IMPACT OF WATER TABLE MANAGEMENT ON GROUND WATER CONTAMINATION BY TWO HERBICIDES

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Studies and Research in partial fulfilment
of the requirements for the degree of
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ABSTRACT

Two field investigations were undertaken to study the role of water table management in reducing herbicide pollution of ground water. One of the three-year studies (1992-1995) was conducted in a sandy field near Joliette (Laurin farm), north-east of Montréal (Québec) to monitor the herbicide metribuzin where potatoes were grown. Two water table management systems were evaluated, namely subsurface drainage and subirrigation. Soil samples were taken at three different depths and water samples were collected from observation wells in 1992 and, with the use of piezometers, at three fixed depths in 1993. The soil and ground water samples were taken at two week intervals, once before and six times after the herbicide application. Water table depths were recorded continuously in both treatments. Three subirrigation experimental plots were used in both years. In the subsurface drainage treatment, one experimental plot was used in 1992 and three were used in 1993.

The results indicate that the amount of rainfall received in the first few weeks following herbicide application is crucial in assessing the extent of ground water contamination. In 1992, fewer rainfall events occurred after the application as compared to 1993, so metribuzin leached slowly. In 1992, it appears that subirrigation reduced ground water contamination by a factor of 10 through enhanced degradation and the greater effect of dilution. However, the role of subirrigation in reducing the metribuzin contamination of ground water was negligible in 1993 due to considerable leaching soon after the application.

The second project was conducted in an organic soil in St-Patrice-de-Sherrington (Van Winden farm) located south of Montréal where the herbicide prometryn was studied. The first two years of this three-year study were carried out by Arjoon (1992). Surface irrigation with a controlled water table was also used as a water table management system. One experimental unit was used for each of the three treatments (subirrigation,

surface irrigation and subsurface drainage). Soil samples were collected at four depths and ground water samples were collected with the use of observation wells.

The herbicide application rate was greater at the Van Winden farm than in the Laurin farm (5.5 kg/ha versus 1.0 kg/ha). However, a higher adsorption coefficient of the organic soil minimized the leaching process. The extent of the ground water contamination was less extensive in the organic deposit. The effect of subirrigation in reducing ground water contamination was significant when the water table was shallow. The prometryn degradation process was relatively slow during the summer. Moreover, significant amounts of prometryn carried-over into the soil after the winter season, so it appears to be a quite persistent herbicide in our climate.

Deux études fûrent entreprises pour déterminer les impacts de l'utilisation d'un système d'irrigation souterraine sur la réduction de la contamination de la nappe phréatique par les herbicides. Une des deux études, d'une durée de trois années, a eu lieu sur les terres sablonneuses de Monsieur Sylvain Laurin dans la région de Joliette (Québec), au nord-est de Montréal. L'herbicide métribuzine fût appliqué pour contrôler le pied-de-coq dans la culture de la pomme de terre. Deux systèmes de gestion de la hauteur de la nappe phréatique fûrent évalués le drainage souterrain libre et l'irrigation souterraine. Les échantillons de sols fûrent pris à trois profondeurs différentes, et les échantillons d'eau souterraine fûrent recueillis via des puits d'observations en 1992, et via des piézomètres à trois profondeurs différentes en 1993. Les échantillons de sol et d'eau souterraine fûrent recueillis à une fréquence d'une journée d'échantillonage à chaque deux semaines, une fois avant, et six fois après l'application de la métribuzine. La hauteur de la nappe phréatique fût enregistrée de façon continue, et ce, à chacun des traitements. Trois unités expérimentales fúrent utilisées pour l'irrigation souterraine durant les deux premières Une seule unité expérimentale fût utilisée pour le traitement de années de l'étude. drainage souterrain libre en 1992, alors que trois unités fûrent utilisées en 1993.

Les résultats obtenus indiquent que la quantité de précipitations reçue durant les premières semaines suivant l'application de la métribuzine est déterminante pour ce qui est du degré de contamination par ledit herbicide. En 1992, la migration de la métribuzine fût lente en comparaison des résultats obtenus en 1993, puisque peu de précipitations ont eu lieu après l'application de l'herbicide. En 1992, il semble que le système d'irrigation souterraine a permis de réduire par un facteur de 10 le niveau de contamination de la métribuzine dans la nappe phréatique. Ceci semble avoir été causé par un processus de dégradation plus marqué ainsi que par l'effet de dilution dans un système où la nappe phréatique est plus élevée. Cependant, le rôle du système d'irrigation souterraine a eu peu d'impacts sur la réduction de la contamination qui fût

négligeable en 1993. Au cours de cette année, la migration de la métribuzine fût importante peu après l'application.

Le deuxième projet de recherche consistait en l'étude de l'herbicide prométryne appliqué sur un sol organique dans la localité de St-Patrice-de-Sherrington (ferme Van Winden) (Québec). Les deux premières années de recherche fûrent entreprises par Arjoon (1992). Un système d'irrigation de surface jumelé avec une chambre de contrôle a été aussi utilisé comme système de gestion de nappe. Une unité experimentale fût utilisée pour chacun des traitements. Les échantillons de sol fûrent recueillis à quatre différentes profondeurs tandis que les échantillons d'eau souterraine fûrent pris via des puits d'observation.

Le taux d'application de l'herbicide fût supérieur à la ferme van Winden qu'à la ferme Laurin (5 5 kg/ha versus 1.0 kg/ha). Cependant, la capacité d'adsorption du dépôt de sol organique étant plus élevé. la migration de la prométryne fût moindre. Le système d'irrigation souterraine a réduit le niveau de contamination de la nappe phréatique seulement lorsque le niveau de la nappe fût élevé. Le processus de dégradation de la prométryne durant l'été fût relativement lent. En plus, d'importantes quantités de prométryne ont résisté à la dégradation durant la saison hivernale.

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LIST OF SYMBOLS AND ABBREVIATIONS

A.I	active ingredient
ave	arıthmetic average
	Best Management Practice
C	carbon content
°C	degrees Celcius
cm	centimetre (10 ² meter)
	coefficient of variability (in percentage)
	diameter of soil particle (millimetre)
	water table tube destroyed by machinery
	Subsurface drainage treatment
	Environmental Protection Agency (United States)
	evapotranspiration (millimetre)
	degrees Fahrenheit
g	-
ĞG	Greenhouse-Geisser epsilon (term in statistics)
	General Linear Model (term in statistics)
ha	
	Huynh-Feldt epsilon (term in statistics)
K	soil-water partition coefficient
	kilogram (10 ³ grams)
K	octanol-water partition coefficient
L	
	Multivariate Analyses of Variance.
	milligram (10 ³ gram)
	millilitre (10 ³ litre)
	millimetre (10 ³ meter)
NA	
ND	
	not read (water table was too deep)
	statistical probability
ppb	
ppm	
	correlation coefficient
	revolutions per minute
•	tandard deviation (term in statistics)
	Subirrigation treatment
	Surface irrigation treatment
	microgram (10-6 gram)
	. micrometer (10 ⁶ meter)
	water table depth (meter)

CHAPTER 1. INTRODUCTION

The installation of subsurface drainage systems is essential in many humid regions of North America to realize the full agricultural potential of soils. In Spring, excess water resulting from snowmelt and frequent rainfalls could prevent heavy machinery from being used on a field. During Summer, the water surplus could damage the crops and, secondly, lead to surface runoff which could carry important quantities of pesticide and fertilizer to rivers (Spencer, 1985 and Bastien, 1991). Farmers understand the benefits of subsurface drainage: about 700,000 ha of agricultural land in Québec was drained by subsurface systems in 1992 (MAPAQ, 1993).

However, the negative impacts of drainage became increasingly important as the input of fertilizers and pesticides increased over the years. The drainage systems are increasingly considered as potential conduits of environmental pollution from agricultural areas as they could carry leached-out fertilizer and pesticide residues into the regional lakes and rivers. Numerous solutions were tried to reduce the environmental impact of this non-point pollution. They included border strips along the farm boundaries (Buttle, 1990), reduction and/or different timing of fertilizer and pesticide applications (McBride, 1989) and, finally, tilling (Isensee, Nash and Helling, 1990 and Patni et al., 1993). Another agricultural practice that may have an impact on non-point pollution is water table management.

By controlling the water table on agricultural lands, it might be possible to reduce environmental pollution by keeping the chemicals within the farm boundaries for extended periods while increasing crop yields as demonstrated by previous studies (von Hoyningen Huene et al., 1985). Most agricultural pesticides have a half-life ranging from a few weeks to a few months, and if drainage water is not allowed to escape farm boundaries during that time, using a controlled drainage or subirrigation system, the water that finally leaves the farm in the fall would contain substantially less contaminants. The microbial degradation process may also be accelerated by the higher soil moisture content

caused by subirrigation and controlled drainage systems. Additionally, less nitrate-N leaching would result due to increased denitrification caused by keeping the drain pipes submerged with these systems. The environmental impact of these systems is substantial because it can bring about a reduction in pollution caused by agricultural chemicals without requiring any drastic changes in current agricultural practices. If found effective, the water table management systems could become on-farm pollution control systems in the humid regions of North America.

In order to assess the efficiency of subirrigation in reducing the ground water contamination by herbicides and fertilizer residues, two three-year studies were initiated. First, the herbicide metribuzin was monitored before and after its application onto a sandy field in the area of Joliette (Québec). Potatoes were grown during the first two years of the study. The second project dealt with the herbicide prometryn applied onto an organic soil of a vegetable farm at St-Patrice-de-Sherrington (Québec).

1 1 Objectives

The primary emphasis of this investigation was to determine environmental benefits of water table management systems. More specifically, the objectives of this study were:

- 1) To assess the efficiency of a subirrigation system in reducing concentration levels of two herbicides in shallow ground water,
- 2) To better understand the leaching and degradation of the herbicide metribuzin in a mineral soil in Québec,
- 3) To better understand the leaching and degradation of herbicide prometryn in an organic soil in Québec,
- 4) To assess the denitrification potential of a subirrigation system.

1.2 Organization of the thesis

After introducing the importance of water table management systems in humid regions in Chapter 1, their agricultural and possible environmental impacts are outlined in Chapter 2. Since the present study focused on environmental pollution from metribuzin

and prometryn, the reviews also contain their properties and some discussion of their threat to ground water supplies.

Chapter 3 focuses on the behaviour of the herbicide metribuzin on a sandy soil (Laurin farm), whereas the study of prometryn in an organic deposit (Van Winden farm) is dealt with in Chapter 4. The site description, the experimental set-up, the soil's physical and chemical properties, the methodology, the meteorological data and the statistical analysis for a given site are described. Chapter 5 contains the summary and conclusion for each experimental location, while Chapter 6 includes the recommendations for future research. The references cited for both experimental sites are included in Chapter 7. The appendix includes the raw experimental data collected at each experimental site (Appendix A and B).

1.3 Scope

The scope of the results obtained in this research is limited to the herbicides used and to the physical and chemical properties of the soil where they had been applied (metribuzin in a coarse-textured soil and prometryn in an organic deposit). The interception of plants is also crucial in the mass balance of the herbicide. Potatoes and celery were grown in the coarse-textured soil and organic soil, respectively. The results are limited to a climate with mostly dry conditions in the Summer and important amount of snowfall during Winter (weather typical to Québec). This climate would affect the time during which the control chamber would be closed or open.

CHAPTER 2. LITERATURE REVIEW

This chapter covers the recent studies concerning agricultural pollution and water table management systems. First, the review will focus on the impact of water table management on pesticide movement towards ground water. The chemical properties and the extent of the use of the herbicides dealt in our study, metribuzin (section 2 and 3) and prometryn (section 4), will follow. Finally, the last part of the review will deal with studies on the impact of water table management on nitrate concentrations in ground water. A summary will conclude this chapter.

Subsurface drainage systems are in gaining popularity as shown in Table 1. In 1992, 700,000 ha of agricultural land were drained (in Québec, 43% of the total cultivated land), a 13% increase in six years. However, surface and subsurface irrigation are still not used extensively which is not surprising considering the Québec climate. The increase in land area that is subsurface drained is also usually accompanied by fertilizer and pesticide applications. Some 3,000 tonnes of pesticides are applied every year on Québec soils (Forrest and Caux, 1988), covering over 620,000 hectares (Statistics Canada, 1992a). Over 30,000 tonnes of pesticides are applied on Canadian soils every year (Forrest and Caux, 1988). In 1991, about 92,000 and 1,200,000 tonnes of nitrogen were applied on Québec and Canadian soils, respectively (Asseltine and Girard, 1992).

Water table management systems have the potential of answering the agricultural needs of the humid regions of Northeastern North America. Excess water resulting from snowmelt in the Spring and frequent rainfalls in late Fall could be drained out of the field by opening the outlet of the control chamber. Moreover, when water deficits are important in the summer months of our region (Gallichand et al., 1990), the control chamber can be closed, allowing rainfall and subirrigation to raise the water level to the desired depth at a very critical time period for the crops.

Table 1. Use of land in Québec farms. The data shown were collected in 1991, except the lower value within a box which are from 1986.

	Province of Québec	Region of Joliette	Region of l'Assompt	Region of Montcalm
Size of land growing potatoes (ha)	17,522 (1)	328 (1)	159 (1)	695 (1)
Size of land where herbicides were applied (ha)	564,330 (1) 541,251 (2)	3,147 (1) 9,761 (2)	4,752 (1) 12,338 (2)	17,224 (1) 9,158 (2)
Size of land where insectic. and/or fungicides were applied (ha)	96,285 (1) 75,901 (2)	1,034 (1) 3,484 (2)	1,388 (1) 3,410 (2)	3,436 (1) 960 (2)
Size of land where surface irrigation was used (ha)	21,848 (1) 15,284 (2)	711 (1) 1,848 (2)	486 (1) 898 (2)	873 (1) 304 (2)
Size of land where subirrigation is used (ha)	650 (3)	N.A.	N.A.	N.A.
Size of land where subsurf. drainage is used (ha)	696,296 (4) 608,674 (2)	9,803 (2)	9,679 (2)	9,720 (2)

Reference: (1) Statistics Canada, 1992a and Statistics Canada, 1992b.

- (2) Statistics Canada, 1986.
- (3) Innotag, 1994.
- (4) MAPAQ, 1993.

2.1 Impact of water table management on pesticide leaching

Most of the studies on water table management are concerned mainly with its impact on denitrification and crop yields, rarely on pesticide residues. From the few publications dealing with the impact on pesticide contamination, both Hatzios and Penner (1988) and Roberts et al. (1979) stated that subsurface drainage does not seem to constitute an

important mean of metribuzin transport toward the ground water because of its low mobility and relatively weak persistence. This is partially confirmed by Muir and Baker (1976) who initiated a study on loamy sand and clay soils where they measured metribuzin concentrations in the subsurface drainage ranging from 0 to 1.65 μ g/L. However, the two most interesting studies on the impact of water table management on the levels of pesticide residues in ground water were made by Arjoon (1992) and Kalita et al. (1992). The focus will be on these two studies in the next few pages as they are similar in nature to this study.

The study by Arjoon (1992) dealt with the effect of the water table management on pesticide movement in two types of Québec soils. The contamination of prometryn in an organic deposit and metolachlor in a sandy soil was monitored in both soil and ground water for two years and one year, respectively. Soil samples were collected at four different depths. Ground water samples were taken from observation wells. The conclusions from her work were as follows:

- 1) Water table management seems to reduce the amount of prometryn leaching into the ground water under an organic soil;
- 2) In an organic soil, the climate, or more specifically, the water balance seems to be the major factor affecting herbicide movement in the soil.
- 3) Organic soils should not be considered as "sponges" for applied contaminants. Results indicate potentially serious contamination problems in the organic deposit. Due to the large quantity of pesticide applied, contamination is potentially more serious than in mineral soils.
- 4) The results of the study of the effect of water table management on metolachlor contamination of ground water under a mineral soil are not conclusive.
- 5) Determination of the major factor affecting herbicide movement through a mineral soil is difficult based on the results of this study. It appears that soil characteristics may be the limiting factor in this case.

6) Metolachlor leaching may be a problem under wet conditions. Again, this cannot be fully substantiated by the results of this study.

The study of Kalita et al. (1992) was performed from 1989 to 1991. Atrazine and alachlor were applied (2.2 kg/ha every year for each herbicide) in a corn field on a silty loam soil in Iowa. The water was pumped from a man-made reservoir and did not come into the subsoil via the subsurface drainage pipes but by irrigation lines (dual-pipe subirrigation system) installed at mid-spacing at a depth of 0.5 to 0.6 m. The subsurface drainage pipes were installed at a depth of 1.2 m. In a water table depth was kept constant for a given field. Five different water table depths were used: 0.2, 0.3, 0.6, 0.9, and 1.1 m. Ground water samples were collected from piezometers installed at depths of 1.2, 1.8 and 2.4 m.

Atrazine concentrations varied between 0 and 67 μ g/L. The highest value was obtained at the 1.2 meter depth before the subirrigation system was used. When subirrigation started, the concentration of the atrazine in the ground water declined. The atrazine concentration decreased with shallow water tables and with increasing soil depths with few exceptions. At the end of the growing season with a shallow water table, the atrazine concentration was 0.34 μ g/L at the 1.2 m depth whereas it was not detected in the two deepest piezometers.

2.2 Properties of metribuzin

Metribuzin is an asymmetric triazinone herbicide which inhibits electron transport. 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 against broadleaf weeds and grasses (in our case, barnyard grass) in the culture of potatoes, alfalfa, sorghum, soybean, corn, barley (Diawara and Banks, 1990). Cross chemical reactions may take place between metribuzin and other pesticides applied the year before or during the same year. This would increase the

phytotoxicity of metribuzin (Pawlak et al., 1987). The partial degradation of metribuzin will lead to the formation of three metabolites: DA (desaminometribuzin), DADK (desamino-diketo-metribuzin) and DK (diketo-metribuzin) (Figure 2) (Bachlechner, 1989).

The degradation of metribuzin in soil has been extensively studied. In an experiment carried out in Saskatchewan, Manitoba, Ontario and Prince Edward Island (Smith, 1982; 1985), 0-20% of the

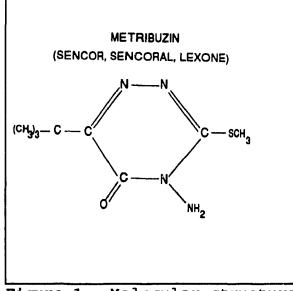


Figure 1. Molecular structure of metribuzin.

total amount of metribuzin applied remained after 5 months. Similar results were obtained (2-20% left after 22 weeks) in clay, clay loam and sandy loam in Saskatchewan (Smith and Hayden, 1982). The half-life of this herbicide is dependant on the soil characteristics, chemical formulation and application rate (U.S. EPA ,1987). Correlations between half-life and soil depth (Moorman and Harper, 1989; Kempson-

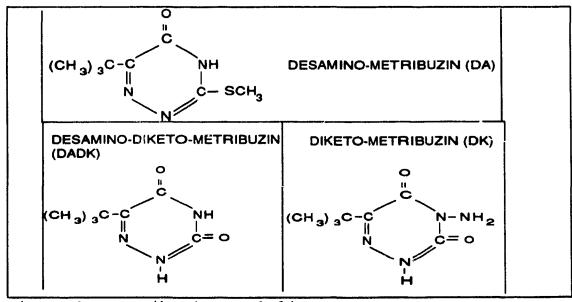


Figure 2. Metribuzin metabolites.

Jones and Hance, 1979) and available potassium (Walker, 1987) confirmed the hypothesis made by Savage (1977) and Bouchard et al. (1982) that the degradation of metribuzin in soil is mostly due to microbiological activity. The degradation in the topsoil followed a first order kinetic reaction in two steps (Ladlie et al. 1976b; LaFleur, 1980). The first phase consisted of a rapid initial loss that started immediately after application. In the second phase, after an equilibrium between the soil and the herbicide had been reached, a slower degradation process followed in which microbial degradation played a major role. Moorman and Harper (1989) found that the degradation rate of metribuzin in the 0-10 cm soil depth followed a second order kinetic, while the slower degradation in the subsoil followed a half-order kinetic. The metribuzin left in the 125-150 cm soil depth was 20.4% (versus 4% in the 0-10 cm soil depth). The conclusion was that metribuzin is not mineralized easily and since mineralization is a microbial process, most of the degradation that occurred in the subsoil was due to abiotic processes.

Moisture content has also been known to affect degradation. In a laboratory experiment done by Smith and Walker (1989), it was found that the degradation rate decreased as the moisture content of the heavy clay soil samples (70% clay, 5% sand) was lowered. At 25°C, the half-life was measured at 28 days with 40% moisture and 300 days with 8% moisture. The degradation rate also slowed down when the temperature was lowered. The latter results confirmed those obtained by Bouchard et al. (1982) and Hv7ak and Zymdahl (1974). Bouchard et al. (1982) measured half-life of 2.6 weeks during the summer in Arkansas, whereas the value rose up to 28 weeks during the winter months. In a study done in Québec, a carry-over of metribuzin after winter was observed (Bastien and Madramootoo, 1992).

The fact that soil characteristics would affect the half-life as stated by the U.S. EPA, was confirmed by the work of Allen and Walker (1987). Strong correlations of half-life with the Freundlich adsorption coefficient, the soil percentage of sand and clay and the soil organic matter content were obtained. The amount of soil organic matter was correlated with metribuzin adsorption (Peter and Weber, 1985). The adsorption rate was

measured in the range of 0.30 to 0.44 cm³/g (Allen and Walker, 1987). Adsorption isotherms were linear, indicating a constant partitioning of the herbicide between the solution phase and the absorbent phase (Peter and Weber, 1985). Soil pH was correlated negatively with adsorption in a study by Ladlie et al. (1976b). They concluded that increased leaching, mobility, degradation (also Hyzak and Zimdahl, 1974) and diffusion will occur when the pH is high because of decreased adsorption. Protonation of the cationic amine group leading to an increase in the adsorption would occur in acidic soils (Ladlie et al., 1976b, Weber, 1980). The maximum adsorption of metribuzin occured when the pH was between 4.0 and 5.0. This herbicide is considered more mobile than atrazine and alachlor because of its higher water solubility (1200 ppm) and lower basicity (Ladlie et al., 1976a; and Jones et al., 1990).

Conflicting results were obtained by different authors about the relationship between adsorption with various characteristics of the soil. Harper (1988) found a correlation with clay content but not with pH, the soil organic matter content and the sand percentage. Savage (1976) also found a correlation with clay content in 16 soil types of the Mississippi valley, but also with the soil organic matter and soil moisture. Peek and Appleby (1989) found a correlation with the sand percentage, leading to the conclusion that metribuzin will have its highest mobility in coarse-textured soils. The U.S. EPA (1988) came to the same conclusion, but also added that adsorption would be very low with low soil organic matter content.

Very few studies have been made on the desorption rate of metribuzin. Boesten and van der Pas (1983) measured desorption after adding a known amount of metribuzin to soil samples. They found that the desorption of the herbicide was 6 times greater, 51 days after the application than after 1 day. This value increases to 8 times after 121 days.

The diffusion of metribuzin was studied by Scott and Paetzold (1978). Their laboratory experiment was done with a silty loam soil. They found that the diffusion of the herbicide would increase with increasing moisture and increasing temperatures. In Iowa, an experiment was done where 0.56 kg/ha of metribuzin was applied in a soybean culture. The results of the study suggested that volatilization of metribuzin is not an important mechanism of transformation (Johnson and Baker, 1984).

The allowable human and animal consumption limit of metribuzin is fairly high, as shown in Table 2. No evidence of carcinogenic, mutagenic, embryonic, teratogenic, or fetotoxic effects were recorded (Pauli et al., 1990). However, aquatic plants seem to be more susceptible to toxic effects than vertebrates. This led to an allowable limit of $1 \mu g/L$ for aquatic life. These results should not undermine the environmental importance of subirrigation since it could promote the degradation of other more toxic pesticides.

Table 2. Recommendations of allowable limit of metribuzin.

Reference	Target media or organism.	Quantity (μg/L)
Santé et Bien-Etre Social Canada, 1989.	Drinking water	80
	Aquatic life	1.0
	Livestock	80
	Irrigation	0.5
U.S. Environmental Protection Agency, 1987.	For whole life	175
	Daily limit for child of 10 kg.	4500

Table 3. Chemical and physical properties of metribuzin.

Properties	Value	Reference	
Molar weight	214.3 g/mole	Worthing and Walker, 1987.	
Density	1.28 g/cm ³	Weed Sci.Soc.Am., 1983	
Fusion point	125.5 - 126.5 ℃	Worthing and Walker, 1987.	
рКа	1.1	Weber, 1980.	
K _{nw}	40	Worthing and Walker, 1987.	
Solubility at 20°C i	n:		
water	1.2 g/kg	Worthing and Walker, 1987.	
acetone	820 g/kg	Worthing and Walker, 1987.	
dichloro- methane	> 200 g/kg	Worthing and Walker, 1987.	
cyclohexanone	1000 g/kg	Worthing and Walker, 1987.	
methanol	450 g/kg	Weed Sci.Soc.Am., 1979.	

2.3 Use of metribuzin in Canada

The use of metribuzin is slowly increasing with time (Table 4). This could be due to increasing soybean production in Canada. Soybeans and potatoes are the crops where most of the metribuzin is being used. In the United States, it has been estimated that 94% of the metribuzin used in agriculture was for soybean production. Potato production accounted for only 1.8% of this herbicide use (U.S. E.P.A., 1985). The quantity of metribuzin applied, as for all other pesticides in Québec, was not available from Statistics Canada. Data for the amount of pesticides sold in Québec are grouped only by family of pesticides. However, from the size of land where potatoes are grown, from the statement that 40% of the potato growers in the 1'Assomption county were using metribuzin (Latreille et al., 1993) and from the application rate of metribuzin (0.25-4.0 kg/ha) (Smith et al., 1982), we can estimate that about 7000 kg of metribuzin was applied in

Québec in 1992 on agricultural land where <u>potatoes</u> were grown (land where soybeans were grown are not included). It is important to note that the application rate will vary with respect to crops and soil textural class (Peek and Appleby, 1989).

The regions of Montcalm and d'Autray (North of Montréal), Napierville (South-West), Nicolet and Drummond (Richelieu-Yamaska) are prone to important metribuzin ground water contamination since these are areas where both potatoes and soybeans, the two crops where most of the metribuzin is being used, are grown extensively (Statistics Canada, 1992). Therefore, the L'Assomption, Richelieu, St-François and Nicolet rivers would be the most prone to metribuzin contamination.

The monitoring of metribuzin in ground water has been limited. It seems that metribuzin is rarely detected in ground water and in the rivers. Baker (1985) stated that annual losses of triazines usually does not exceed 3% of the applied quantity. Metribuzin was not detected in 91 rivers draining in the Great Lakes (Frank et al., 1979). The same authors studied the Grand, Saugeen and Thames rivers located in the agricultural region of south-western Ontario. From 1981 to 1985, only 2% of the wells had detectable concentrations of metribuzin (Frank and Logan, 1988). In the United States, where metribuzin is used more extensively, the herbicide was found in 54 samples out of 240 samples coming from 14 different States. The concentrations were low and the maximum value obtained was 1.25 μ g/L (US EPA, 1987). Most of the high metribuzin concentration values obtained in North America resulted from accidental spills near or into wells. In the ground water of coarse-textured soils, concentrations as high as 3.5 μ g/L have been measured (Bastien and Madramootoo, 1992).

Table 4. Application of Metribuzin by province.

Province	Year of study	Total amount (metric tons)	Reference
Ontario	1978	60	Moxley, 1989
	1983	200	Moxley, 1989
	1988	258	Moxley, 1989
P.E.I.	1986	4.3	Seatech Investigation Services Ltd., 1988
Nova Scotia	1986	0.37	Seatech Investigation Services Ltd., 1988
New Brunswick	1987	2.5	Shanks, 1988.

2.4 Properties of prometryn

Prometryn is stable to hydrolysis in neutral, slightly acidic and slightly alkaline media. It has a lower water solubility and a greater adsorption capacity (K_{ijk}) than metribuzin. The latter characteristic was confirmed in a study done by Lafleur et al. (1975). It showed that prometryn is relatively immobile in soil. The study took place in a sandy loam field with a shallow water table. The soil upper 100 cm contained 31% of the applied prometryn after 16 months. The

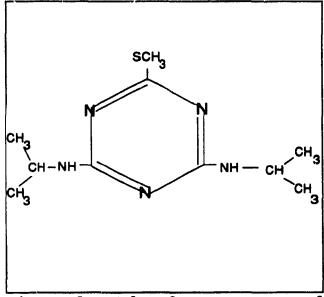


Figure 3. Molecular structure of the herbicide prometryn.

herbicide was measured in the ground water within 2 months of the application.

A study consisting of measuring the outflow of prometryn from lysimeters was also made by Lafleur (1976). One pore volume of water was added to the surface of the soil where prometryn had been applied 24 hours before. Most of the prometryn remained in the upper 40 cm of the soil.

