT and PRZM modules simulate water flow and solute transport.

11. ARS-RZWQM, is Root Zone Water Quality Model (Ahuja et al., 1993). This model was developed to deal with preferential water and chemical transport. Water flow, is based on a simple two-domain approach, namely soil matrix and macropore channels. The soil matrix is subdivided into micropores (immobile), and mesopores (mobile).

The micropores are assumed to have no effect on flow. The soil matrix is partitioned either by input values or by the soil water retention curve at a prescribed suction. The water movement in the soil matrix was determined using the Green-Ampt equation for vertical infiltration; whereas for water movement in the circular or planar macropores the adapted Green-Ampt approach was used.

ARS-RZWQM is the only recently reported mathematical model which considers the macropore flow based on the hydraulic properties of the soil pores. The model incorporates a comprehensive treatment of pesticide transport. There have been recent attempts, to equip this model to study the impact of water table fluctuations (Johnsen et al., 1995). It has been tested against observations from a silty clay loam soil, but further calibration and validation for other types of soils is needed before its application (Kumar and Kanwar, 1996b).

12. PESTFADE, is a Pesticide Fate And Dynamic in the Environment model, which can simulate water and solute movement in the soil (Clemente et al., 1993). In addition to all the processes related to the fate of pesticides, this model also includes macropore flow which is based on two-site non-equilibrium sorption kinetics. The sorption sites in the soil are divided into two parts in order to represent the main soil matric and macropores, and the relationship between them is defined by a fraction called the macropore factor.

The two-domain approach has been introduced to this model by incorporating an empirical correction factor for macropores. Since this model assumes a non-physically based factor of correction, it does not consider the spatial variability of pore size geometry. However, the model employs state-of-the-art mathematical expressions of all the components of the pesticide transport model: adsorption/desorption, leaching, degradation, volatilization, plant uptake, runoff. This model can be used to study the impacts of water table management on the fate of pesticides.

Based on the preceding review of some of the most commonly used pesticide models, the following limitation may be noted:

1. Some existing models do not consider the combined effects of all aspects of fate of pesticides in soil.
2. Certain models do not compute the runoff water quality and quantity (LEACHP).
3. Some models do not consider plant uptake (MOUSE).
4. Some models have excluded the vapour phase partitioning of pesticides, and hence cannot handle volatile pesticides (PRZM).
5. Certain models need the inclusion of agricultural management practices (LEACHP).
6. In some models, the dynamic nature of the soil environment is treated relatively simplistically (PRZM).
7. Certain models have been designed to represent only the transport processes in the root zone; simulation from the bottom of the root zone to the ground water is still to be included (GLEAMS).
8. Some models are suitable only for water flux simulation and do not include solute transport (PREFLO).
9. Certain models are still under further development and need to be validated against further field observations (ARS-RZWQM, PESTFADE).

Among the previously reviewed models, ARS-RZWQM, PESTFADE and PRZM2 seem relatively more complete than the others since they are designed for comprehensive treatment of the pesticide transport in the saturated and unsaturated zones. The ARS-RZWQM model was developed in Fort Collins USA, by the Agricultural Research Service of the United States Department of Agriculture (ARS-USDA), but still needs further verifications. The PESTFADE model has been developed at Macdonald Campus of McGill University, Quebec but needs further verification and better documentation. In general, based on the reasons presented in the previous sections, the PRZM2 computer model was selected for this study due to its following features:

- State-of-the-art deterministic simulation of the fate of pesticides, applied for agricultural purposes, both in the crop root zone and the underlying vadose zone.
- Capacity of simulating multiple pesticides or parent/metabolite relationships.
- The model is also capable of estimating probabilities of concentrations or fluxes from these various media for the purpose of performing exposure assessments.
- Analysis of microbial degradation as a function of soil moisture and temperature distribution.
- Incorporation of two finite-difference numerical solutions, the original backwards-difference implicit scheme , or a Method of Characteristics algorithm that greatly reduces numerical dispersion, but increases model execution time.

PRZM2 consists of four modules, namely PRZM, VADOFT, MONTE CARLO, and EXESUP. PRZM submodel uses finite difference technique to simulate transport and transformation of the parent compound and two metabolites, whereas VADOFT as a one-dimensional, finite element code solves the Richard's equation for flow in the unsaturated zone. PRZM2 links the two computational modules PRZM and VADOFT to perform pollutant fate calculations for the crop root and the vadose zone. The model is also equipped with a module called Monte Carlo processor which performs a probability based exposure assessment.

This module generates further data for the input and output random parameters, then transforms them and performs statistical analysis on the output variables. The EXESUP module is an execution supervisor and controls the simulation processes.

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PREFACE TO CHAPTER 3

The history of the study of the fate of pesticides under water table management and the difficulties involved in the interpretation of some of the field results, was reviewed in the preceding chapter (Chapter 2). Because herbicides usually represent a high percentage of total pesticide use (i.e. 83% in Canada in 1986), it is important to investigate the leaching properties and the risk of environmental pollution from these chemicals in specific soil types under local climatic conditions. There is also a need for further understanding of the fate and transport of commonly used herbicides in subirrigated fields, since this type of water table management has potential in reducing the risk of groundwater pollution, and is also being rapidly implemented in southern Quebec to improve crop production.

To comply with this need, a lysimeter study was planned to determine the fate and transport of one of the most commonly used herbicides in corn farms of southern Quebec. The experiment was carried out to investigate the impact of water table management on the leaching properties and the risk of environmental pollution from atrazine in one of the dominant soil types in this region.

The experimental procedures and the results obtained from the three years experiment on the fate and transport of this herbicide are presented in the next Chapter (Chapter 3). This chapter consists of six sections. Section one introduces the state of water table management and pesticide pollution in Quebec and Canada. Section two reviews some of the physical and chemical properties of atrazine. This section also reviews the previous studies regarding the impact of water table management on the fate and transport of atrazine, and discusses the objectives of this study. The objectives of the study are formulated and explained in section three. The detailed explanation of methodology of the experiment follows in section four. The experimental results for each sampling season are presented and discussed separately in section five. Finally, section six presents the final conclusions for the lysimeter study of the fate of atrazine under different water table management practices. All raw data pertaining to lysimeter studies have been included in Appendix A. A summarised version of this work has been submitted for publication in the Journal of Environmental Quality.

CHAPTER 3

A LYSIMETER STUDY TO DETERMINE THE FATE AND TRANSPORT OF ATRAZINE IN CORN FIELDS UNDER DIFFERENT WATER TABLE MANAGEMENT PRACTICES

Abstract

The role of water table management in reducing water pollution from agricultural herbicides, was investigated in a three year field lysimeter study. Three water table management treatments, in triplicate, were used: shallow subirrigation, deep subirrigation, and free drainage. Nine PVC lysimeters were packed with a sandy soil. Corn (*Zea mays* L.) was grown on each lysimeter, and atrazine was applied to the soil surface at the beginning of each summer. Water and soil samples were collected and analyzed at different time intervals after each natural or simulated rainfall event through 1993-1995. Results indicate that the shallower subirrigation treatment could help speed up atrazine transformation. This chapter also discusses the results of the atrazine mass balance study completed in 1995.

3.1. Introduction

Large areas of Canadian soils and ground waters have become contaminated with different pesticide residues, due to the huge amount of pesticide used and also the large areas sprayed. If appropriate measures are not taken, the soil and ground water may become more and more polluted. Unfortunately, pesticide concentrations in some areas have already exceeded the specified advisory limits in many cases (Frank et al., 1982; Patni et al., 1987).

Various best management practices (BMP) have been examined by researchers to alleviate pollution from pesticides. These include integrated pest management, conservation tillage systems, crop rotation, buffer strips, vegetated streams, and precision farming. Each of these management practices allows for reduced pesticide pollution by reducing surface transport, limiting vertical leaching and controlling the pesticide application. Among the best management practices, water table management may also be used in non-point source pollution control. In this remediation technique, pesticide degradation could be enhanced by managing the soil moisture content in crop root zone with control drainage or subirrigation. In addition, recognizing the site-specific nature of various farming practices, any best management practice must be developed according to the local soil and climatological conditions. Although subirrigation is practised in some agricultural lands in southern Quebec, its environmental impact on the water quality is not yet fully understood.

It has been hypothesised that, during the warm summer months the moisture condition provided by subirrigation, will enhance the chemical, physical, and microbiological activities in the soil profile. The major results of this practice would involve a rapid increase in the population of micro-organisms, which in turn could break down the contaminant molecules, such as fertilizer and pesticide residues, in order to get their required energy growth. The degraded compounds, thus produced, would be less toxic in most circumstances.

So far only about 10,000 ha of agricultural farmland, in the province of Quebec, utilizes some form of water table control (Madramootoo et al., 1993). Installation of subsurface drainage systems, in conjunction with any type of water table management systems in the existing 609,000 ha (Anon., 1986) drained lands will be a win-win situation with: high crop yields due to good water table management during the growing season; low losses of pesticides from subsurface drained farm lands; and the possible reuse of some of the initially leached-out pesticides and fertilizer residues by plants, thus increasing their use-efficiency. In this chapter, the impacts of subirrigation systems on the reduction of atrazine pollution from sandy soils will be discussed.

3.2. Background

Atrazine (2-chloro-4[ethylamino]-6[isopropylamino]-1,3,5-triazine), is a heterocyclic, poorly polar selective herbicide which is widely used in Quebec, Canada, and USA, to control weeds in corn and soybean fields. Figure 3.1. shows chemical structure of atrazine. It has low solubility in water (33 mg/L at 27 °C), and a high microbial decay rate. Except under dry and cold conditions, atrazine residues do not normally last longer than one year in the soil (Colby et al., 1989). Table 3.1 shows the detected and accepted atrazine range in Canadian and American ground waters.

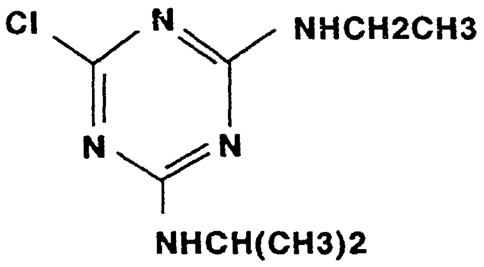

Figure 3.1. Atrazine chemical structure

Atrazine has a half-life of about two months. Therefore, if drainage water containing the dissolved atrazine was kept within the farm boundaries for this period, atrazine would have more time for microbial and chemical transformation. To test the suitability of this idea for atrazine, a field lysimeter study was conducted in a typical sandy soil under southern Quebec climatological conditions.

Table 3.1. Atrazine Residues in Ground Water

	Detected (µg/L)		**Accepted Limits (µg/L)**	
Herbicide	Canada	USA	Canada[1]	USA[2]
Atrazine	0.1 - 74	0.01 - 88	60	3

(1) Anon. (1987a)

(2) Anon. (1987b)

Although other investigators have conducted water table management experiments in Quebec and elsewhere, (Masse et al., 1994; Arjoon et al., 1994; Aubin et al., 1993; Kalita et al., 1992), this research is different from the others since it studies a water table management in the exposed natural climate in combination with advantages of the controlled environment of a large lysimeter setup. The field variability of soil properties and pesticide application, as well as the inflexibility of field setup to research scenarios are among the major reported problems with field plot studies. It was based on the aforementioned reasons that, the need for present research was justified and the following objectives were developed.

3.3. Objectives

The main goal of the present research is to investigate the environmental impact of an on-farm pollution control system that would result in increased crop yields, provide efficient use of herbicides, and more importantly reduce non-point pollution from agricultural herbicides in Quebec. This will be a low-energy water table management system satisfying both agricultural requirements and environmental concerns simultaneously. More specifically, the objectives of this research are:

1. To determine the fate and transport of a most commonly-used herbicide, atrazine, under different water table management practices in a typical sandy soil in Quebec.
2. To analyze the above results and investigate the possible use of subirrigation systems as BMPs for corn farms in Quebec.

In order to fulfil the objectives of this study, a three-year investigation was started in 1993, using a large lysimeter setup to determine the fate of atrazine. At the beginning of each summer, atrazine was applied, soil and water samples were collected and analyzed for herbicide residues. The final results of three years of soil and water sample analysis (1993-1995), will be presented and discussed in this chapter.

3.4. Methodology

The experimental work was conducted in an exposed area beside the Agricultural Engineering Workshop at the Macdonald Campus of McGill University (Figure 3.2). In June 1993, the experiment began with the construction of lysimeter units. The lysimeter setup was completed in early August 1993, and field experiments began in mid August.

3.4.1. Experimental Design

Nine field lysimeters were packed to their original bulk density with a sieved homogeneous sandy soil. Corn (*Zea mays* L.) was grown on each individual lysimeter to represent the pesticide uptake by plant. The lysimeters accommodated three different water tables. Two subirrigation treatments were selected, one with a constant water level at 0.4 m, and the other with the water table at 0.8 m below the soil surface in order to simulate shallow and relatively deep water tables, respectively (Figure 3.3). A free drainage treatment was also used to simulate a subsurface drained field. The statistical scheme consisted of a completely randomized design, in which each treatment was randomly allocated to the lysimeters, and each treatment was supported by three replicates.

3.4.2. Experimental Setup

The experimental setup consisted of nine PVC lysimeters, 1.0 m long x 0.45 m diameter. The PVC lysimeters were welded from the bottom, using 0.6 m x 0.6 m PVC sheets. A 50 mm diameter perforated PVC pipe was installed at the bottom of each lysimeter to allow for either drainage or subirrigation from the bottom (Figure 3.4). Lysimeters were packed with a uniform sandy soil from a farm where no pesticides were applied in the last two years. The soil in the lysimeters was compacted by hand to a field bulk density of 1350 kg/m^3. A 9 mm diameter perforated acrylic plastic tubing was installed, in the subirrigation lysimeters at 0.45 and 0.85 m depths, to collect soil solution (water) samples (Figure 3.4).

All lysimeters were equipped with three 0.22 m long x 3 mm diameter, stainless steel probes. These were utilised for soil moisture content measurements using a TDR instrument (Topp and Davis, 1985). The probes were inserted

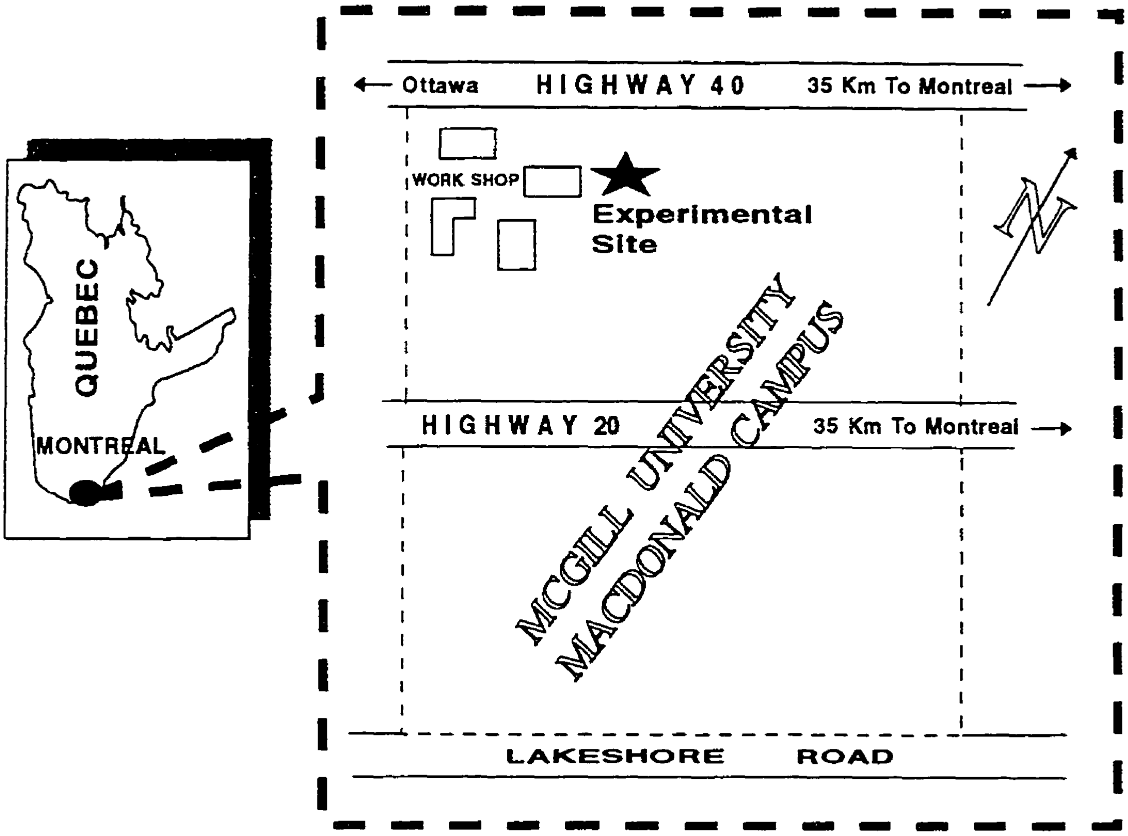

Figure 3.2. Experimental Site

horizontally in the lysimeters at 0.15, 0.3, 0.45, and 0.6 m depths. Four 10 mm horizontal holes were made in all the lysimeters at 0.1, 0.3, 0.5, and 0.7 m depths (summer of 1995), to collect soil samples. All lysimeters were kept above ground in an exposed area in order to locate any possible water leaks that might affect the experimental results. In the subirrigation lysimeters, a 50 mm diameter acrylic plastic riser was connected to the bottom drain and water was supplied from individual water tanks (Figure 3.4). A syphoning supply system (Mariotte System) was used to maintain the water levels at 0.4 and 0.8 m below the soil surface in the subirrigated lysimeters, whereas the free drainage lysimeters were allowed to drain freely from the bottom. Thermocouples were inserted in the soil to measure the unsaturated soil temperature in all lysimeters.

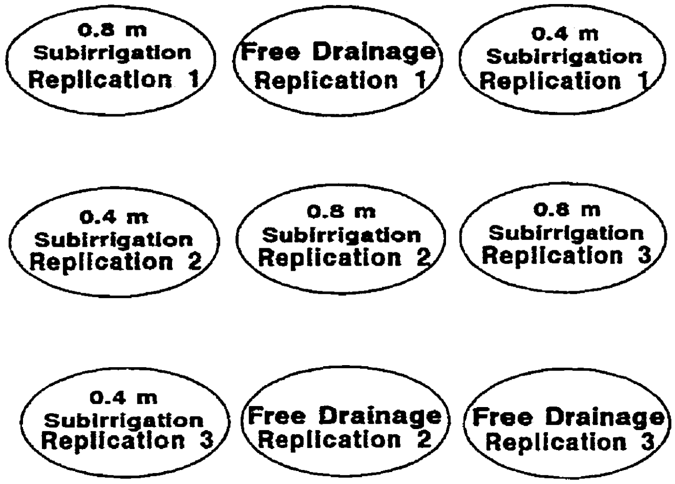

Figure 3.3. Layout of lysimeters in the field

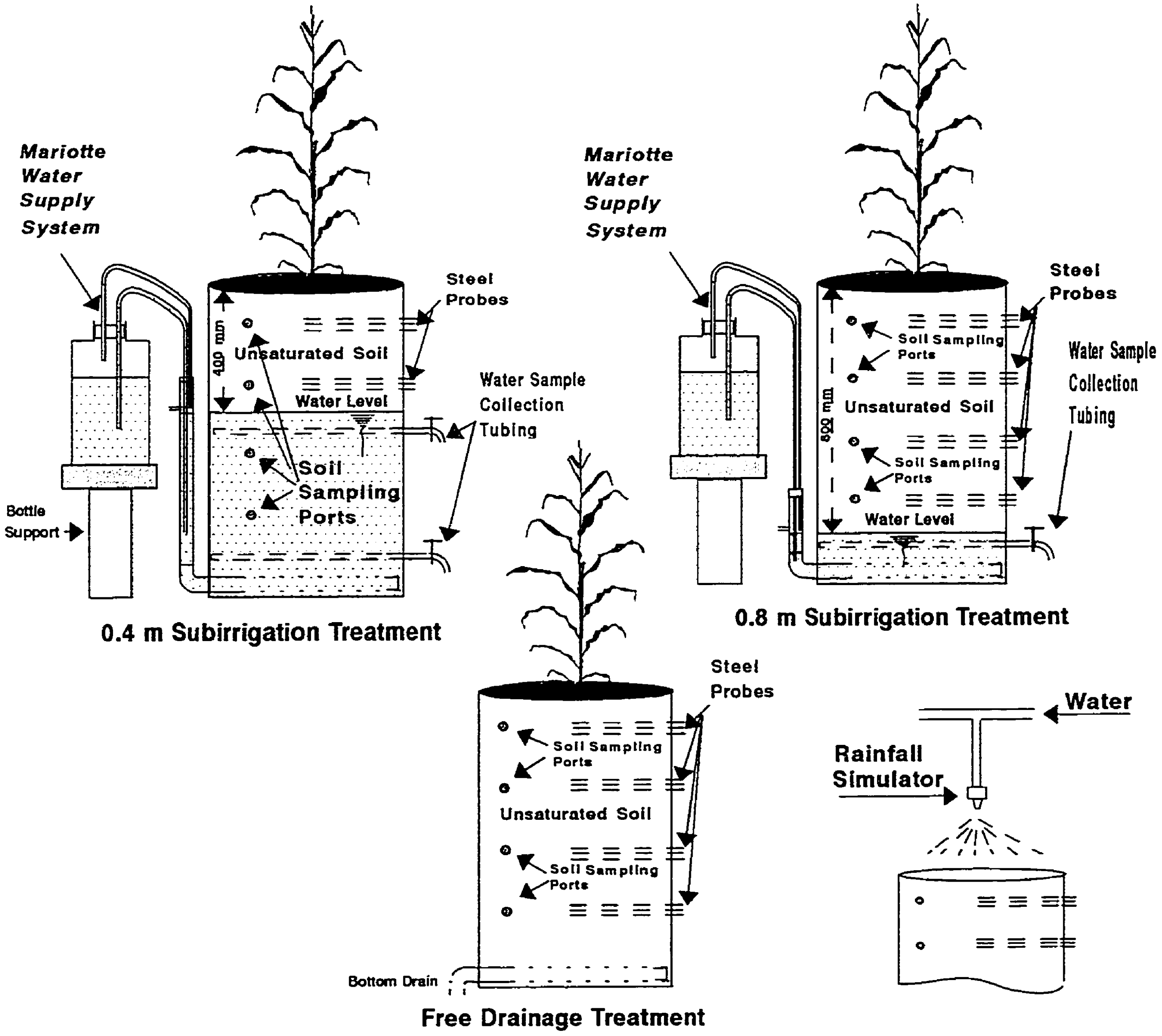

Figure 3.4. Lysimeter setup

A rainfall simulator was constructed and used to perform atrazine leaching studies in 1994 and 1995 . The rainfall simulator consisted of nine brass spray nozzles (product of Spraying Systems Co. USA), directed 0.5 m higher than top of each lysimeter. The nozzles were connected to a copper tubing system equipped with a pressure gage and mounted on a steel frame (Figure 3.4). The pressure gage was used to regulate the tap water pressure required by the spray nozzles. The nozzles inlet size was 12.7 mm with the simulation capacity up to 13 L/min rainfall under 140 kpa.

3.4.3. Soil Characteristics

The soil was obtained from a field at Macdonald College of McGill University, where no herbicides had been applied in the last two years. This soil belongs to St. Amable complex, which has deep sandy deposits of medium to fine texture in its profile (Lajoie, 1960). In order to create a uniform sandy soil profile in the lysimeters, the first 0.1 m of the topsoil was removed and the subsoil was taken to fill the lysimeters. To get the same bulk density as the original soil (1350 kg/m^3), an equivalent weight of soil was used to make each 0.1m layer in the lysimeters.

The disturbed and undisturbed soil samples were taken from the field site to determine the grain size distribution, organic matter content, pH, CEC, and bulk density. The soil saturated hydraulic conductivity was determined on each individual lysimeter using the constant head approach. The average soil temperature at root zone was about 10 °C less than ambient temperature. Undisturbed soil samples were taken from one lysimeter to determine soil moisture retention characteristics. Figures 3.5 to 3.7 show the average (triplicates) soil moisture retention characteristics $\theta(h)$ at 0.1, 0.3 and 0.5 m depths. Table 3.2 shows the results of the tests performed on the soil samples.

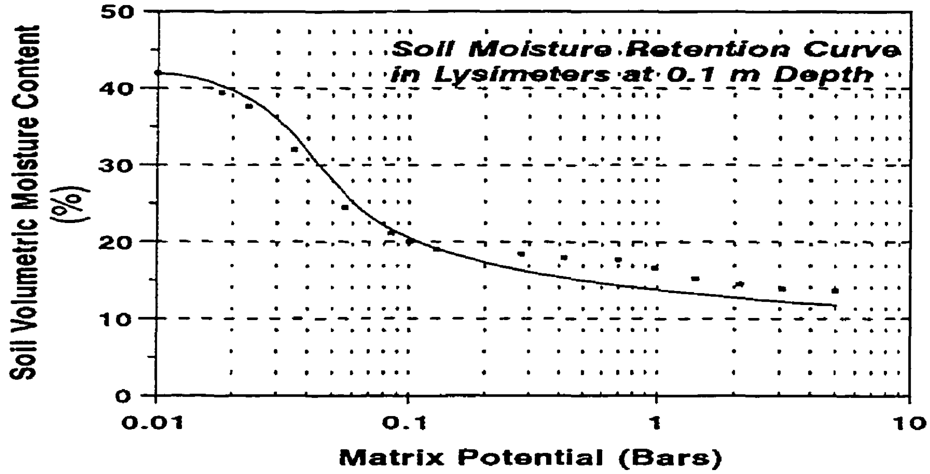

Figure 3.5. Average soil moisture characteristics at 0.1 m depth

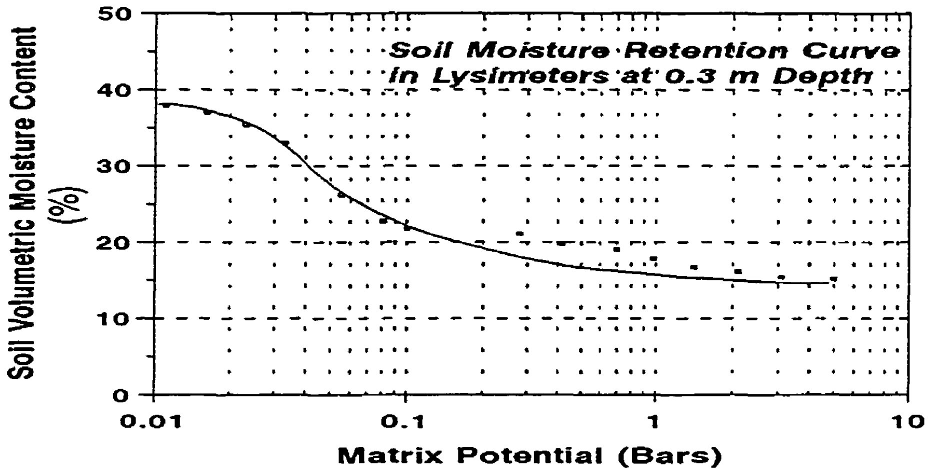

Figure 3.6. Average soil moisture characteristics at 0.3 m depth

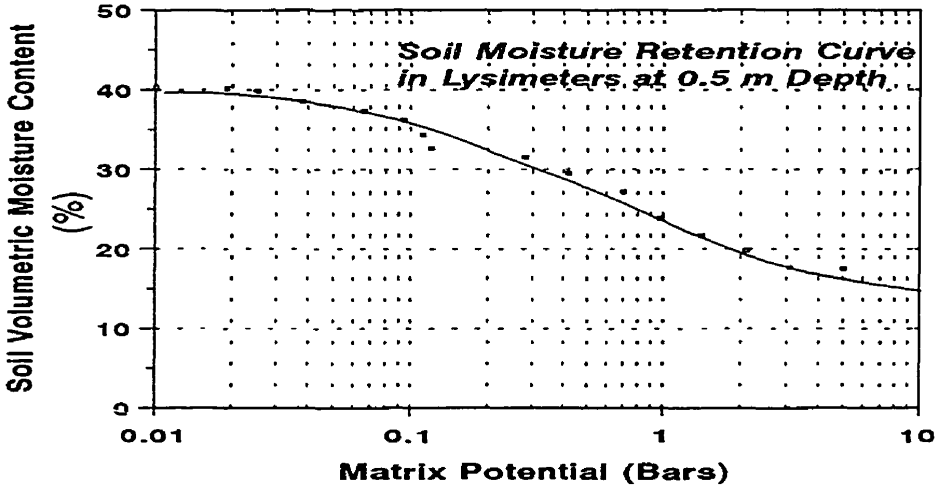

Figure 3.7. Average soil moisture characteristics at 0.5 m depth

Table 3.2. The Physical Characteristics of the Soil

Soil Type	Sand (%)	Silt (%)	Bulk Density (kg/m^3)	Organic Matter (%)	pH	CEC (cmol/kg)	Hydraulic Conductivity* (cm/h)
Sandy Soil	92.2	4.3	1350	3.5	5.5	4.9	6.0 (S.D.** =1.8)

* Average value measured on the lysimeters.

** Stands for standard deviation

3.4.4. Climatological Data

Rainfall, evaporation and the air temperature were measured at the Ste. Anne de Bellevue Weather Station, located less than one kilometre from the experimental area. During the first month of experimentation in August 1993, the average monthly temperature was about 20°C and total rainfall was 42.9 mm (Figure 3.8 presents the daily rainfall for the period of study in 1993). In September, the average monthly temperature was 14°C and total rainfall was 119.2 mm. Data from the nearest Weather Station (Dorval) indicated that August 1993 had the highest monthly temperature and the lowest rainfall in ten years. Six rainfalls with an intensity above 10 mm/day and twenty rainfalls with an intensity of less than 10 mm/day were recorded between the day of herbicide application and the end of the 1993 sampling period. The first rainfall with an intensity of 8.9 mm/day occurred one day after herbicide application. The highest rainfall during this period was 30.4 mm/day and it occurred 23 days after application. There was no surface runoff in the lysimeters.

In the 1994 sampling season, the highest average monthly temperature and evaporation were observed in July. The highest average temperature in this month was 21.3°C, and the total rainfall was 61.3 mm. Total monthly rainfall was 99.9 mm in August and 105.5 in September (Figure 3.11 shows the daily rainfall for the summer period in 1994). In this summer, there were eight rainfalls with an intensity of more than 10 mm/day. The highest daily rainfall occurred on June 29, with 54.9 mm, just six days after the herbicide application. Because a rainfall simulator was constructed and used in 1994, all lysimeters received 260 mm of simulated rainfall in 8 events ranging between 25 to 40 mm. The simulated rainfall intensity was about 25 mm/h. Comparing the monthly average temperature with the past ten years data, for the corresponding months, the summer of 1994 may rank as a mild summer with regard to temperature and rainfall.

In the summer of 1995, the highest average monthly temperature was measured in July. The highest reported evaporation in this summer occurred in June (7.2 mm). Total monthly rainfall in June, July, August and September was measured as 64.5, 138.2, 118.2, 69.5 mm, respectively. Each lysimeter also received 300 mm of simulated rainfall in five events, 60 mm each. The simulated rainfall intensity was about 30 mm/h.

Comparing the monthly average rainfall with the past ten years data, for the corresponding months, the summer of year 1995 may rank as a relatively wet summer. Figure 3.15 shows the daily natural and simulated rainfall for the summer period in 1995.

3.4.5. Atrazine Application

Each summer, all nine lysimeters were sprayed uniformly once with atrazine. Since there were some construction delays in the first year, the pesticide was applied late, on August 11, 1993. In the second year and third year, the pesticide applications were made on June 23, 1994 and June 24, 1995, respectively. Atrazine was applied at a rate of 2.4 kg/ha of active ingredient.

3.4.6. Sampling Methods

In 1993, one-litre water samples (soil solution) were taken at 0, 7, 14, 22, 29, 37, 47, 64, and 84 days after the atrazine application (DAA). In 1994, the soil solution samples were taken at -23, 3, 7, 14, 23, 30, 38, 49, 68, 90 days after the application. The sampling interval for the soil and soil solution samples in the summer of 1995 followed -20, 6, 16, 28, 42, 70, 90 days after application. About 5 to 10 g of soil sample was collected from each port, and samples were kept in the freezer for future extraction and analysis. Before each sampling period, the soil solution sampling tubes were emptied to remove stagnant water, in order to take representative samples of soil solution. About 10 ml of dichloromethane was added to all soil solution samples to stop microbial activity during refrigeration and before analysis. The sampling of the free drainage lysimeters was quite irregular in 1993, since they were completely rain-fed and most rainfall events caused no outflow. To overcome this difficulty and obtain more samples, a rainfall simulator device was constructed and used in 1994.

To collect the soil samples, four sampling ports were made in each lysimeter at 0.1, 0.3, 0.5 and 0.7 m below the soil surface. Each time about 5 to 10 g of soil sample was collected from each port, and samples were kept in the freezer prior to extraction and analysis.

3.4.7. Extraction of Atrazine Residues

The soil solution samples were mixed with 100 ml of dichloromethane (methylene chloride) in a separatory funnel. The mixture was hand shaken for a few minutes and the organic phase, which accumulated at the bottom of the funnel, was collected. The process was repeated twice. The extracted organic phase was evaporated to separate dichloromethane from the herbicides. The residues were then dissolved in about 10 ml of methanol and stored in the refrigerator, for analysis by gas chromatography.

About 5 g of soil sample was transferred to flat bottom flasks. A subsample of about 1 g was placed in the oven at 105° C for 24 hours, for soil moisture determination. Each soil sample received about 100 ml of methanol and was shaken for at least 1 hour. The mixture was transferred to a vacuum flask (Buchner flask) and filtered under negative pressure. The collected organic phase was evaporated in the rotary evaporator for 15 minutes and rinsed with about 10 ml of Hexane. The collected organic phase was then stored in a 15 ml glass vial in the refrigerator to be run by gas chromatography (GC) for pesticide residues.

3.4.8. Gas Chromatography

The gas chromatography was done using a Varian, Model 3400 gas chromatograph, equipped with a column, an injector, a thermionic specific detector (TSD), an autosampler and computer data acquisition system. The column used was a 0.53 mm i.d., fused silica Megabore DB-5 with 1.5 µm film thickness. The injector temperature was set at 250°C and the detector was kept at 300°C. The column temperature was maintained at 180°C for 9 minutes, and then the temperature was increased to 200°C at a rate of 4° C/min; at 200°C it was held for 1 minute, and then it was raised to 280° C at a rate of 20° C/min. The column was kept at this temperature for at least 9 minutes. The nitrogen and helium make up flow rate was 30 mL/min, while the helium carrier gas flow rate was kept at 7.5 mL/min. The hydrogen and the air flow rates were set to 4.5, and 175 mL/min, respectively. The detection limits for soil solution and soil samples were found to be 0.05 and 10 µg/L, respectively. The recovery rate was obtained by fortifying 20g of untreated air dried soil with 0.05, 0.5 and 2 µg/g of atrazine. The samples were left to equilibrate for 24h, after which time they were extracted and analyzed by GC. The recovery rate was estimated to be 93% ± 5%.

3.5. Results and Discussions

To study the fate of atrazine in the lysimeters, only soil solution samples were collected in 1993 and 1994. In 1995, the atrazine residues were investigated in both soil and soil solution samples. The concentration of herbicides was determined from the collected water samples at the 0.85 m depth for all treatments, and also at the 0.45 m depth for the 0.4 m subirrigation treatment. The atrazine concentration in soil was defined at four different depths in each lysimeter. The following section will present and discuss the experimental results obtained from all three sampling seasons, 1993 through 1995.

3.5.1. Atrazine Residues in Soil Solution in 1993

Atrazine concentration in water was measured at two depths in the 0.4 m subirrigation treatment, and at one depth in the 0.8 m treatment. Figure 3.8 shows the plot of atrazine distribution with time (average of three replicates) at the 0.45 and 0.85 m depths, in the subirrigation treatment, with the water table level (WTL) at 0.4 m below the soil surface. The error bars, representing average values ± one standard deviation, are also plotted. Figure 3.9 presents the atrazine distribution with time at the 0.85 m depth, in the subirrigation treatment with 0.8 m WTL. Samples collected from the free drainage treatments were insufficient since natural rainfall did not produce enough outflow.

The distribution of atrazine with depth could only be studied in the 0.4 m subirrigation treatments. In the other two treatments, the soil solution samples were only collected at one depth (0.85 m). Atrazine was relatively mobile in all lysimeters, since it was detected one month after application at both the 0.45 and 0.85 m depths (Figure 3.8). The atrazine leaching was mainly caused by the 30.4 mm natural rainfall which occurred 23 days after the application. Some atrazine was detected at the 0.85 m depth in this treatment, although the concentrations were quite low.

In the 0.4 m WTL subirrigation treatment, the highest average concentration (the average of three replicates) was about 5.6 µg/L, at the 0.45 m depth (Figure 3.8). Almost no atrazine was detected at this depth, 47 days after the application. In a number of studies, researchers have investigated the adsorption and mobility of atrazine in different soils. The mobility of pesticides has been found to be a reverse function of adsorption (Harris, 1965). Kalita et al. (1992) have reported atrazine detection in ground water at 1.2 m depth. In the 0.8 m WTL subirrigation treatment (Figure 3.9), the atrazine levels were higher at the 0.85 m depth compared to those with the 0.4 m WTL.

Figure 3.10 presents this information as bar graphs. Although both treatments had received the same amount of natural rainfall, it is clear that the atrazine level at the 0.85 m depth is higher in the 0.8 m WTL subirrigation lysimeters. The important difference between the two treatments is the higher moisture content at root zone depth (Figure 3.10). This was made possible by the 0.4 m subirrigation treatment. The lower concentration obtained for atrazine at the 0.85 m depth in a 0.4 m subirrigation treatment, may be explained by one of the following processes:

- Since no pesticide could leach out of the lysimeter units, the higher moisture content in the vadose zone may have caused higher biodegradation. This would have left less atrazine available for leaching to the 0.85 m depth.

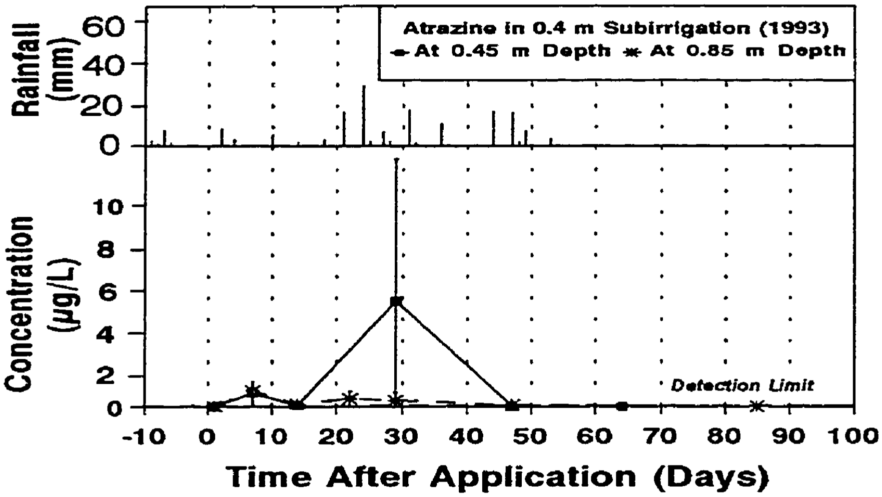

Figure 3.8. Atrazine in soil solution in 0.4m subirrigation treatment (1993)

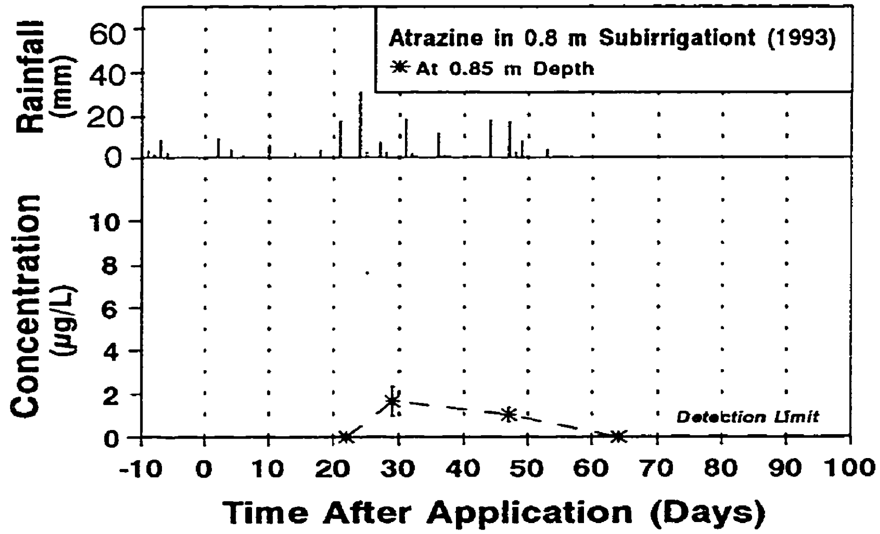

Figure 3.9. Atrazine in soil solution in 0.8m subirrigation treatment (1993)

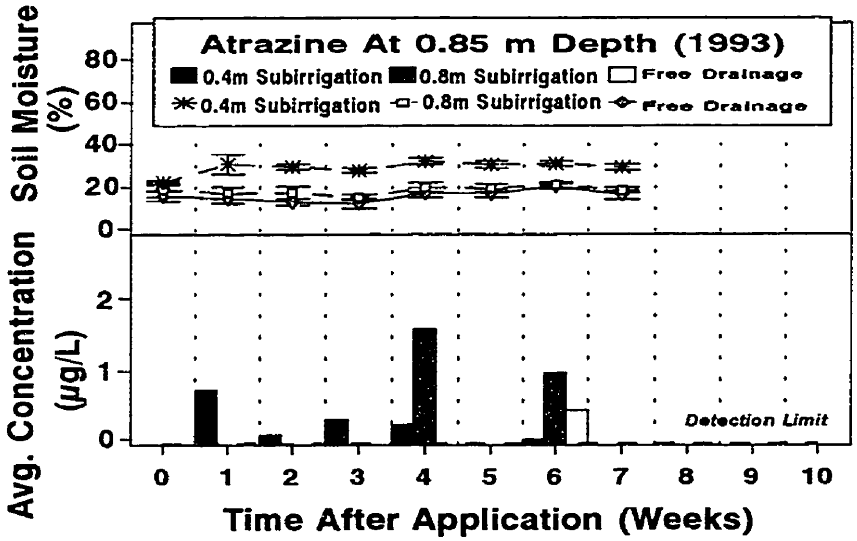

Figure 3.10. Comparison of atrazine insoil solution of all treatments (1993)

- The dilution effects caused by the saturated zone below the 0.4 m depth may give a reduced concentration at the 0.85 m depth.
- It should also be noted that the soil profile in the 0.4 m subirrigation treatment was saturated below 0.4 m. This would have facilitated downward atrazine leaching since higher advection may be expected in the saturated zone.

Another interesting observation can be made by comparing Figures 3.8 and 3.9, which show a different dissipation trend in atrazine concentration. Atrazine dissipated faster at the 0.45 m depth than at the 0.85 m depth; both were 50 mm below the maintained constant water table. This may also be explained by presence of higher moisture content in the root zone depth in 0.4 m subirrigation treatment.

The comparison of the atrazine levels detected in the soil solution samples of three treatments (Figure 3.10) shows less concentration for the 0.4 m subirrigation treatment (shallower water table), with respect to the 0.8 m subirrigation and free drainage treatments. These results have been investigated through a mass balance study, completed in 1995. Figure 3.10 demonstrates the higher moisture levels observed in subirrigation treatment at the root zone depth.

3.5.2. Atrazine Residues in Soil Solution in 1994

Figure 3.11 shows the average atrazine concentration in the 0.4 m subirrigation treatment (average of three replicates). The average background concentration was measured as 1.8 µg/L at 0.45 m depth and 1.1 µg/L at 0.85 m depth. This level decreased to an almost non-detectable limit (0.03 µg/L) within twenty five days. The atrazine concentration then started to increase almost three weeks after the application date, implying that it took almost three weeks for atrazine to leach down to the 0.85 m depth.

Three natural rainfalls of more than 20 mm and one simulated rainfall of 39 mm in the first three weeks after application, did not cause any significant leaching of atrazine, either to the 45 or to the 0.85 m depth. The atrazine concentration increased to 0.7 µg/L at 0.45 m and 0.5 µg/L at 0.85 m depth only 38 days after application. This concentration again reduced to an almost non-detectable level after 11 days, whereas it took almost three weeks to reduce the background concentration from 1.8 µg/L at the 0.45 m and 1.1 µg/L at the 0.85 m depth to a non-detectable level. This may suggest that atrazine residues present in the background from last year's application has undergone less degradation, compared to that which occurred at the beginning of the experiment under the subirrigation treatment. Shortly after the beginning of the experiment, the higher biodegradation contributed to faster pesticide decomposition, when coupled with the higher soil moisture content, provided by the constant water level.

In the 0.8 m subirrigation treatment, the average background concentration before application, was 0.9 µg/L, and it reduced to 0.2 µg/L after twenty five days (Figure 3.12). Only seven days after the surface application of atrazine, the concentration increased to 0.54 µg/L, indicating that the surface applied atrazine had leached down to the 0.85 m depth. Such rapid mobility could be attributed to the occurrence of some form of macropore flow in soil, due to the rainfall that occurred two days after the application.

The average background concentration in the free drainage treatment was about 2.2 µg/L (Figure 3.13). This concentration reduced to a non-detectable level (0.03), within twenty five days. Ten natural and simulated rainfalls were

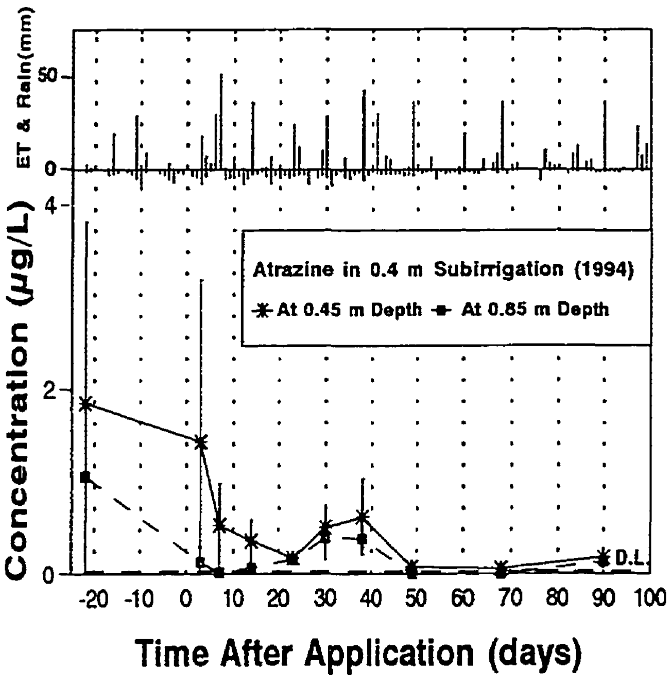

Figure 3.11. Atrazine in soil solution in 0.4m subirrigation treatment (1994)

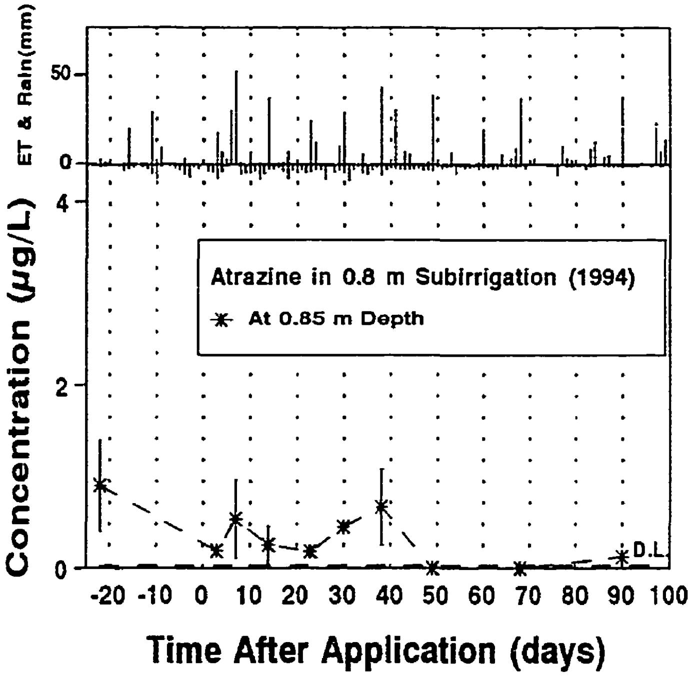

Figure 3.12. Atrazine in soil solution in 0.8m subirrigation treatment (1994)

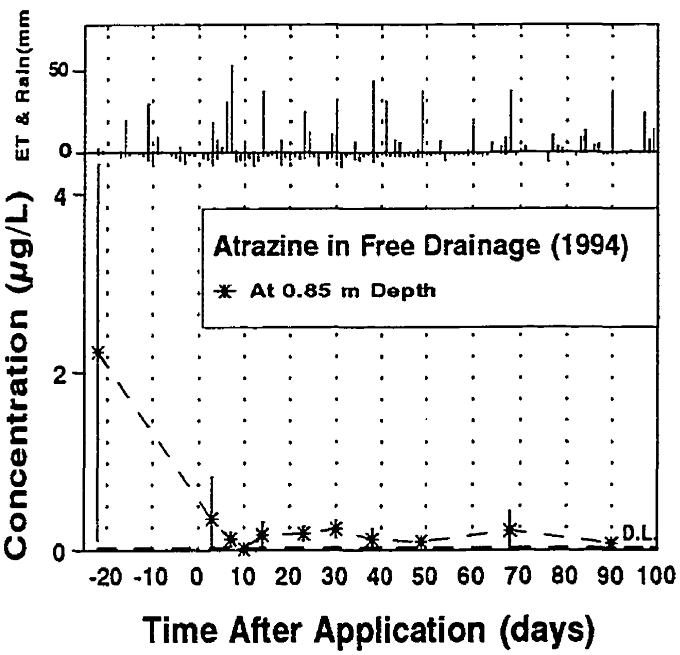

Figure 3.13. Atrazine in soil solution in free drainage treatment (1994)

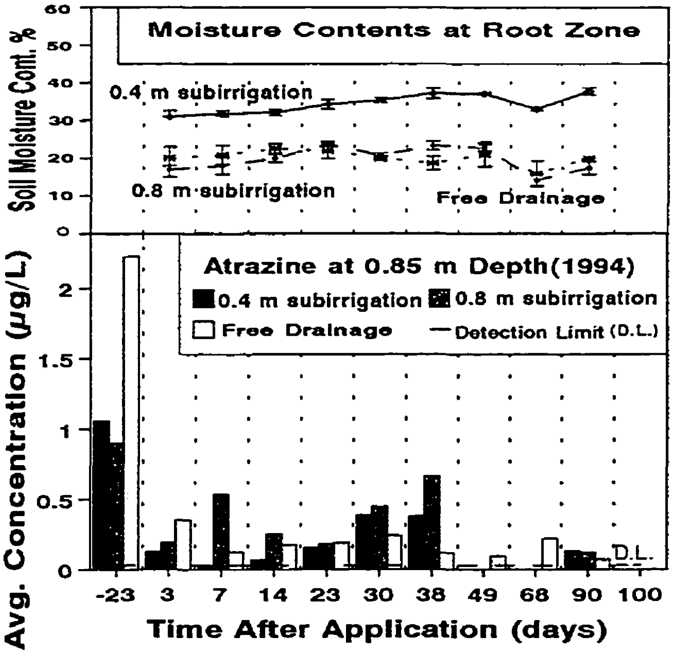

Figure 3.14. Comparison of atrazine residues in soil solution of all treatments (1994)

enough to cause atrazine transportation to the bottom depth. The highest average detected concentration at the 0.85 m depth was only about 0.3 µg/L. This is explained by the fact that no constant water level is maintained in the free drainage treatment, unlike the subirrigated lysimeters, and hence limited mass transfer processes occur between the wetting front and the solid phase. The limited physical and chemical exchange also applies to the fraction of atrazine that has already diffused in the immobile soil solution in the dead ended soil pores (van Genuchten, 1974; Rambow and Lennartz, 1993).

A clear picture of the fate of atrazine has been obtained with the mass balance study at the end of the experimental period in 1995. It could be argued that natural or simulated rainfall pulses create relatively high pore water velocity and the leaching water will only have a limited time span to equilibrate with the atrazine which has either accumulated on the solid phase (soil particles and organic matters) and/or has diffused into the immobile liquid phase, already present in the dead ended pores. The mobile front in the free drainage treatment will not have sufficient contact time for equilibrium, thus the breakthrough curve in this case only represents the instantaneous equilibrium sorption (Ghadiri and Rose, 1992). Hence, the measured concentration is, in fact, a small fraction of the potentially mobile atrazine available in the soil. The higher fraction of atrazine still resides in the soil, which could has been shown by mass balance study. Here atrazine is gradually released as the next water front moves, and hence causing longer tailing effects in the atrazine breakthrough curves. In subirrigation treatments, the time dependent non-equilibrium adsorption/desorption prevails due to presence of moisture, and usually shows higher concentrations.

Comparison of the three atrazine treatments (Figure 3.14) shows less concentration for the 0.4 m subirrigation treatment (shallower water table) compared to the 0.8 m subirrigation; however in some of the cases this demonstrates a lower concentration with respect to free drainage. Figure 3.14 shows the higher moisture levels observed in subirrigation treatment, at the root zone depth.

