VARIABILITY OF SOIL PROPERTIES AND 2,4-D FATE AT FIELD AND REGIONAL SCALES AS AFFECTED BY ECOREGION, LANDSCAPE POSITION AND SOIL DEPTH

BY

JEANETTE GAULTIER

A Thesis
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DOCTOR OF PHILOSOPHY

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FACULTY OF GRADUATE STUDIES

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ABSTRACT

Gaultier, Jeanette. Ph.D., The University of Manitoba, 2007. Variability of soil properties and 2,4-D fate at field and regional scales affected by soil depth, landscape position and ecoregion. Advisor: Annemieke Farenhorst.

This study quantified variations in 2,4-D (2,4-dichlorophenoxyacetic acid) sorption and degradation as influenced by soil properties at field and regional scales. The sorption and degradation of 2,4-D was measured in soil profiles collected from upper, mid, lower and depression landscape positions at the field scale and in surface soils from upper, mid and lower landscape positions in seven ecoregions at the regional scale.

Sorption of 2,4-D varied significantly among soil horizons, as well as among slope positions in the A horizon at the field scale. Although 2,4-D sorption varied among ecoregions and among landscape positions at the regional scale, differences in sorption were generally not significant because of large variability in 2,4-D sorption within ecoregions and within landscape positions. Regardless of scale, variations in 2,4-D sorption were best predicted by regression models containing soil organic carbon content and soil pH as variables. At the field scale, carbonate content was also significant in regressions predicting 2,4-D sorption because sorption was negatively related to carbonate content. At the field scale, segmentation of soils by soil horizon and slope position improved predictions of 2,4-D sorption. At the regional scale, segmentation of soils by ecoregion and landscape position did not greatly improve predictions of 2,4-D sorption.

Compared with sorption, at the field scale, differences in total 2,4-D degradation and degradation rates among slope positions in the A horizon were small. Differences in total 2,4-D degradation and degradation rates among ecoregions and among slope positions at the regional scale were also generally not significant. The most significant differences in 2,4-D degradation occurred with soil depth, for which degradation kinetics were best described by first-order kinetics in the A horizon and by three half-order kinetics in the B and C horizons. Although sorption of 2,4-D limited the bioavailability of 2,4-D for degradation in the A horizon, predictions of 2,4-D degradation parameters were generally poor and not consistently related with 2,4-D sorption or soil properties. Segmentation of soils by ecoregion and by landscape position improved predictions of 2,4-D degradation parameters, however, regression models still had low R^2 values.

Since there is only limited information on the variability of pesticide sorption and degradation in soils, single estimates of pesticide sorption and degradation parameters are used as input parameters in pesticide fate models, even for simulations assessing the environmental risks associated with pesticide use across large areas. Results from this study indicate that determining 2,4-D sorption and degradation parameters as a function of soil properties could be a better approach to obtaining estimates of pesticide input parameters for pesticide fate models. However, determining sorption parameters based on soil properties will be more accurate than determining degradation parameters based on soil properties.

FORWARD

This thesis was prepared in the manuscript format in accordance with the Department of Soil Science guidelines. Thesis chapters were submitted for publication in the following peer reviewed journals:

- 'Spatial variability of soil properties and 2,4-D sorption in a hummocky field as affected by landscape position and soil depth' was published in the Canadian Journal of Soil Science, volume 86, pp. 89–95 in 2006. Dr. Annemieke Farenhorst (advisor) and Dr. Gary Crow, from the Department of Animal Science at the University of Manitoba, co-authored the paper.

- '2,4-D degradation in soil profiles of a cultivated hummocky landscape in Manitoba, Canada' has been accepted for publication in 2007 by the Journal of Environmental Science and Health, Part B. Dr. Annemieke Farenhorst co-authored the paper.

- 'Degradation of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D in 114 agricultural soils as affected by soil organic carbon content ' was submitted to Soil Biology and Biochemistry. Co-authors for this paper were: Dr. Annemieke Farenhorst and Dr. Jason Cathcart and Tom Goddard of AAFRD.

- Variability of soil properties and 2,4-D sorption and degradation parameters in agricultural ecoregions of Alberta, Canada' was submitted to the Journal of

Environmental Quality. Co-authors for this paper were: Dr. Annemieke Farenhorst and Dr. Jason Cathcart and Tom Goddard of AAFRD.

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1. INTRODUCTION

Pesticides have played a significant role in supporting food production and human health throughout history, but it was not until the early 1940s that pesticide use dramatically increased due to the introduction of synthetic organic pesticides. Synthetic organic pesticides are more effective and less expensive as pest control agents than the historically used natural plant extracts and inorganic chemicals. Current pest control practices in agricultural production account for the use of approximately 2.6 billion kilograms of synthetic organic pesticides per annum worldwide (Dich et al., 1997) and 69 million kilograms per annum in Canada (AAFC, 2003).

The growing dependency of modern agriculture on synthetic organic chemicals for pest control has been accompanied by mounting concerns over point source and non-point source pollution (Smith, 1982; Carter, 2000). A study by Newton in 1933 first identified pesticide carry-over problems in agricultural fields, highlighting limitations in re-cropping choices for producers and indicating problems with point-source pesticide persistence and toxicity (Smith, 1982). Non-point source pesticide pollution has been demonstrated by numerous studies that detected a range of trace pesticide residues in surface and groundwater (Hallberg, 1989; Goodrich et al., 1991; Kolpin et al., 1995), precipitation (Nations and Hallberg, 1992; Rawn et al., 1999a) and the atmosphere (Van Dijk and Guicherit, 1999).

A better understanding of pesticide fate in soil is required to determine beneficial management practices that limit pesticide off-site movement but retain the benefits of good pest control. Enhanced knowledge of pesticide fate in soil is also important to improve parameterization of pesticide fate models, including those used for environmental risk assessments and pesticide regulatory purposes.

Pesticide sorption and degradation in soil are two key processes used to predict pesticide fate in the environment (Cheng, 1990) and are sensitive parameters in pesticide fate models (Dubus et al., 2003). The sorption and degradation of pesticides in soil is a function of soil physical, chemical and biological properties, pesticide characteristics, climate and crop management systems (Cheng, 1990). Sorption of pesticides by soil is largely a result of interactions with soil organic matter (Stevenson, 1972; Senesi, 1992; Wauchope et al., 2002), but may also be affected by other soil properties such as soil pH and texture (Calvet, 1989). Degradation of pesticides is primarily mediated by soil microbes (Bollag and Liu, 1990; Topp et al., 1997), and the soil and environmental factors affecting soil microorganisms. Pesticide sorption by soil determines the bioavailability of the pesticide to be degraded. Sorption and degradation affect the persistence and mobility of a pesticide in the environment.

Pesticide fate models were developed to simulate field scale transport of pesticides based on pesticide-soil-water interactions (Rao and Wagenet, 1990). The ability of pesticide fate model simulations to accurately describe pesticide mobility in soil is often limited by the spatial variability of soil properties influencing pesticide fate (Rao and Wagenet,

1985; Elabd et al., 1986). Field scale heterogeneity of soil properties with soil depth and among slope positions result from variations in soil pedogenic factors, such as differences in parent material, hydrology, and physical and chemical weathering (Goderya, 1998; Landi et al., 2004). Differences in soil properties, such as soil organic carbon content and pH, among slope positions in hummocky fields are amplified by erosion and deposition of soil constituents by water, wind and tillage (Gregorich and Anderson, 1985). Research has shown that the distribution of soil properties within fields often vary predictably with landscape position and soil depth (Brubaker et al., 1993) and in response, pesticide fate may vary predictably within fields, as well (Farenhorst et al., 2001).

Evaluation of model ability to simulate pesticide transport at regional scales is required, as pesticide fate models developed at the field scale are currently being used to simulate pesticide transport for much larger areas (Addiscott and Mirza, 1998). Regional scale variability in soil properties encompass the soil pedogenic factors described for the field scale, but also include effects of climate and land use patterns (Parkin, 1993). Studies quantifying spatial variability of soil properties at the regional scale, as by Brejda et al. (2000), are limited and most regional scale research has focused on soil microbial measurements (Parkin, 1993; McCulley and Burke, 2004). Literature concerning pesticide fate at larger scales is virtually non-existent, with the exception of leaching assessments.

The objectives of this study were to determine the spatial variability of soil properties and 2,4-D fate, and the relations among them, at both field and regional scales. The herbicide

2,4-D was selected for this study because it is one of the most widely used herbicides in Canada. Although 2,4-D is quickly degraded in soils, the potential for leaching exists because it is only weakly sorbed by soil (Ahrens, 1994). Studies carried out in the Canadian prairies indicate that 2,4-D is one of the most frequently detected pesticides in surface water (Nicholaichuk and Grover, 1983; Grover et al., 1997; Rawn et al., 1999b; Waite et al., 2002; Cessna and Elliot, 2004) and the atmosphere and precipitation (Rawn et al., 1999a; Waite et al., 2002). So far, there have been no studies on the Canadian prairies that measured groundwater contamination by 2,4-D. Specific research activities were divided into the following 4 chapters:

Chapter 2: A field scale study that quantified 2,4-D sorption in soil profiles (n = 72) along a transect in an agricultural field in Manitoba. This study quantified variations in 2,4-D sorption as influenced by soil properties, landscape position (upper slopes, mid slopes, lower slopes and depressions) and soil depth (A, B and C horizons).

Chapter 3: A field scale study that quantified 2,4-D degradation in soil profiles (n = 25) along a transect in an agricultural field in Manitoba. This study quantified variations in 2,4-D degradation as influenced by 2,4-D sorption, soil properties, landscape position (upper slopes, mid slopes, lower slopes and depressions) and soil depth (A, B and C horizons).

Chapter 4: A study that quantified 2,4-D degradation as both the removal of the carboxyl side chain ([carboxyl-^{14}C] 2,4-D) and cleavage of the phenyl ring ([ring-U-^{14}C] 2,4-D). Degradation of 2,4-D was measured for 114 soils, collected from seven agricultural ecoregions in Alberta. This study quantified variations in 2,4-D degradation as influenced by 2,4-D sorption and soil properties, particularly soil organic carbon content and soil microbial activity. It provided a recommendation for improving pesticide fate modeling at regional scales.

Chapter 5: A regional scale study that quantified 2,4-D sorption and degradation in 123 soils representative of six agricultural ecoregions in Alberta. The sorption and degradation of 2,4-D was measured in both 2002 and 2004, along with a range of soil properties. This study quantified variations in soil properties, 2,4-D sorption and 2,4-D degradation between the two sampling years, the six ecoregions and three landscape positions (upper slopes, mid slopes, lower slopes). Relations between soil properties, 2,4-D sorption and 2,4-D degradation were also examined.

1.1 References

AAFC. 2003. Farm Income and Adaptation Policy: A review of agricultural pesticide pricing and availability in Canada. Available online at: http://www.agr.gc.ca/spb/fiap-dpraa/publications/pesticide/pest_appA_e.php

Addiscott, T.M. and Mirza, N.A. 1998. Modelling contaminant transport at catchment of regional scale. Agric. Ecosyst. Environ., **67:** 211–221.

Ahrens, W. 1994. Herbicide Handbook, 7th edition. Weed Science Society of America, pp. 77–81.

Bollag, J.M. and Liu, S.Y. 1990. Biological transformation processes of pesticides. *In* Cheng, H.H. (Ed). Pesticides in the Soil Environment: Processes, Impacts and Modeling. Soil Science Society of America, Madison, WI. pp. 169–211.

Brejda, J.J., Moorman, T.B., Smith, J.L., Karlen, D.L., Allen, D.L. and Dao, T.H. 2000. Distribution and variability of surface soil properties at a regional scale. Soil Sci. Soc. Am. J., **64:** 974–982.

Brubaker, S.C., Jones, A.J., Lewis, D.T. and Frank, K. 1993. Soil properties associated with landscape position. Soil Sci. Soc. Am. J., **57:** 235–239.

Calvet, R. 1989. Adsorption of organic chemicals in soils. Environ. Health Perspect., **83:** 145–177.

Carter, A.D. 2000. Herbicide movement in soils: principles, pathways and processes. Weed Res., **40:** 113–122.

Cessna, A.J. and Elliot, J.A. 2004. Seasonal variation of herbicide concentrations in prairie farm dugouts. J. Environ. Qual., **33:** 302–315.

Cheng, H. H. (Ed). 1990. Pesticides in the Soil Environment: Processes, Impacts and Modeling. Soil Sci. Soc. Am., Madison, WI. pp. 1–5.

Dich, J., Hoar Zahm, S., Hanberg, A. and Adami, H. 1997. Pesticides and Cancer. Cancer Causes and Control, **8:** 420–443.

Dubus, I.G., Brown, C.D. and Beulke, S. 2003. Sensitivity analyses for four pesticide leaching models. Pest Manag. Sci., **59:** 962–982.

Elabd, H., Jury, W.A. and Cliasth, M.M. 1986. Spatial variability of pesticide adsorption parameters. Environ. Sci. Technol., **20:** 256–260.

Farenhorst, A., Muc, D, Monreal, C. and Florinski, I. 2001. Sorption of herbicides in relation to soil variability and landscape position. J. Environ. Sci. Health Part B, **B36:** 379– 87.

Goderya, F.S. 1998. Field scale variations in soil properties for a spatially variable control: a review. J. Soil. Contam., **7:** 243–264.

Goodrich, J.A., Lykins Jr., B.W. and Clark, R.M. 1991. Drinking water from agriculturally contaminated groundwater. J. Environ. Qual., **20:** 707–717.

Gregorich, E.G. and Anderson, D.W. 1985. Effects of cultivation and erosion of soils of four toposequences in the Canadian Prairies. Geoderma, **36:** 343–354.

Grover, R., Waite, D.T., Cessna, A.J., Nicholiachuk, W., Irvin, D.G., Kerr, L.A. and Best, K. 1997. Magnitude and persistence of herbicide residues in farm dugouts and ponds in the Canadian prairies. Environ. Toxicol. Chem., **16:** 638–643.

Hallberg, G.R. 1989. Pesticide pollution of groundwater in the humid United States. Agric. Ecosyst. Environ., **26:** 299–367.

Kolpin, D.W., Goolsby, D.A. and Thurman, E.M. 1995. Pesticides in near-surface aquifers: an assessment using highly sensitive analytical methods and tritium. J. Environ. Qual., **24:** 1125–1132.

Landi, A., Mermut, A,R. and Anderson, D.W. 2004. Carbon distribution in a hummocky landscape from Saskatchewan, Canada. Soil Sci. Soc. Am. J., **68:** 175–184.

McCulley, R.L. and Burke, I.C. 2004. Microbial community composition across the Great Plains: landscape versus regional variability. Soil Sci. Soc. Am. J., **68:** 106–115.

Nations, B.K. and Hallberg, G.R. 1992. Pesticides in Iowa precipitation. J. Environ. Qual., **21:** 486–492.

Nicholaichuk, W. and Grover, R. 1983. Loss of fall applied 2,4-D in spring runoff from a small agricultural watershed. J. Environ. Qual., **12:** 412–414.

Parkin, T.B. 1993. Spatial variability of microbial processes in soil – a review. J. Environ. Qual., **22:** 409–417.

Rao, P.S.C. and Wagenet, R.J. 1985. Spatial variability of pesticides in field soils: methods for data analysis and consequences. Weed Sci., **33:** 18–24.

Rao, P.S.C. and Wagenet, R.J. 1990. Modeling pesticide fate in soils. *In* Cheng, H.H. (Ed). Pesticides in the Soil Environment: Processes, Impacts and Modeling. Soil Science Society of America, Madison, WI. pp. 351–399.

Rawn, D.F.K., Halldorson, T.H.J., Lawson, B.D. and Muir, D.C.G. 1999a. A multi-year study of four herbicides in air and precipitation from a small prairie watershed. J. Environ. Qual., **28:** 898–906.

Rawn, D.F.K., Halldorson, T.H.J., Turner, W.N., Woychuk, R.N., Zakrevsky, J.-G. and Muir, D.C.G. 1999b. A multi-year study of four herbicides in surface water of a small prairie watershed. J. Environ. Qual., **28:** 906–917.

Senesi, N. 1992. Binding mechanisms of pesticides to soil humic substances. Sci. Tot. Environ., **123/124:** 63–76.

Smith, A.E. 1982. Herbicides and the soil environment in Canada. Can. J. Soil Sci., **62:** 433–460.

Stevenson, F.J. 1972. Organic matter reactions involving herbicides in soil. J. Environ. Qual., **1:** 333–343.

Topp, E., Vallaeys, T. and Soulas, G. 1997. Pesticides: microbial degradation and effects on microorganisms. *In* van Elsas, M.J.D., Welligton, E.M.H. and Trevors, J.T. (Eds), Modern Soil Microbiology. Marcel Dekker Inc., New York, pp. 547–575.

Van Dijk, H.F.G. and Guicherit, R. 1999. Atmospheric dispersion of current-use pesticides: a review of the evidence from monitoring studies. Water, Air, Soil Pollut., **115:** 21–70.

Waite, D.T., Cessna, A.J., Grover, R., Kerr, L.A. and Snihura, A.D. 2002. Environmental concentrations of agricultural herbicides: 2,4-D and Triallate. J. Environ. Qual., **31:** 129–144.

Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W., Gerstl, Z., Lane, M. and Unsworth, J.B. 2002. Pesticide soil sorption parameters: theory, measurements, uses, limitations and reliability. Pest Manag. Sci., **58:** 419–445.

2. SPATIAL VARIABILITY OF SOIL PROPERTIES AND 2,4-D SORPTION IN A HUMMOCKY FIELD AS AFFECTED BY LANDSCAPE POSITION AND SOIL DEPTH

2.1 Abstract

Since pesticide fate and leaching models increasingly incorporate spatial variability, the objective of this study was to quantify the variability of soil properties and 2,4-D sorption within a hummocky field as affected by landscape position and soil depth. Seventy-two soil cores collected at 5 m intervals along a transect were segmented by soil horizon (A, B and C) and landscape position (upper slopes, mid slopes, lower slopes and depressions). As expected, soil organic carbon content significantly decreased, and soil pH and soil carbonate content significantly increased, with soil depth, while clay content was significantly greater in the B horizon than the A and C horizon. Soils from the depressional area generally had higher soil organic carbon content, soil carbonate content, clay content and soil pH than soil samples from other slope positions. Sorption of 2,4-D by soil was positively correlated with soil organic matter content and negatively correlated with soil carbonate content. These soil properties and herbicide sorption varied along the transect and with soil depth. Regardless of whether or not the landscape was segmented by landscape position, for both the A and C horizon, predictions of 2,4-D sorption by soil were generally good using simple regression models that contained soil organic carbon content and carbonate content as the only parameters. However, for the B horizon, the prediction of 2,4-D sorption by soil was very poor when all sampling points along the transect were considered, but greatly improved for the mid and depression slope

positions when soils were segmented by landscape position. We conclude that segmentation by slope position could be an additional tool useful for predicting pesticide fate and leaching at the large-scale. As well, the negative association between soil carbonate content and 2,4-D sorption warrants further attention as a large portion of Canadian agriculture encompasses calcareous soils.

2.2 Introduction

Understanding the fate of herbicides in agricultural fields is imperative to ensure good agricultural performance while limiting chemical movement and potential environmental contamination. The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is a foliar applied herbicide commonly used in Canada and the United States to control broadleaf weeds in annual and perennial grass systems (Ahrens, 1994). Recently, 2,4-D and 2,4-D tank-mixes have been used as pre-seed burn off treatments to control glyphosate-tolerant canola volunteers (Simard and Legere, 2002). Despite the short half-life of 2,4-D in soil (Ahrens, 1994), the risk of 2,4-D movement to groundwater and surface water exist because the herbicide is only weakly sorbed to clay particles and soil organic matter (Ahrens, 1994). The herbicide has been found in surface and ground waters throughout North America (Hallberg, 1989; Goodrich et al., 1991; Kolpin et al., 1995; Rawn et al., 1999; Cox, 1999; Cessna and Elliot, 2004). A recent study detected 2,4-D in rainwater collected in Alberta, indicating measurable levels of the chemical in the atmosphere as well (Hill et al., 2001).

Sorption is a key process that can be used to predict herbicide fate, as it affects herbicide bioavailability, mobility, and persistence in soil (Wagenet and Rao, 1990). Sorption of 2,4-D by soil is largely the result of weak hydrogen bonds and van der Waals interactions with soil organic matter (Calvet, 1989; Senesi, 1992). Other soil properties, including pH and clay content, are also known to affect 2,4-D sorption (Reddy and Gambrell, 1987; Green and Karickhoff, 1990).

Herbicide persistence and mobility may vary in field soils as sorption processes respond to the heterogeneity of soil properties that exists across slope positions and with soil depth (Jacobsen et al., 2001; Strebe and Talbert, 2001; Farenhorst et al., 2003). Factors that affect the variation of soil properties across slope positions and with soil depth include soil pedogenic factors, such as the influence of topography on hydrologic processes, and irregularities in parent material deposition (Goderya, 1998). Cultivation of fields, particularly in hummocky landscapes, increases spatial variability of soil properties due to the redistribution of topsoil from upper slope to lower slope positions by tillage (Gregorich and Anderson, 1985). In addition to tillage erosion, wind and water erosion may amplify spatial differences in soil characteristics within agricultural fields (Lobb et al., 2003).

Although risk assessments of herbicide leaching to groundwater require information on herbicide sorption throughout the entire soil profile, most previous studies have exclusively focused on herbicide sorption processes in the plough layer (de Jonge et al., 2000; Ma et al., 2000; Oliveira Jr. et al., 2001; Gupta and Gajbhiye, 2002). There are

also limited studies on the spatial variability of herbicide sorption within landscapes (Farenhorst et al., 2003). Additional information on the spatial distribution of herbicide fate across slope positions and with depth could enable producers and policy makers to make more informed weed management decisions and reduce environmental contamination by herbicides (Khakural et al., 1994). The objective of this study was to quantify the variability of soil properties and 2,4-D sorption as affected by landscape position and soil depth within an undulating to hummocky terrain in Manitoba. These data were used to determine the associations between 2,4-D sorption and soil properties and landscapes.

2.3 Materials and Methods

2.3.1 Chemicals and analytical techniques

Analytical grade 2,4-D (95% chemical purity) and [ring-U-^{14}C] labelled 2,4-D (99% radiochemical purity; specific activity 9.25 MBq mmol^{-1}) were purchased from Sigma Aldrich Chemical Company (St. Louis, MO.). The amounts of radioactivity in herbicide solutions and samples from experiments were determined by Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (LS 7500 Beckman Instruments, Fullerton, CA). Radioactivity was measured using 10 mL of Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ) and a maximum counting time of 10 minutes.

2.3.2 Site characteristics

The site was located in a field northwest of Miami, Manitoba (6-5-7 1W). The field had been conventionally cultivated for over 100 years by deep tilling in the fall and disking and harrowing in the spring, with a two year cereal-oilseed crop rotation. Herbicides, including 2,4-D, were part of the cropping system in the past 40 years. The soil-landscape is characteristic of a broad region of undulating to hummocky (Soil Classification Working Group, 1998) glacial till landscapes in western Canada (Clayton et al., 1977). The soil is characterized as a Dark Grey Chernozem (Soil Classification Working Group, 1998) developed on shale and calcareous glacial till. Well-drained soils occurring on upper and mid slope positions belong to the Dezwood loam series (Orthic Dark Grey Chernozem; Ap, Btj, Ck horizons). Imperfectly drained soils from lower slope positions are of the Zaplin soil series (Gleyed Dark Grey Chernozem; Ap, Btgj, Ckgj horizons) and soils from depression positions are of the Pouchal soil series (Humic Luvic Gleysol; Ap, Btg, Ckg horizons). The soil texture was sandy loam.

As part of a larger study, the entire field was surveyed using a Trimble AgGPS 214 (Trimble Navigation LTD., Sunnyvale, CA) global positioning system (GPS) at a spacing of 5 m in hummocky portions of the field and 10 m in the more level portions of the field. The Trimble AgGPS 214 is accurate to 1 cm. Field elevation ranged from 440 to 460 m above sea level, with slope gradients of 4 to 9 percent.

2.3.3 Soil sampling and characterization

Seventy-two soil cores (8 cm inner diameter, 50 to 125 cm length) were collected at 5 m intervals along a transect (360 m long) running west to east in the field. The position of sampling points along the transect were mapped using a Sokkia set 4110 Total Station system (Sokkia Co. LTD., Japan) and GPS reference points. The Total Station is accurate to 1 mm. Using the GPS and Total Station output, sample points were classified according to their slope position using the LandMapR software program (MacMillan and Pettepiece, 2000) and placed into one of four slope categories: upper slope (U), mid slope (M), lower slope (L), or depression (D) (Figure 2.1).

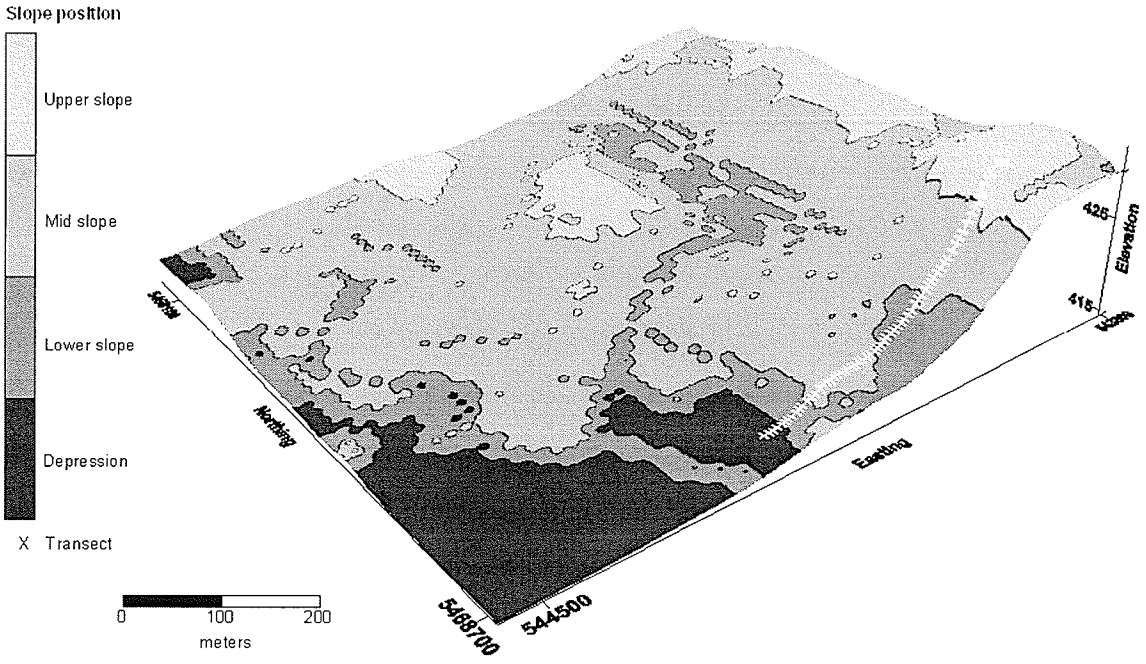


Figure 2.1 Classification of study site and field transect as upper slopes, mid slopes, lower slopes and depressions as determined by LandMapR software.