According to Kozak et al. (1983), prometryn will be more strongly adsorbed to organic matter than metolachlor. Their adsorption experiment demonstrated also that, among all fractions of soil organic matter, the humic substances have the highest affinity for prometryn. The adsorption of this weak base (pK₄ of prometryn is 4.08) is strongly pH-dependant. Moreover, there is a high affinity of the organic matter for the prometryn at low concentrations.

Table 5. Chemical and physical properties of prometryn.

Properties	Value	Reference
Molar weight	241.4 g/mole	Worthing and Walker, 1987
Density	1.157 g/cm ³	Worthing and Walker, 1987.
Fusion point	118-120 ℃	Worthing and Walker, 1987
pK _a	4.1	Worthing and Walker, 1987
K _{ow}	2190	Worthing and Walker, 1987
Solubility at 20°C in:		Worthing and Walker, 1987.
water	0.033 g/kg	
acetone	240 g/kg	
dichloro- methane	300 g/kg	
toluene	170 g/kg	
methanol	160 g/kg	

2.5 Use of prometryn in Canada

The chemical name of prometryn is 2,4 bis(i.opropylamino)-6-methylthio-1,3,5-triazine. Its commercial name is Gesagard, Caparol or Prometrex. It is used as a pre-emergence (1.0-1.5 kg of active ingredient per hectare) or post-emergence (0.5-1.0 kg of A.I. per ha) herbicide for the selective control of annual dicotyledons and monocotyledons in the culture of carrots, celery and potatoes among others. No data concerning the quantity of prometryn sold in Canada or any other countries was available.

2.6 Impact of water table management on nitrate contamination

Nitrate contamination of ground water as a result of intensive fertilizer application has been recognized and confirmed for many decades now. Ground water is still used as the major domestic supply of water for 50% of the United States and 90% of the rural population of North America (Power and Schepers, 1989). Fortunately, between 1984 and 1990, the consumption of commercial fertilizers in Canada and Québec has remained fairly constant at about 2200 thousand tonnes and 260 thousand tonnes respectively (Statistics Canada, 1991).

Since 1989, a few studies have dealt with the relationship of agricultural water management with the quality of drainage effluent. They have primarily focused on ways to correct the situation, not through a reduction in the intensity of the fertilizer application but rather in the scheduling and the techniques used to apply the fertilizer. The evaluation of the Best Management Practice (BMP) has been investigated by many authors.

Best Management Practice studies often include ways to enhance denitrification (Wright et al., 1989) by keeping a high water table during the non-growing season so that a decrease in the nitrate concentration would not affect the crop yields (Protasiewicz et al., 1988). In the irrigated regions of the Great Plains of the United States, much of the leaching will occur during this time period when peak recharge volumes are obtained (Schepers et al., 1985). Ways of reducing the drainage volume was studied by Ritter et

al. (1991) on sandy loam soil. They applied half the optimum water required in irrigation and compared it with a full irrigation treatment. They noticed greater leaching rates in the fall and winter seasons, with the full irrigation system leaching four times more nitrate than the partial irrigation. They concluded that in the future, on that site, the nitrogen and irrigation management practices would have little impact on nitrate leaching, except if one over-irrigated or applied excessive rates of nitrogen.

The movement of nitrate ions through the root zone has been observed to occur in a wave-like fashion (Hubbard et al., 1991). A rainstorm or irrigation water may not move all the nitrate from the soil surface immediately after a nitrogen application. Instead, there may be one wave of nitrate movement by macropore flow following the first major water input after the nitrogen application, and a second more slowly advancing wave of nitrate leaching through the soil matrix from the soil surface zone. Therefore, the study of nitrate contamination in a given ground water supply must be accompanied by soil nitrate determination.

Current studies cover a wide spectrum of related topics. Power and Schepers (1989) noticed that in surface irrigated fields, the top end of a furrow will be irrigated for a longer time compared with the rest of the field leading to a greater recharge volume and, hence, more nitrate leaching. A reduction in the furrow length would, however, not be worthwhile economically.

Judging from the quantity of studies conducted, the research on the impact of nitrogen fertilization methods has been more popular than the studies on water management impact. Water-filled pore space in ploughed soil has been observed to often favour rapid mineralization and nitrification for over several days or even weeks after ploughing (Doran, 1987). It was found by Ritter et al. (1990) that continuous cultivation of soybean (4 years) decreased the nitrate contamination on sixteen irrigated sites where corn was also grown in the same time period. Poultry manure and ammonium nitrate were applied separately or jointly. Nitrate contamination of the ground water was measured

under corn cultivation Nitrate leaching would diminish if the nitrogen was applied on the elevated portion of a ridge (Hamlett et al., 1990). This ridge configuration would concentrate more runoff in the midrows and, therefore, more water would infiltrate below and away from the fertilized zone.

2.7 Summary

The literature review shows quite clearly the lack of studies done in Québec, and elsewhere, on the role of water table management in reducing the herbicide contamination of the ground water, on the behaviour of metribuzin in a coarse-textured soil, and the overall risk of ground water contamination in an organic deposit. This situation justifies the selection of the topic chosen in our research.

Most of the publications deal with the denitrification potential of water table management. This is the reason why analysis for nitrate was less extensive in our project than for herbicides.

CHAPTER 3. IMPACT OF WATER TABLE MANAGEMENT ON METRIBUZIN LEACHING

One of the major points of emphasis in this study was to investigate the role of water table management in reducing pesticide pollution in a mineral soil. Consequently, ar extensive field study was undertaken in 1992 to determine the impact of subirrigation systems on metribuzin leaching, a commonly-used herbicide on potato farms in Québec. This chapter includes site description, experimental set-up, physical and chemical properties of soils, methods of extraction and analysis, meteorological data, statistical analysis, results and discussion and finally, a brief conclusion. The raw data obtained from the Laurin farm in 1992-93 are presented in Appendix A.

3.1 SITE DESCRIPTION

The site description includes the location and pedology of the Laurin farm along with the cultivation practices. It also describes the water table management system at that farm.

3.1.1 Location and pedology of the site

Field experiments were conducted at the Laurin farm in Ste-Marie-Salomée located near Joliette (Québec) in the county of Montcalm, some 40 km north-east of Montréal. In 1992, the study was done using lots 398 and 399 for the subirrigation and lot 151 for the subsurface drainage treatment. The same subirrigated fields were used in 1993, but the subsurface drainage plots under study were relocated onto lots 226, 227 and 228. The experimental units were located on Achigan and St-Thomas soil series according to a pedologic map made by the Ministry of Agriculture of Canada (1965). These soil series cover around 2700 hectares (1.2% of total county area) and 520 hectares (0.23%) respectively in that county (Ministry of Agriculture of Canada, 1965). About 17,000 hectares of Achigan and St-Thomas soil were cultivated in the Northern Montréal region in 1991 (MAPAQ, 1991). The Achigan soil series is dominant in our experimental plots It consist of a ferro-humic orthic podzol which has from 90 to 180 cm layer of very fine

alluvial sand (about 60%), free of rocks, over a flat layer of marine clay (2 0 to 2.5 m deep). Common soil horizons found in our experimental sites are shown on Figure 4. The coarse and fine of fraction this sand soil represents, on average, 90% of the It has a naturally total mass. imperfect drainage occurring (MAPAQ, 1991).

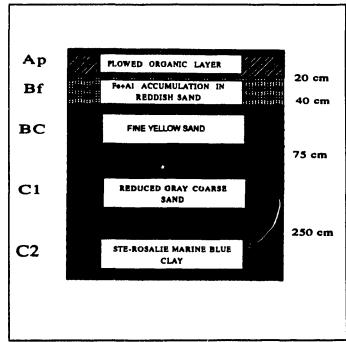


Figure 4. Soil horizons.

3.1.2 Cultivation

Potatoes (Wisconsin variety) are grown on a two-year potato, one-year grain crop rotation. Important fertilizer application is needed for this crop particularly when grown on sandy soils which are usually nutrient poor. The four fertilizer applications made during the growing season, total 1300 kg of 13-13-15-3 (N,P,K,Mg) per hectare. Lime has to be also added in order to slightly neutralize the acidic conditions prevailing in podzol soils so that the pH will be more suitable for potato production.

Metribuzin and other herbicides are used on the Laurin farm to control the growth of barnyard grass which competes with the potatoes. Numerous types of insecticides are used against infestation by the Colorado potato beetles.

Table 6. Typical timetable of agricultural events at the Laurin farm.

End of March, beginning of April.	Start of the snowmelt. Rainfall occurs often.
Beginning of May.	Planting of potatoes.
Beginning of May to the beginning of September.	Application of the herbicides.
End of May.	Ridging.
End of May, beginning of June.	Application of the herbicide metribuzin.
End of May, beginning of June.	Close the drainage control chambers.
Middle of June to the end of July.	Application of the insecticides.
Middle of July to the end of July.	Subirrigation.
Middle of July to the end of August.	Application of the fungicides.
End of August to beginning of October.	Harvesting.

3.1.3 Subsurface drainage system

Subsurface drainage systems are necessary in Quebec. It will remove the excess water resulting from snowmelt in the Spring, in order to allow the heavy machinery to be used on the field for planting and ridging (Table 6). It will also reduce the probabilities of damage to the crop related to shallow water table during the course of the summer. The drainage system was installed in both treatment sites in 1977. It consisted of placing 100 mm plastic tubing at a depth ranging from 90 cm to 150 cm (slope ranging from 0.1% to 0.2%). A drainage tube with a diameter of 150 mm was used for the collectors. Two drain spacing values were used on the subirrigated field. 36 and 18 meters. Only the areas having 18 meters drain spacing were studied for the subirrigation treatment. The fields used for the subsurface drainage treatment had 30 m spacing. In order to install the observation wells, the drainage laterals had to be found. This was done by using a

metal rod probe. This procedure had never been done in the past in these fields, so no records were available. This step was difficult and time consuming since a hard plough pan was present at a depth of about 45 cm. The engineering drainage plan was not helpful since the drain spacing could vary by 4 meters.

3.1.4 Subirrigation system

A subirrigation system was considered necessary in the Laurin farm so that enough moisture would be given to the potatoes during the dry month of July (Table 6). In 1989, control chambers for each drainage units were installed in lots 398 and 399 (area used for the subirrigation treatment analysis). These control chambers were built at the end of the collector and consisted of two wells and a system of panels. The water table in the field was measured using a small pipe installed nearby which acted like a house thermostat. When the water table is higher than the value desired, a system of panels in the control chamber would open the outlet of the collector, letting the excess water drain out. A total of 48 hectares of land had a controlled water table depth. The desired water table depth for a potato crop is between 75 and 90 cm. If it rises above that range, the potatoes could rot as they did partially in 1992. In a typical month of July, the evaporation is high and the amount of rainfall is low. A pump would then be activated by tractor power to bring the water from the nearby Vacher River to the control chambers, in order to raise the water table in the field. It was calculated that an irrigation flow of about 1500 litres per minute (30 litres per hectare per minute) was necessary for the hydrological conditions of this land (Kirschbaum, 1990). The pump power used by the farmer was not sufficient to substantially raise the water table in 1993. There is a 10 meter difference in elevation between the Vacher River from where the water was pumped, and the control chamber. The water table rose only when substantial rainfall occurred during the pumping as it happened in 1992. Metribuzin was not detected upstream from where the water was pumped. An artificial pond, to collect all the water coming out of the drainage system of the subirrigated treatment, was created. A metribuzin concentration of 0.4 μ g/L was measured in that pond on July 30th, 1992. On May 20th 1993, no detectable concentration was measured.

3.2 EXPERIMENTAL SET-UP

This section will first describe the statistical design used in the study and secondly, the actions taken on the field, namely, the installation of equipment and the sampling of ground water and soil (Table 7).

Table 7. Experimental set-up.

	1992	1993
No. of experimental units in subirrigated / subsurface drainage field	3/1	3/3
No. of sampling units per experimental unit	3	4
No. of sampling days	6_	7
Total no. of soil samples analyzed	321	513
Total no. of ground water samples analyzed	54	234
Total no. of samples analyzed	375	747

3.2.1 Statistical design

In 1992, three subirrigation experimental units and one subsurface drainage experimental unit were studied. The subsurface drainage experimental unit used in 1992 changed ownership at the end of our first year of study. Three experimental units were used for each of both treatments in 1993. Each experimental unit covered between 2 and 4 ha. The encircled numbers in the Figures 5 and 6 represent the experimental unit labelling used during our study. Soil and water samples were taken at the same location each time (repetitive measurements).

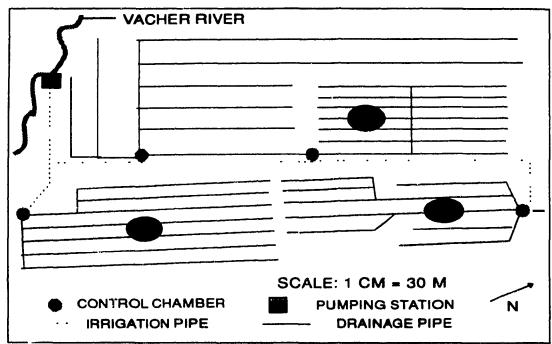


Figure 5. Schematic of the subirrigation experimental test plots used in 1992 and 1993.

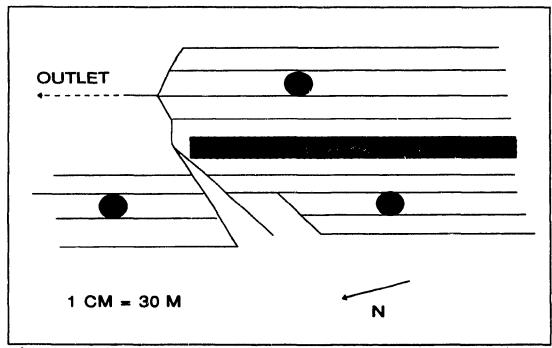


Figure 6. Schematic of the subsurface drainage experimental test plots used in 1993.

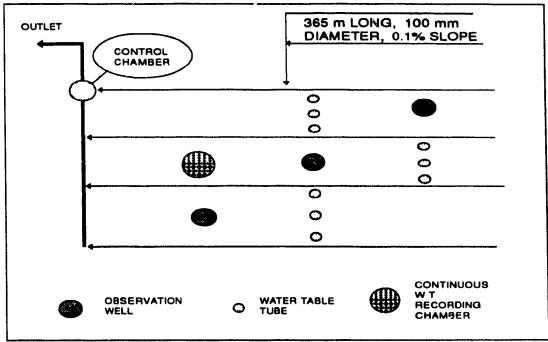


Figure 7. Experimental set-up used for every experimental unit.

3.2.2 Water table depth measurement

Three sets of three perforated PVC pipes (25 mm diameter), roughly 1.8 m long (with extensions), were installed in each experimental unit. For a given set, two pipes were placed one meter from the drain on each side of a corridor of land situated between two laterals (Figure 7). The third pipe was installed at mid-spacing A graduated rod linked with a water sensitive electrode and an audible alarm was used to measure the water level inside the tubes. When this level was too low to be read, the water table depth measurement was taken from inside the closest observation well. Moreover, one perforated, corrugated drainage tubing (250 mm diameter) was installed per treatment. Continuous, automatic water level recorders were installed in these wells. The recorder consisted of a small tensiometer contained within a box. A pulley, which was bolted to the box, supported a wire which had attached to its ends a floater and a counter weight As the water table rose, the pulley turned, affecting the reading of the tension inside the box. A computerized system recorded and converted the tension to water table depths. A portable computer was brought to the field and used to download all of the

readings. Measurements were taken every 6 hours in 1992 and every 4 hours in 1993. Unfortunately, electrical problems occurred in these dataloggers, so that the water table was not monitored in its entirety during both summers

3.2.3 Ground water sampling

Three observation wells, consisting of 100 mm corrugated plastic tubing surrounded by a net, closed at the upper opening by a plastic cap, and sitting at a depth of about 140 cm were installed for each experimental unit in 1992. The pipes were located in the crop rows at mid-spacing. On the sampling day, the water present in the wells was removed with the help of a bailer. A few minutes after, when the water had the time to move back to its original level, the water samples were collected (about 500 ml) with the use of a plunger. The samples were transferred to their respective plastic bottle and kept in a refrigerator (4°C) until analysis for the pesticide could be done. Dichloromethane (10 ml) was added to each sample before storage. The presence of this solvent prevented the decomposition of the pesticide.

In 1992, the water filling up a given observation well after the water had been removed was coming from the saturated zone (from the initial water table depth to the bottom of the observation well). Hence, it was impossible to determine the concentration gradient with respect to the depth from which the water was coming. A different experimental setup was implemented in 1993 for the collection of water samples. Corrugated plastic tubings were replaced by non-perforated sev ge pipes that also had an inner diameter of 100 mm. The upper openings were closed so that pesticides being sprayed would not fall directly into the well. Three sets of four observation wells were installed in each experimental unit of the subirrigated treatment. Three sets of three observation wells were installed in the subsurface drainage treatment. The observation wells for a given set were installed at mid-spacing and were at different depths: 80, 120, 160 and 200 cm below the soil surface. The water coming into the well could enter only from the bottom end of the pipe. About 30 cm of pipe length was coming out of the soil surface in all pipes installed. The 80 cm pipes were not installed in the subsurface drainage treatment

since water had not reached that depth in the same treatment in 1992. Unfortunately, the 1993 season was much drier than in 1992, and the pipes sitting at depths of 80 cm and most of the ones at 120 cm were useless in both treatments since the water table did not reach these depths.

3.2.4 Soil sampling

The soil samples were collected in the crop rows by using a 5 mm auger. The samples were taken always in the vicinity of an observation well (about 10 meters radius) and were labelled accordingly. Therefore, in 1992, three sampling units were under study per experimental unit at four different depths: 0-20 cm, 20-40 cm, 40-60 cm and 60-80 cm. The samples were transferred into their respectively labelled plastic bags where they were frozen until extraction and analysis. The samples were never kept frozen for more than three months. In the first year of the study, the results showed low pesticide concentrations at depths of 40-60 cm and 60-80 cm, leading to the decision that in 1993 the collection of the soil samples would be made at four locations at three depths (0-20 cm, 20-40 cm, 40-60 cm) per experimental units.

3.3 PHYSICAL AND CHEMICAL PROPERTIES OF THE SOIL

One of the most important features of a pesticide behaviour analysis, along with meteorology, is the physical and chemical properties of the soil. They will affect to a great degree the rate at which a given herbicide will leach and be degraded. The following sub-sections will describe several soil properties: the saturated hydraulic conductivity, the soil moisture retention, the soil moisture content, the particle size analysis, the pesticide adsorption coefficient, soil pH and soil organic matter. The predicted behaviour of metribuzin under such a soil environment followed by tables which summarize the chemical and physical properties of the soil (Table 9a and 9b) will conclude this sub-chapter.

3.3.1 Soil saturated hydraulic conductivity

The auger hole method, as described by Van Beers (1983), was used to measure the

saturated hydraulic conductivity of some sites. When digging a vertical hole into the soil, the soil on the sides tended to collapse when the water saturated zone was reached. Consequently, a metallic perforated casing was used wherein an auger could dig the soil from lower depths. This casing had aligned holes at its upper end, so that a metal rod could be inserted through its diameter (100 mm) which served as a handle to twist down the pipe into greater depths. Before starting any measurement of hydraulic conductivity, the observation well had to be at least half full. The only time this condition could be fulfilled was in early Spring, late Fall or during the sub-irrigation period.

The saturated hydraulic conductivity was calculated using the Ernst equation on the portion of the curve where a constant rise of the water table versus time occurred. The calculated saturated hydraulic conductivity values (calculated in soil depths between 1.0 and 1.5 m) were 1.24, 1.40 and 1.33 m/day for the observation wells Sub 2.2, sub 2.1 and dr 2.2 respectively. These results are within the range of the 9 values obtained by the Soconag engineering firm (Kirschbaum, 1990), which had found, in the vicinity of our experimental area, values ranging between 1.1 and 2.1 m/day, with an average value of 1.43 m/day. Hence, drainage in the subsoil is fairly rapid. However, the infiltrating water will accumulate at the impermeable clay layer thereby causing ponding problems in early Spring and late Fall.

3.3.2 Soil moisture retention

The soil moisture retention was performed by using two different techniques: the Hayne's funnel method described by Vocomil (1965) followed by the pressure plate method described by Richards (1965). Soil cores were taken from three depths in two locations from two experimental units of each treatment using a metallic cylinder (diameter of 5 cm and length of 4 cm), a hammer and a wooden plane surface. A piece of geotextile was placed on both ends of the cylinder and attached with a rubber band. The samples were then individually placed in a container which had about 3 cm deep of distilled water. The samples were left for 24 hours to reach water saturation. They were

transferred onto a porous plate of a Havne's funnel that had been previously equilibrated. The geotextile was removed and replaced by a filter paper (Whatman 4). The water level in the burette was read for each increment of 15 cm of negative head. up to a value of 105 cm or 0.105 bar. The system was given enough time (usually 24 hours) for the outflow of water to stop before each change in the tension. The force applied to the sample had to be corrected since it is equal to the difference in height between the soil sample and a fixed point of the burette minus the rise of

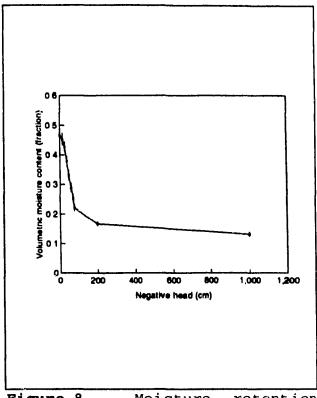


Figure 8. Moisture retention curve.

the water level in that burette. The maximum tension applied with the Hayne's funnels was then: 105 cm - the rise of the water (about 30 cm) = 75 cm. A substantial amount of water was still present in the soil samples with this tension. In order to complete the water retention curves, pressure plates were used.

First, the soil samples were removed from the Hayne's funnels and saturated again. Geotextiles were used again to prevent loss of soil during this 24 hour period. The saturated soil samples were removed from the water container and weighed (the geotextile was replaced by a Whatman 2 filter paper). They were then transferred onto a circular porous plate which had a diameter of about 30 cm that was previously saturated. Finally, this was transferred into a pressure plate system. The latter consists of a circular metal container to which a lid is bolted. A fine metal tube (diameter of about 0.5 cm) is connected to the side of the pressure plate. It is from that opening that compressed air will enter the chamber via a gauge. The pressure applied onto the samples will draw

down the water through the porous plate and out of the chamber by a tube linking the porous plate to an outlet outside the chamber.

The average moisture retention curve of the 12 samples is shown in Figure 10. There was no significant difference in the curve shape with respect to the depth or location of the sample From this curve, we can make the following observations:

- 1) The soil porosity ranges from 45% to 50%.
- 2 Only 70 cm of head applied to a saturated sample is sufficient to draw down 50% of the water contained in that sample.
- 3) About 200 cm of head applied to a saturated sample is sufficient to draw down 60% of the water contained in that sample.

3.3.3 Soil moisture content

Thawed soil samples were weighed and transferred into metallic containers, and were kept in an oven for 24 hours at a temperature of 120°C. The mass of the soil samples was measured after this period of time. The loss of mass was considered to be due solely to water evaporation. The method used was taken from Gardner (1965).

3.3.4 Particle size analysis

Since the proportion of sand was known to be around 90%, it would have been irrelevant to use the hydrometer method to determine its clay and silt fraction (the settlement of the soil particles would have been too rapid). A "wet sieving" procedure was used as described by Day (1965) except that the soil samples were not dispersed with a CALGON solution prior to the analysis. Sieves of 425, 250, 150 and 75 μ m size were weighed and then inserted on top of each other. A weighed soil sample was then placed onto the coarser sieve. A continuous water flow was then applied for about one minute, while shaking the sieves. The sieves were then dried at a temperature of about 120°C for one hour and were then weighed again. The cumulative sand mass measured for each sieve was then transferred to a graph where the coarse and fine sand fraction was read

by intrapolation (Figure 9). However, this is just an approximation since the International Soil Classification use the particle diameter of 20 μ m as the boundary between silt and fine sand. Hence, the calculated silt + clay fraction is slightly overestimated since it covers also the range between 75 μ m (finest sieve used) and 20 μ m. The coarse and fine sand fraction constituted 40% (\pm 17%) and 52% (\pm 13%) respectively.

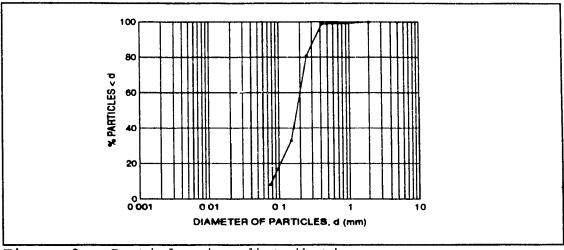


Figure 9. Particle-size distribution curve.

3.3.5 Pesticide adsorption coefficient

The adsorption coefficient of metribuzin on the exchange sites of our soils was determined by the method described by Bowman (1989). Four metribuzin solutions in water were prepared (1.0, 2.5, 5.0 and 10.0 ppm). Then, six grams of oven-dried, sieved soil samples were transferred into a test tube and 30 ml of standard solutions was added. Triplicate samples were prepared. The mixture was then centrifuged at 12,000 rpm for 20 minutes before letting it sit undisturbed for 24 hours A sample was taken from the supernatant from which it was analyzed with the gas chromatograph. The concentration obtained in the solution was subtracted from the pesticide concentration in the standard solution that was applied in order to measure the amount of pesticide that was adsorbed onto the soil. The results obtained best followed the Freundlich adsorption isotherm (Figure 10). Its logarithmic, linear equation is:

$$\log (X|M) = \log K_a + N \log C_s$$
.

where X amount adsorbed by the adsorbent (ug)

M mass of the adsorbent (g)

K_a soil-water partitioning coefficient (μg 'g ml')

N constant indicating degree and direction of curvature of isotherm

C equilibrium concentration (after adsorption) (μg ml)

In this equation, the slope will be equal to N, whereas the Y-intercept will be equal to $\log K_a$. In our analysis, the results obtained were

Depth (cm)	N	K_a (cm ³ /g)	r_
0-20	0.77 + 0.04	2.85 ± 1.07	0 997
20-40	0.85 ± 0.07	2.35 ± 1.13	0 993
40-60	0.87 ± 0.09	2.34 ± 1.17	0 989

As for most pesticides (Bowman, 1989), the N value obtained is lower than 1. Since, it is close to this value, the units of K_d will be cm^3/g . The K_d values obtained show that metribuzin would be more strongly adsorbed by the soil particles at a depth of 0-20 cm. This could be due to higher organic matter content at that depth

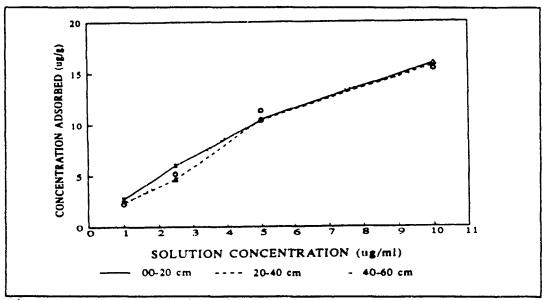


Figure 10. Adsorption isotherm of metribuzin.

3 3 6 Soil pH

The measurement procedure of soil pH was taken from Black, 1965. The soil samples were oven-dried and sieved before measurement of pH. Samples of 10 grams of soil were transferred into a glass bottle. Then 10 ml of distilled water was added to the bottle. After mixing the solution, the sample was left undisturbed for 30 minutes. pH readings were taken in the supernatant phase. The results obtained were

0-20 cm depth
$$5.0 \pm 0.3$$

20-40 cm depth: 4.8 ± 0.4
40-60 cm depth 4.7 ± 0.1

The relatively higher pH values obtained in the upper soil horizon results from liming. The natural pH values of this soil series would have been more acidic at the 0-20 cm horizon, and the pH would have increased with depth (Ministère de l'Agriculture du Canada, 1965).

3.3 7 Soil organic matter content

The soil organic matter content was measured by using a gasometric carbon analyzer (LECO Co., St-Joseph, Michigan, U.S.A.) as described in Carr (1973). A weighed sample (0.10 to 0.20 g. of oven-dried and sieved soil) was placed in a ceramic crucible and burnt in an induction furnace inside a completely enclosed combustion tube through which oxygen passed. Iron and tin were added to the samples to optimize this combustion process in which all of the carbon in the sample is converted to CO. This gas will displace sulphuric acid contained in a burette. The conversion from organic carbon dioxide (% C) to organic matter (% O M) was calculated by the following equation:

$$\% O.M. = \% C * 1 724$$

The volume of liquid displacement in the biuret was corrected for ambient temperature and pressure. The results obtained for our samples were:

Soil depth	# samples	ave. % O.M.	std.dev.
0-20 cm	4	4.46	0.94
20-40 cm	3	3.32	0.27
40-60 cm	4	1.13	0.46

3.3.8 Metribuzin-soil interaction

From the metribuzin properties covered in the literature review and the description of the physical and chemical properties of the soil dominant in our experimental study, a prediction of the mobility of metribuzin in such a soil environment can be made.

