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USE OF SOIL AND VEGETATIVE FILTER STRIPS FOR REDUCING PESTICIDE AND NITRATE POLLUTION

by

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SOIL AND VEGETATIVE FILTERS FOR POLLUTION CONTROL

Abdolmajid Liaghat

ABSTRACT

Ph.D. Abdolmajid Liaghat **Agricultural and Biosystems Engineering**

The use of agricultural chemicals, such as pesticides and nitrogen fertilizers, often results in water pollution. This research, comprising of three parts, was designed to investigate the role of soil and grass strips and water table management in reducing pesticide and nitrate residues in drainage waters. The first part of the research was made on lysimeters to investigate the effects of soil and grass cover under two water table management regimes, subsurface drainage and controlled drainage. The study was done in lysimeters because parameters such as water table level, deep percolation, lateral losses of water, etc, are not easily controlled in field experiments. Twelve PVC lysimeters, 1 m long and 450 mm in diameter were packed with a sandy soil. Four treatments were involved: subsurface drainage, controlled drainage, grass cover, and bare soil. Each treatment consisted of three replicates. Contaminated water containing atrazine, metolachlor, and metribuzin residues was applied to the lysimeters and samples of drain effluent were collected. Significant reductions in pesticide concentrations were found in all treatments.

In the first year (1993), herbicide levels were reduced significantly (1% level), from an average of 250 μg/L to less than 10 μg/L. In the second year (1995), water polluted at a concentration of 50 μg/L, which is considered more realistic and reasonable in natural drainage waters, was applied to the lysimeters, and herbicide residues in drainage waters reduced significantly (1% level) to less than 1 µg/L. It was found that the subsurface drainage and grass cover lysimeters (SDG treatment) reduced herbicide concentration levels to a greater extent than the other treatments. Also, there is an indication that the concentration of nitrate in drain outflows was reduced by one-half. It was found that the controlled drainage lysimeters reduced nitrate concentration levels to a greater extent than the free drainage lysimeters.

The second part of the research was a field study that reports the development and testing of an on-farm pollution control system using soil as a biological filter for trapping herbicide residues. In 1994 and 1995, a field site with four shallow surface ditches, underlain with four perforated drain pipes, was used to carry-out field measurements. Polluted water with concentration levels of 30 mg/L of nitrate and 100 µg/L of three commonly-used herbicides, atrazine, metolachlor, and metribuzin, was applied to the ditches for 10 days continuously (actual daily application lasted for four hours); and no water was applied for the following ten days. This cycle was repeated three times. Water samples were collected both before application and after the water came out of the drains, in an observation chamber. Herbicide levels were reduced significantly (1% level) in drainage waters in comparison to the 100 µg/L level in applied water. In most cases, they were found to be 10 µg/L or less. The average concentration level of nitrate in drainage water was found to be 17 mg/L in comparison to 30 mg/L in applied water. Also, the bio-degradation of herbicide residues in the soil was found to occur between water applications. Thus, it appears that the system would be self-sustainable in the long term.

The third part of the research was a simulation study to estimate the size of grass filter area for removing pesticide residues from agricultural drainage waters. The method utilizes a water table management model, DRAINMOD, for simulating drainage waters from agricultural land and a solute transport model, PRZM2, for simulating pesticide concentrations in the drain effluent coming out of the grass filter area. DRAINMOD was used to estimate the daily drain outflows that would occur in a 100 ha subsurface drained field in the Ottawa-St. Lawrence lowlands by running the model for a 1-in-20 year annual rainfall period. The simulated drain outflows were assumed to contain 50 μg/L of atrazine, metolachlor, and metribuzin residues, and simulations were carried out with PRZM2 to determine the size of grass filter area needed to make drainage water safer for aquatic life. It was found that 6% of the farm area could be used to bring down the concentrations in drainage water from 50 μg/L to less than 1 μg/L for the three herbicides.

RESUME

Ph.D. **Abdolmajid Liaghat** **Génie Rural et Biosystémes**

L'utilisation de pesticides et de nitrates aboutit souvent à la pollution des eaux souterraines. Ce projet de recherche, comprenant trois parties, a été entrepris pour étudier le rôle du sol, le rôle de bandes d'herbe et la gestion du niveau d'eau dans le sol pour réduire la concentration de pesticides et de nitrates dans les eaux de drainage. La première partie de ce projet a été effectué en lysimètres pour étudier l'effet du sol et l'effet de l'herbe lors de deux régimes de gestion de niveau d'eau souterraine. Cet étude a été conduite en lysimètres, car certain paramètres tels que le niveau de l'eau dans le sol, et la perte d'eau aussi bien latérale qu'en profondeur, etc, ne sont pas facile à contrôller dans le champ. Douze lysimètres en PVC de 1 mètre de long et de 0.45 mètre de diamètre fûrent remplis de sol sablonneux. Quatre traitements ont été utilisés: simple drainage, drainage contrôllé, sol avec couverture d'herbe et sol sans couverture d'herbe. Chaque traitement comprenait trois réplicats. De l'eau contaminée avec de l'atrazine, du métolachlore, et du métrabuzine fût appliqée sur les lysimètres et l'effluent des drains fût échantillonné. Une réduction évidente a été observée pour chacun des traitements. Pendant la première année (1993), le niveau d'herbicides a été reduit en moyenne de 250 µg/L à moins de 10 µg/L. Lors de la deuxième année (1995), de l'eau polluée à une concentration de 50 µg/L fût appliquée

sur les lysimétres et une réduction jusqu'à moins de 1 μg/L fût observée. Le traitement de simple drainage avec couverture d'herbe a entrainé une meilleure réduction d'herbicides. De plus, le niveau de nitrate a été réduit de moitié. Le drainage contrôllé a entrainé une meilleure réduction en nitrate que le simple drainage.

La seconde partie de ce projet de recherche consistait du développement et du test d'un système de contrôle de pollution sur le site en utilisant le soil comme filtre biologique pour capturer les résiduts d'herbicides. En 1994 et 1995, un champ comprenant quatre drains et quatre fossés fût utilisé dans ce but. De l'eau polluée à une concentration de 30 mg/L de nitrate et contenant trois herbicides (atrazine, métalochlore, et métrabuzine) à une concentration de 100 μg/L a été appliquée dans les fossés pendant une période de 10 jours. Pendant une période de 10 jours suivant cette application, acune eau était appliquée. Ce cycle fût répèté trois fois. Des échantillons d'eau fûrent collectés avant, et après l'application de l'eau contaminée. Le niveau d'herbicide a été réduit, dans la plupart des cas, jusqu'à une concentration inférieure ou égale à 10 μg/L. La concentration moyenne de nitrate était de 17 mg/L. La bio-dégradation de résidus d'herbicides dans le sol a été observée entre les applications d'eau. Ainsi, il semblerait que le système se maintienne par lui même à long terme.

La troisième partie de cette recherche consistait en l'étude de simulation pour

estimer les dimension du champ utilisé comme filtre pour enlever les résidus de pestcides des eaux de drainage agricole. Pour cela, DRAINMOD, un modèle de gestion du niveau d'eau dans le sol, a été utilisé pour simuler les eaux de drainage dans un champ agricole. PRZM2, un modèle simulant le transport de pesticides dans le sol, a été utilisé pour simuler la concentration de pesticides dans l'effluent des drains provenant du champ utilisé comme filtre. DRAINMOD fût utilisé pour estimer la quantité journalière d'effluent des drains dans un champ de 100 hectares situé dans la région de Ottawa-St.Laurent en simulant une période de précipitation de 1-en-20 ans. La concentration en atrazine, métalochlore, et métrabuzine était fixée à 50 μg/L pour determiner avec PRZM2 les dimensions du champ utilisé comme filtre tout en faisant en sorte que les eaux de drainage soient sans danger pour la vie aquatique. Les résultats montrent que 6% de la surface des champ d'une production agricole est suffisant pour réduire la concentration des trois herbicides de 50 μg/L à moins de 1 μg/L.

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to all who have contributed to this study. In particular, I would like to express my special gratitude and appreciation to Dr. Shiv O. Prasher, my thesis supervisor and professor of Agricultural Engineering and Biosystems, for patiently and skilfully guiding me through my research and thesis preparation. Many thanks to Dr. Broughton who helped me in setting up the field work, including installation of subsurface drainage pipes and pump, and constructing the control chamber. His technical assistance and his willingness to be consulted is greatly appreciated. Appreciation is also extended to the members of my supervisory committee, consisting of Dr. Raghavan, Dr. Alikhani, Dr. Bonnell and Dr. Marshall, who all made useful suggestions during the initial stages of my research.

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It is not fair if I do not acknowledge my wife, Mitra, and my sons, Mehdi, Rasoul, and Amin, for withstanding the hard time and troubles during the course of the present study. This thesis would not be possible without their love, support, understanding, encouragement and patience that gave me the strength to complete what has sometimes appeared to be an overwhelming task. I would like to thank my parents, sisters and brothers for their good wishes and continued moral support in completing this work. They suffered a lot when my brother passed away. They carried the sadness alone and did not inform me until 1 year later so that I could complete this work. In the end, I am feeling very sad that my brother and my father could not live long enough to see me fulfilling their dream. It was due to their blessings and endless affection for me that I have completed this work.

Most of all, I thank God for giving me life to share with others, for giving me abilities to use for the benefit of mankind, and to help preserve the beautiful work of his hands in our environment. I dedicate this thesis to the people of IRAN that contributed in this dissertation indirectly.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Size of filtration area (ha)
A_d	Area of the drained area (m^2)
a.i.	Active ingredient
A_t	Area of the drain pipe (m^2)
AZ	Atrazine
BCD	Bare soil lysimeters with controlled drainage
BSD	Bare soil lysimeters with subsurface drainage
CEC	Cation exchange capacity
D	Lateral drainage from, or subirrigation into, the section (mm)
DP	Dry period
DS	Deep seepage (mm)
EPA	Environmental Protection Agency (United States)
ET	Evapotranspiration (mm/day)
F	Infiltration entering the section (mm)
GC	Gas chromatography
GCD	Grass covered lysimeters with controlled drainage
GSD	Grass covered lysimeters with subsurface drainage
h	Hydraulic head
HPLC	High performance of liquid chromatography
K	Hydraulic conductivity (m/day)
K_d	Soil-water partition coefficient (mg/g)
K_{OC}	Soil sorption coefficient (g/mL)
MT	Metolachlor
MZ	Metribuzin
n	Manning's coefficient
N	Nitrogen

nd	Nondetected
NO_3-N	Nitrate nitrogen
OMOE	Ontario Ministry of the Environment
ppb	Parts per billion
ppm	Parts per million
PVC	Polyvinylchloride
Q	Flow into a unit length of drain per unit time (m/day)
r	Radius to outside of drain (mm)
R	Hydraulic radius (mm)
R_d	Drain outflow rate (mm/day)
R_p	Pumping rate (mm/day)
S	Slope
t	Depth of water ponded on the soil surface (m)
VFS	Vegetative filter strips
Δv_a	Change in the air volume (mm)
θ	Soil water content (cm^3/cm^3)
$	Dollars

MANUSCRIPT AND AUTHORSHIP

The following is a statement from the faculty of Graduate Studies and Research concerning manuscript-based theses:

"Candidates have the option of including, as part of the thesis, the text of a paper(s) submitted or to be submitted for publication, or the clearly-duplicated text of a published paper(s). These texts must be bound as an integral part of the thesis.

"If this option is chosen, **connecting texts that provide logical bridges between the different papers are mandatory**. The thesis must be written in such a way that it is more than a mere collection of manuscript; in other words, results of a series of papers must be integrated.

"The thesis must still conform to all other requirements of the "Guidelines for Thesis Preparation". **The thesis must include:** A Table of Contents, an abstract, in English and French, an introduction which clearly states the rationale and objectives of the study, a comprehensive review of the literature, a final conclusion and summary, and a thorough bibliography or reference list.

"Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

"In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent.** Supervisors must attest to the accuracy of such statement at the doctoral oral defence. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers. **Under no circumstances can a co-author of any component of such a thesis serve as an examiner for that thesis."**

Mrs Chen Li, technician of soil and water quality laboratory of Agricultural and Biosystem Engineering Department, analyzed some the soil and water samples on the GC. Cation exchange capacity (CEC) and organic matter content of the soil were measured by the Soil Testing Laboratory of Natural Resource Science Department.

Professor Shiv O. Prasher contributed in all aspects of this research project. He provided the necessary funds and assistance for this research, including the normal supervisory guidance and the reviewing of manuscripts before their submission for publication. Dr. R.S. Broughton, professor of Agricultural Engineering and Biosystem Department, helped in the field setup, including subsurface drain installation and control chamber construction. He also read one of the papers and gave useful suggestions.

CONTRIBUTION TO KNOWLEDGE

The experimental, lysimeter and field studies, as well as the simulation study in this research provide the following findings as original contributions to knowledge:

1. A new and effective method of reducing agricultural pollution from farmlands in humid regions has been developed. The method uses soil and grass strips as biological filters to remove pesticides and nitrate-N residues in drainage waters.

2. A computer modeling approach has been developed for determining the size of filtration area needed to remove pollutants from agricultural drainage waters. This method can estimate the farm area that will be needed for biological filtration to bring concentration levels of herbicides in drainage waters down to acceptable levels (less than 1 μg/L) for both human consumption and safeguard of aquatic life and marine habitat. For Ste-Amable sandy soil in southwestern Quebec and a 1-in-20 year annual rainfall event, it was found that no more than 6% of the farm area will be needed to bring concentration levels down from 50 μg/L to less than 1 μg/L.

3. The soil and grass filters could be self-sustainable over a long period due to biodegradation of organic chemicals during the dry period when utilizing a water application strategy. In actual practice, the dry period would vary according to rainfall. The adsorption potential of soil for herbicides is high at the beginning of each wet period and tends to decrease during the application of polluted water. This potential also tends to increase during the dry period due to degradation processes in the soil.

4. The trapping efficiency of the system was found to correspond to the total volume of water to be treated and the total mass of pollutants. The trapping ratios for herbicides and nitrates were found to exceed 97% and 85%, respectively.

5. The greatest nitrate reduction was associated with grass covered lysimeters with controlled drainage and water table depth of 0.5 m. However, denitrification, and not plant uptake, was the predominant process for nitrate reduction in this system.

6. More herbicides from polluted water were trapped in lysimeters that were grass-covered and subsurface drained. This is due to grass organic matter with

high sorption potential and the soil with low moisture content in the subsurface drainage lysimeters. The dry soils adsorb pesticides to a greater extent than wet soils. The soil columns in the subsurface drainage lysimeters had lower moisture content, than those with controlled drainage.

7. The concentration of herbicides in drainage waters was found to correspond with the rank order of soil sorption coefficient and water solubility of the herbicides. Metribuzin, with the high water solubility and low soil sorption coefficient, was the herbicide found in the highest concentrations in drainflow water.

CHAPTER 1

INTRODUCTION

1.1 PROBLEM DEFINITION

Widespread agrochemical use, including fertilizer and pesticides, has been brought about by economic factors and farmer's efforts to obtain increased return on their investment in crop production systems. Between 1974 and 1985, agrochemical use has increased by 15% (Hallberg, 1986a). In 1986, U.S. farms had pesticide and fertilizer expenditures of approximately 57% and 75% of the total, respectively (Hallberg, 1986a). Long-term history on tonnage of pesticides use is not available, but the USDA has tracked dollars spent on pesticides over the past 50 years. Pesticide sales to agriculture grew rapidly after the mid-1960s and are currently at about $7 billion annually (John Deere Technical Report, 1995). In Canada, about 500 pesticide active ingredients are currently registered for use. Every year, more than 2 million tonnes of fertilizer and 33000 tonnes of pesticides are applied on farmlands; of this, Quebec accounts for 5.5% (Forrest and Caux, 1988). There is significant potential for extensive surface and groundwater contamination resulting from continued high fertilizer and pesticide applications if current water-management and crop-production practices are followed (Fouss and Willis, 1990).

Half of the people in the United States get their drinking water from ground water. In rural communities, approximately 95% of the population depends on wells for drinking water (Severn and Ballard, 1990). Various estimates suggest that 5% of the US population depends on water supplies contaminated with domestic sewage, agricultural chemicals, and industrial waste. Recent reports suggest that 10% of community drinking water wells and 4% of rural domestic wells in the United States contain detectable levels of pesticide residues (US EPA, 1990). In North America, the ground water provides between 24 and 95% of the drinking water supply (Office of Technology Assessment, 1984). In Quebec, the majority of the people and most of the farmland are located along the Saint-Lawrence River and its tributaries. Some of the tributaries are located in watersheds with intensive agricultural activity. Any activity that changes surface and ground water will impact many people and aquatic life. Contaminated surface and ground water is a multidimensional problem of extraordinary concern.

Research over the last decade has clearly shown that agriculture has become the greatest source of nitrate and pesticides delivered to ground and surface water (Skaggs et al., 1994; Evans et al., 1992; Logan et al., 1993; Hallberg 1986a, 1986b, 1987a, 1987b; Keeney, 1982; Pratt 1984; Gaynor et al., 1995; Bengeston et al., 1990; 1992; Masse et al., 1990). Sharply and Meyer (1994) state that agricultural nonpoint sources now account for more pollution than point source pollution. A number of comprehensive reviews have been published concerning nitrate contamination in the environment and nitrate toxicity and health effects (Aldrich, 1984; Brezonik, 1978; Cast, 1985; Duijvenbooden and Matthijsen, 1987). Over the last 20 years, there has been an almost linear increase in groundwater nitrate-N concentration (Hallberg, 1986a, 1987a; Bock and Hergert, 1991). This has been due primarily to the proliferation of the use of nitrate fertilizers (Bock and Hergert, 1991).

Drainage also carries fertilizer-nitrate residues from agricultural land and contributes significantly to the pollution (Patni et al., 1992; Gilliam et al., 1985; Skaggs, 1989). Some researchers have estimated that between 30 and 60% of the nitrogen fertilizer applied in Quebec is leached out to waterways and ground water after the fall rain and surface runoff (Miller and Mackenzie, 1978; Neilson and Mackenzie, 1977). In some areas, nitrogen pollution in ground water has reached alarming levels. For example, Hubbard and Sheridan (1989) reported that in many agricultural areas, nitrate-N levels in drinking water were significantly higher than the maximum contamination level of 10 mg/L set by the U.S. Environmental Protection Agency (EPA). Nitrate levels as high as 120 mg/L in tile drainage water have been reported under corn in Iowa, Minnesota, and Ohio (Logan et al., 1990). In New Brunswick, Milburn et al. (1990) found concentrations as high as 65 mg/L when associated with potato cropping. In a St. Jude sandy loam soil, Madramootoo et al. (1992) measured values of 2 to 40 mg/L in the drainage water from a potato field. Blue baby syndrome and stomach cancer are two health problems associated with high levels of nitrate in drinking water. Nitrates also promote the growth of algae and other aquatic plants in surface waters. In turn, algae deteriorate the water quality for domestic and recreational uses and also decimate fish populations by reducing the oxygen content of the water.

Pesticides have also been identified in ground water, drainage water, and runoff in US, Canada, and Europe (US Environmental Protection Agency, 1990, 1992; Frank and Sirons, 1979; Pupp, 1985; Bastien, 1991; Logan et al., 1993; Munster et al., 1994; Flury, 1996; Clark et al., 1991; Legrand et al., 1992). Both atrazine and alachlor have been detected in surface and subsurface drainage outflow at concentrations exceeding the EPA maximum contaminant level advisory of 3 μg/L and 2 μg/L, respectively. Pereira and Hostettler (1993) estimated that the Mississippi river carries an annual mass of 160 t atrazine, 71 t simazine, 56 t metolachlor, and 18 t alachlor into the Gulf of Mexico. Wauchope (1978) estimated that 1 to 2% of the applied mass can be lost in a single-runoff event. Loss of pesticides into subsurface drains as high as 3.6% of the applied mass of atrazine (Southwick et al., 1992; Gaynor et al., 1995) and 2.23% of metolachlor have been reported (Gaynor et al., 1995).

Pesticides in waters may be toxic to fish, wildlife, and plants. It is well known that chemicals that may have little direct impact on human health may have potentially severe impacts on fish and wildlife (see Table 1.1). For example, although

DDT was only slightly toxic to mammals, including humans, it was highly toxic to certain species of birds and game fish. Birds, mammals and fish have been killed in large numbers by chemical poisons spread on forests, fields, and over lakes and streams. Fish populations in the United States are presented with many different hazards. One outstanding example is in the treatment of croplands with pesticides. If large quantities reach the fish, they may die immediately.

Table 1.1: Recommended water quality guidelines for nitrate-N, atrazine, metolachlor and metribuzin.

Uses	Atrazine (µg/L)	Metolachlor (µg/L)	Metribuzin (µg/L)	NO_3-N (mg/L)
Drinking water				
CANADA$^{(1)}$	60	50	80	10
US$^{(2)}$	3	10	175	10
Freshwater aquatic life	2	8	1	...
Agricultural uses				
Livestock watering	60	50*	80	...
Irrigation	10	28*	0.5	...

(1) Canadian Water Quality Guidelines (CWQG), 1990, 1991.
(2) United States Environmental Protection Agency (USEPA), 1977.
* Interim

Various chronic conditions may result, if smaller quantities of pesticide reach the fish over a long period of time. The toxicant may accumulate in the fatty tissues and later be released into the body at times of stress, resulting in liver and kidney damage, or reduced red blood cell production. Other effects are depressed growth rates and reduced efficiency of reproduction. Fish populations are sometimes affected by destruction of the food supply. If the invertebrates in a body of water are eliminated by a chemical treatment, the fish are left with little or no food and must subsist on the reserves within their own bodies. This can result in lowered resistance to disease or death due to the release of poisons stored in the body fat.

1.2 EXTENT OF POLLUTION AND ENVIRONMENTAL CONCERNS

The available information in Canada indicates that pesticides have been found in wells across the country (Pupp, 1985). When the Ontario Ministry of the Environment (OMOE, 1987a, 1987b) sampled 15 municipal waterworks in 1985, 6 of 31 samples contained metolachlor with a concentration range of 0.4-5.1 μg/L. A report by the Quebec environment ministry, released in Saint-Hyacinthe in mid-December 1994, states that 6,000 corn producers in Quebec are currently using pesticides on more than 350,000 cultivated hectares. Some of these chemicals are seeping into watercourses and damaging aquatic life. The US Geological Survey (USGS) found that 55 percent of the streams tested in 10 Mid-Western States had detectable levels of pesticides prior to spring planting, when contaminants levels were expected to be lowest (Goolsby, 1991).

Drainage improvement for agricultural purposes is increasingly viewed by the general public and environmentalists as being unfriendly to our environment. In humid regions of North America, where most agricultural fields are subsurface drained, the quality of water from drainage systems has become a major concern. This scepticism has reached such heights in the United States that at a National Conference on wetlands, one official proposed that "agricultural production should not be permitted on any land that requires drainage" (Gilliam, 1987). The assistant deputy minister of the environment of Québec (Michel Paradis) said in a public report in December 1994, "the solution to help ease the increasing environmental headache is for the province's corn producers to drastically reduce the amount of herbicides they currently use, as well as opt for more sustainable cultivation practices".

A new and rapidly expanding field of study in the US, termed "ecotoxicology", is concerned with the fate and impact of toxic compounds in ecosystems. Such studies increased with the establishment of the EPA (U.S. Environmental Protection Agency) and its mandate to protect human health and the environment. In response to growing concerns about the ecological impact of toxic compounds, the EPA's Risk Assessment Council established the Ecotoxicity Subcommittee in 1987 to develop ecological risk assessment guidelines.

In recent years scientists have been working to reduce agricultural chemical use to a minimum. Regulations, limiting the use of crop nutrients and agrochemicals to protect groundwater quality, have been established in several states of the US. The

US Federal clean water Act now includes provisions on ground water. The Quebec Environment Minister has also clearly stated that all polluters, including agricultural farms, will be held responsible and accountable for their part in damaging our natural resources, and for dealing a blow to our freshwater aquatic life and their habitat by year 2000. In North Carolina, regulatory agencies now recommend that agricultural drainage water be pumped into wetland areas.

1.3 REMEDIAL PRACTICES

Today, agricultural scientists have shifted their research emphasis to sound and sustainable systems of crop production. Since reduction in fertilizer and pesticide application rate would result in yield reduction, current research efforts are focused on practices that reduce chemical (such as nitrates and pesticides) leaching without compromising crop productivity. Some pollution control techniques that are still under review include: 1) water table control and subirrigation, identified as best water table management (BWTM) practices, effective in reducing nitrate and pesticide losses; 2) grass border strips, effective in preventing sediment production and consequently reducing pesticide transformation into watercourses; 3) wetlands and ponds, suggested as methods to reduce nitrogen transport from agricultural lands. Cultural practices such as sound fertilizer and pesticide management (time of application, rate of application, method of application), tillage management practices (conventional tillage, reduced tillage, and no tillage), intercropping, as well as crop rotation systems are other management practices in reducing environmental pollutants.

While such management practices help to reduce and minimize the movement of chemicals to ground water, it is virtually impossible to eliminate chemical leaching while keeping food production at a sufficient level. These management practices may not be used to their potential. In addition, some practices are site-specific and may not be technically feasible in other locations. For example, water table management (WTM) practices depend on climatic conditions, soil texture, and shallow ground water or the existence of a shallow impermeable layer. Only 10,000 ha of the cultivated land in the entire province of Quebec utilize some form of water table control. So far, no attempt has been made to treat contaminated agricultural water in situ, probably due to high costs. However, many agricultural fields in humid areas are now tile-drained. Hence, polluted drainage water and surface runoff can be collected at the end of the collector drains, enabling treatment before discharge into the water courses.

The purpose of this research is to investigate the feasibility of cleaning contaminated drainage water and surface runoff in order to improve the quality of water which discharges into our rivers and lakes. The proposal involves using the soil profile as a filter and establishing an on-farm biological pollution control system, in the form of grass border strips that would not only trap sediments but would also adsorb nitrate and pesticide residues from drainage water (Figure 1.1).

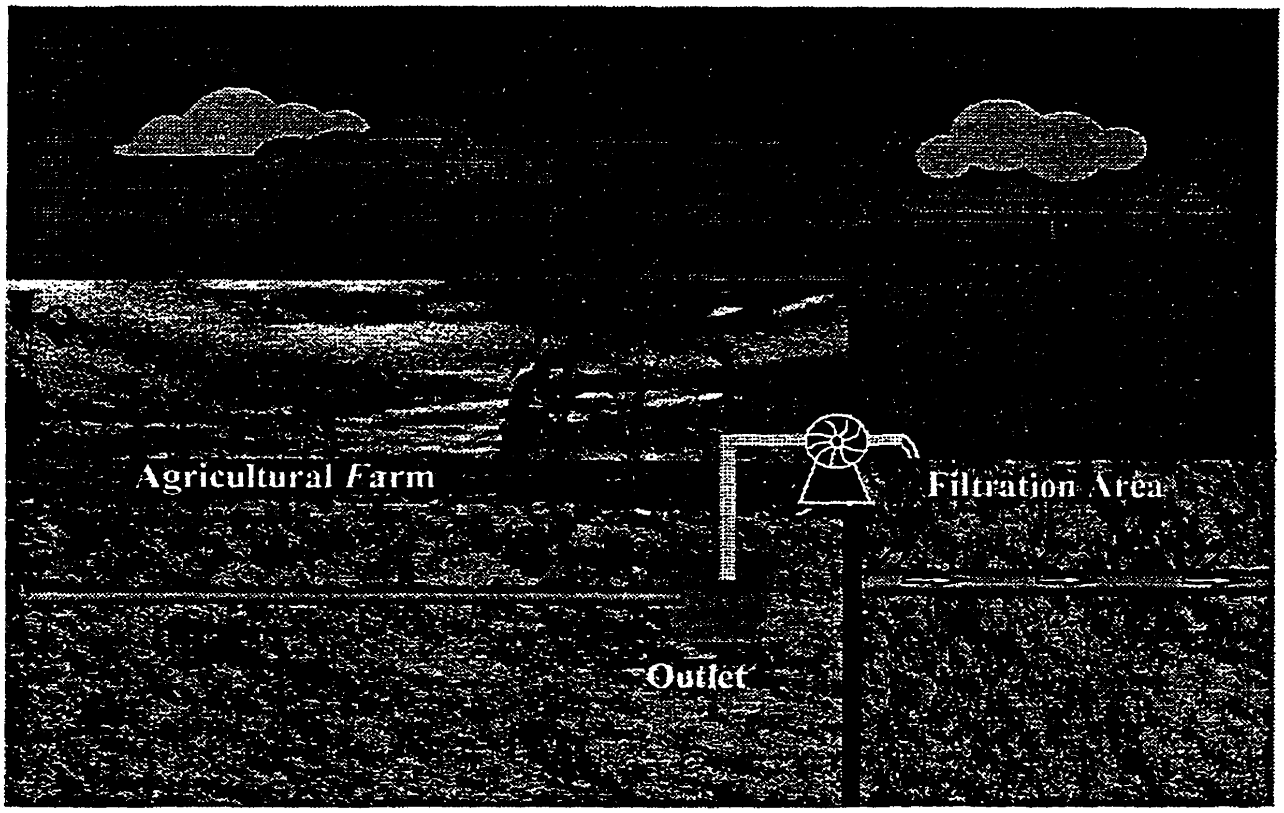

Figure 1.1: Schematic of a filtration area.

Developing pollution control techniques requires some measurements and evaluation of different alternatives. Field-scale and laboratory experimentation can be expensive as well as time consuming. Therefore, computer simulation models have been used as an alternative to physical experiments. DRAINMOD and PRZM2, which have been shown applicable to Quebec conditions, are used to determine the size of filtration area.

1.4 OBJECTIVES

The main objective of this study was to develop an on-farm pollution control and self-sustainable system for reducing pollution loading of surface water by lowering pesticide levels in drain effluent.

This study was based on three hypotheses:

1. Contaminated drainage waters could be passed through the soil system, making it possible to be treated before discharge into the river. In other words, soil profile and grass border strips can act as biological filters for trapping pesticides, fertilizer residues, and sediments in drainage water and surface runoff.
2. Water table management could reduce pesticide and nitrate residues in contaminated drainage waters by enhancing denitrification and biodegradation processes in the soil system,
3. DRAINMOD, a well known water table management model, and PRZM2, a known pesticide transport model, could be used to determine the size of filtration area needed to bring pesticide concentration in drainage water to below threshold levels in Southern Quebec conditions.

Therefore, the objectives of this study were to:

1. Investigate the effectiveness of soil and grass filters in reducing pesticide and nitrate levels in drain effluent based on measurements of nitrate, atrazine, metolachlor, and Metribuzin concentrations (the most commonly-used and problem agrochemicals in Quebec) before and after they pass through the filters in both lysimeter and field studies.
2. Investigate the performance of water table management (free drainage and controlled drainage) in reducing nitrate and pesticide levels in drained effluent, in both grass covered and "bare" soil filters, using large lysimeters.
3. Make investigations to determine the capacity of grass and soil filters to reduce pesticide levels under local geo-hydrologic conditions, in order to assess their effective field life.
4. Develop a modeling approach to determine the size of filter area for pollution control strategies that is applicable at the field scale.
5. Make recommendations in terms of the size, and location of these filters on agricultural farms.
6. Estimate the preliminary cost associated with the filtration area needed to treat agricultural polluted waters.

The above objectives were met through doing study on three parts; lysimeters, field and mathematical models. Objectives 1 and 2, consisted of four treatments (water tables combined with the bare and grass covered soil), were met through the lysimeters study. Objective number 3 was met through the field study in order to reflect field variability. Objectives 4 and 5 were met through the mathematical modeling study in order to determine the size of filtration area.

1.5 THESIS ORGANIZATION

Chapters 1 and 2 present the general introduction and literature review. The results of this research are reported in Chapters 3, 4 and 5 in the form of three papers with connecting texts. The titles of the three papers included in the thesis are:

1. A lysimeter study of grass cover and water table depth effects on pesticide residues in drainage water. Authors: A. Liaghat and S. O. Prasher. Published in Transactions of the ASAE, July 1996 issue, 39(5): 1731-1738.
2. Evaluation of an on-farm pollution control system for reducing pesticide pollution. Authors: A. Liaghat, S. O. Prasher, and R. S. Broughton. Published in Transactions of the ASAE, January 1996 issue, 39(4): 1329-1335.
3. Application of mathematical modeling to determine the size of on-site grass filter strips for reducing pesticide pollution from farms. Authors: A. Liaghat and S. O. Prasher. It has been submitted to Journal of Irrigation and Drainage Engineering for publication.

The data collected in this project as well as the input data files for the mathematical models are available on diskettes from the author or his supervisor upon request.

1.6 SCOPE

In this study, the results are limited to a Ste-Amable sandy soil containing 3.5% organic matter content under Quebec geo-hydrologic conditions. The herbicides used in this study were atrazine, metolachlor, and metribuzin. These chemicals are the most common herbicides used in Quebec. Therefore, the results may not be generally applicable to other herbicides due to differences in their physico-chemical properties. Measurements are restricted to the herbicide residues in the soil and water samples. Metabolites of the three herbicides were not monitored in this study. Polluted water was applied on the filtration area with a 10-day increment, i.e. water was applied for 10 consecutive days (wet period), followed by a 10-day dry period. However, in a real field, these periods depend on daily rainfall. In addition, the lysimeter setup used in this study was above ground and thus would have caused somewhat higher soil temperatures than otherwise. This might have led to greater herbicide and nitrate losses in this study.

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CHAPTER II

LITERATURE REVIEW

National awareness of environmental contamination by agriculture dates back at least to 1962, with the publication of Rachel Carson's 'Silent Spring'. Since that time, considerable national concern has developed concerning the issue of nitrate and pesticide residues in surface and ground water. By the late 1970s, extensive regional studies had clearly identified the causes and extent of agricultural non-point source (NPS) surface water pollution by sediment and nutrients. During the same period, efforts were taken to control agrochemical pollution either using remedial plans or agricultural management practices. This chapter includes a review of previous studies related to environmental impacts of land drainage. Some of the on-farm pollution control systems are presented. In addition, DRAINMOD, a water table management model, as well as PRZM2, a pesticide transport model, are presented.