Soil cores were sectioned based on horizon: A, B and C. Samples were well-mixed and then air-dried and sieved (<2 mm) prior to soil properties and herbicide sorption analyses.

For soil organic carbon content (SOC) analyses, inorganic carbon was removed by digestion with 6 M HCl and organic carbon content was then determined by dry combustion of 0.12 g oven-dried soil using a Leco model CHN 600 C and N determinator (Leco Instruments LTD., Mississauga, ON) (Nelson and Sommers, 1982). Soil pH values were obtained using 10 ml of 0.01 M $CaCl_2$ and 5 g air-dried soil (McKeague, 1978). Total carbonate content was determined using a volumetric calcimeter that measured evolved carbon dioxide upon addition of 6 M HCl · $FeCl_2$ to a soil sample (Loeppert and Suarez, 1996). Soil texture was measured using the hydrometer method (Gee and Bauder, 1986) to determine percent clay content.

2.3.4 Analysis of 2,4-D sorption

Sorption of 2,4-D by soil was determined using batch equilibrium analysis. A 0.01 M $CaCl_2$ solution with 1 μg mL^{-1} 2,4-D and 16.7 Bq mL^{-1} [ring-U-^{14}C] labelled 2,4-D was added (10 mL) to 5 g of soil in Teflon tubes (duplicate) and rotated for 24 hours to establish equilibrium. Samples were then centrifuged at 10,000 rpm for 10 minutes. Aliquots (1 mL) of supernatant (duplicates) were removed from each tube and analyzed by LSC to determine the proportion of 2,4-D remaining in solution. Herbicide sorption by soil was described by the sorption coefficient, *Kd* [mL g^{-1}]:

$$Kd = \frac{Cs}{Ce} \qquad [2.1]$$

where *Cs* = the amount of 2,4-D sorbed by the soil [μg g^{-1}] and *Ce* = the concentration of 2,4-D of the soil solution at equilibrium [μg mL^{-1}]. The amount of 2,4-D sorption per unit soil organic carbon, *Koc* [mL g^{-1}], was also determined:

$$Koc = \frac{Kd}{SOC[\%]} \times 100 \qquad [2.2]$$

2.3.5 Statistical analyses

Since data failed the Kolmogorov-Smirnov normality test, even following transformation, the non-parametric Kruskal-Wallis test was used to describe the effects of slope position and soil depth on soil properties and 2,4-D sorption by soil. However, parametric correlation and regression tests were applied to the data set despite its non-normality due to the robust nature of these analyses (Legendre and Legendre, 1998). Pearson's pairwise correlation analysis was used to determine the existence and strengths of relations among soil properties and 2,4-D sorption. Stepwise regression analysis was carried out to determine the soil properties having the greatest affect on 2,4-D sorption. To be included in a regression model, soil properties had to be significant at $P \leq 0.05$. All statistical analyses were performed in SAS, version 8.01 (SAS Inst., 2000).

Traditionally the mean ± the standard error is reported when means of treatments are compared. In this study the mean ± the coefficient of variation (CV) was used in order to compare variability among variables as well as differences in treatment means.

2.4 Results

SOC was greatest in the A horizon (1.96% ± 42%, reflecting mean value and CV, respectively) and significantly decreased with depth to only 0.54% ± 61% in the B horizon and 0.37% ± 41% in the C horizon (Table 2.1). Both pH and carbonate content

significantly increased with depth, reflecting the calcareous nature of the parent material. However, differences in soil pH among horizons were small because soil pH was on average 6.96 ± 6% in the A horizon, 7.27 ± 4% in the B horizon and 7.46 ± 2% in the C horizon. As expected, carbonate content significantly increased in the order of A horizon < B horizon < C horizon (Table 2.1). Clay content was similar in the A (19.14% ± 29%) and the C (19.80% ± 38%) horizons, but significantly greater in the B horizon (23.49% ± 26%). Sorption capacity of the soil significantly decreased with depth in the order of A horizon > B horizon > C horizon (Table 2.1). *Koc* values followed a similar trend, significantly decreasing in the order A horizon > B horizon > C horizon.

Table 2.1 Means and variability of soil properties and 2,4-D sorption for A, B and C horizons from 72 soil cores

	Soil properties					2,4-D sorption	
	Soil depth (cm)	SOC (g 100 g^{-1} soil)	pH	Carbonate content (g 100 g^{-1} soil)	Clay content (g 100 g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})
A horizon							
Mean		1.96[a]	6.96[c]	1.95[c]	19.14[b]	4.21[a]	211[a]
CV (%)*		42	6	152	29	50	26
Minimum	10	0.54	5.94	0.00	6.45	0.56	103
Maximum	30	3.88	7.58	14.46	32.24	12.54	391
B horizon							
Mean		0.54[b]	7.27[b]	5.73[b]	23.49[a]	0.92[b]	176[b]
CV (%)		61	4	135	26	113	131
Minimum	25	0.14	5.80	0.00	11.29	0.21	48
Maximum	125	1.99	7.66	29.88	42.91	6.51	191
C horizon							
Mean		0.37[c]	7.46[a]	21.90[a]	19.80[b]	0.33[c]	89[c]
CV (%)		41	2	48	38	55	34
Minimum		0.16	6.89	0.07	3.22	0.08	44
Maximum		0.93	7.77	41.15	38.52	0.87	193

*CV = coefficient of variation ([standard deviation/mean] x 100)
[a-c] Column means followed by same letter are not significantly different at $P < 0.05$ (Kruskal-Wallis)

The variability of SOC along the transect was slightly greater in the B horizon compared to the A and C horizons (Table 2.1). Within all soil horizons along the transect, soil pH

was the least variable soil property, with CV values ranging from 2 to 6 percent. Carbonate content was highly variable in the A and B horizons relative to the C horizon (Table 2.1). The variability of clay content was similar for the A and B horizons and only slightly greater in the C horizon. Along the transect, sorption of 2,4-D was most variable in the B horizon, as CV values were 113% and 131% for *Kd* and *Koc*, respectively. Variability in sorption parameters along the transect was similar in the A and C horizons. *Koc* was less variable than *Kd* in the A and C horizons, which is to be expected as *Koc* is known to reduce the variability associated with *Kd* (Gerstl, 2000). However, *Koc* was more variable than *Kd* in the B horizon.

SOC of the A horizon increased significantly with slope position in the order U < M < L < D (Table 2.2). SOC within either B or C horizons did not vary significantly with slope position, with the exception of the L slope position in the C horizon which contained significantly lower levels of organic carbon. Soil pH within the A horizon increased significantly in the order of U < M = L < D slope positions (Table 2.2). Soil pH significantly varied in the same order within the B horizon as within the A horizon, but slope position had no significant affect on soil pH in the C horizon. Carbonate content within the A horizon followed the same trend as pH in that horizon, significantly increasing in the order of U < M = L < D slope positions. In the B horizon, carbonate content was significantly greater in the depression position relative to all other slope positions. In the C horizon, carbonate content significantly increased in the order of U = L < M < D slope positions. For all soil horizons, clay content was significantly higher in depression soils relative to soil from all other slope positions. In the A horizon, *Kd*

increased significantly among slope positions in the order of U < M < L = D (Table 2.2). *Kd* did not respond to slope position in either B or C soil horizons. *Koc* was significantly lower only for the D slope positions, but in all horizons.

Table 2.2 Means and variability of soil properties and 2,4-D sorption as affected by slope position and soil depth in 72 soil cores

	Soil properties				2,4-D sorption	
	SOC (g 100 g^{-1} soil)	pH	Carbonate content (g 100 g^{-1} soil)	Clay content (g 100 g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})
A horizon						
U	0.96 ± 34^{d}	6.49 ± 6^{c}	0.30 ± 90^{c}	21.27 ± 11^{b}	2.03 ± 79^{d}	193 ± 43^{b}
M	1.72 ± 36^{c}	6.94 ± 7^{b}	2.28 ± 155^{b}	18.36 ± 23^{bc}	3.71 ± 42^{bc}	213 ± 27^{ab}
L	2.57 ± 22^{b}	7.07 ± 4^{b}	1.38 ± 124^{b}	16.22 ± 33^{c}	5.99 ± 35^{a}	230 ± 17^{ab}
D	3.09 ± 12^{a}	7.39 ± 3^{a}	4.20 ± 75^{a}	29.26 ± 9^{a}	5.12 ± 20^{ab}	165 ± 15^{c}
B horizon						
U	0.39 ± 35^{a}	6.91 ± 7^{c}	2.74 ± 175^{b}	20.12 ± 15^{b}	0.55 ± 66^{a}	138 ± 37^{a}
M	0.52 ± 58^{a}	7.29 ± 3^{b}	5.56 ± 139^{b}	21.95 ± 23^{b}	0.96 ± 101^{a}	168 ± 55^{a}
L	0.53 ± 47^{a}	7.33 ± 2^{b}	3.70 ± 165^{b}	25.20 ± 19^{b}	1.07 ± 135^{a}	248 ± 175^{a}
D	0.93 ± 65^{a}	7.52 ± 2^{a}	16.48 ± 43^{a}	32.38 ± 28^{a}	0.68 ± 94^{a}	66 ± 25^{b}
C horizon						
U	0.36 ± 21^{a}	7.29 ± 3^{a}	9.55 ± 79^{c}	15.78 ± 30^{b}	0.39 ± 28^{a}	107 ± 22^{a}
M	0.38 ± 43^{a}	7.50 ± 2^{a}	23.87 ± 36^{b}	18.03 ± 31^{b}	0.34 ± 60^{a}	88 ± 29^{a}
L	0.31 ± 35^{b}	7.46 ± 1^{a}	16.37 ± 48^{c}	19.23 ± 34^{b}	0.31 ± 51^{a}	101 ± 36^{a}
D	0.48 ± 42^{a}	7.49 ± 1^{a}	37.28 ± 7^{a}	33.75 ± 11^{a}	0.27 ± 44^{a}	55 ± 20^{b}

Mean ± CV (%)

[a-d] Column means for slope positions within a horizon followed by same letters are not significantly different at $P < 0.05$ (Kruskal-Wallis)

Soil pH had a moderate positive correlation with carbonate content in all horizons (Table 2.3). In the A horizon only, soil pH was also moderately positively correlated with SOC ($r = 0.46$, $P = 0.01$). In the C horizon only, clay content and SOC were weakly, positively correlated ($r = 0.33$, $P < 0.05$). *Kd* was positively correlated with SOC for all soil horizons. The relationship between *Kd* and SOC was strongest in the A horizon and weakest in the B horizon. The positive relation between *Kd* and SOC within the A, B and C horizons was consistent for most slope positions (data not shown). However, *Koc* was

not associated with SOC in any horizon (Table 2.3). For the A and C horizons, *Koc* was negatively correlated to carbonate content, but in the A, B or C horizons, *Koc* was not significantly correlated with soil pH. *Koc* was also negatively correlated with clay content, but in the C horizon only.

Table 2.3 Pearson's pairwise correlation relationships among soil properties and 2,4-D sorption coefficients as affected by soil depth[†]

	Kd	*Koc*	SOC	pH	$CaCO_3$	Clay
A horizon						
Kd	1.00					
Koc	0.60***	1.00				
SOC	0.86***	--	1.00			
pH	0.20*	--	0.46**	1.00		
$CaCO_3$	--	-0.39**	--	0.46***	1.00	
Clay	--	--	--	--	--	1.00
B horizon						
Kd	1.00					
Koc	0.82***	1.00				
SOC	0.41**	--	1.00			
pH	--	--	--	1.00		
$CaCO_3$	--	--	0.43**	0.48***	1.00	
Clay	--	--	--	--	--	1.00
C horizon						
Kd	1.00					
Koc	0.53***	1.00				
SOC	0.75***	--	1.00			
pH	--	--	--	1.00		
$CaCO_3$	--	-0.48***	--	0.53***	1.00	
Clay	--	-0.41**	0.33*	--	0.57***	1.00

*, **, and *** denote $P < 0.05$, $P < 0.01$, and $P < 0.001$ level of significance, respectively, for correlations Ho: $r = 0$; Ha: $r \neq 0$

-- denotes no significant correlation

[†] See Appendix A for graphical representation of significant correlations between soil properties and 2,4-D sorption

Stepwise regression analysis revealed that SOC was responsible for the majority of 2,4-D sorption at all soil depths, and accounted for 73%, 18%, and 60% of 2,4-D sorption in the A, B, and C horizons, respectively. Optimal prediction of 2,4-D sorption in the A horizon was achieved by a regression model containing all measured soil variables. In the B horizon, only SOC and carbonate content were significant in the best regression

model. The best model for the C horizon included the variables of SOC, carbonate content, and clay content. The least complex regression model above (that of the B horizon) contained the variables SOC and carbonate content and explained 79% ($P <$ 0.001) and 73% ($P < 0.001$) of 2,4-D sorption when applied to the A and C horizons, respectively.

Table 2.4 Regression models predicting 2,4-D sorption by depth and landscape position

Horizon	Regression Equation	R^2	P
A horizon			
All slopes	$Kd = 5.93 + 2.45SOC - 0.15CaCO_3 - 0.139Clay - 0.66pH$	0.85	0.048
U	$Kd = -2.332 + 4.57SOC$	0.87	0.001
M	$Kd = 0.49 + 2.02SOC - 0.11CaCO_3$	0.77	0.01
L	$Kd = -1.71 + 3.22SOC - 0.43CaCO_3$	0.83	0.01
D	--		
B horizon			
All slopes	$Kd = 0.221 + 1.787SOC - 0.046CaCO_3$	0.25	0.001
U	--		
M	$Kd = 7.63 + 2.86SOC - 1.09pH - 0.03CaCO_3$	0.74	0.03
L	--		
D	$Kd = -0.27 + 1.01SOC$	0.93	0.05
C Horizon			
All slopes	$Kd = 0.102 + 1.137SOC - 0.004CaCO_3 - 0.008Clay$	0.75	0.05
U	--		
M	$Kd = 0.06 + 1.15SOC - 0.01CaCO_3$	0.84	0.001
L	$Kd = -0.01 + 1.04SOC$	0.51	0.05
D	--		

-- denotes no significant regression at $P \leq 0.05$

When segmented by slope position, the best regression models generally contained the single variable of SOC or again a combination of the variables SOC and carbonate content. Segmentation of samples by slope position greatly improved the predictive power of herbicide sorption in the B horizon, as 74% and 93% of 2,4-D sorption was accounted for by soil properties in the M and D slope positions, respectively. However, no significant regression models existed for predicting 2,4-D sorption in the B horizon of

the U or L slope positions. Regression models were also insignificant for A horizon D, as well as for C horizon U and D.

2.5 Discussion

A change of a factor of two in herbicide sorption input parameters for modeling could result in a ten times difference in herbicide leaching potential within a soil (Boesten and van der Linden, 1991). Such a difference in herbicide sorption occurred in this study with soil depth, and among slope positions within the A horizon. This means that in order to accurately predict the risk of pesticide off-site movement, spatial variability should be taken into consideration when applying pesticide fate and leaching models to hummocky soil-landscapes.

SOC was the single best predictor of a soil's capacity to sorb 2,4-D, regardless of soil depth or slope position. This is in agreement with the findings of previous studies in which SOC was the primary factor influencing 2,4-D sorption in surface soil, both in field and laboratory experiments (Hermosin and Cornejo, 1991; Mallawatantri and Mulla, 1992; Johnson et al., 1995; Farenhorst et al., 2003). The A horizon had significantly greater capacity to sorb the herbicide relative to the B and C horizons, largely as a result of higher SOC. Although SOC had the greatest overall influence on 2,4-D sorption in the B horizon, very little of the sorption could be accounted for by this property or any of the other soil properties. The presence of iron oxides are known to increase 2,4-D sorption in soil (Reddy and Gambrell, 1987; Celis et al., 1999), and were visually observed as rust

flecks in B horizon soil samples, but not quantitatively measured. It is generally accepted that as SOC decreases with soil depth, other soil properties play an increasingly important role in 2,4-D sorption (Reddy and Gambrell, 1987; Green and Karickhoff, 1990; Wauchope et al., 2002). However, despite the fact that sorption in the C horizon was lower due to decreased SOC, soil organic matter still accounted for the majority of 2,4-D sorption ($Kd = -0.031 + 0.985SOC$; $R^2 = 0.60$).

The association between soil carbonates and herbicide sorption by soil has not been previously demonstrated. In this study, carbonate content was found to be the second most significant soil property, negatively affecting the sorption of 2,4-D. Such findings are likely to be significant only in calcareous soils, such as the soil used in this experiment. However, the implication of these finding are widespread because 30% of the world's soil is calcareous (Strom et al., 2001). Studies on the effect of soil carbonates on the sorption of anionic heavy metals and plant nutrients concluded that sorption occurred between carbonate minerals and anions (Wullstein, 1969; Goldberg and Glaubig, 1988; Tunesi et al., 1999). In contrast, we found that the sorption of 2,4-D anions was impeded by the presence of carbonates. There was a negative relation between carbonates and *Koc* in the A and C horizons and it is possible that soil carbonates interacted with soil organic matter, causing 2,4-D sorption per unit organic carbon to decrease. The possible association between the sorption of 2,4-D by organic carbon and soil carbonates warrants further study.

It is also possible that the association between carbonates and herbicide sorption was an indirect effect induced by changes in soil pH. However, the direct effect of soil pH on 2,4-D sorption was limited despite the fact that pH was positively correlated with carbonate content. The dissociation constant (pKa) for 2,4-D is 2.64 (Ahrens, 1994). Since the range in soil pH was neutral to slightly alkaline and well above the pKa of 2,4-D, there was no significant correlation between soil pH and 2,4-D sorption by soil.

Clay content had the least affect on 2,4-D sorption, and was a significant soil property only in the regression model of the A horizon. The soils used in this study were neutral to slightly alkaline in reaction, thus 2,4-D would be present mostly in anionic form and repelled by the negatively charged clay minerals. Sorption reactions between negatively charged clay and 2,4-D are theoretically possible via metal-ion bridges, but did not occur in this case because 2,4-D sorption decreased with increasing clay content in the A horizon. Although some clay minerals enhance the sorption of 2,4-D by soil (Hermosin and Cornejo, 1991), montmorillonite clay, the dominant clay mineral present in Manitoba soils (Madden, 1974), had no effect or a negative effect on 2,4-D sorption in several other studies (Hermosin and Cornejo, 1993; Sannino et al., 1997).

2.6 Conclusions

This study demonstrated that 2,4-D sorption varies significantly with soil depth and landscape position, largely due to similar variability in SOC. The retention of herbicides in the soil profile was particularly low in A, B and C horizons of eroded knolls, and also

within the B and C horizons across other slope positions in the field. Pesticide fate and leaching models utilized at the field scale should recognize this soil-landscape variability as segmentation of soils by landscape position and depth could improve the prediction of 2,4-D fate. In addition, models applicable to pesticide fate and leaching processes in calcareous soils may need to consider soil carbonates as a parameter because this study found a negative association between soil carbonates and 2,4-D sorption. This is a new finding and further studies are required because the exact effect of carbonates on herbicide sorption is not known.

2.7 References

Ahrens, W.H. (Ed.). 1994. Herbicide Handbook. 7th ed. Weed Science Society of America, Champaign, Illinois. 352 pp.

Boesten, J.J.T.I. and van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual., **20:** 425–435.

Calvet, R. 1989. Adsorption of organic chemicals in soils. Environ. Health Persp., **83:** 145–177.

Celis, R., Hermosin, M.C., Cox, L. and Cornejo, J. 1999. Sorption of 2,4-Dichlorophenoxyacetic acid by model particles simulating naturally occurring soil colloids. Environ. Sci. Technol., **33:** 1200–1206.

Cessna, A.J. and Elliot, J.A. 2004. Seasonal variation of herbicide concentrations in prairie farm dugouts. J. Environ. Qual., **33:** 302–315.

Clayton, J.S., Ehrlich, W.A., Cann, D.B., Day, J.H. and Marshall, I.B. 1977. Soils of Canada. Vol. 1. Soil Rep. Res. Branch, Canada Department of Agric., Ottawa, ON. 243 pp.

Cox, C. 1999. 2,4-D: Exposure. J. Pestic. Reform, **19:** 14–19.

de Jonge, H., de Jonge, L.W. and Jacobsen, O.H. 2000. ^{14}C-Glyphosate transport in undisturbed topsoil columns. Pest Manag. Sci., **56:** 909–915.

Farenhorst, A., Florinski, I., Monreal C. and Muc, D. 2003. Evaluating the use of digital terrain modelling for quantifying the spatial variability of 2,4-D sorption within agricultural landscapes. C. J. Soil Sci., **83:** 557–564.

Gee G.W. and Bauder J.W. 1986. Particle-size analysis. *In* Klute, A. (Ed), Methods of soil analysis. Part 1. Physical and Mineralogical Methods. ASA/SSSA, Madison, WI. pp. 383–412.

Gerstl, Z. 2000. An update on the Koc concept in regard to regional scale management. Crop Prot., **19:** 643–648.

Goderya, F.S. 1998. Field scale variations in soil properties for spatially variable control: A review. J. Soil Contam., **7:** 243–264.

Goldberg, S. and Glaubig, R.A. 1988. Anion sorption on a calcareous, montmorillonic soil: Arsenic. Soil Sci. Soc. Am. J., **52:** 1297–1300.

Goodrich, J.A., Lykins, B.W. and Clark, R.M. 1991. Drinking water from agriculturally contaminated groundwater. J. Environ. Qual., **20:** 707–717.

Green, R.E. and Karickhoff, S.W. 1990. Sorption estimates for modeling. *In* Cheng, H.H. (Ed.), Pesticides in the Soil Environment: Processes, Impacts and Modeling. SSSA, Madison, WI. pp. 93–100.

Gregorich, E. and Anderson, D. 1985. Effects of cultivation and erosion on soils of four toposequences in the Canadian prairies. Geoderma, **36:** 343–354.

Gupta, S. and Gajbhiye, V.T. 2002. Adsorption-desorption, persistence, and leaching behaviour of dithiopyr in an alluvial soil of India. J. Environ. Sci. Health Part B, **B37:** 573–586.

Hallberg, G.R. 1989. Pesticide pollution of groundwater in the humid United States. Agric. Ecosyt. Environ., **26:** 299–367.

Hermosin, M.C. and Cornejo, J. 1991. Soil adsorption of 2,4-D as affected by the clay mineralogy. Toxicol. Environ. Chem., **31/32:** 69–77.

Hermosin, M.C. and Cornejo, J. 1993. Binding mechanism of 2,4-Dichlorophenoxyacetic acid by organo-clays. J. Environ. Qual., **22:** 325–331.

Hill, B., Harker, K., Hasselback, P., Moyer, J., Inaba, D. and Byers, S. 2001. Phenoxy herbicides in Alberta rainfall as affected by location, season, and weather patterns. Final Technical Report No. 990059. AAFC Lethbridge Research Centre, Lethbridge, AB. 109 pp.

Jacobsen, C.S., Shapir, N., Jensen, L.O., Jensen, E.H., Juhler, R.K., Streibig, J.C., Mandelbaum, R.T. and Helweg, A. 2001. Bioavailability of triazine herbicides in a sandy soil profile. Biol. Fertil. Soils, **33:** 501–506.

Johnson, W.G, Lavy, T.L. and Gbur, E.E. 1995. Sorption, mobility, and degradation of triclopyr and 2,4-D in four soils. Weed Sci., **43:** 678–684.

Jury, W., Focht, D. and Farmer, W. 1987. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. J. Environ. Qual., **16:** 422–428.

Khakural, B.R., Robert, P.C. and Koskinen, W.C. 1994. Runoff and leaching of alachlor under conventional and soil-specific management. Soil Use Manage., **10:** 158–164.

Kolpin, D.W., Goolsby, D.A. and Thurman, E.M. 1995. Pesticides in near-surface aquifers: an assessment using highly sensitive analytical methods and tritium. J. Environ. Qual., **24:** 1125–1132.

Lobb, D.A., Lindstrom, M.J. and Schumacher, T.E. 2003. Soil erosion processes and their interactions: Implications for environmental indicators. Proc. OECD Expert Meeting on Soil Erosion and Soil Biodiversity Indicators, Rome, Italy.

Loeppert, R.H. and Suarez, D.L. 1996. Carbonate and Gypsum. *In* Bartels, J.M. (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods. ASA/SSSA, Madison, WI. pp. 437–475.

Ma, Q.L., Holland, P.T., James, T.K., McNaughton, D.E. and Rahman, A. 2000. Persistence and leaching of the herbicides acetochlor and terbuthylazine in an allophonic soil: comparisons of field results with PRZM-3 predictions. Pest Manag. Sci., **56:** 159–167.

MacMillan, R.A. and Pettepiece, W.W. 2000. Alberta landforms: Quantitative morphometric descriptions and classification of typical Alberta landforms. Technical Bulletin No. 200-2E. Research Branch, AAFC, Semiarid Prairie Agricultural Research Centre, Swift Current, SK. 118 pp.

Madden, J. 1974. Clay mineralogy and heavy metals in soils and geological sediments of Manitoba. Proc. 18th Annual Manitoba Soil Science Society, Winnipeg, MB.

Mallawatantri, A.P. and Mulla, D.J. 1992. Herbicide adsorption and organic carbon contents on adjacent low-input versus conventional farms. J. Environ. Qual., **21:** 546–551.

McKeague, J.A. (Ed.) 1978. Manual on soil sampling and methods of analysis. Canadian Society of Soil Science, Ottawa, Canada. 212 pp.

Nelson, D.E. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. *In* Page, A.L. (Ed.), Methods of Soil Analysis. Part2. Chemical and microbiological properties. ASA/SSSA, Madison, WI. pp. 539–577.

Novak, J.M., Moorman, T.B. and Cambardella, C.A. 1997. Atrazine at the field scale in to soils and landscape position. J. Environ. Qual., **26:** 1271–1277.

