

AGRICULTURAL PESTICIDE USE TRENDS IN MANITOBA
AND 2,4-D FATE IN SOIL

BY

Janna L. Wilson

A Thesis Submitted to the Faculty of Graduate Studies of
The University of Manitoba
in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science

University of Manitoba

Winnipeg,

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ABSTRACT

Wilson, Janna Leah, Ph.D. The University of Manitoba, October 2012. Agricultural Pesticide Use Trends in Manitoba and 2,4-D Fate in Soil. Major Professor; Annemieke Farenhorst.

In the last century, agricultural intensification on the Canadian prairies has resulted in increased pesticide use with the potential to expose non-target organisms to pesticides as a result of non-point source pollution. In order to minimize risk and implement programs and regulations that promote sustainable agricultural practices, information on the types of pesticides being used and their subsequent fate in soils is essential. In this study, pesticide use trends were summarized and Herbicide Risk Indicators (HRIs) were calculated for the 1996-2006 growing seasons; a time period in which genetically modified herbicide-tolerant (GMHT) crops were commercially adopted. This study also quantified the influence of soil moisture, temperature, slope position, and soil depth within the plough layer on 2,4-D [2,4-(dichlorophenoxy) acetic acid] fate in soil obtained from a cultivated undulating field in Southern Manitoba. Annual pesticide use varied slightly over the 11-year period, but overall, there were no significant increasing or decreasing temporal trends for herbicides, fungicides, or insecticides. Although the total mass of herbicides remained relatively consistent, there was a significant change in the types of herbicides applied associated with the increased adoption of GMHT-canola; the most significant trend being the increase of GLY, from 16% to 45% of the total herbicides used in 1996 to 2006, respectively. HRIs demonstrated that herbicides used in 2006, are on average, more soluble, but less persistent, less volatile, and less acutely toxic

to mammals (inhalation and acceptable daily intake), aquatic invertebrates, fish and algae, than those applied in 1996. Although 2,4-D remains one of the top 10 herbicides applied to agricultural crops in Manitoba, there were no significant increasing or decreasing trends in 2,4-D use between 1996 and 2006. Results from the experimental studies revealed that 2,4-D mineralization half-lives (DT_{50}) in soil varied from 3 days to 51 days with the total 2,4-D mineralization (M_T) ranging from 5.8 to 50.9%, depending on soil moisture, temperature, slope position, and depth. Both DT_{50} and M_T demonstrated a polynomial relationship with temperature, typical of a biological system with minimum, optimum, and maximum temperatures.

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This thesis is dedicated to my loving and supportive
Mom, June Wilson (1945 – 2008).

“Unless someone like you cares a whole awful lot, nothing is going to get better.

It’s not.”

-Dr. Seuss, *The Lorax*

FOREWORD

This is a manuscript style thesis prepared in accordance with the Department of Soil Science, University of Manitoba guidelines. Following the general introduction (Chapter 1) are four chapters prepared in a stand-alone, manuscript format. The final chapter (Chapter 6, Overall Synthesis) integrates the four data chapters by summarizing the research findings and implications, discusses the research limitations, provides future recommendations, and identifies the contribution of this thesis to knowledge.

Versions of Chapters 2 and 3 will be submitted for publication in the near future.

A version of Chapter 4 has been published:

Shymko, J.L. and Farenhorst, A. 2008. 2,4-D mineralization in unsaturated and near-saturated surface soils of an undulating, cultivated Canadian prairie landscape. *J. Environ. Sci. Health Part B* **43**: 34 – 43.

A version of Chapter 5 has been published:

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LIST OF ABBREVIATIONS

2,4-D: [2,4-(dichlorophenoxy) acetic acid]

Θ_{fc} : water retention $\text{cm}^3 \text{ cm}^{-3}$ for field capacity (-0.33 bar);

Θ_w : is the water retention $\text{cm}^3 \text{ cm}^{-3}$ for the wilting point (-15.0 bar)

AAFC: Agriculture and Agri-Food Canada

ACTIVE-DB: Active Ingredient Data Base

ADI: Acceptable Daily Intake

ACUTE-TUs: Acute Toxicity units

ACUTE-TPUs: acute toxicity persistence units

a.i.: active ingredient

ANOVA: Analysis of variance

ASZ: Agassiz Soil Series

AT: herbicide mineralization (as % of applied) at time t

A_t : amount of herbicide mineralized (as % of applied) at time infinity

Ave. Mass: average mass of herbicides

BD: bulk density g cm^{-3}

CANSIM: Canadian Socio-Economic Information Management System

CHRONIC-TUs: Chronic Toxicity Units

CHRONIC-TPUs: chronic toxicity persistence units

DT_{50} : mineralization half-life

EIQ: Environmental Impact Quotient

EIQ_{total} : Environmental Impact Quotient, all compartments

EQ_{con}: Environmental Impact Quotient, consumer

EQ_{ecol}: Environmental Impact Quotient, ecology

EQ_{farm}: Environmental Impact Quotient, farmer

FC: Field Capacity

FPR: formulated product rate

GLU: glufosinate ammonium

GLY: glyphosate

GUS: Ground Water Ubiquity Score

GMHT: Genetically Modified Herbicide-Tolerant

GMHTCs: Genetically Modified Herbicide-Tolerant Crops

HRI: Herbicide Risk Indicator

HPDB: Herbicide Properties Database (HPDB)

IPM: Integrated Pest Management

k₁: First-order mineralization rate constant

k_f: Freundlich sorption coefficient

K_{oc}: Soil organic sorption coefficient

LD₅₀: Lethal Dose

LSC: Liquid Scintillation Counting

MASC: Manitoba Agricultural Services Corporation

MMPP: Manitoba Management Plus Program

M_T: Total Mineralization

NOEL: No-observed-effect-level

OECD: Organization for Economic Co-operation and Development

PEARL: Pesticide Emission Assessment at Regional and Local scales

PERSIST: Persistence units

PAN: Pesticide Action Network

PCPA: Pest Control Products Act

PERL: Practical Extraction and Report Language

PMRA: Pest Management Regulatory Agency

PRZM: Pesticide Root Zone Model

RATE-DB: Herbicide Product Formulation Rate Database

RIV: Red River Soil Series

SOC: Soil organic carbon

SOM: Soil organic matter

TCA: Trichloroacetic acid

TEK: Tee Lake Soil Series

1. INTRODUCTION

1.1 Global Pesticide Use

Although pesticides have been used to control unwanted organisms for over 2,000 years, the intensification of agricultural pesticide use began in the 1940s with the commercial introduction of the insecticide, DDT, the herbicide, 2,4-D, and the fungicide, captan (Mathews 2006; Stephenson and Solomon 2007). This commercial development of synthetic pesticides, combined with the introduction of other technological innovations such as synthetic fertilizers, equipment mechanization and plant variety development, has dramatically increased global crop production (Wilson and Tisdell 2001; Matthews 2006; Uri 2006). For example, the average global food production has increased by 145% since the 1960s, resulting in 25% more food per person (although not evenly distributed) (Pretty 2008).

In the last two decades, global annual pesticide use and expenditures have remained relatively consistent, ranging from 2.3 to 3 billion kg with an estimated global annual market value between 32 and 40 billion US dollars (Figures 1.1 and 1.2) (Aspelin 1997; Aspelin and Grube 1999; Donaldson et al. 2002; Kiely et al. 2004; Pimentel 2005; Grube et al. 2011). Approximately 85% of the pesticides used worldwide are used in agriculture (Luttrell 2007). Current agricultural pesticide use in Canada is estimated to be about 35 million kg (Cessna et al. 2010), which accounts for 1.8% of the total amount of agricultural pesticides used globally (Grube et al. 2011).

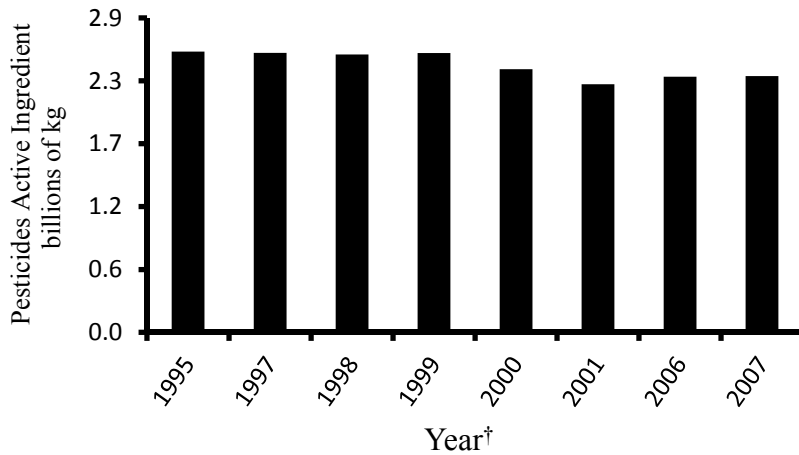


Figure 1.1 Amount of global pesticide active ingredients used.
 Data compiled from the United States Environmental Protection Agency (Aspelin, 1997; Aspelin and Grube 1999; Donaldson et al. 2002; Kiely et al. 2004; Grube et al. 2011).
 †data not available for 1996, 2002-2006

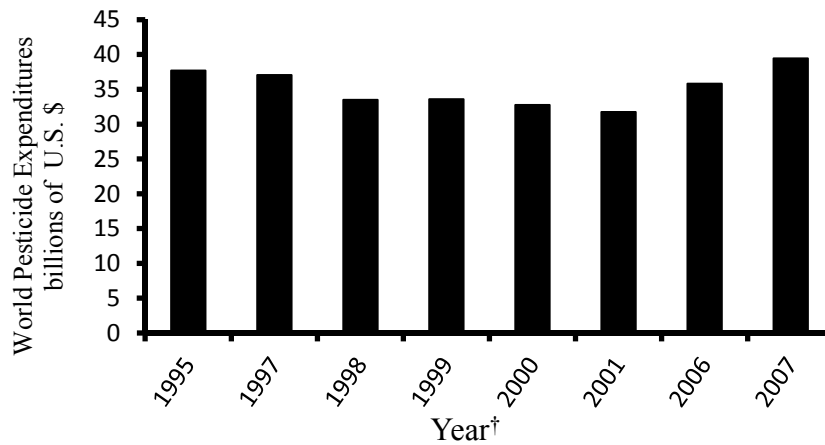


Figure 1.2 Estimates of global pesticide expenditures.
 Data compiled from the United States Environmental Protection Agency (Aspelin, 1997; Aspelin and Grube 1999; Donaldson et al. 2002; Kiely et al. 2004; Grube et al. 2011).
 †data not available for 1996, 2002-2006

1.2 Advantages and Disadvantages of Pesticide Use

The reliance of North American agriculture on pesticides continues to cause controversy due to the potential adverse environmental and public health outcomes. While agricultural pesticides have been shown to provide a significant economic benefit, indirect costs associated with negative impacts on human health and the environment have proven more difficult to quantify (Stemeroff and Culver 1987; McEwan and Deen 1997; Pimentel 2005). Pimentel (2005) estimated a cost-benefit ratio for the United States of 1:4 which means that the \$10 billion annual investment in pest control products in the United States provides \$40 billion in food security benefits, but also results in \$10 billion in environmental and public health risks (Pimentel 2005).

The shift towards more intensive agricultural operations since the second world war has prompted discussions on sustainable agricultural practices in Canada, including the potential for agri-chemicals such as pesticides to move to non-target surface and ground water (Younes and Galal-Gorchev 2000; McKay and Lefebvre 2010). Documented environmental risks associated with pesticide use in Canada include low levels of pesticide residues detected in air, atmospheric dust, rainwater, surface water, groundwater and potable water sources (Wood and Anthony 1997; Rawn et al. 1999ab; Donald et al. 2001; Hill et al. 2002; Cessna and Elliot 2004; Muir et al. 2004; Waite et al. 2004; Tudurri et al. 2006; Donald et al. 2007; Yao et al. 2008; Messing et al. 2011). Pesticide residues in the environment could have an adverse impact on non-target organisms such as invertebrates (Cooper and Roch 2003; Marques et al. 2009; Correia and Moreira 2010), pollinators (Barmaz et al. 2010; Ellis 2010) and fish (Fairchild et al. 2008).

Pesticides have been linked to declines in biodiversity (Gibbs et al. 2009), as well as creating a biodiversity disequilibrium in agricultural systems (Wilson and Tisdell 2001).

Magoon (2006) provides a synthesis of peer reviewed studies representative of agricultural practices in Manitoba that summarizes the potential links between agrarian pesticide use and potential negative public health outcomes. The literature review focused on crops typically grown in Manitoba and included studies from the United States and Canada. Magoon (2006) concluded that there were positive correlations with some cancers, fetal deaths, congenital anomalies, neurodegenerative diseases, mental health, and disorders of the eye. This Canadian study supports the idea that pesticide use has public health risks and may not be sustainable in the long-term.

Knowledge of the types and amounts of pesticides applied to agricultural crops is essential for the development of policies and beneficial agricultural management strategies designed to optimize pest control while reducing environmental and public health risks. However, comprehensive pesticide use information is lacking in Canada and in many other countries around the World (Boyd 2001; Brimble et al. 2005; Cessna et al. 2005; Environment Canada 2011). Although the information on the area of land treated with pesticides is reported in the Agricultural Census for each Canadian province, the census only specifies the general type of pesticide (i.e., herbicide, fungicide, or insecticide) and the area treated with each type (Statistics Canada 1996, 2001, 2006).

As of November 15, 2006, the Pest Control Products Act (PCPA, 2002) was enacted in Canada, requiring that pesticide sales data be reported to Health Canada's Pest Management Regulatory Agency (Pest Control Products Act, S.C. 2002, c. 28). One of the goals of the PCPA Act is to:

“ . . . give Health Canada and Canadians a better understanding of pesticide use in Canada during a given year, as well as trends in pesticide use over a longer period of time. The information provided will also allow the PMRA to validate parameters used in risk assessments and provide guidance for risk reduction strategies.” (Health Canada 2008, 1.0 Introduction section, para. 3)

Although the Public Disclosure clause indicates that Health Canada will report sales data on its website, the release date of this report has not yet been specified (Health Canada, 2008, 1.1 General information, Public Disclosure section, para.1). While sales data may provide more detailed information on the types of pesticides used than is reported in the Agricultural Census, there are limitations with using sales data as a proxy for pesticide use (Brimble et al. 2005; Byrtus 2011).

1.3. Pesticide Risk Assessment

The area treated and the amount of pesticides applied can provide valuable information for risk assessment, but each pesticide varies in its persistence, mobility, and toxicity, and as such, measures other than the mass of pesticides applied or the area treated are needed to adequately assess environmental risks arising from pesticide use (Levitan 2000; Falconer 2002; Uri 2006).

The potential environmental and health impacts of a pesticide are a result of many interacting factors which include the inherent chemical properties of the formulated pesticide product (physicochemical properties), application techniques, application rate (dosage), environmental fate and transport, and toxicological effects to non-target organisms, as well as factors such as weather, soil characteristics, and land management (Carter 2000; Falconer 2002; Leu et al. 2004; Arias-Estévez et al. 2008). In order to simplify the complex nature of pesticide behavior and their effect on the environment and to human health, risk indicators are used to provide a relative measure of the potential of pesticides to cause harm to non-target organisms. A multitude of indicators have been developed to quantify the potential environmental, economic, social and human impacts (Levitan et al. 1995; Levitan 2000; Maud et al. 2001; Falconer 2002; Piorr 2003; Padovani et al. 2004). For example, several indicators have been developed by the Organization for Economic Co-operation and Development (OECD 1999), by the Government of Canada (Cessna et al. 2010) and by governments of other countries including Belgium, Denmark, Germany, the Netherlands, Norway, Switzerland, and the United Kingdom (OECD 2008). Some of these indicators, or components thereof, are used in this study.

1.4 2,4-D [2,4-(dichlorophenoxy) acetic acid]

Two Chapters in this thesis specifically focus on the fate of 2,4-D in soils. 2,4-D was introduced in the 1940s and has been used for over 60 years for the post-emergent control of broadleaf weeds in annual and forage crops (Mathews 2006; Stephenson and Solomon 2007) (Figure 1.3). Recent reports indicate that 2,4-D is the most widely used pesticide

in the world (Industry Task Force II on 2,4-D Research Data 2011), the fourth most widely used herbicide in Canada, the second in Western Canada, and in 2003 the most widely used pesticide in Manitoba (Brimble et al. 2005; Environment Canada 2011). 2,4-D use is an important component of crop production on the Canadian prairies and, if it was removed from the market, estimates suggest that the result would be an annual net loss of \$58-82 million (Krystynak 1983; Stemeroff et al. 1991). In the last decade, 2,4-D and 2,4-D tank-mixes are increasingly being used as pre-seed burn off treatments to control glyphosate-tolerant canola volunteers (Simard and Légère, 2002; Simard et al. 2002). Given the increased incidence of glyphosate tolerant weeds coinciding with the adoption of genetically modified herbicide tolerant crops (GMHTCs) (Powles 2008; Cerdeira and Duke 2009; Heap 2010; Wright et al. 2010), the development of crops that are tolerant to both GLY and other agronomically significant herbicide groups such as 2,4-D will be required to sustain the use and environmental benefits of GMHTCs (Wright et al. 2010).

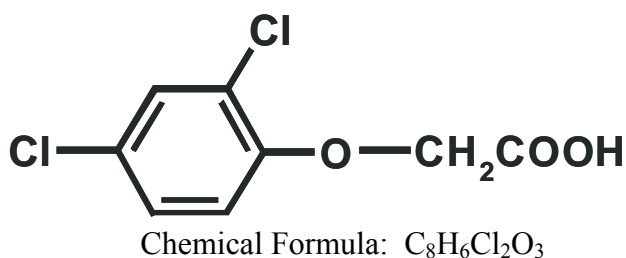


Figure 1.3 2,4-D [2,4-(dichlorophenoxy) acetic acid] molecular structure (PPDB 2009).

2,4-D has been identified as a human carcinogen in some studies (Reuber 1983) as well as linked to developmental and reproductive anomalies (Reuber 1983; Lerda and Rizzi 1991), but other studies have not conclusively recognized such associations with 2,4-D (Ibrahim et al. 1991; Garabrant and Philbert 2002). In some studies, 2,4-D exposure has been linked to greater risks for non-Hodgkin's lymphoma in humans (Hardell et al. 1981; Hoar et al. 1986; Woods et al. 1987; Wigle et al. 1990; Zahm et al. 1990; McDuffie et al. 2001) but there was no such association in other studies (Hardell and Eriksson 1999; Garabrant and Philbert 2002; De Roos et al. 2003).

Given the above potential negative human health impacts, 2,4-D use remains a concern because it is frequently detected as an atmospheric contaminant, as well as a contaminant in surface and ground water, potable water, and rainwater. In a review of 20 peer reviewed studies that tested for herbicides in surface and ground water, rain water, and the atmosphere in Western Canada between 1990 and 2011, 19 of the studies tested for 2,4-D and all studies detected 2,4-D (Waite et al. 1992; Grover et al. 1997; Waite et al. 1995; Anderson et al. 1997; Wood and Anthony 1997; Donald et al. 1999; Rawn et al. 1999ab; Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Waite et al. 2002; Donald et al. 2005; Humphries 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Glozier et al. 2011; Messing et al. 2011). The potential mobility of 2,4-D within the Prairie ecosystem warrants further investigation into the factors affecting retention and degradation in soils to better assess risks and identify agronomic use strategies which minimize contamination of non-target sources.

1.5 2,4-D Properties and Fate in Soil

Pesticide fate is governed by the inherent properties of the chemical and the environmental conditions to which it is exposed. The herbicide 2,4-D has a relatively high water solubility (900 mg l⁻¹ at pH 7, 25°C (McKeague 1998)) and is weakly bound by soil constituents, which suggests that the herbicide may move within the plough layer prior to being degraded in soil (Boivin et al. 2005; Farenhorst et al. 2009). The low pK_a of 2,4-D (pK_a=2.64, Ahrens 1994) coupled with alkaline Manitoban soils (pH typically 6.8 to 7.5 (Manitoba Agriculture, Food and Rural Initiatives 2012)), suggest that 2,4-D is mostly in the ionic form and, therefore, particularly mobile in soils with low organic matter content (Bekbölet et al. 1999). In addition, relatively high soil carbonate content in Manitoba soils has been shown to limit sorption and hence increase the mobility of 2,4-D (Gaultier et al. 2006).

2,4-D is primarily degraded through biological activity by a consortia of soil microorganisms (Soulas 1993; Han and New 1994; Cattaneo et al. 1997; Voos and Groffman 1997; Khalil 2003). The factors influencing the abundance, diversity and activity of 2,4-D degraders is mediated by factors such as soil organic content, soil moisture content (Parker and Doxtader 1983; Ou 1984; Bhanumurthy et al. 1989; Cattaneo et al. 1997; Soulas and Lagacherie 2001) and temperature (Walker 1974).

1.6 Objectives

The overall aim of this study was to improve on agricultural pesticide risk assessment in Manitoba. The specific objectives were: (1) To determine agricultural pesticide use

trends in Manitoba from 1996-2006, and to determine the mass of herbicides applied during this time using crop insurance records from Manitoba Agricultural Services Corporation (Chapter 2). (2) Calculate simple and composite parameter herbicide risk indicators from herbicide mass and determine the changes in relative risk between 1996 and 2006 (Chapter 3). (3) To determine the influence and interaction of soil moisture, slope position, and soil depth within the plough layer on 2,4-D mineralization, and influence of slope position and depth on 2,4-D sorption (Chapter 4). (4) To determine the influence and interaction of temperature, soil moisture, slope position and soil depth within the plough layer on 2,4-D mineralization.

1.7 Hypotheses

The hypotheses are: (1) Agricultural pesticide use in Manitoba has decreased between 1996 and 2006. (2) Herbicides that are less environmentally damaging, and less hazardous to organisms are being used in Manitoba since the adoption of herbicide-tolerant crops. (3) 2,4-D degradation responds to soil moisture and temperature regardless of slope position in the soil landscape, and 2,4-D mineralization is greatest at 20°C at soil moistures near field capacity, and impeded at lower and higher soil moistures and temperatures.

1.8 Thesis Outline

This is a manuscript style thesis prepared in accordance with the Department of Soil Science, University of Manitoba Guidelines. Specific research activities are divided into four, stand alone manuscripts (Chapters 2 through 4).

Chapter 2: Manitoba trends in agricultural pesticide use as a result of the increasing adoption of genetically modified herbicide-tolerant crops from 1996 – 2006.

A study which determined agricultural pesticide use trends in Manitoba for herbicides, insecticides and fungicides. This time period was chosen because herbicide-tolerant canola had been commercially introduced and rapidly adopted on the Canadian Prairies.

Chapter 3: Trends in herbicide risk indicators as a function of changes in herbicide use from 1996-2006 in Manitoba, Canada

The toxicity and physiochemical parameters of 76 herbicide active ingredients used in Manitoba between 1996 and 2006 were used to develop 30 herbicide risk indicators to quantify relative temporal risk trends.

Chapter 4: 2,4-D Mineralization in unsaturated and near-saturated surface soils of an undulating, cultivated, Canadian Prairie landscape

A laboratory study that used microcosms incubation experiments to quantify 2,4-D mineralization using a 4 x 3 x 2 factorial experimental design (soil moisture, 4 levels: 60, 85, 110, 135% of field capacity; slope position, 3 levels: upper-, mid- and lower-slopes; soil depth, 2 levels: 0-5 and 5-15 cm).

Chapter 5: Polynomial response of 2,4-D mineralization to temperature in soils at varying soil moisture contents, slope positions and depths

A laboratory study that used microcosms incubation experiments to quantify 2,4-D mineralization and half-lives using a 4 x 4 x 3 x 2 factorial design (with soil temperature at 4 levels: 5, 10, 20 and 40°C; soil moisture at 4 levels: 60, 85, 110, 135% of field capacity; slope position at 3 levels: upper-, mid- and lower-slopes; and soil depth at 2 levels: 0-5 cm and 5-15 cm). This chapter builds on the work from Chapter 4 by including four different temperature levels.

My contribution to Chapters 2 through 5 include: rate database and herbicide properties database creation and use of these databases for calculations using various software programs including Microsoft Excel and Access (Chapters 2 and 3); conducting field and laboratory experiments (Chapters 4 and 5); statistical analysis using various software programs including SAS, SigmaStat and Microsoft Excel (Chapters 2 through 5); writing, improving, and finalizing two manuscripts submitted to an international peer reviewed journal and responding to and addressing reviewer comments (Chapters 4 and 5); supervising student assistants who assisted with field and laboratory work and with the creation of extensive databases (Chapters 2 through 5). In addition to committee members, statistical assistance was provided by Dr. Francis Zvomuya, Department of Soil Science, University of Manitoba for Chapter 5, mapping assistance was provided by Gary Warkentine, Exceed Analysis, for Chapter 2, PRZM simulations and computer programming for combining the herbicide rate database with the pesticide use database

was conducted by Dr. D.A.R. McQueen, Department of Soil Science, University of
Manitoba.

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2. MANITOBA TRENDS IN AGRICULTURAL PESTICIDE USE AS A RESULT OF THE INCREASING ADOPTION TO GENETICALLY MODIFIED HERBICIDE-TOLERANT CROPS FROM 1996 – 2006

2.1 Abstract

Agricultural pesticides are an essential component of crop production in Canada. Data on the types and amounts of pesticides applied to cropland are important for better understanding trends within an agricultural industry that provides food security with sound environmental management decisions. This paper describes the trends in agricultural pesticide use in the Province of Manitoba, Canada from 1996-2006 during which time the agricultural industry adopted genetically modified herbicide-tolerant crops (GMHTCs). In each of the 11-years, herbicides accounted for the majority of pesticides applied, representing on average 83% of pesticide formulations and 86% of pesticide active ingredients. The area to which herbicides, insecticides, and fungicides are applied has remained relatively consistent between 1996 and 2006. Results further indicate that the adoption of GMHTCs has influenced the types of herbicides used in Manitoba with the greatest change being the increased application of glyphosate (GLY), from 16% to 45% of the total mass of herbicides used in 1996 and 2006, respectively.

2.2 Introduction

A wide range of measures are being used worldwide to control unwanted organisms which cause damage to agricultural crops. The use of synthetic pesticides began on a wide-scale in the 1940s which included the commercial introduction of the herbicide, 2,4-

D (1942), the insecticide, DDT (1944) and the fungicide, captan (1949) (Mathews 2006; Stephenson and Solomon 2007). Synthetic pesticides, combined with the introduction of several other technological innovations has dramatically increased global crop production (Wilson and Tisdell 2001; Phillips and Park 2002; Mathews 2006; Uri 2006). Although not evenly distributed worldwide, on average, global food production has increased by 25% per capita since 1960 (Pretty 2008).

Data on the types and quantities of pesticide active ingredients used in agriculture are important for strengthening programs and policies designed to evaluate agricultural production and promote environmental stewardship. For example, pesticide use data can be used to evaluate the responses of producers to changes in pest pressures or pest resistance, as well as in evaluating the adoption trends of reduced-risk pesticides.

Pesticide use data provides valuable inputs for pesticide fate models that can be utilized as part of risk assessments designed to implement sound environmental management decisions in agriculture. Pesticide use information can also be used to determine the pesticide active ingredients that should be included in local and regional water quality monitoring programs. All these data may be useful to the agrochemical industry for strengthening marketing approaches.

Global pesticide use was estimated to range from 2.3 to 3 billion kg between 1995 and 2006, of which 85% was used in agriculture (Aspelin 1997; Aspelin and Grube 1999; Donaldson et al. 2002; Kiely et al. 2004; Pimentel 2005; Grube et al. 2011). The total market value of pesticides applied globally over this time period is estimated at \$40

billion per year (Pimentel 2005), of which Canada accounts for approximately 3% of pesticides sales (Brimble et al. 2005). In Canada, an estimated 35 million kg of agricultural pesticides are applied every year, and the three Prairie Provinces (Manitoba, Saskatchewan, and Alberta) account for 84% of this total (Cessna et al. 2010).

Genetically Modified Herbicide-Tolerant Crops (GMHTCs) were developed in the 1990s, and are defined as crops that have been genetically modified and can “grow in the presence of foliar-applied, broad spectrum and non-selective herbicides such as glyphosate and glufosinate” (Schwember 2008). The commercial introduction of GMHTCs to the global market has resulted in substantial economic benefits at the farm level; an estimated \$27 billion between 1996 and 2005 (Brookes and Barfoot 2005, 2006). It has been estimated that the introduction of GMHTCs has reduced pesticide use in the European Union by 224 million kg over 10 years (1995-2005), hence reducing the potential impact on human health and the environment (Brookes and Barfoot 2006). In Canada, genetically modified herbicide-tolerant (GMHT) canola was commercially introduced to growers in 1995, and by 2005, 95% of the canola grown in Western Canada consisted of glyphosate (GLY), glufosinate ammonium (GLU), and imidazoline (imazamox and imazethapyr) resistant varieties (Duke 2005; Beckie et al. 2006). Given these significant changes to Canadian Prairie crop production, the objective of this study was to evaluate changes in the types and amounts of pesticide products and active ingredients used between 1996 and 2006.

2.3 Materials and Data

2.3.1 Source data

The foundation of this study was a data set provided by Manitoba Agricultural Services Corporation (MASC) containing 11 years (1996-2006) of pesticide use information with a total of 578,311 records; an average of 52,754 records per year, varying from 40,455 in 2005 to 58,233 in 1998. Each record provided information on the formulated pesticide product applied to a specific crop and the area of that crop grown in a township (36 square miles; 9,324 ha; total of 1,124 townships). A second MASC data set contained the area in each township seeded to insured crops, including areas to which pesticides were not applied with a total of 197,215 records, ranging from a low of 14,598 in 2005 to 20,158 in 2004.

2.3.2 Data processing to calculate the area treated

Two databases were developed: (1) a database containing the active ingredient(s) of each pesticide formulated product that was used in Manitoba between 1996 and 2006 (ACTIVE-DB), and (2) a database containing crop specific minimum and maximum application rates for all active ingredients in each herbicide formulated product that was used in Manitoba between 1996 and 2006 (RATE-DB). These databases were linked to the MASC source data using computer programs written in PERL (Practical Extraction and Report Language). Since many of the pesticide formulation products had more than one active ingredient, there were 245,455 more records (n) in the ACTIVE-DB when compared to the original MASC data set which included 578,311 records containing formulated pesticide product use information.

The classification of pesticide products and active ingredients for the ACTIVE-DB was done using the following sources, in order:

1. 2006 Guide to Crop Protection; Saskatchewan; Weeds; Plant Diseases; Insects (Saskatchewan Agriculture and Food 2006);
2. Guide to Crop Protection; Weeds; Plant Diseases; Insects (Manitoba Agriculture and Food 2000, 2001, 2002, 2003, 2004, 2005, 2007, 2008, 2009);
3. Guide to Crop Protection; Weeds; Plant Diseases; Insects (Manitoba Agriculture 1995, 1996, 1997, 1999);
4. Guide to Crop Protection; Weeds; Plant Diseases; Insects (Saskatchewan Agriculture and Food 1998, 2004);
5. Guide to Crop Protection; Weeds; Insects; Plant Diseases (Manitoba Agriculture 1993, 1994);
6. The Pesticide Management Regulatory Agency (PMRA) “Search Product Label” database, retrieved from Health Canada (2012);
The Pesticide Action Network (PAN) Pesticide Database (Kegley et al. 2011).

Within this dataset, three record sets were excluded. First, from the Crop Protection Guide, fungicide and insecticide seed treatments were excluded because of the difficulty in estimating their application rates (seeding rate is required). Second, 18 herbicide product formulations (Appendix I) were excluded because of lack of product rate information. Last, MASC records referring to unknown products, adjuvants, fertilizers, or no chemicals, were excluded because the listed pesticide product could not be found or the records were not applicable.

The area treated with herbicides, insecticides, and fungicides was calculated by assuming one treatment of the recorded formulated pesticide product was applied to the entire crop area. Although pesticides, in particular fungicides and insecticides, may be applied more than once during the growing season, one application was assumed in this study due to uncertainties regarding the frequency of application rates in specific crops for a wide range of pesticide products. Pesticide use estimates by Brimble et al. (2005) and by Cessna et al. (2010) also assumed one application.

2.3.3 Herbicide Mass and Intensity at Regional Scales

Herbicide rates (comprised of 3,752 crop specific product formulation rates in total) were added to ACTIVE-DB using PERL script and the mass of active ingredient applied on a per hectare basis was further calculated by using the maximum recommended application rates. Herbicide application rates remained consistent among the crop protection guide editions (1996 to 2006). Rates were first obtained from the 2006 Crop Protection Guide and when not available, were obtained from other sources in the order listed above. The mass of herbicide applied on a per hectare basis was calculated using either Equation 2.1 or 2.2, depending on the product formulation:

$$\text{FPR [kg ha}^{-1}\text{]} * \text{a.i. [g kg}^{-1}\text{]} = \text{max a.i. [g ha}^{-1}\text{]} \quad [2.1]$$

$$\text{FPR [L ha}^{-1}\text{]} * \text{a.i. [g L}^{-1}\text{]} = \text{max [g ha}^{-1}\text{]} \quad [2.2]$$

where FPR is the maximum recommended formulated product application rate in either kg ha^{-1} or L ha^{-1} a.i. is the amount of active ingredient in the FPR in either g kg^{-1} or g L^{-1} and max a.i is the maximum amount of active ingredient (g) applied per hectare.

The rates for each crop/product/active ingredient combination were subsequently used to calculate the mass of herbicide active ingredient applied using Equation 2.3:

$$\text{Mass Applied [g]} = \text{area treated [ha]} * \text{max a.i rate [g ha}^{-1}\text{]} \quad [2.3]$$

The area treated with herbicides, insecticides, and fungicides, as well as herbicide mass applied were summarized on a provincial basis using Excel 2007 spreadsheets and pivot tables. Regression analyses were also performed in Excel 2007 to explore general provincial temporal trends in the top 10 herbicides, fungicides, and insecticides.

The five-year average percent change for herbicide mass (kg) and intensity (kg ha⁻¹) between 1996-2001 and 2002-2006 (hereafter referred to as the five-year percent change) was calculated at the township and ecoregion levels for herbicides applied to all crops, using two, five-year periods (Equation 2.4) and results were mapped using Maptitude 6.0 (Caliper Corporation 2011). In addition, the five-year percent change for herbicide use intensity for canola and the mass of GLY, GLU, ethalfluralin, trifluralin, and clopyralid applied to canola crops were calculated and mapped. Herbicide intensity (kg ha⁻¹) was calculated using the total mass of herbicides applied in a mapping unit divided by the total seeded area in the mapping unit.

$$[\text{Ave. Mass}_{(02-06)} - \text{Ave. Mass}_{(96-00)}] / [\text{Ave. Mass}_{(96-00)}] * 100 \quad [2.4]$$

where Ave. Mass₍₀₂₋₀₆₎ is the average mass of herbicides applied in 2002, 2003, 2004, 2005, 2006 and Ave. Mass₍₉₆₋₀₀₎ is the average mass of herbicides applied in 1996, 1997, 1998, 1999, 2000.

At the township level, the five-year percent change was calculated only for townships in which all data years were available. In 21% percent of the cases, data for all years were not available, and these townships were excluded and displayed in black on the maps. Herbicide mass and intensity data were scaled up to the ecoregion level by adding all mass and area seeded data for all the townships in the given ecoregion. Townships were assigned to the ecoregion in which the largest portion of the township was located.

2.4 Results

2.4.1 Area seeded

Between 1996 to 2006, the average area seeded to insured crops (hereafter referred to as insured crops) was 3.76 million hectares, or approximately 80% of the seeded area of field crops as reported by the Canadian Socio-Economic Information Management System (CANSIM) (Statistics Canada, 2010) (Figure 2.1). The percentage of insured crops varied over the 11-year period from 80 to 96% of the field crop area reported by CANSIM, with the percentage varying by crop such as from 83 to 90% for canola, from 80 to 91% for wheat and from 83 to 96% for potatoes (Figure 2.2). The area seeded to insured crops varied for canola from a low of 537 thousand hectares in 1996 to a high of 958 thousand hectare in 2004 (Figure 2.3).

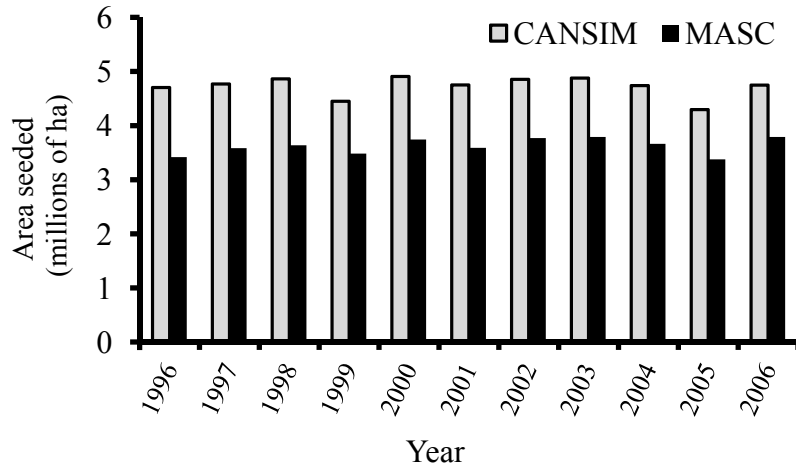


Figure 2.1 Area seeded to agricultural crops in Manitoba as reported by CANSIM (Statistics Canada 2010) and MASC.

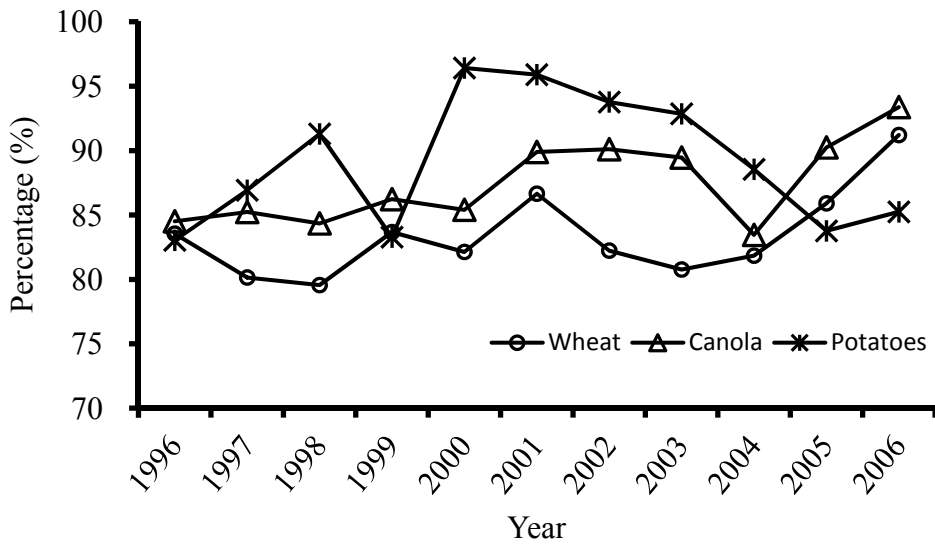


Figure 2.2 Select agricultural crops reported by MASC as a percentage of CANSIM (Statistics Canada 2010).

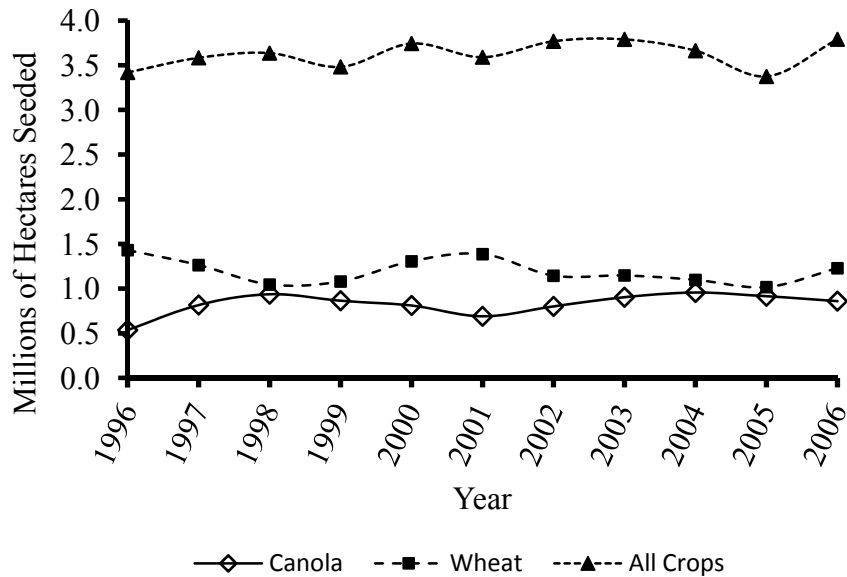


Figure 2.3 Area seeded (millions of ha) to canola, wheat and all crops in Manitoba as calculated from the MASC data.

2.4.2 Pesticide formulated products and active ingredients

There were 245,544 more records when considering active ingredients rather than formulated product because 87 out of 319 commercial pesticide formulations contained more than one active ingredient (Table 2.1). There were also cases in which more than one commercial pesticide product was applied to the same cropped area. For these reasons, the calculated area treated with active ingredients (~ 9.9 million hectares) was approximately 1.4 times greater than the calculated area treated with formulated products (Table 2.1). Between 1996 and 2006, herbicides accounted for the majority of pesticide products applied, 222 different herbicide products out of 316 different pesticide products in total (Table 2.2). The number of pesticide products applied to crops increased from 166 in 1996 to 209 in 2006, while the number of active ingredients for herbicides, insecticides and fungicides remained fairly stable over this 11-year period (Table 2.2).

Table 2.1 Summary of the MASC data set and ACTIVE-DB.

Classification	Product Formulations		Active Ingredients	
	Records (n)	Area Treated (ha)	Records (n)	Area Treated (ha)
herbicide	467,606	57,281,059	700,239	84,233,408
fungicide	57,139	8,807,730	58,788	9,007,597
insecticide	20,794	1,946,386	20,794	1,946,386
adjuvant	378	22,638	378	22,638
organic herbicide	14	890	14	890
seed treatment	9,221	1,013,940	20,483	2,428,331
no application	23,080	1,700,471	23,080	1,700,471
unknown	79	4741	79	4741
Total	578,311	70,777,828	823,855	99,344,434

Table 2.2 Number of different products and active ingredients calculated from the MASC data set and ACTIVE-DB.