2.1 Effects of Agricultural Drainage on Water Quality

In humid regions of North America, the climate is such that there is often an excess of soil water: in the spring due to snowmelt, and in the autumn when rainfall is in excess of evapotranspiration. During these times subsurface drainage is required to remove excess water and provide suitable growth conditions. Land drainage also protects plants from waterlogging and can be used to control salinity in irrigated arid lands (Reeve and Fausey, 1974). For these reasons, farmland is made more productive through the installation of subsurface drainage systems. Although artificial drainage has many benefits, it can also be a major pathway through which soluble and mobile nitrates and pesticides enter the environment and cause eutrophication of surface waters or accumulate toxic substances in the ground water. Artificial drainage is now perceived to be a major contributor to off-site environmental impacts (Skaggs et al., 1994; Evans et al., 1995; Thomas et al., 1995; Fausey et al., 1995; Backlund et al., 1995; Ritter et al., 1995; Shirmohammadi et al., 1995). At present, about 600,000 ha (about 33%) of cultivated land in Quebec is subsurface-drained (Shady, 1989), resulting in a significant potential for increased leaching of agrochemicals to surface and groundwater bodies. Since 23% of the agricultural land requires improved drainage, it is essential to ensure that new systems are designed to reduce off-site impacts.

2.1.1 Pollution from nitrogen fertilizer

Since nitrogen has an essential role in crop yield production, farmers apply excessive quantities of inorganic fertilizer nitrogen in an attempt to ensure maximum yields. Every year in Canada, over $100 million of nitrogen fertilizer is applied (Canadian Fertilizer Institute, 1990), but 20 to 60% of this fertilizer may be lost from the soils through runoff, leaching or denitrification. Some researchers have estimated that 30 to 60% of the nitrogen fertilizer, applied in Quebec, is leached out to waterways and ground water after fall rain and surface runoff (Miller and Mackenzie, 1978; Nielson and Mackenzie, 1977). Leaching is a function of the amount of nitrate-N applied on the soil surface and mineralization of organic N, the amount of precipitation and/or irrigation, the quantity removed by plant uptake and the amount disappearing by denitrification. Gilliam et al. (1985) reported that major losses of nitrate to water bodies occurred on subsurface drained farmland cultivated for several years in North Carolina. Skaggs (1989) reported that a corn field soil with poor subsurface drainage would lose about 17 kg/ha/yr of nitrate-N in North Carolina. However, with improved drainage, the nitrate-N losses would increase from about 22 to 34 kg/ha/yr (Skaggs et al., 1994). Nitrate losses in conventional drainage effluent typically exceeded 20 kg/ha/yr in North Carolina (Evans et al., 1991). Legg and Meisinger (1982) pointed out that nitrate leaching is the most significant loss of nitrogen from soil. An average of 25 to 50% of the N applied in most cropping lands is lost through leaching (McNeal and Pratt, 1978). In the eastern Ontario, Patni et al. (1992) reported total nitrogen loads in subsurface drainage during January to August of 20 to 29 kg/ha.

Nitrate leaching is most common in sandy soils with shallow water tables where excessive water is applied either in the form of precipitation or irrigation. Nitrate levels as high as 120 mg/L in tile drainage water have been reported under corn in Iowa, Minnesota, and Ohio (Logan et al., 1990). In New Brunswick, Milburn et al. (1990) found concentrations as high as 65 mg/L, associated with potato cropping. In the Lower Mississippi Valley, Bengtson et al. (1995) reported nitrate concentration in subsurface drainage water as high as 36 mg/L. Madramootoo et al. (1992) measured nitrogen losses in subsurface drainage from two potato fields. Nitrogen concentrations in the tile effluent ranged from 1.7 to 40.02 mg/L. The total nitrogen loads in subsurface drainage during the growing season (April-November) from the two fields were 14 and 70 kg/ha in 1990.

Reports of nitrate contamination of ground water resulting from agricultural activities can also be found in the literature. In a 1984 study, the U.S. Geological Survey evaluated data from 124,000 wells nationwide. About 6% of the wells exceeded the nitrate-N standard and about 20% had above 3 mg/L (Madison and Brunett, 1985). Nitrate-N concentrations greater than 10 mg/L have been reported in ground water under agricultural areas in Quebec (Madramootoo et al., 1993) and Ontario (Hill, 1982). Many experiments have been conducted to study the effects of cropping system, tillage, and fertility management on subsurface drainage water quality (Kanwar and Baker 1993; Buhler et al., 1993; Randall et al., 1993; Gaynor et al., 1992; and Logan et al., 1993). These studies generally indicate that tillage, cropping system, and fertility management greatly influences the amount and timing of nitrate and total nitrogen in subsurface drainage water.

2.1.2 Pollution from agricultural pesticides

In major field crops, most pesticides are used on row crops such as corn, soybeans, cotton, and potato. Pesticide is a general term used to describe any chemical used to control different types of pests. Pesticides can be divided into three main sub-groups: herbicides, insecticides, and fungicides. Herbicides account for 84% of the current tonnage of pesticides used in major field crops.

Herbicides applied to the soils undergo a series of physical, chemical and biological processes. Most of the herbicide is mixed with the solid phase and is adsorbed on the surface of the soil particles. A fraction of it interacts with the gaseous phase and eventually volatilizes. The remaining herbicide interacts with the liquid phase, which is either transmitted to the water courses, due to surface runoff and tile drainage processes; or leaches down into ground water, due to deep percolation processes. Consequently, these processes are potential sources of contamination of rivers, lakes, and ground water.

Nationally, water contamination from agriculture is most predominant in surface waters (runoff and drainage water). High pesticide concentrations in subsurface flow have generally been attributed to preferential flow (Kladivko et al., 1991; Pivetz and steenhuis, 1989). Groundwater problems exist mainly in areas with either permeable soils or with a shallow water table. In general, herbicide losses in surface and ground waters depends upon three main important parameters: soil properties, herbicides characteristics, and weather conditions (Nicholls, 1988;

Bengtson et al., 1990; Kaldivko et al., 1991). Atrazine, metolachlor, and metribuzin are the most commonly used herbicides in the US and Canada, and have all been detected in both surface and subsurface drainage outflows (Smith and Cullum, 1992; Munster et al., 1994; Logan et al., 1993; Bastien et al., 1990).

Frank and Sirons (1979) analyzed 469 surface water samples from the outlets of 11 watersheds in Ontario: atrazine and deethylatrazine were detected in 77% and 5.7% of the samples, respectively. Atrazine losses as high as 60% were reported in one instance. However, atrazine loss is usually less than 10%, over a growing season (Klaine et al., 1988). Metolachlor in ground water was detected two years after application and found to be at a minimal level (Masse et al., 1994). Arjoon (1993) also found low concentration levels (below 0.01 mg/L) of metolachlor in ground water under two different fields. She also found that metolachlor in the soil samples had disappeared by the last sampling day (total sampling days of 106). Metribuzin concentration in runoff waters sampled 81 to 151 days after metribuzin application, ranged from 2 to 44 μg/L.

Recently, subsurface drainage systems have been examined for their possible contribution to pollution of surface water. It is believed that some of the agricultural chemicals that leach beyond the crop root zone into the shallow ground water migrate with the drain water to the local streams, rivers, and lakes as part of drain effluent. Masse et al. (1990) reported that atrazine and its dealkylated-N metabolites were found in the shallow groundwater zone of a corn field on a clay loam soil in Quebec.

At many times the concentrations were found to be higher than the 3 μg/L advisory limit of the EPA. Another study, conducted by Bastien (1991) under Quebec conditions, revealed metribuzin concentration up to 3.47 μg/L in the tile drain water, and up to 47 μg/L in the surface runoff water. Muir and Baker (1976) observed atrazine concentrations in tile-drain water in the range of 0.2 to 3.85 μg/L in a Quebec corn field. In eastern Ontario, Patni et al. (1987) detected atrazine in 75% and metolachlor in 32% of the tile-drain water samples from a clay loam soil where corn was being grown under conventional tillage. Atrazine and metolachlor concentrations in subsurface drain outflow in southern Louisiana have been reported to vary from 0.015 to 3.53 μg/L and 0.4 to 29.3 μg/L, respectively (Southwick et al., 1990). Baker (1993) reported that tributaries draining agricultural watersheds in northern Ohio had atrazine and alachlor concentrations above the maximum contaminant level. Lakshminarayana et al. (1992) reported atrazine concentration as high as 13.9 μg/L in the subsurface drain outflow and as high as 1.89 μg/L in the stream. Flury et al. (1995) reported that of the total applied atrazine, 4.4% leached below 0.5 m after 90 mm of cumulative infiltration. Hall et al. (1989) reported that 8.4% of the applied simazine and 9.6% of the applied atrazine leached below 1.22 m after 1000 mm of rainfall. There is evidence that even strongly adsorbing chemicals can move as fast through soil as mobile chemicals, but the mass leached seems to be ranked according to the mobility characteristics (Flury, 1996).

2.2 Fate and Transport of Contaminants in the Soil

Processes affecting the movement and fate of contaminants in the subsurface environment include advection, dispersion, sorption, volatilization, and transformation. Advection is the process by which ground water and contaminants flow in response to gravitational, pressure, or density gradients. Dispersion is a mixing process that results both from fluid and molecular motion, resulting in the spreading and dilution of a contaminant within the system. Sorption is the partitioning of a contaminant between a gaseous or liquid phase and a solid phase, and it results in the retardation in the rate of movement of a contaminant with respect to that of the fluid in which it is contained. Volatilization results in a partitioning between liquid or solid and gaseous phases. Transformation causes change in one chemical specie to another and may result from either chemical (abiotic) or biological (biotic) processes or from a combination of both. Sound application of remediation schemes requires knowledge of these processes and generally takes advantage of at least some of them for removal and/or in-situ destruction of the contaminants. In general, contaminant movement and fate is a function of three main important parameters: soil properties, chemical characteristics, and weather conditions (Nicholls, 1988; Bengtson et al., 1990; Kaldivko et al., 1991). The characteristics of the three herbicides, atrazine, metolachlor and metribuzin, and nitrate fertilizer used in this study as well as their fate in the environment will be described in the following sections.

2.2.1 Nitrate and its fate in the environment

The consumption of nitrogen fertilizers in North America has been steadily increasing over the years as a result of placing more land into agricultural production and increasing rate of fertilizer application on a unit area (Baker and Johnson, 1981). They also reported that the application rate of fertilizer to corn fields in Iowa state increased from 115 to 181 kg/ha from 1970 to 1979.

Nitrates in the soil may originate from organic or inorganic fertilizers, or from nitrogen fixation. The major processes governing the fate of nitrate in the soil include plant uptake, incorporation into soil biomass, leaching, volatilization, and microbial denitrification.

Plant uptake decreases the level of nitrate in the soil and helps to convert inorganic N to organic N. Uptake rate depends on fertilization rate, method and timing of fertilizer application, nitrate-N and water availability, and the type of crop (Liang, 1992). Besides plant uptake of soil nitrates, some of the nitrogen may get immobolized and incorporated into soil biomass as organic nitrogen. Nitrogen leaching is one of the most important pathways by which 50% or more of the applied N fertilizer is lost through the soil profile (Baker and Johnson, 1981). Nitrates leach through the vadose layer and get into water supplies. Ingestion of nitrates in drinking water can cause methaemoglobinaemia among infants (Spalding and Exner, 1993). For this reason environmental protection agencies have set limits on the content of nitrates in drinking water. The basis of the limits is usually the non-cancerous acute toxicity of nitrate-N, which is taken by US environmental protection agency to be 10 mg/L.

Nitrogen fertilizer may be lost through volatilization, but only ammonia forming fertilizers in alkaline conditions can be lost through volatilization (Stevenson, 1986).

The soil microorganisms not only produce nitrate; they also destroy it. Denitrification is the process through which nitrates are transformed into gases, which consequently escape into the atmosphere. Soil microorganisms use the nitrate ions (NO_3^-) as electron acceptors and transform them into nitrites (NO_2^-) which can be further reduced to nitrous oxides (N_2O) and eventually nitrogen (N_2) gas (Addiscott et al., 1991). Anaerobic conditions favour the denitrification processes in the soil (Sahrawat and Keeney, 1986). Denitrification is also sensitive to the level of soil moisture and soil temperature. Saturating the soil and increasing the soil temperature increase denitrification substantially. Weil et al. (1990) demonstrated that the combined effect of anaerobic conditions and a good carbon source in a corn field led to denitrification which reduced nitrate levels in ground water to below 0.1 mg/L. Rolston et al. (1979) reported that up to 70% of nitrate fertilizers in the soil could be removed by denitrification.

2.2.2 Atrazine and its fate in the environment

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is a selective herbicide widely used on agricultural crops including corn, sorghum, sugar cane, pineapple, and fruit trees for the control of annual broadleaf and grassy weeds (Weed Science Society of America, 1983). Depending on the crop or the intended use, atrazine may be applied as a pre-plant emergence, or postemergence herbicide. Application rates of active-ingredient atrazine range from 1 to 4 kg/ha. A higher rate is applied when atrazine is used as a non-selective herbicide.

Atrazine was first introduced in Canada in about 1960 to control weeds in corn production. At present, atrazine is one of the most common pesticides used in Canada (Environment Canada/Agriculture Canada, 1987). It is marketed as a liquid, wettable powder, or granular formulations.

Atrazine's formula is $C_8H_{14}ClN_5$. Its molecular weight is 215.7, melting point is 173-175 °C, water solubility is low (33 mg/L at 25 °C), soil sorption coefficient (100 mg/kg of the soil) is low, and its microbial decay rate is high (Colby et al., 1989). The structural formula of atrazine is shown in Figure 2.1. Atrazine is stable in slightly acidic or basic aqueous, but is hydrolyzed to hydroxy derivates by alkali or mineral acids (Windholtz et al., 1983). Henry's law constant and the vapor pressure of atrazine are 2.45×10^{-7} and 6.9×10^{-6} mm Hg at 25°C, respectively (Huckins et al., 1986).

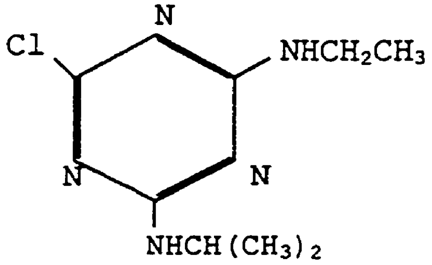

Figure 2.1. Structural formula for atrazine.

The various processes governing the fate of atrazine in the environment include hydrolysis, adsorption, microbial degradation, volatilization, and photodegradation. Chemical hydrolysis of atrazine to hydroxyatrazine has been reported as an important pathway of atrazine degradation in soil (Armstrong et al., 1967). The rate of this first order reaction depends on soil pH and organic matter content. An increased rate of atrazine hydrolysis was reported in acid soils. Half-lives of 95-165 days, 145-350 days, and 3-5 years were estimated for pHs of 4, 7, and 8, respectively (Environment Canada, 1990). Burkhard and Guth (1981) reported that the rate of atrazine degradation by hydrolysis increases as adsorption rate increase.

Clay, organic matter, temperature, and pH play important roles in the adsorption phenomena. Atrazine adsorption increases as clay content or organic matter content of the soil increases. Increasing temperature and soil water content reverses atrazine adsorption. Higher temperature and pH result in lower adsorption of atrazine. Harris and Warren (1964) reported that the organic matter adsorbed more atrazine residues than mineral materials. Desorption of atrazine was found to occur slowly and incompletely on organic soils.

Loss of atrazine due to volatilization is not considered to be a major factor (Burt, 1974; Peter and Weber, 1985). Glotfelty et al. (1989) reported that 2.4% of applied atrazine volatilized in 24 days from a silty loam soil in Maryland. However, loss of atrazine by runoff water and attachment to sediments can be quite extensive when the land exhibits a slope, especially if a storm event occurs shortly after pesticide application (Klaine et al., 1988). For example, the maximum concentrations of atrazine in the tailwater pits were 128 and 250 µg/L in the sorghum and corn fields, respectively (Kadoum and Mock, 1978). Maximum concentrations of atrazine in the pit bottom soil (sediments) were 132.5 and 369 µg/kg in the sorghum and corn fields, respectively. Unfortunately, atrazine application rates and the length of time, that these concentrations remained at that level, were not stated. Atrazine monitoring studies in the surface waters of Canada have mostly been in the southern Ontario region (Frank et al., 1982). In this study, the average rate of atrazine losses to natural streams draining these areas was reported to be 2250 and 1980 mg/ha/year in 1976 and 1977, respectively. The highest reported concentrations of atrazine were 31.7 and 32.8 µg/L in 1976 and 1977, respectively (Frank et al., 1982). Atrazine concentration levels of 0.01 to 26.9 µg/L were found in the Yamaska River basin (Quebec) from April to December in 1974 and 1975 (Muir et al., 1978). Several groundwater studies have reported the presence of atrazine in wells in agricultural areas of Canada (Frank et al., 1987a). They have demonstrated well-water contamination to be the result of atrazine spills, spray drift, and surface runoff. A survey of 91 wells in southern Ontario during 1984 showed atrazine residues ranging from 0.1 to 74 µg/L in 11 wells (Frank et al., 1987b).

Microbial degradation is estimated to be more important than volatilization, chemical breakdown, and leaching (Peter and Weber, 1985). In fact, 90% of herbicide losses have been attributed to microbial degradation (Zimdahl and Clark, 1982). The common half-life of atrazine has been reported to be approximately 60 days. However, the half-life is highly dependent on temperature: i.e., a 10 °C increase in temperature was found to decrease half-life by a factor of approximately 2 (Walker, 1987; Walker and Brown, 1985). Half-life of atrazine in aquatic environments has been reported to range from 3.2 days (Kosinski, 1984) to 3-4 months (Kemp et al., 1985) to 7-8 months (Dewey, 1986). The main products of microbial degradation of atrazine are deethylatrazine and deisopropylatrazine.

Photodegradation of atrazine in surface waters was shown to be very slow and was not expected to be a significant factor in its removal from water (Ghassemi et al., 1981).

2.2.3 Metolachlor and its fate in the environment

Metolachlor (2 – chloro – N - (2-ethyl-6-methylphenyl)´–N -(2-methoxy-1-thylethyl) - acetamide, is another selective herbicide used to control grass weeds in corn, soybean, potatoes, beans, sorghum, and sugar beets fields. The structural formula for metolachlor is shown in Figure 2.2. Metolachlor with a trade name of "Dual", molecular formula of $C_{15}H_{22}ClNO_2$, and molecular weight of 283.8 is found in the market in the form of a colourless, odourless liquid. The Dual product contains 960 g/L of the active ingredient (ai) metolachlor. However, it is also used in combination with atrazine for weed control in corn fields. Application rates of metolachlor active ingredient are 1.4-4.5 kg/ha for crop and noncrop areas, depending on soil and climatic conditions (U.S. EPA, 1988).

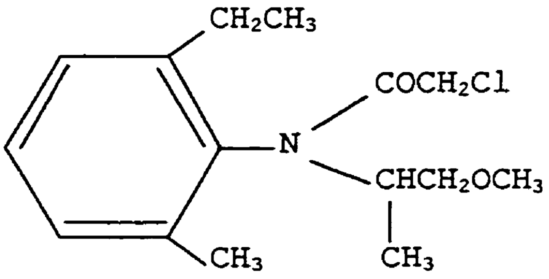

Figure 2.2: Structural formula for metolachlor.

Metolachlor is not manufactured in Canada and was first registered in Canada in 1977 (Agriculture Canada, 1989). Metolachlor imports rose from 4322 t in 1987 to 1724 t in 1989 (Moxley, 1989).

Metolachlor is very soluble in most organic solvents including benzene, dichloromethane, hexane, and methanol. Its solubility in water is about 530 mg/l at 20 °C. It is a relatively non-persistent herbicide. All biological evidence indicates that metolachlor does not persist from one season to the next (Colby et al., 1989). Masse et al. (1994) detected metolachlor in the groundwater samples after only two years. Radio-labelled studies have shown a rapid decline of the parent compound (Liu et al., 1988). The half-life dissipation rate for metolachlor has been determined, in laboratory and field studies, to be 30 to 70 days in northern areas (Patni et al., 1987; Walker and Brown, 1985) and from 15 to 25 days in southern areas of North America (Rao et al., 1986; Liu et al., 1988).

The chemical characteristics of metolachlor, i.e. high solubility and weak adsorption, have led some scientists to conclude that it could easily be leached down the soil profile (Braveman et al., 1986; Obrigawitch et al., 1981). Most studies, however, have reported very low concentration level of metolachlor in drainage and ground water (Masse et al., 1994; Bowman, 1989; Steenhuis et al., 1988; Utulu et al., 1986). Extensive sampling of the Grand, Saugeen, and Thames rivers in southern Ontario showed that of 454 samples, only 21 were contaminated by metolachlor (Frank and Logan, 1988). The average concentrations in these rivers, Grand, Saugeen, and Thames, were 0.9, 0.7, and 3.6 μg/L, respectively. In the United States, metolachlor was detected in 1644 of 1977 (82%) surface water samples tested with a maximum concentration of 138 μg/L (U.S. EPA, 1987). Metolachlor was also found in the treated water. Metolachlor concentrations as high as 16 μg/L and 14 μg/L were found in the drinking water samples and in Sydenham River samples, respectively (Frank et al., 1990). Southwick et al. (1990) reported losses of metolachlor from tile-drained fields with commerce clay loam of about 2.79 g a.i./ha (0.129% of the applied mass) over 240 days. In another study conducted by Gaynor et al. (1995), loss of metolachlor active ingredient from tile-drained fields with clay loam soil ranged from 1.9 to 5.8 g/ha/year (from 0.07% to 2.23% of the applied mass). In 1985, the Ontario Ministry of the Environment (OMOE, 1987a) sampled 351 private wells. Among them, 52 wells (about 15%) showed metolachlor contamination, and 4 of these wells showed metolachlor in concentrations above 105 μg/L. They mentioned that the high concentration was probably the result of infiltration of contaminated surface runoff into poorly located or constructed wells.

Adsorption to the soil is a major factor controlling movement of metolachlor in the environment. Organic matter, clay content, and cation exchange capacity are the most important soil characteristics in terms of increased metolachlor adsorption (Wood et al., 1987). Adsorption is lower in alkaline soil (Environment Canada, 1991), but changes in pH below 7 have little effect on adsorption (Chesters et al., 1989). Generally, soil adsorption increases with increasing organic matter content (Peter and Weber, 1985). However, Chesters et al. (1989) suggested that the type of organic matter may influence adsorption. Within the soil organic fraction, humic substances are the most important adsorbers (Kozak et al., 1983).

Metolachlor was not detected at depths greater than 0.3 m in a field study near Ottawa during a year in which rainfall was unusually heavy (Patni et al., 1987). Volatilization and photodegradation losses of metolachlor from a soil surface are very small, compared to biodegradation in field soils. Factors such as temperature, moisture content, and organic matter favour increased microbial density and activity and decrease the persistence of metolachlor in soil (Bouchard et al., 1982; Zimdahl and Clark, 1982). Major degradation of metolachlor occurs under aerobic conditions, whereas its anaerobic metabolism is rather minimal (Kent et al., 1991).

2.2.4 Metribuzin and its fate in the environment

Metribuzin is used in Canada, United States, and other parts of the world as a herbicide against broadleaf weeds and grasses. Its chemical name is 4-amino-6

(1,1-dimethylethyl)-3-methylthio-1,2,4-triazin-5(4H)-one. Its tradename is "Sencor", "Sencorex" in Great Britain, and "Sencoral" in France. The company DuPont has labelled it as "Lexone". It is used as either a pre-emergence or post-emergence herbicide in potatoes, alfalfa, sorghum, soybean, corn, and barley fields (Diawara and Banks, 1990).

Metribuzin is a white crystalline solid compound with a molecular weight of 214.3, and melting point of 125.5-126.5 °C. The molecular formula of metribuzin is $C_8H_{14}N_4OS$ and its chemical structure is shown in Figure 2.3. The solubility of metribuzin in water is quite high (about 1220 mg/l at 20 °C). Metribuzin has a high solubility in most organic solvents such as acetone (82,000 mg/100g), and methanol (45,000 mg/100g), but it has a low solubility in paraffinic hydrocarbon solvents.

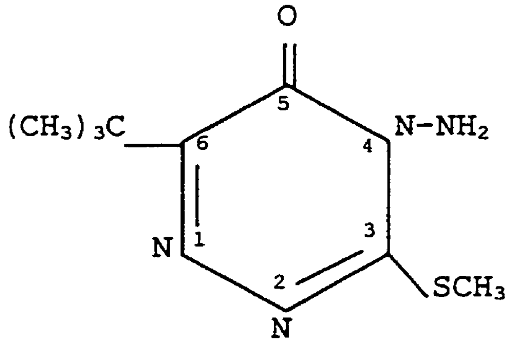

Figure 2.3: Structural formula for metribuzin.

Under field conditions, adsorption of metribuzin to the soil matrix is very important since it influences the persistence and movement of the herbicide in the soil (Hatzios and Penner, 1988). Like other herbicides, adsorption of metribuzin in the soil increases with increased organic matter content. The participation and importance of soil clay colloids in the soil adsorption of metribuzin is less clear. Sharom and Stephenson (1976) did not find any significant correlation between metribuzin adsorption and clay content of several Canadian soils. Other investigators, however, have shown that soil clay colloids are important for the adsorption of this herbicide in selected soils (Albro et al., 1984; Savage, 1976). Soil pH also influences the adsorption of metribuzin to soil particles. Adsorption of metribuzin to soil particles increases with a decrease in soil pH (Ladlie et al., 1976).

Degradation of metribuzin in soil has been extensively studied. The degradation of metribuzin by soil microorganisms is currently considered to be an important process involved in the environmental fate of this herbicide. Although specific studies with soil microorganisms degrading metribuzin are limited, a number of reports have demonstrated the importance of microbiological activity in the degradation of metribuzin in soils (Savage, 1977; and Bouchard et al., 1982). Several environmental factors favoring microbial activity, such as temperature, pH, and soil moisture, are known to influence the degradation of metribuzin in soils. For example, Bouchard et al. (1982) showed that the degradation of metribuzin in soils increased linearly with temperature. The half-life of metribuzin is about 46 days at 20 °C, and 16 days at 35 °C (Hyzak and Zimdahl, 1974). Metribuzin metabolites that have been detected in soils are mostly formed by microbial degradation. These products include DA (deaminated metribuzin), DK (diketo metribuzin), and DADK (deaminated diketo metribuzin) and are usually less biologically active, but more polar than the parent compounds. Thus, they usually have a greater potential for leaching (Nicholls, 1988).

Because metribuzin has high water solubility (1220 mg/L) and low soil sorption coefficient (60 μg/g of the soil), it is expected to leach further downward than atrazine and metolachlor. The mobility of metribuzin in soils is inversely related to the soil adsorptive capacity. In general, metribuzin is relatively mobile in sandy and mineral soils but very immobile in soils with high organic matter (Sharom and Stephenson, 1976). Metribuzin was ranked as the second most frequently detected pesticide with high Relative Mobility Index (RMI) in the Nomini Creek watershed in Virginia (Shukla, et al., 1995). A study conducted at Louisiana showed medium leachability of metribuzin in a soybean field with silty clay loam soil (Orlino, et al., 1994). The mobility of metribuzin increases as the soil pH increases (Hatzios and Penner, 1988).

2.3 Methods for Controlling Nonpoint Sources of Pollution

The majority of environmental problems in agriculture come from nonpoint or diffuse sources. Various methods exist for reducing pollution initiated by agricultural activities. Several preventative practices have been suggested. These management practices are often referred to as Best Management Practices (BMPs). Other methods have been established to control the pollution problems, created by herbicide and fertilizer used in crop production, such as vegetative filter strips, wetlands, and ponds. The following sections will discuss only those methods that have broad applicability and also the ability to bring about significant improvements. One such method is water table management to reduce the movement of the contaminant into ground water and increase the residence time of the contaminant in the soil. Vegetative filter strips, wetlands, and inter-cropping practices are other methods used to reduce contaminant losses into surface runoff.

2.3.1 Water table management practices

Agricultural water management systems include free drainage, controlled drainage and subirrigation. In free (conventional) drainage, rain water is allowed to enter and leave the soil profile freely, while in controlled drainage water is prevented from leaving the soil profile, thus raising the water table. Subirrigation is similar to controlled drainage, but irrigation water is pumped into the field through the subsurface drains. These systems are used primarily to eliminate water related factors that limit crop production or to reduce those factors to an acceptable level, i.e., controlling the duration of either excessive or deficient soil-water conditions in the soil profile. Another major objective is to improve the quality of drainage outflow water. Among these systems, controlled drainage and subirrigation have been identified as capable of reducing movement of the contaminant into ground water (Thomas et al., 1991; Skaggs et al., 1994; Evans et al., 1995). Use of controlled drainage to reduce nitrate outflows from drained agricultural lands was introduced in the 1970s. Evans et al. (1989a) reported that controlled drainage systems reduced nutrient transport to drain outflows. They reported that there was no threat to groundwater pollution from water table management, since virtually no downward movement of nitrate-N occurred below the water table. Other studies (Gilliam et al., 1979; Doty et al., 1986; Evans et al., 1989b) have shown that controlled drainage can be used to promote denitrification and also substantially reduce losses of N to surface waters. It has also been reported that controlled drainage has the potential to reduce losses of plant nutrients and applied chemicals (pesticides) carried in drainage effluent (Bengtson et al., 1988, 1990); especially those which may be transported quickly and directly to subsurface drains through soil cracks. Madramootoo et al. (1993) reported environmental benefits of water table management in terms of reduced nitrate-N pollution from subirrigation systems. They found soil nitrate levels to be higher in conventional drainage lysimeters than the controlled water table lysimeters. Kalita and Kanwar (1993) investigated the effect of water table management on groundwater quality. The concentration of nitrate-N in shallow ground water was a function of water table management practices; the lowest nitrate-N concentrations were reported for shallow water table managed test plots. Thus, controlled drainage has been recommended for use in fertilized lands of many humid regions.

Several field-scale studies have been initiated in the last few years to investigate the role of water table management systems in reducing pesticide residues in drainage outflow. Only a limited amount of information is currently available. The effect of water table management on herbicide transport into ground water has been conducted through field studies (Aubin et al., 1993; Arjoon et al., 1994), and lysimeter study (Jebbellie and Prasher, 1995) in Quebec soils. They reported that both controlled drainage and subirrigation could improve the water quality of shallow ground water. Arjoon et al. (1993) and Kalita and Kanwar (1990) observed lower soil-solution concentrations of prometryn and atrazine, respectively, under controlled drainage when compared with conventional drainage. They hypothesized that water table control slowed vertical leaching of these pesticides to ground water. However, Munster et al., (1994) observed a 25% increase in aldicarb transport in controlled drainage outflows when compared with conventional drainage. Other studies (Arjoon and Prasher, 1993; and Ng et al. 1994) reported that there was no difference in the leaching of atrazine and metolachlor in controlled drainage and conventional drainage.

Mass balance analysis had not been performed in most of the above studies. Also, they did not estimate the dilution effect in controlled drainage and subirrigation systems. In addition, some of the above studies reported that further data were needed to provide more conclusive results. Therefore, adequate conclusions can not be drawn. It has not yet been established whether these methods control pesticide pollution.

2.3.2 Vegetative filter strips

In the search for solutions to prevent sediment production and to reduce sediment yields from agricultural watersheds, grass filtration has gained importance in the last 15 to 20 years. This has also been used to treat food industry wastewater, feedlot runoff, municipal sewage effluent and artificial ground water recharge.

Adam and Lagacé (1986) reported reductions of 99.5% in the total suspended solids, in effluent wastewaters from a settling basin adjacent to a cowshed course, by using a grass filter, 113 m long and 16 m wide with a slope of 0.75%. The cumulative reduction by the settling basin and the grass filter was 99.8%.

Adam and Lagacé (1986) also reported reductions of: 99.9% for BOD, total Kjeldhal nitrogen, ammonium nitrogen and chloride, and 99.4% for potassium. When the cumulative reduction of the basin and the grass were considered, these products were reduced by 99.9, 99.8, 99.9, 99.8, and 99.8%, respectively. In this experiment, the volume of the effluent was also reduced by 90.5% at the exit of the grass filter.

Neibling and Alberts (1979) found that 0.61, 1.22, 2.44, and 4.88 m lengths of sod strips, placed across the base of 6.1 m bare soil plots, reduced total sediment discharge rates by more than a factor of 10. Sediment discharge rates for the < 0.002 mm size fraction were reduced by 37, 78, 82, and 83% for 0.61, 1.22, 2.44, and 4.88 m strips, respectively. The percent reduction for 0.002 to 0.01 mm size fraction were 56, 70, 94, and 95% for the aforementioned respective lengths.

Doyle et al. (1977) used grass buffer strips, 0.5, 1.5 and 4.0 m in length, in order to study whether they effectively improved the water quality of manure-polluted runoff. They showed that grass buffer strips, 3.7 to 4.6 m long, were quite effective in reducing the loading rates of faecal bacteria, and soluble NO, N, P, Na, and K.

Vanderholm and Dickey (1978) studied channelized and overland flow grassed systems for treating feedlot runoff. They reported more than 80% reduction in concentrations of nutrients, solids and oxygen demanding materials, in filter lengths ranging from 91 to 262 m. They also developed a filter design criterion based on residence or contact time concepts. Butler et al. (1974) had previously reported the detention time as the most important parameter for nutrient removal.

Livingston and Hegg (1981) successfully used terraced pasture to treat dairy yard runoff, however with the exception of nitrate removal. Sievers et al. (1975) also used a terraced grass system to treat swine waste. Edwards et al. (1981) used a similar system for beef feedlot runoff. Norman et al. (1978) presented a grass filter design criterion based on making travel time through the filter proportional to BOD concentration in runoff. Young et al. (1982), as cited by Magette et al. (1986), used the concept of residence time to develop empirical relationships for evaluating pollutant reduction potentials of grassed areas. Young et al. (1978) reported on the ability of 24 m long cropped areas to remove pollutants from feedlot runoff.

Bingham et al. (1980) and Overcash et al. (1981) applied chicken manure to grassed areas, and measured runoff quality at numerous distances downslope from the point of application. They concluded that buffer lengths, in a 1:1 ratio to land application area, were necessary to achieve background level of contamination in filters below waste application sites. They developed a mathematical model to predict the filter performance, taking into account dilution, infiltration, and pollution potential of the waste application site.

Vegetative filter strips (VFS) were evaluated on 18 farms by Dillaha et al. (1989), for agricultural nonpoint source pollution control. Vegetative filter strips situated on hill slopes were ineffective since runoff concentrated into natural drainage ways, but were effective for in-place erosion control. VFS were found to be effective for sediment trapping on relatively level lands. In places where the elevation of the VFS was higher than the adjacent fields, because of sediment trapping over the years, water went around the VFS until it found a lower outlet.