Oliveira Jr., R.S., Koskinen, W.C. and Ferreira, F.A. 2001. Sorption and leaching potential of herbicides on Brazilian soils. Weed Res., **41:** 97–110.

Rawn, D., Halldorson, T., Lawson, B. and Muir, D. 1999. A multi-year study of four herbicides in surface water of a small prairie watershed. J. Environ. Qual., **28:** 906–917.

Reddy, K. and Gambrell, R. 1987. Factors affecting the adsorption of 2,4-D and methyl Parathion in soils and sediments. Agric. Ecosyt. Environ., **18:** 231–241.

Sannino, F., Violante, A. and Gianfreda, L. 1997. Adsorption-desorption of 2,4-D by hydroxy aluminium montmorillonite complexes. Pestic. Sci., **51:** 429–435.

SAS Institute Inc. 2000. SAS system for Windows. Version 8.01. SAS Institute Inc., Cary, NC.

Senesi, N. 1992. Binding mechanisms of pesticides to soil humic substances. Sci. Total Environ., **123/124:** 63–76.

Simard, M.J. and Legere, A. 2002. Control of volunteer canola with auxinic herbicides: Does cold hardening or plant size matter? Proc. Canadian Weed Sci. Society National Meeting, Saskatoon, SK.

Soil Classification Working Group. 1998. The Canadian System of Soil Classification. Agric. and Agri-Food Can. Publ. 1646 (Revised). 187 pp.

Strebe, T.A. and Talbert, R.E. 2001. Sorption and mobility of flumetsulam in several soils. Weed Sci., **49:** 806–813.

Strom, L., Owen, A.G., Godbold, D.L. and Jones, D.L. 2001. Organic acid behaviour in a calcareous soil: sorption reaction and biodegradation rates. Soil Biol. Biochem., **33:** 2125–2133.

Tu, M., Hurd, C. and Randall, J.M. 2001. Weed Control Methods Handbook: Tools and Techniques for use in natural areas. [Online] Available: The Nature Conservancy, http://tncweeds.ucdavis.edu. [April 2001].

Tunesi, S., Poggi, V. and Gessa, C. 1999. Phosphate adsorption and precipitation in calcareous soils: the role of calcium ions in solution and carbonate minerals. Nutr. Cycl. Agroecosyst., **53:** 219–227.

Wagenet, R.J. and Rao, P.S.C. 1990. Modeling pesticide fate in soils. *In* Cheng, H.H. (Ed.), Pesticides in the Soil Environment: Processes, Impacts and Modeling. SSSA, Madison, WI. pp. 351–399

Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Gerstl, Z., Lane, M. and Unsworth, J.B. 2002. Review: Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pestic. Manage. Sci., **58:** 419–445.

Wullstein, L.H. 1969. Reduction of nitrate deficits by alkaline metal carbonates. Soil Sci., **108:** 222–226.

3. 2,4-D DEGRADATION IN SOIL PROFILES OF A CULTIVATED HUMMOCKY LANDSCAPE IN MANITOBA, CANADA

3.1 Abstract

The objective of this study was to quantify 2,4-D degradation in soil profiles characteristic of hummocky, calcareous soil-landscapes in western Canada. Twenty-five soil cores were collected along a 360 m transect running west to east in an agricultural field and then segmented by soil-landscape position (upper slopes, mid slopes, lower slopes and depressions) and soil horizon (A, B, and C horizons). In the A horizon, 2,4-D degradation commenced instantaneously and the degradation rate followed first-order kinetics. In both the B and C horizons, 2,4-D degradation only commenced after a lag period of typically 5 to 7 days and the degradation rate was biphasic. In the A horizon, 2,4-D degradation parameters included the first-order degradation rate constant (k_1), the growth-linked degradation rate constant (k_2) and total 2,4-D degradation at the end of the experiment at 56 days (M_{Texp}). These were most strongly correlated to parameters describing 2,4-D sorption by soil, but were also correlated to soil organic carbon content, soil pH, and soil carbonate content. In both B and C horizons, there was no significant correlation between 2,4-D degradation and 2,4-D sorption parameters, and correlations between soil properties and 2,4-D degradation parameters were very poor. The k_1 significantly decreased in sequence of A horizon (0.113% day^{-1}) > B horizon (0.024% day^{-1}) = C horizon (0.026% day^{-1}) and in each soil horizon was greater than k_2. Total 2,4-D degradation also significantly decreased in sequence of A horizon (42%) > B horizon (31%) = C horizon (27%). In the A horizon, slope position had little influence on k_1 or k_2

, except that k_1 was significantly greater in upper slopes (0.170% day^{-1}) than in lower slopes (0.080% day^{-1}). Neither k_1 nor k_2 was significantly influenced by slope position in the B or C horizons. Total 2,4-D degradation was not influenced by slope position in any horizon. Our results suggest that, when predicting 2,4-D transport at the field scale, pesticide fate models should consider the strong differences in 2,4-D degradation between surface and subsurface horizons. This suggests that 2,4-D degradation is best predicted using a model that has the ability to describe a range of non-linear degradation curves. We also conclude that the horizontal variations in 2,4-D degradation at the field scale will be difficult to consider in predictions of 2,4-D transport at the field scale because, within each horizon, 2,4-D degradation was highly variable across the twenty-five soil cores, and this variability was poorly correlated to soil properties or soil-landscape position.

3.2 Introduction

Agricultural use of pesticides has resulted in improved crop quality and quantity, but has also resulted in non-point source pollution. Pesticide fate models have been developed to assess the risk of pesticide transport from agricultural fields into the broader environment. One of the most important input parameters in pesticide fate models are data on pesticide degradation, such as degradation rates or half-lives (Boesten and van der Linden, 1991).

Degradation of pesticides occurs predominantly by the action of soil microorganisms (Bollag and Liu, 1990; Topp et al., 1997), and may be limited by pesticide sorption which controls pesticide concentrations available to microorganisms for breakdown (Shelton et al., 1998; Guo et al., 2000). Therefore, pesticide persistence could be affected by soil properties that affect soil microbial populations and pesticide sorption, such as soil organic carbon content, pH and soil texture (Senesi, 1992; Wardle, 1992; Hermosin and Cornejo, 1993).

Soil properties vary among landscape positions and with soil depth as a result of soil forming factors (Goderya, 1998) and land management practices (Gregorich and Anderson, 1985; Lindstrom et al., 1990; Lobb et al., 2003). The heterogeneous nature of soil properties among landscape positions and with soil depth consequently affects the distribution of soil biological properties and pesticide sorption. It is well established that microbial biomass and activity decrease with increasing soil depth (Tessier, et al., 1998; Vinther et al., 2001) which is largely due to decreased soil organic carbon content. Studies have also shown that microbial biomass and activity varies across landscape positions within a field (Bergstrom et al., 1998; Florinski et al., 2004). Similarly, pesticide sorption by soil decreases with soil depth and increases in the Ap horizon from upper to lower slope positions in response to changes in soil organic carbon contents, soil pH and clay content (Novak et al., 1997; Gaultier et al., 2006).

Previous studies quantified the effects of soil depth on pesticide degradation, not for pedological soil horizons, but for incremental depths that were subjectively chosen

(Willems et al., 1996; Veeh et al., 1996; Shaw and Burns, 1998). Similarly, studies have determined the spatial variability of pesticide degradation in fields (Parkin and Shelton, 1992; Walker et al., 2001; Müller et al., 2003; Rasmussen et al, 2005), but have not looked at differences in degradation by segmenting soil-landscape positions. Previous research has demonstrated that segmentation by landscape positions could be a useful tool when assessing pesticide sorption parameters at the field scale (Chapter 2), but this concept has not been explored for pesticide degradation parameters. Finally, with the exception of Charnay et al. (2005) who examined the degradation of the pesticides atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine], isoproturon [3-(4-isopropylphenyl)-1,1-dimethylurea], and metamitron [4-amino-3-methyl-6-phenyl-l,2,4-triazin-5(4H)-one] in surface and subsurface soils across a large catchment, two-dimensional variations of pesticide degradation in agricultural fields has not been studied.

The purpose of this study was to relate soil properties, 2,4-D (2,4-dichlorophenoxyacetic acid) sorption and 2,4-D degradation in soil profiles of upper slope, mid slope, lower slope and depressions in a cultivated hummocky, calcareous terrain in Manitoba, Canada. The herbicide 2,4-D was selected for this work because it is among the five most used pesticides in Manitoba and, although 2,4-D has relatively low persistence in soil, it has the potential to be transported from the site of application and enter surface and ground waters (Kolpin et al., 1995; Grover et al., 1997; Rawn et al., 1999; Waite et al., 2002).

3.3 Materials and Methods

3.3.1 Chemicals and analytical techniques

Analytical grade 2,4-D (95% chemical purity) and [carboxyl-^{14}C] labelled 2,4-D (99% radiochemical purity; specific activity 632.7 MBq mmol^{-1}) were purchased from Sigma Aldrich Chemical Company (St. Louis, MO.). Sodium hydroxide pellets (98.5% chemical purity) were purchased from Fisher Scientific (Fairlawn, NJ.). The amounts of radioactivity in herbicide solutions and samples from experiments were determined by Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (LS 7500 Beckman Instruments, Fullerton, CA.). Radioactivity was measured using 8 mL of 30% Scintisafe scintillation cocktail (Fisher Scientific, Fairlawn, NJ.) and a maximum counting time of 10 minutes.

3.3.2 Site characteristics

The field site was located northwest of Miami, Manitoba (6-5-7 1W). Conventional agricultural management at the field site included annual cultivation by deep tilling, disking and harrowing over the past 100 years. In the last 40 years there has been a two year cereal-oilseed crop rotation and the use of pesticides, including 2,4-D. The soil-landscape is hummocky (Soil Classification Working Group, 1998), characteristic of a broad region of glacial till landscapes in western Canada (Clayton et al., 1977). Soils from upper and mid slope positions were of the Dezwood loam series (Orthic Dark Grey Chernozem; Ap, Btj, Ck horizons), soils from lower slope positions were of the Zaplin soil series (Gleyed Dark Grey Chernozem; Ap, Btgj, Ckgj horizons) and soils from

depression positions were of the Pouchal soil series (Humic Luvic Gleysol; Ap, Btg, Ckg horizons).

The entire field was surveyed using a Trimble AgGPS 214 (Trimble Navigation LTD., Sunnyvale, CA) global positioning system (GPS) as part of a larger study. Spacing of GPS measurements were 5 m in hummocky portions of the field and 10 m in more level portions of the field. The Trimble AgGPS 214 is accurate to 1 cm. The LandMapR software program (MacMillan and Pettepiece, 2000) was used to classify the soil-landscape according to 4 slope positions, upper slope (U), mid slope (M), lower slope (L), or depression (D) (Figure 2.1). Based on this classification, the 35 ha field consisted of approximately 15% U, 55% M, 15% L and 15% D.

3.3.3 Soil sampling and characterization

A 360 m long transect was positioned along a catena running west to east in the field. Seventy-two soil cores (8 cm inner diameter, 50 to 125 cm length) were collected at 5 m intervals along the transect. Sampling points were referenced using a Total Station system (Sokkia set 4110; Sokkia Co. LTD., Japan) and GPS reference points. The Total Station is accurate to 1 mm.

Twenty-five of the 72 soil cores (approximately every third sample; maximum 15 m spacing) were used for this study. These soil cores were obtained from areas classified as U (n = 3 soil cores), M (n = 13 soil cores), L (n = 6 soil cores), and D (n = 3 soil cores). Each soil core was divided by A, B, and C horizons.

A portion of thoroughly-mixed soil from each horizon was passed through a mesh sieve (<2 mm) and frozen at -22 °C ± 2 °C to be used for herbicide degradation experiments as explained below. The remaining soil was air-dried and sieved (<2 mm) prior to soil properties and herbicide sorption analyses. Determinations of soil properties were as described in Chapter 2.

Sorption of 2,4-D by soil was quantified in duplicate using the batch equilibrium method. A complete description of the 2,4-D sorption experiment is given in chapter 2. An initial herbicide solution containing 1 μg mL^{-1} 2,4-D and 16.7 Bq mL^{-1} [ring-U-^{14}C] 2,4-D was added (10 mL) to 5 g soil in Teflon tubes. After equilibrium conditions were reached (24 h), samples were centrifuged and the amount of ^{14}C-2,4-D remaining in solution was measured by LSC. The amount of 2,4-D sorbed by soil was determined by the difference between the initial and equilibrium herbicide concentrations. Sorption of 2,4-D was calculated by the sorption coefficient, *Kd* and the soil organic carbon sorption coefficient, *Koc* (Equations 2.1 and 2.2). Higher relative values of *Kd* and *Koc* are indicative of greater sorption of 2,4-D by soil and per unit organic carbon content, respectively.

A microcosm incubation study was used to quantify 2,4-D degradation in soil. Triplicate 25 g (dry weight basis) samples of soil were measured into 125 mL glass jars and placed in sealed 1 L mason jars. Soils were brought up to 90 percent of their field capacity and incubated at 20 °C for 14 days, allowing microbial activity to resume after being frozen in storage. Field capacity was estimated using a container method, in which duplicate

containers (15 cm height, 5 cm diameter) of sieved (< 2 mm), air-dried soil were wetted with distilled water and covered with parafilm to reduce water loss by evaporation. A subsample of wet soil (approximately 5 g) was removed from each container after 48 hours (Brady and Weil, 1999) and weighed. Samples were weighed again after being oven-dried at 105 °C for 24 hours. Field capacity was determined as the difference in mass between the wet and oven-dried soil. In addition, microcosms containing 25 g of silica sand were set up in triplicate to assess amounts of abiotic degradation of 2,4-D. Glass tubes containing 3 mL of acidified water (pH ~ 3) were included in each mason jar to maintain humidity. The water was acidified to limit reactions with carbon dioxide. After 14 days, a 2,4-D solution (0.5 mL) was applied and thoroughly mixed into soil or silica sand. The 2,4-D solution contained 18.1 μg mL^{-1} 2,4-D and 16.7 kBq mL^{-1} [carboxyl-^{14}C] 2,4-D in deionised water. This rate corresponds to agronomic application rates assuming distribution of the herbicides to 10 cm depth. Scintillation vials containing 5 mL 0.5 M sodium hydroxide were placed in each microcosm to trap evolved $^{14}CO_2$ as the herbicide was mineralized. Sodium hydroxide traps were replaced at 2, 4, 7, 11, 14, 17, 21, 28, 42, and 56 days post 2,4-D application. Scintillation cocktail (8 mL) was added directly to sodium hydroxide traps and amounts of $^{14}CO_2$ in samples determined by LSC. Sample measurements were adjusted to account for background levels of $^{14}CO_2$ as measured in black microcosms (no 2,4-D added).

Degradation of 2,4-D was calculated as amounts of $^{14}CO_2$ evolved as a percent of initially applied ^{14}C-2,4-D. Cumulative degradation curves were plotted as the percent $^{14}CO_2$ evolved as a function of time. Using a user-defined curve fitter function in SigmaPlot

2000 (Systat Software Inc., 2000), a modified version of Brunner and Focht's (1984) three-half order kinetics model was fit to each degradation curve. This modified version excluded the rates of humus degradation:

$$M_T = M_O(1 - e^{-k_1 t - (k_2 t^2)/2}) \qquad [3.1]$$

where M_T = 2,4-D degradation [%] at time t, M_O = 2,4-D degradation [%] when t approached infinity , k_1 = first-order degradation rate [day^{-1}], k_2 = growth linked degradation rate [day^{-2}] and t = time [days]. The three-half order kinetic model was selected because of its ability to derive meaningful degradation rate constants for a range of non-linear degradation curves, including positive sigmoidal degradation curves (i.e. presence of a lag phase) that are often observed for the disappearance of 2,4-D in soil (Soulas, 1993; Veeh et al., 1996; Shaw and Burns, 1998). In addition to k_1, the three-half order model includes k_2 to account for linear microbial growth over time. If degradation is dependent solely on substrate concentration and not on changes in microbial biomass, then k_2 is zero, and the model simplifies to the first-order degradation kinetic model.

3.3.4 Statistical analyses

All parameters, with the exception of soil pH and degradation rate k_2, were log transformed to achieve normality. Statistical analyses were performed in SAS, version 8.01 (SAS Institute, Inc., 2000) using the following variables: SOC, carbonate content, soil pH, clay content, *Kd*, *Koc*, k_1, k_2, and total 2,4-D degradation (M_{Texp}) at 56 days. Pearson's pairwise correlation analysis was used to measure relations among these variables. Utilizing all 25 soil samples, variables were subjected to a one-way analysis of variances (ANOVA) followed by the Tukey's highly significant difference (HSD) test (*P*

< 0.05) to delineate significant differences in the means of variables across soil depth. Within each horizon, ANOVA and the Tukey's HDS test were also used to delineate significant differences in the means of variables across slope positions. In reporting the significant differences in the means of variables with depth or across slope position, the coefficient of variation (CV) is included as opposed to the more traditional standard deviation. The CV was used because it better allows assessments of the variation in populations depite their significantly different mean values.

3.4 Results and Discussion

SOC decreased significantly from 1.97% in the A horizon to 0.55% in the B horizon and 0.38% in the C horizon (Table 3.1). Soil pH and carbonate content increased significantly with increasing soil depth (Table 3.1), reflecting the calcareous nature of the parent material. Clay content was significantly higher in the B horizon than in the A horizon (Table 3.1), as expected based on the soil profiles at the site (Btj, Btgj and Btg horizons). In all three horizons, 2,4-D sorption by soil was more strongly correlated with SOC than with other soil properties (Table 3.2). Thus, sorption of 2,4-D by soil decreased significantly with increasing soil depth (Table 3.1) in response to decreasing SOC. Sorption of 2,4-D by organic carbon also decreased significantly with increasing soil depth (Table 3.1), suggesting that there were differences in the quality of organic matter among the A, B and C horizons. Sorption of 2,4-D in soil is poorly correlated with pyrophosphate-extractable humic substances but well correlated with alkaline-extracted humic substances (Farenhorst, 2006). Pyrophosphate-extractable humic

substances contain more aromatic C and less aliphatic C than alkaline-extracted humic substances (Piccolo et al., 1998; Pinheiro-Dicket al., 1999). Soil organic matter becomes more aromatic and less aliphatic with increasing soil depth (Xing and Chen, 1999; Chen and Pawluk, 1995; Ding et al., 2002).

Degradation of 2,4-D in the A horizon was immediate and followed first-order degradation kinetics because k_2 values were zero or extremely small (Table 3.1). The lack of a lag phase preceding 2,4-D degradation in the A horizon indicated that degradation was dependent on 2,4-D concentration and not delayed by microbial growth. Degradation independent of microbial growth suggests that 2,4-D was degraded co-metabolically (Fournier et al., 1981). Co-metabolism of pesticides in soil is a process that follows first-order kinetics (Topp et al., 1997). Fournier (1980) found that microorganisms able to co-metabolize 2,4-D were abundant in topsoil and accounted for 1 percent of total soil microorganisms.

The immediate degradation of 2,4-D in the Ap horizon may have resulted from the adaptation of soil microbial populations to 2,4-D as a substrate because topsoils at the study site had received 2,4-D applications over the past 40 years. Studies have shown that repeat applications of 2,4-D lead to enhanced degradation of subsequent applications and elimination of the lag phase because of the increased populations of soil microorganisms able to metabolize 2,4-D (Fournier et al., 1981; Robertson and Alexander, 1994; Shaw and Burns, 1998). Smith and Aubin (1991) demonstrated that the effects of enhanced degradation may be long lived, occurring even after 48 weeks of a previous 2,4-D application.

Table 3.1 Means and variability of soil properties, 2,4-D sorption coefficients and 2,4-D degradation parameters measured on 25 soil cores collected from A, B and C horizons

Horizon	Soil properties and 2,4-D sorption coefficients						2,4-D mineralization parameters		
	SOC (g 100 g^{-1} soil)	pH	Carbonate content (g 100 g^{-1} soil)	Clay content (g 100 g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})	M_{Texp} ($^{14}CO_2$ evolved as % of initial)	k_1 (day^{-1})	k_2 (day^{-2})
A	1.97 ± 47[a]	7.01 ± 6[b]	2.06 ± 155[a]	19.74 ± 30[b]	4.27 ± 58[a]	210 ± 25[a]	41.53 ± 4[a]	0.113 ± 48[a]	0.000 ± 76[b]
B	0.55 ± 52[b]	7.25 ± 5[a]	8.08 ± 116[a]	24.77 ± 26[a]	0.66 ± 71[b]	123 ± 39[b]	30.78 ± 37[b]	0.024 ± 86[b]	0.005 ± 154[a]
C	0.38 ± 35[b]	7.48 ± 2[a]	22.97 ± 46[b]	21.08 ± 36[ab]	0.33 ± 52[c]	86 ± 30[c]	26.46 ± 50[b]	0.026 ± 66[b]	0.004 ± 155[a]

Mean ± CV (%)

[a-c] Column means for horizons followed by same letters are not significantly different at $P < 0.05$ (Tukey's HSD)

Table 3.2 Pearson's pairwise correlations among soil properties, 2,4-D sorption coefficients and 2,4-D degradation parameters in A, B and C horizons of 25 soil cores[†]

	M_{Texp}	k_1	k_2	*Kd*	*Koc*	SOC	pH	$CaCO_3$	clay
A horizon									
M_{Texp}	1.00								
k_1	0.46*	1.00							
k_2	--	0.73***	1.00						
Kd	--	-0.44*	-0.41*	1.00					
Koc	--	--	--	0.67**	1.00				
SOC	--	-0.53**	-0.57**	0.93***	0.31*	1.00			
pH	--	-0.48*	-0.54**	0.27*	--	0.53***	1.00		
$CaCO_3$	--	-0.45*	-0.49*	--	--	--	0.70***	1.00	
clay	--	--	--	--	-0.26*	--	--	--	1.00
B horizon									
M_{Texp}	1.00								
k_1	--	1.00							
k_2	--	--	1.00						
Kd	--	--	--	1.00					
Koc	--	--	--	0.57**	1.00				
SOC	-0.54**	--	--	0.72***	--	1.00			
pH	--	--	--	--	--	0.56**	1.00		
$CaCO_3$	-0.52*	--	--	--	-0.50*	0.63**	0.58**	1.00	
clay	--	--	--	--	-0.61**	--	--	--	1.00
C horizon									
M_{Texp}	1.00								
k_1	--	1.00							
k_2	-0.53**	--	1.00						
Kd	--	--	--	1.00					
Koc	--	--	--	0.69***	1.00				
SOC	--	-0.50*	--	0.79***	--	1.00			
pH	-0.55**	--	--	--	-0.46*	--	1.00		
$CaCO_3$	--	--	--	--	-0.45*	--	0.81***	1.00	
clay	--	--	--	--	--	0.51*	--	--	1.00

*,**, and *** denote $P < 0.05$, $P < 0.01$, and $P < 0.001$, respectively, for correlations Ho: r = 0; Ha: r ≠ 0
-- denotes no significant correlation
[†] See Appendix B for graphical representation of significant correlations between soil properties, 2,4-D sorption and 2,4-D degradation parameters

In the B and C horizons, a phase of rapid 2,4-D degradation began after a lag phase of approximately 5 to 7 days (Figure 3.1). The 2,4-D degradation curves were generally sigmoidal in both horizons, but exponential (first-order) and linear (zero-order) degradation curves were also observed. Deviations from sigmoidal degradation curves occurred within sample replicates, usually due to a single replicate exhibiting a different pattern of 2,4-D degradation relative to the other two replicates. Inconsistent patterns of

2,4-D degradation in subsoil replicates was also reported by Shaw and Burns (1998) and was attributed to small, non-uniform microbial populations in subsoil samples. Shaw and Burns (1998) considered the lag phase in subsurface soils as the time required for small microbial populations to become sufficiently large to degrade 2,4-D by either metabolism or co-metabolism. In contrast, the presence of a lag phase in topsoils is only associated with direct metabolism of 2,4-D by soil microorganisms, and is viewed as the time required for small populations of specific degraders to become active at significant levels (Topp et al., 1997).

The first-order degradation rate, k_1, decreased significantly from the A horizon (0.113% day^{-1}) to the B horizon (0.024% day^{-1}) = C horizons (0.026% day^{-1}) (Table 3.1), and was likely due to decreased soil microbial populations with increased soil depth (Lavy et al., 1973). In contrast, degradation rates dependent on microbial growth, k_2, were extremely small in the A horizon and increased significantly in the B and C horizons, suggesting small microbial population in the B and C horizons were responding to additions of 2,4-D as substrate. Although very small, k_2 was strongly related with k_1 in the A horizon and both degradation rate constants were negatively correlated with SOC and 2,4-D sorption by soil (Table 3.2). Sorption of 2,4-D by soil organic matter therefore reduced the bioavailability of 2,4-D to microorganisms and increased 2,4-D persistence.