Year	<u>Herbicides</u>		<u>Fungicides</u>		<u>Insecticides</u>		<u>Pesticides</u>	
	Prod [†]	Act [‡]	Prod [†]	Act [‡]	Prod [†]	Act [‡]	Prod [†]	Act [‡]
1996	119	67	23	20	24	18	166	105
1997	121	65	18	15	28	20	167	100
1998	126	64	19	16	24	18	169	98
1999	123	62	19	15	25	20	167	97
2000	132	63	25	21	28	22	185	106
2001	134	63	27	22	28	20	189	105
2002	138	62	27	20	27	18	192	100
2003	148	63	30	24	30	21	208	108
2004	142	64	24	20	25	18	191	102
2005	143	62	29	22	25	16	197	100
2006	158	63	26	18	25	18	209	99
11-year Total[§]	222	86	46	34	48	31	316	151

[†]Prod: Pesticide Product Form

[‡]Act: Active Ingredients

[§] unique active ingredients only

On average, applications of active ingredients to wheat (winter wheat, spring wheat and durum) accounted for 63% of the total insured area treated with pesticides, followed by canola (16%), while all other crops accounted for 21% of the area treated with pesticides (Figure 2.4). The area of wheat treated with active ingredients varied by a factor of two, ranging from 9.6 million ha in 1998 to 16.2 million ha in 2001. Similar variability over the 11-year period was observed for herbicide active ingredients applied to canola, with the area treated ranging from 1.8 million ha in 1996 to 3.5 million ha in 2004.

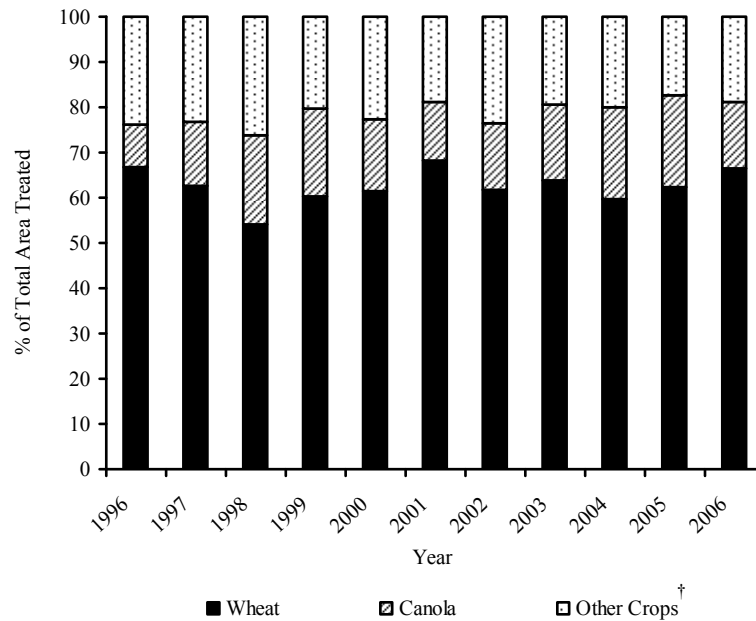


Figure 2.4 Percentage of pesticide (herbicides, fungicides, and insecticides) active ingredients applied to wheat, canola and other crop areas in Manitoba calculated from the MASC data set.
[†]Not including wheat and canola

2.4.3 Area treated with herbicides, insecticides, and fungicides

From 1996 to 2006, the average area treated with herbicide products was 5.2 million hectares (Figure 2.5), which accounted for approximately 85% of the area treated with pesticide products. There were no obvious province wide increasing or decreasing trends in the hectares treated with herbicide products over the 11-year period, however, the area treated with herbicide products did vary from a low of 4.5 million hectares in 1999 to a high of 5.6 million hectares in 2003 (Figure 2.5). On average, the area treated with herbicide active ingredients was 1.5 times greater than that treated with products. Although there were no apparent increasing or decreasing trends, the area treated with

herbicide active ingredients varied from a low of 6.5 million ha in 2005 to a high of 8.2 million ha in 1996 (Figure 2.5).

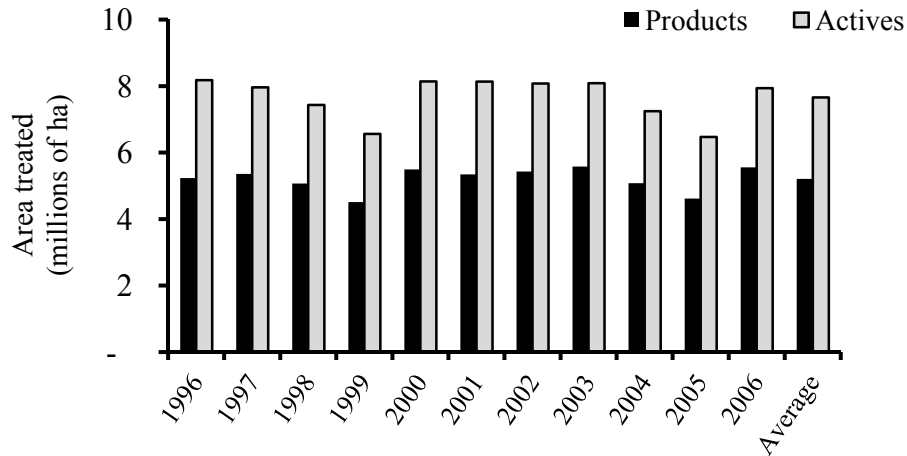


Figure 2.5 Area treated with herbicide product formulations and active ingredients applied to insured crops in Manitoba.

Insecticides were applied to a smaller area than fungicides. On average, insecticides accounted for 2.9% of the treated area, varying from a low of 54,568 ha in 2005, to a high of 278,287 hectares in 1996 (Figure 2.6). Insecticide product formulations did not contain multiple active ingredients; therefore, there were no differences between the area treated with active ingredients and product formulations (Figure 2.6). The area treated with formulated fungicide products ranged from 587,859 ha in 1997 to 1.1 million ha in 2004 (Figure 2.7). Approximately 11% of the formulated fungicide products had more than one active ingredient, and therefore the area treated with active ingredients demonstrated similar fluctuations between years as the area treated with formulated pesticide products (Figure 2.7).

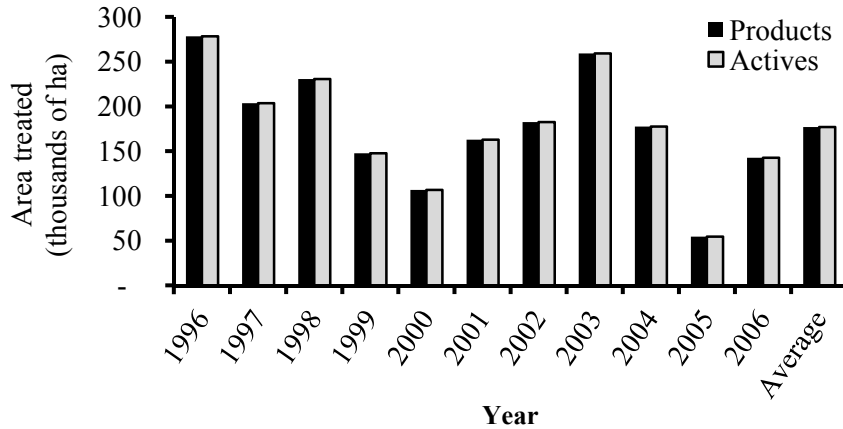


Figure 2.6 Area treated with insecticide product formulations and active ingredients applied to insured crops in Manitoba.

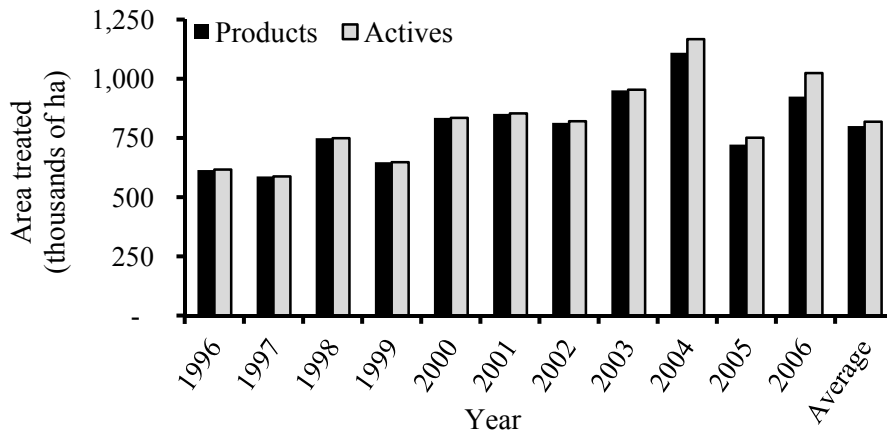


Figure 2.7 Area treated with fungicide product formulations and active ingredients applied to insured crops in Manitoba.

2.4.3.1 Top ten herbicides, insecticides and fungicides based on area

MCPA was the herbicide active ingredient applied to the greatest proportion of the treated area accounting for nearly two times the treated area compared to the next most applied active ingredient, bromoxynil (Table 2.3). MCPA was applied to nearly 5.5 times the area, compared to GLU, the 10th most applied herbicide active ingredient. Over the

Table 2.3 Top 10 pesticide active ingredients applied to insured agricultural crops in Manitoba.

Pesticide	Average Area Treated (ha)	Years of Data	Record Years	Model	r ²	p-value
<u>Herbicides</u>						
MCPA	1,310,612	11	1996-2006	$y = -18,350x + 4 \times 10^7$	0.14	<i>ns</i> [†]
bromoxynil	656,115	11	1996-2006	$y = -11,589x + 2 \times 10^7$	0.39	*
glyphosate	562,474	11	1996-2006	$y = 61,204x - 1 \times 10^8$	0.92	***
fenoxaprop p ethyl	477,389	11	1996-2006	$y = -16,331x + 3 \times 10^7$	0.32	<i>ns</i>
thifensulfuron methyl	423,732	11	1996-2006	$y = -35,893x + 7 \times 10^7$	0.79	***
2,4-D	393,129	11	1996-2006	$y = -10,560x + 2 \times 10^7$	0.27	<i>ns</i>
tribenuron methyl	364,035	11	1996-2006	$y = -14,429x + 3 \times 10^7$	0.30	<i>ns</i>
florasulam	286,098	7	1996, 2001-2006	$y = 51,562x - 1 \times 10^8$	0.85	**
clodinafop propargyl	255,186	11	1996-2006	$y = 5,128x - 1 \times 10^7$	0.05	<i>ns</i>
glufosinate ammonium	239,110	11	1996-2006	$y = 36,565x - 7 \times 10^7$	0.85	***
<u>Insecticides</u>						
chlorpyrifos	33,911	11	1996-2006	$y = -5,163x + 1 \times 10^7$	0.30	<i>ns</i>
carbofuran	24,150	11	1996-2006	$y = -4,766x + 1 \times 10^7$	0.75	***
terbufos	22,644	11	1996-2006	$y = -7,097x + 1 \times 10^7$	0.88	***
cyhalothrin lamda	22,183	10	1997-2006	$y = 2,492x - 5 \times 10^7$	0.34	<i>ns</i>
deltamethrin	20,896	11	1996-2006	$y = 1,513x - 3 \times 10^3$	0.13	<i>ns</i>
dimethoate	15,477	11	1996-2006	$y = -412x + 8 \times 10^5$	0.10	<i>ns</i>
imidacloprid	15,344	8	1999-2006	$y = 2,599x - 5 \times 10^6$	0.67	***
carbaryl	10,777	11	1996-2006	$y = 1,917x - 4 \times 10^6$	0.15	<i>ns</i>
cypermethrin	5,004	11	1996-2006	$y = -502x + 1 \times 10^6$	0.47	*
endosulfan	4,820	11	1996-2006	$y = -581x + 1 \times 10^6$	0.21	<i>ns</i>

[†]*ns*: not significant at $p < 0.05$

*, **, and *** denotes level of significance; $p < 0.05$, $p < 0.01$, and $P < 0.001$, respectively

Table 2.3 continued

	Average Area Treated (ha)	Years of Data	Record Years	Model	r ²	p-value
<u>Fungicides</u>						
propiconazole	274,944	11	1996-2006	$y = 36,376x - 7 \times 10^7$	0.67	**
tebuconazole	131,776	8	1999-2006	$y = 20,296x - 4 \times 10^7$	0.68	**
chlorothalonil	101,888	11	1996-2006	$y = -21,590x + 4 \times 10^7$	0.82	**
iprodione	87,880	11	1996-2006	$y = 13,621x - 3 \times 10^7$	0.67	**
carbathiin	80,468	10	1996-2005	$y = -24,781x + 5 \times 10^7$	0.84	**
vinclozolin	77,747	11	1996-2006	$y = 1,874x - 4 \times 10^6$	0.03	***
trifloxystrobin	61,602	3	2004-2006	$y = 26,826x - 5 \times 10^7$	0.67	ns
mancozeb	42,548	11	1996-2006	$y = 304x - 6 \times 10^5$	0.01	ns
boscalid	28,756	5	1996, 2003-2006	$y = 5,176x - 1 \times 10^7$	0.58	ns
pyraclostrobin	20,790	4	2003-2006	$y = 3,294x - 7 \times 10^6$	0.20	ns

[†]ns: not significant, $p < 0.05$

*, **, and *** denotes level of significance; $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively

11-year period, GLY showed the largest increase in area treated (639,570 ha increase between 1996 and 2006) as demonstrated by a significant, positive linear trend (Table 2.3). Florasulam and GLU were the only other active ingredients in the top 10 list that demonstrated significant increasing linear trends while significant decreasing linear trends were observed for thifensulfuron methyl and bromoxynil (Table 2.3).

Chlorpyrifos was applied to 1.4 times and 1.9 times the area of the second and third most applied insecticide active ingredients, carbofuran and terbufos (Table 2.3). For the top 10 insecticides, three active ingredients showed significant decreasing linear trends over the 11-year period, carbofuran, terbufos, and cypermethrin while imidacloprid had the only significant increasing linear trend (Table 2.3).

Propiconazole emerged as the top ranked fungicide and was applied to 2.1 times and 2.7 times the area of the second and third most applied fungicide active ingredients, tebuconazole and chlorothalonil (Table 2.3). Significant increasing linear trends were found for four active ingredients, propiconazole, tebuconazole, iprodione, and carbathiin. Significant decreasing linear trends were observed for chlorothalonil and carbathiin.

2.4.4 Herbicide mass

Between 1996 and 2011, herbicide intensity averaged 0.75 kg ha^{-1} for all insured crops, varying from a low of 0.6 kg ha^{-1} in 1999 to a high of 0.8 kg ha^{-1} in 1996 (Figure 2.8).

The top ten herbicides applied in Manitoba based on mass (Table 2.4) were slightly different than the top ten herbicides based on area treated (Table 2.3). Over the 11-year

period, the average amount of GLY was 1.7 times greater than the amount of MCPA, and 2.5 times more MCPA was applied as compared to bromoxynil (Table 2.4). GLY and GLU displayed significant increasing linear trends, while six of the top ten active ingredients had significant decreasing linear trends (bromoxynil, dichlorprop, ethalfluralin, imazamethabenz, trifluralin, and sethoxydim) (Table 2.4).

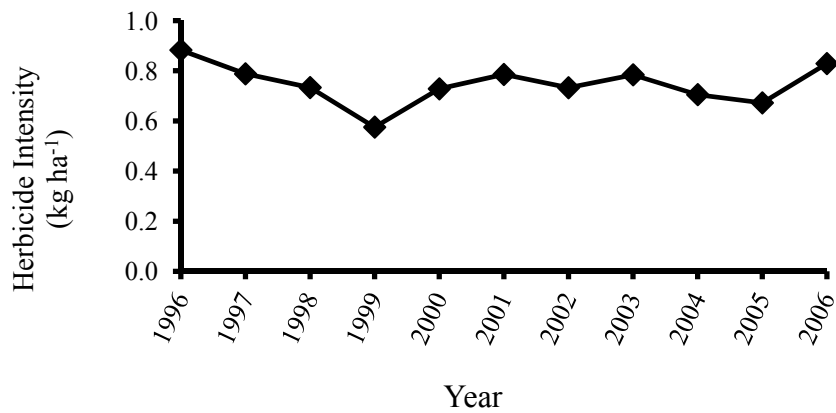


Figure 2.8 Herbicide intensity (kg ha⁻¹) applied to insured crops in Manitoba.

Table 2.4 Top 10 herbicide active ingredients applied to agricultural crops in Manitoba, 1996-2006 based on mass (kg year⁻¹) and least mean squares linear model.

Active Ingredient	Average Mass Applied kg year ⁻¹	Linear Model	r ²	p-value
glyphosate	832,651	$y = 91,950x - 2 \times 10^8$	0.88	***
MCPA	478,520	$y = -5,501x + 1 \times 10^7$	0.10	<i>ns</i> [†]
bromoxynil	191,016	$y = -4177x + 9 \times 10^6$	0.52	*
ethalfluralin	169,077	$y = -12193x + 2 \times 10^7$	0.86	***
2,4-D	164,929	$y = -3487.9x + 7 \times 10^6$	0.20	<i>ns</i> [†]
glufosinate ammonium	141,507	$y = 21624x - 4 \times 10^7$	0.85	***
trifluralin	116,457	$y = -15265x + 3 \times 10^7$	0.87	***
sethoxydim	96,530	$y = -9660x + 2 \times 10^7$	0.83	***
dichlorprop	91,632	$y = -13267x + 3 \times 10^7$	0.89	***
imazamethabenz	68,784	$y = -3953x + 8 \times 10^6$	0.61	**

[†]*ns*: not significant, $p < 0.05$

*, **, and *** denotes level of significance; $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively

2.4.5 Trends associated with herbicide-tolerant crops

The majority of canola (93%) and soybeans (89%) grown in Manitoba are now GMHT varieties (Figure 2.9). The adoption of GMHT-corn varieties has also increased steadily since 1996, now accounting for 47.5% of all corn grown in the province (Figure 2.9). Imidazoline resistant wheat has not been widely adopted remaining below 7% between 1996 and 2006.

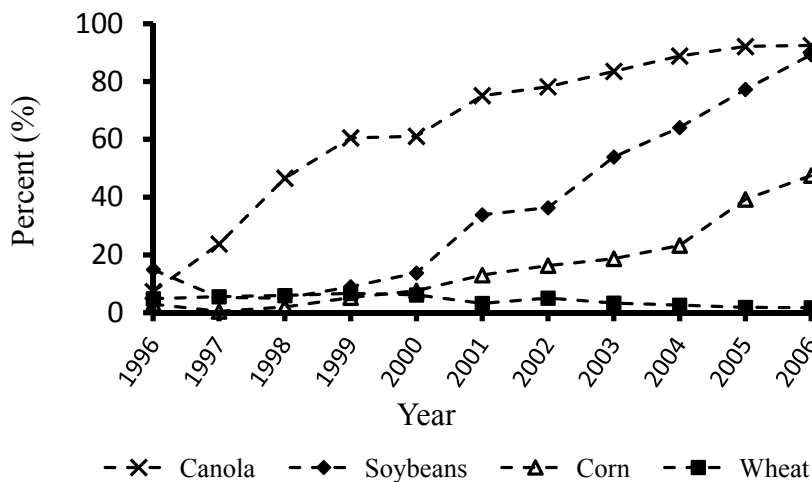


Figure 2.9 Percentage of insured canola, soybeans, corn, and wheat treated with glyphosate, glufosinate ammonium, bromoxynil, imazamox, and/or imazethapyr.

With the increasing adoption of GMHT-canola, the percentage of canola treated with GLY and GLU has also increased since 1996, with there being a greater adoption to GLY-resistant canola than GLU-resistant canola (Figure 2.10). Despite the increase in GMHT-canola, the area seeded has varied from a low of 537 thousand hectares in 1996 to a high of 958 thousand hectares in 2004 (Figure 2.3). The annual mass of GLY and GLU applied displayed significant ($p < 0.0001$) increasing linear trends between 1996 and 2006 (Figure 2.11). Bromoxynil, imazamox, and imazethapyr consistently accounted for a small portion of herbicides applied to GMHT-canola between 1996 and 2006 (Figure

2.10), and a significant ($p < 0.05$) increasing linear trend was observed for imazamox only (Figure 2.12). For the masses of herbicides applied to conventional canola (non-GMHT) between 1996 and 2006, significant ($p < 0.0001$) decreasing linear trends were observed for clopyralid, ethalfluralin, trifluralin, and all herbicides applied to non-GMHT-canola (Figure 2.13).

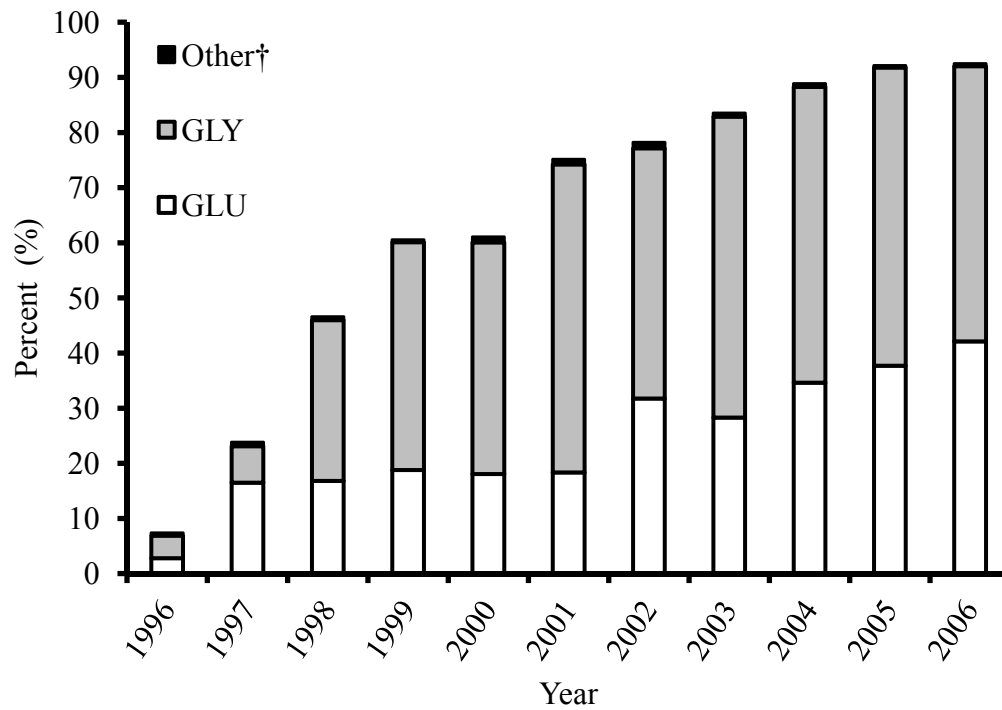


Figure 2.10 Percentage of glyphosate (GLY) and glufosinate ammonium (GLU), and other herbicides applied to GMHT-canola in Manitoba.
[†]Other herbicides applied to GMHT-canola (bromoxynil, imazamox, and imazethapyr)

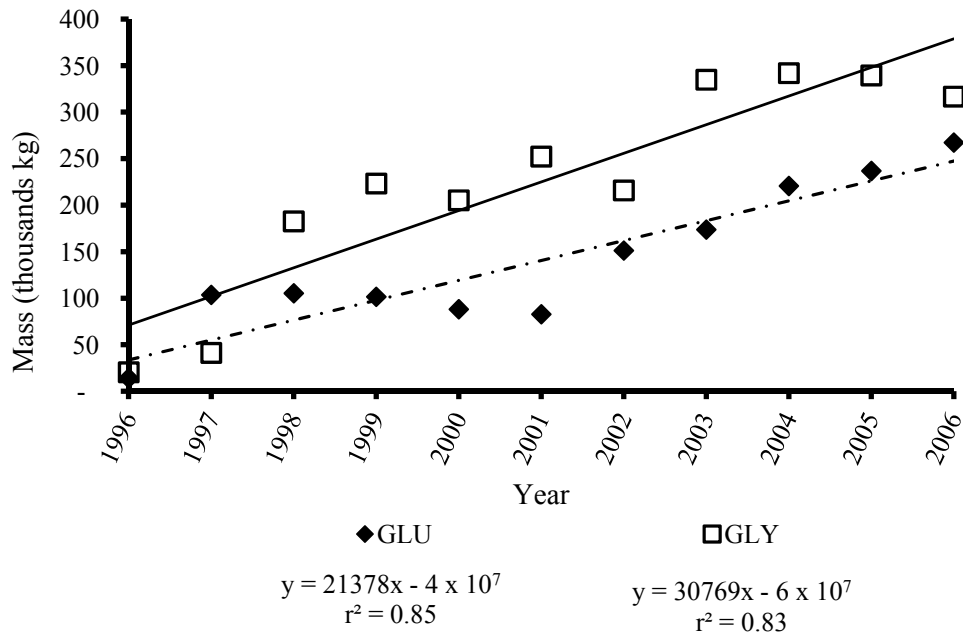


Figure 2.11 Mass of glufosinate ammonium (GLU) and glyphosate (GLY) applied to GMHT-canola in Manitoba.

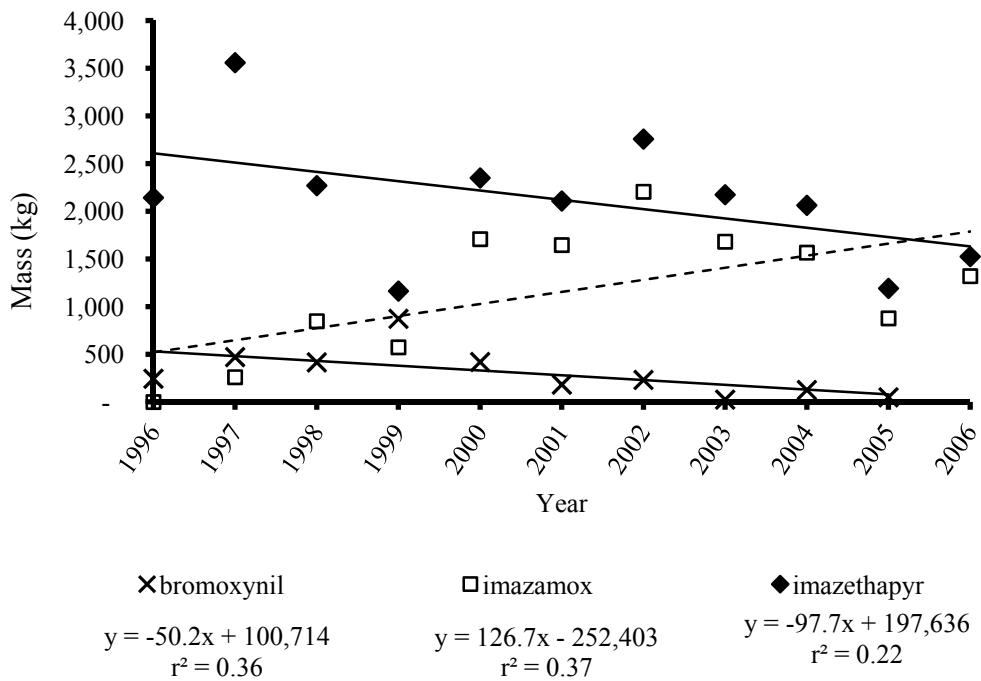


Figure 2.12 Mass of bromoxynil, imazamox, and imazethapyr applied to GMHT-canola in Manitoba.

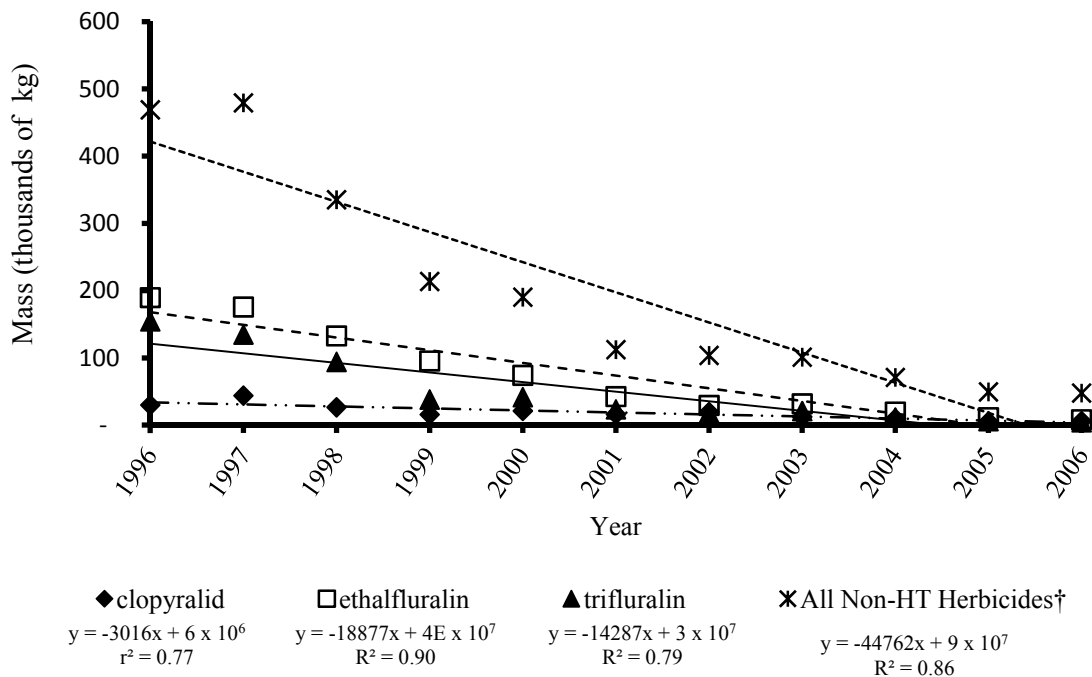


Figure 2.13 Herbicides applied to conventional (non-GMHT) canola.
 †Non-GMHT herbicides applied to canola. Active ingredients listed in Appendix II.

2.4.6 Herbicide use spatial trends

At the township and ecoregion level, the five-year percent change in the mass of herbicides applied to all crops varied by more than $\pm 25\%$ and $\pm 10\%$, respectively (Figures 2.14 and 2.15). On average, at the township and ecoregion level, herbicide use intensity was never greater than $\pm 25\%$ and $\pm 10\%$, respectively (Figure 2.16 and 2.17). The Manitoba Plain and the Aspen parkland region had on average, the highest level of herbicide intensity (0.81 kg ha^{-1} and 0.79 kg ha^{-1}) but no significant increasing or decreasing linear trends were observed over the 11-year time period in these regions (Appendix III). On average, the five-year percent change in GLY mass applied to all

crops at the township level (Figure 2.18) increased by 25%. Similarly, at the ecoregion level, the five-year percent change in GLY mass applied to all crops was always greater than 10% (Figure 2.19) The five-year percent change for herbicide use intensity for canola varied by $\pm 25\%$ at the township level (Figure 2.20), while at the ecoregion level, the intensity varied by $\pm 10\%$ (Figure 2.21).

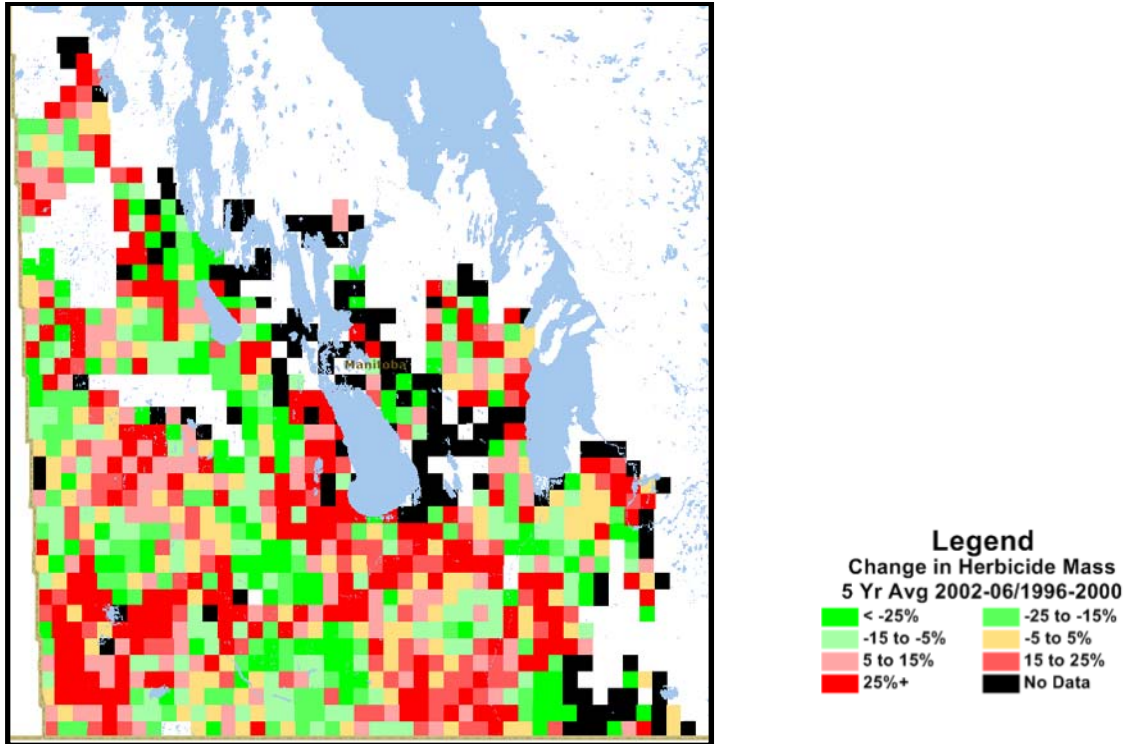


Figure 2.14 Five-year percent change in herbicide mass (all crops) at the township level.

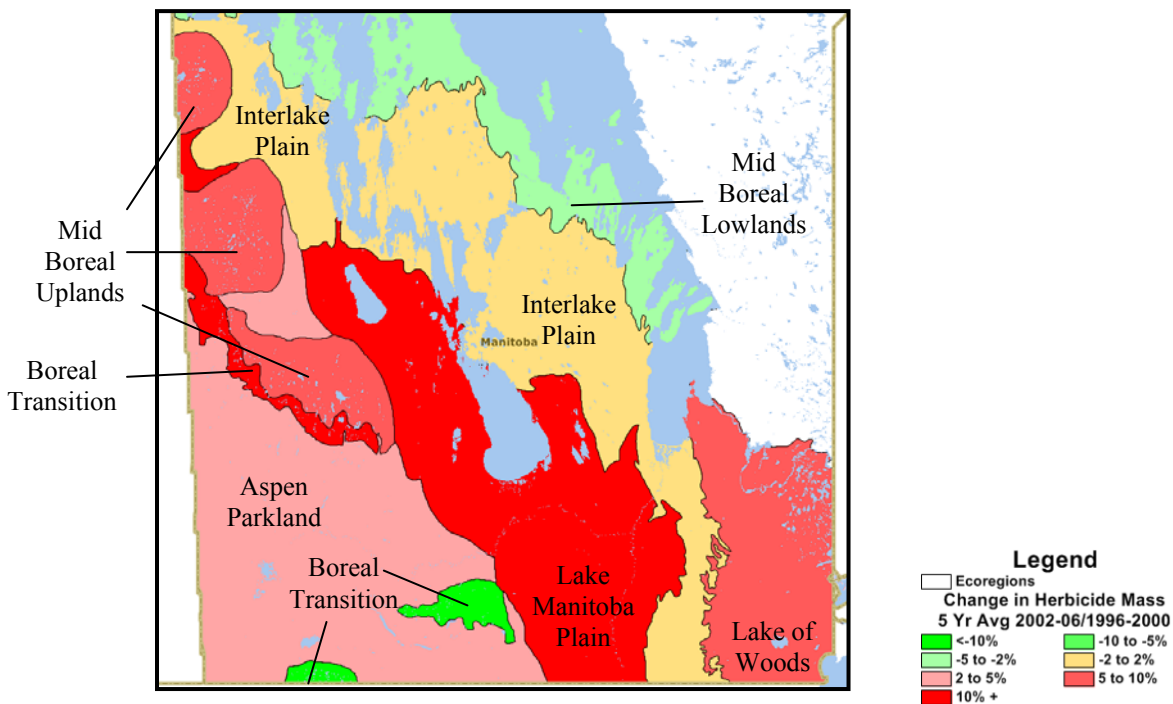


Figure 2.15 Five-year percent change for herbicide mass (all crops) at the ecoregion level.

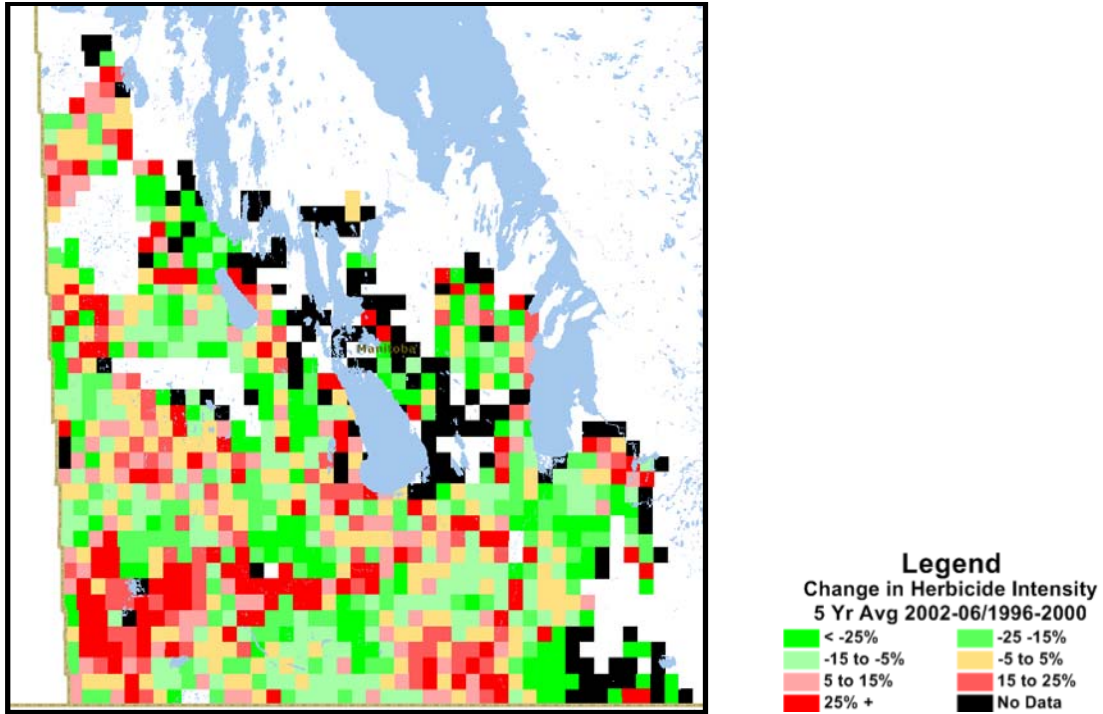


Figure 2.16 Five-year percent change for herbicide use intensity (all crops) at the township level.

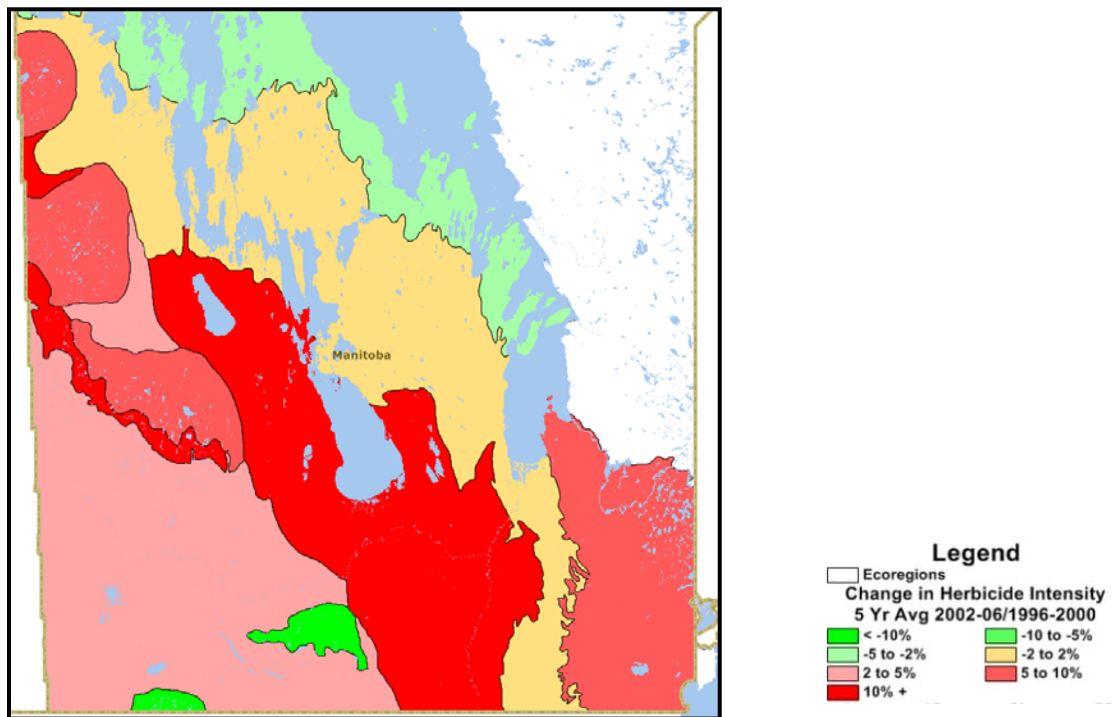


Figure 2.17 Five-year percent change for herbicide use intensity (all crops) at the ecoregion level.

