METHODS TO DETERMINE SPATIAL VARIATIONS OF HERBICIDE AND ESTROGEN SORPTION COEFFICIENTS IN UNDULATING TO HUMMOCKY TERRAINS FOR PESTICIDE FATE MODELING AT THE LARGE SCALE

BY

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ABSTRACT

Baljeet Singh, Ph.D. The University of Manitoba, January 2016. Methods to determine spatial variations of herbicide and estrogen sorption coefficients in undulating to hummocky terrains for pesticide fate modeling at the large scale. Major Professor: Annemieke Farenhorst

To reduce the uncertainty associated with pesticide fate model predictions on the large scale, a rapid method is needed that can generate sorption coefficients (K_d values) with sufficient spatial detail. The feasibility of near-infrared spectroscopy (NIRS) to act as such a method was examined, using weak-acidic (2,4-D), weak-basic (atrazine) and zwitterion (glyphosate) herbicides and the natural steroid estrogen (17β-estradiol). A total of 609 horizons in 140 soil profiles were collected in agricultural fields near Brandon, Manitoba and near Saskatoon, Saskatchewan. In both agricultural fields, K_d values in horizons generally increased in the order of 2,4-D < atrazine < 17β-estradiol < glyphosate. Soil organic carbon content (SOC) followed by the soil pH were the major factors controlling the sorption of 2,4-D, atrazine and 17β-estradiol but glyphosate showed very strong sorption to soil particles regardless of measured SOC and soil pH values. For the chemicals studied, K_d values decreased from A to C horizons regardless of the segment of the slope from which the soil samples were collected, with the exception of glyphosate that showed relatively large K_d values in B-horizons illuviated with clay. Both the Zeiss Corona and the Foss 6500 spectrophotometers produced significantly strong predictive models for soil properties and K_d values of 2,4-D, atrazine and 17β-estradiol. However, models for glyphosate K_d values were weak or not significant. Using a test set approach and either soil spectral or soil properties data as independent variables, partial least squares regressions were successfully developed to estimate K_d values for use in the Pesticide Root Zone Model (PRZM) to calculate the herbicide mass leached. The study concluded that the added benefit of NIRS

will be most useful if the pesticides under study have small sorption potentials and short half-lives in soil. Regional approaches to predicting K_d values from NIRS spectral data can also be developed if the calibration model is derived by combining a set of fields where each has a similar statistical population characteristic in K_d values.

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I dedicate my work to my loving grandmother, the late, Ms. Gurdyal Kaur.

FOREWORD

This manuscript style thesis was prepared in accordance with the guidelines of the Department of Soil Science and the Faculty of Graduate Studies, University of Manitoba. Following the general introduction (Chapter 1) are three chapters prepared in a stand-alone, manuscript style format. The final chapter (Overall Synthesis) integrates the research chapters by summarizing the research findings and implications, discussing the research limitations, providing future recommendations, and identifying the contribution to the knowledge of scientific community.

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LIST OF ABBREVIATIONS

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

a.i.: Active ingredient

AAFC: Agriculture and Agri-Food Canada

ANOVA: Analysis of variance

BD: Bulk density

FC: Field Capacity

FOOTPRINT: IUPAC FOOTPRINT Pesticide Properties Database

GLY: Glyphosate

IROWC-Pest: The Indicator of Risk of Water Contamination by Pesticides

K_d : The sorption coefficient

K_{oc}: The sorption coefficient normalized by soil organic carbon content

LSC: Liquid Scintillation Counting

MCPA: 2-methyl-4-chlorophenoxyacetic acid

MCPB: 4-(4-Chloro-2-methylphenoxy)butanoic acid

MZTRA: Manitoba Zero-Tillage Research Association

NAHARP: National Agri-Environmental Health Analysis and Reporting Program

NIRS: Near-Infrared Reflectance Spectroscopy

PLS: Partial Least Square

PRZM: Pesticide Root Zone Model

RER: Ratio of Range in Validation Set to SEP

RPD: Ratio of Standard Deviation of Reference Values in Validation Sample Set to SEP

SDNWA: St. Denis National Wild-Life Research association

SEE: Standard Error of Estimate

SEP: Standard Error of Prediction

SOC: Soil Organic Carbon

SOM: Soil Organic Matter

USDA: United States Department of Agriculture

US-EPA: United States Environmental Protection Agency

1. Introduction

1.1 Pesticide Applications and Implications

Pesticides are especially designed toxic chemical compounds used to mitigate harmful pest populations. Most pesticides are synthetic chemicals that are integral to today's agro-ecosystem because of the role they play in increasing crop productivity by keeping losses from pests to a minimum level. According to recent market estimates, a total of 2.36 billion kg of pesticide active ingredients were used in the world, of which 40% were herbicides (US-EPA 2011). The United States is the country with the largest share in pesticide use, about 22% of the world total use (US-EPA 2011). Health Canada estimates a total of 88 million kg of pesticide active ingredients sales in Canada in 2010 (Health Canada 2010). Agricultural pesticides accounted for about 60 million kg of these sales, with the herbicide glyphosate having the highest sales volume of more than 25 million kg (Health Canada 2010). About 84% of Canadian agricultural pesticide use was in the three Prairie Provinces of Canada (Alberta, Saskatchewan and Manitoba) (Cessna et al. 2010).

Chemical pest control measures are not always beneficial, with rather controversial studies (Pimental 1995, 2005) suggesting that only 0.1% of applied pesticides in the United States reach their intended target pests and the remaining fraction results in environmental contamination that negatively impacts the health of humans and other organisms. It is estimated that pesticide use in the United States alone results in environmental and public health risks

equivalent to $10 billion per year (Pimental, 2005). In contrast, other North American studies calculated that the movement of pesticides from agricultural land to water is only a small fraction of that applied (Gagnon et al. 2014), which seems to agree with the numerous publications that show that the actual concentrations of pesticides in the broader environment tends to be in the parts per trillion to parts per billion range (Table 1.1). Nevertheless, even within these ranges, environmental concentration can exceed toxicological thresholds of non-target species (Farenhorst 2015ab). The Canadian regulatory system sets limits for individual pesticide active ingredient but not for pesticide mixtures even though this is how pesticides are found in the environment. The European Union has a regulatory system which considers pesticide mixtures in water (Dolan et al. 2013). The European maximum limits for pesticides in drinking water intended for human consumption is 0.1 µg L^{-1} for any individual pesticide compound and 0.5 µg L^{-1} for the total pesticide compounds detected in drinking water (Dolan et al. 2013).

Table 1.1 List of studies detecting a given herbicide (# studies) in environmental samples (surface water, groundwater, rain, or air) and the percent of studies that reported detecting that herbicide in their study (% detect). Data retrieved from studies published in refereed journals over a twenty one year time span (1991-2012). All studies focused on the Prairies provinces in Canada (modified from Wilson 2012).

Pesticide	**# studies**	**% detect**	**References Studies**
2,4-D	19	100	Waite et al. 1992, Waite et al. 1995, Anderson et al. 1997, Grover et al. 1997, Wood and Anthony 1997, Donald et al. 1999, Rawn et al. 1999a, Rawn et al. 1999b, Donald et al. 2001, Hill et al. 2002, Waite et al. 2002, Cessna and Elliot 2004, Donald et al. 2005, Yao et al. 2006, Donald et al. 2007, Yao et al. 2008, Environment Canada 2011, Messing et al. 2011, Glozier et al. 2012
2,4-DB	4	67	Wood and Anthony 1997, Donald et al. 1999, Hill et al. 2002, Glozier et al. 2012

Alachlor	3	67	Rawn et al. 1999a, Yao et al. 2006, Messing et al. 2011
Atrazine	7	83	Wood and Anthony 1997, Donald et al. 1999, Hill et al. 2002, Yao et al. 2006, Donald et al. 2007, Yao et al. 2008, Messing et al. 2011
Bromoxynil	15	100	Waite et al. 1992, Waite et al. 1995, Grover et al. 1997, Wood and Anthony 1997, Donald et al. 1999, Donald et al. 2001, Hill et al. 2002, Cessna and Elliot 2004, Donald et al. 2005, Yao et al. 2006, Donald et al. 2007, Yao et al. 2008, Environment Canada 2011, Messing et al. 2011, Glozier et al. 2012
Clopyralid	6	100	Hill et al. 2002, Cessna and Elliot 2004, Donald et al. 2007, Environment Canada 2011, Messing et al. 2011, Glozier et al. 2012
Dicamba	17	100	Waite et al. 1992, Waite et al. 1995, Anderson et al. 1997, Grover et al. 1997, Wood and Anthony 1997, Donald et al. 1999, Donald et al. 2001, Hill et al. 2002, Cessna and Elliot 2004, 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, Glozier et al. 2012
Dichlorprop	11	100	Wood and Anthony 1997, Donald et al. 1999, Rawn et al. 1999a, Rawn et al. 1999b, Donald et al. 2001, Hill et al. 2002, Cessna and Elliot 2004, Donald et al. 2005, Donald et al.2007, Yao et al. 2008, Glozier et al. 2012
Diclofop-methyl	3	80	Anderson et al. 1997, Donald et al. 2001, Cessna and Elliot 2004
Ethalfluralin	7	83	Rawn et al. 1999a, Hill et al. 2002, Cessna and Elliot 2004, Yao et al. 2006, Yao et al. 2008, Environment Canada 2011, Messing et al. 2011
Ethametsulfuron methyl	1	100	Donald et al. 2007
Fenoxaprop-p-ethyl	3	67	Anderson et al. 1997, Hill et al. 2002, Cessna and Elliot 2004
Glufosinate ammonium	2	50	Messing et al. 2011, Glozier et al. 2012
Glyphosate	3	100	Humphries et al. 2005, Messing et al. 2011, Glozier et al. 2012
Imazamethabenz	3	100	Anderson et al. 1997, Donald et al. 2001, Donald et al. 2007
Imazethapyr	2	100	Hill et al. 2002, Donald et al. 2007
MCPA	17	100	Anderson et al. 1997, Grover et al. 1997, Wood and Anthony 1997, Donald et al. 1999, Rawn et al. 1999a, Rawn et al. 1999b, Donald et al. 2001, Hill et al. 2002, Cessna and Elliot 2004, 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, Glozier et al. 2012
MCPB	5	100	Wood and Anthony 1997, Donald et al. 1999, Donald et al. 2005, Donald et al. 2007, Environment Canada 2011
Mecoprop	7	100	Donald et al. 2001, Hill et al. 2002, Cessna and Elliot 2004, Donald et al. 2007, Environment Canada 2011, Messing et al. 2011, Glozier et al. 2012
Metolachlor	6	100	Wood and Anthony 1997, Rawn et al. 1999a, Yao et al. 2006, Yao et al. 2008, Environment Canada 2011, Messing et al. 2011
Metribuzin	4	100	Cessna and Elliot 2004, Donald et al. 2005, Donald et al. 2007, Environment Canada 2011
Metsulfuron-methyl	2	100	Donald et al. 2007, Environment Canada 2011
Picloram	5	100	Anderson et al. 1997, Wood and Anthony 1997, Donald et al. 2005, Donald et al. 2007, Environment Canada 2011
Quinclorac	1	100	Hill et al. 2002
Simazine	3	100	Wood and Anthony 1997, Donald et al. 2007, Environment Canada 2011
Sulfosulfuron	2	100	Donald et al. 2007, Environment Canada 2011
Thifensulfuron methyl	2	100	Donald et al. 2007, Environment Canada 2011
Triallate	13	100	Waite et al. 1992, Waite et al. 1995, Anderson et al. 1997, Grover et al. 1997, Wood and Anthony 1997, Rawn et al. 1999a, Hill et al. 2002, Cessna and Elliot 2004, Yao et al. 2006, Donald et al. 2007, Yao et al. 2008, Environment Canada 2011, Messing et al. 2011
Tribenuron-methyl	1	100	Donald et al. 2007
Trifluralin	15	93	Waite et al. 1992, Anderson et al. 1997, Grover et al. 1997, Wood and Anthony 1997, Donald et al. 1999, Rawn et al. 1999a, Donald et al. 2001, Cessna and Elliot 2004, 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

In order to control pest populations, pesticides are generally applied in standing crops (post-emergence), or incorporated into the soil (pre-emergence). Pesticides may move to broader environments, with the amount depending on many factors, for example, pesticide physio-

chemical characteristics and interactions with plant surfaces and the soil matrix (Gonzalez et al. 2010). Pesticides may move into the atmosphere because of application drift (Caldwell 2007), post volatilization losses from soils, water or crop surface (Grover et al. 1985), and due to wind erosion of surface soils (Larney et al. 1999). Both atmospheric dry deposition (settling dust particles) and wet deposition (precipitation) contributes to pesticide loadings into surface water sources (Hill et al. 2003, Jantunen et al. 2008, Messing et al. 2011). Pesticides movement from agricultural soils to surface water can also occur by rainfall or snowmelt induced surface runoff (Nicholaichuk and Grover 1983, Brown et al. 1995, Dabrowski et al. 2002, Donald et al. 2005, Ensminger et al. 2013). Movement of pesticides through the soil profile by leaching could result in ground water contamination (Waite et al. 1992, Koplin et al. 1998, Elliot et al. 2000).

Despite the human health and environmental concerns expressed in current scientific literature and popular media, pesticides are still considered to be a vital component of today's pest control measures, particularly in large-scale agriculture in developed and emerging economies. By 2030, the world population is expected to reach more than 8 billion (World Urbanization Prospects 2012), while the size of arable land per capita is shrinking. Therefore, it is likely that pesticide use will continue to be an important component of agricultural production in future, as the agricultural sector needs to improve crop productivity in all regions of the world. Understanding pesticide fate and transport in the environment can help to develop strategies to reduce pesticide loadings from agricultural land to the broader environment, and hence lessen the potential impact of pesticides on fresh and potable water resources.

1.2 Manure Applications and Implications

Manure is an organic amendment added to agricultural land to improve overall health and quality of soils, and as a replacement or supplement to chemical fertilizers. Statistics Canada (2014) reported more than 25 million livestock animals in Canada in 2010, producing millions of tons of manure every year. Manure is organic waste, mainly consisting of feces and urine and is an important source of both micro and macro nutrients benefiting crop production (Schoenau 2006). It also increases the organic matter content and water holding capacity of soils, and hence can contribute to reduced soil erosion in agricultural areas (Schoenau 2006).

Both crop productivity and soil health can be significantly improved by manure applications. Nevertheless, excessive manure applications may pose a serious risk to surface water sources. For example, nutrients such as nitrogen and phosphorus can move from overloaded soils to the broader environment (Stumborg et al. 2005). Increased nutrient loadings and consequent eutrophication in Lake Winnipeg has been linked to increased livestock production near its southern end (Cicek et al. 2006, Hoffman 2008). Lake Winnipeg is the world's 10th largest freshwater lake, spanning more than 1 million km^2 watershed area. Because of the increased nutrient levels and reoccurring algal blooms in water, Lake Winnipeg was cited as the world's most threatened lake in 2013 (Living Lakes of Canada 2013). More recently, increased algal growth in Lake Erie, Ohio, United States, forced millions of people to stop using the lake's water for recreational purposes due to fears of toxicity (Chung 2014). The increased algae growth was linked to increased phosphorous and other nutrient loadings in water. This resulted from

agricultural runoff in the western basin of the lake, which is characterized by intensive livestock farming and application of livestock waste to agricultural land (Chung 2014).

Estrogenic compounds are excreted as a part of normal vertebrate metabolism and hence both biosolids and livestock manure contain complex mixtures of natural steroid hormones, such as 17β-estradiol, estrone, estriol and equol (Ternes et al. 2002, Furuichi et al. 2006, Muller et al. 2008). The main environmental concern is the presence of low concentration of estrogens in surface water can adversely affect the biology of aquatic vertebrates by inducing male feminization (Casey et al. 2003). 17β-estradiol is among the most potent of estrogens (Casey et al. 2003), and can induce vitellogenesis i.e. the process of egg yolk production in males (Sumpter and Jobling 1995) at a concentration as low as 1.0 ng L^{-1} (Purdom et al. 1994, Routledge et al. 1998, Baronti et al. 2000). Kidd et al. (2007) demonstrated in a 7-year whole lake study that low level (5-6 ng L^{-1}) chronic exposures (2 years) of a synthetic estrogen (17α-ethynylestradiol) can produce up to 12,000 µg g^{-1} of vitellogenin (whole body homogenates, 3 time more than the unexposed) in the male fathead minnow, enough to create a population crash as evidenced by the presence of intersex fish in the experimental lake area in north-western Ontario, Canada. In addition, steroid hormone mixtures are known to act synergistically (Brian et al. 2007, Zhang et al. 2009), hence relative to individual exposures, a significant increase in vitellogenin production was observed in male fathead minnows, when they were exposed to a mixture of estrogenic compounds (17β-estradiol, 17α-ethynylestradiol, 4-tert-nonylphenol, 4-tert-octylphenol, and bisphenol A) (Brian et al. 2007).

The primary source of estrogen contamination in the environment comes from applications of biosolids and livestock manure to the soils (Casey et al. 2003, Matthiessen et al. 2006). Studies of Ternes et al. (2002), Fine et al. (2003) and Andaluri et al. (2012) have reported high levels of 17β-estradiol in liquid swine manure lagoons (e.g., 3,000 ng L^{-1}), sewage sludge (e.g., 49,000 ng Kg^{-1}) and biosolids (e.g., 230,000 ng Kg^{-1}), respectively. Estrogens entering the soil due to applications of manure can move to surface water by runoff (Nichols et al. 1997, Finlay-Moore et al. 2000, Yang et al. 2012) or to groundwater by leaching (Finlay-Moore et al. 2000, Kjaer et al. 2007). Following poultry and cattle manure applications to a grassland watershed in the United States, 17β-estradiol has been found in surface runoff water at concentrations up to 3,500 ng L^{-1} (Nichols et al. 1997), in river water up to 38 ng L^{-1} (Khanal et al. 2006) and in ground water up to 66 ng L^{-1} (Finlay-Moore et al. 2000).

1.3 Chemical Fate and Transport in Soils: Importance of Sorption

The fate and transport of most pesticides and estrogenic compounds in soils is mainly controlled by two major processes i.e. sorption and degradation (Caron et al. 2010ab, Bai et al. 2014, Neumann et al. 2014, Prado et al. 2014). An organic chemical can be transformed from a parent molecule into metabolites due to abiotic and biotic degradation. Mineralization is a biological transformation process resulting in the breakdown of an organic molecule or metabolite into CO_2 and other inorganic chemicals (Cheng 1990). Degradation/mineralization and sorption of organic chemicals in soils operates simultaneously and are complex processes. Sorption increases the concentration of an organic chemical in the solid phase resulting from a

reduction in its concentration in the liquid phase mainly due to sorptive interactions such as Van der Waals-London interactions, hydrophobic binding or charge transfer (Pignatello and Xing 1996, Wauchope et al. 2002). Generally, an increase in soil sorption results in decreased degradation/mineralization as sorption can limit the amount of an organic chemical available (Bio-availability) to microorganisms for transformation (Gaultier et al. 2008a, Caron et al. 2010b), for example, sorption and mineralization of 2,4-D were found negatively correlated in surface soil samples obtained from a hummocky calcareous landscape in Alberta (Gaultier et al. 2008a). Nevertheless, in some agricultural soils, the mineralization of 17β-estradiol occurs particularly when in the sorbed phase (Casey et al. 2003). Caron et al. (2010b) found a significant positive correlation between 17β-estradiol sorption and mineralization.

The importance of sorption and its impact on the persistence of pesticides and estrogens in soils has long been recognized worldwide (Yuen and Hilton 1962, Kookana et al. 1992, Caron et al 2010a, Farenhorst et al. 2010, Vallée et al. 2014). The extent of pesticide sorption onto soil surface is usually determined by conducting a conventional batch equilibrium experiment that generates pesticide sorption coefficients such as the pesticide distribution constant, K_d [L kg^{-1}] (Wauchope et al. 2002). The same procedure is used for other potential contaminants such as estrogens (Caron et al. 2010a). The detailed guidelines on conducting a batch equilibrium process for different types of pesticides and soils can be found in the OECD guidelines for the testing of the chemicals (OECD 2000). Generally, in a batch equilibrium experiment, a known amount of pesticide solution is added into a centrifuge tube containing soil and then the centrifuge tube is gently rotated for 24 hours (the typical time period for most pesticides as

recommended by OECD guidelines) under controlled temperature conditions (Wauchope et al. 2002). The pesticide solution is typically prepared in 0.01 M $CaCl_2$ to minimize soil-mineral disruption (Hinds and Lowe 1980). The detailed experimental procedure used in batch equilibrium process used for the research has been listed under section 3.3.2 (Soil characteristics and herbicide sorption).

Pesticide sorption by soil is a rapid process i.e. most of the added pesticide will be sorbed within minutes to few hours because of abundance of sorption sites, followed by slow sorption over time due to reduced availability of sorption sites (Kookana et al. 1992, Wauchope et al. 2002). Sorption is a continuous process. For example, sorption of imidacloprid, an insecticide, was observed to be increased by 4 folds over a 100 day period (Oi 1999).

The K_d value (L kg^{-1}) for a pesticide is calculated by dividing the amount of pesticide sorbed by soil at equilibrium (C_s, µg kg^{-1}) by the amount of pesticide remaining in the equilibrium solution (C_e, µg L^{-1}) (Wauchope et al. 2002). The higher the K_d value for a pesticide, the greater is its potential to be retained by soil sorption and, for many pesticides, that reduces its bioavailability to microorganisms for degradation (Dyson et al. 2002, Jensen et al. 2004).

The extent of pesticide sorption in soils is affected by a number of soil properties such as soil organic carbon content (Gaultier et al. 2008a, Kasozi et al. 2012), soil pH (De Jong and De Jong 1999, Tulp et al. 2009), soil clay minerals (Villaverde et al. 2008, Borggaard and Gimsing 2008), oxides and hydroxides of Fe^{3+} and Al^{3+} (Li et al. 2003, Borggaard and Gimsing 2008), as well as

soil moisture (Reichman et al. 2011, ElGouzi et al. 2012) and soil temperature (Li et al. 2011, Broznic and Milin 2012). Among the numerous studies that have collected data on pesticide K_d values since the work of Hance (1965), a common conclusion is that, for most pesticides, sorption in soils is largely controlled by soil organic matter. As such, another common expression of the sorption of pesticides by soil is the sorption coefficient normalized by soil organic carbon content, K_{oc} value (L kg^{-1}), whereby $K_{oc} = K_d/f_{oc}$ in which f_{oc} is the fraction of soil organic carbon content, that typically ranges from 1.72 to 2.0 (Wauchope et al. 2002). The K_{oc} value is regarded as a universal measure of the ability of a pesticide to be retained in soil (Xing and Pignatello 1997, Wauchope et al. 2002). There are databases available that list a standard K_{oc} value for each pesticide, for example the IUPAC Footprint database (FOOTPRINT 2006). In risk assessments at the large scale, for a given pesticide, the same K_{oc} value is then used regardless of the soil type.

In the past 75 years, numerous pesticide sorption experiments have been conducted focusing mostly on surface soils (Shipinov 1940, Barlow and Hadaway 1955, Bailey and White 1964, Farenhorst et al. 2008), with a number of studies examining the spatial variability of sorption parameters at field or regional scales (Novak et al. 1997, Ahmad et al. 2001, Gaultier et al. 2008a, Farenhorst et al. 2010). It has now been well established that pesticide K_d values are variable within a single field, and between fields in different regions. For example, K_d values for a herbicide 2,4-D ranged from 0.6 to 12.5 L kg^{-1} (n=72) in surface soil horizon samples collected along a 360 meter transect in an undulating hummocky terrain from Alberta (Gaultier et al. 2006) and from 0.6 to 14.5 L kg^{-1} in surface soil samples (n=41) collected within a series of

agricultural fields spanning a 666,000 km^2 area in Alberta (Gaultier et al. 2008a). Studies on spatial variations in K_d values for a range of pesticides and estrogens are summarized in Table 1.2, The K_d values of pesticides and 17β-estradiol vary between regions and within fields due to variations in soil properties. For pesticides, the reported CV of K_d values has ranged from 7 to 131% at the field-scale and 89 to 161% at the regional scale. Relatively fewer studies have examined the spatial variations in K_d values for 17β-estradiol and in these studies, the reported CV of K_d values has ranged from 47 to 60% at the regional scale (Table 1.2).

Table 1.2 Studies examining the spatial distribution of pesticide and 17β-estradiol sorption parameters. Mean and coefficient of variation (CV%) values as reported in the reference stated. H = horizon, which can be A, B or C horizons, n=number of samples, F=Field, U=upper slopes, M=mid slopes, L=lower slopes. The label A-horizon is treated as synonymous to surface soil. S = subsurface soil which is 40-50 depth in Oliver et al. (2003) and 50-60 cm depth in Rodrigues-Cruz et al. (2006).

Sampling protocol	H	n	K_d [L kg^{-1}] mean	K_d CV%	Reference
2,4-dichlorophenoxyacetic acid					
F transect	A	72	4.21	50	Gaultier et al. 2006
	B	72	0.92	113	
	C	72	0.33	55	
F grid – U	A	98	0.90	44	Farenhorst et al. 2008
F grid – M	A	128	1.00	50	
F grid – L	A	61	1.60	25	
Regional	A	123	5.80	89	Gaultier et al. 2008a
Atrazine					
F grid	A	241	5.20	35	Novak et al. 1997
Catchment	A	51	0.80	29	Coquet and Barriuso 2002
Regional	A	19	2.67	121	Oliver et al. 2003
	S	18	0.84	132	
Bentazone					
F grid	A	20	0.06	26	Rodrıguez-Cruz et al. 2006
	S	20	0.11	44	

Carbaryl					
F grid	A	27	10.50	115	Ahmad et al. 2001
Diuron					
Regional	A	43	9.60	161	Liyanage et al. 2006
Regional	A	101	6.49	140	Forouzangohar et al. 2008
Glyphosate					
F grid – U	A	98	108.20	28	Farenhorst et al. 2008
F grid – M	A	128	133.60	36	
F grid – L	A	61	118.70	29	
Imazethapyr					
F grid	A	35	1.56	69	Oliver et al. 2003
Isoproturon					
Catchment	A	51	0.85	30	Coquet and Barriuso 2002
F grid	A	20	1.32	7	Rodrıguez-Cruz et al. 2006
	S	20	0.34	50	
Mecoprop					
F grid	A	20	0.26	26	Rodrıguez-Cruz et al. 2006
	S	20	0.07	24	
Metamitron					
Catchment	A	51	0.96	30	Coquet and Barriuso 2002
Napropamide					
F grid	A	36	2.01	31	Elabd et al. 1986
Phosalone					
F grid	A	27	172.18	131	Ahmad et al. 2001
17β-Estradiol					
Regional - U	A	41	21.00	60	Caron et al. 2010a
Regional - M	A	39	20.80	49	
Regional - L	A	41	26.90	52	
Regional	A	121	22.80	55	
Regional	A	36	24.65	47	Caron et al. 2010b

1.4 Pesticide Fate Models

Pesticide fate models are generally adopted to estimate the fraction of land applied pesticides moving into broader environment especially water bodies (Dubus et al. 2003, Gagnon et al. 2014). The risks of estrogen transport from manure-amended soils to surface and ground water can also be assessed by using pesticide fate models (Casey et al. 2003, Das et al. 2005). K_d values are considered to be among the most sensitive parameters for use in pesticide fate models (Boesten and Van der Linden 1991, Dubus et al. 2003). Field-specific data on K_d values has been recognized to be more important to the success of pesticide risk assessments at the large scale, than the type of pesticide fate model used to complete the calculations (Dann et al. 2006).

Studies of Dubus et al. (2003) and Farenhorst et al. (2009) have demonstrated that failure to efficiently quantify K_d values for pesticides leads to lack of confidence in the fate model predictions. For example, Farenhorst et al (2009) demonstrated that amount of 2,4-D leaching (g ha^{-1}) can increase to more than 29,000% up to a 15 cm depth, when K_d values from toeslopes soil profiles (0.16 to 1.77 L kg^{-1}) were replaced by K_d values from knoll soil profiles (0.12 to 0.50 L kg^{-1}) in an undulating agricultural field from Minnesota, the United States.

Spatial variations in K_d values of pesticides and estrogens are still poorly understood and difficult to estimate particularly when risk assessments are to be conducted at large scales such as fields, watersheds, and regions. In a pesticide risk assessments, the K_d values would need to

be determined using a batch equilibrium process (Wauchope et al. 2002), which is not practical for a large scale analysis, because the technique is time consuming, expensive, and wasteful especially when a large number of samples need to be processed. Therefore, for large scale pesticide risk analysis, deterministic modeling approaches utilize a pesticide properties database to estimate K_{oc} values for input in the risk assessment (Cessna et al. 2010), and then the pesticide K_{oc} value is multiplied in the model by f_{oc} to derive the K_d value for a simulation unit. The f_{oc} is derived for each simulation unit from a soil database. Alternatively, a deterministic modelling approach can utilize the same soil database to obtain SOC, soil pH, and soil textural values for use in pedotransfer functions that calculate K_d values (Weber et al. 2004). Both methods result in only a crude estimation of K_d values in simulation units, and there is no mechanism to take into account the spatial variability of K_d values within simulation units.