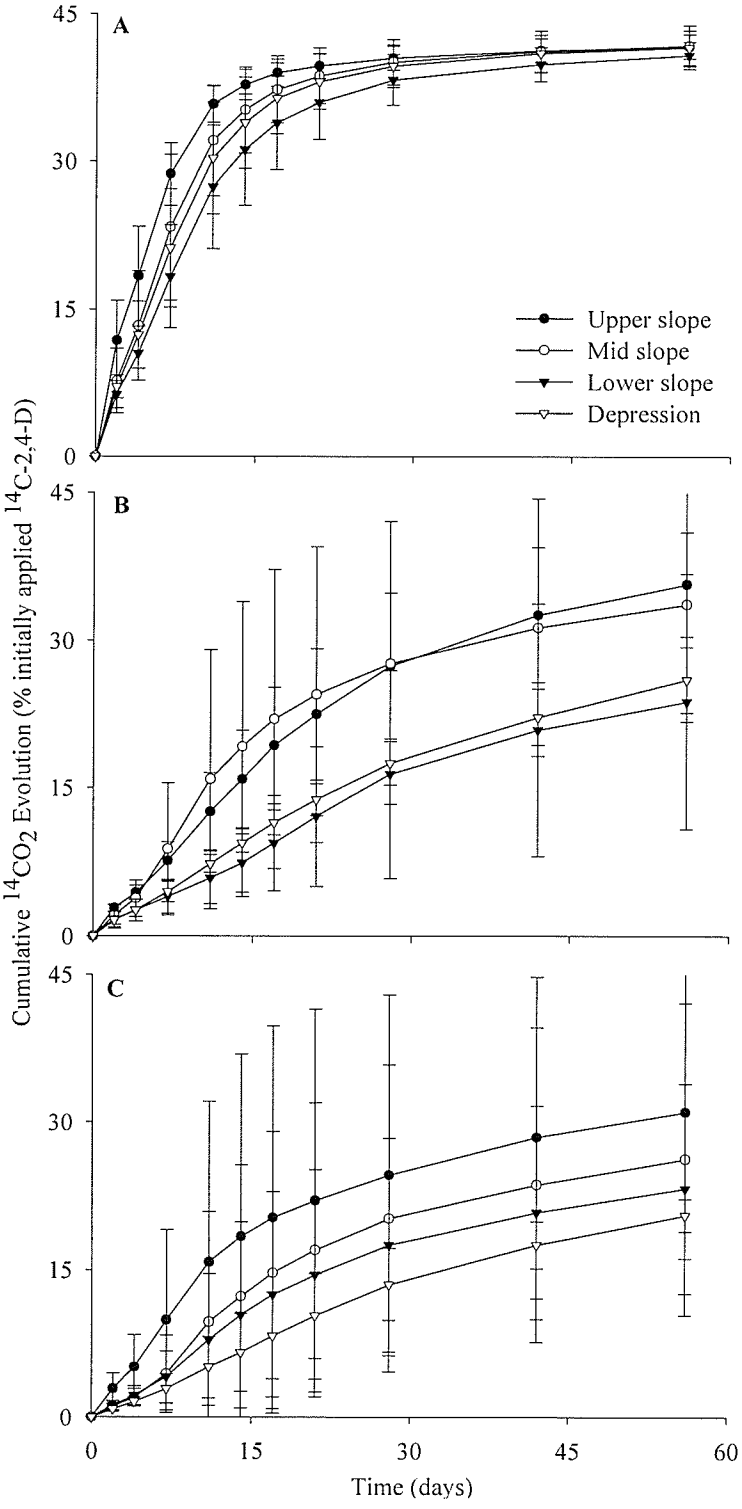


Figure 3.1 Cumulative 2,4-D degradation curves for upper, mid, lower and depression landscape positions in the A) A horizon, B) B horizon and C) C horizon

Both degradation rate constants were also negatively correlated with soil pH and carbonate content. This is interesting, given that the bioavailability of 2,4-D should be increased at neutral and alkaline soil pH due to decreased 2,4-D sorption by soils at these pH (pKa = 2.64). However, the sorption of 2,4-D by soil in the A horizon at this site had a weak, positive correlation with soil pH (Chapter 2) due to positive correlations between SOC and pH and between SOC and 2,4-D sorption. Degradation rate constants in the B or C horizons were not related to soil properties, with the exception of a negative correlation between k_1 and SOC in the C horizon. Degradation rates in the B or C horizons were also not related to 2,4-D sorption by soil, presumably because 2,4-D degradation was rate limited by microbial growth and not by the availability of 2,4-D to microorganisms. Also, the A horizon had a much greater sorption capacity than the B and C horizons (Table 3.1) as previously reported in chapter 2.

Total 2,4-D degradation at the end of the experiment at 56 days, was 41.5% in the A horizon and decreased significantly to 30.8% in the B horizon and 26.5% in the C horizon. The total amount of 2,4-D degraded abiotically, as determined by microcosms containing silica sand, was 1.2% after 56 days, which agrees with previous evidence that 2,4-D degradation occurs mainly by soil microorganisms (Soulas, 1993; Getenga et al., 2004). In the A horizon, there was a weak, positive relation between k_1 and total 2,4-D degradation (0.46, $P < 0.05$). In the B and C horizons, there were no significant correlations between k_1 and total 2,4-D degradation, perhaps because of the initial lag phase in 2,4-D degradation in these horizons. Overall, total 2,4-D degradation was poorly correlated with soil properties in A, B and C horizons (Table 3.2). Also, there

were no significant correlations between 2,4-D sorption and total 2,4-D degradation in the A, B and C horizons (Table 3.2).

SOC increased significantly in the order U < M < L = D slope position in the A horizon, but did not vary significantly with slope position in either the B or C horizon (Table 3.3). Clay content varied significantly between L and D slope positions in the A horizon, but was not influenced by slope position in the B and C horizons (Table 3.3). For all horizons, soil pH was generally more acidic in U slope positions than other slope positions (Table 3.3). Carbonate content did not vary significantly among slope positions in the A and B horizon, but varied significantly among slope positions in the C horizon reflecting the heterogeneous nature of the glacial till parent material. In the A horizon, *Kd* values increased significantly in the order (U = M) < (M = L = D) slope position in response to increasing SOC (Table 3.3). Sorption of 2,4-D by soil did not vary significantly with slope position in either the B or C horizon (Table 3.3), as expected based on the similar SOC across slope positions in these horizons. *Koc* values did not vary among slope positions in the A and C horizon but soil in the B horizon had significantly smaller *Koc* values in the D slope positions than the U, M and L slope positions (Table 3.3).

Table 3.3 Means and variability of soil properties, 2,4-D sorption coefficients and 2,4-D degradation parameters measured on 25 soil cores collected from A, B and C horizons within four landscape positions

	Soil properties and 2,4-D sorption coefficients						2,4-D mineralization parameters		
	SOC (g 100 g^{-1} soil)	pH	Carbonate content (g 100 g^{-1} soil)	Clay content (g 100 g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})	M_{Texp} ($^{14}CO_2$ evolved as % of initial)	k_1 (day^{-1})	k_2 (day^{-2})
A horizon									
U	0.90 ± 41[c]	6.55 ± 8[b]	0.30 ± 43[a]	21.07 ± 8[ab]	2.10 ± 88[b]	207 ± 48[a]	41.72 ± 3[a]	0.170 ± 32[a]	0.000 ± 00[a]
M	1.64 ± 34[b]	7.03 ± 6[b]	2.63 ± 159[a]	19.07 ± 18[ab]	3.58 ± 44[ab]	211 ± 20[a]	41.81 ± 5[a]	0.114 ± 49[ab]	0.000 ± 82[a]
L	2.74 ± 24[a]	7.08 ± 4[b]	1.22 ± 121[a]	15.43 ± 52[b]	6.56 ± 46[a]	232 ± 20[a]	40.75 ± 3[a]	0.080 ± 39[b]	0.000 ± 35[a]
D	3.33 ± 10[a]	7.42 ± 5[a]	3.58 ± 40[a]	29.56 ± 8[a]	5.60 ± 23[a]	167 ± 15[a]	41.64 ± 4[a]	0.099 ± 34[ab]	0.000 ± 35[a]
B horizon									
U	0.34 ± 40[a]	6.65 ± 11[b]	4.64 ± 167[b]	21.08 ± 15[a]	0.39 ± 32[a]	119 ± 15[a]	35.67 ± 15[a]	0.029 ± 26[a]	0.001 ± 93[a]
M	0.53 ± 50[a]	7.31 ± 3[a]	7.28 ± 121[b]	23.17 ± 20[a]	0.76 ± 70[a]	139 ± 28[a]	33.67 ± 36[a]	0.015 ± 77[a]	0.007 ± 119[a]
L	0.52 ± 45[a]	7.31 ± 3[a]	4.68 ± 204[b]	25.81 ± 18[a]	0.67 ± 76[a]	125 ± 53[a]	23.75 ± 55[a]	0.042 ± 85[a]	0.002 ± 103[a]
D	0.88 ± 43[a]	7.52 ± 2[a]	20.36 ± 18[a]	33.09 ± 37[a]	0.51 ± 55[a]	56 ± 16[b]	26.02 ± 13[a]	0.025 ± 24[a]	0.001 ± 103[a]
C horizon									
U	0.39 ± 23[a]	7.20 ± 4[b]	12.51 ± 93[a]	19.30 ± 25[a]	0.37 ± 13[a]	99 ± 15[a]	31.05 ± 48[a]	0.024 ± 13[a]	0.006 ± 170[a]
M	0.39 ± 44[a]	7.55 ± 2[a]	25.16 ± 33[b]	19.24 ± 27[a]	0.35 ± 62[a]	87 ± 32[a]	26.16 ± 61[a]	0.017 ± 80[a]	0.004 ± 168[a]
L	0.34 ± 23[a]	7.47 ± 2[ab]	16.74 ± 51[ab]	19.37 ± 44[a]	0.31 ± 43[a]	91 ± 29[a]	23.16 ± 46[a]	0.035 ± 51[a]	0.005 ± 139[a]
D	0.40 ± 13[a]	7.47 ± 1[ab]	36.43 ± 6[b]	34.22 ± 14[a]	0.24 ± 29[a]	61 ± 23[a]	29.80 ± 9[a]	0.047 ± 21[a]	0.002 ± 102[a]

Mean ± CV (%)

[a-c] Column means for slope positions within a horizon followed by same letters are not significantly different at $P < 0.05$ (Tukey's HSD)

In each horizon, the degradation rate constants were highly variable across the transect, especially k_2 which showed greater variability than any other variable (Table 3.1). Total 2,4-D degradation was less variable across the transect than degradation rate constants, particularly in the A horizon (Table 3.1). Segmentation of soil horizons by slope position reduced the variability of k_2 within all slope positions in the B horizon and within U, L and D slope positions in the A horizon and within L and D slope positions in the C horizon (Table 3.3). Segmentation of soil horizons by slope position also generally reduced the variability of k_1, particularly within U and D positions (Table 3.3). Even though segmentation of soil horizons by slope position reduced the variability of k_1 and k_2, 2,4-D degradation was still highly variable within slope positions, particularly in the B and C horizons (Figure 3.1).

In the A horizon, k_1 was significantly greater in U (0.170% day^{-1}) than in L (0.080% day^{-1}) (Table 3.3). Slope positions had no significant effect on k_1 in the B and C horizons. In all horizons, k_2 was similar across slope positions (Table 3.3). Despite low variability within slope positions in the A horizon, total 2,4-D degradation was not significantly different across slope positions because average values only ranged from 40.8 to 41.8% (Table 3.3). B and C horizons had greater differences in total 2,4-D degradation across slope positions, but these differences were not statistically significant because of the variability of 2,4-D degradation within slope positions (Figure 3.1).

Results of this study indicate that differences in 2,4-D degradation are greater among soil horizons than among slope positions within horizons. As such, pesticide fate models

should focus on differences in 2,4-D degradation among surface and subsurface soils and consider the use of degradation kinetic models that are able to describe a range of non-linear degradation curves, including those with lag phases and decreased degradation rates characteristic of subsurface soil. Decreased 2,4-D degradation rates and increased lag phases in subsurface soils versus topsoils have been previously reported (Willems et al., 1996; Veeh et al., 1996; Shaw and Burns, 1998). Differences in 2,4-D degradation among soils within horizons may be difficult to incorporate in predictions of 2,4-D transport at the field scale because of the high variability in 2,4-D degradation, as found for the 25 soil cores used in this study. This is particularly true since variations in 2,4-D degradation within horizons were poorly correlated with soil properties and landscape position. Soil properties were found to be poorly correlated with 2,4-D degradation in other studies (Willems et al., 1996; Shaw and Burns, 1998).

3.5 Conclusions

The three-half order model was used in addition to laboratory measurements to describe 2,4-D degradation in a cultivated hummocky field as affected by soil properties, 2,4-D sorption, soil depth and landscape position. Degradation in the A horizon was dependent predominantly on 2,4-D concentration while degradation in the B and C horizons was dependent on microbial growth in addition to 2,4-D concentration. With increasing soil depth from A to B to C horizons, both the first-order degradation rate and total 2,4-D degradation at 56 days decreased significantly, but the degradation rate dependent on microbial growth increased significantly. These findings suggest that pesticide fate

models should consider differences in degradation kinetics with increased soil depth by including a kinetics model that has the ability to describe a range of non-linear degradation curves. In each horizon, slope position had no significant effect on 2,4-D degradation except that the first-order degradation rate in the A horizon was significantly greater in U slope positions that contained less soil organic matter than L slope positions. Along the transect, the degradation of 2,4-D was negatively correlated with SOC in the A horizon because of increased sorption of 2,4-D by soil that reduced the availability of the herbicides for microbial breakdown. However, in both B and C horizons degradation of 2,4-D was not affected by 2,4-D sorption and was poorly correlated with soil properties suggesting that 2,4-D degradation was limited by microbial growth.

3.6 References

Bergstrom, D.W., Monreal, C.M., Millette, J.A. and King, D.J. 1998. Spatial dependence of soil enzyme activities along a slope. Soil Sci. Soc. Am. J., **62:** 1302–1308.

Boesten, J.J.T.I. and van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual., **20:** 425–435.

Bollag, J.M. and Liu, S.Y. 1990. Biological transformation processes of pesticides. *In* Cheng, H.H. (Ed). Pesticides in the Soil Environment: Processes, Impacts and Modeling. Soil Science Society of America, Madison, WI. pp. 169–211.

Brady, N.C. and Weil, R.R. 1999. The Nature and Properties of Soils, 12th ed. Prentice-Hall Inc., Upper Saddle River, NJ. 881 pp.

Brunner, W. and Focht, D.D. 1984. Deterministic three-half order kinetic model for microbial degradation of added carbon substrates in soil. Appl. Environ. Microbiol., **47:** 167–172.

Charney, M.-P., Tuis, S., Coquet, Y. and Barriuso, E. 2005. Spatial variability in ^{14}C-herbicide degradation in surface and subsurface soils. Pest Manag. Sci., **61:** 845–855.

Chen, Z., and Pawluk, S. 1995. Structural variations of humic acids in two Alberta Mollisols. Geoderma., **65:** 173–193.

Clayton, J.S., Ehrlich, W.A., Cann, D.B., Day, J.H. and Marshall, I.B. 1977. Soils of Canada. Vol. 1. Soil Rep. Res. Branch, Canada Department of Agric., Ottawa, ON. 243 pp.

Ding, G., Novak, J.M., Amarasiriwardena, D., Hunt, P.G. and Xing, B. 2002. Soil Organic Matter Characteristics as Affected by Tillage Management. Soil Sci. Soc. Am. J., **66:** 421–429.

Farenhorst, A. 2006. Importance of soil organic matter fractions in soil-landscape and regional assessments of pesticide leaching and sorption in soil. Soil Sci. Soc. Am. J., **70:** 1005–1012.

Farenhorst, A., Muc, D, Monreal, C. and Florinski, I. 2001. Sorption of herbicides in relation to soil variability and landscape position. J. Environ. Sci. Health Part B, **B36:** 379–387.

Florinski, I.V., McMahon, S. and Burton, D.L. 2004. Topographic control of sol microbial activity: a case study of denitrifiers. Geoderma, **119:** 33–53.

Fournier, J.C. 1980. Enumeration of the soil microorganisms able to degrade 2,4-D by metabolism or co-metabolism. Chemosphere, **9:** 169–174.

Fournier, J.C., Codaccioni, P. and Soulas, G. 1981. Soil adaptation to 2,4-D degradation in relation to the application rates and the metabolic behaviour of the degrading microflora. Chemosphere, **10:** 977–984.

Gaultier, J., Farenhorst, A. and Crow, G. 2006. Spatial variability of soil properties and 2,4-D sorption in a hummocky field as affected by landscape position and soil depth. Can. J. Soil Sci., **86:** 89–95.

Gee G.W. and Bauder J.W. 1986. Particle-size analysis. *In* Klute, A. (Ed), Methods of soil analysis. Part 1. Physical and Mineralogical Methods. ASA/SSSA, Madison, WI. pp. 383–412.

Getenga, Z.M., Madadi, V. and Wandiga, S.O. 2004. Studies on biodegradation of 2,4-D and metribuzin in soil under controlled conditions. Bull. Environ. Contam. Toxicol., **72:** 504–513.

Goderya, F.S. 1998. Field scale variations in soil properties for spatially variable control: A review. J. Soil Contam., **7:** 243–264.

Greer, L.E. and Shelton, D.R. 1992. Effect of inoculant strain and organic matter content on kinetics of 2,4-dichlorophenoxyacetic acid degradation in soil. Appl. Environ. Microbiol., **58:** 1459–1465.

Gregorich, E. and Anderson, D. 1985. Effects of cultivation and erosion on soils of four toposequences in the Canadian prairies. Geoderma, **36:** 343–354.

Grover, R., Waite, D.T., Cessna, A.J., Nicholaichuk, W., Irvin, D.G., Kerr, L.A. and Best, K. 1997. Magnitude and persistence of herbicide residues in farm dugouts and ponds in the Canadian prairies. Environ. Toxicol. Chem., **16:** 638–643.

Guo, L., Jury, W.A., Wagenet, R,J. and Flury, M. 2000. Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. J. Contam. Hydrol., **43:** 45–62.

Hermosin, M.C. and Cornejo, J. 1993. Binding mechanism of 2,4-Dichlorophenoxyacetic acid by organo-clays. J. Environ. Qual., **22:** 325–331.

Kolpin, D.W., Goolsby, D.A. and Thurman, E.M. 1995. Pesticides in near-surface aquifers: an assessment using highly sensitive analytical methods and tritium. J. Environ. Qual., **24:** 1125–1132.

Lavy, T.L., Roeth, F.W. and Fenster, C.R. 1973. Degradation of 2,4-D and atrazine at three soil depths in the field. J. Environ. Qual., **2:** 132–137.

Lindstrom, M.J., Nelson, W.W., Schumacher, T.E. and Lemme, G.D. 1990. Soil movement by tillage as affected by slope. Soil Tillage Res., **17:** 255–264.

Lobb, D.A., Lindstrom, M.J. and Schumacher, T.E. 2003. Soil erosion processes and their interactions: Implications for environmental indicators. Proc. OECD Expert Meeting on Soil Erosion and Soil Biodiversity Indicators, Rome, Italy.

Loeppert, R.H. and Suarez, D.L. 1996. Carbonate and Gypsum. *In* Bartels, J.M. (Ed.), Methods of Soil Analysis. Part 3. Chemical Methods. ASA/SSSA, Madison, WI. pp. 437–475.

MacMillan, R.A. and Pettepiece, W.W. 2000. Alberta landforms: Quantitative morphometric descriptions and classification of typical Alberta landforms. Technical Bulletin No. 200-2E. Research Branch, AAFC, Semiarid Prairie Agricultural Research Centre, Swift Current, SK. 118 pp.

McKeague, J.A. (Ed.) 1978. Manual on soil sampling and methods of analysis. Canadian Society of Soil Science, Ottawa, Canada. 212 pp.

Moshier, L.J., and Penner, D. 1978. Factors influencing microbial degradation of ^{14}C-glyphosate to $^{14}CO_2$ in soil. Weed Sci., **26:** 686–691.

Müller, K., Smith, R.E., James, T.K., Holland, P.T. and Rahman, A. 2003. Spatial variability of atrazine dissipation in an allophonic soil. Pest Manag. Sci., **59:** 893–903.

Nelson, D.E. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. *In* Page, A.L. (Ed.), Methods of Soil Analysis. Part2. Chemical and microbiological properties. ASA/SSSA, Madison, WI. pp. 539–577.

Novak, J.M., Moorman, T.B. and Cambardella, C.A. 1997. Atrazine at the field scale in to soils and landscape position. J. Environ. Qual., **26:** 1271–1277.

Ogram, A.V, Jessup, R.E., Ou, L.-T. and Rao, P.S.C. 1985. Effects of sorption on biological degradation rates of 2,4-Dichlorophenoxyacetic acid in soils. Appl. Environ. Microbiol., **49:** 585–587.

Parkin, T.B. and Shelton, D.R. 1992. Spatial and temporal variability of Carbofuran degradation in soil. J. Environ. Qual., **21:** 672–678.

Piccolo, A., Conte, P., Scheunert, I. and Paci, M. 1998. Atrazine interactions with soil humic substances of different molecular structure. J. Environ. Qual., **27:** 1324–1333.

Pinheiro-Dick, D., Burba, P. and Herzog, H. 1999. Influence of extractant and soil type on molecular characteristics of humic substances from two Brazilian soils. J. Braz. Chem. Soc., **10:** 140–145.

Rasmussen, J., Aamand, J., Rosenberg, P., Jacobsen, O.S. and Sørensen, S.R. 2005. Spatial variability in the degradation of the phenylurea herbicide linuron within a Danish agricultural field: multivariate correlation to simple soil parameters. Pest Manag. Sci., **61:** 829–837.

Rawn, D.F.K., Halldorson, T.H.J., Turner, W.N., Woychuk, R.N., Zavrevsky, J.-G. and Muir, D.C.G. 1999. A multi-year study of four herbicides in surface water of a small prairie watershed. J. Environ. Qual., **28:** 906–917.

Robertson, B.K. and Alexander, M. 1994. Growth-linked and cometabolic biodegradation: possible reason for occurrence or absence of accelerated pesticide biodegradation. Pestic. Sci., **41:** 311–318.

SAS Institute Inc. 2000. SAS system for Windows. Version 8.01. SAS Institute Inc., Cary, NC.

Senesi, N. 1992. Binding mechanisms of pesticides to soil humic substances. Sci. Total Environ., **123/124:** 63–76.

Shaw, L.J. and Burns, R.G. 1998. Biodegradation of 2,4-D in a noncontaminated grassland soil profile. J. Environ. Qual., **27:** 1464–1471.

Shelton, D.R., Doherty, M.A., Parkin, T.B. and Robinson, J.A. 1998. Modeling of pesticide biodegradation in soil. *In* Koch, A.L., Robinson, J.A. and Milliken, G.A. (Eds), Mathematical Modeling in Microbial Ecology. Chapman & Hall, NY. pp. 124–141.

Smith, A.E. and Aubin, A.J. 1991. Effects of long-term 2,4-D and MCPA field applications on the soil breakdown of 2,4-D, MCPA, mecoprop, and 2,4,5-T. J. Environ. Qual., **20:** 436–438.

Soil Classification Working Group. 1998. The Canadian System of Soil Classification. Agric. and Agri-Food Can. Publ. 1646 (Revised). 187 pp.

Soulas, G. 1993. Evidence for the existence of different physiological groups in the microbial community responsible for 2,4-D degradation in soil. Soil Biol. Biochem., **25:** 443–449.

Systat Software Inc. 2000. SigmaPlot 2000 for Windows. Systat Software Inc., Richmond, CA.

Tessier, L., Gregorich, E.G. and Topp, E. 1998. Spatial variability of soil microbial biomass measured by the fumigation extraction method, and KEC as affected by depth and manure application. Soil Biol. Biochem., **30:** 1369–1377.

Topp, E., Vallaeys, T. and Soulas, G. 1997. Pesticides: microbial degradation and effects on microorganisms. *In* van Elsas, M.J.D., Welligton, E.M.H. and Trevors, J.T. (Eds), Modern Soil Microbiology. Marcel Dekker Inc., New York, pp. 547–575.

Veeh, R.H., Inskeep, W.P. and Camper, A.K. 1996. Soil depth and temperature effects on microbial degradation of 2,4-D. J. Environ. Qual., **25:** 5–12.

Vinther, F.P., Elasgaard, L. and Jacobson, O.S. 2001. Heterogeneity of bacterial populations and pesticide degradation potentials is the unsaturated zone of loamy and sandy soils. Biol. Fertil. Soils. **33:** 514–520.

Waite, D.T., Cessna, A.J., Grover, R., Kerr, L.A. and Snihura, A.D. 2002. Environmental concentrations of agricultural herbicides: 2,4-D and triallate. J. Environ. Qual., **31:** 129–144.

Walker, A., Jurado-Exposito, M., Bending, G.D. and Smith, V.J.R. 2001. Spatial variability in the degradation rate of isoproturon in soil. Environ. Pollut., **111:** 407–415.

Wardle, D.A. 1992. A comparative assessment of factors which influence microbial biomass carbon and nitrogen levels in soil. Biol. Rev., **67:** 321–358.

Wardle, D.A. and Ghani, A. 1995. Why is the strength of relationships between pairs of methods for estimating soil microbial biomass often so variable? Soil Biol. Biochem., **27:** 821–828.

Willems, H.P.L., Lewis, K.J., Dyson, J.S. and Lewis, F.J. 1996. Degradation of 2,4-D and atrazine in the unsaturated and saturated zone of a sandy loam soil. Soil Biol. Biochem., **28:** 989–996.

Xing, B., and Chen, Z. 1999. Spectroscopic evidence for condensed domains in soil organic matter. Soil. Sci., **164:** 40–47.

4. DEGRADATION OF [CARBOXYL-^{14}C] 2,4-D AND [RING-U-^{14}C] 2,4-D IN 114 AGRICULTURAL SOILS AS INFLUENCED BY SOIL ORGANIC CARBON CONTENT

4.1 Abstract

This study compared the degradation of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D in 114 agricultural soils (0 to 15 cm) as affected by 2,4-D sorption and soil properties (organic carbon content, pH, clay content, carbonate content, cation exchange capacity, total microbial activity). The sample area ranged from 49° to 60° north longitude and from 110° to 120° west latitude. Soils were grouped by soil organic carbon content (0 to 0.99%, 1 to 1.99%, 2 to 2.99%, 3 to 3.99% and > 4%). Degradation rates of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D followed first-order kinetics in all soils. Although total microbial activity increased with increasing soil organic carbon content, degradation rates and total degradation of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D decreased with increasing soil organic carbon content. This was likely due to increased sorption of 2,4-D by soil and reduced bioavailability of 2,4-D and its metabolites. Degradation rates of [ring-U-^{14}C] 2,4-D were more limited by sorption than degradation rates of [carboxyl-^{14}C] 2,4-D, possibly because of greater sorption and formation of bound residues of 2,4-D metabolites relative to 2,4-D. Based on the sorption and degradation parameters quantified, there were two distinct groups of soils, those with less than 1% soil organic carbon content and those with more. Specifically, soils with less than 1% SOC had, on average, 2.4 times smaller soil organic carbon sorption coefficients and 1.4 times smaller 2,4-D half-lives than soils with more than 1% SOC. In regional scale model simulations

of pesticide leaching to groundwater, covering many soils, input parameters for each pesticide include a single soil organic carbon sorption coefficient and single half-life value. Our results imply, however, that the approach to these regional scale assessments could be improved by adjusting the values of these two input parameters according to soil organic carbon content. Specifically, this study indicates that for 2,4-D and Alberta soils containing less than 1% SOC, the pesticide parameters obtained from generic databases should be divided by 2.5 (soil organic carbon sorption coefficient) and 1.5 (half-life value).