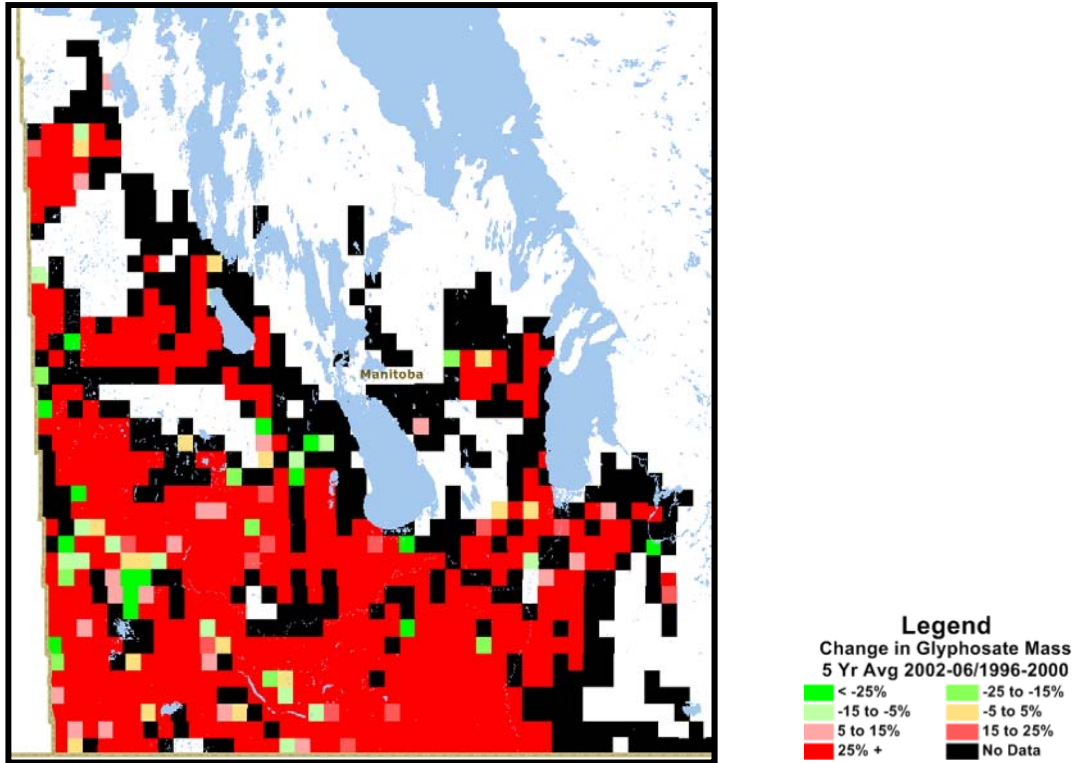


Figure 2.18 Five-year percent change in glyphosate mass (all crops) at township level.

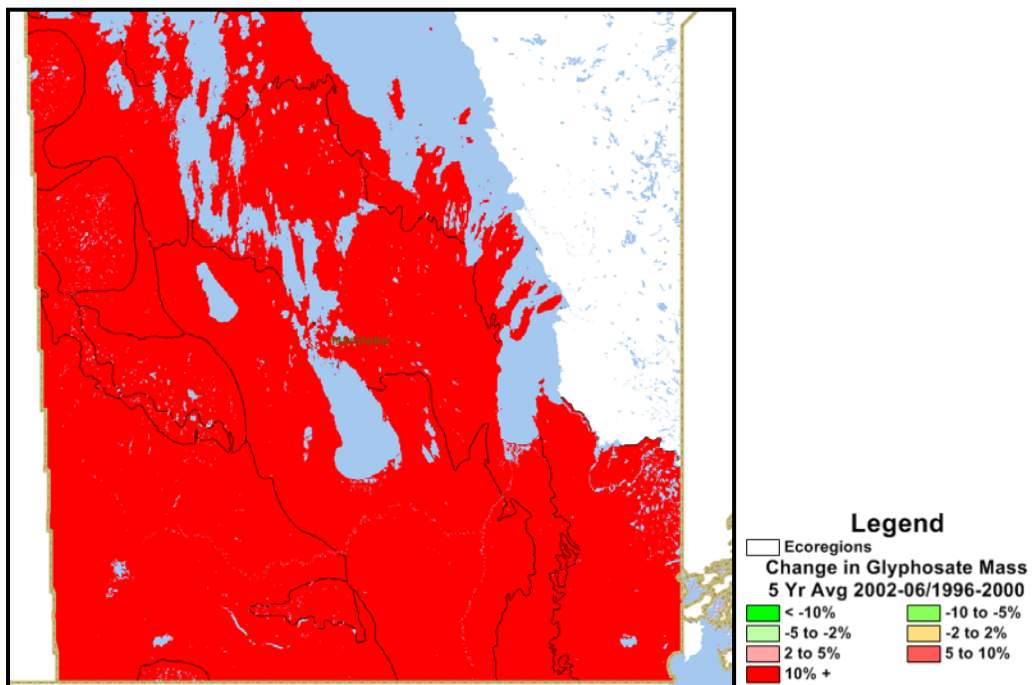


Figure 2.19 Five-year percent change in glyphosate mass (all crops) at ecoregion level.

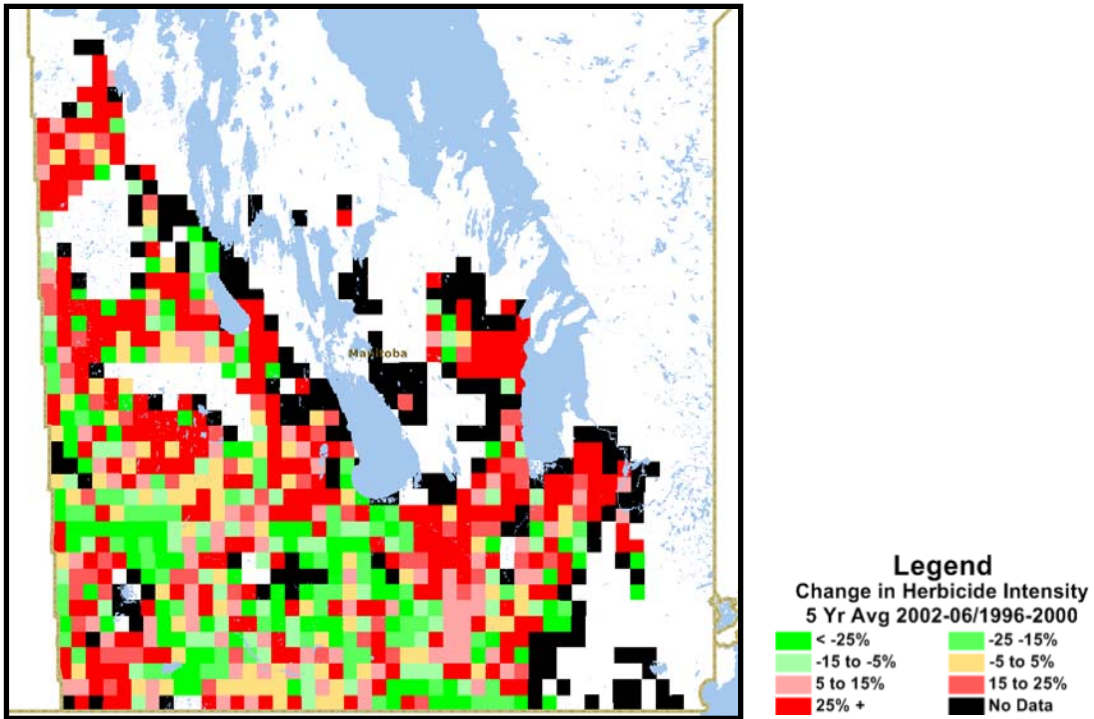


Figure 2.20 Five-year percent change in herbicide use intensity for canola at the township level.

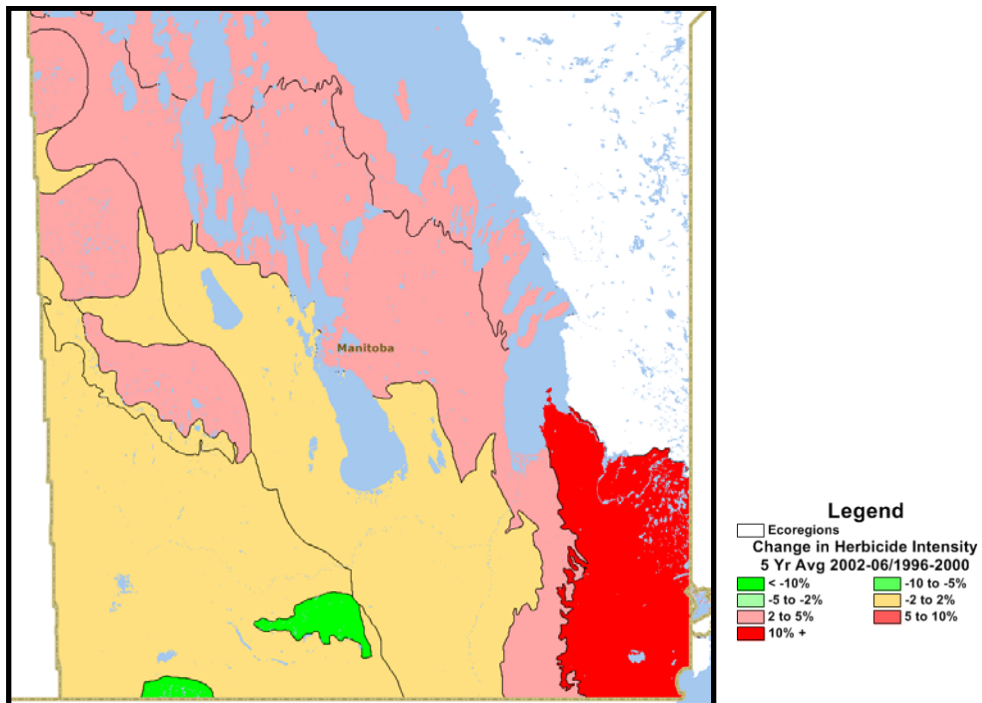


Figure 2.21 Five-year percent change in herbicide use intensity for canola at the ecoregion level.

2.5 Discussion

While several studies suggest that the adoption of GMHTCs has resulted in a reduction in pesticide use globally (Wolfenbarger 2000; Philips and Park 2002; James 2003; Brooks and Barfoot 2005; Beckie et al. 2006), this study suggests that this is not the case in Manitoba as the total mass of herbicide use remained relatively consistent between 1996 and 2006. Of significant note is the increase in GLY and GLU applied to canola and the significant decrease in three herbicides used in non-GMHT canola (clopyralid, ethalfluralin, and trifluralin).

The MASC data indicates that herbicide active ingredients are applied to the largest area, followed by fungicides and insecticides (about 88%, 9%, and 2% of the total pesticide use, respectively). These numbers are consistent with estimations from Cessna et al. (2010) who reported that for the Province of Manitoba in 2006, the percentage pesticides was 92% for herbicides, followed by fungicides (7%), and insecticides (1%). Differences among the percentages likely reflect the differences in source data. These numbers are also consistent with estimations from Brimble et al. (2005) for Manitoba but differ from global pesticide use trends in which the portion of herbicides, insecticides, and fungicides used are 46%, 26%, and 21%, respectively (Stephenson and Solomon 2007).

Casséus (2009) suggests that the elimination of the transportation subsidy for grain in 1995 is responsible for the fewer hectares of wheat being grown in the Prairie Provinces (Figure 2.3) which has resulted in a shift to higher return crops such as canola in which investments in insect and fungal disease control can provide greater cash returns.

However, there was no consistent increase in insecticide and fungicide use observed in the current study. In fact, this study demonstrated fluctuations in insecticide and fungicides throughout the 11-years, likely reflecting annual variations in disease pressures as a result of environmental factors such as weather, rather than crop management practices.

The number of active ingredients for herbicides, insecticides, and fungicides has remained relatively stable over the 11-year period. This likely reflects increasing national and global costs and stricter regulations associated with the development and registration of new pesticides active ingredients (Ollinger and Fernandez-Cornejo 1998; Kraehmer and Drexler 2009). Like other regions of North America, the “golden era” of herbicide discovery and development occurred in the 1960s and 1970s when over half of the currently used 18 modes of action were introduced in Western Canada (Holm and Johnson 2009). The development of new modes of action since the 1990s has slowed considerably, with only four new modes of action being introduced: Groups 10, 14, 15, and 28 (Holm and Johnson 2009). In addition, it has been suggested that the high adoption level of GMHTCs may be responsible for a reduced investment in herbicide discovery because the remaining herbicide market has been substantially reduced (Duke 2005).

Unlike the relatively consistent number of pesticide active ingredients between 1996 and 2006, the increase in the number of product formulations is hypothesized to be the result of patent expiration, which can extend for 20-years for an active ingredient or a product

formulation (McEwan and Deen 1997). The patent for GLY, for example, expired in 2000, resulting in a price decrease of 40% in the United States (Duke and Powles 2008, 2009).

Given the wide variety of pesticides currently used on the Canadian Prairies and the large area to which they are applied, the risk of non-target contamination remains a concern. One of the challenges with environmental monitoring for pesticides in ground and surface water and the atmosphere is determining which pesticides should be included in the analysis (Ferrer and Thurman 2007). Monitoring for all pesticides registered for use on the prairies is cost prohibitive, and therefore, pesticides that are widely used and are of environmental concern should be identified as “priority pesticides” (Environment Canada 2006, 2011). Pesticides which are applied to larger areas such as MCPA, bromoxynil, and GLY should be identified as priority pesticides, not only because they are widely used, but they have the potential to move offsite and contaminate ground and surface water (Humphries et al. 2005; Environment Canada 2011; Glozier et al. 2011; Messing et al. 2011).

Herbicide use data can provide insight into which herbicides should be included in environmental analysis. Out of the 71 herbicides applied to cropland in Manitoba, only 39% have been included in water and atmospheric monitoring studies in western Canada between 1991 and 2011, representing 31 active ingredients and a total mass of 27 million kg of herbicides applied to 65.4 million ha between 1996 and 2006 (Table 2.5). Although

MCPA, bromoxynil and 2,4-D are frequently included in water monitoring studies in western Canada, GLY has only been included in three studies between 1990 and 2011 (Table 2.5). Of the studies that considered MCPA, bromoxynil, 2,4-D, and GLY in water quality studies, 100% of the studies detected these herbicides. Of the pesticides monitored between 1990 and 2011, high use pesticides which are ranked as the top ten herbicides in this study, such as GLY, GLU, and sethoxydim, were infrequently included in environmental analysis (17%, 11%, and 0% of the studies included in Table 2.5).

Widely used herbicides are frequently detected as expected, however less extensively used herbicides are still detected as contaminants. Thus, including as many pesticides as possible is important for monitoring non-target contamination by frequently and less frequently used herbicides. One of the constraints with conventional detection methods such as liquid chromatography and mass spectrometry is narrowing down the list of herbicides which can be included in the analysis (Ferrer and Thurman 2007). Also, GLY is infrequently included in environmental analysis due to analytical difficulties (Sancho et al. 1996; Le Bot et al. 2002; Hidalgo et al. 2004), high costs (Anderson et al. 1997; Byer et al. 2008), and the perception by farmers and researchers that it is a relatively benign herbicide (Baylis 2000; Duke et al. 2003; Cerdeira and Duke 2010). Newer and more cost effective techniques developed for analyzing environmental samples for pesticides include the enzyme-linked immunosorbent assay (ELISA) method and Time-of-Flight mass spectrometry (TOF). Although ELISA is relatively inexpensive, the number of pesticides that can currently be analyzed is limited and the technique often focuses on the analysis of individual compounds rather than multi-residue screening (Baylis 2000). In

Table 2.5 List of active ingredients occurring in the MASC database developed in this study (listed in order by rank) and monitored in Western Canada by other studies. Data from other studies are derived from refereed journal articles and public reports published from 1991 to 2011 (n=19).

Rank	Active ingredient	# of studies that tested for the active ingredient	% of studies that detected the active ingredient	References
1	MCPA	15	100%	Grover et al. 1997; Wood and Anthony 1997; Anderson et al. 1997; Donald et al. 1999; Rawn et al. 1999ab; Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Waite et al. 2004; Donald et al. 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Glozier et al. 2011; Messing et al. 2011
2	glyphosate	3	100%	Humphries et al. 2005; Glozier et al. 2011; Messing et al. 2011
3	bromoxynil	16	100%	Waite et al. 1992; Grover et al. 1997; Waite et al. 1995; Wood and Anthony 1997; Donald et al. 1999; Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Waite et al. 2004; Donald et al. 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Glozier 2011; Messing et al. 2011
4	ethalfluralin	6	83%	Rawn et al. 1999a; Cessna and Elliot 2004; Hill et al. 2002; Yao et al. 2006, 2008; Environment Canada 2011; Messing et al. 2011
5	2,4-D	18	100%	Waite et al. 1992; Grover et al. 1997; Waite et al. 1995; Anderson et al. 1997; Wood and Anthony 1997; Donald et al. 1999; Rawn et al. 1999ab; Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Waite et al. 2002; Donald et al. 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Glozier et al. 2011; Messing et al. 2011

Table 2.5 continued

Rank	Active ingredient	# of studies that tested for the active ingredient	% of studies that detected the active ingredient	References
6	glufosinate ammonium	2	50%	Glozier et al. 2011; Messing et al. 2011
7	trifluralin	15	93%	Waite et al. 1992; Grover et al. 1997; Anderson et al. 1997; Wood and Anthony 1997; Donald et al. 1999; Rawn et al. 1999a; Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Waite et al. 2004; Donald et al. 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Messing et al. 2011
9	dichlorprop	8	100%	Wood and Anthony 1997; Donald et al. 1999; Rawn et al. 1999ab; Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Donald et al. 2005, Donald et al. 2007; Glozier 2011
10	imazamethabenz	3	100%	Anderson et al. 1997; Donald et al. 2001; Donald et al. 2007
12	fenoxaprop p ethyl	3	67%	Anderson et al. 1997; Cessna and Elliot 2004; Hill et al. 2002
13	clopyralid	6	100%	Cessna and Elliot 2004; Hill et al. 2002; Donald et al. 2007; Environment Canada 2011; Glozier 2011; Messing et al. 2011

Table 2.5 continued

Rank	Active ingredient	# of studies that tested for the active ingredient	% of studies that detected the active ingredient	References
14	dicamba	17	100%	Waite et al. 1992; Grover et al. 1997; Waite et al. 1995; Anderson et al. 1997; Wood and Anthony 1997; Donald et al. 1999; Cessna and Elliot, 2004; Donald et al. 2001; Hill et al. 2002; Waite et al. 2002; Waite et al. 2004; Donald et al. 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Glozier 2011; Messing et al. 2011
16	trallate	14	100%	Waite et al. 1992; Donald et al. 1995; Grover et al. 1997; Waite et al. 1995; Anderson et al. 1997; Wood and Anthony 1997; Rawn et al. 1999a; Cessna and Elliot 2004; Hill et al. 2002; Donald et al. 2005; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Environment Canada 2011; Messing et al. 2011;
22	atrazine	6	83%	Wood and Anthony 1997; Rawn et al. 1999a; Hill et al. 2002; Yao et al. 2006; Donald et al. 2007; Yao et al. 2008; Messing et al 2011
23	mecoprop	7	100%	Cessna and Elliot 2004; Donald et al. 2001; Hill et al. 2002; Donald et al. 2007; Environment Canada 2011; Glozier 2011; Messing et al. 2011
27	metribuzin	3	100%	Cessna and Elliot 2004; Donald et al. 2005; Donald et al. 2007; Environment Canada 2011
29	thifensulfuron methyl	2	100%	Donald et al. 2007; Environment Canada 2011

Table 2.5 *continued*

Rank	Active ingredient	# of studies that tested for the active ingredient	% of studies that detected the active ingredient	References
32	imazethapyr	2	100%	Hill et al. 2002; Donald et al. 2007
36	2,4-DB	3	67%	Wood and Anthony 1997; Donald et al. 1999; Hill et al. 2002; Glozier 2011
38	ethametsulfuron methyl	1	100%	Donald et al. 2007
40	diclofop methyl	5	80%	Anderson et al. 1997; Cessna and Elliot 2004; Donald et al. 2001;
47	MCPB	5	100%	Wood and Anthony 1997; Donald et al. 1999; Donald et al. 2005; Donald et al. 2007; Environment Canada 2011
49	metolachlor	5	100%	Rawn et al. 1999a; Wood and Anthony 1997; Yao et al. 2006, 2008; Environment Canada 2011; Messing et al. 2011
50	tribenuron methyl	1	100%	Donald et al. 2007
51	quinclorac	1	100%	Hill et al. 2002

Table 2.5 continued

Rank	Active ingredient	# of studies that monitored for the active ingredient	% of studies that detected the active ingredient	References
55	alachlor	3	67%	Rawn et al. 1999a; Yao et al. 2006; Messing et al. 2011
56	sulfosulfuron	2	100%	Donald et al. 2007; Environment Canada 2011
60	simazine	3	100%	Wood and Anthony 1997; Donald et al. 2007; Environment Canada 2011
66	picloram	5	100%	Anderson et al. 1997; Wood and Anthony 1997; Donald et al. 2005; Donald et al. 2007; Environment Canada 2011
70	metsulfuron methyl	2	100%	Donald et al. 2007; Environment Canada 2011

contrast, TOF allows a wide range of pesticides to be included in environmental analysis, often between 100 and 200 compounds; however, it is more expensive than ELISA (Sancho et al. 2006; Ferrer and Thurman 2007). Donald et al. (2007) consistently detected seven herbicides in prairie reservoirs during the growing season in Manitoba, Saskatchewan, and Alberta in decreasing frequency: 2,4-D, diclofop, bromoxynil, MCPA, triallate, dicamba, and trifluralin. While 45 pesticides and degradation products were monitored in the study by Donald et al. (2007), only four (MCPA, bromoxynil, 2,4-D, and thifensulfuron) of the top ten herbicides (based on mass) from this study were included in their environmental analysis.

Data on the types and amounts of pesticides applied, as well as the crop, area, and geographic location onto which these chemicals are applied are useful to stakeholders involved in environmental monitoring, agricultural policy programs, pesticide product development, and related agri-environmental activities. Canada lacks a comprehensive national system for collecting pesticide use data and although sources of pesticide use and sales data are available in some provinces, the data are collected and reported in a variety of formats making comparisons difficult (Brimble et al. 2005). The Census of Agriculture only collects general pesticide use information, i.e., the area treated with herbicides, insecticides, and fungicides every five years at the provincial level (Statistics Canada, 2006). In Manitoba, pesticide use information is available online from the Manitoba Management Plus Program (MMPP) (MASC 2011). The MMPP provides specific pesticide use data, including the crop and the formulated pesticide product applied at the municipal level, however, only aggregate data from three or more producers or areas greater than 202 ha (500 acres) are included in order to maintain producer anonymity (MASC 2011). The MASC data set used in this study provides pesticide use data at

the township level and is more detailed than either the Census of Agriculture or the MMPP.

While the dataset is a valuable source of pesticide use information, the information provided by producers is not verified, and therefore occasional errors may occur, such as products that cannot be identified (Table 7.1). Despite the valuable pesticide use information provided by the MASC data set, as of 2012, MASC will no longer collect pesticide use data (J. Gaultier personal comm. October 2011).

The data set provided by MASC is novel in that the crop grown and the product applied is recorded on a yearly basis and covers more than 80% of seeded crops in Manitoba. Because the area of crop land treated was not reported, the entire area of crop grown was considered to be the area onto which the pesticide was applied (MASC 2011). This study also assumed maximum application rates. Although such assumptions could lead to an overestimation of pesticide use, the error associated with this assumption is relatively small because the majority of Manitoba producers will typically treat their entire field with one herbicide application using the maximum recommended rate (Gary Martens, personal commun. January 2012). In some instances, GLY may be applied more than once because it is economically feasible and perceived to be beneficial (Gary Martens, Personal commun. January 2012). The implementation of precision farming may further complicate estimating application rates and the area treated, as farmers would vary rates to coincide with localized weed pressures (Faechner et al. 2002). However, the use of precision farming in weed control practices is still relatively uncommon in Manitoba.

GMHT-canola was not explicitly identified in the MASC-data set. Therefore, canola was assumed to be herbicide-tolerant if GLY, GLU, imazamox or imazethapyr were applied. The

estimated area of GMHT-canola grown in Manitoba in this study is in agreement with estimates from several other studies (Brimner et al. 2005; Beckie et al. 2006; O'Donovan et al. 2006; Smyth et al. 2011).

2.6 Conclusion

Herbicides account for the greatest proportion (84%) of pesticides applied in Manitoba ranging from 4.5 million ha in 1999 to 5.6 million ha in 2003. Herbicide use intensity has remained relatively consistent, varying from a low of 0.6 kg ha⁻¹ in 1999 to a high of 0.8 kg ha⁻¹ in 1996. The most significant trend for the top 10 herbicides applied in Manitoba are the increases in GLY from 16 to 45%, and in GLU from 0.5 to 8% of the total herbicides used in 1996 to 2006, respectively. Florasulam was the only other active ingredients in the top 10 list that demonstrated significant increasing linear trends, while significant decreasing linear trends were observed for thifensulfuron methyl and bromoxynil. Information on the types and amount of pesticides used in Manitoba is valuable for determining priority pesticides to include in environmental monitoring programs. Despite the large area and quantities to which GLY is applied in Manitoba, the lack of monitoring for this herbicide as a contaminant likely reflects the preconceived notion that it is a relatively non hazardous pesticide, but could also be related to challenges associated with the more specialized analytical analysis required for detecting this active ingredient. In addition, to move towards more sustainable pesticide use in agriculture, a more centralized system of collecting and disseminating pesticide use data is required not only in Manitoba, but the rest of Canada.

2.7 Acknowledgements

The authors gratefully acknowledge Manitoba Agricultural Services Corporation for providing the data aggregated to the township level. We also wish to acknowledge the contributions of Elaine Slater (University of Manitoba Summer Student), and Gary Warkentine (Exceed Analysis), Ross McQueen (Department of Soil Science, University of Manitoba), and Jeanette Gaultier (Manitoba Agriculture, Food and Rural Initiatives).

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3. TRENDS IN HERBICIDE RISK INDICATORS AS A FUNCTION OF CHANGES IN HERBICIDE USE FROM 1996-2006 IN MANITOBA, CANADA

3.1 Abstract

The introduction of herbicide-tolerant (GMHT) canola to Manitoba growers in 1995 has altered herbicide use on the Canadian Prairies. Over the 11-year study period, GMHT-canola increased from 6% in 1996, to 93% in 2006 of all canola grown in Manitoba. This paper describes the trends in agricultural herbicide risk indicators (HRIs) in Manitoba since the adoption of genetically modified herbicide-tolerant crops (GMHTCs). The annual mass of herbicides applied to agricultural crops was used to calculate 18 simple and 12 composite HRIs, for a total of 11 years (1996-2006) to show changes in potential environmental and health risks associated with herbicide use trends over time. Overall, 67% of the simple parameter indicators, and 83% of the composite HRIs demonstrated that since 1996, producers are using more environmentally benign herbicides which are less mobile, less persistent and less toxic to mammals, aquatic invertebrates, fish, birds, and bees. Many of these trends are related to the replacement of the more mobile, persistent and toxic herbicides used on conventional canola (clopuralid, ethalfluralin, and trifluralin), with seemingly less harmful herbicides such as glyphosate (GLY) and glufosinate ammonium (GLU). This conclusion was derived from time trends calculated using indicators that rely on the input of pesticide physicochemical and toxicological properties derived from databases. Although glyphosate can be regarded as a more environmentally friendly alternative to conventional herbicides, concerns exist regarding the potential of glyphosate to contaminate non-target sources. Several studies indicate that when glyphosate is

included in environmental sample analysis, it is frequently detected in Western Canadian rain and water sources.

3.2 Introduction

Pesticides vary greatly in their persistence, mobility, and toxicity, and it is for this reason measures other than the weight or area treated are needed to adequately assess changes in health or environmental risks arising from pesticide use (Barnard et al. 1997; Levitan 2000; Falconer 2002; Uri 2006). The environmental and human impacts of a pesticide are a result of a multitude of interacting factors which include the inherent physicochemical properties of the active ingredient, application techniques, application rate, environmental fate and transport, toxicological effects to non-target organisms, weather, soil, and land management (Falconer 2002). A variety of literature exists regarding the development and use of pesticide risk indicators (eg. Levitan et al. 1995; van der Werf 1996; Levitan 2000; Maud et al. 2001; Falconer 2002; Padovani et al. 2004; Kookana et al. 2005). A risk indicator provides an estimate of relative risk of resource degradation using mathematical formulas or models (OECD 2001). Pesticide risk indicators aim to simplify the complexities of pesticide impact assessment by providing the best estimate of the potential impact of pesticides on the surrounding environment (Greitens and Day 2006). Simple indicators utilize a single variable, while composite indicators utilize several variables and or a series of simple indicators (Girardin et al. 1999).

The commercial introduction of genetically modified herbicide-tolerant (GMHT) canola to Manitoba growers in 1995 (Duke 2005; Beckie et al. 2006) has resulted in changes to agricultural practices, including the types of herbicide active ingredients that are being used

(Graef et al. 2007; Chapter 2). Many studies have indicated that lower herbicides amounts are used in GMHT cropping systems than conventional cropping systems (Wolfenbarger and Phifer 2000; Shaner 2000; Phipps and Park 2002; James 2003; Brimner et al. 2005; Brookes and Barfoot 2005; Giannessi 2005; Smyth et al. 2011a), however, for the United States, Benbrook (2001, 2003, 2004, 2009) argued that GMHT crops have resulted in an increase in herbicide use. Giannessi (2005) estimated that producers used lower rates of glyphosate (GLY) on GLY resistant canola (average of 0.1 kg less of active ingredient per ha) compared with herbicides rates used on conventional canola. Brimner et al. (2005) estimated that a reduction of 0.35 kg of active ingredient per ha can be achieved in GMHT-canola as compared to conventional canola. The reduction in the amount of active ingredient used on GMHT-canola, coupled with a reduction in application frequency (Smyth et al. 2011b) has been estimated to save producers \$5 per ha when compared to the costs of herbicides used in conventional canola (Giannessi 2005). In addition, Brimner et al. (2005) calculated that the environmental impact per hectare for GMHT-canola as measured by the Environmental Impact Quotient (EIQ) is lower than the EIQ for herbicides applied to conventional canola (Brimner et al. 2005).

Prior to the adoption of GMHT-canola, the options for broadleaf weed control in conventionally grown canola were limited to a few older herbicides such as trifluralin and ethalfluralin introduced in 1965 and 1987, respectively (Brimner et al. 2005; Duke 2005; Beckie et al. 2006; Smyth et al. 2011ab). Although trifluralin and ethalfluralin were significant contributors to the initial success of canola production, their use has decreased substantially since the mid 1990s due to the introduction of GLY and GLU resistant canola (Chapter 2). There are several agronomic limitations associated with herbicides used on conventional canola (Holm and

Johnson 2009), such as the need to incorporate trifluralin and ethalfluralin into the soil before seeding to minimize volatilization (Smith et al. 1997; Holm and Johnson 2009; Smyth et al. 2011a). As such, the switch to GMHT-canola has permitted many Western Canadian producers to adopt zero tillage or minimum tillage systems because soil incorporation is not required since GLY and GLU are foliar applied herbicides (O'Donovan et al. 2006; Smyth et al. 2011a). Unlike GLY and GLU, ethalfluralin and trifluralin have soil residual effects, which may restrict subsequent second-year crops (Smyth et al. 2011a). Another drawback to the use of ethalfluralin and trifluralin in canola is that these are selective herbicides, hence controlling fewer weed species than non-selective herbicides such as GLY and GLU, and therefore limiting producers to growing canola on fields with low weed pressures (Beckie et al. 2006; Smyth et al. 2011a).

According to the pesticide use data provided by Manitoba Agricultural Services Corporation (MASC), the hectares of GMHTCs (canola, soybeans, corn, and wheat) has increased from 57 thousand ha in 1996 to 935 thousand ha in 2006 (Shymko, Chapter 2). The objective of this study was to evaluate changes in the calculated values of herbicide risk indicators (HRIs) as a result of changes to herbicide use since the adoption of GMHTCs in Manitoba.

3.3 Material and Methods

The herbicide properties data base (HPDB) was created in Excel for 76 different herbicide active ingredients applied in Manitoba between 1996 and 2006 (Chapter 2), and included 25 physicochemical and toxicological properties (Appendix IV). The physicochemical and toxicological properties were obtained mainly from the Pesticide Properties Database (PPDB 2009), or when not available, from other sources in the following order:

1. Material Safety Data Sheets (MSDS);
2. Pesticide Management Regulatory Agency (PMRA), Search Product Label Database retrieved from the Health Canada Website:
<http://pr-rp.hc-sc.gc.ca/lr-re/index-eng.php>;
3. The Pesticide Action Network (PAN) Pesticide Database (Kegley et al. 2011);

When a physicochemical or toxicological property could not be found for an active ingredient (1.1% of all properties/active combinations), the missing property was estimated following the methodologies of Kovach et al. (1992) by averaging the values for that property for all the other active ingredients.

3.3.1 Herbicide Risk Indicator calculations

The HPDB compiled in this study and the herbicide masses calculated in Chapter 2 were used to calculate 18 Simple Herbicide Risk Indicators (Simple HRIs) and three Composite HRIs (composed of a total of 12 subcomponents) (Tables 3.1-3.3). These HRIs were calculated annually, for a total of 11 years (1996 – 2006), to show changes in potential risk arising from temporal herbicide use trends. For each of the 18 simple HRIs and one of the composite HRIs (PRZM), the mass of each active ingredient applied in a given year (y) was multiplied by its respective risk property (x). For each year, the product of x times y of each active ingredient was then summed to produce one composite value for all active ingredients used in that year. This composite value was divided by the total mass of active ingredients used in that year to produce a HRI value for that year. For each of the 18 simple HRIs and the HRI PRZM, 11- HRI values were thus calculated, one for each year between 1996 and 2006, inclusively (Equation 3.1).

$$HRI_j = \sum_{i=1}^{76} \left(\frac{x_i * y_{ij}}{\sum_{i=1}^{76} y_{ij}} \right) \quad [3.1]$$

Where HRI is the herbicide risk indicator for the j^{th} year; x is the value of the risk property for active ingredient i ; and y is the mass (kg) of active ingredient i applied in the j^{th} year.

The remaining two composite indicators, the EIQ HRI and PERSIST HRI were calculated using modified versions of Equation 3.1, and are detailed in sections 3.3.1.2 and 3.3.1.3.

Table 3.1 Description of simple physicochemical Herbicide Risk Indicators (HRIs). Physicochemical descriptions compiled from PPDB (2009).

Simple HRI	HRI [§] Type	Description
<u>Physicochemical</u>		
1. K_{ow} (pH 7, 20°C)	M	Octanol-water partition coefficient. Provides an indication of the potential to bioaccumulate. < 2.7 = Low bioaccumulation; 2.7 – 3 = Moderate; > 3.0 = High
2. Water Solubility (20°C)	M	The mass of a given substance (the solute) that can dissolve in a given volume of water. [mg l ⁻¹] < 50 = Low; 50 - 500 = Moderate; > 500 = High
3. Vapour Pressure 25°C	M	A relative measure of the volatility of a pesticide. [mPa] < 1 x 10 ⁻⁶ = Non-volatile; 1 X 10 ⁻⁴ - 1 x 10 ⁻⁶ = Intermediate state ; > 1 X 10 ⁻⁴ = Volatile
4. Henry's Law Constant 25°C	M	Provides an indication of a substances' volatility; the preference of a chemical for air relative to water. [Pa m ³ mol ⁻¹] > 100 = Volatile; 0.1 - 100 = Moderately volatile; < 0.1 = Non-volatile
5. DT ₅₀	P	Half-life. The time (days) taken for the concentration of the pesticide in a defined compartment (e.g. soil, water) to decline by 50%. < 30 = Non-persistent; 30 - 100 = Moderately persistent; 100 - 365 = Persistent; > 365 = Very persistent
6. K _{OC}	P	Organic-Carbon Sorption Coefficient. Measures the affinity for pesticides to sorb to organic carbon. The higher the value, the stronger the tendency to attach to and move with soil. [ml g ⁻¹] < 15 = Very mobile; 15 - 75 = Mobile; 75 - 500 = Moderately mobile; 500 - 4000 = Slightly mobile; > 4000 = Non-mobile
7. GUS	M	Ground Water Ubiquity Score (Gustafson 1989). Indicates the potential for a pesticide to leach into groundwater. It is based on the environmental fate properties of the chemical and takes no account of environmental conditions. Calculated from the soil degradation rate (DT ₅₀) and the organic-carbon sorption coefficient (K _{oc}) where: GUS = log(DT ₅₀) x (4 - log (K _{oc})) > 2.8 = High leachability; 2.8 - 1.8 = Transition state; < 1.8 = Low leachability

[§]M: Mobility; P: Persistence; T: Toxicity

Table 3.2 Description of simple toxicological Herbicide Risk Indicators (HRIs). Toxicity variable descriptions compiled from PPDB (2009).

Simple HRIs	HRI [§] Type	Description
<u>Mammals</u>		
8. Oral	T	Acute [†] LD ₅₀ [§] via oral ingestion (rat) [mg kg ⁻¹]. > 2000 = Low; 100-2000 = Moderate; < 100 = High
9. Dermal	T	LD ₅₀ [§] for dermal penetration studies (rat) [mg kg ⁻¹ body weight].
10. Inhalation	T	LC ₅₀ [‡] for inhalation (rat) [mg l ⁻¹].
11. ADI	T	Acceptable Daily Intake [mg kg ⁻¹ bw day ⁻¹].
<u>Other Organisms</u>		
12. Aquatic Invertebrates	T	Acute [†] 48 hour EC ₅₀ [*] [mg l ⁻¹] for daphnids (<i>Daphnia magna</i>) [mg l ⁻¹]. > 100 = Low; 0.1 - 100 = Moderate; < 0.1 = High
13. Aquatic Plants	T	Acute [†] EC ₅₀ [*] for duckweed (<i>Lemna gibba</i>) [mg l ⁻¹]. > 10 = Low; 0.01 - 10 = Moderate; < 0.01 = High
14. Birds	T	Acute [†] LC ₅₀ [‡] for Mallard duck (<i>Anas platyrhynchos</i>) [mg kg ⁻¹]. > 2000 = Low; 100 - 2000 = Moderate; < 100 = High
15. Fish	T	Acute [†] 96 hour LC ₅₀ [‡] for Rainbow trout (<i>Oncorhynchus mykiss</i>) [mg l ⁻¹]. > 100 = Low; 0.1 - 100 = Moderate; < 0.1 = High
16. Earthworms	T	Acute [†] 14 day LC ₅₀ [‡] for common brandling worm (<i>Eisenia foetida</i>) [mg kg ⁻¹]. > 1000 = Low; 10 - 1000 = Moderate; < 10 - High
17. Algae	T	Acute [†] 72 hour LC ₅₀ [‡] for algae (<i>Raphidocelis subcapitata</i>) [mg l ⁻¹]. > 10 = Low; 0.01 - 10 = Moderate; < 0.01 = High
18. Honey bee	T	Acute [†] 48 hour LD ₅₀ [§] for European honeybee (<i>Apis mellifera</i>) [µg bee ⁻¹]. > 1000 = Low; 10 - 1000 = Moderate; < 10 = High

[†]Acute: Ability of a substance to cause adverse effects within a short period after dosing or exposure.

[§]LD₅₀: Median lethal dose of a toxic substance required to kill half the tested population.

[‡]LC₅₀: Concentration of a toxic substance required to kill half of the test population.

^{*}EC₅₀: The concentration of a chemical that can be expected to cause a defined non-lethal effect in 50% of the tested population.

[§]M: Mobility; P: Persistence; T: Toxicity

Table 3.3 Composite Herbicide Risk Indicators (HRIs).

Composite HRI	HRI [§] Type	Description
<u>Environmental Impact Quotient (EIQ)</u>		
19. EIQ _{ecol}		Developed by Kovach et al. (1992).
20. EIQ _{con}		Utilizes coefficients (based on a one to five scale, with five carrying the most weight and one carrying the least weight) to calculate three equally weighted subcomponents: farm workers (EIQ _{farm}), consumers (EIQ _{con}), and ecological (EIQ _{ecol}) which are averaged to determine the EIQ _{total} . Eleven pesticide parameters are used: dermal toxicity, chronic toxicity, systemicity, fish toxicity, bird toxicity, bee toxicity, beneficial arthropod toxicity, leaching potential, surfaces loss potential, soil half-life. Detailed description and indicator equations found in section 3.3.1.2 and Appendix V.
21. EIQ _{farm}	T	
22. EIQ _{total}		
<u>PERSIST</u>		
23. PERSIST	P	Developed by Barnard et al. (1997).
24. ACUTE TUs	T	A relative index which describes the persistence of pesticide acute and chronic toxicity. ACUTE-TPUs (Acute Toxicity Persistence Units) and CHRONIC-TPUs (Chronic Toxicity Persistence Units) were calculated by multiplying the ACUTE TUs and CHRONIC TUs by PERSIST. The first year for each component is 100 because it is used to compare all subsequent years. Detailed description and indicator equations found in section 3.3.1.3
25. CHRONIC TUs	T	
26. ACUTE TPUs	T	
27. CHRONIC TPUs	T	
<u>Pesticide Root Zone Model (PRZM)</u>		
28. PRZM _{RIV}		Developed by Carsel et al. (1998)
29. PRZM _{ASZ}	P	PRZM simulations providing the amount of pesticide remaining in the 1-metre depth at the end of the growing season using three contrasting Manitoba soil series (TEK: loam; ASZ: sandy loam; RIV: clay) Detailed description found in section 3.3.1.4
30. PRZM _{TEK}		

[§]M: Mobility; P: Persistence; T: Toxicity

3.3.1.2 Statistical Analysis

To investigate the temporal changes in HRIs as a result of the introduction of GMHT-canola, the HRI values were calculated for the mass of active ingredients applied to all crops (AC) and the mass of herbicides applied to all crops excluding canola (ACEC) for each year. Time trend regression analyses were performed for all HRIs using the data analysis tool in Excel 2007 for both AC and ACEC. The rationale for excluding canola was to determine if it was responsible for driving the temporal trends for the HRIs since the adoption rate of GMHT-canola has increased to 95% since its introduction in 1995 (Beckie et al. 2006; Smyth et al. 2011a). Once canola was removed from the time trend analysis, it was deemed to be driving the temporal trends in indicators if the regression slopes for AC and ACEC were significantly different as calculated using the Fitmodel function of JMP 8.01 software (SAS Institute Inc. 2009).