3.5.3. Atrazine Residues in Soil Solution in 1995

Figure 3.15 shows the average atrazine concentration in the soil solution samples in the 0.4 m subirrigation treatment (average of three replicates). The atrazine level at the 0.45 m depth has increased from the background concentration (0.2 µg/L) to about 5 µg/L, following the first rainfall simulation, one week after the atrazine application. After the second rainfall simulation on day 16, the atrazine concentration increased to 5.3 µg/L, and after 28 days, it reduced to 0.3 µg/L. This fast reduction of atrazine concentration in almost 10 days, appears to be result of high moisture content at the soil root zone depth. The higher biodegradation rates, shortly after the beginning of the experiment, contributed to faster atrazine decomposition when coupled with the higher soil moisture contents, provided by the constant water level in the 0.4 m subirrigation treatment.

The atrazine level was always less than 0.3 µg/L, in all soil solution samples collected after day 28, regardless of five natural rainfalls of more than 20 mm, and two simulated rainfalls of about 60 mm, . This implies that the atrazine leached to this depth was either degraded or bound to the soil particles and was not available in the soil solution. The atrazine level at the 0.85 m depth did not vary significantly from the background concentration (0.2 µg/L) in all the sampling periods, suggesting no occurrence of considerable leaching from the upper layers.

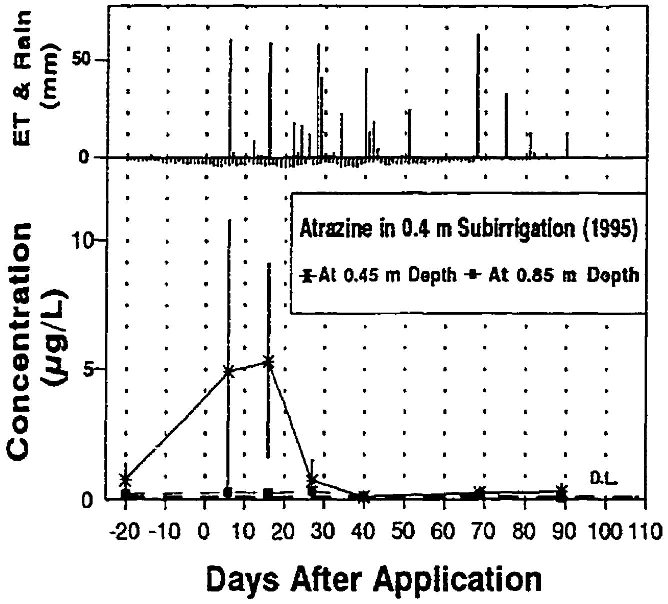

Figure 3.15. Atrazine in soil solution in 0.4m-subirrigation treatment (1995)

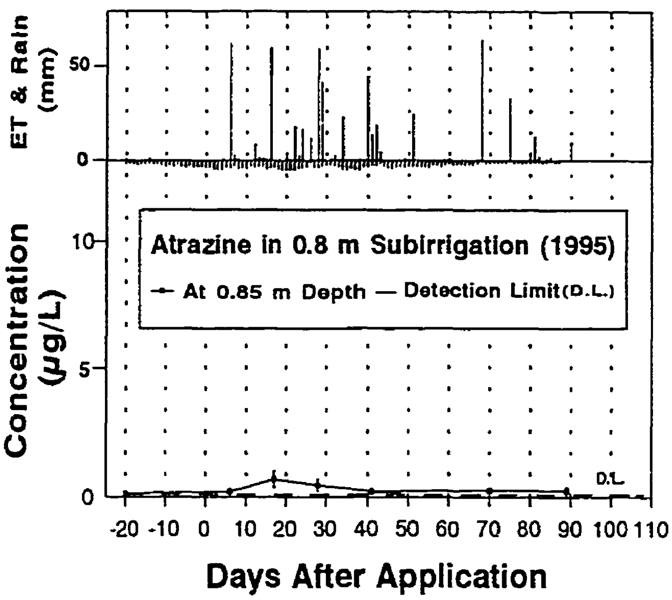

Figure 3.16. Atrazine in soil solution in 0.8m-subirrigation treatment (1995)

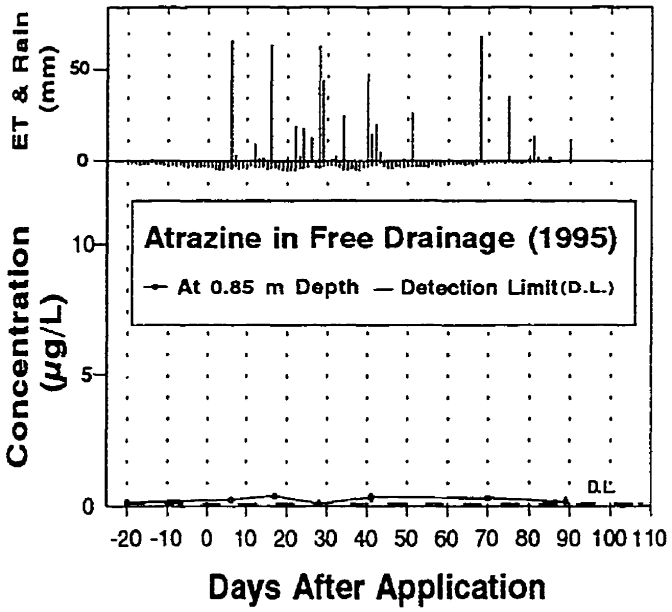

Figure 3.17. Atrazine in soil solution in free drainage treatment (1995)

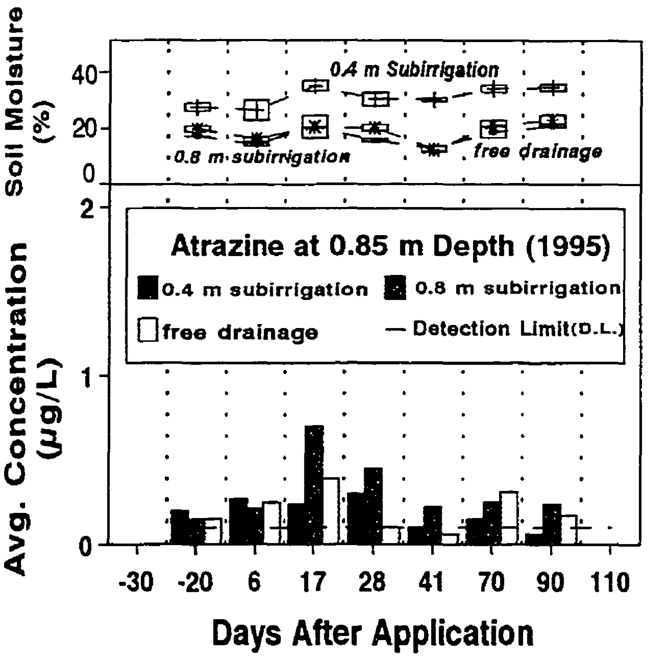

Figure 3.18. Comparison of atrazine residues in soil solution of all treatments (1995)

In the 0.8 m subirrigation treatment, the average background concentration before application, was 0.15 µg/L, and it increased to 0.7 µg/L after eighteen days (Figure 3.16). Atrazine level reduced to 0.22 µg/L in almost three weeks, indicating that the surface applied atrazine has not significantly leached down to the 0.85 m depth.

The average background concentration in the free drainage treatment was about 0.15 µg/L (Figure 3.17). This concentration increased to 0.4 µg/L after eighteen days. At the end of experiment, after ninety days, the atrazine level reduced to 0.17 µg/L, indicating that the surface applied atrazine had not leached significantly in to the 0.85 m depth.

In most cases, the comparison of the three atrazine treatments (Figure 3.18), shows less concentration of 0.4 vs. 0.8 m subirrigation treatment (shallower water table); but a higher concentration with respect to free drainage. Similar to the arguments made for the results in 1994, it could be said that natural or simulated rainfall pulses create a relatively high pore water velocity: that the leaching water will only have a limited time span to equilibrate with the atrazine, which has either accumulated on the solid phase (soil particles and organic matters) and/or has diffused into the immobile liquid phase, already present in the dead ended pores.

This idea maintains that in free drainage treatment the mobile front does not have sufficient contact time for equilibrium, and the breakthrough curve in this case only represents the instantaneous equilibrium sorption. Hence, the measured concentration levels in the free drainage lysimeters is, in fact, a small fraction of the potentially mobile atrazine available in the soil. The higher fraction of atrazine still resides in the soil, and is gradually released as the next water front moves. This causes longer tailing effects in the atrazine breakthrough curves in the soil solution samples. This idea was verified through a mass balance study. Due to presence of moisture in subirrigation treatments, the time dependent non-equilibrium adsorption/desorption might have prevailed, and caused higher concentrations. Figure 3.18 demonstrates the higher moisture content observed in the subirrigation treatment, at the root zone depth.

3.5.4. Atrazine Residues in Soil in 1995

Soil samples were collected from each lysimeter at four different depths on 6, 30 and 90 days after the atrazine application. Tables 3.3 to 3.5, and Figure 3.19 show the average levels and standard deviation of three replicate of atrazine residues, detected in each water table management treatment. A study of the variation of atrazine concentration in the 0.4 m subirrigation on 6, 30 and 90 days after application, can be made by comparing the first row charts. The atrazine residues in soil in the 0.8 m subirrigation and free drainage can be studied, using charts at middle and bottom rows, respectively. The charts in Figure 3.19 can be used in vertical sequence to compare the atrazine levels among the three water table management treatments at each sampling day.

The first three charts in the first column compare the atrazine residues in two subirrigation and one free drainage treatment, 6 days after pesticide application. Lower atrazine concentration was always found in the soil in the 0.4 m subirrigation treatment, especially at the root zone depth. A similar trend is observed when comparing the atrazine levels on day 30 and 90, indicating that the shallower water table in the 0.4 m subirrigation treatment caused a fast reduction in the atrazine levels at the root zone depth. This would leave less pesticide available for leaching to the ground waters. These results are closely allied to the findings of other researchers, in that subirrigation, Table 3. 3

Table 3.3. Atrazine Residues in Soil in 0.4 m-Subirrigation Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (µg/kg)	Standard Deviation(µg/kg)
6	0.10	6.89	0.9
	0.30	0.00	0.0
	0.50	34.35	4.0
	0.70	5.30	7.5
30	0.10	6.89	0.9
	0.30	6.12	4.4
	0.50	17.77	12.9
	0.70	7.49	0.0
90	0.10	9.44	4.4
	0.30	0.00	0.0
	0.50	4.43	6.3
	0.70	36.85	11.9

(1) Zero concentration implies a non-detectable level.

Table 3.4. Atrazine Residues in Soil in 0.8 m-Subirrigation Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (µg/kg)	Standard Deviation(µg/kg)
	0.10	231.45	21.5
6	0.30	49.20	9.2
	0.50	0.00	0.0
	0.70	0.00	0.0
	0.10	155.10	20.4
30	0.30	30.0	24.5
	0.50	0.00	0.0
	0.70	0.00	0.0
	0.10	52.93	14.0
90	0.30	39.17	11.1
	0.50	32.30	2.3
	0.70	47.57	10.3

[1] Zero concentration implies a non-detectable level.

Table 3.5. Atrazine Residues in Soil in Free Drainage Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (µg/kg)	Standard Deviation(µg/kg)
	0.10	280.0	40.0
6	0.30	80.00	10.0
	0.50	5.20	7.4
	0.70	0.00	0.0
	0.10	188.6	20.5
30	0.30	49.20	28.0
	0.50	23.40	40.5
	0.70	29.70	9.7
	0.10	23.70	2.8
90	0.30	42.45	8.0
	0.50	25.90	4.1
	0.70	45.90	5.9

(1) Zero concentration implies a non-detectable level.

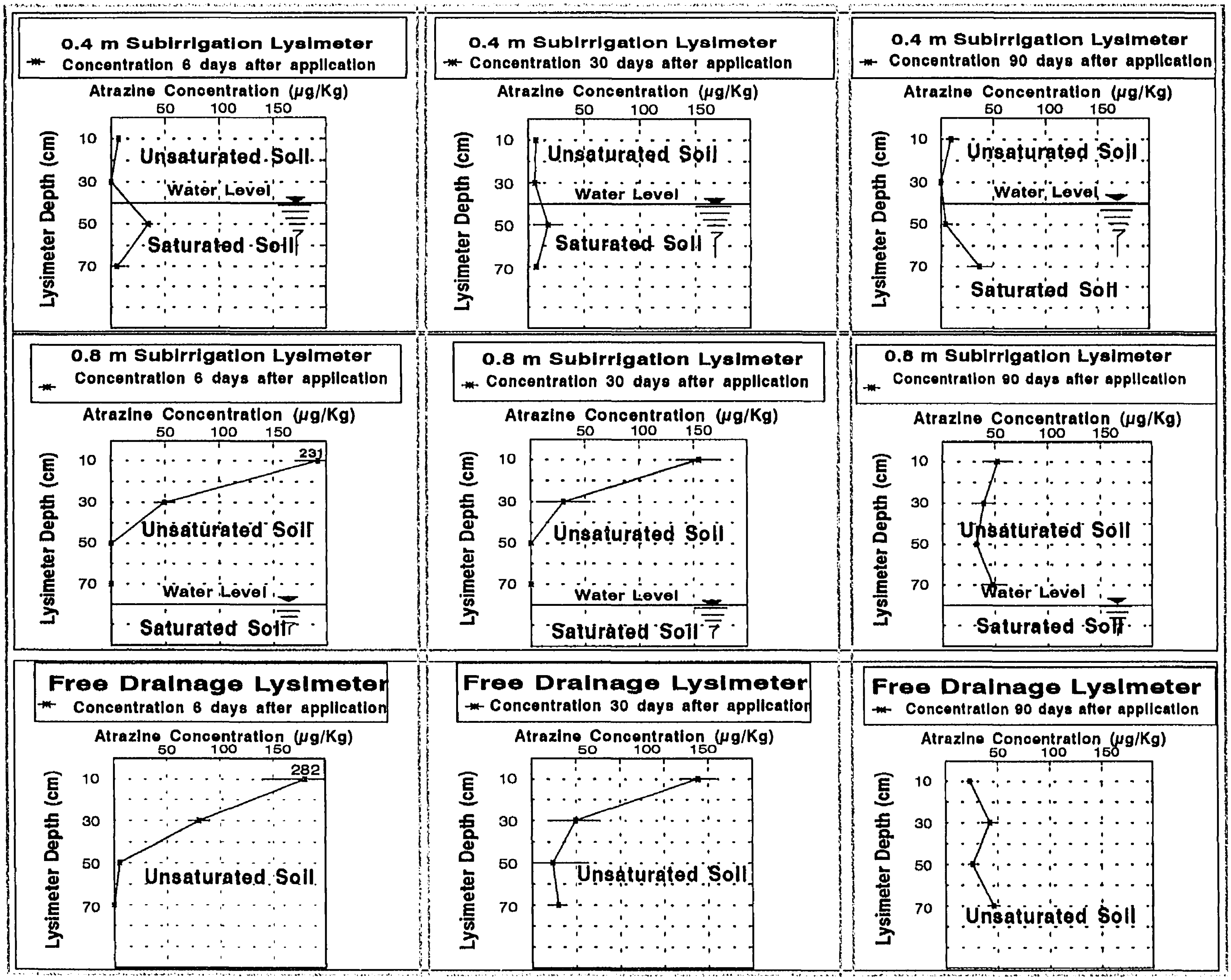

Figure 3.19 The Comparison of Atrazine Residues in the Soil profile of all Treatments in 1995

especially with shallow water tables, would cause a faster breakdown of pesticides (Kalita et al., 1992; Aubin et al., 1993).

Aubin (1994), in his laboratory degradation experiment, found that the metribuzin degradation was enhanced as the soil moisture content increased, due to more suitable conditions provided for the aerobic microbial population. His findings partly support the hypothesis of faster degradation of pesticides, with a shallower water table in the field. To extend these findings to atrazine, a laboratory batch study was carried out in 1995 to investigate atrazine degradation at different soil moisture contents (Jebellie et al., 1996). Results from this batch test indicates that the dissipation of atrazine directly increases with the soil moisture content. These results further support the hypothesis that higher moisture content at the root zone depth reduces the pesticide residues at a much faster rate.

3.5.5. Atrazine Mass Balance

The soil and water samples collected throughout the experiment have shown the leaching of atrazine to the deeper layer. Soil samples were collected from 0.1, 0.3, 0.5 and 0.7 mm depths on 6, 30 and 90 days after application. As Figure 3.18 demonstrates, on any sampling day, the concentration of atrazine residues at each soil depth has changed. This indicates that leaching to the lower layers, degradation or a combination of both processes has occurred. A mass balance study was carried out to gain a true picture of the atrazine dissipation in the soil and water throughout the soil profile.

The mass balance study was performed for each of the sampling days separately. The atrazine residues in the whole lysimeter profile were considered, as well as the mass of atrazine drained or spilled out after either natural or simulated rainfall periods. Table 3.6 shows the summary of the mass balance study of the atrazine in the three water table management treatments. Each lysimeter was sprayed with 38.4 mg of atrazine.

According to Table 3.6, in the 0.4 m subirrigation treatment this amount has been reduced by 95.7%, after 6 days. The corresponding values for the 0.8 m subirrigation and free drainage treatments are 71.7 and 58.6%, respectively, suggesting that fast dissipation of atrazine residues in the 0.4 m subirrigation treatment. A similar trend is identified in the atrazine levels of other sampling days. Figure 3.20 presents these results as an error bar chart. In this figure, the 0.4 m subirrigation treatment shows least amount of remaining atrazine residue. Figure 3.21 demonstrates the percentage of the average (average of three replicate) levels of the remaining atrazine, and Figure 3.22 shows the similar results as a bar chart. The total percentage of loss of atrazine in different treatments is presented in Figure 3.23.

Table 3.6. The mass balance of the atrazine residues in different treatments (mg)

	0.4 m-Subirrigation				**0.8 m-Subirrigation**				**Free Drainage**			
Days	Water	Soil	Total	**Loss%**	Water	Soil	Total	**Loss%**	Water	Soil	Total	**Loss%**
6	0.001	1.651	1.652	**95.7**	0.001	10.850	10.851	**71.7**	0.004	15.896	15.90	**58.6**
30	0.001	1.472	1.473	**96.2**	0.003	7.767	7.77	**79.8**	0.001	13.299	13.30	**65.4**
90	0.017	1.333	1.350	**96.5**	0.003	6.897	6.90	**82.0**	0.002	6.798	6.80	**82.3**

Although atrazine can be applied as a pre or post-emergence herbicide, but with subirrigation systems, a post-emergence application will provide more effective herbicide use and less risk of environmental pollution. In post-emergence spraying, weeds will be killed by diffusion of atrazine into their stomata. The

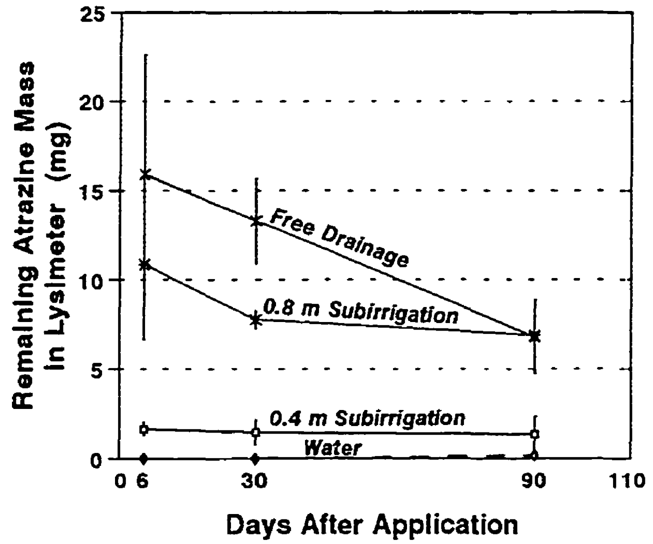

Figure 3.20. Remaining concentration of Atrazine in lysimeters

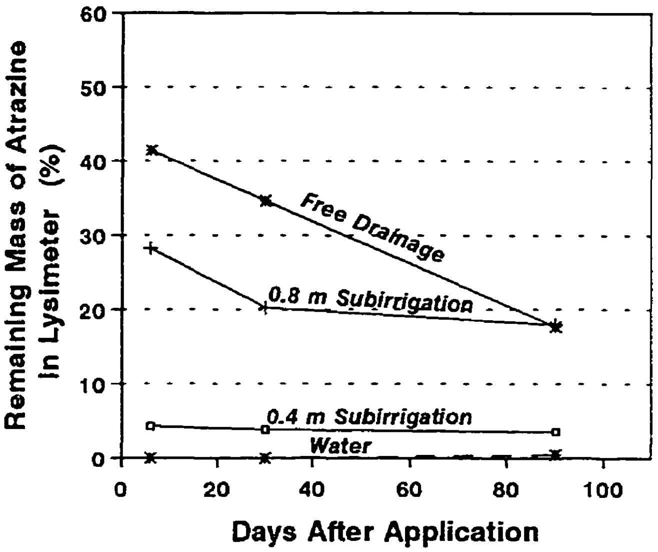

Figure 3.21. Residues of Atrazine in soil

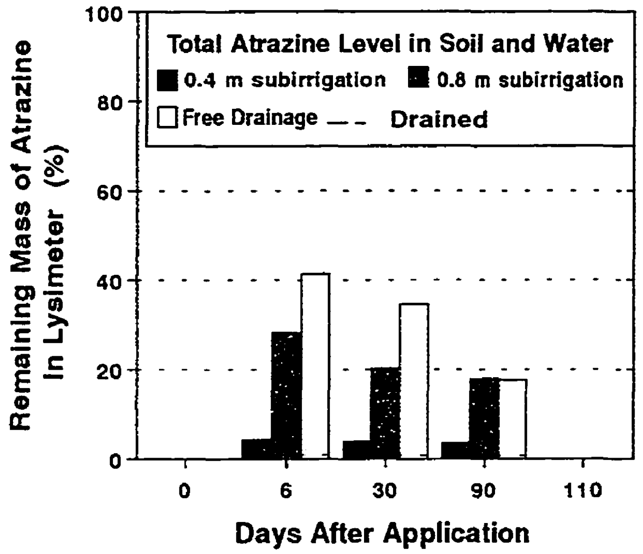

Figure 3.22. Total atrazine levels in soil and water

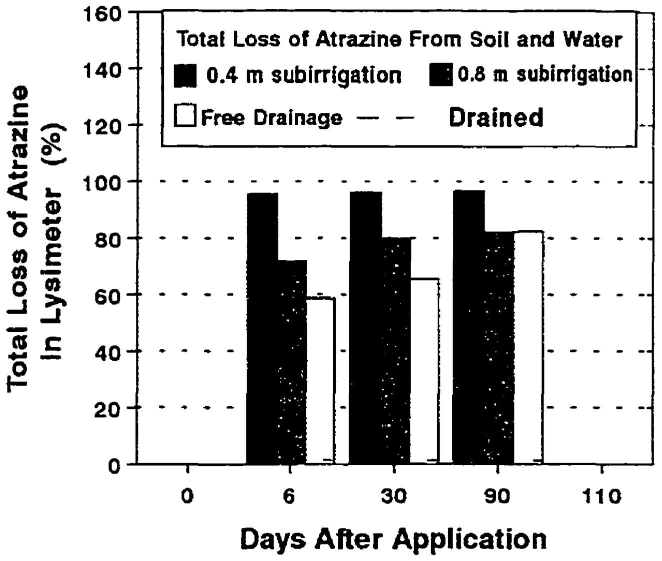

Figure 3.23. Total loss of atrazine in soil profile

subirrigation system can then treat the atrazine residues drifted to the soil surface before it leaches towards the ground water.

3.5.6. Statistical Analysis

A statistical analysis was performed using the SAS program. Since the soil solution samples were taken from the same lysimeter units at predetermined time intervals, the independency of observation and their homoscedasticity could not be maintained. In this situation, the classical statistical analysis of the variance may not produce reliable results. Thus, the Repeated Measures Analysis of Variance was employed instead. The effect of water table management was tested using the Huynh-Feldt (H-F) or Greenhouse-Geisser (G-G) approach for the conservative F test called H-F and G-G test.

The Repeated Measures Analysis of Variance was carried out for the soil moisture contents and total atrazine levels remaining in the soil and water in different treatments. The difference between treatments (WTM), and their contrasts were diagnosed using the classical F test; but the effects of time on the treatments were tested by using the adjusted F test (G-G) and (H-F).

The Huynh-Feldt (H-F) adjusted F test is more applicable than the classical F test for repeated measures of analysis (Dutilleul and legendre, 1993). The calculated Huynh-Feldt epsilon for atrazine (1.0772), reflects a relatively low heterogeneity in the sampling variance. Greater deviation of Huynh-Feldt epsilon from unity indicates higher heterogeneity in the data. The alternative to the null hypothesis has always been considered statistically significant, whenever the probabilities are less than 0.05 ($Pr<0.05$).

Table 3.7 presents results of statistical analysis for soil moisture contents in the crop root zone in 1995. This table shows that moisture level in 0.4 m subirrigation is significantly higher than that of 0.8 m subirrigation and free drainage treatment at 95% level. The contrast between the moisture levels of 0.8 m subirrigation and free drainage was not statistically significant, because 0.8 m water level in the 0.8 m subirrigation could not maintain higher moisture contents in crop root zone.

Table 3.7. General Linear Models Procedure
Repeated Measures Analysis of Variance for **Soil Moisture Contents**
Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WTM	**2**	**2137.56**	**1068.77**	**66.14**	**0.0001**
Error	6	96.95	16.16		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
40-SUB VS. 80-SUB	**1**	**1813.71**	**1813.71**	**112.24**	**0.0001**
40-SUB VS. FREE-DRAI	**1**	**1360.02**	**1360.02**	**84.17**	**0.0001**
80-SUB VS. FREE-DRAI	1	32.60	32.60	2.02	0.2053

Univariate Tests of Hypotheses for Within Subject Effects

Source: TIME

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
6	462.98	77.16	19.51	0.0001	0.0001	0.0001

Source: TIME*WTM

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
12	109.78	9.15	2.31	0.0259	0.1110	0.0456

Table 3.8 shows the statistical analysis for the total atrazine levels found in soil and soil solution samples in 1995. It can be clearly seen that there is a significant difference in total atrazine remaining in the soil among different water table management (WTM) practices. This table shows that the contrast between 0.4 vs. 0.8 m subirrigation, and 0.4 m subirrigation vs. free drainage treatment is statistically significant at the 95% level. Although, relatively lower atrazine residues are found in the 0.8 m subirrigation compared to the free drainage treatment, the contrast between them is not statistically significant.

Table 3.8. General Linear Models Procedure
Repeated Measures Analysis of Variance for **Atrazine**
Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WTM	**2**	**228.84**	**114.42**	**35.55**	**0.0081**
Error	3	9.656	3.21		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
40-SUB VS. 80-SUB	1	**151.84**	**151.84**	**47.17**	**0.0063**
40-SUB VS. FREE-DRAI	1	**149.36**	**149.36**	**46.40**	**0.0065**
80-SUB VS. FREE-DRAI	1	5.46	5.46	1.70	0.2835

Univariate Tests of Hypotheses for Within Subject Effects

Source: TIME

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
2	23.8884434	11.94	2.27	0.1847	0.2273	0.1847

Source: TIME*WTM

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
4	33.07	8.26	1.57	0.2956	0.3395	0.2956

Univariate Tests of Hypotheses for Within Subject Effects

Source: Error(TIME)

DF	Type III SS	Mean Square
6	31.60	5.27

Greenhouse-Geisser Epsilon = 0.5189
Huynh-Feldt Epsilon = 1.0772

Biological activities favour soil higher moisture content as an important stimulant in microbial growth. Higher soil moisture enhances cell metabolism, hydrolysis and hydroxylation reactions of biological compounds. Considering that all lysimeters were identical in terms of soil type and experienced similar climatological conditions, the only significant difference between them was higher moisture content in the crop root zone (Table 3.7). This suggests that significant reduction in the atrazine residues in the 0.4 m subirrigation treatment (Table 3.8) is caused by the higher moisture levels. The higher soil moisture levels in 0.4 m subirrigation may have enhanced the soil biological activity, and thus significantly increased the biodegradation of atrazine residues.

3.6. Conclusions

The distribution of atrazine with depth and time was investigated in this three year study using large field lysimeters. Soil and soil solution samples were collected from different levels of three replicates of 0.4 m subirrigation, 0.8 m subirrigation and free drainage treatments. Atrazine has shown enough mobility to leach down the soil profile, but its concentration diminished with depth. The mass balance study showed a significant difference in the dissipation of atrazine levels in the 0.4 m subirrigation treatment (shallow subirrigation treatment). The contrast between the total remaining mass of atrazine in the 0.4 m subirrigation vs. 0.8 m subirrigation and free drainage was statistically significant at the 95% level. Although relatively lower atrazine residues were found in the 0.8 m subirrigation compared to the free drainage treatment, the contrast between them was not statistically significant. This indicates that most of the pesticide dissipation occurs at the soil root zone depths, and that only shallow subirrigation could significantly reduce the atrazine residues in this sandy soil due to greater supply of moisture to the root zone depth.

These experimental results, which were obtained from large lysimeters in the sandy soil under the Quebec climatological conditions, comply with the findings of other researchers in the field. The study supports the hypothesis that lower atrazine pollution can be expected from the soils of subirrigated farms. These findings also provide adequate support for the recommendation of subirrigation systems as BMPs to control weeds in corn fields in Quebec. The post-emergence application of atrazine in subirrigated corn farms can reduce atrazine pollution from agricultural lands.

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PREFACE TO CHAPTER 4

The fate and transport of atrazine under different water table management systems was presented and discussed in Chapter 3. Potato farms in southern Quebec are sprayed with metribuzin to control weeds. To investigate the impacts of water table management on the leaching properties and the risk of environmental pollution from this herbicide, a lysimeter investigation was carried out on a sandy soil.

The experimental procedures and the results obtained from the three years experiment on the fate and transport of this herbicide are presented in the following chapter (Chapter 4). This chapter comprises of five sections. Section one reviews some of the physical and chemical properties of metribuzin. This section also reviews the previous studies regarding the impact of water table management on the fate and transport of metribuzin. The detailed explanation of methodology of the experiment follows in section two. Although the experimental methodology of study of metribuzin is very similar to that of atrazine, in order to keep the flow material, it is presented and discussed in this section. The experimental results for each sampling season are presented and discussed separately in section three. Finally, in section four the conclusions are presented. All raw data pertaining to lysimeter studies have been included in Appendix A. A summarised version of this work has been submitted for publication in Transactions of the ASAE.

CHAPTER 4

ROLE OF WATER TABLE MANAGEMENT IN REDUCING METRIBUZIN POLLUTION FROM POTATO FARMS

Abstract

The role of water table management systems in reducing pollution from agricultural lands was investigated by measuring metribuzin (4-amino-6(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one) residues in soil in a three year field lysimeter study. Nine PVC lysimeters, 1 m long x 0.45 m diameter, were packed with a sandy soil. Potatoes (*Solanum tuberosum* L.) were grown on each lysimeter to represent the metribuzin uptake by plants. Three water table management treatments were used, consisting of two subirrigation treatments with constant water table depths of 0.4 and 0.8 m and a free drainage treatment. Metribuzin was applied in the summer of each year and soil and soil solution samples were collected at different time intervals after each natural or simulated rainfall event, from the 0.45 and/or 0.85 m depth below the soil surface. The results from the three sampling seasons showed that the metribuzin residues reduced with soil depth and time. A comparison of metribuzin levels in the three treatments showed a significant reduction (95% level) in the soil of 0.4 m subirrigation treatment. The shallower water table in the 0.4 m subirrigation treatment seems to have provided more favourable moisture conditions to the crop root zone enabling the soil biomass to degrade metribuzin faster.

4.1. Introduction

Weeds in potato farms are usually controlled by spraying metribuzin. It is one of the most commonly-used herbicides in potato farms in Quebec. This compound has been detected in various places in Canadian and American ground waters (Shukla et al., 1995; Aubin et al., 1993). Figure 4.1. shows the chemical structure of metribuzin. The solubility of metribuzin in water is about 1220 mg/L. Microbial breakdown is the major mechanism by which metribuzin is lost from the soils. The half-life of metribuzin, at normal usage rates, is about forty six days at 20 °C and sixteen days at 35 °C (Hyzak and Zimdahl, 1974). Aubin et al. (1993) conducted a field study in sandy soil in Quebec, and reported metribuzin levels in ground waters up to 279 µg/L, which is much higher than the advisory limits. Table 4.1 presents the detected and the accepted limits of metribuzin in Canadian and US ground waters.

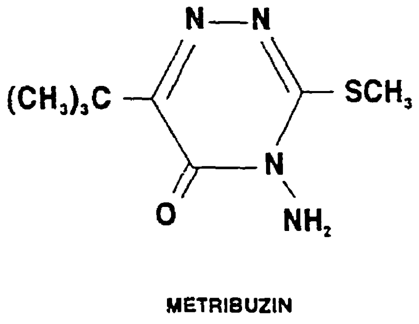


Figure 4.1. Metribuzin chemical structure

Various best management practices such as: integrated pest management, conservation tillage systems, crop rotation, buffer strips, vegetated streams, and precision farming have been examined by researchers to reduce pollution from pesticides. Each of these management practices allows for reduced pesticide pollution by reducing surface transport, limiting vertical leaching and controlling the pesticide application. Among the best management practices, water table management may also be used in non-point source pollution control. In this remediation technique, pesticide degradation could be enhanced by managing the soil moisture content in crop root zone with control drainage or subirrigation. Considering the site-specific nature of various farming practices, any best management practice must be developed according to the local soil and climatological conditions. Although subirrigation is practised in some agricultural lands in southern Quebec, its environmental impact on the water quality is not yet fully understood. It has been hypothesised that, during the warm summer months the moisture condition provided by subirrigation, will enhance the chemical, physical, and microbiological activities in the soil profile. The major results of this practice would involve a rapid increase in the population of micro-organisms, which in turn could break down the contaminant molecules, in order to get their required energy growth. The degraded compounds, thus produced, would be less toxic in most circumstances.

In order to study the impact of water table management on the fate of metribuzin, this lysimeter study was carried out using a typical sandy soil under southern Quebec climatological conditions. Compared to the field plots, the proposed lysimeter setup provided a flexible and reliable environment for

Table 4.1. Metribuzin Trace in Groundwater

	Detected (µg/L)		**Accepted Limits (µg/L)**	
Herbicides	Canada	USA	Canada(1)	USA (2)
Metribuzin	7.8 - 279	1.0 - 4.3	80	175 (for whole life)

(1) Anon. (1987a)

(2) Anon. (1987b)

various study scenarios such as: rainfall simulation to study leaching; the pesticide mass balance; the control of different water levels, and ease of access for close inspection and sample collection. The objectives of this research will be to study the fate and transport of metribuzin under different water table management practices in Quebec. Also, the above results will be analyzed with a view to exploring the possible use of a subirrigation system as BMP for potato farms in Quebec.

To fulfil the above objectives, a three-year investigation began in 1993, using a lysimeter setup. At the beginning of each summer, metribuzin was applied and soil and water samples were collected and analyzed for herbicide residues. The methodology and the results of three years of data are presented and discussed in the following sections.

4.2. Methodology

The experimental work was conducted in an exposed area beside the Agricultural Engineering Workshop at the Macdonald Campus of McGill University. In June 1993, the experiment began, with the construction of lysimeter units. The lysimeter setup was completed in early August 1993, and field experiments began in mid August. The following sections will describe the experimental methodology.

4.2.1. Experimental Design

Nine field lysimeters were constructed and packed to their original bulk density with a homogeneous sandy soil. The lysimeters accommodated three different water table managements. Two subirrigation treatments were selected, one with a constant water level at 0.4 m, and the other with water table at 0.8 m below the soil surface. A free drainage treatment was also used to simulate a subsurface drained field. Potatoes (*Solanum tuberosum* L.) were grown in all nine lysimeters at the beginning of each season. The statistical scheme consisted of a completely randomized design, in which each treatment was randomly allocated to the lysimeters, and each treatment was supported by three replicates (Figure 4.2). In the first year (1993), the experiment began in mid August and ended in mid October. In the second and third year (1994 and 1995), the experiment started in late June and finished in late September.

4.2.2. Experimental Setup

The experimental setup consisted of nine PVC lysimeters, 1.0 m long x 0.45 m diameter. The PVC lysimeters were welded from the bottom, using 0.60 m x 0.60 m PVC sheets. A 50 mm diameter perforated PVC pipe was installed at the bottom of each lysimeter to allow either drainage or subirrigation from the bottom (Figure 4.3). Lysimeters were packed with a uniform sandy soil from a farm where pesticides were not applied in the last two years. The soil in the lysimeters was packed by hand to a field bulk density of 1350 kg/m^3. A 9 mm diameter perforated acrylic plastic tubing was installed in the subirrigation lysimeters at 0.45 and 0.85 m depths, to collect soil solution samples (Figure 4.3).

Each lysimeter was equipped with three, 0.22 m long x 3 mm diameter, stainless steel probes. These were utilised for soil moisture content measurements using a TDR instrument. The probes were inserted horizontally in the lysimeters at 0.15, 0.3, 0.45, and 0.6 m depths. All lysimeters were kept above ground in an exposed area in order to locate possible water leaks that might affect the experimental results.

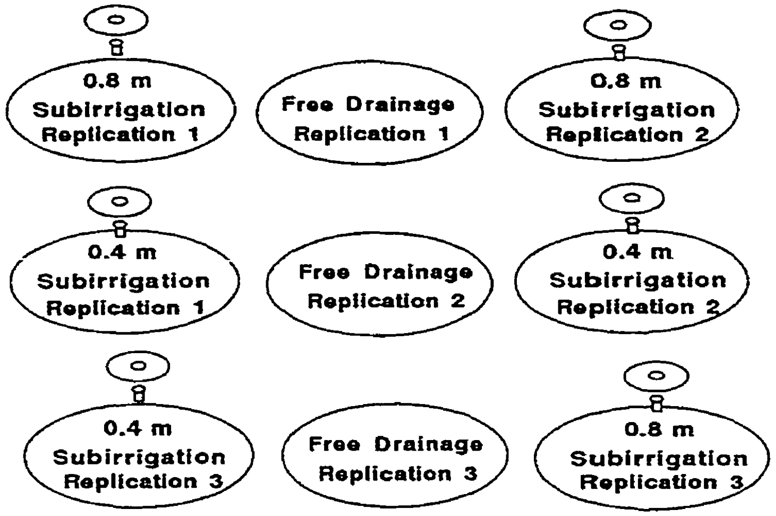
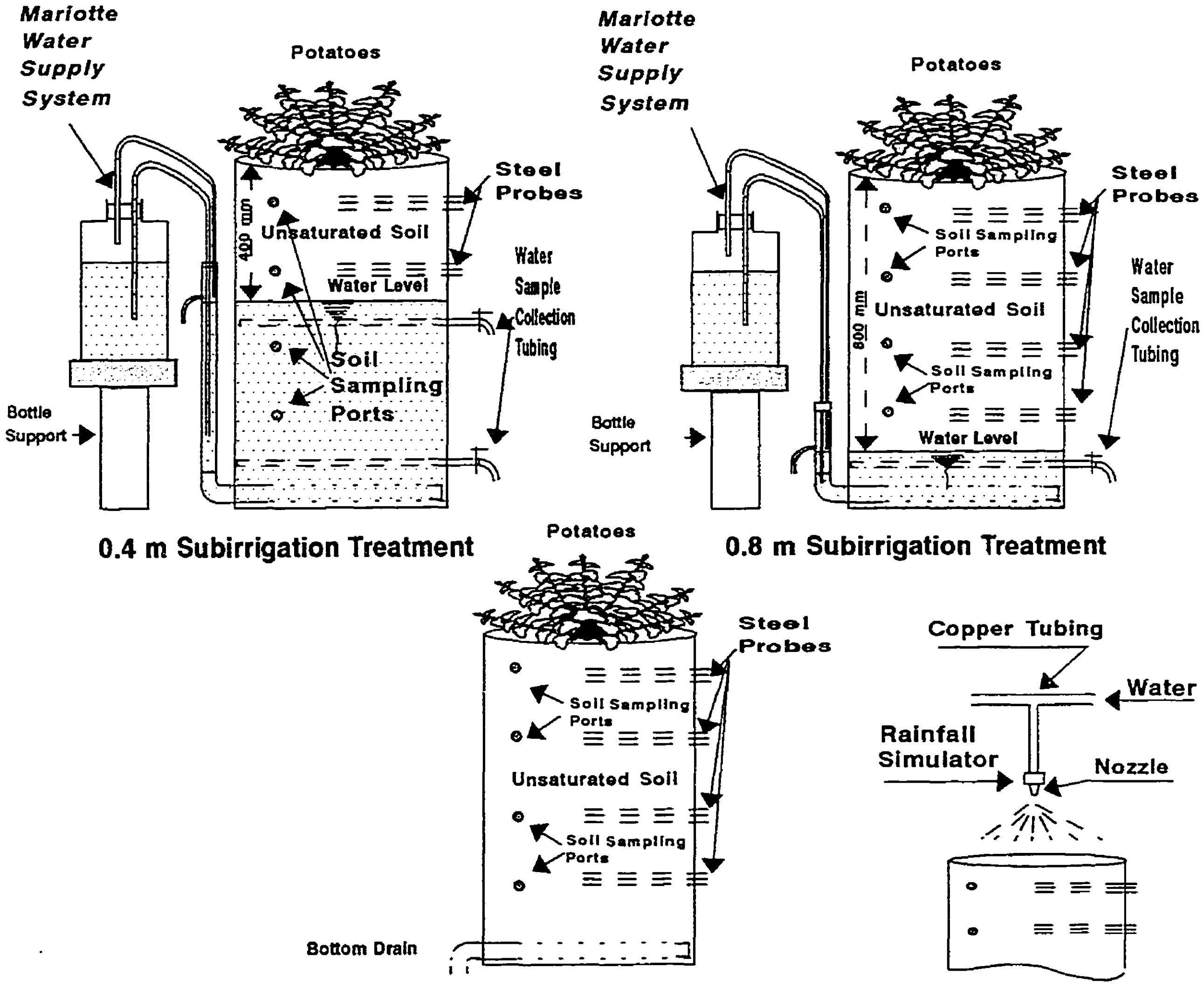


Figure 4.2. Layout of lysimeters in the field



0.4 m Subirrigation Treatment

0.8 m Subirrigation Treatment

Free Drainage Treatment

Figure 4.3. Lysimeter setup

In the subirrigation lysimeters, a 50 mm diameter acrylic plastic riser was connected to the bottom drain and water was supplied from a Mariotte tank (Figure 4. 3). Mariotte tank, based on Mariotte's Law (or Boyle's Law), furnishes a flow of water under a constant head. This syphoning supply system was used to maintain the water levels at 0.4 and 0.8 m below the soil surface in the subirrigated lysimeters, whereas the free drainage lysimeters were allowed to drain freely from the bottom.

A rainfall simulator was also used in 1994 and 1995. The rainfall simulator consisted of nine brass spray nozzles (product of Spraying Systems Co. USA), located 0.5 m higher than top of each individual lysimeter. The nozzles were connected to a flexible copper tubing system equipped with a pressure gage and mounted on a steel frame (Figure 4.3). The pressure gage was used to regulate the tap water pressure required by the spray nozzles. The nozzle inlet size was 12.7 mm, with the simulation capacity up to 13 L/min rainfall under 140 kPa.

4.2.3. Soil Characteristics

The soil was obtained from a field at Macdonald Campus of McGill University, where no herbicides had been applied in the last two years. This soil belongs to St. Amable complex, which has deep sandy deposits of medium to fine texture in its profile (Lajoie, 1960). In order to create a uniform sandy soil profile in the lysimeters, the first 0.1m of the topsoil was removed and the subsoil was taken to fill the lysimeters. To get the same bulk density as the original soil (1350 kg/m^3), an equivalent weight of soil was used to make each 0.1m layer in the lysimeters.

Some disturbed and undisturbed soil samples were taken from the field site to determine: the grain size distribution, organic matter content, pH, CEC, and bulk density. The soil saturated hydraulic conductivity was determined on each individual lysimeter using the constant head approach. The average soil temperature at root zone was about 10 °C less than ambient temperature. Undisturbed soil samples were taken from one lysimeter to determine the average (triplicates) soil moisture retention characteristics (Figures 4.4 to 4.6). Table 4.2 shows results of some of the tests performed on the soil samples.

Table 4.2. The Physical Characteristics of the Soil

Soil Type	Sand (%)	Silt (%)	Bulk Density (kg/m^3)	Organic Matter (%)	pH	CEC (cmol/kg)	Hydraulic Conductivity* (cm/h)
Sandy Soil	92.2	4.3	1350	3.5	5.5	4.9	8.1 (S.D.** =2.4)

* Average value measured on the lysimeters.

** S.D. Stands for standard deviation

4.2.4. Climatological Data

Rainfall, evaporation and the air temperature were measured at the Ste. Anne de Bellevue Weather Station, located less than a kilometre from the experimental area. During the first month of experimentation in August 1993, the average monthly temperature was about 20°C and total rainfall was 42.9 mm (Figure 4.7 presents the daily rainfall for the period of study in 1993). In September, the average monthly temperature was 14°C and total rainfall was 119.2 mm. Data from the nearest Weather Station (Dorval) indicated that August 1993 had the highest monthly temperature and the lowest rainfall in ten years.

Six rainfalls with an intensity above 10 mm/day and twenty rainfalls with an

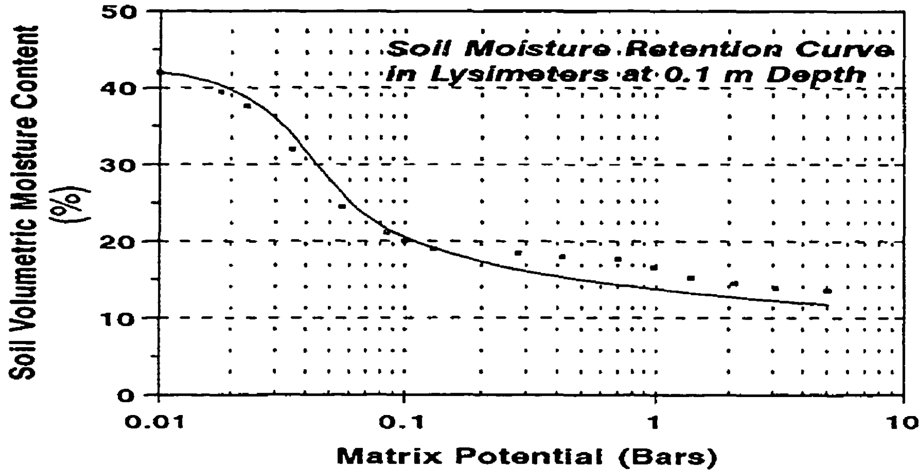


Figure 4.4. Average soil moisture characteristics at 0.1 m depth

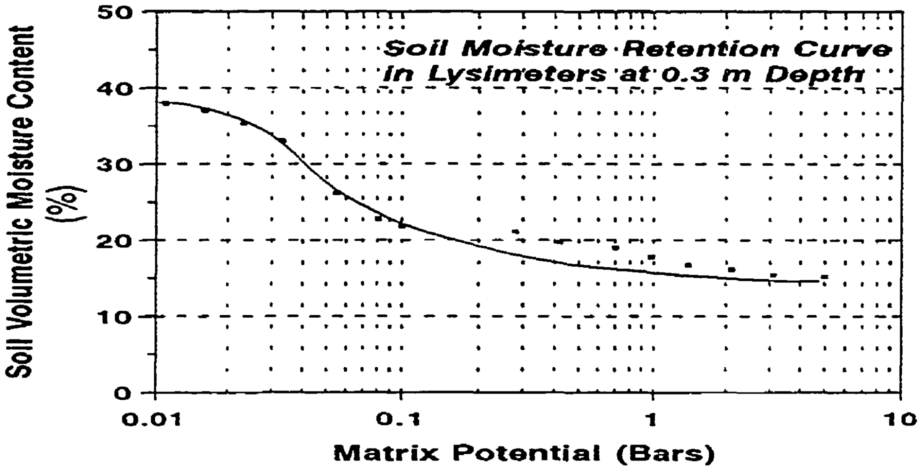


Figure 4.5. Average soil moisture characteristics at 0.3 m depth

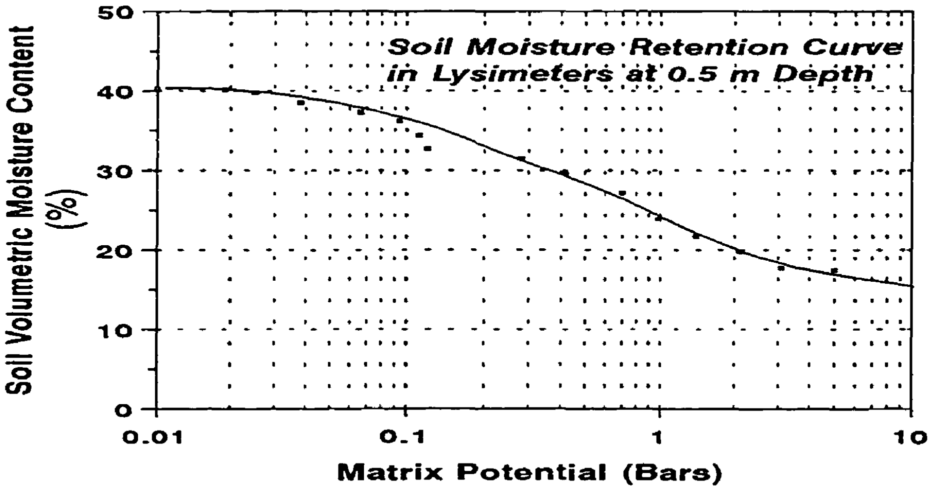


Figure 4.6. Average soil moisture characteristics at 0.5 m depth

intensity of less than 10 mm/day were recorded between the day of herbicide application and the end of the 1993 sampling period. The first rainfall with an intensity of 8.9 mm/day occurred one day after herbicide application. The highest rainfall during this period was 30.4 mm/day and it occurred 23 days after application. There was no surface runoff in the lysimeters.

In the 1994 sampling season, the highest average monthly temperature and evaporation were observed in July. The highest average temperature in this month was 21.3°C, and the total rainfall was 61.3 mm. Total monthly rainfall was 99.9 mm in August and 105.5 in September (Figure 4.10 shows the daily rainfall for the summer period in 1994). In this summer there were eight rainfalls with an intensity of more than 10 mm/day. The highest daily rainfall occurred on June 29, with 54.9 mm just six days after the herbicide application. In 1994, seven rainfalls, each with an intensity of 25 mm/h, were simulated at different intervals. The duration of rainfalls varied from one to 1 to 1.5 hours. The total amount of simulated rainfall in the entire experimental period was about 260 mm. Comparing the monthly average temperature with the past ten years data, for the corresponding months, the summer of 1994 may rank as a mild summer with regard to temperature and rainfall.

In the summer of 1995, the highest average monthly temperature was measured in July. The highest reported evaporation in this summer occurred in June (7.2 mm). Total monthly rainfall in June, July, August and September was measured as 64.5, 138.2, 118.2, 69.5 mm, respectively. (Figure 4.14 shows the daily natural and simulated rainfall for the summer period in 1995). The total amount of simulated rainfall in this year was about 300 mm. The simulated rainfall intensity was about 30 mm/h. Comparing the monthly average temperature with the past ten years of data, for the corresponding months, the summer of year 1995 can be called as a relatively wet summer.

4.2.5. Metribuzin Application

Each summer, the lysimeters received a metribuzin application at a rate of 1 kg/ha of active ingredient. Because there were some construction delays in the first year, the pesticides were applied late, on August 11, 1993. In the second and third year, the pesticide applications were made on June 23 in 1994 and June 24 in 1995.

4.2.6. Sampling Methods

In 1993, one-litre soil solution samples (water) were taken at day 0, 7, 14, 22, 29, 37, 47, 64, and 84 after the metribuzin application (DAA), whereas in 1994, the samples were taken at day -23, 3, 7, 14, 23, 30, 38, 49, 68, and 90 after the application. The sampling interval for soil and soil solution samples in the summer of 1995 followed day -20, 6, 16, 28, 42, 70, and 90 after application.

In order to take representative soil solution samples, the sampling tubes were emptied before each sampling period to remove any stagnant water. Also in order to stop microbial activity, while waiting in the refrigerator for analysis, about 10 ml of dichloromethane was added to all soil solution samples. The sampling for the free drainage lysimeters was quite irregular in 1993, since they were completely rain-fed and most rainfall events caused no outflow. To overcome this difficulty and to obtain more samples, a rainfall simulator was constructed and used in 1994 and 1995.

To collect the soil samples, four sampling ports were made in each lysimeter at 0.1, 0.3, 0.5 and 0.7 m below the soil surface. Each time about 5 to 10 g of soil sample was collected from each port, and samples were kept in the freezer for future extraction and analysis.

4.2.7. Extraction of Metribuzin Residues

The soil solution samples were mixed with 100 ml of dichloromethane (methylene chloride) in a separatory funnel. The mixture was hand shaken for a few minutes, and the organic phase was collected as the accumulation at the bottom of the funnel. The process was repeated twice. The extracted organic phase was evaporated to separate dichloromethane from the herbicides. The residues were then dissolved in about 10 ml of methanol and stored in the refrigerator, prior to gas chromatography analysis.

A soil sample of 5 to 10 g was transferred to a flat bottom flask. A subsample of about 1 g was placed in the oven at 105° C for 24 hours for soil moisture determination. Each soil sample received about 100 ml of methanol and was shaken for at least 1 hour. The mixture was transferred to a vacuum flask (Buchnel flask) and filtered under partial vacuum. The collected organic phase was evaporated in the rotary evaporator for about 15 minutes and rinsed with about 10 ml of hexane. This organic phase was then stored in a 15 ml glass vial in the refrigerator prior to GC analysis.