Nsengiyumva (1994) evaluated three systems (grass covered basin, geotextiles covered basin and flooding a section of the crop land combined with controlled drainage) for filtering polluted river water. It was found that grass filter basins are very efficient in removing sediment from river water. More than 90% of sediments were removed after passage through grass covered basins.

Mickelson and Baker (1993) evaluated the role of filter strips for controlling herbicide runoff losses by applying simulated rainfall. A rainfall intensity of 66 mm/h was used over 4.6 and 9.1 m long buffer strips. Ten minutes after the rain began, the inflow with an atrazine concentration of 1 mg/L, either with or without sediment, was added to the buffer strips. Nearly 72% and 76% of the sediment was trapped by the 4.6-m and 9.1-m long buffer strips, respectively. Atrazine loss reduction averaged 32% and 55% for the two buffer strip lengths, respectively.

Increasing the buffer length by a factor of two resulted in little additional reduction in sediment transport. Moreover, the difference in the reduction in atrazine losses between no-till (without sediment) and conventional tillage (with sediment) plots was not significant. The 9.1-m long buffer strips reduced atrazine concentrations and losses more than the 4.6-m long strips.

This indicates that considerable research efforts have been made to study the role of grass strips in reducing sediment and nutrient loading; however, little work has been done to investigate their effect in reducing pollution from agricultural pesticides. As stated in the hypothesis, a significant reduction can be expected from this method (soil filter integrated with vegetative filter strips). Final concentrations can be as low as 1/1000th of the applied levels. In fact, this can be achieved without requiring the farmers to make significant changes in their current farming and cropping practices. It appears to be a reliable method of significantly minimizing the threats to freshwater aquatic life from agrochemicals.

2.3.3 Wetlands and wastewater treatment

Wetlands can be defined simply as locations in the landscape, characterized by saturated or hydric soils that support mainly hydrophytes. The use of both natural and specially constructed wetlands to treat polluted water is emerging as a relatively new and important technology. By the late 1980s, this became a recognized system for domestic waste treatment. Wetlands are currently used to treat a range of polluted waters including domestic wastewater, agricultural and urban storm runoff, acid rock drainage, mine waters, industrial discharges, and landfill leachates.

Wetlands are important as waterfowl and wildlife habitats, as regulators of water flow, and for their intrinsic natural beauty and contribution to biodiversity (Zoltai, 1988). Another important role of wetlands is the improvement of water quality.

Many studies have demonstrated that major nutrients and sediment from wastewaters can be effectively removed if flow is directed through wetlands (Dolan et al., 1981; Knight et al., 1985; Alexander and Wood, 1987; and Brodrick et al., 1987). Effective pollutant removal by wetlands is very dependent on the hydrology of the system (Sloey et al., 1978; and Tilton and Kadlec, 1979). As the residence time of the water is increased, pollutant removal is enhanced. The residence time depends on the size, shape, slope and hydraulic roughness of the wetland, the size and the land use of the agricultural drainage area, together with the inflow rate of wastewater. The major mechanisms responsible for reducing the concentration of contaminants are: sedimentation, filtration, chemical precipitation and adsorption, ion exchange, biological transformation, and biological uptake through the root systems of the vegetative cover (Watson et al. 1989).

Created wetlands have been suggested as a method of reducing nitrogen transport to the Baltic Sea. A study was undertaken by Arheimer and Wittgren (1994) in the Soderkopingsan drainage basin (882 km^2) which discharges into the Baltic Sea in southeastern Sweden. The objective of this study was to estimate the capacity of created wetlands to reduce nonpoint nitrogen pollution on a regional scale, and to provide guidelines concerning the location and size of such wetlands. It was estimated that conversion of 1% (8.8 km^2) of this basin into wetlands would reduce the nitrogen transport by 10 to 16%, and that more than 5% (45 km^2) conversion to wetlands is required to reduce the transport by 50%. It was concluded that in coastal areas where the summer load is a significant portion of the annual load, wetlands should be created downstream from major lakes.

Removal of nutrients and sediment has also been documented from agricultural drainage water pumped onto wetlands (Kemp et al., 1985; and Chescheir et al., 1991). Drainage water effluent from a relatively large agricultural drainage area is collected by a system of drainage ditches and canals and pumped onto a smaller wetland area for treatment from which it flows to a stream or other receiving water. Chescheir et al. (1992) developed a computer method for predicting nutrient and sediment removal from agricultural drainage water pumped onto wetland buffer areas. The method uses a simulation model of drainage from agricultural lands, coupled with a simulation model of overland flow and nutrient removal on the wetland. This method predicted that the 240 ha wetland buffer at the field research site could be expected to remove over 79% of the nitrate-N, P, and sediment in drainage water from a 1250 ha agricultural watershed.

Ponds and lakes are other types of wetlands, which have the ability to retain nutrients during runoff, at least in the long-term perspective. Jansson et al. (1994) studied nitrogen retention in a small stream, River Raan in southern Sweden, using mass-balance calculations along a 7-km reach with running water and in a small pond. They found that the total annual nitrogen retention was less than 3% of the total nitrogen transport in the stream. The retention in the pond was greater than in the rest of the river. Significant nitrogen retention (20-50%) occurs only during low flow periods in the summer. In addition, they concluded that the discharge was by far the most critical factor determining nitrogen retention, both in running water and the pond.

The combination of ponding and the use of aquatic plants has been identified to be very effective in wastewater treatment (Jong, 1976). The aquatic plants provide attachment sites for microorganisms purifying the sewage and also consume part of the nitrogen and phosphorus supplied to the pond.

To date, Sweden's use of wetlands to reduce the loading of nitrogen on the coast, has been done mainly in the context of decreasing nitrogen transport from farmland streams. Approximately 10% of Sweden's land area consists of lakes, with about 85,000 lakes larger than 1 ha (Arheimer and Wittgren, 1994).

Although experimental work has been in progress for more than 20 years, the technology is still in its infancy and there is still much to learn concerning the design, construction and operation of wetlands (Hammer, 1992). So far, no work has been done to investigate the effects of wetlands in reducing pollution from agricultural pesticides.

2.4 Computer Simulation Models

The fate of agricultural chemicals applied to cultivated fields with subsurface drains is an environmental concern due to potential effects on the health of all living beings. Many pesticide residues have been detected in streams, tile drain effluent and ground water in concentrations far above the standard level for drinking water (Frank and Sirons, 1979; Bastien, 1991; Skaggs et al., 1994; Bengtson et al., 1990). The need to address this problem cannot be understated, since the maximum allowable levels for freshwater aquatic life and marine habitat are usually much less than that for human consumption. For the health of freshwater aquatic life it is suggested that common herbicides be presented in concentrations less than 1 µg/L. In this study, one of the objectives was to determine the filtration area needed to treat polluted drainage water from farms and bring the herbicide levels down to less than 1 µg/L. The requird filtration area for pesticide removal depends on soil characteristics, chemical properties, and climatological regime. Computer simulation models can be useful in computing the required filtration area for different scenarios.

Currently, many models are available to study and manage the pollution of surface and ground waters from nonpoint sources. The most commonly used models are: PRZM; CREAMS; GLEAMS; LEACH-P; ANSWERS; and PESTFADE.

In this study, a watertable management model, DRAINMOD, which simulates drainage from agricultural land and a solute transport model, PRZM2, which simulates the fate of pesticides residues in treated waters were used to determine the filtration area.

DRAINMOD is a well-known field scale water management model, developed by Skaggs (1978). Extensive field testing of DRAINMOD has been done in many areas of Canada and the US (Mackenzie et al., 1988; Mackenzie and Prasher, 1989; Shukla et al., 1994; Skaggs, 1982; Susanto et al., 1987). DRAINMOD was developed for shallow water table soils and is based on a water balance in the soil profile at the midpoint between two drains. The model uses climatological records to simulate the performance of drainage and water table control systems in a field bordered by parallel ditches or subsurface drains. DRAINMOD is a well-documented user-friendly computer software package. Sufficient instructions are given to the user during execution of the program. User inputs are checked throughout the program and a chance to modify faulty entries is provided. More details about DRAINMOD are included in chapter 5 of this thesis.

PRZM (Pesticide Root Zone Model) is a continuous simulation model, developed by Carsel et al. (1985). It is a one-dimensional finite-difference model which accounts for pesticide fate in the crop root zone. PRZM has been tested with field data in New York, Wisconsin, Florida and Georgia and has been used in exposure assessment and other applications (Carsel et al., 1985; Carsel et al., 1986; Carsel et al., 1988; Smith et al., 1989; Banton and Villeneuve, 1989; Jones et al., 1983). The test results demonstrate that PRZM is a useful tool for evaluating groundwater quality. Kaluli et al. (1997) tested the performance of three mathematical models, i.e., PRZM, GLEAMS, and PESTFADE, by comparing the simulated and measured concentrations of the atrazine in a corn field on a clay loam soil in southwestern Quebec. PRZM performed better than the other two models in simulating atrazine behaviour in the root zone.

PRZM has also the capability to simulate a field containing multiple zones. It has two major components: hydrology and chemical transport. The hydrology component calculates runoff and erosion based on the Soil Conservation Service (SCS) curve number technique and the Universal Soil Loss Equation (USLE). The chemical transport component can simulate pesticide application on the soil or on the plant foliage. Dissolved, adsorbed, and vapor-phase concentrations in the soil are estimated by simultaneously considering the processes of pesticide uptake by plants, surface runoff, erosion, decay, leaching, foliar washoff, advection, dispersion, and retardation.

PRZM2, a modified version of the PRZM, was developed by Mullins et al. (1993). PRZM2 links two subordinate models: PRZM, and VADOFT, in order to predict pesticide transport and transformation down through the root zone, and unsaturated zone. PRZM2 incorporates several features in addition to those simulated in the original PRZM code - soil temperature, volatilization and vapor phase transport in soils, irrigation, microbial transformation - and includes a method of characteristics

(MOC) algorithm to eliminate numerical dispersion. VADOFT is a one-dimensional finite element model that solves the Richard's equation for flow in the unsaturated zone. PRZM now has the ability to simulate three chemicals simultaneously as separate compounds or as parent-daughter relationships. This gives the user the option to observe the effects of multiple chemicals without making additional runs or the ability to enter a mass transformation factor from a parent chemical to one or two daughter products. Predictions are made on a daily basis and output can be summarized daily, monthly, or annually. During program execution, daily time series values of various fluxes or storages can be written to sequential files for subsequent analysis.

2.5 Need for the Lysimeter and Field Experiments

The concept of soil and grass filters for reducing agricultural contaminants in water can be investigated in the field, in the laboratory, or in a controlled field environment. Because it is difficult, if not impossible, to control relevant parameters in field experiments (eg. water table level, deep percolation, etc.), lysimeters are a useful alternative. In large-scale field studies, it is also often impractical to get representative data due to difficult access, spatial variability and many other factors. Lysimeters can be used in completely controlled conditions in a laboratory or can be installed in the field where certain parameters pertaining to the soil profile and water table management can be controlled and system outputs can be observed in natural climate conditions. Indeed, Hance and Fuhr (1992) note that lysimeters almost exactly reproduce the environmental conditions that occur in the corresponding field soils. When undisturbed lysimeters are used, there is no significant disturbance of the soil or of microbiological activity. In addition, it is possible to grow crops and simulate agricultural management practices in lysimeters. Finally, where the investigation warrants, lysimeters can be used indoors and variables studied one or a few at a time.

The main disadvantage of the lysimeter technique is that they may not reflect the variability that one would expect in the field. For example, preferential flow pathways due to macropores and cracks are important in the movement of water and solutes in the field, whereas these are usually obliterated during packing of the lysimeters. Also, a gap between the soil and the sidewall of the lysimeter may occur during dry spells and short circuit pathways in the movement of water and solutes. This problem is greater when clay soils are used than when sandy soils are put in the lysimeters.

A comprehensive approach should involve lysimeter experiments to provide information for system design, as well as field experiments to verify the overall approaches being tested.

2.6 Concluding Remarks

Agricultural drainage systems are frequently criticized because of their influence on surface water quality. Herbicides and nitrates are the two major agricultural contaminants drainage waters and are often present, far above the health advisory levels. Without compromising crop yield, there is currently no cost-effective method of controlling this pollution. Water table management (WTM) has been recommended as the best management practice for nitrate reduction. However, limited information is available about its performance on pesticide reduction. In addition, the guidelines for applying the WTM practices are site-specific and difficult to transfer to other soil, agricultural management systems or climatic regions.

Grass filters are recommended for reducing sediment pollution from agricultural land. Limited information is available about their performance on reducing herbicide and nitrate from drainage waters.

Wetlands and ponds have also been identified for nitrate reduction. However, these techniques need the equivalent of 20% or more of the land area, to reduce the contaminant transport by half. In addition, limited information is available on the use of these techniques for herbicide reduction.

The above systems can reduce water pollution from nitrates and pesticides due to increased denitrification or biodegradation. Essentially, these effects are due to increased retention time of the contaminants in an environment which "deactivates" them.

The major objective of this study is to develop a method for pollution control that is widely applicable, brings about significant improvement, is economically feasible and does not require drastic changes to agricultural activities. The main idea is to use the soil and grass strips as biological filters in order to trap pollutants (mostly herbicides) at the top of the soil profile since the bacterial activity is greatest there. Herbicides can be either directly adsorbed by the soil particles or organic matter of the soil or trapped through the sediment-attachment by the grass strips. Their retention time in the system therefore increases, which improves biodegradation. The purpose of vegetation in this system is to provide sites for bacterial growth so as to improve degradation of pollutants. Development of the system is to be based on analysis of experiment results of lysimeter studies and validation through field studies.

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PREFACE TO CHAPTER 3

In order to assess the environmental benefits and costs to the farmer of implementing new techniques of pollution control, it is necessary to have reliable information on the effectiveness of pesticide and fertilizer applications as well as the effectiveness of the pollution control system used. While the analysis of field data requires relatively few assumptions, it may take several years of observation at one site to gain sufficient information for a full understanding of the processes involved. Data from short-term studies are frequently insufficient because they fall in unusually dry, wet, cold or warm years which restrict the range of relevant variables such as water table depths and drain outflows. Field experiments are also subject to lateral losses of water, deep percolation and it may not be possible to control water table depth. Lysimeter experiments can circumvent these and other difficulties, although there are some disadvantages such as unrealistic macropore flow, soil disturbance, and expense. Thus, a full analysis and understanding of water and pesticide transport and degradation is best obtained by a combination of field studies and controlled experiments in lysimeters.

Chapter 3 describes the lysimeter experiments conducted from 1993 to 1995. The results concerning pesticides have been published in the Transactions of the ASAE (Liaghat, A. and S.O. Prasher. 1996. A lysimeter study of grass cover and water table depth effects on pesticide residues in drainage water. Transactions of the ASAE, 39(5): 1731-1738). The nitrate results are the basis of another paper soon to be submitted to the Transactions of the ASAE.

CHAPTER 3

A LYSIMETER STUDY OF GRASS COVER AND WATER TABLE DEPTH EFFECTS ON NITRATE AND PESTICIDE RESIDUES IN DRAINAGE WATER

ABSTRACT

This study was undertaken to investigate the effect of soil and grass cover, when integrated with water table management (subsurface drainage and controlled drainage), in reducing herbicide and nitrate residues in agricultural drainage water. Twelve PVC lysimeters, 1 m long and 450 mm diameter, were packed with a sandy soil and used to study the following four treatments: grass (sod) covered lysimeters with subsurface drainage (GSD), grass covered lysimeters with controlled drainage (GCD), bare soil lysimeters with subsurface drainage (BSD), and bare soil lysimeters with controlled drainage (BCD). Contaminated water containing atrazine, metolachlor, metribuzin, and nitrate residues was applied to the lysimeters and samples of drain effluent were collected. Significant reductions in pesticide concentrations were found in all treatments. Herbicide levels were reduced significantly (1% level), from an average of 250 μg/L to less than 10 μg/L. In the first year, it was also found that the concentrations of herbicides in the drainage waters

tended to increase by continuing application of polluted water. Consequently, in the second year, it was decided to apply polluted water to the lysimeters with a 10-day increments (i.e. flood the lysimeters for 10 consecutive days, followed by a 10-day dry period). The above procedure was repeated three times. Water polluted at 50 µg/L, which is considered more realistic and reasonable in natural drainage waters, was applied to the lysimeters. It was observed that herbicide residues in drainage waters were reduced to less than 1 µg/L. The subsurface drainage lysimeters covered with grass were found to be the most effective treatment system for reducing herbicide residues.

Reductions in nitrate concentrations were also observed in all treatments, but were lower than for pesticides. The controlled drainage lysimeters were found to be more effective in reducing nitrate levels than the subsurface drainage lysimeters. The total amount of nitrate applied to each column was reduced to one-third in the controlled drainage lysimeters, and to one-half in the subsurface drainage lysimeters. The controlled drainage lysimeters covered with grass were found to be the most effective for reducing nitrate residues.

3.1 INTRODUCTION

In humid areas, agricultural drainage water, which originates from precipitation, eventually becomes either runoff from the soil surface or flow from subsurface drains or natural seepages. Pesticides and fertilizers can move with runoff over the land surface either in the solution phase or adsorbed to the sediment and organic matter, or laterally through the soil profile via subsurface flow into surface ditches or streams. The quantity of contaminants can be quite extensive if the agricultural land is sloped and if a rainfall event occurs soon after the herbicide or fertilizer application. In Quebec, the climate is such that there is often an excess of soil water in the spring due to snowmelt and in the autumn when rainfall is in excess of evapotranspiration. During these times, subsurface drainage is required to remove excess water and provide suitable plant growth conditions. More than 600,000 ha (about 30%) of cultivated land in Quebec are subsurface-drained (Shady, 1989), and contribute to contamination of surface and groundwater bodies.

Muir and Baker (1978) and Frank and Sirons (1979) observed that the atrazine concentrations in selected Ontario and Quebec streams ranged from 0.1 to 30.3 μg/L. The most frequently detected herbicides in runoff, ground water, and tile drainage water were atrazine, alachlor, metribuzin, and metolachlor (Triplett et al., 1978; Klaine et al., 1988; Goodrich et al., 1991; Hallberg, 1989). These are among the most heavily used herbicides in the US and Canada (Goolsby et al., 1991; Jayachandran et al., 1994). Frank and Sirons (1979) analysed 469 surface water samples from outlets in 11 watersheds in Ontario, Canada. They found atrazine in 77% of their samples, and reported atrazine losses as high as 60%. On the other hand, Wauchope (1978) studied fields under agricultural conditions and reported herbicide losses in runoff ranging from 2 to 5% of applied amounts, for wettable, powder-formulated herbicides. Metribuzin concentration in surface runoff was reported to be as high as 47 µg/L from a potato field in southwestern Quebec (Bastien, 1991). Atrazine and metolachlor concentrations measured in tile drainage effluent and ground water in Quebec ranged from 0.06 to 10.82 µg/L (Muir and Baker 1976; Masse et al., 1994). Atrazine and metolachlor concentrations in subsurface drain outflow in southern Louisiana have been reported to vary from 0.015 to 3.53 µg/L and 0.4 to 29.3 µg/L, respectively (Southwick et al., 1990). They also found that the total atrazine loss into the drains amounted to 0.038% of that applied. It was estimated that about 0.1 to 2.9% of the total atrazine applied was lost via tile drains in Quebec (Muir et al., 1978, Muir and Baker, 1976).

Nitrogen fertilizer is another source of contaminant to the water bodies. Some researchers have estimated that between 30 and 60% of the nitrogen fertilizer applied in Quebec is leached out to waterways and ground water after the fall rain and surface runoff (Miller and Mackenzie, 1978; Neilson and Mackenzie, 1977). Nitrate levels greater than 10 mg/L have been reported in ground water under agricultural areas in

Quebec (Madramooto et al., 1993) and Ontario (Hill, 1982). Nitrate levels as high as 120 mg/L in tile drainage water have been reported under corn in Iowa, Minnesota, and Ohio (Logan et al., 1980).

Regulations to protect water quality have been established in several states of the US and Canada. For instance, in 1993 the Quebec Environment Minister has clearly stated that all polluters, including agricultural farms, will be held responsible and accountable for their part in damaging our natural resources, and for "dealing a blow" to our freshwater aquatic life and their habitats by year 2000.

Grass filtration has gained importance in the last 20 years as a mean of reducing sediment and nutrient loadings from agricultural watersheds; however, little work has been done to investigate its ability to reduce pollution from agricultural pesticides.

Some work has recently been done on the use of grass filtration to treat surface runoff containing pesticide residues. Mickelson and Baker (1993) used simulated rainfall to evaluate the role of filter strips for controlling runoff losses of herbicide. They reported reductions in atrazine losses of 31.7% and 55.4% for the two buffer strip lengths (4.6 and 9.1 m), respectively.

By the late 1980s, wetlands have also become a recognised system for domestic wastewater treatment. Wetlands are currently used to treat a range of polluted waters including domestic waste waters, agricultural and urban storm runoff, acid rock drainage, mine waters, industrial discharges, and landfill leachates. Many studies have demonstrated that major nutrients and sediment from wastewaters can be removed effectively by wetlands (Dolan et al., 1981; Knight et al., 1985; Alexander and Wood, 1987; Brodrick et al., 1987). Removal of nutrients and sediment has also been documented from agricultural drainage water pumped onto wetlands (Kemp et al., 1985; Chescheir et al., 1992). A system of drainage ditches and canals collects drainage effluent from a relatively large agricultural drainage area. It is then pumped onto a smaller wetland area for treatment and then through the wetland to a stream or other receiving water. So far, no work has been done to investigate the effects of wetlands in reducing pollution from agricultural pesticides.

The concept of controlled drainage to promote denitrification and reduce nitrate (NO_3-N) outflows from drained agricultural lands was introduced in the 1970s (Meek et al., 1970; Willardson et al., 1970; Willardson et al., 1972). By elevating the water table in a moderately well-drained soil during the winter, Gilliam et al. (1979) reported reductions in nitrate levels in drainage effluent by 50%. In the Great Lakes region, Tan et al. (1993) found that controlled drainage could reduce nitrate leaching by 50%. Kaluli (1996) showed that compared to conventional drainage, controlled drainage could enhance denitrification three times and reduce tile drainage losses of N by 70%.

Little work has been done on the effectiveness of water table management on pesticide behaviour. Environmental benefits of water table management on reduced pesticide outflow from subirrigation and controlled drainage systems have been reported on Quebec soils by Aubin et al. (1993), Arjoon and et al. (1994), and Jebbellie and Prasher (1995).

It is well known that the drainage water that escapes the field boundaries through a subsurface drainage system may contain leached-out pesticide and fertilizer residues. Many pesticides are applied at concentrations rates in milligrams per litre (mg/L) (for example, 20 mg/L - it can be calculated from the application rates) and their concentration in drainage water is found in micrograms per litre (µg/L)(e.g., 20 µg/L). Therefore, the drainage water contains about 1/1000 of the applied concentration. This result is obtained after the pesticide has undergone a series of physico-chemical processes while in the soil, such as plant uptake, sorption/desorption, transformation, microbial and chemical degradation, volatilization, photolysis, decay, etc.

It should also be noted that the maximum permissible pesticide concentration for freshwater aquatic life is much lower than that for human consumption, farm animals and irrigation purposes (Environment Canada, 1991). For example, the maximum permissible concentration of metolachlor should not exceed 50 µg/L in drinking water or for farm animals. The limit is 8 µg/L for freshwater aquatic life (Kent at el., 1991). For metribuzin, a herbicide commonly used with potatoes, the maximum concentration is set at 80 μg/L for human and livestock consumption, but at 1 μg/L for aquatic life (Environment Canada, 1991). Such maximum permissible levels are similar for most pesticides. Freshwater aquatic life has a much lower tolerance to contaminants than do humans and animals. Therefore, there is a great need to ensure that any water draining out of farmlands in Quebec is safe for every member of the ecosystem.

Significant reductions in both pesticide and fertilizer concentrations occur during a 'single pass' through the soil (Muir and Baker, 1978; Goodrich et al., 1991; Hallberg, 1989). Under normal circumstances it is rare that pesticide concentrations would reach unacceptable levels. However, if drainage water that is already low in pesticides (probably "safe" for many purposes) is allowed to pass through the soil system again, a further significant reduction is anticipated. The final effluent could have pesticide residues in ng/L, instead of μg/L (i.e., much below the maximum acceptable levels). Thus, one may expect to significantly reduce non-point agricultural pollution from pesticides, without drastic changes in current farming practices.

Many agricultural fields in humid areas are tile-drained. Hence, polluted water (runoff and drainage water) can be collected at the end of the collector drains, enabling treatment before discharge into the water courses. This research project was carried out using lysimeters to enable separate investigation of the effectiveness of bare soil and grass-covered lysimeters. In addition, parameters such as: water table level, deep percolation, lateral losses of water, etc., were easily controlled in the lysimeters. More specifically, the objectives of this research program were to:

1) Investigate the performance of soil and grass filters in reducing pesticide and nitrate levels in drain effluent.
2) Investigate the effectiveness of water table in reducing pesticide and nitrate levels in the drain effluent, in both "grass-covered" and "bare soil" lysimeters.

3.2 MATERIALS AND METHODS

Lysimeter experimentation was started in the summer of 1993 to evaluate various methods of reducing nitrate and pesticide levels in agricultural drainage water. A total of 12 lysimeters were built. Four experimental treatments were planned for the lysimeter study, with three replicates for each treatment. The lysimeters were placed on cement blocks to monitor leakage during the study. The following four treatments were used:

1- BSD: Bare soil lysimeters with Subsurface Drainage
2- GSD: Grass covered lysimeters with Subsurface Drainage
3- BCD: Bare soil lysimeters with Controlled Drainage
4- GCD: Grass covered lysimeters with Controlled Drainage

In controlled drainage lysimeters, the water table level was maintained 0.5 m from the soil surface. This water table depth is considered optimal for corn and soybean fields in southwestern Quebec (Galgannov, 1991; Broughton, 1992).

3.2.1 Lysimeter Construction

The lysimeters were constructed from PVC pipe, 450 mm diameter and 1 m length. A sheet of PVC, 0.65 x 0.65 m^2 was welded to the bottom of the PVC pipe using PVC welding electrodes. The inside joint of the PVC sheet and pipe was glued using a glue gun. A hole was made through the side of the lysimeter using a 50 mm drill, and a polyethylene perforated pipe, 50 mm in diameter and 0.55 m in length, was inserted horizontally into the lysimeter. The outside joint of the perforated pipe and lysimeter was welded using the PVC welding electrodes and the inside joint was glued using PVC glue. A schematic of the lysimeter is given in Figure 3.1.

The soil used in this experiment was St-Amable sand (Ferro-Humic Podzol) taken from the field located at the Macdonald College farm. The soil texture consists of 91.2% sand, 4.2% silt and 1.1% clay. The water holding capacity, saturated hydraulic conductivity, and cation exchange capacity (CEC) of the soil were measured to be 35%, 3 m/day, and 5 meq/100 g of soil, respectively. The soil was repacked in each lysimeter in 100 mm increments and tamped to a bulk density of approximately 1400 kg/m^3. The organic matter in the soil was 3.5% by weight. This was uniform across the whole depth since the soil was homogenized and packed into the lysimeters.

The grass used in this experiment was Sod (Kentucky blue grass) purchased from a local sod company. The sod was transplanted into half of the lysimeters. The grass was cut weekly and the cut grass was taken out of the strips soon after.

In 1993, the lysimeters were placed outdoors and the experiment lasted for two weeks. As the initial results from the 1993 lysimeter study were encouraging, it was decided to conduct a parallel field study in 1994. Thus, no measurements were

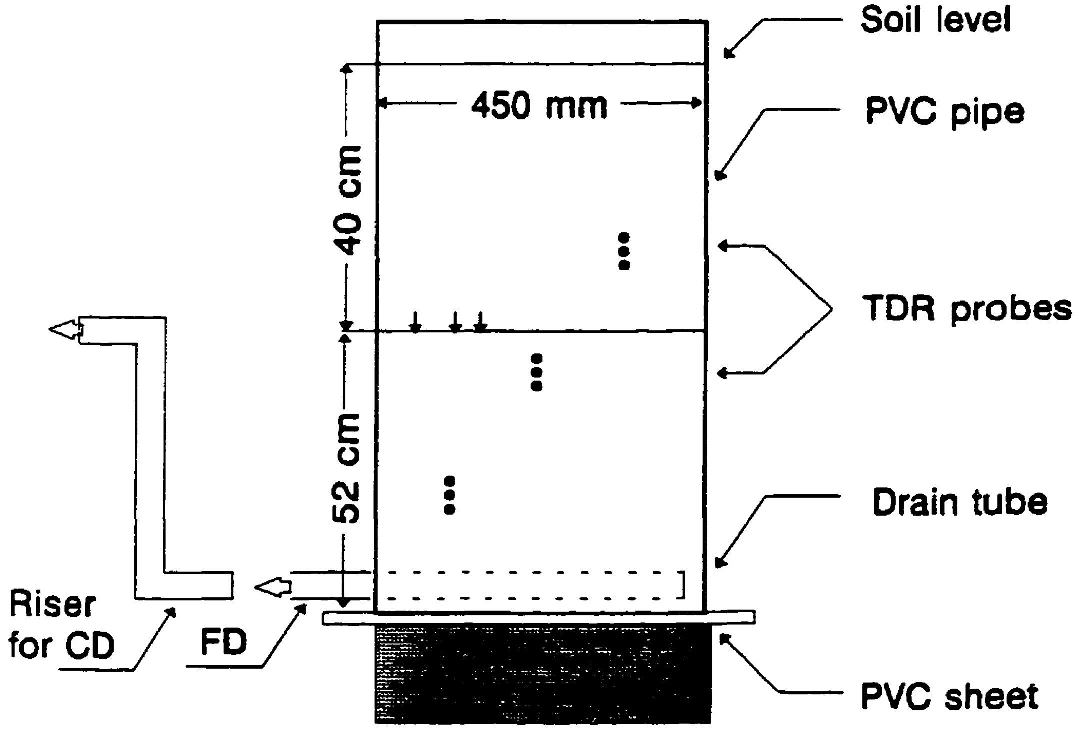

Figure 3.1: Schematic of a lysimeter.

recorded on the lysimeters during this year. However, the lysimeters were left outside in 1994 to allow the pesticides to degrade and leach through the columns. In 1995, the lysimeters were moved indoors. In addition, heating lamps were installed on top of each lysimeter to simulate six hours of sunlight per day. The indoor ambient temperature for the treatments was kept at 25 °C. The moisture content in the lysimeters was measured at different depths (250 mm, 500 mm, and 750 mm) using time-domain reflectometry (TDR).

3.2.2 Water Supply in the Lysimeters

The primary aim of this study was to recycle polluted drainage water through the soil system in order to lower agrochemical levels significantly. In 1993, polluted water was prepared containing herbicides atrazine, metolachlor, and metribuzin, with concentrations close to 250 μg/L for each. In addition, potassium nitrate was added to the solution to bring nitrate-N to about 250 mg/L. The polluted water (10 L/day per lysimeter) was applied from the top of the lysimeters to the soil surface between julian days 261 and 274. It should be noted that the 10 L/day water application was arrived at by considering the maximum daily rainfall in Quebec with a ten-year return period. In other words, each lysimeter was flooded by 60 mm of polluted water on a daily basis, representing a worst case scenario. In fact, the probability of such an occurrence is quite low. Water samples were collected from the drain outlet on days

261, 263, 264, 266, 269, 271, and 274. The drain outflow was not measured in 1993 since the primary objective at that time was to establish the feasibility of using soil as a biological filter in reducing pesticide and nitrate residues.

In 1995, the experiment was carried out indoors. It was decided to apply water at the rate of 10 L/day/lysimeter. The nitrate concentration in the water was set at 50 mg/L and herbicide concentration was set at 50 μg/L, which are close to the maximum levels that would be found in drainage waters in the field. Water was applied in 10-day increments, i.e. flood the lysimeters for 10 consecutive days, followed by a 10-day "dry" period. The above procedure was repeated three times. It should be noted that the 10-day application period was chosen since it represents the worst case scenario, where the drains would flow continuously for 10 days in response to some heavy rainfall events in the fall, or to simulate snowmelt conditions during spring months. Drainage may last longer than 10 days in spring; however, the water may not be as polluted as, for example, in the summer months or early fall.

Graduated buckets were placed under the outlet of each lysimeter to collect and measure the volume of drained water. A one-litre water sample was collected every day from each bucket, for herbicide analysis. A 20-ml sub-sample was taken for nitrate analysis. Methylene chloride was added to the water samples to act as a preservative and the samples were stored in a refrigerator at 4°C.

3.2.3 Extraction of Herbicides and their Metabolites from Water

Water samples were extracted and analyzed according to the methods already established in our previous research projects (Masse et al., 1994; Aubin et al., 1993; Liaghat et al., 1996). The herbicides were extracted from the water samples by adding 100 ml of methylene chloride to 1000 ml of water in a separatory funnel. The mixture was hand shaken for 5 min and the organic layer was collected at the bottom of the funnel. The process was repeated twice with the aqueous layer. The combined extracts were evaporated to dryness and the residues were dissolved in a small volume of methanol, before analysis by gas chromatography. The herbicide concentrations are reported in μg/L of water. The extraction efficiency in water samples was estimated to be 88% ± 5%. The measured values were not adjusted according to the extraction efficiency.

3.2.4 Gas Chromatography

The GC used in this study was a Varian, Model 3400, equipped with a TSD (Thermionic Specific Detector) detector, an autosampler, and an integrator. The column was a 0.53 i.d. fused silica Megabore DB-5. The operating conditions were as follows: the detector and injector temperature were maintained at 290°C and 190°C, respectively; the column temperature was set at 150°C for 2 min, and then it was increased to 190°C at a rate of 5°C/min; at 190°C it was kept for 0.2 min and was then raised to 290°C at a rate of 10°C/min. The helium carrier gas flow rate was set at 15 ml/min.

The concentrations of the herbicides and their metabolites were determined by comparing the response area with that of reference standards. The detection limits of the analytical method were evaluated by injecting analytical standards with decreasing herbicide and metabolite concentrations. The detection limits for water samples were found to be 0.03 µg/L for atrazine, 0.12 µg/L for metolachlor, and 0.05 µg/L for metribuzin.

3.2.5 Analytical Method for Nitrate Analysis

High performance liquid chromatography (HPLC) was used to detect nitrate levels in water samples. The HPLC used in this study was a Waters, equipped with an autosampler and a conductivity detector (Waters 431). The column was an IC-PAK anion; 50 mm in length and 4.6 mm in diameter. The detector was maintained at 35 °C. The mobile phase was sodium borate or gluconate eluent filtered by a 0.2 micron filter paper and degassed by laboratory vacuum simultaneously. The mobile phase flow rate was set at 1.2 ml/min. The concentration of nitrate was determined by comparing the response area with that of a standard.