The adsorption of metribuzin onto the exchange sites of the soil particles would theoretically be very high. The soil pH values found in the field (5.0) are within the range at which protonation of metribuzin will occur, leading to maximum adsorption. A more dominant type of adsorption would be the interaction with amorphous metal oxides of iron and aluminum which have accumulated with time in the podzolic B horizon. The surface charge of these oxides responds to the type and activity of the ions in the ambient solution (pH dependant). The protonated metribuzin would bind with these oxides even if they would be positively charged, indicating that there must be physical (hydration, van der Waals) or chemical (covalent) forces involved in the specific adsorption (Kinniburgh, 1975). However, both types of adsorption are relatively weak when compared with other pesticides, as the metribuzin K_{ow} value indicates (Table 8)(the lower is the K_w value, the greater will be the mobility of the pesticide). Moreover, the low C.E.C. will limit the amount of metribuzin being adsorbed. The portion of the herbicide which is not fixed will be present in the soil solution where it could be easily leached due to its relatively high water solubility and to high soil saturated hydraulic conductivities.

Table 8. Octanol-water partitioning coefficient (K_{ow}) of various pesticides (Worthing and Walker, 1987).

Pesticides	K _{ow}	Pesticides	K _{ow}	
Dicamba	3	Atrazine	219	
Metribuzin	40	Phorate	832	
Simazine	91	Prometryn	2190	
Propanil	193	Metolachlor	2820	

Table 9a. Summary of the chemical and physical properties of the soil. Experimental results.

	SOIL DEPTH					
Properties	0-20 cm		20-40 cm		40-60 cm	
	ave.	std. dev.	ave.	std. dev.	ave.	std. dev.
Bulk density (g/cm ³)	1.32	0.05	1.31	0.11	1.48	0.09
Total porosity	50.7	2.8	50.3	3.5	45.0	5.2
Saturated hydraulic conductivity (m/day)	1.1-2.1 m/day with an average of 1.32 m/day measured at depths ranging from 1.0 to 1.5 m.					
Adsorption coeff.(cm ³ /g)	2.85	1.07	2.35	1.13	2.34	1:17
рН	5.0	0.3	4.8	0,4	4.7	0.1
Organic matter (%)	4.5	1.0	3.3	0.3	1.1	0.5

Table 9b. Results from the description of the St-Thomas soil series (MAPAQ, 1991).

·	SOIL DEPTH		
	0-20 cm 20-40 cm		
Sand, silt, clay proportion (%)	89, 6, 4	94, 2, 4	
Cation Exchange Capacity (meq/100 g.)	11.8	7.0	
C/N ratio	13.9	11.2	

The methods used to determine the chemical properties from the MAPAQ data are: 1) Soil texture wet sieving,

- 2) Cation Exchange Capacity: Mehlich extraction,
- 3) Carbon. Walkley-Black digestion,
- 4) Nitrogen: Sulphuric acid & hydrogen peroxide digestion.

3.4 Methods of extraction and analysis

The methods of extraction and analysis for both metribuzin and nitrate-N are described in this section. Different extraction methods were used not only because we dealt with different compounds, but also with different matrices that of soil and ground water.

3.4.1 Metribuzin extraction

The extraction procedure was that outlined by Dupont and Khan (1992). From 15 to 20 g. of soil, which was initially thawed at room temperature, was transferred into a 250-ml Erlenmeyer flask and mixed with 100 ml of pesticide grade methanol. Each flask was shaken on a rotary shaker for 90 minutes at a speed of 300 rpm. The mixture was filtered under vacuum through a Whatman 5 filter paper supported by a Buchner funnel. The filtrate was transferred into a round-bottom flask and attached to a rotary evaporator in order to remove the methanol. A constant temperature of 40°C was kept in the water bath. After all the organic solvent had evaporated, 8-15 ml of methanol was used to dissolve the pesticide which remained inside the round-bottom flask. Hence, the final concentrations of the pesticides were roughly ten times greater after this step. The final

product was stored in a 20 ml glass container and kept refrigerated until it could be analyzed with a gas chromatograph.

The herbicide was extracted from the ground water samples by the following extraction procedure. About 300-500 ml of water was poured into a separatory funnel along with 100 ml of dichloromethane (pesticide grade). The solution was hand shaken and excess gas was expelled. Two phases will form in the funnel since dichloromethane has a specific density greater than water. The herbicide would collect in the organic solvent phase, since it has a higher solubility in dichloromethane. The dichloromethane phase was transferred into an Erlenmeyer flask. An additional 100 ml of dichloromethane was added to the water left in the funnel. The mixing procedure was repeated, and this extra 100 ml of pesticide-containing organic solvent was added to the volume resulting from the first extraction (total volume of 200 ml). The solutions were kept in the refrigerator until further use. The next step was the evaporation of dichloromethane by using an evaporator as described above. Methanol was used as the final matrix.

3.4.2 Metribuzin analysis

The method used for the analysis of the metribuzin was that described by Dupont and Khan (1992). A Varian 3400 gas chromatograph equipped with a Thermal Specific Detector (TSD) was used with a Megabore DB5 column (30 m length) having a film thickness of 1.5 μm. The detector and injector temperatures were set at 285°C and 190°C respectively. The column had an initial temperature of 90°C which was increased to 260°C by increments of 10°C/min. Under these conditions, the retention time of metribuzin was 13.3 min. The three metabolites of metribuzin (DA, DK, DADK) needed a special extraction procedure for their eventual analysis. Since our financial resources were limited, these metabolites were not examined in this study. Analytical standards of metribuzin and its three metabolites were furnished by Miles Inc., Kansas City. Standard solutions with concentrations of 1.0, 0.5 and 0.2 ppm of metribuzin in methanol were prepared. The standards were injected once for every 12 samples. A strong (97-99%) correlation was obtained when plotting the logarithmic value of the area versus the

logarithmic value of the herbicide concentration. The concentrations in the soil are presented in the thesis on a dry soil basis.

In the extraction and evaporation procedures, losses of the pesticide will occur. The recovery rates were calculated from soil samples. Measured concentrations were divided by the calculated values. The results show recovery rates of 88% \pm 5%. The detection limits were 10 μ g/kg in soil and 0.10 μ g/L in ground water.

3.4 3 Nitrate extraction and analysis

The soil samples were kept in a plastic bag under a sub-zero temperature (-10°C). On the day during which a given sample was to be analyzed, it was thawed at room temperature Between 15 to 20 g. of soil was transferred into a 250 ml Erlenmeyer flask and 100 ml of 1 0 N KCl solution was added. The samples were mixed on a rotary shaker at 300 rpm for one hour. The solutions were filtered through a Whatman 2 filter paper and poured into a light-resistant glass container. The filtrate solutions were kept in a refrigerator until they were analyzed with a Technicon colorimeter (used a Cadmium reducing tube) (Keeney and Nelson, 1989). Nitrate concentration in water was measured directly with the use of an ion-selective electrode.

3.5 METEOROLOGICAL DATA

The rainfall and maximum and minimum temperatures data were acquired from the meteorological station at l'Assomption. The reference evapotranspiration was calculated by using the Baier and Robertson equation (1965):

 $ET_0 = 0.094*[-87.03 + 0.928*T_{max} + 0.933*Range + 0.0486*Q_0]$

where ET_o: Reference evapotranspiration (mm/day),

T_{max}: maximum daily temperature (°F),

Range: difference between the maximum and minimum daily temperature (°F),

O_a: extraterrestrial radiation (Langleys)(latitude of 46°).

The reference evapotranspiration was then multiplied by the crop factor to obtain evapotranspiration (ET). The crop factor changes over time as the vegetative cover varies which was determined by Doorenbos and Pruitt (1977). From the planting (April 28th to May 6th) to a 10% vegetative cover (time period of 30 days), the crop factor remains constant at a value of 0.51. The factor increases linearly from a value of 0.51 to 1.05 after 35 days when the vegetative cover reaches 75%. The value of 1.05 is considered to remain stable until maturity (50 days). Then a linear decline of the crop factor value will occur from a value of 1.05 to 0.70 (31 days), at the day of harvesting (September 9th to September 14th). The daily water balance was calculated by subtracting rainfall with evapotranspiration for a given day. The total amount of rainfall was similar in both summers (363 mm and 338 mm in 1992 and 1993 respectively), but there was 2.4 times

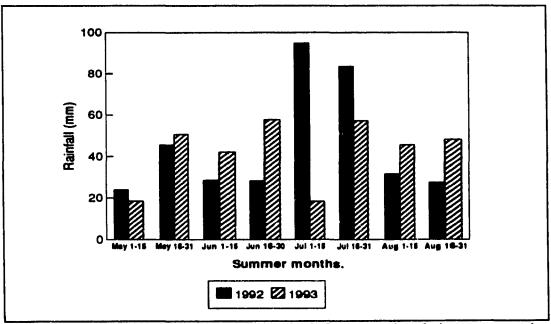


Figure 11. Total amount of rainfall received in two weeks during the summers 1992 and 1993.

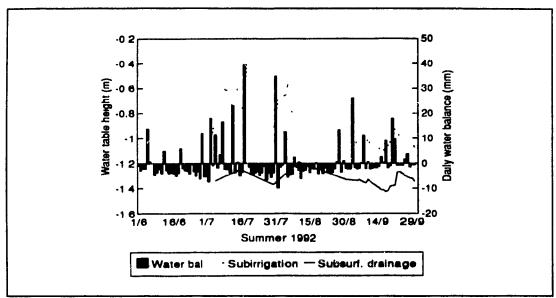


Figure 12. Water table fluctuation in 1992.

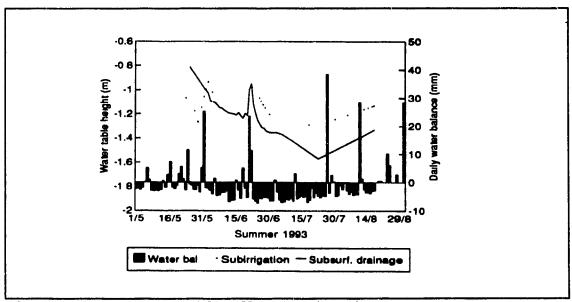


Figure 13. Water table fluctuation in 1993.

more rainfall in the months of July in 1992 than in 1993 (178 mm versus 75 mm)(Figure 11). This is important since July is a critical month when drought can cause the farmers to subirrigate. Even though there was an important amount of rainfall in the summer 1992, the farmer, who participated in the study, did subirrigate, leading to the very high water table values recorded (Figure 12). In addition to the much drier conditions, the

subirrigation system was not very effective in 1993, (the pump broke down after three weeks) and consequently much lower water table depths were recorded in that year during the same period of time (Figure 13). A second observation is that 1.7 times more precipitation occurred in 1993 within 14 days of the pesticide application (59 mm versus 34 mm), when the concentration of the pesticide was at its highest value. This is very important since it would lead to massive leaching to lower soil depths and to the ground water in both treatments in 1993.

3.6 STATISTICAL ANALYSIS

Statistical analysis was performed by the SAS system. Since the soil and water samples were taken at the same location at different times, the analysis was done by using the REPEATED statement. A multivariate analysis was performed (MANOVA) by using the GLM procedure. However, due to a lack in the degree of freedom, some of the multivariate test were not performed. The effect of the treatment, depth, and time were tested individually and in conjunction for its impact on pesticide concentration and soil These statistical probabilities, shown in section 3.7.1 6, moisture content. calculated on two different time scales: the impact on the whole summer (Tables 13 and 14) and on a sampling day basis (Tables 15 and 16). The probabilities shown in the tables are significant if their value is lower than 0.0500. Only the values obtained after pesticide application were used in the statistical analysis. Moreover, since the day of application was not the same for both treatments in 1993, the results were phased accordingly (same number of days after application but not the same day in the calendar). The values of the Greenhouse-Geisser and Huynh Feldt epsilons were calculated in all statistical analysis. Their value was extremely low in the depth*time relationship in the soil analysis in 1993 showing that heteroscedasticity was present (not common variable standard deviation). A "classical" statistical analysis would not have been suitable for such a condition.

3.7 RESULTS AND DISCUSSION

This section is divided into two main sections: 1) the results of metribuzin analysis and 2) the results of the nitrate-N analysis. A brief conclusion will follow each section.

3.7.1 Results of metribuzin analysis

The results of metribuzin analysis will be shown chronologically and will contain values obtained from the ground water and soil samples. All the tables and graphics representing the raw field data are shown in Appendix A. A laboratory metribuzin degradation experiment section is presented between the results sections of 1992 and 1993.

3.7.1.1 Metribuzin in ground water - 1992

The results obtained for the ground water in 1992 were the only group of data in the two-year study for which a significant impact by the treatment was observed (p=0.0134). The maximum metribuzin concentration obtained in the ground water taken from the subirrigated field was 7.8 μ g/L, whereas values of up to 29.4 μ g/L were recorded for the subsurface drainage treatment. In general, higher levels were measured under subsurface drainage than under subirrigation systems.

As expected, the water table was generally higher in the subirrigated plots than in the drainage plots (Figure 12). In addition, as shown in Figures 14 and 15, the herbicide concentration in ground water is low when the water table is at a shallow depth, and viceversa. Thirdly, it appears that the metribuzin concentration in subirrigated plots (Figure 14) is time-independent (p=0.1773) Water samples collected one month and three months after application, with similar water table depths, had similar concentrations. It appears that a continuous downward flow of water containing some herbicide counterbalanced the degradation rate in the ground water. This interpretation could be supported by the observation that there was frequent rainfall during the month of July 1992.

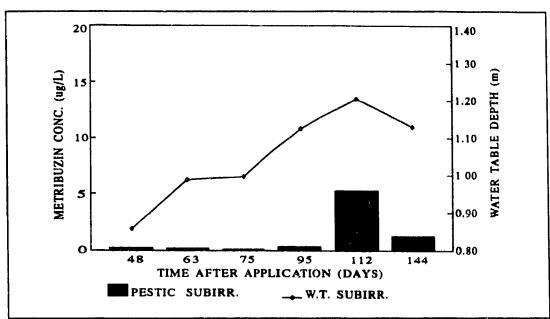


Figure 14. Metribuzin concentration in ground water in the subirrigated field (1992).

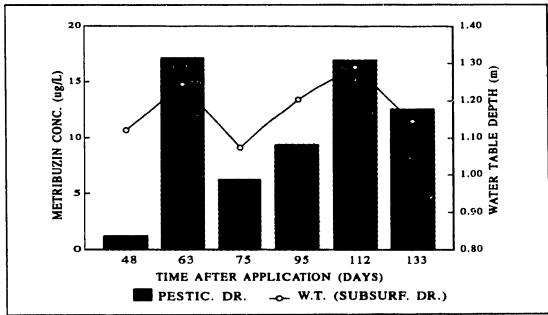


Figure 15. Metribuzin concentration in ground water in the subsurface drainage field (1992).

The metribuzin concentration is plotted in Figure 16 as a function of the water table depth without regard to when these average concentrations were obtained. A direct linear relationship between the logarithmic value of the metribuzin concentration in the ground

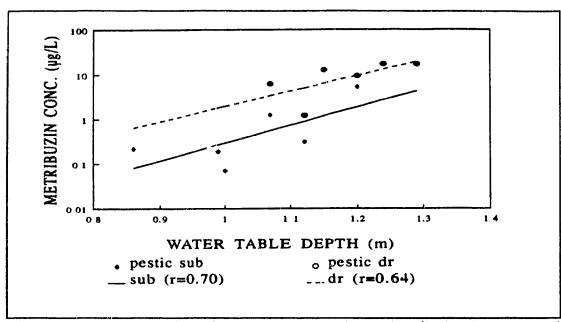


Figure 16. Metribuzin concentration ($\mu g/kg$) in ground water versus water table depth.

water and the water table depth is observed (log-linear relationship). The resulting correlations are good, r=0.64 and 0.70 for subsurface drainage and subirrigation treatment respectively. We can also note from this graph that, for a given water table depth, the metribuzin concentration in the subirrigated field will be lower than in the subsurface drainage field. The reason could be that sufficient moisture is needed for biodegradation to occur, and since the moisture content in the unsaturated zone was greater in the subirrigated plot, we could expect a greater biodegradation rate in this zone. Therefore, when rainfall would occur, less pesticide would have been available in the subsoil to leach downward into the ground water.

3.7.1.2 Metribuzin in soil - 1992

The metribuzin residue left from the previous year's application (carry-over) was low. It was measured to be 12 μ g/kg and 7 μ g/kg in the 0-200 mm and 200-400 mm soil depths respectively.

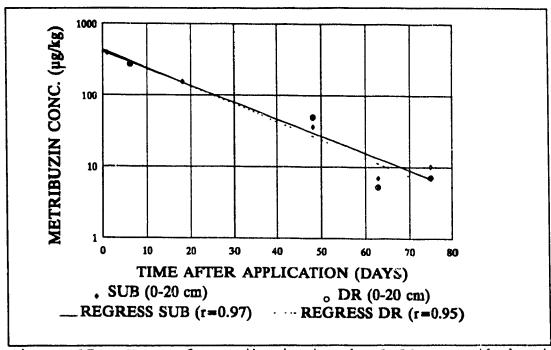


Figure 17. Fate of metribuzin in the 0-20 cm soil depth (1992).

The metribuzin concentration from the application was measured to be 350 μ g/kg. The calculated initial concentration is similar to the values obtained on the field. We can calculate the initial application with the following conversions:

The metribuzin concentration decreased logarithmically with a half-life measured to be 14 days. This disappearance includes the processes of biodegradation, abiotic degradation, volatilization and leaching. The rates of disappearance in the 0-200 mm soil depth from both treatments were found to be almost identical (Figure 17) Moreover, it was noticed that the metribuzin concentration in the topsoil (0-200 mm) was

greater than expected when the cumulative water balance of the soil system was in a net deficit (Figure 18). The cumulative water balance was given an initial reference value of zero on May 1st, and was then calculated by adding up the daily evapotranspiration. The increase in metribuzin concentration could be due to the upward pull of the water by the plants when dry conditions exist. This movement of water would entrain the herbicide that has leached to lower depths (200-400 mm). The second and most probable reason for this result could be the desorption of metribuzin over time which has been described in the literature, as we have seen in our review (Boesten and Van der Pas, 1983).

For the 200-400 mm depth, the concentration levels in both treatments were beginning to deviate from each other but not significantly (p=0.0618). Even when the concentrations were statistically analyzed separately according to the soil depth and sampling day, there was no significant impact of the treatment. Slightly greater metribuzin concentrations in the subsoil were measured in the subsurface drainage system. As mentioned before, this could be due to higher degradation in the subirrigated field.

It seems from the above discussion that subirrigation systems may reduce pollution from agricultural farms. What appears to be happening is that with subirrigation we are maintaining a high moisture content in the soil, which in turn leads to higher adsorption of the herbicide, and thus higher microbial degradation. This could be proven with the laboratory degradation experiment that we have initiated.

3 7 1.3 Laboratory degradation experiment

In 1992, the metribuzin concentration in the ground water was found to be much greater in the subsurface drainage treatment than in the subirrigated treatment. A greater dilution factor in the subirrigated field could not have accounted solely for these results since the relationship between the concentration and the water table depth was logarithmic. A linear increase of the water table depth would have only a linear reduction on the pesticide concentration. Two hypothesis were formed: first, there was

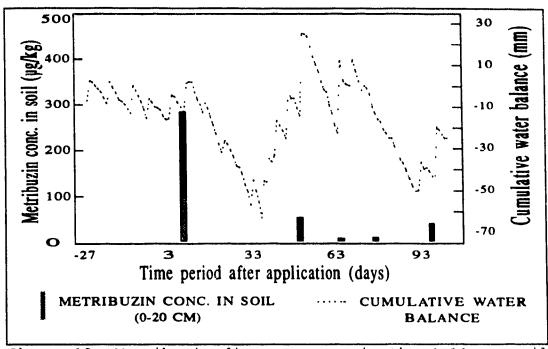


Figure 18. Metribuzin disappearance in the 0-20 cm soil depth with respect to the cumulative water balance (1992).

greater leaching when rainfall occurred in the subsurface drainage treatment due to lower water table depths, and, secondly, there was more degradation in the subirrigated field since the moisture content in the unsaturated soil was greater, and, therefore, there was less pesticide to be leached to the ground water when precipitation occurred. In order to test the second hypothesis, a degradation experiment in the laboratory was performed where leaching and evaporation of the pesticide would be nil. It would include the microbiological and chemical (abiotic) degradation.

Soil samples were collected near our experimental plots, where no metribuzin had been applied. Samples were taken at three different depths, stored separately in plastic bags and brought to the laboratory. The samples were not frozen nor oven-dried, but kept at room temperature. The soil samples were mixed inside their own bag to homogenize the sample as much as possible. Thirty-six (36) soil sample each weighing between 15 and 20 g. from each depth were transferred into 50-ml light resistant glass bottle. Three metribuzin solutions were prepared: 1.5, 2.5 and 5.0 mg/L of metribuzin in water. The

soil samples were subjected to the following treatments:

- T1. Add 1.5 ml of 5.0 mg/L of standard solution.
- T2. Add 3.0 ml of 2.5 mg/L of standard solution.
- T3. Add 5.0 ml of 1.5 mg/L of standard solution.

The total amount of pesticide applied to every sample (volume * concentration) was the same, 7.5 mg. The difference in the treatments comes from the volume of contaminated water being applied, which varies the moisture content of the sample. The soil volumetric water content was calculated to be approximately 40%, 60% and 100% for T1, T2 and T3, respectively. The moisture content was kept constant by sealing the bottle with a lid. This lid was removed only for one minute every week for all samples so that oxygen would not be depleted inside of the bottles. The three different treatments were applied on each of the three depths in triplicate per sampling day. Enough samples were prepared so that the pesticide concentration decline with time could be monitored on four sampling days. Hence, we had:

3 depths * 3 samples per depth * 3 treatments * 4 sampling days

The samples within a given bottle were extracted only once since it contained just enough soil sample to be extracted by following the same extraction procedure as we had followed with the soil analysis from the field. Since all the sample in a given bottle was used in the extraction by methanol, we eliminated the error of heterogeneity of pesticide application to the sample. Concentrations were expressed as percentages of initial metribuzin concentration at their respective depth.

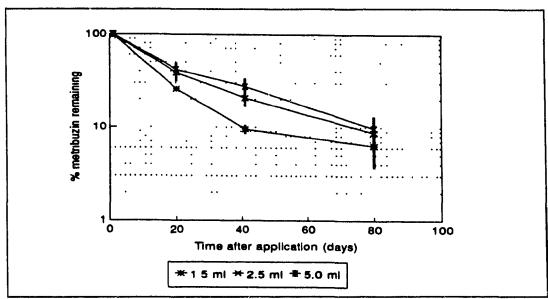


Figure 19. Metribuzin degradation in soil (0-20 cm) in the laboratory experiment.

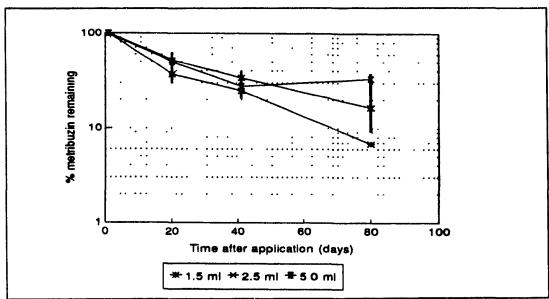


Figure 20. Metribuzin degradation in soil (20-40 cm) in the laboratory experiment.

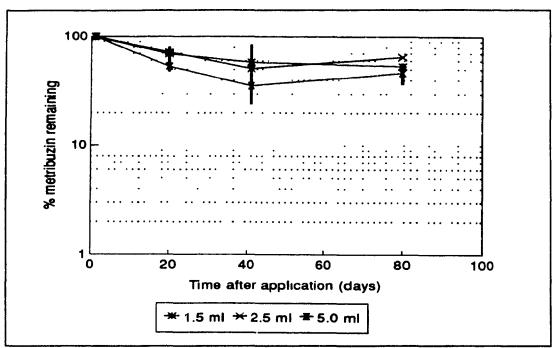


Figure 21. Metribuzin degradation in soil (40-60 cm) in the laboratory experiment.

Table 10. Degradation rates (days-1) of metribuzin in the laboratory experiment.

	0-20	0-20 cm		cm	40-60	cm
Volume	average	std.dev	average	std.dev	average	std.dev
1.5 ml	-0.0255	0.0030	-0.0124	0.0018	-0.0058	0.0014
3.0 ml	-0.0171	0.0026	-0.0118	0.0018	-0.0073	0.0001
5.0 ml	-0.0123	0.0013	0.0140	0.0011	-0.0113	0.0017

Volume: volume of pesticide-water solution added to the soil sample.

std.dev.: standard deviation.

When the logarithmic value of the percentage of metribuzin concentration left in the soil was plotted against the time period after the application, we obtained a linear relationship

for the first two months. The concentration left after that period of time levelled off as it did in the field (desorption). The slope values obtained in the linear portion are presented in the Table 10 and reflect the rate at which the herbicide was degraded in the first two months (the more negative the slope, the faster the degradation). We can notice from Table 10 that:

- 1. At a soil depth of 0-20 cm (Figure 19), the degradation slowed down as the moisture content increased. At a soil depth of 40-60 cm (Figure 21), the degradation was faster as the moisture content increased. In the soil depth of 20-40 cm (Figure 20), the rate of degradation was intermediary
- 2. For a given moisture content, except when the soil was saturated (5 0 ml), the degradation rate was slower in the 40-60 cm soil depth than in the 0-20 cm horizon. When the soil was saturated, there was no noticeable difference in the rate of degradation with respect to the soil depth.

These results show that the degradation of metribuzin occurs predominantly in an aerobic environment. In the 0-20 cm soil depth, the degradation of metribuzin slowed down as the moisture content increased since less oxygen was available for the dominant aerobic microbial populations that exist at that soil depth. In the subsoil, at a depth of 40-60 cm, the degradation was enhanced with an increase of the moisture content since it provided more suitable conditions for anaerobic bacteria population. The decrease of the rate of degradation with respect to the soil depth showed that aerobic bacteria are more efficient at degrading metribuzin; therefore, most of the degradation will occur in the upper soil horizon.

We can compare the rate of disappearance in the laboratory with the values obtained in the field which are presented in Table 11. The rate of disappearance is greater in the upper soil horizon of the field than in the laboratory, since it includes the effect of leaching and, to a lesser degree, volatilization. The high rate obtained in the subsurface drainage field in 1993 suggested a high leaching rate which was confirmed by the

important contamination of the ground water found in this treatment in that year. Secondly, we can notice that the degradation of the herbicide in water is the fastest rate obtained in this two-year study. However, since it is very improbable that important bacterial populations could survive in the ground water, we can hypothesize that the degradation in the saturated zone would have been mostly abiotic.

Table 11. Degradation rates (ppb days⁻¹) of metribuzin in the field; 1992-1993.

Year	Horizon	Rate of degradation	Standard dev.
1993	ground water	Sub: -0.0331	-0.0069
		Dr: -0.0477	-Q.0072
1993	soil (0-200 mm)	Sub: -0.0231	-0.0021
		Dr: -0.0315	-0:0078
1992	soil (0-200 mm)	Sub: -0.0237	-0:0031
		Dr: -0.0252	-0:0060

3.7.1.4 Metribuzin in ground water - 1993

The ground water contamination in 1993 was more important than in 1992. Important precipitations occurred shortly after the application of the metribuzin in all experimental plots (14 days after the application, 34 mm of rain fell in 1992 versus 59 mm in 1993). The highest concentration values recorded in the ground water are presented in Table 12.

Some metribuzin from the previous year's application was present in the ground water. The highest concentrations in the ground water recorded in 1993 were obtained only a day after the application (Figure 22). At that time, in both experimental sites, the water table was not controlled (the control chamber in the subirrigated field was closed only two weeks after the metribuzin application). It is difficult to compare the highest values obtained in the ground water with the ones in 1992, since the water samples during that year were collected starting only one month after the application.

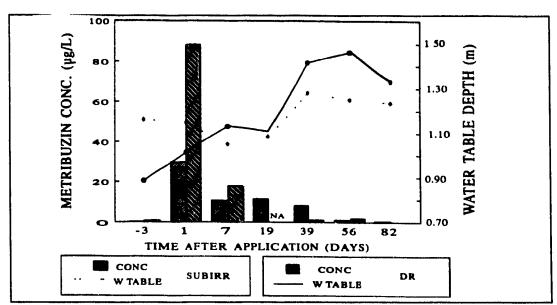


Figure 22. Metribuzin concentration in ground water (1993).

Table 12. Ground water contamination in 1993; worst case scenarios.