In a stochastic modeling approach, the spatial variability of K_d values can be taken into account using a probability density function (Heuvelink et al. 2010), but without having numerous actual measurements of K_d values, the probability density function is a rather hypothetical curve defined by the model user. Thus, the output of both deterministic and stochastic modeling is known to have large uncertainties especially in large scale analysis at the national scale (Dubus et al. 2003, Heuvelink et al. 2010). Improved sufficient detail on the spatial variability of sorption parameters will reduce uncertainty in pesticide leaching predictions.

Pesticide Root Zone Model (PRZM) version 3.12.2 is a one dimensional simulation model (Carsel et al. 1998), used by scientists and policy-makers in North America and the European Union to

estimate the amount of land-applied pesticides entering ground water and surface water (Stewart and Loague 1999, Eason et al. 2004, Gagnon et al. 2014). This model is being used under the National Agri-Environmental Health Analysis and Reporting Program (NAHARP) of Canada as part of the Indicator of Risk of Water Contamination by Pesticides (IROWC-Pest) (McQueen et al. 2007, Cessna et al. 2010). PRZM is a risk assessment tool to assess the effects of beneficial farm management practices on reducing pesticide transport, and to minimize the possible exposure of non-target organisms to pesticides.

1.5 Near-Infrared Reflectance Spectroscopy

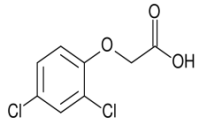
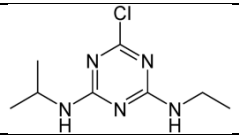
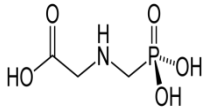
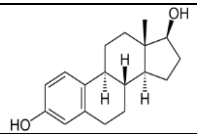
Near-infrared reflectance spectroscopy (NIRS) is a robust analytical technology developed about 50 years ago by Dr. Karl Norris of the United States Department of Agriculture, and subsequently introduced to practical application by Dr. Phil Williams of the Canadian Grain Commission (Williams, 1975). Today, NIRS is well known for its rapid (less than 2 minutes per test), reliable, economical and non-destructive features to measure sample properties. The NIRS technique also offers the possibility of continuous on-line analysis. It has a wide span of applications ranging from the pharmaceutical industry to agriculture sector (Malley et al. 2004, Bengtsson et al. 2007, Burns and Ciurczak, 2007). The principle of the NIRS is that substances containing covalent bonds between O, H, C, and N (and other elements) exhibit molecular vibrations (overtones and combination bands) in the near-infrared region from 700 nm to 2500 nm (Williams, 2001, Workman and Shenk 2004). The mathematical relationship between spectral data and reference data is used in the development of calibration equations for rapid

prediction of composition and some physical parameters (Workman and Shenk 2004).

Among the many advantages of using NIRS is that once calibrations have been developed, multiple parameters can be estimated simultaneously within 1-2 minutes for the same sample, without the use of any chemicals, and the resultant harmful waste (Williams et al. 2009). Previous studies have successfully predicted a number of soil properties with NIRS technology, including soil organic carbon and soil texture. For example, Reeves et al. (2002) successfully predicted organic carbon fractions in 179 soil samples collected from two fields in Maryland, the United States. Martin et al. (2002) were able to predict soil organic carbon fractions in 287 soil samples collected from an A-horizon of an agricultural field near Miniota, Manitoba, Canada. Sorenson and Dalsgaard (2005) developed calibration for the prediction of soil clay content in 179 soil samples collected from Danish soils.

The feasibility of NIRS techniques to estimate the pesticide K_d values in soils has been successfully tested for non-ionic pesticides (lindane and linuron) by Bengtsson et al. (2007). Based on the rapid and precise determination of K_d values by NIRS, this thesis will explore the effectiveness of this tool to predict K_d values of a weakly-basic and a weakly-acidic herbicide, and of a natural steroid hormone. This research also examines whether NIRS can be integrated with pesticide fate modeling to improve spatial estimates of K_d values in fields, and thereby to reduce uncertainties in large scale risk assessments. The four chemicals that are studied are 2,4-D, atrazine, glyphosate and 17β-estradiol. Their molecular structure and physio-chemical properties are listed in Table 1.3 (FOOTPRINT 2006).

Table 1.3 Molecular Structure and physicochemical properties of the chemicals (FOOTPRINT 2006).

	2,4-D	**Atrazine**	**Glyphosate**	**17β-estradiol***
				
Molecular Mass (g mol^{-1})	221.04	215.68	168.07	272.40
Solubility in water (mg L^{-1}) at 20°C	23,180	35	10,500	13***
log K_{ow} at pH 7, 20°C	-0.83	2.70	-3.20	3.94***
pKa at 25°C	2.87	1.70	(2, 2.6, 5.6, 10.6)**	10.50-10.70
Vapor pressure (mPa) at 25°C	1.87×10^{-2}	3.9×10^{-2}	1.31×10^{-2}	3.00×10^{-2}
Soil half-life (days) at 20°C	14	66	49	0.2-9

Where: log K_{ow} = log octanol water partitioning coefficient and pKa = Acid dissociation constant.
*Data taken from Hanselman et al. 2003
**Data taken from Sprankle et al. 1975
***Ying and Kookana 2005

1.6 Chemicals Studied

1.6.1 Herbicide: 2,4-D

1.6.1.1 Use and Properties

2,4-D (Table 1.3) is a selective post emergence herbicide that has been registered for use in North America since the 1940s (Dost 2003, US-EPA 2005). It is applied to control broadleaf weeds in a wide range of agricultural crops, and has also some usage in the urban environment, for example, in lawns and golf courses (Mathews 2006, Stephenson and Solomon 2007). To date, 2,4-D is among the most widely used herbicide in the world (Burns and Swean 2012). Pesticide market estimates in 2007 ranked 2,4-D the seventh most commonly used pesticide in the United States with over 13 million kg of pesticide active ingredients used (US-EPA 2011). Based on pest control products sales, Health Canada (2010) ranked 2,4-D as the fourth most commonly sold pesticide in Canada with over 1 million kg of active ingredient sales. 2,4-D was among the five most commonly used agricultural pesticides in Manitoba between the years 1996 and 2006 with an average of 164,919 kg applied per year (Wilson 2012).

1.6.1.2. Environmental Detection and Exposure Risks:

The use of 2,4-D in North American agriculture systems has resulted in the contamination of the atmosphere and water resources by this herbicide (Waite et al. 2002, Ensminger et al. 2013). A range of Canadian studies have detected 2,4-D in surface water, groundwater, rain, and air samples (Table 1.1). The maximum concentration of 2,4-D detected in water samples in

Canada was 8.2 µg L^{-1} (Environment Canada 2011). The Canadian Water Quality Guidelines for the protection of aquatic life for 2,4-D exposure is 4 µg L^{-1} (CCME 1999a). Exposure to 2,4-D has been suspected to increase risks of Parkinson disease (Hoppin et al. 2002, Kamel et al. 2007) and non-Hodgkin's lymphoma (Wigle et al. 1990, Zahm et al. 1990) in humans, but cause and effect relationships are still under investigation (De Roos et al. 2003).

1.6.1.3. Fate in Soil

Studies have reported the transport of 2,4-D from agricultural soils into the broader environment by processes such as surface runoff (Nicholaichuk and Grover 1983), leaching (Waite et al. 1992), and volatilization (Maybank et al. 1978). The herbicide has a relatively high water solubility (23,180 mg L^{-1} at 20°C, FOOTPRINT 2006) and its weak sorption to soil increases the risk of 2,4-D movement from surface to subsurface horizons before degradation (Boivin et al. 2005, Gaultier et al. 2008b). Thus, despite its relatively short-half live (14 days at 20˚C, FOOTPRINT 2006), 2,4-D can be mobile in soils.

2,4-D is a weak-acid (pKa = 2.87 at 25°C, FOOTPRINT 2006) and hence is in anionic form in alkaline to neutral soils such as those that dominate much of the agricultural land in western Canada. Soil properties such as soil organic carbon content, soil pH, along with soil texture are known to influence the sorption of 2,4-D in western Canadian soils (Farenhorst 2001, Gaultier et al. 2006, Farenhorst et al. 2008). Studies have demonstrated that 2,4-D sorption coefficients vary in response to variations in soil properties across landscape positions and with soil depth (Gaultier et al. 2006, Gaultier et al. 2008a, Farenhorst et al. 2008, Farenhorst et al. 2009).

Wilson (2012) reported a slow mineralization of 2,4-D in Manitoba soils, and total mineralization varied from 6 to 51 %, depending upon slope position, soil depth and environmental factors such as temperature and moisture.

1.6.2 Herbicide: Atrazine

1.6.2.1 Use and Properties:

Atrazine (Table 1.3) is a systemic pre- and post-emergence herbicide primarily used to control broad leaf and grassy weeds in corn and rapeseed crops (Tomlin 1994, Solomon et al. 1996). Atrazine was ranked the second most commonly applied pesticide in United States agriculture, with an estimated over 35 million kg active ingredients sold in 2007 (US-EPA, 2011). Atrazine is most extensively used in the Midwestern Corn Belt watersheds of the United States (Tomlin 1994, Solomon et al. 1996). Atrazine was introduced in Canadian agriculture in the 1960's (CCME 1999b) and is most widely used in southern Ontario as this region is characterized by corn production (Solomon et al. 1996). Health Canada ranked triazines (including atrazine and tetrazines), seventh out of the ten most commonly sold herbicides for the year 2010, with about 500,000 kg triazines active ingredients sold (Health Canada 2010).

1.6.2.2. Environmental Detection and Risks:

Atrazine is among the most commonly detected pesticides in the North American surface water and ground water sources (Barbash et al. 2001, Winchester et al. 2009). For example, the National Resource Defense Council reported that all surface water samples taken across twenty

watersheds in the western United States between 2005 and 2008 contained atrazine at a concentration greater than 1 µg L^{-1}. In the same study (Wu et al. 2010), 90% of the samples violated the EPA's Safe Drinking Water Limit for atrazine (3 µg L^{-1}), and an exceptionally high atrazine concentration of 148 µg L^{-1} was observed in a sample from the Big Blue River Watershed, Nebraska.

Due to its frequent detection and persistent in surface and ground water, atrazine has been banned for use in Europe since 2003 (Sass and Colangelo 2003). Regardless of the ban on atrazine use in Europe, this herbicide still remains registered for use in North America with a precautionary maximum allowable level in drinking water of 3 µg L^{-1} (Dossantes et al. 2004). Scientists have expressed concerns about the continued use of atrazine use in North American agriculture because the herbicide was shown to be an endocrine disruptor in amphibians (Hayes et al. 2002, Hayes et al. 2010), birds (Matsushita et al. 2006), fish and mammals (Suzawa and Ingraham 2008), reptiles (Fan et al. 2007a) and rodents (Rayner et al. 2005). Atrazine exposure has also been hypothesized to increase risks of breast cancer (Kettles et al. 1997), stomach cancer (Van Leeuwen et al. 1999), prostate cancer (MacLennan et al. 2003) and Non-Hodgkin's Lymphoma (De Ross et al. 2003) in humans.

1.6.2.3. Fate in Soil

Atrazine is considered to be a moderate to highly mobile pesticide in soils, in part due to the fact that its leaching potential is enhanced because the herbicide is not readily degraded in soils. Environmental factors such as intensive rainfall events can accelerate atrazine mobility in

soils, especially by preferential flow through earthworm burrows (Edwards et al. 1993, Farenhorst et al. 2000ab). Atrazine is a moderately persistent herbicide and half-lives up to 1 year have been reported in the literature for neutral to alkaline soils (Bouquard et al. 1997, Lesan and Bhandari 2003). Atrazine is more slowly degraded in acidic soils than in neutral or alkaline soils (Pussemier et al. 1997, Houot et al. 1998) because atrazine (pKa 1.70 at 25˚C, FOOTPRINT 2006) is increasingly protonated at lower pH, hence more likely to be sorbed and less bioavailable to microorganisms for degradation.

The sorption of atrazine by soil constituents such as soil organic matter (Barriuso et al. 1992, Kulikova and Perminova 2002) and clay minerals (Laird et al. 1994, Wang and Keller 2008) has been widely studied. Atrazine is particularly retained by humic-clay complexes (Barriuso et al. 1992) because of its hydrophobic binding to aromatic carbon (Kulikova and Perminova 2002). The sorption of atrazine increases over time, i.e., aging (Barriuso et al. 2004) and this reduces the likelihood of atrazine desorption and degradation in soils.

1.6.3 Herbicide: Glyphosate

1.6.3.1 Use and Properties:

Glyphosate is a non-selective systemic herbicide widely used for the post-emergence control of annual broadleaf weeds, grasses, and woody plants (Henderson et al. 2010). Glyphosate was first registered for use in the United States in 1974 (Samsel and Seneff 2013) followed by Canada in 1976 (Trotter et al. 1990), but the actual use has dramatically increased since 1996

with the introduction of genetically-engineered glyphosate resistant soybean, canola, cotton and corn crops (Duke and Powles 2009). Glyphosate is the most popular pesticide in the United States with an estimated 84 million kg of the active ingredient used in 2007 (US-EPA 2011). Health Canada (2010) estimated 25 million kg active ingredient of glyphosate sales in 2010. Glyphosate is considered relatively low-toxic to mammals because its mode of action operates through shikimic acid pathways specific only to plants and microorganisms (Williams et al. 2000).

1.6.3.2. Environmental Detection and Risks:

A number of studies have highlighted the presence of glyphosate residues in air, rainwater, surface water, and ground water (Humphries et al. 2005, Scribner et al. 2007, Messing et al. 2011, Glozier et al. 2012). A maximum concentration of glyphosate of 4.7 µg L^{-1} in groundwater (Scribner et al. 2007) and 430 µg L^{-1} in surface water (Coupe et al. 2012) has been detected in the United States. In Canada, the maximum detected level of glyphosate in surface water was 6.1 µg L^{-1} (Humphries et al. 2005) and this value is at least 10-fold below the Canadian Water Quality guidelines set for the protection of aquatic life (CCME 1999a).

Regardless of the high water solubility (10,500 mg L^{-1}, FOOTPRINT 2006), glyphosate residues are known to be immobile and rapidly inactivated in the soil due to immediate sorption of the molecule by soil constituents (Sprankle et al. 1975). The herbicide is not expected to volatilize from the soil surface because it has a low vapor pressure (1.31×10^{-2} mPa at 25˚C, FOOTPRINT 2006, Henderson et al. 2010). Glyphosate is considered moderately persistent in the soil as its

half-life in soil is 47 days (FOOTPRINT 2006). An increase in soil pH decreases glyphosate degradation in soils (Kools et al. 2005).

Studies have shown K_d values of glyphosate vary from 19 to 547 L kg^{-1} in the soil profiles of a heavily-eroded undulating field in Minnesota, United States (Farenhorst et al. 2008). Sorption capacity of glyphosate by soil decreases with increase in soil pH (De Jonge and De Jonge 1999). Coatings of Fe_2O_3 on the clay in the B-horizons promotes sorption because Fe(III) forms insoluble complexes with the herbicide, and hence the glyphosate molecule shows greater sorption in B-horizons that are enriched in the clay minerals with redoximorphic features due to poor water drainage and periodically reducing conditions (Subramaniam and Hoggard 1988, Gimsing and Borggaard 2002).

1.6.4 Estrogen: 17β-estradiol

1.6.4.1 Concentration in Manure and Properties:

Livestock manure and biosolids contain significant amount of natural steroid hormones (Ternes et al. 2002, Furuichi et al. 2006, Muller et al. 2008), among them most potent is 17β-estradiol, a hormone that is eliminated by vertebrates in both feces and urine (Casey et al. 2003). The amount of 17β-estradiol excreted varies by type of species, and their sex and age (Lorenzen et al. 2006). For example, on a dry weight basis, higher concentrations have been reported for swine waste (1,215 ± 275 µg kg^{-1}) than for dairy cow (239 ± 30 µg kg^{-1}) and poultry (33 ± 12 µg kg^{-1}) wastes (Finlay-Moore et al. 2000, Hanselman et al. 2003). Johnson et al. (2000) reported

the 17β-estradiol excretion rate for humans is much larger for a pregnant woman (259 µg day^{-1}) than for non-pregnant women (2.3 to 3.5 µg day^{-1}) or for men (1.6 µg day^{-1}). 17β-estradiol is an environmental pollutant and has been shown to interfere with the developmental and reproductive processes in wildlife (Jobling et al. 2003, Bevacqua et al. 2011) even at concentrations as low as 1 ng L^{-1} (Routledge et al. 1998, Baronti et al. 2000).

1.6.4.2. Environmental Detection and Risks:

Concentrations for 17β-estradiol in liquid swine manure (5-17 µg kg^{-1}, Furuichi et al. 2006), sewage sludges (1.0-5.5 µg kg^{-1}, Muller et al. 2008) and biosolids (5-17 µg kg^{-1}, Ternes et al. 2002) have been reported. Following the application of these waste products to land, 17β-estradiol can move to fresh and potable water sources from agricultural soils via leaching and surface runoff (Nichols et al. 1997, Kjaer et al. 2007, Yang et al. 2012). Surface runoff occurring over grassland that had received a boiler litter application showed levels of 17β-estradiol up to 2.53 µg L^{-1}, with the soil containing up to 0.67 g kg^{-1} 17β-estradiol (Finlay-Moore et al. 2000). The maximum reported 17β-estradiol concentration in surface water is 5.4 ng L^{-1} (Shore et al. 1993) and in ground water is 66 ng L^{-1} (Peterson et al. 2000).

1.6.4.3. Fate in Soil

The fate of 17β-estradiol in soil is mainly controlled by sorption (Ying and Kookana 2005, Caron et al. 2010a) as well as degradation and mineralization processes (Caron et al. 2010b, Carr et al. 2011). The hydrophobic nature (water solubility of 3.90-13.30 mg L^{-1} at 20°C, Hanselman et al. 2003) along with low vapor pressure ($3x10^{-2}$ mPa at 25°C, Hanselman et al. 2003) results in 17β-

estradiol being strongly retained by soil constituents (Lee et al. 2003, Fan et al. 2007b, Sarmah et al. 2008). Examining the sorption of 17β-estradiol in 121 surface soil samples collected from different ecoregions of Alberta, Caron et al. (2010a) found that 17β-estradiol sorption was mainly controlled by SOC ($r = 0.75$, $p<0.001$).

Microbial degradation has been recognized as a major degradation mechanism for 17β-estradiol in soils (Colucci et al. 2001, Xuan et al. 2008), which can be further influenced by soil moisture (Colucci et al. 2001, Das et al. 2004) and temperature (Colucci et al. 2001, Xuan et al. 2008). Nevertheless, mineralization of 17β-estradiol is relatively a slow process. For example, in silt loam soils of Canada, only 12-17% of the added 17β-estradiol was degraded following a three month laboratory incubation at 30˚C (Casey et al. (2003). In soils with a range of textures, Caron et al. (2010b) observed that 17β-estradiol was always below 30% following three-month laboratory incubation at 20˚C, and reported a significant positive correlation between sorption and maximum mineralization of 17β-estradiol.

1.7 Study Goals

The goal of this study was to examine the spatial variability of the sorption coefficients of 2,4-D, atrazine, glyphosate, and 17β-estradiol at the field-scale and to determine the feasibility of using NIRS as a tool for the rapid quantification of their K_d values in soil samples. Using the two compounds that have the greatest leaching potential in soils (because of their smaller K_d values), this study further investigates whether NIRS could be integrated with a pesticide fate

model to rapidly estimate 2,4-D and atrazine leaching to different depths. The rapid results by NIRS to determine 2,4-D and atrazine K_d values for input parameters in pesticide fate models, at a low cost, could bring an improvement in the accuracy and a wider applications of pesticide fate model predictions in regulatory and environmental assessments of pesticide use.

1.8 Hypotheses

The hypotheses of this study were:

(1) The K_d values of 2,4-D, atrazine, glyphosate and 17β-estradiol are variable across agricultural fields because sorption is largely controlled by soil properties such as soil organic carbon, soil pH and soil texture, all of which are also variable.

(2) Regression equations can be developed to calculate herbicide (2,4-D, atrazine and glyphosate) and 17β-estradiol K_d values from a) soil properties, b) terrain parameters, and c) spectral data, so that the variability in K_d values across agricultural fields can be described without direct measurements of K_d values by batch equilibrium experiments.

(3) The NIRS technique is a rapid, efficient, and cost-effective tool that can be used to determine soil properties and K_d values of herbicide and estrogenic compounds in large numbers of samples, and can therefore, be used to reduce uncertainty in the pesticide fate modeling predictions.

1.9 Thesis outline

This is a manuscript style thesis prepared in accordance with the guidelines of the Department of Soil Science, and Faculty of Graduate Studies of the University of Manitoba, Canada. In addition to Chapter 1 (introduction) and Chapter 5 (Overall Synthesis), specific research activities are divided into three, standalone manuscripts style format (Chapters 2 through 4).

Chapter 2: Feasibility of Using Near-Infrared Spectroscopy for Rapid Quantification of 17β-Estradiol Sorption Coefficients in Soil.

This is the first study to explore the feasibility of NIRS to quantify K_d values of a natural steroid hormone in soil. The study has determined 17β-estradiol K_d values and soil properties in 609 soil samples, collected in a zero-till field and a conventional-till field.

Chapter 3: Soil characteristics and herbicide sorption coefficients in 140 soil profiles of two irregular undulating to hummocky terrains of western Canada.

The uniqueness of the work is the detailed examination of the sorption of three distinct herbicides in soil horizons of the Chernozemic and Gleysolic soils typically found in undulating to hummocky soil-landscapes of western Canada. The herbicides are distinct because of their differences in physio-chemical properties and hence, potentially, the strength of their sorption by soil constituents.

Chapter 4: Near-Infrared Spectroscopy as a tool for generating sorption input parameters for pesticide fate modeling.

This is the first study to integrate NIRS in pesticide fate models. The study contrasts the output of a pesticide fate model under three scenario of determining the sorption input parameter: a) the conventional batch equilibrium method, b) pedotransfer functions, as done in other studies and c) the newly-proposed NIRS method.

My contributions to Chapters 2 through 5 include: planning and conducting laboratory experiments to generate data on soil properties, K_d values for 2,4-D, atrazine, glyphosate and 17β-estradiol, and soil spectral data by NIRS; developing pedotransfer functions and NIRS calibration models; preparing input files for running the pesticide root zone model, understanding the protocols of completing pesticide fate model simulations, subjecting all data obtained to statistical analysis; and preparing drafts of tables and figures that facilitated the interpretation of the data collected. In addition, my contributions were to write, improve, and finalize four manuscripts for submission to peer-reviewed journals and addressing reviewer comments as needed.

Pesticide Root Zone modeling simulations along with computer programming was conducted with the assistance of Dr. Ross McQueen, Department of Soil Science, University of Manitoba. Near-Infrared Spectroscopy training and instruments were provided by Dr. Diane Malley and Dr. Phil Williams, PDK Projects Inc., Winnipeg. Guidance for statistical analysis guidance was

done in collaboration with Dr. Francis Zvomuya, Department of Soil Science, University of Manitoba.

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2. Feasibility of using Near-Infrared Spectroscopy (NIRS) for rapid quantification of 17β-estradiol sorption coefficients in soil

2.1. Abstract

Livestock manure contains natural steroid hormones, the most potent being 17β-estradiol. The transport of steroid hormones from agricultural fields to adjacent water bodies can result in 17β-estradiol environmental contamination impacting aquatic organisms. Sorption coefficients are useful inputs into models that estimate risk of water contamination. The feasibility of applying near-infrared spectroscopy (NIRS) for determining sorption coefficients of 17β-estradiol in soil was investigated for two irregular undulating to hummocky terrain landscapes in Manitoba and Saskatchewan, Canada. A total of 609 soil samples in 140 soil profiles were collected from several horizons to a depth of 1 m. Air-dried and sieved (2 mm) soil samples were analyzed for soil organic carbon (SOC), soil pH, and soil texture. Sorption coefficients of 17β-estradiol were determined by a batch equilibrium process. Spectral data were collected from soil samples (25 g) using two instruments, the 45VISNIR Zeiss Corona diode array (wavelength range 700-1690 nm) and the Foss NIRSystems 6500 (wavelength range 1100-2500 nm). Regardless of the site and instrument, the predictive models were excellent for both SOC and 17β-estradiol sorption coefficients. The data thus generated can be used as input parameters in fate models for efficient risk assessments and decision-making programs for environmental safety where soils may be receiving, or are at risk of receiving, inputs of 17β-estradiol. Calibration results for soil pH were also adequate with the Corona outperforming the

Foss instrument. Soil texture predictions were relatively unsuccessful regardless of the instrument or site.

2.2. Introduction

In 2006, a population of approximately 157 million livestock was reported in Canada (Eillers et al. 2010), producing millions of tonnes of manure every year. Livestock manure is an important source of nutrients for crop production when applied as fertilizer. Nevertheless, poor manure management strategies, especially overly high rates of application, lead to significant environment contamination (Eillers et al. 2010). Loss of livestock manure bearing steroid hormones, such as 17β-estradiol [(17β)-estra-1,3,5(10)-triene-3,17-diol], from manure-treated agricultural soils into water bodies has the potential to adversely affect the quality of fresh water sources (Nichols et al. 1997, Nichols et al. 1998, Peterson et al. 2000, Colucci et al. 2001, Ying et al. 2002). A survey of 139 stream water sources sampled across the United States revealed that 90% of the samples collected contained detectable levels of steroid hormone compounds (Koplin et al. 2002), most likely as a result of both agricultural and urban sources (Nichols et al. 1997, Nichols et al. 1998, Kinney et al. 2006). The presence of as little as 1 ng L^{-1} of 17β-estradiol in water has the potential to trigger feminization in aquatic male wildlife, as well as to produce reproductive disorders in human males (Colucci et al. 2001).

Degradation of 17β-estradiol in soil is dependent on its chemical bioavailability which is reduced by the strong sorption of 17β-estradiol to soil constituents (Colucci et al. 2001,

Hanselman et al. 2003), such as organic matter and silt (Casey et al. 2003). 17β-estradiol transport from soils to the broader environment by water is also limited by soil sorption (Colucci et al. 2001). Sorption coefficients of 17β-estradiol have been reported to be spatially variable across agricultural fields in ecoregions of Alberta, Canada (Caron et al. 2010).

Risks of transport of pesticides and other organic contaminants, from soil to surrounding environments, can be assessed by models such as the Pesticide Root Zone Model (Eillers et al. 2012, Carsel et al. 1998, Cessna et al. 2010). Casey et al. (2003, 2005) describe the application of pesticide fate models for determining estrogen fate in soil. Examples of input parameters for fate models are the physicochemical properties of pesticides or estrogens, including sorption coefficients; weather data, including rainfall and temperature; and soil-landscape characteristics including terrain attributes and management practices (Eillers et al. 2012, Cessna et al. 2010). The uncertainties associated with fate modeling at the large scale are particularly due to the lack of pertinent data on the spatial variation of pesticide or estrogen sorption coefficients in soil-landscapes and regions (Dubus et al. 2003). Generating efficient quality input parameters rapidly and cost-effectively may strengthen the versatility and reliability of chemical fate models when developing beneficial farm management strategies for manure management in agricultural fields. Wet chemistry methods, such as the batch equilibrium process are generally adopted for determining sorption coefficients (K_d) of organic molecules (Wauchope et al. 2002). Such techniques are not only expensive and time consuming but often employ hazardous radiolabeled chemicals (Williams et al. 2001, Williams et al. 2009, Forouzangohar et al. 2009). To reduce the uncertainties in risk assessments, efficient methods are needed that

are not only cost-effective, rapid, and reliable, but also generate quality data to determine spatial distributions of sorption coefficients in soil landscapes.

Near-infrared spectroscopy (NIRS) has been employed for rapid, cost-effective, and accurate determination of soil properties since 1988 (Haaland and Thomas 1988). Many researchers have demonstrated that NIRS can be used to predict total or fractions of carbon in soils obtained from regions in Canada (Malley et al 2000, Martin et al. 2002), United States (Chang et al. 2002, McCarty et al. 2002,Reeves et al. 2002), and Uruguay (Cozzolino and Moron 2006). He et al. (2005) demonstrated the feasibility of NIRS for determination of carbon, nitrogen and phosphorous in soil from a relatively flat agricultural field in China. Sorensen and Dalsgaard (2005) successfully predicted clay content in soil collected across Denmark. Bengtsson et al. (2007) successful employed Near-Infrared Spectroscopy to predict K_d values of lindane and linuron in 27 agricultural soils from Sweden. Similarly, Kookana et al. (2008) highlighted the potential of Mid-Infrared Spectroscopic analysis to predict atrazine K_d values in Australian soils. Where, Forouzangohar et al. (2009) compared the efficiency of both Near-Infrared and Mid-Infrared Spectroscopic techniques to predict K_d values of diuron in 112 agricultural soils collected from Australia.