3.3.1.3 Environmental Impact Quotient (EIQ)

The Environmental Impact Quotient (EIQ) was developed by Kovach et al. (1992) as an Integrated Pest Management (IPM) tool for farmers. The EIQ utilizes coefficients (based on a one to five scale, with five carrying the most weight and one carrying the least weight) to describe eleven pesticide risk parameters (dermal toxicity, chronic toxicity, systemicity, fish toxicity, bird toxicity, bee toxicity, beneficial arthropod toxicity, leaching potential, surfaces loss potential, soil half-life, and plant surface half-life). These parameters are used to determine three equally weighted subcomponents: farm workers (EIQ_{farm}), consumers (EIQ_{con}), and ecological (EIQ_{ecol}) which are averaged to determine the EIQ_{total} (Kovach et al 1992). For the 76 herbicide active ingredients included in the current study, the three compartments (EIQ_{farm} , EIQ_{con} , and

EQ_{ecol}) and the EQ_{total} were obtained from Kovach et al. (2011) and the annual EQ HRIs between 1996 and 2006 were calculated using Equation 3.2.

$$EQ\ HRI_j = \sum_{i=1}^{76} \frac{(x_i(\log y_{ij}))}{\sum_{i=1}^{76} (\log y_{ij})} \quad [3.2]$$

Where EQ HRI is the Environmental Impact Quotient Herbicide Risk Indicator for the j^{th} year, x is either the EQ_{total}, EQ_{farm}, EQ_{con} or EQ_{ecol} for the i^{th} herbicide active ingredient from the HPDB, y is the mass (kg) of herbicide active ingredient i applied in the j^{th} year. Following the recommendations of Levitan et al. (1995) and van der Werf (1996), the mass of individual herbicides and the total mass of all herbicides used for each year were log transformed to prevent biases towards herbicides that have a low EQ_{total}, EQ_{farm}, EQ_{con}, or EQ_{ecol} and are applied extensively. Magoon (2006) used a similar approach to avoid bias towards the untransformed mass data. The EQ values were not available for nine active ingredients (accounting for 12% of all herbicide active ingredients applied by mass) and these values were estimated for each active ingredient by averaging the EQ values for all other available active ingredients in the MASC data set following the methodologies of Kovach et al. (1992).

3.3.1.4 Persistence Index

Barnard et al. (1997) devised an index to describe the persistence of pesticide acute and chronic toxicity. DT₅₀, acute oral LD₅₀ (mammals) and Acceptable Daily Intake (ADI) were used to calculate PERSIST (Pesticide Persistent Units), ACUTE-TUs (Acute Toxicity Units) and CHRONIC-TUs (Chronic Toxicity Units), respectively (Equations 3.3-3.5). ACUTE-TPUs (Acute Toxicity Persistence Units) and CHRONIC-TPUs (Chronic Toxicity Persistence Units)

were calculated by multiplying the ACUTE TUs and CHRONIC TUs by PERSIST (Equations 3.6-3.7).

$$\text{PERSIST}_t = (\sum_i (\text{DT}_{50i} \omega_{it} / \sum_i (\text{DT}_{50i} \omega_{ibase})) \quad [3.3]$$

$$\text{ACUTE-TUS}_t = (\sum_i (\zeta_i \omega_{it} / \sum_i (\zeta_i \omega_{ibase})) \quad [3.4]$$

$$\text{CHRONIC-TUS}_t = (\sum_i (\lambda_i \omega_{it} / \sum_i (\lambda_i \omega_{ibase})) \quad [3.5]$$

$$\text{CHRONIC-TPUS}_t = (\sum_i (\text{DT}_{50i} \zeta_i \omega_{it} / \sum_i (\text{DT}_{50i} \zeta_i \omega_{ibase})) \quad [3.6]$$

$$\text{ACUTE-TPUS}_t = (\sum_i (\text{DT}_{50i} \lambda_i \omega_{it} / \sum_i (\text{DT}_{50i} \lambda_i \omega_{ibase})) \quad [3.7]$$

Where t is the time period, DT_{50} is the active ingredient half-life in soil (days); ω_i is mass (kg) of active ingredient of pesticide i applied in period t ; ω_{ibase} is the kilograms of active ingredient of pesticide i applied in the base period; ζ is the LD_{50} (mg kg^{-1}) of active ingredient, i ; λ is the acceptable daily intake (ADI) ($\text{mg kg}^{-1} \text{ bw day}^{-1}$) of active ingredient, i . The ADI was used for Chronic-TUs, instead of the No-Observed-Effect-Level (NOEL) as originally used by Barnard et al. (1997) because there was a lack of available data for the NOEL (30% of the 76 active ingredients could not be located).

3.3.1.5 Pesticide Root Zone Model (PRZM)

Deterministic simulations were performed using PRZM, version 3.12 (Carsel et al. 1998) to determine the amount of herbicide remaining in the 1-metre depth at the end of the four month growing season. PRZM is an extensively validated, one-dimensional simulation model used by European and North American governments to assess the risk of water contamination by pesticides (Banton and Villeneuve 1989; Zacharias and Heatwole 1994; Ma et al. 1999, 2000; Dubus et al. 2002, 2003; Tiktak et al. 2004; Cessna et al. 2005, 2010). Half-life, K_{OC} , and

Henry's Law constant (dimensionless) were utilized from the HPDB (Appendix IV), while average rates for herbicide applications were utilized from the RATE-DB (Chapter 2). Three contrasting soil series (loam, sandy loam and clay texture) from Manitoba were used in the simulations (Table 3.2).

Table 3.4 Soil series description (Manitoba Agriculture, Food and Rural Initiatives 2010)

Soil Series	Soil Order	Texture
Tee Lake Series (TEK)	Gleyed Gray Luvisol	Loam
Agassiz Series (ASZ)	Orthic Black Chernozem	Sandy Loam
Red River Series (RIV)	Gleyed Rego Black Chernozem	Clay

For the purposes of the PRZM simulations, each soil profile was considered to be one metre deep divided into compartments as recommended by Suarez et al. (2005). Each soil profile was modeled as an individual one-ha field with a slope of 5% with the profile soil drainage set to well-drained for all three soils.

As recommended by Carsel et al. (1998), field capacity (Θ_{fc}) and wilting point (Θ_w) were estimated using the methodology from Rawls et al. (1982) (Equations 3.9-3.10).

$$\Theta_{fc} = 0.3486 - (\% \text{ sand} * 0.0018) + (\% \text{ clay} * 0.0039) + (\% \text{ SOM} * 0.0228) - (\text{BD} * 0.0738) \quad [3.9]$$

$$\Theta_w = 0.0854 - (\% \text{ sand} * 0.0004) + (\% \text{ clay} * 0.0044) + (\% \text{ SOM} * 0.0122) - (\text{BD} * 0.0182) \quad [3.10]$$

Where Θ_{fc} is the water retention $\text{cm}^3 \text{ cm}^{-3}$ at field capacity (-0.33 bar); Θ_w is the water retention $\text{cm}^3 \text{ cm}^{-3}$ at the wilting point (-15.0 bar), SOM is soil organic matter, and BD is soil bulk density (g cm^{-3}).

SOC and texture were used to determine the erodibility factor (K), and was determined using Table 5.3 of the PRZM manual (Carsel et al. 1998). The universal soil loss cover management factor (C) was set to 0.14 assuming a spring wheat stubble mulch rotation based on Table 5.7 of the PRZM manual (Carsel et al. 1998). The universal soil loss equation (P) practice factor was set at 0.40 assuming a 2.1-7.0% land slope and a row-crop/row-crop/fall-seeded grain/wheat/meadow practice based on Table 5.6 of the PRZM manual (Carsel et al. 1998).

Temperature, precipitation and potential evapotranspiration for Miniota were obtained from the Agriculture and Agri-Food Canada (AAFC) ecodistrict climate database (1:7,500,000 map scale). These data were created by AAFC by aggregating data from weather stations within and close to each ecodistrict. Potential evapotranspiration was calculated using the method of Hargreaves and Samani (1985).

PRZM simulations were conducted with all three soils set at field capacity at the start but allowing for a one-year warm up time which ensured more realistic soil moisture conditions when simulating herbicides applied on May 1 in the following year. Preliminary PRZM simulations using a longer warm-up time (up to five years) showed no significant influence on modeling results.

3.4 Results

Of the 18 simple HRIs calculated for this study, 13 of the HRIs were influenced by changes to the types of herbicides applied to canola (Table 3.5). In addition, of the 12 composite HRIs calculated, ten had significant linear trends of which seven were driven by the changes in

herbicides applied to canola (Table 3.6). While 67% of the simple parameter indicators demonstrated that over the 11-year study period, producers are using less environmentally hazardous herbicides, four of the herbicide indicators, which were also driven by the changes in the types of herbicides applied to GMHT-canola, showed otherwise. The water solubility HRI increased, while the acute oral LD₅₀ and dermal LD₅₀, and the aquatic vascular plant HRIs decreased.

Overall, shifts in the types of agricultural herbicides used in Manitoba have occurred since the introduction of GMHT-canola in 1995. The change in the ratio of GLY and GLU to clopyralid, ethalfluralin and trifluralin applied to all crops has increased from 1.1 to 9.9 over the 11-year study period (Figures 2.11-2.13; Table 3.7). The mass of GLY and GLU applied to agricultural crops increased by 334%, while clopyralid, ethalfluralin and trifluralin decreased by 280%. The conventional herbicides clopyralid, ethalfluralin, and trifluralin are more volatile (declining vapour pressure and Henry's law constant), more soluble (increasing water solubility), less toxic to mammals via inhalation LC₅₀ and ADI, more toxic via acute oral LD₅₀ and dermal LD₅₀, and less toxic to birds, fish, earthworms, honey bees and algae than the herbicides that were used in 1996. This shift in herbicide use has impacted many of the indicators calculated in this study.

3.4.1 Mobility and Persistence Herbicide Risk Indicators

The HRIs demonstrated significant linear decreasing trends for both the K_{ow} and K_{OC} and as expected, a corresponding significant increasing trend in the water solubility HRI (Table 3.5). In addition, significant linear decreasing trends for both the vapour pressure and Henry's Law Constant HRIs were observed. The regression slope for the water solubility and the K_{ow} HRIs

were driven by changes in the types of herbicides applied to canola. Relative to 1996, farmers in 2006 used herbicides that are less likely to leach through the soil profile as demonstrated by the significant decreasing linear trend in the GUS HRI (Table 3.5). Although a significant decreasing linear trend for the K_{OC} HRI suggests that more mobile herbicides are being used, the DT_{50} HRI and the PERSIST HRI (calculated using DT_{50}) demonstrated a significant decreasing linear trend as well, indicating that less persistent herbicides are being used and thus herbicides would overall, be less mobile (Table 3.6). In addition, the PRZM HRI demonstrated a significant decreasing linear trend supporting the trends observed for the DT_{50} and PERSIST HRIs. The PRZM HRI further showed that less herbicide would remain in soil at the end of the growing season, most likely reflecting greater pesticide degradation rates for the chemicals used in 2006 versus 1996. The amount of herbicide remaining in the 1-m depth during the PRZM simulation ranged from a low of 0% for several active ingredients (clodinafop propargyl, desmediphamin, diclofop methyl, and difenzoquat) in all three soils, to 59% for chlorosulfuron in the AIZ soil.

Table 3.5 Regression equations, r² and p-values for Simple Herbicide Risk Indicators (HRIs).

HRI	All Crops (AC)			All Crops Except Canola (ACEC)			Comparison of Regression lines for AC and ACEC p-value
	Model	r ²	p-value	Model	r ²	p-value	
<u>Physicochemical Properties</u>							
1. K _{ow}	y = -1648x + 3x 10 ⁶	0.94	***	y = 197.5x - 385,177	0.12	ns [†]	***
2. Water Solubility (20°C)	y = 3064x - 6 x 10 ⁶	0.72	***	y = 197x - 385,177	0.12	ns	***
3. Vapour pressure 25°C	y = -7.9x + 15,764	0.83	***	y = -14x + 275,64	0.72	***	**
4. Henry's law constant 25°C	y = -0.14x + 287	0.92	***	y = 0.04x - 86.2	0.42	***	***
5. DT ₅₀ (typical)	y = -1.25x + 2,519	0.80	***	y = -0.2723x + 572	0.02	ns	ns
6. K _{OC}	y = -1648x + 3 x 10 ⁶	0.94	***	y = 197.05x - 385,177	0.12	*	***
7. GUS	y = -0.04x + 86	0.88	***	y = 650.99x - 10 ⁶	0.42	**	***
<u>Toxicity to Mammals</u>							
8. Acute oral LD ₅₀	y = -31.7x + 65,161	0.89	***	y = 17.658x - 33,793	0.53	*	***
9. Dermal LD ₅₀	y = -22.0x + 44,489	0.62	**	y = -2.2783x + 7,103	0.41	ns	*
10. Inhalation LC ₅₀	y = 0.05x - 97	0.78	***	y = 0.047x - 90.0	0.70	*	ns
11. ADI (Acceptable Daily Intake)	y = 0.0085x - 17	0.94	***	y = 0.0072x - 14.3	0.89	***	**
<u>Toxicity to Other Organisms</u>							
12. Aquatic invertebrates	y = 3.8x - 75,29	0.80	***	y = -1.70x + 3,499.	0.87	***	*
13. Aquatic Plants Acute EC ₅₀	y = -0.10x + 199	0.82	***	y = 0.0020x - 1.11	0.001	ns	*
14. Birds	y = 12.3x - 23,157	0.58	**	y = 19.0x - 36,830	0.86	***	***
15. Fish	y = 3.4x - 6,793	0.58	**	y = -0.476x + 1,007	0.09	ns	***
16. Earthworms	y = 2.3x - 4,174	0.32	ns [†]	y = -5.82x + 12,078	0.69	**	***
17. Honey bee	y = 2.8x - 5,448	0.94	***	y = 1.43x - 2,755	0.87	***	***
18. Algae	y = 0.16x - 300	0.11	ns	y = -0.667x + 1,361	0.48	*	*

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[†]ns: no significant regression at p<0.05

*, **, and *** denotes level of significance; p< 0.05, p<0.01, and p<0.001, respectively

See Appendix VI in Chapter 7 for graphical representation of herbicide indicators.

Table 3.6 Regression equations for Composite Herbicide Risk Indicators.

Indicator	All Crops			All Crops Except Canola			Comparison of Regression lines for AC and ACEC p-value
	Regression Equation	r ²	p-value	Regression Equation	r ²	p-value	
<u>EIQ</u>							
19. EIQ _{ecol}	y = -0.1495x + 314	0.63	**	y = -0.106x + 226	0.54	**	***
20. EIQ _{con}	y = -0.043x + 90	0.56	**	y = -0.0404x + 84.6	0.67	**	***
21. EIQ _{farm}	y = -0.0267x + 55	0.60	**	y = -0.0213x + 44.5	0.61	**	***
22. EIQ _{total}	y = -0.0753x + 157	0.67	**	y = -0.0589x + 124	0.65	**	***
<u>PERSIST</u>							
23. PERSIST	y = -3.38x + 6844	0.73	***	y = -0.353x + 824	0.003	<i>ns</i> [†]	***
24. ACUTE TUs	y = -1.34x + 2771	0.27	<i>ns</i> [†]	y = 1.28x - 2467	0.14	<i>ns</i>	*
25. CHRONIC TUs	y = 9.09x - 18054	0.83	***	y = 6.58x - 13068	0.56	**	***
26. ACUTE TPU _s	y = -5.86x + 11780	0.86	***	y = -2.21x + 4524	0.24	<i>ns</i>	***
27. CHRONIC TPU _s	y = -1.85x + 3798	0.27	<i>ns</i>	y = -2.47x + 5046	0.31	<i>ns</i>	<i>ns</i>
<u>PRZM</u>							
28. Sept _{RIV}	y = -0.194x + 391	0.89	***	y = -0.170x + 341	0.80	**	<i>ns</i>
29. Sept _{ASZ}	y = -0.195x + 393	0.89	***	y = -0.172x + 346	0.66	**	<i>ns</i>
30. Sept _{TEK}	y = -0.184x + 371	0.88	***	y = -0.165x + 333	0.601	**	<i>ns</i>

[§]M: Mobility; P: Persistence; T: Toxicity

[†]*ns*: no significant regression at p<0.05

*, **, and *** denotes level of significance; p< 0.05, p<0.01, and p<0.001, respectively

See Appendix VII in Chapter 7 for graphical representation of herbicide indicators.

Table 3.7 Herbicides applied to GMHT- and conventional canola and selected physicochemical and toxicity parameters obtained from the HPDB (Table 7.3)

Active Ingredient		Amount Applied [kg]		Water Solubility 20°C [mg l ⁻¹]	DT ₅₀ [days]	K _{oc} [ml g ⁻¹]	Vapour pressure 25° C [mPa]	Oral LD ₅₀ [mg kg ⁻¹]	Dermal LD ₅₀ [mg kg ⁻¹ body weight]	Aquatic Vascular Plants Acute EC ₅₀ [mg l ⁻¹]	EIQ _{total} [§]
		1996	2006								
glufosinate ammonium	GMHT [†]	14,398	268,730	416	7.4	755	0.031	416	>2,000	1.47	20.2
glyphosate	GMHT [†]	493,314	1,427,382	10,500	12	21,699	0.013	1,760	>2,000	12	15.3
clopyralid	CON [‡]	29,989	6,275	143,000	39	5	1.36	2676	>5000	89	18.12
ethalfluralin	CON [‡]	232,343	102,458	>5,000	45	5,356	12	>5000	>2,000	0.08	21.5
trifluralin	CON [‡]	215,858	62,355	>5,000	181	8,765	9.5	>5000	>2,000	0.435	18.9

[†]GMHT: genetically modified herbicide-tolerant canola

[‡]CON: conventional canola

[§]EIQ_{total}: values obtained from Kovach et al. 2011

3.4.2 Toxicity Herbicide Risk Indicators

There was a significant increasing linear trend for the inhalation and the ADI HRIs for AC and ACEC (Table 3.5). In addition, the EIQ_{farm} , EIQ_{con} , and EIQ_{ecol} HRIs also all had significant decreasing trends driven by changes in herbicides applied to canola, suggesting that the types of herbicides being used have become less harmful to farmers, consumers, and the environment (Table 3.6). The exception to these were the significant decreasing linear trends for both the oral LD_{50} and dermal LD_{50} HRI for herbicides applied to AC. The change in herbicides used on GMHT-canola have driven the decreasing trends observed for the oral LD_{50} , but not for the dermal LD_{50} (Table 3.5).

The aquatic invertebrates, birds, fish and honeybee HRIs all showed significant increasing linear trends, suggesting that overall, the types of herbicides being used are less toxic to these organisms (Table 3.5). While the earthworms and algae HRIs did not have significant linear relations, the aquatic plants HRI demonstrated a significant decreasing linear trend over time (Table 3.5). Herbicides applied to canola over the 11-year study were the driving forces behind the weighted indicator trends for aquatic invertebrates, aquatic plants, fish, earthworms, and algae.

3.5 Discussion

The decrease in the acute oral LD_{50} HRI could be explained by the replacement of the conventional herbicides clopyralid, ethalfluralin and trifluralin, with GLY and GLU used on GMHT-canola. Although the perception is that GLU and GLY are benign herbicides with low mammalian toxicities (Baylis 2000; Duke et al. 2003; Duke 2005; Cerdeira and

Duke 2010), they have replaced chemicals such as clopyralid, ethalfluralin and trifluralin which all have larger acute oral LD₅₀ values (lesser mammalian toxicity) (Table 3.7).

While clopyralid has a smaller acute oral LD₅₀ compared to ethalfluralin and trifluralin, its use on canola was relatively small compared to ethalfluralin and trifluralin and hence had minimal impact on the oral LD₅₀ HRI.

Pesticides have been linked to species endangerment in Canada (Kerr and Cihlar 2004).

Declining bird populations due to agricultural intensification have raised concerns in North America and the European Union (Donald et al. 2001; Vickery et al. 2004; Mineau et al. 2005; Wilson et al. 2005). Pimentel (2005) estimated that bird losses in the United States amounted to \$2.1 billion year⁻¹. While herbicides are typically less acutely toxic to bird species compared to insecticides, the elimination of habitat and food sources appear to be the major reason for declining bird populations (Freemark and Boutin 1995; Jobin et al. 1996; Blus and Henny 1997; Wilson et al. 2005). In this study, a decline in bird toxicity over the 11-years suggests that overall, the potential risk for herbicides to cause acute harm to bird populations has decreased.

Declining bee populations in North America have also raised concerns regarding intensified agricultural practices. Kuldna et al. (2009) determined that the most significant influence on pollinators were land use practices and agrochemical use.

Herbicide use most likely affects bee populations through the modification of forage habitat rather than direct toxicity (Johansen 1977; Bohan et al. 2005; Kuldna et al. 2009). Regardless, over the 11-year study period, herbicides which are acutely less toxic to bees are increasingly being used.

The environmental impact of herbicides, as measured by the EIQ_{total} in this study, showed decreasing linear trends and a 10% decrease since 1996. Studies conducted by Brimmer et al. (2005) and Kletter et al. (2007) also demonstrated that the EIQ_{total} for GMHT-canola has decreased over time as compared to conventionally grown canola. Brookes and Barfoot (2006) further determined that globally, a 23% decrease in the environmental impact of herbicide use occurred due to the adoption of GMHT-canola, and while the resulting change in pesticides applied to crops was -9.7%, the reduction in EIQ_{total} was greater, at -20.7% (Brookes and Barfoot 2005).

The effect of herbicides on human health and the environment are difficult to assess due to the complexity and variability of many interacting physicochemical properties and their effects on different environmental compartments and human health. For this reason, herbicide indicators, rather than the mass of herbicides used or area treated were chosen to provide a relative measure of potential herbicide risk (Barnard et al. 1997; Levitan 2000; Falconer 2002; Uri 2006). Indicators can be used to simplify the complex nature of pesticides properties by mathematically incorporating various physicochemical and toxicity parameters (Greitens and Day 2006). As more environmental compartments are included, the complexity of the indicator increases (Bol et al. 2003). Coupled with this increase in complexity is the increasing uncertainties due to potential variance among pesticide physicochemical properties that are influenced by soil properties (Dubus et al. 2003). For example, the K_{OC} values for GLU (755 ml g⁻¹) and GLY (21,699 ml g⁻¹) were utilized from the PPDB (2009). However, the K_{OC} may vary from 0.6 to 1,299 ml g⁻¹ for GLU and from 9 to 60,000 ml g⁻¹ for GLY (Battaglin et al. 2005).

In addition to the potential variability of physicochemical parameters, the environmental effects, such as soil moisture, temperature, and soil properties affect the variability of pesticide parameters (Reus et al. 2002). A DT_{50} of 7.4 was used for GLU and 12 for GLY, but have been reported to range from 4 to 34 days for GLU (Accinelli et al. 2004; Screpanti et al. 2005), 7 to 174 days for GLY depending on environmental conditions such as soil type, temperature and moisture (Giesy et al. 2000; Accinelli et al. 2004; Mamy et al. 2005; Laitinen et al. 2006; Cerdeira and Duke 2010; Druart et al. 2011). As a further example, 2,4-D mineralization is heavily influenced by soil moisture, temperature, depth and landscape position, with values ranging from 5.8 % to 51% within a single field (Shymko and Farenhorst 2008; Shymko et al. 2011). In addition, 2,4-D sorption varies significantly enough within a single field at different landscape positions due to changes in the amount of SOC (Farenhorst et al 2003; Gaultier et al. 2006). Given the potential infield variability of sorption and mineralization values, the use of a single value to calculate the HRIs in this study provides a general indication of risk over a broad area, and site specific parameters will be required to use this method at the field level.

In this study, GMHT-canola was not explicitly identified in the MASC-data set.

Therefore, canola was assumed to be herbicide-tolerant if GLY, GLU, imazamox or imazethapyr were applied. The estimates of GMHT-canola in this study are in agreement with other researchers (Beckie et al. 2006; Brimner et al. 2005; Smyth et al. 2011b). In addition, the mass of herbicides applied assumed a single application (Chapter 2). In Manitoba, the majority of producers will typically apply herbicides to the entire crop reported using one application (Garry Martens, personal commun. January 2012). Given that GLY is relatively inexpensive, some producers may treat their crop with a second

application (Gary Martens, personal commun. 2012). GLU, imazamox, and imazethapyr are typically applied once (Brimner et al. 2005) and the majority of producers (70-80%) growing GMHT-canola use one application (James 1997; Brimner et al. 2005). In non-GMHT-canola, ethalfluralin and trifluralin are typically applied as pre-emergent soil incorporated treatments at rates averaging 0.8 kg of active ingredient per hectare, and other herbicides are often used later in the growing season as needed (Brimner et al. 2005). While Smyth et al. (2011b) determined that producers are using fewer GLY applications on GMHT-canola, further research is required to pinpoint application frequency as well as rates used in Manitoba.

3.6 Conclusion

Herbicide risk indicators provide a relative measure for comparing the risk that herbicides pose to non-target organisms and the environment. Over this 11-year period, the adoption of GMHT-canola increased from 6% in 1996, to 93% in 2006, and has resulted in the replacement of herbicides such as clopyralid, ethalfluralin, and trifluralin used on conventional canola with GLY and GLU, which are used on GMHT-canola. This study calculated the impact of this change through a series of simple parameter and composite parameter indicators. Of particular interest is the significant increase in the use of herbicides which are less persistent and consequently, less mobile overall as defined by GUS. In addition, although the amount of herbicides being used has remained relatively stable, the calculated risk indicators demonstrate that the types of herbicides used have become less toxic to mammals via inhalation and ADI, and less toxic to aquatic invertebrates, fish, birds, and bees.

3.7 Acknowledgements

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4. 2,4-D MINERALIZATION IN UNSATURATED AND NEAR-SATURATED SURFACE SOILS OF AN UNDULATING, CULTIVATED, CANADIAN PRAIRIE LANDSCAPE

4.1 Abstract

The herbicide 2,4-D [2,4-(dichlorophenoxy) acetic acid] is one of the most widely used pesticides in the Canadian Prairies and is frequently detected as a ground and surface water contaminant. The objective of this paper was to determine the magnitude and extent of variation of 2,4-D mineralization in a cultivated undulating prairie landscape.

Microcosm incubation experiments, using a 4 x 3 x 2 factorial experimental design (soil moisture, 4 levels: 60, 85, 110, 135% of field capacity; slope position, 3 levels: upper-, mid- and lower-slopes; soil depth, 2 levels: 0-5 and 5-15 cm), were used to assess 2,4-D mineralization. The first-order mineralization rate constant (k_1) varied from 0.03 to 0.22 day⁻¹, while total 2,4-D mineralization varied from 31 to 52% after 103 days. At near-saturated conditions (110 and 135% of field capacity), the onset of 2,4-D degradation was delayed in soil obtained from the upper- and mid-slopes but not in soils obtained from the lower-slope position. The k_1 and total 2,4-D mineralization was significantly influenced by all three factors and their interactions. The Freundlich sorption coefficient of 2,4-D ranged from 0.83 to 2.46 ug^{1-1/n} g⁻¹ mL^{1/n} and was significantly influenced by variations in soil organic carbon content across slope positions. The infield variability of 2,4-D sorption and mineralization observed across slope positions in this undulating field was comparable in magnitude and extent to the regional variability of 2,4-D sorption and mineralization observed in surface soils across Manitoba. The large variability of 2,4-D mineralization and sorption at different slope positions in this cultivated undulating field

suggests that landform segmentation models, which are used to delineate slope positions, are important considerations in pesticide fate studies.

4.2 Introduction

The herbicide 2,4-D [2,4-(dichlorophenoxy) acetic acid] is one of the most widely used pesticides in western Canada. Since the late 1940s, it has been used for the post-emergent control of broadleaf weeds and it is increasingly being used to control glyphosate tolerant canola volunteers (Simard and Légère 2003). 2,4-D is frequently detected in potable water, rainwater and farm dugouts in western Canada (Rawn et al. 1999; Hill et al. 2002; Cessna and Elliot 2004) indicating that the offsite movement of 2,4-D from agricultural fields is an environmental concern.

Although it has been suggested that the majority of herbicide biodegradation occurs in the top 0-5 cm soil layer (Topp et al. 1997), information regarding herbicide mineralization has been mostly derived from studies that investigated the entire 0-15 cm (Han and New 1994; Fomsgaard and Kristensen 1999) or 0-30 cm soil layers (Veeh et al. 1996; Willems et al. 1996; Foomsgaard 1997; Dejonghe et al. 2000). In general, there is a lack of scientific evidence on the variability of 2,4-D mineralization with respect to depth in surface soils (Shaw and Burns 1998).

Sorption influences herbicide transformation by limiting herbicide bioavailability (Ogram et al. 1985; Benoit et al. 1999; Guo et al. 2000). The variability of soil properties across landscape positions, such as soil organic carbon content (SOC), influences 2,4-D

sorption. 2,4-D sorption is positively correlated with SOC (Reddy and Gambrell 1987; Hermosin and Cornejo 1991; Voos and Groffman 1997; Bekbölet et al 1999; Farenhorst et al. 2001; Picton and Farenhorst 2004; Gaultier et al. 2006). The sorption of 2,4-D in surface soils of undulating agricultural fields typically increases from upper- < mid -< lower-slopes (Farenhorst et al 2003; Gaultier et al. 2006), coinciding with increases in SOC (da Silva et al. 2001; Manning et al. 2001). In conventionally tilled fields, lower-slope positions exhibit deeper A horizon profiles, at times extending beyond the depth of the plough layer (Manning et al. 2001; VandenBygaart et al. 2001; Papiernik et al. 2005).

Microorganisms are primarily responsible for the transformation of 2,4-D and its metabolites in surface soil (Wood et al. 1987; Soulas 1993; Han and New 1994; Voos and Groffman 1997). A diverse consortia of soil microorganisms are capable of degrading 2,4-D (Sinton et al. 1986; Han and New 1994; Cattaneo et al. 1997; Khalil 2003), but the diversity, abundance and activity of 2,4-D degraders vary with SOC and soil moisture conditions (Parker and Doxtader 1983; Ou 1984; Bhanumurthy et al. 1989; Cattaneo et al. 1997; Soulas and Lagacherie 2001).

The surface soil layer is subject to spatial and temporal variations in soil moisture content because it is strongly coupled with the atmosphere. Slope position is a significant factor further affecting the variability of soil moisture content in an agricultural field (Mohanty and Skaggs 2001). Soil moisture directly affects the diversity and abundance of 2,4-D degrading soil microorganisms which may vary across slope positions. Although it is known that 2,4-D mineralization rates increase with increasing moisture contents (Han and New 1994; Willems et al. 1996; Parker and Doxtader 1983, Bhanumurthy et al.

1989), the influence of slope position and soil moisture, and their interaction on 2,4-D mineralization has not been previously studied.

The objective of this study was to assess the impact of soil moisture (60, 85, 110, 135% of field capacity), slope position (upper-slope, mid-slope and lower-slope positions), soil depth (0-5 and 5-15 cm), and their interactions, on the magnitude and extent of variability of 2,4-D mineralization in soil obtained from a cultivated undulating prairie landscape.

4.3 Materials and Methods

Approximately 5 kg of soil was collected from both the 0-5 and 5-15 cm soil depth at three slope positions (upper-, mid-, and lower-slopes) along a transect running west to east in an agricultural field near Deerwood (49° 23' N, 98° 23' W; 6-5-7 1W), Manitoba, Canada. Slope positions were determined using a landscape segmentation model software program, LandMapR (MacMillan and Pettepiece 2000). Samples collected from the upper- and mid-slopes were 43.5 meters apart, while the distance between the mid- and lower-slope positions were 250 meters apart. To prevent the intermixing of soil between each sampling location, the shovel used to obtain each 5-kg bulk soil sample was disinfected with bleach and the bleach residue was removed with distilled water between each sample. Soil samples were immediately stored in plastic bags and transported on ice to the University of Manitoba where the soil was subsequently frozen at -35°C. Mortensen and Jacobsen (2004) determined that the freezing of soils prior to experimentation does not significantly affect herbicide mineralization data when compared to data obtained using fresh soils. Prior to use, bulk soil samples from each

slope and depth position were thawed, air-dried, passed through a <2mm sieve, and thoroughly mixed to ensure soil homogeneity.

The soil-landscape at the field site is undulating (boulder till intermixed with shale) ranging from 458 to 441 meters above sea level from west to east. The field had been cultivated for more than 100 years by deep tilling in the fall and disking and harrowing in the spring, with a two year cereal-oilseed crop rotation. Pesticides, including 2,4-D, have been part of the cropping system for the past 40 years. Well-drained soils occurring on upper- and mid-slope positions belong to the Dezwood loam series (Orthic Dark Grey Chernozem; Ap, Btj, Ck horizons) (Soil Classification Working Group 1998).

Imperfectly-drained soils from lower-slope positions are of the Zaplin soil series (Gleyed Dark Grey Chernozem; Ap, Btgj, Ckgj horizons) (Soil Classification Working Group 1998). Soil properties were determined using air-dried, sieved (<2mm) soil. Soil pH was determined using 10 mL of 0.01 M CaCl₂ and 5 g of air-dried soil (McKeague 1978). Soil organic carbon content (SOC) was determined using the dichromate oxidation method (Nelson and Sommers 1982) while soil texture was measured using the hydrometer method (Sheldrick and Wang 1993). Field capacity was determined using laboratory leaching columns (11 cm in height, 2.7 cm radius) to determine the amount of gravity retained soil moisture after 96 hours.

The batch equilibrium technique was used to determine the Freundlich sorption coefficient (k_f) in triplicates. Five herbicide solutions were prepared in 0.01 M CaCl₂ by combining analytical grade 2,4-D (95% chemical purity, Sigma Chemical, St. Louis, MO) with ¹⁴C-ring labeled 2,4-D (99% radiochemical purity; specific activity 250 μCi; Sigma

Aldrich Chemical Company, St. Louis, MO). The concentrations were 1, 2, 4, 8 and 16 mg L⁻¹ of 2,4-D with a radioactivity of 17, 34, 68, 136 and 272 Bq mL⁻¹, respectively. A CaCl₂ solution was used instead of water to minimize disruption of the soil mineral environment (Wauchope et al. 2002). Following standard batch equilibrium technique procedures, five grams of air-dried soil was combined with each herbicide solution (10 mL) in Teflon tubes and rotated for 24 hours in the dark to establish equilibrium. The 2,4-D solution slurry was then centrifuged for 10 minutes at 10,000 rev min⁻¹ after which 1 mL sub-samples of supernatant (duplicates) were removed from each tube. Scintillation cocktail (8 mL) (30% Scintisafe scintillation cocktail; Fisher Scientific, Fairlawn, NJ) was added to the sub-samples to quantify the amount of 2,4-D remaining in the supernatant by Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (Tri Carb 2100TR, Beckman Instruments, Fullerton, CA). Radioactivity was measured using a maximum counting time of 10 minutes.

The Freundlich sorption coefficient, k_f [$\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$], was calculated by nonlinear regression using the empirical Freundlich equation (log transformed): $\text{Log } C_s = \text{log } k_f + 1/n \text{ log } C_e$, where C_s is the concentration of 2,4-D sorbed to soil [$\mu\text{g g}^{-1}$], C_e is concentration of 2,4-D in the equilibrium solution [$\mu\text{g mL}^{-1}$] and $1/n$ is the dimensionless Freundlich constant describing nonlinearity. These units were chosen to ensure that all isotherm lines crossed $C_e = 1$, which is an important criterion for calculating k_f (Bowman 1981,1982).

Microcosm incubation experiments were conducted using a 4 x 3 x 2 factorial experimental design with four replicates. The three factors were soil moisture (4 levels: 60, 85, 110, 135% of field capacity), slope position (3 levels: upper-, mid- and lower-slopes) and soil depth (2 levels: 0-5 and 5-15 cm). The microcosm consisted of a 500-mL sealed jar which contained a 50-mL flint jar with 25 g of soil (oven dried weight). The air-dry moisture content of each soil was determined gravimetrically and then distilled water was added to each 50-mL flint jar to bring the soil to 50, 75, 100 or 125% of field capacity. In addition, a glass vial containing 5 mL of acidified water (pH of 3 using 6 N HCl) was inserted into the microcosm to keep the environment moist. Previous microcosm incubation experiments demonstrated that soil moisture loss at 20°C was negligible and the replacement of soil moisture throughout the duration of the experiment was not required. The soil samples were pre-incubated for 14 days at 20°C to stimulate microbial growth. Stock solutions were prepared using analytical grade 2,4-D and ¹⁴C-ring labeled 2,4-D to apply herbicide solutions at an agronomic rate of 0.63 g m⁻³ soil of active ingredient (a.i) and 333 Bq g⁻¹ soil. The agronomic rate was determined using a 2,4-D product formulation of 500 g a.i. L⁻¹ and an application rate of 0.50 L ac⁻¹ (average of recommended application rates; 0.28 to 0.71 L ac⁻¹) obtained from the 2002 Crop Protection guide (Manitoba Agriculture and Food 2002). The addition of the 2,4-D stock solution (1 mL) resulted in a soil moisture increase of the four treatments to: 60, 85, 110, and 135% of field capacity. A 20-mL scintillation vial containing 5 mL of 0.5 M NaOH was used to trap the ¹⁴CO₂ evolved during incubation. Traps were changed every 2 or 3 days until degradation rates began to slow down at 48 days. Following this, traps were changed on days 55, 71, 87 and 103. Radioactivity in samples was determined by LSC as described above.

Herbicide mineralization rate constants were calculated in SigmaStat for Windows, Version 3.5 (Systat Software Inc. 2006) assuming first-order kinetics: $MT = M_T(1 - e^{-k_1 t})$, where MT = herbicide mineralization (as % of applied) at time t ; M_T = amount of herbicide mineralized (as % of applied) at time infinity; k_1 = first-order mineralization rate constant [day^{-1}]; and t = time in days [day].

Analysis of variance (ANOVA) and multiple means comparison were conducted using Proc GLM, SAS software, Version 8.02 of the SAS System for Windows (SAS Institute Inc. 2002-2003). Statistical analyses included a two-way ANOVA on SOC, pH and k_f with the factors slope position (upper-, mid- and lower-slopes) and soil depth (0-5 and 5-15 cm). A three-way ANOVA was conducted on M_T and k_1 with the factors soil moisture, slope position and soil depth. Data for k_1 was log transformed to achieve normality. Multiple means comparisons were conducted using the Student-Newman-Keuls test ($\alpha=0.05$).

4.4 Results and Discussion

4.4.1 2,4-D Sorption

The Freundlich sorption coefficient, k_f , significantly increased in the sequence of upper- ($0.83 \mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$) < mid- ($1.71 \mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$) < lower-slopes ($2.46 \mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$) (Table 4.1). Despite the wide range in soil pH (5.4 to 7.7, Table 4.1), there was no significant correlation with k_f because the observed soil pH was well above the 2,4-D dissociation constant ($\text{pK}_a=2.64$) (Ahrens 1994). The slopes of the Freundlich isotherms ($1/n$) were less than unity, ranging from 0.96 in soil obtained from the upper-slope, to 0.75 in the lower-slope (Table 4.1). These values ($1/n < 1$) demonstrate that the

saturation of the sorption sites limited further sorption as herbicide concentration increased, indicating that the Freundlich fitting of the 2,4-D isotherm was L-type (Giles et al. 1960). k_f was significantly affected by slope position but soil depth, and the interaction slope position x soil depth, were not significant (Table 4.2).

Table 4.1 Soil characteristics at the three slope position and two soil depths.

Slope Position	Depth (cm)	Texture ^a	FC ^b (%)	pH ^c	Organic Carbon ^d %	k_f^e [$\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$]
Upper	0-5	SCL	42.46	6.2a*	1.43a*	0.90
	5-15	SCL	43.39	5.9b	0.63b	0.72
Mid	0-5	SCL	43.90	5.5c	1.90c	1.72
	5-15	CLAY	38.84	5.4c	1.23a	1.69
Lower	0-5	SCL	31.81	7.7d	2.52d	2.63
	5-15	SCL	34.91	7.7d	2.97e	2.29

^a Hydrometer method; SCL= sandy clay loam

^b Field Capacity (gravimetric) determined using laboratory leaching columns

^c Determined using a 2:1, 0.01 M CaCl₂:soil

^d Determined using dichromate oxidation method (Nelson and Sommers 1982)

^e Freundlich sorption coefficient

* Means within columns with the same letter are not significantly different (Student-Newman Keuls Test, $\alpha = 0.05$)

Table 4.2 Abbreviated three-way and two-way analysis of variance (ANOVA).

Variable	Source	df	MS	F	P>F ^a
SOC	MODEL	4	1.49	51.43	<0.0001
	Slope	2	3.08	106.31	<0.0001
	Depth	1	0.35	12.18	0.0130
	Slope x Depth	1	0.47	16.17	0.0038
pH	MODEL	4	2.16	6.90	0.014
	Slope	2	3.89	12.40	0.005
	Depth	1	0.45	1.43	0.27
	Slope x Depth	1	0.43	1.36	0.28
k_f	MODEL	4	1.65	7.78	0.0018
	Slope	2	4.01	18.88	0.0002
	Depth	1	0.17	0.81	0.39
	Slope x Depth	1	0.037	0.17	0.84
Mineralization (M_T)	MODEL	23	96.2	15.41	<0.0001
	Soil Moisture	3	381.5	61.09	<0.001
	Slope	2	220.0	35.23	<0.001
	Depth	1	132.5	21.22	<0.001
	Soil Moisture x Slope	6	31.4	5.03	<0.001
	Soil Moisture x Depth	3	67.8	10.86	<0.001
	Slope x Depth	2	3.6	0.58	0.565
	Soil Moisture x Depth x Slope	6	16.3	2.60	0.024
k₁	MODEL	23	0.28	42.18	<0.0001
	Soil Moisture	3	1.1	162.3	<0.001
	Slope	2	0.3	49.9	<0.001
	Depth	1	1.4	211.7	<0.001
	Soil Moisture x Slope	6	0.1	19.4	<0.001
	Soil Moisture x Depth	3	0.05	7.33	<0.001
	Slope x Depth	2	0.008	1.21	0.305
	Soil Moisture x Depth x Slope	6	0.03	5.13	<0.001

^a Significant p-values are given in boldface ($\alpha=0.05$).

As expected, there were no significant associations between clay content and 2,4-D sorption in this study, and the differences in 2,4-D sorption across slope positions were likely due to differences in soil organic carbon content as suggested by the positive correlation between k_f and SOC ($r=0.87$, $p<0.05$). In this study, SOC significantly decreased with soil depth in the upper- and mid-slopes, but conversely, increased with soil depth in the lower-slope (concave depositional area) (Table 4.1). Regardless of slope

position, differences in SOC between the 0-5 and 5-15 cm depths were relatively small so that k_f was similar for the 0-5 and 5-15 cm depth in each slope-position. The high degree of infield variability of k_f observed across slope positions in this agricultural field (0.72 to $2.63 \text{ ug}^{1-1/n} \text{ g}^{-1} \text{ mL}^{1/n}$) was comparable in magnitude and extent to the regional variability of k_f observed in surface soils across the agricultural growing region of Manitoba, ranging from $0.81 \text{ ug}^{1-1/n} \text{ g}^{-1} \text{ mL}^{1/n}$ in an Almassippi sand to $2.89 \text{ ug}^{1-1/n} \text{ g}^{-1} \text{ mL}^{1/n}$ in a Hoddinott silty clay (Picton and Farenhorst 2004). Therefore, the large infield variability of k_f and SOC, and their strong correlation, suggest that sampling by soil horizon and slope position is the best approach for pesticide sorption studies in this undulating prairie landscape (Gaultier et al. 2006).