4.2.8. Gas Chromatography

The gas chromatography was done using a Varian, Model 3400 gas chromatograph. The column used was a 0.53 mm i.d., fused silica Megabore DB-5, 1.5 µm film thickness, made by J&W Scientific. The injector temperature was set at 250°C and the detector was kept at 300°C. The column temperature was maintained at 180°C for 9 minutes, and then increased to 200°C at a rate of 4° C/min. At 200°C it was held for 1 minute, and then raised to 280° C at a rate of 20° C/min. The column was kept at this temperature for at least 9 minutes. The nitrogen and helium make up flow rate was 30 mL/min, while the helium carrier gas flow rate was kept at 7.5 mL/min. The hydrogen flow rate was 4.5

mL/min, and air flow was set to 175 mL/min. The detection limits for water and soil samples were found to be 0.03 µg/L and 10 µg/kg, respectively. The recovery rate of metribuzin extraction and evaporation, was 88% ± 5%.

4.2.9. Statistical Analysis

Statistical analysis was performed using the SAS program. Because samples had to be taken from the same lysimeter units at predetermined time intervals, therefore, time series approach was used to analyze the data. The Repeated Measures Analysis of Variance was employed to study the effect of water table management on the loss of herbicides. The hypothesis was tested using the Huynh-Feldt (H-F) or Greenhouse-Geisser (G-G) approach for the conservative F test called H-F and G-G test.

4.3. Results and Discussions

In 1993 and 1994 sampling seasons, only soil solution samples were collected from the lysimeters, whereas, in 1995, both soil solution and soil samples were collected and analyzed for metribuzin residues. The results obtained for each sampling season are presented and discussed separately in the following sections:

4.3.1. Metribuzin Residues in Soil Solution in 1993

Metribuzin distribution with depth and time was examined by collecting soil solution samples at two depths (0.45 and 0.85 m) in the 0.4 m-subirrigation treatment, and at one depth (0.85 m) in the 0.8 m-subirrigation and free drainage treatments. Figures 4.7 and 4.8 respectively show the distribution of metribuzin with depth and time for subirrigation treatment with water table level (WTL) at 0.4 m and 0.8 m below the soil surface. The error bars, representing average values ± one standard deviation are also plotted. However, the distribution of metribuzin with depth could only be studied in the 0.4 m subirrigation treatment since soil solution samples with depth could not be collected for other treatments. In 1995, soil samples were also collected and they facilitated the study of metribuzin leaching in lysimeters.

The highest observed average concentration (average of three replicates) at the 0.45 m depth in the 0.4 m-subirrigation, was 1.8 μg/L (Figure 4.7). Metribuzin had also leached down into the 0.85 m depth, and the highest average concentration of metribuzin at this depth was 1.7 μg/L.

In the 0.8 m-subirrigation treatment (Figure 4.8), the highest average metribuzin concentration was 3.7 μg/L, detected almost four weeks after herbicide application. Metribuzin demonstrated high mobility after rainfall in both subirrigation treatments. Metribuzin is relatively soluble in water, which partly explains its higher mobility.

In both subirrigation treatments, metribuzin also degraded fast. In the 0.4 m subirrigation treatment, it took only one week to reduce the concentration of soil solution at the 0.45 m depth, from the highest average value (1.8 μg/L) to 0.1 μg/L (Figure 4.7). A similar dissipation trend was observed at the 0.85 m depth in the 0.4 m WTL subirrigation treatment (Figure 4.7).

In the subirrigation treatment with 0.8 m WTL, metribuzin concentration at the 0.85 m depth was reduced from 3.7 to 0.4 μg/L within eighteen days (Figure 4.8). The comparison of dissipation trends at 0.45 and 0.85 m depths reveals that in the subirrigation treatment with 0.4 m WTL, metribuzin dissipates faster at the 0.45 m depth compared to the 0.85 m depth (Figure 4.7). Since

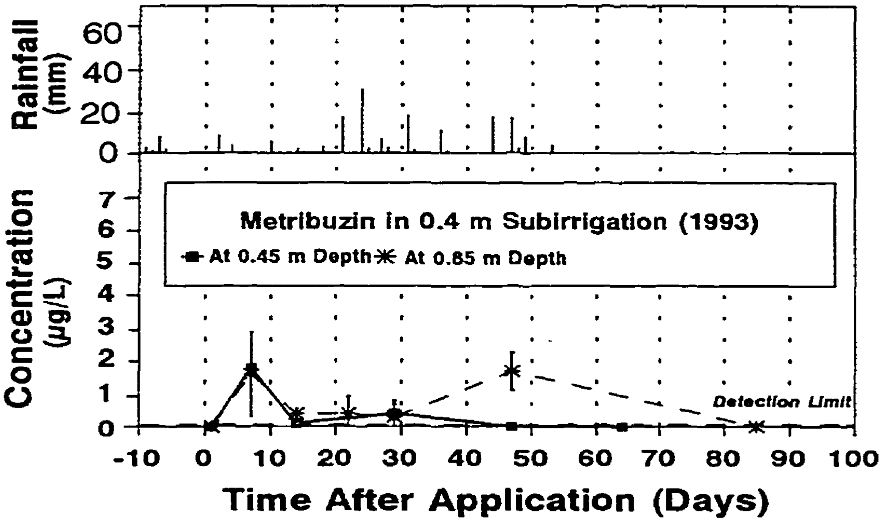


Figure 4.7. Metribuzin in soil solution in 0.4m subirrigation treatment (1993)

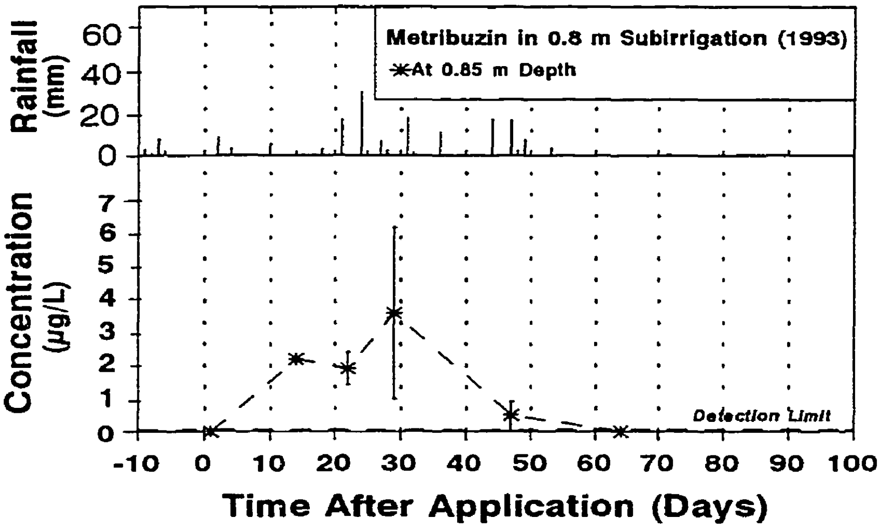


Figure 4.8. Metribuzin in soil solution in 0.8m subirrigation treatment (1993)

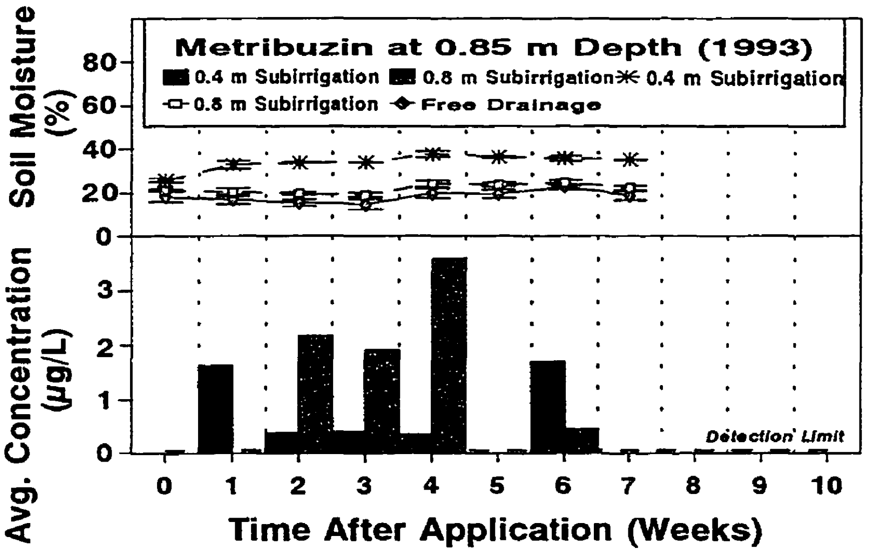


Figure 4.9. Comparison of metribuzin residues in soil solution of all treatments (1993)

metribuzin has a relatively low adsorption rate (Bouchard et al., 1982), its dissipation in the soil solution may be caused by faster degradation, due to higher moisture content in the root zone in the shallower subirrigation treatment.

Aubin et al. (1993) reported a longer persistence of metribuzin under drainage plots as compared to subirrigation plots. They also reported higher adsorption and microbial degradation at higher soil moisture content. Lack of samples from the free drainage treatments did not permit the comparison of these findings with the free drainage treatments. However, a comparison of two subirrigation treatments (Figure 4.9) showed a lower concentration in the shallower subirrigation treatment. Figure 4.9 demonstrates the higher moisture content observed in the subirrigation treatment at the root zone depth.

4.3.2. Metribuzin Residues in Soil Solution in 1994

Figure 4.10 shows metribuzin distribution with depth and time, in the 0.4 m-subirrigation treatment. The average background concentration (average of three replicates) of metribuzin at the 0.45 and 0.85 m depths was measured as 0.33 μg/L and 0.15 μg/L, respectively. The measured concentration reduced to almost non-detectable limits (0.03 μg/L) after twenty five days, and then increased to 0.44 μg/L at the 0.45 m and 0.15 μg/L at the 0.85 m depth just one week after application. Rapid leaching from the upper layers occurred only six and seven days after the application with 32 and 54.9 mm of natural rainfall, respectively. This rapid leaching may be attributed to either macropore flow occurrence in the soil matrix or the high mobility of metribuzin. Due to high mobility, the metribuzin breakthrough curve demonstrates several peaks. These correlates with periods of significant rainfall. In this sampling season, the highest detected concentration, was 0.4 μg/L, three weeks after application.

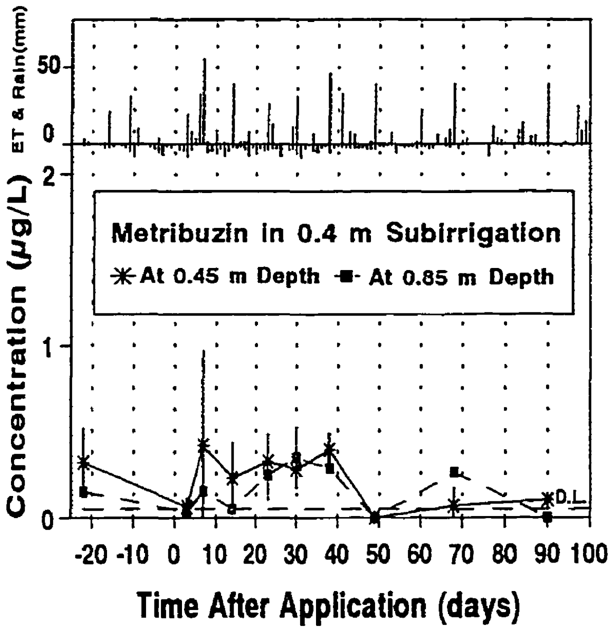


Figure 4.10. Metribuzin in soil solution in 0.4m subirrigation treatment (1994)

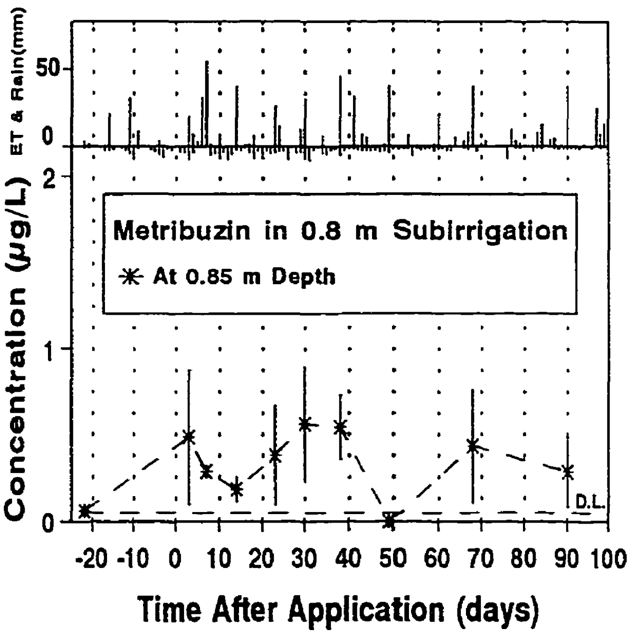


Figure 4.11. Metribuzin in soil solution in 0.8m subirrigation treatment (1994)

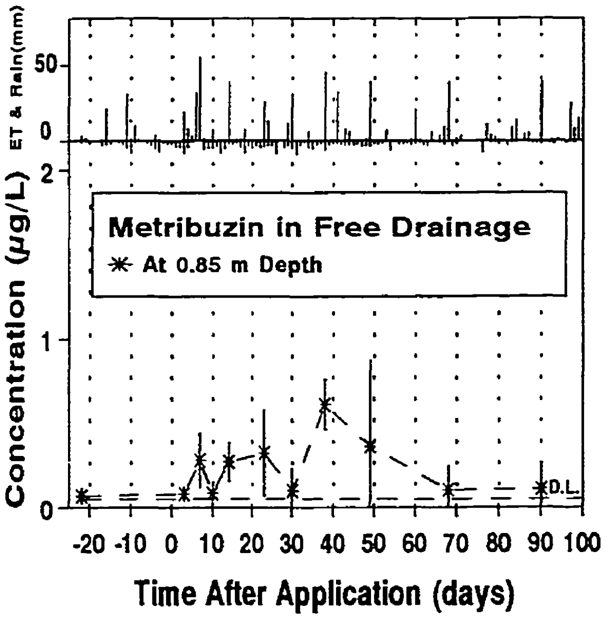


Figure 4.12. Metribuzin in soil solution in free drainage treatment (1994)

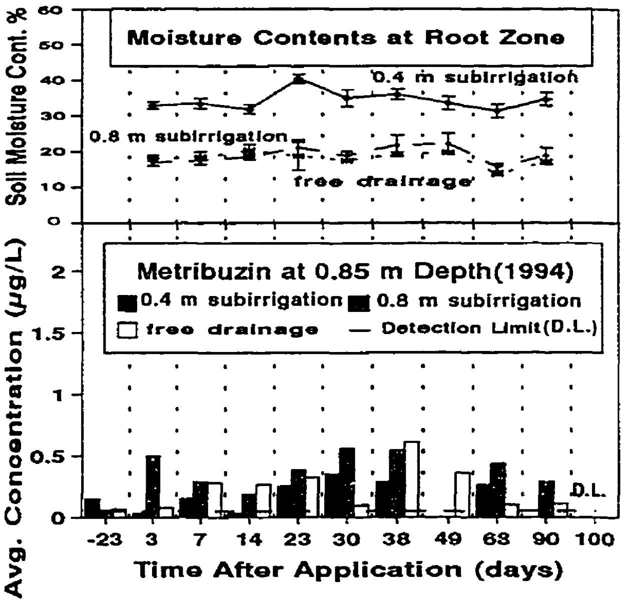


Figure 4.13. Comparison of metribuzin residues in the soil solution of all treatments (1994)

Figure 4.11 demonstrates metribuzin distribution with time, in the 0.8 m subirrigation treatment. The highest average concentration was 0.55 µg/L. Metribuzin was detected at the 0.85 m depth only three days after surface application. This again demonstrates either the occurrence of preferential flow in the soil profile or high mobility. Metribuzin concentration reduced to 0.2 µg/L after two weeks, and increased again to 0.6 µg/L after sixteen days of water application.

The rapid leaching of metribuzin was also observed in the free drainage treatment (Figure 4.12), where metribuzin was detected at the 0.85 m depth, only three days after application. It should be noted that only 19.3 mm of rainfall occurred in this period. The average metribuzin concentration in free drainage lysimeters was 0.1 µg/L, three days after application. Then, with leaching of new metribuzin from the upper layers, it increased to 0.28 µg/L within seven days. The highest average concentration (average of three replicates) of metribuzin was measured at about 0.65 µg/L, thirty eight days after surface application; this concentration was expected to be higher since less degradation loss was anticipated in the free drainage lysimeters.

Unlike the subirrigated lysimeters, a constant water level was not maintained in the free drainage lysimeters; hence, a downward movement of simulated rainfall will have only a limited contact time to equilibrate with the solid phase, and with the immobilized metribuzin molecules already diffused and trapped in the dead-ended voids (Rambow and Lennartz, 1993; Ghadiri and Rose, 1992; van Genuchten et al., 1974). However, the adsorbed/trapped metribuzin residues may not degrade as fast as those in subirrigation. This was supported by a mass balance study and a laboratory batch study carried out in 1995.

Figure 4.13 demonstrates that higher moisture content was observed at all times at the root zone depth in the subirrigation treatments. The comparison of the three treatments (Figure 4.13) indicates a lower metribuzin concentration in the shallow water table subirrigation treatment.

4.3.3. Metribuzin Residues in Soil Solution in 1995

Figure 4.14 shows the average metribuzin concentration in the soil solution samples in the 0.4 m-subirrigation treatment (average of three replicates). The metribuzin level at the 0.45 m depth increased from the background concentration (0.2 µg/L) to about 0.9 µg/L, following the second rainfall simulation sixteen days after the metribuzin application. The metribuzin level was always less than 0.9 µg/L, in all soil solution samples collected after day 16, regardless of the three natural rainfalls of more than 20 mm, and the five simulated rainfalls of about 60 mm. This implies that the metribuzin leached to this depth was either degraded or bound to the soil particles and was not available in the soil solution. The maximum metribuzin level at the 0.85 m depth was about 0.5 µg/L.

In the 0.8 m subirrigation treatment, the highest concentration was 0.5 µg/L, twenty-eight days after application (Figure 4.15). The metribuzin level reduced to a non-detectable limit in almost two weeks, indicating that the surface applied metribuzin had leached to the 0.85 m depth and then dissipated.

The highest metribuzin concentration in the free drainage treatment was about 1.2 µg/L (Figure 4.16), indicating that the surface applied metribuzin had continuously leached and accumulated at the 0.85 m depth. In most cases, the comparison of the three metribuzin treatments (Figure 4.17) shows a lower concentration in the 0.4 vs. 0.8 m-subirrigation treatment; but a higher concentration with respect to free drainage. Similar to the arguments made for

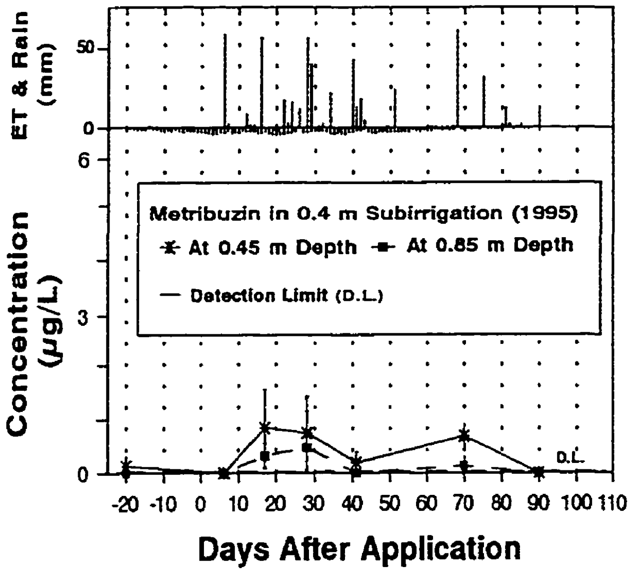


Figure 4.14. Metribuzin in soil solution in 0.4m subirrigation treatment (1995)

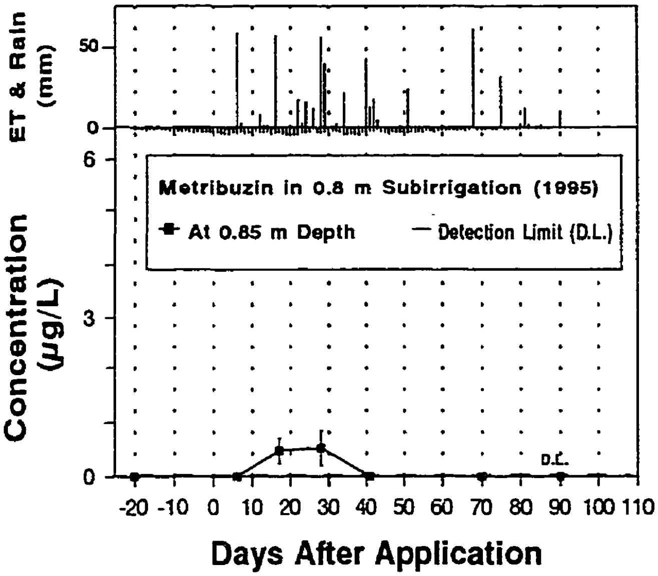


Figure 4.15. Metribuzin in soil solution in 0.8m subirrigation treatment (1995)

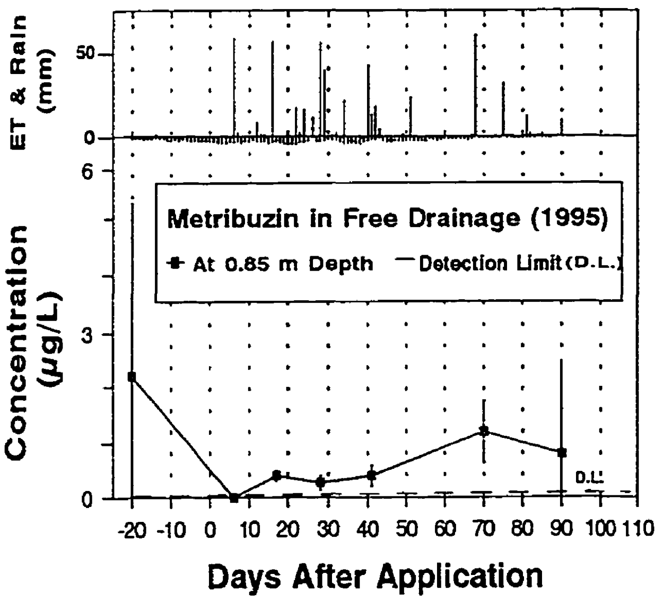


Figure 4.16. Metribuzin in soil solution in free drainage treatment (1995)

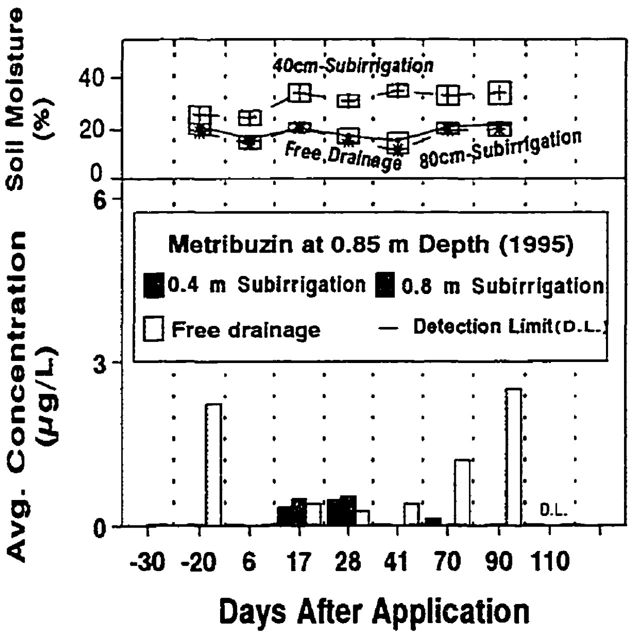


Figure 4.17. Comparison of metribuzin residues in soil solution of all treatments (1995)

the results in 1994, it could be said that: natural or simulated rainfall pulses create a relatively high pore water velocity; the leaching water will only have a limited time span to equilibrate with the metribuzin, which has either accumulated on the solid phase (soil particles and organic matters) and/or has diffused into the immobile liquid phase, already present in the dead-end pores.

This idea maintains that, in the free drainage treatment, the mobile front does not have sufficient time contact for equilibrium, and the breakthrough curve in this case only represents the instantaneous equilibrium sorption. Hence, the measured concentration levels in the free drainage lysimeters is, in fact, a small fraction of the potentially mobile metribuzin available in the soil. The higher fraction of metribuzin still resides in the soil and is gradually released with the movement of the next water front. This causes longer tailing effects in the metribuzin breakthrough curves in the soil solution samples. Retention of metribuzin residues in the profile of free drainage lysimeters has been verified through a mass balance study. Due to the presence of moisture in subirrigation treatments, the time dependent non-equilibrium adsorption/desorption prevailed, and usually showed higher concentrations. Figure 4.17 demonstrates the higher moisture content observed in subirrigation treatment at the root zone depth.

4.3.4. Metribuzin Residues in Soil in 1995

Soil samples were collected from each lysimeter at four different depths on 6, 30 and 90 days after the metribuzin application. Tables 4.3 to 4.5 show metribuzin residues and their standard deviation in all treatments. Figure 4.18 shows the average levels of three replicates of metribuzin residues detected in the soils of each water table management treatment at various depths. A study of the variation of metribuzin concentration in the 0.4 m-subirrigation on day 6, 30

Table 4.3. Metribuzin Residues in Soil in 0.4 m-Subirrigation Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (μg/kg)	Standard Deviation(μg/kg)
6	0.10	15.00	14.0
	0.30	11.33	16.0
	0.50	0.00	0.0
	0.70	2.97	4.2
30	0.10	0.00	0.0
	0.30	1.53	2.2
	0.50	0.00	0.0
	0.70	0.00	0.0
90	0.10	0.00	0.0
	0.30	0.00	0.0
	0.50	0.00	0.0
	0.70	0.00	0.0

(1) Zero concentration implies a non-detectable level.

Table 4.4. Metribuzin Residues in Soil in 0.8 m-Subirrigation Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (μg/kg)	Standard Deviation(μg/kg)
6	0.10	81.3	18.7
	0.30	4.95	1.1
	0.50	0.00	0.0
	0.70	0.00	0.0
30	0.10	47.0	7.0
	0.30	0.00	0.0
	0.50	0.00	0.0
	0.70	2.77	0.1
90	0.10	8.60	1.4
	0.30	4.90	1.1
	0.50	0.00	0.0
	0.70	0.00	0.0

(1) Zero concentration implies a non-detectable level.

Table 4.5. Metribuzin Residues in Soil in Free Drainage Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (μg/kg)	Standard Deviation(μg/kg)
	0.10	185	15.0
6	0.30	0.00	0.0
	0.50	0.00	0.0
	0.70	0.00	0.0
	0.10	92.5	7.5
30	0.30	51.0	9.0
	0.50	17.0	1.5
	0.70	23.0	1.0
	0.10	42.5	7.5
90	0.30	52.5	7.5
	0.50	30.0	5.0
	0.70	15.0	0.0

(1) Zero concentration implies a non-detectable level.

and 90 after application, can be made by comparing the first row of charts. The metribuzin residues in soil in the 0.8 m subirrigation and free drainage may be studied, using charts in the middle and bottom rows, respectively. The charts in Figure 4.18 could be used in a vertical sequence, to compare the metribuzin levels among the three water table management treatments at each sampling day.

The first three charts in the first column compare the metribuzin residues in two subirrigation and one free drainage treatment, six days after pesticide application. Lower metribuzin concentration was always found in the soil in the 0.4 m-subirrigation treatment, especially at the root zone depth. A similar trend is observed when comparing the metribuzin levels on day 30 and 90, indicating that the shallower water table, in the 0.4 m-subirrigation treatment, caused a very fast reduction in the metribuzin levels at the root zone depth. This would leave less pesticide available for leaching to the ground waters.

These results are closely allied to the findings of other researchers, i.e. subirrigation, especially with shallow water tables, would cause a faster breakdown of pesticides (Aubin et al., 1993; Kalita et al., 1992). Aubin (1994), in a laboratory degradation experiment, found that the metribuzin degradation was enhanced as the soil moisture content increased. His findings partly support the hypothesis of faster degradation of pesticides, with a shallower water table in the field.

To extend these findings to metribuzin, a laboratory batch study was carried out in 1995 to investigate metribuzin degradation at different soil moisture contents (Jebellie et al., 1996). Results from this batch test indicate that the dissipation of metribuzin directly increases with the increase of soil moisture content. These results further support the hypothesis that higher moisture content at the root zone depth reduces the pesticide residues at a much faster rate.

4.3.5. Metribuzin Mass Balance

The soil and soil solution samples collected throughout the experiment have shown the leaching of metribuzin to the deeper layer. Soil samples were collected from 0.1, 0.3, 0.5 and 0.7 m depths on day 6, 30 and 90 after application. Figure 4.18 demonstrates that on any sampling day there is a change in concentration of metribuzin residues at each soil depth. This indicates the simultaneous occurrence of leaching to the lower layers and degradation. A mass balance was carried out to obtain further information about, metribuzin dissipation.

The mass balance was performed for three separate sampling days. The metribuzin residues in the whole lysimeter profile were considered, as well as the mass of metribuzin drained or spilled out after either natural or simulated rainfall periods. Figure 4.19 compares the metribuzin residue among the three water table management treatments at different times. Table 4.6 contains the summary of the mass balances of the metribuzin in all water table management treatments. Each lysimeter was sprayed with about 16 mg of metribuzin at the

Table 4.6. The Residue Levels and Loss of Metribuzin in Different Treatments (mg)

	0.4 m-Subirrigation				**0.8 m-Subirrigation**				**Free Drainage**			
Days	Water	Soil	Total	**Loss%**	Water	Soil	Total	**Loss%**	Water	Soil	Total	**Loss%**
6	0.0	1.575	1.575	**90.2**	0.0	3.642	3.642	**77.2**	0.0	7.992	7.992	**50.1**
30	0.014	0.099	0.113	**99.3**	0.002	2.085	2.087	**87.0**	0.001	7.927	7.928	**50.4**
90	0.014	0.0	0.014	**99.9**	0.0	0.583	0.583	**96.4**	0.0	5.832	5.832	**63.6**

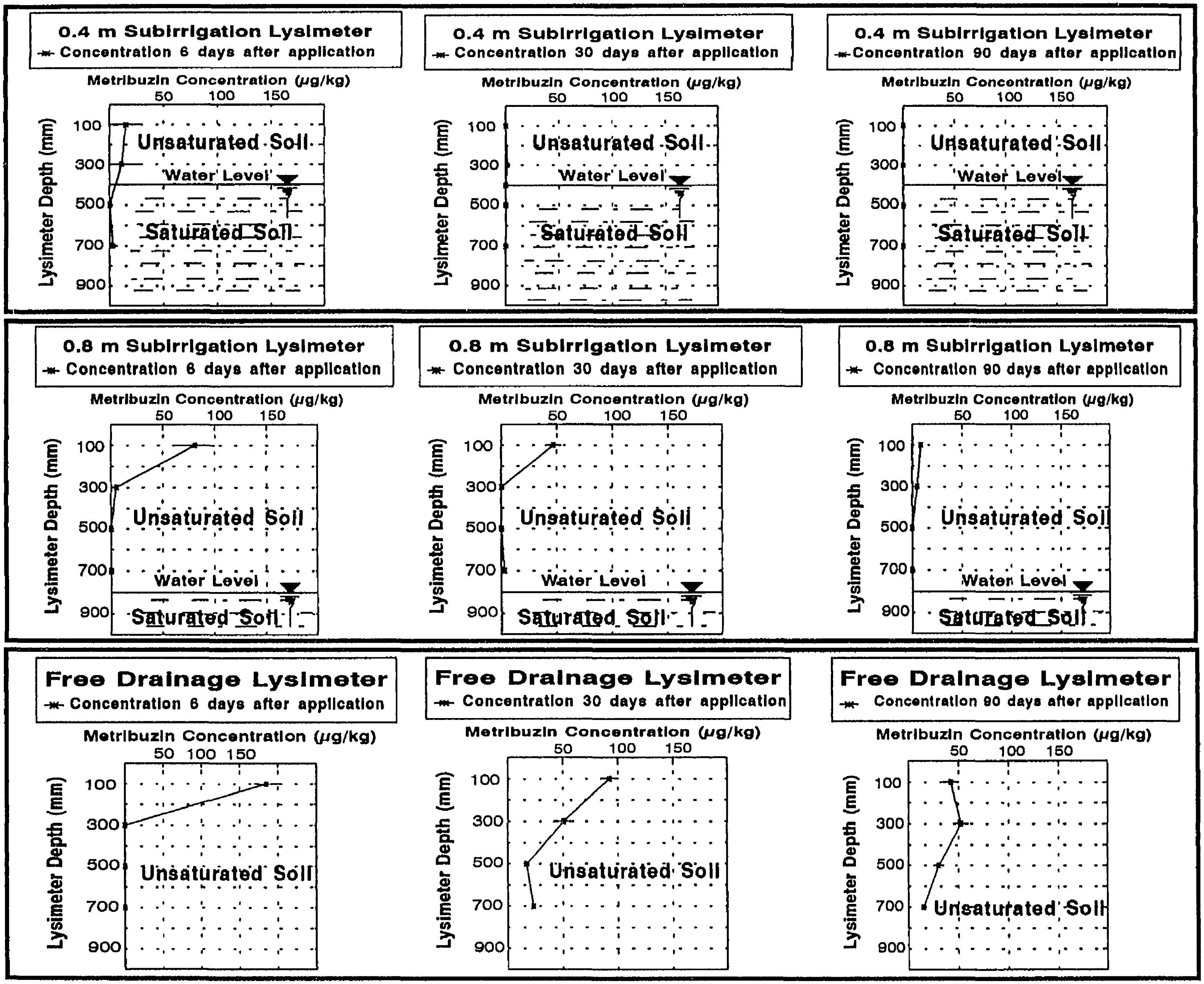


Figure 4.18. Comparison of metribuzin residues in the soil profile of all treatments in 1995

beginning of summer 1995. According to Table 4.6, in the 0.4 m-subirrigation treatment, this amount has been reduced by 90.2%, after six days. The corresponding values for the 0.8 m-subirrigation and free drainage treatments are 77.2 and 50.1%, respectively; suggesting faster dissipation of metribuzin residues in the 0.4 m subirrigation treatment. A similar trend is identified in the metribuzin levels of other sampling days. The total percentage of loss of metribuzin in different treatments is presented in Figure 4.20.

Although metribuzin can be applied as a pre or post-emergence herbicide, but with subirrigation systems, a post-emergence application will provide more efficient herbicide use and lesser risk of environmental pollution. In post-emergence spraying, weeds will be killed by diffusion of metribuzin through their stomata, and subirrigation system can treat the metribuzin residues drifted to the soil surface before it leaches towards the ground water.

4.3.6. Statistical Analysis

The statistical analysis for the 1993 data could not be done, due to lack of data (missing data). However, the Repeated Measures Analysis of Variance was carried out using the SAS program for the series of nine soil solution sample data, collected in the summer of 1994 and the series of seven soil moisture contents, soil solution and soil samples in 1995. The difference between treatments (WTM), and their contrasts were diagnosed using the classical F test; but the effects of time on the treatments were tested by using the adjusted F test, known as Greenhouse-Geisser (G-G) and Huynh-Feldt (H-F) tests (Dutilleul and Legendre, 1993). The alternative to the null hypothesis is considered statistically significant whenever the probabilities are less than 0.05 ($Pr<0.05$).

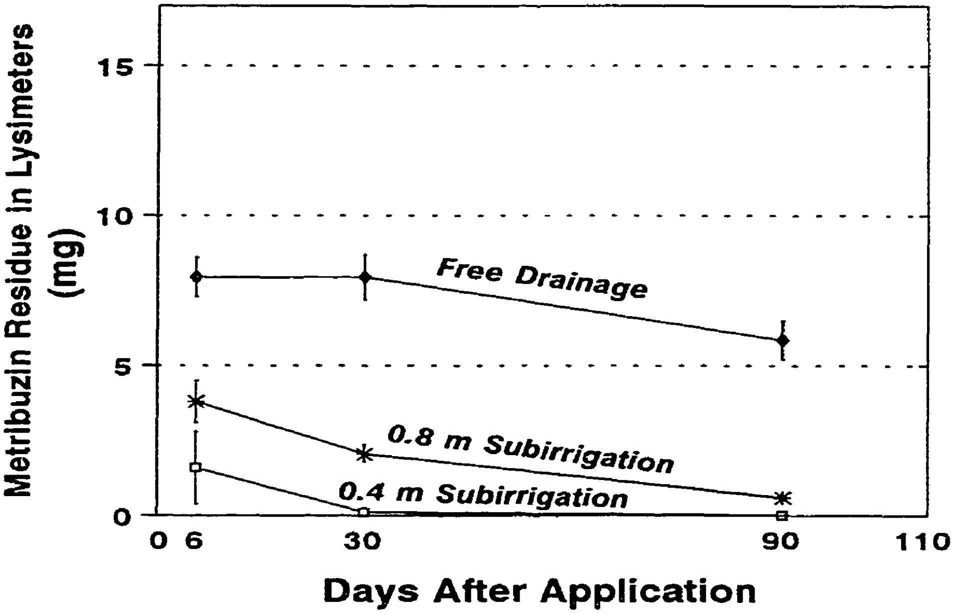


Figure 4.19. Metribuzin residues in soil

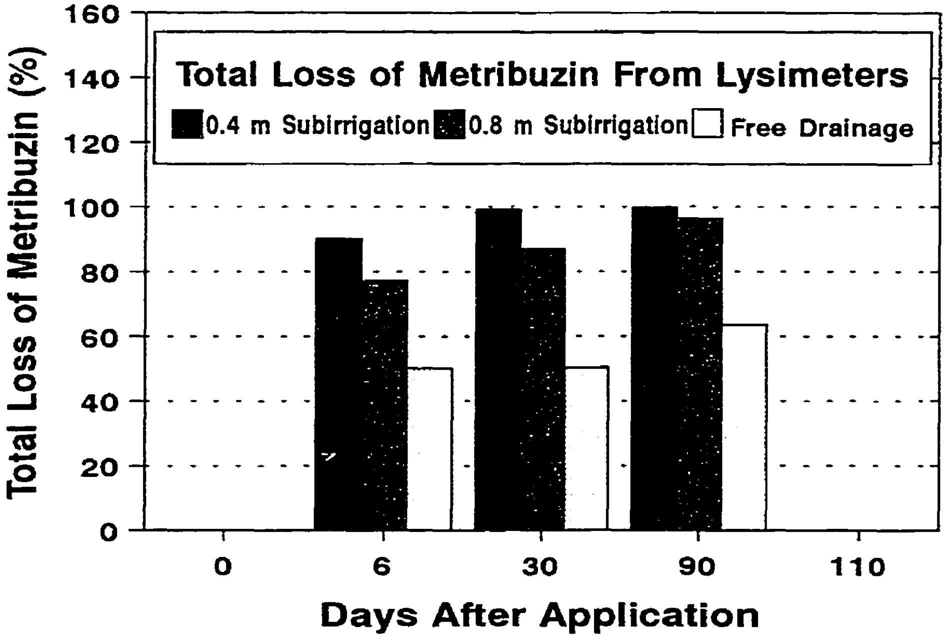


Figure 4.20. Total loss of metribuzin in the soil profile

Table 4.7 shows the statistical analysis of soil moisture content in the crop root zone. There is a significant difference in soil moisture contents between different water table management (WTM) practices. The contrast between 0.4 m subirrigation vs. free drainage and 0.4 m vs. 0.8 m subirrigation is statistically significant at the 95% level. The contrast between 0.8 m subirrigation treatments vs. free drainage is not statistically significant, because the 0.8 m subirrigation treatment could not provide as much moisture to the crop root zone, and thus acted, more or less like a subsurface drainage treatment.

Table 4.7. General Linear Models Procedure
Repeated Measures Analysis of Variance for **Soil Moisture Contents**
Lysimeters, Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WTM	**2**	**1955.52**	**977.76**	**28.65**	**0.0009**
Error	6	204.76	34.12		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
40-SUB VS. 80-SUB	**1**	**1226.88**	**1226.88**	**35.95**	**0.0010**
40-SUB VS. FREE-DRAI	**1**	**1672.02**	**1672.02**	**48.99**	**0.0004**
80-SUB VS. FREE-DRAI	1	34.38	34.38	1.01	0.3543

Univariate Tests of Hypotheses for Within Subject Effects

Source: **TIME**

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
6	322.22	53.73	15.36	0.0001	0.0002	0.0001

Source: TIME*WTM

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
12	269.58	22.47	6.42	0.0001	0.0030	0.0001

Table 4.8 presents the statistical analysis for metribuzin in soil. This table shows that there is a significant difference in metribuzin residues between different water table management (WTM) practices; also, the contrast between 0.4 and 0.8 m subirrigation vs. free drainage is statistically significant at the

Table 4.8. General Linear Models Procedure
Repeated Measures Analysis of Variance For **Metribuzin Residues** in Lysimeters, Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WTM	**2**	**141.7433**	**70.8716**	**51.50**	**0.0048**
Error	4	4.1283	1.3761		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
40-SUB VS. 80-SUB	1	10.6408	10.6408	7.73	0.0689
40-SUB VS. FREE-DRAI	**1**	**133.3333**	**133.3333**	**96.89**	**0.0022**
80-SUB VS. FREE-DRAI	**1**	**68.6408**	**68.64083**	**49.88**	**0.0058**

Univariate Tests of Hypotheses for Within Subject Effects

Source: **TIME**

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
8	20.32	10.16	6.94	0.0275	0.0467	0.0275

Source: TIME*WTM

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
16	5.92	1.48	1.01	0.4704	0.4670	0.4704

95% level. The contrast between 0.4 and 0.8 m subirrigation treatment was not statistically significant, because the 0.8 m subirrigation treatment was as relatively effective as the 0.4 m subirrigation, in the reduction of metribuzin residues.

A favourable soil moisture content is required to stimulate and contribute to soil biological activities. Microbial population use soil moisture as a medium for cell metabolism, hydrolysis and hydroxylation reactions of biological compounds (Tate, 1995). Considering that all lysimeters were identical (same soil type and same climatological conditions), and the only significant difference between them was higher moisture content in the crop root zone of 0.4 m subirrigation (Table 4.7), the significant reduction in the metribuzin residues in the 0.4 m subirrigation treatment (Table 4.8) can be directly related to higher moisture levels. The higher soil moisture levels in the 0.4 m subirrigation appears to have could helped the soil biological activity, and thus increased significantly the biodegradation of metribuzin residues.

4.4. Conclusions

The fate and transport of metribuzin was investigated with depth and time, under three different water table management scenarios, using two subirrigation and one free drainage treatment. Metribuzin was found to be quite mobile as it leached down the soil profile in all treatments. Therefore, it may be concluded that there is a risk of groundwater pollution from the use of this herbicide on potato farms in Quebec.

The mass balance study showed a significant difference in the dissipation of metribuzin levels in the 0.4 m subirrigation treatment (shallow subirrigation treatment) vs. the others. The contrast between the total residue levels of metribuzin in the 0.4 and 0.8 m subirrigation vs. free drainage was statistically significant at the 95% level. These results support the idea that lower metribuzin pollution may be expected from the soils of subirrigated farms, leaving less chemicals for transportation to the water bodies. These findings also provide adequate support for the recommendation of subirrigation systems as BMP for potato farms in Quebec. Subirrigation in potato farms can reduce the non-point source pollution from metribuzin.

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PREFACE TO CHAPTER 5

In the previous two chapters, the fate and transport of atrazine and metribuzin under different water table management systems were presented and discussed. This chapter presents the experimental procedures and the results obtained from a three year lysimeter experiment on the fate and transport of metolachlor under different water table management systems.

This chapter is composed of four sections. Section one reviews some of the physical and chemical properties of metolachlor as one of the important herbicides in corn and soybean farms of Quebec. This section also reviews the previous studies regarding the impact of water table management on the fate and transport of metolachlor. The explanation of methodology of the experiment follows in section two. Although experimental methodology of study of metolachlor is not very much different from that of atrazine and metribuzin, still in order to keep the flow of material it has been presented and discussed in section two. The experimental results for each of the three sampling seasons have been presented and discussed separately in section three. At the end, section four presents the conclusions for the study of the fate of metolachlor under different water table management systems. All raw data pertaining to lysimeter studies have been included in Appendix A. A summarised version of this work has been submitted for publication in the Journal of Irrigation and Drainage Engineering, American Society for Civil Engineers.

CHAPTER 5

A LYSIMETER STUDY OF FATE OF METOLACHLOR IN SANDY SOIL UNDER SUBSURFACE IRRIGATION SYSTEMS

Abstract

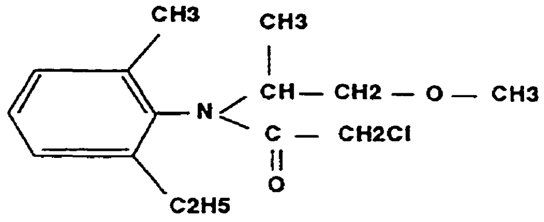
A three-year field lysimeter study was undertaken to investigate the role of subirrigation systems in reducing the risk of water pollution from metolachlor (2-chloro-N-(2-ethyl-6-methlphenyl)-N-(2-methoxy-1-methylethyl)acetamide), a very commonly used herbicide in corn and soybean fields in Canada. Nine PVC lysimeters, 1m tall x 0.45m diameter, were packed with a sandy soil. Three water table management treatments, i.e. two subirrigation treatments with constant water table depths of 0.4 and 0.8 m, respectively, and a free drainage treatment in a completely randomized design with three replicates were used. Corn (*Zea mays* L.) was grown on each lysimeter and metolachlor was applied each year at the locally recommended rate of 2.75 kg/ha of active ingredient, in the beginning of summer season. Both soil and soil solution samples were collected at different time intervals after each natural or simulated rainfall event. Metolachlor was extracted from soil solution samples and was analyzed using Gas Chromatography.

From the final results of the three years of experiment (1993-1995), it can be concluded that metolachlor was quite mobile, as it leached to the 0.85 m depth below the soil surface quite early in the growing season. Metolachlor concentrations decreased with depth as well as with time. Although the shallower water table in the 0.4 m-subirrigation treatment showed less residues in the soil solution than that of other treatments, a mass balance study showed that there was no statistically significant effect of water table management on the reduction of metolachlor residues in this sandy soil.

5.1. Introduction

Pesticides are frequently used to increase agricultural crop production. Although they have received more attention than other toxic substances, toxicological and environmental data about them are still not readily available (Pearse et al., 1985). Detection of pesticides in Canadian and American groundwater aquifers have led scientists to study the fate of pesticides and define the processes by which the surface and groundwater body contamination occurs.

Metolachlor (2-chloro-N-(2-ethyl-6-methlphenyl)-N-(2-methoxy-1-methylethyl)acetamide), is a highly polar selective herbicide with an aromatic benzene ring in its chemical structure, which is used to control weeds in corn (*Zea mays* L.), and soybean [*Glycine Max* (L.) Merr.] fields. Figure 5.1. shows metolachlor chemical structure. Its solubility in water is about 530 mg/L at 20°C. Metolachlor is a relatively non-persistent herbicide. Radio-labelled studies have shown a rapid decline of the parent compound. Biological evidence indicates that metolachlor does not persist from one season to the next (Colby et al., 1989). The half-life dissipation rate for metolachlor has been determined from both laboratory and field studies to be 30 to 50 days in northern areas, and from 15 to 25 days in southern areas of North America. In a number of cases, metolachlor residues have been detected in Canadian and American ground waters. For instance, Cohen et al. (1986) reported that metolachlor levels in Pennsylvania ground water ranged from 0.1 to 0.5 µg/L. Metolachlor concentrations in subsurface drain outflow in southern Louisiana has been reported to be varying from 0.4 to 29.3 µg/L (Southwick et al., 1988). Patni et al. (1987) reported the metolachlor maximum concentration of 12 µg/L in the drainage water in a field study near Ottawa. It must be noted that based on USEPA, the maximum recommended level of this herbicide in drinking water is about 10 µg/L. Studies conducted by Masse et al. (1994) on a St-Amble sandy soil in Montreal, Quebec, found metolachlor concentration in shallow ground waters to be 5 µg/L.



METOLACHLOR

Figure 5.1. Metolachlor chemical structure

Metolachlor is reported to be a mobile herbicide with high leaching capability (Arjoon et al., 1994; Braverman et al., 1986). From laboratory and greenhouse studies, Obrigawitch et al. (1981) reported low adsorption and high mobility of metolachlor in soils containing less than 1% organic matter. However, Smith and Parrish (1993) found no significant leaching below 0.3 m in sandy loam and loamy sand field plots. A slower transformation (degradation) rate at lower soil depth was reported by Bouchard et al. (1982) and Smith and Parrish (1993).

Different management practices such as integrated pest management, conservation tillage systems, crop and chemical rotation, buffer strips, vegetated streams, precision farming have been exploited by researchers to reduce pollution from pesticides. Water table management is being also used in some locations to reduce non-point source pollution from fertilizer residues. However, the impact of water table management systems on pesticide pollution has not been clearly established thus far (Kanwar, 1996).

Most agricultural pesticides, including metolachlor, have a field half life of about 4 to 8 weeks. Therefore, if drainage water containing dissolved pesticides is kept within soil for this period by subirrigation systems, pesticides would have more time for microbial and chemical degradation, and their toxicity to the surface and groundwater resources would decrease at the time of release in late September.

Although other investigators have conducted water table management experiments in Quebec and elsewhere, (Masse et al., 1994; Arjoon et al., 1994; Aubin et al., 1993; Kalita et al., 1992), this research is different from the others since it studies a water table management in the exposed natural climate in combination with advantages of the controlled environment of a large lysimeter setup. More specifically, the objectives of this research are:

a. To determine the fate and transport of a most commonly-used herbicides, metolachlor in corn and soybean farms under different water table management practices in a typical sandy soil in southern Quebec.

b. To analyze the results and investigate the possible use of subirrigation systems as BMPs for corn and soybean farms in southern Quebec.

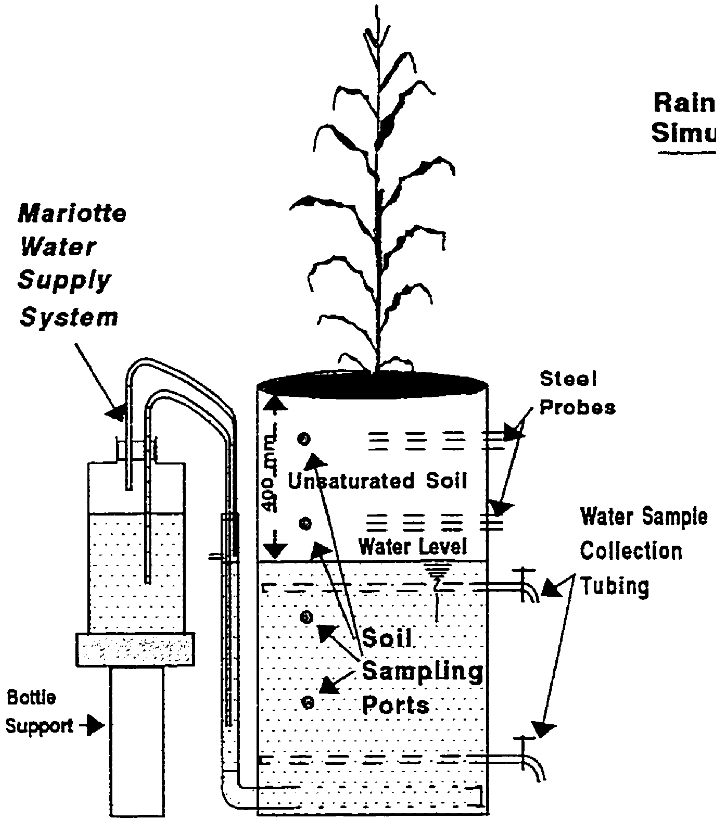
In order to fulfil the objectives of this study, a three-year investigation was metolachlor. The following sections will present and discuss the experimental procedures and the results obtained from three year investigation of fate and transport of metolachlor under different water table management.

5.2. Methodology

The experimental work was conducted in an exposed area beside the Agricultural Engineering Workshop at the Macdonald Campus of McGill University. It started in June 1993 with the construction of nine field lysimeter units. The lysimeters accommodated three different water table managements. Two subirrigation treatments were selected, one with a constant water level at 0.4 m; and the other with water table at 0.8 m below the soil surface. A free drainage treatment was also used to simulate a subsurface drained field. The statistical scheme consisted of a completely randomized design, in which each treatment was randomly allocated to the lysimeters, and each treatment was also supported by three replicates (Figure 5.2). Corn (*Zea mays* L.) was grown on all nine lysimeters in the beginning of each season to simulate plant uptake. In the first year (1993), the experiment began in mid August and ended in mid October. In the second and third year, the experiment started in late June and finished in late September.