The objectives of the present study were to determine the feasibility of NIRS as a rapid tool to quantify the spatial variability of soil properties and 17β-estradiol sorption coefficients in the soil profiles of irregular undulating to hummocky terrain landscapes of Canada.

2.3. Materials and Methods

2.3.1. Soil sampling and analysis

Soil samples were collected from two irregular undulating to hummocky terrain landscapes in the prairie pothole region of western Canada. One landscape at the Manitoba Zero Tillage Research Association (MZTRA) (49° 53'N latitude, 99° 58'W longitude) situated in the province of Manitoba consisted of a zero-tilled agricultural field, 16 ha in area. The second landscape at the St. Denis National Wildlife Research Area (SDNWA) (106° 5'N longitude, 52° 12'W latitude), situated in the province of Saskatchewan, consisted of one conventionally-tilled agricultural field, 20 ha in area. Conventional tillage here refers to typical field operations with surface disturbance and incorporation of a portion of the previous year's crop residues into surface soil. Pesticides and synthetic fertilizers were applied in both of the landscapes, following typical field practices in the Prairie region.

At both MZTRA and SDNWA, ten soil profiles of 1 m depth were collected from each of seven landform elements, including convergent or divergent shoulders, convergent or divergent backslopes, convergent or divergent footslopes, and depressions. The landform element classification was performed using Digital Elevation Models with a 5 x 5 m^2 grid and the landform segmentation technique described in Pennock and colleagues (Pennock et al. 1987, Pennock 2003). Soil profiles were collected with a truck-mounted hydraulic probe, 5-cm in diameter. Each profile was classified into soil horizons. A total of 609 soil samples from MZTRA (n=314) and SDNWA (n=295) landscapes were collected.

Soil samples were air dried and sieved (<2 mm) and analyzed for soil organic carbon (SOC), soil pH, and soil texture (% sand, % silt, and % clay) by a Leco CR-12 Carbon Analyzer (LECO Corporation, Ontario, Canada), pH meter (Acumen 50 pH meter; Thermo Fisher, Texas, USA), and Horiba LA-950 laser particle size analyzer (Horiba, California, USA), respectively.

2.3.2. 17β-estradiol sorption analysis

17β-estradiol of 99 % chemical purity, 6,7-^{3}H(N), 99 % radiochemical purity, and specific activity of 13.51 x 10^{-10} Bq $mmol^{-1}$ (American Radiolabelled Chemicals Inc., St. Louis, MO, USA) was used in batch-equilibrium experiments as described by Caron et al. (2010). These experiments were used to quantify the K_d values of 17β-estradiol for each soil sample. All soil samples, glassware, and de-ionized water used for stock solution preparation were sterilized by autoclaving at 121°C for 30 min to minimize the risk of 17β-estradiol degradation during the batch experiment (Caron et al. 2010). Preliminary batch experiments revealed that the equilibrium time of 24 h was appropriate for sorption analysis of 17β-estradiol. 17β-estradiol stock solutions with a specific activity of 16.70 Bq mL^{-1} were prepared by dissolving both analytical grade and radiolabelled 17β-estradiol in 0.01 M $CaCl_2$ solution. 17β-estradiol stock solution of 10 mL volume was added to 5 g of soil in 50 mL glass tubes in duplicates and rotated in the dark for 24 h under controlled temperature conditions of 5°C to achieve the equilibrium between the concentration of 17β-estradiol sorbed by soil (C_s in g kg^{-1}) and the concentration of 17β-estradiol remaining in solution (C_e g L^{-1}). Samples were centrifuged at 10,000 rpm for 10 min. Then 1 mL supernatant aliquots were transferred to scintillation vials (duplicates) containing 5

mL of scintillation cocktail. After 24 h in the dark, scintillation vials were counted in a Beckman Liquid Scintillation Counter (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) with automated quench correction using the #H method for determining remaining radioactivity in the samples. The sorption partitioning coefficients (K_d) were determined as $K_d = C_s/C_e$.

2.3.3. Near-Infrared Reflectance Spectroscopy

Spectra were obtained in triplicate for each soil sample by scanning 25 g samples that had been air-dried and sieved (2 mm). Samples were presented in a 5-cm diameter glass petri dish or in a 3-cm diameter glass scintillation vial, to the 45VISNIR Zeiss Corona (Carl Zeiss, Jena, Germany) spectrometer with a wavelength range of 380 to 1690 nm at 2 nm intervals and to the Foss NIR Systems 6500 spectrometer equipped with the Rapid Content Sampler (RCS) at a wavelength range of 1100 to 2500 nm at 2 nm intervals. The samples were placed on the scanning window of each instrument and the spectral data were collected through the bottom of the sample containers. Each sample was rotated 120° between triplicate scans.

Spectra for each instrument/sample holder combination were imported into The Unscrambler® multivariate statistical analysis software version 9.8 (2008, CAMO Process ASA). Triplicate spectra for each sample were averaged and the reference data for each sample were added prior to calibration development. Spectral precision of both instruments was monitored by scanning the same three check samples after every 10 unknown samples. Although the samples stored in the vials were scanned more rapidly than those in petri dishes, the petri dishes provided a more optically-uniform interface and larger area of sample scanned than did the

vials. The “noisy” region (380-700 nm) of the Corona spectra was removed before mathematical pre-treatments were performed on the raw spectral data of petri dishes. Wavelength ranges were thus 700-1690 nm for the Corona and 1100-2500 nm for the Foss 6500 instrument. Partial Least Squares Regression (PLS1) in the Unscrambler® software was used to develop calibrations for each property/constituent. Calibrations were developed using the test set method in which all the samples were sorted from low to high for each property or constituent and were divided into calibration (2/3rd of the total samples) and validation (1/3rd of the total samples) data sets by selecting every 3rd sample for the validation sets. Consequently, the range of values for each property or constituent was approximately the same in the calibration file and the corresponding validation file. A total of 37 calibration trials were made for every property or constituent by performing mathematical pretreatments on raw spectra by smoothing over 5, 11, 21 or 41 wavelength points followed by transformation to first or second derivative, and using derivative gaps of 5, 11, 21 or 41 wavelength points. Wavelength points were 2 nm apart. The best calibration for each parameter was selected based on highest coefficient of determination (r^2), lowest standard error of prediction (SEP) and highest RPD value. The RPD value is the ratio of SD of the constituent values in the validation set to the SEP (Williams et al. 1987). In environmental samples, values of RPD >4 are judged as indicating excellent calibrations, >3 are successful, and between 2.25 to 3.0 are moderately successful. In addition, the RER (ratio of range of validation set to SEP) values was also considered with RER values of greater than 10 generally being judged as moderately successful (Starr et al. 1981, Malley et al. 2004).

2.4 Results and Discussion

The 609 soil samples collected from A, B and C horizons of the 140 soil profiles demonstrated widely ranging soil properties and 17β-estradiol K_d values (Table 2.1). The 17β-estradiol K_d values in MZTRA ranging from 8.28 to 58.71 L Kg^{-1}, and those in SDNWA ranging from 4.01 to 33.48 L Kg^{-1} (Table 2.1). These values were significantly ($p<0.001$) positively correlated with SOC and significantly ($p<0.001$) negatively correlated with soil pH and clay content (Table 2.2). Mean SOC and mean 17β-estradiol K_d values decreased from A > B > C-horizon, while the mean soil pH and mean clay content increased with soil depth (Table 2.1). Under the zero-tillage management practices at MZTRA, soils contained on average of two times greater SOC and 17β-estradiol K_d values than the conventional-tillage soils at SDNWA (Table 2.1).

Both NIRS instruments demonstrated satisfactory spectral precision, although the Corona marginally outperformed the Foss 6500 instrument when the coefficient of variation of the spectra of 3 check samples were compared at four wavelengths points (1186, 1210, 1410 and 1510 nm) (Table 2.3). The soil spectra displayed absorbance peaks at three major wavelength points, i.e. 1400 nm, 1900 nm and 2200 nm, related to O-H bonds of water present in the air dried soil samples (Figure 2.1). The average spectra of samples from the A, B and C horizons in MZTRA (and SDNWA, data not shown) were distinctively different in absorbance values (Figure 2.1). This is reflected in clustering of samples from A (mean SOC=3.41), B (mean SOC=1.97) and C (mean SOC=0.94) horizons in MZTRA (and SDNWA, data not shown) in the Principal Component Analysis, reflecting differences in SOC and average particle size in the respective horizons (Figure 2.2).

Table 2.1 Constituents in the 609 soils samples from the MZTRA and SDNWA sites. Values are mean ± S.D. The K_d values are given for 17β-estradiol.

Site	Horizon	17β-estradiol	SOC%	pH	Sand%	Silt%	Clay%
MZTRA	**ABC(n=314)**	24.26±10.18	1.99±1.33	7.78±0.33	69.55±15.70	18.58±8.36	11.88±8.94
	A(n=120)	33.38±6.47	3.41±1.03	7.54±0.23	73.09±12.64	18.40±7.49	8.52±6.35
	B(n=79)	22.47±9.36	1.37±0.48	7.79±0.27	73.93±14.91	15.75±8.48	10.32±7.95
	C(n=115)	15.98±4.64	0.94±0.34	8.03±0.26	62.84±16.90	20.72±8.59	16.45±9.97
SDNWA	**ABC(n=295)**	13.22±6.09	1.01±0.96	8.19±0.67	48.21±10.80	40.74±8.56	11.06±7.14
	A(n=109)	18.85±5.06	2.06±0.75	7.91±0.60	53.59±7.78	41.09±6.67	5.32±4.44
	B(n=74)	10.96±4.85	0.57±0.32	8.04±0.58	45.87±8.80	41.01±7.78	13.12±6.31
	C(n=112)	9.22±2.66	0.28±0.26	8.56±0.61	44.51±12.37	40.21±10.52	15.28±6.03

Table 2.2 Pearson correlation coefficients (r) among 17β-estradiol (K_d values) and soil properties in MZTRA and SDNWA.

Site	Constituent or Property	SOC%	pH	Sand%	Silt%	Clay%
MZTRA	**17β-estradiol**	0.79***	-0.58***	0.18***	NS	-0.28***
	SOC%		-0.62***	0.19***	NS	-0.33***
	pH			-0.25***	NS	0.37***
	Sand%				-0.90***	-0.91***
	Silt%					0.65***
SDNWA	**17β-estradiol**	0.81***	-0.24***	0.35***	NS	-0.60***
	SOC%		-0.40***	0.38***	NS	-0.65***
	pH			NS	-0.32***	0.25***
	Sand%				-0.75***	-0.61***
	Silt%					NS

***Correlation is significant at the 0.001 level,

NS Correlation is not significant at the 0.05 level.

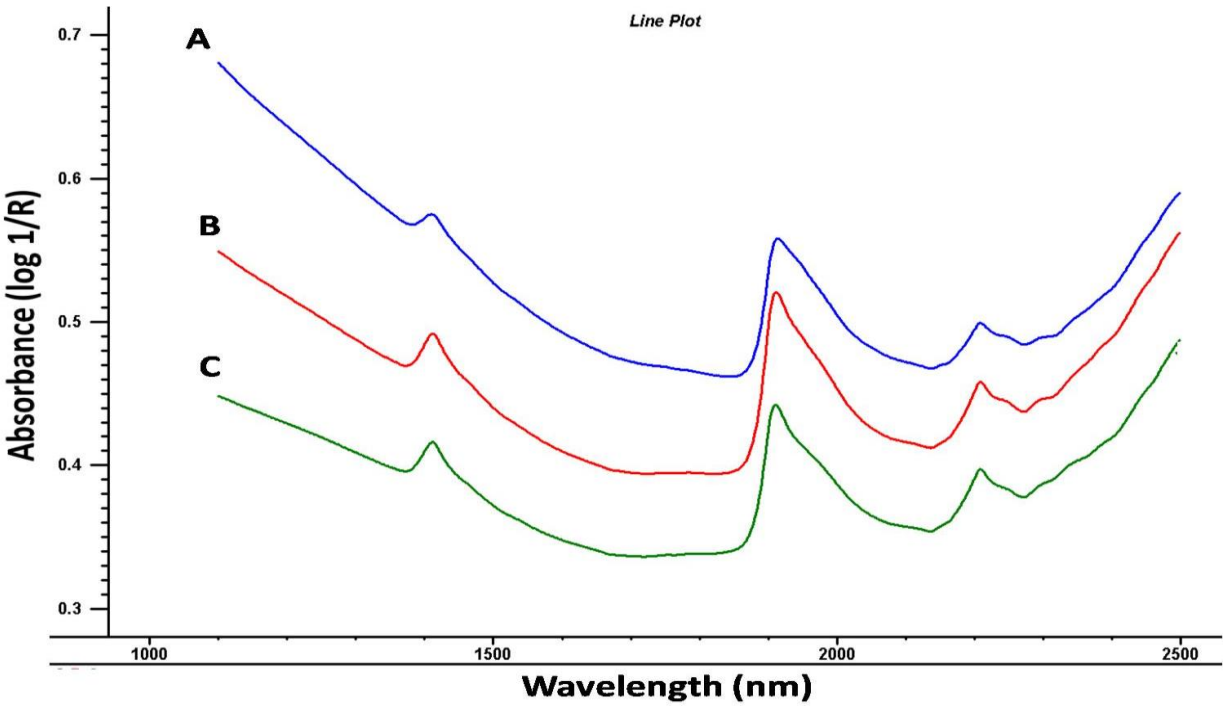


Figure 2.1 Spectra of soil samples from the A, B and C horizon in MZTRA recorded by the Foss 6500.

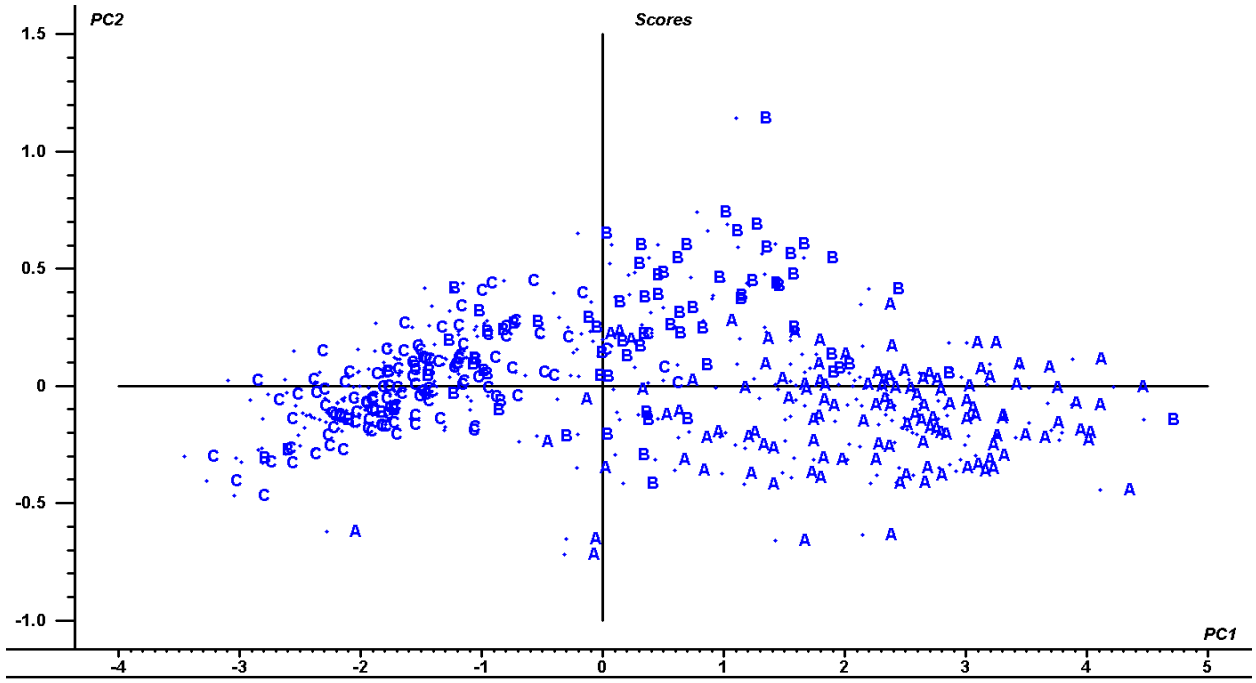
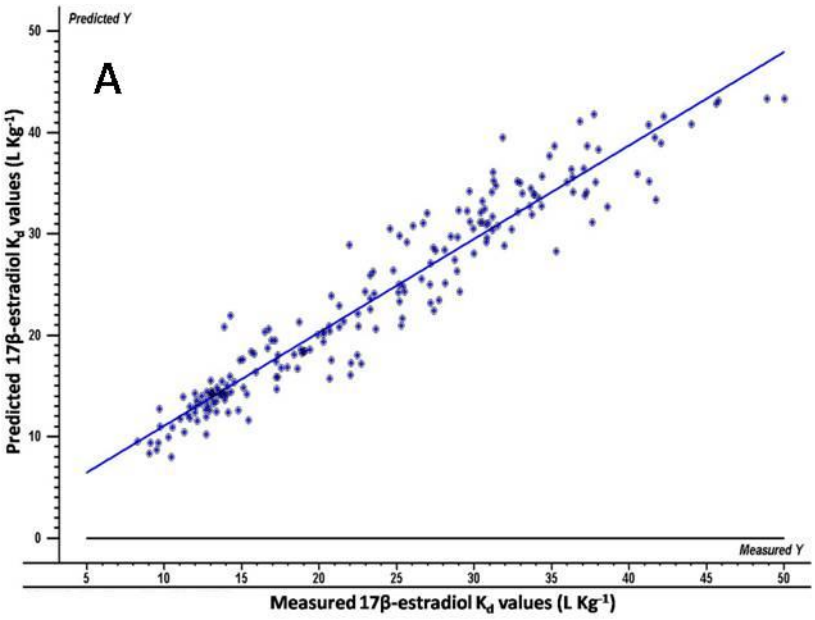
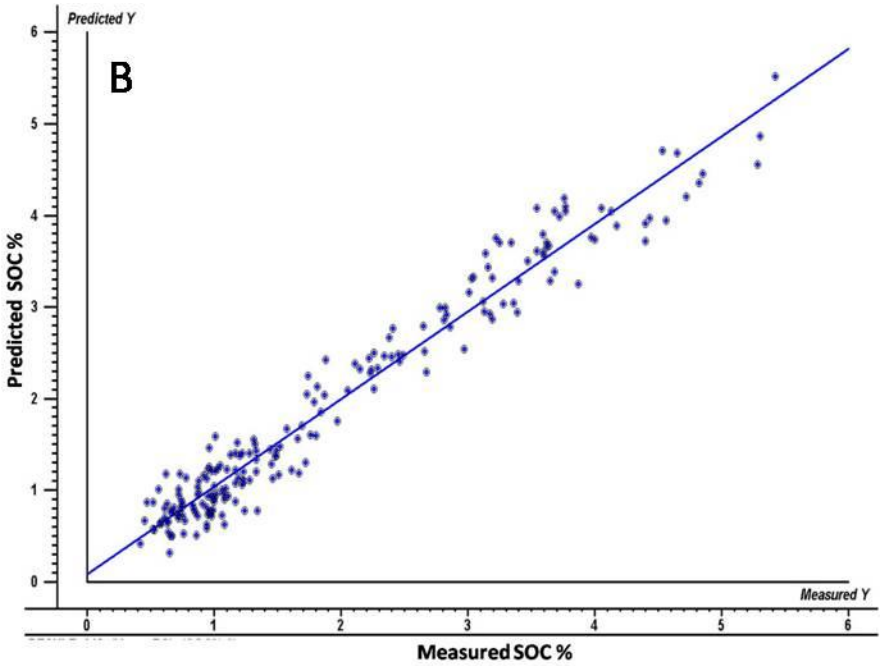


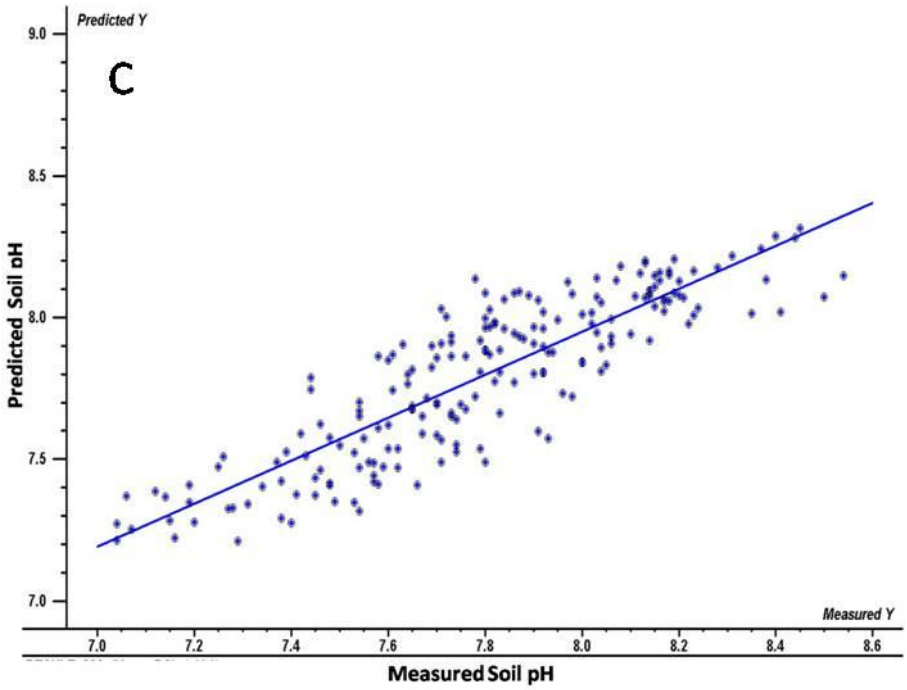
Figure 2.2 Scores plot from Principle Component Analysis of 314 soil samples of MZTRA belonging to A, B and C horizons using spectra recorded by the Foss 6500.

Regardless of the site location and instrument, successful to moderately successful calibration results were obtained for K_d values of 17β-estradiol and for SOC. Soil pH and clay content were generally predicted moderately usefully. Results for soil samples scanned in petri dishes with the Foss 6500 instrument demonstrated the most successful results in MZTRA (r^2 = 0.92, RPD = 3.78) when the spectra (1100 to 2498 nm) were smoothed over 11 wavelength points, using the 2nd derivative (Figure 2.3A, Table 2.4), where 96 % of the variance in the measured 17β-estradiol K_d values was explained by the 1st principal component. Similarly, in the SDNWA soil landscape, the Foss 6500 successfully predicted 17β-estradiol with r^2 of 0.84 and RPD of 2.53 (Table 2.4). Comparatively, the Foss 6500 marginally outperformed the Corona (r^2=0.81, RPD=2.37) in SDNWA and the differences between the two instruments were even smaller for MZTRA (Table 2.4).

This was the first study to explore the feasibility of NIRS application for landscape-scale quantification of 17β-estradiol K_d values in soil. Nevertheless, near infrared and mid infrared spectroscopy has successfully been applied to estimate sorption coefficients for other organic chemicals (pesticides) in agricultural soils at the regional scale in Sweden (Bengtsson et al. 2007) and Australia (Kookana et al. 2008, Forouzangohar et al. 2009).


A
Predicted Y
Measured Y
Predicted 17β-estradiol K_d values (L Kg^{-1})
Measured 17β-estradiol K_d values (L Kg^{-1})
0
10
20
30
40
50
5
10
15
20
25
30
35
40
45
50


B
Predicted Y
Measured Y
Predicted SOC %
Measured SOC %
0
1
2
3
4
5
6



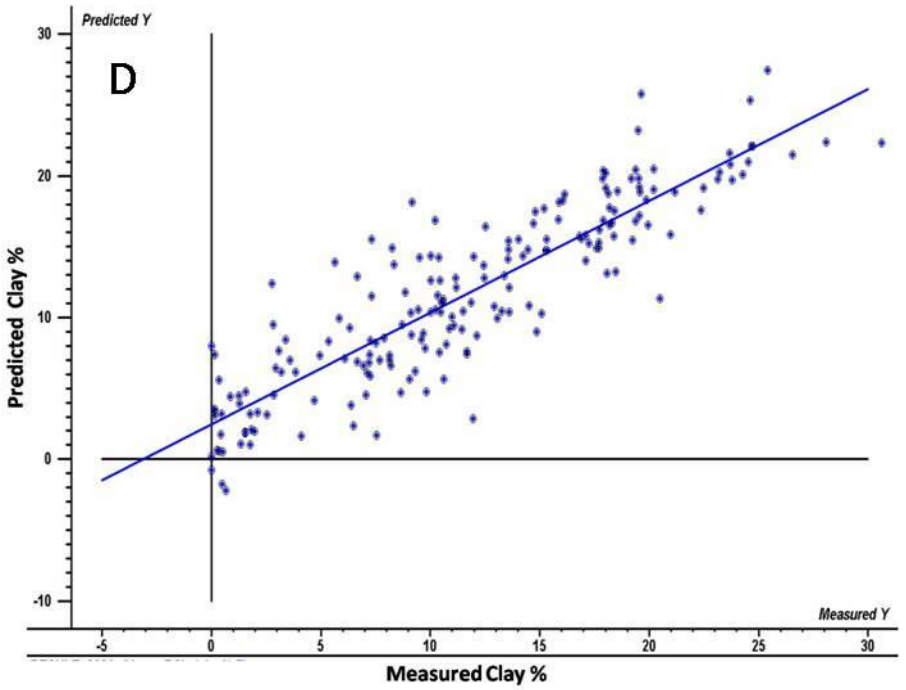


Figure 2.3 Linear regression relationship between NIR-predicted and measured values for sorption coefficients of 17β-estradiol (A), soil organic carbon (B), soil pH (C), and soil clay (D).

Table 2.3 Spectral precision comparison of Zeiss Corona and Foss 6500 instruments using check sample means (Absorbance Log 1/R) in petri dishes.

Sample		Zeiss Corona				Foss 6500			
		1186nm	1210nm	1410nm	1510nm	1186nm	1210nm	1410nm	1510nm
Check-1	Mean	0.5925	0.5802	0.4628	0.4367	0.6371	0.6263	0.5602	0.5091
(n=13)	SD	0.0034	0.0034	0.0032	0.0031	0.0030	0.0034	0.0032	0.0031
	CV%	0.5738	0.5860	0.6914	0.7099	0.4709	0.5429	0.5712	0.6089
Check-2	Mean	0.6181	0.6058	0.4898	0.4623	0.6661	0.6555	0.5908	0.5386
(n=13)	SD	0.0030	0.0029	0.0029	0.0028	0.0048	0.0048	0.0052	0.0054
	CV%	0.4854	0.4787	0.5921	0.6057	0.7206	0.7323	0.8802	1.0026
Check-3	Mean	0.6028	0.5917	0.4868	0.4588	0.6423	0.6326	0.5783	0.5254
(n=13)	SD	0.0028	0.0028	0.0032	0.0034	0.0049	0.0049	0.0048	0.0047
	CV%	0.4645	0.4732	0.6574	0.7411	0.7629	0.7746	0.8300	0.8946

Excellent calibration results were obtained for SOC by the Foss 6500, in the MZTRA (r^2 = 0.96, and RPD = 5.34) and a successful calibration was obtained in the SDNWA (r^2 = 0.91 and RPD = 3.21) (Figure 2.3B, Table 2.4). Comparatively, the Foss 6500 marginally outperformed the Corona for both MZTRA and SDNWA (Table 2.4). The results of the present study support results of previous studies (Sudduth and Hummel 1993, Malley et al. 2000, Martin et al. 2002, Chang and Laird 2002, McCarty et al. 2002, Malley et al. 2004, Sorensen and Dalsgaard 2005, Cozzolino and Moron 2006, Vasques et al. 2009), all of which researchers successfully determined the content of carbon fractions in soils by NIRS. Moderately useful calibrations were developed for soil pH in MZTRA (r^2=0.76, RPD=2.08) and SDNWA (r^2=0.76, RPD=2.05) with the Corona (Figure 2.3C, Table 2.4). Soil clay was moderately usefully predicted by the Foss 6500 in SDNWA (r^2=0.79, RPD=2.13), but the results were relatively poor for clay by the Corona (r^2=0.73, RPD=1.91) and by either instruments in MZTRA (Figure 2.3D, Table 2.4). Soil sand and silt content were not successfully predicted by either instrument (Table 2.4).

The present study demonstrated that NIRS is a rapid and cost effective technology that could be used efficiently to estimate sorption coefficients of 17β-estradiol, together with some soil properties. It presents a promising substitute for costly and time-consuming conventional wet chemistry techniques. The data generated by NIRS can readily be used as input parameters in the chemical fate models for efficient risk assessments and effective decision making programs for environmental safety.

Table 2.4 Calibration results of 17β-estradiol (K_d values) and soil properties on MZTRA and SDNWA soil samples presented in Petri dishes to the Foss 6500 and the Zeiss Corona.