Location	Time period vs applic	Range (μg/L)	Ave. (μg/L)	Std. dev.	Media n value (μg/L)	No. of wells
Sub 2, 160 cm depth	+ 1 day	15-37	24	. 9	20	3
Sub 2, 200 cm depth	+ 1 day	51-98	69	21	59	3
Sub 4&5, 160&200 cm depth	+ 10 day	1.2-32	15	13	7	9
Dr 2,3,4 at 160 cm depth	+ 1 day	11.7- 279	95	93	47	9
Dr 2,3,4 at 200 cm depth	+ 1 day	13-247	88	65	80	9

Sub: subirrigation treatment

Dr: subsurface drainage treatment

Applic.: time period after application

The leaching in 1993 could not have been due to direct spraying of the herbicide into the observation well since plastic sheets were placed onto their upper openings and the water inside the wells was pumped out before sampling. Moreover, the observation wells in the Dr 4 experimental plot were installed only after the pesticide application. The concentration values obtained in this experimental plot are similar to the ones of the same treatment on the same sampling day. Important rainfall occurred two days before the application, so that the water could have carried the applied pesticide to the subsoil. There was no significant difference in concentration with respect to the depth at which the water samples were collected (p=0.5620).

The high initial concentration and the low amount of rainfall in the remaining part of the summer (100 and 75 mm of rain in the months of June and July respectively) resulted in minimal leaching and a logarithmic decay of the metribuzin in the ground water with time (p=0.0387). The decay rate was extremely rapid (slope=-0.0331 and -0.0477 in the subirrigated and in the subsurface drainage treatment respectively).

3.7.1.5 Metribuzin in soil - 1993

The carry-over concentrations were measured before the application at levels of 60 μ g/kg and 5 μ g/kg in the 0-200 mm and the 200-400 mm soil depths respectively. These values were greater than the carry-over values obtained in 1992. After the application, the trend in the disappearance of the metribuzin concentration in the 0-200 mm soil depth was similar to 1992. There was again a logarithmic disappearance before the herbicide concentration levelled off after two months as shown on Figure 23. There was no significant difference in the disappearance rate when comparing both treatments.

There was a greater leaching process in 1993 (Figures 24 to 27). This is confirmed by the higher ground water concentrations measured in the same year. However, when the results were tested against the treatment, it was found to be not statistically significant (p=0.1136). It could have been due, as we have explained in the results for the ground water, to the important rainfall that occurred immediately after the application when the

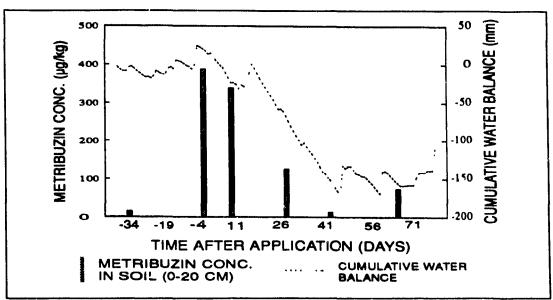


Figure 23. Metribuzin disappearance in the 0-20 cm soil depth with respect to the cumulative water balance (1993).

pesticide concentration was at its highest value in the topsoil. Similar to the results obtained for the soil in 1992, there was a strong significant difference in the pesticide concentration with respect to the depth at which they were collected (without considering the treatment)(p=0.0001).

There was no significant impact of the treatment on the pesticide values recorded in the soil in 1993 (global probability considering all depths and sampling days). However, some statistically significant impact of the treatment occurred when the values obtained at a given depth and sampling day were taken separately. We obtained a significant impact of the treatment on the third sampling day at the soil depth of 0.200 mm, and at the third, fourth and fifth (final) sampling day in the 200-400 mm soil depth. There was no significant difference obtained in the 400-600 mm soil depth. These results are quite interesting since the farmer had started to subirrigate two days after the third sampling day. Hence, the effect of this treatment would have carried down to the fourth and fifth sampling day. The lack of effect of the treatment on the deepest soil horizon studied is not surprising since the values recorded at that depth are very small and therefore cannot

be easily compared. Moreover, because the concentrations at that depth were sometimes close to our gas chromatograph detection limit, erroneous results might have been included.

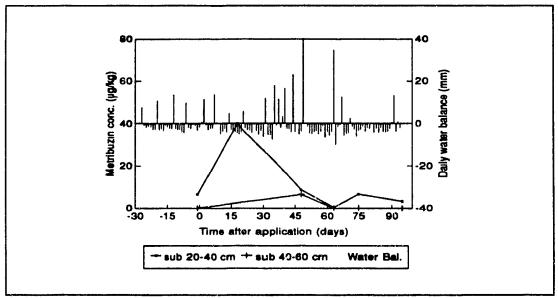


Figure 24. Subsoil contamination in the subirrigated field -1992.

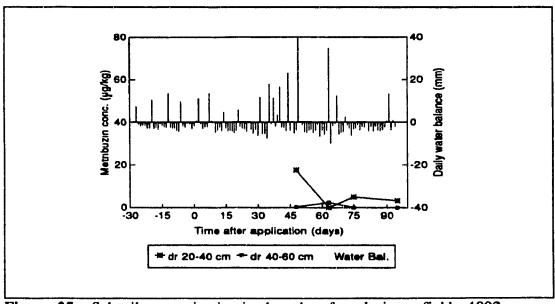


Figure 25. Subsoil contamination in the subsurface drainage field - 1992.

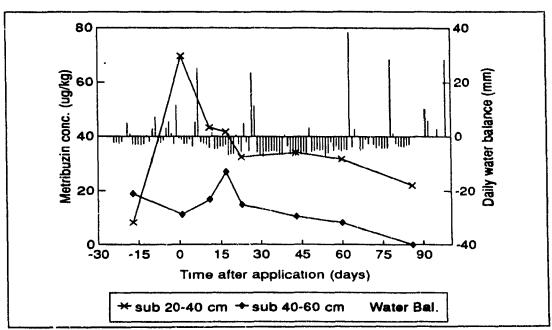


Figure 26. Subsoil contamination in the subirrigated field - 1993.

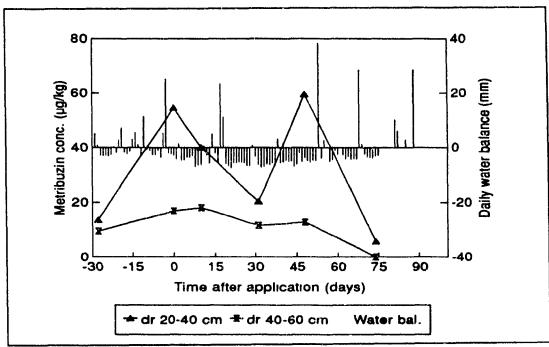


Figure 27. Subsoil contamination in the subsurface drainage field - 1993.

3.7.1.6 Statistical results

Table 13. Statistical analysis concerning pesticide concentrations in soil and water; 1992-1993. The values in bold are significant at a level of confidence of 95%.

		soil 1992	water 1992	soil 1993	water 1993
Treatment		0.1439	0.0134	0.4075	0.1731
Depth	(GG)	0.0002		0.0001	0.5620
	(HF)	0.0002		0.0001	
Depth * Treatment	(GG)	0.0628		0.1487	0.4314
	(HF)	0 0618		0.1136	
Time	(GG)	0.1168	0.1773	0.0066	0.2236
	(HF)	0.0390		0.0017	0.0387
Time * Treatment	(GG)	0.2896	0.2431	0.42/44	0.3421
	(HF)	0.2347	·	0.4548	6.1700
Depth * Time	(GG)	0.1037		0.0089	0.3373
	(HF)	0.0093		0.0023	•
Depth*Time*Treat.	(GG)	0.2403		0.4326	0.2105
	(HF)	0.1150		0.4667	

GG: probability corrected with the Greenhouse-Geisser epsilon.

Table 14. Statistical analysis concerning soil moisture content; 1992-1993. The values in bold are significant at a level of confidence of 95%

	1992	1993
Treatment	0.0246	0.6216
Depth (GG)	0.1866	0.0039
(HF)	0.1214	0.0009
Depth * Treatment (GG)	0.1514	0.2199
(HF)	0.0879	0 2044
Time (GG)	0.1296	0.0001
(HF)	0.0387	0.0001
Time * Treatment (GG)	0.1034	0 7267
(HF)	0.0228	0.8664
Depth * Time (GG)	0.1193	0 3125
(HF)	0.0079	0.2709
Depth*Time*Treat. (GG)	0 3904	0.1387
(HF)	0.3573	0.0586

GG: probability corrected with the Greenhouse-Geisser epsilon.

Table 15. Statistical analysis concerning pesticide concentrations and soil moisture content per day and soil depth; 1992. The values in bold are significant at a level of confidence of 95%

Day, DAA	SOIL DEPTH (cm)					
	00-20		20-40		40-60	
	PESTIC.	MOIST	PESTIC	MOIST.	PESTIC	MOIST
15 JUL, +48	0.2206	0.0922	0.5627	0.1248	0.5521	0.0152
30 JUI , +63	0.6297	0.0379	0.6667	0.0663	0.9999	0.0434
11 AUG, +75	0.7961	0.0836	0.9552	0.0241	0.9999	0.0680
31 AUG, +95	0.0947	0 2645	0.9716	0.9824	0.9999	0.2401
18 SEP, +112	0.2905	0.8696	0.1300	0.5551	0.6667	0.0018

DAA: days after herbicide application

Table 16. Statistical analysis concerning pesticide concentrations and soil moisture content per day and soil depth: 1993. The values in bold are significant at a level of confidence of 95%.

Day, DAA	SOIL DEPTH (cm)						
	00-20		20	20-40		40-60	
	PESTIC.	MOIST	PESTIC	MOIST.	PESTIC	MOIST	
04 JUN, +1	0 7623	0.6954	0 8122	0.3491	0.4990	0 6641	
16 JUN, +11	0.0580	0 1448	0 6912	0.6255	0.6217	0.9933	
06 JUL, +31	0.0078	0.7138	0.0248	0.0930	0.6184	0 3727	
23 JUL, +48	0.0997	0.4930	0.02/6	0.4186	0.8195	0.6809	
18 AUG, +74	0.7367	0.6445	0.0352	0.2968	0.9999	0.1055	

DAA: days after herbicide application.

3.7.1.7 Summary

The disappearance of metribuzin from a given depth will be mainly a function of the water regime. As shown in the degradation experiment done in the laboratory, faster degradation rates will occur as the soil moisture content increases. Greater degradation occurred in 1992, in which about 87% of the initial metribuzin concentration in both treatments was degraded 45 days after the application (Figures 28 and 29). In 1993, which was overall a drier summer, from 67% to 80% of the metribuzin was degraded in the same period of time (Figures 30 and 31). However, since more rainfall events occurred in the first few days after the application in 1993, more leaching occurred. In 1992, from 4.4% (Sub) to 5.9% (Dr) of the metribuzin applied was still present in the subsoil (200-400 mm, 400-600 mm and ground water) 45 days after the application. The values obtained in 1993 ranged from 10.0% (Sub) to 17.6% (Dr).

From 15% (Sub) to 31% (Dr) of the metribuzin applied was found in the ground water only one day after the application in 1993. These results show that metribuzin is relatively mobile in coarse-textured soils. If few rainfall events occur in the few days following the application, most of the herbicide will remain for the rest of the year in the 0-200 mm soil depth (from 54% to 64% in 1992, and from 47% to 50% in the second year). The proportions of metribuzin in the ground water 45 days after the application ranged from 0.06% (Sub) to 0.30% (Dr) in 1992 and from 0.26% (Sub) to 0.43% (Dr) in 1993. These low proportions are due to relatively fast degradation rates in the ground water.

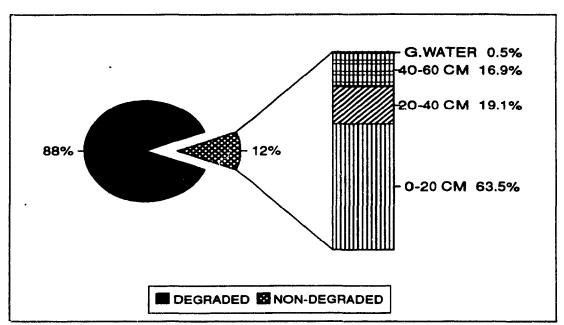


Figure 28. Distribution of the metribuzin 45 days after the application in the subirrigated field (1992).

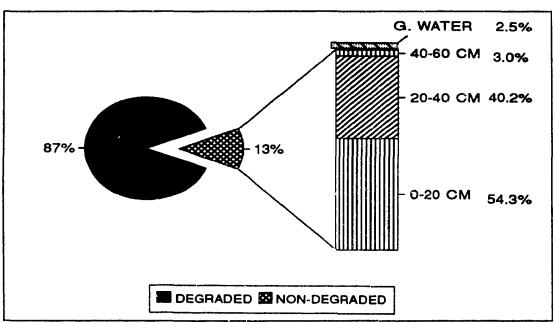


Figure 29. Metribuzin distribution 45 days after the application in the subsurface drainage field (1992).

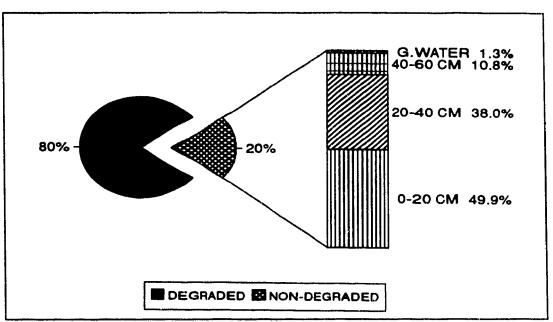


Figure 30. Metribuzin distribution 45 days after the application in the subirrigated field (1993).

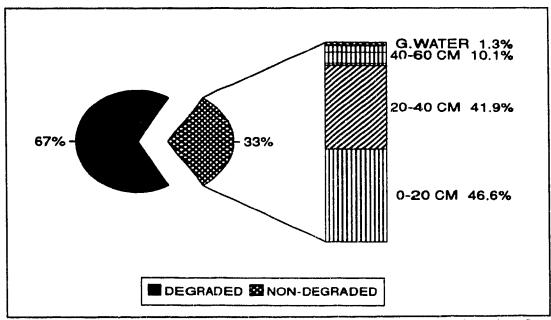


Figure 31. Metribuzin distribution 45 days after the application in the subsurface drainage field (1993).

3.7.2 Results of nitrate analysis

The nitrate-N concentrations were monitored in both soil and round water but only in 1992. The total amount of fertilizers applied per year at both treatment sites was 1300 kg/ha of 13-13-15-4 (N-P-K-Mg). Numerous applications were made during the growing season to reach this value:

Subirrigated field Mid May: 20 L/ha of 18-0-0

End of June: 20 L/ha of 18-0-0 Mid August: 5 L/ha of 8-25-3

Subsurface drainage Mid June: 28 L/ha of 18-0-0

End of June: 10 L/ha of 18-0-0

Beginning of July: 5 L/ha of 8-25-3 End July: 5 L/ha of 8-25-3

Hence, it would be impossible to study the nitrate-N fluctuation with respect to the water table management (e.g.: a rise of nitrate-N concentration in ground water could be due to a change of water table depth and/or application of fertilizer). This is the main reason why the soil and ground water samples were not analyzed for nitrate in 1993. The data obtained in 1992 is presented to give an idea of the extent of the nitrate contamination.

3.7.2.1 Ground water nitrate-N results in 1992

The highest nitrate-N concentrations in the ground water were measured in the month of July, two to four weeks after 20 (Sub) to 40 (Dr) L/ha of 18-0-0 fertilizer had been applied. The average values shown on Figure 32, show that concentrations ranging from 40 to 60 ppm of nitrate-N were recorded. These values are well in excess of the drinking water limit of 10 ppm of nitrate-N. From the end of August to the end of October, the values ranged in the vicinity of the allowable drinking limit. This is understandable since only 5 L/ha of fertilizer 18-0-0 had been applied two weeks before August 31st on the subirrigated field and no fertilizer had been applied after the end of July in the subsurface drainage field.

There was no significant difference in nitrate-N concentrations with respect to the water table management. It seems that denitrification was a slow process in our experimental site since similar nitrate-N values were recorded from the end of August to the end of October time period when no fertilizer was applied.

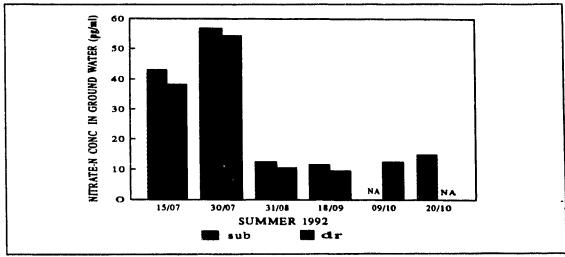


Figure 32. Nitrate-N concentration in ground water.

3.7.2.2 Soil nitrate-N results in 1992

The nitrate-N levels in the soil are shown on Figures 33 and 34. In the subirrigated field, some nitrification occurred between the end of May and mid June. This could be explained by the waterlogged conditions, resulting from the catchment of snowmelt water, that still exists in the end of May. At this period of time, the control chambers had just been opened to allow the machinery to be used on the field. The drop in the water table led to the oxidation of the fertilizer that had been previously applied. No fertilizer input was made between the end of May and mid June. The second observation from Figure 33 is the decrease of nitrate-N concentrations in the second half of the month of July This denitrification process is explained by the fact that this was the time period during which the water table was at its highest values resulting from subirrigation events and frequent rainfalls. During the same period, an important decrease of nitrate-N levels in

soil occurred also in the subsurface drainage field (Figure 33). It could be due to the frequent rainfall received in July 1992 or to the fact that only 5 L/ha of 8-25-3 fertilizer had been applied in the second half of the month.

In both treatments, a rise in the nitrate-N concentrations occurred in mid August. This nitrification could be due to the lowering of the water table, resulting from the non-use of the subirrigation system in the subirrigated field and to fewer rainfall events in August.

The soil nitrate-N values in the subsurface drainage field were slightly higher than in the subirrigated field. Moreover, the overall values in the soil for both treatments were lower than their respective ground water levels.

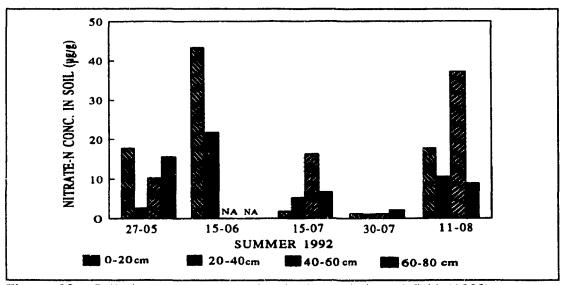


Figure 33. Soil nitrate-N concentration in the subirrigated field (1992).

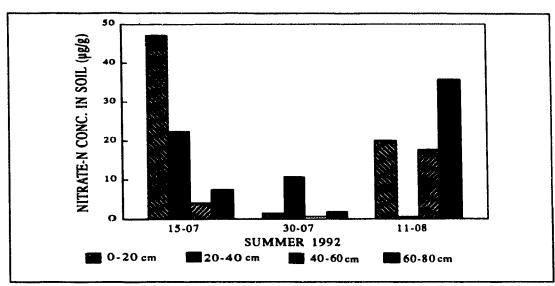


Figure 34. Soil nitrate-N concentration in the subsurface drainage field (1992).

3.7.2.3 **Summary**

The opening of the control chambers in late May led to a nitrification process. Subirrigation accompanied with frequent rainfalls in July did succeed in reducing the nitrate-N levels. A slower denitrification process occurred in the subsurface drainage system where deeper water table levels were recorded. The drop of this water table in both treatments lead to a nitrification process starting from the second half of the month of August.

3.9 CONCLUSIONS

The impact of the water table management on the leaching of metribuzin in a mineral soil should be assessed with great caution. The amount of rainfall occurring in the first few days after the metribuzin application is crucial in determining the capacity of the subirrigation system to reduce the herbicide concentration in the ground water. While the leaching process was minor as in 1992, the herbicide levels recorded in the saturated zone of the subirrigated field were ten times smaller than in the subsurface drainage field because of an enhanced degradation process and dilution. Both of these factors are due to the higher water table values recorded on the field. However, if substantial rainfall occurs in the first few days after the application as in 1993, contamination of the ground water will occur in both treatment fields. The enhanced degradation occurring in the subsoil due to the subirrigation system seems to be a minor aspect when levels of contamination such as in 1993 are recorded. In this year, the degradation rates were equivalent in both treatments.

One might conclude that the benefits of the subirrigation treatment are not only its dilution and enhanced degradation attributes but also the retention of the ground water on site until the end of the summer so that the outflow water would be less contaminated. This is true except that the retention of the ground water on site did not differ, in our case, with respect to the water table management. In the subsurface drainage treatment, the water table was almost always lower than the drains so that no outflow of contaminated water occurred. The situation would have been different with a fine-textured soil or with a shallower impermeable layer under a coarse-textured soil.

CHAPTER 4. IMPACT OF WATER TABLE MANAGEMENT ON PROMETRYN LEACHING

The second major focus of this investigation was herbicide pollution in an organic soil located in St-Patrice-de-Sherrington (Québec)(Van Winden farm) In Québec, about 80 000 ha of organic deposit is exploitable as peat for market production. In southwestern Québec, where most of the exploitable organic deposits are located, about half of the organic deposit is exploited (10 000 ha)(CPVQ, 1986).

The general belief among environmentalists is that less ground water contamination would occur in a peatland for a given pesticide even though the application rates are slightly higher than in a mineral soil. This belief is based on the assumption that the high adsorption capacity of the organic material will limit the extent of the contaminant leaching process. However, very few studies concerning ground water contamination under such conditions has been made. This is the main reason why an organic deposit was chosen as one of the experimental site.

The fourth chapter will describe the site, the experimental set-up, the soil's physical and chemical properties, the methodology and the meteorology of the second experimental site. The statistical analysis, the results and, finally, a conclusion will conclude the chapter. Since only one year of prometryn and nitrate-N data was collected by the author of this thesis, less attention will be paid on the results obtained at the Van Winden farm. Since, two years of data were collected by another student, a summary of the results obtained after three years will be included in the results.

4.1 SITE DESCRIPTION

The description of the Van Winden organic deposit includes its location, pedology, cultivation practices and, finally, an overview of the subsurface drainage, subirrigation, and surface irrigation systems used.

4 1 1 Location and pedology of the site

The Van Winden farm is located in St-Patrice-de-Sherrington, south of Montréal. It is a part of the Napierville organic soil deposit which has a total area of 4500 hectares, 2600 hectares of which are presently cultivated (Arjoon, 1992). The degree of decomposition of the organic material varies with depth. The top 40 cm of deposit is well decomposed, whereas the next 40 cm is a fibrous non-decomposed material. Then, another layer of varying depth of well decomposed material is present before reaching an orange-clay sand deposit. This dense layer is at its shallowest depth in the subirrigated field (80-90 cm). In the other two experimental plots used, the clay layer is deeper, ranging from 1.0 to 1.2 meters.

4.1.2 Cultivation

The Van Winden farm has been cultivated since 1953. The principal cultures are carrots (30%), celery (30%), lettuce (30%), and to a lesser extent onions (10%). In 1992, celery was grown in all the experimental fields.

4.1.3 Subsurface drainage system

The subsurface drainage system in an organic deposit serves three purposes: (1) to remove excess water so as to allow the use of machinery. (2) to optimize plant growth and, finally, (3) to reduce the wind erosion that would occur if the soil were dry. The drainage system in the Van Winden farm consisted of 100 mm diameter corrugated plastic tubing spaced 18 meters apart and having lengths ranging from 122 to 420 meters (Figure 34) The collectors have a diameter of 150 mm with an outlet emerging at a depth of about 1 6 meters into the trenches that edge the fields. The slope of the side of these trenches was quite steep (about 45°) so that erosion occurred extensively in Spring. The

water table in the subsurface drainage field should not be considered as "freely draining" (Kirschbaum, 1991). The water table in the adjacent trench would substantially control the height of the water in that field.

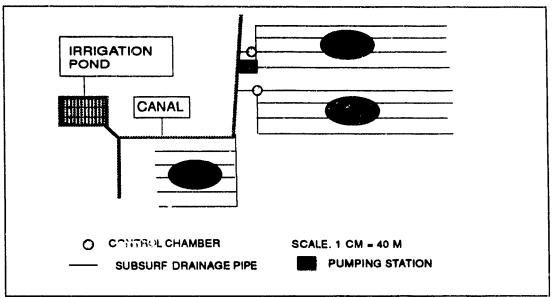


Figure 35. Schematic of the experimental test plots used in 1992.

4.1.4 Subirrigated and surface irrigated systems

The water table was controlled in the subirrigation and surface irrigation fields with a chamber located between the end of the collector and the outlet. The water pumped into the subirrigation field was taken from the irrigation pond via the trenches. The pumping event occurred for about two weeks at the end of June.

4.2 EXPERIMENTAL SET-UP

The experimental set-up describes the statistical design used at this location along with the means used to measure the water table depths and to collect the ground water and soil samples.

4.2.1 Statistical design

The experimental set-up is quite similar to the one used in the first year of study at the Laurin farm. Three sampling units were taken per experimental plot. Soil samples were collected from four depths per sampling unit. One experimental unit, which measured from 1 to 3 ha, was used for each of the three treatments (Table 17). The effect of each of these treatments on moisture content and pesticide concentration were statistically tested.

Table 17. Experimental set-up.

	1990	1991	1992
No of experimental units in subirrigated/ surface irrigated / subsurface drainage field	1/1/1	1/1/1	1/1/1
No of sampling units per experimental unit	3-5	3-5	3
No of sampling days	5	6	6
Total no of soil samples analyzed	150	307	281
Total no of ground water samples analyzed	144	75	61
Total no of samples analyzed	294	382	342

4 2 2 Water table depth measurement

Three sets of three water table tubes consisting of 25 mm diameter PVC pipes were installed per treatment. One pipe was located at mid-spacing and the two other ones were located one meter from a subsurface drainage lateral. The machinery used to harvest the celery destroyed almost all of these water table tubes near the end of our study. But since we had the intention of continuing to monitor the water table depth, we reinstalled some of the water table tubes. At the places where they were not reinstalled, the water level was obtained from the observation wells.

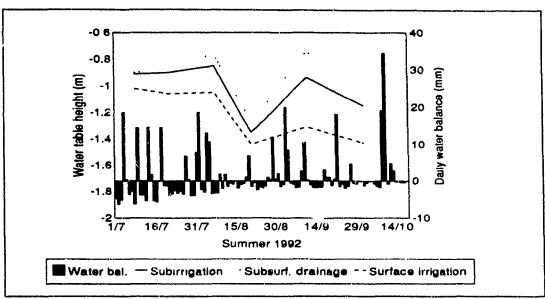


Figure 36. Water table fluctuations at the Van Winden farm in 1992.

4.2.3 Ground water and soil sampling

For the collection of ground water samples, three observation wells consisting of corrugated and perforated drainage plastic tubing were installed per treatment. A cap was placed on the top of the wells so that no pesticide application would directly contaminate the ground water contained in the wells. Moreover, in order to reduce the risk of such contamination, the water in the wells was first removed before sampling with the use of a bailer, as for the Laurin farm. Only a few minutes were necessary for the ground water to reach its initial water table depth. The water samples were then taken with the use of a plunger and transferred into labelled plastic bottles.

The soil samples were collected at four different depths, 0-200 mm, 200-400 mm, 400-600 mm and 600-800 mm, from three fixed areas per treatment. The sample were taken in the vicinity of an observation well and labelled accordingly. The samples were transferred from the 50 mm auger to plastic bags and brought into the laboratory to be frozen until extraction and analysis could be done.

4.3 SOIL PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of the soil were determined in the same manner as described in the Laurin section except for the soil moisture content. What follows is a summary of the results obtained at the Van Winden farm by Arjoon (1992).

Table 18. Soil physical and chemical properties.

Properties	
Saturated hydraulic conductivity (m/day)	From 0.9-1.3 meters deep: 1.0-6.3 m/day 1.3-2.1 meters deep: 0 3-4.3 m/day
Prometryn adsorption coefficient	18 cm ³ /g at equilibrium concentration of 1 ppm.
рН	5.5 - 5.8 (both soil and water)

4.3.1 Soil saturated hydraulic conductivity

The soil saturated hydraulic conductivity at the Van Winden farm was performed by the Soconag engineering firm. They measured the hydraulic conductivity at two soil depths by using the method described by Van Beers (1983) which is explained in greater details in the section 3.3.1. The readings taken in the organic deposit show a lower soil saturated hydraulic conductivity in the subsoil than in the topsoil. This could be explained by the clay layer present in the deep soil horizons. A "floatation" effect in the upper soil layer could also contribute to higher hydraulic conductivity in that soil horizon.

4.3.2 Soil moisture retention

The soil moisture retention curves were also measured by the Soconag engineering firm. Unfortunately, the method used is not described in Arjoon's thesis (1992). It should have been the same described in section 3.3.2. Tension up to 1 bar was used to draw the curves (Figure 37).