5.2.1. Experimental Setup

The experimental setup consisted of nine PVC lysimeters, 1.0 m long x 0.45 m diameter. The PVC lysimeters were welded from the bottom, using 0.6 m x 0.6 m PVC sheets. A 50 mm diameter perforated PVC pipe was installed at the bottom of each lysimeter to allow for either drainage or subirrigation from the bottom (Figure 5.3). Lysimeters were packed with a uniform sandy soil from a



0.4 m Subirrigation Treatment

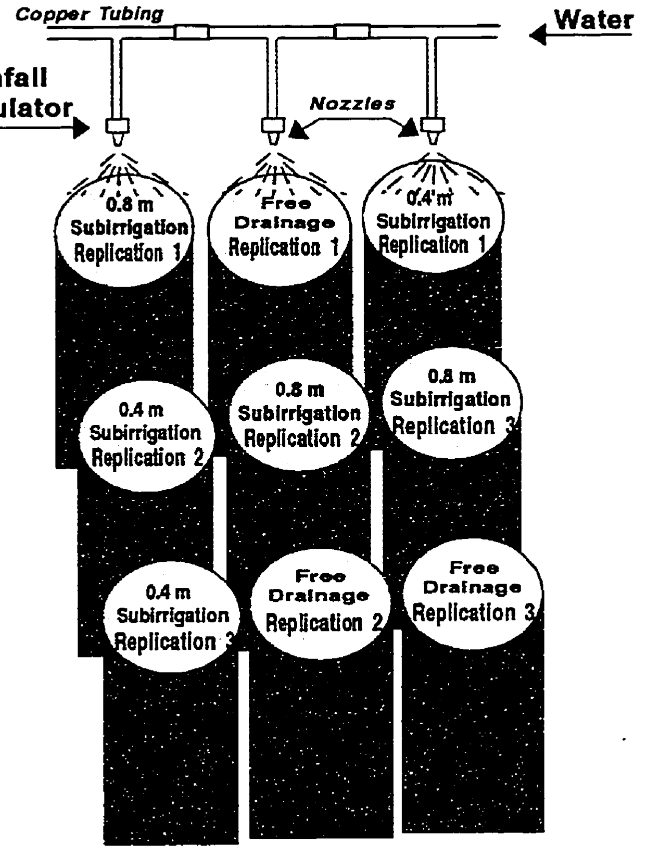
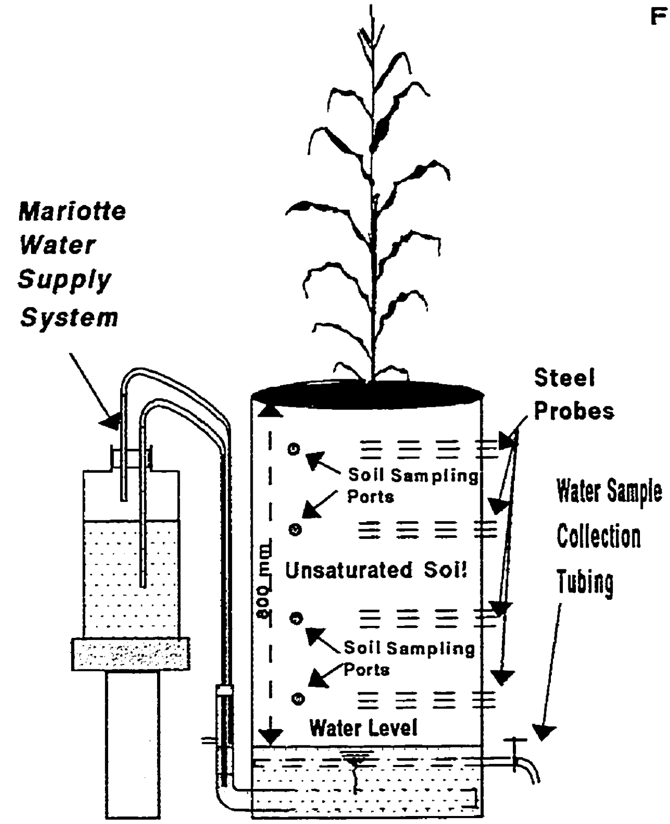
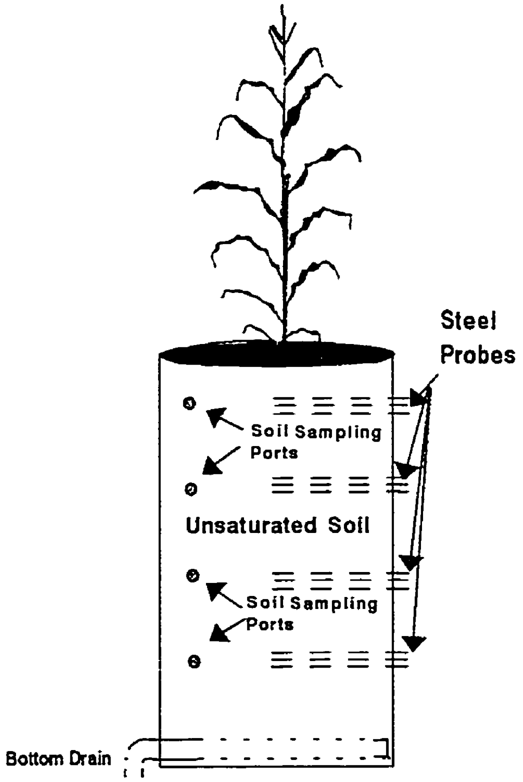


Figure 5.2. Layout of lysimeters in the field



0.8 m Subirrigation Treatment



Free Drainage Treatment

Figure 5.3. Lysimeter setup

farm where no pesticides were applied in the previous two years. The soil in the lysimeters was compacted by hand to a field bulk density of 1350 kg/m^3. A 9 mm diameter perforated acrylic plastic tubing was installed in the subirrigation lysimeters at depths of 0.45 and 0.85 m, to collect soil solution samples (Figure 5.3). All lysimeters were equipped with 0.22 m long x 3 mm diameter, stainless steel probes, to measure soil moisture content using a TDR instrument (Topp and Davis, 1985). The probes were inserted horizontally in the lysimeters at 0.15, 0.3, 0.45, and 0.6 m depths. All lysimeters were kept above ground in an exposed area in order to locate any possible water leakages that might affect the experimental results.

In the subirrigation lysimeters, a 50 mm diameter acrylic plastic riser was connected to the bottom drain to supply water from individual water tanks (Figure 5.3). A syphoning supply system (Mariotte system) was used in the subirrigated lysimeters, to maintain the water levels at 0.4 and 0.8 m below the soil surface, whereas the free drainage lysimeters were allowed to drain freely from the bottom.

In 1994 and 1995 a rainfall simulator was constructed and used to perform metolachlor leaching studies. The rainfall simulator consisted of nine brass spray nozzles (product of Spraying Systems Co.), directed 0.5 m higher than top of lysimeters. The nozzles were connected to a copper tubing system, equipped with a pressure gage and mounted on a steel frame (Figure 5.2). The pressure gage was used to regulate the tap water pressure required by the spray nozzles. The nozzles inlet size was 12.7 mm with the simulation capacity up to 13 L/min rainfall under 140 kPa.

5.2.2. Soil Characteristics

The soil was obtained from a field at Macdonald Campus of McGill University, where no herbicides had been applied in the last two years. This soil belongs to St. Amable complex, which has deep sandy deposits of medium to fine texture in its profile (Lajoie, 1960). In order to create a uniform sandy soil profile in the lysimeters, the first 0.1m of the topsoil was removed and the subsoil was taken to fill the lysimeters. To get the same bulk density as the original soil (1350 kg/m^3), an equivalent weight of soil was used to make each 0.1m layer in the lysimeters.

The disturbed and undisturbed soil samples were taken from the field to determine the particle size distribution, organic matter content, pH, CEC, and bulk density. The soil saturated hydraulic conductivity was determined on each individual lysimeter using the constant head approach. The average soil temperature at root zone was about 10 °C less than ambient temperature. Undisturbed soil samples were taken from the lysimeters to determine soil average (triplicates) moisture retention characteristics (Figures 5.4 to 5.6). Table 5.1 shows results of some of the tests performed on the soil samples.

Table 5.1. The Physical Characteristics of the Soil

Soil Type	Sand (%)	Silt (%)	Bulk Density (kg/m^3)	Organic Matter (%)	pH	CEC (cmol/kg)	Hydraulic Conductivity* (cm/h)
Sandy Soil	92.2	4.3	1350	3.5	5.5	4.9	6.0 (S.D.** =1.8)

* Average value measured on the lysimeters.

** S.D. Stands for standard deviation

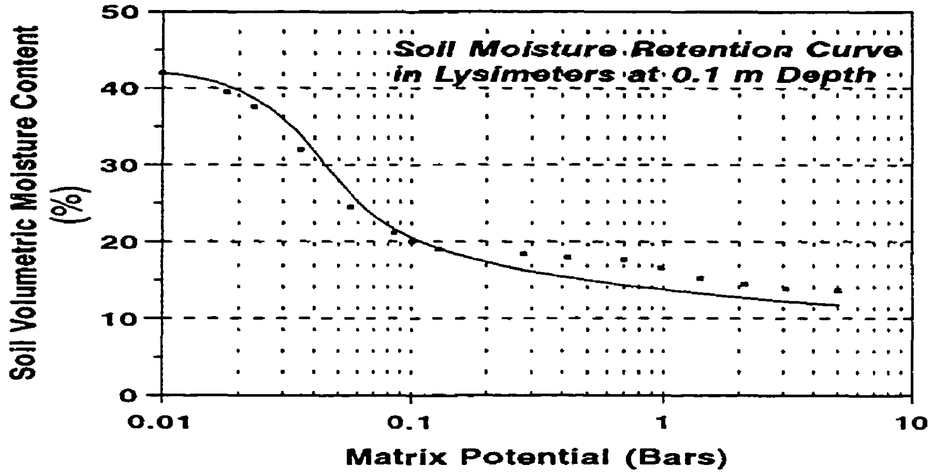


Figure 5.4. Average soil moisture characteristics at 0.1 m depth

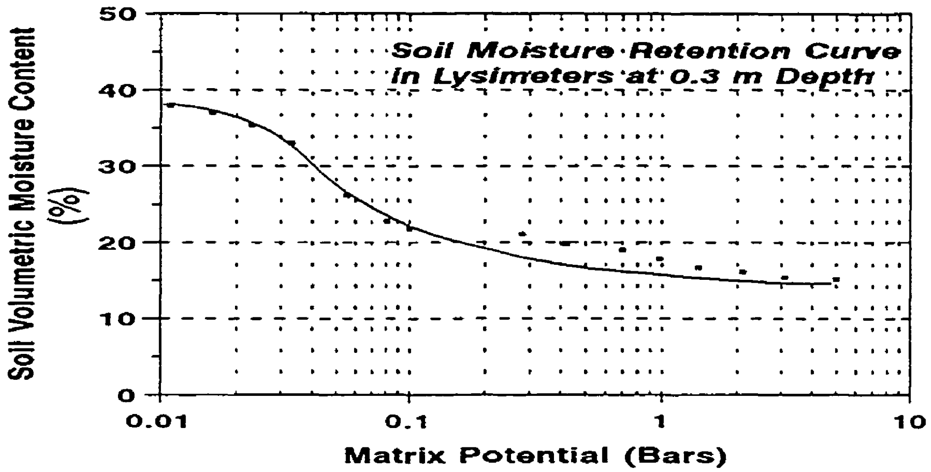


Figure 5.5. Average soil moisture characteristics at 0.3 m depth

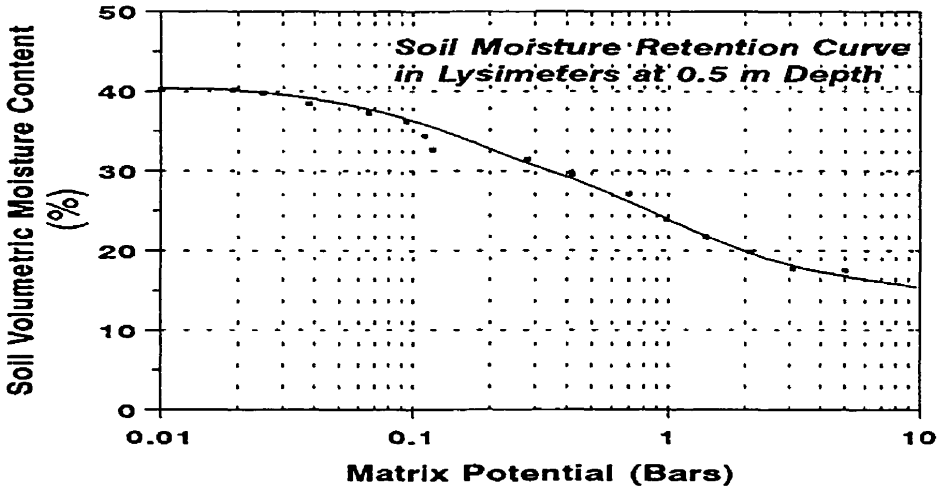


Figure 5.6. Average soil moisture characteristics at 0.5 m depth

5.2.3. Climatological Data

Rainfall, evaporation and air temperature were measured at the Ste. Anne de Bellevue Weather Station, located less than a kilometre from the experimental site. During the first month of experimentation in August 1993, the average monthly temperature was about 20°C and total rainfall was 42.9 mm (Figure 5.7 presents the daily rainfall for the period of study in 1993). In September, the average monthly temperature was 14°C and total rainfall was 119.2 mm. Data from the nearest Weather Station (Dorval) indicated that August 1993 had the highest monthly temperature and the lowest rainfall in ten years. Six rainfalls with an intensity above 10 mm/day and twenty rainfalls with an intensity of less than 10 mm/day were recorded between the day of herbicide application and the end of the 1993 sampling period. The first rainfall with an intensity of 8.9 mm/day occurred one day after herbicide application. The highest rainfall during this period was 30.4 mm/day and it occurred 23 days after application. There was no surface runoff in the lysimeters.

In the 1994 sampling season, the highest average monthly temperature and evaporation were observed in July. The highest average temperature in this month was 21.3°C, and the total rainfall was 61.3 mm. Total monthly rainfall was 99.9 mm in August, and 105.5 mm in September. Figure 5.10 shows the daily rainfall for the summer period in 1994. In this summer, there were eight rainfalls with an intensity of more than 10 mm/day. The highest daily rainfall occurred on June 29, with 54.9 mm, just six days after the herbicide application. In 1994 because a rainfall simulator was used, seven rainfalls, each with an intensity of 26 mm/h, were simulated at different intervals. The duration of rainfalls varied from 1.0 to 1.5 hours. In this sampling season each lysimeter received 260 mm of simulated rainfall in 8 events, ranging from 25 to 40 mm. The simulated rainfall intensity was about 25 mm/h. Comparing the monthly average temperature with the past ten years data for the corresponding months, the summer of 1994 may rank as a mild summer with regard to temperature and rainfall.

In the summer of 1995, the highest average monthly temperature was measured in July. The highest reported evaporation in this summer occurred in June (7.2 mm). Total monthly rainfall in June, July, August and September was measured as 64.5, 138.2, 118.2, 69.5 mm, respectively. Each lysimeter also received 300 mm of simulated rainfall in five events, 60 mm each. The simulated rainfall intensity was about 30 mm/h. Comparing the monthly average temperature with the past ten years data, for the corresponding months, the summer of year 1995 may rank as a relatively wet summer. Figure 5.14 shows the daily natural and simulated rainfall for the summer period in 1995.

5.2.4. Metolachlor Application

Each summer all lysimeters received postemergence metolachlor application in liquid form. Because there were some construction delays in the first year, the pesticide was accordingly applied late on August 11, 1993. In the second year (1994) and third year (1995), the pesticide applications were made on June 23, and June 24, respectively. The rate of application was 2.75 kg/ha of active ingredient.

5.2.5. Sampling Methods

On each sampling day, about one-litre soil solution sample (water) was taken from all lysimeters. In 1993, the soil solution samples were taken on 0, 7, 14, 22, 29, 37, 47, 64, and 84 days after application (DAA), whereas in 1994, the samples were taken on -23, 3, 7, 14, 23, 30, 38, 49, 68, 90 days after the application. The order of soil and soil solution sample collection in the summer of 1995 was as follows: -20, 6, 16, 28, 42, 70, 90 days after application. In order to take representative samples of soil solution, sampling tubes were emptied first to remove any stagnant water. About 10 ml of dichloromethane was added to all soil solution samples to stop microbial activity while stored in the refrigerator for GC analysis. The sampling for the free drainage lysimeter was quite irregular in 1993, because they were completely rain-fed and most rainfall events caused no outflow. To overcome this difficulty and obtain more regular samples, a rainfall simulator device was constructed and used in 1994 and 1995, which simulated rainfall about 24 hours prior to each sampling period (Figure 5.2).

Four soil sampling ports were made in each lysimeter at 0.1, 0.3, 0.5 and 0.7 m below the soil surface to take the soil samples. Each time, 5 to 10 g of soil sample was collected from an individual port, and samples were kept frozen until one hour prior their extraction and analysis.

5.3.6. Extraction of Metolachlor Residues

The soil solution samples were mixed with 100 ml of dichloromethane (methylene chloride) in a separatory funnel. The mixture was hand shaken for a few minutes and the organic phase was collected. The process was repeated twice for each sample. The extracted organic phase was evaporated to separate dichloromethane from the herbicides. The residues were then dissolved in about 10 ml of hexane and stored in the refrigerator, prior to gas chromatography analysis.

Between 5 to 10 g of soil sample was transferred to a flat bottom flask. A subsample of about 1 g was placed in the oven at 105° C for 24 hours for soil moisture determination. Each soil sample received about 100 ml of methanol and was shaken for at least 1 hour. The mixture was transferred to a vacuum flask (Buchnel flask) and filtered under partial vacuum. The collected organic phase was evaporated in the rotary evaporator for about 15 minutes and rinsed with about 10 ml of hexane. The collected organic phase was then stored in a 15 ml glass vial in the refrigerator prior to GC analysis.

5.2.7. Gas Chromatography

The gas chromatography was done using a Varian, Model 3400 gas chromatograph, equipped with a column and NPD (TSD) detector. The column used was a 0.53 mm i.d., fused silica Megabore DB-5, 1.5 µm film thickness, made by J&W Scientific. The injector temperature was set at 250°C and the detector was kept at 300°C. The column temperature was maintained at 180°C for 9 minutes, and then the temperature was increased to 200°C at a rate of 4° C/min; at 200°C, it was held for 1 minute, and then raised to 280° C at a rate of 20° C/min. The column was kept at this temperature for 9 minutes. The nitrogen and helium make up flow rate was 30 mL/min, while the helium carrier gas flow rate was kept at 7.5 mL/min. The hydrogen flow rate was 4.5 mL/min, and air flow was set to 175 mL/min. The detection limits for soil solution and soil samples were found to be 0.12 µg/L and 10 µg/kg, respectively. The recovery rate was obtained by fortifying 5 g of untreated oven dry soil with 0.05, 0.5 and 5 µg/g of herbicides. The samples were left to equilibrate for 24h, after which time they were extracted and analyzed by GC. The recovery rate was estimated to be 97% ± 2%.

5.3.8. Statistical Analysis

Statistical analysis was performed using the SAS program. Since the soil and soil solution samples had to be taken from the same lysimeter units at predetermined time intervals, the independency of observation and their homogeneity of sampling variance could not be maintained. The classical statistical analysis of the variance might not produce reliable results in this situation. Thus, the Repeated Measures Analysis of Variance was employed instead. The difference between treatments (WTM) and their contrasts were diagnosed using the classical F test; but the effect of time on the treatments were tested by using the adjusted F test, known as Greenhouse-Geisser (G-G), and Huynh-Feldt (H-F) tests (Dutilleul and Legendre, 1993). The alternative to the null hypothesis is considered statistically significant whenever the probabilities are less than 0.05 ($Pr<0.05$).

5.3. Results and Discussions

In 1993 and 1994 sampling season, only soil solution samples were collected from the lysimeters, whereas in 1995 soil solution and soil samples were collected and analyzed to perform a mass balance for metolachlor residues. The results obtained for each sampling season are presented and discussed separately in the following sections:

5.3.1. Metolachlor Residues in Soil Solution in 1993

Figure 5.7 shows the metolachlor distribution with time (average concentration of three replicates) at depths 0.45 and 0.85 m in the subirrigation treatment, with water table level (WTL) 0.4 m below the soil surface. The error bars, represent the average values ± one standard deviation. The highest measured average concentration at 0.45 m depth in the 0.4 m-subirrigation was 13 µg/L, which is higher than USEPA recommended limit of 10 µg/L. Metolachlor had also leached down to the 0.85 m depth, and the highest average concentration

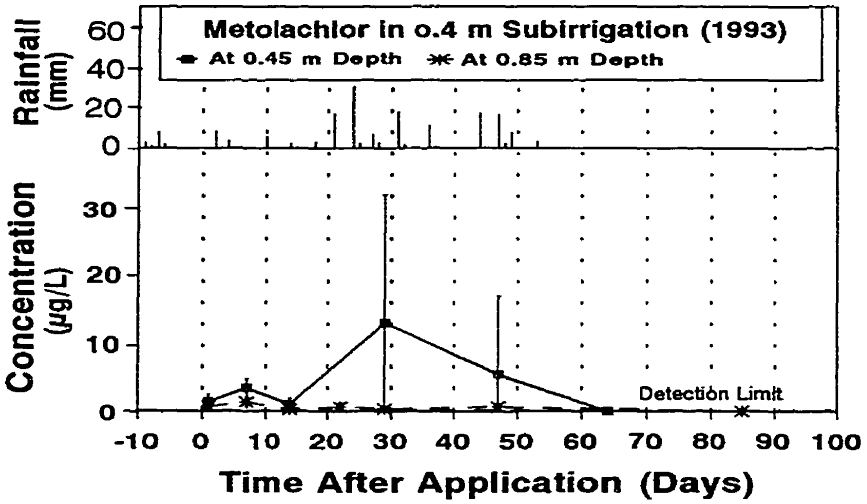


Figure 5.7. Metolachlor in soil solution in 0.4m subirrigation treatment (1993)

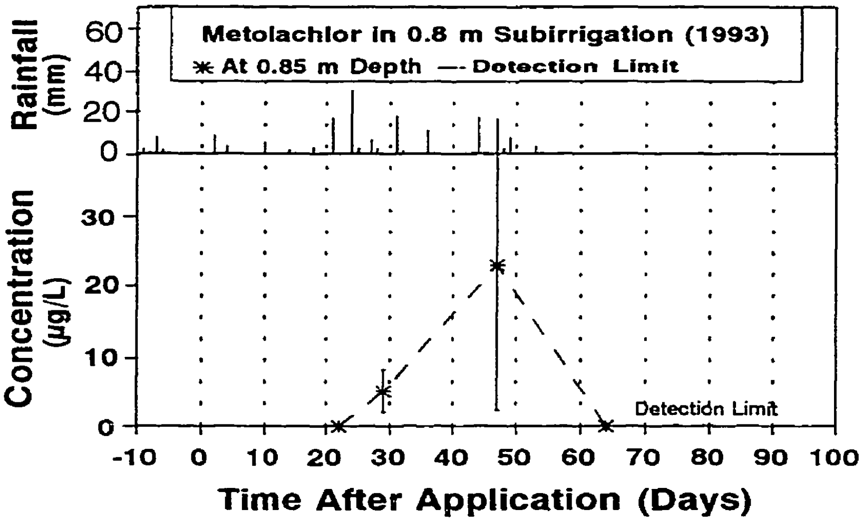


Figure 5.8. Metolachlor in soil solution in 0.8m subirrigation treatment (1993)

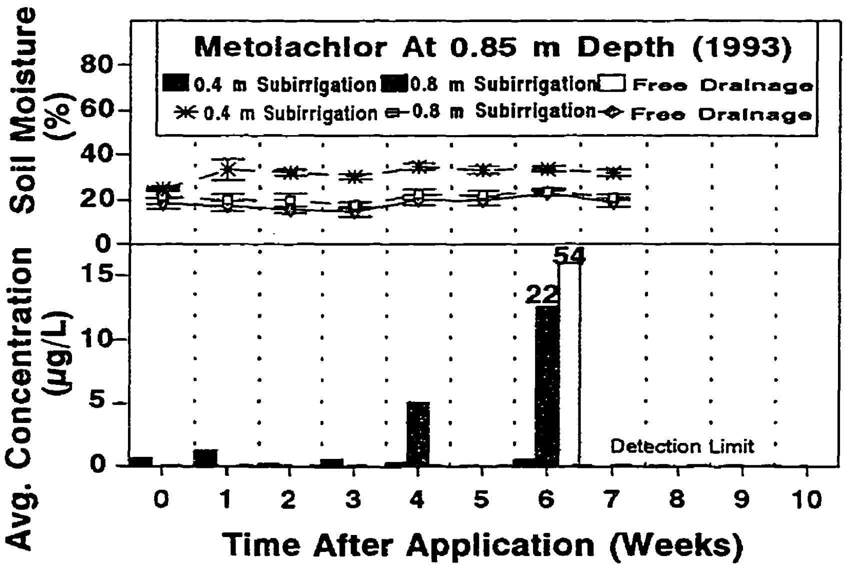


Figure 5.9. Comparison of metolachlor residues in soil solution of all treatments (1993)

almost seven weeks after the herbicide application.

Leaching of metolachlor in subirrigation treatments (Figures 5.7 and 5.8) was due to 5 rainfall events in a period of 3 to 7 weeks after application. Since almost no metolachlor was detected in the solution phase two months after application, neither at 0.45 nor at 0.85 m depths, it may imply that metolachlor was dissipating quite fast in these lysimeters. Not many soil solution samples could be collected from the free drainage treatments in this season, since they were rainfed and in most cases the natural rainfall was not enough to produce any discharge.

Figure 5.9 compares this information as bar graphs. Although, both subirrigation treatments were subjected to the same amount of natural rainfall, it is clear that the metolachlor levels at 0.85 m depth are considerably lower in 0.4 m WTL subirrigation lysimeters (shallower water table). Again, the only difference between the two treatments is the higher moisture content in the vadose zone that was made possible by the 0.4 m WTL subirrigation treatment (Figure 5.9). Since metolachlor has a lower adsorption capability (Obrigawitch et al., 1981), it seems that the higher moisture content would have caused higher microbial decay in the crop root zone, and this, in turn, would have produced lower metolachlor levels at the 0.85 m depth in the 0.4 m WTL subirrigation treatments.

5.3.2. Metolachlor Residues in Soil Solution in 1994

Metolachlor background in the soil solution was close to the detection limit in all treatments. After metolachlor application it leached into the soil profile after two weeks and the highest average detected concentration (average of three replicates) was about 1.5 µg/L at 0.45 m and 0.75 µg/L at 0.85 m depth (Figure

5.10) in 0.4 m-subirrigation treatment. This concentration reduced to a non-detectable limit (0.12 µg/L), after 11 days, indicating rapid decay of metolachlor at that depth. Even with the 39 mm simulated rainfall on day 38, no metolachlor was detected in soil solution at the next sampling period. This was possibly due to a high degradation rate during that period. It seems that high temperature in early August could lead to such rapid degradation of this free metolachlor molecules in the lysimeters. However, metolachlor leached again to 0.85 m depth due to simulated rainfall on day 49.

In 0.8 m-subirrigation treatments, the first leaching was observed only 3 days after the application, where metolachlor concentration was about 0.21 µg/L (Figure 5.11), and increased to 0.3 µg/L after one week. This rapid leaching of metolachlor to 0.85 m depth could have been caused by the macropore flow in the lysimeters.

Metolachlor was also detected at 0.85 m depth in the free drainage treatment ten days after the application, although the concentration was not as high as expected (Figure 5.12). Following the 32 and 54.9 mm rainfall occurrences, six and seven days after the application, metolachlor leached down to 0.85 m depth. The highest average metolachlor concentration was about 0.75 µg/L, 68 days after the application. It can be seen from Figure 5.12 that even after four rainfall simulations, between the first week and the sixth week, not much metolachlor could be detected in the soil solution. This may be due to the fact that in the free drainage treatment, unlike the subirrigated lysimeters, no constant water level is maintained, and limited mass transfer between mobile water and solid phase has occurred. This limitation also applies to the fraction of metolachlor that has already diffused in immobile soil water in the dead ended soil pores (Rambow and Lennartz, 1993; van Genuchten, 1974).

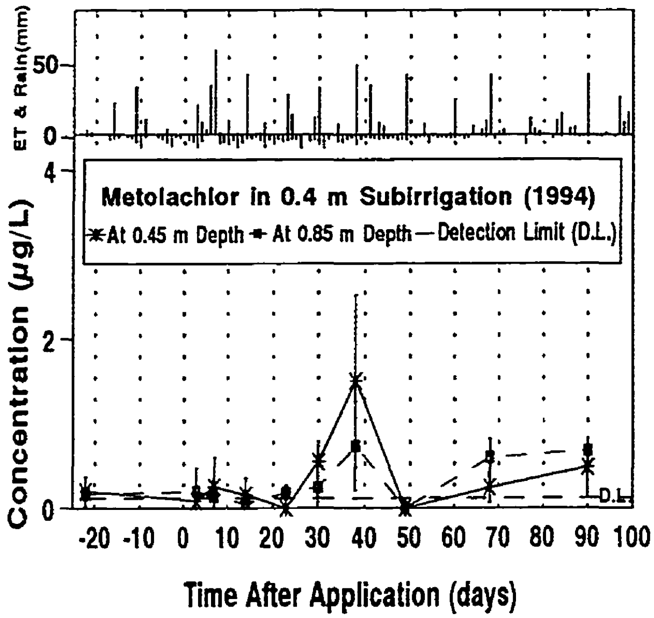


Figure 5.10. Metolachlor in soil solution in 0.4m subirrigation treatment (1994)

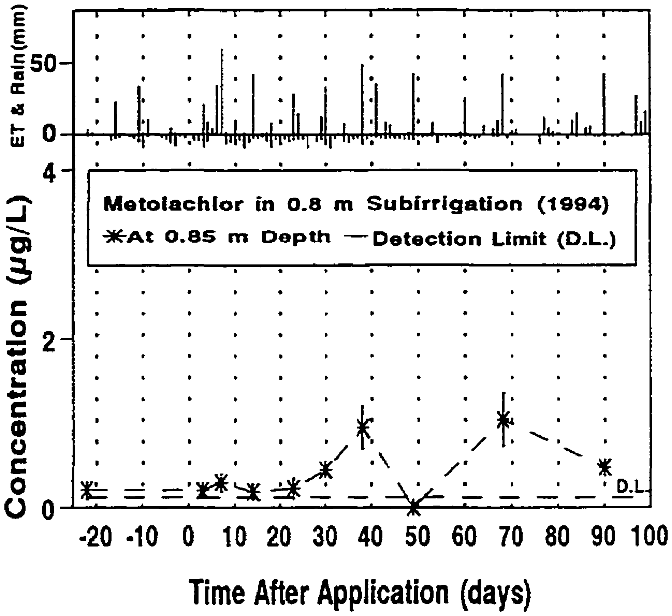


Figure 5.11. Metolachlor in soil solution in 0.8m subirrigation treatment (1994)

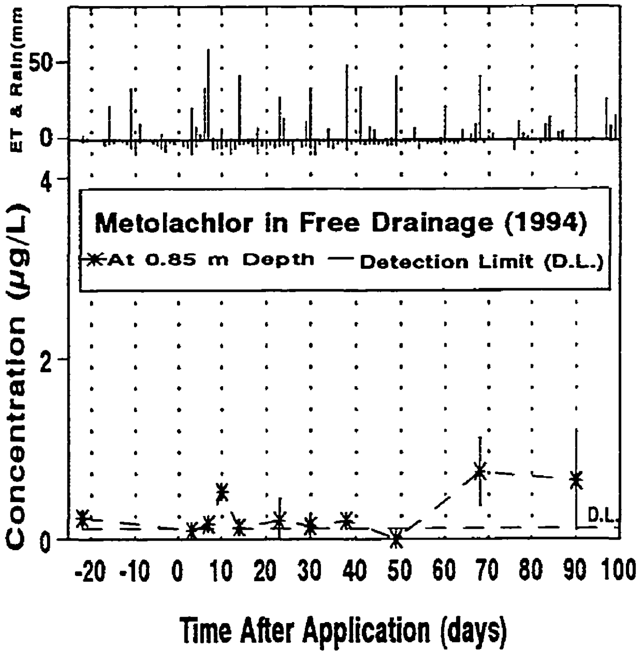


Figure 5.12. Metolachlor in soil solution in free drainage treatment (1994)

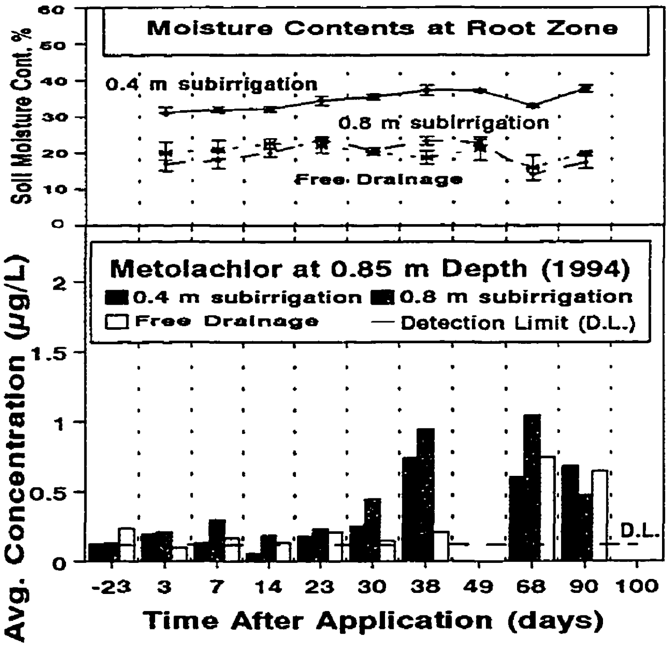


Figure 5.13. Comparison ofmetolachlor residues in the soil solution of all treatments (1994)

It is proposed that under the simulated rainfall events the leaching water had limited time to equilibrate with metolachlor adsorbed to soil particles and/or diffuse into immobile liquid phase trapped in the dead ended pores (Ghadiri and Rose, 1992). In other words, while in subirrigation treatments the time dependent non-equilibrium adsorption/desorption prevails, the breakthrough curves in free drainage treatment may represent the instantaneous equilibrium sorption. Thus, the detected concentration in free drainage treatment is in fact a small fraction of potentially mobile metolachlor available in the soil. The higher fraction of metolachlor still remains in the soil, which could be released gradually in subsequent rainfall events and thus cause longer tailing effects in the metolachlor breakthrough curve. This was examined by a mass balance study in 1995 sampling season.

The comparison of three metolachlor treatments (Figure 5.13) shows substantially less concentration for the 0.4 m-subirrigation treatment (shallower water table) with respect to the 0.8 m-subirrigation; but lower concentration with respect to free drainage in most of the cases. Figure 5.13 also demonstrates the higher moisture contents observed in subirrigation treatment at the root zone depth.

5.3.3. Metolachlor Residues in Soil Solution in 1995

Metolachlor background in the soil solution of all treatments were almost negligible. Figure 5.14 shows the average metolachlor concentration in the soil solution samples in the 0.4 m subirrigation treatment as a function of time and the corresponding error bars (average values of three replicates ± one standard deviation). The metolachlor level at the 0.45 m depth has increased to about 6.7 µg/L, following the second rainfall simulation 16 days after the metolachlor application. The metolachlor level hereafter remained less than 0.7 µg/L, regardless of three natural rainfall of more than 20 mm, and three simulated rainfall of about 60 mm, in all soil solution samples collected after day 16. This implies that the metolachlor leached to this depth was either degraded or bound to the soil particles and was not available in the soil solution. Metolachlor did leach down to 0.85 m depth and its maximum level at the 0.85 m depth was 3.8 µg/L.

In the 0.8 m subirrigation treatment, the highest average concentration was 8.8 µg/L, twenty-eight days after application (Figure 5.15). The concentration became non-detectable after almost four weeks, indicating that the surface applied metolachlor had leached to the 0.85 m depth and then slowly dissipated.

The highest average metolachlor concentration in the free drainage treatment was about 9 µg/L (Figure 5.16), indicating that the surface applied metolachlor had continuously leached and accumulated at the 0.85 m depth while its degradation was also occurring. In some cases, the 0.4 m-subirrigation treatment (shallower water table) showed less concentration. This may lead to the same arguments made for the results in 1994 that natural or simulated rainfall pulses create a relatively high pore water velocity therefore, the leaching water will only have a limited time span to equilibrate with the metolachlor, which has either accumulated on the solid phase (soil particles and organic matters), and/or has diffused into the immobile liquid phase, already present in the dead ended pores. This idea maintains that in free drainage treatment the mobile front does not have sufficient contact time for equilibrium, and the breakthrough curve in this case only represents the instantaneous equilibrium sorption. Hence, the measured concentration levels in the free drainage lysimeters is, in fact, a small fraction of the potentially mobile metolachlor available in the soil.

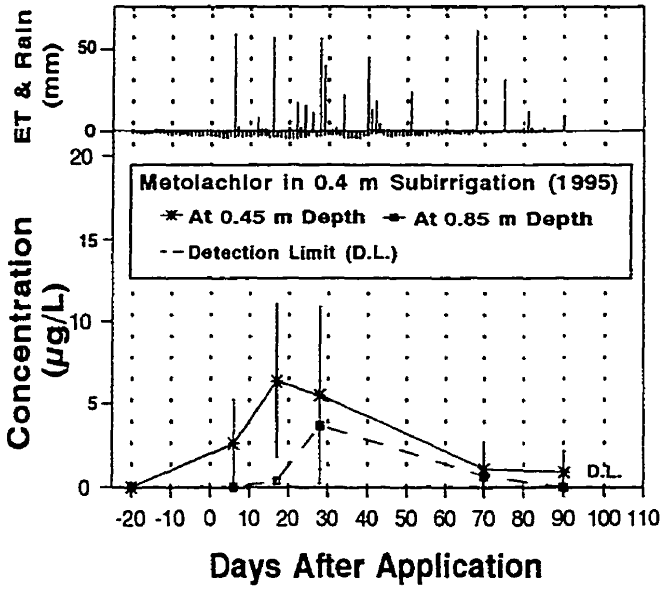


Figure 5.14. Metolachlor in soil solution in 0.4m-subirrigation treatment (1995)

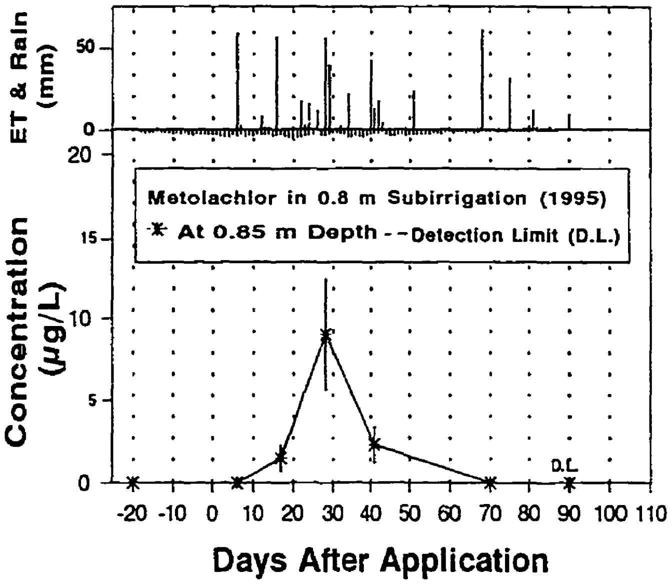


Figure 5.15. Metolachlor in soil solution in 0.8m-subirrigation treatment (1995)

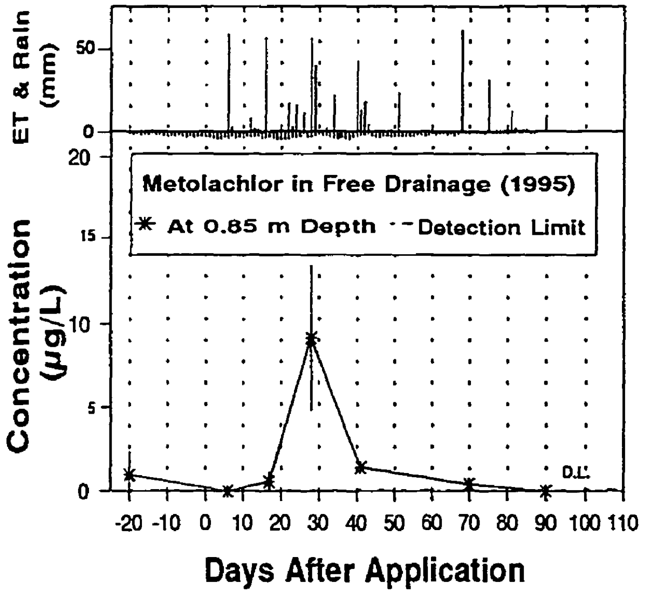


Figure 5.16. Metolachlor in soil solution in free drainage treatment (1995)

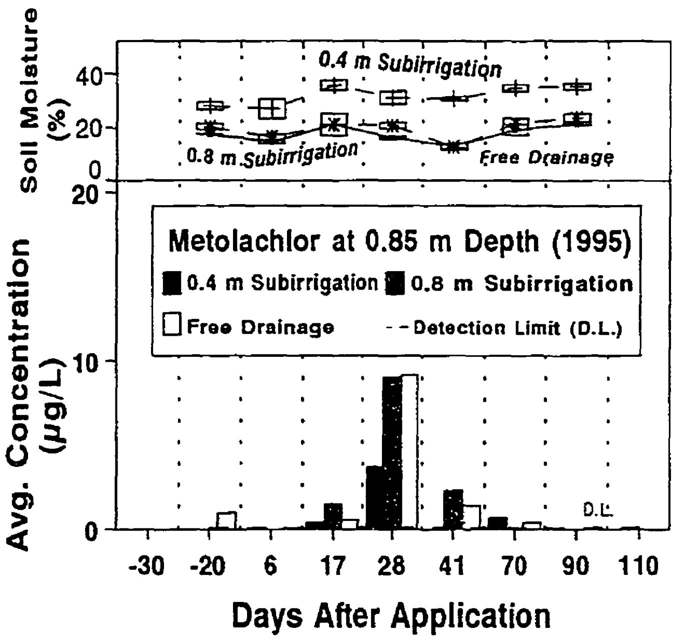


Figure 5.17. Comparison of metolachlor residues in soil solution of all treatments (1995)

The higher fraction of metolachlor still resides in the soil, and is gradually released as the next water front moves. This causes longer tailing effects and shifted peak concentration in the metolachlor breakthrough curves in the soil solution samples (Figures 5.15 and 5.16). Whereas, in shallow subirrigation treatment due to presence of higher moisture content, the time dependent non-equilibrium adsorption/desorption prevails, and usually shows higher concentrations in the soil solution samples taken one day after the leaching study. This proposed idea was verified by taking soil samples and conducting a mass balance study, which is discussed in the next section. Figure 5.17 demonstrates the moisture contents observed at the root zone depth of different treatments as function of time.

5.3.4. Metolachlor Residues in Soil in 1995

Soil samples were collected from each lysimeter at four different depths on 6, 30 and 90 days after the metolachlor application. Tables 5.2 to 5.4 present the average and standard deviation of analyzed samples at various depths. Figure 5.18 shows the same results in graphical form. A study of the variation of metolachlor concentration in the 0.4 m subirrigation on 6, 30 and 90 days after application, can be made by comparing the first-row charts. The metolachlor residues in soil in the 0.8 m subirrigation and free drainage can be studied, using charts in the middle and bottom rows, respectively. The charts in Figure 5.18, could be used in vertical sequence to compare the metolachlor levels among the three water table management treatments on each sampling day.

The first column compares the metolachlor residues in two subirrigation and one free drainage treatment, 6 days after pesticide application. Higher metolachlor concentration was found in the soil profile of the free drainage treatment. A similar trend was observed when comparing the metolachlor levels

Table 5.2. Metolachlor Residues in Soil in 0.4 m-Subirrigation Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (µg/kg)	Standard Deviation(µg/kg)
6	0.10	50.0	10.0
	0.30	65.0	15.0
	0.50	62.3	12.3
	0.70	0.00	0.0
30	0.10	58.9	8.9
	0.30	0.00	0.0
	0.50	0.00	0.0
	0.70	0.00	0.0
90	0.10	0.00	0.0
	0.30	54.5	4.5
	0.50	0.00	0.0
	0.70	0.00	0.0

(1) Zero concentration implies a non-detectable level.

Table 5.3. Metolachlor Residues in Soil in 0.8 m-Subirrigation Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (μg/kg)	Standard Deviation(μg/kg)
6	0.10	96.3	3.7
	0.30	100	20.0
	0.50	0.00	0.0
	0.70	0.00	0.0
30	0.10	69.2	20.5
	0.30	0.00	0.0
	0.50	0.00	0.0
	0.70	0.00	0.0
90	0.10	23.93	10.7
	0.30	91.60	8.4
	0.50	18.30	3.8
	0.70	0.00	0.0

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[1] Zero concentration implies a non-detectable level.

Table 5.4. Metolachlor Residues in Soil in Free Drainage Lysimeters (1995)

Days After Application	Depth (m)	Average Concentration[1] (μg/kg)	Standard Deviation(μg/kg)
6	0.10	95.00	15.0
	0.30	65.00	5.0
	0.50	49.25	4.8
	0.70	0.00	0.0
30	0.10	40.0	10.0
	0.30	40.0	10.0
	0.50	106.5	16.5
	0.70	6.75	3.3
90	0.10	47.15	2.9
	0.30	0.00	0.0
	0.50	15.95	16.0
	0.70	68.65	39.1

[1] Zero concentration implies a non-detectable level.

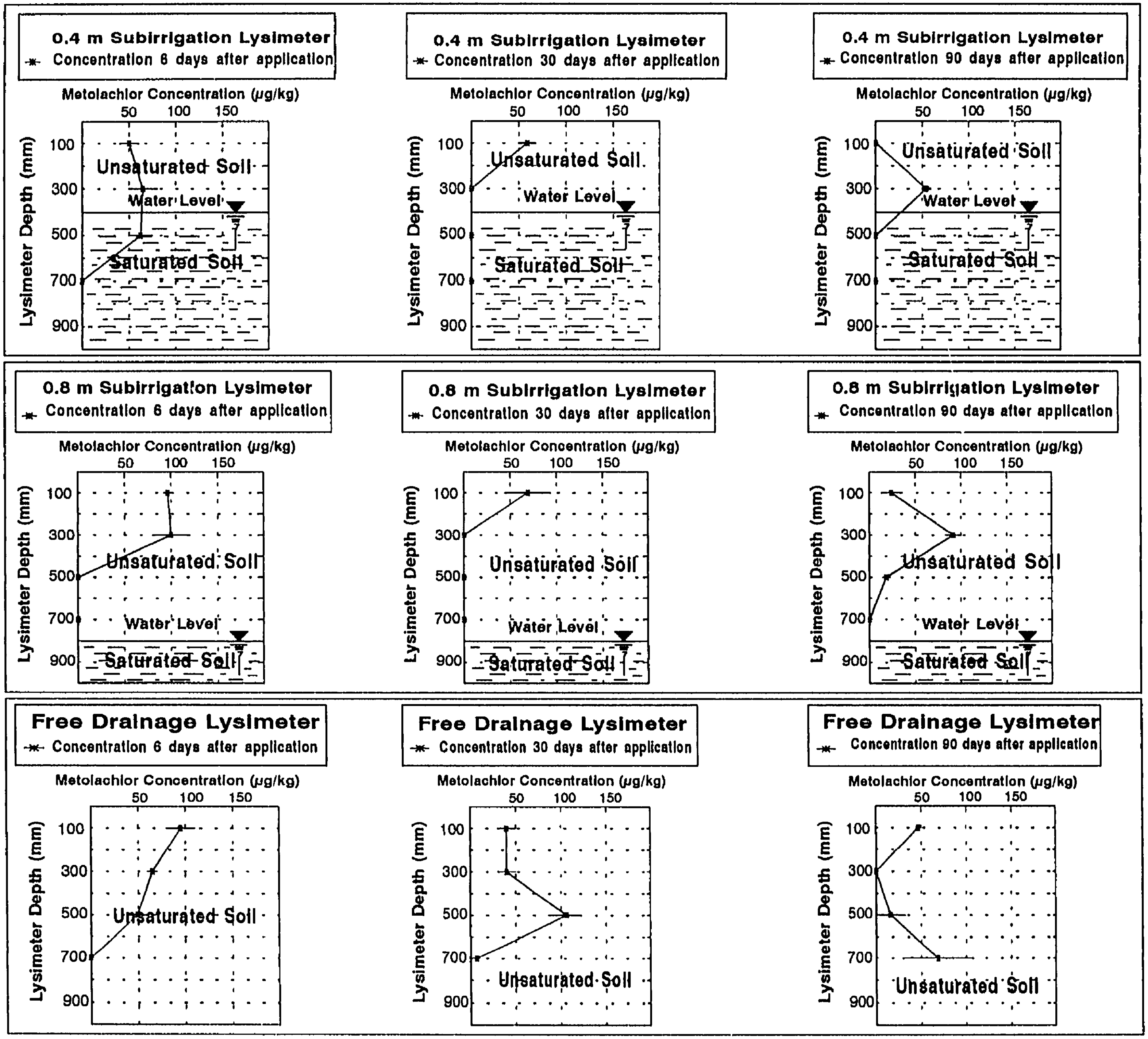

Figure 5.18. Metolachlor residues in soil (1995)

on day 30 and 90, indicating that the shallower water table in the 0.4 m subirrigation treatment in some occasions caused faster reduction in the metolachlor levels in the soil profile. This would leave relatively less pesticide available for leaching to the ground waters.

As Figure 5.18 illustrates, on any sampling day the concentration of metolachlor residues at each soil depth had changed. This reflects the simultaneous processes of leaching to the lower layers, and degradation on that depth. Comparison of three columns in Figure 5.18 shows the variation of the metolachlor residue in the soil with respect to time. In general, relatively less residues were found in 0.4 m-subirrigation lysimeter.

A mass balance study was carried out for three sampling days separately to obtain a deep insight of metolachlor dissipation in the soil and soil solution throughout the soil profile. In the mass balance study, the metolachlor residues in the whole lysimeter profile were considered, as well as the mass of metolachlor drained or spilled out after either natural or simulated rainfall periods. Table 5.5 shows the summary of the mass balance study of metolachlor in the three water table management treatments.

Table 5.5. The Mass Balance of Metolachlor in Different Treatments (mg)

	0.4 m-Subirrigation				**0.8 m-Subirrigation**				**Free Drainage**			
Days	Water	Soil	Total	**Loss%**	Water	Soil	Total	**Loss%**	Water	Soil	Total	**Loss%**
6	0.0	7.659	7.659	**83.0**	0.001	8.48	8.481	**81.2**	0.003	9.042	9.045	**79.9**
30	0.027	2.549	2.576	**94.3**	0.003	7.759	7.762	**82.8**	0.001	8.351	8.352	**81.4**
90	0.031	2.350	2.385	**94.7**	0.003	6.886	6.889	**84.7**	0.002	5.659	5.661	**87.4**

Figure 5.19 shows the total metolachlor residues deposited in the soil profile of different treatments. Each lysimeter was sprayed with about 45 mg of metolachlor at the beginning of summer. According to Table 5.5, in the 0.4 m subirrigation treatment this amount has been reduced by 83%, after 6 days. In the 0.8 m subirrigation and free drainage treatments the dissipation of metolachlor was also quite high and amounted 81.2 and 79.9%, respectively. A similar trend is identified in the metolachlor levels of other sampling days except that 0.4 m subirrigation always showed higher percentage of metolachlor loss. The total percentage of loss of metolachlor in different treatments is presented in Figure 5.20.

The Repeated Measures Analysis of Variance was carried out for the nine series of soil solution sample data, collected in the summer of 1994. The same statistical method was used to analyze seven series of soil moisture contents, seven series of soil solution and three sets of soil data in 1995. Table 5.6 presents results of the statistical analysis for soil moisture contents in the crop

Table 5.6. General Linear Models Procedure
Repeated Measures Analysis of Variance for **Soil Moisture Contents**
Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WTM	**2**	**2137.56**	**1068.77**	**66.14**	**0.0001**
Error	6	96.95	16.16		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
40-SUB VS. 80-SUB	1	**1813.71**	**1813.71**	**112.24**	**0.0001**
40-SUB VS. FREE-DRAI	1	**1360.02**	**1360.02**	**84.17**	**0.0001**
80-SUB VS. FREE-DRAI	1	32.60	32.60	2.02	0.2053

Univariate Tests of Hypotheses for Within Subject Effects

Source: TIME

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
6	462.98	77.16	19.51	0.0001	0.0001	0.0001

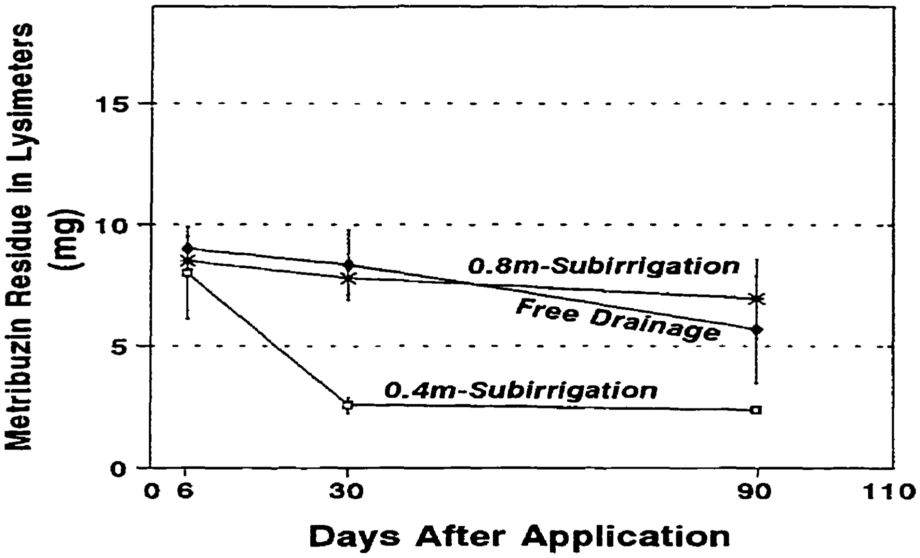

Figure 5.19. Metolachlor residues in the soil

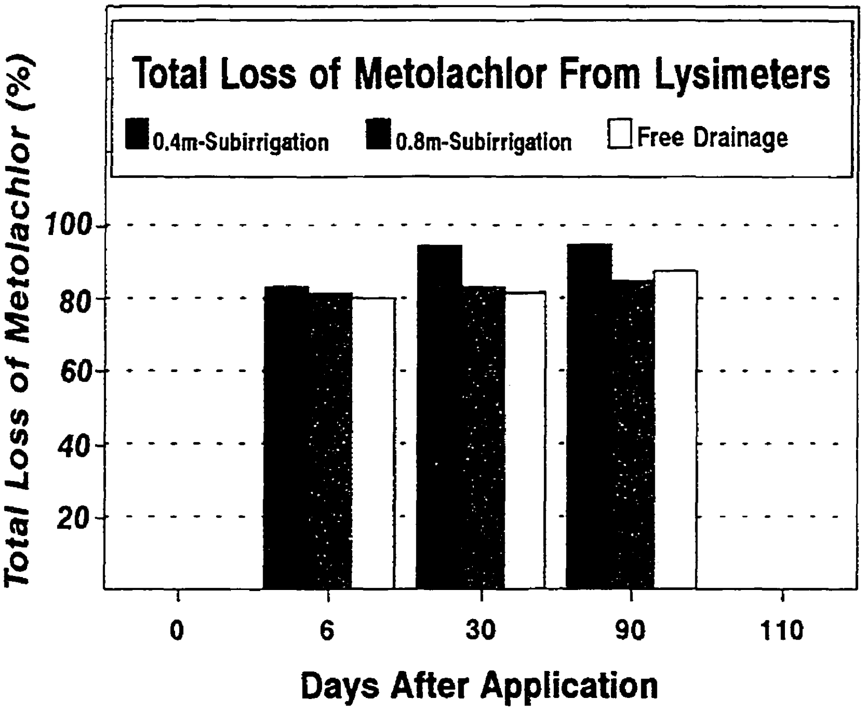

Figure 5.20. Total loss of metolachlor in the soil profile

root zone in 1995. This table shows that moisture level in 0.4 m subirrigation was significantly higher than that of other treatments at 95% level. The contrast between the moisture levels of 0.8 m subirrigation and free drainage was not statistically significant, because the 0.8 m water level in the 0.8 m subirrigation could not provide high moisture content at crop root zone.