3.3 RESULTS AND DISCUSSION

3.3.1 Herbicide Results Obtained in 1993

In 1993, the main objective was to verify the hypothesis that continuous application of polluted drainage water to soil and grass filters reduce the contaminant residues. For this reason, mass balance analysis was not carried out during 1993. Only the concentration levels of herbicides (atrazine, metolachlor, and metribuzin) were determined in water samples taken from polluted application water and drainage outflow water. It should be noted that measured values of 0.0 μg/L did not necessarily indicate that a herbicide was not present in the sample. Rather, this indicated that the level of extractable herbicide was below the detection limit of the GC. The lysimeters were located outside and there were rainfall events on days 266 and 269, with 13 mm and 17 mm of rain, respectively. Figure 3.2 shows daily concentration levels of atrazine, metolachlor, and metribuzin for the applied water and drained water of different treatments. It illustrates that the concentration levels of herbicides in the effluent were reduced significantly (1% level), from an average of 250 μg/L to less than 10 μg/L, for all the treatments. In most cases, the concentration levels were lowered to less than 5 μg/L. These results support the hypothesis that there is a significant reduction (up to 1000 times) in the concentration level of initial applied water, by passing it through the soil system. The highest concentration level (10 μg/L) in drainage waters was found for metribuzin which has higher water solubility (1220 mg/L) and lower soil sorption coefficient (60 g/ml) than the other two herbicides (Wauchope et al., 1991). They reported the water solubility and soil sorption coefficient for atrazine to be 33 mg/L and 100 g/ml, respectively. For metolachlor, these parameters were 520 mg/L and 200 g/ml, respectively.

Repeated-Measures Analysis of Variance was performed to test for differences between treatments and whether the concentration level in drainage water for each treatment changed during the application of polluted water. A significant difference (1% level) was found between the bare soil and grass covered lysimeters. Significant differences (1% level) in herbicide levels in drainage waters were also found over time. This indicates that the concentrations in drainage water tended to increase with continuing application of polluted water. This trend can be seen in Figure 3.3 which shows daily concentrations of atrazine, metolachlor, and metribuzin for different treatments. The error bars in this figure show the minimum and maximum concentrations of the three herbicides in drainage waters. Figure 3.3 also indicates that the grass-covered lysimeters with subsurface drainage (GSD) reduced the concentration level of the three herbicides to a greater extent when compared to the other treatments. This can be explained by the fact that the dry soils adsorb pesticides to a greater extent than wet soils. The soil columns in subsurface drainage lysimeters had lower moisture content, compared to the controlled drainage lysimeters. Another explanation for this reduction could be attachment-adsorption to grass and roots in the

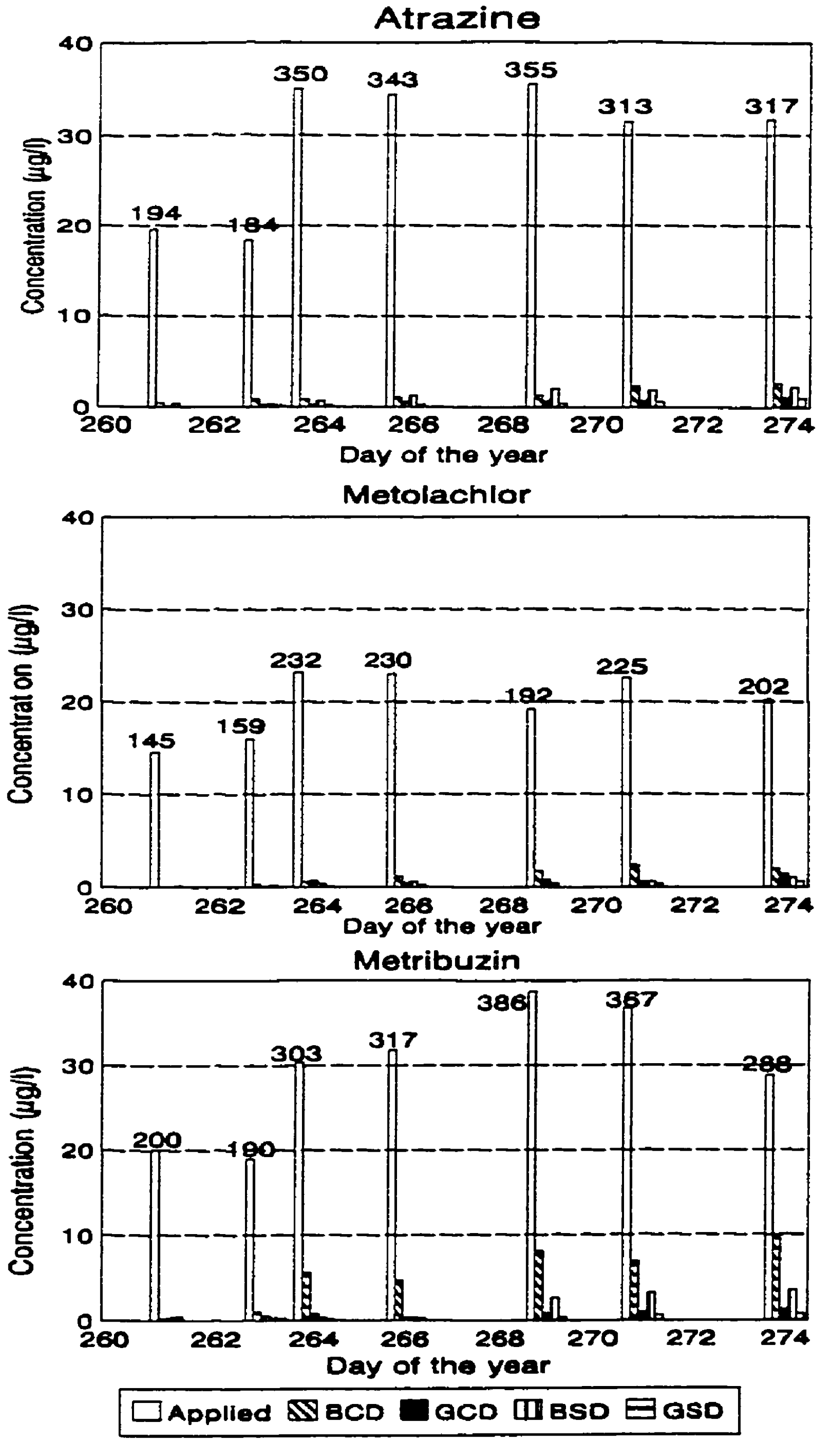

Figure 3.2: Herbicide levels in applied water and drained waters for different treatments (1993).

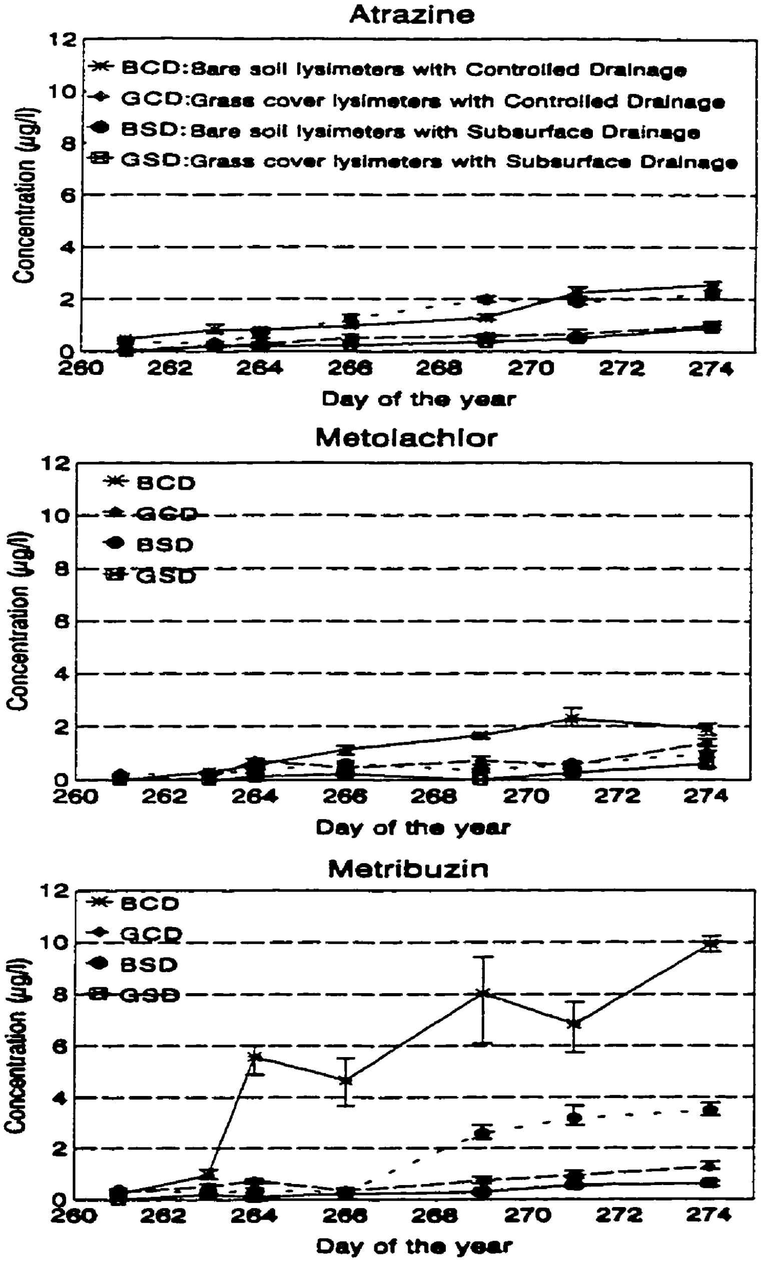

Figure 3.3: Daily concentration levels of atrazine, metolachlor, and metribuzin in drainage waters for different treatments (1993).

Lysimeters.

3.3.2 Herbicide Results Obtained in 1995

In this year, the cumulative volume of applied water and drain outflow was determined and the average ET was estimated for different treatments and over the time of experiment. The average ET's were 4.7, 5.8, 5.9, and 6.9 mm/day for bare soil lysimeters with subsurface drainage, grass covered lysimeters with subsurface drainage, bare soil lysimeters with controlled drainage, and grass covered lysimeters with controlled drainage, respectively. The daily average, minimum, and maximum concentration levels of atrazine, metribuzin, and metolachlor detected in drain outflow are shown in Figures 3.4, 3.5, and 3.6, respectively. The black bars in these figures show the minimum and maximum concentrations and the asterisks show average concentrations of the three herbicides. The average concentration levels of the three herbicides in the drainage effluent was reduced significantly from 50 μg/L to less than 1.2 μg/L, which was not only lower than the maximum permissible level for human beings, but also lower than the water quality guideline for aquatic life. Repeated-Measures Analysis of Variance was used to determine the correlation among the dependent variables (concentration levels of herbicides in drainage water over time). It was found that the concentration levels changed over the experimental period. It is postulated that the soil has a potential capacity for chemical adsorption.

This potential is high at the beginning of each wet period and tends to decrease during the application of polluted water. This potential also tends to increase during the dry period due to degradation processes in the soil. These trends are generally indicated in Figures 3.4, 3.5, and 3.6. Thus, it is concluded that the system can be self-sustainable over the long term, utilising a water application strategy (i.e. allowing a dry period between polluted water applications). It may be noted that the 10-day dry period was chosen arbitrarily. The dry period would vary according to rainfall. More experiments may be needed to determine the minimum dry period needed for sustainability of the system. It is also possible to use computer simulation to determine this period for local conditions.

The total amount of atrazine, metribuzin, and metolachlor trapped by the different treatments was determined and is shown in Table 3.1. Table 3.1 clearly indicates that the soil filters out most of the herbicides. In all lysimeters, there was a significant difference (1% level) between applied masses and those coming out at the outlet. Also, there was a significant difference (1% level) between the grass covered lysimeters and bare soil lysimeters. Table 3.1 indicates that the grass-covered lysimeters trapped herbicides more successfully than the bare soil lysimeters. This may be explained by the attachment-adsorption to grass vegetation. The grass-covered lysimeters were thus shown to be more effective in the reduction of herbicides.

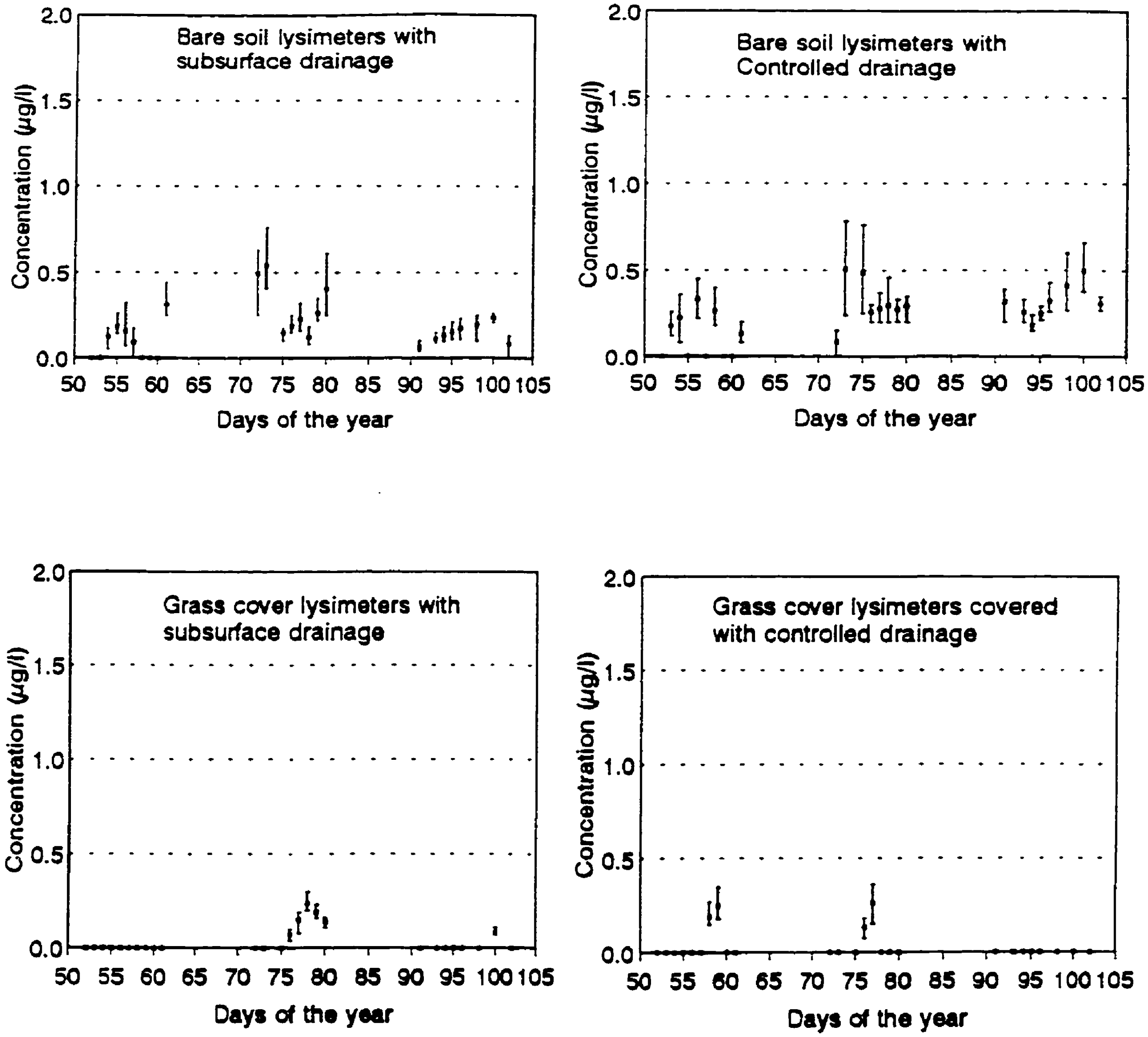

Figure 3.4: Atrazine levels in drainage waters for different treatments (1995).

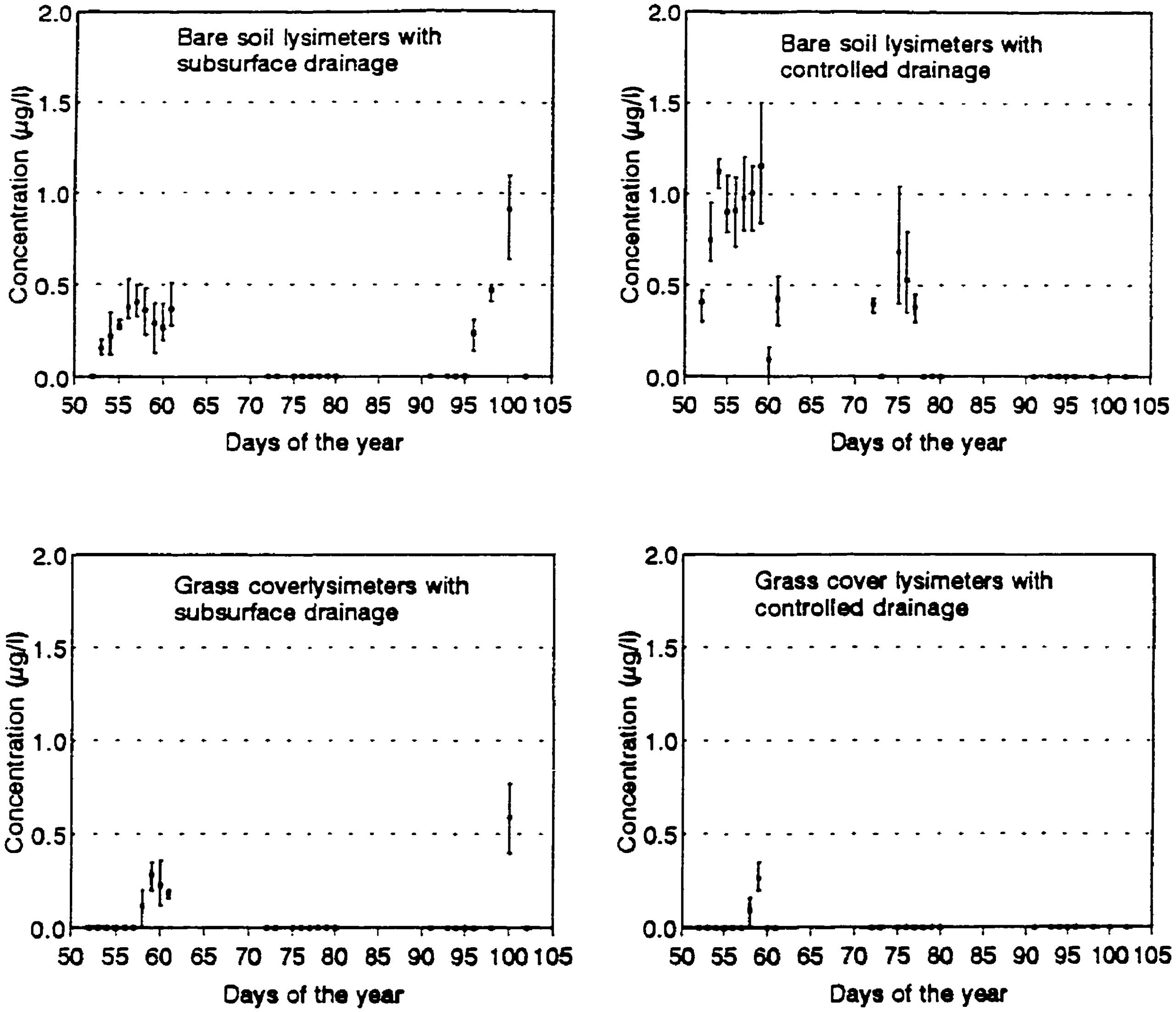

Figure 3.5: Metolachlor levels in drainage waters for different treatments (1995).

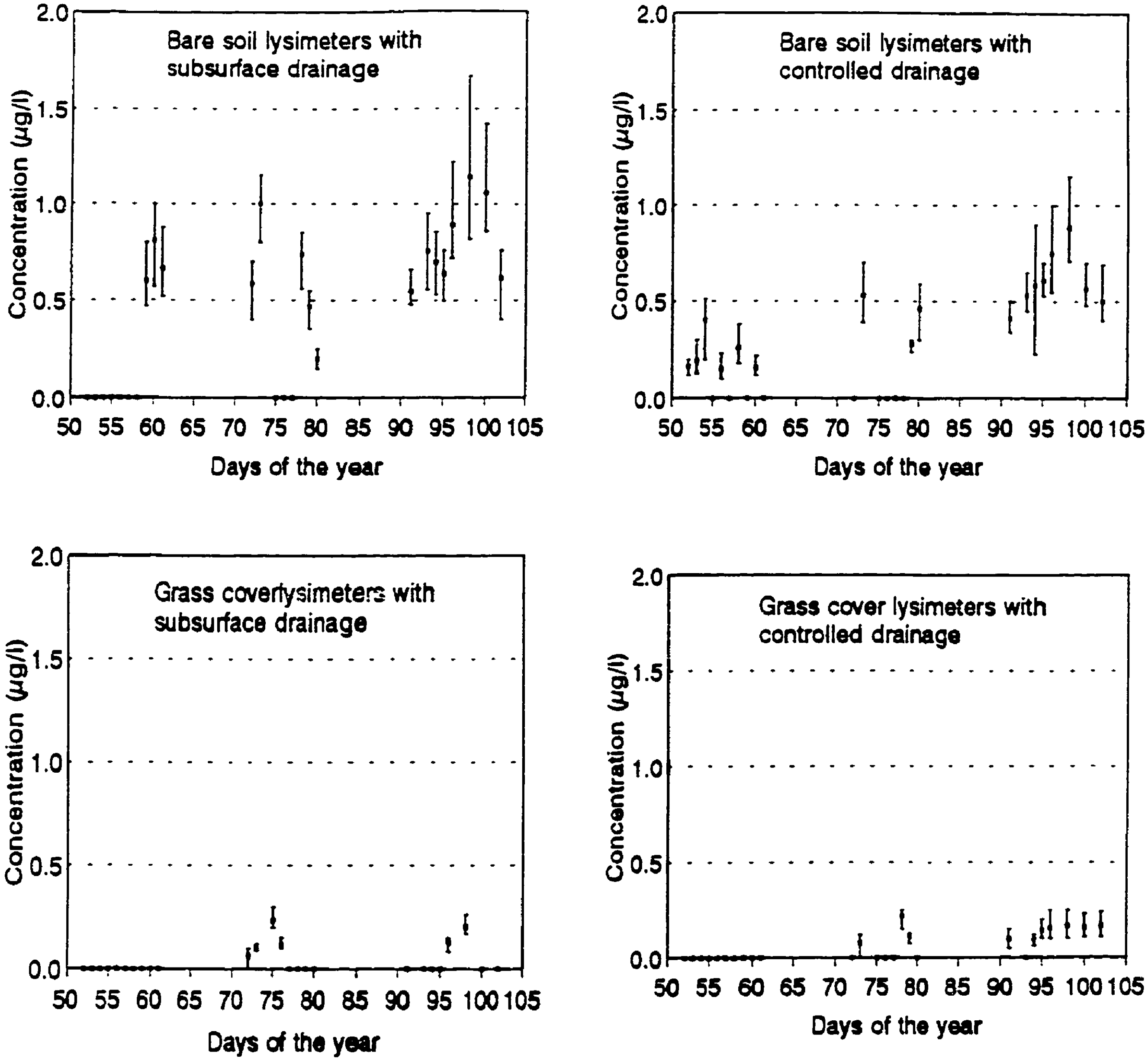

Figure 3.6: Metribuzin levels in drainage waters for different treatments (1995).

Table 3.1: Total amount of atrazine, metribuzin and metolachlor applied to the columns and trapped by different treatments during winter 1995.

Herbicides		BSD	GSD	BCD	GCD
Applied (mg) AZ/MZ/MT		13	13	13	13
Trapped	AZ	99.7	99.9	99.6	99.9
(% of applied)	MZ	99.2	99.9	99.5	99.9
	MT	99.7	99.9	99.3	99.9

AZ: Atrazine; MZ: Metribuzin; and MT: Metolachlor

3.3.3 Nitrate results obtained in 1993

In this study, the main emphasis was on the cleaning of herbicide-contaminated water. Since, nitrate is also a major source of pollution it was decided to investigate the performance of this technique (soil and grass strips filters integrated with water table management) on nitrate residues as well. In 1993, the main objective was to verify the hypothesis that continuous application (daily application for two weeks) of polluted drainage water to soil and grass filters reduces the contaminants. For this reason, mass balance analysis was not carried out in 1993. The concentration of nitrate was only determined in water samples taken from polluted application water and drainage outflow water. Figure 3.7 shows daily concentration levels of nitrate for the applied water and drained water of different treatments. It illustrates that the concentrations of nitrate in the effluent were reduced somewhat, but not as much as the herbicide levels. The reason is that the nitrate ions with

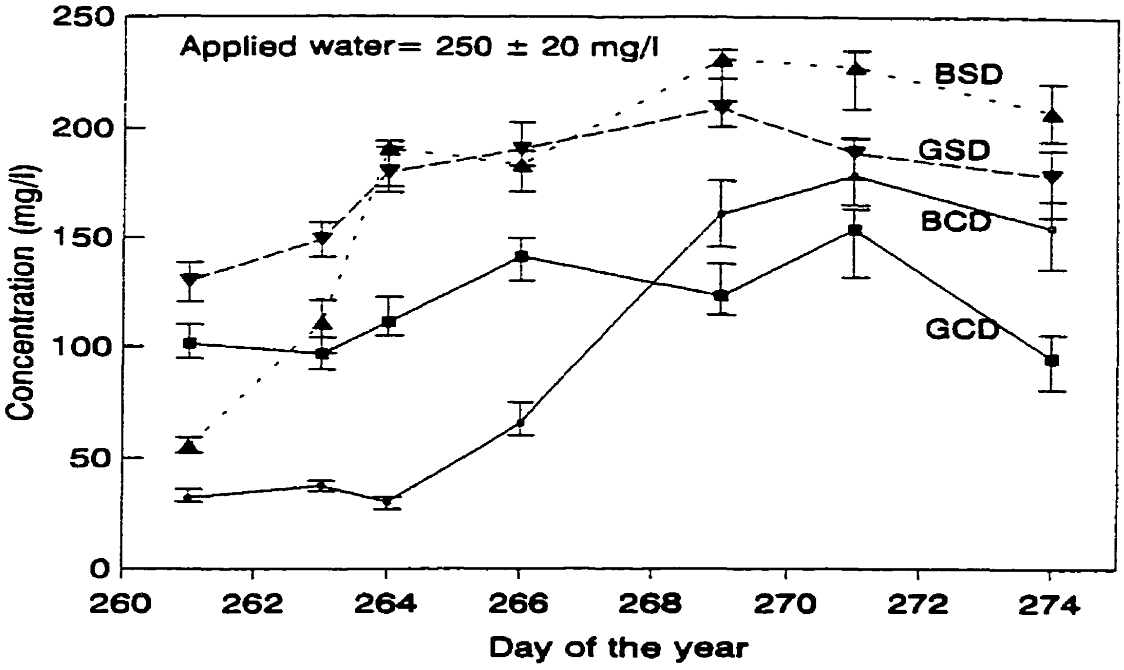

Figure 3.7: Nitrate levels in applied water and drained waters for different treatments (1993).

negative charges and high water solubility can leach easily through the soil profile. Repeated-Measure Analysis of Variance was performed to test for differences among the treatments and whether the concentration level in drainage water for each treatment changed during the application of polluted water. The results of this analysis are shown in Table 3.2. A significant difference (1% level) was found between the controlled drainage and subsurface drainage lysimeters. Nitrate levels in drained waters for different treatments are shown in figure 3.7. Controlled drainage lysimeters show better performance for reducing nitrate levels in drainage waters than the subsurface drainage lysimeters over time. This is due to greater denitrification in the controlled drainage systems (Shirmohammadi et al., 1993; Thomas et al., 1991; Kalita and Kanwar, 1989; Gilliam and Skaggs, 1986). Significant differences (1% level) in nitrate levels in drainage waters were also found over time. This indicates that the concentrations in drainage water tended to increase with continuous application of polluted water (figure 3.7). Repeated-Measure Analysis (Table 3.2) shows a significant difference (5% level) between the bare soil and grass-covered soil in controlled drainage lysimeters.

This is expected since the grass roots may take up some of the nitrate in applied water. Nevertheless, the effect of grass cover on nitrate reduction was not significant in subsurface drainage lysimeters probably because the leaching rate was much greater than the rate of uptake by plants. Figure 3.7 indicates that the concentration levels of nitrate in drainage waters are initially high in grass-covered lysimeters. The reason could be that these were the fertilizer residues in the sod strips when we bought them.

Table 3.2: Repeated-Measure Analysis of Variance for the nitrate levels in drainage waters for different treatments (1993).

Source	Pr>F	Level
Time	*	1%
Time*Treatment	*	1%
Treatment	*	1%
BCD vs BSD	*	1%
BCD vs GCD	*	5%
GCD vs GSD	*	1%
BSD vs GSD	NS	

* Effect significant NS Not significant

3.3.4 Nitrate results obtained in 1995

In 1995, the cumulative volume of applied water and drain outflow was determined in order to analyze the mass balance and estimate the nitrate dissapation rate in different treatments. Figure 3.8 shows daily concentration levels of nitrate in applied water and drain outflow of different treatments. All treatments indicate a reduction in nitrate levels in drainage waters. The dissipation rates of nitrate for different treatments were estimated to be 125, 144, 173, and 181 mg per day per lysimeter (mg/day/lysimeter) for BSD, GSD, BCD, and GCD treatments, respectively.

Nitrate losses could be due to denitrification in the bare soil lysimeters or both plant uptake and denitrification in the grass-covered lysimeters. The estimated dissipation rates in different treatments indicate that the denitrification losses were greater extent than the plant uptake losses. Rolston et al. (1979) reported that the denitrification losses vary from 0-70% of applied N. Addiscott et al. (1991) stated that water-logged soils kept at 25°C in the laboratory and supplied with plenty of easily-decomposable organic matter, may destroy nitrate at a rate equivalent to 30 kg N/ha per day. Rates of denitrification in soils in the field, however, are more likely to be of the order of 3 kg N/ha per day.

Repeated-Measure Analysis of Variance was performed to test for differences among the treatments and whether the concentration in drainage water for each treatment changed during the application of polluted water. The results of this analysis are shown in Table 3.3. A significant difference (1% level) was found between the controlled drainage and subsurface drainage lysimeters. It was found that the controlled drainage lysimeters reduced nitrate level in drainage waters to a greater extent than in the subsurface drainage lysimeters (Figure 3.8). The mass balance also indicates that the total mass of nitrate applied on each column was reduced to one-third in the controlled drainage lysimeters, but to one-half in the subsurface drainage lysimeters. Increased denitrification could be a contributing factor in the case of the controlled drainage lysimeters. The lysimeters with controlled drainage had about one-half of the soil profile saturated, making a conducive environment for denitrification. In addition, the applied contaminated water containing nitrate remained in the saturated zone of controlled drainage lysimeters until the day after water application. However, some of the water applied to the subsurface drainage lysimeters was drained during the day of application. Thus, extent of denitrification was directly related to residence time. There were no significant differences between the concentrations of nitrate in drainage waters during the application of polluted water. This could be due to high solubility of nitrate ions (NO_3^-) in water that prevents retention by humus and clay complexes and is quite different than for the pesticides in which potential sorption capacity of the soil is initially high and reduces in time by continued application of polluted water.

While the dissipation rate of nitrate in the grass-covered lysimeters tended to be higher than that of the bare soil lysimeters, the effect of grass strips on reducing nitrate was not statistically significant. This could be due to the fact that there is an interaction between plant uptake and denitrifier bacteria for a limited source of nitrate in the soil profile. Plants uptake some of the nitrate from the soil profile, thus reducing the availability of nitrate for denitrification.

Table 3.3: Repeated-Measure Analysis of Variance for the nitrate levels in drainage waters for different treatments (1995).

Source	Pr>F	Level
Time	NS	
Time*Treatment	NS	
Treatment	*	1%
BCD vs BSD	*	1%
BCD vs GCD	NS	
GCD vs GSD	*	1%
BSD vs GSD	NS	

*	Effect significant
NS	Not significant

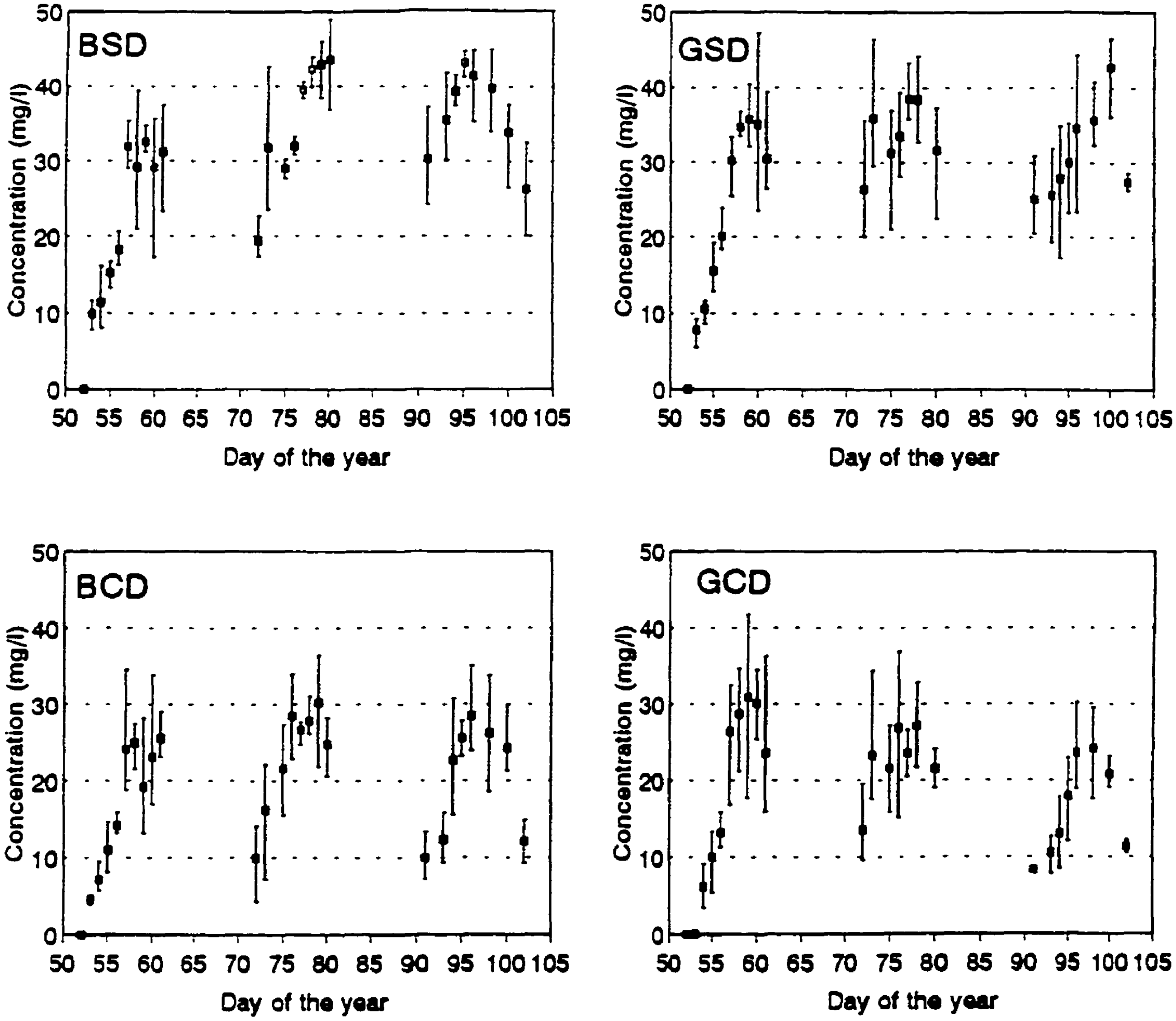

Figure 3.8: Nitrate level in applied waters (50 ± 4 mg/L) and drained waters for different treatments.