MZTRA	Calibration	r^2	SEP	Bias	RPD	RER	Math Treatment
Foss 6500	**17β-estradiol**	0.92	2.71	8.75E-07	3.78	14.77	s11e5
	SOC%	0.96	0.26	3.89E-07	5.34	18.89	s5e5
	pH	0.67	0.19	2.76E-06	1.70	8.22	s5e5
	Sand%	0.51	10.9	5.48E-06	1.25	6.39	s5e11
	Silt%	0.43	5.51	-6.90E-05	1.35	7.17	s41e5
	Clay%	0.48	6.83	4.12E-06	1.05	4.83	s5e5
Corona	**17β-estradiol**	0.93	2.69	8.06E-05	3.75	15.27	s5e5
	SOC%	0.92	0.37	2.14E-08	3.49	13.04	s21e41
	pH	0.76	0.16	-1.80E-07	2.08	9.18	s5e41
	Sand%	0.55	9.37	7.41E-05	1.83	9.99	s5e5
	Silt%	0.49	5.2	-4.03E-05	1.64	10.6	s11e5
	Clay%	0.59	5.25	-1.20E-05	1.93	9.09	s11e11
SDNWA	**Calibration**	**r^2**	**SEP**	**Bias**	**RPD**	**RER**	**Math Treatment**
Foss 6500	**17β-estradiol**	0.84	2.42	-4.42E-07	2.53	10.89	s41d21
	SOC%	0.91	0.29	-1.86E-06	3.21	12.16	s5e5
	pH	0.65	0.39	-2.32E-05	1.71	6.55	s41e5
	Sand%	0.70	5.89	-8.01E-06	1.76	10.00	s5e11
	Silt%	0.51	5.92	1.36E-04	1.44	9.03	s41e5
	Clay%	0.79	3.28	-6.04E-05	2.13	8.87	s5e5
Corona	**17β-estradiol**	0.81	2.58	-6.99E-07	2.37	10.21	s5e5
	SOC%	0.90	0.31	-5.60E-08	2.98	11.26	s41e41
	pH	0.76	0.33	-2.88E-07	2.05	7.83	s5e21
	Sand%	0.52	7.31	2.22E-05	1.39	8.06	s41d5
	Silt%	0.41	6.59	3.24E-05	1.29	8.12	s5e5
	Clay%	0.73	3.69	-7.35E-06	1.91	7.89	s41d11

Where; r^2 = coefficient of determination, SEP = standard error of prediction, Bias = difference between the means of the NIR-predicted data and the reference data, RPD = ratio of standard deviation of values in the validation set to SEP, RER = ratio of range of values in the validation set to SEP, Segment = number of wavelength points over which the spectra were smoothed and designated as “s”, Gap = number of wavelength points over which the derivative was calculated and designated as “d” for first derivative and “e” for second derivative.

Although both instruments successfully demonstrated the feasibility of predicting 17β-estradiol K_d values along with SOC, pH and clay content in air-dried and sieved soil samples, the most effective use of NIRS technology will be in generating on-site data from field-moist soil. This explains why field portable instruments such as the Corona are receiving increased attention in carbon monitoring and environmental studies (Williams et al. 1987, Sudduth and Hummel 1993, Malley et al. 2000, Martin et al. 2002, Vasques et al. 2009). Field portable instruments, such as the Corona, have the advantage of further decreasing costs associated with sample collection, handling, and storage and may provide a rapid on-site assessment of the chemical properties of field-moist samples.

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3. Soil characteristics and herbicide sorption coefficients in 140 soil profiles of two irregular undulating to hummocky terrains of western Canada

3.1 ABSTRACT

Sensitive input parameters such as herbicide sorption coefficients are seldom quantified in sufficient spatial detail, leading to large uncertainties in pesticide fate model predictions at regional and national scales. This study examined the spatial variability of soil characteristics and herbicide sorption coefficients (K_d) in a total of 609 soil samples obtained from 140 soil profiles in two undulating to hummocky soil-landscapes of western Canada. In all soil horizons, K_d values were always largest for glyphosate followed by atrazine then 2,4-D. In each soil-landscape, soil organic carbon content (SOC), 2,4-D and atrazine K_d values, all strongly associated, numerically decreased with A > B > C mineral horizons, regardless of the segment of the slope in which the soil profile was located. SOC, 2,4-D K_d and atrazine K_d values were typically smaller in the eluvial A-horizons (Ae, Aej) than in other A-horizons. In several landform elements, glyphosate K_d values were numerically greater in the B, rather than the A or C mineral horizons. Glyphosate K_d values were particularly large in B-horizons with redoximorphic features such as in illuvial B-horizons enriched with clay (Btg, Btgj). When the soil properties and sorption values of similar horizons were compared across the soil-landscapes, SOC and 2,4-D K_d demonstrated greater coefficients of variation than atrazine K_d and glyphosate K_d. The strength of prediction equations for 2,4-D K_d and atrazine K_d was strong in each soil-landscape when all samples in the soil profile were included in the model. Nevertheless, the strength of

prediction equations by mineral horizon was generally weaker and in some cases not significant. The in-field variability of glyphosate K_d values could not be predicted from the measured soil properties data, or from calculated digital terrain attributes. Terrain attributes also showed little to no correlation, or predictive strength for describing the variability of 2,4-D and atrazine sorption in the soil-landscapes.

3.2 Introduction

Pesticide sorption coefficients such as K_d values are among the most sensitive input parameters in pesticide fate models (Boesten and Van der Linden 1991, Dubus et al. 2003, Farenhorst et al. 2008). The K_d values of herbicides 2,4-D, alachlor, atrazine, glyphosate and mesotrione all vary across slope positions in surface soils of fields and watersheds (Novak et al. 1997, De Jonge and De Jonge 1999, Liu et al. 2002, Dyson et al. 2002, Dorado et al. 2003, Farenhorst et al. 2008). It is, therefore, that digital terrain models have been shown to improve in some cases the predictions of herbicide fate parameters in surface soils of fields (Farenhorst et al. 2003). Few studies have focused on the spatial variability of K_d values in subsurface soils (Gaultier et al. 2006, Farenhorst et al. 2008).

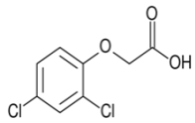
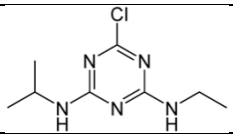
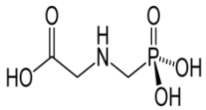
The Prairie pothole region of Canada consists of 390,000 km^2 of undulating to hummocky agricultural landscapes with millions of wetlands (Wrubleski and Ross, 2011). These Prairie wetlands act as fresh water filtration systems and provide habitats for aquatic and terrestrial wildlife. Pesticides have been detected in Prairie wetlands (Messing et al. 2011), sometimes at

levels violating the Canadian Aquatic Water Quality guidelines (Donald et al. 1999). Knowledge of the spatial variability of herbicide sorption parameters in terrains typical of the Prairie pothole region of Canada is important when pesticide fate models are used in assessing the impact of improved farm management practices on the risk of water contamination by pesticides (Cessna et al. 2010).

Approximately 94 % of the agriculture applied pesticides in Canada are herbicides (Environment Canada, 2011). Three herbicides, 2,4-D (weak-acid), atrazine (weak-base), and glyphosate (zwitterion) with contrasting physicochemical characteristics were used in this study (Table 3.1). Previous studies have demonstrated that sorption of 2,4-D and atrazine is largely controlled by soil organic carbon content (SOC) while soil pH has been shown to influence the sorption of all three herbicides (Sprankle et al. 1975, Calvet, 1989, Sensi, 1992, De Jonge and De Jonge, 1999, Dorado et al. 2003). 2,4-D, atrazine and glyphosate are commonly detected in surface and ground water sources of North America (Humphries et al. 2005, Donald et al. 2007, Messing et al. 2011).

The objective of this study was to quantify the spatial variability of sorption parameters of 2,4-D, atrazine and glyphosate in 1 m deep soil profiles of irregular undulating to hummocky terrain landscapes, as influenced by soil depth and landform elements.

Table 3.1 Molecular Structure and physicochemical properties of the herbicides used in the study (FOOTPRINT 2009).

	2,4-D	**Atrazine**	**Glyphosate**
			
Molecular Mass (g mol^{-1})	221.04	215.68	168.07
Solubility in water (mg L^{-1}) at 20°C	23,180	35	10,500
log Kow at pH 7, 20°C	-0.83	2.70	-3.20
pKa at 25°C	2.87	1.70	(2, 2.6, 5.6, 10.6)*
Vapor pressure (mPa) at 25°C	1.87×10^{-2}	3.9×10^{-2}	1.31×10^{-2}
Soil half-life (days) at 20°C	14	66	49

Where: log Kow = log octanol water partitioning coefficient and pKa = Dissociation constant.
*Sprankle et al. 1975

3.3. Materials and Methods

3.3.1 Research site and soil sampling

Soil sampling was conducted at research sites representative of agricultural fields in the Prairie pothole region of Canada and classified as irregular undulating to hummocky terrain landforms (Pennock et al. 1987, Podolsky and Schindler, 1994). Two parallel fields (8-ha each) were selected at the Manitoba Zero Tillage Research Association Research Farm (MZTRA) (49° 53'N latitude, 99° 58'W longitude), located about 17 km north of Brandon in the Province of Manitoba. One field (20-ha) was selected at the St. Denis National Wildlife Research Area (SDNWA) (106° 5'N Longitude, 52° 12'W latitude), located about 50 Km East of Saskatoon in the Province of Saskatchewan. Both MZTRA (zero-tilled) and SDNWA (conventional-tilled) fields are in a grain and oilseed rotation and pesticides and synthetic fertilizers were used following typical farm practices (Xu et al. 2009). Conventional tillage, as the term is used here, refers to shallow surface disturbance and incorporation of a portion of the previous year's crop residues into surface soil.

The study design was set up such that the impact of landform elements on soil properties and herbicide sorption could be tested. Digital elevation models (grid size 5x5 m^2) and digital terrain modeling software (Pennock 2003) were used to classify the MZTRA and SDNWA landscapes into convergent and divergent shoulders (CSH and DSH), convergent and divergent backslopes (CBS and DBS), convergent and divergent footslopes (CFS and DFS) and depression (DEP)

landform elements. Within each landform element, 10 sampling points (latitude and longitude) were randomly selected to collect soil profiles to a depth of 1 m (truck mounted hydraulic probe with a 5 cm diameter). At each of the 70 sampling points, ten terrain attributes were also calculated (Pennock 2003) to explore the association between terrain attributes and herbicide sorption in the A-horizon. These terrain attributes were elevation (Z, m), gradient (G, degree), aspect (A, degree), profile curvature (PROFILE, degree m^{-1}), plan curvature (PLAN, degree m^{-1}), mean curvature (MEAN, degree m^{-1}), specific catchment area (SCA, m^2 m^{-1}), specific dispersal area (SDA, m^2 m^{-1}), compounded topographic index (CTI) and steam power index (SPI).

Soil profiles were classified following the Canadian System of Soil Classification (Soil Classification Working Group, 1998) and sectioned by horizon yielding 609 soil samples. The 314 soil samples from MZTRA were from one of 23 designated horizons (i.e., AB, AC, Ae, Aej, Ah, Ap, Apk, Apksa, Apsa, BC, Bg, Bgk, Bm, Bmk, Btg, Btj, CA, Cca, Cg, Cgca, Cgk, Ck and Csa). The 295 soil samples from SDNWA were from one of 22 of such designated horizons (i.e., Ae, Aeg, Aegj, Ah, Ahk, Ap, Apca, Apk, Bcagj, BCca, BCg, Bg, Bm, Bmk, Bt, Btg, Btgj, Cca, Ccagj, Cg, Ck and Ckg).

3.3.2 Soil characteristics and herbicide sorption

The 609 soil samples were air dried and sieved to 2 mm (mesh size) prior to the analysis of soil properties and herbicide sorption. Soil organic carbon (SOC) was determined by the dry combustion method, employing a Leco CR-12 Carbon Analyzer (LECO Corporation, Ontario, Canada). A 2:1 ratio of soil to 0.01 M $CaCl_2$ (McKeague, 1978) was used in determining soil pH

(Acumen 50 pH meter; Thermo Fisher, Texas, USA). Soil texture was determined using Horiba LA-950 laser particle size analyzer (Horiba, Irvine, California, USA).

The batch equilibrium process was used to determine herbicide sorption by soil (Wauchope et al. 2002). 2,4-D (95% chemical purity, ^{14}C U-ring-labeled, 99% radiochemical purity and specific activity 13.97 x 10^{-14} Bq $mmol^{-1}$), glyphosate (99% chemical purity, ^{14}C U-ring-labeled, 95% radiochemical purity and specific activity 5.94 x 10^{-14} Bq $mmol^{-1}$) and atrazine (95% chemical purity, ^{14}C U-ring-labeled, 99% radiochemical purity and specific activity 25.14 x 10^{-14} Bq $mmol^{-1}$) were purchased from Sigma Aldrich Co., St. Louis, MO, USA. For each herbicide, a stock solution (1 mg herbicide L^{-1} and 16.70 Bq ^{14}C-herbicide mL^{-1}) was prepared by dissolving analytical grade and radiolabeled herbicide in 0.01 M $CaCl_2$. Herbicide solution (10 mL) was added to soil (5 g) in 50 mL Teflon tubes (duplicates) and rotated in dark for 24 hour at 5 °C to establish equilibrium between the concentration of herbicide sorbed by soil (Cs) and the concentration of herbicide remaining in solution (Ce). Samples were centrifuged at 10,000 rpm for 10 minutes and supernatant aliquots (1 mL) were removed (duplicates) and added to 5 mL of scintillation cocktail in 7 mL vials. Vials were manually lightly shaken and stored in the dark for 24 hours to dissipate the chemiluminescence. Radioactivity was then quantified using a Liquid Scintillation Counter (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) with automated quench correction (#H method). Herbicide sorption coefficient, K_d values (L kg^{-1}) was determined by C_s/C_e, where C_s is the amount of chemical sorbed on the soil at equilibrium (g kg^{-1}) and C_e is the amount of chemical remaining in the solution at equilibrium (g L^{-1}).

3.3.3 Statistical analysis

Horizons at each site (MZTRA or SDNWA) were grouped into one of three mineral horizons: A, B, or C. Box plots in SigmaPlot for Windows Version 11.0 (2008 Systat Software, Inc. Germany) were used to visualize the data by mineral horizon. Pearson pairwise correlations (SigmaPlot Version 11.0) were used to determine the strength of significant correlations (associations) between soil properties and herbicide K_d values for the 314 soil samples from MZTRA and the 295 soil sample from SDNWA. Pearson pairwise correlations were also applied to the samples from A-horizons to determine the strength of significant correlations (associations) between terrain attributes and herbicide K_d values. Forward stepwise multi-linear regression with partial least square (PLS1) was done in the Unscrambler® version 9.8 (CAMO Software ASA, Norway) to predict K_d values from soil properties and/or terrain attributes (A-horizon only) for MZTRA, SDNWA, and the two soil-landscapes combined. In these PLS1 analyses, every third sample in a set, e.g., 609 soil samples, was used to validate, while the remaining two-thirds of the samples were used to calibrate. During calibration independent variables contributing less than $R^2 = 0.1$ to the equation were sequentially removed to simplify the regression equation while maintaining the approximate prediction power. A three-way ANOVA (Analysis of Variance) using Proc Mixed in SAS institute 9.2 for Windows was performed to explore the significant effects of factors site (MZTRA and SDNWA), mineral horizon (A, B and C) and landform elements (CSH, DSH, CBS, DBS, CFS, DFS and DEP) on soil properties and herbicide K_d values. Similar three-way ANOVAs were run with landform element data grouped by shoulder (CSH+DSH), backslopes (CBS+DBS), footslopes (CFS+DFS) and depressions (DEP).

3.4 Results

The herbicide sorption in soils numerically increased from 2,4-D K_d < atrazine K_d < glyphosate K_d (Table 3.2). At both MZTRA and SDNWA, SOC and sorption values demonstrated large variations among horizons (Figure 3.1). SOC and 2,4-D K_d typically showed larger coefficient of variations within horizons than atrazine K_d and glyphosate K_d (Figure 3.1). In both soil-landscapes, atrazine K_d and 2,4-D K_d were strongly positively associated with SOC, and with each other (Table 3.3). Percentage clay and soil pH showed negative correlations with SOC at both MZTRA and SDNWA (Table 3.3) since SOC decreased but %Clay and soil pH increased with depth (Figure 3.2). Therefore, atrazine and 2,4-D K_d were also negatively associated with %Clay and soil pH (Table 3.3). Glyphosate K_d was not significantly associated with soil properties, except for a very weak negatively association with SOC and %Silt in MZTRA (Table 3.3).

SOC was a consistently significant parameter in predicting K_d for 2,4-D and atrazine with a prediction power (R^2) being generally stronger when all samples were included, as opposed to when samples were included from each mineral horizon separately (Table 3.4). A prediction equation for glyphosate K_d value was not derived (not significant, data not shown) because glyphosate sorption was found to be poorly correlated with soil properties used in the current study at both the MZTRA and SDNWA soil-landscapes (Table 3.3).

Table 3.2 Mean (coefficient of variance %) of K_d values and SOC by soil horizons and landform element down the soil profiles and along a catenary sequence in MZTRA and SDNWA.

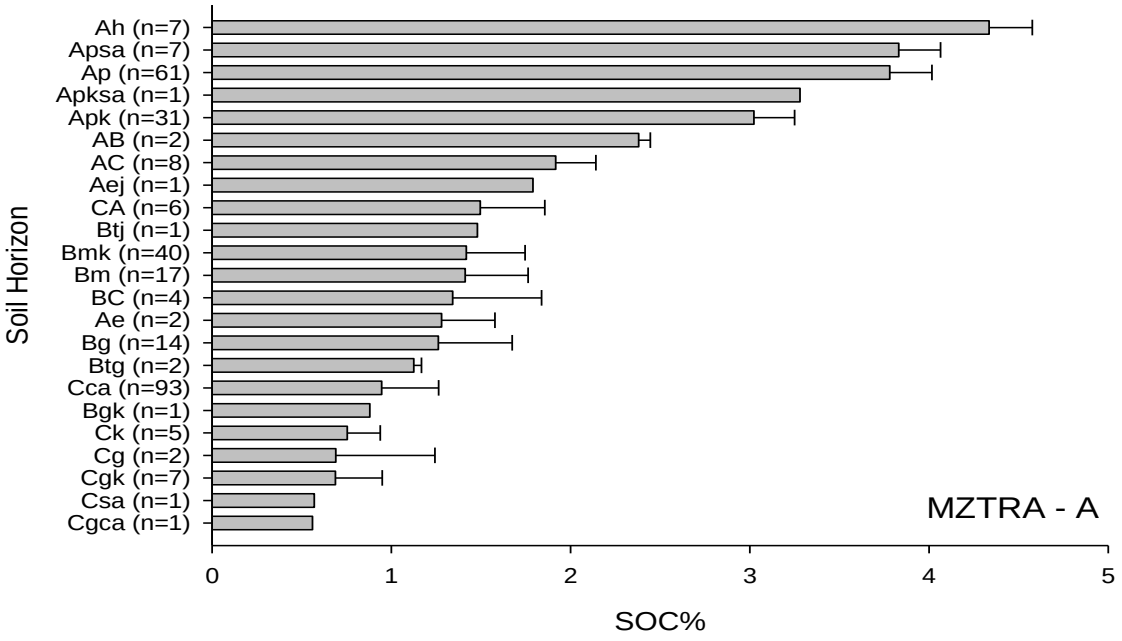
	Landform Elements							
	MZTRA				SDNWA			
Soil Profiles	**Shoulder**	**Backslopes**	**Footslopes**	**Depression**	**Shoulder**	**Backslopes**	**Footslopes**	**Depression**
SOC	(Landscape Range 0.42-5.81 %)				(Landscape Range 0.00-3.52 %)			
A-Horizon	3.30(28)	3.45(30)	3.17(26)	4.04(36)	1.92(33)	2.11(32)	2.14(31)	2.07(49)
B-Horizon	1.54(37)	1.40(31)	1.29(33)	1.26(37)	0.80(39)	0.58(52)	0.58(62)	0.41(51)
C-Horizon	1.05(34)	0.93(33)	0.91(37)	0.72(33)	0.25(192)	0.33(124)	0.27(33)	0.29(41)
Profile Mean	1.97(61)	1.99(67)	1.95(63)	2.11(81)	0.86(99)	1.01(94)	1.00(94)	1.26(89)
2,4-D	(Landscape Range 0.03-7.70 L Kg^{-1})				(Landscape Range 0.01-5.11 L Kg^{-1})			
A-Horizon	2.48(38)	3.28(47)	2.59(40)	3.84(47)	1.68(25)	2.16(34)	1.95(45)	2.07(53)
B-Horizon	0.70(80)	0.55(65)	0.54(67)	0.66(109)	0.73(100)	0.64(33)	0.56(116)	0.41(68)
C-Horizon	0.31(94)	0.27(78)	0.25(56)	0.24(54)	0.37(100)	0.44(75)	0.28(54)	0.35(69)
Profile Mean	1.18(101)	1.47(116)	1.30(101)	1.68(118)	0.84(77)	1.09(85)	0.94(103)	1.26(92)
Glyphosate	(Landscape Range 13.63-222.70 L Kg^{-1})				(Landscape Range 5.36-842.01 L Kg^{-1})			
A-Horizon	35.55(35)	39.83(91)	49.74(62)	49.33(47)	150.81(140)	18.40(91)	83.48(140)	45.74(140)
B-Horizon	49.85(34)	57.05(46)	72.60(60)	64.94(47)	100.00(129)	35.50(57)	73.09(69)	191.73(108)
C-Horizon	48.32(36)	37.57(27)	55.27(42)	48.64(39)	100.89(74)	41.23(74)	75.93(72)	73.53(83)
Profile Mean	43.99(38)	43.24(63)	56.80(58)	55.33(47)	116.96(120)	31.91(81)	77.73(103)	101.63(146)
Atrazine	(Landscape Range 1.01-52.49 L Kg^{-1})				(Landscape Range 0.08-9.12 L Kg^{-1})			
A-Horizon	13.64(42)	15.76(45)	14.70(45)	25.98(47)	4.00(33)	4.37(45)	4.31(41)	4.72(55)
B-Horizon	4.51(59)	3.45(47)	3.76(55)	3.87(82)	1.43(31)	1.21(37)	1.05(32)	1.02(49)
C-Horizon	2.71(49)	2.46(57)	2.12(36)	1.73(30)	0.76(36)	0.79(39)	0.69(49)	0.94(51)
Profile Mean	7.05(89)	7.71(100)	7.81(95)	11.17(119)	1.90(88)	2.13(95)	2.04(97)	2.94(90)

Table 3.3 Pearson correlation coefficients among soil properties and K_d values (L Kg^{-1}) for MZTRA (n=314) and SDNWA (n=295).

MZTRA(n=314)	K_d_Glyphosate	K_d_Atrazine	SOC%	pH	Sand%	Silt%	Clay%
K_d_2,4-D	-0.19***	0.90***	0.93***	-0.64***	0.15***	NS	-0.30***
K_d_Glyphosate		-0.16***	-0.21***	NS	NS	-0.11**	NS
K_d_Atrazine			0.90***	-0.61***	0.13*	NS	-0.28***
SOC%				-0.62***	0.19***	NS	-0.33***
pH					-0.25***	NS	0.37***
Sand%						-0.90***	-0.91***
Silt%							0.65***

SDNWA(n=295)	K_d_Glyphosate	K_d_Atrazine	SOC%	pH	Sand%	Silt%	Clay%
K_d_2,4-D	NS	0.89***	0.90***	-0.32***	0.37***	NS	-0.57***
K_d_Glyphosate		NS	NS	NS	NS	NS	NS
K_d_Atrazine			0.89***	-0.30***	0.36***	NS	-0.59***
SOC%				-0.40***	0.38***	NS	-0.65***
pH					NS	-0.32***	0.25***
Sand%						-0.75***	-0.61***
Silt%							NS