4.4.2 2,4-D Mineralization

Total 2,4-D mineralization at 103 days ranged from 32% to 52% of that initially applied. The modelled $^{14}\text{CO}_2$ mineralization showed a very good fit to the measured data for all treatments, with coefficients of determination (r^2) ranging from 0.90 to 0.99. In this study, there were no significant associations between measured soil properties (SOC and clay content) and 2,4-D mineralization. The saturated conditions had a significant influence on delaying the onset of 2,4-D degradation in soil obtained from the upper- (Figures 4.1A, B) and mid-slopes (Figures 4.1C, D) but not in soil from the lower-slope (Figures 4.1E, F). Due to topographical influences (concave depositional areas), soils in lower-slopes are more frequently exposed to saturated field conditions. Our study suggests that due to previous exposure to saturated conditions, microbial communities might be

inherently present in lower-slopes and thus preconditioned to rapidly degrade 2,4-D in near-saturated soil conditions.

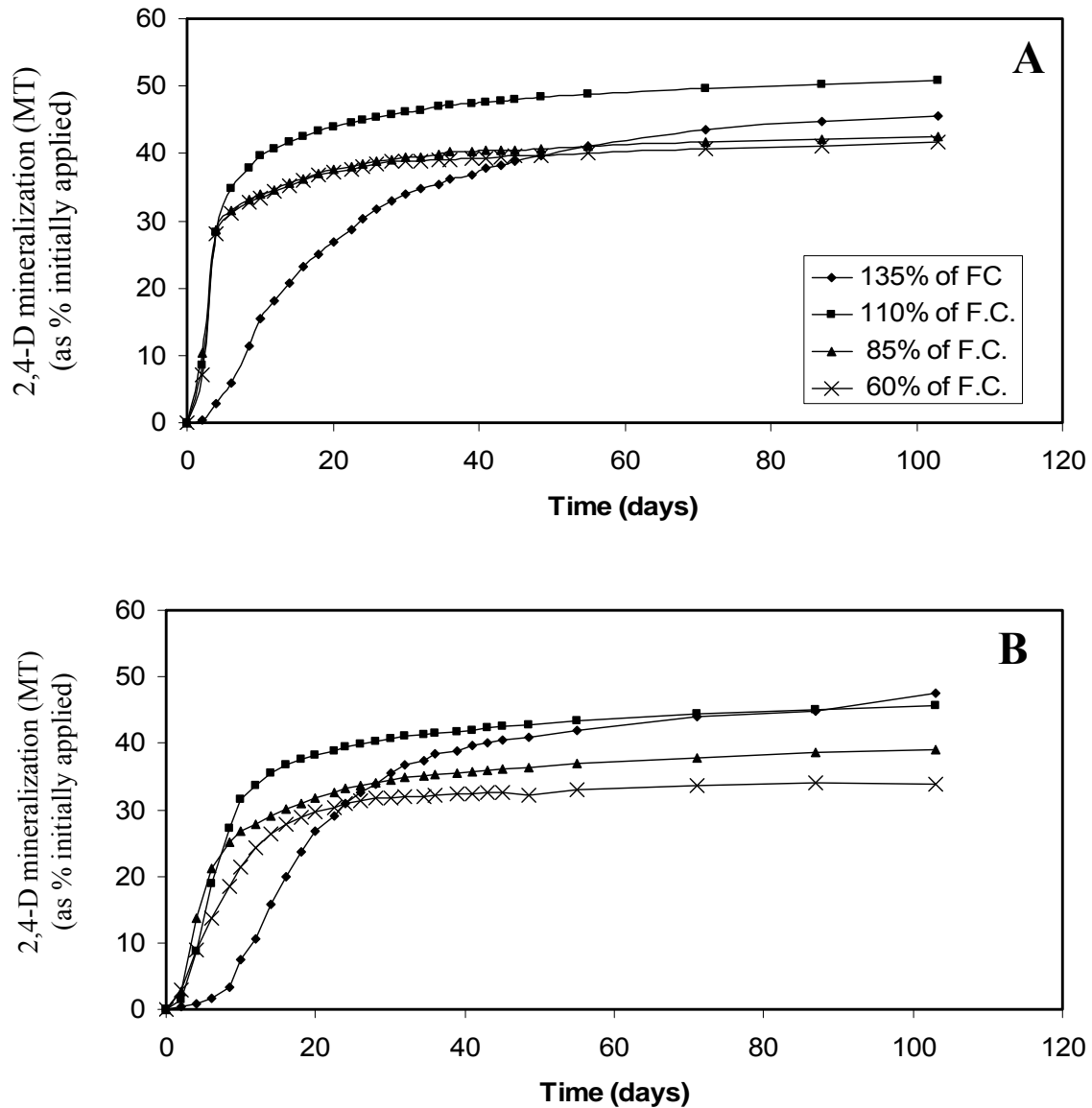


Figure 4.1 2,4-D mineralization (MT, as % initially applied) as a function of time at four soil moisture contents for A: upper-slope (0-5 cm), B: upper-slope (5-15 cm), C: mid-slope (0-5 cm), D: mid-slope (5-15 cm), E: lower-slope (0-5 cm), F: lower-slope (5-15 cm).

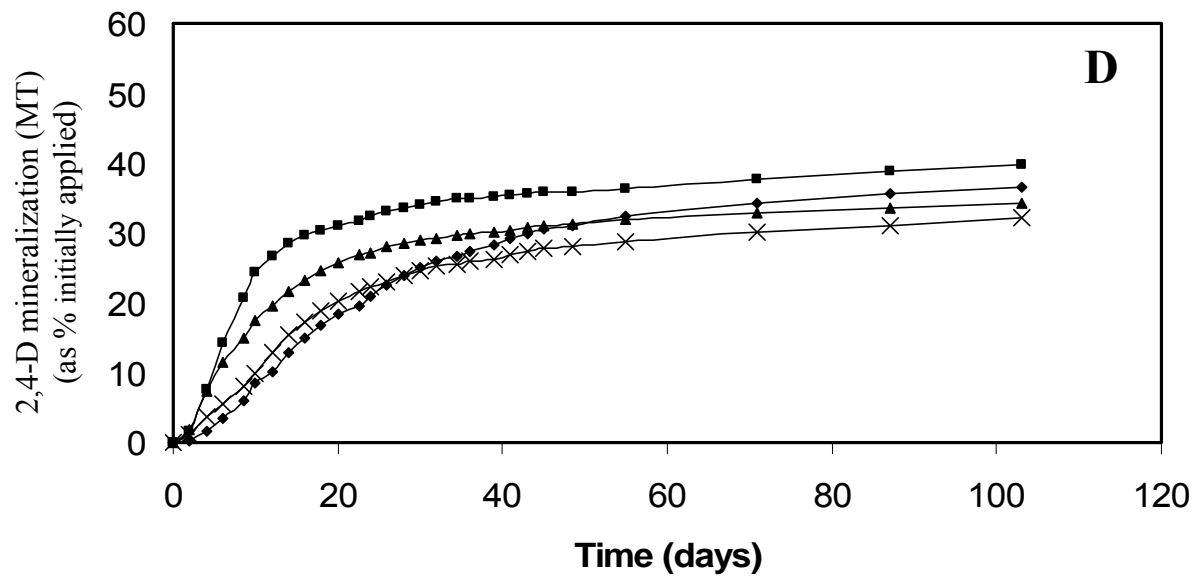
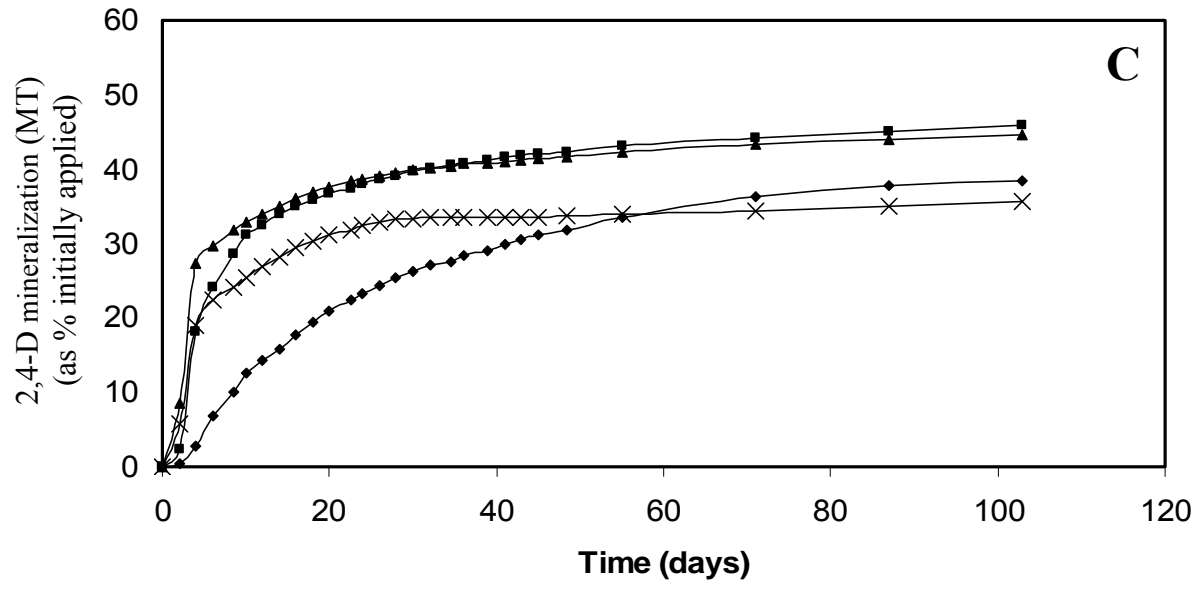


Figure 4.1 *continued*

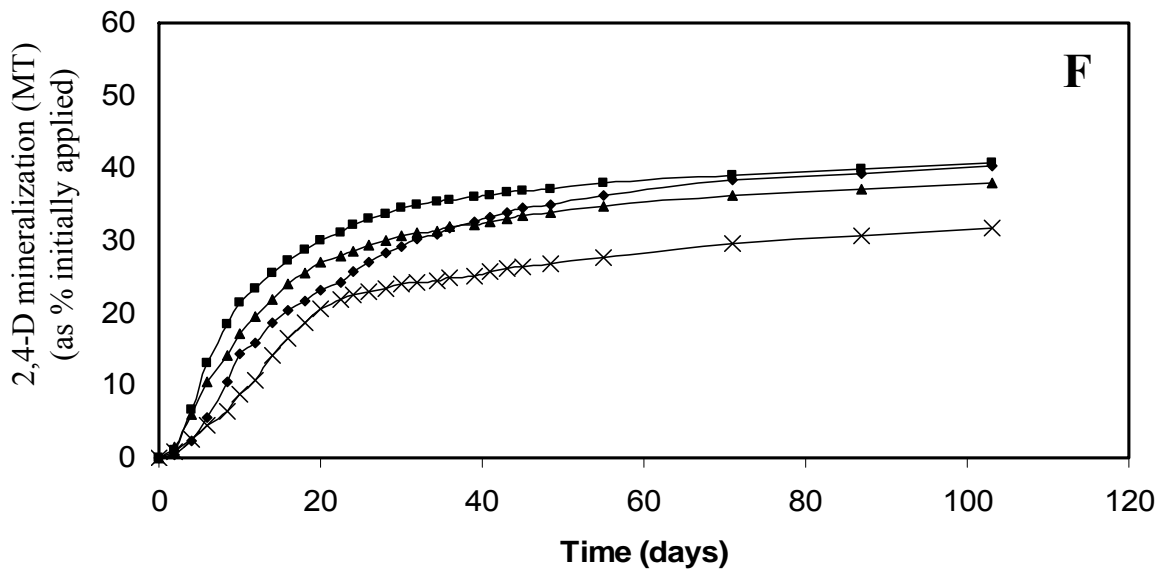
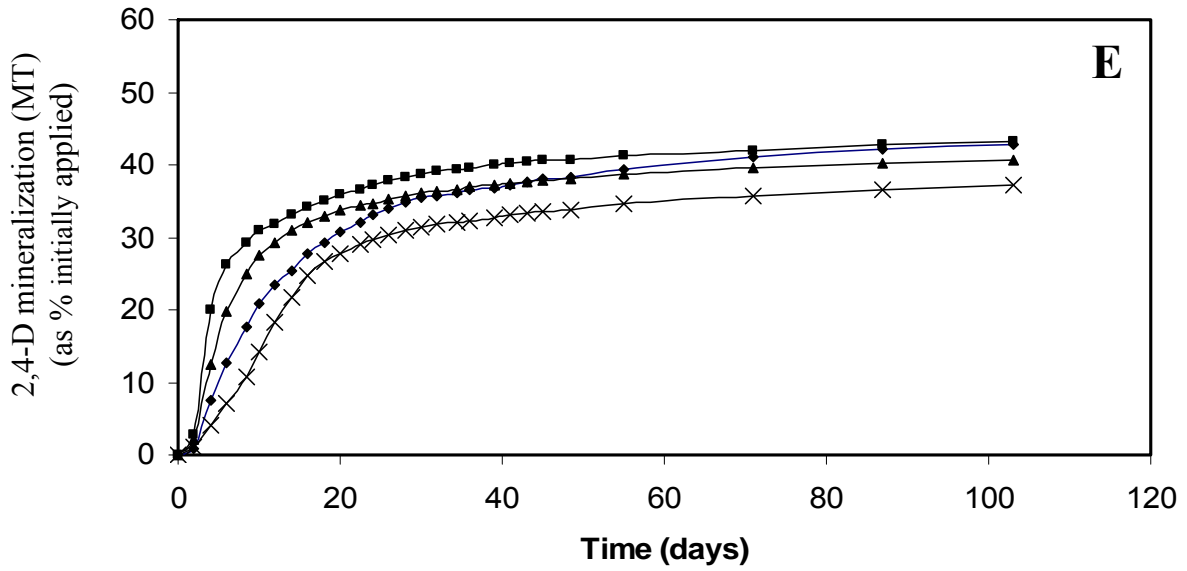


Figure 4.1 *continued*

Although 2,4-D mineralization was significantly influenced by the three-way interaction, soil moisture x soil depth x slope position, the interaction was weak, as the p-value was close to the 5% significance level (Table 4.2). Drier soils (60% of field capacity) had

significantly lesser 2,4-D mineralization than wetter soils (135% of field capacity), except in the lower-slope position at 0-5 cm depth (Table 4.3). Dry soil conditions could inhibit microbial activity but also decrease herbicide bioavailability through increased sorption (Shelton and Parkin 1991).

Table 4.3 Pair-wise comparisons of total 2,4-D mineralized at four soil moistures at time infinity, as determined by fitting the evolved $^{14}\text{CO}_2$ in surface soils obtained from three slope positions and two depths, to the equation: $MT = M_T(1 - e^{-k_1 t})$, where MT = herbicide mineralization (as % of applied) at time t ; M_T = amount of herbicide mineralized (as % of applied) at time infinity; k_1 = first-order mineralization rate constant [day^{-1}]; and t = time in days [day].

Soil Moisture % of Field Capacity	Upper		Mid		Lower	
	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm
60	39*a**	33*a**	34*a**	32*a**	37*a**	32*a**
85	40a	36ab	41b	33ab	38a	36b
110	47b	44c	42b	37c	40a	39bc
135	46b	52d	39b	41d	41a	41c

*Means of four replicates.

**Means within columns with the same letter are not significantly different (Student-Newman Keuls Test, $\alpha = 0.05$)

The difference in 2,4-D mineralization among slope positions was generally more pronounced in wetter than drier soils (Figure 4.2). 2,4-D mineralization in near-saturated soils (110 and 135% of field capacity) was significantly greater in soil obtained from the upper- than the lower-slope (Table 4.4), possibly due to greater SOC in the lower-slope position which increased sorption and limited the bioavailability of 2,4-D over time (Ogram et al. 1985; Bolan and Baskaran 1996; Benoit et al. 1999; Guo et al. 2000). In contrast, there were no significant differences in 2,4-D mineralization between slope

positions in dryer soils (60 and 85% of field capacity) (Table 4.4). This further suggests that, under dryer conditions, mineralization was limited by sorption in all soils or that microbes became stressed due to insufficient moisture conditions.

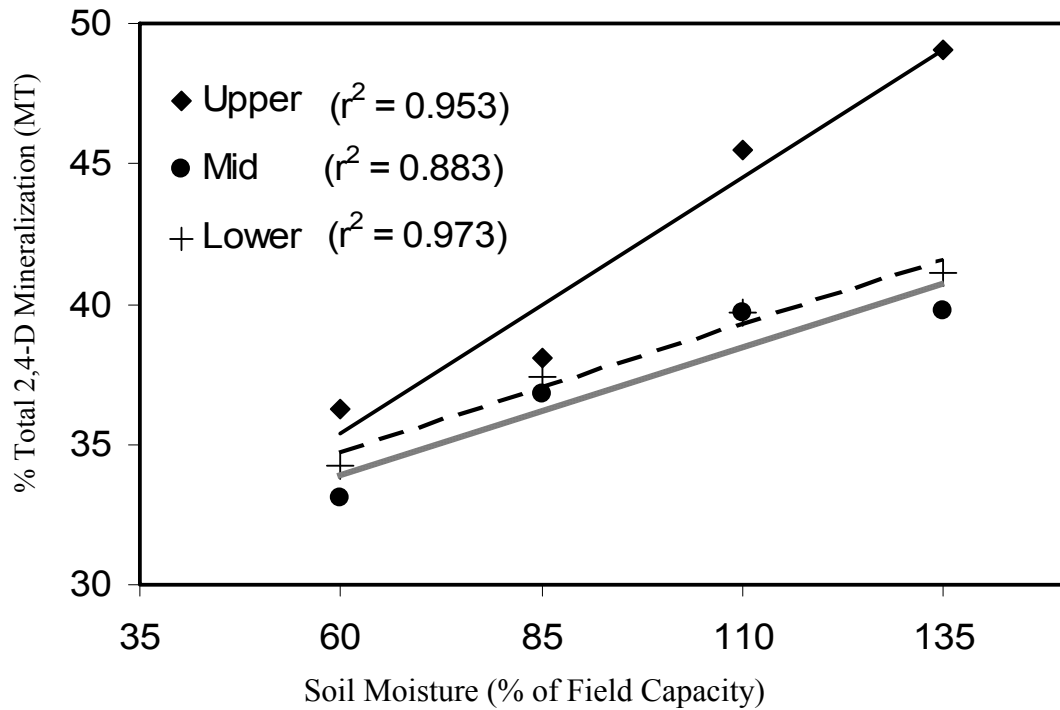


Figure 4.2 Amount of 2,4-D mineralized (M_T) at different soil moistures at three slope positions. Points in graph reflect experimental values of maximum 2,4-D mineralization averaged over two soil depths (0-5 and 5-15 cm).

Table 4.4 Pair-wise comparisons of total 2,4-D mineralized at four soil moistures time infinity, as determined by fitting the evolved $^{14}\text{CO}_2$ in surface soils obtained from three slope positions and two depths, to the equation: $MT = M_T(1 - e^{-k_1 t})$, where MT = herbicide mineralization (as % of applied) at time t ; M_T = amount of herbicide mineralized (as % of applied) at time infinity; k_1 = first-order mineralization rate constant [day^{-1}]; and t = time in days [day].

Slope Position	Soil Moisture (% of Field Capacity)							
	60		85		110		135	
	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm
Upper	39A	33a	40a	36a	47a	44a	46a	52a
Mid	34A	32a	41a	33a	42b	37b	39b	41b
Lower	37A	32a	38a	36a	40b	39b	41b	41b

* Means of four replicates.

**Means within columns with the same letter are not significantly different (Student-Newman Keuls Test, $\alpha = 0.05$)

2,4-D mineralization always decreased with depth, except under near-saturated conditions (135% of field capacity) (Table 4.4). The numerical difference in 2,4-D mineralization between soil depth increased with decreasing soil moisture conditions (Figure 4.3). Since 2,4-D sorption was similar for the 0-5 and 5-15 cm layers regardless of slope position, these results suggest that, under a wide range of soil moisture conditions, microbial activity varies over very small distances with depth in surface soils.

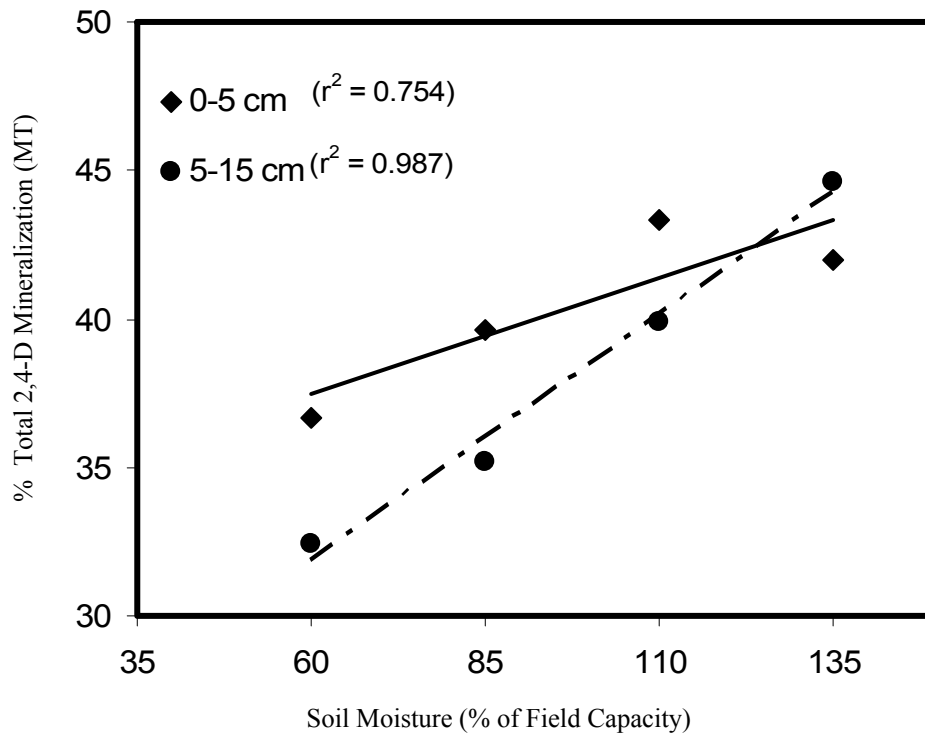


Figure 4.3 Amount of 2,4-D mineralized (M_T) at different soil moistures at two soil depths. Points in graph reflect experimental values of maximum 2,4-D mineralization averaged over three slope positions (upper-, mid-, and lower-slopes).

The first-order mineralization rate constant (k_1) varied between slope positions by as much as a factor of 3.5 (Table 4.5). Using a similar microcosm set-up as in our study, k_1 varied by a factor of 3 in surface soils across Agro-Manitoba when these soils were incubated at 75% of field capacity (Farenhost et al. 2006). The k_1 was significantly affected by the three-way interaction between soil moisture x soil depth x slope position (Table 4.2). The difference in k_1 between depth (Figure 4.4), or between slope positions (Figure 4.5), was generally more pronounced in drier than wetter soils. At the 0-5 cm depth, k_1 was significantly slower in the lower-slope than in the upper-slope (Table 4.5), except at 135% of field capacity, where there was a delay in the onset of 2,4-D

mineralization in the upper-slope (Figures 4.1A, B). At the 5-15 cm depth, k_1 was also significantly lower in the lower-slope compared to the upper-slope, but only in unsaturated soils (60 and 85% of field capacity) (Table 4.5). In the upper- and mid-slopes, regardless of soil depth, k_1 was significantly slower at 135% field capacity than at 60% field capacity (Table 4.6). However, in the lower-slope, no significant differences in k_1 values were observed between these two moisture contents, and mineralization rates were generally slow (Table 4.6). Relative to the other slope positions, enhanced 2,4-D sorption in the lower-slope likely inhibited 2,4-D mineralization and thus reduced mineralization rates.

Table 4.5 Pair-wise comparisons of the first-order mineralization rate constant (k_1) at four soil moistures at time infinity, as determined by fitting the evolved $^{14}\text{CO}_2$ in surface soils obtained from three slope positions and two depths, to the equation: $\text{MT} = \text{M}_T(1 - e^{-k_1 t})$, where MT = herbicide mineralization (as % of applied) at time t; M_T = amount of herbicide mineralized (as % of applied) at time infinity; k_1 = first-order mineralization rate constant [day^{-1}]; and t = time in days [day].

Slope Position	Soil Moisture (% of Field Capacity)							
	60		85		110		135	
	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm
Upper	0.21* a**	0.10* a**	0.22* a**	0.12* a**	0.20* a**	0.11* a**	0.04* a**	0.04* a**
Mid	0.16b	0.05b	0.18a	0.07b	0.12b	0.09a	0.04a	0.03a
Lower	0.06c	0.04b	0.11b	0.06b	0.14b	0.07a	0.07b	0.04a

*Means of four replicates.

**Means within columns with the same letter are not significantly different (Student-Newman Keuls Test, $\alpha = 0.05$)

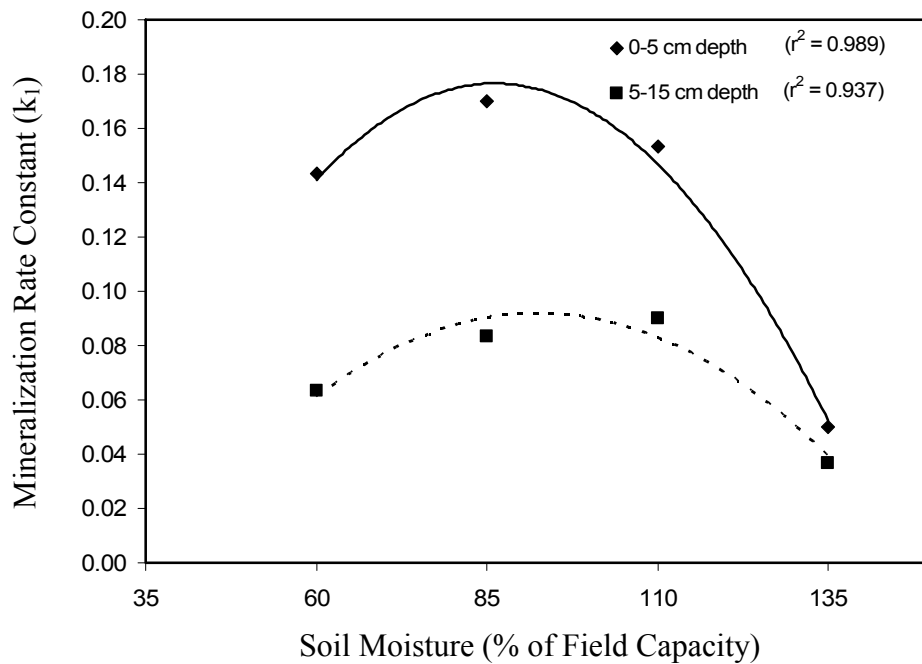


Figure 4.4 First-order mineralization rate constant (k_1) at different soil moistures at two soil depths. Points in graph reflect calculated first-order mineralization rate constants averaged over three slope positions (upper-, mid-, and lower-slopes).

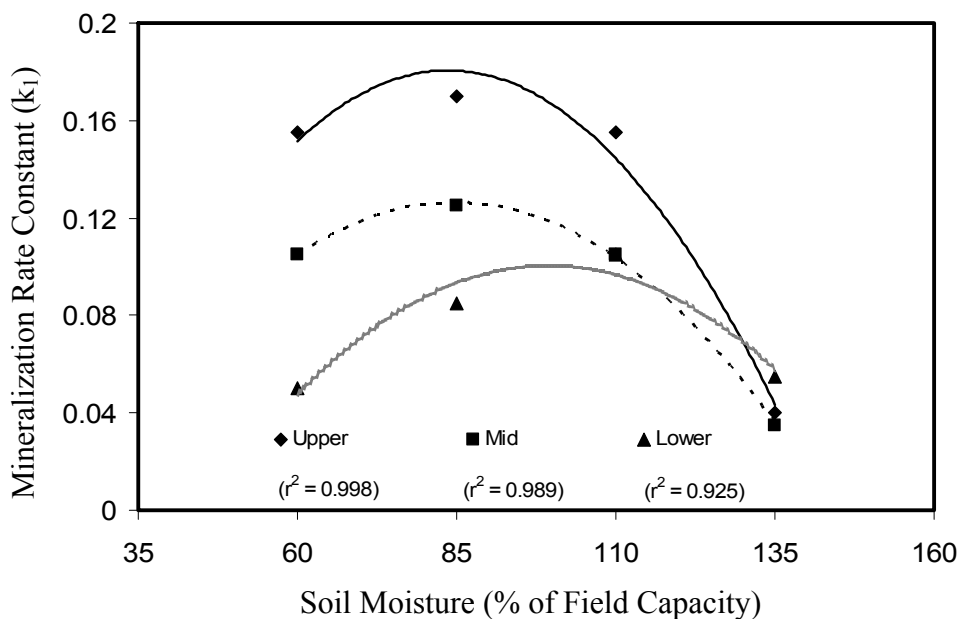


Figure 4.5 First-order mineralization rate constant (k_1) at different soil moisture at three slope positions. Points in graph reflect calculated first-order mineralization rate constants (k_1) averaged over two soil depths (0-5 and 5-15 cm).

Table 4.6 Pair-wise comparisons of the first-order mineralization rate constant at four soil moistures at time infinity, as determined by fitting the evolved $^{14}\text{CO}_2$ in surface soils obtained from three slope positions and two depths, to the equation: $MT = M_T(1 - e^{-k_1 t})$, where MT = herbicide mineralization (as % of applied) at time t ; M_T = amount of herbicide mineralized (as % of applied) at time infinity; k_1 = first-order mineralization rate constant [day^{-1}]; and t = time in days [day].

Soil Moisture % of Field Capacity	Upper		Mid		Lower	
	0-5 cm	5-15 cm	0-5 cm	5-15 cm	0-5 cm	5-15 cm
60	0.21*a**	0.10*a**	0.16*ab**	0.05*a**	0.06*a**	0.04*a**
85	0.22a	0.12a	0.18a	0.07b	0.11b	0.06b
110	0.20a	0.11a	0.12b	0.09b	0.14b	0.07b
135	0.04b	0.04b	0.04c	0.03c	0.07ac	0.04ac

*Means of four replicates.

**Means within columns with the same letter are not significantly different (Student-Newman Keuls Test, $\alpha = 0.05$)

4.5 Conclusion

Our results indicate that differences in 2,4-D mineralization within the plough layer (0-15 cm) may be great enough to warrant sampling in smaller depth increments (5 cm). The variability of sorption and mineralization within this undulating, cultivated, Canadian Prairie landscape suggests that the segmentation of the landscape (upper-, mid-, lower-slopes) using digital elevation models may be useful for appropriate field sampling and estimates of 2,4-D fate. Both k_f and k_1 are important input parameters in pesticide fate models, thus segmentation by landscape position, rather than the use of a single value to describe an entire agricultural field, should be considered when modeling 2,4-D fate in undulating fields. Under field conditions, the spatial distribution of 2,4-D sorption and mineralization will be dependent on the spatial distribution of soil properties (e.g. SOC) and environmental factors (e.g. soil moisture content) which are, in turn, controlled by

landscape processes. Areas of the undulating landscape, such as concave depositional areas or lower-slope positions, generally would be higher in SOC and soil moisture content. Landform segmentation models can be used to delineate these areas, and therefore could be used to provide proxy estimates of 2,4-D sorption and mineralization parameters.

4.6 Acknowledgements

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5. POLYNOMIAL RESPONSE OF 2,4-D MINERALIZATION TO TEMPERATURE IN SOILS AT VARYING SOIL MOISTURE CONTENTS, SLOPE POSITIONS AND DEPTHS

5.1 Abstract

The herbicide 2,4-D [2,4-(dichlorophenoxy) acetic acid] is a widely used broadleaf control agent in cereal production systems. Although 2,4-D soil-residual activity (half-lives) are typical less than 10 days, this herbicide also has as a short term leaching potential due to its relatively weak retention by soil constituents. Herbicide residual effects and leaching are influenced by environmental variables such as soil moisture and temperature. The objective of this study was to determine impacts of these environmental variables on the magnitude and extent of 2,4-D mineralization in a cultivated undulating Manitoba prairie landscape. Microcosm incubation experiments were utilized to assess 2,4-D half-lives and total mineralization using a 4 x 4 x 3 x 2 factorial design (with soil temperature at 4 levels: 5, 10, 20 and 40°C; soil moisture at 4 levels: 60, 85, 110, 135% of field capacity; slope position at 3 levels: upper-, mid- and lower-slopes; and soil depth at 2 levels: 0-5 cm and 5-15 cm). Half-lives (DT_{50}) varied from 3 days to 51 days with the total 2,4-D mineralization (M_T) ranging from 5.8 to 50.9%. The four-way interaction (temperature x moisture x slope x depth) significantly ($p < 0.001$) influenced both DT_{50} and M_T . Second-order polynomial equations best described the relations of temperature with DT_{50} and M_T as was expected from a biological system. However, the interaction and variability of DT_{50} and M_T among different temperatures, soil moistures, slope positions, and soil depth combinations indicates that the complex nature of these

interacting factors should be considered when applying 2,4-D in agricultural fields and in utilizing these parameters in pesticide fate models.

5.2 Introduction

Soil temperature and moisture content impacts herbicide sorption and bioavailability (Dao and Lavy 1978), microbial communities and activities (Blume et al. 2002) and, consequently, herbicide biodegradation rates (Smith and Cullimore 1975; Schroll et al. 2006). Since soil moisture and temperature are among the dominant environmental variables affecting herbicide fate in soil, some herbicide fate models such as PRZM (Pesticide Root Zone Model) version 3.12.2 (Carousel et al. 2005) include equations for simulating the effects of soil temperature and soil moisture on herbicide degradation. Equations for temperature include the Arrhenius equation and the Q_{10} relationship (Boesten 2000), while soil moisture include the use of empirical equations (Walker 1974; Walker 1987). In PEARL (Pesticide Emission Assessment at Regional and Local scales), herbicide degradation is calculated using factors to correct for moisture, temperature and soil depth in reference to the half-life of a pesticide determined in a well moistened plough layer at a set temperature (van der Linden et al 2009). Utilizing this model in spatial assessments (GeoPEARL), soil properties available in soil information systems are further used as factors to calculate the reference pesticide half-life in a wider range of soils (van der Linden et al. 2009). Given the increasing interest to refine equations dealing with herbicide degradation as part of pesticide fate models used in agricultural-environmental regulatory and programming analyses, experimental studies are required to ensure that the interactive effects of soil properties, temperature and moisture on

herbicide degradation is better understood. Such experimental studies, and their potential impact on improving pesticide fate model equations, are particularly important under the current realization of increasing climate fluctuations and change.

The majority of herbicide biodegradation in agricultural soils occurs in the plough layer (0-15 cm) where herbicide residues tend to reside and microbial communities proliferate (Walker et al. 1989; Larsen et al. 2000). Although the top 5 cm of the soil surface is presumed to be the primary location of herbicide transformation (Topp et al. 1997), there have been few experimental studies comparing herbicide degradation rates across depths in the plough layer (Shymko and Farenhorst 2008). Many factors influence the temperature and moisture content of plough layers such as atmospheric conditions, slope position and aspect, as well as cropping system and tillage management (Ayyad and Dix 1964; da Silva et al. 2001; Mohanty and Skaggs 2001). Even on a single day, herbicide residues in the plough layer are exposed to a wide range of soil temperatures, for example, for an agricultural soil set in a temperate climate, temperatures may range from -2 to 20°C during a day in mid-April or from 15 to 45°C during a day in late-May (Stoller and Wax 1973).

The herbicide 2,4-D continues to be one of the most widely applied agricultural pesticides in western Canada. Although 2,4-D biodegrades quickly in moist, warm soil (Smith and Muir 1980; Han and New 1994; Johnson et al. 1995), this herbicide has potential soil residual activity and the timing of application as well as factors such as soil temperature and moisture influences soil residual activity at levels that may adversely impact subsequent sensitive crops (Walker et al. 1992). 2,4-D has a relatively large water

solubility (900 mg l⁻¹ at pH 7, 25°C (McKeague 1998)) and its weak binding by soil constituents particularly in alkaline soils appears to suggest that the herbicide moves to depth in the plough layer prior to being degraded in soil (Farenhorst et al. 2009). 2,4-D sorption and degradation in Canadian prairie landscapes have been shown to vary among slope positions and with soil depth because of variations in soil organic carbon content (Gaultier and Farenhorst 2007; Farenhorst et al. 2008ab). The objective of this study is to assess the impact of soil temperature (5, 10, 20 and 40°C), soil moisture (60, 85, 110 and 125% of field capacity), slope position (upper-, mid- and lower-slopes), and soil depth (0-5 and 5-15 cm), and their interactions, on 2,4-D mineralization in an undulating Canadian prairie landscape. Although studied for more than 40 years, to our knowledge, this is the first study to examine all of these factors concurrently on 2,4-D mineralization.

5.3 Materials and Methods

5.3.1 Site

The agricultural field site is situated within the South Tobacco Creek Watershed located near Deerwood (49° 23' N, 98° 23' W; 6-5-7-W1) in south central Manitoba. This watershed drains 7,638 hectares of land, of which 71% is under cultivation (Hope et al. 2002). The field (approximately 55 hectares) is an undulating soil-landscape based on boulder till intermixed with shale (Soil Classification Working Group 1998), and ranges from a high of 458 meters above sea level in an upper-slope position in the west and decreases to 441 meters above sea level in the lower-slope position in the east. The upper- and mid-slopes consist of the Dezwood loam series (Orthic Dark Grey Chernozem; Ap, Btj, Ck horizons), while the lower-slopes contain soils from the Zaplin series (Gleyed

Dark Grey Chernozem; Ap, Btgj, Ckgj horizons) (Soil Classification Working Group 1998). The site has been cultivated for over 100 years, using a regime of deep tilling in the fall, and disking and harrowing in the spring. Cultivation over the past 40 years has included a two year cereal-oilseed crop rotation in which 2,4-D has been used regularly for weed control.

5.3.2 Soil Sampling and Characterization

Samples were collected from three slope positions (upper-, mid- and lower-slopes) in an eastward transect. The upper- and mid-slope positions were 43.5 meters apart while the lower-slope position was situated 250 meter from the mid-slope position. Approximately 5 kg of soil was obtained from both the 0-5 and 5-15 cm soil depth at each slope position. In order to minimize intermixing of soil samples, the shovel used to collect the samples was disinfected with bleach, and then sprayed with distilled water to remove bleach residue between each 5-kg sample. Soil was immediately placed in plastic bags and stored on ice in a cooler for transport to the University of Manitoba where soil was subsequently frozen at -35°C. The freezing of soils prior to experimentation has been shown not to significantly affect the mineralization data obtained when compared to data obtained using fresh soils (Mortensen and Jacobsen 2004).

Soil characteristics, including soil organic carbon content (SOC), texture and pH, as well as soil field capacity and 2,4-D sorption parameters were determined and published in a previous study conducted by Shymko and Farenhorst (2008) (Table 5.1). Soil properties were determined using air-dried, sieved (<2 mm) soil in which the gravimetric soil

Table 5.1 Soil characteristics at the three slope positions and two soil depths (adapted from Shymko and Farenhorst 2008).

Slope Position	Depth (cm)	Soil Texture [†]	Field Capacity (%)	Soil pH	Soil organic Carbon %	K_f [‡] [$\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$]
Upper	0-5	SCL	42.46	6.2d*	1.43c	0.90b
	5-15	SCL	43.39	5.9c	0.63d	0.72b
Mid	0-5	SCL	43.90	5.5b	1.90bc	1.72ab
	5-15	CLAY	38.84	5.4b	1.23cd	1.69ab
Lower	0-5	SCL	31.81	7.7a	2.52ab	2.63a
	5-15	SCL	34.91	7.7a	2.97a	2.29a

[†]SCL=sandy clay loam.

[‡]Freundlich coefficient.

* Means within columns with the same letter are not significantly different. To be consistent with the multiple comparison test used in the current mineralization study, data on soil properties and K_f values were reanalyzed using Tukey's multiple comparison test ($\alpha = 0.05$) rather than the Student-Newman-Keuls test ($\alpha = 0.05$), which was used in Shymko and Farenhorst (2008).

moisture varied between 7 and 14%. Soil organic carbon content (SOC) was determined using the dichromate oxidation method (Nelson and Sommers 1982). Soil texture was measured using the hydrometer method (Sheldrick and Wang 1993). Soil pH was determined in 0.01 M CaCl_2 (10 mL) with 5 g of air-dried soil (McKeague 1998). Laboratory leaching columns (11 cm in height, 2.7 cm radius) were used to determine field capacity, defined as the amount of gravity retained soil moisture measured at 96 hours after the columns had been saturated. 2,4-D sorption was described by the Freundlich coefficient as determined by batch-equilibrium techniques using a 1:2 soil:solution ratio. The Freundlich sorption coefficient, K_f [$\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$], was calculated by nonlinear regression using the log transformed empirical Freundlich equation: $\text{Log } C_s = \text{log } K_f + \frac{1}{n} \text{log } C_e$, where C_s is the concentration of 2,4-D sorbed to soil [$\mu\text{g g}^{-1}$], C_e is concentration of 2,4-D in the equilibrium solution [$\mu\text{g mL}^{-1}$] and $1/n$ is

the dimensionless Freundlich constant describing nonlinearity. The units of C_s and C_e ensure that all isotherm lines crossed $C_e = 1$, an important criterion when calculating K_f (Bowman 1981, 1982).

5.3.3 Mineralization Experiments

2,4-D mineralization was assessed using microcosm incubation experiments with a $4 \times 4 \times 3 \times 2$ factorial experimental design. The four factors were soil temperature (4 levels: 5, 10, 20 and 40 °C), soil moisture (4 levels: 60, 85, 110 and 135% of field capacity), slope position (3 levels: upper-, mid- and lower-slopes) and soil depth (2 levels: 0–5 and 5–15 cm). Three replicates were used for treatments at 5, 10 and 40°C, while 4 replicates were used for treatments at 20°C as this was part of a previous experiment (Shymko and Farenhorst 2008).