Table 5.7 shows the result of statistical analysis for metolachlor residues in soil. Although, in all three sampling years less metolachlor residues were found in the soil solution of 0.4 m-subirrigation treatment, the metolachlor mass balance study has shown that neither the effect of water table management, nor the contrast between metolachlor residues in the soils of three treatments, are statistically significant at the 95% level.

Soil biomass population favours soil higher moisture content as an important stimulant in its cell metabolism. The higher soil moisture level could help to enhance the soil biological activity, and increase significantly the biodegradation of herbicide residues. Although the soil moisture content in the crop root zone of 0.4 m subirrigation was significantly higher than that of the other treatments (Table 5.6), the reduction in the metolachlor residues was not statistically significant (Table 5.7).

To further investigate these findings, a laboratory batch study was carried out in 1995 to study the metolachlor degradation at various soil moisture contents (Jebellie et al., 1996). Results from this batch test indicated that metolachlor degradation was not moisture sensitive, and the degradation of metolachlor at different soil moisture contents did not show a statistically significant difference. This laboratory finding confirms the lysimeter results that metolachlor residues in the soils of subirrigated corn and soybean farms of Quebec may not reduce significantly. Therefore, other BMPs must be exploited

Table 5.7. General Linear Models Procedure
Repeated Measures Analysis of Variance For **Metolachlor Residues** in Lysimeters, Tests of Hypotheses for Between Subjects Effects

Source	**DF**	**Type III SS**	**Mean Square**	**F Value**	**Pr > F**
WTM	2	72.07	36.03	1.27	0.3459
Error	6	169.74	28.29		

Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
40-SUB VS. 80-SUB	1	72.00	72.00	2.55	0.1618
40-SUB VS. FREE-DRAI	1	20.05	20.05	0.71	0.4321
80-SUB VS. FREE-DRAI	1	16.05	16.05	0.57	0.4798

Univariate Tests of Hypotheses for Within Subject Effects

Source: **TIME**

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
2	13.982963	6.99148	1.18	0.3411	0.3388	0.3411

Source: TIME*WTM

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
4	31.69481	7.923703	1.34	0.3128	0.3170	0.3128

to examine the possibility of reduction of environmental pollution from agricultural lands which use metolachlor herbicide.

5.4. Conclusions

The fate and transport of metolachlor was investigated, with depth and time, under three different water table management scenarios, using two subirrigation and one free drainage treatment. Metolachlor was found to be quite mobile as it leached down the soil profile in all treatments. Therefore, it may be concluded that there is a risk of surface and groundwater pollution from the use of this herbicide, in the sandy soils under the Quebec climatological conditions.

The results of three years of lysimeter study, which is also supported with a laboratory batch investigation, showed no significant difference in metolachlor residues among the water table management treatments. This suggests that water table management may not reduce the risk of environmental pollution from metolachlor residues from corn and soybean farms of Quebec. Therefore, other BMPs must be exploited to examine the possibility of non-point pollution from agricultural farms which use metolachlor herbicide.

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PREFACE TO CHAPTER 6

In the last three chapters, the impact of subirrigation systems on the fate of three most commonly-used herbicides in southern Quebec, namely atrazine, metribuzin and metolachlor, was explained and discussed. The experimental results showed that atrazine and metribuzin herbicides are mobile enough to leach down in the soil profile, and the residue levels of these chemical at any specific soil depth varied with time in all water table management treatments. This result was also applicable to metolachlor residues to a certain extent. The changes in herbicide concentration at a certain soil depth, either in adsorbed or solution phases could be caused by: leaching of herbicide from upper layer or to a deeper soil depth, further adsorption or desorption, pesticide transformation, and/or combination of some of the above factors.

To clarify the three years lysimeter findings, there was a need to conduct a laboratory study in 1995. This would enable the explanation of the impact of soil moisture content on the processes occurring in the soil. Since biotransformation plays an important role in the dissipation of pesticide residues from soils, the laboratory test was planned in a way to investigate the effects of soil moisture content on the biodegradation of the three herbicides used in the field lysimeter study.

Chapter 6 comprises of four different sections. These sections explain how the laboratory study was done and how the results support the lysimeter findings. Section one discusses the impact of different parameters including soil moisture content on the degradation of pesticide residues. The detailed explanation of methodology of the experiment follows in section two. The experimental results for each of the three chemicals, atrazine, metribuzin, and metolachlor are presented and discussed separately in section three. At the end, section four concludes the final results of this laboratory study. This work was reviewed, accepted in 1996 and published in the Canadian Water Resources Journal 21(4): 79-87. This paper is co-authored by Drs. Prasher and Clemente. Dr. Prasher is my research supervisor and he provided the overall guidance for this study. Dr. Clemente helped in the analysis of data and made editorial corrections to the manuscript.

CHAPTER 6

ROLE OF SOIL MOISTURE CONTENT IN REDUCING ENVIRONMENTAL POLLUTION FROM PESTICIDES

Abstract

The role of soil moisture content in reducing groundwater pollution from agricultural chemicals was investigated under laboratory conditions. Specifically, the effects of different soil moisture content levels on the dissipation rates of three commonly-used herbicides, namely, atrazine, metolachlor, and metribuzin, were analyzed using a batch degradation study in the laboratory. The soil samples were taken from a sand field in southern Quebec, where no herbicides had previously been applied in the past two years. Four soil moisture content treatments, i.e., 20%, 35%, 50% and a slurried condition, were simulated to represent different moisture regimes that might occur in humid regions.

Our results indicate that the degradation rates of atrazine and metribuzin were higher at 35% and 50% soil moisture contents than at 20%, whereas that for metolachlor remained unaffected. The half life of atrazine was found to be 1 week at 50% moisture content, and two weeks at 20% and 35% moisture

content. In the slurried soil, the half life was measured at more than 9 weeks. For metribuzin, it ranged from 3 to 5 days for the unsaturated soil conditions and about 10 days for the slurried condition. The half life of metolachlor was not affected by moisture content; it was found to be about 2 weeks at 20%, 35%, and 50% moisture contents. Under slurried conditions, the half life was 4 weeks. From the results of this study, it can be concluded that a water table management system which can maintain higher levels of moisture in the soil profile may reduce groundwater pollution from atrazine and metribuzin in sandy soils of Quebec.

6.1. Introduction

Chemical and microbial degradation is one of the major pathways by which herbicides are dissipated in soils. Some herbicides have low persistence and thus they are either dissipated quickly or are transformed to their daughter products or metabolites. Depending on the chemical structure and environmental conditions, the degradation can take place by such processes as oxidation, hydrolysis, N-dealkylation, dechlorination, ring hydroxylation, etc. (Coats, 1991).

Biodegradation of chemicals occurs through the activities of naturally occurring microorganisms population. Soil factors, such as nutrients, moisture content, pH, and temperature may be used as growth stimulants to enhance biological activities. Exponential growth of microbial population in soil may be achieved due to provision of these stimulants to the soil (Tate, 1995). In addition to that, electron acceptors are also needed for the oxidation of food (organic compounds) by microorganisms. The most available electron acceptor used by microorganisms, is oxygen in the air. That is why the highest biological activity is usually observed under aerobic environment. Nitrate, sulphate and carbon dioxide are other electron acceptors found in soil in the absence of air, when anaerobic conditions prevail. The energy thus, obtained from the oxidation/reduction reactions by microorganisms, is used for cell maintenance and growth (Coats, 1991).

The degradation is enhanced in the soil pH range of 5.5-8.0, with an optimal pH value of about 7 (Sparks, 1995). Biodegradation also tends to increase with temperature (Hyzak and Zimdahl, 1974; Savage, 1977). The effect of soil moisture content on biodegradation of pesticides, however, is not fully understood. It is known that the availability of soil moisture is required for enhanced biomass activity. The rate of pesticide degradation under saturated soil conditions is also known to be very slow (Goswami and Green, 1971).

In humid regions of North America, farmers are adapting their subsurface drainage systems for subirrigation in increasing numbers. A subirrigation system is needed to meet crop water requirements during the hot summer months when rainfall events are less frequent. Several studies have reported increased crop yields with subirrigation in Quebec, B.C., and in many states in the US (Memon, 1985; Ahmad and Kanwar, 1991; Kalita and Kanwar, 1993; Prasher et al., 1994).

It is possible that biodegradation of pesticides may be occurring at a higher rate on farms undergoing subirrigation since the soil moisture maintained at a higher level through the soil profile. With higher soil moisture content and soil temperature during the summer months, the pesticides may degrade rapidly thus reducing the risk of water pollution. It may, however, be noted that the moisture content in the soil profile is not maintained at the same level during subirrigation; it is close to saturation near the water table and decreases with distance above the water table. Thus, the biodegradation may not occur uniformly in the soil profile.

This study was undertaken to investigate the effects of different soil moisture contents on the biodegradation of three commonly-used herbicides, namely atrazine, metribuzin and metolachlor in a sandy soil. These herbicides are examined because of their extensive use in corn, soybean and potato farms in Quebec. The results will help us to determine the environmental impacts of water table management systems in Quebec.

6.2. Materials and Methods

The experimental was conducted in a laboratory at the Macdonald Campus of McGill University in 1995. The following sections will explain the experimental procedures and discuss the results.

6.2.1. Sampling Scheme

The soil was a St. Amable sand (Humic Haplorthod), and it was collected from a sand field where no herbicide had been applied in the previous two years. In order to minimize the effect of organic matter in the top soil, the first 100 mm of the soil was removed before sampling. Table 6.1 shows some of the physical characteristics of this soil.

Table 6.1. The Physical and Chemical Characteristics of the Soil

Soil Type	Sand (%)	Silt (%)	Bulk density (kg/m^3)	Organic matter (%)	pH	CEC cmol/kg
Sandy Soil	92.2	4.3	1350	3.5	5.5	4.9

Four different moisture levels were chosen to determine the degradation of pesticides. The volumetric moisture contents reflect the different moisture content regimes that might occur during water table management. The 20% soil moisture content was used to represent the moisture levels at the root zone depth in a free drainage or a subirrigation system. Since the moisture content in the soil would decrease with height above the water table, two other levels, i.e., 35% and 50%, were also used. In addition, another treatment was added to the experimental protocol to simulate slurried soil conditions.

With three herbicides and four moisture content levels, there were 12 treatments. A completely randomized design was used in this study, with three replicates for each treatment. Each experiment was carried out in the laboratory at 21 °C ± 2 °C in a 200 ml glass bottle, wrapped with an aluminum foil to prevent any photo decomposition.

Some initial estimates were made as to how much soil would be needed in each glass bottle. It was assumed that the soil would be sampled four times during the experimental period, each sample requiring 20 g of soil for herbicide (15 g) and soil moisture content (5 g) determinations. Therefore, 80 g of air-dried soil was added to each bottle. In addition, it was decided to add 0.03 mg of herbicide to each bottle, yielding a startup concentration of 0.375 mg/kg.

Some further calculations were necessary to ascertain the required moisture content levels in each bottle. Four different concentrations of atrazine, metolachlor and metribuzin solution were prepared: 0.5, 1.0, 1.5 and 2.5 mg/L. The herbicides were first dissolved in 5 ml of methanol and then tap water was added to obtain a 2.5 mg/L stock solution. The stock solution was diluted with tap water to obtain the remaining three concentrations. To obtain 20% moisture content, 12 ml of 2.5 mg/L stock solution was added to the bottles. Similarly, 20 ml of 1.5 mg/L, 30 ml of 1.0 mg/L, and 60 ml of 0.5 mg/L were added to various bottles to obtain 35%, 50%, and slurried soil moisture levels, respectively.

The soil in each bottle was sampled at the following time intervals: 1 week, 2 weeks, 4 weeks, and 9 weeks. It was mixed properly with a spatula prior to each sampling. Though the glass bottles were covered with a rubber stopper, two small holes were made in them for aeration. They were weighed periodically to maintain constant moisture content.

6.2.2. Extraction and Analysis of Herbicide Residues

In each sampling, 20 g of soil was removed from each bottle. Five grams of this soil was placed in the oven at 105° C for 24 hours to determine the soil moisture content. The remaining soil was put in a flat bottom flask to which 100 ml of methanol was added, and the mixture was shaken for 1 hour. The mixture was transferred to a Buchnel flask and filtered under partial suction. The collected organic phase was evaporated in a rotary evaporator for about 15 minutes, and the dried residues were dissolved in 10 ml of hexane. The extracts were stored in 15 ml glass vials in the refrigerator prior to the GC analysis.

The samples were analyzed using a Varian, Model 3400, gas chromatograph. The column used was a 0.53 mm i.d., fused silica Megabore DB-5, 1.5 µm film thickness, made by J&W Scientific. A Thermionic Specific Detector (TSD), also known as nitrogen-phosphorus detector (NPD), was used to detect the herbicide residues. The injector temperature was set at 250°C and the detector was kept at 300°C. The column temperature was maintained at 180°C for 9 minutes, and then the temperature was increased to 200°C at the rate of 4° C/min; at 200°C it was held for 1 minute, and then it was raised to 280°C at the rate of 20° C/min. The column was kept at this temperature for 9 minutes. The detection limit for the soil samples, evaluated by injecting extracts with decreasing herbicide concentrations, was estimated to be 10 µg/kg. The recovery rate was obtained by fortifying 5 g of untreated oven dry soil with 0.05, 0.5 and 5 µg/g of herbicides. The samples were left to equilibrate for 24 h., after which time they were extracted and analyzed by GC. The calculated recovery rate was 97% ± 2%.

6.2.3. Statistical Analysis

The statistical analysis of the data was performed using the SAS program. Since the soil subsamples had to be taken from the same bottles at predetermined time intervals, the independency of observations and homogeneity of sampling variance could not be maintained. The classical statistical analysis of the variance may not produce reliable results in this situation. Thus, the Repeated Measures Analysis of Variance was employed instead. The effects of various soil moisture contents were tested using the Huynh-Feldt (H-F), or Greenhouse-Geisser (G-G), approach for the conservative F test, called the H-F and G-G test. It has been reported that the Huynh-Feldt (H-F) adjusted F test is more applicable for repeated measures of analysis (Dutilleul and Legendre, 1993).

6.3. Results and Discussions

The mechanisms affecting the fate and behaviour of pesticides under field conditions include adsorption, leaching, degradation, surface transport, plant uptake, volatilization, and photodecomposition. However, only the degradation process was allowed to occur in this study. The background concentration of all three herbicides in the soil was found to be below the detection limit of the GC.

6.3.1. Atrazine

Figure 6.1 illustrates the average concentration of atrazine remaining in the soil as a function of time at four different moisture contents. The error bars, representing average values ± one standard deviation are also plotted. The initial degradation of atrazine during the first two weeks was fast, and then it slowed down. It is also clear from the Figure that atrazine did not degrade rapidly under the slurried soil condition. However, it seems to have degraded quickly at the other soil moisture contents. Though the degradation was quite uniform during the first week at these moisture contents, the highest degradation occurred at 50% moisture content in the 9 week period, followed by 35% moisture content, and then by 20% moisture content.

Atrazine half life in the soil at 50% moisture content was found to be about one week. The half lives at the 20% and 35% soil moisture contents were between one and two weeks. Under the slurried condition, the half life was estimated to be more than nine weeks. It can also be inferred from Figure 6.1 that whereas about 80% of atrazine had degraded within two weeks, it only degraded by about 40% in the slurried soil during the same time period.

Table 6.2 presents the statistical analysis for atrazine. This table shows that the effect of moisture content on the degradation of atrazine is statistically significant. The contrast between 50% vs. 20% moisture content is statistically significant at the 95% level. The contrast between 35% vs. 20% moisture content is also statistically significant at the 95% level. This suggests that atrazine degradation is highly dependent on soil moisture content. This behaviour was also reported by Ghassemi et al. (1981), who found higher soil moisture content enhances soil microbial activity.

Table 6. 2. General Linear Models Procedure
Repeated Measures Analysis of Variance For **Atrazine**
Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Moisture	**3**	**0.0909**	**0.030**	**16.56**	**0.0050**
Error	5	0.0091	0.001		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
50%-Mois vs. 20%-Mois	**1**	**0.0392**	**0.0392**	**21.43**	**0.0057**
50%-Mois vs. 35%-Mois	1	0.0009	0.0009	0.49	0.5145
50%-Mois vs. 100%-Mois	1	0.0064	0.0064	3.50	0.1205
35%-Mois vs. 20%- Mois	**1**	**0.0273**	**0.0273**	**14.91**	**0.0119**

Univariate Tests of Hypotheses for Within Subject Effects

Source: TIME

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
3	0.06453750	0.0215	14.05	0.0001	0.0067	0.0003

Source: TIME*MOIS

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
16	0.0159	0.0017	1.16	0.3856	0.4088	0.3911

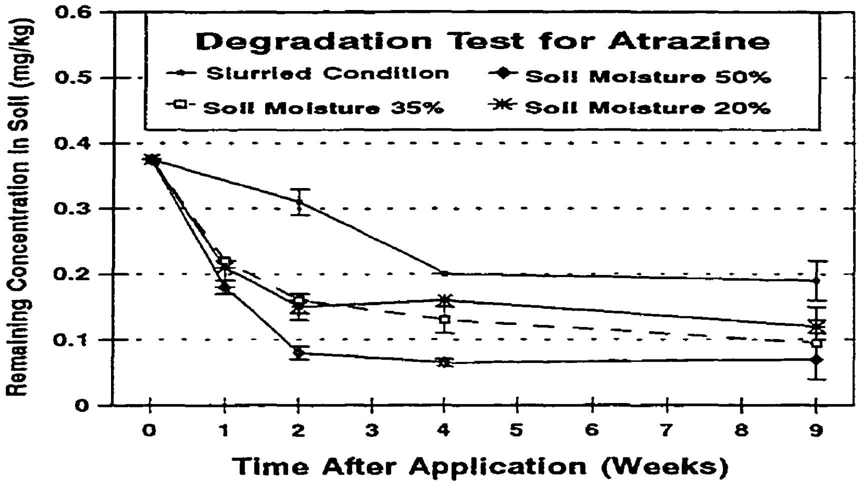

Figure 6.1. Remaining concentration of atrazine in soil

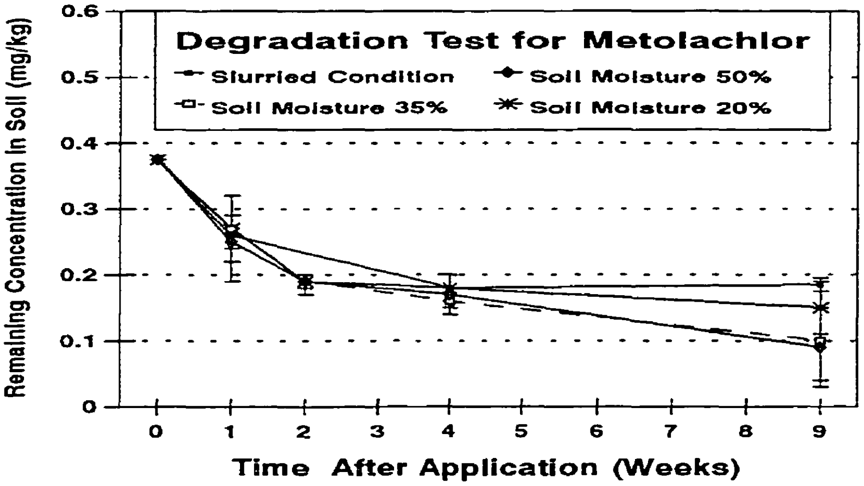

Figure 6.2. Remaining concentration of metolachlor in soil

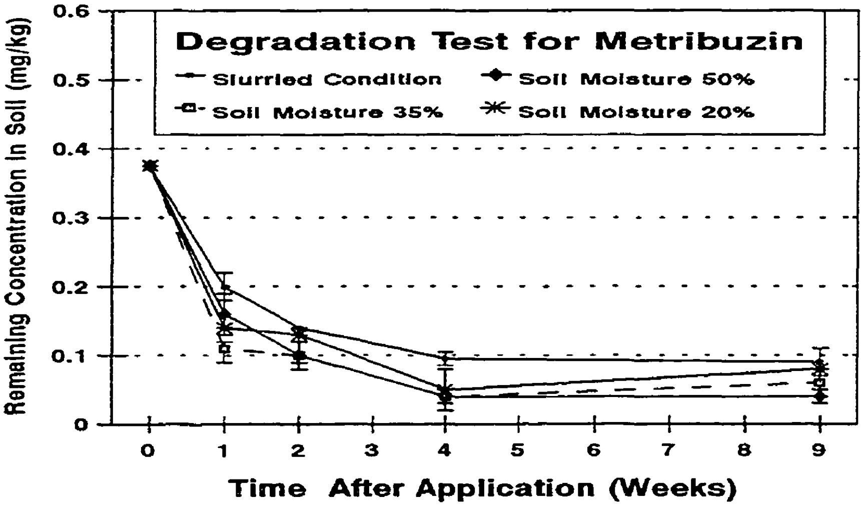

Figure 6.3. Remaining concentration of metribuzin in soil

From the above results, it appears that subirrigation systems in the corn growing areas of Quebec may also enhance atrazine degradation. By maintaining higher soil moisture content in the unsaturated zone of soil, atrazine dissipation will be very rapid, thus lowering the risk of water pollution.

6.3.2. Metolachlor

The results of metolachlor experiment are given in Figure 6.2. The average metolachlor concentration is plotted against time for the four different moisture conditions. In addition, error bars, showing the average value ± one standard deviation, are also drawn. There does not seem to be much impact of different moisture conditions on metolachlor degradation. The degradation process appears to be similar for all four moisture conditions for the first four weeks. Thereafter, more degradation seems to have occurred under 50% and 35% moisture conditions, however, it is not as conclusive as was found for atrazine.

Metolachlor half life at the various moisture contents appears to be about two weeks. It also appears that the degradation process started quite quickly in the beginning but it slowed down after about two weeks.

Table 6.3 presents the results of the statistical analysis for metolachlor. The impact of soil moisture content on the degradation of metolachlor is not found to be statistically significant. None of the four contrasts in the moisture levels were found to be statistically significant at the 95% level. Therefore, subirrigation systems do not enhance metolachlor degradation in sandy soils. These results comply with the findings of other researchers (Chesters et al., 1989; Braverman et al., 1986) who also found no correlation between metolachlor degradation and soil moisture content. Arjoon et al. (1995) had found similar results under field conditions on a sandy loam soil in Quebec.

Table 6.3. General Linear Models Procedure
Repeated Measures Analysis of Variance For **Metolachlor**
Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Moisture	3	0.0032	0.0010	0.98	0.4708
Error	5	0.0055	0.0011		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
50%-Mois vs. 20%-Mois	1	0.00200	0.00200	1.79	0.2381
50%-Mois vs. 35%-Mois	1	0.00102	0.00102	0.91	0.3828
50%-Mois vs. 100%-Mois	1	0.00002	0.00002	0.01	0.9075
35%-Mois vs. 20%- Mois	1	0.00034	0.00034	0.30	0.6060

Univariate Tests of Hypotheses for Within Subject Effects

Source: TIME

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
3	0.084	0.028	16.28	0.0001	0.0030	0.0001

Source: TIME*MOIS

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
9	0.009	0.001	0.60	0.7805	0.6876	0.7805

6.3.3. Metribuzin

Figure 6.3 gives the average metribuzin concentrations remaining in the soil as a function of time. In addition, the error bars, representing the average values ± one standard deviation, are also drawn. The trend in the results is similar to the one found for atrazine. Although metribuzin seems to degrade quite rapidly for all moisture content conditions, the fastest and the highest degradation occurs at the 50% moisture content, followed by 35% and 20% moisture contents. The degradation rate was slowest for the slurried soil condition.

The half life in the unsaturated soil samples was between 3-5 days. However, it was about 10 days for the slurried soil. In soil samples with 20%, 35% and 50% moisture content, nearly 90% of the applied metribuzin was degraded in four weeks, while 73% of the herbicide was degraded in the slurried condition during the same time.

Table 6.4 presents the results of statistical analysis for metribuzin. This table shows that the effects of different soil moisture contents on metribuzin degradation is highly significant. It also shows that the degradation contrast between the 50% vs 20% soil moisture content is statistically significant at the 95% level. The contrast between the 35% vs 20% moisture content is also statistically significant at the 95% level.

From the above results, we can conclude that subirrigation systems can be used to enhance degradation of metribuzin herbicide in sandy soils. These findings also agree with the experimental results of Aubin (1993) who found higher metribuzin degradation rates under subirrigation in a sandy soil under field conditions.

The comparison of the degradation rates of the three herbicides at various soil moisture contents shows that metribuzin degradation was the highest of the three in the sandy soil, followed by atrazine. There was no significant effect of moisture content on metolachlor degradation. Thus, subirrigation systems seem

Table 6.4. General Linear Models Procedure
Repeated Measures Analysis of Variance For **Metribuzin**
Tests of Hypotheses for Between Subjects Effects

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Moisture	**3**	**0.0106**	**0.0035**	**5.86**	**0.0432**
Error	5	0.0030	0.0006		

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
50%-Mois vs 20%-Mois	**1**	**0.0106**	**0.0104**	**17.25**	**0.0089**
50%-Mois vs 35%-Mois	1	0.0013	0.00133	2.20	0.1981
50%-Mois vs 100%-Mois	1	0.0008	0.0008	1.32	0.3023
35%-Mois vs 20%- Mois	**1**	**0.0036**	**0.0036**	**5.94**	**0.0588**

Univariate Tests of Hypotheses for Within Subject Effects

Source: TIME

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
3	0.056	0.018	45.65	0.0001	0.0001	0.0001

Source: TIME*MOIS

					Adj Pr > F	
DF	Type III SS	Mean Square	F Value	Pr > F	G - G	H - F
9	0.0073	0.0008	2.00	0.1126	0.1915	0.1126

to have significant environmental benefits in addition to the agricultural benefits. For both atrazine and metribuzin, they would cause rapid degradation and consequently reduce the risk of water pollution in a significant way.

6.4. Conclusions

This study focused on the evaluation of the effects of different soil moisture contents on the degradation rates of three herbicides, namely, atrazine, metolachlor, and metribuzin, in a sandy soil. Four soil moisture content scenarios were simulated: 20%, 35%, 50%, and a slurried condition.

Our results indicate that the degradation rate of two herbicides, metribuzin and atrazine, increased significantly when the soil moisture level was raised from 20% to 50%. However, metolachlor degradation was not affected by different moisture contents. Between atrazine and metribuzin, the highest and the fastest degradation rate was observed for metribuzin. Given that a subirrigation system can maintain suitable moisture contents in the soil profile, it can be concluded that this system could also be very effective in the quick degradation of atrazine and metribuzin in sandy soils. Further investigations, however, are needed for fine-textured soils before any concrete conclusions are drawn.

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PREFACE TO CHAPTER 7

The studies described in chapters 3 through 6 showed that atrazine, metribuzin and metolachlor leached readily through a sandy soil in southern Quebec climatic conditions. Lysimeter experiments nevertheless showed that non-point source pollution of ground water by atrazine and metribuzin can be significantly reduced when the residence time in the soil is lengthened and high soil moisture levels are maintained by subirrigation. The high soil moisture favours microbial growth and permits more extensive microbial degradation of the herbicide residues.

There are many contaminant transport models that can simulate non-point source pollution (NPS) in soils. Among them, PRZM2 is a more recent and well documented model. It is designed for comprehensive treatment of pesticide transport in the unsaturated zone. PRZM2 can deal with three pesticides simultaneously and its component models have been tested at several Canadian and US locations.

In the chapter that follows, the ability of PRZM2 to simulate fate and transport of atrazine, metribuzin and metolachlor will be examined. The theoretical basis of PRZM2 is described, and the input data requirements are explained. The simulation results for the three herbicides, based on inputs from the lysimeter studies are presented and discussed. In its current form, PRZM2 cannot be used for subirrigation due to its inability to simulate upward water movement. Therefore, the model was only tested in this study for pesticide transport in subsurface drainage lysimeters.

CHAPTER 7

MATHEMATICAL SIMULATION OF HERBICIDE TRANSPORT WITH PRZM2

Abstract

Detection of pesticide residues in ground waters has led to concerns over non-point source pollution from agricultural lands. Researchers are exploiting all means, including mathematical models, to study the fate and transport of pesticides. A computer simulation model (PRZM2) was used to simulate atrazine, metribuzin, and metolachlor leaching in sandy soil columns under subsurface drainage conditions. The input parameters and the observed data were obtained from a lysimeter study conducted on a sandy soil in southern Quebec. The model outputs were statistically analyzed using several statistical methods, including the coefficient of performance (C.P.).

According to simulated results, none of the three herbicides leached below 0.2 m depth, whereas herbicide residues had been detected in the soil solution at 0.85 m depth in the lysimeters. The calculated Coefficient of Performance values (C.P.) show that the simulated atrazine concentration at 0.1 m depth was in good agreement with the corresponding measured data over the entire experimental period (CP=0.2). Although the simulated metribuzin and metolachlor results at 0.1 m depth followed observed time and depth patterns, the model did not perform as well since it either under- or over-estimated

herbicide concentrations (CP>0.5). The model also performed poorly in simulating the leaching of the three herbicides to depths greater than 0.1 m.

Under- and/or over-estimation of atrazine, metribuzin, and metolachlor concentrations by model, may be due to simplistic treatment of matrix flow and the lack of a realistic macropore flow component. The existing approaches to handle transport and transformation processes may not adequately reflect the fate and transport of chemicals in soil. This emphasises the need for further calibration and validation of PRZM2 for these three herbicides in sandy soil under Quebec climatical condition.

7.1. Introduction

Non-point source pollution from agriculture is characterized by extensive loadings from agrochemicals leaching below the root zone. The widespread nature of agricultural contamination makes remedial actions very difficult, because there is no single moving plume as in "point source" pollution that can be isolated and controlled. The prevention or reduction of groundwater contamination by agrochemicals, especially pesticides, must be based on understanding of the chemical properties, soil system properties, and the climatic variables that combine to induce the leaching.

Because of the spatial variability of soil characteristics and pesticide properties, it is neither possible nor practical to carry out too many experiments, to study the fate and transport of various pesticides on all soil types. However, mathematical models may be used in these instances to examine a series of alternative scenarios.

Contaminant transport modelling started almost two decades ago, when a rapid increase in the use of agrochemicals was observed. Several mathematical models have been developed and tested since that time. However, these simulations have not always been successful due to the complexity of soil and pesticide behaviour in the vadose zone. That is why contaminant transport models usually under-estimate or over-estimate actual conditions.

Although the existing mathematical models have been successful in simulating simple aspects of contaminant transport processes to a reasonable level, there are still difficulties in the simulation of realistic pesticide flux in the soil. Mathematical models may not always give a complete picture of the various aspects of the complex processes occurring in the soil. But the efforts to develop new models or improve the performance of existing ones, should not be stopped, since the dynamic nature of environmental problems cannot otherwise be easily studied. The purpose of this study was to review some of the existing mathematical models, select the most comprehensive one, and simulate the transport of atrazine, metribuzin and metolachlor in a sandy soil under southern Quebec climatic conditions.

7.2. Background

Computer modelling is increasingly being used to predict the fate and transport of pesticides in soil systems. Models, validated and calibrated with experimental results, are the vehicles for transferring these results to other unexamined scenarios. However, successful model development, testing, and application to real fields must be based upon a comprehensive understanding of the dynamic nature of transport processes (Wagenet and Rao, 1985).

Investigators have studied the factors contributing to pesticide leaching since the 1980's. Results of these investigations have shown that pesticide solubility in water, sorptive properties, volatility, and the chemical structure determine the tendency of pesticides to leach through the soil profile. The hydrologic cycle also interacts with the pesticides to transform and transport them within and out of the root zone. Vertical transport of pesticides beyond the crop root zone, can result in groundwater contamination and has been the target of investigation in most mathematical models.

There are many contaminant transport models which simulate non-point source pollution (NPS) in soils (Donigian and Rao, 1988). However most models have some limitations with respect to a comprehensive treatment of pesticide transport. For instance, some models do not consider macropore flow and plant uptake (LEACH-P, MOUSE). Some models have excluded the vapour phase partitioning of pesticides, and hence cannot handle volatile pesticides (PRZM). Certain models do not permit consideration of agricultural and water table management practices (PRZM, LEACHP, PRZM2). In some models, the dynamic nature of the soil environment is treated rather simplistically (most models). Some models have been designed to represent only the transport processes in the root zone; simulation from the bottom of the root zone to the ground water is still to be included (GLEAMS). There are models suitable only for water flux simulation and do not include solute transport (PREFLO). Some models are still under development and need to be validated against further field observations (ARS-RZWQM, PESTFADE).

Among the above models, ARS-RZWQM, PESTFADE and PRZM2 seem relatively more complete than the others since they are designed for comprehensive treatment of pesticide transport in the saturated and unsaturated zones. The ARS-RZWQM model was developed in Fort Collins USA by the Agricultural Research Service (ARS-USDA), but it is a new model and still needs further testing and verifications. The PESTFADE model has been developed at Macdonald Campus of McGill University Quebec, and can handle water table management studies. However, it needs better documentation and further verification. Based on the above reasons the PRZM2 computer model was selected for this study due to the following features:

a) Good documentation and technical support.

b) State-of-the-art deterministic simulation of the fate of agricultural pesticides, both in the crop root zone and the underlying vadose zone.

c) Capacity of simulating multiple pesticides or parent/metabolite relationships.

d) Capabilities of the model to estimate probabilities of concentrations or fluxes from these various media for the purpose of performing exposure assessments.

e) Analysis of microbial degradation as a function of soil biomass characteristics.

f) Incorporation of two finite-difference numerical solutions, the original backwards-difference implicit scheme, or a Method of Characteristics algorithm that greatly reduces numerical dispersion, but increases model execution time.

PRZM2, a new release of original PRZM (Carsel et al., 1984), is a field-scale hydrology and transport model, developed by the US-EPA (Mullins et al., 1992). PRZM2 is a water flow and pesticide transport model, which incorporates several new features in addition to those used in the original PRZM. Compared to PRZM, there are several improvements in PRZM release 2, which may be broken into four categories:

- Hydrology
- Soil hydraulics
- Method of solution of the transport equation
- Deterministic nature of the model

Hydraulic computations in PRZM were performed on a daily basis. However, some of the processes, including evaporation, runoff and erosion may be simulated on a smaller time step to ensure greater accuracy. This depends to some extent upon the duration of the rainfall events. PRZM2 still retains the daily time step, primarily due to the relative availability of daily meteorological data (Mullins et al. 1992).

PRZM2 has been equipped to simulate soil temperature in order to correct Henry's constant which is used to calculate vapour-phase transport at various depths in the soil.

In PRZM, the soil hydraulics were over-simplified by assuming that all drainage to field capacity occurs within 1 day. This had the effect of inducing a greater-than-anticipated movement of chemical through the profile, especially in larger soil cores. While this feature of soil hydraulics has been retained in PRZM2, the option of coupling PRZM to the VADOFT module has also been added. The PRZM module is then used to represent the root zone depth, whereas VADOFT represents the unsaturated soil domain.

The required parameters for the solution of Richard's equation for unsaturated flow in VADOFT are obtained by using either soil textural information, which can generate soil water characteristic curves, or the van Genuchten technique which fits an appropriate curve to the measured soil moisture retention data. One of the limitations that remained untouched in PRZM2 is the inability to simulate upward flux. The PRZM2 model, can only simulate advective, downward movement of water and does not consider diffusive movement due to soil water gradients (Mullins et al., 1992). Because of this limitation, PRZM2 cannot simulate flow processes in a subirrigation system. Therefore, the model was tested in this study for atrazine, metribuzin and metolachlor fate and transport in subsurface drained lysimeters only.

The inadequacy of the backward difference technique in solving the transport equations in advection-dominated systems has been overcome in PRZM2. The backward difference technique for the advection term tends to produce a high degree of numerical dispersion in such systems. This results in over-prediction of downward movement due to smearing of the peak and subsequent over-estimation of chemical loadings to ground water. In PRZM2, a new formulation is also available for advection-dominated systems. The advective terms are decoupled from the rest of the transport equation and solved separately using a Method of Characteristics (MOC) formulation. The remainder of the transport equation is then solved as before, using the fully implicit scheme. This approach effectively eliminates numerical dispersion, but increases the computation time. In low-advection systems, the MOC approach reduces to the original PRZM solution scheme, which is exact for very small velocities (Mullins et al. 1992). The final improvement in PRZM2 is that values of water and chemical transport parameters are generated by the Monte Carlo module to represent spatial variability of soil characteristics. These, distributional, rather than field-averaged values will produce distributional outputs of the relevant variables (i.e. flux to the water table).

With all improvements, PRZM2 now consists of four major modules: PRZM, VADOFT, MONTE CARLO, and EXESUP which can be used under a user-friendly environment. The PRZM submodel uses the finite difference technique to simulate transport and transformation of the parent compound and two metabolites, whereas VADOFT as a one-dimensional, finite element code, solves the Richard's equation for flow in the unsaturated zone (vadose zone). PRZM2 links the two computational modules, PRZM and VADOFT, to simulate the pollutant fate for the crop root and the vadose zone. The model is also equipped with a module, called the Monte Carlo processor, which performs a probability based exposure assessment. This module generates further data for the input and output random parameters, then transforms them and performs statistical analysis on the output variables. The EXESUP module is an execution supervisor and controls the simulation procedures.

7.3. Transport Processes in PRZM2

Pesticide transport and transformation in PRZM2 is performed by two major computational modules, the improved PRZM and VADOFT. The Pesticide Root Zone Model (PRZM) is a one-dimensional, dynamic, compartmental model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the plant root zone. PRZM itself has two major components, hydrology and chemical transport. The hydrologic component calculates runoff and erosion based on the Soil Conservation Service (SCS) curve number technique and the Universal Soil Loss Equation (USLE). Evapotranspiration is estimated either directly from pan evaporation data, or using an empirical formula.

Evapotranspiration is further divided into evaporation from crop interception, evaporation from the soil surface, and transpiration by the crop. Water movement simulation is based on generalized soil parameters such as field capacity, wilting point, saturation water content, and saturated hydraulic conductivity . Pesticide biodegradation can also be simulated in the root zone. Adsorbed, dissolved, and vapour-phase pesticide concentrations in the soil are calculated by simultaneous consideration of pesticide partitioning among the various processes, such as: uptake by plants, surface runoff, erosion, decay, volatilization, foliar washoff, advection, dispersion, and retardation.

The mathematical expression of the governing equations of various processes incorporated in PRZM2 can be grouped into the following categories:

- Pesticide Transport
- Water Movement
- Soil Erosion
- Volatilization
- Irrigation

7.3.1. Pesticide Transport

PRZM2 considers the mechanisms responsible for the transport of pesticides, including convection (mass flow) and hydrodynamic dispersion-diffusion. When considering these processes simultaneously, the general convective-dispersive transport equation for a non-adsorbing solute and for steady water flow can be expressed as:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (7\text{-}1)$$

where

C = solute concentration (g/cm^3),
D = hydrodynamic dispersion coefficient (cm^2/h),
v = pore-water velocity (cm/h), and
x and t are distance (cm) and time (h), respectively.

The hydrodynamic dispersion coefficient in this equation combines the influences of molecular diffusion and velocity-induced "mechanical" dispersion, which results from the interaction of large and small pores during flow (Wagenet and Rao, 1985). This basic transport equation, with modifications for reactive solutes (such as pesticides) and various transformation processes, has been used in PRZM2 to describe transfer of a solute that interacts with the soil. In this situation, the general solute transport equation may be written as:

$$\frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \phi \qquad (7\text{-}2)$$

where

S = adsorbed concentration (g/g), and
ϕ = a sink term which combines all solute losses due to degradation (chemical or biological), plant uptake, volatilization, removal by runoff and leaching, as expressed in equation 7-3).

Various functional relationships between S and C which explain fundamental interactions between solute and the soil have been explored and applied to many pesticide models, including PRZM2. The equation 7-2 has been adapted for both surface and subsurface transport based on the concept of compartmentalized representation of the soil profile (Figure 7.1). Thus, the governing equation for one-dimensional transport of a nonconservative solute species in a variably saturated soil for dissolved phases takes the following form in PRZM2:

$$A \ \Delta z \ \frac{\partial (C_w \theta)}{\partial t} = J_D - J_v - J_{DW} - J_U - J_{QR} + J_{APP} + J_{FOF} \pm J_{TRN} \qquad (7\text{-}3)$$

The transport and transformation for the adsorbed phase is written as:

$$A \ \Delta z \ \frac{\partial (C_s \rho)}{\partial t} = J_{DS} - J_{ER} \qquad (7\text{-}4)$$

Finally, the vapour phase transport and transformation is expressed as:

$$A \ \Delta z \ \frac{\partial (C_g a)}{\partial t} = J_{GD} - J_{DG} \qquad (7\text{-}5)$$

where

A = cross sectional area of the column (cm^2)

Δz = depth of compartment (cm)

C_w = dissolved concentration of pesticide (g/cm^3)

C_s = sorbed concentration of pesticide (g/g)

C_g = gaseous concentration of pesticide (g/cm^3)

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

a = volumetric air content of the soil (cm^3/cm^3)

ρ_s = soil bulk density (g/cm^3)

t = time (d)

J_D = represents the effect of dispersion and diffusion phase (g/day)

J_V = represents the effect of advection of dissolved phase (g/day)

J_{GD} = represents the effect of dispersion and diffusion in vapour phase (g/day)

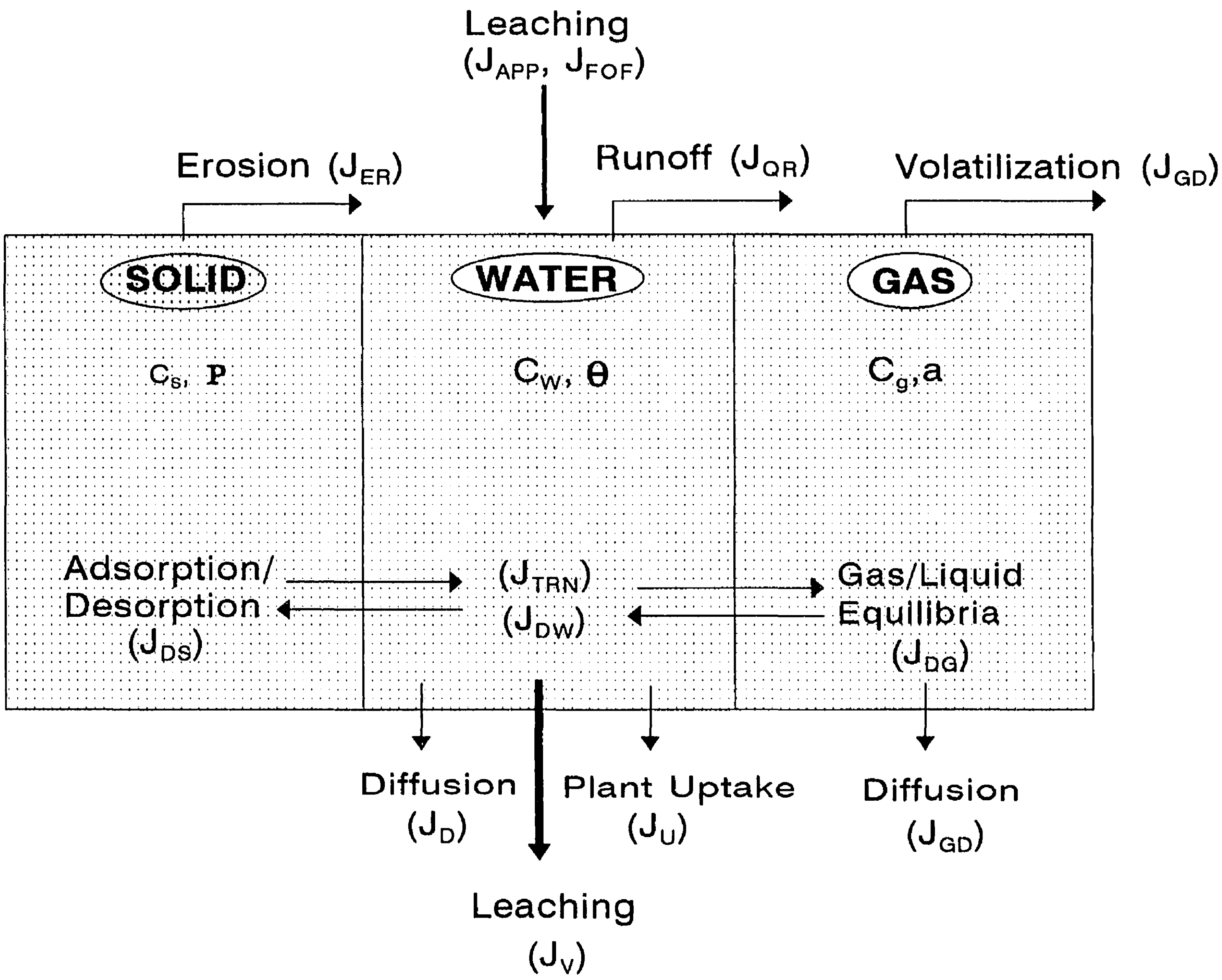

Figure 7.1. Schematic representation of fate of pesticides in PRZM2

J_{DW} = mass loss due to degradation in the dissolved phase (g/day)
J_{DG} = mass loss due to degradation in the vapour phase (g/day)
J_U = mass loss by plant uptake of dissolved phase (g/day)
J_{QR} = mass loss by removal in runoff (g/day)
J_{APP} = mass gain due to pesticide deposition on the soil surface (g/day)
J_{FOF} = mass gain due to washoff from plants to soil (g/day)
J_{DS} = mass loss due to degradation of sorbed phase chemical (g/day)
J_{ER} = mass loss by removal on eroded sediments (g/day)
J_{TRN} = mass gain or loss due to parent/daughter transformation

Adsorption and desorption in equations 7-3 through 7-5 are treated as instantaneous, linear, and reversible processes. The relationship between sorbed phase concentration and dissolved-phase can be expressed as:

$$C_s = k_d \, C_w \tag{7-6}$$

where

K_d = partition coefficient between the dissolved and solid phases (cm^3/g)

Degradation of a pesticide in or on soil is assumed to be result of such processes as hydrolysis, photolysis, and microbial decay. PRZM2 considers pseudo first-order kinetics, and the rate coefficient is combined into a single decay coefficient as follows:

$$J_{DW} = K_s \, C_W \, \theta \, A \, \Delta z \tag{7-7}$$

and

$$J_{DS} = K_s \, C_S \, \rho_S \, A \; \Delta z \tag{7-8}$$

where

K_s = lumped, first-order decay constant for solid and dissolved phases (day^{-1})

7.3.2. Water Movement

PRZM2 assumes the conventional darcian flow in the soil system, and exploits the well known Richard's equation, based on Darcy's law and the continuity equation. Thus, the governing equation of downward movement of water in the vadose zone may be expressed as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\frac{\partial h}{\partial z}\right] \tag{7-9}$$

where

$K(\theta)$ = hydraulic conductivity at various heads (cm/sec)

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

h = hydraulic gradient (cm/cm)

z and t are vertical distance (cm) and time (sec), respectively

PRZM and VADOFT modules solve the Richard's equation in the root zone and below the root zone either by backwards finite difference formulation or by the method of characteristics algorithm, considering initial and boundary condition for pressure head in the soil profile (Mullins et al. 1992).

7.3.3. Soil Erosion

Soil erosion involves the removal of sorbed pesticides from soil surface. This process is a major source of pesticide loading to the water bodies. The Modified Universal Soil Loss Equation (Williams, 1975) is used to calculate the soil loss in PRZM2. This equation can be expressed as:

$$X_e = a(V_r\ q_p)^{0.56}\ K\ LS\ C\ P \qquad (7\text{-}10)$$

where

X_e = the event soil loss (t/day)
V_r = volume of daily runoff (m^3)
q_p = peak storm runoff (m^3/sec)
k = soil erodability factor
LS = length-slope factor
C = soil cover factor
P = conservation practice factor
a = units conversion factor

7.3.4. Volatilization

Most of the pesticide volatilization occurs from the soil surface. When a pesticide is incorporated into the soil, its initial volatilization rate is a function of the vapour pressure of the chemical at the soil surface. As the concentration of the chemical at the soil surface changes, volatilization will depend upon the rate of the transport of pesticide to the soil surface (Mullins et al., 1992). The governing equation for the pesticide volatilization flux from the soil profile can be expressed as:

$$J_1 = \frac{D_a A}{d} (C_{g,1} - C^{*}_{g,d}) \qquad (7\text{-}11)$$

where

J_1 = volatilization flux from soil (g/day)

D_a = molecular diffusivity of the chemical in air (cm^2/day)

A = cross sectional area of the soil column (cm^2)

d = thickness of stagnant air boundary layer (cm)

$C_{g,1}$ = vapour-phase concentration in the surface soil layer (g/cm^3)

$C^{*}_{g,d}$ = vapour-phase concentration above the stagnant air boundary layer (g/cm^3)

7.3.5. Irrigation

PRZM2 irrigation algorithms compute depths of irrigation water to be applied at the soil surface. The irrigation water requirements are calculated from the soil water deficit and are added as infiltration to the first PRZM soil compartment. Irrigation is triggered when the average root-zone soil moisture content reduces to a level of user defined available water capacity. The soil moisture deficit, D, is then calculated based on the following equation (Mullins et al., 1992):

$$D = (\theta_{fc} - \theta_z) Z_r \qquad (7\text{-}12)$$

where

D = soil moisture deficit (cm)

θ_{fc} = average root zone soil moisture content at field capacity (cm^3/cm^3)

θ_z = average root zone soil moisture content (cm^3/cm^3)

where

D = soil moisture deficit (cm)

θ_{fc} = average root zone soil moisture content at field capacity (cm^3/cm^3)

θ_z = average root zone soil moisture content (cm^3/cm^3)

Z_r = root zone depth (cm)

Figure 7.2 shows the schematic view of the various processes occurring in the lysimeters.

7.4. Model Input Data Requirements

The input parameters required by transport and transformation modules or PRZM and VADOFT for the lysimeters can be broadly classified into the four following categories:

- **Meteorological parameters,** provide information for the hydrologic component of PRZM to calculate runoff, erosion, and evapotranspiration (Table 7.1). Meteorological inputs for lysimeter simulation consist of precipitation, evaporation, and average temperature for 1995, from the Macdonald Campus weather station. Meteorological data covers the entire experimental period in the 1995 sampling season, starting from the day of planting (June 4, 1995) to harvest (September 28, 1995).

- **Media parameters** are necessary to calculate water and pesticide leaching in the soil profile. Examples of these variables include the groundwater velocity, soil porosity, organic carbon content, dispersivity values, etc., which were either obtained from laboratory and lysimeter measurements or collected from the literature (Table 7.1).