*, **, and *** = correlation is significant at the 0.05, 0.01, and 0.001 level, respectively. NS = correlation is not significant.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Soil Horizon
MZTRA - A
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2
3
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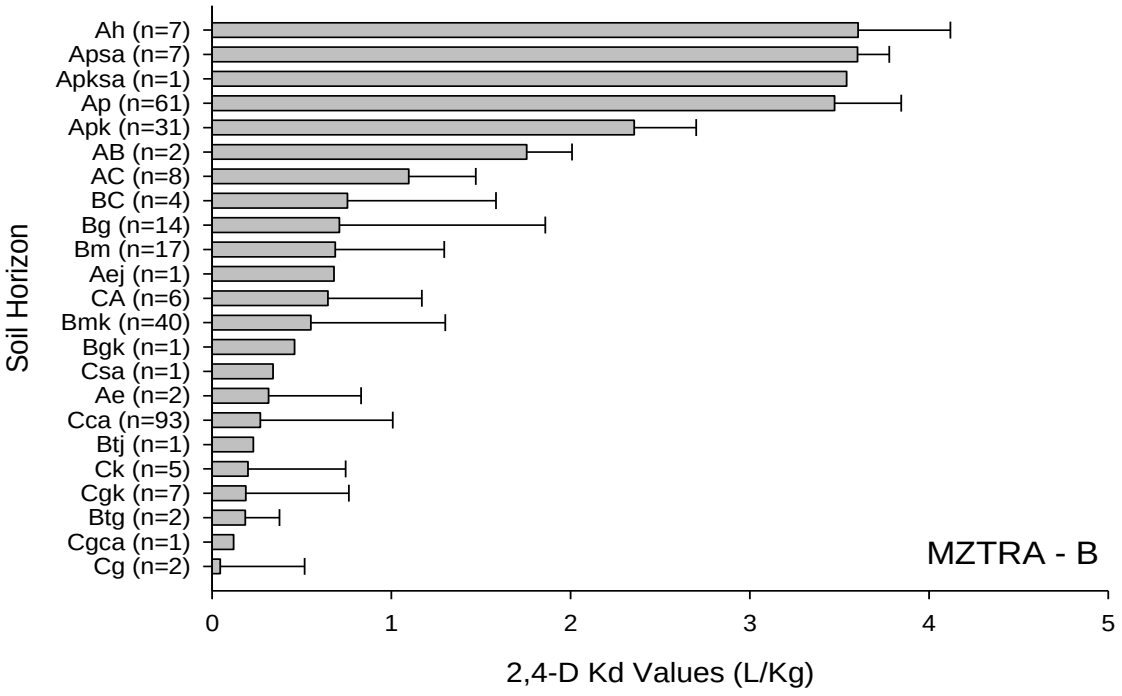
SOC%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Soil Horizon
MZTRA - B
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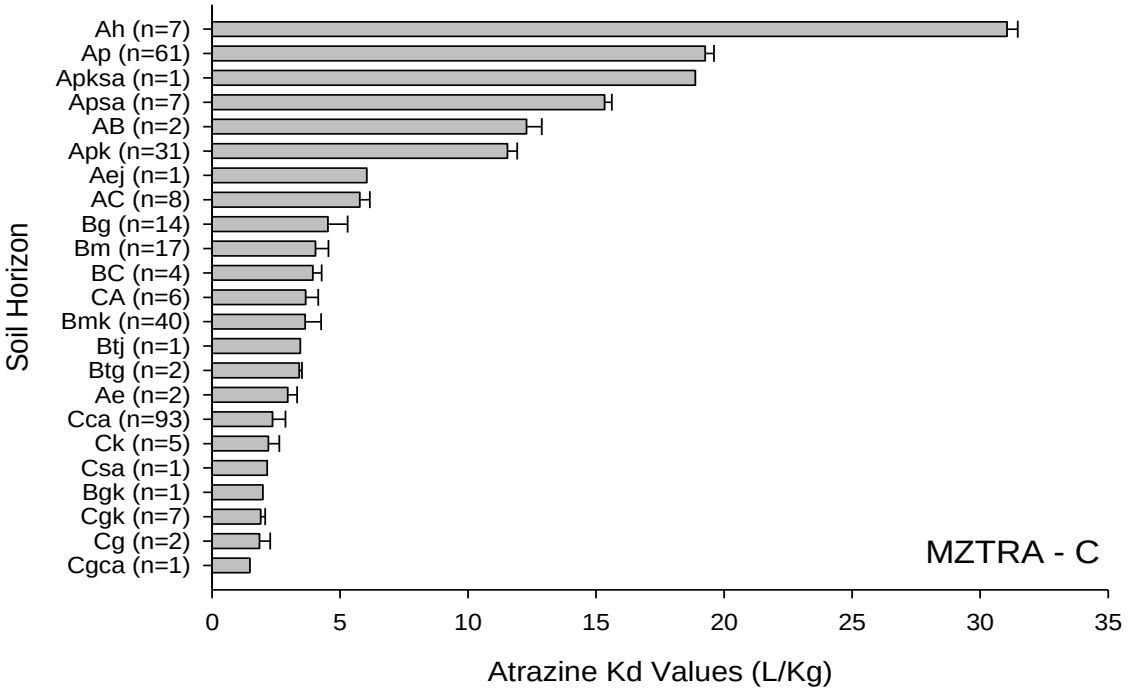
5
2,4-D Kd Values (L/Kg)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Csa (n=1)
Bgk (n=1)
Cgk (n=7)
Cg (n=2)
Cgca (n=1)
Soil Horizon
MZTRA - C
0
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10
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20
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30
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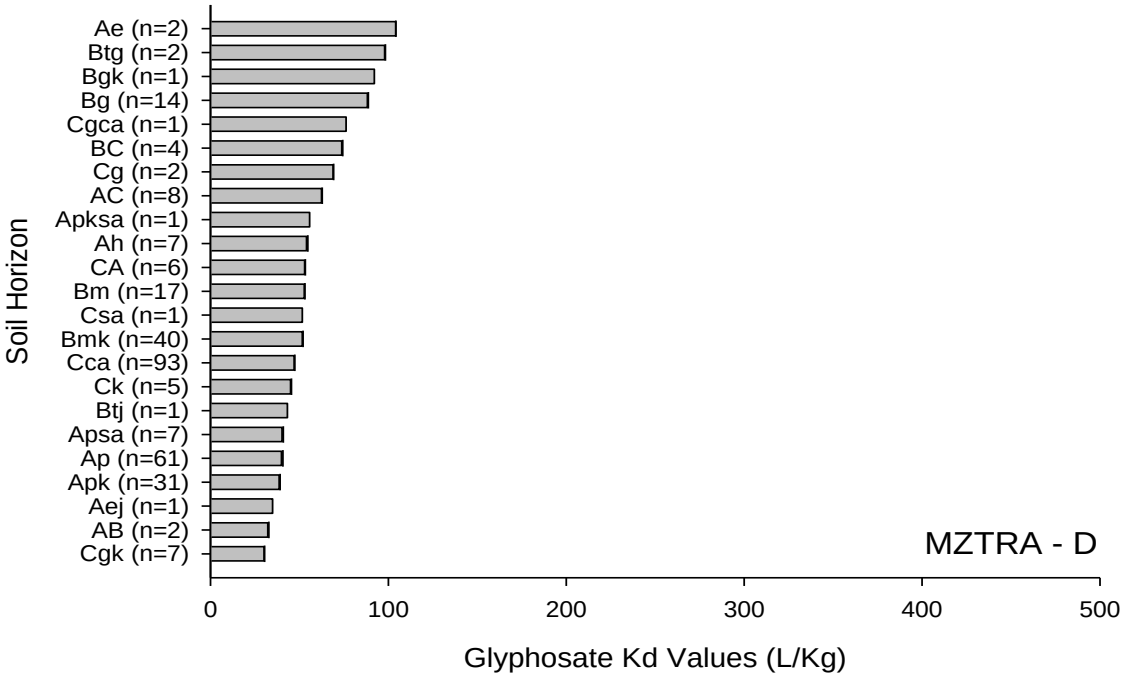
Atrazine Kd Values (L/Kg)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Soil Horizon
MZTRA - D
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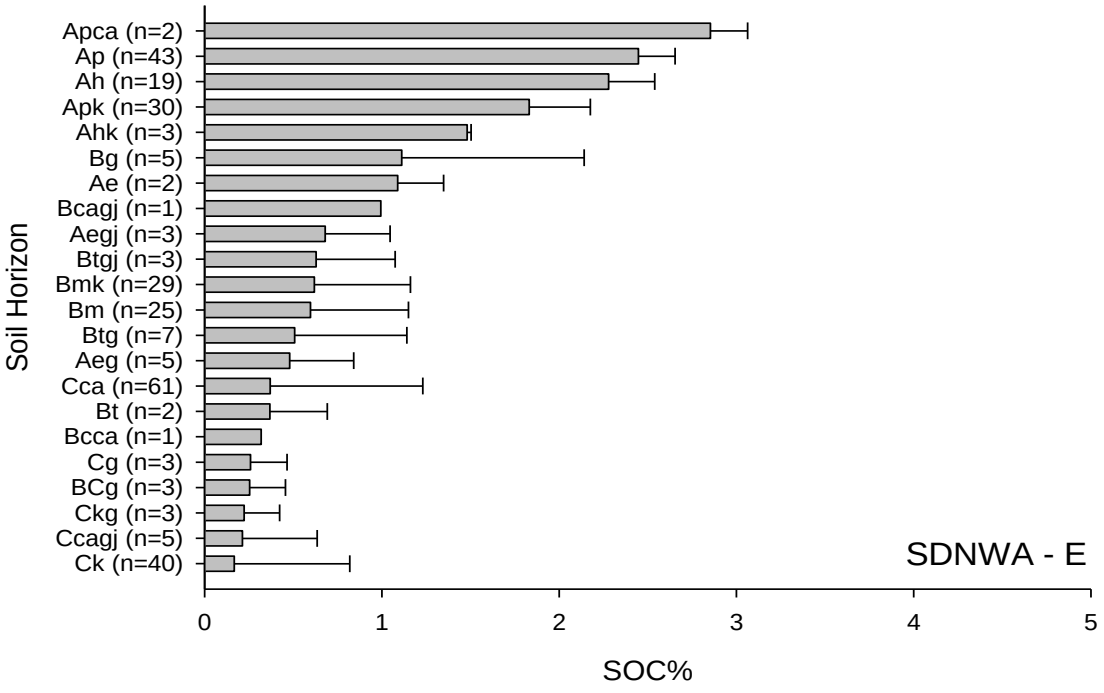
200
300
400
500
Glyphosate Kd Values (L/Kg)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SDNWA - E
0
1
2
3
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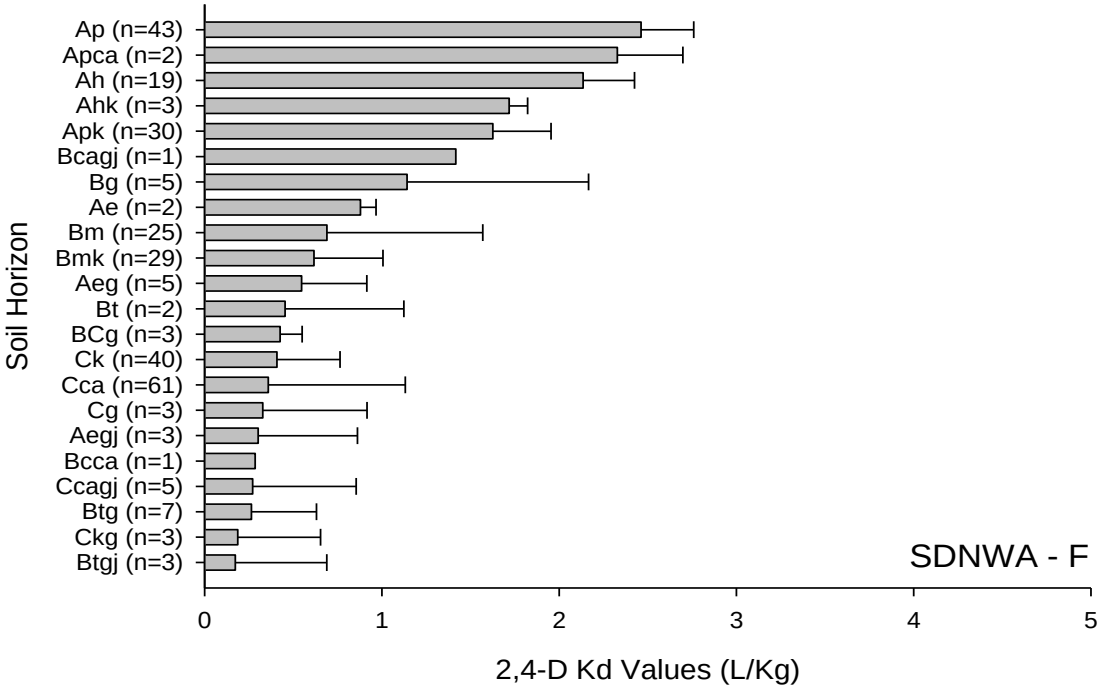
5
SOC%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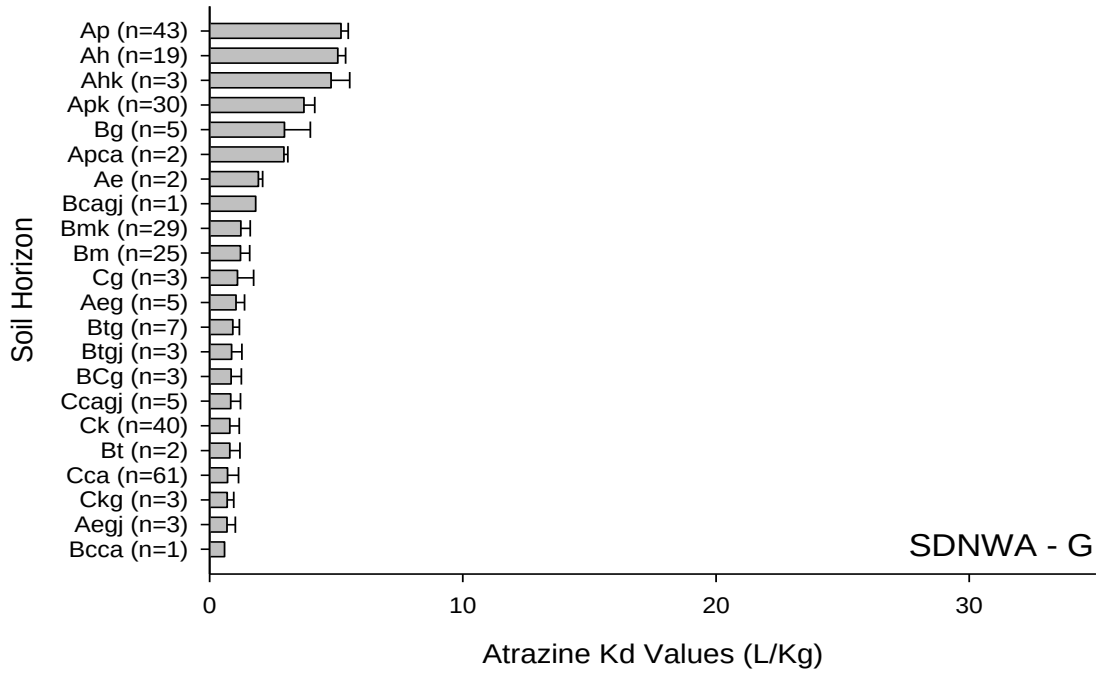
Bcca (n=1)
Ccagj (n=5)
Btg (n=7)
Ckg (n=3)
Btgj (n=3)
Soil Horizon
SDNWA - F
0
1
2
3
4
5
2,4-D Kd Values (L/Kg)



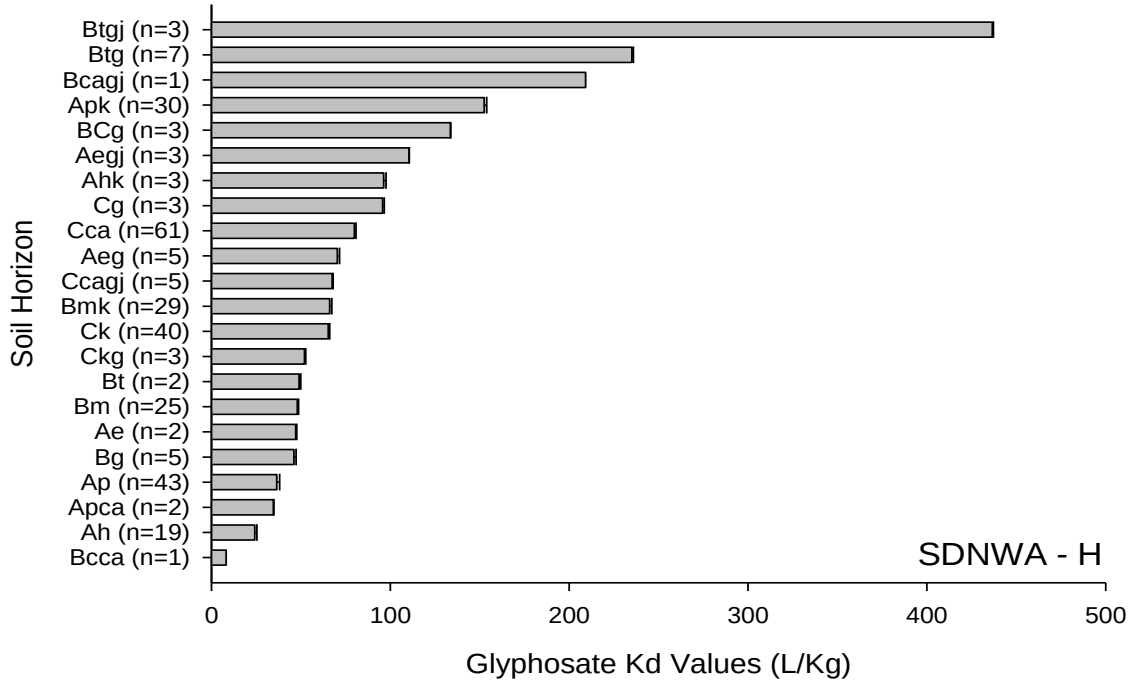
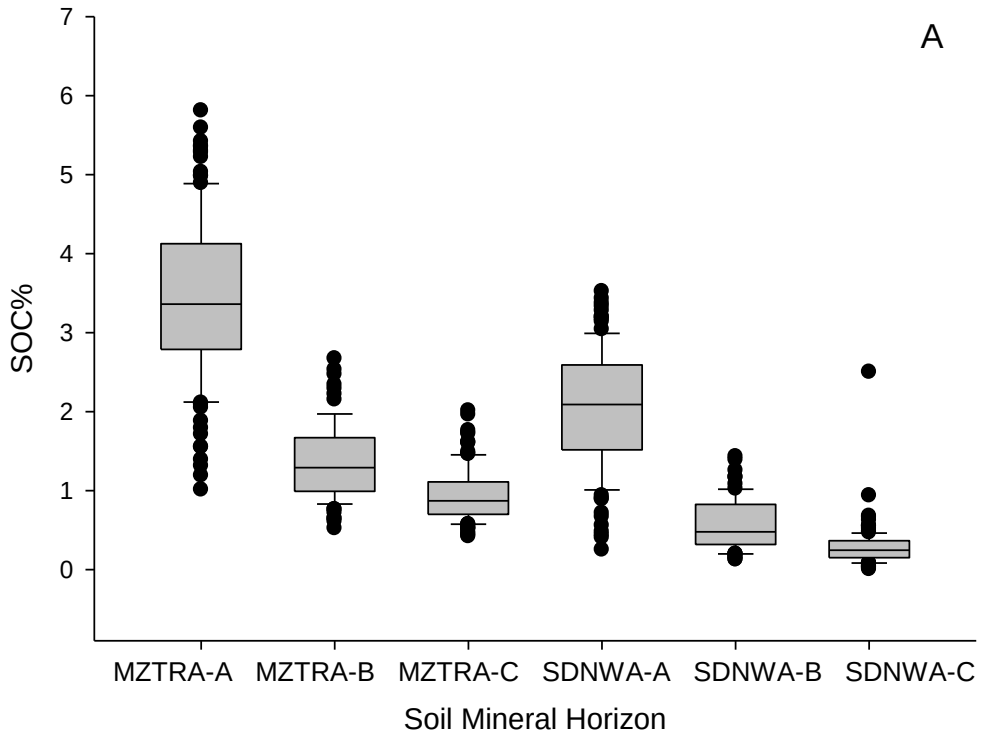
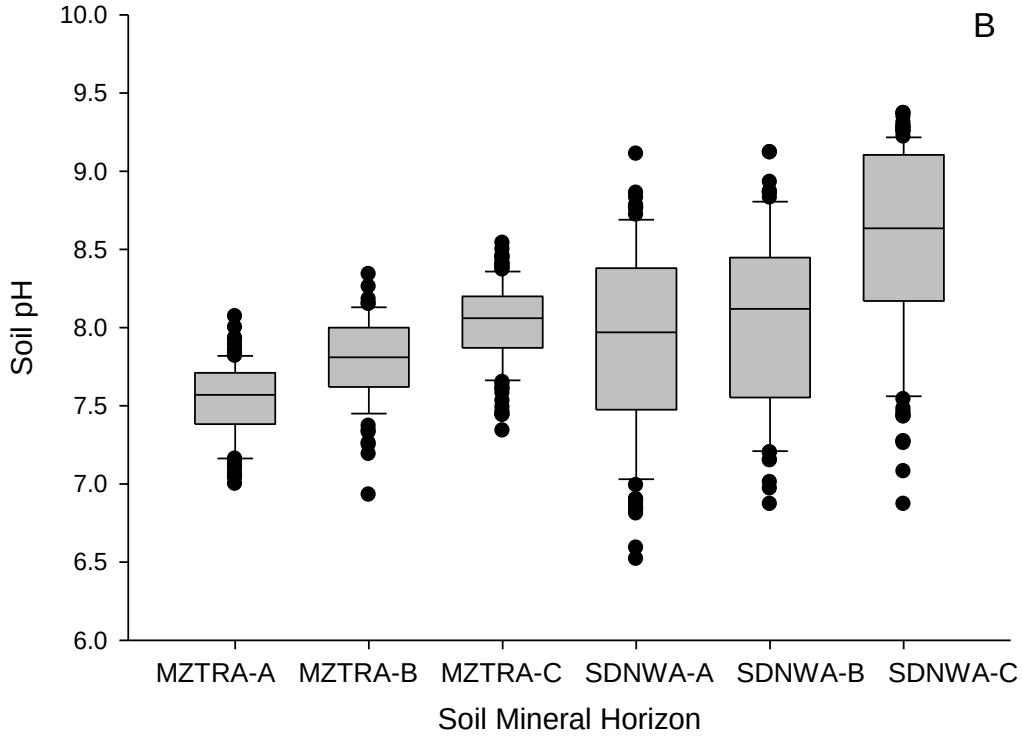


Figure 3.1 Mean SOC% and K_d values (L Kg^{-1}) in soil horizons at MZTRA (A to D) and SDNWA (E to H). Coefficient of variation is given as error bars.


A
SOC%
7
6
5
4
3
2
1
0
MZTRA-A
MZTRA-B
MZTRA-C
SDNWA-A
SDNWA-B
SDNWA-C
Soil Mineral Horizon


B
Soil pH
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
MZTRA-A
MZTRA-B
MZTRA-C
SDNWA-A
SDNWA-B
SDNWA-C
Soil Mineral Horizon

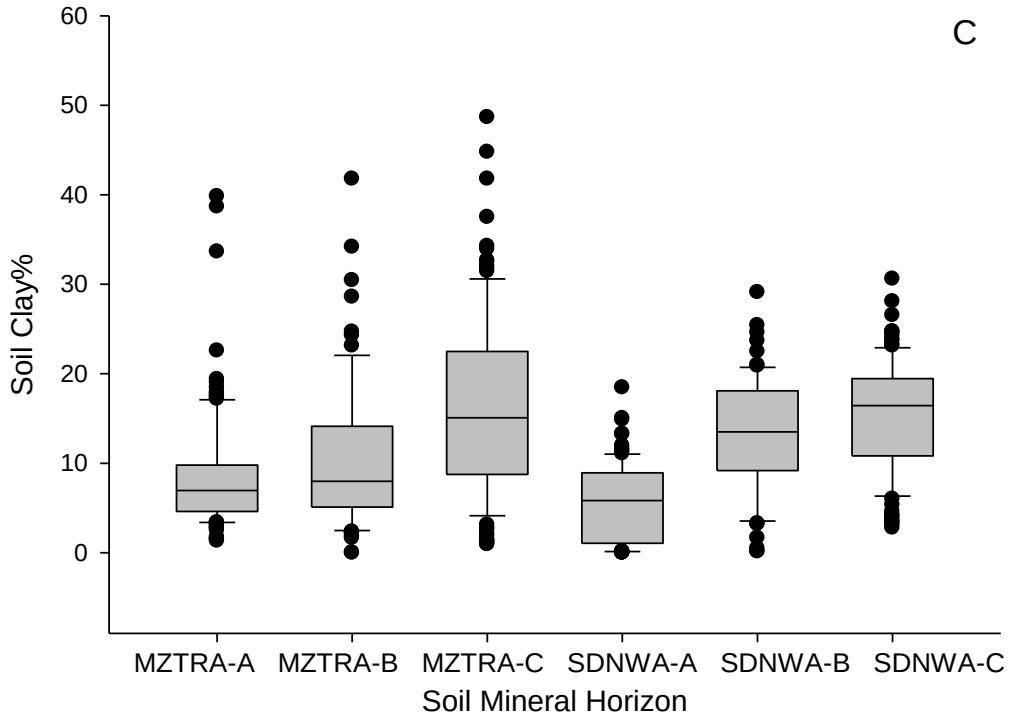


Figure 3.2 Box plot distributions of soil organic carbon (A), soil pH (B) and soil clay% (C) in different horizons in MZTRA and SDNWA landscapes.

Table 3.4 Prediction Models for K_d values (L Kg^{-1}) from soil properties in MZTRA and SDNWA.

MZTRA		PLS1-Models	R^2	RMSEP	Bias	Var-PC
2,4-D	Profiles	K_d=0.67+1.01(SOC%)-0.17(pH)	0.87	0.60	-0.01	96%,4%
	A Horizons	K_d=0.34+1.13SOC%-0.16(pH)	0.76	0.59	0.18	96%,4%
	B Horizons	K_d=0.23+0.84(SOC%)-0.10(pH)	0.70	0.29	-0.05	74%,26%
	C Horizons	K_d=1.51+0.34(SOC%)-0.18(pH)-0.002(Sand%)+0.004(Silt%)-0.003(Clay%)	0.50	0.15	0.04	94%,6%
Atrazine	Profiles	K_d=3.94+5.68(SOC%)-0.91(pH)	0.82	3.45	0.36	96%,4%
	A Horizons	K_d=0.747+6.70(SOC%)-0.94(pH)	0.49	5.25	0.73	96%,4%
	B Horizons	K_d=1.27+4.55(SOC%)-0.47(pH)	0.82	0.87	-0.11	74%,26%
	C Horizons	K_d=-1.195+1.47(SOC%)+0.29(pH)	0.32	0.96	0.42	67%,33%
SDNWA		**PLS1-Models**	**R^2**	**RMSEP**	**Bias**	**Var-PC**
2,4-D	Profiles	K_d=0.14+0.86(SOC%)	0.87	0.33	0.001	100%,100%
	A Horizons	K_d=0.40+0.80(SOC%)	0.61	0.51	0.24	100%,100%
	B Horizons	--NS--	--	--	--	--
	C Horizons	K_d=0.63+0.2(SOC%)-0.003(Sand%)-0.004(Silt%)-0.0005(Clay%)	0.36	0.27	-0.02	46%,54%
Atrazine	Profiles	K_d=3.63+1.70(SOC%)-0.39(pH)	0.78	1.00	-0.14	74%,26%
	A Horizons	K_d=0.73+1.78(SOC%)	0.57	0.57	0.18	100%,100%
	B Horizons	K_d=-0.61+0.40(SOC%)+0.193(pH)	0.16	0.42	0.07	53%,47%
	C Horizons	K_d=2.52+0.27(SOC%)+0.13(pH)-0.03(Sand%)-0.02(Silt%)-0.02(Clay%)	0.20	0.30	-0.02	84%,16%
MZTRA+SDNWA		**PLS1-Models**	**R^2**	**RMSEP**	**Bias**	**Var-PC**
2,4-D	Profiles	K_d=-0.75+0.98(SOC%)	0.86	0.45	0.08	81%,19%
	A Horizons	K_d=1.27+0.99(SOC%)+0.18(pH)	0.63	0.74	0.09	89%,2%
	B Horizons	K_d=0.24+0.59(SOC%)	0.24	0.46	0.05	87%,13%
	C Horizons	--NS--	--	--	--	--
Atrazine	Profiles	K_d=8.10+4.65(SOC%)-0.98(pH)	0.78	3.06	0.26	86%,12%
	A Horizons	K_d=10.96+5.36(SOC%)-1.04(pH)-0.16(Silt%)+0.22(Clay%)	0.65	5.62	-0.52	85%,15%
	B Horizons	K_d=3.08+3.35(SOC%)-0.41(pH)	0.68	1.18	-0.05	85%,15%
	C Horizons	K_d=1.03+1.60(SOC%)	0.49	0.88	-0.01	89%,11%

Where; R^2=Coefficient of determination, RMSEP=Root Mean Square Error of Prediction, Bias= Mean difference between measured and predicted variable, Var-PC=variance explained by first two principal components around independent variable. NS= No significant model equation.

Soil properties and K_d values were generally weakly or not significantly associated with terrain attributes (Table 3.5). When soil samples from the top horizon were used (n=70 for both MZTRA and SDNWA), PLS analysis produced no significant models that would predict herbicide sorption from terrain attributes, with the exception of a weak model to predict atrazine K_d in MZTRA (R^2=0.14, variables G and PROFILE) and to predict 2,4-D K_d (R^2=0.15, variables PLAN and MEAN) and glyphosate K_d (R^2=0.28, variables G and SDA) in SDNWA. Including soil properties data to these terrain attributes improved the predictive power to a R^2 of 0.51 for atrazine K_d in MZTRA and to a R^2 of 0.56 for 2,4-D K_d in SDNWA, but resulted in not-significant models for glyphosate K_d. When all A-horizon samples in the PLS analysis (n=120 for MZTRA and n=109 for SDNWA) were included, only MZTRA showed significant models to predict herbicide sorption from terrain attributes, and again the models were very weak with a R^2 of 0.10 for 2,4-D K_d (variable G) and a R^2 of 0.15 for atrazine K_d (variables Z, G, PROFILE and CTI). Combining terrain attributes and soil properties data in predicting sorption values in the A-horizon improved the prediction for 2,4-D K_d from a R^2 of 0.76 with soil properties data alone (Table 3.4) to 0.80 and for atrazine K_d values from a R^2 of 0.49 with soil properties data alone (Table 3.4) to 0.53.

Table 3.5 Pearson correlations coefficients among K_d values (L Kg^{-1}), soil properties and topographic attributes for the A-horizons in MZTRA (n=120) and SDNWA (n=109).

MZTRA	Z	GRADIENT	ASPECT	PROFILE	PLAN	MEAN	SCA	SDA	CTI	SPI
K_d_2,4-D	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
K_d_Glyphosate	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
K_d_Atrazine	NS	-0.33**	NS	NS	NS	NS	NS	NS	0.25*	NS
SOC%	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
pH	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Sand%	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Silt%	NS	-0.30*	NS	NS	NS	NS	NS	NS	NS	NS
Clay%	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

SDNWA	Z	GRADIENT	ASPECT	PROFILE	PLAN	MEAN	SCA	SDA	CTI	SPI
K_d_2,4-D	-0.30*	NS	NS	NS	-0.29*	-0.29*	NS	NS	NS	NS
K_d_Glyphosate	0.28*	0.36**	NS	NS	NS	NS	NS	0.30*	-0.29*	NS
K_d_Atrazine	-0.29*	NS	NS	NS	NS	NS	NS	NS	NS	NS
SOC%	-0.38***	NS	NS	-0.27*	-0.37**	-0.38**	NS	-0.31**	0.25*	NS
pH	0.40***	0.27*	NS	0.44***	0.27*	0.29*	NS	0.35**	-0.34**	NS
Sand%	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Silt%	NS	NS	-0.26*	NS	NS	NS	NS	NS	NS	NS
Clay%	0.24*	0.31**	NS	NS	0.30**	0.31**	NS	NS	-0.38**	NS

*, **, and *** = correlation is significant at the 0.05, 0.01, and 0.001 level, respectively. NS = correlation is not significant.

Each of the seven landform elements had Chernozemic soils. 90% of the soil profiles at MZTRA than SDNWA were Chernozemic soils (Table 3.6). At both sites, many of the Chernozemic soils experienced discharge of solute-rich groundwater, as indicated by the high number of profiles with calcium carbonate in the A (e.g. Apsa, Apk, Apksa, Apsa) and B (e.g. Bmk, Bgk) horizons. (Pennock et al. 2011). Gleysolic soils (10%) were predominantly located in depressions, and never in shoulder positions (Table 3.6). The ANOVAs with either four (Table 3.7) or seven (Table 3.8) landform elements demonstrated that spatial variations in soil properties and sorption values were significantly ($P<0.05$) influenced by two or three-way interactions of site, mineral horizon and/or landform element.

In the analysis with four landform elements (Table 3.7), site and horizon was the only significant interactive factor in the case of SOC and 2,4-D K_d, while the three-way interaction was significant for %Clay and the K_d values of atrazine and glyphosate. Site and landform element was the only significant interactive factor for soil pH, and site and horizon was the only significant interactive factor for %sand and %silt (Table 3.7). In all four landform elements, SOC, 2,4-D K_d, and atrazine K_d values (Table 3.2) were always significantly greater in the A-horizon of MZTRA than in other mineral horizons at MZTRA, and relative to all mineral horizons at SDNWA, (Table 3.2). The A-horizon of SDNWA showed significantly larger SOC and 2,4-D K_d values, and often numerically larger atrazine K_d values, than subsurface horizons at MZTRA and SDNWA (Table 2.2). In contrast, within the four landform elements, glyphosate K_d values were frequently numerically greater in B- and C-horizons than in A-horizons (Table 2.2).