Microcosms consisted of a 50-mL flint jar placed in a 500-mL sealed glass jar. Soil was thawed for four days at 20°C and passed through a 2-mm sieve. Soil moisture content was determined on a portion of soil and another portion of soil was used to add 25 g of soil (oven-dried weight) to a 50-mL flint jar. Distilled water was added to each soil to bring the soil moisture to 50, 75, 100 and 125% of field capacity. The soils were pre-incubated at 20°C for 14 days to stimulate microbial activity. To maintain adequate humidity in the microcosm, 5 mL of acidified water (pH of 3 using 6NHCL) was added to a glass vial and inserted into the 500-mL sealed glass jar. The acidified water prevented the reaction between carbon dioxide and water. Evaporation of water, as determined by weighing, was observable at 40°C, but not in the 5 to 20°C treatments. Consequently,

distilled water was added at day 2 to bring the 40°C treatment back up to the appropriate soil moisture level and parafilm was placed over each jar. Holes were poked in the parafilm to allow the exchange of CO₂ with negligible evaporation.

To assess 2,4-D mineralization, a 2,4-D stock solution was prepared by combining analytical grade 2,4-D with ¹⁴C-ring labeled 2,4-D (99% radiochemical purity; specific activity 250 μCi; Sigma Aldrich Chemical Company, St. Louis, MO). The herbicide solution (1 ml) was thoroughly mixed into soil at an agronomic rate of 0.63 g m⁻³ of soil and 333 Bq g⁻¹ of soil and subsequently increased the soil moisture of the four soil moisture treatments to: 60, 85, 110 and 135% of field capacity. The agronomic rate was determined using a 2,4-D product formulation of 500 g a.i. L⁻¹ and an average application rate of 0.5 L acre⁻¹ (Manitoba Agriculture and Food 2002).

The amount of ¹⁴CO₂ evolved during incubation was trapped using a 20-mL scintillation vial containing 5 mL of 0.5 M NaOH. Traps were inserted into the 500-mL microcosm jar and changed every 2 or 3 days until degradation rates began to taper off at 46 days. Traps were then changed on days 51, 55, 60, 67, 74, 89 and 103. Radioactivity in each trap was assessed by adding 8-mL of scintillation fluid (30% Scintisafe scintillation cocktail; Fisher Scientific, Fairlawn, NJ) to the 5-mL of 0.5 M NaOH in the vials so that the radioactivity could be determined using Liquid Scintillation Counting (LSC), with automated quench correction (#H method) (Tri Carb 2100TR, Beckman Instruments, Fullerton, CA). A maximum counting time of 10 minutes was used to determine radioactivity.

Mineralization was expressed as a percentage of the amount of $^{14}\text{CO}_2$ evolved as a function of time, relative to the amount of ^{14}C -2,4-D initially applied. Half-lives (DT_{50}) were graphically determined using half of the total 2,4-D mineralized at 103 days. Initially, the widely-used first-order kinetic model typically used in pesticide leaching models (Vanclooster et al. 2000; Beulke and Brown 2001), as well as the three-half-order kinetic model (Brunner and Focht 1984), were fitted to the data but not used in this study because in either models, about 5% of the data (predominantly at 5 and 40 °C) resulted in unrealistic model parameters for inclusion in statistical analysis.

5.3.4 Statistical analyses

Half-lives (ln-transformed to achieve normality and homoscedasticity) and total mineralization at 103 days were analyzed using a four-way ANOVA using Proc Mixed in SAS Version 9.2 for Windows (SAS Institute Inc. 2002-2008). Temperature, soil moisture and slope and their interactions were treated as fixed effects, while depth nested within the site was modeled as random effects along with its interaction with the fixed effects. The Tukey-Kramer multiple pair-wise comparison procedure ($\alpha = 0.05$) was used for all pair-wise comparisons. To be consistent with the multiple comparison test used in the current mineralization study, data on soil properties and K_f values were reanalyzed using Tukey's multiple comparison test rather than Student-Newman Keuls ($\alpha = 0.05$) which was used in Shymko and Farenhorst (2008). Polynomial equations were developed using EXCEL 2007 (Microsoft) to relate soil temperature to half-lives and total mineralization at 103 days, as influenced by soil moisture, soil depth and slope position factors.

5.4 Results

Half-lives varied from 3 days to 51 days with the total 2,4-D mineralization (MT) ranging from 5.8 to 50.9% (Figures 5.1A, B). The four-way interaction (temperature x moisture x slope x depth) significantly influenced both DT_{50} and MT at the 1% significance level (Table 5.2). The relationship between temperature and either DT_{50} (r^2 varied between 0.76 and 1.00) or MT (r^2 varied between 0.95 and 1.00) followed a second-order polynomial function for all moistures, slopes and depths (Figures 5.2, 5.3 and Table 5.3). To adequately fit a polynomial relationship between temperature and DT_{50} in the 0-5 cm depth of the upper-slope at 135% moisture, the data point at 5°C was omitted (Table 5.5).

5.4.1 Temperature

Considering all of the 72 temperature, moisture, slope and depth combinations, DT_{50} was often numerically and significantly shorter at 20°C than at 5, 10 or 40°C (Table 5.4), particularly at 60, 85 and 110% moisture when DT_{50} was always statistically shorter at 20°C than at 5°C or 10°C (except for 1 case). DT_{50} was numerically longer at 20°C than 40°C and differences were significant 87.5% of the time across the 24 possible cases. DT_{50} was statistically similar between 5 and 10°C in 83.3% across the 24 possible cases, but exceptions occurred most frequently in the upper-slope at the 5-15 cm depth in which DT_{50} was significantly longer at 5 than 10°C at 85, 110 and 135% moisture. DT_{50} was numerically shorter at 5 than 40°C in 62.5% of the 24 possible cases, but the differences were often not significant and lacked any obvious trends. In several instances, DT_{50} was numerically longer at 5 than 40°C (37.5% of the 24 possible cases) but, differences were only statistically significant at 60% moisture in the mid-slope (5-15 cm) and upper-slope

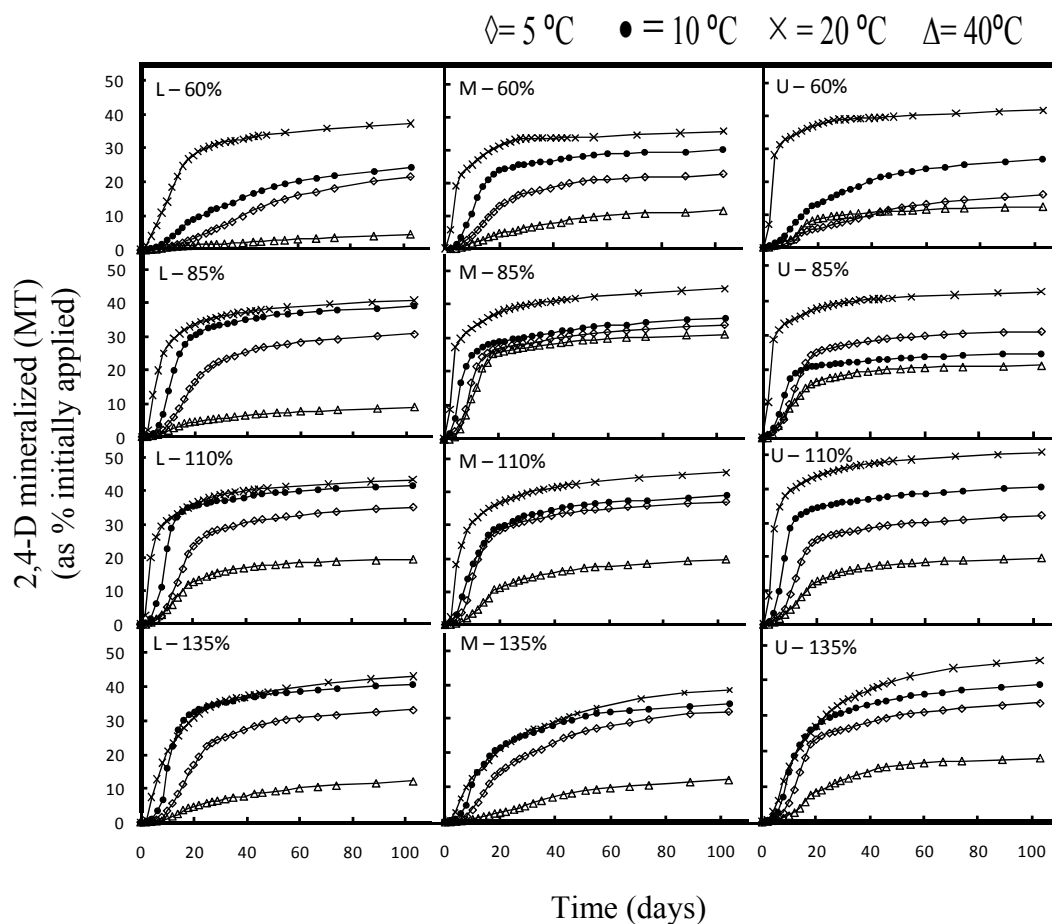


Figure 5.1a Mean 2,4-D mineralization rates (MT, as % initially applied) as a function of time at four soil moisture contents (60, 85, 110 and 135% of field capacity) for lower-slope (L) (0-5 cm), mid-slope (M) (0-5 cm) and upper-slope (U) (0-5 cm).

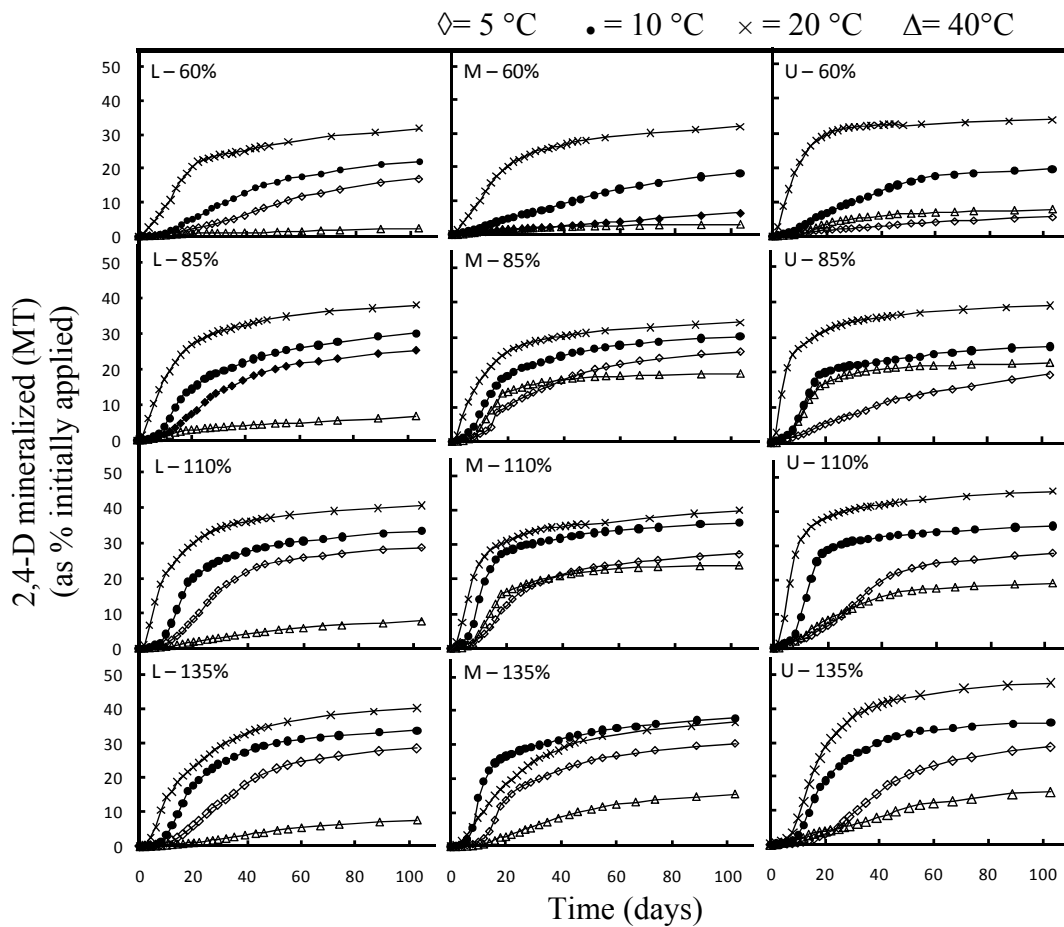


Figure 5.1b Mean 2,4-D mineralization rates (MT, as % initially applied) as a function of time at four soil moisture contents (60, 85, 110 and 135% of field capacity) for lower-slope (L) (5-15 cm), mid-slope (M) (5-15 cm) and upper-slope (U) (5-15 cm).

Table 5.2 Abbreviated four-way analysis of variance (ANOVA) for experimental mineralization data (MT) and half-lives (DT₅₀).

Source	Df	DT ₅₀		MT	
		f- value	Pr > F [†]	f- value	Pr > F [†]
Depth	1	519.4	<0.0001	308.3	<0.0001
Slope	2	99.3	<0.0001	25.6	<0.0001
Moisture	3	225.7	<0.0001	382.3	<0.0001
Temperature	3	624.4	<0.0001	1623.8	<0.0001
Slope * Depth	2	3.4	0.03	0.9	0.03
Moisture * Depth	3	22.4	<0.0001	16.6	<0.0001
Temperature * Depth	3	26.6	<0.0001	11.7	<0.0001
Moisture * Slope	6	24.4	<0.0001	8.2	<0.0001
Temperature * Slope	6	17.6	<0.0001	42.6	<0.0001
Moisture * Slope * Depth	6	18.0	<0.0001	8.3	<0.0001
Temperature * Slope * Depth	6	11.5	<0.0001	2.3	<0.0001
Moisture * Temperature	9	32.7	<0.0001	19.4	<0.0001
Moisture * Temperature * Depth	9	6.6	<0.0001	0.9	<0.0001
Moisture * Temperature * Slope	18	3.7	<0.0001	3.8	<0.0001
Moisture * Temperature * Slope * Depth	18	4.9	<0.0001	3.7	<0.0001

[†]Significant p-values are given in boldface ($\alpha=0.05$)

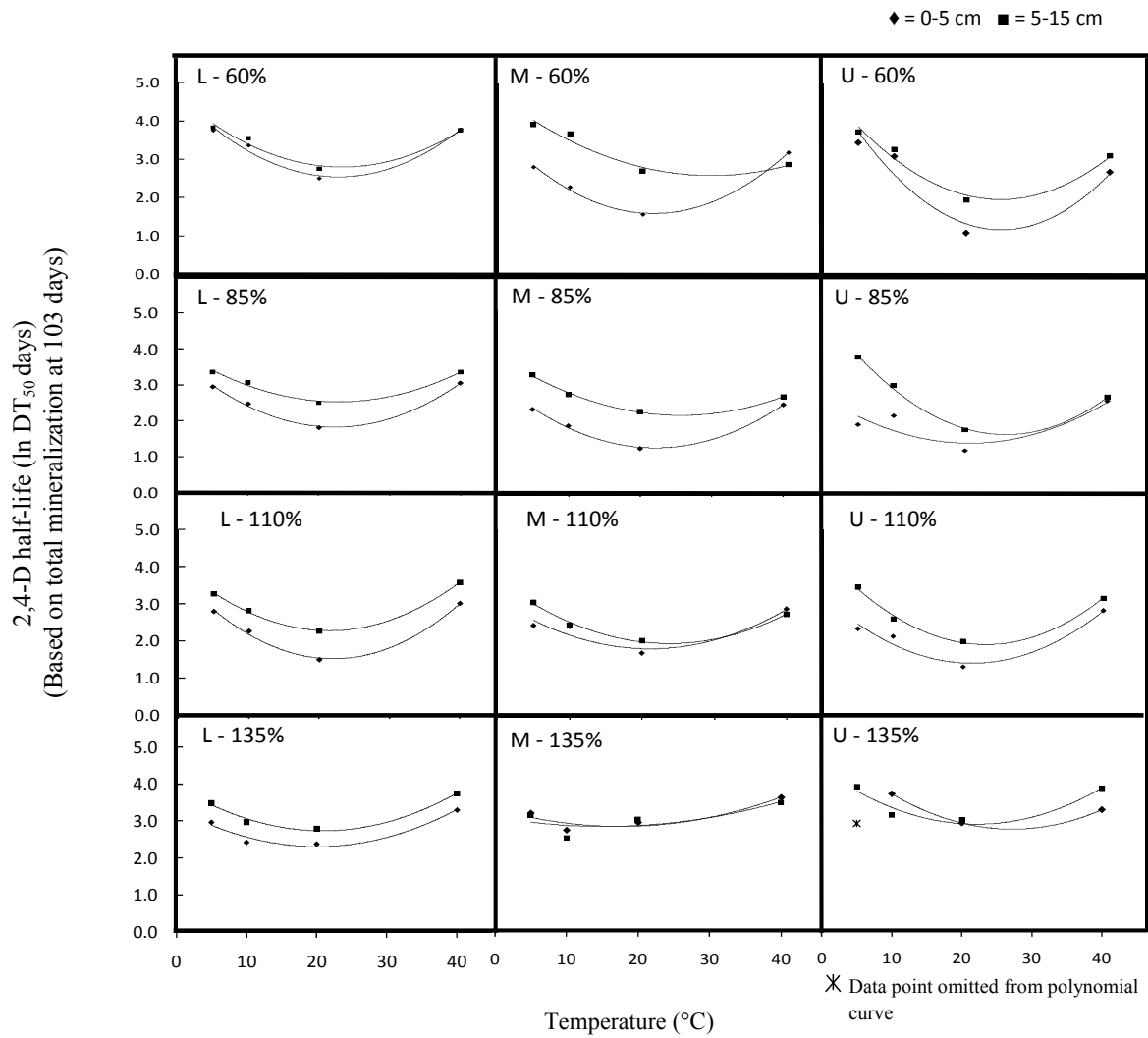


Figure 5.2 2,4-D half-life (ln DT₅₀, days) (LS Means estimate), as a function of temperature for lower-slope (L), mid-slope (M) and upper-slope (U).

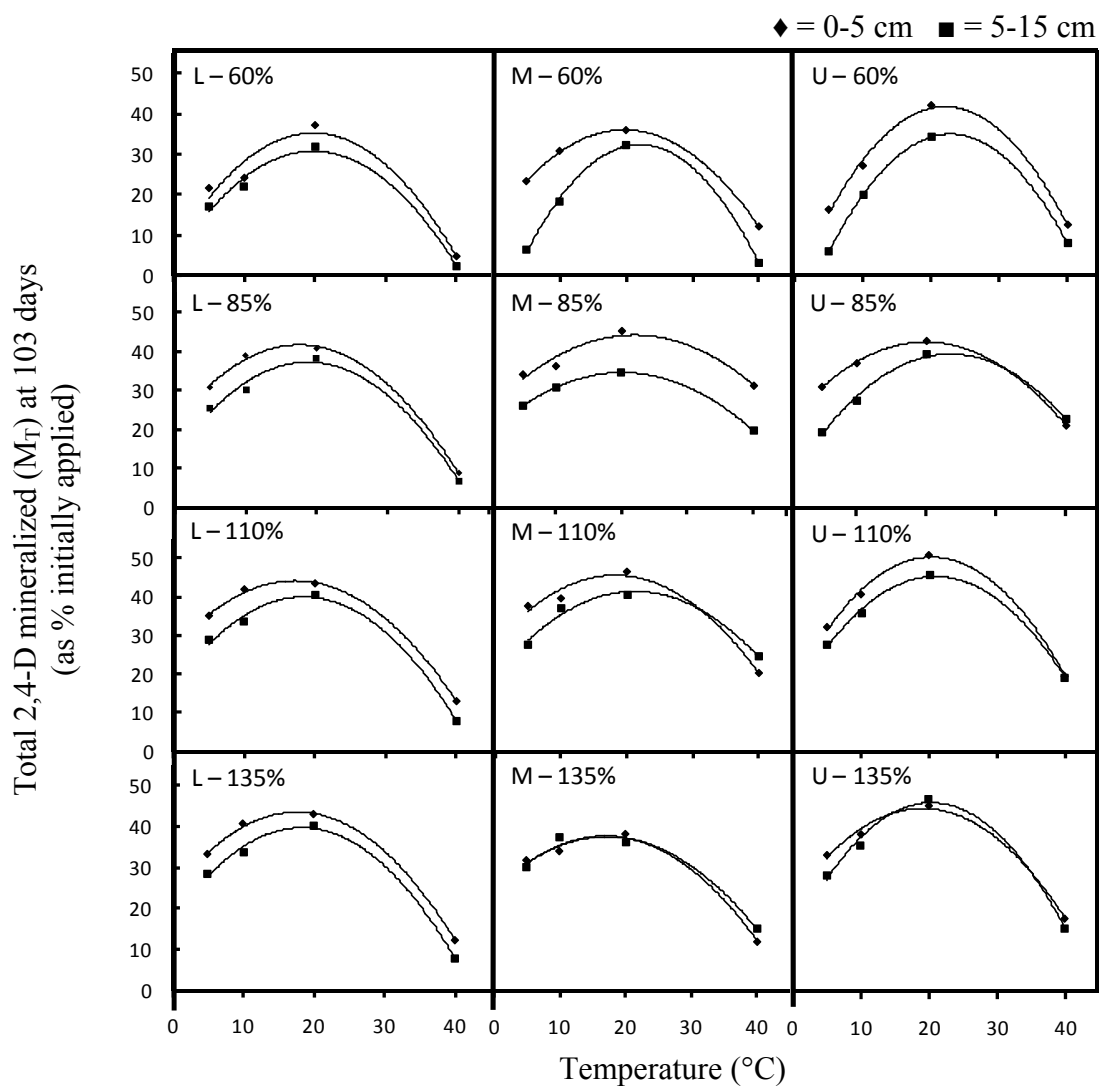


Figure 5.3 Total 2,4-D mineralization rates (M_T , as % initially applied) (LS Means estimate) as a function of temperature for lower-slope (L), mid-slope (M) and upper-slope (U).

Table 5.3 Second-order polynomial equations and r^2 vales for the polynomial relationships of 2,4-D mineralization half-life (DT_{50}) and total mineralization (M_T) relationship with temperature (t) for Figures 2.3 and 2.4.

Soil Moisture	Depth (cm)	Lower-slope		Mid-slope		Upper-slope	
		Equation	r^2	Equation	r^2	Equation	r^2
DT_{50}							
60%	0-5	$\ln DT_{50} = 0.004t^2 - 0.19t + 4.68$	0.97	$\ln DT_{50} = 0.002t^2 - 0.143t + 4.70$	0.95	$\ln DT_{50} = 0.005t^2 - 0.24t + 4.95$	0.94
	5-15	$\ln DT_{50} = 0.003t^2 - 0.16t + 4.63$	0.94	$\ln DT_{50} = 0.005t^2 - 0.201t + 3.74$	0.99	$\ln DT_{50} = 0.006t^2 - 0.33t + 5.17$	0.89
85%	0-5	$\ln DT_{50} = 0.004t^2 - 0.17t + 3.75$	0.99	$\ln DT_{50} = 0.004t^2 - 0.164t + 3.08$	0.99	$\ln DT_{50} = 0.005t^2 - 0.26t + 4.88$	0.73
	5-15	$\ln DT_{50} = 0.003t^2 - 0.13t + 3.97$	0.97	$\ln DT_{50} = 0.003t^2 - 0.128t + 3.80$	0.99	$\ln DT_{50} = 0.005t^2 - 0.26t + 4.88$	0.99
110%	0-5	$\ln DT_{50} = 0.005t^2 - 0.20t + 3.73$	0.99	$\ln DT_{50} = 0.003t^2 - 0.124t + 3.12$	0.88	$\ln DT_{50} = 0.004t^2 - 0.17t + 3.19$	0.94
	5-15	$\ln DT_{50} = 0.004t^2 - 0.16t + 4.02$	1.00	$\ln DT_{50} = 0.003t^2 - 0.142t + 3.65$	0.98	$\ln DT_{50} = 0.005t^2 - 0.21t + 4.31$	0.99
135%	0-5	$\ln DT_{50} = 0.003t^2 - 0.10t + 3.33$	0.95	$\ln DT_{50} = 0.002t^2 - 0.054t + 3.25$	0.87	$\ln DT_{50} = 0.003t^2 - 0.17t + 4.84^*$	1.00
	5-15	$\ln DT_{50} = 0.003t^2 - 0.12t + 3.95$	0.97	$\ln DT_{50} = 0.001t^2 - 0.033t + 3.02$	0.61	$\ln DT_{50} = 0.003t^2 - 0.13t + 4.13$	0.87
M_T							
60%	0-5	$M_T = -0.0897t^2 + 3.96t - 2.34$	0.99	$M_T = -0.058t^2 + 2.27t + 13.3$	1.00	$M_T = -0.074t^2 + 2.91t + 6.6$	0.95
	5-15	$M_T = -0.0906t^2 + 4.14t - 12.7$	1.00	$M_T = -0.090t^2 + 3.98t - 11.7$	1.00	$M_T = -0.069t^2 + 2.71t + 3.9$	0.98
85%	0-5	$M_T = -0.0526t^2 + 2.09t + 21.6$	1.00	$M_T = -0.039t^2 + 1.71t + 25.0$	0.92	$M_T = -0.065t^2 + 2.28t + 21.5$	0.99
	5-15	$M_T = -0.0605t^2 + 2.84t + 6.12$	0.99	$M_T = -0.037t^2 + 1.50t + 19.2$	1.00	$M_T = -0.067t^2 + 2.53t + 13.4$	0.99
110%	0-5	$M_T = -0.0795t^2 + 3.24t + 17.4$	1.00	$M_T = -0.053t^2 + 1.92t + 27.4$	0.98	$M_T = -0.060t^2 + 2.03t + 26.7$	0.99
	5-15	$M_T = -0.0719t^2 + 3.01t + 13.9$	1.00	$M_T = -0.048t^2 + 2.02t + 19.3$	0.98	$M_T = -0.068t^2 + 2.52t + 16.8$	0.99
135%	0-5	$M_T = -0.0618t^2 + 2.36t + 22.6$	0.99	$M_T = -0.049t^2 + 1.65t + 24.2$	0.99	$M_T = -0.063t^2 + 2.21t + 24.1$	1.00
	5-15	$M_T = -0.0800t^2 + 3.26t + 13.2$	0.99	$M_T = -0.044t^2 + 1.50t + 25.1$	0.98	$M_T = -0.068t^2 + 2.48t + 17.1$	1.00

*Data point for DT_{50} (5°C) was omitted from equation in order to adequately fit a polynomial curve.

(0-5 cm), and at 85% moisture in the upper-slope (5-15 cm). Between 10 and 40°C, DT_{50} was statistically similar in 58% of the 24 possible cases, but there were no obvious trends when significant differences occurred.

In agreement with half-lives, M_T was numerically greater at 20°C than at 5, 10 or 40 °C in 71 of 72 temperature, moisture, slope and depth combinations and the differences were significant in 76.4% of the 72 cases (Table 5.5). Out of the 22.2% of the 72 cases that demonstrated statistically similar results, M_T was most often statistically similar at 10 and 20°C (58.3% out of 24 possible cases). M_T was numerically smaller at 5° than 10°C for all 24 possible cases, but statistically similar in 79.2% of these cases. M_T was numerically greater at 10°C than at 40°C in all 24 possible cases, and these cases were statistically greater 87.5% of the time. Although M_T was numerically greater at 5 than 40°C in 95.8% of the 24 possible cases, these differences were only significantly greater 66.7% of the time.

Table 5.4 Least square mean estimates of 2,4-D half-life (DT₅₀= days, values back transformed from ln DT₅₀) compared among temperatures, slopes, and depth within the same moisture treatment (Tukey's multiple comparison test, $\alpha = 0.05$).

Temperature	0-5 cm						5-15cm					
	Lower-slope		Mid-slope		Upper-slope		Lower-slope		Mid-slope		Upper-slope	
60% of Field Capacity												
5°C	42.7	A [†] x [‡] a [§]	16.7	AB [†] y [‡] b [§]	31.7	A [†] x [‡] a [§]	46.3	A [†] x [‡] a [§]	51.3	A [†] x [‡] a [§]	41.6	A [†] x [‡] a [§]
10°C	28.7	Axa	9.8	Byb	22.1	ABxa	34.9	Axa	40.0	Axa	26.6	Axa
20°C	12.1	Axa	4.8	Cyb	3.0	Cyb	15.7	Bxa	15.1	Bxa	7.1	Cya
40°C	43.7	Axa	24.5	Axya	14.7	Bya	42.9	Axa	17.7	Bya	22.4	Aya
85% of Field Capacity												
5°C	19.0	A [†] x [‡] a [§]	10.2	A [†] xy [‡] a [§]	6.3	B [†] y [‡] b [§]	28.5	A [†] x [‡] a [§]	25.9	A [†] x [‡] a [§]	39.3	A [†] x [‡] a [§]
10°C	11.8	Axa	6.5	Axb	8.0	ABxb	21.6	Axa	15.2	ABxa	18.0	B [†] xa
20°C	6.1	Bxb	3.5	Bya	3.1	Cyb	12.2	Bxa	9.6	Bxa	5.4	C [†] ya
40°C	21.0	Axa	11.6	Axa	11.9	Axa	28.7	Axa	14.3	ABya	13.3	Bya
110% of Field Capacity												
5°C	16.3	AB [†] x [‡] a [§]	11.5	A [†] x [‡] a [§]	10.0	AB [†] x [‡] a [§]	26.5	AB [†] x [‡] a [§]	21.3	A [†] x [‡] a [§]	30.9	A [†] x [‡] a [§]
10°C	9.7	Bxa	11.2	Axa	8.2	Bxb	16.8	B [†] xa	11.5	ABCxa	13.2	Bxa
20°C	4.5	Cxa	5.5	Bxa	3.6	Cxa	9.6	Cxa	7.7	Cxa	7.2	Cxb
40°C	20.3	Axa	17.9	Axa	16.5	Axb	36.0	Axa	15.5	ABya	23.0	ABxya
135% of Field Capacity												
5°C	19.4	AB [†] x [‡] a [§]	22.7	AB [†] x [‡] a [§]	15.6	B [†] x [‡] b [§]	32.8	AB [†] x [‡] a	21.7	AB [†] x [‡] a [§]	39.6	A [†] x [‡] a [§]
10°C	11.3	Bya	14.5	Bya	32.8	Axa	19.4	BCxa	11.8	Bxa	19.1	Bxa
20°C	10.8	Bxa	17.7	Bxa	15.7	Bxa	16.2	BCxa	19.4	Bxa	17.0	Bxa
40°C	27.1	Axa	34.3	Axa	22.0	ABxa	42.3	Axa	30.1	Axa	37.6	Axa

[†]Means with the same capital letter (A, B, C, D) are not significantly different within columns of the same slope and moisture content.

[‡]Means with the same lower case letter (x, y, z) are not significantly different within rows of the same depth and moisture content.

[§]Means with the same lower case letter (a, b) are not significantly different between depths within the same slope, moisture content and temperature.

5.4.2 Moisture

Regardless of the temperature, slope and depth treatments, DT_{50} was always statistically similar between 85 and 110% moisture contents (Table 5.4). This was in close agreement with the results for M_T for which 85 and 110% moisture was statistically similar in 91.7% of the 24 possible cases (Table 5.5). DT_{50} and M_T were also often statistically similar between 110 and 135% moisture, 58.3 and 95.8% of the 24 possible cases, respectively. DT_{50} was often statistically similar between 60 and 85% (70.8% of the 24 possible cases) and between 60 and 110% (62.5% of the 24 possible cases), but M_T was always numerically less at 60 than 85% moisture (and significantly less in 50% of the cases), and at 60 than 110% (and significantly less in 79.2% of the cases). No obvious trends for numerical or statistical differences were observed for DT_{50} between 60 and 135% moisture. In contrast, M_T was always numerically smaller at 60 than 135%, although these differences were only significant in 58.3% of the 24 possible cases, more often at both 5 and 10°C.

5.4.3 Slope and Depth

Slope position had no significant effect on DT_{50} (62.5% of the cases) and M_T (71.9% of the cases) for the majority of the temperature, moisture, and depth combinations (Tables 5.4, 5.5). In instances where significant differences occurred among slope positions, there were no obvious trends for either DT_{50} or M_T .

Soil depth minimally influenced DT_{50} and M_T at all slope positions. DT_{50} was numerically longer at the 5-15 cm depth in 85.4% of the cases but was statistically similar 70.8% of the time (Table 5.4). In instances where DT_{50} was numerically smaller in the 5-15 cm

depth, the differences were not statistically significant. In agreement with DT_{50} , M_T was numerically greater in the 0-5 cm depth as compared to the 5-15 cm depth in 89.6% of the instances, but these differences were often not statically significant (Table 5.5). There were no apparent trends for cases in which M_T and DT_{50} were significantly different between depths.

Table 5.5 Least squares mean estimate of 2,4-D total mineralization (MT = as % applied) compared among temperature, slopes and depth within the same moisture treatment (Tukey's multiple comparison test, $\alpha = 0.05$).

Temperature	0-5 cm						5-15cm					
	Lower-slope		Mid-slope		Upper-slope		Lower-slope		Mid-slope		Upper-slope	
60% of Field Capacity												
5°C	21.6	B [†] x [‡] a [§]	23.1	B [†] x [‡] a [§]	16.0	C [†] x [‡] a [§]	17.0	B [†] x [‡] a [§]	6.3	C [†] y [‡] b [§]	5.8	C [†] y [‡] a [§]
10°C	24.1	Bxa	30.5	ABxb	26.8	Bxa	22.0	Bxa	18.2	Bxb	19.6	Bxa
20°C	37.3	Axa	35.6	Axa	41.6	Axb	31.8	Axa	32.1	Axa	33.8	Axb
40°C	4.6	Cxa	12.0	Cxya	12.3	Cya	2.4	Cxa	3.1	Cxa	7.9	Cxa
85% of Field Capacity												
5°C	30.8	B [†] x [‡] a [§]	33.8	B [†] x [‡] a [§]	30.9	B [†] x [‡] a [§]	25.4	B [†] x [‡] a [§]	25.8	AB [†] x [‡] a [§]	19.4	B [†] x [‡] b [§]
10°C	38.9	Axa	35.9	Bxb	36.9	ABxa	30.1	ABxa	30.3	Axa	27.4	Bxa
20°C	40.7	Axa	44.7	Axa	42.5	Axa	38.0	Axa	34.3	Axb	39.1	Axa
40°C	8.9	Cza	31.0	Bxa	21.1	Cya	6.8	Cya	19.5	Bxb	22.6	Bxa
110% of Field Capacity												
5°C	35.0	B [†] x [‡] a [§]	37.0	B [†] x [‡] a [§]	32.2	C [†] x [‡] a [§]	28.7	B [†] x [‡] a [§]	27.3	B [†] x [‡] b [§]	27.7	BC [†] x [‡] a [§]
10°C	41.8	ABxa	39.0	ABxa	40.7	Bxa	33.4	AB [†] xa	36.4	ABxa	35.7	Bxa
20°C	43.3	Aya	45.9	Axya	50.9	Axa	40.7	Axa	39.9	Axa	45.8	Axa
40°C	13.1	Cxa	19.8	Cxa	19.5	Dxa	7.9	Cya	24.1	Bxa	19.0	Cxa
135% of Field Capacity												
5°C	33.2	B [†] x [‡] a [§]	32.1	A [†] x [‡] a [§]	33.5	B [†] x [‡] a [§]	28.5	B [†] x [‡] a [§]	30.3	A [†] x [‡] a [§]	28.7	B [†] x [‡] a [§]
10°C	40.6	ABxa	34.3	Axa	38.7	ABxa	33.7	ABxa	37.8	Axa	35.8	Bxa
20°C	42.9	Axya	38.5	Aya	45.7	Axa	40.2	Axya	36.6	Aya	47.5	Axa
40°C	12.3	Cxa	12.3	Bxa	18.0	Cxa	7.6	Cxa	15.4	Bxa	15.6	Cxa

[†]Means with the same capital letter (A, B, C, D) are not significantly different within columns of the same slope and moisture content.

[‡]Means with the same lower case letter (x, y, z) are not significantly different within rows of the same depth and moisture content.

[§]Means with the same lower case letter (a, b) are not significantly different between depths within the same slope, moisture content, and temperature.

5.5 Discussion

The variation in DT_{50} and M_T among the varying environmental factors of soil temperature, soil moisture content, slope position and soil depth shows that these interacting factors are important when determining the fate of 2,4-D. The consortia of soil microorganisms responsible for degrading 2,4-D has been well documented (Sinton et al. 1986; Soulas 1993; Ka et al. 1994) and the ability of these degraders to mineralize 2,4-D are a reflection of the combined biological response to a myriad of interacting environmental factors. Other researchers, studying factors independently, also concluded that soil depth and SOC (Veeh et al. 1996; Gaultier and Farenhorst 2007), temperature (Veeh et al. 1996), water availability and soil moisture (Ou 1984; Han and New 1994) and landscape position (Boivin et al. 2005) influence 2,4-D DT_{50} and/or M_T .

Both DT_{50} and M_T demonstrated a strong polynomial relationship with temperature. These polynomial relationships demonstrate a typical biological system (in this instance, the consortia of 2,4-D degraders) which reacts to temperature and are influenced by minimum, optimum, and maximum temperatures (Paul and Clark 1996). Studies conducted by Stoller and Wax (1973) demonstrated that soil temperatures on bare soil surfaces fluctuate between 5 and 40°C during the growing season indicating that temperatures used in this study are realistic agricultural field temperatures.

The optimal temperature for DT_{50} and M_T (shortest DT_{50} and greatest M_T) in this experiment was 20°C and followed an increasing trend between 20°C and 5°C for DT_{50} and a corresponding decreasing trend for M_T . These results are in agreement with Veeh et

al. (1996) who also found a decrease in 2,4-D degradation with decreasing soil temperatures between 24° to 10°C. In addition, Ou (1984) found that 2,4-D degradation was smaller in soils incubated at 35° as compared to 25°C, which corresponds to the trends found in this experiment in which DT_{50} was typically longer and M_T was smaller at 40°C than 20°C. 2,4-D mineralization studies are typically carried out at 20°C (Smith 1978; Han and New 1994; Boivin et al. 2005; Picton and Farenhorst 2004) because this is considered to be the optimum temperature for pesticide mineralization. While 20°C was the optimal 2,4-D mineralization temperature in this study, the temperatures between 20° and 40°C were not investigated, and previous studies suggest that optimal 2,4-D degradation temperatures are between 22 and 27°C (Parker and Doxtader 1983; Sinton et al. 1986). In addition, while M_T was greatly reduced at 40°C, other researchers have found that 2,4-D will continue to biodegrade at thermophilic temperatures beyond 40°C (Michel et al. 1995). Further studies which investigate 2,4-D mineralization below 5°C, above 40°C, and between 5° and 40°C are recommend to improve the polynomial relationship by refining the minimum, maximum, and optimum temperatures for 2,4-D mineralization under varying moisture conditions.

The lower-slope at 60% moisture and 40°C resulted in the lowest 2,4-D mineralization rates and the longest DT_{50} , demonstrating that dryer, warmer soils rich in SOC limit 2,4-D mineralization, and thus prolong DT_{50} . This finding is in agreement with Maurice and Kirkland (2003) who found that herbicide mineralization is reduced in dryer soils because of lesser microbial activity. In addition, other researchers have found that dryer soils reduced 2,4-D bioavailability due to increased sorption onto SOC (Ogram et al. 1985; Shelton and Parkin 1991; Estrella et al. 1993; Guo et al. 2000; Gaultier and Farenhorst

2007) and slower herbicide diffusion rates towards the degrader microorganisms (Parker and Doxtader 1983; Han and New 1994;). Our study also suggests that, with predicted increases in air temperatures and possible drier conditions due to climate change in the prairie region of Canada (Shepard and McGinn 2003; Motha and Baier 2005), the resulting warmer and drier soil conditions could potentially lead to decreases in herbicide mineralization.

The range of total 2,4-D mineralization observed from a single agricultural field in this study (5.8 to 50.9%) was greater than regional studies which maintained constant temperature and soil moisture content (i.e. 20°C and 80% of field capacity). For example, Picton and Farenhorst (2004) demonstrated that total 2,4-D mineralization among agricultural fields ranged between 31 and 50% in soils obtained from 5 agricultural soils across Manitoba. Our results thus suggest that the influence of slope position, soil depth, temperature and moisture merit consideration when modeling 2,4-D fate and when applying this herbicide to agricultural fields particularly because the studied temperature and moisture ranges can be expected to occur during the growing season.

The majority of treatments demonstrated a rapid mineralization phase (first-order reaction) in the first 10 days after 2,4-D application followed by a slow mineralization phase similar to the findings of Parker and Doxtader (1983). In agreement with Parker and Doxtader (1983), at warmer temperatures, a first-order reaction was not observed, in this case, at the 40°C temperature treatment. In this study, the upper-slope position at 110% of field capacity at 20°C was the only treatment in which half of the initially applied 2,4-D was mineralized by the end of the experiment at 103 days and

demonstrated the fastest first-order reaction phase (approximately 2 weeks). Similarly, soil microcosm experiments conducted by Boivan et al. (2005) also showed that half of the applied 2,4-D was mineralized by 2 weeks in soils obtained from the 0-15 cm layer and incubated at $20 \pm 1^\circ\text{C}$ and 80% of field capacity.

2,4-D mineralization is often described as being sorption limited, meaning that rates of mineralization will decrease because sorption processes are limiting herbicide availability to microorganisms (Ogram et al. 1985; Johnson et al. 1995; Guo et al. 2000).

Mineralization at 40°C proceeded slowly in all moisture and slope positions which may have been a result of decreased microorganism activity at this high temperature rather than the result of increased sorption limiting 2,4-D bioavailability.

In general, there were no significant differences in total 2,4-D mineralization between the 0-5 and 5-15 cm depths in near-saturated soil (110 and 135% moisture). When differences in total 2,4-D mineralization were significant between depths, these differences more often occurred in upper-slopes, at lower temperatures and lower soil moistures. Total 2,4-D mineralization did not differ significantly between the 0-5 and 5-15 cm depths in the lower-slope, most likely due to a deeper, more homogeneous A horizon. The lower-slope position (concave depositional area) had significantly higher SOC as compared to the upper-slope, which is in agreement with previous studies (Gregorich and Anderson 1985; Pennock et al. 1994; Burke et al. 1995; Gaultier et al. 2006). In addition, greater microbial activities associated with soils richer in SOC increase the potential for greater rates of mineralization (Parker and Doxtader 1983), but will also promote 2,4-D sorption, which is highly linked to SOC (Reddy and Gambrell 1987; Bolan and Baskaran 1996;

Gaultier et al. 2006). Thus, higher moisture contents may reduce sorption of 2,4-D to soil constituents due to competition for sorption sites, resulting in higher total mineralization rates due to increased bioavailability. In addition, the water solubility of 2,4-D has been reported to decrease with increasing temperatures, resulting in a negative association between temperature and 2,4-D sorption by soil (Aksu and Kabasakal 2004; Gupta et al. 2006).