4.2 Introduction

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is widely used in western Canada to control broadleaf weeds in cereals and other crops. The persistence of 2,4-D in soil is low because a wide range of soil microorganisms are capable of transforming the herbicide (Audus, 1949; Soulas, 1993; Getenga et al., 2004). Ester formulations of 2,4-D has persistence in soil similar to amine salt formulations because they are rapidly converted to the acid or anionic form (Grover, 1973; Wilson et al., 1997). Microbial breakdown of 2,4-D in soil begins with the removal of the carboxyl side chain (1-C position) or the ether linkage (2-C position) (Foster and McKercher, 1973; Roberts et al., 1998), resulting in the formation of 2,4-dichlorophenol (2,4-DCP) and other phenolic metabolites that are further degraded by cleavage and oxidation of the phenyl ring (Smith and Aubin, 1991a; Roberts et al., 1998). Complete mineralization of 2,4-D is desirable

from an agri-environmental standpoint because the entire herbicide molecule is reduced to carbon dioxide and other inorganic compounds.

The majority of laboratory studies examining the impact of soil properties on the persistence of 2,4-D in soil have used [ring-U-^{14}C] 2,4-D (e.g. Willems et al., 1996; Shaw and Burns, 1998; Boivin et al., 2005). Parameters describing the degradation of [ring-U-^{14}C] 2,4-D in soil are assumed to be representative of 2,4-D persistence in soils because concentrations of 2,4-DCP and other phenyl metabolites in soil are generally small (Ou, 1984). Consequently, there have been few laboratory studies determining the impact of soil properties on the removal of the carboxyl side chain by microorganisms. Notable exceptions include Smith and Muir (1980) and Smith and Aubin (1991a).

Not all 2,4-D in soil is degraded because a portion of the parent molecule and metabolites are bound within the organic matter matrix making them unavailable to microorganisms (Smith and Aubin, 1991; Barriuso et al., 1997). In addition, soils with greater organic matter contents have greater 2,4-D sorption by soil (Reddy and Gambrell, 1987; Hermosin and Cornejo, 1991; Gaultier et al., 2006), which could result in reduced herbicide degradation (Moshier and Penner, 1978; Ogram et al., 1985; Greer and Shelton, 1992). There is also evidence that soils with greater organic carbon contents have significantly greater 2,4-D degradation rates because of increased soil microbial activities (Bolan and Baskaran, 1996; Getenga et al., 2004) which results in a positive correlation between 2,4-D degradation and the amount of 2,4-D sorbed per unit organic carbon (Benoit et al., 1999; Picton and Farenhorst, 2004). Other studies have demonstrated that

2,4-D degradation is poorly correlated with soil organic carbon content (Voos and Groffman, 1997). Understanding the discrepancy between studies is complicated by the fact that in each of the above studies the experimental work on 2,4-D degradation was conducted utilizing only a small number of soil samples that were obtained from one (Benoit et al., 1999; Getenga et al., 2004), three (Ogram et al., 1985), five (Voos and Groffman, 1997; Picton and Farenhorst, 2004), or ten (Bolan and Baskaran, 1996) research sites. There has been no regional scale study that compared the effects of soil organic carbon content and herbicide sorption on 2,4-D degradation across a wide-range of agricultural soils.

There is an increasing interest among governments and the scientific community to assess the risk of pesticide off-site movement at regional, provincial and national scales (Hutson, 1993; Wilson et al., 1996; Stewart and Loague, 1999; Dubus et al., 2003; Eason et al., 2004; Cessna et al., 2005). The risk of pesticide off-site movement can be assessed using mathematical models such as PRZM (Pesticide Root Zone Model) (Carsel et al., 2003) and MACRO (Jarvis, 2001). These models have been used to assess the risk of pesticide leaching to groundwater as part of policy analyses on pesticide registrations in the European Union (Dubus et al., 2003). PRZM is being used to assess the risk of pesticide contamination by groundwater at a national scale in Canada (Cessna et al. 2005). The most sensitive input parameters required by these models are soil organic carbon content, the pesticide soil organic carbon sorption coefficient (*Koc*) and pesticide half-life (Boesten and van der Linden 1991; Dubus et al., 2003).

Although variations in soil organic carbon content were considered in these risk assessments through data derived from provincial and national soil databases, it was assumed that each pesticide has a specific *Koc* and half-life regardless of the region in which the simulation is performed. It is likely that such approach to regional scale assessments creates uncertainties because the *Koc* values of some pesticides have been shown to vary by a factor of 22 and 33 across agricultural soils of different ecoregions in Australia and Pakistan, respectively (Ahmad et al., 2001). Knowledge of the impact of soil organic carbon content on pesticide input parameters could improve risk assessments because this knowledge could be used to develop correction factors that would help account for variations in pesticide parameters caused by differences in soil organic carbon content.

There are no data available in Canada on regional differences in *Koc* and soil half-life. The objective of this study was to evaluate the transformation of 2,4-D across 114 soils samples from seven ecoregions in Alberta, Canada to better understand the effects of soil organic carbon content, microbial activity and 2,4-D sorption on 2,4-D dissipation in western Canadian soils.

4.3 Materials and Methods

4.3.1 Herbicides and analytical techniques

Analytical grade 2,4-D (95% chemical purity), [ring-U-^{14}C] 2,4-D (99% radiochemical purity; specific activity 191.3 MBq mmol^{-1}) and [carboxyl-^{14}C] 2,4-D (99%

radiochemical purity; specific activity 632.7 MBq $mmol^{-1}$) were purchased from Sigma Aldrich Chemical Company (St. Louis, MO.) (Figure 4.1). Amounts of radioactivity in herbicide solutions and experimental samples were quantified by liquid scintillation counting (LSC) with automated quench correction (#H method) (LS 6500 Beckman Instruments, Fullerton, CA.) and a maximum 10 minute counting time. Readysafe scintillation cocktail was purchased from Beckman Coulter (Fullerton, CA.)

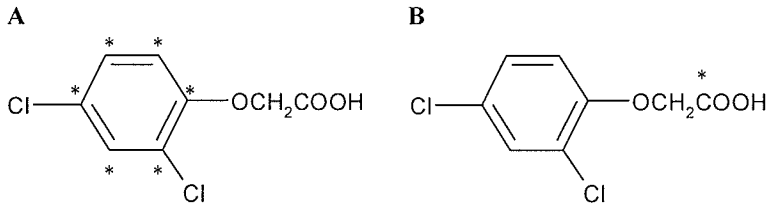


Figure 4.1 2,4-D molecule, with asterisks marking the position(s) of the ^{14}C in A) [ring-U-^{14}C] 2,4-D and B) [carboxyl-^{14}C] 2,4-D

4.3.2 Soil sampling and characterization

The Alberta Environmentally Sustainable Agriculture (AESA) Soil Quality Program was established in 1998 to monitor the state of soil quality of agricultural soil-landscapes representative of seven ecoregions in Alberta: Peace Lowland (PL), Boreal Transition (BT), Mid Boreal Uplands (MBU), Aspen Parkland (AP), Moist Mixed Grassland (MMG), Fescue Grassland (FG), and Mixed Grassland (MG) (Figure 4.2). Detailed site descriptions are given in Leskiw et al. (2000).

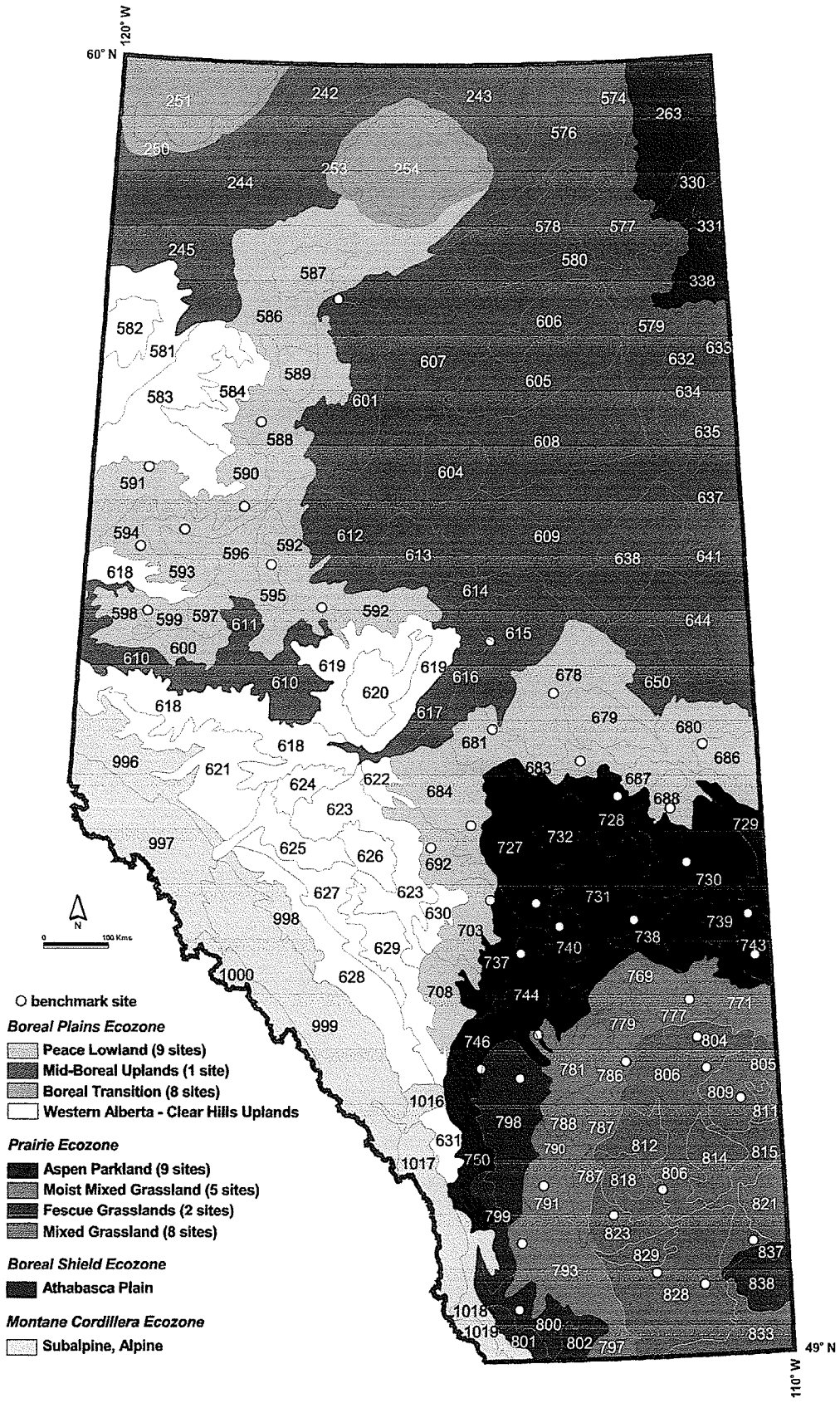


Figure 4.2 Location of soil sample sites, ecodistricts and ecoregions within the province of Alberta, Canada

One-hundred fourteen soil samples (0 to 15 cm) were collected in 2004 from upper, middle and lower slope positions of 38 agricultural fields located in these seven ecoregions (Table 4.1). The sample area ranged from 49° to 60° north longitude and from 110° to 120° west latitude. The number of agricultural fields sampled was 7 in PL, 8 in BT, 1 in MBU, 8 in AP, 5 in MMG, 2 in FG and 7 in MG. Each soil sample was a composite of six soil cores collected within a 2 m radius. Augers were rinsed with a 10% bleach solution to limit cross-contamination between soil samples. Samples collected were representative of the followed soil great groups: Brown Chernozems, Dark Brown Chernozems, Black Chernozems, Dark Grey Chernozems, Gray Luvisols and Luvic Gleysols (Soil Classification Working Group, 1998) (Table 4.1).

Table 4.1 Soil great groups, average climate and cropping systems typical in 7 ecoregions in Alberta (Adapted from Cathcart et al.).

Ecoregion	Soil Great Groups	Mean Temperature (°C)		GDD > 5°C	Precipitation (mm)	Cropping system
		January	July			
PL	Gray Luvisols (n=12), Dark Gray (n=6) and Black Chernozems (n=3)	-17.2	13.3	1118–1305	435–517	Annual crops
MBU	Gray Luvisols (n=2), Luvic Gleysol (n=1)	-16.4	15.5	1225	508	Annual crops or forages
BT	Gray Luvisols (n=15), Dark Gray (n=4) and Black Chernozems (n=4), Luvic Gleysol (n=1)	-15.0	15.9	1287–1384	428–535	Annual crops and forages
AP	Black (n=21) and Dark Brown Chernozems (n=3)	-14.3	16.4	1280–1486	391–478	Annual crops and forages
MMG	Black (n=3) and Dark Brown Chernozems (n=12)	-10.8	17.0	1482–1556	368–422	Annual crops and forages
FG	Black Chernozems (n=6)	-9.5	15.6	1290–1362	427–537	Annual crops
MG	Brown Chernozems (n=21)	-12.8	17.9	1459–1774	314–363	Annual crops and forages

GDD = Growing Degree Days

Soil samples were kept cool (4 °C) and transported back to the laboratory where samples were passed through a 2 mm mesh sieve. A portion of the samples (approximately 200 g) were frozen (-20 ± 2 °C) for use in 2,4-D degradation experiments and to determine the total soil microbial activity. The remaining portion of the soil samples (approximately 800 g) was air-dried for use in 2,4-D sorption experiments, and to determine soil texture, cation exchange capacity, soil organic carbon content, soil pH and carbonate content.

Soil texture, pH, soil organic carbon content (SOC) and carbonate content for samples were measured as described in chapter 2. Cation exchange capacity (CEC) was determined using the method described in McKeague (1978). Total soil microbial activity was measured by the hydrolysis of fluorescein diacetate (FDA) (Adam and Duncan, 2001). Duplicate 2 g samples of fresh soil (dry weight basis) were brought up to 90% field capacity and incubated for 14 days at 20 °C to simulate 2,4-D degradation experiment conditions (see below). Total microbial activity was then determined by the amount of fluorescein in sample filtrate as measured at 490 nm by a spectrophotometer (Biochrom Ultrospec 3100 pro, Cambridge, UK).

Sorption of 2,4-D by soil was quantified using the batch equilibrium method described in chapter 2. Duplicate soil samples (5 g) in Teflon tubes were rotated for 24 hours in the dark with a herbicide solution (10 mL) containing 1 μL 2,4-D and 16.7 Bq mL^{-1} of [ring-U-^{14}C] 2,4-D in 0.01 M $CaCl_2$. Equilibrium conditions were obtained (24 hr) and samples were centrifuged for 10 minutes at 10,000 rpm after which 1 mL sub-samples of supernatant (duplicates) were analyzed by LSC to determine the amount of ^{14}C-2,4-D

remaining in solution. The sorption coefficient, *Kd*, was used to quantify the sorption of 2,4-D by soil, and the soil organic carbon sorption coefficient, *Koc*, was used to quantify the sorption of 2,4-D per unit soil organic carbon (Equations 2.1 and 2.2). Higher relative values of *Kd* and *Koc* are indicative of greater sorption of 2,4-D by soil and per unit organic carbon content, respectively.

Degradation of 2,4-D in soil was quantified over a 42 day period using soil microcosms. Soil samples (25 g dry weight basis) were added to 125 mL glass jars in triplicates, wetted to 90% field capacity (refer to Chapter 3) and placed in sealed 1 L mason jars. Samples were incubated at 20 °C for 14 days allowing microbial activity to equilibrate after being frozen in storage. Microcosms with blank jars (no soil) and jars with 25 g silica sand were used to monitor background levels of $^{14}CO_2$ and assess amounts of abiotic degradation of 2,4-D, respectively. Glass vials containing 3 mL acidified water (pH ~ 3) were included in microcosms to maintain humidity. The acidic pH of the water ensured the absence of reaction between the water and carbon dioxide. After 14 days, a herbicide solution (0.5 mL) containing 17.9 μg mL^{-1} analytical grade 2,4-D and 16.7 MBq mL^{-1} [carboxyl-^{14}C] 2,4-D was added to a set of soil samples (triplicates) and thoroughly mixed so that the degradation rates of 2,4-D upon removal of the carboxyl side chain by microorganisms could be measured. A herbicide solution (0.5 mL) containing 4.5 μg mL^{-1} analytical grade 2,4-D and 16.7 MBq mL^{-1} [ring-U-^{14}C] 2,4-D was added to another set of soil samples (triplicates) and thoroughly mixed to measure degradation of 2,4-D upon cleavage of the phenyl ring. The amount of 2,4-D added to the microcosms represented average field application rates of 2,4-D to soils in western

Canada (Manitoba Agriculture and Food, 2000). Scintillation vials containing 0.5 M NaOH (5 mL) were placed in microcosms to trap evolved $^{14}CO_2$ as 2,4-D was degraded. Microcosms continued to incubate in the dark at 20 °C and sodium hydroxide traps were replaced at 2, 4, 6, 8, 11, 14, 17, 21, 28 and 42 days after 2,4-D application. Scintillation cocktail was added (8 mL) to the vials of NaOH and the amount of radioactivity in the traps determined by LSC. The radioactivity counts were adjusted to account for background levels of $^{14}CO_2$.

Degradation of 2,4-D was expressed as the amount of $^{14}CO_2$ evolved as a percent of initially applied ^{14}C-2,4-D. Cumulative degradation curves were plotted as the percent $^{14}CO_2$ evolved as a function of time. Using the non-linear regression exponential rise to the max curve fitter function in SigmaPlot 2000 (Systat Software Inc., 2000), each degradation curve was fit with the first-order kinetic model:

$$M_T = M_O(1 - \exp^{-kt}) \qquad [4.1]$$

where M_T = 2,4-D degradation at time, t [%], M_O = percent 2,4-D degradation when t approaches infinity [%] , k = first-order degradation rate constant [day^{-1}] and t = time [days]. Half-lives, $t½$ [days], for degraded portions of 2,4-D were determined by:

$$t_{1/2} = \frac{\ln 2}{k} \qquad [4.2]$$

4.3.3. Statistical analyses

All parameters, with the exception of soil pH, were log transformed to achieve normality. Pearson's pairwise correlation analysis was conducted in SAS, version 8.01 (SAS Inst.,

2000) to quantify relations among the following variables: SOC, soil pH, carbonate content, percent clay, CEC, total microbial activity, *Kd*, *Koc*, [carboxyl-^{14}C] 2,4-D degradation rate, [ring-U-^{14}C] 2,4-D degradation rate, and total [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation at 42 days (M_{Texp}).

Following these preliminary analysis, soils were classified into 5 groups according to their SOC: 0 to 0.99% (n=19), 1 to 1.99% (n=45), 2 to 2.99% (n=24), 3 to 3.99% (n=11) and > 4% SOC (n=13). Soils were divided this way because SOC was the only soil parameter that had a consistently significant correlation with the [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation rates, and with total [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation (see results section). In addition, it has been previously shown that SOC is the most important soil property influencing 2,4-D sorption (Mallawatantri and Mulla, 1992; Farenhorst et al., 2003; Gaultier et al., 2006) and that SOC is an important soil property affecting microbial biomass and activity (Wardle and Ghani, 1995; Milne and Haynes, 2004).

Redundancy analysis (RDA), a multivariate ordination method, was used to further assess the relations among variables. Redundancy analysis was conducted using CANOCO, version 4.53 (ter Braak and Šmilauer, 2002). Redundancy analysis is a form of canonical principal component analysis, where a set of response variables is linearly constrained by a set of factor variables (Kenkel et al., 2002). The [carboxy^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation parameters were considered the response variables constrained by the factor variables which were 2,4-D sorption and soil properties. The five classes of SOC

were included as dummy factor variables so that their relation with [carboxy^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation parameters and the response variables could be determined. In addition, the 2,4-D degradation parameters, [carboxyl-^{14}C] 2,4-D degradation rate, [ring-U-^{14}C] 2,4-D degradation rate, and total [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation 42 days, were subjected to a two-way analysis of variance (ANOVA) in SAS, version 8.01. The two factors considered were the percentage of SOC in soil (0 to 0.99, 1 to 1.99%, 2 to 2.99, 3 to 3.99, and > 4%) and the type of 2,4-D applied ([carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D). Comparisons of treatment means were made using the Tukey's Highly Significant Difference (HSD) test ($P < 0.05$).

4.4 Results

There was a strong, positive correlation between SOC and *Kd* (Table 4.2) so that *Kd* increased significantly in sequence of (soils with 0 to 0.99% SOC) < (soils with 1 to 1.99% SOC) < (soils with 2 to 2.99% SOC and 3 to 3.99% SOC) < (soils with 3 to 3.99% SOC and greater than 4% SOC) (Table 4.3). The sorption of 2,4-D per unit soil organic carbon was significantly smaller in soils with less than 1% SOC than in soils with greater than 1% SOC (Table 3). Both *Kd* and *Koc* were strongly negatively correlated with soil pH but not negatively correlated with clay content (Table 4.2, Figure 4.2).

Table 4.2 Relations between [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation parameters, 2,4-D sorption coefficients and soil properties†

	M_{Texp} carboxyl	*k* carboxyl	M_{Texp} ring	*k* ring	*Kd*	*Koc*	SOC	pH	$CaCO_3$	% clay	CEC
M_{Texp} carboxyl	1.00										
k carboxyl	0.23*	1.00									
M_{Texp} ring	0.63***	0.43***	1.00								
k ring	0.34**	0.71***	0.82***	1.00							
Kd	-0.28**	-0.37***	-0.58***	-0.69***	1.00						
Koc	-0.22*	-0.22*	-0.53***	-0.63***	0.88***	1.00					
SOC	-0.26**	-45***	-0.47***	-0.56***	0.85***	0.51***	1.00				
pH	--	--	0.50***	0.46***	-0.62***	-0.81***	-0.22*	1.00			
$CaCO_3$	--	--	0.26**	0.22*	-0.34***	-0.43***	--	0.52***	1.00		
% clay	--	0.27**	--	--	--	--	--	--	--	1.00	
CEC	-0.23*	-0.29**	-0.23*	-0.28**	0.47***	0.24*	0.60***	--	--	0.34***	1.00
Microbial activity	--	-0.19*	-0.42***	-0.43***	0.58***	0.56***	0.44***	-0.51***	-0.26**	-0.46***	--

*,**, and *** denote $P < 0.05$, $P < 0.01$, and $P < 0.001$, respectively, for correlations Ho: r = 0; Ha: r ≠ 0

-- denotes no significant correlation

† See Appendix C for graphical representation of significant correlations between soil properties, 2,4-D sorption and 2,4-D degradation parameters

Table 4.3 Average soil properties and 2,4-D sorption as affected by percent soil organic carbon content

% SOC level	Soil properties						2,4-D sorption	
	SOC (g 100 g^{-1} soil)	pH	Carbonate content (g 100 g^{-1} soil)	Clay content (g 100 g^{-1} soil)	CEC (meq 100 g^{-1} soil)	Microbial activity (µg fluorescein g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})
0.00 to 0.99	0.76 ± 18^{e}	6.73 ± 13^{a}	1.97 ± 115^{a}	24.64 ± 14^{ab}	15.79 ± 24^{c}	0.16 ± 37^{b}	0.61 ± 73^{d}	80.78 ± 70^{b}
1.00 to 1.99	1.44 ± 21^{d}	5.43 ± 13^{b}	0.71 ± 9^{b}	22.41 ± 42^{b}	17.90 ± 29^{bc}	0.38 ± 53^{a}	3.17 ± 60^{c}	215.45 ± 51^{a}
2.00 to 2.99	2.43 ± 10^{c}	5.31 ± 14^{b}	0.72 ± 14^{b}	29.46 ± 43^{ab}	24.28 ± 34^{b}	0.38 ± 59^{a}	6.62 ± 46^{b}	274.50 ± 47^{a}
3.00 to 3.99	3.27 ± 9^{b}	5.37 ± 11^{b}	0.71 ± 4^{b}	34.49 ± 37^{a}	32.96 ± 18^{a}	0.32 ± 58^{a}	9.93 ± 44^{ab}	303.90 ± 42^{a}
> 4.00	5.72 ± 59^{a}	5.97 ± 14^{b}	1.05 ± 75^{ab}	22.17 ± 33^{b}	35.64 ± 36^{a}	0.47 ± 52^{a}	14.52 ± 39^{a}	295.45 ± 51^{a}

Mean ± CV

[a-e] Column means followed by the same letter are not significantly different as determined by Tukey's HSD ($P < 0.05$)

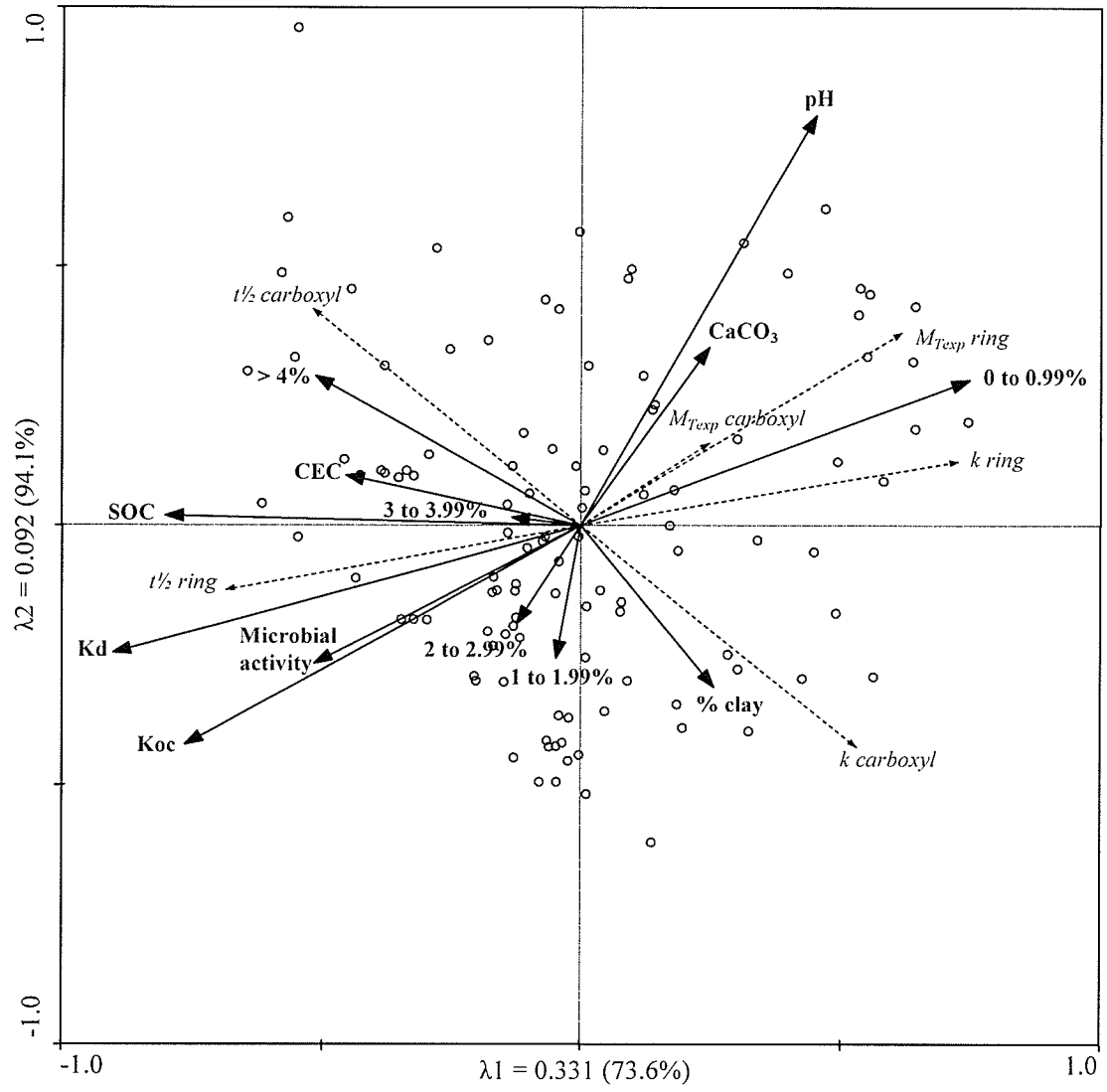


Figure 4.3 Redundancy analysis ordination triplot of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation parameters (vectors with dashed lines) constrained by 2,4-D sorption and soil properties (vectors with solid lines). Soil samples indicated by open circles. Eigenvalues for each axis are indicated by λ followed by cumulative percent variance of response-factor variable relation in brackets. Response-factor variable canonical correlations are 0.707 for axis 1 and 0.689 for axis 2. Redundancy is 42.3%.