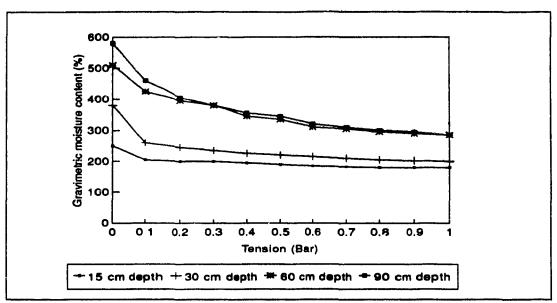


Figure 37. Moisture retention curve of the organic soil at the Van Winden farm.

4.3.3 Soil moisture content

The determination of the soil moisture content was different for the organic material. The temperature in the oven was set at 80°C instead of 120°C. If the temperature exceeded 80°C, the combustion of the organic matter could start.

4.3.4 Pesticide adsorption coefficient

A modified batch equilibrium method in which the soil-pesticide solution in water is not shaken but left undisturbed for 24 hours was used. A more detailed description of the method is included in section 3.3.5.

4.3.5 pH

The pH values were determined from both soil and ground water samples. A detailed method for pH measurement is included in section 3.3.6.

4.3.6 Prometryn-organic deposit interaction

The interaction between the sorbent and the herbicide was very different than the situation described in the Laurin farm (section 3.3.8). The organic deposit found at the

Van Winden farm has a greater cation exchange capacity than the sandy field of the Laurin farm (250 cmol/kg versus 16 cmol/kg), a higher soil pH (5.5-5.8 versus 4 7-5.0), a shallower impermeable layer (1.2 m versus 2.5 m) leading to greater soil moisture content, and, of course, a greater soil organic matter content which in turn, leads to higher adsorption coefficient (18 cm 3 /g versus 3 cm 3 /g). Moreover, the herbicide prometryn is 35 times less water soluble than metribuzin (0 033 g/kg versus 1 2 g/kg) and has a higher K_{ow} (2190 versus 40) leading to greater adsorption rates. All of these soil and herbicide properties show that for a given rainfall distribution, the leaching process of prometryn is much slower than metribuzin.

4.4 Procedures of extraction and analysis

Different extraction and analysis methods were used at the second experimenta' site, which will be described in this sub-chapter.

4.4.1 Prometryn extraction

Soil samples were thawed, extracted with methanol, and filtered. The resulting solution was partially evaporated and reconstituted with methanol as a final matrix. The ground water samples were extracted twice with dichloromethane. The organic phase was also partially evaporated and reconstituted with methanol. The method of extraction from soil and ground water, which is the same as the metribuzin extraction, is described in detail in section 3.4.1.

4.4.2 Prometryn analysis

The herbicide prometryn was analyzed in the soil and water samples by a technique different from the one used for metribuzin analysis, which had been done by gas chromatograph. Analysis of prometryn was done by using the RaPID Assay kit (Ohmicron Company, Pennsylvania). This kit applies the principles of enzyme linked immunosorbent assay (ELISA) to the determination of triazines. First, prometryn is extracted from the soil sample by methanol (18 grams of soil in 100 ml). The solution is filtered and reduced by the rotary evaporator. The resulting solution must be diluted

in water since this technique cannot accept a matrix of pure methanol. The water samples were extracted in the same way as with the samples analyzed for metribuzin. The final sample is then mixed with an enzyme conjugate in a disposable test tube. Paramagnetic particles bound to antibodies specific to triazines were added. The enzyme labelled prometryn in the enzyme conjugate compete for antibody sites on the magnetic particles. After an incubation period (15 minutes), a magnetic field is applied to hold the paramagnetic particles (with atrazine and labelled atrazine analog bound to the antibodies on the particles, in proportion to their original concentration) in the tube and the unbound reagents are decanted. After decanting, the particles are washed with a Washing Solution (deionized water).

The presence of prometryn is detected by adding the enzyme substrate, hydrogen peroxide, and a chromagen to generate a coloured product. After an incubation period (20 minutes), the reaction is stopped and stabilized by the addition of a diluted sulphuric acid solution. Since the labelled atrazine was in competition with the unlabelled (sample) atrazine for the antibody sites, the intensity of the colour developed is inversely proportional to the concentration of atrazine in the sample. Hence, the accuracy of the method will level off as the concentration of the pesticide in the solution increases. The pesticide concentrations were determined from a calibration curve (4 points) which was made for every 30 samples. Dilutions of sample solution were made when its pesticide concentration exceeded the highest standard used (5 ppb). The detection limit was 0.05 ppb.

4.4.3 Nitrate extraction and analysis

Nitrate-N was extracted from the organic soil by mixing a thawed sample with a solution of KCl. The solution was filtered and transferred into a glass container where it was stored in a fridge until it was analyzed with a colorimeter. The nitrate-N concentrations in ground water were determined with a ion-selective electrode. A more detailed method of extraction and analysis is described in section 3.4.3.

4.5 METEOROLOGICAL DATA

More evapotranspiration will occur in a celery field than in a field of potatoes. The crop coefficients (ratio of actual evapotranspiration by the potential evapotranspiration) for celery, which was the culture used in the Van Winden farm for the 1992 season, are 0.49, 1.00, and 0.90 for the initial stage, mid-season stage and at the end of maturity respectively. The celery seedlings were transplanted in the subsurface dramage, surface irrigated and subirrigated fields on May 4th, 8th and 13th respectively. The harvesting occurred between August 1st and August 10th.

4.6 STATISTICAL ANALYSIS

The statistical analysis performed on the Van Winden data was slightly different than the one used for the Laurin farm data. The "Repeated measurements" statement was still used inside the MANOVA (multivariate) analysis but the data were used in a different way. Since there was only one experimental unit available for each of the three treatments, the three sample units taken per experimental unit were considered as average values of an experimental unit. Hence, the scale of analysis is much smaller than for the Laurin farm, so that the results obtained in the Van Winden organic deposit should be interpreted with caution.

4.7 RESULTS AND DISCUSSION

The results will be presented in two main portions: the results of prometryn analysis and nitrate-N analysis. The raw data collected in 1992 at the Van Winden farm are presented in Appendix B.

4.7.1 Results of prometryn analysis

The prometryn results obtained in 1992, the last year of the study, will be presented first, followed by their statistical results. Then, an overview of all the prometryn results obtained during the three years of the study will be made, ending with a brief summary.

4 7.1 1 Prometryn in ground water - 1992

The carry-over concentrations measured in the outlets of the drainage systems at the end of April and at the beginning of May were in the range of 0.2 to 1.6 μ g/L. There was no significant treatment impact on the levels recorded (p ranging from 0.22 to 0.41). The leaching process seemed to have been quite slow since the maximum concentrations readings were obtained late in the season. However, we should accept this information with precaution since no ground water measurements were taken in the month following the application. The maximum values obtained are shown in Table 19.

Table 19. Worst case scenarios in the ground water.

Treatment	Maximum conc. (μg/L)	Days after application (days)	Median value on that day (μg/L)
subirrigation	13.0	+ 48	4.9
surface irrigation	7.8	+ 101	*
subsurface drainage	5.6	+ 80	3.6

^{*:} only sample was taken in this treatment on that day.

Regardless of when the ground water samples were taken, the prometryn contamination in the saturated zone is extremely small when considering the application rate (0.2% of initial application found in ground water). On September 11th, the prometryn concentrations in the water coming out of the outlets were not detectable. A total of 17 mm of rain had fallen in the three days prior to the sampling. On the other hand, concentrations of 3.6 and 2.6 μ g/L were recorded in the outlet water of the subirrigated and surface irrigated fields respectively on October 2nd. No precipitation had occurred for the last five days before the sampling. Prometryn appeared to be strongly bonded onto the organic matter exchange sites and water will had a limited effect upon the leaching process. However, when rainfall occurs, it will raise the water table and dilute

the prometryn that had already leached into the saturated zone.

4.7.1.2 Prometryn in soil - 1992

The carry-over of prometryn in the soil after the winter season is very high. It has been measured in the range of 600 to 750 μ g/kg. Its concentration diminishes by a two fold factor for each 200 mm soil depth except in the 600-800 mm soil depth where its concentration is similar to that in the 400-600 mm soil depth

The statistical analysis confirms that the prometryn levels decrease with respect to the soil depth (p=0.0004, 0.1750 and 0.0058), and that there was a treatment effect on the pesticide levels between the subirrigation and subsurface drainage fields (p=0.0325). Lower prometryn levels are found in the soil in the subirrigated field.

The maximum concentration values in soil (0-200 mm depth) obtained after the application does not occur on our first sampling day, but on the second. This phenomenon has to be attributed to the celery interception of the herbicide during the application since the crop had already been grown in a greenhouse before planting. Rainfall, which occurred between the first and second sampling day, would have washed out the herbicide from the plants onto the soil surface, increasing its concentration. Little precipitation had occurred between the day of application and the first sampling day.

The first thing to be noticed from our results is the scale of the prometryn concentration in the soil. Two applications of 2.75 kg/ha were made, far beyond the application rate of metribuzin in the Laurin farm (1 kg/ha). If we consider that the bulk density in the upper soil horizon equal 0.5 g/cm³, we would calculate that 0 88 million kilograms of soil would occupy the upper 15 cm of soil per hectare. From that value, we would obtain an initial application of 6250 μ g/kg of prometryn. The concentration in the topsoil (0-200 mm) disappeared at a rate which could be linear as well as logarithmic since the correlation values are similar in either case. Without regards to the order of the disappearance rate, the fastest disappearance was recorded in the subsurface

drainage field. The lowest rate was recorded from the subirrigated field when considering a linear disappearance. Table 20 shows the logarithmic disappearance rate of prometryn from the 0-200 mm soil depth.

Table 20. Rates of prometryn disappearance (ppb days⁻¹) from the 0-200 mm soil depth.

Treatment	rate of disappearance	correlation with time (r)
subirrigated field	-0.0034	0.964
surface irrigation	-0.0029	0.866
subsurface drainage	-0.0052	0.943

We can see that the disappearance of prometryn from the upper soil horizon was far-slower than for metribuzin (10 times). This would suggest slower leaching process because of a greater adsorption or a slower degradation rate. However, this slower leaching process was not due to the treatment since it was not significant. It could have been due solely to the higher cationic exchange capacity of the soil organic matter.

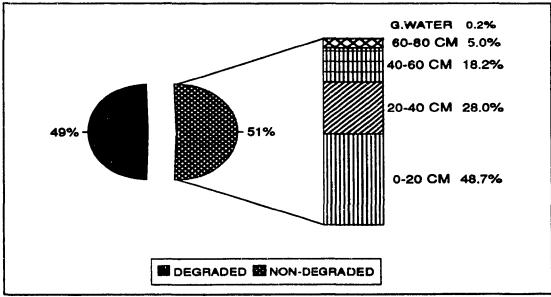


Figure 38. Prometryn distribution in the subirrigated field 45 days after the application.

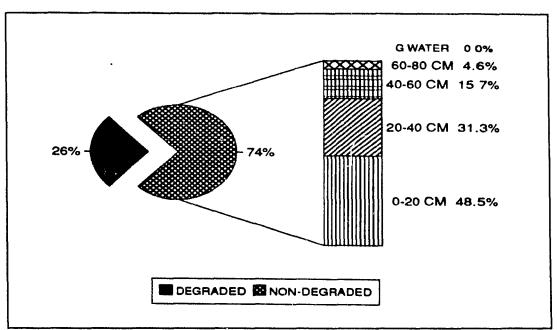


Figure 39. Prometryn distribution in the surface irrigated field 45 days after the application.

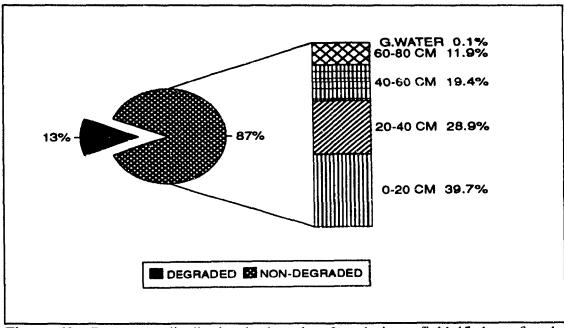


Figure 40. Prometryn distribution in the subsurface drainage field 45 days after the application.

4 7.1.3 Statistical results

The statistical probabilities on the impact of various variables on the herbicide concentrations found in ground water, soil and the soil moisture content are presented in Table 21, 22 and 23.

Table 21. Statistical analysis. Probabilities on the significance of the impact of variables on pesticide concentration in the ground water.

Ground water. 1992.	subirr. vs subsurface drainage	surface irr. vs subsurface drainage	subirr. vs surface irrigation
Treatment	0.4070	0.2185	0.2596
Time (GG)	0.2705	0.3470	0.8003
(HF)	0 2383	0.3030	0.9780
Time*Treatment (GG)	0.3107	0.1604	0 3856
(HF)	0.2958	0.0508	0.3667

GG: probability corrected with the Greenhouse-Geisser epsilon.

Table 22. Statistical analysis. Probabilities on the significance of the impact of variables on pesticide concentration in soil. The values in bold are significant at the 95% level.

Soil. 1992.	subirr. vs subsurf. drainage	subirr. vs surface irrigation	surface irrigation vs subsurf drainage
Treatment	0.0325	0 5617	0 1702
Depth (GG)	0.0004	0 1750	0.0058
(HF)	0.0001		0.0003
Depth * Treatment (GG)	0 1052	0.4605	0 9127
(HF)	0.0775		0 9764
Time (GG)	0.0671	0 6292	0 3042
(HF)	0.0129		0 2161
Time * Treatment (GG)	0.0883	0 6063	0 2482
(HF)	0.0231		0 1313
Depth * Time (GG)	0.3209	0 4286	0 3475
(HF)	0.2149	0.1955	0 2043
Depth*Time*Treat. (GG)	0.3447	0 3870	0 6641
(HF)	0.2668	0.0858	0 9624

GG: probability corrected with the Greenhouse-Geisser epsilon.

Table 23. Statistical analysis. Probabilities on the significance of the impact of variables on soil gravimetric moisture content. The values in bold are significant at the 95% level

Soil. 1992.	subirr. vs subsurf. drainage	subirr. vs surface irrigation	surface irrigation vs subsurf drainage
Treatment	0 3557	0.0923	0 8703
Depth (GG)	0.6019	0.0001	0.0002
(HF)	0.0001	0.0001	0.0001
Depth * Treatment (GG)	0.2741	0 3310	0 1040
(HF)	0 2075	0 3191	0 0618
Time (GG)	0 1267	0.0540	0 0819
(HF)	0.0196	0.0060	0.0196
Time * Treatment (GG)	0 0650	0.0243	0 1328
(HF)	0.0025	0.0009	0.0537
Depth * Time (GG)	0 0911	0.0084	0.0284
(HF)	0.0001	0.0001	0.0001
Depth*Time*Treat (GG)	0.2192	0.0591	0.0569
(HF)	0.0200	0.0001	0.0015

GG: probability corrected with the Greenhouse-Geisser epsilon.

4.7 1 4 Overall results (1990-1991)

The meteorology, water table readings and herbicide concentrations obtained at the Van Winden farm during the three years period are summarized in Table 24

Table 24. Summary of Van Winden farm results: 1990-1992.

CHARACTERISTICS	1990	1991	1992
RAINFALL (mm): MAY 21-31	2 9	35.5	23-8
JUNE 1-10	36 3	0.0	51.2
JUNE 11-20	18.7	26 3	16.8
JIJNE 21-30	51 9	27 6	2.2
JULY 1-10	25 8	20 8	50 4
JULY 11-20	27 9	7 ()	47.6
WATER TABLE (cm). SUB	41-78	70-80	85 109
SURF	68-75	80-90	102-145
DR	68-110	80-120	80-130
APPLICATION RATE (kg/ha) SUB	3 0	0.0	5 5
SURF	5 2	0 ()	5.5
DR	5 2	0.0	5 5
GROUND WATER PROMETRYN CONC. RANGE (µg/L)			
SUB	2-12	0 1-1 8	2-12
SURF	5-10	0 1-2 7	2-6
DR	8-22	0 3-2 0	1-4
GROUND WATER PROMETRYN CONC MEDIAN (µg/L)			
SUB	4 0	1 1	2 9
SURF	5 0	1 7	3 8
DR	12 0	0.5	3 6

There was no prometryn application in 1991. Soil and ground water samples were collected during the course of the summer to assess the importance of carry-over concentrations. The results obtained in that year suggest a slow prometryn degradation rate and leaching process in an organic deposit. The prometryn application rates in 1990 and 1992 were much higher than the recommended levels (1.0-1.5 kg/ha).

The meteorological conditions in 1990 and 1992 were similar with respect to the amount of rainfall received, which was higher than normal. The water table readings were, however, quite different. In all water table management treatments, the water table was generally deeper year after year.

The shallowest water table readings were always obtained in the subirrigated field. However, when comparing the water table readings in the subirrigated field versus the subsurface drainage field, the difference diminished with time. This was due to a break in the pump in 1991 so that the quantity of water brought to the field was limited. This was also due to surface irrigation which was applied to all treatments (from 20 mm to 45 mm per year) in the first two years. Since the subirrigated and surface irrigated fields possess a control chamber, the water level will differ to a greater degree than in the subsurface drainage field in which ground water is freely draining.

Similar prometryn concentrations were obtained in the ground water in 1990 and 1992. They ranged from 2 to 12 μ g/L in the subirrigated and surface irrigated fields. The major difference lies in the subsurface drainage treatment. In 1992, it showed the greatest contamination of all treatments with values ranging from 8 to 22 μ g/L. In 1993, the concentrations obtained were much smaller (1 to 4 μ g/L) and, moreover, not significantly different from the two other treatments. It seems that subirrigation succeeded in reducing the prometryn contamination in the ground water only when high water tables were recorded as in 1990. Even when the water table was shallower in the subirrigated field than in the subsurface drainage field as in 1992, the overall water table readings were deeper. This situation seems to minimize the impact of the subirrigation

treatment.

4.7.1.5 **Summary**

The extent of the prometryn contamination in the ground water of an organic deposit will be much lower than for metribuzin in the saturated zone of a coarse-textured soil. The slower leaching process is mainly due to the high adsorption capacity of the organic material and the low water solubility of prometryn. Water table management did not affect the degree of the prometryn contamination in the ground water. However, subirrigation did result in a higher degradation rate in the soil by ways of increasing the soil moisture content.

4.7.2 RESULTS OF NITRATE-N ANALYSIS

The fertilizer input in the Van Winden farm consisted of an initial application in early May of 400 kg per hectare of 15-10-15. A second application of 200 kg/ha of the same fertilizer mixture took place in the middle of the month of July. Hence, we could study the impact of the water table management on the denitrification process only from the sampling day of July 21st.

4.7.2.1 Nitrate-N in ground water - 1992

The nitrate-N levels in the ground water are presented on Figure 41. The highest levels recorded in the first week of July were recorded in the surface irrigated field. That treatment continued to have very high values till the middle of August. The allowable nitrate-N level for drinking water was exceeded on July 8th and August 7th. The subirrigated field was the second most contaminated treatment from the beginning of July to the middle of August.

The overall trend of the nitrate-N levels for both the subirrigated and surface irrigated fields is its decline with time. This trend is the reverse of the situation in the subsurface drainage field, where peak values were reached from the middle of August to the beginning of October. This time period coincides with the deepest water table values

recorded. The concentration levels in the subsurface drainage treatment were lower than the two other water table managements before the middle of July. After this, when the second application of fertilizer was made, more contamination occurred in the subsurface drainage field.

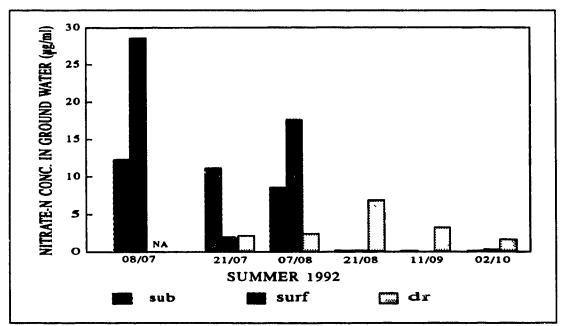


Figure 41. Ground water nitrate-N concentration.

4.7.2.2 Nitrate-N in soil - 1992

The nitrate-N levels in the soil (Figures 42,43 and 44) are generally greater than in the ground water system. In all the three treatments, there was a decline of the nitrate level from the 21st of July (the second fertilizer application was made in the middle of July). The highest values were recorded in the subirrigated field whereas the lowest values were in the subsurface drainage field. An homogeneous distribution of the nitrate-N levels versus the soil depth was found in the surface irrigated field.

There was a slight trend where the concentrations were decreasing as the soil depth increased. The lowest nitrate-N levels obtained in the subsurface drainage field coincide with shallow water table values.

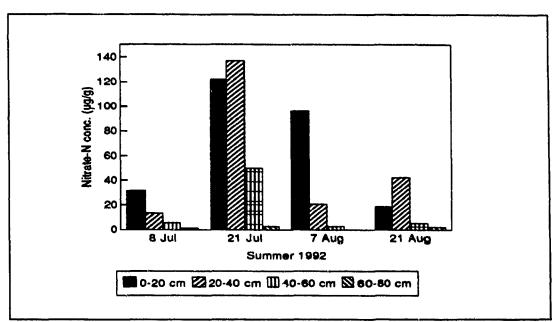


Figure 42. Soil nitrate-N concentration in the subirrigated field.

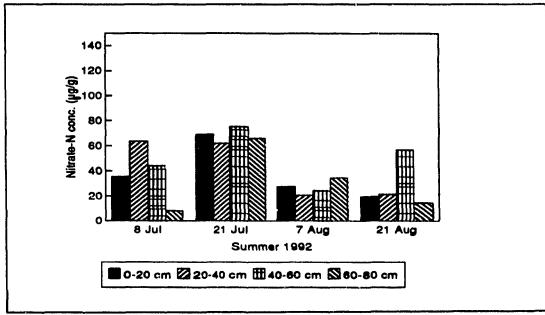


Figure 43. Soil nitrate-N concentration in the surface irrigated field.

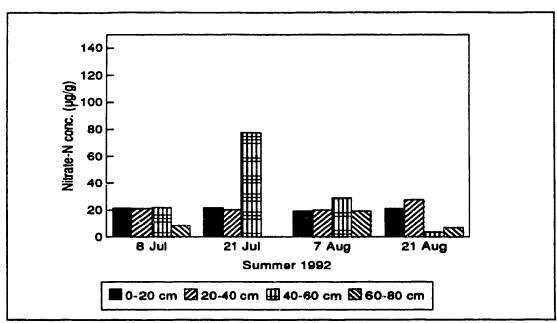


Figure 44. Soil nitrate-N concentration in the subsurface drainage field.

4.7.2.3 **Summary**

Denitrification was a function of the water table depth and not of the upward movement of water occurring in a subirrigation treatment. Nitrate-N levels were at their lowest in the treatment where the highest water table values were recorded: the subsurface drainage field. The 40 cm water table difference measured between the surface irrigated field and the subsurface drainage field led to 4 times less nitrate-N contamination in the shallow water treatment.

4.8 CONCLUSION

The higher soil organic matter content, the higher adsorption rate and lower water solubility of prometryn led to a slower leaching process of the herbicide and indirectly to lower ground water contamination. Subirrigation did succeed in reducing ground water contamination by increasing the degradation rate of prometryn. It has been calculated that 49% of the initial herbicide application had been degraded in the subirrigated field. A value as low as 13% was obtained in the subsurface drainage field.

More denitrification occurred in the subsurface drainage field treatment where the shallowest water table values were recorded.

CHAPTER 5. SUMMARY AND CONCLUSIONS

Two three-year studies were initiated in order to assess the role of subirrigation in reducing ground water contamination by two herbicides. At the first experimental site, the herbicide prometryn was applied onto an organic deposit at the Van Winden farm in St-Patrice-de-Sherrington (Québec) where celery and lettuce were grown. The second location, Ste-Marie-Salomée (Québec), consisted of a deep fine sand deposit where metribuzin was applied to where potatoes were grown.

Soil and ground water samples were taken along with water table measurements at two-week intervals during the course of the three growing seasons. The chemical and physical properties of the soil and of the organic deposit were determined. The conclusions drawn from our two experiments are as follows:

- 1) The high mobility of metribuzin in a coarse-textured soil will lead to important ground water contamination if rainfall occurs in the first few days following the herbicide application. This situation will occur most probably in all water table management systems in Québec since the application of metribuzin takes place in the Spring, when the water table is not significantly different with respect to the treatment.
- 2) If the water table is sufficiently high and if there is no important initial ground water contamination, subirrigation systems will substantially reduce the herbicide concentration found in the ground water.
- 3) The degradation rate and leaching process of prometryn in an organic deposit were relatively slower than for metribuzin in a mineral soil.
- 4) According to our laboratory degradation experiment, the degradation rate of metribuzin slows down as the moisture content decreases and as the soil depth

increases. Most of the degradation seems to be due to the activity of aerobic bacteria.

5) The sudden opening of the control chamber in May will lead to a nitrification process. During the summer, when the water table will be at its highest level with the help of a subirrigation system, a denitrification process will occur.

CHAPTER 6. RECOMMENDATIONS FOR FUTURE RESEARCH

Future research should include the study of the chemical cross-reactions that will most probably occur between the numerous pesticides used in a potato field. These byproducts could be more toxic than the original pesticides used.

Secondly, research should focus on the biodegradation of numerous pesticides in an oxygen depleted and moist soil environment. These conditions will dominate in the subsoil of a subirrigated system. If pesticides are found to be degraded under such conditions, then one would expect subirrigation to reduce the ground water concentration of the given pesticide.

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APPENDIX

APPENDIX A

RESULTS OBTAINED AT THE LAURIN FARM (SAND DEPOSIT)

- N.B.: 1) The abbreviations LA92 and LA93 used in the identification of the tables presented in the appendix signifies the location (LA: Laurin farm) and the year (92: 1992) at which the samples and or readings were taken.
 - 2) Two sub-sections are included in this appendix. The results obtained in 1992 and 1993 are presented in the sections A.1 and A.2, respectively.
 - 3) The blanks left in tables signify that no measurement were taken for that given location and day.
 - 4) The coefficient of variability (C.V.) will be presented in a percentage form in the shaded areas of the tables.
 - 5) Most of the metribuzin and nitrate-N results presented in the tables are average values (from 3 samples in 1992, and from 4 samples in 1993).
 - 6) The abbreviations used in the appendix are explained in the list of abbreviations and symbols section in the beginning of the thesis.

APPENDIX A

A.1 Results in 1992. A.1.1 Pesticide application (1992)

Insect	Ici	d	AR
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Common name	Commercial name	Applic. rate	Applic.day
Deltamethrin	Decis	1.2 L/ha	Sub: 14/06
		250 ml/ha	Sub: 29/06
Endosulfan	Thiodan	2.5 L/ha	Dr: 16/06
		2.0 L/ha	Sub: 08/07
		200 ml/ha	Sub: 07/08
Phorate	Thimet	22 kg/ha	Dr: 28/04
Cypermethrin	Cymbush	200-250 ml/ha	Dr: 23/06
			Dr: 02/07
Permethrin	Ambush	100 ml/ha	Dr: 15/07
			Sub: 15/07

Fungicides

Common name	Commercial name	Applic. rate	Applic.day
Zn ammoniate ethylenebis(dithioca		2 kg/ha	Dr: 15/07 Dr: 24/07
poly(ethylenethiura	m alsulfiae)		Sub: 15/07 Sub: 22/07
			Sub: 25/08
Metalaxyl	Ridomil	0.2 kg/ha	Sub: 07/08
Mancozeb	Manzate	1.6 kg/ha	Sub: 07/08

Herbicides

Common name	Commercial name	Applic. rate	Applic.day
Fluazifop-butyl	Fusilade	1.5 L/ha	Sub: 17/05
Bentazone	Basagran	1.1 kg/ha	Dr: 04/05 Sub: 04/05
Diquat	Regione	0.25 kg/ha	Dr: 10/08 Sub: 26/08
Metribuzin	Sencor	1 kg/ha	Sub: 02/09 Dr: 26/05
		1 kg/ha	Sub: 26/05

A.1.2 Metribuzin concentrations in soil (1992)

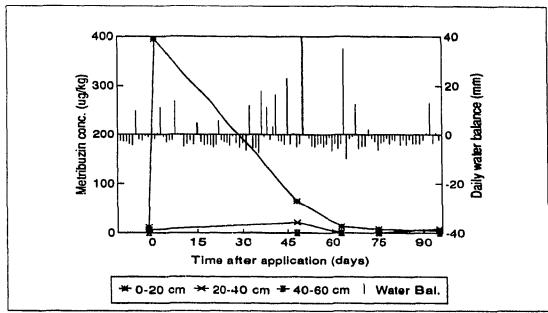


Figure 45. Soil metribuzin concentration in the field Sub 2 (1992).