3.4 Summary and Conclusions

This study was carried out to investigate the performance of bare soil and grass-covered lysimeters as biological filters in reducing non-point source pollution from agricultural drainage waters. Two water table management practices, i.e., subsurface drainage and controlled drainage, were used in combination with the bare soil and grass covered lysimeters.

The following conclusions can be drawn from this two year study:

1. A significant reduction (1% level) in herbicide and nitrate levels was found in all treatments during both years of the study. However, reduction in the nitrate levels was not as high as reduction in the herbicide levels.
2. Repeated Measures Analysis of Variance for the herbicide levels indicated a significant difference (1% level) between the grass covered lysimeters and bare soil lysimeters, irrespective of the water table management. The grass covered lysimeters reduced herbicide levels in drainage waters to a greater extent. There was a greater herbicide reduction in the grass covered lysimeters with subsurface drainage (GSD treatment) compared to other treatments.
3. Repeated Measures Analysis of Variance for the nitrate levels indicated a significant difference (1% level) between the controlled drainage lysimeters and the subsurface drainage lysimeters. The controlled drainage lysimeters reduced the nitrate level in drainage waters to a greater extent as compared to

the subsurface drainage lysimeters. In addition, there was more nitrate reduction in the controlled drainage lysimeters covered with grass (GCD treatment) as compared to other treatments.

4. Denitrification was the predominant process for reducing nitrate levels.
5. It was found that the concentration level of herbicides in drainage water increased by continued application of polluted water. This situation was remedied by introducing dry periods between the wet periods. In contrast, the concentration levels of nitrate in drainage water did not differ statistically by continued application of polluted water.
6. It was found that of the total applied atrazine, metolachlor, and metribuzin, more than 99% was trapped by the soil filter and of the total applied nitrate more than 48% was dissipated by the soil filter. Results to date reinforce the contention that dual-passage of drainage water could dramatically reduce environmental pollution from agricultural farms, and, concurrently, safeguard freshwater aquatic habitats.

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PREFACE TO CHAPTER 4

Our surface waters are classified according to "designated use": 1) drinking water, 2) swimming and fishing, and 3) transportation and agriculture. Most of our surface waters are in the swimming and fishing category, and pollution control of these waters is important to make such a use possible. In the previous chapter (3), the lysimeters study showed very promising results. However, we felt it necessary to conduct a field study to evaluate the performance of the proposed system.

Chapter 4 presents the procedure and results of a field-scale experiment designed to investigate the performance of soil as a biological filter, for reducing pesticide and nitrate residues in polluted drainage waters. This chapter consists of pesticide and nitrate results obtained from the field in 1994 and 1995. A part of this chapter (Pesticide results of 1994) has been published in the Transactions of the ASAE (Liaghat, A., S.O. Prasher, and R.S. Broughton. 1996. Evaluation of an on-farm pollution control system for reducing pesticide pollution. Transactions of the ASAE, 39(4): 1329-1335).

CHAPTER 4

EVALUATION OF AN ON-FARM POLLUTION CONTROL SYSTEM FOR REDUCING NITRATE AND PESTICIDE POLLUTION

ABSTRACT

This two-year field study concerns the development and testing of an on-farm pollution control system using soil as a biological filter for trapping herbicide and nitrate residues. Measurements were carried out at a field site with four shallow surface ditches, under-lain with four perforated drain pipes. Polluted water with concentrations of 30 mg/L of nitrate and 100 µg/L of three commonly-used herbicides, atrazine, metolachlor, and metribuzin, was applied to the ditches for 10 days continuously (actual daily application lasted for four hours); and no water was applied for the following ten days. This cycle was repeated three times. Water samples were collected before application and after the water came out of the drains.

The average level of nitrates residues in the lake, in which runoff and drainage effluent of some of the cultivated farms on the campus drain, was found to be 30 mg/L. When the lake water was pumped to the soil system, the concentration in the effluent dropped significantly (1% level) to 15 mg/L. Herbicide concentrations were also reduced significantly (1%), from 100 µg/L to

10 µg/L or less in most cases. Herbicide levels in the soil samples indicated that the herbicide residue in the polluted water was trapped mostly by the surface layer of the soil filter, where microbial activity is higher than in the subsurface layers. Bio-degradation of herbicides was also found to occur between water applications. Thus, it appears that the system would be self-sustaining in the long term. It was found that of the total applied atrazine, metolachlor, and metribuzin in 1994, 98.1, 97.6, and 97%, respectively, were trapped by the soil system. The trapping ratios in 1995 were 98.4, 98.6, and 98.1% for atrazine, metolachlor, and metribuzin, respectively. These results reinforce the contention that dual-passage of drainage water could dramatically reduce environmental pollution from agricultural farms and, at the same time, safeguard freshwater aquatic habitats.

4.1 INTRODUCTION

In Quebec, the majority of the population and much of the farmland are located along the Saint-Lawrence river and its tributaries. Some of the tributaries are located in watersheds with intensive agricultural activity. Any activity that changes surface and ground water will impact many people and also aquatic life. Pesticide and nitrate fertilizer in surface and ground water are a major environmental problem in such areas. A report by the Quebec environment ministry released in Saint-Hyacinth in mid-December 1994, states that 6,000 corn producers in Quebec are using pesticides on more than 350,000 ha of cultivated land, and that these are seeping directly into watercourses and destroying aquatic life. Muir and Baker (1978) and Frank and Sirons (1979) observed that the atrazine concentrations in selected Ontario and Quebec streams ranged from 0.1 to 30.3 µg/L. Aubin et al. (1993) reported metribuzin levels in ground water as high as 279 µg/L in Quebec. Pesticides have been found in wells all across Canada (McRae, 1985; Pupp, 1985). Widespread contamination of drinking water (particularly ground water) by nitrates and herbicides has been found in many countries. The most frequently detected herbicides in the largest concentrations in the US and Canada were: atrazine, alachlor, metribuzin, and metolachlor. These are among the most heavily used herbicides in the US (Goolsby et al., 1991). More recently, the US Geological Survey (USGS) found that 55 percent of the streams tested in 10 Mid-Western States had detectable levels of pesticides prior to spring planting, when contaminants levels were expected to be lowest (Goolsby et al., 1991).

In humid areas, agricultural drainage water, which originates from precipitation, eventually becomes either runoff from the soil surface or flow from subsurface drains or natural seepages. Pesticides and fertilizers can move with runoff over the land surface, either in the solution phase or adsorbed to the sediment and organic matter, or laterally through the soil profile via subsurface flow into surface ditches or streams and pose a direct threat to surface water quality. The quantity of contaminants can be quite extensive if the agricultural land is sloped and if a rainfall event occurs soon after the herbicide or fertilizer application. Frank and Sirons (1979) analyzed 469 surface water samples from outlets in 11 watersheds in Ontario, Canada. They found atrazine in 77% of their samples, and atrazine losses were reported to be as high as 60%. On the other hand, Wauchope (1978) observed herbicide losses in agricultural runoff ranging from 2 to 5% for wettable powder-formulated herbicides. In an average year, the herbicide losses through surface runoff on a typical farm are expected to be around 10% over a growing season (Klaine et al., 1988). Triplett et al. (1978) monitored the losses of atrazine and simazine in surface runoff from conventional and no-till corn fields. The largest quantities of atrazine and simazine transported in runoff from any watershed-year was 64 g/ha (5.7%) and 123 g/ha (5.4%), respectively. These concentrations were detected for rainfall occurring soon after herbicide application and declined quickly for later events. Metribuzin concentration in surface runoff was reported by Bastien (1991) to be as high as 47 µg/L on a potato field in southwestern Quebec.

Southwick et al. (1990) reported atrazine concentration in drainage waters to be up to 3.53 µg/L in a Commerce clay loam in Louisiana. They also found that the total atrazine loss into the drains amounted to 0.038% of that applied. It was estimated that about 0.1 to 2.9% of the total atrazine applied was lost via tile drains in Quebec (Muir et al., 1978, Muir and Baker, 1976).

Research over the last decade has clearly shown that agriculture has become the greatest source of nitrate delivered to ground and surface water (Hallberg, 1987a, 1987b; Keeney, 1982; Pratt, 1984). In some areas, nitrogen pollution in ground water has reached alarming levels. For example, Hubbard and Sheridan (1989) reported that in many agricultural areas, nitrate-N levels in drinking water were significantly higher than the maximum contamination level of 10 mg/L, set by the U.S. Environmental Protection Agency (EPA). Research has shown that subsurface drainage enhances nitrate-N leaching loss from the soil profile (Carter et al., 1971, Devitt et al., 1976). In a St. Jude sandy loam soil, Madramootoo et al. (1992) measured values of 2 to 40 mg/L of nitrate-N in the drainage water from a potato field. Some researchers have estimated that between 30 and 60%, of the nitrogen fertilizer applied in Quebec, is leached out to waterways and ground water after the fall rain and surface runoff (Miller and Mackenzie, 1978; Neilson and Mackenzie, 1977).

Regulations, limiting the use of crop nutrients and agrochemicals, to protect groundwater quality have been established in several states of the US and Canada. The US Federal clean water Act now includes provisions on ground water. The Quebec Environment Minister has also clearly stated that all polluters, including agricultural farms, will be held responsible and accountable for their part in damaging our natural resources, and for dealing a blow to our freshwater aquatic life and their habitat.

While there are many known management practices which help to reduce and minimize the movement of chemicals to water bodies, it is virtually impossible to eliminate chemical leaching while keeping food production at a sufficient level. So far, no attempt has been made to treat contaminated agricultural water in-situ, probably due to high costs. However, many agricultural fields in humid areas are now tile-drained. Hence, polluted water (runoff and drainage water) can be collected at the end of the collector drains, enabling treatment before discharge into the water courses.

The objective of this research was to investigate the feasibility of cleaning contaminated drainage water and surface runoff in order to improve the quality of water which is discharged finally into our rivers and lakes. The proposal involves using the soil profile as a filter and establishing an on-farm biological pollution control system, in the form of grass border strips that would not only trap sediments but would also adsorb pesticide and nitrate residues from drainage waters and surface runoff.

4.2 HYPOTHESIS

It is well known that drainage water escaping the field boundaries through a subsurface drainage system may contain leached-out pesticides and fertilizer residues. Many pesticides are applied at concentrations of mg/L and found in drainage water in µg/L. This is the result of the pesticide having undergone a series of physico-chemical processes while in the soil, such as plant uptake, sorption/desorption, transformation, microbial and chemical degradation, volatilization, photolysis, decay, etc.

It should be noted that the maximum allowable pesticide concentration for freshwater aquatic life is much lower than that for human consumption, farm animals and irrigation purposes. For example, the most commonly-used herbicide in Quebec for corn and soybeans is metolachlor. The maximum permissible level for drinking water is 50 µg/L but only 8 µg/L for freshwater aquatic life. For metribuzin, a herbicide used in potato production, the limit is 80 µg/L for human and livestock consumption, and 1 µg/L for aquatic life. Standards for the other pesticides are in the same range.

According to a "traditionally-held" environmental viewpoint, significant reductions in both pesticide and fertilizer concentrations occur during a 'single pass' through the soil. It is rare that pesticide concentrations would reach unacceptable levels for human under normal circumstances but they often exceed limits for aquatic life. However, if drainage water is allowed to pass through the soil system again, a reduction to levels safe for aquatic life is anticipated. The final effluent could have concentrations in ng/L, instead of µg/L. Thus, the expectation is to significantly reduce non-point agricultural pollution from pesticides without drastic changes in current farming practices.

4.3 MATERIALS AND METHODS

4.3.1 Field Site

In order to carry-out field measurements, a field site (100 m wide and 150 m long), with St-Amable sandy soil (Ferro-Humic Podzol), was selected at the farm at Macdonald Campus of McGill University. The farm was chosen for the following reasons: 1) The field was surrounded by four roads which act as barrier boundaries; 2) An impermeable layer (clay layer) existed at a depth of 1 m; 3) It was close to the Campus so the site could be accessed easily for the frequent field measurements with minimum time and expenses; 4) None of the herbicides to be used in this study were applied on this field in the previous six years; and 5) A source of polluted water (lake) was located adjacent to the field. The runoff and drainage effluent of some of the cultivated farms on the Campus drain into this lake. The general land slope of the field is toward the lake which is located at the west side.

In September 1993, five perforated drainage pipes, 100 mm in diameter, were installed at the site at an average depth of 70 cm from the surface, at 16 m spacing. A wooden observation chamber (2.5 m x 2.5 m x 2.5 m) was constructed near the western boundary of the site. All the newly- installed drains come into the observation chamber before they drain into the lake, via a 0.2 m diameter non-perforated drain. The chamber permitted collection of water samples from individual drains.

Four shallow surface ditches, parallel to the drain laterals, were constructed on the farm using a tractor plow and grader. Each ditch was constructed on top of the lateral drain with a 2 m lateral offset (Figure 4.1). The ditches were not located directly above the drains since the soil above the drains was disturbed during drainage system installation. Also, they were not located at midspacing so that we could have at least four replicates. Each ditch was 80 m long and had an average depth of 0.3 m.

Atrazine and metolachlor are normally applied to the corn-growing area of the Macdonald Campus Farm, according to the locally recommended rates and in pre- or post-emergence applications. Atrazine and metolachlor are applied at the rate of 2.4 and 2.7 kg/ha of active ingredient, respectively, and metribuzin is applied on potato farms at the rate of 1 kg/ha of active ingredient. The drainage

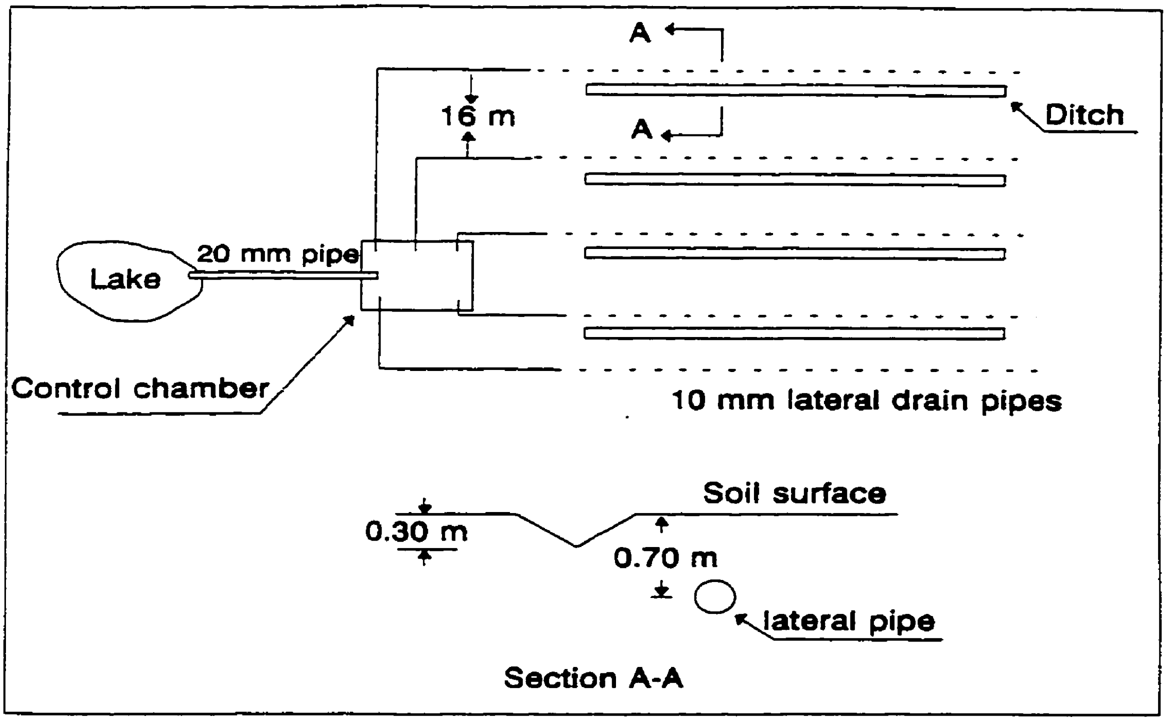

Figure 4.1: Schematic of the field layout.

water from the corn-growing area enters into the lake. This pond water was pumped into the shallow surface ditches of the field site.

In fall 1994, before starting the experiment, the base (initial) levels of the three herbicides (atrazine, metolachlor and metribuzin) were measured in field plots. It was found that the base levels of the three herbicides were below the minimum detection level. The lake water was also initially tested for herbicide and nitrate residues. It was found to contain only trace levels of the three herbicides.

Therefore, it was decided to use an "intravenous" system to bring the herbicide levels to about 100 μg/L in the water that was to be applied to the ditches. This simulated the maximum levels of herbicides that could be present in drainage waters at any time. It should be noted that it is not anticipated that herbicide levels in drainage waters would be this high under normal circumstances. Nitrate levels in the lake water were found to average 30 mg/L. Therefore, no nitrate was added to the applied water.

In addition, it was decided to apply water in 10-day increments, i.e. flood the ditches for 10 days continuously, followed by a 10-day "dry" period. In the fall of 1994, the above procedure was repeated three times. It should be noted that the 10-day application period was chosen, since it represents the worst case scenario; where the drains would be flowing continuously for 10 days because of some heavy rainfall events in the fall, or to simulate snowmelt conditions during spring months. Drainage may last longer than 10 days during spring time; however, the water may not be as polluted as, for example, in the summer months or early fall.

Water was applied to the field ditches on the following Julian days: 253 to 263, 276 to 286, and 302 to 304. The water was not applied to the ditches during Julian days 305 to 310 due to a major rainfall event; but water samples were collected from subsurface drains during this period. The periods during which water was applied are defined as "recycling periods" or wet periods" and the in-between periods are called "dry periods". The volume of water applied to ditches and the effluent from the drains were measured using a flowmeter and a tipping bucket setup, respectively.

One-litre water samples were collected daily from the application water to the ditches and from the water coming out of the drains in the observation chamber. For sampling drainage water, one-liter bottles were placed under tipping buckets to collect drainflow gradually (5 ml per tipping of the tipping bucket). These samples were supposed to be representative of the total water coming out of the drains during a particular day. Three samples of applied water were collected per day from the delivery pipe. A 20-ml sub-sample was taken from each sample for nitrate analysis. Methylene chloride was added to the water samples to act as a preservative; then the samples were stored in a refrigerator at 4°C.

When the pump was stopped after a ten-day application period, soil samples were collected from the ditches at regular intervals (on day 1, 5, and 9 after the pump was stopped). Soil samples were taken at three depths: 0 to 0.2 m, 0.2 to 0.4 m, and 0.40 to 0.6 m. For each depth, the soil samples were taken at three different locations (beginning, middle, and end of the ditch) per test plot. The soil samples were stored in a freezer.

In the summer of 1995, soil samples were taken at three depths: 0 to 0.2 m, 0.2 to 0.4 m, and 0.40 to 0.6 m. For each depth, soil samples were taken at three different locations (beginning, middle, and end of the ditch) per test plot. These three samples were thoroughly mixed and a sub-sample was taken to represent the given depth per test plot.

In 1995, water was applied to the field ditches on the following Julian days: 216 to 225, 237 to 246, and 281 to 286. The third cycle of application of polluted water was started late (35 days) due to mechanical problems with the pump. On the Julian days of 217, 226, 243, 250, 277, 278, 288, 295, and 302, rainfall occurred and water samples were collected from subsurface drains.

Both the soil and water samples were extracted and analyzed according to the methods already established in our previous research projects (Masse, 1990; Arjoon, 1993; and Aubin, 1993). Tables 4.1 and 4.2 include the measured physical and chemical properties of the soil and herbicides used in this study; these data help to explain the role of the soil filter in reducing pesticide pollution.

Table 4.1: Soil Characteristics of the Field.

Soil Type	Sand (%)	Silt (%)	Bulk density (g/cm^3)	Organic matter (%)
Sand	91.2	4.2	1.4	3.5

Table 4.2: Physicochemical properties and soil sorption coefficients of organic chemicals.

Property	Atrazine	Metolachlor	Metribuzin	Source
Solubility (mg/L)	33	530	1220	Wauchope et al. (1991)
Soil sorption Coef. K_{oc} (g/mL)	133	246	80	Measured
Soil half life (day^{-1})	60	90	40	Wauchope et al. (1991)

4.3.2 Herbicide extractions from soil samples

The soil samples were thawed and thoroughly mixed before moisture content was determined on a sub-sample at 105°C for 24 hours. A sub-sample (20 g, oven-dry weight basis) at field moisture content was mechanically shaken in 100 ml of methanol for 30 min and filtered under suction. This process was repeated twice. The combined filtrate was then evaporated to dryness in a rotary evaporator at 40°C. The residues sticking to the round bottom flask were dissolved in 10 ml of methanol and stored at 4°C. The extracts were then analyzed on GC and GC/MS, and the results are reported in ng/g of dry soil. The recovery rate of pesticides from the extraction and evaporation process was estimated to be 98% ± 4% for soil samples.

4.3.3 Extraction of herbicides and their metabolites from water

The herbicides and/or metabolites were extracted from the water samples by adding 100 ml of methylene chloride to 1000 ml of water in a separatory funnel. The mixture was hand shaken for 5 min and the organic layer was collected at the bottom of the funnel. The process was repeated twice with the aqueous layer. The combined extracts were evaporated to dryness and the residues were dissolved in a small volume of methanol, before analysis by gas chromatography. The herbicide concentrations are reported in µg/L of water. The extraction efficiency in water samples was estimated to be 88% ± 5%.

4.3.4 Gas chromatography

The gas chromatography (GC) used in this study is a Varian, Model 3400, equipped with a TSD (Thermionic Specific Detector) detector, an autosampler, and an integrator. The column is a 0.53 i.d. fused silica Megabore DB-5 column. The operating conditions were as follows: the detector and injector temperature were maintained at 290°C and 190°C, respectively; the column temperature was set at 150°C for 2 min, and then it was increased to 190°C, at a rate of 5°C/min; at 190°C it was kept for 0.2 min and then it was raised to 290°C at a rate of 10°C/min. The helium carrier gas flow rate was set at 15 ml/min.

The concentrations of the herbicides were determined by comparing the response areas with reference standards. The detection limits of the analytical method were evaluated by injecting extracts with decreasing herbicide and metabolite concentrations. The detection limits for water samples were found to be 0.03 μg/L for atrazine, 0.12 μg/L for metolachlor, and 0.05 μg/L for metribuzin. In the soil samples, the detection limits were 0.01 μg/g for atrazine, 0.05 μg/g for the metolachlor, and 0.01 μg/g for the metribuzin. Some pesticide extractions were randomly chosen to be run on a Varian Saturn III GC/MS.

4.3.5 Analytical method for nitrate analysis

High performance liquid chromatography (HPLC) was used to detect nitrate levels in water samples. The HPLC used in this study was a Waters, equipped with an autosampler and a conductivity detector (Waters 431). The column was an IC-Pak anion; 50 mm in length and 4.6 mm in diameter. The operation conditions for nitrate were as follow: the detector was maintained at 35 °C, the mobile phase was sodium borate or gluconate eluent, filtered by a 0.2 micron filter paper and degassed by laboratory vacuum simultaneously, the mobile phase flow rate was set at 1.2 ml/min. The concentration of nitrate was determined by comparing the response area with that of reference standard.

4.4 RESULTS AND DISCUSSION

This section consists of the results of herbicides and nitrate obtained in 1994 and 1995. Herbicide results are presented first and nitrate results are presented second on the year order.

4.4.1 Analysis of Herbicide Data Obtained in 1994

In the fall of 1994, soil and water samples were collected from the field experiment. The results of the herbicide levels in water and soil samples are presented below.

4.4.1.1 Herbicide Trapping by the Ditches in 1994

The cumulative volume of the applied water and drainflow during the fall of 1994 is given in Figures 4.2. This figure indicates that about 25% of the applied water

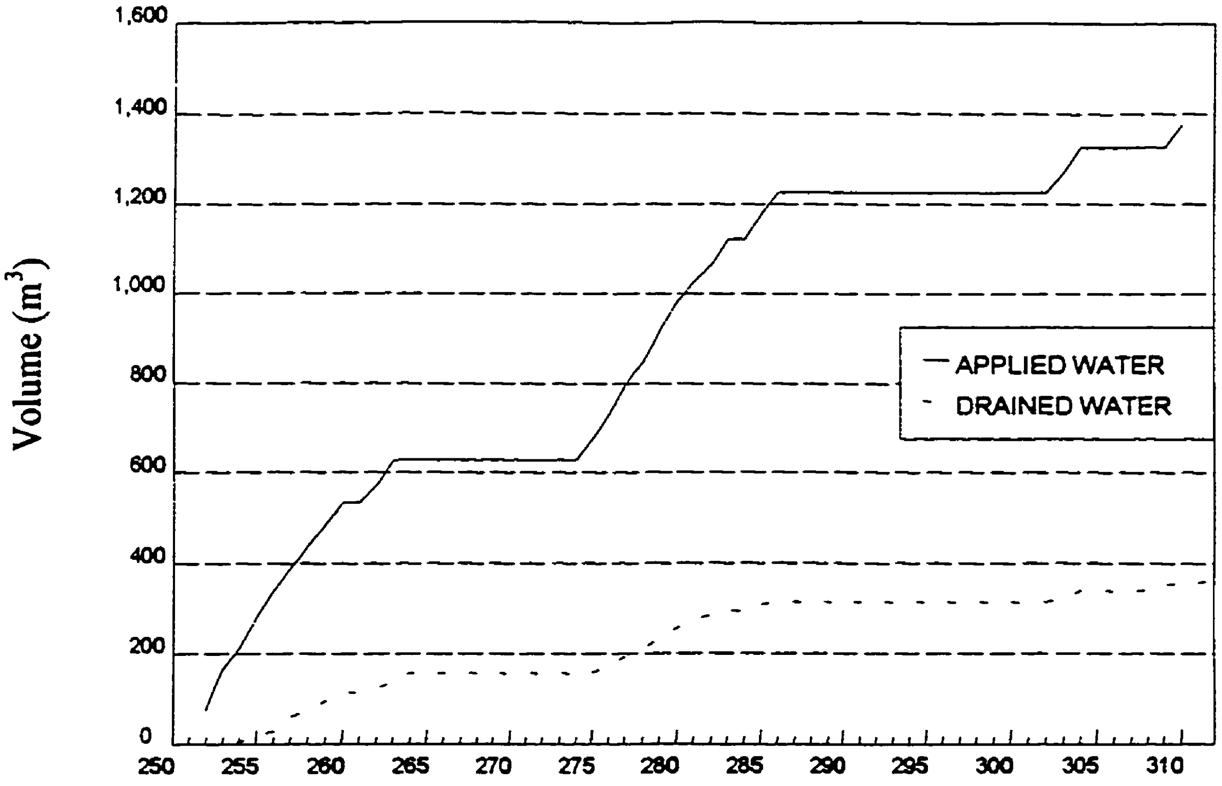

Figure 4.2: Cumulative volume of applied water and drainflow in 1994.

passed into the drains and the remaining 75% were lost to the atmosphere via evapotranspiration. The high evapotranspiration was due to the presence of an impermeable layer at the depth of 1 m or less, which caused water to be maintained at the rootzone and evapotranspirate more readily, and the presence of alfalfa and grass cover on the soil surface. Polluted water was initially pumped to the ditches on Julian day 253 of 1994, however, drainflow appeared two days later. Almost all the herbicides (atrazine, metribuzin, and metolachlor) applied to the ditches were detected in the drain flow, four days after the start of the application. All three detected herbicides reached the drains at the same time, in spite of differences in adsorption coefficients. It is generally expected that compounds with higher sorption should have a slower travel time, as well as attenuated concentrations.

Tyherefore, the data collected indicates that both preferential flow and nonequilibrium sorption are occurring on a field-scale. Bottcher et al. (1981) also found small amounts of two chemicals with different sorption coefficients in drainflow within four days of application. Everts et al. (1989) irrigated a loam soil with a solution of two non-sorbed tracers and two differently sorbed tracers, and they detected all four tracers in drainflow within one hour of initiation of the irrigation.

Herbicide levels in the ditch and drainage water samples measured on the GC, are given in Figures 4.3 to 4.5. These figures show daily concentration levels of atrazine, metribuzin, and metolachlor, respectively, in drainage waters. It should be noted that measured values of 0.0 μg/L do not mean that herbicide is not present in the sample. Rather, this indicates that the level of extractable herbicide is below the detection limit of the GC. During the fall of 1994, typical concentration ranges for the herbicides were: atrazine, 0 to 25.60 μg/L; metribuzin, 0 to 34 μg/L; metolachlor, 0.9 to 24.79 μg/L. Using the t-test, it was found that the average concentration levels in the drainage waters reduced significantly (1%), from 100 μg/L to about 10 μg/L.

The concentration levels in drainage waters still appear to be above the desirable levels. It should, however, be noted that only about 0.4 m of the soil profile depth was used for bio-filtering at the field site (0.7 m average drain depth and 0.3 m average depth of surface ditches). Typically, the average depth of subsurface drains in Québec is 1.2 m. Confidence is expressed in this method, since the results were obtained with 0.4 m bio-filtering coupled with the fact that the field reduced herbicide levels from over 100 μg/L to around 10 μg/L or less.

Figures 4.3 to 4.5 show that the concentrations in drainage waters tend to increase with continuous water applications during each recycling period. This could be the result of continuous water application in ditches; however, due to the variability in data, it cannot be confirmed statistically. In any case, the concentration levels in drainage waters stay around 10 μg/L or less, and this represents a reduction of at least 90%.

Also, the pesticide concentration on the last day of a wet period tends to be higher than the concentration on the first day of the next consecutive wet period, though it was found to be true statistically in only about half of the cases. This may imply that there could be some biodegradation, chemical and/or biotransformation occurring during a dry period. Biodegradation would be highly desirable for this system since it would make it self-sustainable However, no specific measurements were made in this respect in the current study.

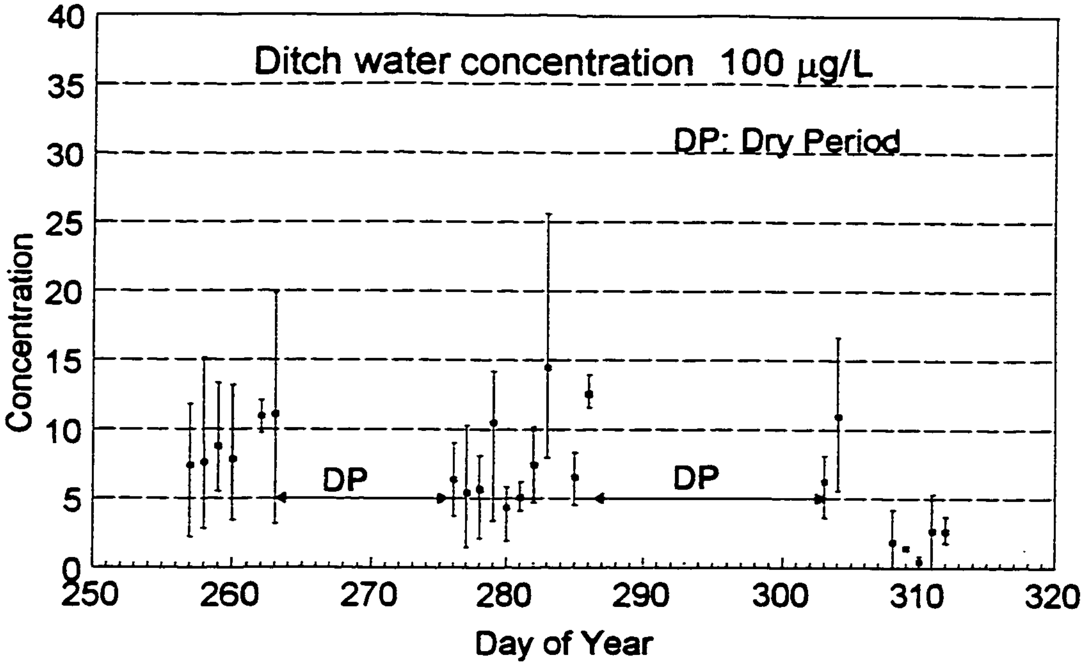

Figure 4.3: Atrazine concentration in applied water and drainflow (1994).