Herbicide degradation was biologically mediated since total abiotic 2,4-D degradation was only 0.4% and 0.3% of initially applied [carboxyl-^{14}C] and [ring-U-^{14}C] 2,4-D, respectively. Experimental data of both [carboxyl-^{14}C] 2,4-D (average R^2 = 0.99; P < 0.0001) and [ring-U-^{14}C] 2,4-D (average R^2 = 0.98; P < 0.0001) followed first-order degradation kinetics. Soils with higher 2,4-D degradation rates had greater total amounts of 2,4-D degraded because k and M_{Texp} were positively correlated for both [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D (Table 4.2).

SOC was negatively correlated with total amounts and rates of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation (Table 4.2). Due to the positive relation between SOC and CEC, degradation parameters for both [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D were negatively related with CEC. Rates of [ring-U-^{14}C] 2,4-D degradation and total [ring-U-^{14}C] 2,4-D degradation had strong, positive relations with soil pH. As a result of this relation with soil pH, [ring-U-^{14}C] 2,4-D degradation parameters were also related to soil carbonate content (Table 4.2). In addition, degradation rates of [carboxyl-^{14}C] 2,4-D were correlated with clay content, but not due to soil textural effects on 2,4-D sorption or microbial activity because clay content was related to neither (Table 4.2). Total 2,4-D degradation and the rates of degradation were negatively correlated to 2,4-D sorption for both [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D. However, the correlation was stronger for [ring-U-^{14}C] 2,4-D than for [carboxyl-^{14}C] 2,4-D (Table 4.2). Regardless of the type of labelled 2,4-D, degradation rates were negatively correlated with total microbial activity.

Both total 2,4-D degradation and 2,4-D degradation rates in soil were significantly influenced by the % SOC level and the type of 2,4-D applied. However, there were also significant interactions between the % SOC level and the type of 2,4-D (Table 4.4). Degradation rates of [ring-U-^{14}C] 2,4-D and total 2,4-D degradation of both [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D were significantly greater in soils with less than 1% SOC relative to soils with more than 1% SOC (Table 4.4, Figure 4.1). Although rates of [carboxyl-^{14}C] 2,4-D degradation also numerically decreased with increasing SOC levels, there were no significant differences in [carboxyl-^{14}C] 2,4-D degradation rates among soils with 0 to 3.99% SOC but soils with > 4% SOC had significantly smaller [carboxyl-^{14}C] 2,4-D degradation rates than other soils (Table 5.4). Degradation rates of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D were similar in soils with less than 1% SOC, but the degradation rates of [carboxyl-^{14}C] 2,4-D were greater than that of [ring-U-^{14}C] 2,4-D in soils with greater than 1% SOC (Table 4.4). Regardless of the SOC, total [carboxyl-^{14}C] 2,4-D degradation was always greater than total [ring-U-^{14}C] 2,4-D degradation (Table 4.4). However, the numerical differences between total [carboxyl-^{14}C] 2,4-D degradation and total [ring-U-^{14}C] 2,4-D degradation increased with increasing SOC. Differences were about 13% in soils with less than 1% SOC, about 19% in soils with 1.00-3.99% SOC and about 21% in soils with larger than 4% SOC (Table 4.4).

When constrained by 2,4-D sorption and soil properties variables, the ordination of [carboxy-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation parameters, also differentiated soils with less than 1% SOC (to the right of the second ordination axis) from soils with greater than 1% SOC (to the left of the second ordination axis) (Figure 4.2). Soils with

less than 1% SOC were characterized by greater carbonate contents (Figure 4.2) and had significantly greater soil pH (Table 4.3) than soils with more than 1% SOC. These soils also had significantly less microbial activity than samples with more than 1% SOC (Table 4.3, Figure 4.2) probably because microbial activity was positively correlated with SOC and negatively correlated with soil pH (Table 4.2).

Table 4.4 Means and variability of the total 2,4-D degraded at 42 days (M_{Texp}) and the 2,4-D first-order degradation rate constant (k) as affected by soil organic carbon content and type of 2,4-D applied

	M_{Texp} (% of initial ^{14}C applied)		k (day^{-1})	
% SOC level	[carboxyl-^{14}C] 2,4-D	[ring-U-^{14}C] 2,4-D	[carboxyl-^{14}C] 2,4-D	[ring-U-^{14}C] 2,4-D
0.00 to 0.99	47.76 ± 3^{aA}	35.27 ± 16^{aB}	0.39 ± 39^{aA}	0.31 ± 46^{aA}
1.00 to 1.99	45.00 ± 8^{bA}	26.30 ± 18^{bB}	0.31 ± 33^{aA}	0.16 ± 46^{bB}
2.00 to 2.99	44.56 ± 6^{bA}	25.66 ± 17^{bB}	0.30 ± 34^{aA}	0.14 ± 34^{bcB}
3.00 to 3.99	44.99 ± 2^{bA}	26.06 ± 11^{bB}	0.27 ± 28^{abA}	0.14 ± 39^{bcB}
> 4.00	44.52 ± 3^{bA}	23.75 ± 15^{bB}	0.19 ± 25^{bA}	0.10 ± 42^{cB}
Statistical analysis	F-statistics and P values		F-statistics and P values	
SOC level	F-value 18.1 ($P < 0.0001$)		F-value 21.2 ($P < 0.0001$)	
^{14}C label	F-value 733.1 ($P < 0.0001$)		F-value 120.6 ($P < 0.0001$)	
SOC level × ^{14}C label	F-value 8.0 ($P < 0.0001$)		F-value 2.8 ($P = 0.028$)	

Mean ± CV (%)

[a-c] Means in the same column followed by the same lower-case letters are not significantly different as determined by Tukey's HSD ($P < 0.05$).

[A-B] For M_{Texp}, and k, respectively, the means in the same row followed by the same upper-case letters are not significantly different as determined by Tukey's HSD ($P < 0.05$)

4.5 Discussion

Results of this study were consistent with previous research that demonstrated degradation of 2,4-D occurs mainly by microbial processes (Audus, 1949; Soulas, 1993; Getenga et al., 2004). Degradation of both [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D began immediately, with neither exhibiting the lag phase sometimes observed for 2,4-D degradation (Parker and Doxtader, 1983; Soulas, 1993; Veeh et al., 1996; Shaw and

Burns, 1998). The range of observed half-lives of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D were similar to that in Veeh et al. (1996) and Picton and Farenhorst (2004) but lower than in Bolan and Baskaran (1996). Enhanced degradation of 2,4-D may have occurred because applications of 2,4-D in many of these agricultural soils allowed the microorganisms to adapt to 2,4-D as a substrate (Fournier et al., 1981; Smith and Aubin, 1991b; Robertson and Alexander, 1994).

There was strong evidence that soil microbial activities increased with increasing SOC. Previous studies have shown that soils generally contain a consortium of soil bacterial species able to degrade 2,4-D (Fulthorpe et al., 1995; Tonso et al., 1995) and 2,4-D metabolites (Puhakka et al., 1995; Haggblöm, 1998; Gallego et al., 2003). Soils with a greater activity of microorganisms capable of removing the carboxyl side chain also had a greater activity of microorganisms capable of cleaving the phenyl ring. However, not all bacterial strains capable of degrading 2,4-D will degrade 2,4-D metabolites (Short et al., 1991; Daugherty and Karel, 1994). The [carboxyl-^{14}C] degradation parameters were less variable across soils, relative to [ring-U-^{14}C] 2,4-D degradation parameters. Thus, there was a higher concentration of microorganisms capable of removing the carboxyl side chain than microorganisms capable of removing the phenyl ring.

In this study, although the degradation of 2,4-D in soil was carried out by soil microorganisms, 2,4-D degradation rates were negatively related with total microbial activity due to the positive effect of SOC on 2,4-D sorption. Increased SOC resulted in increased sorption which limited the availability of 2,4-D for breakdown. Thus, the

degradation of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D was limited by herbicide sorption and not by microbial activity. The limiting effect of sorption on degradation was greater for [ring-U-^{14}C] 2,4-D than [carboxyl-^{14}C] 2,4-D most likely because, over the range of soil pH in this study, 2,4-D metabolites are more strongly sorbed by soil than 2,4-D (Benoit et al., 1996; Haberhauer et al., 2000). Additionally, phenolic 2,4-D metabolites are incorporated into soil as bound residues to a greater extent than the 2,4-D parent molecule (Benoit and Barriuso, 1997). Although amounts of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D bound to soil were not measured, the difference between total [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation suggests that a significant portion of the metabolites were not degraded but incorporated into soil organic matter. In studies that quantified the fractions of 2,4-D bound to soil, Smith and Muir (1980) and Xie et al. (1997) also showed 15 to 20 percent more [ring-U-labelled] 2,4-D bound to soil compared with [carboxyl-^{14}C] 2,4-D.

The Alberta soils ranged in pH from 4.3 to 7.6 so that the portion of 2,4-D (pKa of 2.64: Ahrens, 1994) in molecular form was small. In contrast, over the range of soil pH studied, the phenolic metabolites (e.g. 2,4-DCP pKa = 7.89: Smith, 1985) were largely in molecular form. Increased soil pH resulted in decreased 2,4-D sorption due to increasing amounts of 2,4-D in anionic form relative to molecular form. Soil pH increased [ring-U-^{14}C] 2,4-D degradation suggesting that, at increasing soil pH, also an increasing portion of 2,4-D metabolites became in anionic form, thereby decreasing their relative sorption onto soil and increasing their bioavailability for transformation.

In regional scale assessments, single *Koc* and half-life values, obtained from a pesticide database, are used as input parameters in pesticide fate models to estimate leaching risk of pesticides in soil. For a sensitivity analysis on pesticide fate modeling, Boesten and van der Linden (1991) demonstrated that changing the value of either pesticide sorption coefficients or half-lives by a factor of 2 will increase pesticide leaching by a factor of 10. In our study, averaged 2,4-D half-lives in soils with more than 1% SOC were 1.4 times greater than in soils with less than 1% SOC. Additionally, averaged 2,4-D *Koc* values in soils with more than 1% SOC were 2.4 times greater than in soils with less than 1% SOC. Given the sensitivity of pesticide fate models to *Koc* and half-life values, our results at the provincial level indicate that values of 2,4-D half-lives and sorption coefficients should be adjusted to improve the accuracy of estimates of pesticide leaching at regional scales. Since *Koc* and half-life values in databases are usually determined on soils that contain more than 1% SOC, the accuracy of estimating pesticide leaching in soils with less than 1% SOC could be improved by dividing these input parameters by about 2.5 and 1.5, respectively.

4.6 Conclusions

Quantification of [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation in 114 soils from the province of Alberta, Canada revealed two distinct groups of soils based on their SOC content: those with less than 1% SOC and those with greater than 1% SOC. Soils with less than 1% SOC generally had greater total [carboxyl-^{14}C] 2,4-D and [ring-U-^{14}C] 2,4-D degradation and greater degradation rates compared with other soils. This is

because soils with less than 1% SOC had significantly less 2,4-D sorption than soils with higher SOC and, for both types of labelled 2,4-D, this lesser sorption increased the availability of 2,4-D and its metabolites to be degraded. Even though soil microbial activity increased with increasing SOC, total microbial activity was negatively correlated with 2,4-D degradation because increasing 2,4-D sorption by soil limited herbicide bioavailability. Averaged 2,4-D half-lives were 1.4 times smaller than in soils with less than 1% SOC than in soils with more than 1% SOC. Also, averaged 2,4-D *Koc* values were 2.4 times smaller in soils with less than 1% SOC than in soils with more than 1% SOC. These results have implications for pesticide fate modeling and 2,4-D environmental risk assessments at the regional scale whereby 2,4-D half-lives and *Koc* values should be adjusted in soils with less than 1% SOC.

4.7 References

Adam, G. and Duncan, H. 2001. Development of a sensitive and rapid method for the measurement of microbial activity using fluorescein diacetate (FDA) in a range of soils. Soil Biol. Biochem., **33:** 943–951.

Ahmad, R., Kookana, R.S., Alston, A.M. and Skjemstad, J.O. 2001. The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by ^{13}C CPMAS spectroscopy. Environ. Sci. Technol., **35:** 878–884.

Ahrens, W.H. (Ed.) 1994. Herbicide Handbook. 7th ed. Weed Science Society of America, Champaign, Illinois. 352 pp.

Audus, L.J. 1949. The biological detoxification of 2,4-dichlorophenoxyacetic acid in soil. Plant Soil, **2:** 31–36.

Barriuso, E., Houot, S. and Sierra-Wittling, C. 1997. Influence of compost addition to soil on the behaviour of herbicides. Pestic. Sci., **67:** 211–221.

Benoit, P., Barriuso, E. and Soulas, G. 1999. Degradation of 2,4-D, 2,4-Dichlorophenol, and 4-Chlorophenol in soil after sorption on humified and nonhumified organic matter. J. Environ. Qual., **28:** 1127–1135.

Benoit, P. and Barriuso, E. 1997. Fate of ^{14}C-ring-labelled 2,4-D, 2,4-Dichlorophenol and 4-Chlorophenol during straw composting. Biol. Fertil. Soils, **25:** 53–59.

Benoit, P., Barriuso, E., Houot, S. and Calvet, R. 1996. Influence of the nature of soil organic matter on the sorption-desorption of 4-chlorophenol, 2,4-dichlorophenol and the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). Eur. J. Soil Sci., **47:** 567–578.

Boesten, J.J.T.I. and van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual. **20:** 425–435.

Boivin, A., Amellal, S., Schaivon, M. and van Genuchten, M.T. 2005. 2,4-Dichlorophenoxyacetic acid (2,4-D) sorption and degradation dynamics in three agricultural soils. Environ. Pollut., **138:** 92–99.

Bolan, N.S. and Baskaran, S. 1996. Biodegradation of 2,4-D herbicide as affected by its adsorption-desorption behaviour and microbial activity of soils. Aust. J. Soil Res., **34:** 1041–1053.

Carsel, R.F., Imhoff, J.C., Hummel, P.R., Cheplick, J.M. and Donigan, A.S.J. 1998. PRZM-3. A model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: User manual for release 3.0, National Exposure Research Laboratory, Office of Research and development, U.S. Environmental Protection Agency, Athens, GA. 420 pp.

Cathcart, R.J., Cannon, K.R., Heinz, J.L. 2007. Selection and establishment of the Alberta soil quality benchmark sites. AAFRD Technical report. 31 pp.

Daugherty, D.D. and Karel, S.F. 1994. Degradation of 2,4-dichlorophenoxyacetic acid by *Pseudomonas cepacia* DBO1 (pRO101) in a dual-substrate chemostat. App. Environ. Microbiol., **60:** 3261–3267.

Dubus, I.G., Brown, C.D. and Beulke, S. 2003. Sensitivity analyses for four pesticide leaching models. Pest Manag. Sci., **59:** 962–982.

Eason, A., Tim, U.S. and Wang. X. 2004. Integrated modeling environment for statewide assessment of groundwater vulnerability from pesticide use in agriculture. Pest Manag. Sci., **60:** 739–745.

Farenhorst, A., Florinski, I., Monreal, C. and Muc, D. 2003. Evaluating the use of digital terrain modelling for quantifying the spatial variability of 2,4-D sorption within agricultural landscapes. Can. J. Soil Sci., **83:** 557–564.

Foster, R.K. and McKercher, R.B. 1973. Laboratory incubation studies of chlorophenoxyacetic acids in Chernozemic soils. Soil Biol. Biochem., **5:** 333–337.

Fournier, J.C., Codaccioni, P. and Soulas, G. 1981. Soil adaptation to 2,4-D degradation in relation to the application rates and the metabolic behaviour of the degrading microflora. Chemosphere, **10**: 977–984

Fulthorpe, R.R., McGowan, C., Maltseva, O.V., Holben, W.E. and Tiedje, J.M. 1995. 2,4-Dichlorophenoxyacetic acid-degrading bacteria contain mosaics of catabolic genes. Appl. Environ. Microbiol., **61:** 3274–3281.

Gallego, A., Fortunato, M.S., Foglia, J., Rossi, S., Gemini, V., Gomez, L., Gomez, C. E., Higa, L.E. and Korol, S.E. 2003. Biodegradation and detoxification of phenolic compounds by pure and mixed indigenous culture in aerobic reactors. Int. Biodeterior. Biodegrad., **52:** 261–267.

Gaultier, J., Farenhorst, A. and Crow, G. 2006. Spatial variability of soil properties and 2,4-D sorption in a hummocky field as affected by landscape position and soil depth. Can. J. Soil Sci., **86:** 89–95.

Gee, G.W. and Bauder, J.W. 1986. Particle-size analysis. I*n* Klute, A. (Ed), Methods of soil analysis. Part 1. Physical and mineralogical methods. ASA, SSSA, Madison, WI. pp. 383–412.

Getenga, Z.M., Madadi, V. and Wandiga, S.O. 2004. Studies on biodegradation of 2,4-D and metribuzin in soil under controlled conditions. Bull. Environ. Contam. Toxicol., **72:** 504–513.

Goh, T.B., St. Arnaud, R.J. and Mermut, A.R. 1993. Carbonates. *In* Carter, M.R. (Ed), Soil Sampling and Methods of Analysis. Canadian Society of Soil Science, Lewis Pulblishers, Boca Raton, FL. pp. 177–186.

Greer, L.E. and Shelton, D.R. 1992. Effect of inoculant strain and organic matter content on kinetics of 2,4-Dichlorophenoxyacetic acid degradation in soils. Appl. Environ. Microbiol., **58:** 1459–1465.

Grover, R. 1973. The adsorptive behaviour of acid and ester forms of 2,4-D on soils. Weed Res., **13:** 51–58.

Haberhauer, G., Pfeiffer, L., Gerzabek, M. H. 2000. Influence of molecule structure on sorption of phenoxyalkanoic herbicides on soil and its particle size fractions. J. Agric. Food Chem., **48:** 3722–3727.

Häggblom, M.M. 1998. Reductive dechlorination of halogenated phenols by a sulfate-reducing consortium. FEMS Microbiol. Ecol., **26:** 35–41.

Hermosin, M.C. and Cornejo, J. 1991. Soil adsorption of 2,4-D as affected by the clay mineralogy. Toxicol. Environ. Chem., **31/32:** 69–77.

Inskeep, W.P., Wraith, J.M., Wilson, J.P., Snyder, R.D., Macur, R.E., and Gaber, H.M. 1996. Input parameter and model resolution effects on predictions of solute transport. J. Environ. Qual., **25:** 453–462.

Jarvis, N.J. 2001. The MACRO model. V. 4.3. Technical description. Swedish University of Agricultural Science, Uppsala, Sweden.

Kenkel, N.C., Derksen, D.A., Thomas, A.G. and Watson, P.R. 2002. Multivariate analysis in weed science research. Weed Sci., **50:** 281–292.

Leskiw, L.A., Yarmuch, M.S., Waterman, L.P. and Sansom, J.J. 2000. Baseline soil physical and chemical properties of forty-three soil quality benchmark sites in Alberta. File #99-042, Can-Ag Enterprises Ltd., 175 pp.

Liu, Z., Clay, S.A. and Clay. D.E. 2002. Spatial variability of atrazine and alachlor efficacy and mineralization in an eastern South Dakota field. Weed Sci., **50:** 662–671.

Manitoba Agriculture and Food. 2000. Guide to Crop Protection.

Mallawatantri, A.P. and Mulla, D.J. 1992. Herbicide adsorption and organic carbon contents on adjacent low-input versus conventional farms. J. Environ. Qual., **21:** 546–551.

McKeague, J.A. (Ed.), 1978. Manual on soil sampling and methods of analysis. Canadian Society of Soil Science, Ottawa, ON. 212 pp.

Milne, R.M. and Haynes, R.J. 2004. Soil organic matter, microbial properties, and aggregate stability under annual and perennial pastures. Biol. Fertil. Soils, **39:** 172–178.

Moshier, L.J. and Penner, D. 1978. Factors influencing microbial degradation of ^{14}C-glyphosate to $^{14}CO_2$ in soil. Weed Sci., **26:** 686–691.

Nelson, D.E. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. *In* Page, A.L. (Ed.), Methods of Soil Analysis. Part 2. Chemical and microbiological properties. ASA, SSSA, Madison, WI. pp. 539–577.

Ogram, A.V., Jessup, R.E., Ou, L.-T. and Rao, P.S.C. 1985. Effects of sorption on biological degradation rates of 2,4-dichlorophenoxyacetic acid in soils. Appl. Environ. Microbiol., **49:** 582–587.

Parker, L.W. and Doxtader, K.G. 1983. Kinetics of the microbial degradation of 2,4-D in soil: effects of temperature and moisture. J. Environ. Qual., **12:** 553–558.

Picton, P. and Farenhorst, A. 2004. Factors influencing 2,4-D sorption and mineralization in soil. J. Environ. Sci. Health Part B, **B39:** 367–379.

Puhakka, J.A., Herwig, R.P., Koro, P.M., Wolfe, G.V. and Ferguson, J.F. 1995. Biodegradation of chlorophenols by mixed and pure cultures from a fluidized-bed reactor. Appl. Microbiol. Biotechnol., **42:** 951–957.

Reddy, K. and Gambrell, R. 1987. Factors affecting the adsorption of 2,4-D and methyl parathion in soils and sediments. Agric. Ecosyst. Environ., **18:** 231–241.

Roberts, T.R., Hutson, D.H., Lee, P.W., Nicholls, P.H. and Plimmer, J.R. (Eds). 1998. Metabolic pathways of Agrochemical Part 1: Herbicides and Plant Growth Regulators. The Royal Society of Chemistry, Cambridge, UK. pp. 66–74.

Robertson, B.K. and Alexander, M. 1994. Growth-linked and cometabolic biodegradation: possible reason for occurrence or absence of accelerated pesticide biodegradation. Pestic. Sci., **41:** 311–318.

SAS Institute Inc. 2000. SAS system for Windows. Version 8.01. SAS Institute Inc., Cary, NC.

Shaw, L.J. and Burns, R.G. 1998. Biodegradation of 2,4-D in a non-contaminated grassland profile. J. Environ. Qual., **27:** 1464–1471.

Short, K. A., Doyle, J.D., King, R.J., Seidler, R.J., Stotzky, G. and Olsen, R.H. 1991. Effects of 2,4-dichlorophenol, a metabolite of a genetically engineered bacterium, and 2,4-dichlorphenoxyacetate on some microorganism mediated ecological processes in soil. App. Environ. Microbiol., **57:** 412–418.

Smith, A.E. and Aubin, A.J. 1991a. Metabolites of [^{14}C]-2,4-dichlorophenoxyacetic acid in Saskatchewan soils. J. Agric. Food Chem., **39:** 2019–2021.

Smith, A.E. and Aubin, A.J. 1991b. Effects of long-term 2,4-D and MCPA field applications on the soil breakdown of 2,4-D, MCPA, mecoprop, and 2,4,5-T. J. Environ. Qual., **20:** 436–438.

Smith, A.E. and Muir, D.C.G. 1980. Determination of extractable and non-extractable radioactivity from prairie soils treated with carboxyl- and ring-labelled [^{14}C]2,4-D. Weed Res., **20:** 123–129.

Soil Classification Working Group. 1998. The Canadian system of soil classification, 3rd ed. Agriculture and Agri-Food Canada, National Research Council Research Press, Ottawa, ON. pp. 187

Soulas, G. 1993. Evidence for the existence of different physiological groups in the microbial community responsible for 2,4-D mineralization in soil. Soil Biol. Biochem., **25:** 443–449.

Stewart, I.T. and Loague, K. 1999. A type of transfer function approach for regional-scale pesticide leaching assessments. J. Environ. Qual., **28:** 378–387.

Systat Software Inc. 2000. SigmaPlot 2000 for Windows. Systat Software Inc., Richmond, CA.

ter Braak, C.J.F. and Šmilauer, P. 2002. CANOCO and CanoDraw for Windows, version 4.53. Wageningen University and Research Centre, Wageningen, The Netherlands.

Tonso, N.L., Matheson, V.G and Holben, W.E. 1995. Polyphasic characterization of a suite of bacterial isolates capable of degrading 2,4-D. Microb. Ecol., **30:** 3–24.

Veeh, R.H., Inskeep, W.P. and Camper, A.K. 1996. Soil depth and temperature effects on microbial degradation of 2,4-D. J. Environ. Qual., **24:** 5–12.

Voos, G. and Groffman, P.M. 1997. Relationships between microbial biomass and dissipation of 2,4-D and dicamba in soil. Biol. Fertil. Soils, **24:** 106–110.

Wardle, D.A. and Ghani, A. 1995. Why is the strength of relationships between pairs of methods for estimating soil microbial biomass often so variable? Soil Biol. Biochem., **27:** 821–828.