Table 3.6 Summary of soil profiles classified at the subgroup level according to Canadian System of Soil Classification (CSSS 1998). Numbers refer to the number of soil profiles in each of the landform elements at MZTRA and SDNWA. Nearest equivalents to the *U.S. Soil Taxonomy* are: Black Chernozems = *Udic Boroll subgroups*; Dark Brown Chernozems = *Typic Boroll subgroups*; Humic Gleysol = *Aquolls, Humaquepts*; Luvic Gleysoil = *Argiaboll, Argiaquolls, Aqualfs*.

		Shoulder		**Backslope**		**Footslope**		**Depression**	
		MZTRA	**SDNWA**	**MZTRA**	**SDNWA**	**MZTRA**	**SDNWA**	**MZTRA**	**SDNWA**
Chernozemic[1]	**Rego**	4	10	6	5	6	3	0	0
	Orthic / Calcareous	15	10	13	15	13	13	4	0
	Eluviated / Gleyed Eluviated / Gleyed	1[2]	0	0	0	0	4	0	3
Gleysolic[2]	**Orthic Humic**	0	0	1	0	0	0	5	3
	Humic Luvic	0	0	0	0	1	0	1	4

[1] MZTRA has Black Chernozems and SDNWA has Dark Brown Chernozems; [2] Located in a fairly leveled area in the field (anomaly).

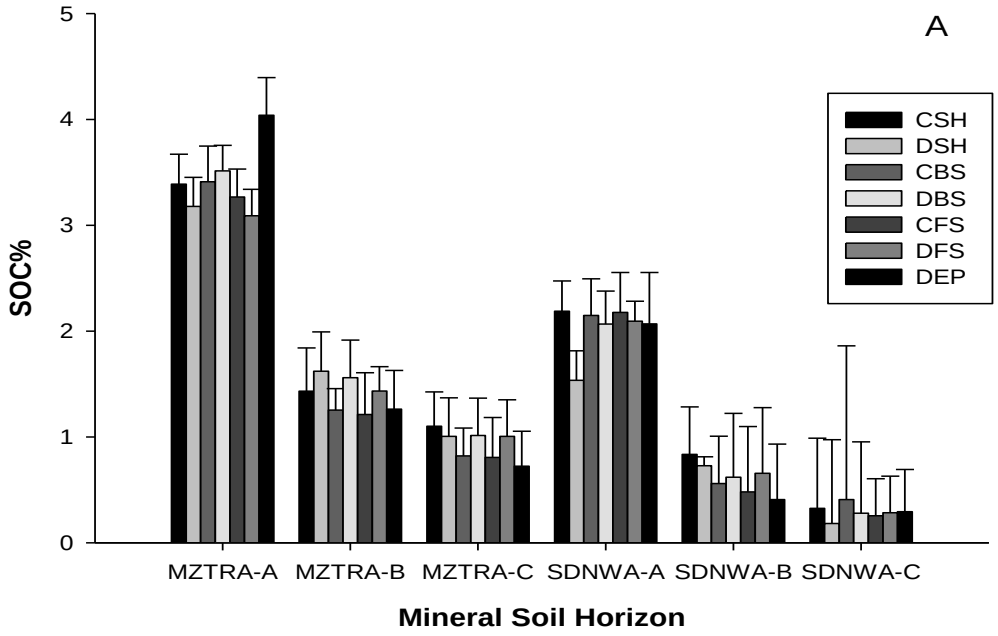
Table 3.7 Three-way ANOVAs on soil properties and K_d values (L Kg^{-1}), examining the factors Site (MZTRA and SDNWA), Horizon (A, B and C horizon) and Landform Elements (shoulder, backslopes, footslopes and depressions).

4 Landform Element		**SOC**		**2,4-D**		**Glyphosate**		**Atrazine**	
Effect	**Num DF**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**
SITE	1	351.85	<.0001	0.25	0.6214	0.44	0.5080	445.23	<.0001
LE	3	0.85	0.4689	0.53	0.6629	10.28	<.0001	0.02	0.9954
HOR	2	466.44	<.0001	479.72	<.0001	27.00	<.0001	653.21	<.0001
SITE*LE	3	1.19	0.3196	1.03	0.3863	5.69	0.0016	0.73	0.5390
SITE*HOR	2	20.01	<.0001	17.99	<.0001	3.89	0.0210	4.86	0.0081
LE*HOR	6	0.73	0.6274	0.65	0.6895	4.18	0.0004	2.36	0.0294
SITE*LE*HOR	6	1.52	0.1685	0.79	0.5743	5.65	<.0001	2.62	0.0162
		Soil pH		**Sand%**		**Silt%**		**Clay%**	
Effect	**Num DF**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**
SITE	1	21.25	<.0001	155.39	<.0001	401.20	<.0001	4.09	0.0461
LE	3	6.78	0.0005	2.92	0.0386	1.31	0.2775	1.90	0.1356
HOR	2	73.26	<.0001	34.12	<.0001	7.73	0.0005	58.67	<.0001
SITE*LE	3	5.31	0.0024	0.62	0.6018	0.10	0.9573	0.07	0.9741
SITE*HOR	2	1.27	0.2812	5.30	0.0053	9.11	0.0001	13.98	<.0001
LE*HOR	6	0.22	0.9708	0.59	0.7372	0.78	0.5829	1.84	0.0885
SITE*LE*HOR	6	0.80	0.5690	1.83	0.0919	0.85	0.5302	2.69	0.0140

Table 3.8 Three-way ANOVAs on soil properties and K_d values (L Kg^{-1}), examining the factors Site (MZTRA and SDNWA), Horizon (A, B and C horizon) and Landform Elements (CSH, DSH, CBS, DBS, CFS, DFS and DEP).

7 Landform Element		**SOC**		**2,4-D**		**Glyphosate**		**Atrazine**	
Effect	**Num DF**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**
SITE	1	370.44	<.0001	0.08	0.7797	0.78	0.3798	564.65	<.0001
LE	6	1.56	0.1642	4.16	0.0007	13.13	<.0001	1.43	0.2073
HOR	2	657.37	<.0001	796.96	<.0001	52.85	<.0001	826.41	<.0001
SITE*LE	6	1.10	0.3667	4.2	0.0006	14.3	<.0001	0.44	0.8505
SITE*HOR	2	34.88	<.0001	25.25	<.0001	5.04	0.0068	3.69	0.0257
LE*HOR	12	1.25	0.2462	2.91	0.0006	5.53	<.0001	1.61	0.0856
SITE*LE*HOR	12	1.47	0.1329	0.92	0.5239	8.37	<.0001	2.09	0.0161
		Soil pH		**Sand%**		**Silt%**		**Clay%**	
Effect	**Num DF**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**	**F Value**	**Pr > F**
SITE	1	45.40	<.0001	184.74	<.0001	546.02	<.0001	4.24	0.0412
LE	6	7.56	<.0001	2.54	0.0229	0.89	0.5076	3.82	0.0015
HOR	2	250.09	<.0001	54.38	<.0001	9.06	0.0001	79.53	<.0001
SITE*LE	6	5.12	<.0001	1.63	0.1429	1.26	0.2798	0.80	0.5737
SITE*HOR	2	2.89	0.0574	3.04	0.0489	9.14	0.0001	13.57	<.0001
LE*HOR	12	2.18	0.0134	0.39	0.9665	0.61	0.8316	1.35	0.1935
SITE*LE*HOR	12	2.44	0.0052	1.93	0.0292	1.58	0.0940	2.61	0.0028

When seven landform elements were considered for the ANOVA analysis, soil properties and herbicide K_d values were again significantly influenced by two-way or three-way interactions (Table 3.8). Site and horizon was the only significant interactive factor for SOC, whereas 2,4-D K_d was influenced by interactions of site and horizon, and site and landform elements (Table 3.8). K_d values of atrazine and glyphosate, as well as the soil pH, %Sand and %Clay were significantly influenced by the three-way interaction (Table 3.8). SOC and 2,4-D K_d values significantly increased from A-horizon at MZTRA > A-horizon at SDNWA > subsurface soils (Figure 3.3). Atrazine K_d values in all seven landform elements were also significantly greater in the A-horizon of MZTRA than in other mineral horizons at MZTRA and in any horizon at SDNWA (Figure 3.3). In the A-horizons of MZTRA, the DEP landform element demonstrated particularly large SOC, 2,4-D K_d and atrazine K_d values, relative to most other landform elements (Figure 3.3). At both MZTRA and SDNWA, Ae horizons typically displayed smaller SOC, 2,4-D and atrazine K_d values than other A-horizons (Figure 3.1). The C-horizon at MZTRA, had on average, significantly greater SOC values than the C-horizon of SDNWA. In all landform elements, except DEP, atrazine K_d values were significantly greater in C-horizons of MZTRA than of SDNWA (Figure 3.3). In contrast, 2,4-D K_d values were on average significantly greater in the C-horizon of SDNWA than in the C-horizon at MZTRA. For the ANOVA analysis with seven landform elements, regardless of the mineral horizon or landform element, glyphosate K_d values were statistically similar across MZTRA soils (Figure 3.3). At SDNWA, the Apk, Bmk, Cca and Ck horizons from a range of soil profiles in DSH (Figure 3.3), and Bg, Btg and Btgj horizons in DEP landform elements particularly demonstrated numerically large glyphosate K_d values (Figure 3.1).


A
SOC%
0
1
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4
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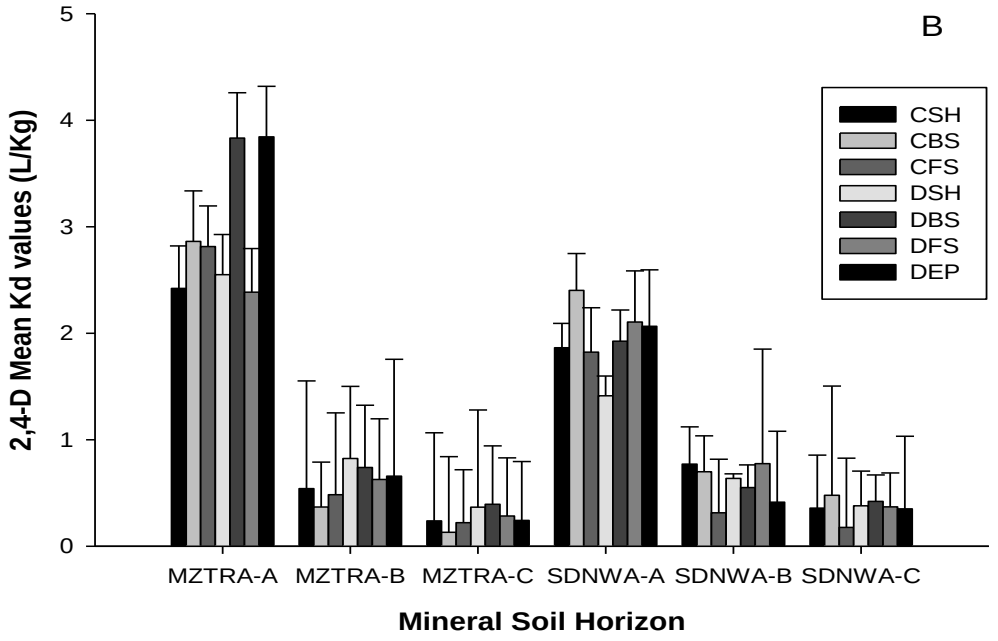
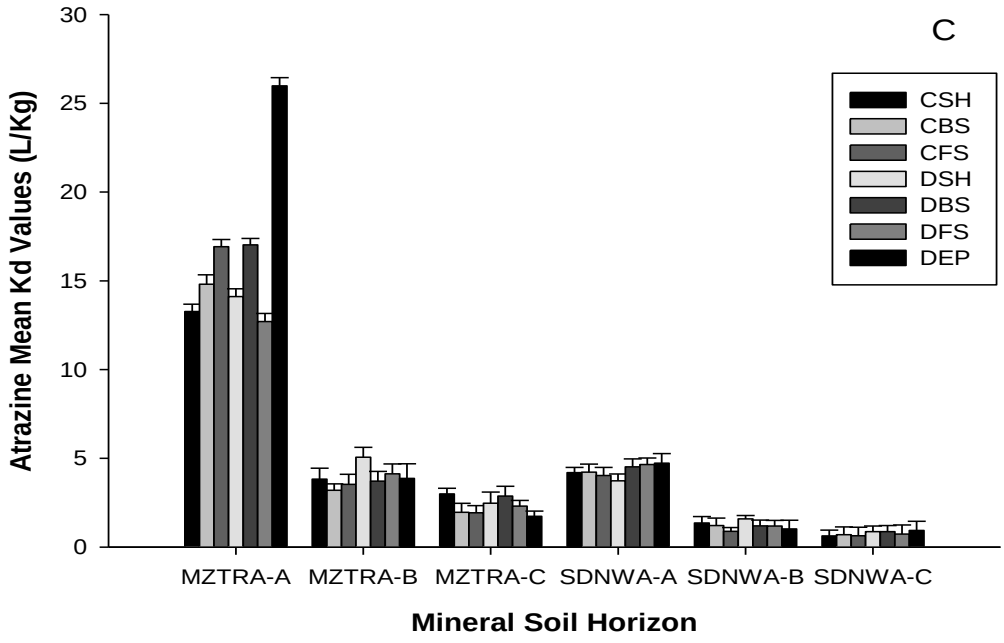
CSH
DSH
CBS
DBS
CFS
DFS
DEP
MZTRA-A
MZTRA-B
MZTRA-C
SDNWA-A
SDNWA-B
SDNWA-C
Mineral Soil Horizon


B
2,4-D Mean Kd values (L/Kg)
0
1
2
3
4
5
CSH
CBS
CFS
DSH
DBS
DFS
DEP
MZTRA-A
MZTRA-B
MZTRA-C
SDNWA-A
SDNWA-B
SDNWA-C
Mineral Soil Horizon



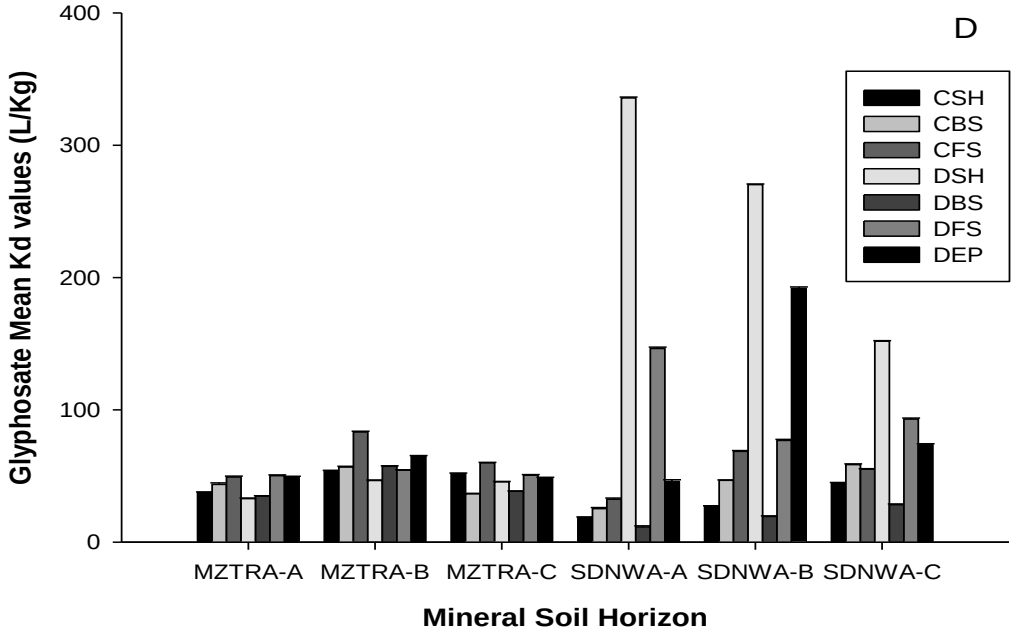


Figure 3.3 Mean SOC% (A) and K_d values L Kg^{-1} (coefficient of variance as error bars) of 2,4-D (B), atrazine (C) and glyphosate (D) belonging to different horizons in their respective landform elements (CSH, DSH, CBS, DBS, CFS, DFS and DEP) on MZTRA and SDNWA landscapes.

3.5 Discussion

Glyphosate K_d values ranged from 5 to 842 L Kg^{-1}. This is in agreement with the range of 19 to 547 L Kg^{-1} found for soil profiles in a heavily-eroded undulating field in Minnesota, United States (Farenhorst et al. 2008) and with the 5 to 810 L Kg^{-1} range reported for glyphosate in the IUPAC Footprint database (PPDB, 2009). Glyphosate sorption was largest in the B-horizons of soil profiles that showed evidence of poor drainage and periodic reduction, particularly when these B-horizons with redoximorphic features were also illuvial horizons enriched with clay. The polar functional groups of the glyphosate molecule are expected to show an affinity for clay minerals (Borggaard and Gimsing 2008). In addition, Fe_2O_3 coatings in B horizons with redoximorphic features promote glyphosate sorption because Fe(III) forms insoluble complexes with glyphosate molecules under pH conditions relevant to our soils (Subramaniam and Hoggard 1988, Gimsing and Borggaard 2002). Glyphosate K_d values were weakly or not significantly associated with SOC and soil pH, which is in agreement with another soil landscape study in undulating to hummocky terrain (Farenhorst et al. 2008).

Sorption parameters significantly impact the outcome of pesticide fate models particularly for soluble to moderately soluble pesticides such as 2,4-D and atrazine (Boesten and van der Linden 1991, Farenhorst et al. 2009). 2,4-D K_d values ranged from 0.03 to 7.70 L Kg^{-1} which is in close agreement with the range found for soil profiles in the Dark Grey Chernozemic soil zone of Manitoba (Gaultier et al. 2006). Atrazine K_d values ranged from 0.1 to 52.5 L Kg^{-1}. Weakly-basic herbicides are typically more strongly sorbed by soil than weakly-acidic herbicides

(Wauchope et al. 2002). There are different bonding mechanisms involved by which 2,4-D and atrazine are retained by soil (Senesi 1992). Also, weakly-acidic herbicides can be repelled by clay minerals, particularly under neutral and alkaline conditions (Celis et al. 1997).

SOC was the most significant soil property in explaining the spatial variability of 2,4-D and atrazine K_d within and between the research sites. Other studies which investigated a wide range of soils have shown strong positive associations between SOC and the sorption of 2,4-D (Benoit et al. 1996, Dorado et al. 2003, Gaultier et al. 2006, Farenhorst et al. 2008) and atrazine (Paya-Perez et al. 1992, Celis et al. 1997, Dorado et al. 2003, Kasozi et al. 2012). The lack of information on the spatial variability of sorption parameters within and between simulation units is one of the largest sources of uncertainty when pesticide fate models are used in regulatory and environmental risk assessments at the large-scale (Debus et al. 2003). The study results indicate that the data on SOC can be used to improve 3-dimensional information of 2,4-D and atrazine K_d values at the soil-landscape level.

SOC ranged from 0.4 to 5.8 % at MZTRA but from < 0.1 to 3.5% at SDNWA. SOC, 2,4-D and atrazine K_d values of A-horizons were smaller at SDNWA than at MZTRA, and the differences were particularly large for atrazine K_d values. Across all landform elements, atrazine K_d values were four to five fold greater in the A-horizons of MZTRA than in the A-horizons of SDNWA. Black Chernozems (MZTRA) have, by definition, a darker A-horizon than Dark Brown Chernozems (SDNWA) as a result of the greater net soil organic matter accumulation during soil development in a wetter climate (Pennock et al. 2011). In addition to the intrinsic factor of soil development, extrinsic factors such as summer fallow practices have impacted SOC levels in

Prairie soils (Rasmussen et al. 1980; Shrestha et al. 2013). Thus, the frequent summer fallow used prior to the 1980s at SDNWA reduced crop residues returns and has promoted loss of SOC from surface soils at this site (Smith et al. 1997, van der Kamp et al. 2003), thereby also impacting the potential retention of herbicides in surface soils.

Topography is a soil-forming factor and affects the redistribution of water based on the morphological features of the soil-landscape and hence influences soil development and the characteristics of the soil layers particularly the surface soil. Classified at the subgroup level, the distributions of soils across landform elements were in agreement with that generally reported for undulating to hummocky till landscapes in the Canadian Prairies. For example, upland and lower slopes typically show Rego / Orthic / Calcareous Chernozems (Miller et al., 1985, van der Kamp et al. 2003). Footslopes and depressions typically reveal a mixture of Eluviated / Gleyed Eluviated / Gleyed Chernozemic and Gleysolic profiles (Bedard-Haughn and Pennock 2002). Many of the lower slopes soils at both sites were carbonated and/or saline due to discharge of solute-rich groundwater, but neither carbonation nor salinization are recognized at the subgroup level in the Canadian System of Soil Classification.

The correlations between terrain attributes and herbicide K_d were more often significant for SDNWA than for MZTRA. In a previous study which included 2,4-D only (Farenhorst et al. 2003), the correlations between terrain attributes and 2,4-D K_d values were also more consistent in the conventional-tilled than in the zero-tilled field. Nevertheless, in the current study, terrain attributes explained only 15% of the spatial variability of 2,4-D K_d values in SDNWA, and none of

the variability of 2,4-D K_d values in MZTRA, while this ranged from 50 to 56% in other landscapes we have examined (Farenhorst et al. 2003, 2008). Both SDNWA and MZTRA landscapes contain numerous wetlands and these open water sources have been shown to challenge the application of terrain attributes in soil characteristics predictions because the discharge of solute-rich water from wetlands is a major soil-forming factor (Pennock et al. 2011, Bedard-Haughn and Pennock 2002). We also recognize the need to explore further the impact of sampling design on the usefulness of terrain attributes in pesticide fate studies. In the current study, sampling units were defined based on digital terrain analyses such that 10 sampling locations could be chosen in each of the seven landform elements. In contrast, a grid-sampling approach was used for a total of 76 surface soil samples (50x50m grid) in Farenhorst et al. (2003), and 287 surface soil samples (10x10m grid) in Farenhorst et al. (2008). Hence, capturing the shorter-interval variability in fields may be important to the success of the application of terrain attributes to pesticide fate studies.

3.6 Conclusion

Herbicide variability within the soil landscapes was strongly influenced by the morphological and chemical properties of horizons in soil profiles. 2,4-D (weak-acid) and atrazine (weak-base) K_d values decreased from A > B > C mineral horizons because of similar decreases in SOC. SOC, 2,4-D K_d and atrazine K_d values were numerically smaller in the eluvial A-horizons than other A-horizons. Glyphosate (zwitterion) K_d values were particularly large in illuvial B-horizons with redoximorphic features and enriched with clay. The A-horizon of Black Chernozems characteristic of the MZTRA site demonstrated significantly larger SOC, 2,4-D K_d and atrazine K_d

values than the A-horizon of Dark Brown Chernozems characteristic of the SDNWA site, and hence the soil-forming factor climate had a clear impact on influencing herbicide variability at a regional scale. Digital terrain attributes demonstrated weak correlations with herbicide sorption parameters.

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4. Near-infrared spectroscopy as a tool for generating sorption input parameters for pesticide fate modeling

4.1 Abstract

Sorption parameters (such as K_d values) are among the most sensitive input parameters in pesticide fate models. This study demonstrates that near-infrared spectroscopy (NIRS), in combination with batch equilibrium techniques, can be used to estimate K_d values, thereby increasing throughput of the many samples required to characterize spatial variability of pesticide sorption within fields. The Pesticide Root Zone Model (v. 3.12.2) was used to compare scenarios that used NIRS spectral data, pedotransfer functions and batch equilibrium methods as inputs for the calculation of 2,4-D and atrazine leaching in 591 soil horizons. Based on the 3,564 simulation runs conducted, we concluded that the added benefit of NIRS is most useful when the pesticides under study have small sorption potentials and short half-lives in soil. 2,4-D and atrazine sorption by soil was highly correlated to soil organic carbon content (SOC) in the fields under study. The feasibility of using NIRS to predict pesticide K_d values largely relies on the sorption of the pesticide being significantly correlated to SOC. In addition, successful regional approaches to predicting K_d values from NIRS spectral data can also be developed when the calibration model is derived by combining a set of fields where each has a similar statistical population characteristic in K_d values.

4.2 Introduction

Sorption parameters (K_d values) are among the most sensitive input parameters in pesticide fate models used to calculate pesticide transport to depth (Boesten and Van der Linden 1991, Villeneuve et al. 1998, Dubus et al. 2003a, Dubus et al. 2003b, Farenhorst et al. 2009). There are large variations in sorption parameters within and between agricultural fields. For example, for the herbicide 2,4-D in surface soils, its sorption parameter K_d ranged from 0.56 to 12.5 L kg^{-1} (n=72) along a 360-m long transect in a single field and from 0.6 to 14.5 L kg^{-1} (n=41) across fields spanning a 660,000 km^2 area (Gaultier et al. 2006, Gaultier et al. 2008). Because sorption parameters are seldom quantified in sufficient spatial detail within and between simulation units (Huber et al. 2000, Gagnon et al. 2014), there have been large uncertainties in risk assessments, regardless of the pesticide fate model used (Dubus et al. 2003b, Dann et al. 2006, Farenhorst et al. 2009).

To reduce uncertainties in large-scale risk assessments, efficient methods are needed that can rapidly, and inexpensively, estimate sorption parameters for a large number of samples. The sorption of a pesticide is dependent on soil characteristics (MacKay and Vasudevan 2012) and so pesticide K_d values are usually assigned to simulation units by applying pedotransfer functions to soil geographical databases. Weber et al. (2004) established pedotransfer functions to calculate K_d values for a wide range of non-ionic or ionizable pesticides, with equations based on up to three soil properties that were the most consistently reported in soil geographical databases: soil organic carbon content (SOC), soil pH and clay content.

Near-infrared spectroscopy (NIRS) can be used to estimate one or more soil properties from spectral data, including SOC, soil pH, clay content, carbonate content, cation exchange capacity, as well as aluminum and iron concentrations in minerals (Ben-Dor and Banin 1990a, Ben-Dor and Banin 1990b, Malley et al. 2000, Chang and Laird 2002, Martin et al. 2002, Sorensen and Dalsgaard 2005, Singh et al. 2012). These soil properties play an important role in the sorption of pesticide chemical structures (MacKay and Vasudevan 2012) and so NIRS could be used to rapidly estimate pesticide K_d values from spectral data. For fields and regions, NIRS has been previously used to estimate the sorption of nonionic (lindane, linuron) (Bengtsson et al. 2007) and ionizable (atrazine and 2,4-D) (Singh et al. 2010) pesticides in soils. Similarly, mid-infrared spectroscopy has been successfully used to estimate the sorption of atrazine (Kookana et al. 2008) and the nonionic pesticide, diuron (Forouzangohar et al. 2008) in soils. However, no study has integrated the use of infrared spectroscopy with pesticide fate models and hence the impact of estimating sorption input parameters by infrared spectroscopy on calculated pesticide transport is unknown.

In this study, the base (or reference) scenario for calculating downward vertical pesticide transport consisted of using K_d values measured in the laboratory by batch equilibrium experiments. The measured K_d values were used for input in the Pesticide Root Zone Model version 3.12.2 (PRZM-3) (Carsel et al. 1998) which is an extensively validated model used by both European and North American governments to assess the risk of water contamination by pesticides in fields and regions (Dubus et al. 2003a, Gaultier et al. 2008, Cessna et al. 2010,

Water Models). The objective of this study was to compare the base scenario with scenarios that used NIRS spectra or pedotransfer functions (see Weber et al. 2004) as inputs for estimating K_d values and leaching estimates using PRZM-3.

4.3 Material and Methods

4.3.1. Soil samples and characteristics. This study utilized 591 soil samples collected from two irregular undulating to hummocky terrains in the Canadian Prairies. Sites were a 16-ha zero-tilled agricultural area at the Manitoba Zero Tillage Research Association research farm (49° 53'N latitude**,** 99° 58'W longitude) near Brandon, Manitoba, Canada, and a 20-ha conventionally-tilled area at the St. Denis National Wildlife Association (52° 12'N latitude, 106° 5'W longitude) near Saskatoon, Saskatchewan, Canada. Both the Manitoba and Saskatchewan fields were mapped (grid size 5x5 m^2) using digital terrain modeling software (Pennock 2003) to identify seven landform elements in which soil profiles were sampled. Landform elements were convergent and divergent shoulders, convergent and divergent backslopes, convergent and divergent footslopes, and depressions, with the general topography and soil profile sampling locations presented in Figure 4.1. Soil profiles were sampled to 1 m depth by horizon in 70 locations at both sites using a truck mounted 5 cm diameter hydraulic probe. The 307 soil samples collected from Manitoba were from 23 different horizons. The 284 soil samples collected from Saskatchewan were from 22 different horizons. The ranges in %SOC, soil pH, %sand, %silt, and %clay at both the Manitoba and Saskatchewan fields are presented in Table 4.1.