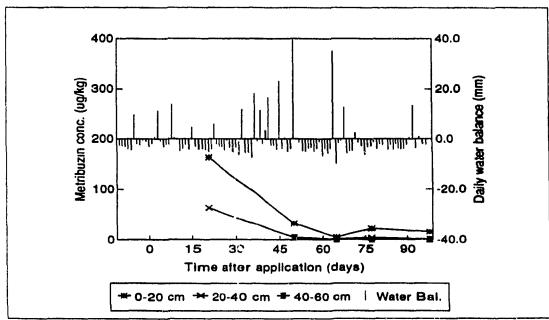


Figure 46. Soil metribuzin concentration in the field Sub 4 (1992).

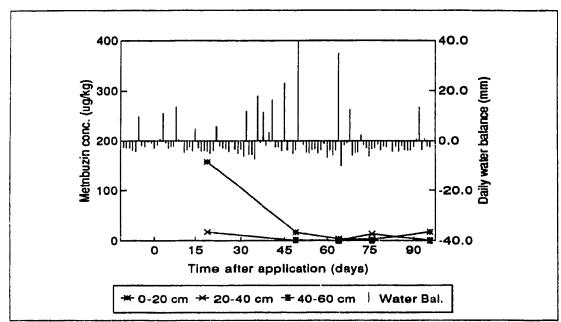


Figure 47. Soil metribuzin concentration in the field Sub 5 (1992).

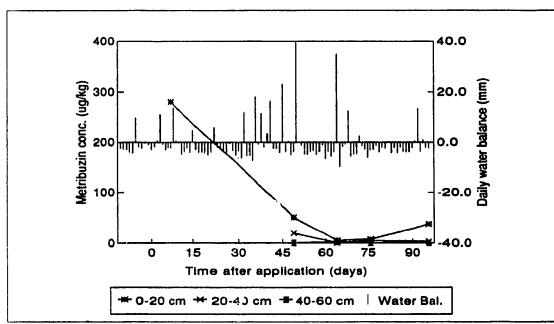


Figure 48. Soil metribuzin concentration in the field Dr 1 (1992).

Table LA92-1. Metribuzin concentration (µg/kg) in the soil in the field Sub 2.

Day	DAA	0-20 c	m	20-40 cm		40-60 c	m
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 27	-1	11.9	101	6.5	82	nd	
May 29	+1	394.7	32				
Jul 15	+48	64.4	102	21.7	160	0.7	171
Jul 30	+63	13.2	77	nd	` `	nd	
Aug 11	+75	7.9	39	nd		nd	
Aug 31	+95	4.6	63	8.5	125	nd	

DAA: Days after application. conc.: Metribuzin concentration.

% C.V.: coefficient of variation in percentage.

Table LA92-2. Metribuzin concentration ($\mu g/kg$) in the soil in the field Sub 4.

Day	y DAA 0-20 cm		DAA	OAA 0-20 cm 20-40 cm		cm	40-60	cm
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.	
Jun 15	+18	163.3	70	62.8	38	,	Cale Service	
Jul 15	+48	32.2	105	4.5	113	4.4	141	
Jul 30	+63	4.5	96	1.1	173	nd	saya didik	
Aug 11	+75	21.9	46	3.8	92	nd		
Aug 31	+95	15.6	53	1.0	170	nd	1.77.37.07.78 1.77.37.00.78	

DAA: Days after application. conc.: Metribuzin concentration.

Table LA92-3. Metribuzin concentration (µg/kg) in the soil in the Sub 5 field.

Day DA	DAA		0-20 cm	20-40	cm	40-60 c	m
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
Jun 15	+18	158.0	59	17.0	36		
Jul 15	+ 48	16.7	73	nd		1.4	36
Jul 30	+63	4.0	56	nd	,	nd	
Aug 11	+75	2.5	140	13.3	66	nd	
Aug 31	+95	17.4	118	0.3	167	nd	

DAA: Days after application. conc.: Metribuzin concentration.

% C.V.: coefficient of variation in percentage.

Table LA92-4. Metribuzin concentration (µg/kg) in the soil in the Dr 1 field.

Day	DAA	0-20 cm		0-20 cm 20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
Jun 03	+6	280.5	100		,		
Jul 15	+48	50.6	123	17.5	70	0.3	(200 , °
Jul 30	+63	5.3	¹ 15	nd		2.4	175
Aug 11	+75	7.4	45	4.9	173	nd	
Aug 31	+95	37.5	36	3.2	97	nd	

DAA: Days after application. conc.: Metribuzin concentration.

A.1.3 Metribuzin concentrations in ground water (1992)

Table LA92-5. Metribuzin concentration (µg/L) In ground water.

Day	DAA	Sub 2 S		ub 4	s	ub 5	D	r 1	
		conc.	%C.V.	conc.	%C.V	conc.	%C.V	conc.	%C.V.
Jul 15	+48	0 20	140	0.35	6	0.10	140	1.21	15
Jul 30	+63	0.17	30	0.23	91	0.18	*	17.12	67
Aug 11	+75	0.04	150	0.18	172	0.00	0	6.24	82
Aug 31	+95	0.93	173	0.00	0	0.00	,O	9.38	96
Sep 18	+113					7.77	•	16.93	74
Oct 09	+134		1					12.59	138
Oct 20	+145	2.97	118	0.21	+	0.53	*		

DAA: Days after application. conc.: Metribuzin concentration.

% C.V.: coefficient of variation in percentage.

*: only one sample was taken in the experimental unit (no % C.V.)

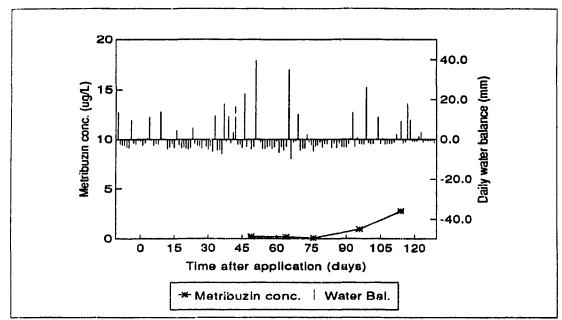


Figure 49. Ground water metribuzin concentration in the Sub 2 field (1992).

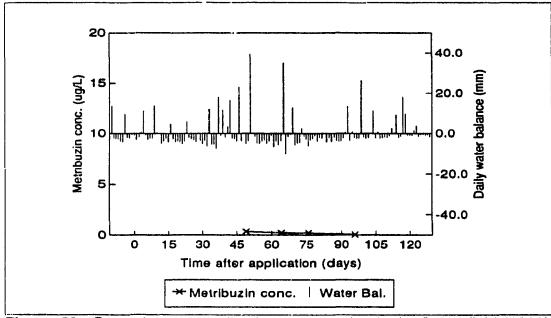


Figure 50. Ground water metribuzin concentration in the Sub 4 field (1992).

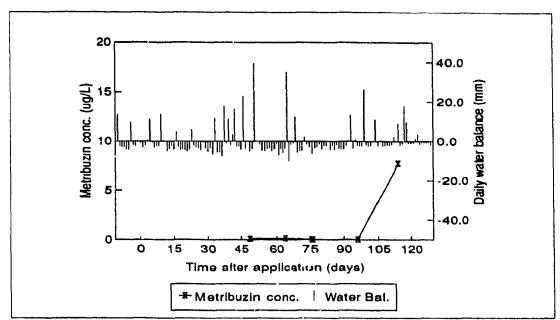


Figure 51. Ground water metribuzin concentration in the Sub 5 field (1992).

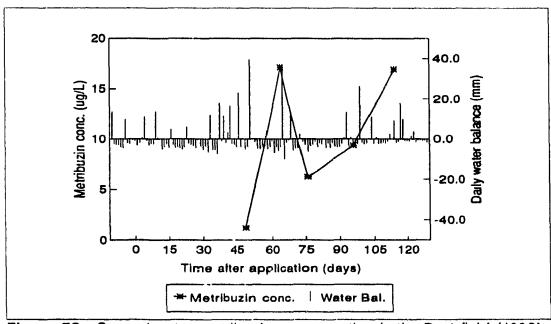


Figure 52. Ground water metribuzin concentration in the Dr 1 field (1992).

A.1.4 Nitrate-N concentrations in soil (1992).

Table LA92-6. Nitrate-N concentration (µg/g) in the soil in the field Sub 2.

Day	Day 0-20 cm				40)-60 cm
	conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 29	25.9	9				*
Jul 15	1.1	64	6.0	65	28.1	80 ~
Jul 30	2.3	56	1.9	16	2.5	40
Aug 11	0.5	20	6.2	116	58.0	48

conc.: Nitrate-N concentration.

% C.V.: coefficient of variation in percentage.

Table LA92-7. Nitrate-is concentration (µg/g) in the soil in the field Sub 4.

Day	0-20 cm		20-40	cm	40-60 cm	
	conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
Jun 15	61.5	77	74.2	180		X 127
Jul 15	1.0	110	1.6	60 100	7.6	14 4 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
Jul 30	0.9	33	0.6	83	1.0	40 ~ ~ .
Aug 11	20.3	26	9.1	170	15.6	.89

conc.: Nitrate-N concentration.

Table LA92-8. Nitrate-N concentration (µg/g) in the soil in the field Sub 5.

Day	0-20	0-20 cm		cm	40-60 cm	
	conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
Jun 15	21.5	106	6.3	33		
Jul 15	2.4	58	6.7	115	9.1	37
Jul 30	0.6	67	0.7	57	00	1111
Aug 11	28.8	9	14.2	142	30.5	17

conc.: Nitrate-N concentration.

% C.V.: coefficient of variation in percentage.

*: only one sample was taken in the experimental unit (no % C.V.)

Table LA92-9. Nitrate-N concentration (µg/g) in the soil in the field Dr 1.

Day	Day 0-20 cm			cm	40-60 c	m
	conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
Jun 03	20.8	64				J. ryog
Jul 15	46.4	100	21.7	87	4.0	88
Jul 30	1.4	36	10.5	90 1	0.6	83
Aug 11	19.3	31	0.5	120	17.1	27

conc.: Nitrate-N concentration.

A.1.5 Nitrate-N concentrations in ground water (1992).

Table LA92-10. Nitrate-N concentration (µg/ml) in ground water.

Day	Sub 2	Sub 2		4	Sub	5	Dr 1		
	conc.	%C.V.	conc.	%C.V	conc.	%C.V.	conc.	%C.V.	
Jul 15	60.0	36	27.5	46	41.8	60	38.2	5	
Jul 30	49.4	.22	31.6	88	89.3	#	54.3	e1 🔷	
Aug 11									
Aug 31	15.5	28	4.4	30	17.9	* .	10.6	52	
Sep 18	9.1	53			14.1	*	9.6	44	
Oct 09							12.6	80%	
Oct 20	17.2	42	6.5	*	21.1	•			

conc.: Nitrate-N concentration.

^{*:} only one sample was taken in the experimental unit (no % C.V.)

A.1.6 Water regime (1992).

N.B.: WT : Water table depth (m)

Dr : Subsurface drainage treatment

Sub: Subirrigation treatment

ET: Evapotranspiration (mm)
Bal: Water balance (rainfall minus

evapotranspiration) (mm)

Crop coefficient: From Doorenbos and Pruitt, 1977.

DAY	WT DR	WT SUB	RAIN	ET	BAL	CROP
	(m)	(m)	(mm)	(mm)	(mm)	COEFF
_						
01-May			1.8	1.3	0.5	0.51
02-May			9.2	1.5	7.7	0.51
03-May			0.0	0.9	-0.9	0.51
04-May			0.0	1.8	-1.8	0.51
05-May			0.0	1.4	-1.4	0.51
06-May			0.0	1.6	-1.6	0.51
07-May			0.0	2.8	-2.8	0.51
08-May			0.0	2.7	-2.7	0.51
09-May			11.2	0.6	10.6	0.51
10-May			0.0	2.9	-2.9	0.51
11-May			0.0	2.4	-2.4	0.51
12-May			0.0	3.4	-3.4	0.51
13-May			1.6	2.4	-0.8	0.51
14-May			0.0	1.5	-1.5	0.51
15-May			0.0	2.1	-2.1	0.51
16-May			0.0	2,3	-2.3	0.51
17-May			17.4	3.8	13.6	0.51
18-May			0.0	2.4	-2.4	0.51
19-May			0.0	2.7	-2.7	0.51
20-May			0.0	2.8	-2.8	0.51
21-May			0.0	3.9	-3.9	0.51
22-May			0.0	4.3	-4.3	0.51
23-May			13.8	4.1	9.7	0.51
24-May			0.0	1.8	-1.8	0.51
25 - May			0.0	2.4	-2.4	0.51
26-May			0.0	0.5	-0.5	0.51
27-May			0.0	0.9	-0.9	0.51
28-May			0.0	3.0	-3.0	0.51
29-May			0.0	1.7	-1.7	0.53
30-May			3.0	2.3	0.7	0.54
31-May			11.4	0.2	11.2	0.56
01-Jun			0.4	1.2	-0.8	0.56
02-Jun			0.0	2.9	-2.9	0.57
03-Jun			0.0	2.1	-2.1	0.59
04-Jun			0.2	2.4	-2.2	0.60

DAY	WT DR	WT SUB	RAIN_	et	BAL	CROP
	(m)	(m)	(mm)	(mm)	(mm)	COEFF
05-Jun			15.4	1.7	13.7	0.62
06-Jun			1.6	1.0	0.6	0.63
07-Jun			1.8	1.9	-0.1	0.65
08-Jun			0.0	4.8	-4.8	0.66
09Jun			0.0	3.7	-3.7	0.68
10-Jun			0.0	2.3	-2.3	0.70
11-Jun			0.0	4.1	-4.1	0.71
12-Jun			8.6	3.8	4.8	0.73
13-Jun			0.6	3.4	-2.8	0.74
14-Jun			0.0	4.1	-4.1	0.76
15-Jun			0.0	3.8	-3.8	0.77
16-Jun			0.0	4.3	-4.3	0.79
17-Jun			0.0	5.1	-5.1	0.80
18-Jun			0.2	4.2	-4.0	0.82
19-Jun			8.0	2.1	5.9	0.83
20-Jun			0.2	2.2	-2.0	0.85
21-Jun			0.0	2.9	-2.9	0.86
22-Jun			0.0	3.2	-3.2	0.88
23-Jun			0.0	4.3	-4.3	Ö.90
24-Jun			2.0	2.5	-0.5	0.91
25-Jun			0.0	3.3	-3.3	0.93
26-Jun			0.0	5.1	-5.1	0.94
27 - Jun			0.4	3.7	-3.3	0.96
28-Jun			0.0	6.3	-6.3	0.97
29-Jun			17.4	5.5	11.9	0.99
30-Jun			0.0	5.4	-5.4	1.00
01-Jul			0.0	5.4	-5.4	1.05
02-Jul			0.0	7.4	-7.4	1.05
03-Jul		-0.98	20.8	2.8	18.0	1.05
04-Jul		-0.95	0.6	1.4	-0.8	1.05
05-Jul	-1.34	-0.77	16.8	5.4	11.4	1.05
06-Jul	1.5.	-0.76	1.8	3.6	-1.8	1.05
07-Jul		-0.77	5.8	2.4	3.4	1.05
08-Jul		-0.77	21.6	5.0	16.6	1.05
09-Jul		-0.60	0.0	2.4	-2.4	1.05
10-Jul		-0.63	0.8	3.3	-2.5	1.05
11-Jul		-0.68	0.0	3.9	-3.9	1.05
12-Jul		-0.77	25.6	2.5	23.1	1.05
13-Jul		-0.53	0.0	3.8	-3.8	1.05
14-Jul		-0.62	0.8	0.5	0.3	1.05
15-Jul	-1.25	-0.65	0.0	5.0	-5.0	1.05
16-Jul	1.23	-0.77	0.4	4.1	-3.7	
17-Jul		-0.72	41.2	1.7		1.05
17-5ul 18-Jul		-0.39	3.2	3.3	39.5	1.05
19-Jul		-0.41			-0.1	1.05
19-5u1 20-Jul			2.2	3.6	-1.4	1.05
		-0.56	0.4	5.0	-4.6	1.05
21-Jul		-0.60	0.0	4.9	-4.9	1.05
22-Jul		-0.67	0.0	3.8	-3.8	1.05
23-Jul		-0.74	0.0	3.3	-3.3	1.05

DAY	WT DR	WT SUB	RAIN	4 6	5.	
	(m)	(m)	(mm)	ET (mm)	BAL	CROP
			(4444)	(11111)	(mm)	COEFF
24-Jul		-0.80	0.0	4.9	-4.9	1.05
25-Jul		-0.85	0.0	3.8	-3.8	1.05
26-Jul		-0.89	0.8	1.9	-1.1	1.05
27-Jul		-0.90	0.0	6.6	-6.6	1.05
28-Jul		-0.91	0.0	3.8	-3.8	1.05
29-Jul		-0.91	0.0	5.7	-5.7	1.05
30-Jul	-1.37	-0.91	0.0	3.8	-3.8	1.05
31-Jul		-0.90	35.3	0.4	34.9	1.05
01-Aug		-0.69	5.2	15.1	-9.9	1.05
02-Aug		-0.68	1.0	2.5	-1.5	1.05
03-Aug		-0.61	2.8	3.5	-0.7	1.05
04-Aug		-0.69	14.6	2.0	12.6	1.05
05-Aug		-0.57	0.0	5.7	-5.7	1.05
06-Aug		-0.70	0.0	4.7	-4.7	1.05
07-Aug		-0.82	0.0	4.4	-4.4	1.05
08-Aug		-0.90	6.0	3.6	2.4	1.05
09-Aug		-0.87	0.0	1.4	-1.4	1.05
10-Aug	-1.19	-0.86	1.2	3.9	-2.7	1.05
11-Aug		-0.98	0.0	6.1	-6.1	1.05
12-Aug		-1.01	0.0	3.2	-3.2	1.05
13-Aug		-1.03	0.0	2.7	-2.7	1.05
14-Aug		-1.04	0.0	1.3	-1.3	1.05
15-Aug		-1.04	0.8	4.5	-3.7	1.05
16-Aug		-1.05	1.2	3.2	-2.0	1.05
17-Aug		-1.05	0.2	2.5	-2.3	1.05
18-Aug		-1.05	3.0	2.8	0.2	1.05
19-Aug		-1.05	0.4	4.6	-4.2	1.05
20-Aug		-1.05	0.0	2.0	-2.0	1.05
21-Aug		-1.05	0.4	4.5	-4.1	1.04
22-Aug		-1.05	0.0	1.8	-1.8	1.02
23-Aug		-1.05	0.0	3.6	-3.6	1.01
24-Aug		-1.05	0.0	3.9	-3.9	0.99
25-Aug		-1.05	0.0	3.7	-3.7	0.98
26-Aug		-1.05	1.6	3.8	-2.2	0.97
27-Aug		-1.05	2.0	1.4	0.6	0.95
28-Aug		-1.05	15.4	2.0	13.4	0.94
29-Aug		-1.05	0.6	4.2	-3.6	0.92
30-Aug		-1.05	2.0	1.1	0.9	0.91
31-Aug	-1.33	-1.05	0.6	2.6	-2.0	0.90
01-Sep		-1.10	0.0	2.2	-2.2	0.88
02-Sep		-1.10	0.0	2.2	-2.2	0.87
03-Sep		-1.08	26.6	0.5	26.1	0.85
04-Sep		-1.04	0.0	1.6	-1.6	0.84
05-Sep	-1.34	-1.03	0.0	2.2	-2.2	0.83
06-Sep	-1.33	-1.03	0.0	1.9	-1.9	0.81
07-Sep	-1.34	-1.04	1.2	1.0	0.2	0.80
08-Sep	-1.35	-1.04	14.8	3.6	11.2	0.78
09-Sep	-1.36	-1.03	0.2	2.3	-2.1	0.77
10-Sep	-1.33	-1.01	1.4	0.8	0.6	0.76

DAY	WT DR	WT SUB	RAIN	ET	BAL	CROP
	(m)	(m)	(mm)	(mm)	(mm)	COEFF
11-Sep 12-Sep 13-Sep 14-Sep 15-Sep 16-Sep 16-Sep 17-Sep 19-Sep 21						

A.1.7 Soil moisture content (1992)

Table LA92-11. Soil gravimetric moisture content in the field Sub 2.

Day	0-20 cm		20-40	:m	40-60	cm	60-80 cm		
	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.	
May 27	0.129	16	0.137	29	0.151	40	0.138	22 \	
May 29	0.095	2							
Jul 15	0.167	9	0.179	G	0.201	10	0.207	5	
Jul 30	0.155	19	0.160	14	0.172	5	0.194	3	
Aug 11	0.171	15	0.169	7	0.192	13	0.186	2	
Aug 31	0.161	0.6	0.152	13	0.130	30	0.188	12	

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA92-12. Soil gravimetric moisture content in field Sub 4.

Day	0-20 cm		20-40	cm	40-60	cm	60-80	%C.V.	
	ave.	%C.V.	ave.	%C.V.	8ve.	%C.V.	8ve.	%C.V.	
Jun 15	0.151	17	0.161	14				And a	
Jul 15	0.181	14	0.152	38	0.185	15	0.189	7	
Jul 30	0.167	8	0.161	27~ //3	0.169	12	0.190		
Aug 11	0.186	12	0.177	29	0.184	16	0.189	8	
Aug 31	0.160	5	0.140	18	0.127	46	0.148	34	

ave.: average

Table LA92-13. Soil gravimetric moisture content in field Sub 5.

Day	0-20 cm		20-40) cm	40-60	cm	60-80	60-80 cm		
	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.		
Jun 15	0.132	3	0.152	9						
Jul 15	0.199	3	0.193	3	0.198	9	0.216	6		
Jul 30	0.164	2	0.177	8	0.156	20	0.193	5		
Aug 11	0.179	6	0.184	9	0.174	6	0.189	1		
Aug 31	0.177	10	0.163	15	0.161	12	0.139	0		

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA92-14. Soil gravimetric moisture content in the field Dr 1.

Day	0-	0-20 cm		0-40 cm	4	0-60 cm	60	-80 cm
	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.
Jun 03	0.127	14						
Jul 15	0.122	12	0.113	35	0.106	52	0.087	~ 90° ~
Jul 30	0 125	24	0.126	33	0.119	20	0.156	17 , 3 %
Aug 11	0.149	8	0.115	48	0.143	7	0.176	3
Aug 31	0.182	16	0.152	22	0.105	. 26	0.118	~, 15

ave.: average

A.1.8 Water table depths in observation wells (1992).

Table LA92-15. Water table depth (m) in the observation wells.

Day	Sub 2		Sı	Sub 4		Sub 5		Dr 1	
	DEPTH	%C.V.	DEPTH	%C.V	DEPTH	%C.V.	DEPTH	%C.V.	
Jul 15	0.69	*	0.93		0.95	•	1 12	16	
Jul 30	1.10	9	0.81	2	1.06	•	1.24	10	
Aug 11	0.80	19	1.10	16	1.09	20	1.07	10	
Aug 31	1.09	9	1 05	8	1.24	•	1.20	10	
Sep 18	1.13	4			1.28	* .	1.29	9	
Oct 09						,	1.15	15	
Oct 20	1.00	4	1.07	*	1.15	A .		1000	

depth: depth of the water table (m)
% C.V.: coefficient of variation in percentage.
*: only one reading was taken in the experimental unit (no % C.V.)

A.1.9 Water table tubes readings (1992).

Table LA92-16. Water table tubes readings (m).

Day	Jul 15	Jul 30	Aug 10	Aug 31	Sept 18	Oct 20
S2,1 L1	1.16	NR	1.37	D	D	D
S2,1 C	1.08	1.48	1.31	1.45	1.46	1.32
S2,1 L2	1.17	NR	NR	D	D	D
S2,2 C		1.32	0.98	1.30	1.28	1.13
S2,3 C		1.07	0.70	1.06	1.24	1.10
S4,1 L1		NR	1.43	D	D	D
S4,1 C		1.08	1.43	1.24	1.39	1.31
S4,1 L2		NR	1.39	D	D	D
S4,2 C				1.30		NR
S4,3 L1	1.27	1 41	1.31	D	D	D
S4,3 C	1.41	1.27	1.45	1.50	1.85	1.88
S4,3 L2	1.33	NR	1.40	D	D	D
S5,1 L1	1.43	NR	NR	D	D	D
S5,1 C	1.33	1 44	NR	1.38	1.42	1.29
S5,1 L2	1.49	NR	NR	D	D	D
S5,2 L1	1.34	NR	NR	D	D	D
S5,2 C	1.37	NR	1.40	1.25	D	D
S5,2 L2	1.17	NR	NR	D	D	D

S : subirrigation treatment

L1,L2: reading taken one meter from a cirainage lateral

C : reading taken at mid-spacing (centre) NR : water table was too deep to be read.

D : water table tube had been destroyed by machinery.

DAY	Jul 15	Jul 30	Aug 10	Aug 31	Sep 18	Oct 09	Oct 20
Dr 1C	1.37	1.49	1.31	1.45	1.52	1.56	1.27
Dr 2C	1 24	1.50	1.31	1.44	1.53	1.50	
Dr 3C	1.14	1.31	1.19	1.31	1.41	1.38	

Dr: reading taken in the subsurface drainage treatment

A.2 Results in 1993.

A.2.1 Pesticide application in : 993.

. Insecticides

Common name Co	mmercial name	Applic. rate	Applic.day
Deltamethrin Endosulfan	Decis Thiodan	500 ml/ha 2.0 L/ha	Dr: 06/08 Sub:14/07
Cypermethrin Azinphos-methyl	Cymbush Guthion	300 ml/ha 660 g/ha	Sub:12/06 Sub:20/06 05/07
Oxamyl	Vydate	600 g/ha	Dr: 29/06 Dr: 13/07

Fungicides

Common name	Commercial name	Applic, rate	Applic.day
Metalaxyl	Ridomil	2.5 kg/ha	Sub: 06/08 Dr: 06/08
Mancozeb	Manzate	1.6 kg/ha	Sub: 14/07
			Dr: 13/07 26/08

Herbicides

Common name	Commercial name	Applic. rate	Applic.day
Diquat	Reglone	0.25 kg/ha	Sub: 25/08
•	•	•	Dr; 01/09 Sub: 24/05
Metribuzin	Sencor	1 kg/ha	Dr: 03/06

A.2.2 Metribuzin concentrations in soil (1993)

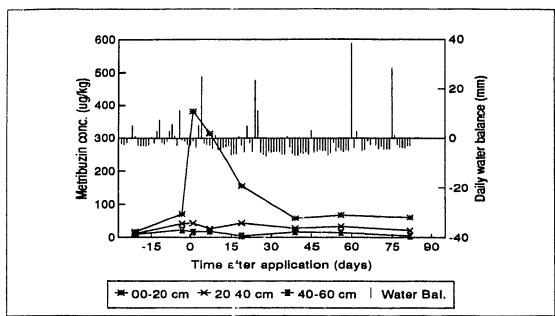


Figure 53. Soil metribuzin concentration in the field Sub 2 (1993).

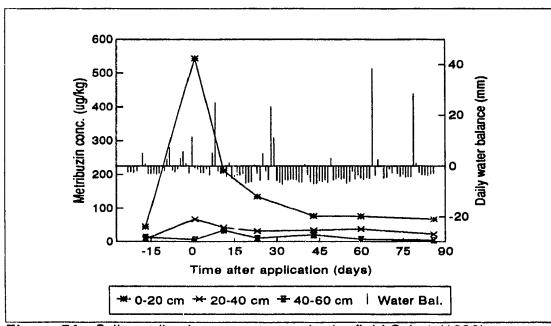


Figure 54. Soil metribuzin concentration in the field Sub 4 (1993).

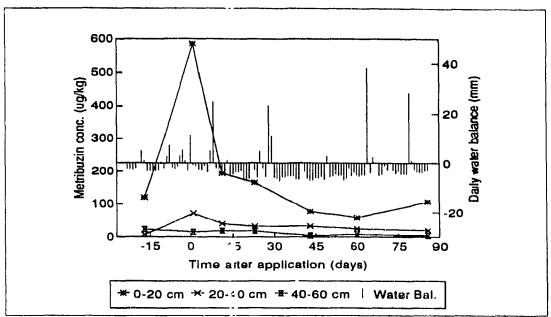


Figure 55. Soil metribuzin concentration in the field Sub 5 (1993).

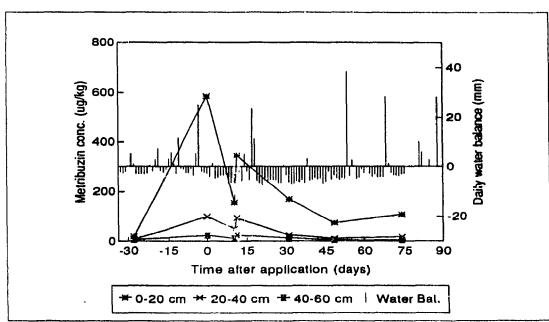


Figure 56. Soil metribuzin concentration in the field Dr 2 (1993).