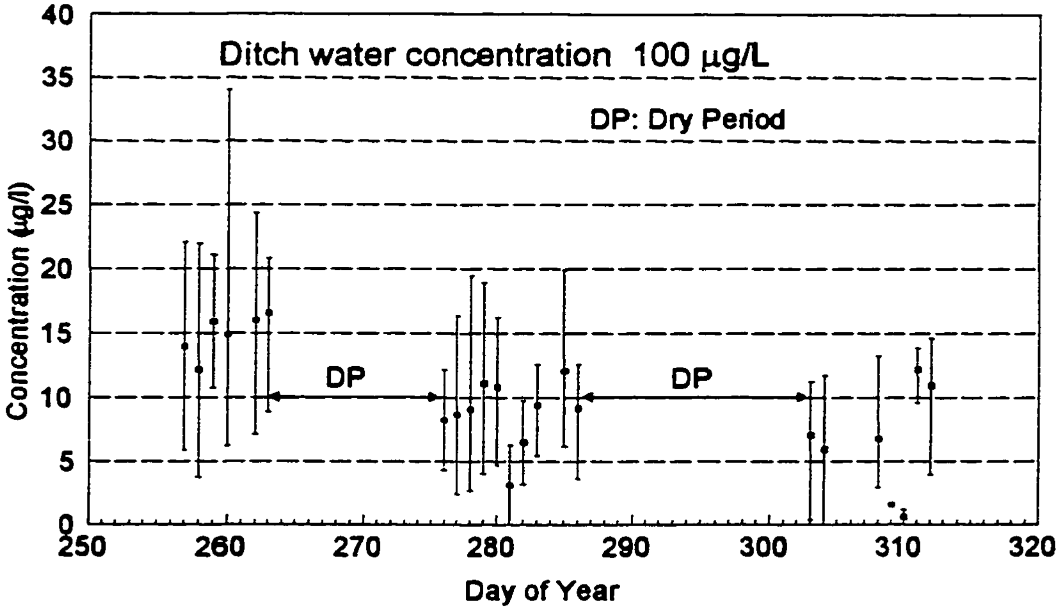

Figure 4.4: Metribuzin concentration in applied water and drainflow (1994).

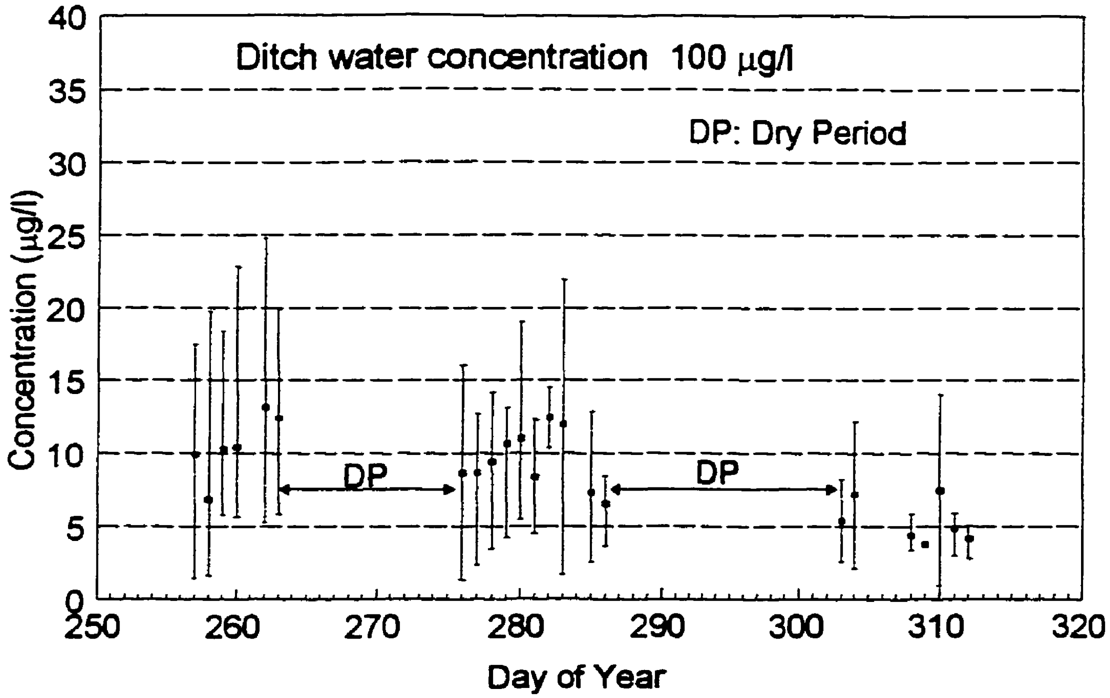

Figure 4.5: Metolachlor concentration in applied water and drainflow (1994).

The cumulative masses of herbicides (atrazine, metribuzin, and metolachlor) in applied and drainflow water and coming during the experiment period, are illustrated in Figure 4.6. The herbicide concentrations in the drainflow samples were found to be statistically different at 1% level using the t-test. This indicates that they correspond with the rank-order of their water solubility (Table 4.2). Metribuzin, with high solubility, was sorbed the least and it was the herbicide found in the highest concentrations in the drainflow (34 µg/L). The total amount of atrazine, metolachlor, and metribuzin trapped by the soil during the experiment period was estimated to be about 98.1, 97.6, and 97.0%, respectively, of the total applied herbicides (Table 4.3).

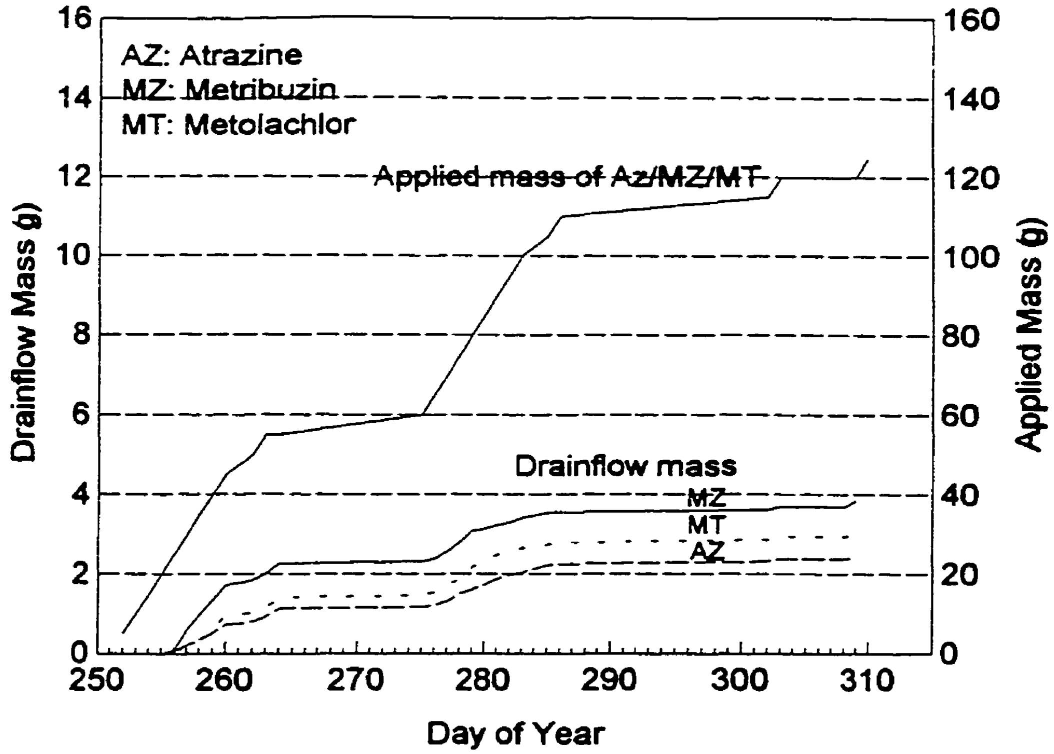

Figure 4.6: Cumulative masses of herbicides in applied water and drainflow (1994).

Table 4.3: Total amount of atrazine, metolachlor and metribuzin applied to the ditches and lost through subsurface drainflow during fall 1994.

Herbicides	Atrazine	Metolachlor	Metribuzin
Applied (g)	125.0	125.0	125.0
Leached (% of applied)	1.9	2.4	3.0
Trapped (% of applied)	98.1	97.6	97.0

4.4.1.2 Herbicide Levels in the Soil in 1994

As already indicated, soil samples were taken at three different locations (beginning, middle, and end of the ditch) per test plot, and this data is presented in Table 4.4. Both the average values and the corresponding standard deviations are provided. Overall, it appears that most of the herbicides remained in the upper 0.0 to 0.2 m layer of the soil, with little leaching to lower layers. These data also show that the concentrations of metribuzin in the soil layers are lower than those of atrazine and metolachlor. The explanation could relate to the higher water solubility, lower soil sorption coefficient, and lower persistence of metribuzin. This result agrees with those obtained from the drainflow analysis, in which the total mass of metribuzin was higher than those of atrazine and metolachlor. Although the soil filter trapped over 97% of the three herbicides, there were wide differences in the soil herbicide residues (Table 4.4). It should be noted that the polluted water was pumped to the middle site of the ditch, from which point the water moved to both sides of the ditch. In addition, some grass and weeds grew inside the ditches. Both of these factors may have caused these intra-ditch differences. Another explanation could be a greater infiltration of the polluted water in the middle part of the ditch or a nonuniform distribution of water within the ditch.

As already stated, soil samples were taken from the field before the experiment commenced, in order to find the base level of herbicide concentration in the soil. None of the samples showed a detectable concentration. Table 4.4 indicates that the concentration of herbicides in the soil tends to decrease over time during the dry periods (from 265 to 274 days and from 288 to 302 days). In most cases, it is quite pronounced at 0.0 to 0.2 m depth which could be the result of higher concentration of the herbicide. This reduction may be explained, for the most part, by microbial and chemical degradation, and to a lesser extent, by volatilization and plant uptake. Therefore, the results obtained from this study indicate that the system should be self-sustainable in the long term.

4.4.2 Analysis of Herbicide Data Obtained in 1995

In the summer of 1995, soil and water samples were collected from the field experiment. The results of the herbicide levels in water and soil samples are presented below.

4.4.2.1 Herbicide Trapping by the Ditches in 1995

In the spring of 1995, drainage outlet discharged on the following Julian days: 118, 124, 139, 153 days, due to snow melt and rainfalls. Water samples were collected during those days for determining herbicide levels in the drainage waters. Herbicide levels in the drainage waters were found to be less than 3.38, 1.25, and 1.31 μg/L for atrazine, metribuzin, and metolachlor, respectively. On the

Table 4.4: Average and standard deviation of herbicides levels in the soil in 1994.

	Atrazine (µg/kg)			Metribuzin (µg/kg)			Metolachlor (µg/kg)		
Day of Year	0.0-0.2 (m)	0.2-0.4 (m)	0.4-0.6 (m)	0.0-0.2 (m)	0.2-0.4 (m)	0.4-0.6 (m)	0.0-0.2 (m)	0.2-0.4 (m)	0.4-0.6 (m)
Beginning of the ditch									
265	82.4*	nd	nd	37.3	11.8	nd	60.7	11.8	nd
	(27.2)**			(12.6)	(5.3)		(22.5)	(6.8)	
270	84.4	10.9	9.0	20.8	nd	nd	53.5	9.7	27.2
	(14.1)	(2.1)	(2.5)	(7.4)			(13.8)	(4.1)	(5.8)
274	64.1	nd	nd	nd	nd	nd	37.7	nd	nd
	(14.0)						(19.7)		
288	207.4	12.3	nd	65.9	nd	nd	209.4	12.2	nd
	(34.2)	(2.9)		(9.4)			(42.5)	(3.8)	
296	169.4	11.7		36.3	9.6	17.0	144.0	nd	nd
	(29.3)	(6.8)		(8.6)	(1.7)	(5.4)	(22.2)		
302	180.4	22.9	nd	35.5	8.9	nd	155.8	nd	nd
	(37.7)	3.1		(7.8)	(2.1)		(23.7)		
Middle of the ditch									
265	212.5	122.0	49.0	32.8	47.0	32.2	414.6	228.8	113.8
	(55.8)	(33.1)	(7.0)	(10.1)	(17.8)	(8.2)	(107)	(89.9)	(29.1)
270	195.5	105.4	38.2	16.4	27.5	15.6	297.4	169.1	148.6
	(65.8)	(18.9)	(16.3)	(4.4)	(5.5)	(7.3)	(75.0)	(31.5)	(39.5)
274	122.7	65.3	63.0	16.6	13.8	16.8	178.8	112.1	97.0
	(24.8)	(12.5)	(22.2)	(6.6)	(5.0)	(4.6)	(58.1)	(21.0)	(26.0)
288	186.8	100.4	99.9	57.3	49.2	44.8	220.3	119.1	105.6
	(34.9)	(41.3)	(37.7)	(17.6)	(7.1)	(20.2)	(30.4)	(29.8)	(30.7)
296	163.5	123.6	35.7	34.9	45.9	24.4	181.4	122.3	39.8
	(27.8)	(46.3)	(7.0)	(9.9)	(13.7)	(7.3)	(26.1)	(38.5)	(14.9)
302	159.9	85.8	20.1	30.1	42.6	18.2	115.7	113.4	34.8
	(30.1)	(19.1)	(4.1)	(13.5)	(22.5)	(6.6)	(33.7)	(23.2)	(11.8)
End of the ditch									
265	63.0	17.8	11.3	20.1	12.9	nd	50.9	nd	15.8
	(28.1)	(5.2)	(6.6)	(8.6)	(6.0)		(19.6)		(8.8)
270	48.1	nd	nd	13.2	nd	8.2	36.6	10.5	18
	(13.7)			(3.3)		(3.1)	(10.4)	(3.9)	(5.0)
274	41.0	nd	nd	nd	nd	nd	nd	nd	nd
	(7.0)								
288	142	34.6	nd	48.3	11.5	10.6	99.1	26.7	22.
	(50.3)	(8.9)		(19.6)	(4.1)	(2.9)	(27.4)	(4.5)	(7.2)
296	129.1	nd	nd	36.4	8.4	nd	99.9	nd	nd
	(34.3)			(10.3)	(1.7)		(15.8)		
302	111.5	nd	nd	22.8	nd	nd	91.9	nd	nd
	(24.0)			(7.0)			(17.8)		

* Average value ** Standard deviation nd Non detected(< 10 µg/kg).

below the detection level. Therefore, no sample was collected after that day. Soil samples were also collected from the field plots on 215th day, a day before starting the experiment, to measure the herbicide residues remained in the soil system from the last year (1994). Atrazine, metribuzin, and metolachlor concentrations in the soil were found to be respectively 25.7, 2.2, and 56.3 µg/kg for the surface layer (0.0 to 0.2 m), 23.2, 3.2, and 4.7 µg/L for the subsurface layer (0.2 to 0.4 m), and 16.5, 6.3, and 22.3 µg/L for the bottom layer (0.4 to 0.6 m). Polluted water was initially pumped to the ditches on 216th day of 1995 and drainflow appeared at the same day. Appearance of drainflow in the first day of water application was because the soil was wet due to rainfall occurred two days before starting the experiment. Also, the three herbicides were detected in the drain outflow at the same day of water application. The reason could be due to pesticide residues remained in the soil profile from the last year (1994). The cumulative volume of the applied water and drainflow during the summer and fall of 1995 is given in Figure 4.7. This figure indicates that about 25% of the applied water passed into the drains and the remaining 75% was lost to the atmosphere via evapotranspiration. These results are similar to those obtained in 1994.

Water samples were collected from the drain outflow on the daily basis and during the experiment. Herbicide levels in the drainage water samples, measured on GC, are given in Figures 4.8 through 4.10. These figures show daily concentration levels of atrazine, metribuzin, and metolachlor, respectively.

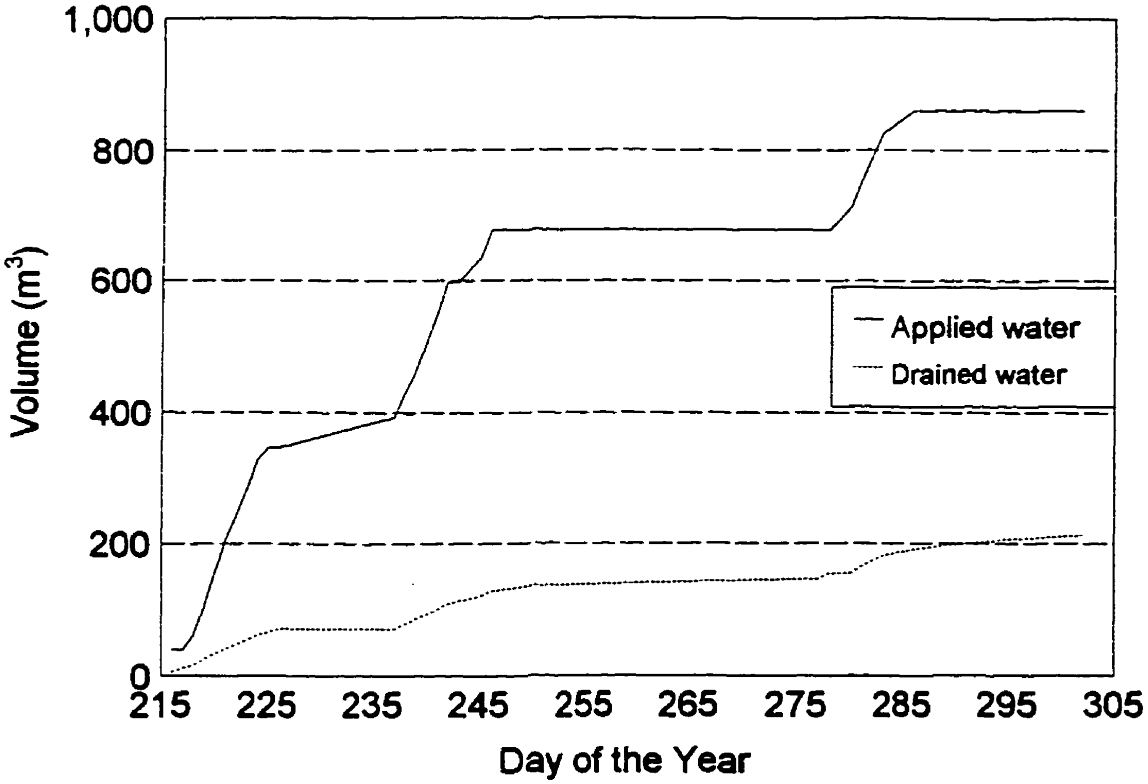

Figure 4.7: Cumulative volume of applied water and drainflow in 1995.

During the experiment period in 1995, typical concentration ranges for the herbicides were: atrazine 2 to 16 μg/L; metribuzin 2 to 17 μg/L; and metolachlor 0 to 15 μg/L. These ranges were lower than those obtained in 1994 due to higher organic matter (vegetation) contents inside the ditches in 1995. Using the T-test, it was found that the average concentration levels in the drainage waters reduced significantly (1%), from 100 μg/L to about 10 μg/L. Figures 4.8 to 4.10 show that the concentration levels in drainage waters tend to increase with continuous water applications during each recycling period. This result was confirmed by

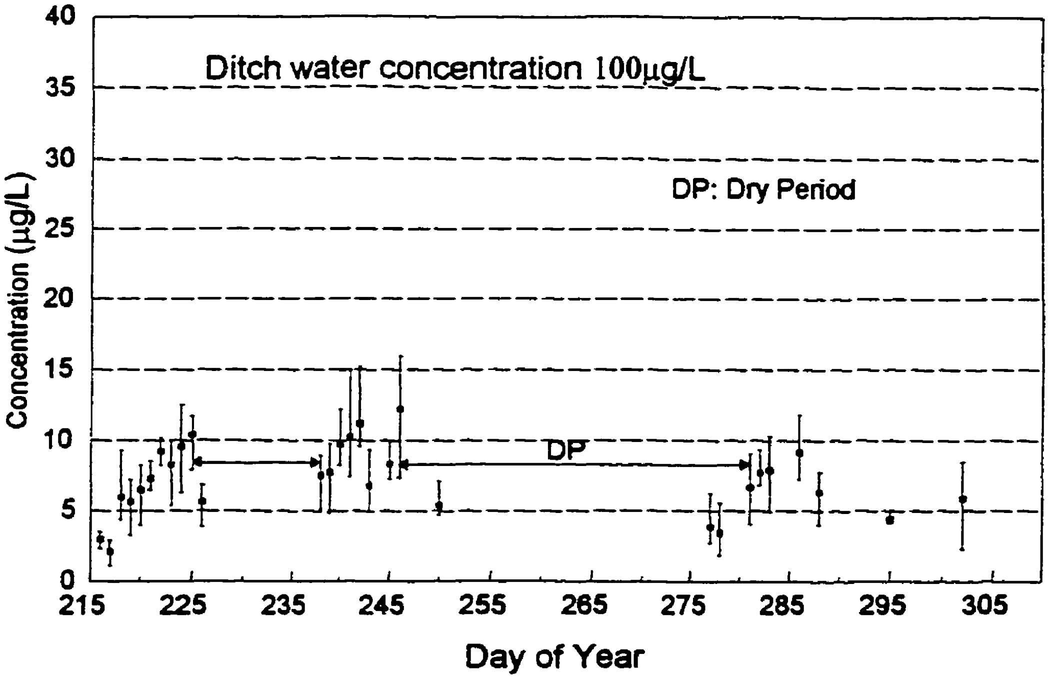

Figure 4.8: Atrazine concentration in applied water and drainflow (1995).

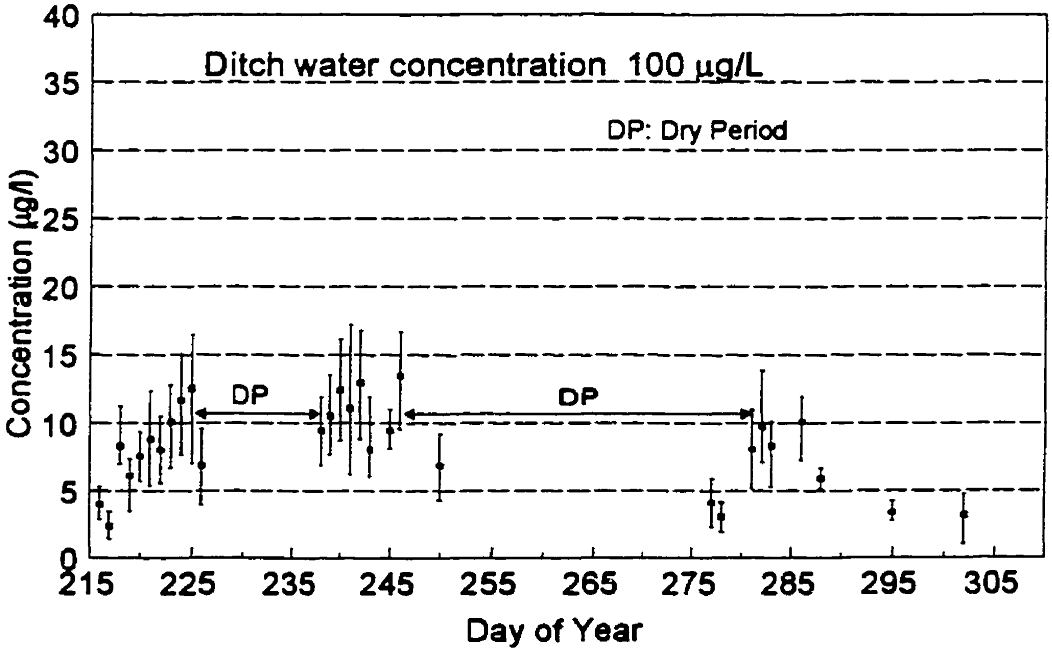

Figure 4.9: Metribuzin concentration in applied water and drainflow (1995).

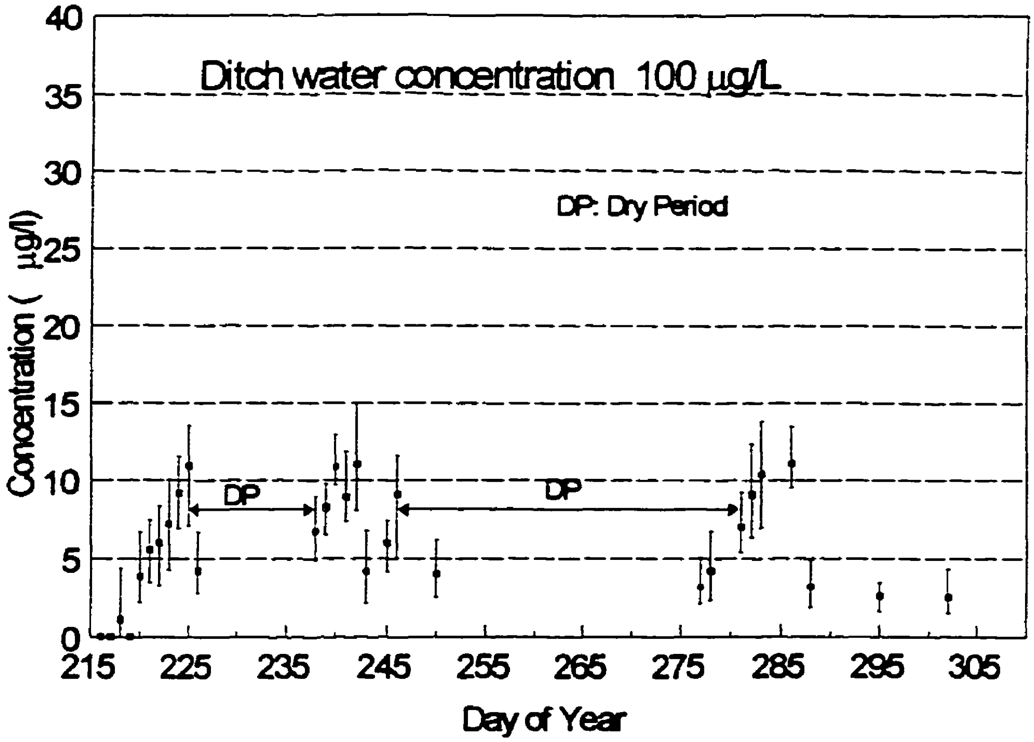

Figure 4.10: Metolachlor concentration in applied water and drainflow (1995).

Repeated-measures analysis of variance, which was used to determine the correlations among the dependent variables (concentration levels of herbicides in drainage water over time). It was found that the concentration levels changed over the experiment period. This could be the result of continuous application of water, containing herbicides, in ditches during each recycling period and biodegradation of herbicides in the soil during the dry periods. It is postulated that the soil has a potential capacity for chemical adsorption. This potential is high at the beginning of each wet period and tends to decrease during the application of polluted water. This potential also tends to increase during the dry period due to degradation processes in the soil. These trends are generally indicated in figures 4.8 to 4.10. Thus, it is concluded that the system can be self-sustainable over the long term, utilizing a water application strategy (i.e., allowing a dry period between polluted water applications). It may be noted that the 10-day dry period was chosen arbitrary. The dry period would vary according to rainfall.

The cumulative masses of herbicides in applied and drainflow water and coming during the experiment period are illustrated in Figure 4.11. This figure shows that the concentrations in the drainflow samples correspond with the rank-order of soil sorption coefficients (Table 4.2), instead of their water solubility (the results obtained in 1994). The reason could be due to higher organic matter (vegetation cover) content inside the ditches and lower preferential flow to the drains in 1995, compared with those in 1994. The less variability in the data also indicates the low preferential flow to the drains in 1995. Metribuzin, with low soil sorption coefficient, was sorbed the least and metolachlor, with high soil sorption coefficient, was sorbed the most.

The total amount of atrazine, metolachlor, and metribuzin trapped by the soil during the experiment period was estimated to be about 98.4, 98.6, and 98.1%, respectively, of the total applied herbicides (Table 4.5). These values are higher than those obtained in 1994 (98.1, 97.6, and 97%) due to higher volume of application of polluted water. Therefore, it can be concluded that the trapping efficiency corresponds to the total volume of water, and also to the total mass of pollutants applied into the system.

Table 4.5. Total amount of atrazine, metolachlor and metribuzin applied to the ditches and lost through subsurface drainflow in 1995.

Herbicides	Atrazine	Metolachlor	Metribuzin
Applied (g)	86.0	86.0	86.0
Leached (% of applied)	1.6	1.4	1.9
Trapped (% of applied)	98.4	98.6	98.1

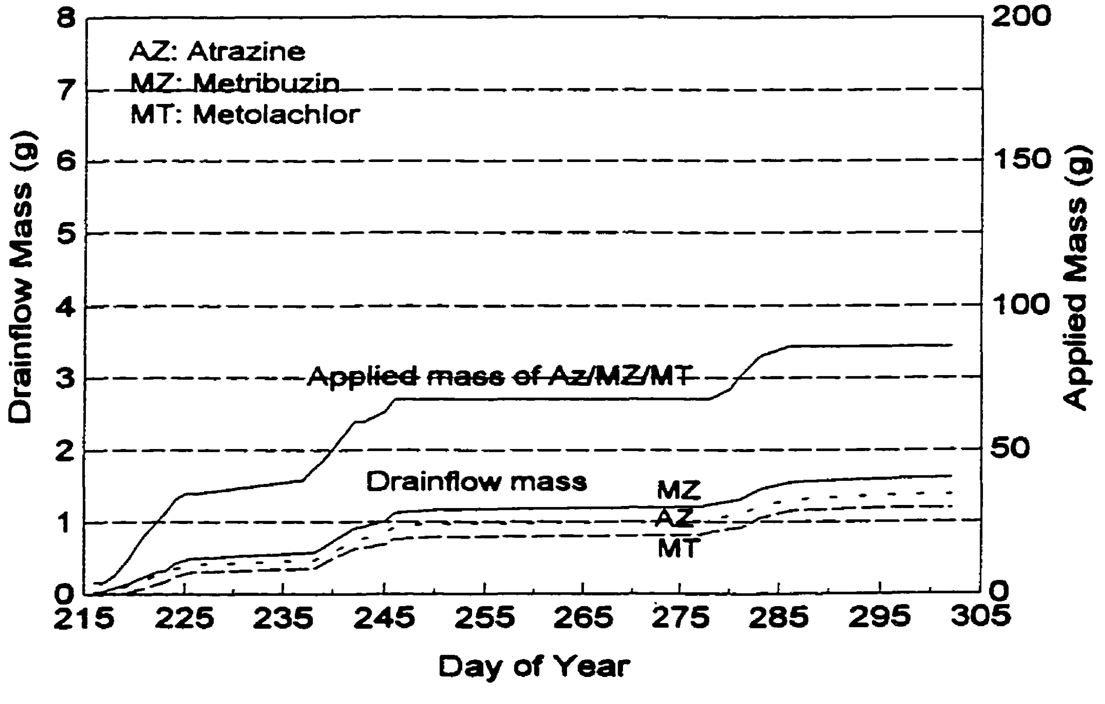

Figure 4.11: Cumulative masses of herbicides in applied water and drainflow during the experiment period in 1995.

4.4.2.2 Herbicide Levels in the Soil in 1995

Collecting soil samples from the field plots was started the day (215th of Julian day) before the experiment commenced in the summer of 1995 and continued over the experiment time during the dry periods. As already indicated, soil samples were taken from different depths (0 to 0.2 m, 0.2 to 0.4 m, and 0.4 to 0.6 m) per test plot, and this data is presented in Table 4.6. Both the average values and the corresponding standard deviations are provided. Comparing the last day-data of table 4.4 with the first day-data of table 4.6, indicate that the herbicide residues remained in the soil system from the last year (1994). However, degradation was occurred during the time in between the two years of experiment. Atrazine, metribuzin, and metolachlor residues in the soil surface (0 to 0.2 m), were reduced from an average of 150.6 to 25.7 µg/kg, 29.5 to 2.2 µg/kg, and 121.1 to 56.2 µg/kg, respectively. Degradation rates in the upper layer of soil were found to be greater than those in the lower layers, due to greater microbial activities. These two days-data also indicate that the concentrations of metribuzin in the soil layers are lower than those of atrazine and metolachlor. The reason could be due to lower persistence of metribuzin in the soil, compared to those of atrazine and metolachlor.

Table 4.6 shows that most of the herbicides remained in the upper 0.0 to 0.2 m layer of the soil, with little leaching to lower layers. This table also shows that the concentrations of metribuzin in the soil layers are lower than those of atrazine and metolachlor. The explanation could relate to the higher water solubility, lower soil sorption coefficient, and lower persistence of metribuzin. These results agree well with those obtained in 1994. Although the soil filter trapped over 98% of the three herbicides, there were wide differences in the soil herbicide residues (table 4.6). This could be due to non-uniform distribution of the chemical into ditches, differences in herbicide properties such as water solubility, soil sorption coefficient, persistence, and vapor pressure. Table 4.6 indicates that the concentration of herbicides in the soil tends to decrease over time during the dry periods (from 225 to 236 days, from 246 to 259 days, and 290 to 305 days). This reduction may be explained, for the most part, by microbial and chemical degradation, and to a lesser extent, by volatilization and plant uptake. Therefore, the results obtained from this study indicate that the system should be self-sustainable in the long term.

Data shown in Table 4.6 indicate that the amount of herbicides retained in the soil differs for the atrazine, metribuzin, and metolachlor. Metribuzin concentration levels in the soil show the least values, however, metolachlor concentration levels show the maximum values. Atrazine concentration levels in the soil are in-between metribuzin and metolachlor concentrations. Therefore, it can be concluded that the amount of herbicides retained in a soil differs when a different herbicide contaminant solution is used and when more than one species is present in the leachate. When more than one species of herbicides is introduced as

Table 4.6 Average and standard deviation of herbicides levels in the soil (1995).

	Atrazine (µg/kg)			Metribuzin (µg/kg)			Metolachlor (µg/kg)		
Day of Year	0.0-0.2 (m)	0.2-0.4 (m)	0.4-0.6 (m)	0.0-0.2 (m)	0.2-0.4 (m)	0.4-0.6 (m)	0.0-0.2 (m)	0.2-0.4 (m)	0.4-0.6 (m)
215	25.7*	23.2	16.5	2.2	3.2	6.3	56.2	4.7	22.3
	(5.1)**	(13.6)	(9.3)	(2.3)	(1.9)	(6.8)	(56.3)	(8.1)	(38.6)
225	87.5	42.2	38.7	16.6	23.3	20.3	158.3	33.2	32.1
	(22.6)	(27)	(15.8)	(1.6)	(12.8)	(9.2)	(100.1)	(28.7)	(32)
230	67.8	34.8	21.7	11.5	17.6	6.7	136.3	7.4	nd
	(18.2)	(9.3)	(6.8)	(4.5)	(2.5)	(2.2)	(108.9)	(12.8)	
236	60.2	27.6	18.8	16.5	10.6	8.5	120.6	6.2	nd
	(18.6)	(9.3)	(8.2)	(7.8)	(6.5)	(1.8)	(82.6)	(10.7)	
246	138.8	74.9	51.8	36.8	12.4	22.1	219.4	92.2	60.9
	(25.8)	(27.8)	(19.2)	(7.7)	(2.7)	(2.2)	(22.4)	(27.2)	(48)
251	125.8	56.9	27.1	26.9	13.7	14	169.8	48.5	nd
	(25.1)	(16.8)	(3.8)	(6.6)	(4.7)	(7)	(10.7)	(14.5)	
259	112.8	43.4	21.8	17.5	9.8	7.2	121.1	23.5	13.1
	(28.8)	(18.8)	(15.3)	(6.4)	(3.6)	(1.7)	(5.8)	(33.3)	(18.5)
290	131	38.3	20.5	28.4	12.4	12.3	142.1	38.3	19.2
	(4.7)	(24.5)	(6.9)	(1.8)	(8.9)	(4.2)	(18.4)	(27.7)	(27.1)
298	110.4	33.8	17.4	20.5	8.8	10.2	111.2	21.9	20.5
	(26.7)	(22.6)	(9.8)	(4.5)	(3.2)	(6.1)	(30.2)	(12.4)	(8.8)
305	79.9	24.1	10.5	10.9	6.1	11.4	86.5	16.7	15.9
	(14.6)	(7.6)	(6.2)	(3.3)	(2.1)	(4.2)	(22.2)	(9.7)	(12.8)

* Average value
nd Nondetected (< 10 µg/kg)
** Standard deviation

a contaminant leachate into the soil, competition between herbicide molecules for adsorption sites occurs. Therefore, it is expected that the system performance improve when only one specie present in the leachate. Typically, one kind of herbicide exists in the drainflow water of a particular field. Therefore, the concentration of herbicide in the drainflow may reduce to a greater extent, compared with the one presented with other species.