Willems, H.P.L., Lewis, K.J., Dyson, J.S. and Lewis, F.J. 1996. Mineralization of 2,4-D and Atrazine in the unsaturated zone of a sandy loam soil. Soil Biol. Biochem., **28:** 989–996.

Wilson, J.P., Inskeep, W.P., Wraith, J.M. and Snyder, R.D. 1996. GIS-based solute transport modeling applications: Scale effects of soil and climate data input. J. Environ. Qual., **25:** 445–453.

Wilson, R.D. Geronimo, J. and Armbruster, J.A. 1997. 2,4-D dissipation in field soils after applications of 2,4-D dimethylamine salt and 2,4-D 2-ethylhexyl ester. Environ. Toxicol. Contam., **16:** 1239–1246.

Xie, H., Guetzloff, T.F. and Rice, J.A. 1997. Fractionation of pesticide residues bound to humin. Soil Sci., **162:** 421–429.

5. VARIABILITY OF SOIL PROPERTIES AND 2,4-D SORPTION AND DEGRADATION PARAMETERS IN AGRICULTURAL ECOREGIONS OF ALBERTA, CANADA

5.1 Abstract

Knowledge of the spatial variability of pesticide fate data at regional scales, and their consistency over time, is required to improve estimates of pesticide leaching to groundwater at regional scales. This study quantified the spatial variability and repeatability (2002 versus 2004) of soil properties and 2,4-D sorption and degradation measurements made in 123 soils collected from across the province of Alberta, Canada. These data were also used to determine if grouping soils by ecoregion (Peace Lowland, Boreal Transition, Aspen Parkland, Moist Mixed Grassland, Fescue Grassland, Mixed Grassland) or slope position (upper slopes, mid slopes, lower slopes) would decrease the variability associated with and improve predictions of 2,4-D fate parameters. Despite a high degree of variation in 2,4-D sorption across all 123 soils, 2,4-D sorption coefficients were well predicted by regression models with soil organic carbon content and soil pH as variables. Although segmentation of soils by ecoregion and slope position decreased spatial variations in 2,4-D sorption relative to all soils, it did not greatly improve predictions of 2,4-D sorption. Variations in 2,4-D degradation parameters across all 123 soils were smaller than variations in sorption but predictions of total 2,4-D degradation and degradation rates were generally poor and only weakly related to 2,4-D sorption and other soil properties. Segmentation of soils by ecoregion and slope position also led to decreased variations in 2,4-D degradation parameters and improved predictions of total

2,4-D degradation and degradation rates. However, large variations among repeated measures of 2,4-D degradation parameters between two years were not consistently related with soil properties may further complicate predictions of these parameters. Results of this study indicate that single values for 2,4-D *Koc* and half-life are not suitable as input parameters in models providing leaching estimates at regional scales because a wide range in 2,4-D sorption and degradation was measured for the soils at the provincial scale for Alberta. Additionally, variations in repeated 2,4-D degradation measurements may cause further inconsistencies for estimates of 2,4-D leaching risk.

5.2 Introduction

The contamination of groundwater by pesticides is a concern because pesticides in groundwater persist for many years (e.g. > 10 years for atrazine: Spalding et al., 2002) and decrease the quality of potable water used by rural communities and their livestock. Large datasets (> 2,000 sites) generated by water quality assessment programs in the United States have been used to better understand the factors that influence the risk of groundwater contamination by pesticides. Relative to other pesticides, the frequency of detection of a specific pesticide in shallow groundwater was significantly correlated with its soil organic carbon partition coefficient (*Koc*) (Kolpin et al., 1998) and its soil half-life (Barbash et al., 2001).

The aqueous contamination of a specific pesticide in groundwater has been shown to vary across regions as a result of several factors such as nearby agricultural use and

groundwater depth (Barbash and Resek, 1996; Spalding et al., 2002), but factors such as *Koc* and soil half-life have not been considered because there is limited data on regional variations in *Koc* and soil half-life values. Agricultural soils from different ecosystems in Australia and Pakistan showed wide ranging *Koc* values for both carbaryl (1-naphthyl methylcarbamate) and phosalone (*S*-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-ylmethyl *O*,*O*-diethyl phosphorodithioate) herbicides, whereby minimum and maximum *Koc* values among soils differed by a factor of 22 for carbaryl and by a factor of 33 for phosalone (Ahmad et al., 2001). It is possible that such variations in *Koc* values additionally contribute to the observed variations in groundwater contamination across regions because changing the sorption coefficient by a factor of two changes the amount of pesticides leached by a factor of 10 (Boesten and van der Linden, 1991).

Achieving environmental sustainability is a high priority in Canada, as evident by federal government initiatives such as the National Agri-Environmental Health Analysis and Reporting Program (NAHARP). NAHARP is bridging the gap between science and policy by developing strategic indicators that can be used to assess the performance and risks associated with agricultural systems. One strategic indicator being proposed is the national Indicator of Risk of Water Contamination by Pesticides (IROWC-Pest) which includes the pesticide fate model PRZM version 3.2 (Pesticide Root Zone Model) (Carsel et al., 1998) to simulate the risk of groundwater contamination by pesticides (McQueen et al., 2007). As in other regional scale assessments of pesticide leaching to groundwater (Wilson et al., 1996; Stewart and Loague, 1999; Eason et al., 2004), it is assumed that each pesticide has a specific *Koc* and half-life, regardless of the region in which the

simulation is performed. It is well-known that this approach to regional scale assessments creates uncertainties (Loague, 1991; Loague, 1994; Soutter and Musy, 1998) but there are no comprehensive data available in Canada on regional differences in *Koc* and soil half-life. In addition, there are no data on the repeatability of pesticide input parameters, creating additional uncertainties in regional scale analyses of the risk of groundwater contamination by pesticides.

Assessments of regional differences in pesticide *Koc* need to consider the spatial variations in pesticide fate that exist among soil-landscape positions at the field scale level (Chapter 2). Pesticide sorption within a field varies among slope positions in response to topographic and anthropogenic induced differences in soil properties such as soil organic carbon content, pH or soil texture. The spatial distribution of herbicide sorption within agricultural fields has been examined for atrazine (2-chloro-4-17-ethylamino-6-isopropylamino-1,3,5-triazine) (Novak et al., 1997), imazethapyr (2-4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-lH-imidazol-2-yl-5-ethyl-3 pyridine carboxylic acid) (Oliveira et al., 1999), 2,4-D (2,4-dichlorophenoxyacetic acid) (Farenhorst et al., 2001), and other herbicides (Wood et al., 1987; Mallawatantri and Mulla, 1992), but translating information from the field level to a regional scale remains challenging (Inskeep et al., 1996; Wilson et al., 1996; Wagenet and Hutson, 1996). Soil-landscape position also influenced the half-lives of the herbicides atrazine and alachlor (2-Chloro-2'-6'-diethyl-N-(methoxymethyl)-acetanilide) in soil, thereby affecting their soil-residual activity and efficacy in controlling weed populations (Liu et al., 2002) and possibly their leaching potential to groundwater.

The objective of this study was to determine the influence of soil properties on the spatial variability of 2,4-D sorption and degradation in upper, mid, and lower slopes of 41 agricultural fields across six ecoregions in Alberta, Canada. These data were also used to compare the repeatability of 2,4-D sorption and degradation measurements between two sampling years. The herbicide 2,4-D was selected because it is among the most frequently used pesticides in this region and other parts of western Canada. The herbicide is used for the post-emergent control of broadleaf weeds in annual and forage crops and to control glyphosate-tolerant canola volunteers (Simard and Legere, 2002).

5.3 Materials and Methods

5.3.1 Soil sampling and characterization

The AESA (Alberta Environmentally Sustainable Agriculture) Soil Quality Program was established in 1998 to monitor the state of soil quality of agricultural soil-landscapes typical of six ecoregions in Alberta: Peace Lowland (PL), Boreal Transition (BT), Aspen Parkland (AP), Moist Mixed Grassland (MMG), Fescue Grassland (FG), and Mixed Grassland (MG) (Table 5.1, Figure 4.2). The PL and BT ecoregions are part of the Boreal Plains ecozone and are predominantly characterized by Grey Luvisolic, Dark Grey Chernozemic, Brunisolic and Gleysolic soils. The AP, MMG, FG and MG ecoregions are part of the Prairie ecozone and are predominantly characterized by Brown, Dark Brown and Black Chernozemic and Solenetzic soils. Detailed site descriptions are given in Leskiw et al. (2000).

Table 5.1 Soil great groups, average climate and cropping systems typical in 7 ecoregions in Alberta (Adapted from Cathcart et al.).

Ecoregion	Soil Great Groups	Mean Temperature (°C)		GDD* > 5 °C	Precipitation (mm)	Cropping systems
		January	July			
PL	Gray Luvisols, Dark Gray and Black Chernozems	-17.2	13.3	1118–1305	435–517	Annual crops
BT	Gray Luvisols, Dark Gray and Black Chernozems, Luvic Gleysol	-15.0	15.9	1287–1384	428–535	Annual crops and forages
AP	Black and Dark Brown Chernozems	-14.3	16.4	1280–1486	391–478	Annual crops and forages
MMG	Black and Dark Brown Chernozems	-10.8	17.0	1482–1556	368–422	Annual crops and forages
FG	Black Chernozems	-9.5	15.6	1290–1362	427–537	Annual crops
MG	Brown Chernozems	-12.8	17.9	1459–1774	314–363	Annual crops and forages

*GDD = Growing Degree Day

As part of the AESA program, soil samples (0 to 15 cm) were collected in October of 2002 and 2004 from upper, mid and lower slopes in 41 agricultural fields. The sample area ranged from 49° to 60° north longitude and from 110° to 120° west latitude (Figure 4.1). A Differential Global Positioning System (DGPS) (Trimble AgGPS 132; Trimble Navigation LTD., Sunnyvale, CA and Satloc SLXg; Hemisphere GPS, Calgary, AB) with sub-meter accuracy on the x, y plane was used to locate and relocate sampling positions. At each DGPS reference point, six soil cores were collected within a 2 m radius. A 10% bleach solution was used to rinse soil augers between reference points thereby minimizing cross-contamination among slope positions and among field sites. Composite soil samples from each DGPS reference point were kept cool (4 °C) and transported to the laboratory where samples were passed through a 2 mm mesh sieve in preparation for soil property and herbicide analyses. A portion of each soil sample (approximately 800 g) was air-dried for the following analyses: soil organic carbon content (SOC), soil texture, cation exchange capacity (CEC), carbonate content, soil pH,

electrical conductivity (EC), and 2,4-D sorption by soil. The remaining soil (approximately 200 g) was not air-dried and was stored frozen (-22 ± 2 °C) for herbicide degradation and total microbial activity analyses. Soil texture, CEC and carbonate content are relatively static soil properties, therefore these soil properties were only measured once. SOC, soil pH, EC, total soil microbial activity, 2,4-D sorption by soil and 2,4-D degradation half-lives in soil were measured on samples collected in both 2002 and 2004 because these variables are less static.

Soil samples were characterized by soil texture, pH, SOC, and carbonate content as described in chapter 2. CEC and EC were determined using the methods described in McKeague (1978). Total microbial activity in samples was measured by the fluorescein diacetate hydrolysis assay (FDA) (Adam and Duncan, 2001). This measurement reflects the microbial activity that was present at the time of sample collection and differences among soils may be due to regional differences in soil moisture, temperature, pH and substrate availability (Wardle, 1992). Duplicate 2 g samples of soil (dry weight basis) were brought up to 90% field capacity and incubated for 14 days at 20 °C to simulate microcosm experiment conditions. The FDA assay was carried out as per Adam and Duncan (2001) and amounts of fluorescein in sample filtrate measured at 490 nm on a spectrophotometer (Biochrom Ultrospec 3100 pro, Cambridge, UK). Total microbial activity was measured as the amount of fluorescein hydrolysed.

5.3.2 Herbicide sorption and degradation analyses

The batch equilibrium method was used to measure 2,4-D sorption by the soils. Herbicide solutions were prepared by mixing analytical grade 2,4-D (95% chemical purity; Sigma Aldrich Chemical Company, St. Louis, MO.) with [ring-U-^{14}C] 2,4-D (99% radiochemical purity; specific activity 191.3 MBq mmol^{-1}; Sigma Aldrich Chemical Company, St. Louis, MO.). A solution containing 1μg mL^{-1} 2,4-D and 16.7 Bq mL^{-1} [ring-U-^{14}C] 2,4-D in 0.01 M $CaCl_2$ was added (10 mL) to duplicate 5 g samples of soil in Teflon tubes. The 2,4-D solution and soil mixture were rotated for a 24 hour time period to equilibrate. Samples were centrifuged (10,000 rpm for 10 minutes) and duplicate 1 mL subsamples of supernatant removed from each tube to quantify the amount of 2,4-D remaining in solution. Amounts of radioactivity in herbicide solutions and samples from experiments were determined by Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (LS 7500 Beckman Instruments, Fullerton, CA.). Radioactivity was measured using a 5:1 ratio of Scintisafe scintillation cocktail to sample supernatant (Fisher Scientific, Fairlawn, NJ.) and a maximum counting time of 10 minutes. Herbicide sorption was described by the sorption coefficient, *Kd* [mL g^{-1}]:

$$Kd = \frac{Cs}{Ce} \qquad [5.1]$$

where *Cs* = the amount of 2,4-D sorbed by the soil [μg g^{-1}] and *Ce* = the concentration of 2,4-D of the soil solution at equilibrium [μg mL^{-1}]. The amount of 2,4-D sorption per unit soil organic carbon, *Koc* [mL g^{-1}], was also determined:

$$Koc = \frac{Kd}{SOC[\%]} \times 100 \qquad [5.2]$$

Degradation of 2,4-D was quantified using soil microcosm incubation experiments. Herbicide solutions were prepared by mixing analytical grade 2,4-D (95% chemical purity; Sigma Aldrich Chemical Company, St. Louis, MO.) with [carboxyl-^{14}C] 2,4-D (99% radiochemical purity; specific activity 632.7 MBq mmol^{-1}; Sigma Aldrich Chemical Company, St. Louis, MO.). Triplicate 25 g samples of soil (dry weight basis) were measured into 125 mL glass jars, wetted to 90% field capacity (refer to Chapter 3) and placed in 1 L mason jars. Microcosms containing no sample or 25 g of silica sand (triplicates) were used to monitor background levels of $^{14}CO_2$ and abiotic degradation of 2,4-D, respectively. The samples were allowed to incubate at 20 °C for 14 days to stimulate microbial communities. A glass vial containing 3 mL acidified water (pH ~ 3) was included in each microcosm to maintain humidity. After 14 days, microcosms received 0.5 mL herbicide solution containing 2.4 μg mL^{-1} analytical grade 2,4-D and 16.7 MBq mL^{-1} [carboxyl-^{14}C] 2,4-D in deionised water. The herbicide solution was thoroughly mixed into the soil samples. The concentration of the herbicide solution was selected to represent average field application rates of 2,4-D (Manitoba Agriculture and Food, 2000). Soil moisture (90% field capacity) and temperature (20 °C) were maintained during the experiment. Scintillation vials containing 5 mL of 0.5 M NaOH (98.5% chemical purity; Fisher Scientific, Fairlawn, NJ.) were placed in microcosms immediately after 2,4-D application to trap evolved $^{14}CO_2$ as 2,4-D was degraded. Sodium hydroxide traps were replaced at 2, 4, 6, 8, 11, 14, 17, 21, 28, and 42 days post herbicide application. Scintillation cocktail (8 mL) was added to NaOH vials and the

amount of radioactivity measured by LSC as described above. Background levels of $^{14}CO_2$, monitored by the blank microcosms were subtracted from sample counts.

Cumulative amounts of $^{14}CO_2$ evolved, as a percent of initially applied ^{14}C-2,4-D, was plotted as a function of time using the non-linear regression curve fitting function in SigmaPlot 2000 (Systat Software Inc., 2000). The resulting degradation curves were described by first-order degradation kinetics:

$$M_T = M_O(1 - e^{-kt}) \qquad [5.3]$$

where M_T = 2,4-D degradation [%] at time t, M_O = 2,4-D degradation [%] when t approached infinity, k = degradation rate [day^{-1}] and t = time [days]. Degradation rates were used to derive half-life values for the degraded fraction of 2,4-D, $t½$ [days]:

$$t^1/_2 = \frac{\ln 2}{k} \qquad [5.4]$$

5.3.3 Statistical analyses

All soil properties (except pH) and herbicide parameters were log transformed to achieve normal distributions. Data was summarized (mean, coefficient of variation (CV)) using SAS, version 8.01 (SAS Inst., 2000). A pair-wise t-test (SAS, version 8.01; SAS Inst., 2000) was used to determine if selected soil properties and 2,4-D sorption and degradation differed between sample years 2002 and 2004. For each sampling year, the multivariate linear ordination method redundancy analysis (RDA) was run on the data set to determine the ability of the selected soil properties to predict 2,4-D sorption and degradation and to compare trends in the data between years. The RDA was conducted using CANOCO for Windows, version 4.53 (ter Braak and Šmilauer, 2002). RDA is a

form of constrained principal component analysis that maximizes predictions of a set of response variables by a set of factor variables (Kenkel, 2002). Thus, the 2,4-D sorption and degradation parameters (*Kd*, *Koc*, M_{Texp}, *k* and *t½*) were the response variables constrained by selected soil properties (SOC, soil pH, EC, soil texture, CEC, carbonate content, and total soil microbial activity) which were the factor variables. The influence of ecoregion (PL, BT, AP, MMG, FG and MG) and slope position (U, M, L) on the predictability of 2,4-D sorption and degradation were subsequently determined by RDA by including these groups as a dummy factor variables in the analysis. In addition to the RDA results, for both 2002 and 2004 data, 2,4-D sorption and degradation measurements among ecoregions and slope positions were subjected to a two-way analysis of variance (ANOVA) followed by a comparisons of treatment means using the Tukey's Highly Significant Difference (HSD) test ($P < 0.05$) in SAS, version 8.01 (SAS Inst., 2000). Finally, correlation and stepwise regression analysis (SAS Inst., 2000) were used to determine the soil properties that best predicted 2,4-D sorption and degradation parameters in each ecoregion and landscape position.

5.4 Results

5.4.1 Repeatability of 2,4-D fate and soil property measurements

SOC and soil pH did not differ significantly between sampling years while EC and microbial activity were significantly different in 2002 and 2004 (Table 5.2). Ordination of SOC and soil pH was similar in 2002 and 2004 (Figure 5.1), in agreement with the t-test results. Although ordination of the other soil properties differed slightly between

2002 and 2004 (indicated by the shift in vector position for these soil properties in the triplots), overall trends in the data were similar for both years, with microbial activity related to SOC and soil texture, and EC and carbonate content related to soil pH (Figure 5.1).

Table 5.2 Pair-wise t-test results for means of soil properties and 2,4-D fate parameters measured in 2002 and 2004

	Mean		t statistic	$P > t^*$
	2002	2004		
Soil parameters				
SOC	2.3 ± 70	2.2 ± 62	1.90	0.0604
pH	5.6 ± 16	5.7 ± 16	0.56	0.5739
EC	0.60 ± 57	0.45 ± 68	7.07	<0.0001
Total microbial activity	0.42 ± 65	0.34 ± 61	5.35	<0.0001
2,4-D fate parameters				
Kd	5.9 ± 87	5.6 ± 91	4.40	<0.0001
Koc	241.5 ± 57	228.5 ± 60	3.08	0.0026
M_{Texp}	54.9 ± 6	45.2 ± 7	26.96	<0.0001
k	0.36 ± 38	0.30 ± 40	4.58	<0.0001
t½	2.26 ± 38	2.72 ± 48	4.54	<0.0001

Mean ± CV (%)
*when $P = 0.05$, t = 1.98 (Degrees of freedom = 122)

The eight soil properties included in the RDA accounted for 59.5% and 50.3% of the total variability associated with 2,4-D sorption and degradation measurements in 2002 and 2004, respectively (Table 5.3). Sampling year had a significant influence on 2,4-D sorption and degradation parameters (Table 5.2), but in both 2002 and 2004, SOC and pH were the most important soil properties affecting 2,4-D sorption and degradation parameters (note the length of the arrows and their position parallel to the first axis) (Figure 5.1). The influence of soil texture on 2,4-D sorption and degradation parameters decreased in 2004 compared with 2002, as demonstrated by the decreased vector length in the triplots, but the positions of percent sand and percent clay in the triplots were similar in both years.

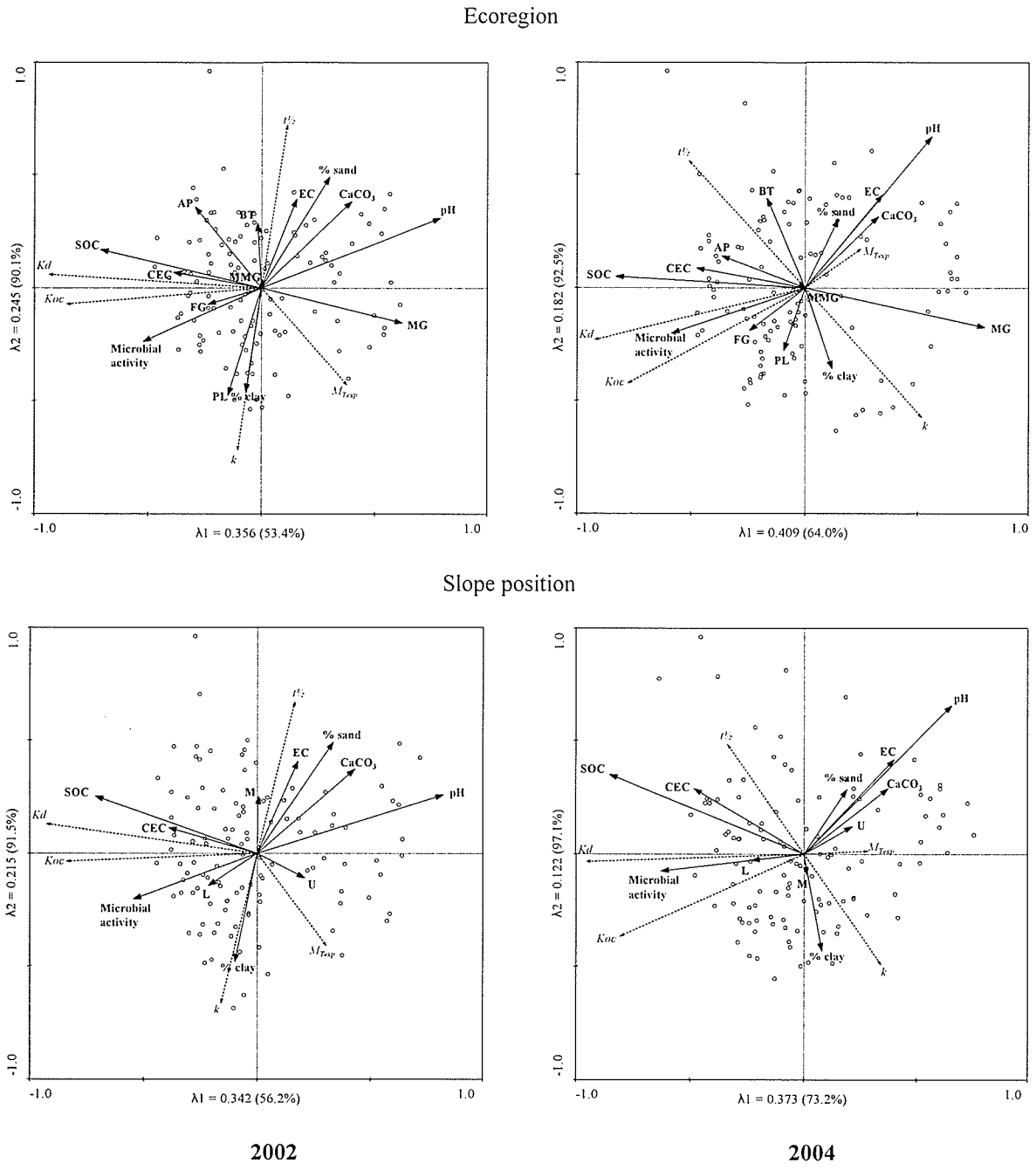


Figure 5.1 Redundancy analysis ordination triplots of 2,4-D sorption and degradation parameters (vectors with dashed lines) constrained by soil properties and ecoregions or slope positions (vectors with solid lines) in 2002 and 2004. Samples indicated by open circles. Eigenvalues for each the first and second ordination axes are indicated by λ followed by cumulative percent variance of response-factor variable relation in brackets. Redundancy is 66.6% and 63.9% for 2002 and 2004, respectively, when ecoregion dummy variables were included in the analysis. Redundancy is 60.9% and 51.0% in 2002 and 2004, respectively, when slope position dummy variables were included in the analysis.

Table 5.3 Ability of soil properties to predict 2,4-D fate parameters as determined by Redundancy analysis (RDA).

	RDA canonical axes			
	1	2	3	4
2002				
Cumulative Redundancy*	34.1	54.4	57.8	59.5
Cumulative fraction fitted**				
Kd	85.5	87.6	89.1	92.3
Koc	70.2	70.3	77.5	78.9
M_{Texp}	8.8	26.1	32.2	35.7
k	3.0	43.5	44.5	44.7
t½	3.2	44.6	45.7	45.8
2004				
Cumulative Redundancy	37.3	49.0	50.1	50.3
Cumulative fraction fitted				
Kd	91.0	91.0	92.2	92.6
Koc	65.1	78.1	80.0	80.0
M_{Texp}	7.9	7.9	9.9	10.7
k	11.5	34.7	34.9	34.9
t½	11.1	33.3	33.5	33.5

*Redundancy is an expression of the ability of all soil properties to explain the pesticide parameters

**The cumulative fraction fitted describes the fit of each pesticide parameter as a fraction of variance of pesticide parameters (i.e., parameters with higher fitted values are responding more strongly to soil properties)

Sorption of 2,4-D was more strongly influenced by the soil properties than 2,4-D degradation (Table 5.3). The overall trends in the association between herbicide sorption and soil properties was the same in 2002 and 2004, with *Kd* and *Koc* positively related to SOC and CEC, and negatively related to soil pH, carbonate content, EC and sand content (Figure 5.1). The ability of the soil properties to explain 2,4-D degradation parameters, especially total 2,4-D degradation, was greater in 2002 than in 2004 (Table 5.3). In both 2002 and 2004, total 2,4-D degradation was negatively associated with 2,4-D sorption and SOC (Figure 5.1). However, degradation rates and half-lives appeared to be more strongly affected by pH in 2002 and by SOC in 2004 (Figure 5.1).