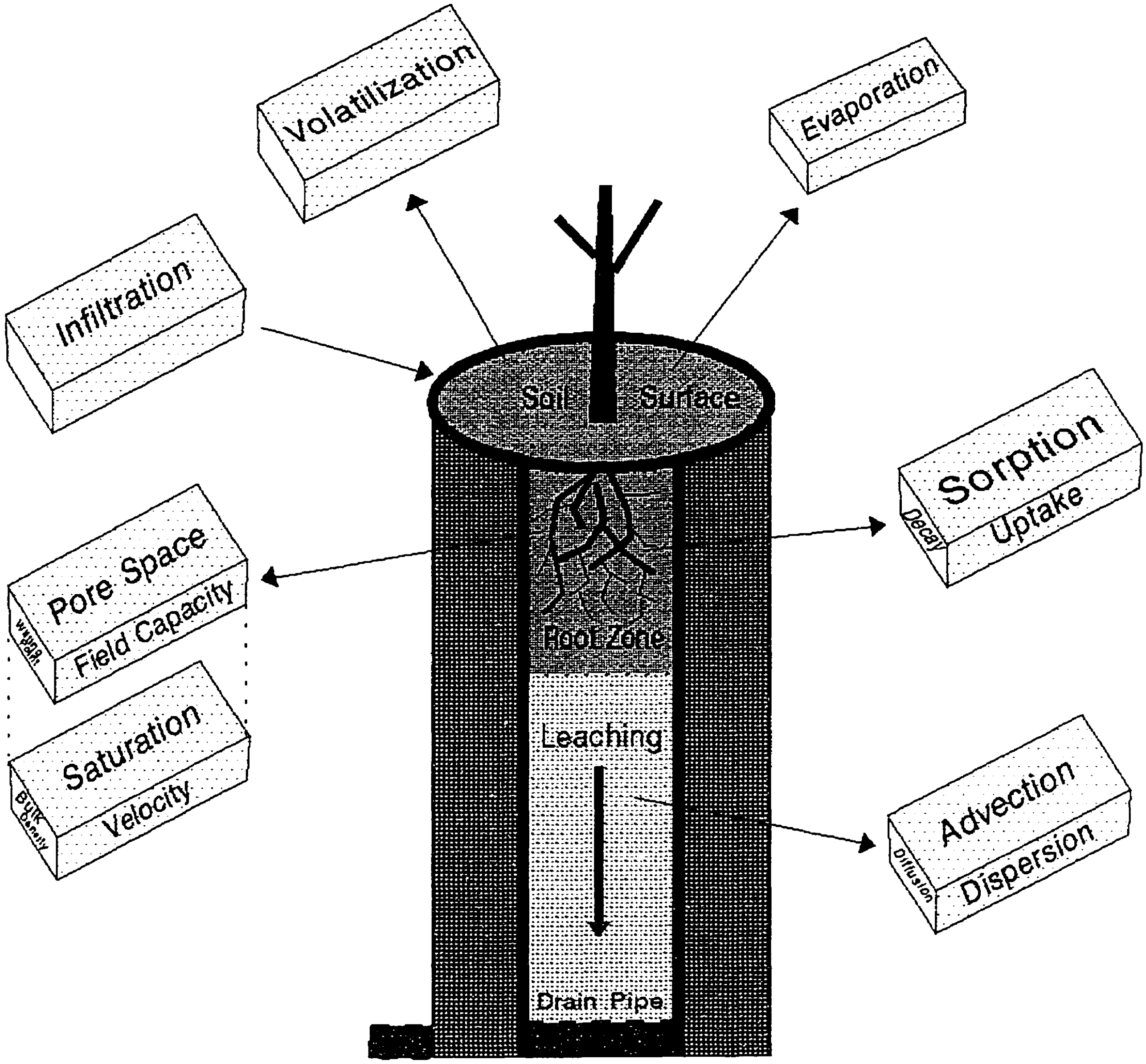

Figure 7.2. Simulation of various processes in lysimeter by PRZM2 model

Table 7.1. Sources of PRZM2 Model Input Data

Input	Source of Data
Meteorological parameters: - Precipitation - Pan evaporation - Temperature - Wind speed	Direct measurement from Ste-Anne-de-Bellevue, Weather Station, Quebec.
Media parameters:	
- Hydraulic conductivity	- Measured on the lysimeters
- Saturated water content	- Measured in the laboratory
- Residual water content	- Measured in the laboratory
- Permeability	- Estimated from soil program (El-Kadi, 1987)
- Retardation coefficient	- PRZM2 user manual page 5-72
- Longitudinal dispersion	- PRZM2 user manual page 5-66
- Organic carbon content	- Observation
Chemical parameters:	
- Partition coefficient	- Measured in our laboratory
- Hydrodynamic dispersion	- Estimated (Biggar and Nielsen, (1976)
- Henry's constant	- Estimated (Donigian et al., 1986)
- Decay rates	- Estimated (Sparks, 1989)
Management parameters:	
- Pesticide application timing	- Observed data
- Pesticide application	- Observed data
- Crop cover	- Observed data

- **Chemical parameters** provide information for the computation of various transport and transformation processes such as advection, dispersion, decay, erosion, and plant uptake. Examples of these variables include the soil-adsorption coefficient, Henry's Law constant, etc. This information was mainly collected from literature (Table 7.1).

- **Management parameters** include irrigation timing, pesticide application timing, etc., which were available from the measurements made in the experiment (Table 7.1).

To prepare the input file data for PRZM and VADOFT modules in proper format, the soil profile was partitioned into two horizons and several nodal points. Nodal points are the computational units within the unsaturated flow model and are equally spaced in each horizon. The soil column in lysimeter study was divided into 2 horizons, as shown in Figure 7.3. Horizons 1 and 2 were each 0.4 and 0.5 m thick, respectively. Horizon 1 represented the root zone, where the simulated rainfall and the pesticides were applied. Horizon 2 represented the vadose zone, which mainly contributed to the transport (leaching) of pesticides.

7.5. Results and Discussion

The output from PRZM2 is summarized in Tables 7.1 to 7.5 in the following pages and B.1 to B.14 in the appendix B. The simulated and measured data were evaluated by both graphical and statistical approaches. In the graphical approach, the measured and simulated values were plotted against time and depth.

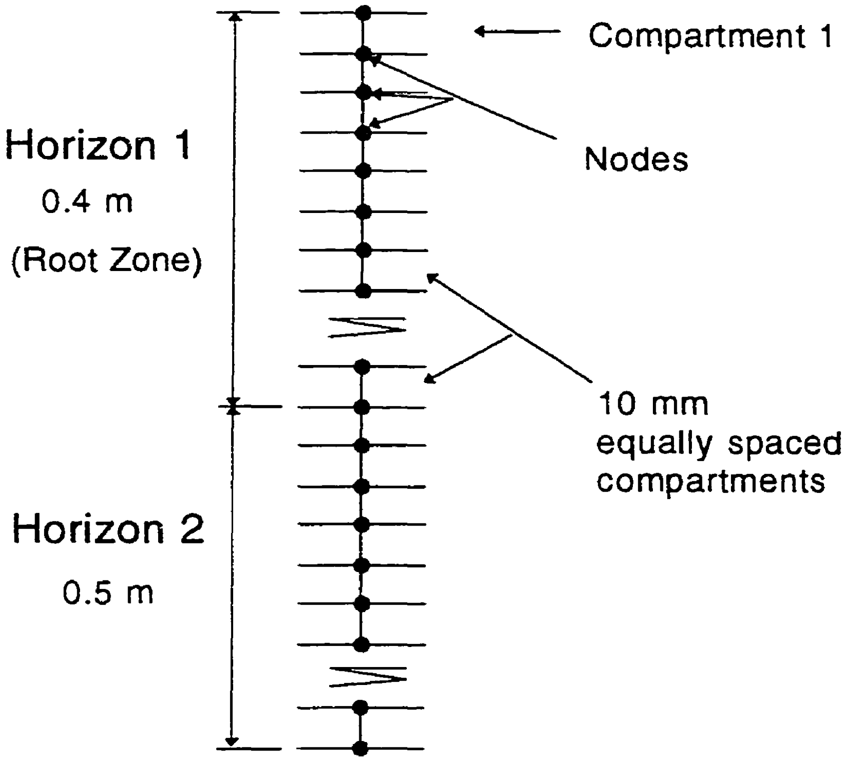

Figure 7.3. Schematic diagram of nodal structure for one dimensional PRZM2 model in lysimeters.

Because the mobility and transport of pesticide mass are functions of soil moisture fluxes, the study and comparison of simulated soil moisture contents with measured data is essential prior to the investigation of chemical transport. If simulated and measured moisture levels are in good agreement, then the chemical processes can be evaluated. The simulated and measured soil moisture contents from lysimeters are plotted in Figures 7.4 and 7.5. It can be seen from the graphs that the simulated moisture levels are in good agreement with measured ones. Based on this good agreement, it was decided to compare simulated and measured pesticide levels in the soil.

Figure 7.6 shows the total simulated and measured atrazine concentration in adsorbed and liquid phases at 0.1 and 0.3 m depths vs. time. This figure shows that simulated and observed data at 0.1 m on same days are in fairly good agreement, whereas those at 0.30 m depth do not match well. The model under-estimated metribuzin leaching (Figure 7.7), and on the other hand, over-estimated metolachlor transport (Figure 7.8). Like measured value patterns, the model also responded to first and second simulated rainfall, since considerable atrazine and metribuzin leaching occurred right after these rainfall events.

To study the distribution of herbicide concentration with depth (soil profile), the snapshots of total simulated and observed herbicide concentrations 6, 30, and three months after application at 0.1, 0.3, 0.5, and 0.7 m depth were plotted. Tables 7.2 to 7.4 compare these results for atrazine, metribuzin, and metolachlor residues. Figures 7.9 to 7.17 present these results as plotted charts. Figures 7.9 to 7.11 show the variation of simulated and observed soil atrazine concentration with depth at 6, 30, and three months after atrazine application (AA). Comparison among Figures 7.9 to 7.11 defines the distribution of atrazine with time. Although, the simulated and measured values at 0.1 m are in fairly close agreement, the model under-estimated atrazine concentration at other depths and times. This agrees with results found by other researchers (Kaluli et al., 1997; Smith et al., 1989). According to the simulated results presented in Tables B6 to B8 in Appendix B, atrazine hardly leached below 0.2 m depth in the entire simulation period. However, the simulated results always followed the leaching pattern of measured data. Accumulation of atrazine above the 0.2 m depth could be caused by the high adsorption rate simulated by the linear adsorption/desorption isotherm in PRZM2. The higher atrazine concentration

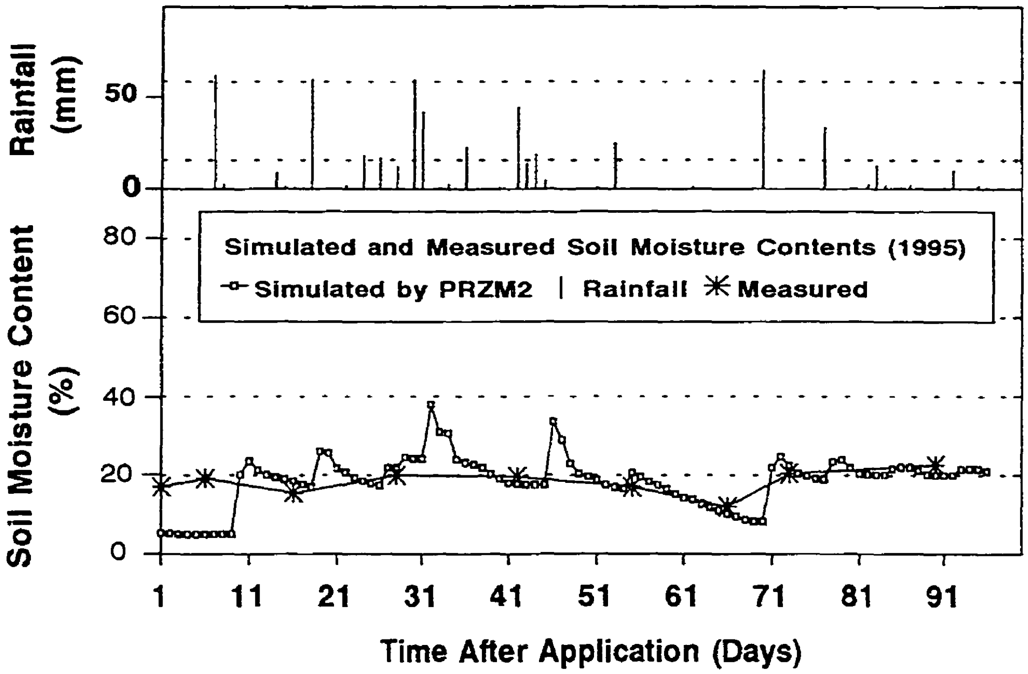

Figure 7.4. Soil moisture content in atrazine and metolachlor lysimeters

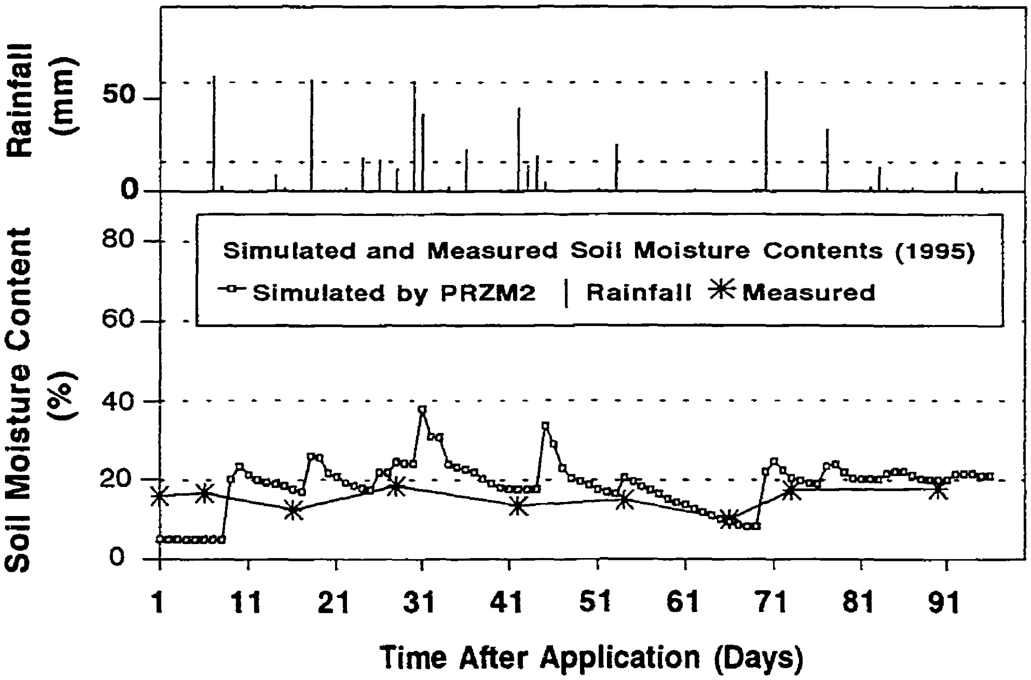

Figure 7.5. Soil moisture content in metribuzin lysimeters

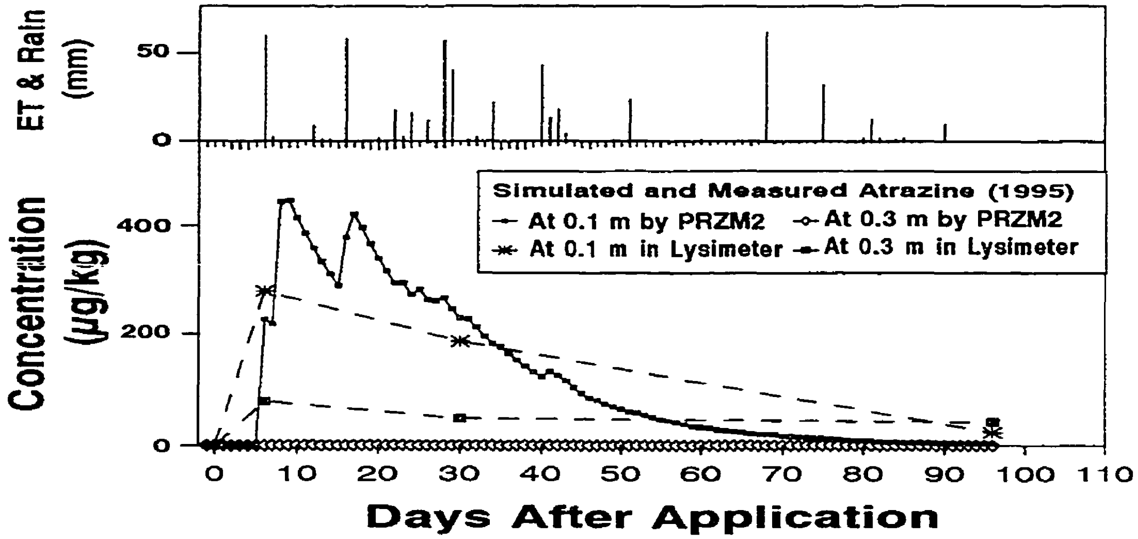

Figure 7.6. Comparison of simulated and measured atrazine

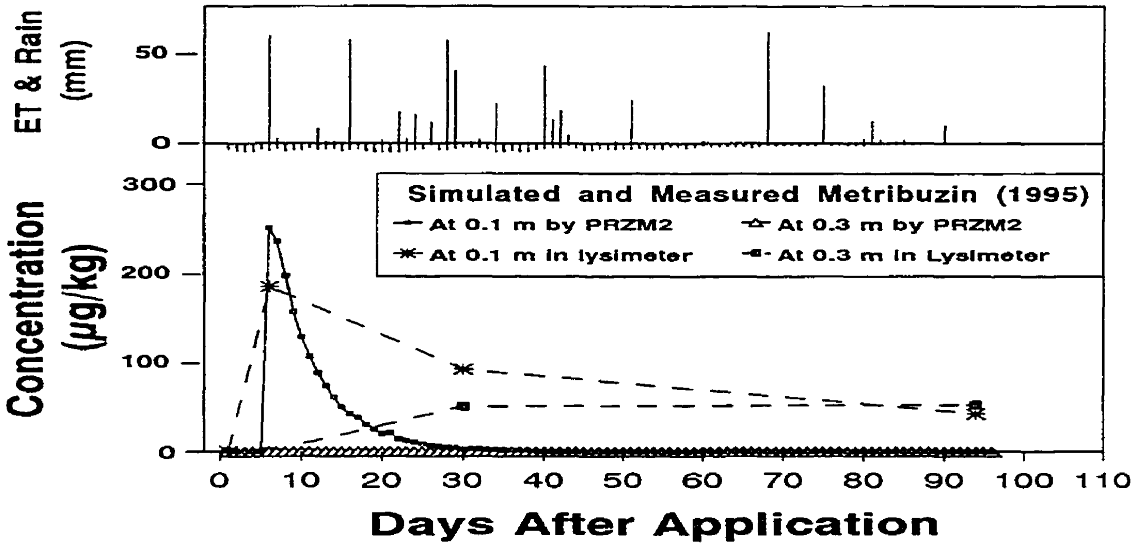

Figure 7.7. Comparison of simulated and measured metribuzin

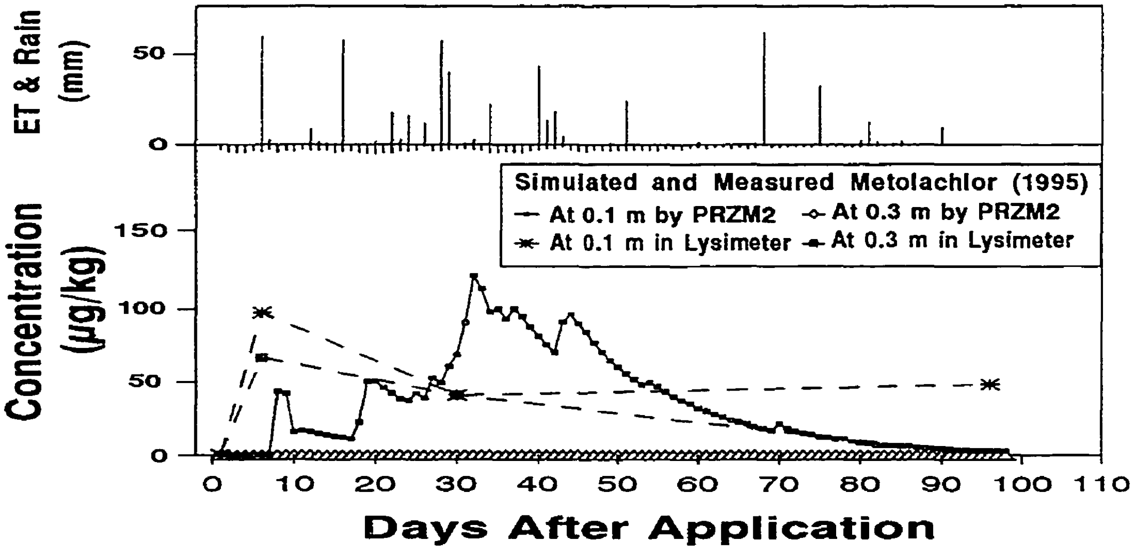

Figure 7.8. Comparison of simulated and measured metolachlor

Table 7.2. Comparison of Simulated and Measured Atrazine Residues in Soil in Free Drainage Lysimeters in 1995.

Days After Application	Depth (m)	**Average Measured** Conc. (μg/kg)	**Simulated** Conc.(μg/kg)
	0.10	280 (40.0*)	228.3
6	0.30	80 (10.0)	0.2E-15
	0.50	5.2 (7.40)	0.0
	0.70	0.0 (0.00)	0.0
	0.10	188.6(20.5)	247.3
30	0.30	49.2 (28.0)	0.2E-10
	0.50	23.4 (40.5)	0.0
	0.70	29.7 (9.70)	0.0
	0.10	23.70 (2.80)	2.99
90	0.30	42.45 (8.00)	0.2E-5
	0.50	25.90 (4.10)	0.0
	0.70	45.90 (5.90)	0.0

* Standard Deviation

Table 7.3. Comparison of Simulated and Measured Metribuzin Residues in Soil in Free Drainage Lysimeters in 1995

Days After Application	Depth (m)	**Average Measured** Conc. (μg/kg)	**Simulated** Conc. (μg/kg)
	0.10	185 (15.0*)	236.0
6	0.30	0.0 (0.00)	0.1E-16
	0.50	0.0 (0.00)	0.0
	0.70	0.0 (0.00)	0.0
	0.10	92.5 (7.50)	3.08
30	0.30	51 (9.00)	0.6E-15
	0.50	17 (1.50)	0.0
	0.70	23 (1.00)	0.0
	0.10	42.5 (7.50)	0.2E-4
90	0.30	52.5 (7.50)	0.1E-12
	0.50	30 (5.00)	0.0
	0.70	15 (0.00)	0.0

* Standard Deviation

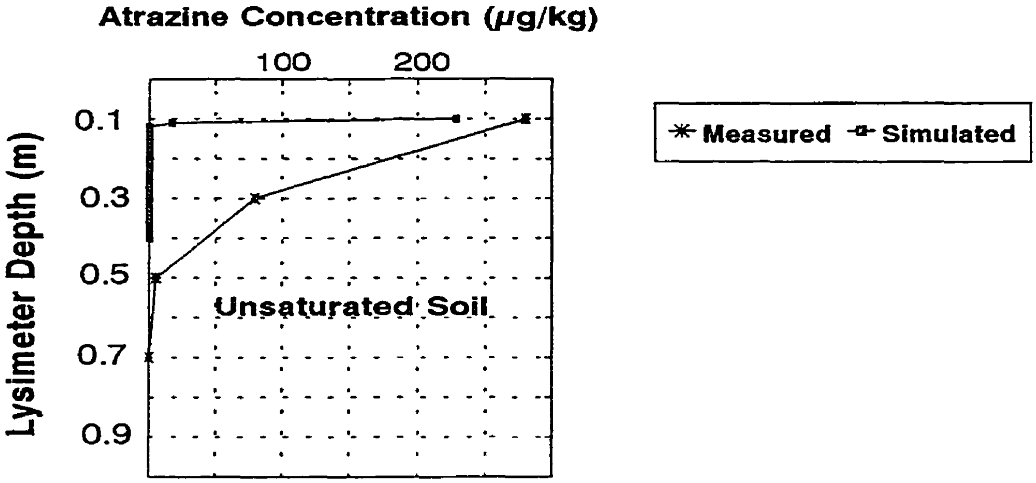

Figure 7.9. Comparison of simulated and measured atrazine in free drainage lysimeter, 6 days after application

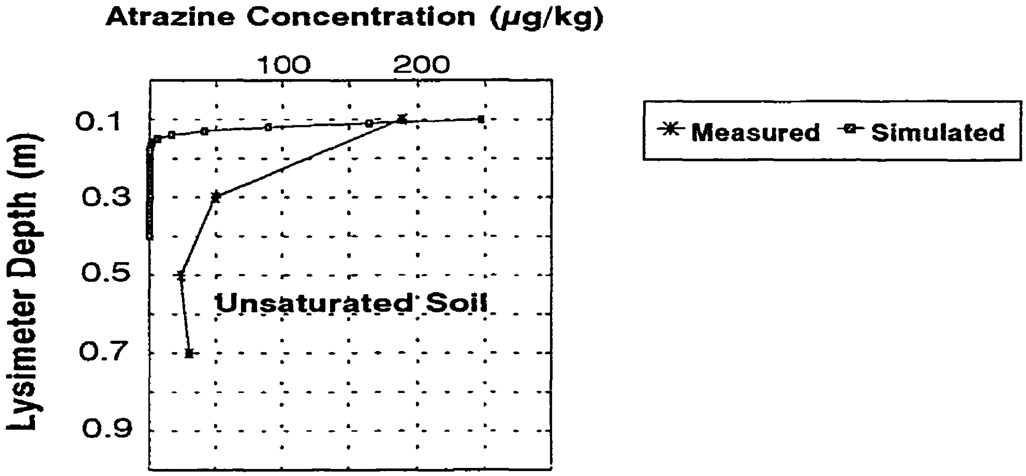

Figure 7.10. Comparison of simulated and measured atrazine in free drainage lysimeter, 30 days after application

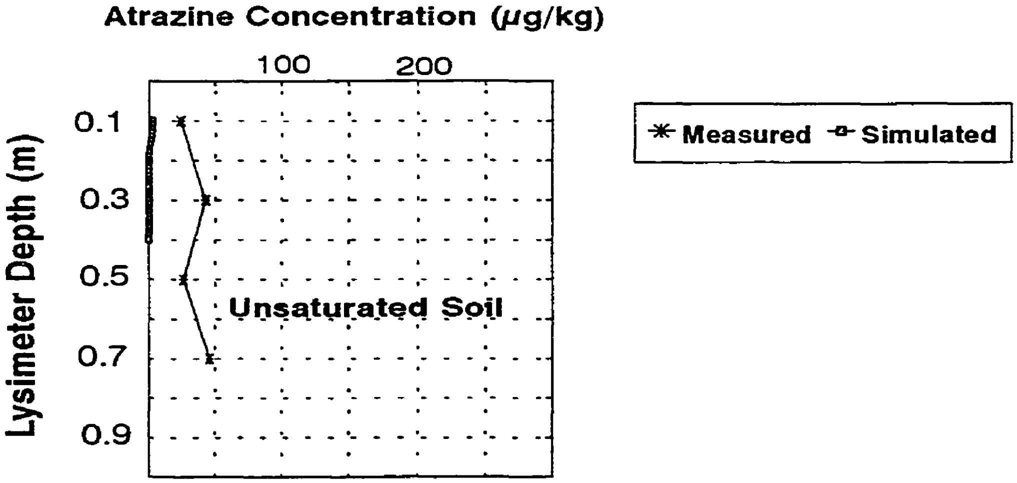

Figure 7.11. Comparison of simulated and measured atrazine in free drainage lysimeter, 90 days after application

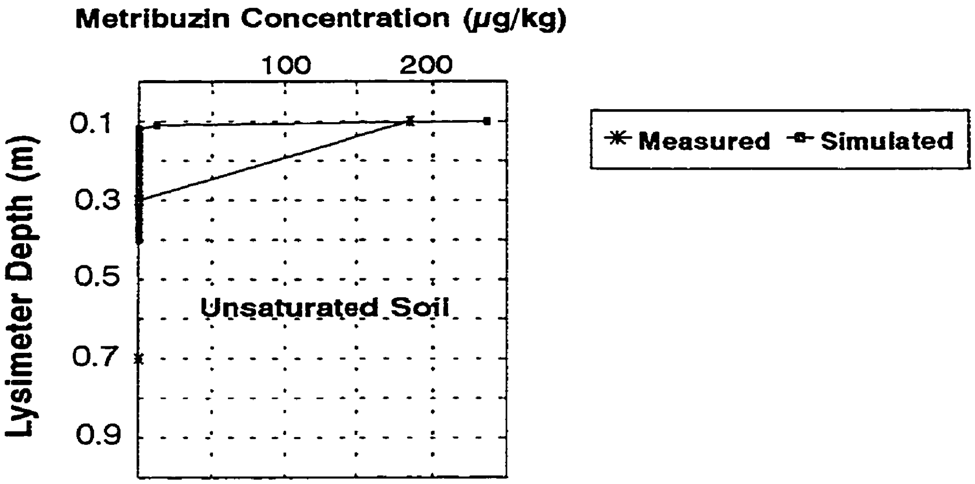

Figure 7.12. Comparison of simulated and measured metribuzin in free drainage lysimeter, 6 days after application

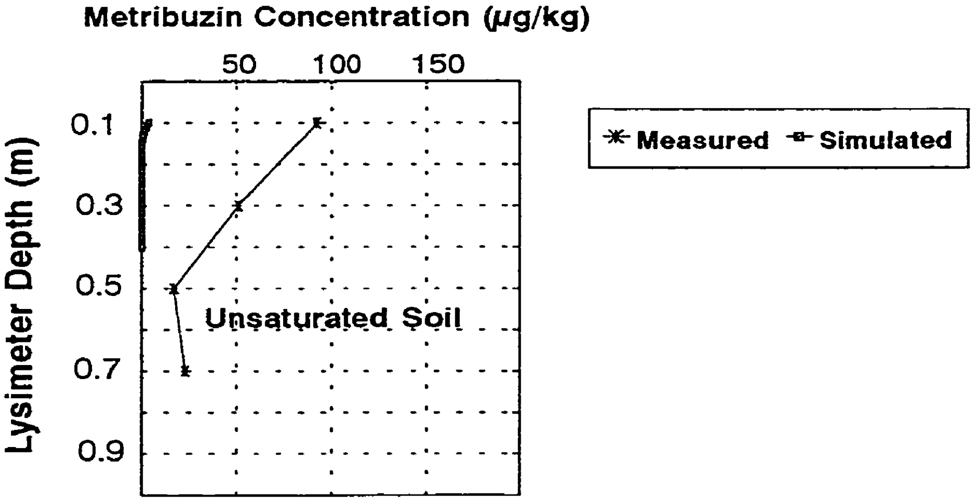

Figure 7.13. Comparison of simulated and measured metribuzin in free drainage lysimeter, 30 days after application

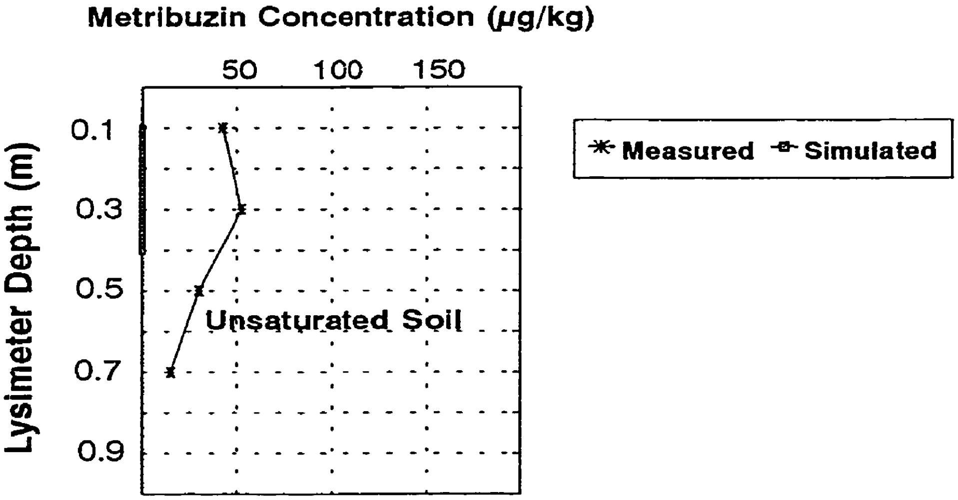

Figure 7.14. Comparison of simulated and measured metribuzin in free drainage lysimeter, 90 days after application

at 0.1 m depth on day 30 (Figure 7.10) could be caused either by leaching from upper layers or higher desorption rate. The comparison of simulated and measured atrazine levels in Figure 7.10 and 7.11 demonstrates faster dissipation of simulated atrazine residues, which may suggest over-estimation of degradation, plant uptake and volatilization by PRZM2. Since the degradation is mainly responsible for loss of pesticide in soil, this implies that the degradation module in PRZM2 may require further testing.

Figures 7.12 to 7.14 show the variation of simulated and observed metribuzin with depth on 6, 30, and three months after application (AA). The arguments used for atrazine also hold for metribuzin, except that shorter half life and faster metribuzin dissipation occurred in the soil profile 30 days after metribuzin application.

Metolachlor results are presented in Figures 7.15 to 7.17. The model demonstrated similar behaviour as atrazine. The model over-estimated the leaching metolachlor concentration at 0.1 m depth on day 30, and under-estimated on all simulation period. These results somewhat agrees with results obtained by other researchers. Dale et al. (1990), who found that PRZM overestimated chemical movement in the silt loam soil of Maryland's Wye Research Station. Smith (1991) reported under-estimation of atrazine levels near the soil surface, and over-estimation below that depth.

Agreement between the simulated and measured herbicide concentrations were quantified with several statistical methods such as the average mean of differences (A.M), average absolute deviation (A.D.), standard error (S.E.), and the coefficient of performance (C.P.). The coefficient of performance determines the accumulated errors of the differences, and is an indicator of the dispersivity between the simulated and observed data (James and Burges, 1982). The

Table 7.4. Comparison of Simulated and Measured Metolachlor Residues in Soil in Free Drainage Lysimeters in 1995

Days After Application	Depth (m)	**Average Measured** Conc. (μg/kg)	**Simulated** Conc. (μg/kg)
6	0.10	95.00 (15.0*)	42.4
	0.30	65.00 (5.00)	0.1E-18
	0.50	49.25 (4.80)	0.0
	0.70	0.00 (0.00)	0.0
30	0.10	40.00 (10.0)	88.19
	0.30	40.00 (10.0)	0.7E-8
	0.50	106.5 (16.5)	0.0
	0.70	6.75 (3.30)	0.0
90	0.10	47.15 (2.90)	2.75
	0.30	0.0 (0.00)	0.2E-3
	0.50	15.95 (16.0)	0.0
	0.70	68.65 (39.1)	0.0

* Standard Deviation

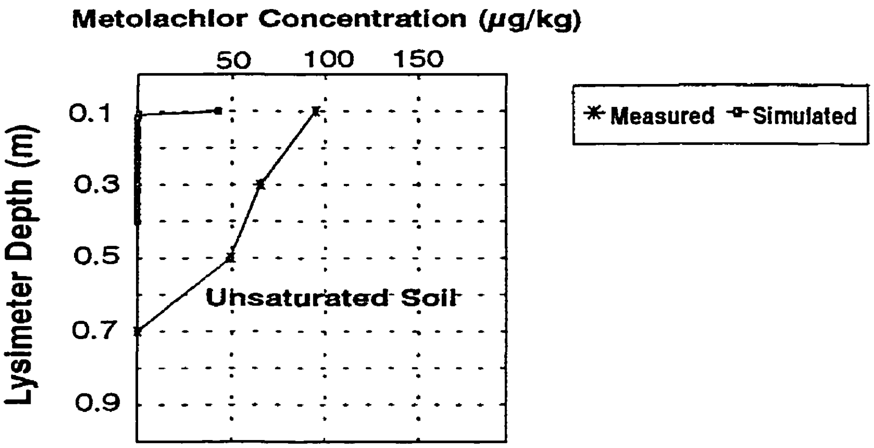

Figure 7.15. Comparison of simulated and measured metolachlor in free drainage lysimeter, 6 days after application

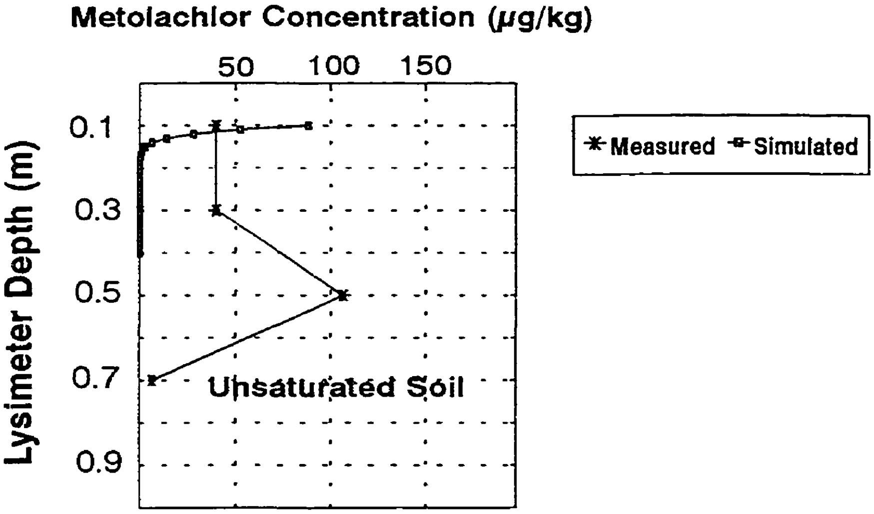

Figure 7.16. Comparison of simulated and measured metolachlor in free drainage lysimeter, 30 days after application

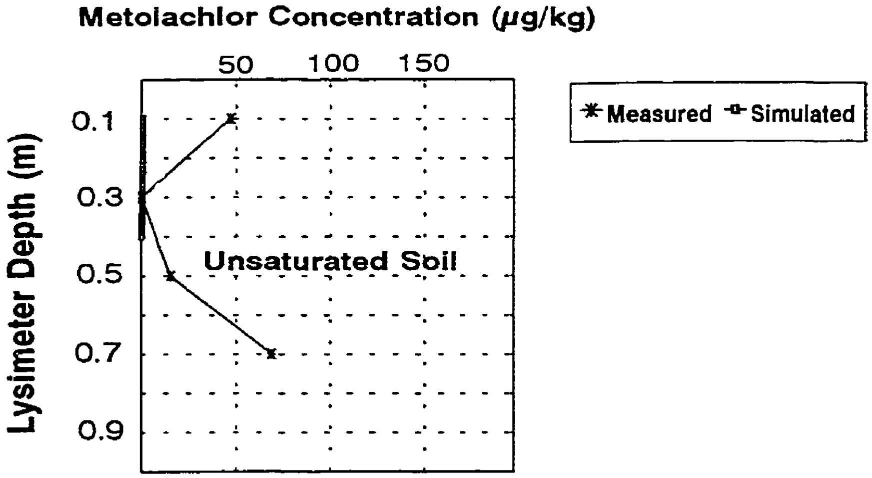

Figure 7.17. Comparison of simulated and measured metolachlor in free drainage lysimeter, 90 days after application

average mean of differences was calculated using the following equation:

$$A.M. = \frac{\sum_{i=1}^{i=n} (O_i - S_i)}{n} \qquad i=1 \; .... \; n \tag{7-13}$$

where

O_i = observed value
S_i = simulated value
n = number of observations

The average absolute deviation was calculated as:

$$A.D. = \frac{\sum_{i=1}^{i=n} |O_i - S_i|}{n} \qquad i=1 \; .... \; n \tag{7-14}$$

The standard error was computed using the following expression:

$$S.E. = \frac{\sqrt{\sum_{i=1}^{i=n} (O_i - S_i)^2}}{n} \qquad i=1 \; .... \; n \tag{7-15}$$

The coefficient of performance of model was calculated as:

$$C.P. = \frac{\sum_{i=1}^{i=n} (S_i - O_i)^2}{\sum_{i=1}^{i=n} (O_i - O_{avg})^2} \qquad i=1 \; .... \; n \tag{7-16}$$

where

O_{avg} = average observed value

The calculated A.M., A.D., S.E. and C.P.'s for atrazine, metribuzin, metolachlor and the soil moisture contents are listed in Tables 7.5 to 7.7. The performance of a model is considered satisfactory when $C.P. \leq 0.5$. The performance of PRZM2 with regard to soil moisture levels was good, since the CP values were always less than 0.5 and A.M., A.D., and S.E. values were low (Tables 7.5 to 7.7). According to Table 7.5, PRZM2 performed well only at 0.1 m depth for atrazine simulation since it demonstrated least A.M. (A.M.=4.5 μg/kg), and CP=0.2. Performance was poor at all depths for metribuzin and metolachlor (CP>0.5).

According to graphical and statistical evaluations, the flow component in PRZM2 did perform well in simulating soil moisture contents, but the transport module under- or over-estimated the pesticide flux simulation. Various processes are coupled together in PRZM2 to determine the fate and transport of pesticides in soil profile. Among the different processes, the convection-dispersion, transformation and adsorption/desorption relations are the most important governing processes. Although neither model verification nor sensitivity analysis were accomplished in this study, the interpretation of time series outputs indicate that the under- or over-estimation of atrazine, metribuzin, and metolachlor leaching, can be mainly attributed to the unrealistic performance of the following processes:

First, inadequacy of the conventional darcian approach for the treatment of advection-dispersion of pesticide transport in the soil matrix. This may cause higher pesticide accumulation on the upper layer and less leaching in to the soil profile.

Table 7.5. Statistical Analysis for The Simulation of Soil Moisture Contents and Atrazine Residues by PRZM2

Simulation	Depth (m)	Days After Application	A.M.	A.D.	S.E.	**C.P.**
Moisture	Root Zone	Entire Sampling Period	0.2	1.7	1.9	0.1
Atrazine	0.10	6, 30, 90	4.5	43.7	46.7	0.2
	0.30	6, 30, 90	57.2	57.2	59.5	13.3
	0.50	6, 30, 90	18.2	18.2	20.4	4.9
	0.70	6, 30, 90	25.2	25.2	31.6	2.8

Table 7.6. Statistical Analysis for The Simulation of Soil Moisture Contents and Metribuzin Residues by PRZM2

Simulation	Depth (m)	Days After Application	A.M.	A.D.	S.E.	**C.P.**
Moisture	Root Zone	Entire Sampling Period	2.7	2.7	3.0	0.5
Metribuzin	0.10	6, 30, 90	27	61	64.3	1.2
	0.30	6, 30, 90	34.5	34.5	42.3	3.0
	0.50	6, 30, 90	15.7	15.7	19.9	2.6
	0.70	6, 30, 90	12.7	12.7	15.9	2.8

Table 7.7. Statistical Analysis for The Simulation of Soil Moisture Contents and Metolachlor Residues by PRZM2

Simulation	Depth (m)	Days After Application	A.M.	A.D.	S.E.	**C.P.**
Moisture	Root Zone	Entire Sampling Period	0.2	1.7	1.9	0.1
Metolachlor	0.10	6, 30, 90	16.3	48.4	48.5	3.9
	0.30	6, 30, 90	35.0	35.0	44.1	2.7
	0.50	6, 30, 90	57.2	57.2	68.4	3.3
	0.70	6, 30, 90	25.1	25.1	39.8	1.7

Secondly, simplistic instantaneous linear treatment of the adsorption/desorption isotherm, which causes unrealistic retardation or desorption of chemicals, resulting in higher or lesser pesticide concentrations at a particular soil depth.

Thirdly, unrealistic treatment of pesticide transformation mechanisms, which might result in fast dissipation and lesser leaching.

This emphasises the importance of incorporation of more realistic adsorption/desorption isotherm and macropore flow component in the PRZM2 model.

7.6. Summary and Conclusions

The performance of PRZM2 in simulating atrazine, metribuzin, metolachlor residues and moisture contents in soil was evaluated using graphical and statistical methods. The average mean of differences (A.M.), absolute deviation (A.D.), standard error (S.E.) and coefficient of performance (C.P.) at each depth were estimated. The model performance was good in estimating soil moisture contents and atrazine residues at 0.1 m depth (CP<0.5). But the model did poorly at other depths for atrazine, and at all depths for metribuzin and metolachlor.

In general, the simulated values for all three herbicides in most of the cases followed the leaching pattern of observed data. But model either under- or over-estimated the herbicide concentrations in soil. This confirms findings of some other researchers who found similar function for PRZM model (i.e. Smith et al., 1989; Dale et al., 1990; Smith, 1991; Kaluli et al., 1997). Under and/or over-estimation of atrazine, metribuzin, and metolachlor concentration by model, is attributed to simplistic instantaneous linear adsorption/desorption, inadequacy of conventional darcian approach for the treatment of matrix flow, and unrealistic treatment of pesticide transformation pathways. This emphasises the importance of incorporation of more realistic adsorption/desorption isotherm and macropore flow component in the model.

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CHAPTER 8

SUMMARY AND OVERALL CONCLUSIONS

A three-year field lysimeter study was undertaken to evaluate the role of subirrigation in reducing pollution from three herbicides, namely atrazine, metribuzin, and metolachlor. Eighteen PVC lysimeters, 1.0 m high x 0.45 m diameter, were packed with a sandy soil. Three water table management treatments in three replicates were used, i.e. subirrigation with a constant water table depth of 0.4 m, subirrigation with a constant water table depth of 0.8 m, and free drainage. Nine lysimeters received atrazine and metolachlor, while the remaining nine received metribuzin only. Soil and water samples were collected and analyzed from the different treatments at different time intervals.

A laboratory batch test was also conducted on the same sandy soil to study the role of soil moisture content on the degradation of these three herbicides. A mathematical model PRZM2 was used to simulate fate and transport of the three herbicides in the soil profile of subsurface drained lysimeters.

Based on the findings from these studies, the following final conclusions were drawn:

1. From the experimental results obtained from the lysimeter study, it can be concluded that lower pesticide pollution can be expected from the soils of subirrigated farms. These findings support the environmental benefits of subirrigation systems for corn and potato farms that use atrazine and metribuzin. These findings also provide adequate support for the recommendation of subirrigation systems as BMPs for corn and potato farms in Quebec, in order to reduce non-point pesticide pollution from agricultural lands.

2. According to results of repeated measure analysis of variance, the concentration of pesticides in the soil and soil solutions in the 0.4 m subirrigation treatment were significantly reduced for atrazine and metribuzin. This indicates that a shallower water table causes a faster dissipation of atrazine and metribuzin in the soil profile and hence may reduce environmental pollution from corn and potato fields, respectively.

3. Results of three years of lysimeter study supported with a laboratory batch investigation, showed no significant difference between the metolachlor residues among different water table management treatments. This suggests that the metolachlor residues and the associated risk of environmental pollution from subirrigated corn and soybean farms of Quebec, may not reduce significantly. Therefore, other BMPs must be exploited to examine the possibility of non-point pollution from agricultural farms which use metolachlor herbicide.

4. Results of laboratory studies on the degradation of atrazine, metribuzin, and metolachlor herbicides at various soil moisture content have shown that the degradation of atrazine and metribuzin is closely related to soil moisture content. But the effect of soil moisture content on the degradation of

metolachlor was not statistically significant.

5. In all water table management treatments, the surface applied atrazine, metribuzin, and metolachlor were found to be quite mobile in the St. Amable sandy soil, as they leached to lower soil depths, following the natural or simulated rainfall events. This suggests that the potential leaching of these three herbicides from corn, soybean, and potato farms of southern Quebec can be a real threat to the groundwater contamination.

6. The concentration of pesticides in the solid and liquid phases reduced with soil depth in all treatments. The brief explanation for this is that: pesticides were lost by biodegradation or were retarded by adsorption at the shallower depth, leaving less pesticide available for leaching to the deeper soil depth.

7. The concentration of pesticides in soil and soil solutions of different water table treatments reduced with time at all depths at different rates. This suggests that pesticides degrade mainly through soil physical, chemical and biological activities.

8. A computer simulation model (PRZM2) was used to simulate atrazine, metribuzin, and metolachlor leaching in sandy soil columns under subsurface drainage condition. In general, the simulated values for all three chemicals followed the leaching pattern of observed data in most cases. But the model either under- or over-estimated the herbicide concentrations in soil. Under- and/or over-estimation of atrazine, metribuzin, and metolachlor concentration by PRZM2, may be due to simplistic instantaneous linear adsorption/desorption, inadequacy of conventional darcian approach for the treatment of matrix flow, and unrealistic treatment of pesticide transformation pathways. This emphasises the necessity of incorporation of

more realistic adsorption/desorption isotherm, and macropore flow component in this model.

CHAPTER 9

RECOMMENDATIONS FOR FUTURE RESEARCH

Although, the lysimeter and laboratory experiments were successfully conducted as planned, but like many other research work few additional observations and some shortcomings were also encountered during the course of this study. The results from both experiments and computer simulation revealed the following areas for further investigation:

(i) This lysimeter study was successfully conducted in packed sandy soil columns to study fate of atrazine, metribuzin, and metolachlor. Since there are some other dominant soil types in southern Quebec (i.e. sandy loam and loamy soils), it is recommended that similar experiment be conducted to study the fate of above-mentioned herbicides under subirrigation in these soils.

(ii) Since with the results of this experiment, it is evident that subsurface irrigation systems can significantly reduce the atrazine and metribuzin pollution from uniform sandy soils in southern Quebec, it may be then appropriate to extend this study to intact (undisturbed) soil columns for loamy and sandy loam soils.

(iii) The environmental impact of subirrigation systems on the reduction of pollution from of atrazine, metribuzin, and metolachlor parent compound was studied, it is recommended that in the future investigations fate of metabolites be also included in the studies.

(iv) With the expansion of subirrigation in southern Quebec, there is need for a computer model that can simulate environmental impact of water table management with regard to pesticide and fertilizer loadings. It is, therefore, recommended that a well documented computer model, which can handle water table management systems be tested and calibrated for different soil types and chemicals under southern Quebec climatological conditions. This will facilitate the development of best management practices based on local conditions, to better demonstrate the environmental impacts of water table management.