4.4.3 Analysis of Nitrate Data obtained in 1994 and 1995

As aforementioned, the lake water was initially tested for the nitrate residues. Nitrate-N concentration level was found to be high and exceeded the standard level for drinking water (10 mg/L). The total volume of applied water in 1994 and 1995 were 1378 and 860 m^3, respectively. Lower application of water in 1995 was due to mechanical problems with the pump. Figures 4.12 and 4.14 show the concentration levels of nitrate in daily applied and drained water in 1994 and 1995, respectively. The standard deviations of nitrate concentrations in drained water in 1994 and 1995 are presented in Tables 4.7 and 4.8, respectively. The average concentration levels of nitrate in the applied water (lake water) were found to be 30 and 21 mg/L in 1994 and 1995, respectively. The lower concentration levels in 1995 could be due to higher rainfall events during the experiment period.

Nitrate residues in the applied water reduced after passage through the soil system. The average concentration levels of nitrate in the drainflow were about 17 and 13 mg/L for 1994 and 1995, respectively. This reduction could be attributed to many factors: greater denitrification, plant uptake, less transportation to a deeper depth and volatilization. Herbicides can enhance denitrification when they are applied at the rate of 50 μg/g of soil or more (Mills, 1984; and McElhannon et al., 1984). Polluted water applied in this study was a mixture of three herbicides (atrazine, metolachlor, and metribuzin) with the lake water.

Repeated-Measures Analysis of Variance was performed to test whether the concentration level of nitrate in drainage water changed during the application of polluted water. It was found that the nitrate levels in the drainage waters did not change significantly over the time of experiment. As expected, unlike herbicide adsorption, the soil tendency for nitrate adsorption was found to be low. The cumulative masses of nitrate in the applied and drainflow water in 1994 and 1995 are illustrated in Figures 4.13 and 4.15, respectively. These figures indicate that of the total applied nitrate in 1994 and 1995, 85 and 90% respectively disappeared in the soil and grass filters. The higher value of disappeared-nitrate in 1995 (90%) could be due to higher vegetation cover inside the ditches and lower amount of application of polluted water in 1995, compared to that in 1994. Williford and Cardon (1971) also demonstrated that significant amounts of nitrate were removed from water flowing through a field of water grass. They found that of the total nitrate loading to the site 73% was trapped by the system. They reported that about

50-60% of the nitrogen removal occurred through bacterial denitrification and the reminder was by way of algal uptake. The disappeared-nitrate in the field study (85%) was found to be greater than the one in the lysimeters study (48%). The reason may be due to lower rate of water application (about 10mm/day) in the field than the rate of application (60 mm/day) in the lysimeters and also could be due to more intensive vegetation cover in the field.

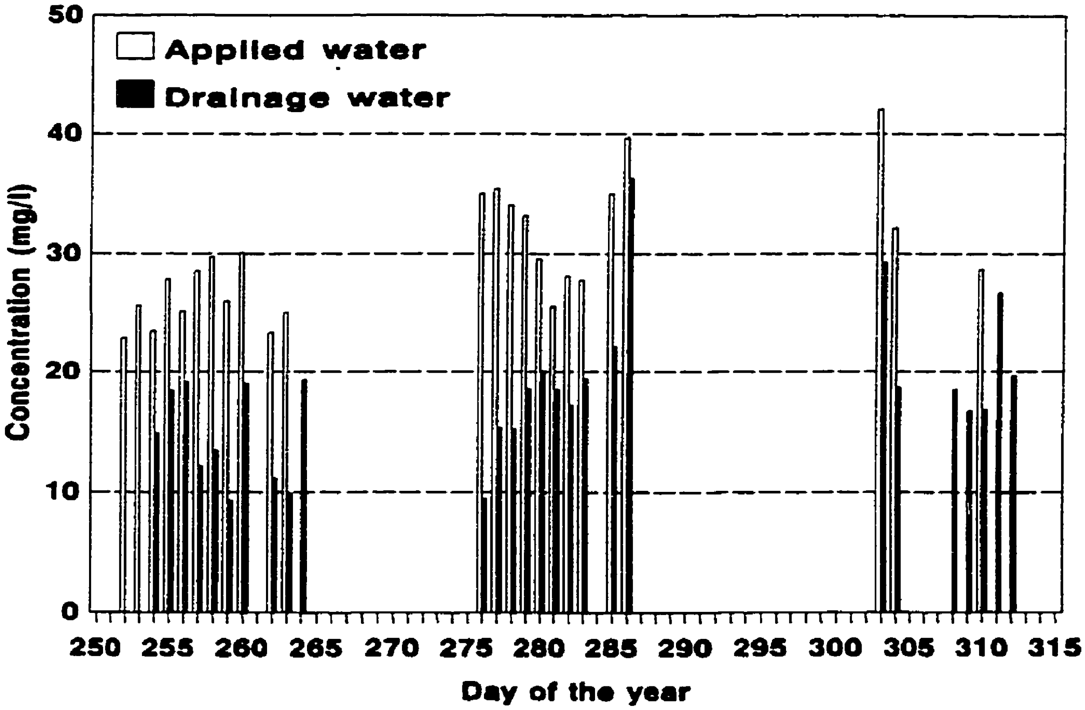

Figure 4.12: Nitrate-N concentrations in applied and drainflow water in 1994.

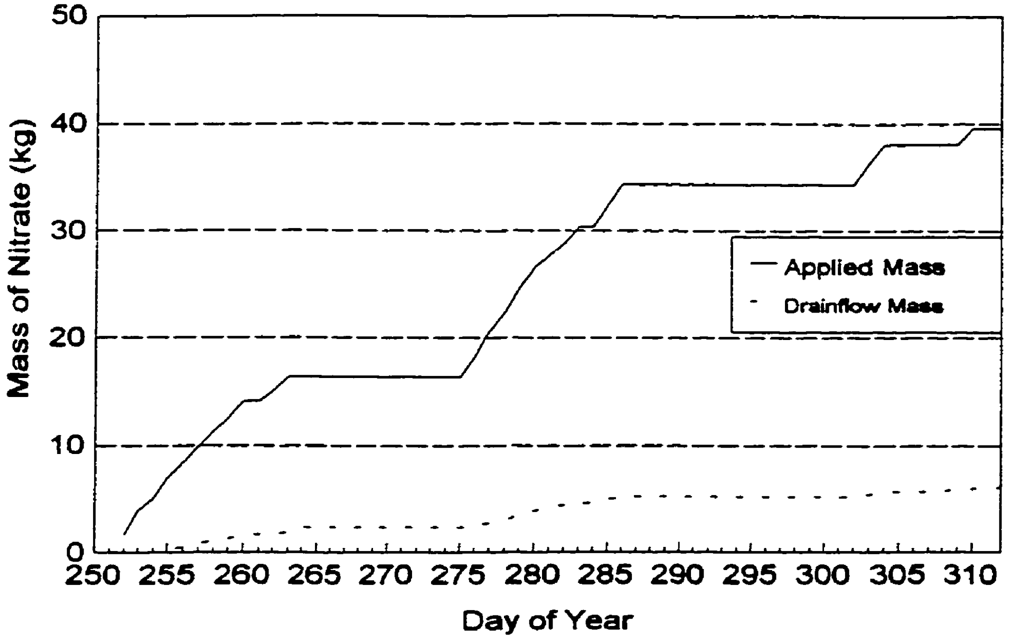

Figure 4.13: Cumulative masses on nitrate in applied and drainflow waters in 1994.

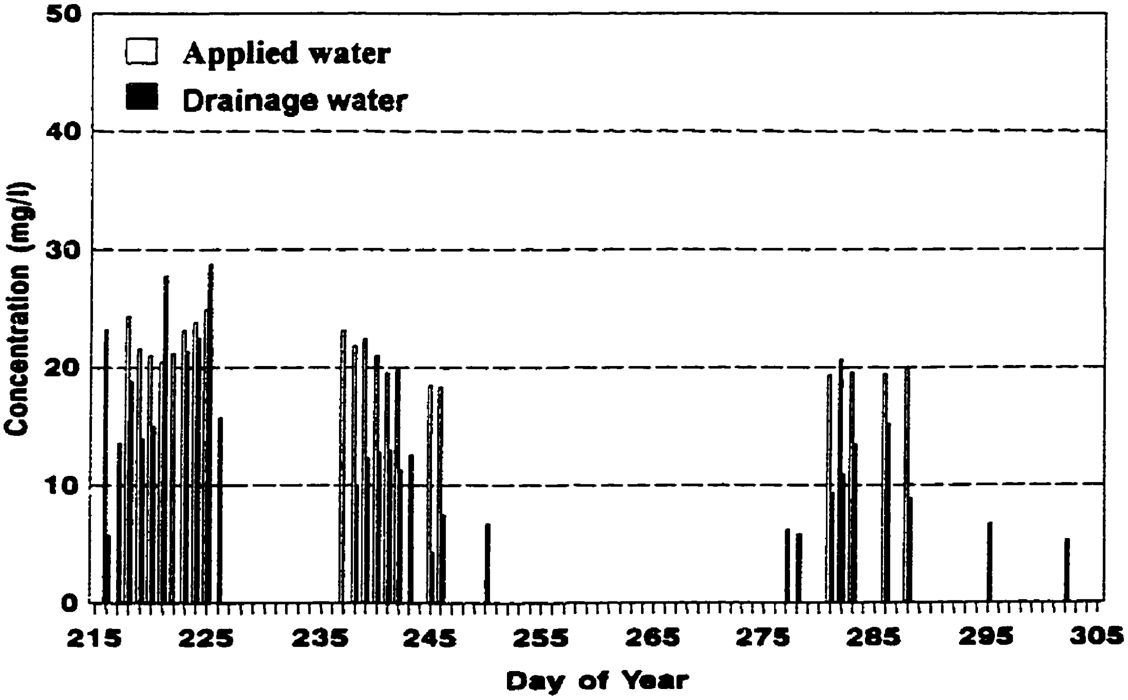

Figure 4.14: Nitrate-N concentrations in applied and drainflow water in 1995.

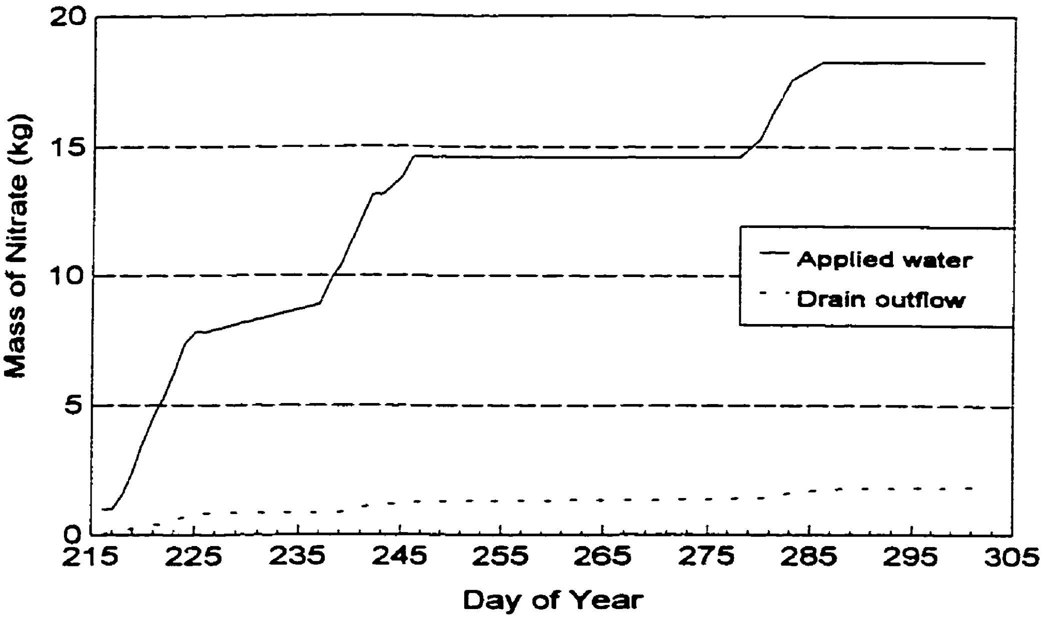

Figure 4.15: Cumulative masses of nitrate in applied and drainflow water in 1995.

Table 4.7: Average and standard deviation of nitrate-N concentrations in the drainage water (1994).

Day of year	Average	Standard deviation	Day of year	Average	Standard deviation
254	14.89	3.24	280	20.04	2.35
255	18.36	5.24	281	18.51	7.21
256	19.12	4.25	282	17.15	4.68
257	12.18	1.99	283	19.43	7.52
258	13.46	2.85	285	22.14	-
259	9.32	5.19	286	36.26	10.21
260	19	1.20	303	29.25	7.25
262	11.13	3.45	304	18.66	6.58
263	9.87	2.89	308	18.49	-
264	19.32	-	309	16.72	2.21
276	9.45	4.26	310	16.75	1.74
277	15.28	2.36	311	18.68	4.65
278	15.21	3.99	312	19.67	8.21
279	18.55	4.22			

Table 4.8: Average and standard deviation of nitrate-N concentrations in the drainage water (1995).

Day of year	Average	Standard deviation
216	5.727	1.13
217	13.59	0.29
218	18.86	4.52
219	13.89	1.72
220	14.97	0.62
221	27.82	1.72
223	21.33	8.31
224	22.48	8.17
225	28.75	-
226	15.71	2.46
238	10.02	-
239	12.24	-
240	12.75	3.72
241	12.91	4.26
242	11.27	2.86
243	12.52	2.10
245	4.34	1.99
246	7.49	4.05
250	6.74	1.97
277	6.25	1.40
278	5.85	2.50
281	9.36	6.43
282	10.92	5.49
283	13.42	8.77
286	15.13	9.70
288	8.86	1.50
295	6.73	1.89
302	5.34	1.56

4.5 Summary and Conclusions

This study was undertaken to investigate a novel method of reducing non-point source pollution from agricultural farms. This was initiated by using soil as a biological filter, for removal of pesticide residues. Measurements were made on four test plots in the field.

The results of this study are very encouraging. A significant reduction (1%) in herbicide levels was measured in the field study. In 1994 and 1995, concentrations of atrazine, metolachlor and metribuzin were lowered from 100 μg/L to less than 10 μg/L in most cases. This occurred when the ditches were flooded continuously for 10 days (a worst case scenario for our local conditions).

Bio-degradation of herbicides was also noted between water applications; thus it appears that the system could be self-sustainable in the long term. It was found that of the total applied herbicide, more than 97% trapped by the soil filter. The concentration of herbicides in drainage waters was found to correspond with the rank-order of soil sorption coefficient and water solubility of the herbicides. Metribuzin, with the high water solubility and low soil sorption coefficient, was the herbicide found in the highest concentrations in drainflow water.

Nitrate concentration levels were also reduced from an average of 30 mg/L to 17 mg/L. It was found that of the total applied nitrate, more than 85% disappeared through the soil system. Generally, the results obtained from the nitrate analysis were similar to that found for the herbicide residues in water samples analysis. However, the trapping ratio for the nitrate was less than that obtained for the herbicides.

Trapping efficiency of the system was found to correspond to the total volume of applied water and total masses of applied pollutant. Trapping ratios for the herbicide and nitrate respectively were more than 97 and 85%. It was found that the results to-date reinforce the contention that dual-passage of drainage water could dramatically reduce environmental pollution from agricultural farms; and, at the same time, safeguard freshwater aquatic habitats.

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PREFACE TO CHAPTER 5

In the previous chapters (3 and 4), it was shown that the soil and grass strip can be used as a biological filter for reducing pesticides from agricultural drainage waters. Having a certain amount of polluted water, the concentrations of pesticide in treated water depends on the size of filtration area.

Therefore, the last objective of this research was to determine the size of filtration area needed to reduce the concentrations of the three herbicides (atrazine, metolachlor, and metribuzin used in this study) to levels safe for human and aquatic life. While field-scale experiments such as the one described in chapter 4 can be used to determine the size of filtration area, they are time consuming and very expensive. Computer simulations offer a cheaper and faster alternative to physical experiments. In Chapter 5, the DRAINMOD and PRZM2 models were used to determine the size of filtration area for removing pesticide residues from agricultural drainage waters.

This paper has been submitted to Journal of Irrigation and Drainage Engineering for publication.

CHAPTER 5

Application of Mathematical Modeling to Determine the Size of On-Site Grass Filters for Reducing Pesticide Pollution from Farms

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ABSTRACT

This paper presents a mathematical approach for estimating the size of a grass filter area for removing pesticide residues from agricultural drainage waters. The method utilizes a water table management model, DRAINMOD, for simulating drainage waters from agricultural land and then a solute transport model, PRZM2, for simulating pesticide concentrations in drain effluent coming from grass filters.

DRAINMOD was used to estimate daily drain outflows that occurred in a 100 ha subsurface drained field in the Ottawa-St. Lawrence lowlands by running the model for a 1-in-20 year annual rainfall period. The simulated drain outflows were assumed to contain 50 µg/L of atrazine, metolachlor, and metribuzin residues, and simulations were carried out with PRZM2 to determine the required size of grass filter area to make drainage waters safer for aquatic life and marine habitat. It was found that no more than 6% of the farm area would be needed to bring down the concentrations in drainage waters from 50 µg/L to less than 1 µg/L for the three herbicides.

5.1 INTRODUCTION

The fate of agricultural chemicals applied to cultivated fields with subsurface drains is an environmental concern with potential effects on the health of all living beings. Many pesticide residues have been detected in streams, tile drain effluent and ground water with concentrations far above the standard level for drinking water (McRae, 1989; Gilliam and Skaggs, 1985; Deal et al., 1986; Bengston and Southwick, 1989; Muir and Baker, 1976; Frank and Sirons, 1979; Klaine et al., 1988; Bastien, 1991). Flury (1996) has done a comprehensive review concerning pesticide contamination in runoff waters, subsurface drainage waters, and ground waters. Moreover, the need to address this problem cannot be understated since the maximum allowable levels for freshwater aquatic life and marine habitat are usually much less than that for human consumption.

In the last few decades, soil scientists and engineers have developed technologies to reduce pollution from contaminated waters. For example, sand filtration has been identified as an effective method for purification of drinking water (Steel and McGhee, 1979; Clark et al., 1971; Huisman, 1978). Grass filtration (grass border strips) is also used in prevention of sediment production, in reduction of sediment yields from agricultural watersheds, in food industry wastewater treatment, in feedlot runoff treatment, and in municipal sewage effluent. Filter strips have also been evaluated for their ability to control herbicide runoff losses (Mickelson and Baker, 1993).

The combination of sand and grass filters was found to be effective in reducing herbicides from agricultural runoff and drainage water (Liaghat et al., 1996; Liaghat and Prasher, 1996) and in removing sediment from river water (Nsengiyumva, 1996). In such a system, polluted waters, drained from a large agricultural drainage area, are collected by a system of drain pipes, ditches and canals, and then pumped on to a smaller filtration area, underlain by a subsurface drainage system, for treatment. The water infiltrates through the grass filter into the soil profile and the treated water, coming out of tile drains from the filtration area, can be discharged to streams or other receiving waters. The efficiency of combined systems for pesticide removal depends on meteorological data, soil characteristics, chemical properties, and mainly size ratio of filter area to farm area.

Given that the pollutant removal effectiveness of combined system depends on many factors, methods are needed to determine the size of filtration area and to determine its performance in treating agricultural drainage water. Due to the costs and time involved in a field-scale experiment, alternative methods are needed. A cheaper and faster alternative is the use of computer simulation models.

5.2 OBJECTIVES

In this study, a computer modelling approach for determining the size of filtration area for removing pesticide residues from agricultural drainage waters was investigated. Determination of the optimum size of filtration area was not possible in the field or lysimeter study. Therefore, the objectives of this paper were to:

1. Determine the optimum size of filtration area for removing pesticide residues from agricultural polluted waters in Eastern Canada, under a worst case scenario (a one-in-20 year annual rainfall),
2. Determine the optimum size of filtration area for different concentration levels of polluted water (10, 20, 30, 40, and 50 μg/L),
3. Estimate the preliminary cost associated with the filtration area needed to treat agricultural polluted waters.

The method utilizes a watertable management model, DRAINMOD, for simulating drainage waters from agricultural land and a solute transport model, PRZM2, for simulating pesticide residues in treated waters.

5.3 MODEL DESCRIPTION

5.3.1 DRAINMOD Simulation Model

DRAINMOD is a well-known field scale water management model, developed by Skaggs (1978). Extensive field testing of DRAINMOD has been done in many areas of Canada and US (Skaggs, 1982; Susanto et al., 1987; Mackenzie et al., 1988; Mackenzie and Prasher, 1989; Shukla et al., 1994). DRAINMOD was developed for shallow water table soils and is based on a water balance in the soil profile at the midpoint between two drains. The model uses climatological records to simulate the performance of drainage and water table control systems in a field bordered by parallel ditches or subsurface drains.

Input data to DRAINMOD includes soil properties, crop parameters, drainage system, site parameters, and weather data. Soil property inputs include saturated hydraulic conductivity for each layer, relationships between drainage volume and water table depth, and information concerning upward flux from the water table. The effective root zone depth as a function of time is also an input.

The model uses approximate methods to quantify the hydrologic components: infiltration, surface runoff, subsurface drainage, subirrigation, actual evapotranspiration (ET), and water table position over a long period of climatological data. For example, equations developed by Hooghoudt (Luthin, 1978), Kirkham (1957), and Ernst (1975) are used to calculate drainage and subirrigation rates, and infiltration rates are predicted by the Green and Ampt (1911) equation. Complex numerical methods are avoided by assuming a drain-to-equilibrium situation.

Hourly precipitation and daily maximum and minimum temperatures for estimating daily PET are read from weather records and the water balance is calculated on an hour-by-hour basis. Another option is to read in daily PET directly. The water balance for a time increment of t is given as:

$$\Delta V_a = D + ET + DS - F \qquad (1)$$

where ΔV_a = change in the air volume (mm), D = lateral drainage from, or subirrigation into, the section (mm),

ET = evapotranspiration (mm),

DS = deep seepage (mm), and

F = infiltration entering the section (mm).

In general, the basic time increment used for simulation in the model is one hour. However, it could be two hours or one day depending on drainage and ET rates under no rainfall conditions. During rainfall events, depth of infiltration and surface runoff are predicted in three-minute increments. Number of trafficable days, sum of excess water table rises above a 300 mm depth (SEW_{30}), and planting date are estimated and stress-day-index methods are used to calculate yield response to excessive and deficient soil water conditions. Output of model predictions is available on a daily, monthly, or annual basis. The performance of a given system design or management alternative can be simulated for a long period of climatological record (i.e. 20 to 40 years) to consider the effects of year-to-year and seasonal variabilities.

DRAINMOD is a well-documented user-friendly computer software package. Sufficient instructions are given to the user during execution of the program. User inputs are checked throughout the program and a chance to re-enter any faulty entry is provided. It runs on an IBM PC or compatible with at least 640 KB RAM. A math co-processor is strongly recommended. For further details, the reader is referred to Skaggs (1978, 1980, 1989a, 1989b).

5.3.2 PRZM2 Simulation Model

PRZM2 model provides state-of-the-art deterministic simulation for movement of solutes in porous media for steady state, transient, and multil-ayered conditions. It simulates the fate of pesticides in crop root and vadose zones taking into account the effects of agricultural management practices. PRZM2 links two subordinate models: PRZM and VADOFT, in order to predict pesticide transport and transformation down through the crop root and unsaturated zones. For the movement of water, these two modules are based on the combination of Darcy's law and the continuity equation that yields the Richards equation given as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}[K(\theta)\frac{\partial h}{\partial z}] \quad \text{......} \quad (2)$$

where θ = Soil water content (m^3/m^3)

K = Hydraulic conductivity (m/day), and

h = Hydraulic head (m).

In order to perform probability-based exposure assessments, PRZM2 is also equipped with a Monte Carlo (MCARLO) pre- and post-processor. These three modules are written in ANSI FORTRAN 77.

PRZM (Pesticide Root Zone Model) is a well-known continuous simulation model, which was developed at the EPA Laboratory in Athens, Georgia. It is a one-dimensional finite-difference model, which accounts for pesticide fate in the crop root zone. PRZM is able to simulate multiple zones, transport and transform the parent compound and as many as two daughter species within and immediately below the plant root zone.

The model has two major components: hydrology and chemical transport. The hydrology 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 based on an empirical formula. Evapotranspiration is divided among evaporation from crop interception, evaporation from soil, and transpiration by the crop. Water movement is simulated using generalized soil parameters, including field capacity, wilting point, and saturated water content.

The chemical transport component can simulate pesticide application on soil or on plant foliage as well as biodegradation in the root zone. Dissolved, adsorbed, and vapor-phase concentrations in the soil are estimated by simultaneously considering the processes of pesticide uptake by plants, surface runoff, erosion, decay, leaching, foliar wash-off, advection, dispersion, and retardation.

The model has been tested with field data in New York, Wisconsin, Florida, and Georgia and has been used in exposure assessment and other applications (Carsel et al., 1985; Carsel et al., 1986; Carsel et al., 1988; Smith et al., 1989; Banton and Villeneuve, 1989; Jones et al., 1983). The test results demonstrate that PRZM is a useful tool for evaluating groundwater quality. Smith et al. (1991) tested the performance of PRZM with data obtained from soil columns in Quebec, Canada. They reported that the PRZM required calibration due to simplistic linear adsorption equations and lack of macropore flow subroutine.

PRZM2 incorporates several additional features to those simulated in the original PRZM code; especially soil temperature simulation, volatilization and vapor phase transport in soil, irrigation simulation, microbial transformation, and a method of characteristics (MOC) algorithm to eliminate numerical dispersion.

VADOFT is a one-dimensional, finite element code that solves Richard's equation for flow in the unsaturated zone. VADOFT simulates the movement of pesticides within and below the plant root zone and assesses subsequent groundwater contamination. VADOFT can also simulate the fate of two parent and two daughter products.

VADOFT code contains both a flow model (solving Richard’s equation) and a solute transport model (following Fick's law). These models simulate single-phase moisture and solute transport in unconfined and variably saturated porous media. The user may make use of constitutive relationships between pressure, water content, and hydraulic conductivity to solve the flow equation. Transport processes include hydrodynamic dispersion, advection, linear equilibrium sorption, and first-order decay. The model simulates infiltration or recharge rate and solute mass flux entering the saturated zone.

The Monte Carlo processor (MCARLO) reads the standard deterministic input data sets for each model, then reads a Monte Carlo input file that specifies which parameters are to be varied. The processor is capable of preparing statistics of specified output variables, including mean and boundary values of output distribution. Application of the Monte Carlo simulation requires that at least one of the parameters be uncertain. This method involves the repeated generation of pseudo-random values of input variables that are used by the models. Therefore, the output can be represented as probability distribution.

PRZM2 predictions are made on a daily basis. Output can be summarized for a daily, monthly, or annual period. Daily time series values of various fluxes can be reported to sequential files during program execution for subsequent analysis.

5.4 MATERIALS AND METHODS

5.4.1 Field Site

In order to determine the size ratio of filtration area to farm area, calculations were carried out for a hypothetical 100 ha field located at the Macdonald Campus Farm. Local meteorological data and soil properties were used in these computations (Table 5.1). It was assumed that three herbicides, namely atrazine, metolachlor and metribuzin, would be applied on the farm. The herbicide characteristics are given in Table 5.2 (Liaghat et al., 1996).

Atrazine and metolachlor are normally applied to the corn-growing area of Quebec in pre- or post-emergence applications. Atrazine and metolachlor are applied at a rate of 2.4 and 2.7 kg/ha of active ingredient, respectively, and metribuzin is applied on potato farms in Quebec at a rate of 1 kg/ha of active ingredient.

Table 5.1: Soil Characteristics of the Field.

Soil Type	Sand (%)	Silt (%)	Bulk density (g/cm^3)	Organic matter (%)
Sandy Soil	91.2	4.2	1.4	3.5

Table 5.2: Chemical properties of atrazine, metolachlor, and metribuzin.

Property	Atrazine	Metolachlor	Metribuzin	Source
Solubility (mg/L)	33	530	1220	Wauchope et al., 1991
Partition Coef., K_d (ml/g)	2.7	5.0	1.6	measured
Soil Half Life day^{-1}	60	90	40	Wauchope et al., 1991
Henry's Constant	2.5E-7	3.8E-7	9.8E-8	PRZM Manual (Mullins et al., 1993)

5.4.2 Design Procedure

Figure 5.1 illustrates the design procedure for determination of filter size. This procedure contains two components; hydrology and test analysis. These components are explained in more detail in the following sections.

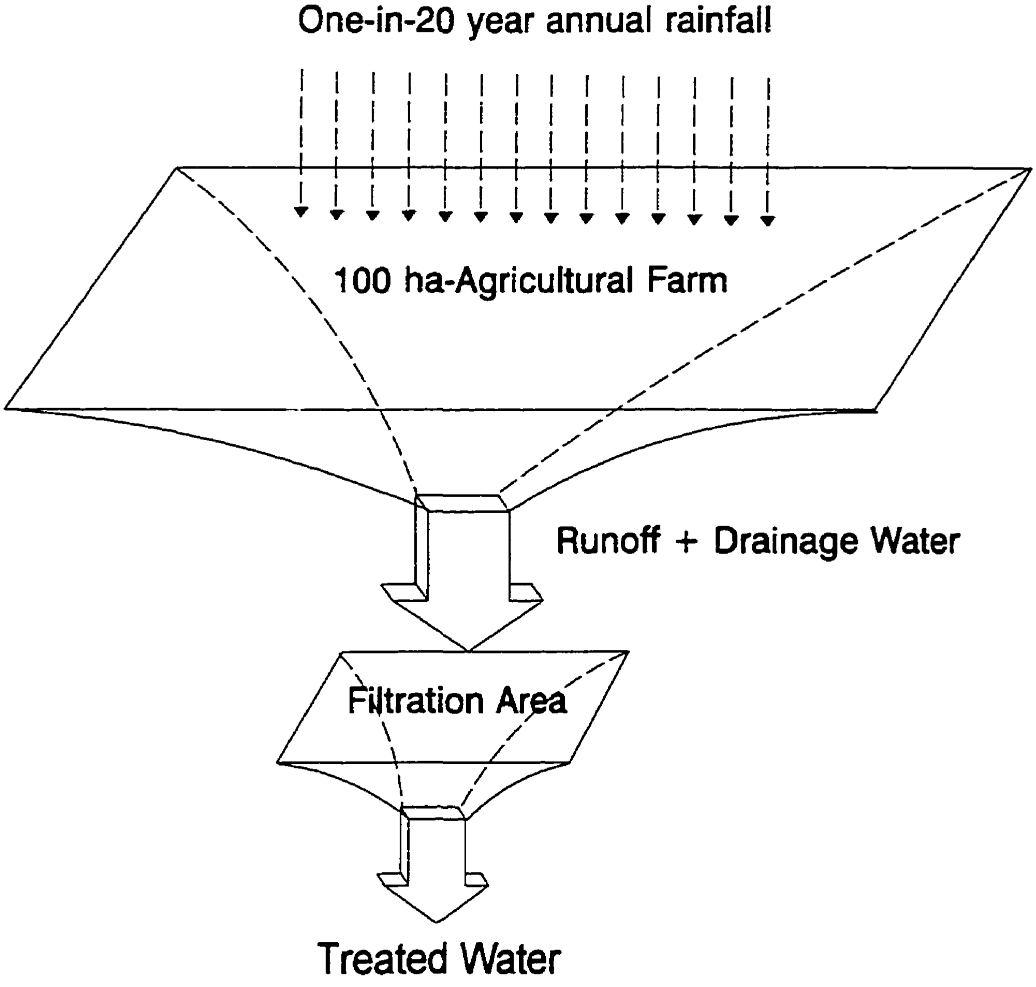

Figure 5.1: Design steps to determine the site of a filtration area.

5.4.2.1 Hydrology

Forty years of annual rainfall data (1955 to 1995), measured at the Dorval Airport weather station (Montreal, Quebec, Canada) were used to predict a 1-in-20 year annual rainfall. This station is about 10 km far from Macdonald Campus. The rainfall data was sorted in a descending order and a 1-in-20 year annual rainfall was chosen to use its daily rainfall and maximum and minimum temperatures for running the DRAINMOD model. The concept of 1-in-20 year annual rainfall was to consider the worst case scenario of rainfall that could occur on site. The 1-in-20 year annual rainfall is a conservative return period for any drainage project (Broughton, 1996). The year 1972, with an annual rainfall of 685 mm, was the one with a 20-year return period.

DRAINMOD was used to estimate daily drainage water (runoff and subsurface drainage water) that would occur in a 100 ha subsurface drained field by running the model for 1972 meteorological data. The drainage parameters required are drain spacing, drain depth, and drainage coefficient, which were 20 m, 1 m, and 10 mm/day, respectively. These are common values for southern Quebec agricultural lands.

Daily rainfall and maximum and minimum temperatures were entered into DRAINMOD as the weather input data. Hydraulic conductivity of the soil was measured in lysimeter study (Liaghat and Prasher, 1996) and was found to be 3 m/day. Soil moisture retention data was measured in the laboratory by Haines Funnel and pressure plate apparatuses, and the curve is shown in Figure 5.2.