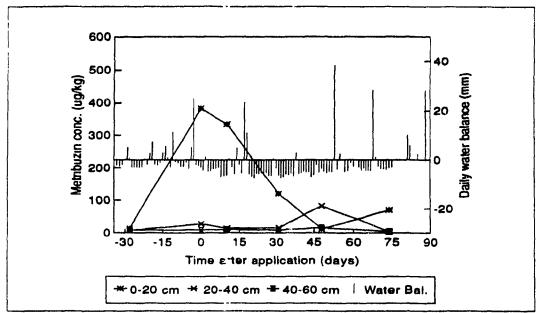


Figure 57. Soil metribuzin concentration in the field Dr 3 (1993).

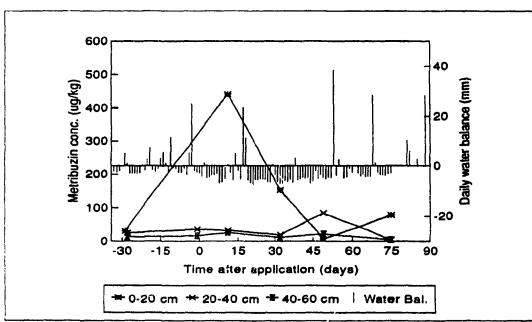


Figure 58. Soil metribuzin concentration in the field Dr 4 (1993).

Table LA93-1. Metribuzin concentration (µg/kg) In the soil in the field Sub 2.

Day	DAA	DAA 0-20 cm		20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 07	-21	16.2	89	11.9	100	9.5	.82
May 25	-3	71.7	38	42.4	3 1	22.8	48
May 29	+1	382.6	28	43.3	45	16.8	.47
Jun 04	+7	315.1	23	26.8	44	18.6	86
Jun 16	+19	155.1	52	43.4	Ì 13	nd	***************************************
Jul 06	+39	58.3	32	28.1	67	16.6	76
Jul 23	+56	68.4	51	33.8	64	14.8	68
Aug 18	+82	59 9	60	21.7	133	nd	

DAA: Days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd: not detectable.

Table LA93-2. Metribuzin concentration (µg/kg) in the soil in the field Sub 4.

Day	DAA	0-20 cm		20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 07	-17	44 9	41	8.8	76,	13.9	78
May 25	+1	543.1	32	67.5	83	7.2	
Jun 04	+17	212.0	24	42.6	79	34.6	136
Jun 16	+23	1348	23	32.1	126	11.3	56.
Jul 06	+43	76.8	17	34.6	-24	20.9	182%
Jul 23	+60	76.0	16	38.1	87	7.8	62
Aug 18	+86	67.5	54	23.0	136	nd	1. If the fighter of

DAA: days after application.

conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd: not detectable.

Table LA93-3. Metribuzin concentration (µg/kg) in the soil in the field Sub 5.

Day	DAA	0-20 cm		20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 07	-17	120.0	53	7.7	61	23.6	136
May 25	+1	584.9	43	71.7	111	15.2	93
Jun 04	+17	194.7	20	40.8	80	19.4	44
Jun 16	+23	165.8	25	32.9	62	18.5	38
Jul 06	+43	78.0	23	33.8	. 40	nd	
Jul 23	+60	59.0	15	25.7	101	8.5	72
Aug 18	+86	108.0	87	21.1	108	nd	

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

Table LA93-4. Metribuzin concentration (µg/kg) in the soil in the field Dr 2.

Day	DAA	0-20 cm		20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 07	-28	19.2	81	7.5	57	5.6	42
Jun 04	0	585.9	21	99.6	108	23.9	85
Jun 15	+9	155.0	32	50.5	55	11.6	67
Jun 16	+10	345.7	49	93.9	123	24.4	107
Jul 06	+31	169.0	62	25.1	47	12.9	87
Jul 23	+48	73.9	41	11.3	97	nd	` ` ` ` `
Aug 18	+74	107.3	37	17.2	123	nd	- myanana

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

Table LA93-5. Metribuzin concentration (µg/kg) in the soil in the field Dr 3.

Day	DAA	0-20 cm		20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 07	-28	13.4	79	7.7	-81	8.7	74
Jun 04	0	383.6	15	28.3	32	9.6	83
Jun 15	+9	334.3	31	14.8	96	10.9	63
Jul 06	+31	121.0	15	15.7	63	9 4	81
Jul 23	+48	12.2	102	83.4	25	16.5	70
Aug 18	+74	70.9	56	nd		nd	

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

Table LA93-6. Metribuzin concentration (µg/kg) in the soil in the field Dr 4.

Day	DAA	0-20 cm		20-40 cm		40-60 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 07	-28	30.9	40	25.2	114	13.1	, 82 (1)
Jun 04	0	168.4	97	36.1	73	17.1	· 60 ·
Jun 15	+9	440.8	10	32.9	80	26.0	98
Jul 06	+31	152.9	38	20.1	64	124	103
Jul 23	+48	7.0	50	83.8	50	21.8	/114
Aug 18	+74	78.3	, 55	nd		nd	

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

A.2.3 Metribuzin concentrations in ground water (1993)

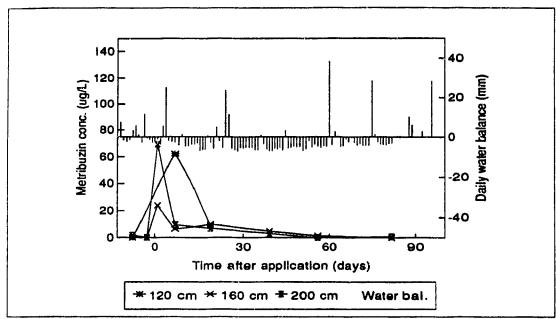


Figure 59. Ground water metribuzin concentration in the field Sub 2 (1993).

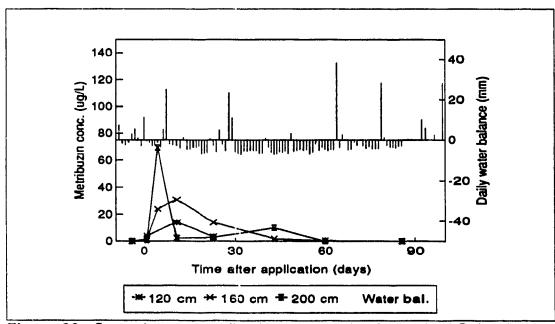


Figure 60. Ground water metribuzin concentration in the field Sub 4 (1993).

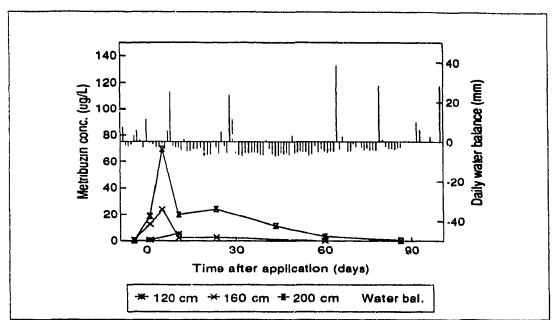


Figure 61. Ground water metribuzin concentration in the field Sub 5 (1993.)

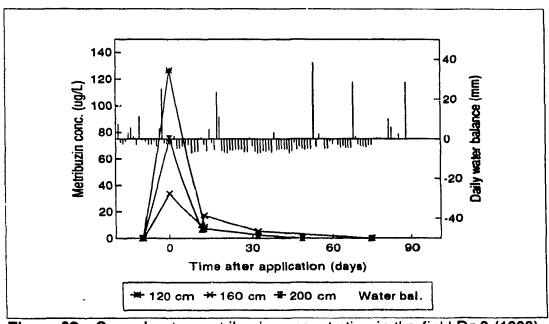


Figure 62. Ground water metribuzin concentration in the field Dr 2 (1993).

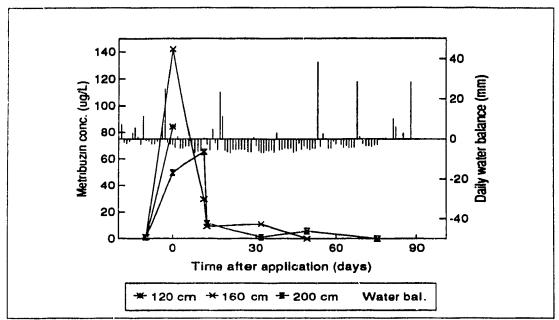


Figure 63. Ground water metribuzin concentration in the field Dr 3 (1993).

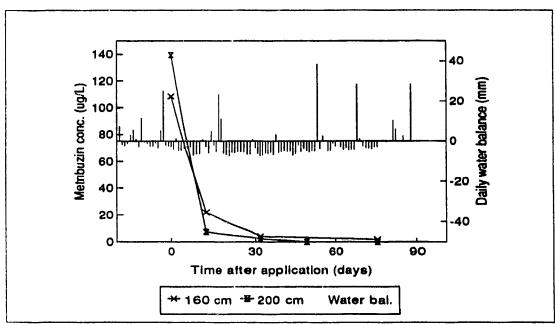


Figure 64. Ground water metribuzin concentration in the field Dr 4 (1993).

Table LA93-7. Metribuzin concentration ($\mu g/L$) in ground water in the field Sub 2.

Day DAA	DAA	120 cm		160 cm		200 cm	
	1.	conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 20	-8			nd		1.7	89
May 25	-3	0.29	127	nd		0.3	126
May 29	+1			24.0	40	69 4	30
Jun 04	+7	62.3	65	6.4	12	9.6	. 88 45.45
Jun 16	+19	8.9	27	10.0	63	6.9	53
Jul 06	+39			4.8	*	3.1	64
Jul 23	+56			1.4	98 💉 🗸	nd	***************************************
Aug 18	+82			nd	, , , , , , , , , , , , , , , , , , ,	0.8	92

DAA: days after application.

conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

* : only one sample was taken in the experimental unit (no %C.V.)

Table LA93-8. Metribuzin concentration (μ g/L) in the ground water in the field Sub 4.

Day	DAA	120 cm		160	cm	200 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 20	-4			nd	,	0.1	103
May 25	+1	3.9	92	1.7	29	1.0	92
Jun 04	+17		54	30.7	4	2.4	37
Jun 16	+23	3.5	99	14.0	84	3.0	48
Jul 06	+43			2.0		10.1	76
Jul 23	+60			0.6	95	nd	
Aug 18	+86			nd		nd	11. 14. 14. 15.

DAA: days after application.

conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

Table LA93-9. Metribuzin concentration ($\mu g/L$) in the ground water in the field Sub 5.

Day DAA		120 cm		16	160 cm		200 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.	
May 20	-4			0.9	*	nd	(3)	
May 25	+1	0.8	14	12.7	133	18.8	140 1	
Jun 04	+17	5.7	•	2.4	. •	20.1	49 👙	
Jun 16	+23		,	2.7	*	24.3	102	
Jul 06	+43					11.5	•	
Jul 23	+60		***************************************	nd		3.4	72 ;	
Aug 18	+86			nd	,	0.5	133	

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

* : only one sample was taken in the experimental unit (no %C.V.)

Table LA93-10 . Metribuzin concentration ($\mu g/L$) in the ground water in the field Dr 2.

Day DA	DAA	120 cm		160	cm	200 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 25	-10	nd		0.2	117 .	0.3	127
Jun 04	0	126.6	50	33.8	47 ()	75.6	59
Jun 15	+9			9.9	43	6.7	45
Jun 16	+10	8.9	*	17.3	77	7.1	28
Jul 06	+31			5.2	76	2.6	27 %
Jul 23	+48				/ 11 /	nd	7743
Aug 18	+74			nd	1	nd	32.73

DAA: days after application.

conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

* : only one sample was taken in the experimental unit (no %C.V.)

Table LA93-11. Metribuzin concentration (µg/L) in the ground water in the field Dr 3.

Day	DAA	120 cm		1	160 cm)0 cm
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
May 25	-10	1.1	126	1.4	134	1.2	136
Jun 04	0	84.3	*	142.0	69	49.8	44
Jun 15	+9			29.4	32	65.2	51
Jun 16	+10			9.1	69	11.5	85
Jul 06	+31			10.9	115	1.1	78
Jul 23	+48		``	nd		5.7	53
Aug 18	+74			nd	, , ,	nd	100000000000000000000000000000000000000

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

* : only one sample was taken in the experimental unit (no %C.V.)

Table LA93-12. Metribuzin concentration ($\mu g/L$) in the ground water in the field Dr 4.

Day	DAA	120 cm		160 cm		200 cm	
		conc.	% C.V.	conc.	% C.V.	conc.	% C.V.
Jun 04	0			108.7	493	139.4	57
Jun 16	÷10		,	21.9	51 ···	7.4	
Jul 06	+31			4.2	47	2.6	62
Jul 23	÷48					nd	
Aug 18	+74			1.9		nd	

DAA: days after application. conc: Metribuzin concentration.

%C.V.: coefficient of variation in percentage.

nd : not detectable

* : only one sample was taken in the experimental unit (no %C.V.)

A.2.4 Water regime (1993).

N.B.: WT : Water table depth (m)
Dr : Subsurface drainage treatment
Sub: Subirrigation treatment

ET : Evapotranspiration (mm)
Bal: Water balance (rainfall minus

evapotranspiration) (mm)
Crop coefficient: From Doorenbos and Pruitt, 1977.

DAY	WT DR	WT SUB	RAIN	ET	BAL	CROP
	(m)	(m)	(mm)	(mm)	(mm)	COEFF
01-May			0.0	2.2	-2.2	0.51
02-May			0.0	2.1	-2.1	0.51
03-May			0.0	2.5	-2.5	0.51
04-May			0.0	1.9	-1.9	0.51
05-May			1.6	1.5	0.1	0.51
06-May			7.0	1.9	5.1	0.51
07-May			2.4	1.5	0.9	0.51
08-May			0.0	2.9	-2.9	0.51
09-May			0.0	3.0	-3.0	0.51
10-May			0.0	2.8	-2.8	0.51
11-May			0.0	3.1	-3.1	0.51
12-May			0.0	2.6	-2.6	0.51
13-May			2.8	2.3	0.5	0.51
14-May			0.0	1.8	-1.8	0.51
15-May			4.6	1.8	2.9	0.51
16-May			8.8	1.5	7.3	0.51
17-May			0.0	1.6	-1.6	0.51
18-May			0.0	2.3	-2.3	0.51
19 -M ay			0.6	1.8	-1.2	0.51
20-May		-1.15	4.6	1.5	3.1	0.51
21-May			7.4	1.8	5.6	0.53
22-May			3.4	2.3	1.1	0.55
23-May			0.0	2.7	-2.7	0.57
24-May			13.6	2.1	11.5	0.59
25 -Ma y	-0.81	-1.02	1.2	1.9	-0.7	0.61
26-May			1.2	2.3	-1.1	0.63
27-May			0.0	2.6	-2.6	0.65
28-May			0.0	2.5	-2.5	0.67
29-May		-1.28	1.2	2.2	-1.0	0.69
30-May			0.0	3.5	-3.5	0.71
31-May			8.6	3.3	5.3	0.73
01-Jun		•	27.4	2.3	25.1	0.75
02-Jun			1.2	3.1	-1.9	0.77
03-Jun	-1.03	-0.92	0.4	2,8	-2.4	0.79
04-Jun	-1.09	-0.99	0.2	3.0	-2.8	0.81
05-Jun	-1.10	-1.02	0.0	4.1	-4.1	0.83

DAY	WT DR	WT_SUB	RAIN	ET	BAL	CROP
	(m)	(m)	(mm)	(mm)	(mm)	COEFF
06-Jun	-1.10	-1.01	4.2	2.8	1.4	0.85
07-Jun	-1.12	-1.00	0.0	4.7	-4.7	0.87
08-Jun	-1.15	-1.01	0.0	4.4	-4.4	0.89
09-Jun	-1.15	-1.00	0.4	4.0	-3.6	0.91
10-Jun	-1.17	-1.02	0.4	3.9	-3.5	0.93
11-Jun	-1.18	-1.04	1.2	4.1	-3.0	0.95
12-Jun	-1.19	-1.05	0.0	6.8	-6.8	0.97
13-Jun	-1.20	-1.07	0.0	6.4	-6.4	0.98
14-Jun	-1.20	-1.08	0.0	6.3	-6.3	1.01
15-Jun	-1.21	-1.09	6.6	6.0	0.6	1.03
16-Jun	-1.19	-1.09	2.2	4.9	-2.7	1.05
17-Jun	-1.22	-1.10	0.0	5.7	-5.7	1.05
18-Jun 19-Jun	-1.24	-1.11	9.6	4.6	5.0	1.05
20-Jun	-1.20	-1.03	3.2	5.2	-2.0	1.05
20-3un 21-Jun	-1.21 -1.00	-1.00	0.0	5.4	-5.4	1.05
21-Jun 22-Jun	-1.00 -0.95	-0.94	27.4	4.0	23.5	1.05
23-Jun	-0.95 -1.12	-0.99 -0.97	15.2	4.0	11.2	1.05
24-Jun	-1.12	-0.97	0.0	5.8	-5.8	1.05
25-Jun	-1.25	-1.00 -1.03	0.0	6.6	-6.6	1.05
26-Jun	-1.28	-1.03	0.0	7.3	-7.3	1.05
27-Jun	-1.31		0.0	5.5	-5.5	1.05
28-Jun	-1.32	-1.10 -1.14	0.0	5.6	-5.6	1.05
29-Jun	-1.32	-1.14	0.0	5.2	-5.2	1.05
30-Jun	-1.35	-1.16	0.0	5.3	-5.3	1.05
01-Jul	-1.35	-1.21	0.0	5.4	-5.4	1.05
02-Jul	-1.35	-1.21	0.0 0.0	6.5	-6.5	1.05
03-Jul	-1.35	-1.27	6.0	6.5	-6.5	1.05
04-Jul	-1.36	-1.28	2.6	5.2	0.8	1.05
05-Jul	1.50	1.20		6.0	-3.4	1.05
06-Jul	-1.37	-1.28	0.0 0.0	6.1	-6.1	1.05
07-Jul	1.57	1.20	0.0	7.1 6.9	-7.1 -6.0	1.05
08-Jul			0.6	6.4	-6.9	1.05
09-Jul			0.0	6.2	-5.8 6.2	1.05
10-Jul			0.0	5.5	-6.2	1.05
11-Jul			0.0	6.6	-5.5 -6.6	1.05
12-Jul			8.8	5.7	3.2	1.05
13-Jul			0.2	5.8	-5.6	1.05
14-Jul			0.0	5.2	-5.0 -5.2	1.05
15-Jul			0.0	4.6	-3.2 -4.6	1.05
16-Jul			0.0	5.1	-4.0 -5.1	1.05
17-Jul			0.0	4.8	-4.8	1.04
18-Jul			0.0	6.9	-6.9	1.03
19-Jul			0.0	6.1		1.02
20-Jul			2.6	4.5	-6.1	1.01
21-Jul			0.0		-1.9 -5.1	1.00
22-Jul			0.0	5.1	-5.1 -3.6	0.99
23-Jul	-1.57	-1.29	0.4	4.0	-3.6 -4.7	0.98
24-Jul		± ,	0.0	4.7	-4.7 -5.4	0.97
			V . Z	5.6	-5.4	0.96

DAY	WT DR	WT SUB	RAIN	ET	BAL	CROP
	(m)	(m)	(mm)	(mm)	(mm)	COEFF
25-Jul 26-Jul 27-Jul 28-Jul 29-Jul 30-Jul 31-Jul 01-Aug 02-Aug 03-Aug 04-Aug 05-Aug 07-Aug			(mm) 0.0 0.0 41.8 1.0 7.0 4.2 0.0 0.0 3.4 1.6 3.8 0.6 0.0 0.0 0.0	(mm) 4.6 4.8 3.4 4.7 4.3 4.0 4.9 4.5 4.4 4.1 3.9 3.4 4.1 3.9	(mm) -4.6 -4.8 38.4 -3.8 2.7 0.2 -4.9 -4.5 -1.0 -2.5 -0.1 -2.8 -4.1 -3.2 -4.3	0.95 0.94 0.93 0.92 0.91 0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83 0.82 0.81
09-Aug 10-Aug 11-Aug 12-Aug 13-Aug 14-Aug 15-Aug 16-Aug 17-Aug 20-Aug 21-Aug 22-Aug 24-Aug 25-Aug 26-Aug 27-Aug 27-Aug 27-Aug 28-Aug 27-Aug 28-Aug 21-Aug	-1.33	-1.13	0.0 0.0 31.4 4.2 0.6 0.0 0.0 0.0 0.4 0.0 0.0 0.0 0.0 0.0 0.0	4.2 3.0 3.6 3.6 3.8 3.9 3.5 8 3.9 3.8 3.9 3.8 3.8 3.8 3.8 3.8	-4.2 -4.2 28.4 1.2 -3.4 -3.6 -3.8 -3.8 -3.9 -2.5 -3.5 -3.5 -3.6 -3.6 -3.6 -3.6 -3.6 -3.6 -3.6	0.80 0.79 0.78 0.77 0.76 0.75 0.74 0.71 0.71 0.71 0.71 0.71 0.71 0.71 0.71

A.2.5 Soil moisture content (1993).

Table LA93-13. Soil gravimetric moisture content in the field Sub 2.

Day	0-2	0-20 cm		20-40 cm		60 cm
	ave.	%C.V.	ave.	%C.V.	ave.	%C.V.
May 7th	0.193	19	0.235	9	0.223	8
May 25th	0.187	6	0.242	23	0.221	9
May 29th	0.113	19	0.207	15	0.193	16
June 4th	0.137	10	0.220	19	0.203	10
June 16th	0.125	8	0.178	8 .	0.192	9
July 6th	0.081	10	0.133	9	0.173	19
July 23rd	0 083	14	0.129	15	0.125	25
Aug 18th	0.106	8	0.165	6	0.15ย	11

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA93-14. Soil gravimetric moisture content in the field Sub4.

Day	0-2	0-20 cm		20-40 cm		60 cm
	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.
May 7th	0.157	3	0.179	32	0.171	43
May 25th	0.181	\$	0.174	22	0.144	28
June 4th	0.141	1	0.203	22	0.172	26
June 16th	0.141	16	0.158	25	0.140	42
July 6th	0.090	16	0.120	13	0.122	27
July 23rd	0.056	34	0.086	30	0.104	35
Aug 18th	0.123	8	0.120	27	0.131	38 *** -

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA93-15. Soil gravimetric moisture content in the field Sub5.

Day	0-	0-20 cm		20-40 cm		-60 cm
	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.
May 7th	0.193	17	0.178	19	0.214	18 **
May 25th	0.207	11	0.194	8	0.230	5
June 4th	0.137	20	0.192	24.	0.200	14.
June 16th	0.152	17	0.194	14	0.165	12
July 6th	0.146	10	0.166	11	0.149	14
July 23rd	0.097	31	0.122	27	0.093	23
Aug 18th	0.124	10	0.162	10	0.169	10

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA93-16. Soil gravimetric moisture content in the field Dr 2.

Day	0-2	20 cm	20	-40 cm	40-60 cm	
	ave.	% C.V.	ave.	% C.V.	ave,	% C.V.
May 7th	0.244	8	0.256	4.	0.245	1100
June 4th	0.192	7	0.272	12;	0.231	1 // //
June 15th	0.156	3	0.216	27	0.198	7
June 16th	0.199	3	0.223	8	0.223	1877
July 6th	0.133	5	0.183	13.	0.171	12 4
July 23rd	0.083	23	0.145	7 CA	0.113	8 2/1/9
Aug 18th	0.146	12	0.209	23	0.143	9 //

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA93-17. Soil gravimetric moisture content in the field Dr 3.

Day	0-2	20 cm	20	-40 cm	40-60 cm		
	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.	
May 7th	0.190	6	0.202	8	0.208	14', 1	
June 4th	0.132	4.	0.214	. ,12	0.194	10	
June 15th	0.158	11	0.226	25	0.177	11000	
July 6th	0.075	16	0.160	4	0.148	9.1	
July 23rd	0.124	9	0.056	16	0.115	13	
Aug 18th	0.097	19	0.142	4	0.107	11	

ave.: average

%C.V.: coefficient of variation in percentage.

Table LA93-18. Soil gravimetric moisture content in the field Dr 4.

Day	0-	20 cm	20)-40 cm	40-60 cm	
	ave.	% C.V.		% C.V.	ave.	% C.V.
May 7th	0.168	11	0.212	\$ 7 3/2	0.149	37
June 4th	0.134	17	0.180	25 🐬	0.183	310
June 15th	0.086	9 ,	0.129	13	0.124	24
July 6th	0.075	4	0.175	22	0.174	18
July 23rd	0.113	20	0.065	4. 38 (%)	0.122	35
Aug 18th	0.132	17	0.184	419 "	0.108	28

ave.: average

%C.V.: coefficient of variation in percentage.

A.2.6 Water table depths in observation wells (1993).

Table LA93-19. Water table depth (m) in observation wells.

	Sub 2		Sub 4		Sub 5	
	Depth	% CV	Depth	% CV	Depth	% CV
May 20th	1.15	6	1.25	. 5	1.28	5 }
May 26th	1.03	3	0.96	9	1.20	11,**
May 29th	1.06	*				
June 04th	1.05	4	1.04	6	1.19	+
June 16th	1.02	4	1.04	9 '	1.18	*
July 06th	1.28	4	1.31	7,	1.32	5 ***
July 23rd	1.28	4	1.29	8 0.	1.17	627
Aug 18th	1.11	5	1.40	J. 9 (% 5)	1.17	5

		or 2		Dr 3	Dr 4		
	Depth	% CV	Depth	% CV	Depth	% CV	
May 26th	0.81	8	0.96	10			
June 04th	0.89	5	1.01	9		4.38	
June 15th	1.16	1	1.17	9			
June 16th	1.04	4	1.11	10/1/2	1.10	•	
July 06th	1.38	1	1.28	8.	1.40	9.5%	
July 23rd	1.61	2	1.44	38 / //	1.50	3,4	
Aug 18th	1.33	1	1.24	9	1.38	2 9 7/2/5	

depth: depth of the water table (m)

% C.V.: coefficient of variation in percentage.

^{* :} only one reading was taken in the experimental unit (no % C.V.)

A.2.7 Water table tube readings (1993).

Table LA93-20. Water table tube readings (m) in the subirrigated fields.

Day	May 20	May 26	May 29	June 04	June 16	July 06	July 23	Aug 18
S2,1 L	1.15	1.06	NR	1.07	1.00	1.23	1.20	1.10
S2,1 C	1.15	1.03	NR	1.06	1.06	1.27	1.24	1.10
S2,2 L	1.19	NR	NR	NR	NR	1.29	1.29	1.14
S2,2 C	1.23	1.07	NR	1.09	NR	1.35	1.35	1.19
S2,3 C	1.06	0.99	1.06	1.00	0.98	1.22	1.24	1.05
S2,3 L	1.06	0.96	1.05	0.98	1.00	1.21	1.23	1.05
S4,1 L	1.23	0.90		1.12	1.00	1.27	1.22	D
\$4,1 C	1.20	0.90		1.02	0.97	1.24	1.20	D
S4,2 L	1.22	0.91		1.07	0.96	1.25	1.19	. D
S4,2 C	1.20	0.90		0.98	0.98	1.25	1.23	1.28
S4,3 L	1.32	1.05		1.16	1.12	1.39	1.39	1.45
S4,3 C	1.34	1.09		1.12	1.18	1.43	1.44	1.52
S5,1 L	1.23	1.16		1.19	1.19	1.29	1.18	1.16
S5,1 C	1.26	1.21		NR	NR	1.31	1.17	1.17
S5,2 L	1.18	1.15		1.16	1.16	1.21	NF	1.08
S5,2 C	1.21	1.18		1.19	1.18	1.25	1.08	1.10
S5,3 L	1.20	1.06		1.07	1.15	NF	NF	NF
S5,3 C	1.36	NR		NR	NR	1.40	1.25	1.24

S: subirrigation treatment

L : reading taken one meter from a drainage lateral

C: reading taken at mid-spacing (centre)
NR: water table was too deep to be read.
NF: water table tube not found in vegetation.

D : water table tube had been destroyed by machinery.

Table LA93-21. Water table tube readings (m) in the subsurface drainage fields.

Day	May 26	Jun 04	Jun 15	Jun 16	Jul 06	Jul 23	Aug 18
Dr 2,1 L	1.03	1.05	1.18	1.11	1.33	1.52	1.32
Dr 2,1 C	0.88	0.95	NR	1.09	1.37	1.57	1.35
Dr 2,2 L	0.90	0.93	1.14	1.01	1.31	NR	1.28
Dr 2,2 C	0.78	0.86	1.15	1.01	1.36	1.61	1.32
Dr 2,3 L	0.72	0.75	NR	NR	1.25	NR	1.20
Dr 2,3 C	0.78	0.86	1.17	1.01	1.40	1.64	1.32
Dr 3,1 L	NR	NR	NR	NR	1.31	NF	1.29
Dr 3,1 C	1.02	1.09	1.25	1.19	1.36	1.51	1.34
Dr 3,2 L	1.10	1.13	NR	1.15	1.29	1.44	1.26
Dr 3,2 C	0.82	0.88	1.02	0.95	1.13	1.28	1.09
Dr 3,3 L	1.03	1.05	1.09	1.06	1.20	1.35	1.14
Dr 3,3 C	1.03	1.07	1.23	1.18	1.36	1.52	1.29
Dr 4,1 L				NR	1.52	NR	1.49
Dr 4,1 C				NR	1.57	NR	1.54
Dr 4,2 L				1.15	1.30	1.47	1.25
Dr 4,2 C				1.10	1.27	1.45	1.24
Dr 4,3 L				NR	1.55	NR	1.50
Dr 4,3 C				NR	1.37	1.55	1.35

Dr : subsurface drainage treatment

L : reading taken one meter from a drainage lateral

C: reading taken at mid-spacing (centre)
NR: water table was too deep to be read.
NF: water table tube not found in vegetation.