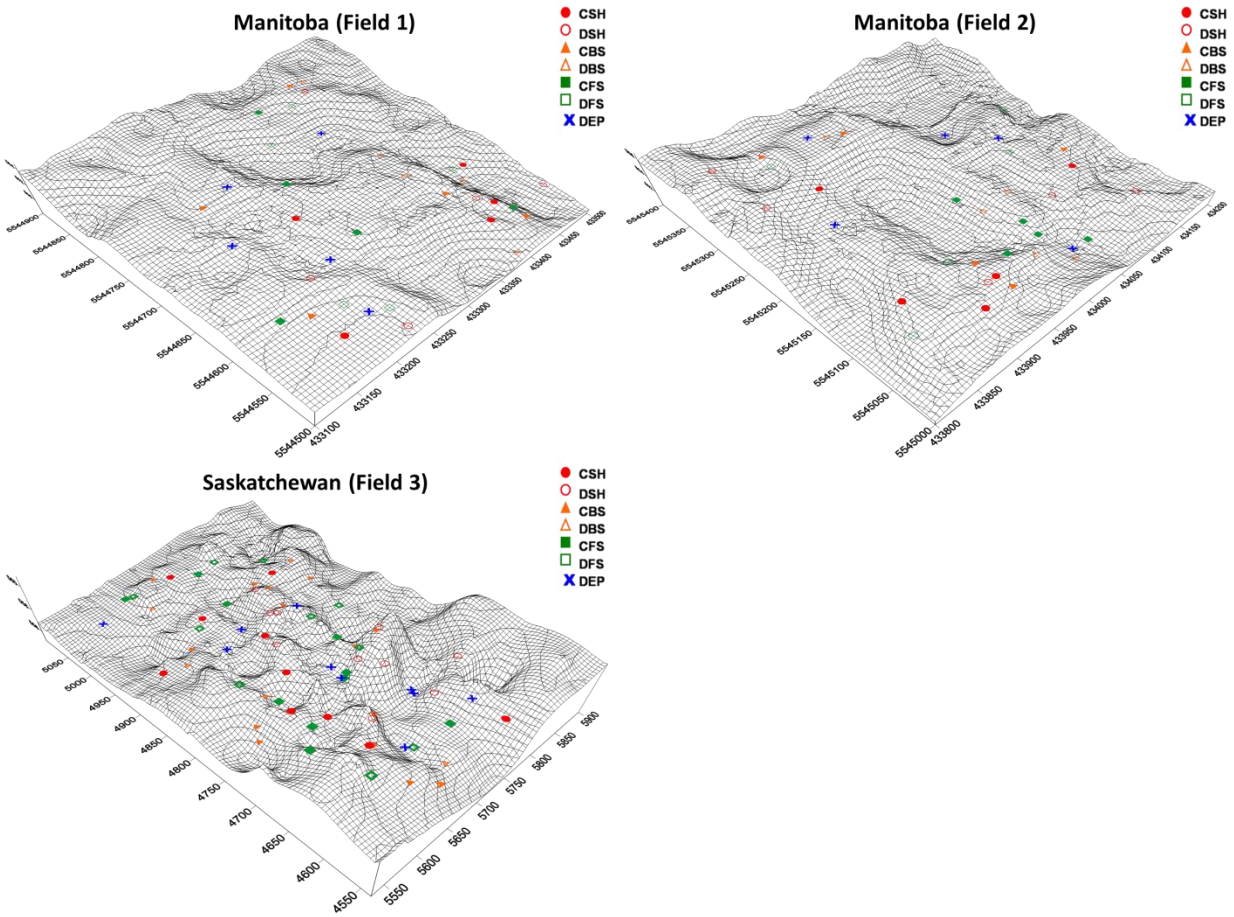

Figure 4.1. Topography and soil sampling locations at Manitoba (Field 1 and 2) and Saskatchewan (Field 3) sites. Landform elements were convergent (CSH) and divergent (DSH) shoulders, convergent (CBS) and divergent (DBS) backslopes, convergent (CFS) and divergent (DFS) footslopes, and depressions (DEP).

Table 4.1. Range (minimum to maximum) of soil properties at Manitoba and Saskatchewan sites.

Soil Physical Properties	Manitoba (n=307)*	Saskatchewan (n=284)*
%SOC	0.42 to 5.42%	<0.01** to 3.52%
Soil pH	6.93 to 8.54	6.52 to 9.37
%Sand	<0.01 to 97.41%	9.25 to 87.32%
%Silt	2.60 to 61.30%	9.28 to 76.14%
%Clay	<0.01 to 48.65%	<0.01 to 30.60%

*n= total number of samples collected at the soil-landscape.
**<0.01% = below detection limits.

4.3.2. Near-Infrared Spectroscopy (NIRS) and batch equilibrium data. Near-Infrared spectra were recorded for each horizon using a 25 g subsample and the Foss NIRS Systems model 6500 spectrophotometer (Carl Zeiss, Jena, Germany) equipped with a rapid content sampler. Soil was presented in 5 cm diameter glass petri dishes to collect data over the wavelength range of 1100 to 2500 nm at 2 nm intervals, which resulted in 700 absorbance values for each spectrum. Triplicate spectra were obtained for each sample by rotating the petri dish 120 degrees between scans. Subsamples of horizons were also analyzed for soil properties (%SOC, soil pH, %clay, %silt and %sand) as well as for 2,4-D and atrazine K_d values. Those results have been previously published (Singh et al. 2014). K_d values were determined by batch equilibrium experiments using 50 mL Teflon tubes containing 5 g soil and 10 mL of either a 2,4-D or atrazine solution prepared in 0.01 M $CaCl_2$ at a concentration of 1 mg herbicide L^{-1}. K_d value (L kg^{-1}) was calculated using C_s/C_e, where C_s is the amount of chemical sorbed on the soil at equilibrium (g kg^{-1}), and C_e is the amount of chemical remaining in the solution at equilibrium (g L^{-1}). Throughout this paper, the 2,4-D and atrazine K_d values determined in the laboratory by batch-equilibrium experiments will be referred to as LAB-K_d values.

4.3.3. Calibration and validation sets. The triplicate spectra for each sample were imported into Unscrambler® multivariate statistical analysis software version 9.8 (2008, CAMO Process ASA, www.camo.com/products) and averaged. Soil properties (%SOC, soil pH, %sand, %silt and %clay) and 2,4-D and atrazine K_d values were also imported. K_d values were predicted using either NIRS spectra (see 4.3.3.1.) or pedotransfer functions (see 4.3.3.2.). All calibrations used a test set method in which LAB-K_d values were sorted from low to high values and divided into

calibration (two-thirds of the total samples) and validation (one-third of the total samples) sets by selecting every third sample for the validation set. As indicated in Table 4.2, for each site and herbicide combination, the test set method resulted in approximately the same distribution of LAB-K_d values in the calibration and validation sets.

4.3.3.1. Use of NIRS to predict sorption. Calibration development was done in Unscrambler® software using protocols similar to those previously described (Dunn et al. 2002, Malley et al. 2004, Singh et al. 2010, Singh et al. 2012) except that in this study the test set method allowed for validation evaluation. The software allowed us to consecutively apply partial least squares regression (PLS1 method) to optimize the prediction of K_d values from spectral data for the calibration set, the resulting optimized calibration equation within the software then generated the prediction of K_d values from spectral data derived from the validation samples. Trial calibrations consisted of performing mathematical pretreatments (using moving average method) on the raw spectra by smoothing over 5, 11, 13, 21, or 41 wavelength points, and transforming the spectra to the first or second derivative using derivative gaps of either 5, 11, 13, 21, or 41 wavelength points (Figure 4.2). Higher coefficients of determinations (R^2), higher ratios of prediction to deviation (RPD), and lower standard error of predictions (SEP) (Dunn et al. 2002, Malley et al. 2004) were generally achieved with a mathematical pretreatment that used transformation of the spectra to the first derivative using 13 wavelength points, was applied to each of the calibration/validation scenarios to estimate 2,4-D and atrazine K_d values in the validation samples. The predicted 2,4-D and atrazine K_d values as applied to the soil horizons in the validation sets will be referred to as NIRS-K_d values.

Table 4.2. Summary statistics of the 2,4-D and atrazine LAB-K_d values obtained for the soil horizons used in the calibration and validation data sets.

Herbicide and Data Set	n*	Mean	CV%	Median	Minimum	Maximum	Q1	Q3
					2,4-D			
Manitoba – Calibration	204	1.34	110%	0.53	0.04	6.78	0.23	2.36
Manitoba – Validation	103	1.36	112%	0.53	0.03	6.78	0.24	2.33
Saskatchewan - Calibration	189	0.98	90%	0.55	0.05	3.88	0.34	1.59
Saskatchewan – Validation	95	0.97	90%	0.53	0.01	3.60	0.34	1.57
					Atrazine			
Manitoba – Calibration	204	7.74	100%	3.78	1.08	33.02	2.07	12.25
Manitoba – Validation	103	7.84	102%	3.75	1.01	35.14	2.06	12.07
Saskatchewan - Calibration	189	2.15	94%	1.11	0.29	8.71	0.74	3.25
Saskatchewan – Validation	95	2.14	95%	1.11	0.08	8.70	0.74	3.26

*n = number of samples in the validation or calibration data set, CV% = coefficient of variation, Q1 = lower quartile and Q3 = upper quartile.

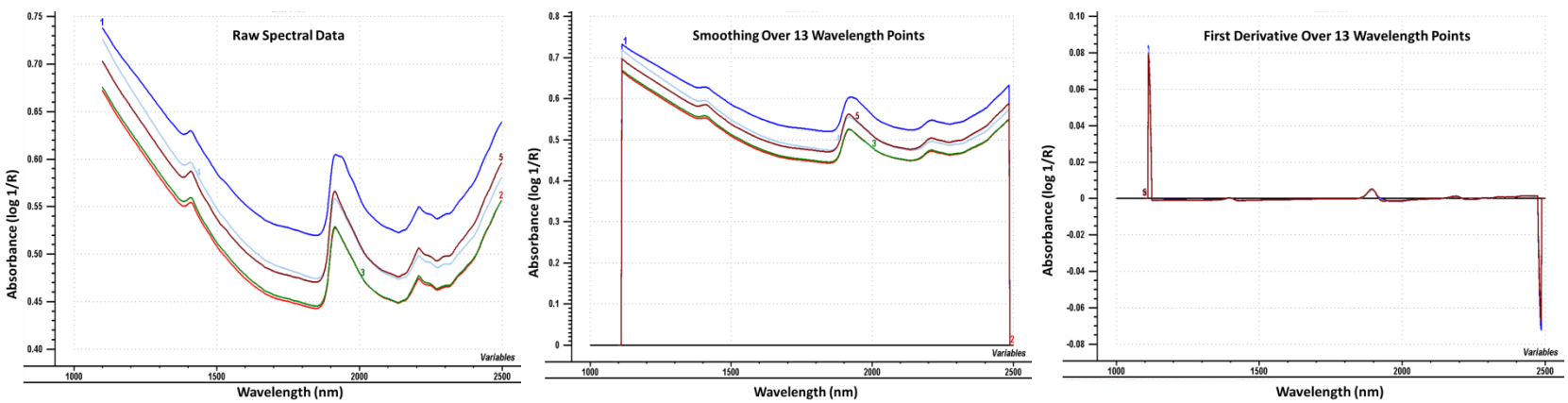

Figure 4.2. Examples of the raw spectral data of five A-horizon samples collected at the Manitoba site and subsequent math-pretreatment results.

4.3.3.2. Pedotransfer functions. Using the same calibration and validation sets as for the NIRS method, partial least squares regression (PLS1 method in Unscrambler® software) was applied to two-thirds of calibration samples to establish pedotransfer functions using 2,4-D or atrazine LAB-K_d values as the dependent (response) variable and soil properties (%SOC, soil pH, %sand, %silt and/or %clay) as the independent variables. During calibration, independent variables that contributed ≤ 0.1 to the coefficient of determination were sequentially removed, which simplified the regression equations but maintained the same approximate prediction power. For each of the calibration and validation scenarios, the best pedotransfer function was selected based on the largest R^2 and the lowest SEP and bias values in the calibration model. Pedotransfer functions were subsequently applied to the measured soil properties data of the validation samples in order to calculate herbicide K_d values for the soil horizons in the validation set. Throughout this paper, calculated 2,4-D and atrazine K_d values as applied to the soil horizons in the validation sets will be referred to as SOIL-K_d values.

4.4. PRZM simulations. Each validation sample was set as a simulation unit with a 10 cm depth and 0.1 cm compartments (PRZM simulation layers). The herbicide mass leached (referred as L_m, kg ha^{-1}) below 10 cm depth was set as the output parameter to be tested. Each validation sample in the ten calibration and validation scenarios had a measured LAB-K_d value, a predicted NIRS-K_d and a calculated SOIL-K_d value. These LAB-K_d, NIRS-K_d, or SOIL-K_d values were used as input parameters in PRZM to calculate the herbicide mass leached as LAB-L_m, NIRS-L_m and SOIL-L_m, respectively. A total of 3,564 PRZM simulations were conducted. AutoPRZM (McQueen et al.

2007) was used to automate the construction of the PRZM input file, the running of PRZM, and the extraction of data from the PRZM output file.

A detailed description of the PRZM model including how its input parameters are used in equations is described in Carsel et al. (1998). Briefly, PRZM is a one-dimensional model in which water moves from one compartment to the next after field capacity is exceeded. K_d value is a sensitive parameter in the model as it is inversely related to the amount of the pesticide moving with leachate (Farenhorst et al. 2009). Simulations were performed using a 24-h time step for temperature and precipitation data. Temperature and precipitation data were obtained from a meteorological station at the Brandon airport that is located about 14 km from the Manitoba site. The same weather data were used for both Manitoba and Saskatchewan sites to allow for a more direct comparison in PRZM simulation outputs between sites.

Field capacity and wilting point are key variables describing vertical water flow and evapotranspiration in the model. Field capacities and wilting points were calculated for each horizon by applying measured %SOC, %sand, %clay, and bulk density to equations based on the work of Rawls et al. (1982) and provided in the PRZM manual (Carsel et al. 1998). Potential evapotranspiration was calculated using the method of Hargreaves and Samani (1985) using REF-ET© given by Allen (2001). Soil profile drainage was set as well-drained for all horizons. All simulations were started with soils at field capacity, but a warm-up time of one year was used to provide for more realistic moisture conditions at the time of application of the herbicides in year one. Preliminary PRZM simulations indicated that a longer warm-up time of up to five

years had no significant influence on modeling results. The herbicide application rates were 445 g ha^{-1} for 2,4-D and 1,073 g ha^{-1} for atrazine, which approximate the recommended rates. We assumed that the herbicides were applied at the beginning of a growing season (May 3rd), and the end of the simulation was set at November 31st, which is the average date when there is permanent snow cover in the Prairie region where the field sites are located (Potter 1965). Degradation was calculated in the model assuming first-order kinetics and using half-lives of 66 days for atrazine and 14 days for 2,4-D as obtained from the Pesticide Properties DataBase (University of Hertfordshire 2013).

4.4.1. Statistical evaluations of the success of the prediction methods used. For each validation set, coefficient of determination (R^2) was calculated between LAB-K_d vs. NIRS-K_d, and LAB-K_d vs. SOIL-K_d, and LAB-L_m vs. NIRS-L_m, and LAB-L_m vs. SOIL-L_m. Linear regression plots were also developed with NIRS-K_d, SOIL-K_d, NIRS-L_m or SOIL-L_m as independent variables and LAB-K_d or LAB-L_m as dependent variables to determine regression equations along with the root mean square error of prediction (RMSE). For each herbicide, calibration/validation scenarios with larger R^2 and smaller RMSE values were deemed the more successful approaches to estimating 2,4-D and atrazine K_d values for use in PRZM. For some samples in the validation sets, a few predictions resulted in negative NIRS-K_d, and/or SOIL-K_d values. These soil horizons were removed prior to the statistical evaluations.

4.5 Results and Discussion

The RPDs of NIRS validations ranged from 2.15 to 3.17 in the site-specific approach (Table 4.3). Dunn et al. (2002) suggests three categories for RPD in soil analysis: poor, < 1.6; acceptable, 1.6-2.0; and excellent, > 2.0. In the regional approach, NIRS validations also had RPD > 2 in all cases, except for atrazine in the Saskatchewan validation data (RPD = 1.26) (Table 4.4). Atrazine and 2,4-D LAB-K_d values were significantly positively associated with SOC in both Manitoba and Saskatchewan with correlation coefficients (R) ranging from 0.89 to 0.94. NIRS predictions for SOC often yield RPD values > 2.0 (Malley et al. 2000, Chang and Laird 2002) and the feasibility of using NIRS to predict herbicide sorption largely relies on the sorption of the herbicide being highly significantly correlated to SOC.

SOC and pH were represented in all pedotransfer functions, both in the site-specific approach (Table 4.5) and in the regional (Table 4.6). Atrazine and 2,4-D LAB-K_d values were significantly negatively associated with soil pH in both Manitoba and Saskatchewan with correlation coefficients ranging from -0.30 to -0.63. Other researchers have reported that 2,4-D and atrazine sorption increases with increasing SOC and decreasing soil pH (Novak et al. 1997, Rodriguez-Rubio et al. 2006, Hiller et al. 2008, Villaverde et al. 2008, Prado et al. 2014).

Table 4.3. Accuracy of prediction for 2,4-D and atrazine NIRS-K_d values at Manitoba and Saskatchewan sites using a site-specific approach to calibration. Reported R^2, SEP, Bias and RPD parameters are based on the evaluation of the validation data set (at each site, one-third of the total samples).

Herbicide and Site	n*	R^2	SEP	Bias	RPD
2,4-D constituent					
Manitoba validation	103	0.90	0.47	-1.00×10^{-2}	3.17
Saskatchewan validation	95	0.86	0.33	3.00×10^{-2}	2.66
Atrazine constituent					
Manitoba validation	103	0.87	2.86	-1.80×10^{-1}	2.72
Saskatchewan validation	95	0.79	0.94	-1.00×10^{-2}	2.15

*n = number of samples in the validations data set, R^2 = coefficient of determination, SEP standard error of prediction, Bias = mean difference between predicted and measured values, RPD = ratio of prediction to deviation.

Table 4.4. Accuracy of prediction for 2,4-D and atrazine NIRS-K_d values at Manitoba and Saskatchewan sites using a regional approach to calibration. Reported R^2, SEP, Bias, and RPD parameters are based on the evaluation of the validation data set (at each site, one-third of the total samples).

Herbicide and Site	n*	R^2	SEP	Bias	RPD
2,4-D constituent					
Manitoba validation	103	0.87	0.55	-4.00×10^{-2}	2.77
Saskatchewan validation	95	0.84	0.36	4.00×10^{-2}	2.44
Manitoba + Saskatchewan validation	198	0.86	0.47	4.19×10^{-5}	2.70
Atrazine constituent					
Manitoba validation	103	0.90	2.73	-1.20×10^{-1}	2.86
Saskatchewan validation	95	0.79	1.61	1.10×10^{-1}	1.26
Manitoba + Saskatchewan validation	198	0.87	2.35	-3.08×10^{-3}	2.79

*n = number of samples in the validations data set, R^2 = coefficient of determination, SEP standard error of prediction, Bias = mean difference between predicted and measured values, RPD = ratio of prediction to deviation.

Table 4.5. Calibration models developed using a site-specific approach to calculate SOIL-K_d values for soil horizons in the validation sets at Manitoba and Saskatchewan sites. Reported R^2, SEP, and Bias parameters are based on the evaluation of the calibration data set (at each site, two-thirds of the total samples).

Herbicide and Site	Calibration Model	R^2*	SEP	Bias
2,4-D constituent				
Manitoba calibration	SOIL-K_d = 0.54 + 1.05*(SOC%) - 0.15*(pH)	0.90	0.48	2.00×10^{-2}
Saskatchewan calibration	SOIL-K_d = -0.54 + 0.89*(SOC%) + 0.08*(pH)	0.87	0.32	3.50×10^{-3}
Atrazine constituent				
Manitoba calibration	SOIL-K_d = 4.32 + 5.21*(SOC%) - 0.78*(pH)	0.82	3.35	4.30×10^{-1}
Saskatchewan calibration	SOIL-K_d = 0.04 + 1.90*(SOC%) + 0.03*(pH)	0.80	0.92	6.77×10^{-4}

*R^2 = coefficient of determination, SEP standard error of prediction, Bias = mean difference between predicted and measured values.

Table 4.6. Calibration models developed using a regional approach to calculate SOIL-K_d values for soil horizons in the validation sets at Manitoba and Saskatchewan sites. Reported R^2, SEP, and Bias parameters are based on the evaluation of the calibration data (at each site, two-thirds of the total samples).

Herbicide and Site	Calibration Model	R^2*	SEP	Bias
2,4-D constituent				
Manitoba calibration	SOIL-K_d = -1.69 + 0.98*(SOC%) + 0.16*(pH)	0.89	0.50	1.10×10^{-1}
Saskatchewan calibration	same as above	0.81	0.38	-1.10×10^{-1}
Manitoba + Saskatchewan calibration	same as above	0.87	0.47	3.00×10^{-3}
Atrazine constituent				
Manitoba calibration	SOIL-K_d = 7.77 + 4.25*(SOC%) - 0.92*(pH)	0.79	3.90	2.80×10^{-1}
Saskatchewan calibration	same as above	0.60	2.25	1.80×10^{-1}
Manitoba + Saskatchewan calibration	same as above	0.76	3.21	2.30×10^{-1}

*R^2 = coefficient of determination, SEP standard error of prediction, Bias = mean difference between predicted and measured values.

2,4-D LAB-K_d ranged from 0.03 to 6.78 L kg^{-1} in Manitoba and from 0.01 to 3.88 L kg^{-1} in Saskatchewan (Table 4.2) and the medians of the 2,4-D LAB-K_d data at the two sites were not significantly different (Mann-Whitney test, P = 0.92). For 2,4-D, the mean K_{oc} value (sorption coefficient normalized by soil organic carbon content) was 56 L kg^{-1} for Manitoba and 170 L kg^{-1} for Saskatchewan, where NIRS (57 L kg^{-1} for Manitoba and 181 L kg^{-1} for Saskatchewan) and the pedotransfer functions (57 L kg^{-1} for Manitoba and 146 L kg^{-1} for Saskatchewan) also produced a similar mean K_{oc}. These K_{oc} values were in agreement with the literature 2,4-D K_{oc} range of 31-275 L kg^{-1} (University of Hertfordshire 2013).

The soil horizons in the validation sets showed strong agreement between measured and predicted 2,4-D K_d values (Figure 4.3), ranging from R^2 = 0.83 to 0.90 in the site-specific approach (Table 4.7) and from R^2 = 0.82 to 0.90 regional approach (Table 4.8). For 2,4-D, agreement between LAB-L_m and either NIRS-L_m or SOIL-L_m ranged from R^2 = 0.57 to 0.78 in the site-specific approach (Table 4.7) and from R^2 = 0.52 to 0.78 in the regional approach (Table 4.8). Agreement were always weaker for L_m than K_d because, like other pesticide fate models (Dubus et al. 2003a), PRZM is very sensitive to K_d values, so small differences between measured and predicted K_d values lead to proportionally larger differences in the herbicide mass leached (Farenhorst et al. 2009).

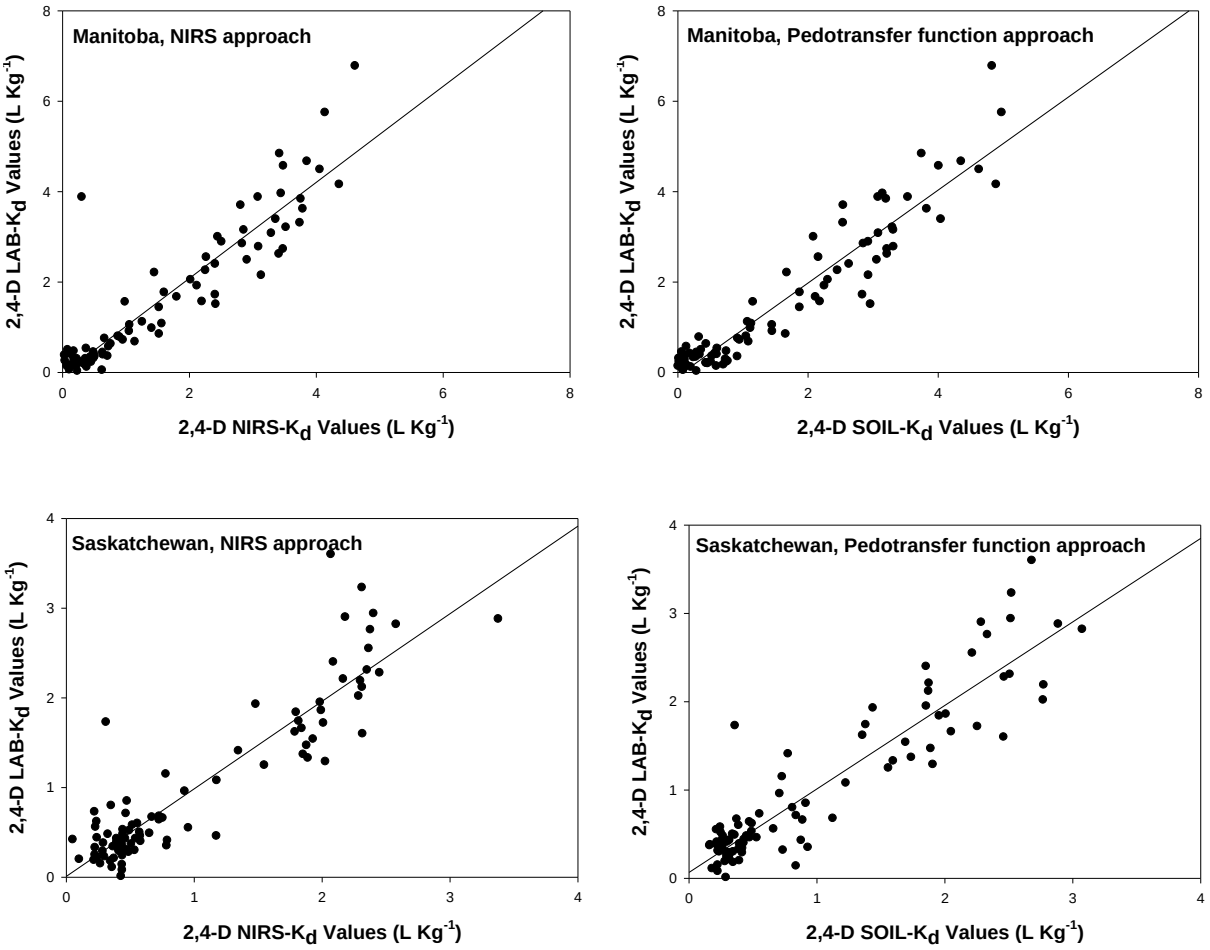

Figure 4.3. Showing the relation between predicted K_d values (NIRS-K_d or SOIL-K_d) and measured K_d values (LAB-K_d) at Manitoba and Saskatchewan soil-landscapes for the herbicide 2,4-D.

Table 4.7. Regression equations showing the relation between predicted K_d values (NIRS-K_d or SOIL-K_d) and measured K_d values (LAB-K_d), and, for the calculated mass of herbicide leached, showing the relation between model outputs when using the predicted K_d (NIRS-L_m or SOIL-L_m) and measured K_d (LAB-L_m) values as input parameters in the Pesticide Root Zone Model. Utilizing a site-specific approach to calibration, the reported RMSE and R^2 parameters are based on the evaluation of the validation data set (at each site, one-third of the total samples).