Among the most sensitive input parameters into pesticide fate models is the rate of pesticide degradation in soil (Boesten and van der Linden 1991; Boesten 2000; Dubus et al. 2003). Changes in the degradation parameter by a factor of 2 can result in a 10-fold increase in leaching (Boesten and van der Linden 1991). Although pesticide fate models may adjust for the effect of temperature and moisture on degradation using generic relationships such as those derived by Walker (1974) for moisture and the Arrhenius equation and the Q_{10} relationship for temperature (Boesten 2000; Vanclooster et al. 2000; Dubus et al. 2003), specific data are lacking for the biodegradations of individual pesticides, including 2,4-D. The polynomial relationships developed in this study could be useful for further refining pesticide fate models and spatial assessments such as GeoPEARL.

We acknowledge that further studies are required on the impact of the storage and pre-incubation conditions used on subsequent experimental results. In this and other studies (Reimer et al. 2005; Shymko and Farenhorst 2008), we utilized a pre-incubation period that is within the mid-range of what is recommended by the OECD (between 2 to 28 days) (2001). We chose a pre-incubation temperature of 20°C because such a pre-

incubation temperature was used in a previous study examining pesticide mineralization in soils under temperatures ranging from 10 to 40°C (Vischetti et al. 2002). Using a different approach, Mervosh and collaborators (1995) pre-incubated soil for 4 days at 5, 15, 25, or 30°C prior to applying ¹⁴C-pesticides to soil and kept these same temperatures for the duration of the experiment. In another study, Walker and collaborators (1996) demonstrated that pre-incubation temperatures ranging from 5 to 25°C had no impact on ¹⁴C-pesticides mineralization in soils subsequently incubated at 5, 10 and 25°C. There appears to be a lack of standardization in the types of storage and pre-incubation conditions used because in a range of other soil microcosm studies, soils were not pre-incubated prior to pesticide applications in the laboratory. The storage conditions of the soils used in these latter studies ranged from storing fresh soil at 4°C for up to 28 days (Entry et al. 1994; Völkel et al. 1994), freezing soil at - 4°C for up to 6 months (Topp and Starratt 2000; Colucci et al. 2001), or air-drying soil and storing it up to 3 years prior to use (Parker and Doxtader 1983; Ferrell and Vencill 2003).

5.6 Conclusions

This study demonstrated that total 2,4-D mineralization was highly influenced by temperature and soil moisture. A significant four-way interaction between soil temperature, soil moisture, slope position and soil depth was also observed ($\alpha = 0.001$), suggesting that the variability observed (DT_{50} varied from 3 days to 51 days; M_T varied from 5.8 to 50.9%) because of these interactive variables in this cultivated, undulating, Canadian prairie landscape are important considerations when using M_T and DT_{50} as input parameters for pesticide fate models. Specific polynomial relationships relating DT_{50} and

M_T to temperature at four soil moisture contents (60, 85, 110 and 135% of field capacity), three slope positions (upper-, mid- and lower-slopes) and two soil depths (0-5 and 5-15 cm) are provided. 2,4-D mineralization was highest at temperatures of 20°C, and lowest at temperatures of 5°C and 40°C.

The sensitivity of 2,4-D degradation to soil temperature and moisture warrants further attention to the effect of seasonal and diurnal variations in soil temperature and moisture in undulating prairie landscapes, particularly with increasing climate fluctuations and change in this and other regions. The seasonal timing of 2,4-D application to agricultural crops on the Canadian prairies should be considered as temperature, soil moisture, slope position and soil depth will influence the amount and variation of 2,4-D mineralization in an undulating landscape and therefore the potential for offsite leaching and soil residual effects.

5.7 Acknowledgements

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6. OVERALL SYNTHESIS

6.1 Summary of Research Findings

The research presented in Chapter 2 indicates that herbicide use in Manitoba accounts for 84% of the area treated with pesticides, followed by fungicides (13%), and insecticides (3%). The area treated with fungicides, herbicides, and insecticides in Manitoba did not significantly increase or decrease between 1996 and 2006. For herbicides, MCPA was applied to the largest area, followed by bromoxynil and glyphosate (GLY). With respect to herbicide mass, the ranking differed with GLY being the top herbicide, followed by MCPA and bromoxynil. Two of the top ten herbicides applied on a mass basis had significant ($p < 0.0001$) increasing linear trends; glufosinate ammonium (GLU) and GLY, while other herbicides in the top 10, bromoxynil, dichlorprop, ethalfluralin, imazamethabenz, sethoxydim, and trifluralin had significant ($p < 0.001$) decreasing linear trends. These trends are due to the adoption of genetically modified herbicide-tolerant (GMHT) canola, which increased from 6 to 89% of the total area seeded to canola between 1996 and 2006, respectively.

This research further tested the hypothesis that less environmentally damaging, and less harmful herbicides are being used in Manitoba since the adoption of GMHT-canola by calculating a series of simple and composite Herbicide Risk Indicators (HRIs) (Chapter 3). A total of 18 simple and 12 composite HRIs were calculated using the mass of herbicide applied in a given year. Of the 18 simple HRIs calculated for this study, 16 of the HRIs were influenced by changes to the types of herbicides applied to canola. Of the 12 composite HRIs calculated, ten of the indicators had significant linear trends, of which only seven were driven by the changes in herbicides applied to canola. While 67% of the

simple HRIs demonstrate that since 1996, producers are using more environmentally benign herbicides, four of the herbicide indicators, which were driven by the changes in the types of herbicides applied to GMHT-canola, showed otherwise. The water solubility HRI increased (increased mobility), while the HRIs for acute oral LD₅₀, dermal LD₅₀, and aquatic vascular plants decreased (increased toxicity). Over this 11-year period, the adoption of GMHT-canola has resulted in the replacement of more persistent and toxic herbicides such as clopyralid, ethalfluralin and trifluralin, with GLU and GLY, which are perceived as less harmful herbicides (Williams et al. 2000; Mauro and McLachlan 2008).

Chapters 4 and 5 involved microcosm incubation studies to assess the fate of the herbicide 2,4-D as influenced by slope position, soil depth within the plough layer, soil moisture, and soil temperature. The batch equilibrium technique was used to determine the Freundlich sorption coefficient of 2,4-D at three slope positions and two soil depths for Chapter 4. The Freundlich sorption coefficient for 2,4-D ranged from 0.83 to 2.46 ug^{1-1/n} g⁻¹ mL^{1/n}, and as expected, was significantly influenced by variations in soil organic carbon content across slope positions. Total mineralization (M_T) at 20°C varied from 31 to 52% at four soil moisture contents (60, 85, 110 and 135% of field capacity). At near-saturated conditions (110 and 135% of field capacity), the onset of 2,4-D degradation was delayed in soil obtained from the upper- and mid-slopes but not in soils obtained from the lower-slope position. Including a wider range of soil temperatures (5, 10, 20 and 40°C), M_T ranged from 5.8 to 52%, while 2,4-D mineralization half-lives (DT₅₀) varied from 3 days to 51 days. Both M_T and DT₅₀ demonstrated a polynomial relationship with temperature, indicating that DT₅₀ and M_T responded similar to a biological system with minimum, optimum, and maximum temperatures. The variability of sorption and mineralization

among slope positions and depth within in the plough layer suggests the segmentation of the landscape (upper-, mid-, lower-slopes) using digital elevation models may be useful for appropriate field sampling and estimates of 2,4-D fate, and differences in 2,4-D mineralization within the plough layer (0-15 cm) may be great enough to warrant sampling in smaller depth increments (5 cm).

6.2 Present and Future Implications

Given the interest in using pesticide fate models to direct regulatory policies, it is essential that accurate information be utilized so that policy makers can be directed appropriately (Arias-Estévez et al. 2008). One of the challenges with developing agri-environmental indicators is the lack of available comprehensive pesticide use information in Canada (Brimble et al. 2005; Cessna et al. 2005; Environment Canada 2011). The results of this PhD thesis provides one of the more detailed pesticide use studies conducted in Canada. The MASC data set used in Chapters 2 and 3 is a valuable source of pesticide use information because it provides details regarding the hectares of crop grown and the product formulation used, which is typically not available. This data set provides greater detail than the Agricultural Census of Canada in which producers are required to report the area treated with herbicides, fungicides, and insecticides. Although the present study focused primarily on provincial herbicide use trends, the MASC dataset includes detailed pesticide use information for fungicide, herbicide, insecticides, and seed treatments, georeferenced at the township level and provides many opportunities for additional pesticide use analysis. In addition, the mass of fungicides, insecticides, and

seed treatments can be calculated using the information available in the MASC dataset to provide a broader understanding of pesticide use and risk trends.

Agri-environmental indicators have been applied in Canada to track trends in agricultural pesticide use and are important for policy development and the evaluation of pesticide risk reduction programs (MacRae et al. 2000; Eilers et al. 2010). The HRIs applied in this study provide an additional methodology for tracking the evolution of relative herbicide risk in Manitoba. This methodology could be utilized in other agricultural regions across the Canadian Prairies to provide a consistent measure of herbicide risk and may be useful in comparing regional, national, and international herbicide risk trends. Given the fine detail of the MASC data set, the information could be used at the township level, or scaled up to larger areas such as ecoregions, ecoclimatic regions, or soil landscape polygons.

The changes in herbicides applied to GMHT-canola have impacted the majority of the HRIs calculated in this study. The replacement of more volatile and toxic herbicides such as clopyralid, ethalfluralin and trifluralin, with GLY and GLU, have overall, reduced risks associated with herbicide use. Despite GLY being considered a relatively non-hazardous herbicide, it is frequently detected in environmental sample analysis (Humphries 2005; Glozier et al. 2011; Messing et al. 2011), but is infrequently included in sample analysis. This suggests that GLY is mobile and the potential off-site movement into the broader environment warrants further investigation.

While the use of GMHTCs have been linked to reduced herbicide use when compared to conventional cropping systems (Wolfenbarger and Phifer 2000; Shaner 2000; Phipps and Park 2002; James 2003; Brimmer et al. 2005; Brookes and Barfoot 2005; Giannessi 2005; Gardner and Nelson 2008; Duke and Powles 2009; Smyth et al. 2011a) concerns exist regarding the development of herbicide resistant weeds (Powles 2008; Cerdeira and Duke 2009; Webster and Nichols 2012). In the United States, 24 glyphosate resistant weeds, coinciding with the use of GLY as an in-crop selective herbicide have been identified (Powles 2008; Cerdeira and Duke 2009; Heap 2010; Wright et al. 2010). Although weed management on GLY tolerant crops is more environmentally benign than conventionally weed management systems, the intensive use of GLY has lead to strong selection intensity for weeds with gene traits that permit GLY survival (Powles 2008; Harker et al. 2012). Thus, the use of GLY on GLY tolerant crops will become less efficacious as more GLY resistant weeds develop, and less environmentally friendly because additional herbicide modes of action will be required to control GLY tolerant weeds (Dill et al. 2008; Duke and Powles 2008; Powles 2008; Duke and Powles 2009; Duke 2011). As such, the efficacy of GLY in controlling weed species will begin to decline, and thus reduce the benefit of using GLY tolerant crops because other herbicides, such as synthetic auxin class herbicides (i.e. 2,4-D, dicamba, MCPA etc.) and ALS-inhibiting herbicides will be required to maintain effective weed control (Green et al. 2008; Mortenson et al. 2012). While Green et al. (2008) and Write et al. (2010) believe that adding additional herbicide modes of action into glyphosate tolerant weed control systems is a viable

solution to GLY resistant weeds, Harker et al. (2012) and Egan et al. (2011) believe that other strategies, such as Integrated Weed management is a more sustainable option.

Given the variability in 2,4-D mineralization observed in Chapters 4 and 5, factors which include site specific degradation rates and site landscape characteristics such as slope position and soil depth and further integrate adjustments for soil moisture and temperature, may be important in improving pesticide fate models (Gottesbuèren et al. 2000; Leu et al. 2004; Farenhorst et al. 2009). The reliance on pesticide fate models to direct environment policy and the inclusion of factors such as temperature and soil moisture can have a significant impact on model outcome (Garratt et al. 2002). As such, the equations developed in this study can be incorporated into pesticide fate models. Other sensitive input parameters for pesticide fate models include sorption values (Boesten and van der Linden 1991; Soutter and Musy 1998; Dust et al. 2000; Gottesbuèren et al. 2000; Klein et al. 2000; Dubus et al., 2003; Malone et al. 2004; Dan et al. 2006) and given the link with organic matter content which varies by slope position, this relationship may be used to refine pesticide fate models.

Refinement of pesticide fate input parameters in relation to changes in temperature and moisture could be valuable for forecast modeling in determining potential contamination of non-target sources as a result of human induced climate change. Changes in agronomic practices related to the introduction of new crops such as GMHT-canola, precision farming, and climate change may require more precise application of pesticides at different rates within a field based on site characteristics such as weed pressures

(Faechner et al. 2002) and variables which affect pesticide fate such as slope, temperature, and soil moisture (Carter 2000). It has been suggested that climate change will increase human exposure to agricultural contaminants such as pesticides (Schiedek et al. 2007; Boxall et al. 2009). The largest impact on the partition of contaminants in the environment are believed to be related to changes in temperature and precipitation (Boxall et al. 2009) and therefore, information on how temperature and moisture affect 2,4-D will assist with pesticide risk reduction strategies as the agricultural industry adapts to a changing climate.

6.3 Study Limitations and Future Recommendations

Although the two MASC data sets provide an important resource, there are several limitations with this data. The data set contains information on the area of a crop grown and that a pesticide was applied, not the actual area treated. In Chapter 2, it was assumed that the pesticides were applied once, to the entire crop. While this is typically the case for herbicides, fungicides and insecticides are often applied more frequently during the growing season. Despite these limitations, the data collected by MASC is a valuable source of information and MASC should continue to collect these data because it can also be used to validate pesticide sales data which is purported to be collected by PMRA. Unfortunately, as of 2012, MASC will no longer collect pesticide use data (J. Gaultier personal comm. October 2011), and other proxies such as sales data, provided it is available, will need to be used. The current MASC data set could be used to look at the relationship to sales data to verify its accuracy as a proxy for actual pesticide use from 1996-2006.

In addition, the calculation of herbicide mass (Chapter 2) assumed that only one application was made, and that the maximum recommended rates were used. While Manitoba farmers typically use one herbicide application, GLY is becoming increasingly popular to apply more than once because it is inexpensive and perceived to be less hazardous to organisms and the environment, resulting in increased crop yield (G. Martens personal comm. January 2012). Hence, surveys investigating herbicide use rates and frequency should be conducted to determine typical herbicide application rates and treatment frequency.

While the mass of herbicides applied was calculated in Chapter 2, the mass of insecticides, fungicides and seed treatments were not. Although these pesticides account for a small portion of all pesticides applied in Manitoba, the inclusion of these chemicals in risk indicators would provide a better synopsis of pesticide use trends in Manitoba. One of the challenges with estimating application rates and treatment frequency for insecticides and fungicides is that they vary considerably based on the crop and type of pest. The mass of fungicide and insecticides resulting from seed treatments are also challenging because the seeding rate is required. To further estimate the mass of fungicides, insecticides and seed treatments, a survey which examines fungicide and insecticide application rates and frequency, as well as seeding rates associated with crops that utilize seed treatments would be beneficial. In addition to the pesticide use information provided in the MASC data set, information on application rate and frequency could be obtained from producer surveys and further used to develop a set of equations (pesticide transfer functions) that relate the mass of pesticides applied as a

function of area. These transfer functions could possibly be extrapolated to estimate pesticide use masses in other prairie regions such as Alberta and Saskatchewan.

Although the HRIs calculated in Chapter 3 provide a relative means of assessing temporal risk trends, thresholds for the risk indicators need to be developed to provide a better understanding of what is considered reduced risk and whether current risk levels are acceptable. In addition to the HRIs, Pesticide Risk Indicators should also be calculated for fungicides, insecticides, and seed treatments to track temporal changes in risk. Given that the MASC data will no longer be collected after 2012 and the lack of application rate and frequency information available, the area treated should be used to recalculate the HRIs to determine if there is a significant relationship with the HRIs calculated using mass. This would provide an alternate method for tracking changes in risk associated with pesticide use, particularly when mass information is unavailable. Finally, it is recommended that Pesticide Risk Indicators be calculated for all years of available MASC data. This is for assessing past and predicting future temporal trends.

Limitations for Chapters 4 and 5, which studied 2,4-D mineralization in soils include the use of only three slope positions with three or four experimental repetitions, and the limited range in soil moistures and temperatures. More samples from each slope position from different soil-landscapes and a wider range of soil moisture and temperatures would provide more insight into the in-field variability of 2,4-D mineralization and possibly permit the development of a universal set of equations that could be applied to broad classes of soil types. In addition to methodological limitations with microcosm incubation experiments, future contributions to this area should also examine

mineralization of a wider variety of pesticides using fluctuating temperatures and moistures similar to field conditions observed during the Canadian Prairie growing season. This could be done using growth chambers to regulate temperatures as well as in-field studies which look at fluctuation temperatures and further developing a set of heat units which could potentially predict pesticide fate more accurately.

6.4 Contribution to Knowledge

The first component of this study (Chapters 2 and 3) was the first study to utilize Crop Insurance Records from Manitoba Agricultural Services to summarize pesticide use in Manitoba by calculating the area treated with herbicides, fungicides, and insecticides. This study determined that crop insurance records are a valuable source of pesticide use information because it provides details as to the type of crop and product formulation applied and covers more than 80% of crops grown in Manitoba. This data provides pertinent information on pesticide use trends that would be of interest to government agencies at the provincial and federal level, as well as agrochemical companies.

This was also the first study to calculate the mass of herbicides applied using specific crop and product formulation rates, and to calculate a series of Herbicide Risk Indicators (HRI) for Manitoba. The HRIs provide a relative measure as to how changes in agricultural cropping practices are affecting the types of herbicides being used, and could further be used to design and evaluate pesticide risk reduction programs. This study also revealed that the area treated by pesticides and the mass of herbicides applied annually between 1996 and 2006 have neither increased nor decreased, but the types of pesticides

being applied have changed. In particular, based on the risk indicators calculated in this study, less toxic and less environmentally harmful herbicides such as GLY and GLU have increased significantly, replacing more toxic and persistence herbicides such as clopyralid, ethalfluralin, and trifluralin. While this can be seen as a beneficial outcome from the rapid adoption of GMHT-canola, attention should be paid to more recent studies providing evidence of the mobility of GLY in the environment and the need for including GLY more often in environmental sample analysis (Chapter 2). Studies that have included GLY in sample analysis have determined that this herbicide is moving from the site of application into the broader environment including surface waters (Humphries 2005; Glozier et al. 2011; Messing et al. 2011).

Chapters 4 and 5 were the first studies to look at 2,4-D degradation variability as a result of four interacting factor: slope position, soil depth within the plough layer, soil moisture, and soil temperature. This research also confirmed previous studies that concluded 2,4-D sorption was positively correlated with organic matter content, which varied according to slope position (Farenhorst et al. 2003; Picton and Farenhorst 2004; Gaultier et al. 2006). A series of site specific degradation rates for each slope position, depth, soil moisture and temperature were developed which can be used to improve on pesticide fate model input data.

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7. APPENDICES

Appendix I. MASC data set unidentified products.

Table 7.1 Products in which insufficient information was available regarding either the type of pesticide (insecticide, herbicide, Fungicide) or application rates.

Product formulation	Type	Active Ingredients	Number of Records (n)	Hectares (ha)
2,4,5-T	I	2,4,5-T	51	2,137
AMIBEN	H	chloramben sodium salt	3	138
ARAMO	H	tepraloxym	5	306
BASFAPON	H	dalapon sodium salt	5	368
BETENAL	H	phenmedipham	8	403
BIOMAL	H	colletotrichum gloeosporioides	6	190
CAN 0 COTE		unknown	1	17
CARBYNE240	H	barban	9	201
COBEX	H	dinitramine	4	84
DLC		unknown	3	282
DY AMINE		unknown	6	259
GUARDSMAN	H	dimethenamid, atrazine	1	127
HOEFLURAN		unknown	4	190
KILMORE	H	2,4-D	1	65
RANDOX	H	allidochlor	8	329
SINOX PE	H	dinoseb	4	158
TOK RM	H	nitrofen	2	71
YELLOW STUFF PE		unknown	1	36
ZINC CHELATE		unknown	64	3,931
Total			122	5,360

Appendix II. Product formulations and active ingredients applied to canola.

Table 7.2 Product formulations and active ingredients applied to canola.

Product	Active Ingredient(s)
ABSOLUTE	clopyralid ,imazamox, imazethapyr
ACCENT	nicosulfuron
ACCORD	quinclorac
ACHIEVE DG	tralkoxydim
ACHIEVE EXTRA GOLD	bromoxynil, MCPA, tralkoxydim
ADVANCE	trifluralin
ALLY	metsulfuron methyl
AMITROL	amitrol
ARROW	clethodim
ASSERT	imazamethabenz
ASSURE	quizalofop p ethyl
ATRAZINE	atrazine
ATTAIN	fluroxypyr, 2,4-D
AVADEX BW	triallate
AVADEX BW & TREFLAN	triallate, trifluralin
BANVEL	dicamba
BASAGRAN	bentazon
BENAZOLIN	dimethylamine
BEYOND	imazamox
BLADEX	cyanazine
BONANZA	trifluralin
BROMOX 450M	bromoxynil, MCPA
BUCTRIL M	bromoxynil, MCPA
CASORON	dichlobenil
CENTURION	clethodim
CHAMPION EXTRA	fenoxaprop p ethyl, thifensulfuron methyl, tribenuron methyl
CHAMPION PLUS	fenoxaprop p ethyl, MCPA, thifensulfuron methyl, 2,4-D
CLEAROUT 41	glyphosate
COMPAS	bromoxynil
CREDIT	glyphosate
CURTAIL M	clopyralid, MCPA
DICHLORPROP D	dichlorprop, 2,4-D
DUAL	metolachlor

Table 7.2 continued

Product	Active Ingredient(s)
DYVEL	dicamba, MCPA
ECLIPSE	clopyralid, glyphosate
EDGE	ethalfluralin
EKKO	atrazine, related triazines, simazine
ELIM	rimsulfuron
ESTAPROP	dichlorprop, 2,4-D
EVEREST	flucarbazone sodium
EXCEL	fenoxaprop p ethyl
EXPRESS	tribenuron methyl
EXPRESS PACK	tribenuron methyl, 2,4-D
FACTOR	glyphosate
FLAX MAX	clopyralid, MCPA, sethoxydim
FORTRESS	trallate, trifluralin
FREEDOM GOLD	quizalofop p ethyl, thifensulfuron methyl
FRONTIER	dimethanamid
FRONTLINE	florasulam, MCPA
FUSILADE	fluazifop p butyl
FUSILADE II	fluazifop p butyl
FUSION	fenoxaprop p ethyl, fluazifop p butyl
GLEAN	chlorsulfuron
GLYFOS	glyphosate
GLYPHOSATE	glyphosate
GRAMOXONE	paraquat
GRAMOXONE PDQ	diquat, paraquat
HARMONY TOTAL	clodinafop propargyl, thifensulfuron methyl, tribenuron methyl
HARVEST	glufosinate ammonium
HOEGRASS	diclofop methyl
HOEGRASS 284	diclofop methyl
HOEGRASS II	bromoxynil, diclofop methyl
HORIZON	clodinafop propargyl
KERB	propyzamide
LADDOK	atrazine, bentazon
LASER	bromoxynil, fenoxaprop p ethyl, MCPA
LEXONE DF LEXONE L	metribuzin
LIBERTY	glufosinate ammonium

Table 7.2 continued

Product	Active Ingredient(s)
LONTREL	clopyralid
LOROX L	linuron
MARKSMAN	atrazine, dicamba
MATAVEN	flamprop m methyl
MATAVEN L	flamprop m methyl
MAVERICK	glyphosate
MCPA AMINE	MCPA amine
MECOPROP	mecoprop
MIRAGE	dicamba, MCPA , mecoprop
MUSTER	ethametsulfuron methyl
MUSTER GOLD	ethametsulfuron methyl, quizalofop p ethyl
ODYSSEY	imazamox, imazethapyr
ODYSSEY DLX	imazamox, imazethapyr, tepraloxym
PAR III	dicamba, mecoprop, 2,4-D
PARDNER	bromoxynil
PINNACLE	thifensulfuron methyl
PLATINUM	MCPA
POAST	sethoxydim
PRE PASS	florasulam, glyphosate
PRESTIGE	clopyralid, fluroxypyr, MCPA
PREVAIL	clopyralid, MCPA, tralkoxydim
PRISM	rimsulfuron
PUMA	fenoxaprop p ethyl
PUMA ONEPASS	bromoxynil, fenoxaprop p ethyl, MCPA
PUMA SUPER	fenoxaprop p ethyl
PURSUIT	imazethapyr
PURSUIT ULTRA	imazethapyr, sethoxydim
REFINE	thifensulfuron methyl
REFINE EXTRA	thifensulfuron methyl, tribenuron methyl
REFLEX	fomesafen
REGLONE	diquat
RENEGADE	glyphosate
RIVAL	trifluralin
ROUNDUP	glyphosate
ROUNDUP FASTFORWARD	glufosinate ammonium, glyphosate

Table 7.2 continued

Product	Active Ingredient(s)
ROUNDUP LOW RATE	glyphosate
RUSTLER	dicamba, glyphosate
SABRE	MCPA
SELECT	clethodim
SELECT BUCTRIL VIRTUAL PAK	bromoxynil, clethodim, MCPA
SENCOR	metribuzin
SOLO	imazamox
SPECTRUM	clopyralid, florasulam, MCPA
STAMPEDE	propanil
STAMPEDE EDF	propanil
SUNDANCE	sulfosulfuron
TARGET	dicamba, MCPA, mecoprop
TCA SOLUTION	TCA
TELAR	chlorsulfuron
THUMPER	bromoxynil, 2,4-D
TORCH	bromoxynil
TOUCHDOWN	glyphosate
TREFLAN	trifluralin
TREFLAN HALF RATE	trifluralin
TRIFLURALIN	trifluralin
TRIFLUREX	trifluralin
TRIUMPH PLUS	fenoxaprop p ethyl, MCPA, thifensulfuron methyl
TROPOTOX	MCPB
TURBOPROP	dichlorprop, 2,4-D
2,4-D	2,4-D
TWFOURD AMINE	2,4-D
TWFOURD LVESTER	2,4-D
ULTIM	nicosulfuron, rimsulfuron
VANTAGE	glyphosate
VENTURE	fluazifop p butyl
VICTOR	glyphosate

Appendix III. Herbicide Intensity

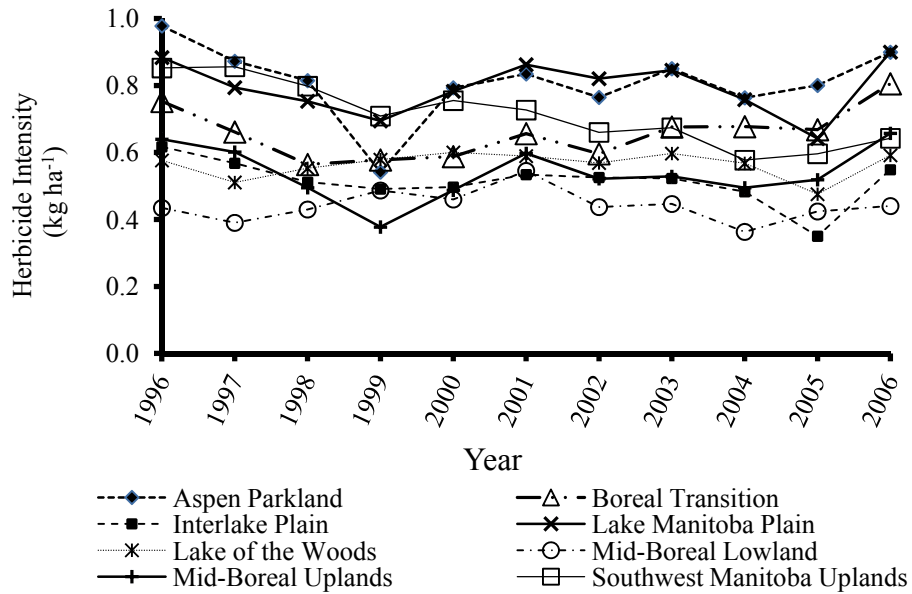


Figure 7.1 Herbicide intensity (kg ha⁻¹) use at the ecoregion level.

Appendix IV. Herbicide Properties Database (HPDB)

Table 7.3 Herbicide Properties Database (HPDB) – physicochemical properties.

Active Ingredient	Chemical Group	Mode of Action	Classification		Kow pH 7 20°C	Water Solubility 20°C (mg l ⁻¹)	Vapour pressure 25° C [mPa]	Henry's law constant 25°C [Pa m ³ mol ⁻¹]	DT ₅₀ typical [days]	KOC ml/g	GUS
			Classification								
			US EPA	WHO							
acifluorfen	nitrophenyl ether	14	No Con.	II	15	250,000	0.133	8.31X 10 ⁻¹³	54	113	3.4
alachlor	chloroacetamide	15	III	II	1230	240	2.9	3.20 X 10 ⁻³	14	124	2.2
amitrol	triazole	11	IV	U	0	264,000	0.033	1.76 X 10 ⁻⁸	18	111	2.5
asulam	carbamate	18	IV	III	1	962,000	0.192	1.73 X 10 ⁻⁷	9	20	2.6
atrazine	triazine	5	III	III	501	35	0.039	1.50 X 10 ⁻⁴	75	100	3.8
bentazon	benzothiazinone	6	III	II	0	570	0.17	7.20 X 10 ⁻⁵	13	51	2.6
bromoxynil	hydroxybenzoxynil	6	II	II	11	90	0.17	5.30 X 10 ⁻⁴	1	174	0.0
chlorsulfuron	sulfonylurea	2	IV	U	0	12,500	3.07 X 10 ⁻⁶	3.50 x 10 ⁻¹¹	160	36.3	5.4
clethodim	cyclohexanedione	1	III	na	13,800	5,450	1.00 X 10 ⁻²	3.50 X 10 ⁻⁶	3	22.7	1.3
clodinafop propargyl	aryloxyphenoxypropionate	1	No Con.	NL	7,940	4	3.19 X 10 ⁻³	2.79 X 10 ⁻⁴	0.8	1,466	-0.1
clopyralid	pyridine compound	4	IV	III	0	143,000	1.36	1.80 x 10 ⁻¹¹	34	5	5.1
cyanazine	triazine	5	II, III	II	126	171	0.000213	6.60 X 10 ⁻⁶	16	190	2.1
desmedipham	bis-carbamate	5	III	U	2,450	7	0.000041	4.30 X 10 ⁻⁷	8	10,542	0.0
dicamba	benzoic acid	4	III	II	0	250,000	1.67	1.00 X 10 ⁻⁴	8	2.64	3.2
dichlobenil	benzoxynil	20	III	III	501	21.2	0.00014	1.317	70	237	3.0
dichlorprop	aryloxyalkanoic acid	4	III	II	195	350	0.01	8.80 X 10 ⁻⁶	10	170	1.8
diclofop methyl	aryloxyphenoxypropionate	1	III	II	63,100	0.39	0.46	0.219	1	20,869	0.0
difenzoquat	unclassified	8	I	II	0	765,000	0.01	5.70 X 10 ⁻¹¹	90	30,000	-0.9

Table 7.3 continued

Active Ingredient	Chemical Group	Mode of Action	Classification		K _{ow} pH 7 20°C	Water Solubility 20°C (mg l ⁻¹)	Vapour pressure 25° C [mPa]	Henry's law constant 25°C [Pa m ³ mol ⁻¹]	DT ₅₀ typical [days]†	K _{oc} ml/g	GUS
			US EPA	WHO							
dimethanamid	chloroacetamide	15	II	II	158	1,200	0.37	8.60 X 10 ⁻³	13	108	2.2
dimethylamine	benzothiazolone	Un-known	No Con.	III	22	500	1.00 X 10 ⁻⁴	4.87 X 10 ⁻⁸	21†	36	3.2
diquat	bipyridylum	22	II	II	0	718,000	1.00 X 10 ⁻³	5.00 X 10 ⁻¹²	1,000	2,000	2.1
endothall	dicarboxylicacid	Un-known	II	II	81	100,000	2.09 X 10 ⁻⁵	3.90 X 10 ⁻¹¹	5	85	1.4
EPTC	thiocarbamate	8	III	II	15,80	370	4500	5.00 X 10 ⁻⁶	6	300	1.2
ethalfluralin	dinitroaniline	3	II	U	129,000	0.01	12	18	45	5,356	0.4
ethametsulfuron methyl	triazinylsulfonyleurea	2	No Con.	NL	8	50	7.70 X 10 ⁻¹⁰	6.34 X 10 ⁻¹²	70	73	3.9
ethofumesate	benzofuran	16	IV	U	501	50	0.65	6.80 X 10 ⁻⁴	70	147	3.4
fenoxaprop p ethyl	aryloxyphenoxypropionate	1	Na	O	38,000	0.7	5.30 X 10 ⁻⁴	2.74 X 10 ⁻⁴	0.4	1,1354	0.0
flamprop m methyl	aryaminopropionic acid	25	Na	III	794	18.2	2.39 X 10 ⁻⁴	4.32 X 10 ⁻⁷	63†	280	2.8
florasulam	triazolopyrimidine	4	No Con.	U	0	6,360	0.01	4.35 X 10 ⁻⁷	8.5	22	2.5
fluzafop p butyl	aryloxyphenoxypropionate	1	III	III	31,600	0.93	0.12	0.056	1	3394	0.0
flucarbazone sodium	triazolone	2	No Con.	U	0	44,000	1.00 X 10 ⁻⁶	1.00 X 10 ⁻¹¹	17	20	3.3
flumetsulam	triazolepyrimidine	2	III	U	2	5,650	3.70 X 10 ⁻⁷	2.00 X 10 ⁻¹⁴	45	28	4.2
fluroxypyr	pyridine compound	4	No Con.	U	1	6,500	3.80 X 10 ⁻⁶	1.10 X 10 ⁻⁸	3	66	1.0
fomesafen	organochlorine	14	III	II	0	50	4.00 X 10 ⁻³	2.00 X 10 ⁻⁷	86	50	4.5
foramsulfuron	pyrimidinylsulfonyleurea	2	III	NL	0	3293	4.20 X 10 ⁻⁹	5.80 X 10 ⁻¹²	5.5	78	1.6
glufosinate ammonium	phosphinic acid	10	III	II	0	500,000	0.0131	4.48 X 10 ⁻⁹	7.4	755	1.0
glyphosate	phosphonoglycine	9	III	III	0	10,500	0.0131	2.10 X 10 ⁻⁷	12	21,699	-0.4

7.3 continued

Active Ingredient	Chemical Group	Mode of Action	Classification		K_{ow} pH 7 20°C	Water Solubility 20°C (mg l ⁻¹)	Vapour pressure 25°C [mPa]	Henry's law constant 25°C [Pa m ³ mol ⁻¹]	DT ₅₀ typical [days]†	K _{oc} ml/g	GUS
			US EPA	WHO							
hexazinone	triazinone	5	II	II	15	33,000	0.03	1.10 X 10 ⁻⁷	105	54	4.6
imazamethabenz	imidazolinone	2	III	U	35	1,114	1.50 X 10 ⁻³	5.05 X 10 ⁻⁷	47	35	4.1
imazamox	imidazolinone	2	No Con.	NL	229,000	626,000	0.0133	9.76 X 10 ⁻⁷	25	67	3.0
imazethapyr	imidazolinone	2	III	U	31	1,400	1.33 X 10 ⁻²	1.30 X 10 ⁻²	90	52	4.5
isoxaflutole	isoxazole	27	III	NL	209	6.2	1.00 X 10 ⁻³	1.87 X 10 ⁻⁵	2	112	0.6
linuron	urea	7	Na	III	1,000	63.8	5.1	2.00 X 10 ⁻⁴	48	620	2.0
MCPA	aryloxyalkanoic acid	4	III	II	0	29,390	0.4	5.50 X 10 ⁻⁵	15	74	2.5
MCPB	aryloxyalkanoic acid	4	III	II	21	4,400	0.004	3.00 X 10 ⁻⁵	7	108	2.5
mecoprop	aryloxyalkanoic acid	4	III	II	1	250,000	1.6	2.20 X 10 ⁻⁴	8.2	31	2.5
metolachlor	chloroacetamide	15	III	III	2,510	530	1.7	2.40 X 10 ⁻³	90	200	1.7
metribuzin	triazinone	5	III	II	45	1,165	0.121	2.00 X 10 ⁻⁵	11.5	38	2.3
metsulfuron methyl	sulfonylurea	2	III	U	0	2,790	1.10 X 10 ⁻⁷	4.50 X 10 ⁻¹¹	10	39.5	3.3
nicosulfuron	sulfonylurea	2	IV	U	4	7,500	8.00 X 10 ⁻⁷	1.48 X 10 ⁻¹¹	26	21	2.6
oxyfluorfen	diphenyl ether	14	IV	II	72,400	0.116	0.026	0.02382	35	12,233	2.4
paraquat	bipyridylum	22	No Con.	U	0	620,000	0.01	4.00 X 10 ⁻¹²	3,000	1 X 10 ⁶	3.8
phenmedipham	bis-carbamate	5	IV	U	3,890	1.8	7.00 X 10 ⁻⁷	5.00 X 10 ⁻⁸	18	888	-0.1
picloram	pyridine compound	4	I	U	0	560	8.00 X 10 ⁻⁵	3.00 X 10 ⁻⁷	82.8	35	-7.0
pinoxaden	unclassified	1	No Con.	NL	1,580	200	4.60 X 10 ⁻⁴	9.20 X 10 ⁻⁷	0.5	323	1.3
propanil	anilide	7	III	II	195	95	0.02	1.74 X 10 ⁻⁴	2	400	4.7

Table 7.3 continued

Active Ingredient	Chemical Group	Mode of Action	Classification		K_{ow} pH 7 20°C	Water Solubility 20°C (mg l ⁻¹)	Vapour pressure 25° C [mPa]	Henry's law constant 25°C [Pa m ³ mol ⁻¹]	DT ₅₀ typical [days]†	K _{oc} ml/g	GUS
			US EPA	WHO							
propyzamide	benzamide	15	IV	U	2,000	9	0.0267	7.60 X 10 ⁻⁴	47	840	-0.4
pyridate	phenylpyridazine quinolinecarboxylic acid	6	III	III	3	1.49	0.000998	1.21 X 10 ⁻⁴	5	55	0.4
quinclorac	aryloxyphenoxy- propionate	4	III	III	0	0.065	0.01	3.72 X 10 ⁻²	450	50	1.8
quizalofop p ethyl	aryloxyphenoxy- propionate	1	Na	II	40,700	0.61	1.10 X 10 ⁻⁴	6.70 X 10 ⁻⁵	2	1816	1.6
rimsulfuron	sulfonylurea	2	III	U	0	7,300	8.90 X 10 ⁻⁴	8.30 X 10 ⁻⁸	24.3	47	6.1
sethoxydim	cyclohexadione	1	III	III	45	4,700	0.013	1.39 X 10 ⁻⁶	1.2	100	0.2
simazine	triazine	5	IV	U	200	5	0.00081	5.60 X 10 ⁻⁵	60	130	
sulfosulfuron	sulfonylurea halogenated aliphatic compound	2	III	NL	0	1,627	3.05 X 10 ⁻⁵	8.83 X 10 ⁻⁹	24	33	3.2
TCA	halogenated aliphatic compound	26	III	III	21	120,000	0.01332	1.37 X 10 ⁻³	55	3	0.2
tepraloxymid	cyclohexadione oxime	2	No Con.	NL	2	430	1.10 X 10 ⁻²	8.74 10 ⁶	10	20	3.4
terbacil	uracil	5	IV	U	78	710	0.0625	1.30 X 10 ⁻⁵	115	55	3.4
thifensulfuron methyl	sulfonylurea	2	IV	U	0	2240	9.00 X 10 ⁻¹¹	1.30 X 10 ⁻¹²	4	100	6.1
tralkoxydim	cyclohexadione oxime	1	III	II	126	6.1	3.70 X 10 ⁻⁴	2.00 X 10 ⁻⁵	1.9	120	2.7
triallate	thiocarbamate	8	III	III	11,500	4.1	12	0.89	82	4,301	4.7
tribenuron methyl	sulfonylurea	1	III	U	6	2,040	5.30 X 10 ⁻⁵	1.00 X 10 ⁻⁸	14	31	1.2

Table 7.3 continued

Active Ingredient	Chemical Group	Mode of Action	Classification		K_{ow} pH 7 20°C	Water Solubility 20°C (mg l ⁻¹)	Vapour pressure 25° C [mPa]	Henry's law constant 25°C [Pa m ³ mol ⁻¹]	DT ₅₀ typical [days] †	K _{oc} ml/g	GUS
			US EPA	WHO							
trifluralin	dinitroaniline	3	III, IV	U	18,6000	0.221	9.5	10.2	181	8,765	0.5
2,4-D	alkylchlorophenoxy aryloxyalkanoic	4	II - III	II	0	23,180	0.0187	1.30 X 10 ⁻⁵	10	56	0.7
2,4-DB	acid	4	III	II	22	4,385	9.44 X 10 ⁻³	3.10 X 10 ⁻⁴	16	224	2.9
vernolate	thiocarbamate	8	III	O	6,920	90	1,390	3.13	16	260	0.1

† DT₅₀: typical half-live Mean of all field and laboratory values quoted in the general literature. This is the value normally used in the regulatory modelling studies and is for aerobic conditions (Kegley et al. 2011)

‡ field half-life used

Table 7.4 Eco-toxicological values for mammals and other organisms.