D : water table tube had been destroyed by machinery.

APPENDIX B

RESULTS OBTAINED AT THE VAN WINDEN FARM (ORGANIC DEPOSIT)

- N.B.: 1) The abbreviations VW92 used in the identification of the tables presented in the appendix signifies the location (VW: Van Winden farm) and the year (92: 1992) at which the samples and or readings were taken.
 - 2) Only the results obtained in 1992 will be presented in this thesis.

 The raw data obtained from the first two years of study are presented in Arjoon (1992).
 - 3) The blanks left in tables signify that no measurement were taken for that given location and day.
 - 4) The coefficient of variability (C.V.) will be presented in a percentage form in the shaded areas of the tables.
 - 5) Most of the prometryn and nitrate-N results presented in the tables are average values (from 3 samples in 1992).
 - 6) The abbreviations used in the appendix are explained in the list of abbreviations and symbols section in the beginning of the thesis.

APPENDIX B

B.1 Results in 1992 B.1.1 Pesticide application (1992).

Herbicides

Common name	Commercial	name Applic	. rate	Applic	. day
Prometryn	Gesagard	2.75 kg/ha	(80WP)	Dr:	25-05 Dr:
08-06				Sub, Surf: Sub, Surf:	
Linuron	Lorox	3.0 kg/ha		Sub	: ?

Insecticide

Common name	Commercial name	Applic. rate	Applic. day
Cypermethrin	Cymbush	250 ml/ha	Dr: 22-06 Sub: 22-06

B.1.2 Prometryn concentration in soil

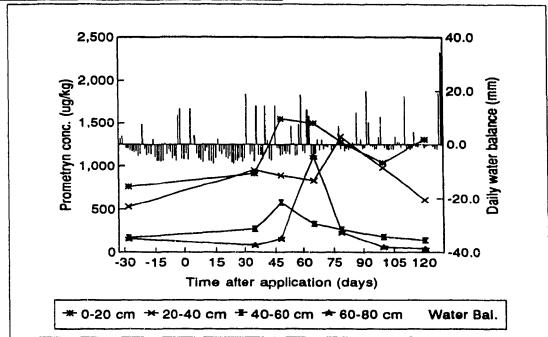


Figure 65. Soil prometryn concentration in the subirrigated field.

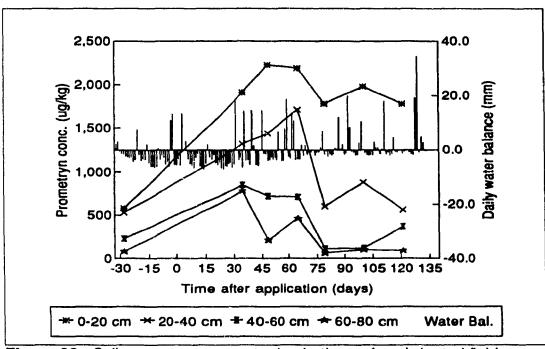


Figure 66. Soil prometryn concentration in the surface irrigated field.

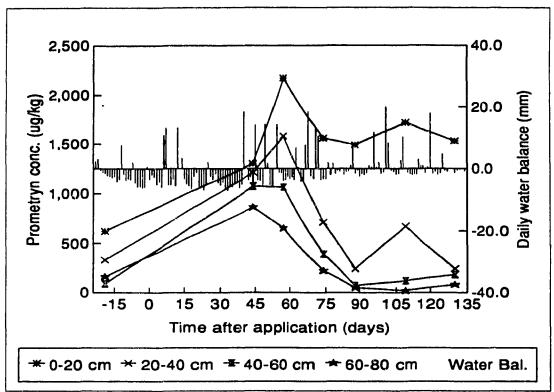


Figure 67. Soil prometryn concentration in the subsurface drainage field.

Table VW92-1. Prometryn concentration (µg/kg) in the subirrigation field.

Day	DAA 0-20 cm		0 cm	20-40 cm		40-60 cm		60-80 cm	
		conc.	%C.V.	conc.	% C.V.	conc.	%C.V.	conc.	%C.V.
May 06	-28	760	25	530	75 .	170	c 212	160	69.
Jul 08	+35	910	18	950	. 33 · · · ·	270	22	80	100
Jul 21	+48	1550	49	890	45	580	69	160	63
Aug 07	+66	1500	49	830	13	330	45	1110	77(> }
Aug 21	+80	1280	28	1340	34	260	19	230	74
Sep 11	+101	1040	36	980	47	180	83 、	60	.: 50 %
Oct 02	+122	1310	29	610	46	140	57	40	75

DAA: days after application.

conc.: Prometryn concentration.

% C.V.: coefficient of variation in percentage.

Table VW92-2. Prometryn concentration ($\mu g/kg$) in soil in the surface irrigation field.

Day	DAA	DAA 0-20 cm		20-40 cm		40-	40-60 cm		80 cm
		conc.	%C.V.	conc.	%C.V.	conc.	%C.V	conc.	%C.V.
May 06	-28	580	19	530	15	230	61	80	13
Jul 08_	+35	1910		1320	66	850	98	780	103
Jul 21	+48	2230		1440	48	720	67	210	71
Aug 07	+66	2190	27	1710	19	710	69	460	107
Aug 21	+80	1780	30	600	88	110	55.	60	50
Sep 11	+101	1980	25	880	35	120	92	100	90
Oct 02	+122	1780	24	560	32	370	95	90	100

DAA: days after application. conc.: Prometryn concentration.

% C.V.: coefficient of variation in percentage.

Table VW92-3. Prometryn concentration ($\mu g/kg$) in soil in the subsurface drainage field.

Day	DAA	0-20 cm		20-	20-40 cm		40-60 cm		BO cm
		conc.	%C.V.	conc.	%C.V.	conc.	%C.V.	conc.	%C.V.
May 06	-28	620	45	330	33	90	44	160	113
Jul 08	+35	1300	73	1210	es	1070	39	860	3)
Jul 21	+48	2170	22	1580	13	1060	65	650	75
Aug 07	+66	1560	42	710	32	390	56	220	50
Aug 21	+80	1490	32	240	58	70	71 ::	50	80
Sep 11	+101	1720	12	670	76	120	33	20	50
Oct 02	+122	1530	10	240	91	180	61	80	163

DAA: days after application. conc.: Prometryn concentration.

% C.V.: coefficient of variation in percentage.

B.1.3 Prometryn concentration in the ground water.

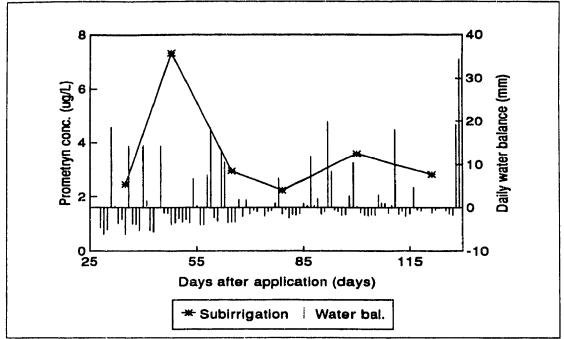


Figure 68. Ground water prometryn concentration in the subirrigated field.

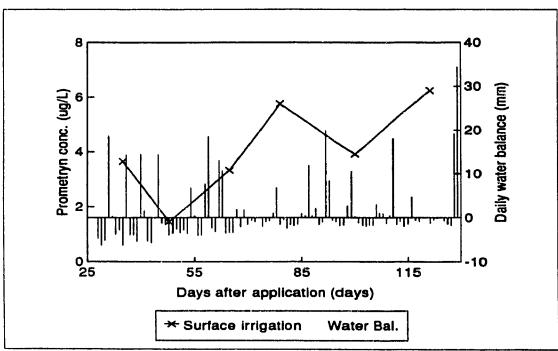


Figure 69. Ground water prometryn concentration in the surface irrigated field.

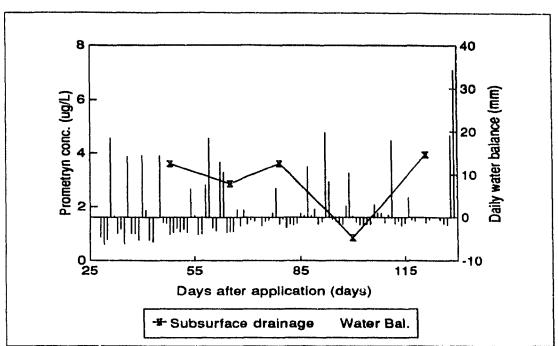


Figure 70. Ground water prometryn concentration in the subsurface drainage field.

Table VW92-4. Prometryn concentration (µg/L) in the ground water.

Day	DAA	Subirrigation			Su	ırf.irrigati	on	Su	Subsurf.drainag		
		conc.	% CV	out	conc.	%CV	out	conc.	% CV	out	
Apr 23	-39			0.21		1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	1.5			1.81	
May 06	-28			0.18		136.72	0.7			0.23	
Jul 08	+35	2.46	108		3.65	39					
Jul 21	+48	7.32	67		1.46			3.62	85		
Aug 07	+66	2.96	90		3.32	70		2.86	67		
Aug 21	+80	2.24	108		5.76	:15		3 62	\$5		
Sep 11	+101	3.61	39	0.00	3.92	141	0.0	0.84	173	0.00	
Oct 02	+122	2.83	67	3.57	6.25	South State of State	2.5	3.96	S2		

DAA: days after application.

conc.: Prometryn concentration.

% C.V.: coefficient of variation in percentage.

out: Prometryn concentration measured at the drainage outlet.

* : only one sample was taken in the experimental unit (no %C.V.)

B.1.4 Nitrate-N concentration in soil.

Table VW92-5. Nitrate-N concentration (µg/g) in soil in the subirrigation field.

Day	0-20 cm		20-40 cm		40-	60 cm	60-80 cm	
	conc.	%C.V.	conc.	%C.V.	conc.	%C.V	conc.	%C.V.
May 06	4.5	107	17.2	134	3.0	163	2.8	114
Jul 08	31.2	7	13.0	42.00	5.4	30	1.2	75
Jul 21	122.1	110	137.0	-44	49.5	32	2.6	•
Aug 07	96.2	121	20.5	24	2.6	92		
Aug 21	18.6	30	42.1	3 / 4	5.0	60	2.1	110

conc.: Nitrate-N concentration.

% C.V.: coefficient of variation in percentage.

Table VW92-6. Nitrate-N concentration ($\mu g/g$) in soil in the surface irrigated field.

Day	0-20 cm		20-40 cm		40-60 cm		60	60-80 cm	
	conc.	%C.V.	conc.	%C.V.	conc.	%C.V.	conc.	%C.V.	
May 06	12.4	44	14.6	47/200	6.3	. 98	2.1	81	
Jul 08	35 5	103	63.2	127	43.9	149	7.9	24///	
Jul 21	68.8	137	61.7	125	75.3	500. **	65.7	121	
Aug 07	27.4	71	20.5	14.	24.2	185	34.4	<151	
Aug 21	19.5	40	21.4	18	56.6	80	14.4	128°	

conc.: Nitrate-N concentration.

% C.V.: coefficient of variation in percentage.

^{* :} only one sample was taken in the experimental unit (no %C.V.)

Table VW92-7. Nitrate-N concentration ($\mu g/g$) in soil in the subsurface drainage field.

Day	0-20 cm		20-40 cm		40	40-60 cm		60-80 cm	
	conc.	%C.V.	conc.	%C.V.	conc.	%C.V.	conc.	%C.V	
May 06	11.6	42	20.1	55	12.4	123	4.7	111	
Jul 08	21.2	95	21.0	1	21.8	. 8	8.6	* 133	
Jul 21	21.6	30	20.1	•	77.3	48		Animipers and the second	
Aug 07	19.2	24	20.0	64	28.8	86	19.1	18	
Aug 21	21.0	40	27.5	18	3.5	26	6.8	129	

conc.: Nitrate-N concentration.

% C.V.: coefficient of variation in percentage.

*: only one sample was analyzed in the experimental unit (no %C.V.).

B.1.5 Nitrate-N concentration in ground water

Table VW92-8. Nitrate-N concentration in ground water.

Day	Subtrrigation			Surf.irrigation			Sub	surf. drainage		
	conc.	%CV	out	conc.	%CV	out	conc.	%CV	out	
Jul 08	12.0	27		28.3	84			,,		
Jul 21	11.0	122		1.8	41		2.0	39		
Aug 07	8.4	47		174	44		2.3	4		
Aug 21	0.1	71		0.1	78		6.7	78		
Sep 11	0.1	23		0.02	*		3.1	108		
Oct 02	0.06	*		0.22	*		1.5	130		

* : only one sample was taken per experimental plot (no C.V.)

conc.: Nitrate-N concentration.

% C.V.: coefficient of variation in percentage.

out: Nitrate-N concentration measured at the drainage outlet.

B.1.6 WATER REGIME

N.B.: WT : Water table depth (m)

Dr : Subsurface drainage treatment Surf: Surface irrigation treatment

Sub: Subirrigation treatment

ET : Evapotranspiration (mm)
Bal: Water balance (rainfall minus

evapotranspiration) (mm)

Crop coefficient: From Docrenbos and Pruitt, 1977.

DAY	WT	WT	WT	RAIN	ET	WATER	CROP
	DR	SURF	SUB	(mm)	(mm)	BALANCE	COEFF
***************************************	(m)	<u>(n)</u>	(m)	 		(mm)	
01-May				0.0	1.0	-1.0	0.49
02-May				3.0	0.8	2.2	0.49
03-May				3.8	0.8	3.0	0.49
04-May				0,8	1.2	-0.4	0.49
05-May				0.0	1.3	-1.3	0.51
06-May			,	0.0	1.4	-1.4	0.53
07-May				0.0	2.2	-2.2	0.56
08-May				0.0	2.5	-2.5	0.58
09-May				0.0	2.8	-2.8	0.60
10-May				0.0	2.5	-2.5	0.62
11-May				0.0	4.1	-4.1	0.65
12-May				0.0	3.5	-3.5	0.67
13-May				11.0	3.5	7.5	0.69
14-May				0.8	2.5	-1.7	0.71
15-May				0.0	3.8	-3.8	0.73
16-May				0.0	3.2	-3.2	0.76
17-May				0.0	3.4	-3.4	0.78
18-May				5.6	3.6	2.0	0.80
19-May				0.0	4.5	-4.5	0.82
20-May				0.0	5.9	-5.9	0.84
21-May				0.0	5.8	-5.8	0.87
22-May				0.0	6.2	-6.2	0.89
23-May				0.0	6.0	-6.0	0.91
24-May				5.6	5.0	0.6	0.93
25-May				0.0	3.4	-3.4	0.96
26-May				1.8	3.7	-1.9	0.98
27-May				0.8	3.5	-2.7	1.00
28-May				0.0	5.0	-5.0	1.00
29-May				0.0	4.2	-4.2	1.00
30-May				0.0	5.9	-5.9	1.00
31-May				15.6	4.7	10.9	1.00
01-Jun				16.2	2.9	13.3	1.00
02-Jun				0.0	5.2	- 5.2	1.00
03-Jun				0.0	5.3	- 5.3	1.00
04-Jun				1.4	4.8	-3.4	1.00
05-Jun				0.0	5.6	-5.6	1.00

DAY	WT	WT	WT	RAIN	ET	WATER	CROP
	DR	SURF	SUB	(mm)	(mm)	BALANCE	COEFF
	(m)	(m)	(m)			(mm)	
06-Jun				17.8	4.6	13.3	1.00
07-Jun				5.6	5.6	0.0	1.00
08-Jun				8.0	4.8	3.2	1.00
09-Jun				2.2	5.5	-3.3	1.00
10-Jun				0.0	5.0	-5.0	1.00
11-Jun				0.0	5.6	-5.6	1.00
12-Jun				0.0	6.6	-6.6	1.00
13-Jun				3.4	5.9	-2.5	1.00
14-Jun				4.2	5.5	-1.3	1.00
15-Jun				0.0	5.9	-5.9	1.00
15-Jun				0.0	6.2	-6.2	
10-Jun				0.0	7.0	-7.0	1.00
							1.00
18-Jun				0.0	5.0	-5.0	1.00
19-Jun				6.6	4.6	2.0	1.00
20-Jun				2.6	5.1	-2.5	1.00
21-Jun				0.0	3.4	-3.4	1.00
22-Jun				1.2	3.0	-1.8	1.00
23-Jun				0.0	4.6	-4.6	1.00
24-Jun				0.0	5.2	-5.2	1.00
25-Jun				0.0	4.4	-4.4	1.00
26-Jun				0.0	6.6	-6.6	1.00
27-Jun				0.0	7.0	-7.0	1.00
28-Jun				0.0	5.8	-5.8	1.00
29-Jun				0.0	5.9	-5.9	1.00
30-Jun				1.0	6.0	- 5.0	1.00
01-Jul				0.0	4.7	-4.7	1.00
02-Jul				0.0	6.2	-6.2	1.00
03-Jul				0.4	5.5	-5.1	1.00
04-Jul				22.6	4.0	18.6	1.00
05-Jul				4.4	4.1	0.3	1.00
06-Jul				0.8	4.5	-3.7	1.00
07-Jul				2.2	4.9	-2.7	1.00
08-Jul	-0.9	-1.02	-0.91	0.0	6.2	-6.2	1.00
09-Jul				18.8	4.5	14.3	1.00
10-Jul				1.2	5.0	-3.8	1.00
11-Jul				0.8	4.7	-3.9	1.00
12-Jul				0.0	5.3	- 5.3	1.00
13-Jul				19.2	4.7	14.5	1.00
14-Jul				6.0	4.4	1.6	1.00
15-Jul				0.0	5.3	-5.3	1.00
16-Jul				0.0	5.6	-5.6	1.00
17-Jul				1.8		-0.1	1.00
18-Jul				16.6		14.4	1.00
19-Jul				1.0		-1.2	0.99
20-Jul				2.2		-1.4	0.99
21-Jul	-0.87	-1.06	-0.90			-3.9	0.98
	-0.0/	-1.00	-0.30	0.0		-3.5	0.98
22-Jul							
23-Jul				0.0	2.6	-2.6	0.98

DAY	WT	WT	WT	RAIN	ET	WATER	CROP
	DR	SURF	SUB	(mm)	(mm)	BALANCE	COEFF
	(m)	(m)	(m)			(mm)	
24-Jul 25-Jul 26-Jul 27-Jul 28-Jul 29-Jul				0.0 0.0 1.0 11.2 4.2 0.0	3.3 2.8 4.6 4.5 3.8 4.0	-3.3 -2.8 -3.6 6.7 0.4 -4.0	0.97 0.97 0.97 0.96 0.96
30-Jul 31-Jul 01-Aug 02-Aug 03-Aug 04-Aug 05-Aug 06-Aug				0.0 8.6 20.8 0.0 0.0 15.0 14.4	3.9 1.0 2.3 2.3 3.1 2.0 3.8 3.5	-3.9 7.6 18.5 -2.3 -3.1 13.0 10.6 -3.5	0.95 0.95 0.94 0.94 0.93 0.93 0.93
07-Aug 08-Aug 09-Aug 10-Aug 11-Aug 12-Aug 13-Aug	-0.76	-1.05	-0.85	0.0 0.0 4.0 0.0 6.2 0.0 0.0	3.3 3.3 2.2 2.0 4.5 1.5 0.6 0.9	-3.3 -3.3 1.8 -2.0 1.7 -1.5 -0.6 -0.9	0.92 0.92 0.91 0.91 0.90 0.49 0.49
15-Aug 16-Aug 17-Aug 18-Aug 19-Aug 20-Aug 21-Aug	-1.27	-1.44	-1.35	0.0 0.0 0.0 0.0 2.4 8.0 0.0	0.0 1.9 1.0 0.7 1.4 1.2	0.0 -1.9 -1.0 -0.7 1.0 6.8 -1.5	0.49 0.49 0.49 0.49 0.49 0.49
22-Aug 23-Aug 24-Aug 25-Aug 26-Aug 27-Aug 28-Aug				0.0 0.0 0.0 0.0 2.2 1.2	0.5 2.4 1.6 1.8 1.4 1.3 0.8	-0.5 -2.4 -1.6 -1.8 -1.4 0.9 0.4 11.9	0.49 0.49 0.49 0.49 0.49 0.49
30-Aug 31-Aug 01-Sep 02-Sep 03-Sep 04-Sep 05-Sep 06-Sep 07-Sep 08-Sep 09-Sep				1.8 3.0 0.0 20.2 9.6 0.0 0.0 0.0	1.3 1.0 1.5 1.0 0.3 1.3 0.5 0.9 1.8 1.7	0.5 2.0 -1.5 -1.0 19.9 8.3 -0.5 -0.9 -1.8 -1.7	0.49 0.49 0.49 0.49 0.49 0.49 0.49 0.49

DAY	WT	WT	WT	RAIN	ET	WATER	CROP
	DR	SURF	SUB	(mm)	(mm)	BALANCE	COEFF
	(m)	(m)	(m)			(mm)	
10-sep 11-sep 12-sep 13-sep 14-sep 15-sep 16-sep 16-sep 19-sep 21-sep 21-sep 21-sep 22-sep 23-sep 24-sep 25-sep 26-sep 27-sep 28-sep 29-sep 20-ct 28-ct 29-ct 20-ct 20-ct 20-ct 20-ct 20-ct 20-ct 20-ct	DR	SURF	SUB	14.2 1.0 0.0 0.0 0.0 0.0 0.0 4.2 2.6 2.8 0.0 1.6 19.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	3.8 0.7 1.1 1.7 1.9 1.6 1.7 1.2 1.6 1.9 1.3 1.1 0.9 1.5 0.9 1.9 1.4 0.5 0.6 0.8 0.0 0.1 1.2 0.7	10.4 0.3 -1.1 -1.7 -1.9 -1.6 -1.7 3.0 1.0 0.9 -1.3 0.5 18.1 -1.5 -0.9 -1.4 4.7 -0.6 -0.8 0.0 -0.1 -1.2 -0.5 -0.1	0.49 0.49 0.49 0.49 0.49 0.49 0.49 0.49
03-Oct 04-Oct 05-Oct 06-Oct	-0.32	-1.43	1.13	0.0 0.0 0.0	0.5 0.1 0.0 0.7	-0.5 -0.1 0.0 -0.7	0.49 0.49 0.49 0.49
10-Oct 11-Oct 12-Oct 13-Oct 14-Oct 15-Oct 16-Oct 17-Oct				34.8 0.0 4.8 3.0 0.0 0.0 0.0	0.4 0.8 0.1 0.2 0.3 0.2 0.4	34.4 -0.8 4.7 2.8 -0.3 -0.2 -0.4 -0.5	0.49 0.49 0.49 0.49 0.49 0.49 0.49

B.1.7 SOIL MOISTURE CONTENT

Table VW92-9. Gravimetric soil moisture content in the subirrigated field.

Day	. 0	. 0-20 cm		20-40 cm 40		-60 cm	60	0-80 cm	
	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.	
May 06	2.178	6.3	2.474	16.9	3.454	19.5	4.514	3,4	
Jul 08	1.819	9.2	2.337	9.5	3.895	12.7	4.757	14.0	
Jul 21	1 956	4.8	2.244	6.7	3.475	10.9	4.551	9.8	
Aug 21	1.591	6.3	2.011	6.3	3.562	7.3	4.329	2.3	
Sep 11	1.555	•	1.762	14.2	3.177	•	4.095	3.1	
Oct 02	1.567	4.9	2.117	14.5	3.489	14.7	3.822	0.5	

ave.: average value

% C.V.: coefficient of variation in percentage.

*: only one sample was analyzed in the experimental unit (no %C.V.).

Table VW92-10. Gravimetric soil moisture content in the surface irrigated field.

Day	0-20 cm		20-40 cm		40-	-60 cm	60-80 cm	
	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.
May 06	1.689	27.8	2.383	33.8	3.589	23. 5	4.028	8.3
Jul 08	1.691	6.3	1 901	6.7	3.412	2.0	4.210	14,8
Jul 21	1 745	48.3	1.930	1.6	2.885	6.4	4.014	2.3
Aug 21	1.505	6.1	2.028	6.0	3.549	1.5	4.213	3.5
Sep 11	1.713	5.4	2.313	#,	3.185	13.3	3.920	•
Oct 02	1.583	7.8	2.035	10.6	3.366	5,3	3.618	~ 6.9 ~ « ×

ave.: average value

% C.V.: coefficient of variation in percentage.

*: only one sample was analyzed in the experimental unit (no %C.V.).

Table VW92-11. Gravimetric soil moisture content in the subsurface drainage field.

Day	0-:	0-20 cm		20-40 cm		60 cm	60-80 cm	
	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.	ave.	% C.V.
May 06	1.618	23.0	2.009	30.2	3.408	28.1	3.910	13.2 <
Jul 08	1.660	21.8	2.242	18.2	3.248	5.4	3.777	3.7
Jul 21	1.678	10.1	2.084	23.4	3.439	8.0	3.826	7.5
Aug 21	1.640	16.1	2.627	12.9	3.877	10.8	4.415	1.5
Sep 11	1.363	7.5	2.217	16.2	3.751	2.7	3.956	5.8 🗵
Oct 02	1.569	17.7	2.956	15.2	3.575	6.9	4.211	0.0

ave.: average value

% C.V.: coefficient of variation in percentage.

B.1.8 Water table depth in the observation wells

Table VW92-12. Water table depth (m) in the observation wells.

Date	Subirrigation		Surf.irrigation		Subst	Subsurf.drainage	
	Depth	% CV	Depth	% CV	Depth	% CV	
July 08	0.91	6	1.02	6			
July 21	0.90	5	1.06	7	0.86	2	
Aug 07	0.85	18	1.05	9	0.76	12	
Aug 21					1.27	5	
Sep 11	0.94	*	1.30	7.7	33° W	8	
Oct 02	1.09	15	1 45	*	1.09	5	

% C.V.: coefficient of variation in percentage.

^{*:} only one reading was taken in the experimental unit (no %C.V.).

B.1.9 Water table tube readings

Table VW92-13. Water table readings (m).

Day	Jul 08	Jul 21	Aug 07	Sep 11	Oct 02
Sub 1 L1	0.98	0.96	1.00	D	D
Sub 1 C	0.98	0.94	0.93	D	1.25
Sub 1 L2	1.02	0.98	0.98	D	D
Sub 2 L1	0.89	0.86	0.89	1.16	D
Sub 2 C	0.85	0.84	0.64	0.94	0.93
Sub 2 L2	0.87	0.84	0.93	1.17	D
Sub 3 L1	0.83	0.85	1.03	D	D
Sub 3 C	0.89	0.92	0.98	D	D
Sub 3 L2	0.95	0.98	1.09	D	D

Table VW92-13. Water table readings (m).

Day	Jul 08	Jul 21	Aug 07	Sep 11	Oct 02
Surf 1 L1	0.96	0.98	1.03	1.41	D
Surf 1 C	0.94	0.95	0.92	1.20	1.45
Surf 1 L2	1.12	1.14	1.12	1.25	D
Surf 2 L1	1.14	1.20	1.21	1.45	D
Surf 2 C	1.07	1.13	1.12	1.42	D
Surf 2 L2	0.96	1.02	1.01	1.33	D
Surf 3 L1	1.04	1.08	1.13	1.37	D
Surf 3 C	1.06	1.10	1.10	1.29	D
Surf 3 L2	1.14	1.19	1.26	D	D

Table VW92-13 . Water table readings (m).

Day	Jul 08	Jul 21	Aug 07	Aug 21	Sep 11	Oct 02
Dr 1 L1		0.87	0.67	1.29	0.91	1.12
Dr 1 C		0.84	0.63	1.20	0.75	0.99
Dr 1 L2			0.71	D	0.72	0.99
Dr 2 L1			0.96	D	D	D
Dr 2 C		0.86	0.84	D	D	D
Dr 2 L2			0.80	D	D	D
Dr 3 L1						1.09
Dr 3 C		0.89	0.81	1.33	0.88	1.09
Dr 3 L2			1.03	1.26	0.95	1.19

Sub: subirrigation treatment Surf : surface irrigation treatment

Dr : subsurface drainage treatment
L : reading taken one meter from a drainage lateral
C : reading taken at mid-spacing (centre)
D : water table tube had been destroyed by machinery.