APPENDIX A

EXPERIMENTAL DATA

Table A.1. Climatological data (1993)

(Macdonald Campus)

Day	Month	Water added (mm)	Water removed (mm)	Precip. (mm)	Water loss pan	Accum. wind run (km)	Daily wind run (km)	Water maximum temp	Water minimum temp
4	6								
7	6	start	start	start	-	7980.7	-	-	-
8	6	-	-	-	-	-	-	-	-
9	6	5.65	0	21	26.65	8099.4	118.7	-	-
10	6	0	0.05	12	11.95	8190.4	91	-	-
11	6	3.8	0	2	5.8	8294.9	104.5	-	-
12	6	2.4	0	0	2.4	8341.3	46.4	25	15.5
13	6	6.7	0	0	6.7	8398.2	56.9	35	19
14	6	6.45	0	0	6.45	8433.2	35	35	19
15	6	7.2	0	0	7.2	8488.2	55	34	19.5
16	6	0	17	18.5	1.5	8545.9	57.7	23.5	16.5
17	6	4	0	0	4	8598.5	52.6	27	15.5
18	6	2	0	2.2	4.2	8637.8	39.3	30.5	19.5
19	6	0	8.5	9.8	1.3	8666.5	28.7	30	18
20	6	0	18.5	25	6.5	8769	102.5	30	19
21	6	0	0.2	6.3	6.1	8771.6	2.6	21	19.5
22	6	0	21.6	26.7	5.1	8820.2	48.6	26	20
23	6	4.7	0	1.1	5.8	8961.1	140.9	26.5	12
24	6	7.2	0	0	7.2	9029	67.9	31	15
25	6	2.9	0	0	2.9	9061.9	32.9	28.5	16
26	6	6.4	0	0	6.4	9149.9	88	35	19
27	6	6.5	0	0	6.5	9237.3	87.4	31.5	18
28	6	0	1.35	7.4	6.05	9320.9	83.6	32.5	20
29	6	3.6	0	1.5	5.1	9377.1	56.2	29	20
30	6	2.05	0	0	2.05	9424.3	47.2	28	16.5
1	7	7.4	0	0	7.4	9471.8	47.5	34	18.5
2	7	5	0	0	5	9506	34.2	34	18
3	7	0	1	2.8	1.8	9570	64	30	18.5
4	7	2.2	0	0	2.2	9609.6	39.6	31	18.5
5	7	6.8	0	0	6.8	9642	32.4	34.5	19
6	7	4.35	0	0	4.35	9686.1	44.1	33	22.5
7	7	6.8	0	0	6.8	9766.7	80.6	37	22.5
8	7	4.8	0	1.2	6	9805.1	38.4	37	22.5
9	7	0	0.4	3.3	2.9	9848.1	43	31	24
10	7	5	0	0.4	5.4	9904.9	56.8	35.5	24
11	7	7.8	0	0	7.8	9973.5	68.6	35.5	21
12	7	0	2	8	6	10023.9	50.4	35.5	22
13	7	2.6	0	2.3	4.9	10083.4	59.5	34	20
14	7	7.2	0	0	7.2	10138.1	54.7	33.5	19.5
15	7	1.6	0	0.4	2	10174.9	36.8	29.5	19
16	7	7.1	0	0.6	7.7	10250.5	75.6	30.5	17
17	7	5.6	0	0.2	5.8	10361.7	111.2	28	15
18	7	4.6	0	0	4.6	10402.8	41.1	30.5	18.5
19	7	5.2	0	0	5.2	10436.6	33.8	34.5	20
20	7	4.2	0	0	4.2	10492.9	56.3	32	21.5
21	7	0	22.8	29.6	6.8	10544.6	51.7	29.5	19.5
22	7	4.6	0	0.2	4.8	10617.9	73.3	30	16.5
23	7	0	0.7	3.6	2.9	10692.4	74.5	30.5	15.5
24	7	3.1	0	0	3.1	10701.5	9.1	31	18.5
25	7	5.3	0	0	5.3	10753.4	51.9	32	18
26	7	6.3	0	0	6.3	10803.7	50.3	33	17
27	7	0	14.9	20.8	5.9	10938.4	134.7	31.5	19.5
28	7	0	7.85	10.7	2.85	10967.4	29	31.5	21
29	7	0	3.65	7.7	4.05	11014.5	47.1	34.5	23
30	7	4.2	0	0.4	4.6	11073.8	59.3	32.5	21
31	7	0	1.7	1	-0.7	11108.5	34.7	30.5	20.5

Table A.1. Climatological data (1993)

1	8	4.6	0	0	4.6	11144.7	36.2	32.5	20.5
2	8	2.2	0	3	5.2	11173.2	28.5	33	21
3	8	5.2	0	0	5.2	11226.7	53.5	36.5	20.5
4	8	2.2	0	1	3.2	11277.6	50.9	34	18.5
5	8	1	0	3.3	4.3	11330.3	52.7	32.5	17.5
6	8	2.6	0	0.4	3	11374.4	44.1	25.5	15.5
7	8	4.8	0	0	4.8	11418.4	44	31.5	17.5
8	8	4.8	0	0	4.8	11458.1	39.7	32	17.5
9	8	5	0	0	5	11489.3	31.2	34	19
10	8	5.6	0	0.2	5.8	11518.9	29.6	34	18.5
11	8	1.2	0	0.6	1.8	11582.3	63.4	28	19
12	8	0	2.15	6.4	4.25	11651.2	68.9	30	21
13	8	1.2	0	1.2	2.4	11680.3	29.1	29.5	21.5
14	8	3.4	0	0	3.4	11708.8	28.5	33	21
15	8	4.3	0	0	4.3	11750.1	41.3	35	18.5
16	8	4.2	0	0	4.2	11793.7	43.6	36	19
17	8	2.1	0	2.4	4.5	11822.1	28.4	36	19.5
18	8	3.7	0	0.4	4.1	11910.1	88	35	21
19	8	1.4	0	0.2	1.6	11942.4	32.3	26.5	18
20	8	2.4	0	0	2.4	11989.7	47.3	30	16
21	8	1.7	0	5.8	7.5	12043.3	53.6	30	14.5
22	8	1.3	0	0	1.3	12095.7	52.4	30.5	13.5
23	8	1.5	0	0	1.5	12137.6	41.9	30.5	16.5

Table A.2. Soil volumetric moisture content at root zone (1993)

(%)

0.4 m Subirrigation

Metribuzin

Days	at 0-40 m			High	Low	Avg.	Sd.Dev.
after Appl	Lysi#7	Lysi#9	Lysi#13				
0	24.6	26.14	26.54	27	25	26	0.83
7	30.59	33.37	34.65	35	31	33	1.69
14	33.51	33.72	34.16	34	34	34	0.27
22	34.02	33.72	33.87	34	34	34	0.12
29	36.2	37.5	39.53	39	36	38	1.37
37	36.94	36.47	35.64	37	36	36	0.54
47	37.26	34.16	35.89	37	35	36	1.27
64	35.42	35.42	34.89	35	35	35	0.25

0.4 m Subirrigation

Atrazine & Metolachlor

Days	at 0-40 m			High	Low	Avg.	Sd.Dev.
after Appl	Lysi#6	Lysi#10	Lysi#16				
0	24.86	25.77	23.3	26	24	25	1.021
7	29.71	39.81	30.12	38	29	33	4.67
14	30.99	33.8	31.09	33	31	32	1.302
22	30.43	28.76	31.54	31	29	30	1.146
29	34.59	32.81	36.47	36	33	35	1.496
37	34.34	30.78	34.34	35	31	33	1.679
47	33.51	32.19	35.12	35	32	34	1.199
64	33.24	29.78	32.41	33	30	32	1.473

0.8 m Subirrigation

Metribuzin

Days	at 0-40 m			High	Low	Avg.	Sd.Dev.
after Appl	Lysi#1	Lysi#5	Lysi#17				
0	21.54	20.26	21.37	22	20	21	0.566
7	22.75	18.33	19.44	22	18	20	1.876
14	20.54	18.88	19.43	20	19	20	0.689
22	19.98	17.77	18.88	20	18	19	0.903
29	24.41	22.19	25.52	25	23	24	1.385
37	24.41	22.2	24.38	25	23	24	1.035
47	24.41	23.3	26.05	26	23	25	1.129
64	23.3	21.09	22.19	23	21	22	0.901

0.8 m Subirrigation

Atrazine & Metolachlor

Days	at 0-40 m			High	Low	Avg.	Sd.Dev
after Appl	Lysi#4	Lysi#8	Lysi#12				
0	16.52	24.98	21.98	25	18	21	3.501
7	15.73	20.54	22.43	22	17	20	2.818
14	15.73	20.54	22.75	23	17	20	2.931
22	15.64	17.77	18.87	19	16	17	1.342
29	18.96	23.3	24.42	25	20	22	2.356
37	20.01	21.09	24.42	24	20	22	1.878
47	21.63	24.97	23.87	25	22	23	1.387
64	18.91	21.09	22.2	22	19	21	1.366

Free Drainage

Metribuzin

Days	at 0-40 m			High	Low	Avg.	Sd.Dev.
after Appl	Lysi#2	Lysi#11	Lysi#14				
0	19.6	14.72	19.98	20	16	18	2.397
7	18.61	13.85	18.32	19	15	17	2.18
14	16.69	13.09	16.12	17	14	15	1.582
22	15.58	11.43	16.66	17	12	15	2.253
29	19.99	16.84	22.19	22	17	20	2.195
37	19.98	16.75	21.37	21	17	19	1.935
47	23.3	21.09	23.87	24	22	23	1.198
64	19.99	15.73	19.98	21	17	19	2.006

Free Drainage

Atrazine & Metolachlor

Days	at 0-40 m			High	Low	Avg.	Sd.Dev
after Appl	Lysi#3	Lysi#15	Lysi#18				
0	23.09	22.2	23.86	24	22	23	0.678
7	19.43	19.43	19.99	20	19	20	0.263
14	17.21	18.33	18.88	19	17	18	0.697
22	15.56	16.66	18.87	18	16	17	1.375
29	22.2	23.3	22.2	23	22	23	0.518
37	23.32	21.09	21.09	23	21	22	1.048
47	23.87	23.87	26.07	26	24	25	1.036
64	19.98	19.98	21.09	21	20	20	0.523

Table A.3. Herbicide concentration in soil solution (1993)

(µg/L)

0.4 m Subirrigation

Metribuzin

Days after Appl	at 0.45 m				at 0.85 m			
	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
0	0	0	0	0.00	0	0	0	0.00
7	2.5	1.1	1.8	0.74	2.9	0.3	1.6	1.29
14	0.1	0	0.1	0.06	0.6	0.2	0.4	0.18
22	0	0	0	0.00	0.9	-0	0.4	0.54
29	0.8	0	0.4	0.40	0.7	0	0.3	0.34
37	none	none	none	none	none	none	none	none
47	none	none	none	none	2.3	1.1	1.7	0.59
64	0	0	0	0.00	none	none	none	none

0.4 m Subirrigation

Atrazine

Days after Appl	at 0.45 m				at 0.85 m			
	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
0	0	0	0	0.00	0	0	0	0.00
7	1.2	0.1	0.679	0.55	1	0.6	0.8	0.20
14	0.1	-0	0.048	0.05	0.2	0.1	0.1	0.04
22	none	none	none	none	0.7	0	0.4	0.37
29	12	-2	5.234	7.07	0.7	-0	0.3	0.41
37	none	none	none	none	none	none	none	none
47	0	0	0	0.00	0.2	0	0.1	0.08
64	0	0	0	0.00	none	none	none	none

0.4 m Subirrigation

Metolachlor

Days after Appl	at 0.45 m				at 0.85 m			
	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
0	2.5	0.4	1.4	1.07	1.6	-0	0.7	0.94
7	4.8	2	3.4	1.43	2	0.5	1.3	0.75
14	1.9	-0	1	0.98	0.4	0.1	0.3	0.14
22	none	none	none	none	1.2	0	0.6	0.58
29	32	-5	13	18.54	0.7	-0	0.3	0.41
37	none	none	none	none	none	none	none	none
47	17	-6	5.4	11.82	1.1	0	0.6	0.57
64	0	0	0	0.00	none	none	none	none

0.8 m Subirrigation

	Metribuzin				Atrazine				Metolachlor			
	at 0.85 m				at 0.85 m				at 0.85 m			
Days after Appl	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
0	0	0	0	0.00	0	0	0	0.00	0	0	0	0.00
7	0	0	0	0.00	0	0	0	0.00	0	0	0	0.00
14	2.2	2.2	2.2	0.00	0	0	0	0.00	0	0	0	0.00
22	2.4	1.4	1.9	0.50	0	0	0	0.00	0	0	0	0.00
29	6.2	1	3.6	2.60	2.3	1	1.7	0.69	8.086	2	5	3.06
37	none	none	none	none	none	none	none	none	none	none	none	none
47	0.9	0	0.5	0.45	1.4	0.7	1	0.33	42.8	2.3	23	20.24
64	0	0	0	0.00	0	0	0	0.00	0	0	0	0.00

Free Drainage

	Atrazine	Metola.
Days after Appl	-0.85 m 'Lysi#3	-0.85 m Lysi#3
0	none	none
7	none	none
14	none	none
22	none	none
29	none	none
37	none	none
47	0.499	54.85
64	none	none

Table A.4. Climatological data (1994)
Macdonald Campus (Seed Farm)

	Days	Rain(mm)	EP(mm)
June	23	0.0	5.9
	24	0.0	4.9
	25	19.3	5
	26	8.0	0
	27	3.5	1.8
	28	32.0	0
	29	54.9	5
	30	1.5	6.7
July	1	0.0	5.6
	2	7.5	5.6
	3	0.0	4.2
	4	1.0	11
	5	0.0	6
	6	0.0	2.9
	7	0.0	3.1
	8	1.2	2
	9	1.3	3.7
	10	7.7	9.4
	11	0.0	4.3
	12	0.0	6.4
	13	0.0	4.1
	14	0.0	6.2
	15	0.0	4.5
	16	13.1	3.6
	17	0.0	3.6
	18	0.0	9.8
	19	0.0	0.7
	20	0.0	5.7
	21	11.4	4
	22	4.8	5.6
	23	0.0	10.6
	24	0.0	3.8
	25	0.0	1.4
	26	6.9	6.2
	27	0.0	7
	28	0.0	3.3
	29	0.0	2.6
	30	6.4	7
	31	0.0	3.3
August	1	0.0	2.4
	2	32.4	2.9
	3	0.0	3
	4	8.0	3.8
	5	6.2	4
	6	0.0	4.4
	7	0.0	3
	8	0.0	5
	9	1.7	5.1
	10	0.0	6
August	11	0.0	2.8
	12	0.0	3.6
	13	0.0	2.4
	14	7.4	2.6
	15	0.0	10.7
	16	0.0	2.3
	17	0.0	3.9
	18	0.0	3.3
	19	0.0	2.5
	20	1.7	4.8
	21	20.7	3.4
	22	0.0	2.8
	23	0.0	5
	24	0.0	4.1
	25	6.2	1.4
	26	0.0	0.3
	27	3.8	2.3
	28	9.6	5
	29	0.0	1.6
	30	0.0	6.2
	31	2.2	1
September	1	3.8	1.1
	2	0.0	0
	3	0.0	0
	4	0.0	0
	5	0.0	0
	6	0.0	13.6
	7	11.2	0
	8	3.9	2.4
	9	2.5	2.4
	10	1.1	0
	11	0.0	0
	12	0.0	6.1
	13	9.3	2.5
	14	14.0	2.5
	15	0.0	0.2
	16	4.6	1.6
	17	5.6	2.7
	18	0.0	3.6
	19	0.0	3.2
	20	0.0	3.5
	21	0.0	2.3
	22	0.0	3.1
	23	0.0	3.8
	24	1.5	0
	25	0.0	1
	26	0.0	3.1
	27	24.9	0
	28	8.4	2.6
	29	14.8	1.2
	30	0.0	5.9

Table A.5. Evapotranspiration data (1994)

Date	R. hum. %	Wind km/day	Ep (mm/d)	kp	ETo mm/day	Kc Potatoes	Kc Corn	ET(pota) mm/day	ET(corn) mm/day
June 1	66.5	139.14	4.8	0.75	3.6	0.43	0.43	1.55	1.55
June 2	77.5	93.08	2.7	0.85	2.295	0.45	0.45	1.03	1.03
June 3	62.5	67.9	0.1	0.75	0.075	0.47	0.47	0.04	0.04
June 4	59.5	83.74	0	0.75	0	0.49	0.49	0.00	0.00
June 5	57	93.08	1.9	0.75	1.425	0.51	0.51	0.73	0.73
June 6	79	67.9	7.5	0.85	6.375	0.53	0.53	3.38	3.38
June 7	84.5	55.01	5.8	0.85	4.93	0.55	0.55	2.71	2.71
June 8	64.5	96.62	4.7	0.75	3.525	0.57	0.57	2.01	2.01
June 9	50.5	74.19	0	0.75	0	0.59	0.59	0.00	0.00
June 10	55.5	76.48	3.5	0.75	2.625	0.61	0.61	1.60	1.60
June 11	55.5	41.96	5.8	0.75	4.35	0.63	0.63	2.74	2.74
June 12	79	107.04	9.3	0.85	7.905	0.65	0.65	5.14	5.14
June 13	71	51.82	14.9	0.85	12.665	0.67	0.67	8.49	8.49
June 14	81.5	41.37	2.9	0.85	2.465	0.69	0.69	1.70	1.70
June 15	73	22.49	0.2	0.85	0.17	0.71	0.71	0.12	0.12
June 16	74	34.89	0	0.85	0	0.73	0.73	0.00	0.00
June 17	70.5	36.1	3.7	0.85	3.145	0.75	0.75	2.36	2.36
June 18	73.5	65.51	5.5	0.85	4.675	0.77	0.77	3.60	3.60
June 19	62.5	88.35	9.5	0.75	7.125	0.79	0.79	5.63	5.63
June 20	63	10.48	12.1	0.75	9.075	0.82	0.82	7.44	7.44
June 21	60	43.68	3	0.75	2.25	0.84	0.84	1.89	1.89
June 22	64.5	145.22	4.2	0.75	3.15	0.86	0.86	2.71	2.71
June 23	64.5	111.27	5.9	0.75	4.425	0.88	0.88	3.89	3.89
June 24	67.5	52.79	6.9	0.75	5.175	0.9	0.9	4.66	4.66
June 25	85.5	157.7	10.7	0.85	9.095	0.93	0.93	8.46	8.46
June 26	79	44.615	5.8	0.75	4.35	0.95	0.95	4.13	4.13
June 27	94	44.615	0.9	0.85	0.765	0.97	0.97	0.74	0.74
June 28	84.5	93.7	0	0.85	0	0.99	0.99	0.00	0.00
June 29	82.5	53.96	0.2	0.85	0.17	1.01	1.01	0.17	0.17
June 30	82.5	65.4	6.7	0.85	5.695	1.03	1.03	5.87	5.87
July 1	74.5	20.35	5.6	0.85	4.76	1.05	1.05	5.00	5.00
July 2	76.5	29.99	5.6	0.85	4.76	1.05	1.05	5.00	5.00
July 3	70.5	11.26	4.2	0.85	3.57	1.05	1.05	3.75	3.75
July 4	64.5	51.34	11	0.75	8.25	1.05	1.05	8.66	8.66
July 5	74.5	39.85	6	0.85	5.1	1.05	1.05	5.36	5.36
July 6	75.5	44.14	2.9	0.85	2.465	1.05	1.05	2.59	2.59
July 7	74.5	30.08	3.1	0.85	2.635	1.05	1.05	2.77	2.77
July 8	83	36.68	2	0.85	1.7	1.05	1.05	1.79	1.79
July 9	73	75.9	4.6	0.85	3.91	1.05	1.05	4.11	4.11

Table A.5. Evapotranspiration data (1994)

July 10	76.5	113.1	9.4	0.85	7.99	1.05	1.05	8.39	8.39
July 11	64.5	53.13	4.3	0.75	3.225	1.05	1.05	3.39	3.39
July 12	66	52.2	6.4	0.75	4.8	1.05	1.05	5.04	5.04
July 13	69.5	88.3	4.1	0.75	3.075	1.05	1.05	3.23	3.23
July 14	64.5	57.9	6.2	0.75	4.65	1.05	1.05	4.88	4.88
July 15	79.5	67.73	4.5	0.85	3.825	1.05	1.05	4.02	4.02
July 16	74	63.89	3.6	0.85	3.06	1.05	1.05	3.21	3.21
July 17	72.5	19.97	3.6	0.85	3.06	1.05	1.05	3.21	3.21
July 18	75	39	9.8	0.85	8.33	1.05	1.05	8.75	8.75
July 19	71	18.17	0.7	0.85	0.595	1.05	1.05	0.62	0.62
July 20	67	74.36	5.7	0.75	4.275	1.05	1.05	4.49	4.49
July 21	76	29.63	4	0.85	3.4	1.05	1.05	3.57	3.57
July 22	78	38.03	5.6	0.85	4.76	1.05	1.05	5.00	5.00
July 23	70.5	141.48	10.6	0.85	9.01	1.05	1.05	9.46	9.46
July 24	69	77.31	3.8	0.75	2.85	1.05	1.05	2.99	2.99
July 25	68	46.99	1.4	0.75	1.05	1.05	1.05	1.10	1.10
July 26	69.5	38.56	6.2	0.75	4.65	1.05	1.05	4.88	4.88
July 27	66	69.58	7	0.75	5.25	1.05	1.05	5.51	5.51
July 28	76	39.58	3.3	0.85	2.805	1.05	1.05	2.95	2.95
July 29	69.5	34.1	2.6	0.75	1.95	1.05	1.05	2.05	2.05
July 30	76	87.82	7	0.85	5.95	1.05	1.05	6.25	6.25
July 31	76	27.31	3.3	0.85	2.805	1.05	1.05	2.95	2.95
Aug 1	69.5	271.2	2.4	0.7	1.68	1.04	1.04	1.75	1.75
Aug 2	88.5	235.2	2.9	0.75	2.175	1.03	1.03	2.24	2.24
Aug 3	82.5	148.8	3	0.85	2.55	1.02	1.02	2.60	2.60
Aug 4	79.5	216	3.8	0.75	2.85	1.01	1	2.88	2.85
Aug 5	68	206.4	4	0.7	2.8	1	0.98	2.80	2.74
Aug 6	69.5	136.8	4.4	0.65	2.86	0.99	0.96	2.83	2.75
Aug 7	70.5	67.2	3	0.85	2.55	0.98	0.95	2.50	2.42
Aug 8	69.5	100.8	5	0.75	3.75	0.97	0.93	3.64	3.49
Aug 9	68.5	288	5.1	0.7	3.57	0.96	0.91	3.43	3.25
Aug 10	69.5	292.8	6	0.7	4.2	0.95	0.88	3.99	3.70
Aug 11	67.5	348	2.8	0.7	1.96	0.94	0.87	1.84	1.71
Aug 12	74	189.6	3.6	0.75	2.7	0.93	0.85	2.51	2.30
Aug 13	79	240	2.4	0.75	1.8	0.92	0.84	1.66	1.51
Aug 14	70	511.2	2.6	0.6	1.56	0.91	0.83	1.42	1.29
Aug 15	75.5	499.2	10.7	0.65	6.955	0.9	0.79	6.26	5.49
Aug 16	70	304.8	2.3	0.7	1.61	0.89	0.78	1.43	1.26
Aug 17	72.5	280.8	3.9	0.75	2.925	0.88	0.8	2.57	2.34
Aug 18	79.5	242.4	3.3	0.75	2.475	0.87	0.78	2.15	1.93
Aug 19	75.5	141.6	2.5	0.85	2.125	0.86	0.77	1.83	1.64
Aug 20	78.5	196.8	4.8	0.75	3.6	0.85	0.74	3.06	2.66

Table A.5. Evapotranspiration data (1994)

Aug 21	89	175.2	3.4	0.75	2.55	0.84	0.71	2.14	1.81
Aug 22	73	216	2.8	0.75	2.1	0.83	0.7	1.74	1.47
Aug 23	65	134.4	5	0.75	3.75	0.82	0.67	3.08	2.51
Aug 24	72	91.2	4.1	0.85	3.485	0.81	0.64	2.82	2.23
Aug 25	88	213.6	1.4	0.75	1.05	0.8	0.63	0.84	0.66
Aug 26	87	196.8	0.3	0.75	0.225	0.79	0.62	0.18	0.14
Aug 27	71	266.4	2.3	0.75	1.725	0.78	0.61	1.35	1.05
Aug 28	77	492	5	0.65	3.25	0.77	0.59	2.50	1.92
Aug 29	64	571.2	1.6	0.6	0.96	0.76	0.58	0.73	0.56
Aug 30	65.5	408	6.2	0.7	4.34	0.75	0.56	3.26	2.43
Aug 31	82.5	88.8	1	0.85	0.85	0.74	0.55	0.63	0.47
Sep 1	83	242.4	1.1	0.75	0.825	0.73	0.55	0.60	0.45
Sep 2	78	302.4		0.75	0	0.72	0.55	0.00	0.00
Sep 3	69	148.8		0.75	0	0.71	0.55	0.00	0.00
Sep 4	77	151.2		0.85	0	0.7	0.55	0.00	0.00
Sep 5	68	244.8		0.7	0	0.7	0.55	0.00	0.00
Sep 6	84	141.6	13.6	0.85	11.56	0.7	0.55	8.09	6.36
Sep 7	92	223.2	-0.6	0.75	-0.45	0.7	0.55	-0.32	-0.25
Sep 8	93	297.6	2.4	0.75	1.8	0.7	0.55	1.26	0.99
Sep 9	86	268.8	2.4	0.75	1.8	0.7	0.55	1.26	0.99
Sep 10	84	355.2		0.75	0	0.7	0.55	0.00	0.00
Sep 11	80	376.8		0.75	0	0.7	0.55	0.00	0.00
Sep 12	80	338.4	6.1	0.75	4.575	0.7	0.55	3.20	2.52
Sep 13	91	290.4	2.5	0.75	1.875	0.7	0.55	1.31	1.03
Sep 14	87	148.8	2.5	0.85	2.125	0.7	0.55	1.49	1.17
Sep 15	79	103.2	0.2	0.85	0.17	0.7	0.55	0.12	0.09
Sep 16	99	91.2	1.6	0.85	1.36	0.7	0.55	0.95	0.75
Sep 17	81	422.4	2.7	0.75	2.025	0.7	0.55	1.42	1.11
Sep 18	73	295.2	3.6	0.75	2.7	0.7	0.55	1.89	1.49
Sep 19	75	398.4	3.2	0.75	2.4	0.7	0.55	1.68	1.32
Sep 20	77	403.2	3.5	0.75	2.625	0.7	0.55	1.84	1.44
Sep 21	76	220.8	2.3	0.75	1.725	0.7	0.55	1.21	0.95
Sep 22	79	242.4	3.1	0.75	2.325	0.7	0.55	1.63	1.28
Sep 23	74	300	3.8	0.75	2.85	0.7	0.55	2.00	1.57
Sep 24	94	249.6		0.75	0	0.7	0.55	0.00	0.00
Sep 25	93	134.4	1	0.85	0.85	0.7	0.55	0.60	0.47
Sep 26	93	180	3.1	0.75	2.325	0.7	0.55	1.63	1.28
Sep 27	95	316.8	-1.5	0.75	-1.125	0.7	0.55	-0.79	-0.62
Sep 28	87	228	2.6	0.75	1.95	0.7	0.55	1.37	1.07
Sep 29	99	218.4	1.2	0.75	0.9	0.7	0.55	0.63	0.50
Sep 30	73	523.2	5.9	0.65	3.835	0.7	0.55	2.68	2.11

Table A.6. Soil volumetric moisture content at root zone (1994)

(%)

0.4 m Subirrigation

Metribuzin

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#7	Lysi#9	Lysi#13				
5	33.38	32.19	35.01	35	32	34	1.16
7	30.43	32.64	32.64	33	31	32	1.04
23	41.24	39.16	41.24	42	40	41	0.98
30	36.2	32.41	36.67	37	33	35	1.91
38	36.2	34.59	37.5	37	35	36	1.19
49	32.41	32.64	35.81	35	32	34	1.55
66	32.41	29.32	32.64	33	30	31	1.51

0.4 m Subirrigation

Atrazine & Metolachlor

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#6	Lysi#10	Lysi#16				
5	32.73	31.43	31.43	32	31	32	0.61
7	32.81	31.3	32.13	33	31	32	0.62
23	33.91	33.38	35.67	35	33	34	0.98
30	34.89	35.12	36.2	36	35	35	0.57
38	36.67	38.71	36.2	38	36	37	1.09
49	36.8	37.26	37.25	37	37	37	0.22
66	32.91	32.64	33.51	33	33	33	0.36

0.8 m Subirrigation

Metribuzin

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#1	Lysi#5	Lysi#17				
5	18.88	16.69	17.23	19	17	18	0.93
7	18.88	17.77	18.87	19	18	19	0.52
23	23.32	21.09	18.87	23	19	21	1.82
30	19.98	17.77	18.88	20	18	19	0.90
38	24.41	18.88	22.2	24	20	22	2.27
49	23.3	18.88	24.41	25	20	22	2.39
66	16.69	14.53	15.56	16	15	16	0.88

0.8 m Subirrigation

Atrazine & Metolachlor

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#4	Lysi#8	Lysi#12				
5	16.69	20.54	16.66	20	16	18	1.82
7	19.99	21.09	18.87	21	19	20	0.91
23	23.31	24.42	23.32	24	23	24	0.52
30	19.99	21.09	21.09	21	20	21	0.52
38	23.3	24.41	22.2	24	22	23	0.90
49	23.3	22.21	none	23	22	23	0.55
66	14.53	12.35	15.58	15	13	14	1.35

Free Drainage

Metribuzin

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#2	Lysi#11	Lysi#14				
5	16.69	18.33	19.98	20	17	18	1.34
7	18.88	19.98	22.2	22	19	20	1.38
23	22.21	23.29	14.48	24	16	20	3.92
30	17.77	19.99	19.98	20	18	19	1.04
38	19.99	21.09	20.54	21	20	21	0.45
49	19.99	22.19	22.21	23	20	21	1.04
66	13.51	14.53	13.4	14	13	14	0.51

Free Drainage

Atrazine & Metolachlor

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev
	Lysi#3	Lysi#15	Lysi#18				
5	23.32	21.09	18.33	23	19	21	2.04
7	23.32	23.32	21.09	24	22	23	1.05
23	24.98	22.76	23.31	25	23	24	0.94
30	25.52	24.42	19.98	26	21	23	2.39
38	25.52	24.42	23.32	25	24	24	0.90
49	24.38	26.62	23.3	26	23	25	1.38
66	18.88	17.76	12.35	19	13	16	2.85

Table A.7. Herbicide concentration in soil solution (1994)

(μg/L)

	0.4 m Subirrigation Metribuzin								0.4 m Subirrigation Atrazine								0.4 m Subirrigation Metolachlor							
	at 0.45 m				at 0.85 m				at 0.45 m				at 0.85 m				at 0.45 m				at 0.85 m			
Days after Appl	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
-23	0.5	0.1	0.3	0.20	0.2	0.2	0.2	0	3.8	-0	1.853	1.963	1.8	0.3	1.1	0.75	0.4	0.0	0.2	0.17	0.2	0.1	0.2	0.03
3	0.1	0.0	0.1	0.05	0.0	0.0	0.0	0.009	3.2	-0	1.433	1.748	0.3	-0	0.1	0.17	0.2	-0	0.1	0.12	0.5	-0	0.2	0.28
7	1	-0	0.4	0.55	0.3	0.0	0.2	0.136	1	0.1	0.527	0.457	0.0	-0	0.0	0.02	0.6	-0	0.3	0.35	0.2	0.0	0.1	0.10
14	0.4	0.0	0.2	0.21	0.1	0.0	0.1	0.03	0.6	0.1	0.36	0.226	0.1	-0	0.1	0.07	0.4	-0	0.2	0.20	0.1	-0	0.1	0.08
23	0.5	0.2	0.3	0.16	0.4	0.1	0.3	0.145	0.2	0.1	0.173	0.033	0.2	0.1	0.2	0.04	0	0	0	0.00	0.3	0.1	0.2	0.09
30	0.3	0.2	0.3	0.04	0.5	0.2	0.4	0.175	0.7	0.3	0.503	0.243	0.6	0.1	0.4	0.24	0.8	0.3	0.6	0.24	0.5	-0	0.2	0.26
38	0.5	0.3	0.4	0.10	0.3	0.3	0.3	0.025	1	0.2	0.617	0.411	0.5	0.3	0.4	0.09	2.5	0.5	1.5	1.02	1.3	0.2	0.7	0.53
49	0	0	0	0.00	0	0	0	0	0.1	0.0	0.073	0.066	0	0	0	0.00	0	0	0	0.00	0	0	0	0.00
68	0.2	-0	0.1	0.11	0.3	0.2	0.3	0.02	0.1	0.0	0.057	0.049	0	0	0	0.00	0.4	0.1	0.2	0.18	0.8	0.4	0.6	0.22
90	0.1	0.1	0.1	0.00	0	0	0	0	0.3	0.1	0.18	0.102	0.2	0.1	0.1	0.06	0.8	0.1	0.5	0.35	0.8	0.6	0.7	0.13

0.8 nm Subirrigation

	Metribuzin				Atrazine				Metolachlor			
	at 0.85 m				at 0.85 m				at 0.85 m			
Days after Appl	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
-23	0.1	0.1	0.1	0.00	19	-3	8.1	10.57	3.548	-0	1.5	2.008
3	0.9	0.1	0.5	0.39	0.2	0.2	0.2	0.00	0.222	0.2	0.2	0.015
7	0.3	0.3	0.3	0.00	0.6	0	0.3	0.28	0.402	0.2	0.3	0.105
14	0.3	0.1	0.2	0.07	0.5	0.0	0.3	0.21	0.277	0.1	0.2	0.09
23	0.7	0.1	0.4	0.29	0.2	0.1	0.2	0.06	0.345	0.1	0.2	0.12
30	0.9	0.2	0.6	0.33	0.5	0.4	0.5	0.02	0.457	0.4	0.4	0.01
38	0.7	0.4	0.5	0.19	1.1	0.3	0.7	0.42	1.197	0.7	0.9	0.25
49	0	0	0	0.00	0	0	0	0.00	0	0	0	0
68	0.8	0.1	0.4	0.33	0	0	0	0.00	1.358	0.7	1	0.315
90	0.5	0.1	0.3	0.20	0.1	0.1	0.1	0.03	0.473	0.5	0.5	0

Free Drainage

	Metribuzin				Atrazine				Metolachlor			
	at 0.85 m				at 0.85 m				at 0.85 m			
Days after Appl	High	Low	Avg.	St. Dev	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev
3	0.1	0.0	0.08	0.04	0.8	-0	0.4	0.48	0.1	0.1	0.1	0.035
7	0.4	0.1	0.28	0.16	0.2	0.0	0.1	0.08	0.2	0.1	0.2	0.05
10	0.1	0.0	0.083	0.07	0.0	0.0	0.0	0.01	0.6	0.5	0.5	0.06
14	0.4	0.2	0.27	0.11	0.3	0.0	0.2	0.15	0.2	0.1	0.1	0.07
23	0.6	0.1	0.323	0.26	0.3	0.1	0.2	0.08	0.5	-0	0.2	0.25
30	0.2	-0	0.097	0.14	0.3	0.1	0.2	0.10	0.3	0	0.1	0.145
38	0.8	0.5	0.61	0.15	0.2	0	0.1	0.12	0.2	0.2	0.2	0.02
49	0.9	-0	0.363	0.51	0.1	0.1	0.1	0.03	0	0	0	0
68	0.2	-0	0.103	0.15	0.4	0	0.2	0.22	1.1	0.4	0.7	0.375
90	0.3	-0	0.11	0.16	0.1	0.1	0.1	0.00	1.2	0.1	0.6	0.54
90	0.3	-0	0.11	0.16	0.1	0.1	0.1	0.00	1.2	0.1	0.6	0.54

Table A.8. Soil temperature in lysimeters (1994)

(C)

		Below	Ground	
		0.8 m	Subirrigation	
	Temp	at	Centre	
Days	0.1m	0.3m	0.5m	0.7m
3	20.7	19.5	18.6	17.6
7	22.9	19.5	18.7	17.9
14	22	28.7	19	17.7
23	21.1	20.9	19.6	18.2
30	22.7	22.7	21.1	19.3
37	21.2	20.5	19.6	18.7

		Above	Ground	
		0.8 m	Subirrigation	
	Temp	at	Centre	
Days	0.1m	0.3m	0.5m	0.7m
3	21.5	22.9	21.4	21.6
7	26.2	26.1	24.2	23.4
14	22.9	24.2	24	24.1
23	25.4	26.2	24	23.8
30	22.1	24	25.8	26.1
37	27.8	29.1	26.7	25

		Below	Ground	
		Free	Drain	
	Temp	at	Centre	
Days	0.1m	0.3m	0.5m	0.7m
3	20.9	19.7	-	17.7
7	24.9	20	-	18.2
14	23.3	21.3	-	18.7
23	23.9	21.5	-	18.5
30	21.8	23.2	-	19.8
37	23.9	20.8	-	19.1

		Above	Ground	
		Free	Drain	
	Temp	at	Centre	
Days	0.1m	0.3m	0.5m	0.7m
3	21.9	22.4	21.8	21.3
7	24.8	23.5	23.3	25
14	22.5	23.2	23.8	23.8
23	23.2	23.3	24.4	25.3
30	23	25	25.7	24.3
37	26	25	25.5	27.9

		Below	Ground	
		0.4 m	Subirrigation	
	Temp	at	Centre	
Days	0.1m	0.3m	0.5m	0.7m
3	20.8	19.3	-	-
7	23.7	19.7	-	-
14	22.2	21.1	-	-
23	21.3	21.2	-	-
30	22.4	22.6	-	-
37	21.4	20.7	-	-

		Above	Ground	
		0.4 m	Subirrigation	
	Temp	at	Centre	
Days	0.1m	0.3m	0.5m	0.7m
3	21.7	21.5	-	-
7	26.8	24	-	-
14	23.2	23.6	-	-
23	24.3	23.1	-	-
30	22.6	25.2	-	-
37	28	25.4	-	-

Table A.9. Climatological data (1995)

(Macdonald Campus)

Date	Time	Rain	Water		Pan Evap.	Temp.	
	hr. min		added	removed	mm	max	min
MAY							
31	9	0.0	3.9		3.9	25.0	10.0
JUNE							
1	9		5.2		5.2	30.0	16.0
2	9.15	34.5		30.4	4.1	25.5	16.0
3	9.15	25.0		24.0	1.0	19.5	12.0
4	9.1	1.0	3.8		4.8	26.0	13.5
5	9.1		3.8		3.8	26.0	14.5
6	9		4.6		4.6	32.0	16.5
7	9		6.8		6.8	33.0	11.0
8	9		5.2		5.2	25.5	10.5
9	9.15		5.2		5.2	27.0	11.5
10	9	1.2	2.3		3.5	28.0	16.0
11	9		4.2		4.2	26.0	16.0
12	9		4.4		4.4	26.0	12.5
13	9		6.0		6.0	28.0	14.0
14	9		7.2		7.2	29.5	11.0
15	9.1		5.5		5.5	29.0	13.0
16	9.2		7.1		7.1	29.5	16.0
17	9.3		4.8		4.8	29.5	15.0
18	9		6.2		6.2	32.0	15.0
19	9		7.2		7.2	34.5	19.0
20	9		5.7		5.7	29.0	15.0
21	9		5.8		5.8	29.0	14.0
22	9		5.6		5.6	32.5	15.5
23	9.3		5.6		5.6	35.0	13.0
24	9.3		5.2		5.2	34.5	20.0
25	9.3		6.7		6.7	37.0	20.0
26	9		7.2		7.2	31.0	14.0
27	9		6.5		6.5	31.0	16.0
28	9		4.7		4.7	31.0	16.5
29	9		5.8		5.8	35.0	19.0
30	9	2.8	2.4		5.2	35.0	20.0
JULY							
1	9	2.8	1.0		3.8	31.0	18.0
2	9		5.8		5.8	28.0	13.0
3	9		4.8		4.8	30.0	14.0
4	9		5.2		5.2	33.0	16.0
5	9		3.6		3.6	30.5	21.0
6	9	9.0		4.6	4.4	34.0	20.0

Table A.9. Climatological data (1995)

7	8.3	1.6	2.9		4.5	31.0	21.0
8	9	1.4	2.8		4.2	31.0	14.0
9	9	0.5	5.4		5.9	28.0	14.0
10	9	0.6	4.4		5.0	31.0	16.0
11	9		4.4		4.4	29.5	16.0
12	9		5.8		5.8	32.0	18.0
13	9		6.8		6.8	32.0	17.0
14	9	2.1	4.8		6.9	36.0	22.0
15	9		6.7		6.7	35.0	14.0
16	9	18.4		12.8	5.6	27.0	13.0
17	9	2.8	2.4		5.2	22.0	13.0
18	9	17.0		12.0	5.0	24.0	12.0
19	9		4.0		4.0	29.0	13.0
20	9	12.5		11.2	1.3	22.0	18.0
21	9		4.7		4.7	33.0	19.0
22	9		4.8		4.8	34.0	22.0
23	9	42.3		39.5	2.8	24.0	21.0
24	9		3.1		3.1	31.0	22.0
25	9	1.0	2.4		3.4	35.0	22.0
26	9	2.6	1.0		3.6	31.0	21.0
27	9	0.2	4.2		4.4	32.0	18.5
28	9	23.4		17.0	6.4	33.0	20.0
29	10		6.2		6.2	33.0	19.0
30	10		5.4		5.4	33.0	18.0
31	9		6.4		6.4	33.0	18.0
August							
1	9	0.6	6.3		6.9	33.5	14.0
2	9		4.8		4.8	29.0	13.5
3	9	45.4		41.3	4.1	27.5	16.5
4	9	14.0		10.6	3.4	31.0	13.0
5	10	19.2		15.8	3.4	24.0	15.0
6	9	4.8		2.4	2.4	26.0	14.5
7	9		4.8		4.8	32.5	16.0
8	9		6.0		6.0	34.0	17.0
9	9		6.2		6.2	35.0	18.0
10	9		4.8		4.8	35.0	19.0
11	9	0.3	3.7		4.0	31.0	21.0
12	9	1.2	4.8		6.0	33.0	15.0
13	9		5.4		5.4	30.5	18.0
14	9	25.2		19.6	5.6	31.0	19.0
15	9		5.3		5.3	35.5	21.0
16	9		5.6		5.6	35.0	20.0
17	9.25		5.1		5.1	35.5	19.0
18	9		6.5		6.5	32.0	16.0

Table A.9. Climatological data (1995)

19	9		4.0		4.0	32.0	16.0
20	9		4.8		4.8	34.0	21.0
21	9		6.0		6.0	32.5	14.0
22	9		4.2		4.2	26.0	15.0
23	8	1.4	2.5		3.9	25.0	14.0
24	9		5.2		5.2	23.0	10.0
25	9		4.0		4.0	21.0	11.0
26	9		4.0		4.0	21.0	11.0
27	9		5.4		5.4	29.0	11.5
28	9		4.0		4.0	29.0	12.5
29	9		5.8		5.8	29.0	12.0
30	9	1.0	3.6		4.6	29.0	15.0
31	9	5.1		3.4	1.7	22.0	15.0
September							
1	9	0.2	4.0		4.2	27.0	11.0
2	9		4.0		4.0	25.0	11.0
3	9		3.1		3.1	28.0	14.0
4	9		3.5		3.5	30.0	14.0
5	9		3		3.0	27.0	14.0
6	9		3.5		3.5	26.0	9.0
7	9	33.8		31.9	1.9	25.0	7.0
8	9		3.2		3.2	22.0	6.0
9	9		3.1		3.1	23.0	7.0
10	9		3.3		3.3	24.0	7.0
11	9		3.2		3.2	22.0	10.0
12	9	2.4	1.2		3.6	26.0	10.0
13	9	13.2		10.8	2.4	22.0	17.0
14	9	2.2	0	0	2.2	22.0	12.0
15	9		2.5		2.5	21.0	10.0
16	9	1	1		2.0	22.0	8.0
17	9	2.2	0		2.2	21.0	7.0
18	9	0.2	2.3		2.5	20.0	7.0
19	9		2.5		2.5	19.0	9.0
20	9		0.6		0.6	20.0	10.0
21	9	0.5	0		0.5	20.0	10.0
22	9	10.4		9.4	1.0	19.0	9.0
23	9		2.3		2.3	19.0	7.0
24	9		2.4		2.4	19.0	7.0
25	9	2.0		1.5	0.5	19.0	8.0
26	9	1.0	0.5		1.5	18.0	8.0
27	9		1.6		1.6	16.0	6.0
28	9	0.4	1.6		2.0	17.0	6.0
29	9		2.1		2.1	18.0	7.0
30	9		2.3		2.3	20.0	8.0

Table A.9. Climatological data (1995)

October							
1	9.0		2.4		2.4	22.0	10.0
2	9.0		2.8		2.8	22.0	10.0
3	10.0	4.4		1.8	2.6	21.0	9.0
4	9.0	47.0		45.5	1.5	16.0	10.0
5	9.0	25.0		23.5	1.5	15.0	9.0
6	9.0	4.0		2.8	1.2	16.0	10.0
7	9.0		1.2		1.2	15.0	9.0

Table A.10. Evapotranspiration data (1995)

Exper. Days	Date	Rain* mm	Pan Eva. mm	Kp	ET0	Kc	ET
-20	JUNE 4	1.0	4.8	0.75	3.6	0.5	1.80
-19	5		3.8	0.75	2.9	0.5	1.43
-18	6		4.6	0.75	3.5	0.5	1.73
-17	7		6.8	0.75	5.1	0.5	2.55
-16	8		5.2	0.75	3.9	0.5	1.95
-15	9		5.2	0.75	3.9	0.5	1.95
-14	10	1.2	3.5	0.75	2.6	0.5	1.31
-13	11		4.2	0.75	3.2	0.6	1.89
-12	12		4.4	0.75	3.3	0.6	1.98
-11	13		6.0	0.75	4.5	0.6	2.70
-10	14		7.2	0.75	5.4	0.6	3.24
-9	15		5.5	0.75	4.1	0.6	2.48
-8	16		7.1	0.75	5.3	0.6	3.20
-7	17		4.8	0.75	3.6	0.6	2.16
-6	18		6.2	0.75	4.7	0.7	3.26
-5	19		7.2	0.75	5.4	0.7	3.78
-4	20		5.7	0.75	4.3	0.7	2.99
-3	21		5.8	0.75	4.4	0.8	3.48
-2	22		5.6	0.75	4.2	0.8	3.36
-1	23		5.6	0.75	4.2	0.8	3.36
0	24		5.2	0.75	3.9	0.9	3.51
1	25		6.7	0.75	5.0	0.9	4.52
2	26		7.2	0.75	5.4	0.9	4.86
3	27		6.5	0.75	4.9	1	4.88
4	28		4.7	0.75	3.5	1	3.53
5	29		5.8	0.75	4.4	1	4.35
6	30	62.8	5.2	0.75	3.9	1.05	4.10
7	JULY 1	2.8	3.8	0.75	2.9	1.05	2.99
8	2		5.8	0.75	4.4	1.05	4.57
9	3		4.8	0.75	3.6	1.05	3.78
10	4		5.2	0.75	3.9	1.05	4.10
11	5		3.6	0.75	2.7	1.05	2.84
12	6	9.0	4.4	0.75	3.3	1.05	3.47
13	7	1.6	4.5	0.75	3.4	1.05	3.54
14	8	1.4	4.2	0.75	3.2	1.05	3.31
15	9	0.5	5.9	0.75	4.4	1.05	4.65
16	10	60.6	5.0	0.75	3.8	1.05	3.94
17	11		4.4	0.75	3.3	1.05	3.47

Table A.10. Evapotranspiration data (1995)

18	12		5.8	0.75	4.4	1.05	4.57
19	13		6.8	0.75	5.1	1.05	5.36
20	14	2.1	6.9	0.75	5.2	1.05	5.43
21	15		6.7	0.75	5.0	1.05	5.28
22	16	18.4	5.6	0.75	4.2	1.05	4.41
23	17	2.8	5.2	0.75	3.9	1.05	4.10
24	18	17.0	5.0	0.75	3.8	1.05	3.94
25	19		4.0	0.75	3.0	1.05	3.15
26	20	12.5	1.3	0.75	1.0	1.05	1.02
27	21		4.7	0.75	3.5	1.05	3.70
28	22	60.0	4.8	0.75	3.6	1.05	3.78
29	23	42.3	2.8	0.75	2.1	1.05	2.20
30	24		3.1	0.75	2.3	1.05	2.44
31	25	1.0	3.4	0.75	2.6	1.05	2.68
32	26	2.6	3.6	0.75	2.7	1.05	2.84
33	27	0.2	4.4	0.75	3.3	1.05	3.47
34	28	23.4	6.4	0.75	4.8	1.05	5.04
35	29		6.2	0.75	4.7	1.05	4.88
36	30		5.4	0.75	4.1	1.05	4.25
37	31		6.4	0.75	4.8	1.05	5.04
38	August1	0.6	6.9	0.75	5.2	1	5.18
39	2		4.8	0.75	3.6	1	3.60
40	3	45.4	4.1	0.75	3.1	1	3.08
41	4	14.0	3.4	0.75	2.6	1	2.55
42	5	19.2	3.4	0.75	2.6	1	2.55
43	6	4.8	2.4	0.75	1.8	0.9	1.62
44	7		4.8	0.75	3.6	0.9	3.24
45	8		6.0	0.75	4.5	0.9	4.05
46	9		6.2	0.75	4.7	0.9	4.18
47	10		4.8	0.75	3.6	0.9	3.24
48	11	0.3	4.0	0.75	3.0	0.9	2.70
49	12	1.2	6.0	0.75	4.5	0.8	3.60
50	13		5.4	0.75	4.1	0.8	3.24
51	14	25.2	5.6	0.75	4.2	0.8	3.36
52	15		5.3	0.75	4.0	0.8	3.18
53	16		5.6	0.75	4.2	0.8	3.36
54	17		5.1	0.75	3.8	0.8	3.06
55	18		6.5	0.75	4.9	0.7	3.41
56	19		4.0	0.75	3.0	0.7	2.10
57	20		4.8	0.75	3.6	0.7	2.52
58	21		6.0	0.75	4.5	0.7	3.15
59	22		4.2	0.75	3.2	0.7	2.21

Table A.10. Evapotranspiration data (1995)

60	23	1.4	3.9	0.75	2.9	0.6	1.76
61	24		5.2	0.75	3.9	0.6	2.34
62	25		4.0	0.75	3.0	0.6	1.80
63	26		4.0	0.75	3.0	0.6	1.80
64	27		5.4	0.75	4.1	0.6	2.43
65	28		4.0	0.75	3.0	0.6	1.80
66	29		5.8	0.75	4.4	0.6	2.61
67	30	1.0	4.6	0.75	3.5	0.6	2.07
68	31	65.1	1.7	0.75	1.3	0.55	0.70
69	Sept 1	0.2	4.2	0.75	3.2	0.55	1.73
70	2		4.0	0.75	3.0	0.55	1.65
71	3		3.1	0.75	2.3	0.55	1.28
72	4		3.5	0.75	2.6	0.55	1.44
73	5		3.0	0.75	2.3	0.55	1.24
74	6		3.5	0.75	2.6	0.55	1.44
75	7	33.8	1.9	0.75	1.4	0.55	0.78
76	8		3.2	0.75	2.4	0.55	1.32
77	9		3.1	0.75	2.3	0.55	1.28
78	10		3.3	0.75	2.5	0.55	1.36
79	11		3.2	0.75	2.4	0.55	1.32
80	12	2.4	3.6	0.75	2.7	0.55	1.49
81	13	13.2	2.4	0.75	1.8	0.55	0.99
82	14	2.2	2.2	0.75	1.7	0.55	0.91
83	15		2.5	0.75	1.9	0.55	1.03
84	16	1	2.0	0.75	1.5	0.55	0.83
85	17	2.2	2.2	0.75	1.7	0.55	0.91
86	18	0.2	2.5	0.75	1.9	0.55	1.03
87	19		2.5	0.75	1.9	0.55	1.03
88	20		0.6	0.75	0.5	0.55	0.25
89	21	0.5	0.5	0.75	0.4	0.55	0.21
90	22	10.4	1.0	0.75	0.8	0.55	0.41

* Simulated rainfall added

Table A.11. Soil volumetric moisture content at root zone (1995)

(%)

0.4 m Subirrigation

Metribuzin

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#7	Lysi#9	Lysi#13				
6	18.88	23.27	26.6	26	20	23	3.16
16	20	20	25.4	24	19	22	2.54
28	26.46	32.41	33.51	34	28	31	3.10
42	27.46	25.35	30.63	30	26	28	2.17
66	32.19	28.69	33.62	34	29	32	2.07
73	28.41	26.46	34.59	33	26	30	3.47
90	28.41	27.46	36.47	35	27	31	4.05

0.4 m Subirrigation

Atrazine & Metolachlor

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#6	Lysi#10	Lysi#16				
6	28.57	26.35	25.44	28	25	27	1.32
16	29.61	21.09	26.35	29	22	26	3.51
28	36.67	32.41	33.51	36	32	34	1.81
42	32.81	27.46	28.57	32	27	30	2.31
66	30.08	28.49	29.43	30	29	29	0.65
73	33.72	31.54	34.34	34	32	33	1.20
90	35.12	33.51	32.41	35	33	34	1.11

0.8 m Subirrigation

Metribuzin

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#1	Lysi#5	Lysi#17				
6	19	16.75	19.98	20	17	19	1.34
16	14	13.57	15.61	15	14	14	0.87
28	18	16.75	19.98	20	17	18	1.35
42	19	13.64	13.43	18	13	15	2.54
66	16	15.68	9.27	17	11	14	3.01
73	19	16.75	19.99	20	17	19	1.35
90	19	19.99	19.98	20	19	20	0.53

0.8 m Subirrigation

Atrazine & Metolachlor

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#4	Lysi#8	Lysi#12				
6	16.69	16.66	16.66	17	17	17	0.01
16	13.46	13.41	14.5	14	13	14	0.50
28	19.98	19.98	19.98	20	20	20	0.00
42	15.58	15.58	14.53	16	15	15	0.50
66	11.31	12.37	13.41	13	12	12	0.86
73	15.58	18.87	19.98	20	16	18	1.87
90	19.98	19.98	21.09	21	20	20	0.52

Free Drainage

Metribuzin

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#2	Lysi#11	Lysi#14				
6	16	16.75	17.76	18	16	17	0.87
16	10	14.57	12.37	14	11	12	1.69
28	17	19.99	18.87	20	17	19	1.37
42	12	14.53	13.43	14	13	13	0.86
66	9	11.37	9.27	11	9	10	0.97
73	16	18.88	17.76	19	16	17	1.35
90	14	19.98	18.87	20	15	18	2.38

Free Drainage

Atrazine & Metolachlor

Days after Appl	at 0-40 m			High	Low	Avg.	Sd.Dev.
	Lysi#3	Lysi#15	Lysi#18				
6	19.99	19.98	17.77	20	18	19	1.05
16	15.61	16.72	14.5	17	15	16	0.91
28	22.2	23.3	14.5	24	16	20	3.91
42	18.88	18.87	21.09	21	19	20	1.04
66	11.31	11.31	13.41	13	11	12	0.99
73	21.09	22.21	17.81	22	18	20	1.87
90	24.41	22.2	21.09	24	21	23	1.38

Table A.12. Herbicide concentration in soil solution (1995)

(µG/L)

0.4 m Subirrigation

Metribuzin

Days after Appl	at 0.45 m High	Low	Avg.	St. Dev.	at 0.85 m High	Low	Avg.	St. Dev.
-20	0.3	-0	0.1	0.19	ND	ND	ND	0.00
6	ND	ND	ND	0.00	ND	ND	ND	0.00
17	1.6	0.1	0.9	0.74	0.6	0.1	0.3	0.25
28	1.5	0.1	0.8	0.71	1.2	-0	0.5	0.68
41	0.4	0	0.2	0.20	ND	ND	ND	0.00
70	0.9	0.5	0.7	0.22	0.3	-0	0.1	0.19
90	ND	ND	ND	0.00	ND	ND	ND	0.00

0.4 m Subirrigation

Atrazine

at 0.45 m High	Low	Avg.	St. Dev.	at 0.85 m High	Low	Avg.	St. Dev.
1.4	0.1	0.747	0.63	0.3	0.1	0.2	0.05
11	-1	4.933	5.81	0.4	0.1	0.3	0.13
9.1	1.6	5.333	3.74	0.3	0.2	0.2	0.06
1.5	-0	0.7	0.79	0.3	0.3	0.3	0.00
0.2	-0	0.1	0.14	0.2	-0	0.1	0.14
0.3	0.2	0.24	0.07	0.3	0.0	0.2	0.12
0.6	-0	0.297	0.31	0.1	0	0.1	0.06

0.4 m Subirrigation

Metolachlor

at 0.45 m High	Low	Avg.	St. Dev.	at 0.85 m High	Low	Avg.	St. Dev.
0	0	0	0.00	ND	ND	ND	0.00
20	-3	8.4	11.93	ND	ND	ND	0.00
11	1.8	6.4	4.62	0.4	0.4	0.4	0.00
11	0.2	5.6	5.34	6.4	1.1	3.7	2.64
ND	ND	ND	0.00	ND	ND	ND	0.00
2.7	-0	1.1	1.56	1.6	-0	0.7	0.96
2.2	-0	0.9	1.31	ND	ND	ND	0.00

0.8 nm Subirrigation

Days after Appl	Metribuzin at 0.85 m High	Low	Avg.	St. Dev.	Atrazine at 0.85 m High	Low	Avg.	St. Dev.	Metolachlor at 0.85 m High	Low	Avg.	St. Dev.
-20	ND	ND	ND	0.00	0.2	0.1	0.2	0.07	ND	ND	ND	0.00
6	ND	ND	ND	0.00	0.3	0.1	0.2	0.10	ND	ND	ND	0.00
17	0.7	0.2	0.5	0.24	1	0.4	0.7	0.34	2.271	0.7	1.5	0.80
28	0.9	0.2	0.5	0.33	0.7	0.2	0.5	0.22	12.42	5.6	9	3.39
41	ND	ND	ND	0.00	0.3	0.1	0.2	0.11	3.384	1.2	2.3	1.08
70	ND	ND	ND	0.00	0.3	0.2	0.3	0.09	ND	ND	ND	0.00
90	ND	ND	ND	0.00	0.4	0.1	0.2	0.17	ND	ND	ND	0.00