5.4.2.2 Test analyses

The filtration area was tested for two purposes; a) infiltration test: the filtration site was tested for the maximum infiltration rate and its size was increased so as to pass all drainage water draining from a 100 ha agricultural farm, and b) trapping test:

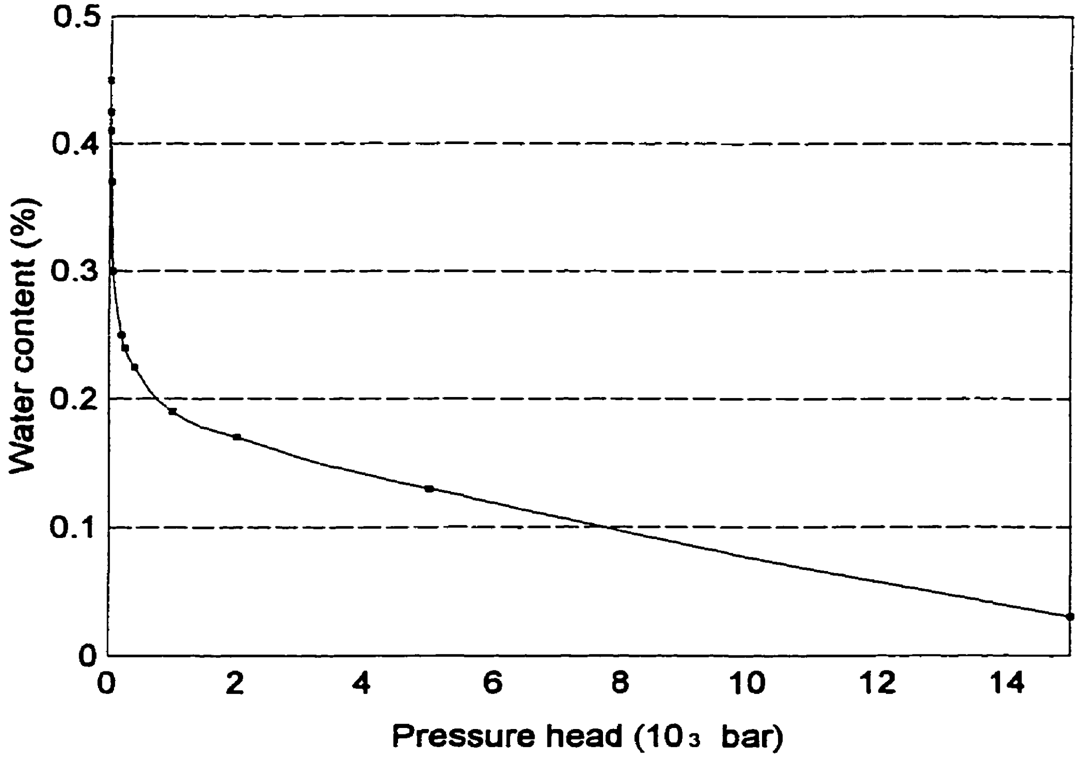

Figure 5.2: Soil moisture retention curve for the sandv soil of Macdonald Campus farm.

the filtration site was tested for trapping herbicides and its size was increased so as to trap most of the pesticides in drainage waters and bring the levels down to acceptable levels that would be safe for aquatic life and marine habitat.

5.4.2.2.1 Infiltration Test

In our case, the filtration area should be able to accommodate daily drainage waters from a 100 ha agricultural farm. Therefore, the pumping rate should be equal to or smaller than the infiltration rate of the filtration site in order to eliminate storage needs for drainage waters. The pumping rate depends on size of the filtration area and it can be expressed as follows:

$$R_p = R_d \times 100 \times A / a \qquad (3)$$

where R_p = pumping rate (mm/day),

R_d = drain outflow rate from agricultural land (mm/day), and

A = size of Agricultural farm (ha), and

a = size of filtration area (ha).

The investigation started with A = 1 ha and the DRAINMOD model was used to evaluate this test for every day of the year. Though, typical drain spacing used in Quebec for sandy soils is 20 m, a 10 m spacing was chosen for the filtration area to increase the infiltration rate and consequently reduce the filtration area. The drain depth for the filtration area was chosen to be 1 m. The drainage coefficient was calculated from equation 4 (Kirkham, 1949), which describes drain flow in homogeneous and saturated soils.

$$Q = \frac{2\pi\kappa(t + h - r)}{\ln(2h/r)} \qquad (4)$$

Where Q = flow into a unit length of drain per unit time (m^3/day), K = hydraulic conductivity (m/day),

t = depth of water ponded on the soil surface (m),

h = depth from soil surface to center of drain (m), and

r = radius to outside of drain (m).

Use of equation 4 assumes that drainage is limited by the rate of soil water movement to the lateral drains and not by the hydraulic capacity of the drain tubes or of the outlet. The maximum depth of water ponded on the filtration area was chosen to be 0.3 m. Therefore, the drainage coefficient was calculated to be 0.7 m/day. Usually, the size of the drain tubes is chosen to provide a design flow capacity, also called the drainage coefficient. The drainage coefficient (m/day) for a given slope and size of drain can be obtained from Manning's equation, expressed as follows:

$$Q = 86{,}400\, R^{2/3}\, S^{1/2}\, A_t \,/\, (A_d\, n) \quad \text{.......} \quad (5)$$

where n = Manning's coefficient,

R = Hydraulic radius (= D/4 in which the D is drain pipe diameter (m)),

S = Slope,

A_t = Area of the drain pipe (m^2), and

A_d = Area of the drained area (m^2)(= L*S in which L is the length of drain pipe (m) and S is the drain spacing (m)).

Manning's coefficient, slope, length, and size of drain pipes for the filtration area were 0.015, 0.0025, 100 m, and 0.15 m, respectively. Therefore, the drainage coefficient, estimated by Manning's equation, was 0.25 m/day. However, a conservative input value for the drainage coefficient was set at 0.2 m/day.

5.4.2.2.2 Trapping test

It was assumed that the simulated drain outflows from the farm area (100 ha) contained 50 μg/L of atrazine, metolachlor, and metribuzin residues, and simulations were carried out with PRZM2 to determine the required size of the grass filter area to make drainage water safer for aquatic life and marine habitat. The nodal spacing for PRZM was chosen to be 1 cm and pesticide movement was simulated to a depth of 100 cm, which is equal to the drain depth. Plant growth was introduced to the simulation model by inducing cropping soil conditions over the simulation period. The root depth and plant uptake factor for the grass strips were chosen to be 15 cm and 0.3, respectively (Mullins et al., 1993).

Soil properties, such as organic matter content and bulk density, were previously measured to be 3.5% by weight and 1400 kg/m^3, respectively (Liaghat et al., 1996). Values of decay rate, solubility and partition coefficient for the three herbicides are shown in Table 2. The dispersion coefficients for the three herbicides were chosen to be zero, as suggested by the PRZM Manual.

5.5 RESULTS AND DISCUSSIONS

Among the 40 years of annual rainfall data (1955 to 1995), the data of 1972 presented a 1-in-20 year annual rainfall. DRAINMOD was run with 1972 meteorological data to simulate the daily drain outflow from the 100 ha typical agricultural field. Figure 5.3 shows daily rainfall and drain outflows simulated by DRAINMOD for 1972. This figure shows occurring of one or two rainfall events per week during 1972. The maximum rainfall occurred in the fall (August and September) and was 30 mm. Figure 5.3 also shows that the drains would have flown continuously during the summer, thus representing a worst case scenario for this analysis. The maximum outflow was 6.5 mm which occurred in the fall.

The drainage coefficient for the filtration area, using equations 4 and 5, was estimated to be 0.7 (as determined by Kirkham equation) and 0.25 m/day (as determined by the hydraulic capacity of drain pipes), respectively. This indicates that the drainage or infiltration rate for the soil was limited by the hydraulic capacity of the drain pipes, and not by the rate of soil-water movement towards the drains.

The infiltration test revealed that at least a 2 ha filtration area is required in order to pass all drainage water through the soil profile without causing any surface runoff. The trapping test was performed for the 2 ha filtration area, running the PRZM2 model. However, the efficiency of the filtration area was found to be inadequate in lowering the concentration level of pesticides in drainage waters to the maximum acceptable level of 1 µg/L for aquatic life.

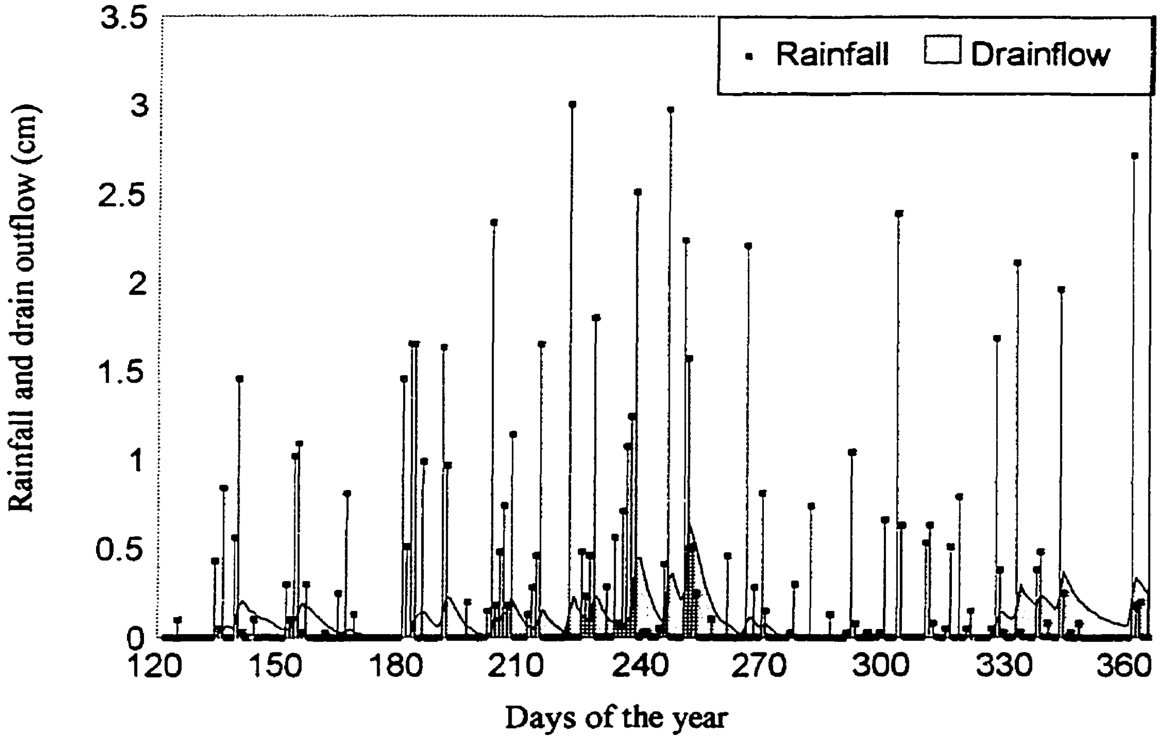

Figure 5.3: Daily rainfall and simulated drain outflow per unit area for 1972.

This test was also performed for 3, 4, 5, and 6 ha filtration areas. Figure 5.4 shows simulated pesticide concentrations in treated water from a 6 ha filtration area on a daily basis. It was found that 6% of the farm area can be used to bring down the concentration level in drainage waters from 50 µg/L to less than 1 µg/L for the three herbicides under the local meteorological conditions and for two consecutive years, assuming that the 1-in-20 year annual rainfall occurred in two consecutive years. This represents an even more worst case scenario for an agricultural field in the region. Figure 5.4 indicates that the concentration of atrazine and metolachlor could be reduced considerably more with a 6% filtration area. The maximum concentration of atrazine

lachlor in treated water was estimated to be less than 0.4 and 0.1 µg/L. It , therefore, that lesser filtration area will be needed for atrazine and chlor contaminated waters to reach levels that are considered safe for aquatic nd marine habitat. These herbicides have lower water solubility and higher soil ption coefficient. Therefore, the size of filtration area depends on chemical aracteristics and soil properties.

It should be noted that a worst case scenario was considered in this study, such as contaminant levels in drainage waters to be 50 µg/L. In actual practice, the concentrations will fluctuate, depending on the time of year. In addition, the contaminant level in drainage waters during wet years, or following heavy rainfalls, would be low due to a dilution effect, while the total loss of pesticides may be greater for such years.

One should also note that the simulation was performed such that the system need not require any on-site water storage. However, in many regions, natural lakes or ponds are available, and may be used, for storage of polluted drainage waters during heavy rainfalls and later on may be pumped onto the filtration area. This can reduce the required size of the filtration area.

The size of filtration area was determined for different levels of contaminants, such as 20 µg/L, 30 µg/L, and 40 µg/L, that may be found in drainage waters under various circumstances. Figure 5.5 illustrates the maximum concentration levels of atrazine, metolachlor and metribuzin in treated water according to the size ratio (filtration area to farm area) and the level of contaminant in drainage water. Knowing the contaminant level in polluted water (say 30 µg/L) and the maximum acceptable level (say 1 µg/L, which is safe for aquatic life), one can determine the size of filtration area from this figure. For the above case, 5% of the farm will be needed for the filtration area.

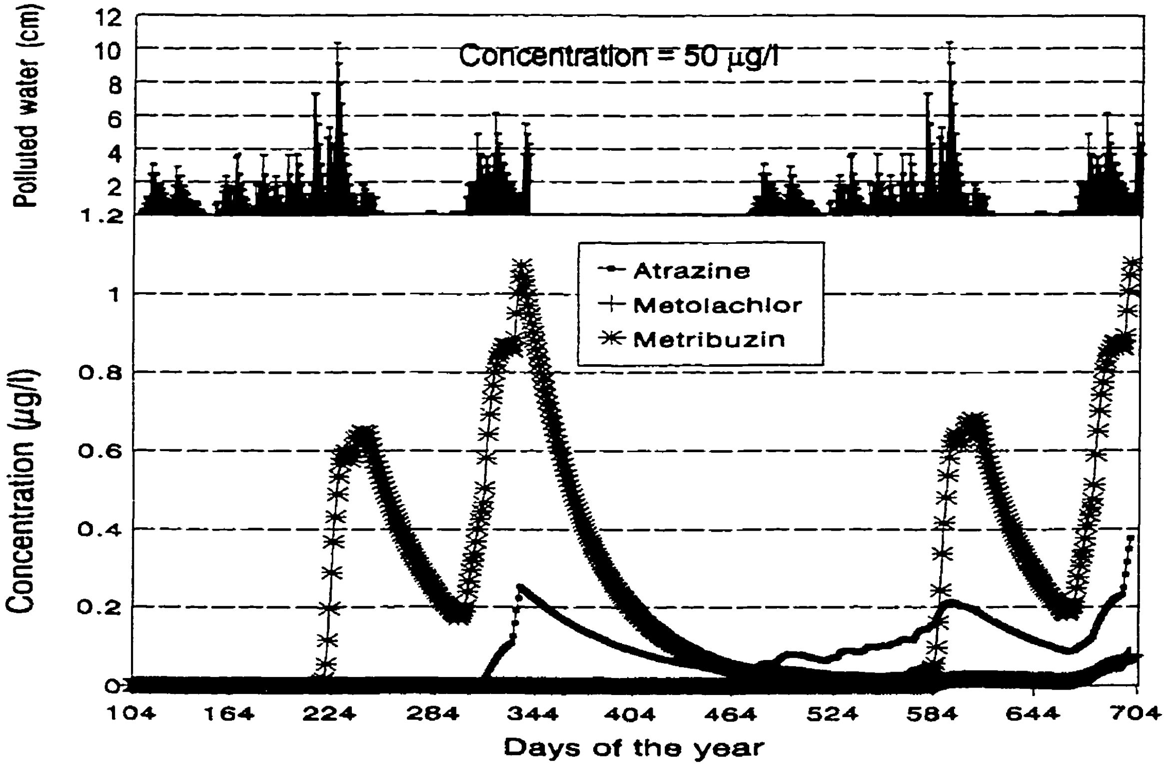

Figure 5.4: Predicted pesticide concentrations in treated water escaped from filtration area on the daily basis.

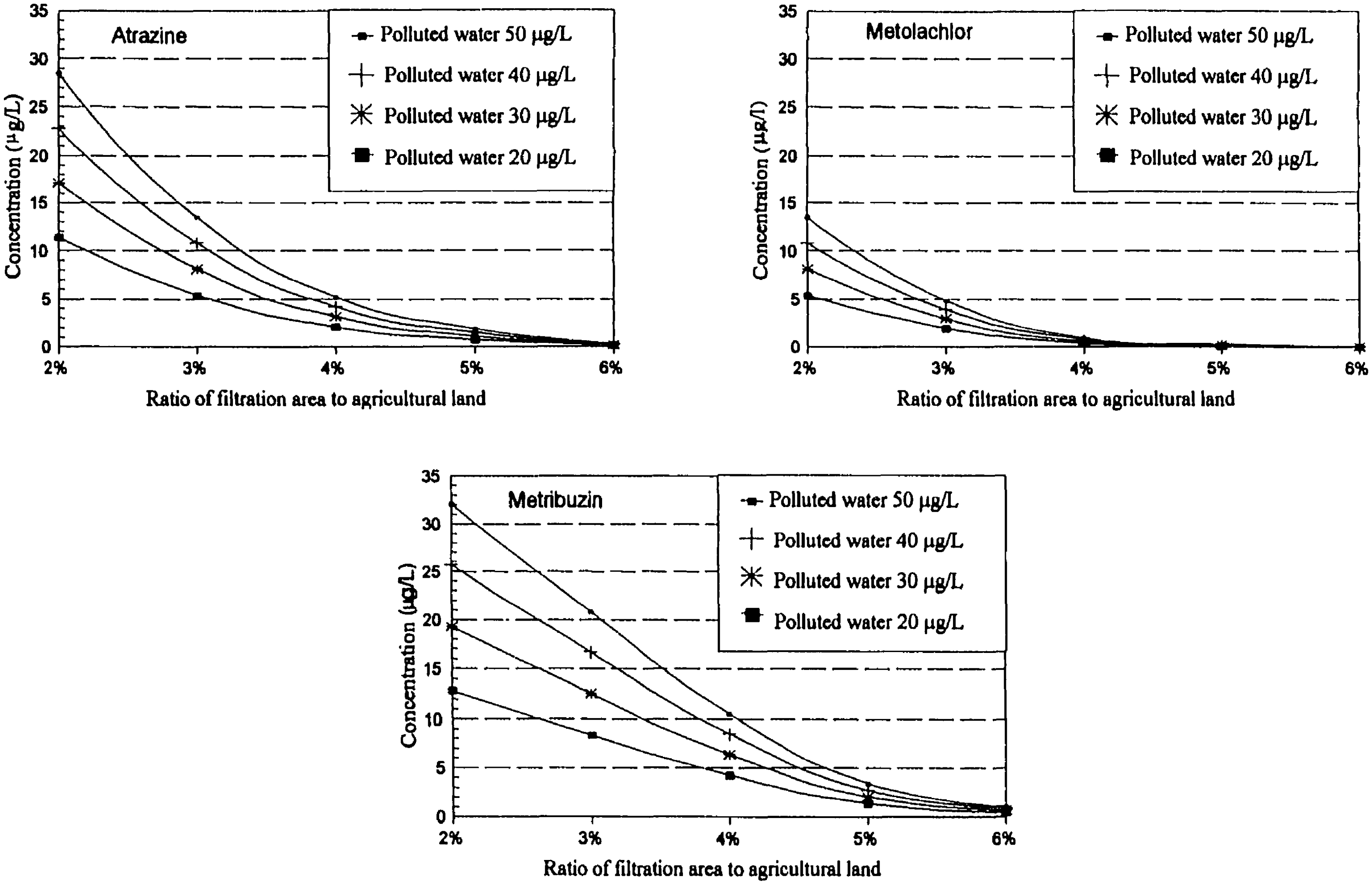

Figure 5.5: Maximum concentration level of atrazine, metolachlor, and metribuzin in treated water for the different filtration size and different contaminant levels of drainage waters.

5.6 PRELIMINARY COST ESTIMATION

The simulations described in this chapter indicate that a filtration area, equal to 6% of the total farmed area, would be sufficient to reduce the herbicide levels in drainage water to safe levels for humans, livestock and aquatic life. There is a cost involved, and one can analyze the situation in various ways, depending on what alternatives the farmer chooses and how society perceives the responsibility of ensuring that ground and surface waters remain clean. The cost of a soil and grass filtration system involves:

1) The cost of installation of the subsurface drainage system for the filtration area,
2) The cost of operating and maintaining the system,
3) Financing cost,
4) The lost opportunity of production on the 6% land area set aside.

The first two items are presented in detail in Tables 5.3 and 5.4, based on a subsurface-drained 100 ha field in Quebec with a 6 ha filtration area. The drain spacing in the filtration area is assumed to be 10 m and the drain outflow from 100 ha field is based on the 1972 annual rainfall (a 1-in-20 year case). The cost of drainage pipes was obtained from Plasti-DRAIN LTEE, while the cost of installation, maintenance and pump were given by Broughton (1996) and Prasher et al., (1994). The average net benefit of corn for the southern Quebec agricultural lands was estimated to be 400 $/ha (Serge, 1997).

Item 3 can be handled in several ways:

a) The farmer could pay cash for the system, in which case he would incur a cost of lost investment opportunity,

b) The farmer could borrow from the bank, in which case there may be a cost equivalent to difference between interest paid on the loan and interest accrued on investment (if one has that much investment capital).

c) The government partly or fully finances the interest on the loan since it is in the public interest to maintain a clean environment as well as produce food and livestock feed.

For purposes of this estimate, we assume the second scenario with no investment capital buffering and a 10% medium term interest rate at the bank for 5 years (Table 5.4).

Item 4 can represent a loss equivalent to 6% of the 100 ha profit the farmer would normally get, minus the savings in his production cost for the 6 ha. Here, we assume that the filtration area is not harvested for hay because it will be saturated for a substantial part of the year. Although the grass possibly could be harvested and sold as cattle feed, no value for such a benefit was assumed in the cost estimates.

Detailed cost estimations are presented in Table 5.4. In this table, the costs were amortized over a 15-year expected life span of the items.

The analysis was carried out to provide the cost per cubic meter of polluted water or the cost per hectare of agricultural land. Total drainage waters coming out of a 100 ha cultivated land was estimated by DRAINMOD to be 243,700 m^3/year. Therefore, the total cost for the filtration of polluted drainage waters is estimated to be about 2.38 cent/m^3/year or 58 $/ha/year.

The above estimation was based on an assumption that the filtration area needs to be subsurface drained. However, most agricultural lands in humid regions may already be subsurface drained in which the cost of subsurface drainage system for the filtration site as well as the related cost will be reduced by one-half. In this case, the total cost is estimated to be 1.83 cent/m^3 /year or 44.75 $/ha/year.

Table 5.3: Capital cost including drain pipes, installation, and land leveling.

Materials	units (m)	Cost $/m	Installation cost $/m	Total cost $
15 mm drain pipe	6000	2.72	0.4	18720
20 mm drain pipe	600	5.05	0.5	3330
Connections of lateral drains to collectors				1000
Land Leveling				600
Sump				100
Total x 15% tax				3560
Total				27310

Table 5.4: Annual cost of filtration area.

Items	$/year
Subsurface drainage system	1820
Diesel engine pump	100
Maintenance	50
Fuel and lubricants	300
Labour	120
Miscellaneous	100
Financing cost	910
Benefit lost of 6 ha corn production	2400
Total cost per year	5800

5.7 SUMMARY AND CONCLUSIONS

A computer modeling approach was used to determine the size of filtration area required for removing pollutants from agricultural drainage waters. DRAINMOD and PRZM2 models were used to determine the required size of filtration area for an agricultural farm in South-western Quebec and for a 1-in-20 year rainfall period. The results of this study show that no more than 6% of farm area can be used to reduce pesticide concentration in drainage waters from 50 μg/L to less than 1 μg/L. This procedure can also be used at other sites in determining the required size of filtration area.

In this study, the 6% of land area for the filtration site was obtained based on a worst case scenario. However, it may be noted that the actual land area required for filtration will be less than 6% since this figure was derived for a 1-in-20 year annual rainfall event and by assuming 50 μg/L pesticide concentration in drainage waters. In typical drainage designs, a 5-year return period is used and this will most certainly reduce the land area required for filtration. In addition, the herbicide concentration in drainage waters will seldom remain at 50 μg/L level throughout the drainflow period. In most cases, it will be much less than 50 μg/L, and thus lesser area will be needed for filtration purposes, as can be seen from figure 5. The mathematical approach given in this paper can be used to perform these types of analyses.

Preliminary cost for the filtration area was estimated to be about $23.8 per 1000 m^3 of polluted water. If the filtration area is already subsurface drained, the cost will reduce to $18.3 per 1000 m^3.

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CHAPTER 6

SUMMARY AND CONCLUSIONS

The aim of this entire study was to establish an on-farm pollution control system for reducing herbicides and nitrate residues from agricultural drainage waters. This study consisted of three parts: a lysimeter study, a field study, and a computer simulation.

Twelve lysimeters were used to evaluate the performance of four treatments, bare soil and grass covered lysimeters combined with water table management (free drainage and controlled drainage), for reducing contaminants in agricultural waters.

To verify the proposed method and the results obtained from the lysimeter study, a field study was used to investigate the performance of the soil and grass strips as a biological filter for trapping contaminant from agricultural polluted waters.

Simulation was used to estimate the size of grass filter area for removing pesticide residues from agricultural drainage waters. The method uses a water table management model, DRAINMOD, for simulating drainage waters from agricultural land and a solute transport model, PRZM2, for simulating pesticide concentrations in the drain effluent coming out of the grass filter area. Preliminary cost for the filtration area was estimated in terms of $\$/m^3$.

From the lysimeter, field, and simulation studies done in this research, the following general conclusions can be drawn:

1. The proposed system (soil and grass filter) showed a significant (1% level) reduction for both herbicides and nitrate levels in polluted drainage waters. However, reduction of the herbicides levels was greater than the nitrate levels.

2. Simulations suggest that no more than 6% of a farm area is needed to reduce pesticide concentration in drainage waters from 50 mg/L to less than 1 mg/L. In this study, 6% of land area for the filtration site was obtained, based on a worst case scenario.

3. Biodegradation of herbicides was confirmed by soil samples taken from the field during the dry period. This indicates that the system could be self-sustainable in the long term.

4. Trapping efficiency of the system corresponds to the total volume of applied water and total masses of applied pollutant. Trapping ratios for the herbicides and nitrate, respectively, were more than 97% and 85% in the field study.

5. The grass covered lysimeters reduced herbicide levels in the drainage waters

to a greater extent than the bare soil lysimeters. Also, there was greater herbicide reduction in the grass covered lysimeters with subsurface drainage (GSD) compared to other treatments.

6. The controlled drainage lysimeters reduced nitrate levels in the drainage waters to a greater extent than the subsurface drainage lysimeters. In addition, there was greater nitrate reduction in the controlled drainage lysimeters covered with grass (GCD).

7. In this system, denitrification was found to be the predominant process for nitrate reduction compared to plant uptake.

8. The concentration level of herbicides in drainage waters tended to increase by continued application of polluted water. This situation was remedied by introducing dry periods between the wet periods.

9. The results of this study are very encouraging and reinforce the contention that dual-passage of drainage water could dramatically reduce environmental pollution from agricultural farm; and at the same time, safeguard freshwater aquatic habitats.

CHAPTER 7

SUGGESTIONS FOR FUTURE RESEARCH

From the field, lysimeter, and model studies in this research, the following area of further research are suggested:

1. In the field study, polluted water was applied into four ditches. Therefore, only a fraction of the filtration area (surface area inside the ditches) was effective for trapping herbicides. The efficiency of the system increases if the entire filtration area is involved. Therefore, there is a need to apply polluted water on the entire filtration area and determine the effectiveness of this system.

2. Grass covered lysimeters were found to have better performance for trapping nitrate and herbicides. However, grass may not survive under saturation conditions. Therefore, there is a need to find some species to be tolerance under saturation conditions and be also suitable for microbial growth.

3. Free drainage lysimeters covered with grass showed better performance for herbicide trapping. In contrast, controlled drainage lysimeters covered with grass showed better performance for nitrate reduction. Thus, there is a need

to find an optimum case for both systems; for example, managing a free drainage system during the wet period and a controlled drainage system during the dry period.

4. Controlled drainage lysimeters, with water table settings of 0.5 m, showed better effectiveness for reducing nitrate pollution as compared to free drainage lysimeters. There is a need to set different water table levels in controlled drainage and to test their effectiveness.

5. Soil sorption potential for adsorbing nitrate is very low because of negative charges of both nitrate and soil particles. It is known that nitrate leaching losses are less in the acidic soils due to the effect of pH on denitrification rate or because of predominantly positive charges of ions in these soils. Therefore, there is a need to test the system with different ranges of soil pH.

6. Lysimeter and field studies showed that more than 97% of the total applied herbicide can be trapped by the Ste-Amable sandy soil containing 3.5% organic matter. Further work is needed to test trapping efficiency on different soils with different organic matter contents. It should be noted that the soils with high infiltration rate and high adsorption capacity are best for this technique.

7. Runoff waters from agricultural land normally contain some sediment or soil particles. These particles have the potential to adsorb organic chemical on their surfaces. The water applied in this study was free of particles. It is expected that if some particles (soil or solid organic) are present in the polluted water, the efficiency of the system increases. Therefore, there is a need to test the performance of filters using polluted water containing different amounts of particles.

8. Measurements on the soil samples collected from the field showed a very high spatial variability of herbicides in the soil. Soil samples collected from the middles of the ditches, where polluted water was pumped, showed higher herbicide concentration compared to samples collected from other locations. It is expected that if polluted water is applied uniformly on the filtration area, a better performance can be obtained using this system. Therefore, there is a need to test the influence of irrigation methods for application of polluted water on the field.

9. The amount of herbicides retained in a soil differ when a different herbicide contaminant solution is used. Therefore, it is needed to find the system performance for other pesticides.

IMAGE EVALUATION
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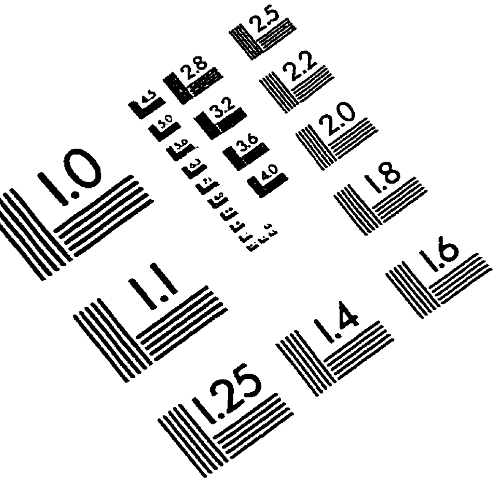

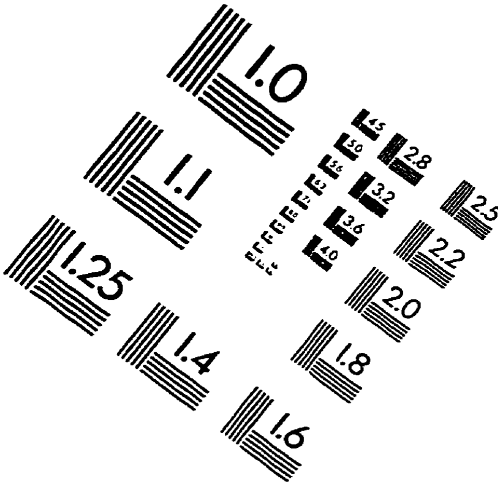

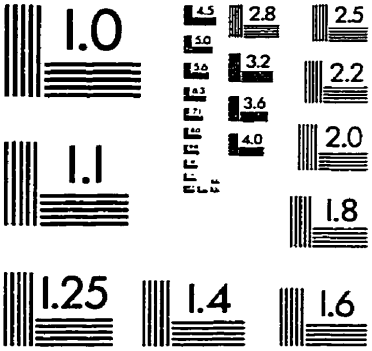

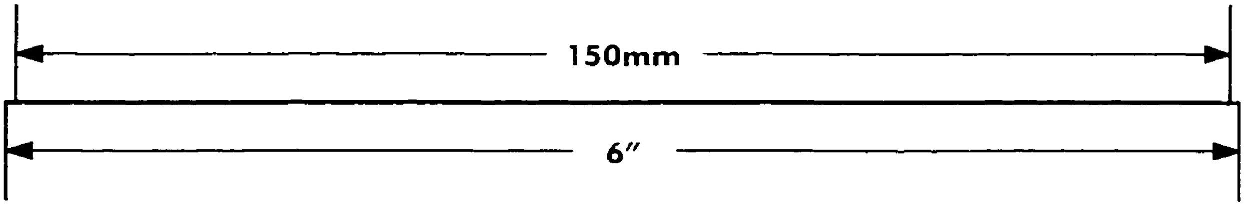

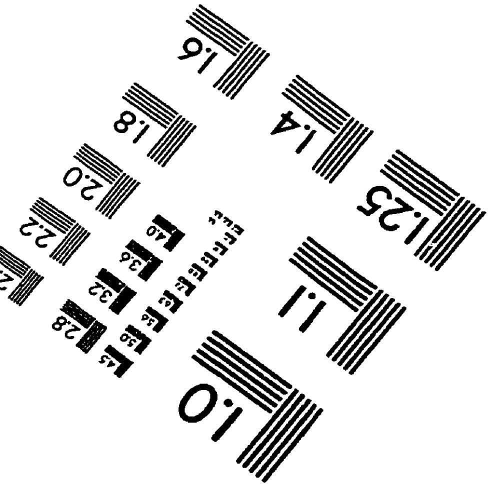

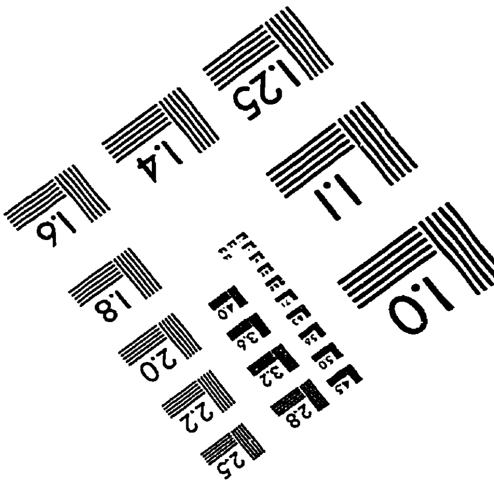

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