Active	Mammals					Other organisms								
	Acute oral LD ₅₀ [mg kg ⁻¹]	Dermal LD ₅₀ [mg kg ⁻¹ body weight]	Inhalation LC ₅₀ [mg l ⁻¹]	ADI [mg kg ⁻¹ bw day ⁻¹]	invertebrates <i>Daphnia</i> 48 hour EC ₅₀ [mg l ⁻¹]	Birds Acute LD ₅₀ [mg kg ⁻¹]	Fish Acute 96 hour LC ₅₀ [mg l ⁻¹]	Earth-worms Acute 14 day LC ₅₀ [mg kg ⁻¹]	Honey bee Acute 48 hour LD ₅₀ (µg bee ⁻¹)	Aquatic Vascular Plants (<i>lemna gibba</i>) Acute 7 day EC ₅₀ , biomass (mg l ⁻¹)	Fresh-water algae (<i>Selenastrum</i>) Algae EC ₅₀	Skin Irritant	Carcinogen	Eye Irritant
acifluorfen	1,370	2,001	6.9	0.013	28	2,821	54	821 [†]	505	0.23 [†]	261	1	1	1
alachlor	1,200	13,301	1.04	0.01	10	1,536	1.8	387	16	0.01	0.966	0	1	1
amitrol	5,001	2,501	0.439	0.001	6.1	2,151	1,001	449	101	2.5	2.3	0	1	0
asulam	5,001	10,001	1.8	0.36	2	2,001	175	1,004	101	0.27	0.67	1	0	1
atrazine	1,869	3,101	5.8	0.02	85	4,237	4.5	79	100	0.019	0.059	1	1	1
bentazon	500	5,001	5.1	0.1	64	1,140	100	870	200	5.4	10.1	1	0	0
bromoxynil	81	2,001	0.0002	0.01	12.5	217	29.2	45	5	0.033	0.12	0	1	0
chlorsulfuron	5,001	3,401	5.6	0.2	113	5,001	123	751	101	0.0004	0.068	0	1	1
clethodim	1,133	4,168	3.24	0.01	101	1,641	25	454	44	1.9	12.1	1	0	0
clodinafop propargyl	234	2,001	2.33	0.003	0.77	1,363	0.21	197	94.7	1.5	1.7	1	1	1
clopyralid	2,676	5,001	1.01	0.15	100	1,465	101	1,001	99.1	89	30.5	1	1	1
cyanazine	182	2,001	2.46	0.002	49	400	10	600	100	0.051	0.2	0	1	1
desmedipham	5,001	2,001	7.4	0.03	0.45	2,001	0.25	80	26	5.3	0.01	1	1	1
dicamba	1,581	2,001	4.46	0.3	111.7	1,373	101	1,001	101	0.987	1.8	1	1	1
dichlobenil	2,001	2,001	0.25	0.005	6.2	698	7.2	135	11	0.0279	111	0	1	0
dichlorprop diclofop methyl	825	1,401	0.65	0.06	100	504	0.5	1,000	16	0.23 [†]	1100	1	0	1
difenzoquat	373	3,541	0.36	0.001	2.63	4,640	694	400	36	0.23 [†]	0.54	1	1	1

Table 7.4 continued

Active	Mammals					Other organisms								
	Acute oral LD ₅₀ [mg kg ⁻¹]	Dermal LD ₅₀ [mg kg ⁻¹ body weight]	Inhalation LC ₅₀ [mg l ⁻¹]	ADI [mg kg ⁻¹ bw day ⁻¹]	Aquatic invertebrates <i>Daphnia</i> 48 hour EC ₅₀ [mg l ⁻¹]	Birds Acute LD ₅₀ [mg kg ⁻¹]	Fish Acute 96 hour LC ₅₀ [mg l ⁻¹]	Earth-worms Acute 14 day LC ₅₀ [mg kg ⁻¹]	Honey bee Acute 48 hour LD ₅₀ (µg bee ⁻¹)	Aquatic Vascular Plants (<i>lemna gibba</i>) Acute 7 day EC ₅₀ , biomass (mg l ⁻¹)	Fresh-water algae (<i>Selenastrum</i>) Algae EC ₅₀	Skin Irritant	Carcinogen	Eye Irritant
dimethanamid	397	2,001	4.99	0.02	16	1,908	2.6	147	94	0.028	0.062	1	1	0
dimethylamine	5,001	5,001	1.43	0.87	233.4	10,200	27	821 [†]	480	0.23 [†]	16	0	1	0
diquat	214	4,01	0.122	0.008	1.2	83	21	130	13	1.2	0.16	1	0	1
endothall	51	2,001	0.68	0.02	32.5	5000	78	821 [†]		0.23 [†]	50	1	0	1
EPTC	916	2,001	3.8	0.09	14	1000	14	267	0.011	2.9	5.46	1	0	1
ethalfuralin	5,001	2,001	2.81	0.042	1.13	2001	0.136	25	110.9	0.08	0.009	1	1	1
ethametsulfuron methyl	5,001	2,001	5.7	0.87	34	2250	601	1,001	12.6	0.23 [†]	0.421	1	0	1
ethofumesate	5,001	2,001	3.97	0.07	14	2001	11	134	51	51	3.9	0	0	0
fenoxaprop p ethyl	3,151	2,001	1.23	0.01	1.06	2001	0.19	501	200	2.76	0.54	1	1	1
flamprop m methyl	5,001	1,801	21	0.0002	77	1000	4	821 [†]	505	0.23 [†]	6.8	1	0	1
florasulam	5,000	2,001	5	0.05	293	1046	101	1,321	101	0.001	0.009	1	0	1
fluazifop p butyl	2,001	2,001	5.21	0.01	2	3961	3961	501	201	1.5	1.9	0	0	0
flucarbazone sodium	5,001	5,001	5.13	0.36	109	2000	96.7	1,000	200	0.0126	6.4	0	0	1
flumetsulam	5,001	2,001	1.2	1	254	2250	300	1,001	100	0.0021	10.68	1	0	1
fluroxypyr	2,406	2,001	1.01	0.8	101	2001	14.3	1,001	101	12.3	49.8	0	0	0
fomesafen	1,250	1,001	4.97	0.003	330	5000	170	1,000	50	0.23 [†]	0.17	1	0	1
foramsulfuron	5,001	2,001	5.04	0.5	100	2001	101	453	226	0.0007	3.3	1	0	1
glufosinate ammonium	416	2,001	1.26	0.021	668	2001	710	1001	346	1.47	46.5	1	0	1
glyphosate	1,760	2,001	5	0.3	40	2001	38	481	100	12	4.4	1	0	1

Table 7.4 continued

Active	Mammals					Other organisms								
	Acute oral LD ₅₀ [mg kg ⁻¹]	Dermal LD ₅₀ [mg kg ⁻¹ body weight]	Inhalation LC ₅₀ [mg l ⁻¹]	ADI [mg kg ⁻¹ bw day ⁻¹]	Aquatic invertebrates <i>Daphnia</i> 48 hour EC ₅₀ [mg l ⁻¹]	Birds Acute LD ₅₀ [mg kg ⁻¹]	Fish Acute 96 hour LC ₅₀ [mg l ⁻¹]	Earth-worms Acute 14 day LC ₅₀ [mg kg ⁻¹]	Honey bee Acute 48 hour LD ₅₀ (µg bee ⁻¹)	Aquatic Vascular Plants (<i>lemna gibba</i>) Acute 7 day EC ₅₀ , biomass (mg l ⁻¹)	Fresh-water algae (<i>Selenastrum</i>) Algae EC ₅₀	Skin Irritant	Carcinogen	Eye Irritant
hexazinone	1,690	5,001	7.48	0.05	85	2258	320	821 [†]	60	0.072	0.0145	1	0	1
imazamethabenz	5,001	2,001	5.8	0.0625	220	2150	100	123	100	0.23 [†]	89.1	1	0	1
imazamox	5,001	4,001	6.3	9	123	1847	123	902	41	0.011	0.038	1	0	1
imazethapyr	5,001	2,001	3.27	0.44	1,000	2150	340	1,0000	0.1	0.008	71	1	0	1
isoxaflutole	5,001	2,001	5.23	0.02	2.5	2,151	2.7	1,001	101	0.016	0.12	0	1	0
linuron	1,146	2,001	0.85	0.003	0.31	314	3.15	1,001	161	0.017	0.016	1	1	1
MCPA	9,62	4,001	6.37	0.05	191	270	50	325	201	0.051	79.8	1	1	1
MCPB	4,300	2,001	1.15	0.01	55	282	4.3	253	83	37	41	1	1	1
mecoprop	1,166	4,001	12.5	0.01	201	501	240	988	101	40.2	237	1	1	1
metolachlor	1,200	5,051	2.02	0.1	23.5	2,000	3.9	140	111	0.043	57.1	1	1	1
metribuzin	32	5,001	2.05	0.013	49	164	74.6	427	53	0.008	0.02	0	0	0
metsulfuron methyl	5,001	2,001	5	0.22	151	2,511	151	1,001	26	0.0004	0.045	1	0	1
nicosulfuron	5,001	2,001	5.48	2	90	2,001	65.7	1,001	76	0.002	7.8	1	0	1
oxyfluorfen	5,001	5,001	3.72	0.003	0.72	948	0.25	1,001	101	0.0014	2.1	0	1	0
paraquat	110	201	0.6	0.004	4.4	35	19	1,001	10	0.037	0.0002	1	1	1
phenmedipham	8,001	2,001	7	0.03	0.41	2,101	1.71	244	51	0.23	0.086	1	0	0
picloram	4,012	2,001	0.036	0.3	44.2	1,945	8.8	4,476	75	102	60.2	0	0	1
pinoxaden	5,001	2,001	4.64	0.1	5.87	2,251	10.3	1,001	101	3.5	0.91	1	0	1

Table 7.4 continued

	Mammals					Other organisms					Aquatic Vascular Plants (<i>lemna gibba</i>) Acute 7 day EC ₅₀ , biomass (mg l ⁻¹)†	Fresh-water algae (<i>Selenastrum</i>) Algae EC ₅₀ †	Skin Irritant	Carcinogen	Eye Irritant	
	Acute oral LD ₅₀ [mg kg ⁻¹]†	Dermal LD ₅₀ [mg kg ⁻¹ body weight]†	Inhalation LC ₅₀ [mg l ⁻¹]†	ADI [mg kg ⁻¹ bw day ⁻¹]	Aquatic invertebrates <i>Daphnia</i> 48 hour EC ₅₀ [mg l ⁻¹]†	Birds Acute LD ₅₀ [mg kg ⁻¹]†	Fish Acute 96 hour LC ₅₀ [mg l ⁻¹]†	Earth-worms Acute 14 day LC ₅₀ [mg kg ⁻¹]†	Honey bee Acute 48 hour LD ₅₀ (µg bee ⁻¹)†							
Active																
propanil	1,080	5,001	1.25	0.005	4.8	196	2.3	734	240	5.8	0.11	0	1	1		
propyzamide	2,501	2,001	2.1	0.02	6.6	6,600	5.7	174	137	1.4	2.8	1	1	1		
pyridate	3,589	2,001	4.37	0.036	0.83	1,269	2.2	3	101	2.1	2.1	1	0	0		
quinclorac	2,680	2,001	5.2	0.3	29.8	2,000	100	821 [†]	181	0.5	6.53	1	0	1		
quizalofop p ethyl	1,182	5,001	5.8	0.009	0.29	2,001	0.21	501	101	0.098	0.021	0	0	1		
rimsulfuron	5,001	2,001	5.5	0.1	361	2,251	391	1001	101	0.009	0.029	1	0	1		
sethoxydim	2,676	5,001	6.28	0.14	1.5	5,000	170	542	10	0.28	0.64	1	0	1		
simazine	5,001	2,001	5.5	0.005	1.1	4,640	90	1,000	97	0.3	0.04	1	1	1		
sulfosulfuron	5,001	5,001	3	0.24	97	2,251	92	849	26	0.0010	0.221	0	1	1		
TCA	3,200	2,001	365	3.65	3100	4,280	11,000	0	1,141	100	0.23 [†]	8	1	0	1	
tepraloxydim	2,001	2,001	5.1	0.025	7.44	2,000	100	100	25	6.5	78.2	0	1	1		
terbacil	5,001	2,001	4.4	0.0125	65	2,250	46.2	821 [†]	50	0.14	0.042	1	0	1		
thifensulfuron methyl	2,001	2,001	2.02	0.01	98.6	2,000	104	2,001	8.1	0.0013	0.0159	1	0	1		
tralkoxydim	934	2,001	3.6	0.005	176	2,024	7.1	1,001	101	1	5.2	1	1	1		

Table 7.4 continued

Active	Mammals				Other organisms									
	Acute oral LD ₅₀ [mg kg ⁻¹]#	Dermal LD ₅₀ [mg kg ⁻¹ body weight]#	Inhalation LC ₅₀ [mg l ⁻¹]#	ADI [mg kg ⁻¹ bw day ⁻¹]	Aquatic invertebrates <i>Daphnia</i> 48 hour EC ₅₀ [mg l ⁻¹]#	Birds Acute LD ₅₀ [mg kg ⁻¹]#	Fish Acute 96 hour LC ₅₀ [mg l ⁻¹]#	Earth-worms Acute 14 day LC ₅₀ [mg kg ⁻¹]#	Honey bee Acute 48 hour LD ₅₀ (µg bee ⁻¹)#	Aquatic Vascular Plants (<i>lemna gibba</i>) Acute 7 day EC ₅₀ , biomass (mg l ⁻¹)#	Fresh-water algae (<i>Selenastrum</i>) Algae EC ₅₀ #	Skin Irritant	Carcinogen	Eye Irritant
trilalate	1,100	5,001	5.4	0.025	0.091	1,560	0.95	276	101	2.3	0.0022	0	1	0
tribenuron methyl	5,001	5,001	6	0.01	894	2,251	738	1,001	10	0.0099	0.11	1	1	1
trifluralin	5,001	2,001	1.25	0.015	0.245	2,251	0.088	501	101	0.0435	0.0122	0	1	0
2,4-D	469	2,001	1.79	0.05	100	501	100	350	94	0.58	24.2	1	1	1
2,4 DB	877	2,001	2.3	0.02	25	1,545	3.5	1,001	101	68.8	1.2	0	0	0
vernolate	1,500	1,956	8.7 [†]	0.05	1.8	14,500	4.6	821 [†]	11	14	0.54	1	0	1

[†]Value estimated using average value for all available active ingredients

Appendix V. Environmental Impact Quotient (EIQ)

The general equations used to calculate the EIQ values are provided for reference.

Values were obtained online from Kovach et al. (2011):

<http://nysipm.cornell.edu/publications/eiq/>

$$\text{Total EIQ}_{\text{total}} = (\text{EIQ}_{\text{farm}} + \text{EIQ}_{\text{con}} + \text{EIQ}_{\text{ecol}}) / 3$$

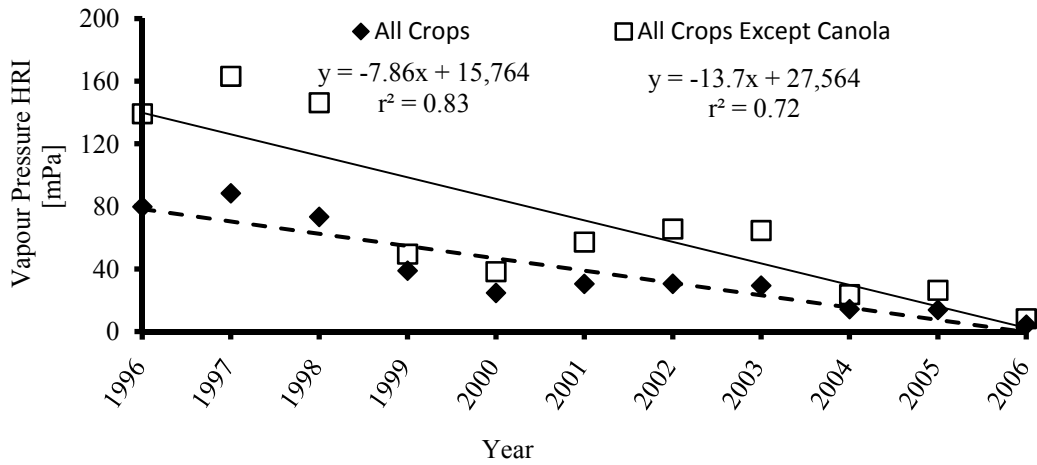
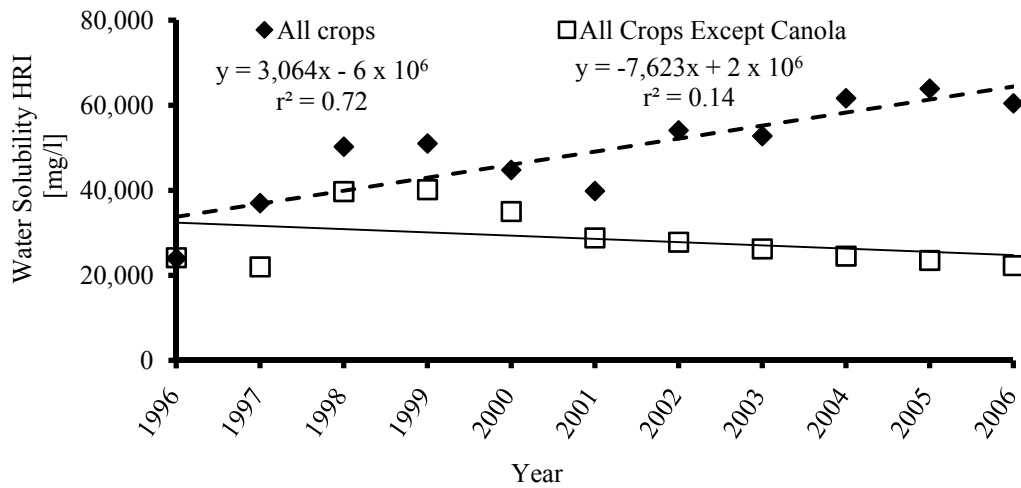
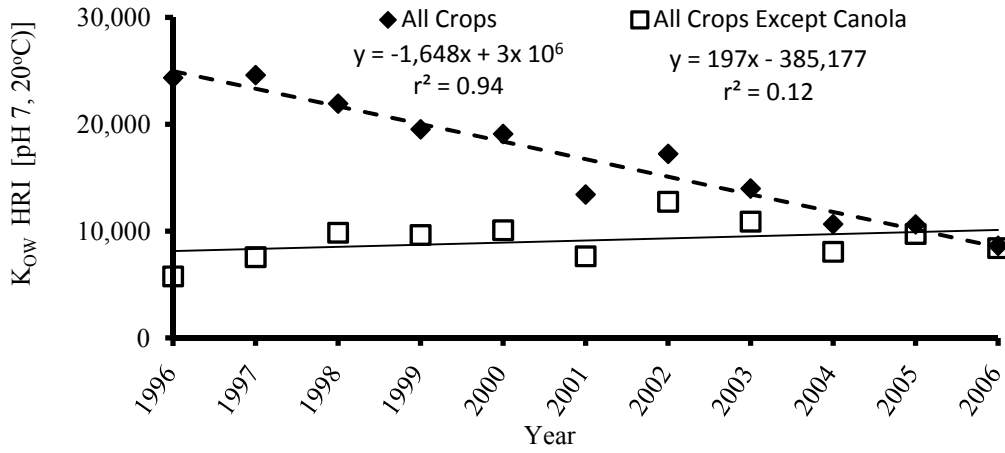
$$\text{EIQ}_{\text{farm}} = \{C[(DT * 5) + (DT * P)]\}$$

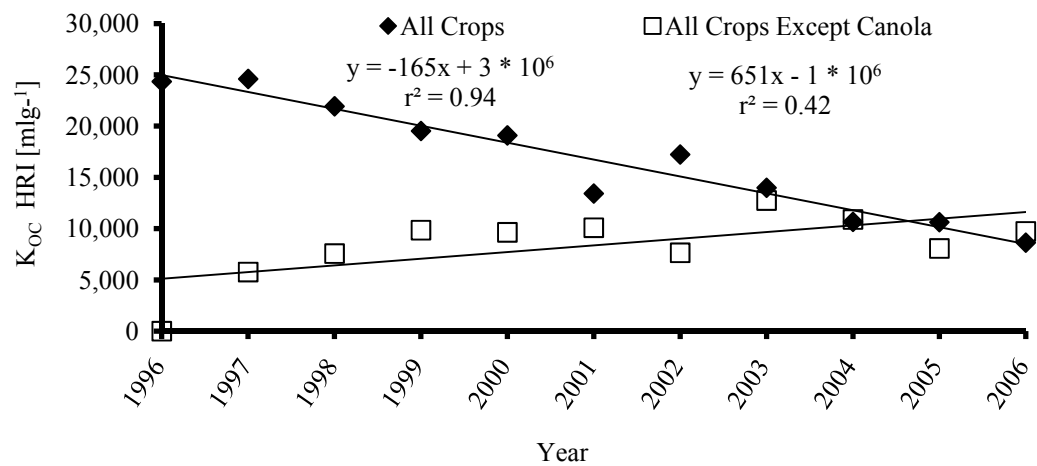
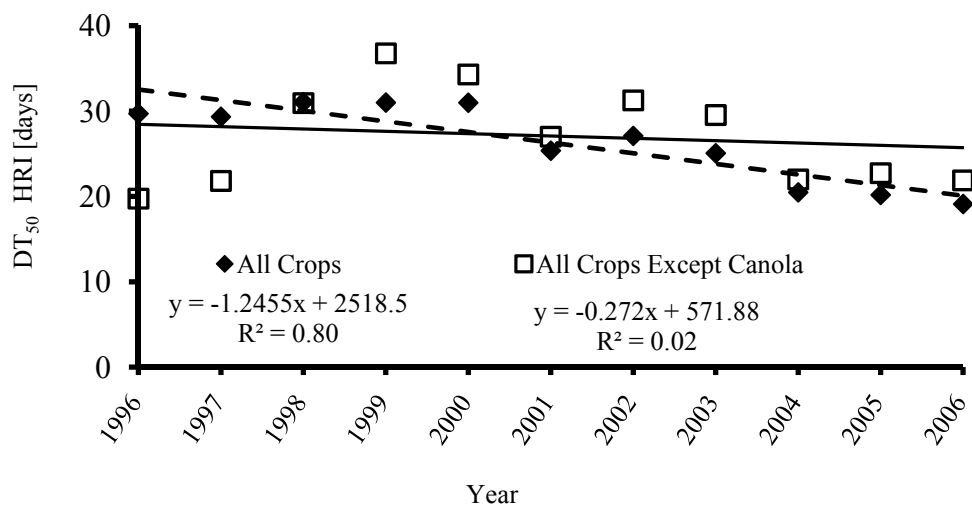
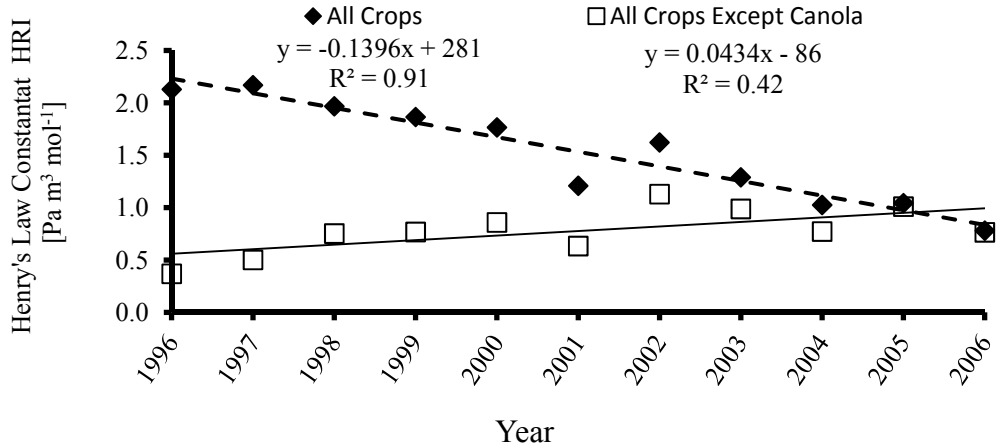
$$\text{EIQ}_{\text{con}} = [(C * ((S + P) / 2) * SY) + (L)]$$

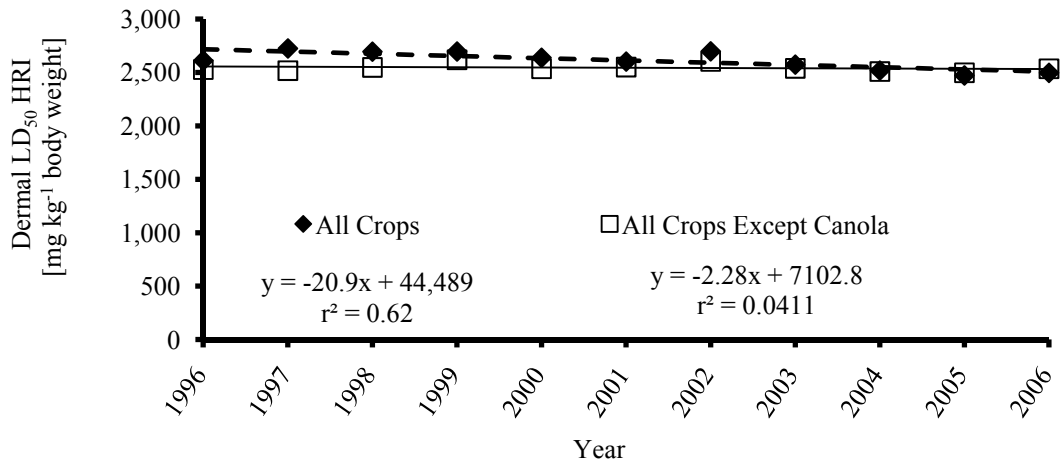
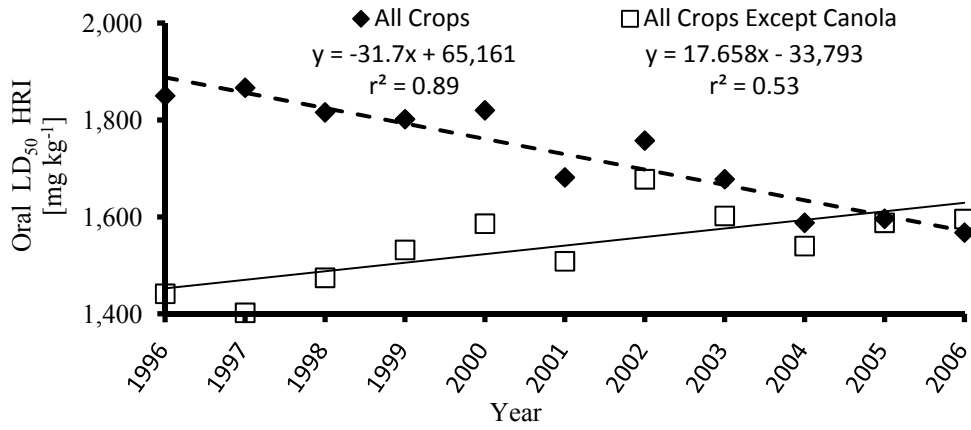
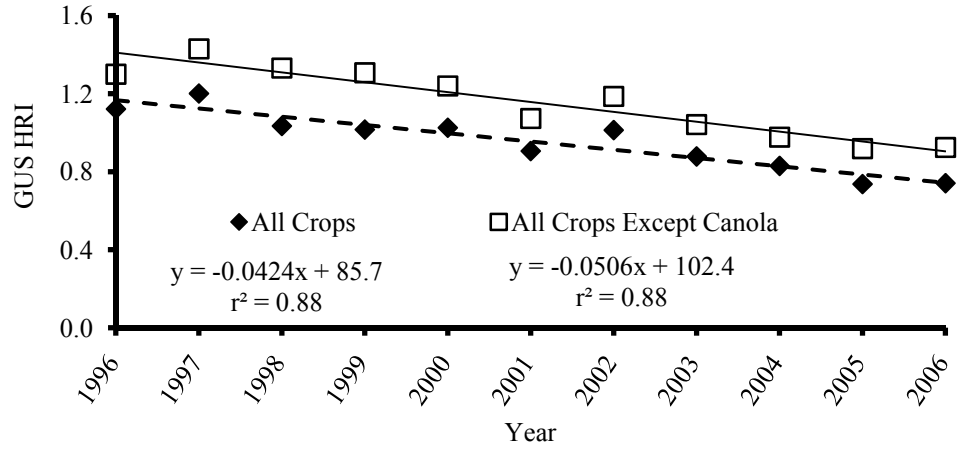
$$\text{EIQ}_{\text{ecol}} = [(F * R) + (D * ((S + P) / 2) * 3) + (Z * P * 3) + (B * P * 5)]$$

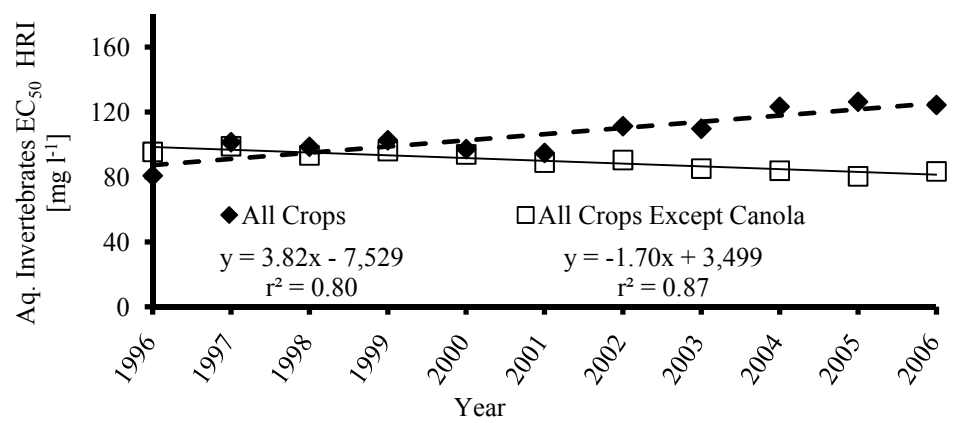
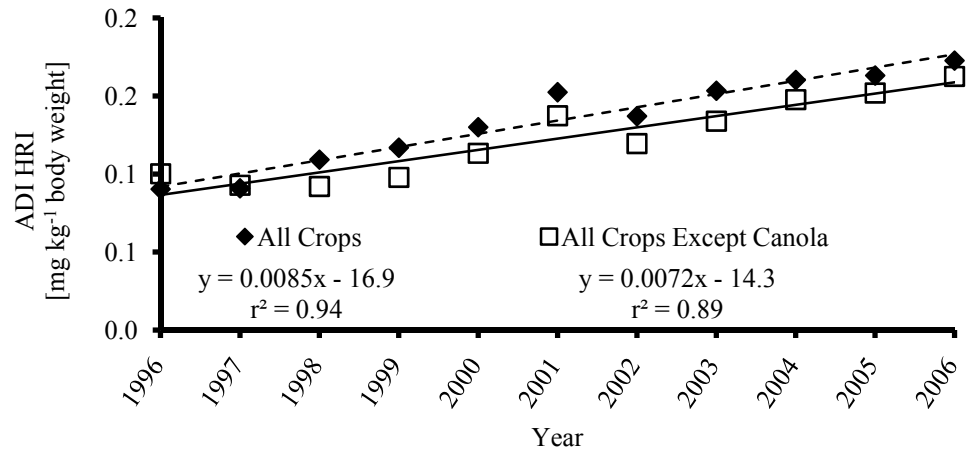
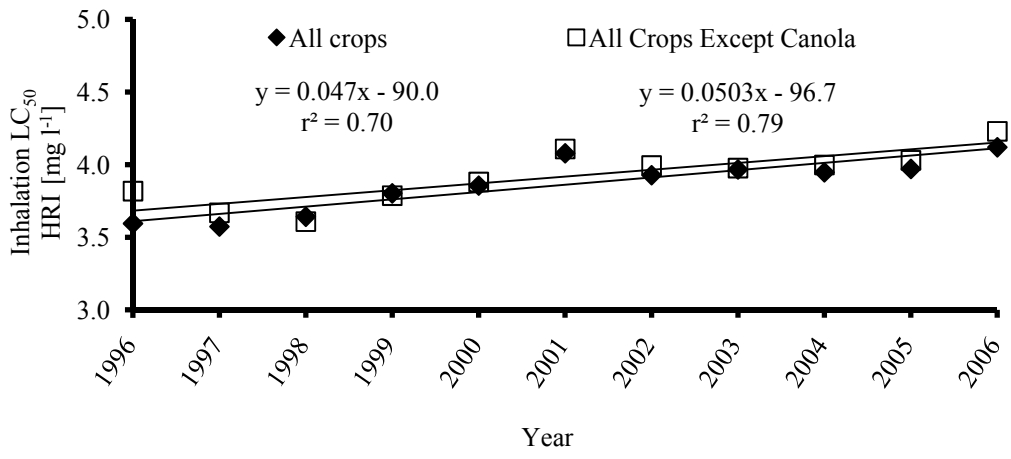
Where:	Index Rating
DT: dermal toxicity	>2000: 1 200 – 2000: 3 0 – 200: 5
C: chronic toxicity	little or none: 1; possible: 3; definite: 5
SY: Systemicity	non-systemic: 1; all herbicides: 1; systemic: 3
F: fish toxicity	> 10 ppm: 1; 1-10 ppm: 3; < 1 ppm: 5
L: leaching potential (ground water and leaching potential)	Small: 1; Medium: 3; Large: 5
R: surface loss potential	
D: bird toxicity	> 1000 ppm: 1; 100-1000 ppm: 3; 1-100 ppm: 5
S: soil residue half-life	DT ₅₀ <30 days: 1; DT ₅₀ =30-100 days: 3; DT ₅₀ >100 days: 5
Z: bee toxicity	relatively nontoxic: 1; moderately toxic: 3; highly toxic: 5
B: beneficial arthropod toxicity	low impact: 1; moderate impact: 3; severe impact: 5
P: plant surface half-life	1-2 weeks: 1; 2-4 weeks: 3; > 4 weeks: 5; pre-emergent herbicides: 1; post-emergent herbicides: 3

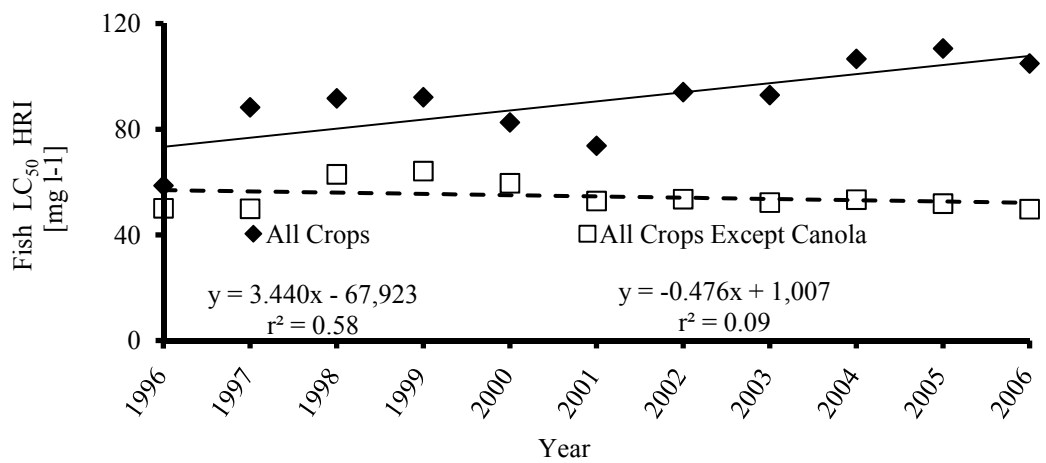
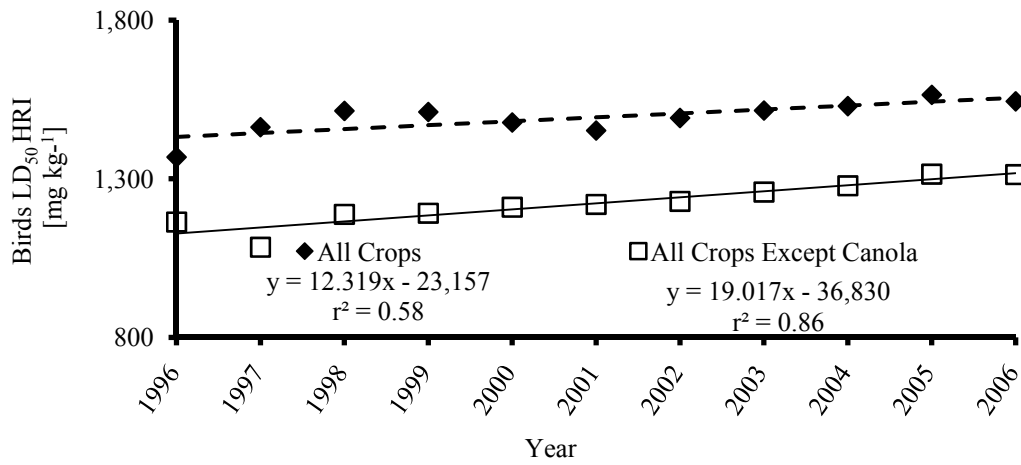
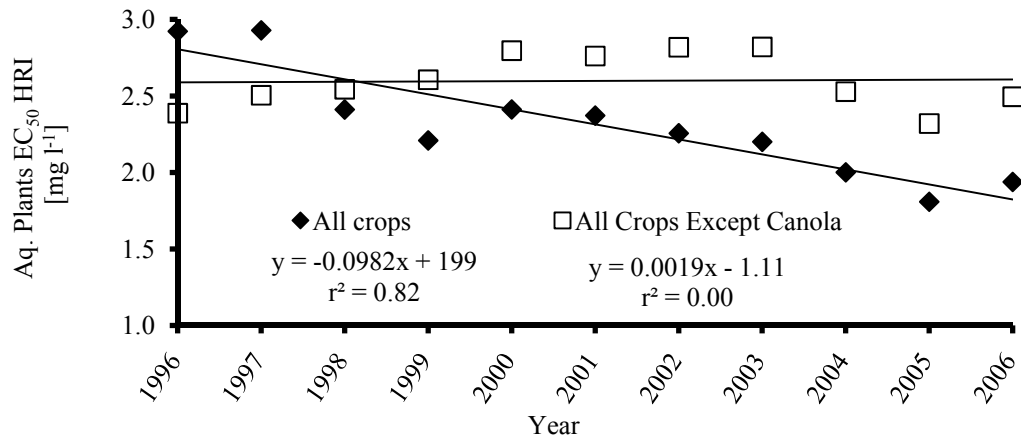
Appendix VI. Regression Equations for Simple Herbicide Risk Indicators
(Table 3.5)

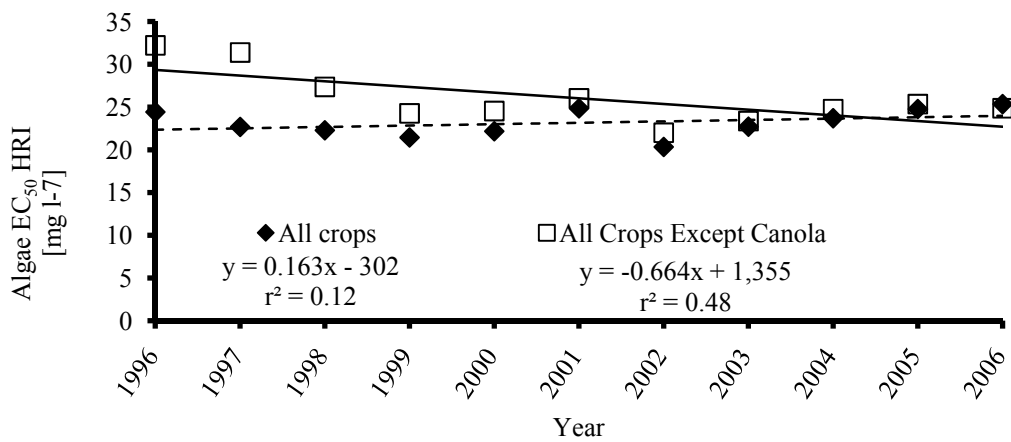
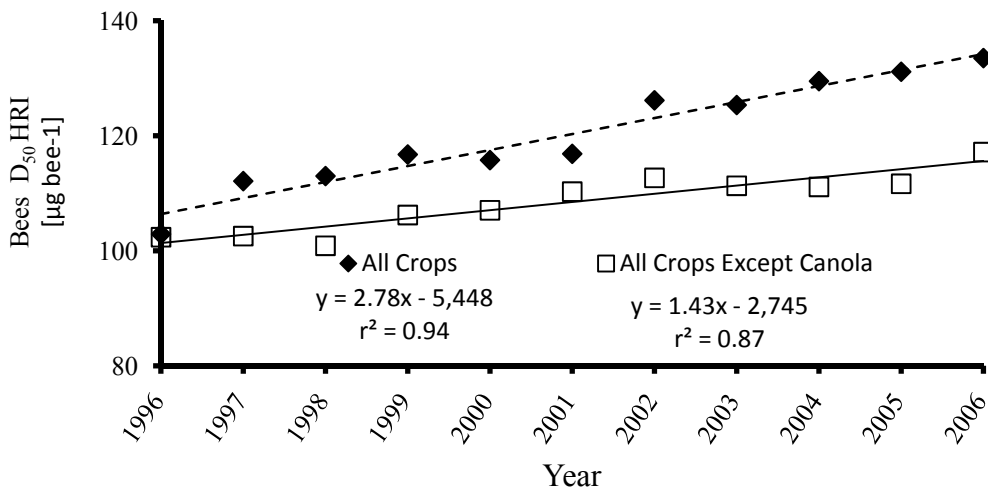
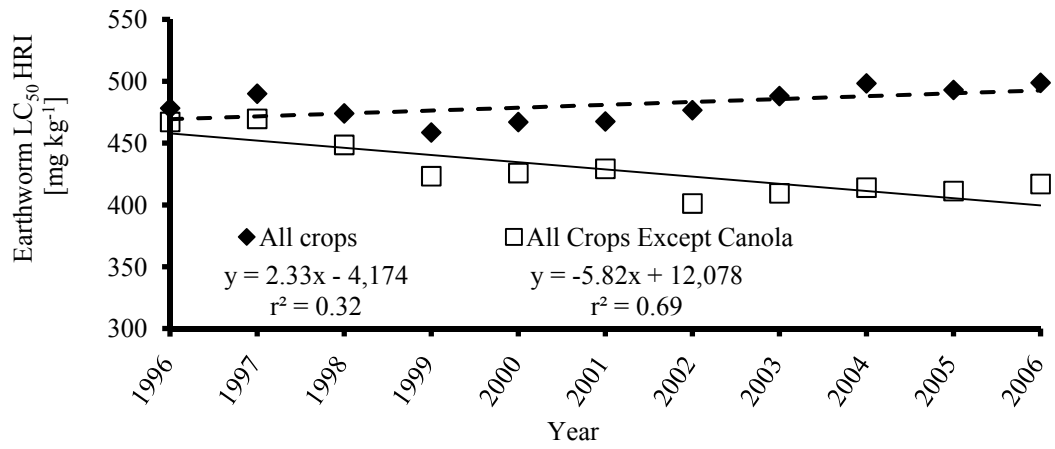












**Appendix VII. Regression Equations for Composite Herbicide Risk Indicators
(Table 3.6)**