Free Drainage

Days after Appl	Metribuzin at 0.85 m High	Low	Avg.	St. Dev.	Atrazine at 0.85 m High	Low	Avg.	St. Dev.	Metolachlor at 0.85 m High	Low	Avg.	St. Dev
-20	5.4	-1	2.233	3.16	0.2	0.1	0.1	0.08	2.4	-0	1	1.39
6	ND	ND	ND	0.00	0.4	0.2	0.3	0.10	ND	ND	ND	0.00
17	0.5	0.3	0.4	0.10	0.5	0.3	0.4	0.09	1.1	0.0	0.6	0.55
28	0.4	0.1	0.27	0.13	0.2	-0	0.1	0.14	13	4.8	9.2	4.33
41	0.6	0.2	0.4	0.19	0.5	0.2	0.3	0.16	1.5	1.3	1.4	0.08
70	1.8	0.6	1.2	0.57	0.4	0.2	0.3	0.07	0.8	0.0	0.4	0.38
90	ND	ND	2.5	0.00	0.3	-0	0.2	0.17	ND	ND	ND	0.00

Table A.13. Herbicide concentration in soil (1995)

(µg/kg)

0.4 m Subirrigation

		Metribuzin				Atrazine				Metolachlor			
Days after Appl	Depth	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.	High	Low	Avg.	St. Dev.
	0.1	30.0	0.0	15.0	15.0	7.8	6.0	6.9	0.0	6.9	0.0	3.4	3.4
6	0.3	27.4	-4.7	11.3	16.0	0.0	0.0	0.0	8.9	8.9	0.0	4.4	4.4
	0.5	0.0	0.0	0.0	0.0	38.3	30.4	34.4	0.0	34.4	0.0	17.2	17.2
	0.7	7.2	-1.2	3.0	4.2	12.8	-2.2	5.3	2.3	4.9	-1.3	1.8	3.1
	0.1	0.0	0.0	0.0	0.0	7.8	6.0	6.9	0.0	6.9	0.0	3.4	3.4
30	0.3	3.7	-0.6	1.5	2.2	10.5	1.8	6.1	1.2	5.2	0.8	3.0	2.2
	0.5	0.0	0.0	0.0	0.0	30.6	4.9	17.8	0.0	15.0	0.1	7.6	7.5
	0.7	0.0	0.0	0.0	0.0	7.5	7.5	7.5	0.0	8.5	1.5	5.0	3.5
	0.1	0.0	0.0	0.0	0.0	13.8	5.1	9.4	0.0	8.7	1.0	4.8	3.9
90	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.5	0.0	0.0	0.0	0.0	10.7	-1.8	4.4	0.0	3.5	-1.8	0.9	2.6
	0.7	0.0	0.0	0.0	0.0	48.7	25.0	36.9	0.0	36.0	5.3	20.6	15.4

0.8 m Subirrigation

		Metribuzin				Atrazine				Metolachlor			
Days after Appl	Depth	High	Low	Avg.	St. Dev	High	Low	Avg.	St. Dev	High	Low	Avg.	St. Dev.
	0.1	100.0	62.6	81.3	18.7	252.9	210.0	231.5	21.5	231.5	210.0	220.7	10.7
6	0.3	6.0	3.9	5.0	1.1	58.4	40.0	49.2	9.2	120.0	40.0	44.6	4.6
	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.1	54.0	40.0	47.0	7.0	175.5	134.7	155.1	20.4	155.1	134.7	144.9	10.2
30	0.3	0.0	0.0	0.0	0.0	54.5	5.5	30.0	24.5	30.5	9.5	20.0	10.5
	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.7	2.9	2.6	2.8	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.1	10.0	7.2	8.6	1.4	67.0	38.9	52.9	14.0	51.4	19.2	35.3	16.1
90	0.3	6.0	3.8	4.9	1.1	50.2	28.1	39.2	11.1	39.2	28.1	33.6	5.5
	0.5	0.0	0.0	0.0	0.0	34.6	30.0	32.3	2.3	32.3	30.0	31.2	1.1
	0.7	0.0	0.0	0.0	0.0	57.9	37.3	47.6	10.3	47.4	16.0	31.7	15.7

Free Drainage

		Metribuzin				Atrazine				Metolachlor			
Days after Appl	Depth	High	Low	Avg.	St. Dev	High	Low	Avg.	St. Dev	High	Low	Avg.	St. Dev.
	0.1	200	170	185	15	320.0	240.0	280.0	40.0	280.0	240.0	260.0	20.0
6	0.3	0	0	0	0	90.0	70.0	80.0	10.0	80.0	70.0	75.0	5.0
	0.5	0	0	0	0	12.6	-2.2	5.2	7.4	5.2	-2.2	1.5	3.7
	0.7	0	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.1	100	85	92.5	7.5	209.1	168.1	188.6	20.5	188.6	168.1	178.4	10.3
30	0.3	60	42	51	9	77.2	21.2	49.2	28.0	49.2	21.2	35.2	14.0
	0.5	19	15	17	2	63.9	-17.1	23.4	40.5	23.4	-17.1	3.1	20.3
	0.7	24	22	23	1	39.4	20.0	29.7	9.7	29.7	20.0	24.9	4.9
	0.1	50	35	42.5	7.5	26.5	20.9	23.7	2.8	20.9	2.8	11.9	9.1
90	0.3	60	45	52.5	7.5	50.4	34.5	42.5	8.0	42.5	34.5	38.5	4.0
	0.5	35	25	30	5	30.0	21.8	25.9	4.1	25.9	21.8	23.9	2.1
	0.7	15	15	15	0	51.8	40.0	45.9	5.9	40.0	5.9	23.0	17.1

Table A.14. Soil moisture retention curve (for soil in lysimeters)

at 0.1 m depth		at 0.3 m depth		at 0.5 m depth	
Pressure (h) (Bar)	Volumetric soil moisture (θ) (%)	Pressure (h) (Bar)	Volumetric soil moisture (θ) (%)	Pressure (h) (Bar)	Volumetric soil moisture (θ) (%)
0	42.6	0	42.0	0	42.6
0.010	42.0	0.011	37.9	0.010	40.3
0.018	39.5	0.016	37.0	0.019	40.2
0.023	37.6	0.023	35.4	0.025	39.8
0.035	32.0	0.033	33.0	0.038	38.5
0.056	24.5	0.055	26.2	0.066	37.3
0.085	21.1	0.081	22.8	0.094	36.2
0.105	20.0	0.100	21.8	0.111	34.4
0.129	19.0	0.280	21.1	0.120	32.7
0.280	18.4	0.420	19.8	0.280	28.3
0.420	17.9	0.70	19.0	0.420	26.2
0.700	17.7	0.980	17.8	0.700	25.3
0.980	16.6	1.40	16.7	0.980	22.4
1.40	15.2	2.10	16.1	1.40	19.6
2.10	14.5	3.08	15.0	2.10	18.3
3.08	13.9	5.00	14.5	3.08	17.4
5.0	13.6			5.0	17.2

APPENDIX B

PRZM2 INPUT AND OUTPUT DATA

Table B.1. PRZM2 execution advisor

```
*****************************************************************************
*** PRZM2 version 1.02 | Date: Thursday, 11 February 1993. Time: 13:10:35.***
*** ------------------------------------------------------------------ ***
*** File PRZM2.RUN, run time supervisor file for PRZM2 model, required    ***
*** for all model runs.  This file, as distributed by CEAM, is configured ***
*** for the data sets PRZM3.INP and VADF3.INP.  Modify this file, as     ***
*** as shown below within comment lines, to execute PRZM2 model with     ***
*** other test input data sets distributed with PRZM2 model system.     ***
*** Lines beginning with *** (i.e., three asterisks) are comment lines.   ***
*****************************************************************************
*** option records
PRZM              ON
VADOFT            ON

*** To execute the PRZM2 model with MONTE CARLO simulation,
*** 1) turn the MONTE CARLO option switch to ON.  The MONTE
***    CARLO input file that will be read from option MCIN
***    is MC.INP.
*** 2) Set the PRZM2 INPUT file option to read the files
***    PRZM3.INP and VADF3.INP.
MONTE CARLO              OFF
TRANSPORT SIMULATION     ON
*** zone records
PRZM ZONES           1
VADOFT ZONES         1
ENDRUN
*** input file records
PATH                C:\FDPRZM2\INPUT\
MCIN                MC.INP
METEOROLOGY         1  METO95.INP
*** Change the next two lines to reflect the file names of the PRZM2
*** and/or VADOFT input files (e.g., PRZM.INP, PRZM1.INP, PRZM2.INP,
*** PRZM3.INP or VADF.INP, VADF1.INP, VADF2.INP, VADF3.INP).
PRZM INPUT        1  PRZM-FD.INP
VADOFT INPUT      1  VADF95.INP
*** ouptut file records
PATH                C:\FDPRZM2\OUTPUT\
TIME SERIES         1  TIMES95.OUT
PRZM OUTPUT         1  PRZM-FD.OUT
VADOFT OUTPUT       1  VADF95.OUT
MCOUT               MC.OUT
MCOUT2              MC2.OUT
```

Table B.1 cont'd

```
*** scratch file records
PRZM RESTART         1  RESTART.PRZ
VADOFT FLOW RST      1  VFLOW95.RST
VADOFT TRANS RST     1  VTRANS95.RST
VADOFT TAPE10        1  VADF95.TAP
ENDFILES
*** global records
START DATE          080695
END DATE            280995
*** For input files PRZM.INP and PRZM1.INP the number of chemicals
*** must be set to a value of one; for PRZM2.INP and PRZM3.INP the
*** number of chemicals must be set to a value of 3.
 NUMBER OF CHEMICALS    3
*** For input files PRZM.INP and PRZM1.INP comment out the next
*** two lines; for PRZM2.INP and PRZM3.INP uncomment the next
*** two lines (i.e., PARENT OF 2... and PARENT OF 3...).
PARENT OF 2         1
PARENT OF 3         2
ENDDATA
*** display records
ECHO              4
TRACE            OFF
```

Table B.2. Input file for PRZM module

```
*******************************************************

3 CHEMICALS, 1 HORIZON, SIMULATION DATA FOR LYSIMETERS AT
MACDONALD CAMPUS (1995)
HYDROLOGY PARAMETERS
   0.75   0.03     2  30.000     1     2
    9.6    9.7   12.2   13.6   15.4   15.5
   15.7   14.5   12.5   11.3    9.5    9.0
     0
     1
     1   0.25   40.0  80.000     3  86  78  74 0.0 0.0 0.0      100.0      1
   240695  240795  280995      1

PESTICIDE TRANSPORT AND TRANSFORMATION AND APPLICATION
PARAMETERS
     1     3     0
ATRAZINE         METRIBUZIN         METOLACHLOR
  240695     0    9.0    9.0    1.0    2.40    1.00    2.75
     1     1
SOILS PARAMETERS
   40.0     0.3   0   0   0   1   0   0   0   0   0
  4.3E3  2.5E-7  9.8E-8  3.8E-7  5.5E-3  5.5E-3  5.5E-3
     1
     1    40.0    1.35   0.200    2.7     0.0     0.0     0.0
        0.070   0.200   0.070   0.070   0.200   0.070   0.230   0.230   0.000
          1.0    .200    .050    3.5    3.2    4.3    1.7
        0.000   0.000   0.000
     0     0
   WATR    DAY      1    PEST    DAY      1    CONC    DAY      1
     6    DAY
   TPST1   TSER10      0.74E09
   TPST1   TSER30      0.74E09
   SPST1   TSER10      0.74E09
   SPST1   TSER30      0.74E09
   PRCP    TSER
   THET    TSER20
PESTICIDE CONCENTRATION IN DAY 6, 30, AND 90
 300695 SNAPSHOT   1
 230795 SNAPSHOT   1
 280995 SNAPSHOT   1
```

TABLE B.3. Input files for VADOFT module

```
**********************************FLOW***********************************
3 CHEMICAL, 1 HORIZON, VADOSE ZONE FLOW SIMULATION FOR
LYSIMETERS AT MACDONALD CAMPUS (1995)
  51   1   0   1   1   1   1   0   0   0
  20   2   1     .01
   1   1   1   1   0   1   2   1   0
     0.0      1.0      1.0      1.0
   1      0.0      1.0
   1
   1  50   1     50.0
   0.0E00   0
   1   1     0.0   0.0E00   0   0       0      0.5
  2.00E02   .30E00   0.0E00   0.0E00
 0.100E00  -1.0E00  0.035E00  2.02E00  0.626E00
  11  31
 DAY
********************************TRANSPORT*******************************
3 CHEMICAL, 1 HORIZON, VADOSE TRANSPORT SIMULATION AT
MACDONALD CAMPUS
  51   1   0   1   0   1   1   0   0   0
   0   1   1   0   0   1   2   1
     0.0      1.0      1.0      1.0
   1      0.0      1.0
   1
   1  50   1     50.0
   0.0E00   0   0.0E00   0   0.0E00   0
   0   0     0.0      0.0   0   0   0   0
  0.50E01   .39E00
 1.100E01 1.450E01 0.530E01   0.0E00   0.0E00   0.0E00
   1      0.0      1.0   0.0E00
   1  7.000E-2  0.200E00  7.000E-2   0.15E00   0.15E00   0.15E00
   1   1
  11  31
 DAY
```

Table B.4. Simulated and measured moisture contents in free drainage lysimeters at Macdonald Campus (1995)

Date	Rainfall (mm)	Simulated Moisture Contents (%)	Measured Moisture Contents in Lysimeters Received Atrazine and Metolachlor (%)	Measured Moisture Contents in Lysimeters Received Metribuzin (%)
1995 6 23	0.00	5.2	17.0	16.0
1995 6 24	0.00	5.2		
1995 6 25	0.00	5.1		
1995 6 26	0.00	5.0		
1995 6 27	0.00	5.0		
1995 6 28	0.00	5.0		
1995 6 29	0.00	5.0		
1995 6 30	62.8	5.0	19.2	16.7
1995 7 1	2.80	5.0		
1995 7 2	0.00	20.1		
1995 7 3	0.00	23.5		
1995 7 4	0.00	21.3		
1995 7 5	0.00	20.1		
1995 7 6	0.90	19.4		
1995 7 7	1.60	18.9		
1995 7 8	1.40	18.5	15.6	12.5
1995 7 9	0.50	17.7		
1995 7 10	60.6	17.1		
1995 7 11	0.00	26.1		
1995 7 12	0.00	25.6		
1995 7 13	0.00	21.7		
1995 7 14	2.10	20.7		
1995 7 15	0.00	19.3		
1995 7 16	18.4	18.5		
1995 7 17	0.28	17.9		
1995 7 18	17.0	17.5		
1995 7 19	0.00	21.9		
1995 7 20	12.5	21.9	20.0	18.5
1995 7 21	0.00	24.6		
1995 7 22	60.0	24.3		
1995 7 23	42.3	24.6		
1995 7 24	0.00	38.0		
1995 7 25	1.00	30.9		
1995 7 26	2.60	30.7		
1995 7 27	0.20	23.9		
1995 7 28	23.4	23.2		
1995 7 29	0.00	22.7		
1995 7 30	0.00	21.9		
1995 7 31	0.00	20.2		
1995 8 1	0.60	19.0		
1995 8 2	0.00	18.0		
1995 8 3	45.4	17.7	19.6	13.5
1995 8 4	14.0	17.6		
1995 8 5	19.2	17.6		
1995 8 6	4.80	17.6		
1995 8 7	0.00	33.6		
1995 8 8	0.00	29.0		

Table B.4 Cont'd

1995 8 9	0.00	23.3		
1995 8 10	0.00	20.4		
1995 8 11	0.30	20.0		
1995 8 12	1.20	18.7		
1995 8 13	0.00	17.6		
1995 8 14	25.2	17.0		
1995 8 15	0.00	16.6		
1995 8 16	0.00	20.6	17.0	15.0
1995 8 17	0.00	19.6		
1995 8 18	0.00	18.3		
1995 8 19	0.00	17.5		
1995 8 20	0.00	16.5		
1995 8 21	0.00	15.2		
1995 8 22	0.00	14.2		
1995 8 23	1.40	13.8		
1995 8 24	0.00	12.6		
1995 8 25	0.00	11.8		
1995 8 26	0.00	11.1		
1995 8 27	0.00	10.1	12.0	10.0
1995 8 28	0.00	9.0		
1995 8 29	0.00	8.6		
1995 8 30	1.00	8.2		
1995 8 31	65.1	8.2		
1995 9 1	2.00	22.0		
1995 9 2	0.00	24.8		
1995 9 3	0.00	22.4		
1995 9 4	0.00	20.4		
1995 9 5	0.00	19.8		
1995 9 6	0.00	19.1		
1995 9 7	33.8	19.0	20.4	17.4
1995 9 8	0.00	23.4		
1995 9 9	0.00	23.9		
1995 9 10	0.00	21.8		
1995 9 11	0.00	20.3		
1995 9 12	2.40	20.1		
1995 9 13	13.2	20.1		
1995 9 14	2.20	20.1		
1995 9 15	0.00	21.6		
1995 9 16	1.00	22.1		
1995 9 17	2.20	22.1		
1995 9 18	0.20	21.1		
1995 9 19	0.00	20.1		
1995 9 20	0.00	20.0		
1995 9 21	0.50	20.0		
1995 9 22	10.4	20.0		
1995 9 23	0.00	21.4		
1995 9 24	0.00	21.5		
1995 9 25	2.00	21.5		
1995 9 26	1.00	21.1		
1995 9 27	60.0	21.1		
1995 9 28	0.40	28.1	22.6	17.8

Table B.5. Time series output from przm2 for lysimeter study at Macdonald Campus (1995)

TIME SERIES	TOTAL ATRAZINE IN SOIL (µg/kg), AT		TOTAL METRIBUZIN IN SOIL (µg/kg), AT		TOTAL METOLACHLOR IN SOIL (µg/kg), AT	
	0.10 m DEPTH	**0.30 m** DEPTH	**0.10 m** DEPTH	**0.30 m** DEPTH	**0.10 m** DEPTH	**0. 30 m** DEPTH
6 23	0.0000	0.00000	0.00000	0.00000	0.00000	0.00000
6 24	0.0511	0.00000	621.600	0.1E-17	0.1E-16	0.1E-18
6 25	0.0910	0.3E-15	518.100	0.1E-17	0.6E-15	0.1E-18
6 26	0.1343	0.2E-15	431.200	0.1E-17	0.7E-15	0.1E-18
6 27	0.1669	0.9E-15	359.500	0.1E-16	0.5E-14	0.1E-18
6 28	0.1946	0.3E-15	300.400	0.1E-16	0.8E-14	0.1E-18
6 29	0.2180	0.9E-15	250.800	0.1E-16	0.7E-13	0.1E-18
6 30	228.33	0.2E-15	236.000	0.1E-16	42.4600	0.1E-18
7 1	220.51	0.2E-15	197.400	0.1E-16	41.4000	0.1E-18
7 2	441.86	0.1E-15	156.500	0.1E-16	15.3900	0.1E-18
7 3	444.81	0.6E-15	128.800	0.1E-16	16.5800	0.1E-18
7 4	412.56	0.2E-15	106.500	0.1E-16	15.4400	0.1E-18
7 5	384.28	0.5E-15	88.3200	0.1E-16	14.4900	0.1E-18
7 6	357.99	0.1E-15	73.6400	0.1E-16	13.4400	0.1E-18
7 7	333.84	0.3E-15	61.0200	0.1E-16	12.5500	0.1E-18
7 8	310.78	0.6E-15	50.1700	0.1E-16	11.7200	0.1E-18
7 9	289.99	0.1E-15	42.9600	0.1E-16	10.9400	0.1E-18
7 10	377.97	0.9E-15	38.6000	0.1E-16	21.9700	0.1E-18
7 11	420.07	0.4E-15	30.7700	0.1E-16	49.0300	0.6E-18
7 12	394.85	0.1E-11	25.6300	0.4E-15	49.1900	0.1E-08
7 13	365.65	0.2E-11	20.0600	0.1E-14	45.0300	0.4E-08
7 14	339.30	0.4E-11	21.5100	0.1E-14	41.2100	0.4E-08
7 15	316.06	0.6E-11	14.1800	0.9E-15	37.5500	0.4E-08
7 16	294.43	0.9E-11	12.7300	0.8E-15	36.3800	0.4E-08
7 17	295.11	0.1E-11	10.6100	0.6E-15	41.0800	0.4E-08
7 18	274.31	0.2E-11	8.89600	0.5E-15	38.0600	0.4E-08
7 19	283.00	0.3E-11	7.04600	0.5E-15	51.4700	0.3E-08
7 20	264.49	0.6E-11	6.40900	0.4E-15	48.0700	0.4E-08
7 21	262.02	0.7E-10	4.81700	0.9E-15	59.0400	0.8E-08
7 22	267.48	0.3E-10	4.36030	0.8E-15	67.0004	0.7E-08
7 23	247.30	0.2E-10	3.08100	0.6E-15	88.1920	0.7E-08
7 24	251.81	0.3E-06	3.71800	0.3E-10	119.600	0.4E-04
7 25	229.41	0.2E-05	3.41800	0.2E-09	110.900	0.2E-03
7 26	214.25	0.2E-05	2.17100	0.8E-09	95.4300	0.2E-03
7 27	198.04	0.3E-05	2.96730	0.2E-09	97.4200	0.4E-03
7 28	184.61	0.3E-05	1.81460	0.2E-09	90.6600	0.3E-03
7 29	178.79	0.4E-05	1.67220	0.2E-09	97.4400	0.4E-03
7 30	166.09	0.4E-05	1.55500	0.2E-09	92.1500	0.4E-03
7 31	154.41	0.4E-05	1.45830	0.2E-09	85.3800	0.4E-03
8 1	143.76	0.4E-05	0.87870	0.1E-09	79.3800	0.4E-03
8 2	133.13	0.4E-05	0.61300	0.1E-09	73.3800	0.4E-03
8 3	124.90	0.3E-05	0.46570	0.9E-10	68.5700	0.3E-03
8 4	133.89	0.3E-05	0.42120	0.8E-10	88.5200	0.3E-03
8 5	126.39	0.3E-05	0.38430	0.7E-10	93.6600	0.3E-03
8 6	117.10	0.3E-05	0.35230	0.5E-10	87.6200	0.3E-03
8 7	104.80	0.4E-05	0.22570	0.8E-10	82.0100	0.5E-03
8 8	93.890	0.9E-05	0.20370	0.2E-09	74.7300	0.9E-03
8 9	86.510	0.1E-04	0.15001	0.2E-09	68.7500	0.1E-02
8 10	81.430	0.1E-04	0.12701	0.2E-09	63.0600	0.1E-02

Table B.5 Cont'd

8 11	74.610	0.1E-04	0.10701	0.2E-09	58.6300	0.1E-02
8 12	70.010	0.1E-04	0.9E-01	0.1E-09	54.4000	0.1E-02
8 13	65.620	0.1E-04	0.7E-01	0.1E-09	50.3700	0.1E-02
8 14	60.980	0.1E-04	0.6E-01	0.9E-10	47.0700	0.1E-02
8 15	58.820	1.0E-05	0.5E-01	0.8E-10	48.2400	0.1E-02
8 16	54.850	0.9E-05	0.4E-01	0.6E-10	45.5600	0.9E-03
8 17	51.050	0.9E-05	0.4E-01	0.5E-10	42.0400	0.8E-03
8 18	46.400	0.8E-05	0.3E-01	0.4E-10	38.6400	0.8E-03
8 19	43.880	0.8E-05	0.2E-01	0.4E-10	36.3800	0.8E-03
8 20	41.490	0.7E-05	0.2E-01	0.3E-10	34.2100	0.7E-03
8 21	38.210	0.7E-05	0.2E-01	0.3E-10	31.1500	0.7E-03
8 22	34.030	0.6E-05	0.1E-01	0.2E-10	29.1700	0.6E-03
8 23	32.950	0.6E-05	0.1E-01	0.2E-10	27.2900	0.6E-03
8 24	31.940	0.6E-05	1.0E-02	0.1E-10	25.4600	0.6E-03
8 25	28.010	0.5E-05	0.8E-02	0.1E-10	23.0100	0.5E-03
8 26	27.160	0.5E-05	0.7E-02	0.1E-10	22.0300	0.5E-03
8 27	25.370	0.4E-05	0.6E-02	0.9E-11	20.5800	0.4E-03
8 28	23.400	0.4E-05	0.5E-02	0.7E-11	18.6600	0.4E-03
8 29	21.640	0.4E-05	0.4E-02	0.6E-11	17.5700	0.4E-03
8 30	20.410	0.4E-05	0.3E-02	0.5E-11	16.3300	0.4E-03
8 31	20.810	0.3E-05	0.3E-02	0.4E-11	20.7400	0.3E-03
9 1	19.790	0.3E-05	0.2E-02	0.3E-11	17.6700	0.3E-03
9 2	17.240	0.3E-05	0.2E-02	0.3E-11	15.9900	0.3E-03
9 3	16.130	0.3E-05	0.2E-02	0.2E-11	14.7000	0.3E-03
9 4	15.410	0.3E-05	0.1E-02	0.2E-11	13.7400	0.3E-03
9 5	14.060	0.3E-05	0.1E-02	0.2E-11	12.1200	0.3E-03
9 6	13.040	0.2E-05	0.9E-03	0.2E-11	11.7800	0.2E-03
9 7	12.930	0.2E-05	0.8E-03	0.1E-11	10.8500	0.2E-03
9 8	11.870	0.2E-05	0.7E-03	0.1E-11	10.9300	0.2E-03
9 9	10.790	0.3E-05	0.5E-03	0.1E-11	9.22500	0.3E-03
9 10	9.8070	0.3E-05	0.4E-03	0.1E-11	7.97900	0.3E-03
9 11	8.5270	0.3E-05	0.4E-03	0.1E-11	7.75300	0.3E-03
9 12	8.2700	0.3E-05	0.3E-03	0.9E-12	6.54700	0.3E-03
9 13	8.0540	0.3E-05	0.3E-03	0.7E-12	6.37200	0.3E-03
9 14	7.8300	0.2E-05	0.2E-03	0.6E-12	6.19300	0.2E-03
9 15	6.6220	0.2E-05	0.2E-03	0.5E-12	6.02900	0.2E-03
9 16	6.4300	0.3E-05	0.2E-03	0.5E-12	5.87800	0.2E-03
9 17	5.2530	0.2E-05	0.1E-03	0.4E-12	5.24000	0.2E-03
9 18	5.0890	0.2E-05	0.1E-03	0.4E-12	4.61200	0.2E-03
9 19	5.9380	0.2E-05	0.9E-04	0.3E-12	4.49400	0.2E-03
9 20	4.7980	0.2E-05	0.7E-04	0.3E-12	4.38600	0.2E-03
9 21	4.6690	0.2E-05	0.6E-04	0.2E-12	3.88700	0.2E-03
9 22	4.5550	0.2E-05	0.5E-04	0.2E-12	3.59800	0.2E-03
9 23	3.4430	0.2E-05	0.4E-04	0.2E-12	3.31200	0.2E-03
9 24	3.3400	0.2E-05	0.3E-04	0.2E-12	3.03200	0.2E-03
9 25	3.2440	0.2E-05	0.3E-04	0.1E-12	2.95920	0.2E-03
9 26	3.1550	0.2E-05	0.2E-04	0.1E-12	2.89130	0.2E-03
9 27	3.0710	0.2E-05	0.2E-04	0.1E-12	2.80860	0.2E-03
9 28	2.9950	0.2E-05	0.2E-04	0.1E-12	2.75040	0.2E-03

Table B.6. Output file from PRZM2
Atrazine concentration profile in lysimeter for
6 days after application (JUNE 30, 1995)

HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.2074	0.1863	0.5821E-01	0.1455E-07
1	11	0.1680E-01	0.1516E-01	0.4738E-02	0.1184E-08
1	12	0.2743E-11	0.2712E-11	0.8475E-12	0.2119E-18
1	13	0.1623E-15	0.1604E-15	0.5013E-16	0.1253E-22
1	14	0.9216E-20	0.9110E-20	0.2847E-20	0.7117E-27
1	15	0.0000	0.0000	0.0000	0.0000
1	16	0.0000	0.0000	0.0000	0.0000
1	17	0.0000	0.0000	0.0000	0.0000
1	18	0.0000	0.0000	0.0000	0.0000
1	19	0.0000	0.0000	0.0000	0.0000
1	20	0.0000	0.0000	0.0000	0.0000
1	21	0.0000	0.0000	0.0000	0.0000
1	22	0.0000	0.0000	0.0000	0.0000
1	23	0.0000	0.0000	0.0000	0.0000
1	24	0.0000	0.0000	0.0000	0.0000
1	25	0.0000	0.0000	0.0000	0.0000
1	26	0.0000	0.0000	0.0000	0.0000
1	27	0.0000	0.0000	0.0000	0.0000
1	28	0.0000	0.0000	0.0000	0.0000
1	29	0.0000	0.0000	0.0000	0.0000
1	30	0.0000	0.0000	0.0000	0.0000
1	31	0.0000	0.0000	0.0000	0.0000
1	32	0.0000	0.0000	0.0000	0.0000
1	33	0.0000	0.0000	0.0000	0.0000
1	34	0.0000	0.0000	0.0000	0.0000
1	35	0.0000	0.0000	0.0000	0.0000
1	36	0.0000	0.0000	0.0000	0.0000
1	37	0.0000	0.0000	0.0000	0.0000
1	38	0.0000	0.0000	0.0000	0.0000
1	39	0.0000	0.0000	0.0000	0.0000
1	40	0.0000	0.0000	0.0000	0.0000

Table B.7. Output file from PRZM2
Atrazine concentration profile in lysimeter for
30 days after application (JULY 23, 1995)

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HORZ  COMPART.  TOTAL       ADSORBED    DISSOLVED   GAS CONC.
                (MG/KG)     (MG/KG)     (MG/L)      (MG/L)

 1      10      0.2473      0.2220      0.6939E-01  0.1735E-07
 1      11      0.1650      0.1482      0.4630E-01  0.1157E-07
 1      12      0.8973E-01  0.8058E-01  0.2518E-01  0.6295E-08
 1      13      0.4105E-01  0.3686E-01  0.1152E-01  0.2880E-08
 1      14      0.1607E-01  0.1443E-01  0.4509E-02  0.1127E-08
 1      15      0.5422E-02  0.4869E-02  0.1522E-02  0.3804E-09
 1      16      0.1579E-02  0.1418E-02  0.4430E-03  0.1108E-09
 1      17      0.3958E-03  0.3555E-03  0.1111E-03  0.2777E-10
 1      18      0.8557E-04  0.7685E-04  0.2401E-04  0.6004E-11
 1      19      0.1542E-04  0.1458E-04  0.4555E-05  0.1139E-11
 1      20      0.3255E-05  0.3083E-05  0.9634E-06  0.2409E-12
 1      21      0.6397E-06  0.6061E-06  0.1894E-06  0.4735E-13
 1      22      0.1168E-06  0.1107E-06  0.3460E-07  0.8649E-14
 1      23      0.1991E-07  0.1888E-07  0.5900E-08  0.1475E-14
 1      24      0.3183E-08  0.3019E-08  0.9436E-09  0.2359E-15
 1      25      0.4798E-09  0.4554E-09  0.1423E-09  0.3557E-16
 1      26      0.6841E-10  0.6495E-10  0.2030E-10  0.5074E-17
 1      27      0.9230E-11  0.8767E-11  0.2740E-11  0.6849E-18
 1      28      0.1180E-11  0.1122E-11  0.3505E-12  0.8762E-19
 1      29      0.1424E-12  0.1354E-12  0.4230E-13  0.1057E-19
 1      30      0.1582E-13  0.1505E-13  0.4702E-14  0.1176E-20
 1      31      0.1594E-14  0.1517E-14  0.4739E-15  0.1185E-21
 1      32      0.1466E-15  0.1395E-15  0.4359E-16  0.1090E-22
 1      33      0.1245E-16  0.1184E-16  0.3701E-17  0.9253E-24
 1      34      0.9865E-18  0.9391E-18  0.2935E-18  0.7336E-25
 1      35      0.7374E-19  0.7021E-19  0.2194E-19  0.5485E-26
 1      36      0.5245E-20  0.4995E-20  0.1561E-20  0.3902E-27
 1      37      0.3573E-21  0.3403E-21  0.1064E-21  0.2659E-28
 1      38      0.2347E-22  0.2236E-22  0.6987E-23  0.1747E-29
 1      39      0.0000      0.0000      0.0000      0.0000
 1      40      0.0000      0.0000      0.0000      0.0000
```

Table B.8. Output file from PRZM2
Atrazine concentration profile in lysimeter for
Three months after application (SEPT. 28, 1995)

HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.2995E-02	0.2797E-02	0.7749E-03	0.1937E-09
1	11	0.2824E-02	0.2616E-02	0.8174E-03	0.2044E-09
1	12	0.2715E-02	0.2520E-02	0.7876E-03	0.1969E-09
1	13	0.2366E-02	0.2200E-02	0.6876E-03	0.1719E-09
1	14	0.1862E-02	0.1734E-02	0.5419E-03	0.1355E-09
1	15	0.1323E-02	0.1234E-02	0.3857E-03	0.9643E-10
1	16	0.8524E-03	0.7964E-03	0.2489E-03	0.6222E-10
1	17	0.5016E-03	0.4693E-03	0.1467E-03	0.3667E-10
1	18	0.2719E-03	0.2547E-03	0.7960E-04	0.1990E-10
1	19	0.1368E-03	0.1283E-03	0.4010E-04	0.1003E-10
1	20	0.6433E-04	0.6041E-04	0.1888E-04	0.4720E-11
1	21	0.2843E-04	0.2672E-04	0.8350E-05	0.2087E-11
1	22	0.1186E-04	0.1116E-04	0.3488E-05	0.8719E-12
1	23	0.4698E-05	0.4424E-05	0.1383E-05	0.3457E-12
1	24	0.1775E-05	0.1673E-05	0.5227E-06	0.1307E-12
1	25	0.6422E-06	0.6057E-06	0.1893E-06	0.4732E-13
1	26	0.2234E-06	0.2109E-06	0.6589E-07	0.1647E-13
1	27	0.7499E-07	0.7083E-07	0.2214E-07	0.5534E-14
1	28	0.2438E-07	0.2304E-07	0.7201E-08	0.1800E-14
1	29	0.7698E-08	0.7279E-08	0.2275E-08	0.5687E-15
1	30	0.2366E-08	0.2239E-08	0.6995E-09	0.1749E-15
1	31	0.7099E-09	0.6721E-09	0.2100E-09	0.5250E-16
1	32	0.2085E-09	0.1975E-09	0.6172E-10	0.1543E-16
1	33	0.6011E-10	0.5695E-10	0.1780E-10	0.4449E-17
1	34	0.1703E-10	0.1614E-10	0.5044E-11	0.1261E-17
1	35	0.4744E-11	0.4498E-11	0.1406E-11	0.3514E-18
1	36	0.1302E-11	0.1235E-11	0.3860E-12	0.9651E-19
1	37	0.3532E-12	0.3351E-12	0.1047E-12	0.2618E-19
1	38	0.9490E-13	0.9008E-13	0.2815E-13	0.7038E-20
1	39	0.2530E-13	0.2402E-13	0.7506E-14	0.1877E-20
1	40	0.6702E-14	0.6366E-14	0.1989E-14	0.4973E-21

Table B.9. Output file from PRZM2 Metribuzin concentration profile in lysimeter for 6 days after application (JUNE 30, 1995)

HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.2360	0.2189	0.4707E-01	0.4613E-08
1	11	0.1212E-01	0.1122E-01	0.2609E-02	0.2557E-09
1	12	0.2218E-09	0.2199E-09	0.5115E-10	0.5012E-17
1	13	0.5806E-14	0.5757E-14	0.1339E-14	0.1312E-21
1	14	0.1093E-18	0.1084E-18	0.2521E-19	0.2471E-26
1	15	0.0000	0.0000	0.0000	0.0000
1	16	0.0000	0.0000	0.0000	0.0000
1	17	0.0000	0.0000	0.0000	0.0000
1	18	0.0000	0.0000	0.0000	0.0000
1	19	0.0000	0.0000	0.0000	0.0000
1	20	0.0000	0.0000	0.0000	0.0000
1	21	0.0000	0.0000	0.0000	0.0000
1	22	0.0000	0.0000	0.0000	0.0000
1	23	0.0000	0.0000	0.0000	0.0000
1	24	0.0000	0.0000	0.0000	0.0000
1	25	0.0000	0.0000	0.0000	0.0000
1	26	0.0000	0.0000	0.0000	0.0000
1	27	0.0000	0.0000	0.0000	0.0000
1	28	0.0000	0.0000	0.0000	0.0000
1	29	0.0000	0.0000	0.0000	0.0000
1	30	0.0000	0.0000	0.0000	0.0000
1	31	0.0000	0.0000	0.0000	0.0000
1	32	0.0000	0.0000	0.0000	0.0000
1	33	0.0000	0.0000	0.0000	0.0000
1	34	0.0000	0.0000	0.0000	0.0000
1	35	0.0000	0.0000	0.0000	0.0000
1	36	0.0000	0.0000	0.0000	0.0000
1	37	0.0000	0.0000	0.0000	0.0000
1	38	0.0000	0.0000	0.0000	0.0000
1	39	0.0000	0.0000	0.0000	0.0000
1	40	0.0000	0.0000	0.0000	0.0000

Table B.10. Output file from PRZM2
Metribuzin concentration profile in lysimeter for
30 days after application (JULY 23, 1995)

HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.3417E-02	0.3150E-02	0.7326E-03	0.7180E-10
1	11	0.2355E-02	0.2171E-02	0.5049E-03	0.4948E-10
1	12	0.1170E-02	0.1079E-02	0.2510E-03	0.2460E-10
1	13	0.4524E-03	0.4172E-03	0.9702E-04	0.9508E-11
1	14	0.1421E-03	0.1310E-03	0.3046E-04	0.2985E-11
1	15	0.3705E-04	0.3416E-04	0.7945E-05	0.7786E-12
1	16	0.8112E-05	0.7480E-05	0.1739E-05	0.1705E-12
1	17	0.1498E-05	0.1381E-05	0.3212E-06	0.3148E-13
1	18	0.2349E-06	0.2166E-06	0.5037E-07	0.4936E-14
1	19	0.3085E-07	0.2958E-07	0.6879E-08	0.6741E-15
1	20	0.4640E-08	0.4455E-08	0.1036E-08	0.1015E-15
1	21	0.6458E-09	0.6202E-09	0.1442E-09	0.1414E-16
1	22	0.8316E-10	0.7989E-10	0.1858E-10	0.1821E-17
1	23	0.9963E-11	0.9575E-11	0.2227E-11	0.2182E-18
1	24	0.1117E-11	0.1073E-11	0.2496E-12	0.2446E-19
1	25	0.1177E-12	0.1132E-12	0.2633E-13	0.2580E-20
1	26	0.1172E-13	0.1127E-13	0.2621E-14	0.2569E-21
1	27	0.1102E-14	0.1060E-14	0.2465E-15	0.2416E-22
1	28	0.9796E-16	0.9428E-16	0.2193E-16	0.2149E-23
1	29	0.8194E-17	0.7889E-17	0.1835E-17	0.1798E-24
1	30	0.6290E-18	0.6057E-18	0.1409E-18	0.1380E-25
1	31	0.4363E-19	0.4202E-19	0.9773E-20	0.9577E-27
1	32	0.2755E-20	0.2654E-20	0.6173E-21	0.6050E-28
1	33	0.1604E-21	0.1546E-21	0.3594E-22	0.3523E-29
1	34	0.8644E-23	0.8331E-23	0.1937E-23	0.1899E-30
1	35	0.0000	0.0000	0.0000	0.0000
1	36	0.0000	0.0000	0.0000	0.0000
1	37	0.0000	0.0000	0.0000	0.0000
1	38	0.0000	0.0000	0.0000	0.0000
1	39	0.0000	0.0000	0.0000	0.0000
1	40	0.0000	0.0000	0.0000	0.0000

Table B.11. Output file from PRZM2
Metribuzin concentration profile in lysimeter for
Three months after application (SEPT. 28, 1995)

HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.1689E-07	0.1594E-07	0.3708E-08	0.3634E-15
1	11	0.1659E-07	0.1567E-07	0.3644E-08	0.3571E-15
1	12	0.1469E-07	0.1389E-07	0.3229E-08	0.3165E-15
1	13	0.1139E-07	0.1079E-07	0.2508E-08	0.2458E-15
1	14	0.7682E-08	0.7284E-08	0.1694E-08	0.1660E-15
1	15	0.4525E-08	0.4296E-08	0.9990E-09	0.9791E-16
1	16	0.2353E-08	0.2236E-08	0.5199E-09	0.5095E-16
1	17	0.1094E-08	0.1041E-08	0.2421E-09	0.2373E-16
1	18	0.4616E-09	0.4396E-09	0.1022E-09	0.1002E-16
1	19	0.1786E-09	0.1702E-09	0.3958E-10	0.3879E-17
1	20	0.6391E-10	0.6097E-10	0.1418E-10	0.1389E-17
1	21	0.2132E-10	0.2035E-10	0.4733E-11	0.4639E-18
1	22	0.6674E-11	0.6376E-11	0.1483E-11	0.1453E-18
1	23	0.1973E-11	0.1886E-11	0.4387E-12	0.4299E-19
1	24	0.5543E-12	0.5302E-12	0.1233E-12	0.1208E-19
1	25	0.1486E-12	0.1423E-12	0.3308E-13	0.3242E-20
1	26	0.3822E-13	0.3660E-13	0.8512E-14	0.8342E-21
1	27	0.9466E-14	0.9070E-14	0.2109E-14	0.2067E-21
1	28	0.2267E-14	0.2173E-14	0.5053E-15	0.4952E-22
1	29	0.5261E-15	0.5045E-15	0.1173E-15	0.1150E-22
1	30	0.1187E-15	0.1139E-15	0.2649E-16	0.2596E-23
1	31	0.2613E-16	0.2508E-16	0.5833E-17	0.5716E-24
1	32	0.5624E-17	0.5400E-17	0.1256E-17	0.1231E-24
1	33	0.1186E-17	0.1139E-17	0.2649E-18	0.2596E-25
1	34	0.2456E-18	0.2359E-18	0.5487E-19	0.5377E-26
1	35	0.4994E-19	0.4799E-19	0.1116E-19	0.1094E-26
1	36	0.9997E-20	0.9610E-20	0.2235E-20	0.2190E-27
1	37	0.1976E-20	0.1900E-20	0.4418E-21	0.4330E-28
1	38	0.3866E-21	0.3718E-21	0.8646E-22	0.8473E-29
1	39	0.7498E-22	0.7213E-22	0.1677E-22	0.1644E-29
1	40	0.1444E-22	0.1390E-22	0.3232E-23	0.3167E-30

Table B.12. Output file from PRZM2
Metolachlor concentration profile in lysimeter for
6 days after application (JUNE 30, 1995)

HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.4250E-01	0.3502E-02	0.2060E-02	0.7828E-09
1	11	0.5945E-03	0.4940E-03	0.2906E-03	0.1104E-09
1	12	0.1239E-12	0.1213E-12	0.7133E-13	0.2711E-19
1	13	0.9610E-17	0.9405E-17	0.5532E-17	0.2102E-23
1	14	0.7454E-21	0.7295E-21	0.4291E-21	0.1631E-27
1	15	0.0000	0.0000	0.0000	0.0000
1	16	0.0000	0.0000	0.0000	0.0000
1	17	0.0000	0.0000	0.0000	0.0000
1	18	0.0000	0.0000	0.0000	0.0000
1	19	0.0000	0.0000	0.0000	0.0000
1	20	0.0000	0.0000	0.0000	0.0000
1	21	0.0000	0.0000	0.0000	0.0000
1	22	0.0000	0.0000	0.0000	0.0000
1	23	0.0000	0.0000	0.0000	0.0000
1	24	0.0000	0.0000	0.0000	0.0000
1	25	0.0000	0.0000	0.0000	0.0000
1	26	0.0000	0.0000	0.0000	0.0000
1	27	0.0000	0.0000	0.0000	0.0000
1	28	0.0000	0.0000	0.0000	0.0000
1	29	0.0000	0.0000	0.0000	0.0000
1	30	0.0000	0.0000	0.0000	0.0000
1	31	0.0000	0.0000	0.0000	0.0000
1	32	0.0000	0.0000	0.0000	0.0000
1	33	0.0000	0.0000	0.0000	0.0000
1	34	0.0000	0.0000	0.0000	0.0000
1	35	0.0000	0.0000	0.0000	0.0000
1	36	0.0000	0.0000	0.0000	0.0000
1	37	0.0000	0.0000	0.0000	0.0000
1	38	0.0000	0.0000	0.0000	0.0000
1	39	0.0000	0.0000	0.0000	0.0000
1	40	0.0000	0.0000	0.0000	0.0000

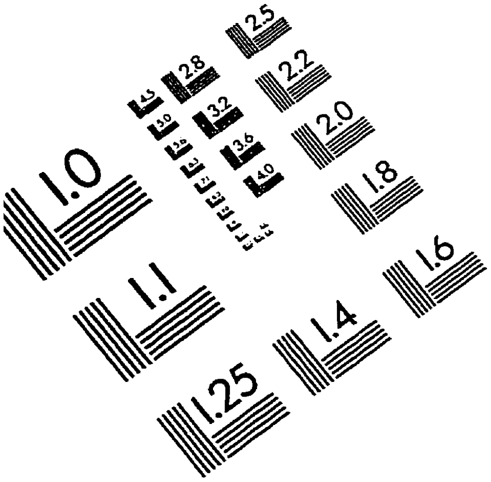
Table B.13. Output file from PRZM2
Metolachlor concentration profile in lysimeter for
30 days after application (JULY 23, 1995)

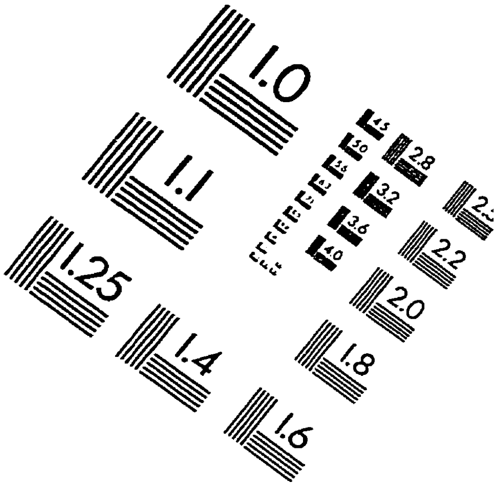
HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.8819E-01	0.7266E-01	0.4274E-01	0.1624E-07
1	11	0.5245E-01	0.4321E-01	0.2542E-01	0.9659E-08
1	12	0.2861E-01	0.2357E-01	0.1387E-01	0.5269E-08
1	13	0.1436E-01	0.1183E-01	0.6959E-02	0.2644E-08
1	14	0.6624E-02	0.5457E-02	0.3210E-02	0.1220E-08
1	15	0.2798E-02	0.2305E-02	0.1356E-02	0.5152E-09
1	16	0.1075E-02	0.8860E-03	0.5212E-03	0.1980E-09
1	17	0.3736E-03	0.3078E-03	0.1811E-03	0.6880E-1
1	18	0.1170E-03	0.9636E-04	0.5668E-04	0.2154E-10
1	19	0.3060E-04	0.2761E-04	0.1624E-04	0.6171E-11
1	20	0.1008E-04	0.9124E-05	0.5367E-05	0.2040E-11
1	21	0.3140E-05	0.2843E-05	0.1673E-05	0.6356E-12
1	22	0.9189E-06	0.8327E-06	0.4898E-06	0.1861E-12
1	23	0.2533E-06	0.2297E-06	0.1351E-06	0.5135E-13
1	24	0.6597E-07	0.5988E-07	0.3522E-07	0.1339E-13
1	25	0.1630E-07	0.1481E-07	0.8709E-08	0.3310E-14
1	26	0.3830E-08	0.3481E-08	0.2048E-08	0.7782E-15
1	27	0.8556E-09	0.7783E-09	0.4578E-09	0.1740E-15
1	28	0.1820E-09	0.1657E-09	0.9746E-10	0.3703E-16
1	29	0.3677E-10	0.3350E-10	0.1970E-10	0.7487E-17
1	30	0.6906E-11	0.6294E-11	0.3702E-11	0.1407E-17
1	31	0.1185E-11	0.1081E-11	0.6356E-12	0.2415E-18
1	32	0.1866E-12	0.1702E-12	0.1001E-12	0.3805E-19
1	33	0.2723E-13	0.2485E-13	0.1462E-13	0.5555E-20
1	34	0.3720E-14	0.3397E-14	0.1998E-14	0.7593E-21
1	35	0.4802E-15	0.4387E-15	0.2580E-15	0.9806E-22
1	36	0.5906E-16	0.5397E-16	0.3175E-16	0.1206E-22
1	37	0.6972E-17	0.6374E-17	0.3749E-17	0.1425E-23
1	38	0.7950E-18	0.7270E-18	0.4276E-18	0.1625E-24
1	39	0.8804E-19	0.8053E-19	0.4737E-19	0.1800E-25
1	40	0.9512E-20	0.8702E-20	0.5119E-20	0.1945E-26

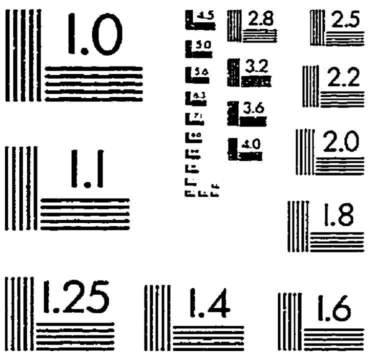
Table B.14. Output file from PRZM2
Metolachlor concentration profile in lysimeter for
Three months after application (SEPT. 28, 1995)

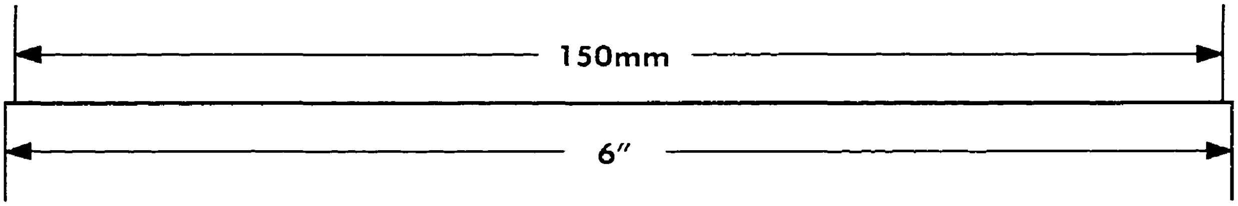
HORZ	COMPART.	TOTAL (MG/KG)	ADSORBED (MG/KG)	DISSOLVED (MG/L)	GAS CONC. (MG/L)
1	10	0.2701E-02	0.2440E-02	0.1024E-02	0.3889E-09
1	11	0.2231E-02	0.1940E-02	0.1141E-02	0.4338E-09
1	12	0.2265E-02	0.1977E-02	0.1163E-02	0.4419E-09
1	13	0.2123E-02	0.1859E-02	0.1094E-02	0.4157E-09
1	14	0.1847E-02	0.1623E-02	0.9545E-03	0.3627E-09
1	15	0.1498E-02	0.1320E-02	0.7764E-03	0.2950E-09
1	16	0.1138E-02	0.1005E-02	0.5911E-03	0.2246E-09
1	17	0.8120E-03	0.7190E-03	0.4229E-03	0.1607E-09
1	18	0.5475E-03	0.4859E-03	0.2858E-03	0.1086E-09
1	19	0.3504E-03	0.3117E-03	0.1833E-03	0.6967E-10
1	20	0.2140E-03	0.1907E-03	0.1122E-03	0.4263E-10
1	21	0.1252E-03	0.1117E-03	0.6572E-04	0.2498E-10
1	22	0.7034E-04	0.6290E-04	0.3700E-04	0.1406E-10
1	23	0.3810E-04	0.3412E-04	0.2007E-04	0.7627E-11
1	24	0.1994E-04	0.1789E-04	0.1052E-04	0.3998E-11
1	25	0.1011E-04	0.9083E-05	0.5343E-05	0.2030E-11
1	26	0.4979E-05	0.4478E-05	0.2634E-05	0.1001E-11
1	27	0.2386E-05	0.2149E-05	0.1264E-05	0.4803E-12
1	28	0.1116E-05	0.1006E-05	0.5917E-06	0.2249E-12
1	29	0.5103E-06	0.4605E-06	0.2709E-06	0.1029E-12
1	30	0.2286E-06	0.2065E-06	0.1215E-06	0.4616E-13
1	31	0.1006E-06	0.9093E-07	0.5349E-07	0.2032E-13
1	32	0.4353E-07	0.3938E-07	0.2317E-07	0.8804E-14
1	33	0.1857E-07	0.1682E-07	0.9893E-08	0.3759E-14
1	34	0.7824E-08	0.7091E-08	0.4171E-08	0.1585E-14
1	35	0.3256E-08	0.2953E-08	0.1737E-08	0.6600E-15
1	36	0.1340E-08	0.1216E-08	0.7151E-09	0.2717E-15
1	37	0.5460E-09	0.4958E-09	0.2916E-09	0.1108E-15
1	38	0.2210E-09	0.2008E-09	0.1181E-09	0.4488E-16
1	39	0.8896E-10	0.8087E-10	0.4757E-10	0.1808E-16
1	40	0.3566E-10	0.3244E-10	0.1908E-10	0.7251E-17

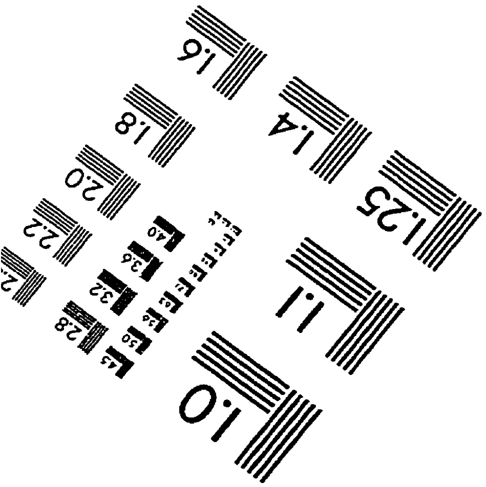
IMAGE EVALUATION
TEST TARGET (QA-3)











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