Herbicide and Site	Prediction Method	n*	Linear Regression Equation	RMSE	R^2
2,4-D constituent					
Manitoba	Near-infrared spectroscopy	90	LAB-K_d = -4.04 x 10^{-2} + 1.06 x NIRS-K_d	3.86 x 10^{-1}	0.85
Manitoba	Near-infrared spectroscopy	90	LAB-L_m = 7.66 x 10^{-3} + 0.89 x NIRS-L_m	6.37 x 10^{-4}	0.78
Saskatchewan	Near-infrared spectroscopy	94	LAB-K_d = 9.79 x 10^{-3} + 0.98 x NIRS-K_d	1.33 x 10^{-1}	0.83
Saskatchewan	Near-infrared spectroscopy	94	LAB-L_m = 1.31 x 10^{-2} + 0.80 x NIRS-L_m	8.07 x 10^{-4}	0.57
Manitoba	Pedotransfer function	90	LAB-K_d = -7.74 x 10^{-2} + 1.03 x SOIL-K_d	2.59 x 10^{-1}	0.90
Manitoba	Pedotransfer function	90	LAB-L_m = 1.18 x 10^{-2} + 0.79 x SOIL-L_m	7.37 x 10^{-4}	0.74
Saskatchewan	Pedotransfer function	94	LAB-K_d = 6.68 x 10^{-2} + 0.95 x SOIL-K_d	1.21 x 10^{-1}	0.85
Saskatchewan	Pedotransfer function	94	LAB-L_m = 7.94 x 10^{-3} + 0.83 x SOIL-L_m	6.48 x 10^{-4}	0.65
Atrazine constituent					
Manitoba	Near-infrared spectroscopy	98	LAB-K_d = 2.68 x 10^{-1} + 0.99 x NIRS-K_d	1.26 x 10^{1}	0.81
Manitoba	Near-infrared spectroscopy	98	LAB-L_m = 1.70 x 10^{-2} + 0.15 x NIRS-L_m	3.28 x 10^{-3}	0.27
Saskatchewan	Near-infrared spectroscopy	93	LAB-K_d = 2.98 x 10^{-2} + 0.98 x NIRS-K_d	8.99 x 10^{-1}	0.79
Saskatchewan	Near-infrared spectroscopy	93	LAB-L_m = 6.27 x 10^{-2} + 0.76 x NIRS-L_m	2.03 x 10^{-2}	0.63
Manitoba	Pedotransfer function	98	LAB-K_d = -5.02 x 10^{-1} + 1.03 x SOIL-K_d	1.22 x 10^{1}	0.81
Manitoba	Pedotransfer function	98	LAB-L_m = 2.28 x 10^{-2} + 0.21 x SOIL-L_m	3.47 x 10^{-3}	0.23
Saskatchewan	Pedotransfer function	93	LAB-K_d = -1.18 x 10^{-1} + 1.04 x SOIL-K_d	8.59 x 10^{-1}	0.80
Saskatchewan	Pedotransfer function	93	LAB-L_m = 7.12 x 10^{-2} + 0.85 x SOIL-L_m	2.29 x 10^{-2}	0.59

*n = number of samples in the validations data set, RMSE = root mean square error of regression, and R^2 = coefficient of determination. All regression equations are significant at $p<0.001$.

Table 4.8. Regression equations showing the relation between predicted 2,4-D K_d values (NIRS-K_d or SOIL-K_d) and measured 2,4-D K_d values (LAB-K_d), and, for the calculated mass of 2,4-D leached, showing the relation between model outputs when using the predicted K_d (NIRS-L_m or SOIL-L_m) and measured K_d (LAB-L_m) values as input parameters in the Pesticide Root Zone Model. K_d values were predicted using either near-infrared spectroscopy (NIRS-K_d) or pedotransfer functions (SOIL-K_d). Utilizing a regional approach to calibration, the reported RMSE and R^2 parameters are based on the evaluation of the validation data set (at each site, one-third of the total samples).

Validation Site	n*	Linear Regression Equation	RMSE	R^2
		Near-infrared spectroscopy		
Manitoba	97	LAB-K_d = -1.57 x 10^{-1} + 1.16 x NIRS-K_d	2.77 x 10^{-1}	0.89
Manitoba	97	LAB-L_m = 8.84 x 10^{-3} + 0.95 x NIRS-L_m	6.61 x 10^{-4}	0.78
Saskatchewan	76	LAB-K_d = 3.65 x10^{-2} + 0.94 x NIRS-K_d	1.51 x 10^{-1}	0.82
Saskatchewan	76	LAB-L_m = 1.18 x 10^{-2} + 0.76 x NIRS-L_m	6.62 x 10^{-4}	0.62
Manitoba + Saskatchewan	175	LAB-K_d = -8.40 x 10^{-2} + 1.07 x NIRS-K_d	2.45 x 10^{-1}	0.86
Manitoba + Saskatchewan	175	LAB-L_m = 9.40 x 10^{-3} + 0.87 x NIRS-L_m	7.24 x 10^{-4}	0.71
		Pedotransfer function		
Manitoba	97	LAB-K_d = -2.29 x 10^{-1} + 1.11 x SOIL-K_d	2.34 x 10^{-1}	0.90
Manitoba	97	LAB-L_m = 1.55 x 10^{-2} + 0.94 x SOIL-L_m	9.51 x 10^{-4}	0.69
Saskatchewan	76	LAB-K_d = 1.84 x 10^{-1} + 0.87 x SOIL-K_d	1.25 x 10^{-1}	0.85
Saskatchewan	76	LAB-L_m = 1.28 x 10^{-2} + 0.57 x SOIL-L_m	8.32 x 10^{-4}	0.52
Manitoba + Saskatchewan	175	LAB-K_d = -6.50 x 10^{-2} + 1.04 x SOIL-K_d	2.01 x 10^{-1}	0.89
Manitoba + Saskatchewan	175	LAB-L_m = 1.39 x 10^{-2} + 0.76 x SOIL-L_m	1.04 x 10^{-3}	0.58

*n = number of samples in the validations data set, RMSE = root mean square error of regression, and R^2 = coefficient of determination. All regression equations are significant at $p<0.001$.

Atrazine LAB-K_d values ranged from 0.08 to 8.71 L kg^{-1} in Saskatchewan but from 1.01 to 35.14 L kg^{-1} in Manitoba (Table 4.2). For atrazine, the mean K_{oc} value was 333 L kg^{-1} for Manitoba and 267 L kg^{-1} for Saskatchewan, where NIRS (339 L kg^{-1} for Manitoba and 270 L kg^{-1} for Saskatchewan) and the pedotransfer functions (344 L kg^{-1} for Manitoba and 262 L kg^{-1} for Saskatchewan) also produced a similar mean K_{oc}. The atrazine K_{oc} reported in the literature ranges from 89 to 513 L kg^{-1} (University of Hertfordshire 2013). Under the pH conditions studied, atrazine is primarily in non-ionic form, thus promoting hydrophobic interactions with organic matter. As discussed in Singh et al. (2014), SOC increased significantly from A-horizons in Manitoba > A-horizons in Saskatchewan > all other horizons. In Manitoba, Ap and Ah horizons in depressions showed particularly large SOC and atrazine LAB-K_d values (> 20 L kg^{-1}) (Singh et al. 2014). The medians of the atrazine LAB-K_d data at the two sites were significantly (Mann-Whitney test, P = <0.001) different and the regional approach for atrazine was not successful, with correlations between LAB-L_m and either NIRS-L_m or SOIL-L_m being $R^2 \leq 0.25$, regardless of the validation scenario used.

For the site-specific analyses, the soil horizons in the validation sets showed strong ($R^2 \geq 0.79$) agreement between measured and predicted atrazine K_d values for both Manitoba and Saskatchewan (Table 4.8, Figure 4.4). For atrazine, the agreement between LAB-L_m and either NIRS-L_m or SOIL-L_m were stronger for Saskatchewan than Manitoba (Table 4.7) because of the relatively large SEP and bias observed for the models predicting atrazine K_d values in Manitoba (Tables 4.3 and 4.5). In addition, for herbicides that have relatively long half-lives such as atrazine, variations in sorption input parameters, in particular, can lead to differences in the

predicted herbicide mass leached when K_d values are large. For example, for a hypothetical soil horizon, reducing the K_d value by 10% increased the mass of atrazine leached by a factor of 2.2 when atrazine's K_d value was set to 3.75 L kg^{-1} (the median atrazine LAB-K_d in Manitoba, Table 4.2), but by a factor of only 1.2 for a K_d of 1.11 L kg^{-1} (the median atrazine LAB-K_d in Saskatchewan, Table 4.2).

Soil properties vary in fields or catchments because of intrinsic (e.g., irregularities in parent material deposition) and extrinsic (e.g., tillage) factors (Lindstrom et al. 1992, Goderya 1998, Phillips 2001, Park and Vlek 2002, Li et al. 2007). Sorption processes respond to the heterogeneity of soil properties that exists in fields or catchments, as shown in studies for pesticides 2,4-D, atrazine, bentazone, glyphosate, imazethapyr, isoproturon, mecoprop, metamitron, napropamide and trifluralin (Elabd and Jury 1986, Novak et al. 1997, Oliveira et al. 1999, Coquet and Barriuso 2002, Rodrıguez-Cruz et al. 2006, Farenhorst et al. 2008, Singh et al. 2014). The strength of the current study is that it demonstrates that NIRS spectra can be used as a tool to rapidly measure large numbers of samples for sorption parameters, and that such data can be integrated into pesticide fate models. Relative to LAB-K_d values, the NIRS spectra and pedotransfer function approaches were equally successful in characterizing the spatial variability of herbicide sorption in soil-landscapes, and hence in predicting the mass of 2,4-D or atrazine in the soil horizons of the validation data sets.

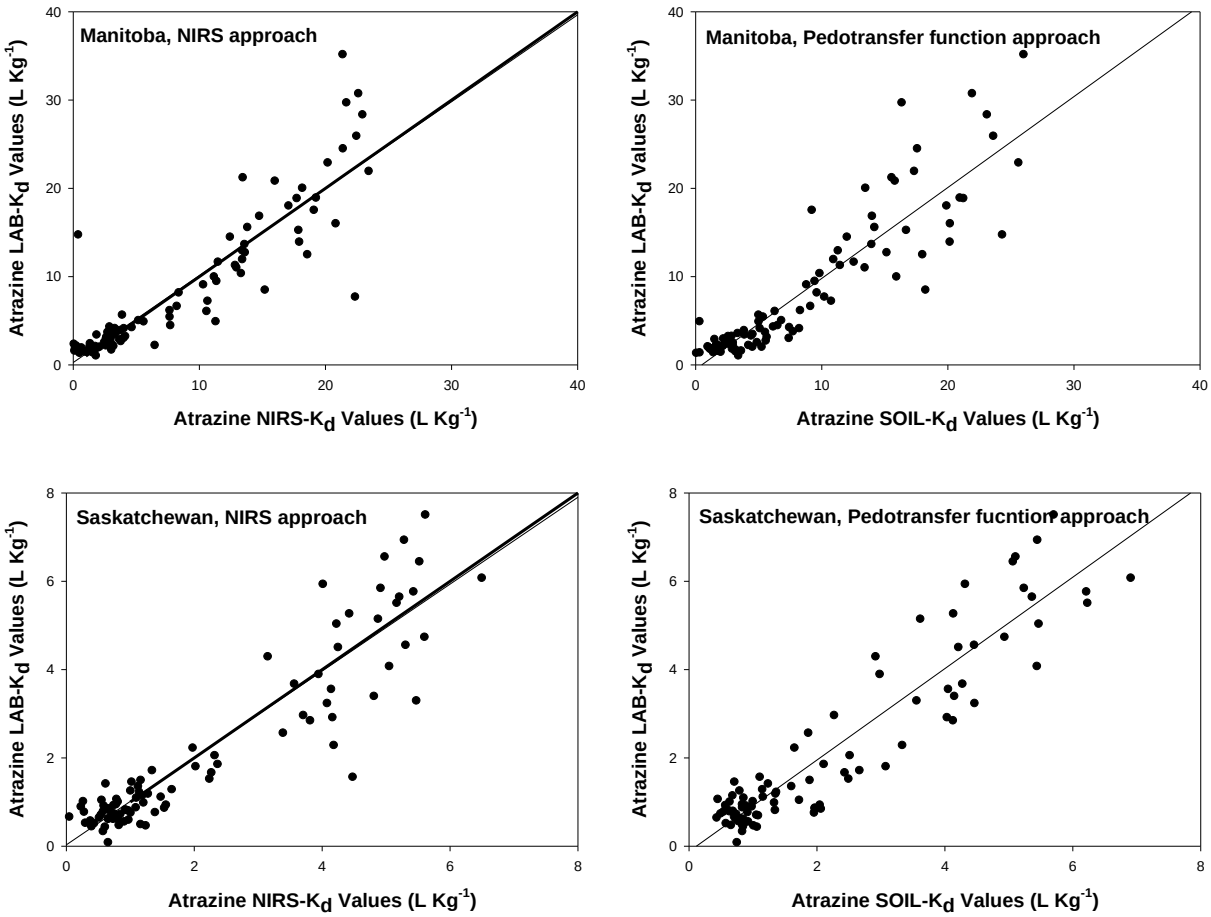

Figure 4.4. Showing the relation between predicted K_d values (NIRS-K_d or SOIL-K_d) and measured K_d values (LAB-K_d) at Manitoba and Saskatchewan soil-landscapes for the herbicide atrazine.

An added benefit to NIRS is the non-destruction of samples and the rapid nature of the analysis, leading to more rapid throughput of the many samples needed to characterize spatial variability of herbicide sorption in field or catchments. Also, NIRS spectra can be used to predict the values of a range of soil properties in soil-landscapes, including SOC and soil pH (Malley et al. 2000, Martin et al. 2002, Singh et al. 2012).

Governments use pesticide fate models to evaluate the impact of agriculture on water resources, and to augment national water monitoring programs in the regulatory practices of pesticide environmental exposure assessments (Dubus et al. 2003a, Gagnon et al. 2014). There are several ways by which NIRS can be integrated with these large-scale assessments. Regional approaches to predicting K_d values from NIRS spectral data can be developed providing that the calibration model is derived from a combined set of fields that each have similar statistical population characteristics in K_d values. In its simplest form, NIRS can be used as a screening tool in which K_d values in soil horizons are predicted from NIRS spectral data and used as input parameters in pesticide fate models to calculate the herbicide mass leached in soil profiles. Regression equations (examples in Tables 4.7 and 4.8) can be applied prior to the pesticide fate simulations to adjust the predicted NIRS-K_d values to approximate LAB-K_d values, or applied after the pesticide fate simulations to calculate the approximate herbicide mass leached that would have been predicted when using LAB-K_d values as input parameters.

In stochastic risk assessments, probability density functions (PDFs) help account for spatial variations in sorption input parameters (Berg et al. 2008, Heuvelink et al. 2010). This allows for

a deterministic pesticide fate model to be run repeatedly within a simulation unit, each time using a different sorption input parameter derived from a statistical distribution that is represented by the PDF. Model users typically assume a normal, log-normal, or uniform distribution to describe variability in sorption parameters at the large scale (Nofziger et al. 1994, Dubus and Brown 2002, Warren-Hicks et al. 2002). However, because PDFs are typically developed using K_d data obtained from a small number of soil profiles (Berg et al. 2008, Heuvelink et al. 2010), the construction of PDFs is strongly influenced by subjective decisions made by the model user (Dubus et al. 2002). For example, although presented with the same K_d data from 18 soils, different modelers chose to use different statistical distributions (log-normal, normal, or triangular)(Beulke et al. 2006), and this user-subjective decision towards sorption input parameters can have a more significant impact on the model predictions than the type of pesticide fate model used (Boesten 2000). Through the use of NIRS spectra, numerous K_d values can be estimated in the simulation area of interest, which should lead to better decisions about the type of distribution assigned to the sorption input data as well as which minimum and maximum K_d values to use in truncating PDFs (Beulke et al. 2006). Improvements to sorption input data will reduce uncertainties in risk assessments of pesticide transport in fields and regions (Dubus et al. 2003b).

4.6 Conclusion

Pesticide K_d values are highly variable in soil-landscapes and this spatial variability is difficult to delineate especially when risk assessments are to be conducted for large agricultural regions. In

combination with batch equilibrium techniques, NIRS is a quick, economical and efficient tool to optimize estimates of spatially variable pesticide K_d values in agricultural fields. The results showed that NIRS can be easily integrated with pesticide fate models to estimate input K_d values for herbicides 2,4-D and atrazine and calculate the approximate herbicide mass leached. NIRS calibrations were most successful for 2,4-D, which has a smaller K_d values and smaller half-life than atrazine. Regional scale calibrations were also successfully developed for 2,4-D because the K_d data sets from the fields in Manitoba and Saskatchewan had similar statistical distributions. To reduce uncertainties in large-scale risk assessments of pesticide transport in fields and regions, NIRS will be an appropriate tool for improving on sorption input data.

4.6 Acknowledgements

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5. OVERALL SYNTHESIS

5.1 Summary of Research Findings

This research study examined the spatial variations in K_d values of 2,4-D, atrazine, glyphosate and 17β-estradiol in two agricultural fields in the Canadian Prairies. Considering all soil samples, the average K_d values increased in the order of 2,4-D < atrazine < 17β-estradiol < glyphosate. The K_d values for 2,4-D, atrazine and 17β-estradiol significantly decreased from surface to subsurface soils in response to change in soil properties, regardless of the slope position from which the soil profiles were sampled, whereas glyphosate showed the largest K_d values in clay enriched illuviated B-horizons. In both soil landscapes (MZTRA and SDNWA), K_d values of 2,4-D, atrazine and 17β-estradiol were positively correlated with SOC. Whereas, regardless of SOC content, glyphosate showed strong sorption (>98%) in all soil samples, suggesting that the herbicide is relatively immobile in soil matrix.

Partial Least Square regression equations developed to predict 2,4-D and atrazine K_d values always included SOC as an independent variable and revealed stronger predictive power when including all soil samples in the profile, relative to equations based on a specific mineral horizon. Glyphosate sorption coefficients could not be predicted from measured soil properties data. Calculated digital terrain attributes showed weak or non-significant correlations with soil properties or sorption coefficients and hence failed to describe spatial variability of 2,4-D, atrazine, and glyphosate. For example, digital terrain attributes explained only 15 % of spatial

variability in 2,4-D K_d values in the SDNWA landscape, and none of the variability in 2,4-D K_d values in the MZTRA landscape.

The research examined the feasibility of using NIRS to estimate a range of soil properties data, as well as 17β-estradiol K_d values in soils. NIRS was generally an excellent technology for estimating SOC and 17β-estradiol K_d values, and was moderately successful for predicting soil pH, but generally resulted in weak predictive models for %sand, %silt or %clay. The Foss 6500 spectrophotometer marginally outperformed the smaller-sized field portable Zeiss Corona in predicting SOC and K_d values, while for determinations of soil pH, the Zeiss Corona marginally outperformed the Foss 6500 spectrophotometer.

Research further focused on the use of NIRS to predict K_d values, for herbicides 2,4-D (weakly-acidic), atrazine (weakly-basic) and glyphosate (zwitterion). Excellent calibrations were obtained for 2,4-D and atrazine, nevertheless calibrations were poor for glyphosate as the sorption of this herbicide was not strongly influenced by SOC. Our results built on previous studies (Malley et al. 2000, Martin et al. 2002, Bengtsson et al. 2007, Kookana et al. 2008) that have successfully used near-infrared spectroscopy and mid-infrared spectroscopy to predict a range of soil properties and the K_d values of non-ionic pesticides in soils.

Using the Foss 6500 spectrophotometer, research further focused on the application of NIRS to predict 2,4-D and atrazine K_d values and use these as input parameters in a pesticide fate model. For each field site and both field sites combined (regional approach), the study used a

test set method with two-third of the samples considered to be calibration set and one-third considered as validation set. NIRS-K_d values (determined using NIRS spectral data), Soil-K_d values (determined using pedotransfer functions and measured soil properties) or Lab-K_d values (determined with the batch equilibrium method) of validation data were used as input parameters in more than 3,500 PRZM simulations to calculate the amount of 2,4-D and atrazine leached to 15 cm depth (Kg ha^{-1}). For 2,4-D, for each field site and also for the regional approach, there was an adequate to good correlation of r >0.7 between the leaching predicted using Lab-K_d values as input parameters and the leaching predicted using either NIRS-K_d values or Soil-K_d values as input parameters. Results were less satisfactory for atrazine, particularly for Manitoba, because the Lab-K_d values were not always in close agree agreement with NIRS-K_d values or Soil-K_d values and for herbicides that have relatively long half-lives such as atrazine, variations in sorption input parameters lead to proportionally larger differences in the predicted herbicide mass leached. In general, this study suggests that the added benefit of NIRS, to rapidly process soil samples and determine K_d input parameters, is most efficient for pesticides that have small sorption potentials and short half-lives in soil. Most importantly, for these pesticides, NIRS can also be used to generate regional scale calibration equations providing that the fields included have a similar range in K_d values.

5.2 Research Implications

Pesticide fate models are important tools in registering agrochemicals, and in broader risk assessment tools to estimate which portion of agricultural applied pesticides or manure borne

estrogens move to water due to leaching, surface runoff, and erosion (Carsel et al. 1998, Das et al 2005, Wolf et al. 2008, Cessna et al. 2010). Pesticide and estrogen sorption coefficients (K_d values) are among the most sensitive input parameters for use in such risk assessment tools (Boesten and Van der Linden 1991, Dubus et al. 2003, Gagnon et al. 2014). This Ph.D. thesis focused on determining such sensitive input parameters. The research demonstrates that there are large variations in K_d values in surface and subsurface soils at the field-specific level, and that these variations need to be known to improve the confidence in using pesticide fate models for regulatory practices and decision-making at the large-scale of watersheds and regions. This study is among the most detailed study to have been conducted on variations in sorption of surface soils, and for a diverse range of chemical compounds including 2,4-D, atrazine, glyphosate or 17β-estradiol. Although a large number of sorption studies have been conducted in the past 75 years (Shipinov 1940, Yuen et al. 1962, Novak et al. 1997, Casey et al. 2003, Forouzangohar et al. 2008, Gaultier et al. 2008, Caron et al. 2010ab), relatively few studies have quantified variations in K_d values in subsurface soils (Oliver et al. 2003, Gaultier et al. 2006, Rodriguez-Cruz et al. 2006).

Unavailability of field-specific data on K_d values continues to present a major challenge for pesticide fate model users and policy makers especially when risk assessments are to be conducted for large geographical areas such as Canadian landscapes (Dubus et al. 2003, Cessna et al. 2010). K_d values for pesticides or estrogenic compounds are typically determined by batch equilibrium experiments (Wauchope et al. 2002), which are expensive, laborious, time consuming, and generate significant amounts of toxic waste. When applying pesticide fate

models to large-scale risk assessments, K_d values are more conveniently estimated from a pesticide properties databases (Cessna et al. 2010), or from soil geographical databases by applying pedotransfer functions (Weber et al. 2004), but these methods fail to capture the spatial variability in K_d values and this contributes to uncertainty in pesticide fate model predictions (Dubus et al. 2003). This Ph.D. study demonstrates that NIRS is an efficient supplementary method to batch equilibrium experiments and can more readily determine pesticide and estrogen K_d values in a large number of samples to capture the variability associated with sorption in landscapes. Moreover, field portable NIRS instruments such as Zeiss Corona, which can simultaneously analyze large number of samples for soil properties and K_d values on-site can be seen as future instruments for conducting spatial research as samples would not have to be transported to the laboratory.

Scientists have previously demonstrated that NIRS can be used to predict K_d values of non-ionic pesticides, but this is the first study to demonstrate that NIRS can be successfully used for determining the sorption of ionizable pesticides. Moreover, this is also the first study to demonstrate how NIRS can be integrated with pesticide fate models in large scale risk assessments. In the simplest approach, once calibrations are in place, NIRS instruments can analyze large number of soil horizons for pesticide K_d values and use these values in pesticide fate models for predicting pesticide leaching in soil profiles. Calibrations can be developed for a single field or for multiple fields at the same time, providing that such fields having similar ranges in K_d values. Alternatively, the pesticide K_d values generated can also be used in stochastic risk assessment techniques, such as to develop probability density functions from

which the pesticide K_d values are sampled by the model user. Stochastic modeling is particularly useful in the evaluation and registration process of new pesticide products and in calculating the efficiency of specific farm management strategies in reducing off-site pesticide movement.

5.3 Study Limitations and Future Recommendations

The research presented in this thesis covers detailed landscape-scale studies of the sorption of three herbicides and an estrogen. Herbicides 2,4-D and atrazine and estrogen 17β-estradiol K_d values all showed significant positive association with SOC and significant negative association with soil pH. Nevertheless, although the herbicide glyphosate showed stronger sorption in B-horizon having redoximorphic features, the associations between soil properties and glyphosate K_d values were not significant or otherwise weak. The soil properties analysis in this study was limited to SOC, soil pH and texture, but Al and Fe oxides are known to play an important role in glyphosate sorption in B-horizons with redoximorphic features (Subramanium and Hoggard 1988, Gimsing and Borggaard 2002, Gimsing et al 2004). Thus, the analysis of soil samples for Al and Fe oxides should be included in future studies focusing on the spatial variability of glyphosate sorption in agricultural fields of western Canada, particularly when studies include B-horizons with redoximorphic features.

The study demonstrated a wide range in glyphosate K_d values in soil-landscapes, ranging from 13.63 – 222.70 L Kg^{-1} for MZTRA, and 5.36 – 842.01 L Kg^{-1} for SDNWA. Regardless of such a wide range in both the landscapes, the current study failed to establish an understanding of the

impact of topography on glyphosate K_d values. For example, in MZTRA, the glyphosate mean K_d value of surface soils was 1.4 times larger in the depressional area than in shoulders; however, in SDNWA, the glyphosate mean K_d value of surface soils was 3.3 times smaller in the depressional area than in shoulders. For ionizable herbicides such as atrazine and 2,4-D, studies always find larger mean K_d values in the depressional area than in shoulders (Novak et al. 1997, Farenhorst et al. 2003, Gaultier et al. 2008) and our contradictory results for glyphosate, at least for SDNWA, suggest the need to examine spatial variability of glyphosate sorption in additional soil-landscapes.

The study presented in this thesis is the first research study to quantify 17β-estradiol K_d values in surface and subsurface soils at the landscape scale. With the exception of measuring the spatial variability of 17β-estradiol sorption in surface soils at the regional scale (Caron et al. 2010ab), no substantial data have been published on 17β-estradiol K_d values in western Canadian soils, or elsewhere. There is the scarcity of information on spatial variability of 17β-estradiol K_d values at the landscape scale especially in subsurface soils and future studies should focus on quantifying the fate of this and other steroid estrogenic compounds in agricultural fields in western Canada.

Studies on the spatial variability of sorption coefficients in agricultural fields have almost exclusively focused on surface soils and, as indicated above, conclude that for a range of pesticides, including 2,4-D and atrazine, sorption is typically greater in depressions (lower slopes) than on shoulders (upper slope) (Novak et al. 1997, Farenhorst et al. 2003, Gaultier et

al. 2008). This Ph.D. research indicates that such pattern does not hold for subsurface soils. For example, in both landscapes, the B-horizon samples in shoulder elements had numerically greater average 2,4-D K_d and atrazine K_d values than in depressional elements. Future research should focus on a better understanding of the role of landscape position on the fate of pesticides in sub-surface soils, and whether consistent patterns could be observed between digital terrain parameters or landform elements and K_d values in B-horizons. In the studies conducted for this Ph.D. research project, digital terrain parameters or landform elements failed to explain the spatial variability in K_d values in the studied fields, both in A and B mineral horizons. This may be because sampling design used in the current study collected 10 samples in each of seven predefined landform elements, rather than using a grid sampling design, for example 50 x 50 m^2 (Farenhorst et al. 2003) and 10 x 10 m^2 (Farenhorst et al. 2008). Thus, this Ph.D. study also indicated the need for future studies to examine the impact of sampling design on associations between digital terrain attributes and pesticide sorption coefficients.

This was the first study to use NIRS for predicting the sorption parameters of ionizable and the subsequent use of these K_d values in pesticide fate models to access herbicide leaching potential. The results demonstrated that such applications of NIRS were more successful for 2,4-D than atrazine, most likely because atrazine has larger K_d values and a longer half-life than 2,4-D. Nevertheless, the integration of NIRS with pesticide fate models was only investigated for two herbicides, and there is a need to examine a much broader range of pesticides to determine whether the conclusion of this study holds under such broader investigation. Much work also needs to be completed on how to develop and refine NIRS equations such that this

technique can be applied at multiple fields at the regional scale and, hence, is most likely to benefit the process of new pesticide product registrations. The initial findings of this study suggest that NIRS can be integrated with pesticide fate models by including two fields that are more than 700 km apart, is promising and warrants additional investigations for regional scale studies.

5.4 Contribution to Scientific Knowledge

The research presented in this thesis provides more detailed data than has ever before been reported on how K_d values of four chemically different compounds (2,4-D, atrazine, glyphosate and 17β-estradiol) vary with soil depth and across slope positions in undulating to hummocky terrains of western Canada. This detailed information of spatial variations in K_d values has not been reported for any soil-landscape and thus the data set so generated could lead to developing approaches to adjust pesticide K_d values by horizon in modeling approaches.

The research presented in this Ph.D. thesis indicate that NIRS is a rapid and economical alternate to conventional wet chemistry methods for estimating ionizable pesticide and estrogen K_d values for use in risk assessment tools. To the best of our knowledge, only one previous study (Bengtsson et al. 2007) has been published on the use of NIRS to predict pesticide K_d values in soils, and this study examined only non-ionic pesticides. One of the other major strengths of the present study is that it is the first one to outline how NIRS can be integrated in risk assessments and hence can lead to changes in the way governments evaluate

new pesticides for registered use. The detailed information now provided in the scientific literature because of this Ph.D. research could increase the use of NIRS technology to quickly, economically and accurately estimate pesticide K_d values for large scale analysis.

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