Table 5.4 Stepwise linear regression models for the prediction of the 2,4-D sorption coefficient, *Kd*

	Model, $P < 0.0001$	R^2	Model, $P < 0.05$	R^2
2002				
All soils	log*Kd* = 1.83 + 1.29logSOC - 0.23pH	0.91	log*Kd* = 1.83 + 1.29logSOC - 0.23pH - 0.22logclay	0.92
PL	log*Kd* = 1.29 - 0.18pH	0.44	log*Kd* = 1.29 + 1.06logSOC - 0.18pH	0.74
BT	log*Kd* = 1.97 +1.40logSOC - 0.23pH	0.91	log*Kd* = 1.97 +1.40logSOC - 0.23pH -0.44logclay – 0.77log$CaCO_3$	0.95
AP	log*Kd* = 1.71 + 1.43logSOC	0.80	log*Kd* = 1.71 + 1.43logSOC - 0.16pH – 0.42logclay	0.93
MMG	log*Kd* = 1.79 - 0.26pH	0.81	log*Kd* = 1.79 + 1.12logSOC - 0.26pH	0.90
FG	--	--	log*Kd* = 0.88 – 0.16pH + 0.67logCEC	0.99
MG	log*Kd* = 1.61 - 0.24pH	0.86	log*Kd* = 1.61 +0.68logSOC – 0.24pH + 0.31logEC	0.96
U	log*Kd* = 1.40 + 1.31logSOC - 0.21pH	0.94	--	--
M	log*Kd* = 1.87 + 1.47logSOC - 0.20pH	0.93	log*Kd* = 1.87 + 1.47logSOC - 0.20pH - 0.41logclay	0.95
L	log*Kd* = 2.75 + 1.31logSOC - 0.34pH	0.87	log*Kd* = 2.75 + 1.31logSOC - 0.34pH - 0.55logclay - 0.23logFDA	0.92
2004				
All soils	log*Kd* = 1.09 +1.24logSOC - 0.21pH	0.91	log*Kd* = 1.09 +1.24logSOC – 0.21pH – 0.18logEC + 0.25logCEC + 0.16logFDA	0.93
PL	log*Kd* = 1.49 + 0.63logCEC	0.41	log*Kd* = 1.49 + 0.50logSOC - 0.31pH + 1.19log$CaCO_3$ + 0.63logCEC	0.88
BT	log*Kd* = 2.12 + 1.47logSOC – 0.35pH	0.87	--	--
AP	log*Kd* = 1.23 + 1.54SOC – 0.18pH	0.96	--	--
MMG	log*Kd* = 1.79 – 0.29pH	0.78	log*Kd* = 1.79 +1.32logSOC – 0.29pH	0.89
FG	--	--	log*Kd* = 0.86 – 0.27logEC	0.69
MG	log*Kd* = 1.45 – 0.28pH	0.87	log*Kd* = 1.45 – 0.28pH – 1.02logclay + 0.24log$CaCO_3$ +1.60logCEC + 0.43logFDA	0.96
U	log*Kd* = 1.41 + 1.47logSOC – 0.22pH	0.92	--	--
M	log*Kd* = 0.79 + 0.98logSOC – 0.23pH	0.92	log*Kd* = 0.79 + 0.98logSOC – 0.23pH + 0.39log$CaCO_3$ – 0.21logEC + 0.73logCEC + 0.38logFDA	0.97
L	log*Kd* = 1.21 + 1.36logSOC – 0.27pH	0.88	log*Kd* = 1.21 + 1.36logSOC – 0.27pH + 0.33logsand	0.90

Table 5.5 Stepwise linear regression models for the prediction of the 2,4-D soil organic carbon sorption coefficient, *Koc*

	Model, $P < 0.0001$	R^2	Model, $P = 0.05$	R^2
2002				
All soils	log*Koc* = 3.83 + 0.29logSOC – 0.23pH	0.76	log*Koc* = 3.83 + 0.29logSOC – 0.23pH – 0.22logclay	0.78
PL	log*Koc* = 3.31 – 0.18pH	0.65	--	--
BT	log*Koc* = 3.97 – 0.23pH	0.52	log*Koc* = 3.97 + 0.40logSOC - 0.23pH – 0.44logclay – 0.77log$CaCO_3$	0.80
AP	--	--	log*Koc* = 3.71 + 0.43logSOC - 0.16pH – 0.42logclay	0.73
MMG	log*Koc* = 3.84 – 0.27pH	0.86	--	--
FG	--	--	log*Koc* = 3.45 – 0.17pH	0.86
MG	log*Koc* = 3.40 – 0.21pH	0.88	log*Koc* = 3.40 – 0.21pH + 0.22logEC	0.90
U	log*Koc* = 3.40 – 0.21pH	0.77	log*Koc* = 3.40 + 0.31logSOC – 0.21pH	0.83
M	log*Koc* = 3.87 – 0.20pH	0.69	log*Koc* = 3.87 + 0.47logSOC – 0.20pH – 0.41logclay	0.84
L	log*Koc* = 4.75 – 0.33pH	0.66	log*Koc* = 4.75 + 0.31logSOC – 0.34pH – 0.55logclay – 0.23logFDA	0.81
2004				
All soils	log*Koc* = 3.09 + 0.24logSOC – 0.21pH	0.77	log*Koc* = 3.09 + 0.24logSOC – 0.21pH -0.17logEC + 0.25logCEC + 0.16logFDA	0.80
PL	log*Koc* = 3.44 – 0.20pH	0.66	--	--
BT	--	--	log*Koc* = 4.13 – 0.34pH – 0.69logclay + 0.75logCEC	0.79
AP	--	--	log*Koc* = 3.23 + 0.54logSOC – 0.18pH	0.84
MMG	log*Koc* = 3.94 – 0.30pH	0.83	--	--
FG	--	--	log*Koc* = 2.30 – 0.61logEC	0.93
MG	log*Koc* = 3.38 – 0.23pH	0.81	--	--
U	log*Koc* = 2.84 – 0.26pH + 0.63logCEC	0.81	--	--
M	log*Koc* = 2.81 – 0.23pH + 0.71logCEC	0.83	log*Koc* = 2.81 – 0.23pH + 0.40log$CaCO_3$ – 0.21logEC + 0.71logCEC + 0.37logFDA	0.91
L	log*Koc* = 3.21 – 0.27pH	0.56	log*Koc* = 3.21 +0.36logSOC – 0.27pH + 0.33logsand	0.72

Table 5.6 Stepwise linear regression models for the prediction of total 2,4-D degradation, M_{Texp}

	Model, $P < 0.0001$	R^2	Model, $P = 0.05$	R^2
2002				
All soils	$\log M_{Texp} = 1.87 - 0.04\log Kd - 0.04\log CaCO_3$	0.29	$\log M_{Texp} = 1.87 - 0.04\log Kd - 0.05\log sand - 0.04\log CaCO_3 - 0.03\log CEC + 0.02\log FDA$	0.41
PL	--	--	$\log M_{Texp} = 1.86 - 0.08\log CEC$	0.31
BT			$\log M_{Texp} = 1.87 - 0.10\log CEC$	0.69
AP	--	--	$\log M_{Texp} = 1.75 - 0.03\log Kd$	0.31
MMG	--	--	$\log M_{Texp} = 1.75 - 0.02\log Kd$	0.38
FG	--	--	$\log M_{Texp} = 1.78 - 0.06\log Kd$	0.95
MG	--	--	--	--
U	--	--	$\log M_{Texp} = 1.80 - 0.05\log CEC$	0.11
M	--	--	$\log M_{Texp} = 1.75 - 0.03\log Kd - 0.07\log CaCO_3$	0.34
L	$\log M_{Texp} = 1.81 - 0.04\log Kd$	0.42	$\log M_{Texp} = 1.81 - 0.04\log Kd - 0.03\log sand - 0.4\log CaCO_3$	0.60
2004				
All soils	--	--	$\log M_{Texp} = 1.66 - 0.02\log Kd$	0.08
PL	--	--	$\log M_{Texp} = 1.99 - 0.03\text{pH} - 0.13\log clay$	0.59
BT	--	--	$\log M_{Texp} = 1.74 + 0.03\log EC - 0.05\log CEC$	0.50
AP	--	--	$\log M_{Texp} = 1.68 - 0.02\log Kd$	0.39
MMG	--	--	--	--
FG	--	--	--	--
MG	--	--	$\log M_{Texp} = 1.13 + 0.39\log clay$	0.26
U	--	--	--	--
M	--	--	$\log M_{Texp} = 1.67 - 0.02\log Kd$	0.17
L	--	--	$\log M_{Texp} = 1.67 - 0.03\log Kd$	0.11

Table 5.7 Stepwise linear regression models for the prediction of the 2,4-D degradation rate, *k*

	Model, $P < 0.0001$	R^2	Model, $P = 0.05$	R^2
2002				
All soils	$\log k = -0.25 - 0.32\log\text{sand} + 0.24\log\text{FDA}$	0.27	$\log k = -0.25 - 0.23\log\text{SOC} + 0.27\log\text{clay} - 0.32\log\text{sand} - 0.18\log\text{EC} + 0.24\log\text{FDA}$	0.43
PL	--	--	$\log k = 0.26 - 0.64\log\text{sand} - 1.69\log CaCO_3$	0.58
BT	--	--	$\log k = 0.67 - 0.57\log\text{sand} - 0.27\log\text{CEC}$	0.66
AP	--	--	--	--
MMG	--	--	--	--
FG	--	--	$\log k = -0.59 - 0.47\log\text{EC}$	0.97
MG	--	--	$\log k = -0.42 - 0.27\log CaCO_3$	0.34
U	--	--	$\log k = -0.84 - 0.13\log Kd + 0.39\log\text{clay} - 0.27\log\text{EC} + 0.36\log\text{FDA}$	0.42
M	--	--	$\log k = 0.31 - 0.30\log\text{SOC} - 0.52\log\text{sand} - 0.40\log CaCO_3$	0.39
L	$\log k = 0.96 - 0.81\log\text{sand}$	0.35	$\log k = 0.96 - 0.31\log\text{SOC} - 0.81\log\text{sand} + 0.18\log\text{FDA}$	0.61
2004				
All soils	--	--	$\log k = -0.26 - 0.24\log Kd - 0.10\text{pH} + 0.29\log\text{clay}$	0.38
PL	$\log k = -0.73 - 1.73\log CaCO_3$	0.73	--	--
BT	--	--	$\log k = 2.42 - 0.45\log Koc - 0.30\text{pH} - 0.20\log\text{sand} + 0.62\log CaCO_3$	0.66
AP	--	--	$\log k = -0.61 + 0.29\log Kd - 0.72\log\text{SOC}$	0.48
MMG	--	--	--	--
FG	--	--	$\log k = -1.08 - 1.28\log\text{EC}$	0.68
MG	--	--	$\log k = -0.35 - 0.19\log CaCO_3$	0.35
U	--	--	--	--
M	--	--	$\log k = -0.46 - 0.35\log\text{SOC}$	0.24
L	$\log k = -1.21 + 0.57\log\text{clay}$	0.25	$\log k = -1.21 - 0.38\log\text{SOC} + 0.57\log\text{clay}$	0.54

Regardless of sampling year, when considering all 123 soils, predictions of 2,4-D sorption by soil (Table 5.4) and per unit organic carbon (Table 5.5) were best achieved with regression models that contained both SOC and soil pH (Appendix D). In both 2002 and 2004, the addition of other soil properties to SOC and pH reduced the significance of the regression models and did not improve model R^2 values (Tables 5.4 and 5.5). Although the regression models demonstrated excellent prediction ability for *Kd* (R^2 = 0.91, $P < 0.001$ and 0.92, $P < 0.05$) and good prediction ability for *Koc* (R^2 = 0.76 $P <$ 0.001 and 0.78, $P < 0.05$), the regression models for pesticide degradation parameters were very poor, particularly for the 2004 samples (Tables 5.6 and 5.7).

5.4.2 Spatial variability of 2,4-D fate and soil property measurements

Regardless of the sampling year, across the 123 soils, the variability of SOC, EC and total microbial activity were similar (CV = 57–70%) and greater than the variability in soil pH (CV = 16%) (Tables 5.8 and 5.9). Among the soil properties that were measured once, carbonate content was the most variable soil property (CV = 108%), while soil texture and CEC had lesser and similar variability (CV = 38–42%). The variability of SOC, microbial activity, and soil pH were similar in 2002 (Table 5.8) and 2004 (Table 5.9), but EC was less variable in 2002 than 2004. Normalizing sorption by SOC decreased the variability associated with *Kd* in both sampling years. Regardless of the sampling year, both *Kd* (CV = 87–91%) and *Koc* (CV = 57–60%) were more variable than 2,4-D degradation parameters. Total 2,4-D degradation (CV = 6–7%) always demonstrated less variation compared to degradation rate (CV = 30–38%) and half-lives (CV = 38–48%).

Table 5.8 Means and variability of the soil properties and 2,4-D fate parameters measured on 2002 soil samples as affected by ecoregion and slope position

	Soil properties				2,4-D fate parameters				
	SOC (g 100 g^{-1} soil)	pH	EC (dS m^{-1})	Microbial activity (µg fluorescein g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})	M_{Texp} (%)	*k* (day^{-1})	*t½* (days)
All soils	2.3 ± 70	5.6 ± 16	0.60 ± 57	0.42 ± 65	5.9 ± 87	241.5 ± 57	54.9 ± 6	0.36 ± 38	2.26 ± 38
Ecoregion									
PL	3.1 ± 28[a]	5.5 ± 14[b]	0.57 ± 44[a]	0.40 ± 49[ab]	7.0 ± 47[a]	228.8 ± 40[a]	56.0 ± 4[a]	0.45 ± 32[a]	1.75 ± 37[b]
BT	2.5 ± 105[b]	5.5 ± 11[b]	0.56 ± 48[a]	0.30 ± 53[b]	5.5 ± 87[a]	228.4 ± 40[a]	54.7 ± 7[ab]	0.29 ± 32[b]	2.61 ± 31[a]
AP	2.6 ± 54[ab]	5.4 ± 13[b]	0.68 ± 78[a]	0.43 ± 51[ab]	9.1 ± 72[a]	321.7 ± 39[a]	53.4 ± 4[b]	0.30 ± 34[b]	2.63 ± 32[a]
MMG	1.6 ± 27[b]	5.5 ± 22[b]	0.58 ± 52[a]	0.62 ± 57[a]	5.4 ± 90[a]	301.7 ± 69[a]	55.5 ± 3[ab]	0.32 ± 23[ab]	2.30 ± 24[ab]
FG	2.4 ± 12[ab]	5.3 ± 16[b]	0.42 ± 66[a]	0.81 ± 60[a]	8.8 ± 29[a]	370.7 ± 29[a]	52.3 ± 3[ab]	0.42 ± 33[ab]	1.80 ± 32[ab]
MG	1.0 ± 31[c]	6.4 ± 16[a]	0.64 ± 43[a]	0.31 ± 77[b]	1.2 ± 85[b]	108.5 ± 54[b]	55.9 ± 7[ab]	0.39 ± 40[ab]	2.15 ± 47[ab]
Slope position									
U	1.9 ± 57[b]	5.8 ± 17[a]	0.64 ± 67[a]	0.38 ± 81[b]	4.3 ± 84[b]	205.9 ± 54[a]	55.2 ± 6[a]	0.36 ± 34[ab]	2.17 ± 34[ab]
M	2.1 ± 54[b]	5.6 ± 16[a]	0.56 ± 43[a]	0.38 ± 56[b]	6.1 ± 91[ab]	255.4 ± 58[a]	54.9 ± 6[a]	0.32 ± 34[b]	2.47 ± 35[a]
L	3.1 ± 88[a]	5.5 ± 15[a]	0.59 ± 51[a]	0.53 ± 59[a]	7.6 ± 76[a]	258.6 ± 56[a]	54.7 ± 5[a]	0.39 ± 41[a]	2.13 ± 43[b]
Statistical analysis	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values
Ecoregion	21.87 (*P* < 0.0001)	5.19 (*P* = 0.0003)	1.25 (*P* = 0.2897)	5.91 (*P* < 0.0001)	28.47 (*P* < 0.0001)	17.07 (*P* < 0.0001)	3.07 (*P* = 0.0132)	5.54 (*P* = 0.0002)	5.49 (*P* = 0.0002)
Slope	5.88 (*P* = 0.0038)	1.22 (*P* = 0.2994)	0.75 (*P* = 0.4740)	2.79 (*P* = 0.0667)	5.38 (*P* = 0.0060)	1.66 (*P* = 0.1960)	0.15 (*P* = 0.8588)	3.08 (*P* = 0.0507)	2.97 (*P* = 0.0560)
Ecoregion × slope	1.87 (*P* = 0.0578)	1.37 (*P* = 0.2053)	0.61 (*P* = 0.7988)	0.76 (*P* = 0.6626)	1.09 (*P* = 0.3750)	0.96 (*P* = 0.4848)	1.37 (*P* = 0.2084)	0.63 (*P* = 0.7876)	0.61 (*P* = 0.8003)

Mean ± CV (%)

[a-c] Column means for ecoregions and slope positions, respectively, followed by the same letter are not significantly different as determined by Tukey's HSD ($P < 0.05$)

Table 5.9 Means and variability of the soil properties and 2,4-D fate parameters measured on 2004 soil samples as affected by ecoregion and slope position

	Soil properties				2,4-D fate parameters				
	SOC (g 100 g^{-1} soil)	pH	EC (dS m^{-1})	Microbial activity (µg fluorescein g^{-1} soil)	*Kd* (mL g^{-1})	*Koc* (mL g^{-1})	M_{Texp} (%)	*k* (day^{-1})	*t½* (days)
All soils	2.2 ± 62	5.7 ± 16	0.45 ± 68	0.34 ± 61	5.6 ± 91	228.5 ± 60	45.2 ± 7	0.30 ± 40	2.72 ± 48
Ecoregion									
PL	2.7 ± 35[a]	5.5 ± 14[b]	0.40 ± 43[b]	0.26 ± 49[b]	6.4 ± 48[ab]	243.3 ± 40[a]	43.7 ± 8[ab]	0.32 ± 26[b]	2.41 ± 45[b]
BT	2.3 ± 82[ab]	5.6 ± 10[b]	0.39 ± 73[b]	0.27 ± 48[b]	5.2 ± 104[b]	215.5 ± 59[a]	45.8 ± 4[a]	0.23 ± 31[c]	3.33 ± 31[a]
AP	2.8 ± 50[a]	5.4 ± 14[b]	0.40 ± 74[b]	0.42 ± 49[b]	9.1 ± 71[a]	305.7 ± 41[a]	45.7 ± 3[a]	0.24 ± 31[c]	3.20 ± 29[a]
MMG	1.6 ± 26[b]	5.5 ± 19[b]	0.40 ± 39[ab]	0.51 ± 50[a]	4.4 ± 85[b]	249.5 ± 67[a]	45.6 ± 3[a]	0.29 ± 20[bc]	2.53 ± 19[ab]
FG	2.7 ± 16[ab]	4.9 ± 4[b]	0.43 ± 46[ab]	0.58 ± 46[a]	9.4 ± 15[a]	367.7 ± 28[a]	40.1 ± 14[b]	0.32 ± 52[bc]	3.53 ± 102[ab]
MG	0.9 ± 31[c]	6.5 ± 15[a]	0.66 ± 68[a]	0.23 ± 60[b]	1.0 ± 105[c]	90.2 ± 65[b]	46.4 ± 10[a]	0.45 ± 28[a]	1.70 ± 30[c]
Slope position									
U	1.7 ± 54[b]	5.8 ± 17[a]	0.46 ± 76[a]	0.30 ± 67[b]	3.9 ± 91[b]	191.0 ± 61[b]	45.2 ± 9[a]	0.30 ± 32[a]	2.61 ± 30[a]
M	2.1 ± 55[b]	5.6 ± 15[a]	0.43 ± 61[a]	0.35 ± 63[ab]	5.8 ± 98[b]	239.8 ± 62[ab]	45.6 ± 6[a]	0.31 ± 41[a]	2.63 ± 42[a]
L	3.0 ± 89[a]	5.6 ± 14[a]	0.47 ± 64[a]	0.41 ± 53[a]	7.3 ± 76[a]	250.5 ± 54[a]	44.8 ± 7[a]	0.30 ± 44[a]	2.92 ± 60[a]
Statistical analysis	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values
Ecoregion	21.30 (*P* < 0.0001)	6.66 (*P* < 0.0001)	3.74 (*P* = 0.0037)	10.92 (*P* < 0.0001)	33.87 (*P* < 0.0001)	20.65 (*P* < 0.0001)	4.88 (*P* = 0.0005)	12.15 (*P* < 0.0001)	11.29 (*P* < 0.0001)
Slope	5.49 (*P* = 0.0054)	0.55 (*P* = 0.5797)	0.01 (*P* = 0.9883)	3.58 (*P* = 0.0318)	6.34 (*P* = 0.0025)	2.72 (*P* = 0.0708)	1.47 (*P* = 0.2357)	0.40 (*P* = 0.6709)	0.49 (*P* = 0.6140)
Ecoregion × slope	1.26 (*P* = 0.2609)	1.33 (*P* = 0.2247)	0.74 (*P* < 0.6816)	0.67 (*P* = 0.7492)	1.22 (*P* = 0.2863)	1.22 (*P* = 0.2898)	1.22 (*P* = 0.2867)	0.84 (*P* = 0.5947)	0.92 (*P* = 0.5218)

Mean ± CV (%)

[a-c] Column means for ecoregions and slope positions, respectively, followed by the same letter are not significantly different as determined by Tukey's HSD ($P < 0.05$)

Table 5.10 Means and variability of static soil properties

	Clay content (g 100 g^{-1} soil)	Sand content (g 100 g^{-1} soil)	Carbonate content (g 100 g^{-1} soil)	CEC (meq 100 g^{-1} soil)
All soils	26.1 ± 39	37.1 ± 38	0.92 ± 108	23.1 ± 42
Ecoregion				
PL	36.9 ± 24[a]	23.1 ± 25[c]	0.74 ± 17[b]	29.4 ± 29[a]
BT	25.6 ± 43[b]	38.1 ± 44[b]	0.78 ± 42[b]	24.1 ± 58[ab]
AP	21.1 ± 32[b]	40.8 ± 33[ab]	0.72 ± 11[b]	24.6 ± 32[a]
MMG	18.5 ± 32[b]	49.4 ± 24[a]	0.70 ± 0[b]	18.0 ± 36[b]
FG	29.4 ± 53[ab]	33.1 ± 26[bc]	0.70 ± 0[b]	26.1 ± 23[ab]
MG	24.3 ± 15[b]	41.0 ± 19[ab]	1.71 ± 121[a]	16.0 ± 16[b]
Slope position				
U	26.8 ± 39[a]	38.2 ± 35[a]	1.11 ± 133[a]	22.6 ± 39[a]
M	24.8 ± 40[a]	37.8 ± 39[a]	0.83 ± 83[a]	22.2 ± 44[a]
L	26.1 ± 41[a]	35.0 ± 38[a]	0.88 ± 71[a]	24.5 ± 44[a]
Statistical analysis	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values	F-statistics and *P* values
Ecoregion	F = 12.83	F = 13.11	F = 4.71	F = 8.18
	P < 0.0001	*P* < 0.0001	*P* = 0.0006	*P* < 0.0001
Slope	F = 0.41	F = 0.39	F = 0.52	F = 0.02
	P = 0.6619	*P* = 0.6758	*P* = 0.5943	*P* = 0.9758
Ecoregion × slope	F = 0.19	F = 0.19	F = 1.50	F = 1.70
	P = 0.9965	*P* = 0.9964	*P* = 0.1503	*P* = 0.0909

Mean ± CV (%)

[a-c] Column means (± coefficient of variation) for ecoregions and slope positions, respectively, followed by the same letter are not significantly different as determined by Tukey's HSD ($P < 0.05$)

The two-way analysis of variance indicated that the interaction between slope position and ecoregion was not significant for any soil property or 2,4-D fate parameter. Differences in soil properties and 2,4-D sorption and degradation were significant among ecoregions, and to a lesser extent, among slope positions (Tables 5.8 to 5.10). Specifically, in both 2002 (Table 5.8) and 2004 (Table 5.9), the MG ecoregion had significantly lower SOC and significantly higher pH and carbonate contents relative to all other ecoregions. The PL ecoregion had significantly higher clay content and significantly lower sand content relative to all other ecoregions. Regardless of the sampling year, the MG region also had significantly lower *Kd* and *Koc* values than other

ecoregions (Tables 5.8 and 5.9). Differences in total 2,4-D degradation were small, but significant differences existed between the PL and AP ecoregions in 2002 (Table 5.8) and between ecoregions FG and (BT=AP=MMG=MG) in 2004 (Table 5.9). In both 2002 and 2004, significant differences in degradation rates and half-lives existed between the PL and (BT=AP) ecoregions. In 2004 only, the MG ecoregion had significantly greater 2,4-D degradation rates and significantly shorter half-lives compared with all other ecoregions.

In both 2002 and 2004, average SOC was significantly higher in L slope positions than U and M slope positions. In both 2002 and 2004, total microbial activity was significantly smaller in U slope positions than L slope positions (Tables 5.8 and 5.9). Regardless of the sampling year, L slope positions had significantly higher *Kd* values than U slope positions. All other soil properties were statistically similar among slope positions (Tables 5.8 and 5.9). Slope position generally had no effect on 2,4-D degradation, except that 2,4-D degradation rates and half-lives were significantly different between M and L position in 2002 (Table 5.8).

Inclusion of ecoregions as variables in the RDA, in addition to soil properties, improved the total amount of variability of 2,4-D fate parameters accounted for, from 59.5% to 66.6% in 2002 and from 50.3% to 63.9% in 2004. The MG ecoregion, which was significantly different from other ecoregions with respect to SOC, pH and carbonate content, and the PL ecoregion, which had significantly higher clay content, were pulled out by the RDA ordination (Figure 5.1). Differences between other ecoregions were

small, but visually observable in the triplot (Figure 5.1). Inclusion of slope positions as variables in the RDA, in addition to the soil properties, only slightly improved the total amount of variability of 2,4-D fate parameters accounted for, from 59.5% to 60.9% in 2002 and from 50.3% to 51.0% in 2004. In agreement with the ANOVA results, differences in SOC and microbial biomass between U and L slope positions were most evident in the RDA triplots (Figure 5.1).

Regardless of the sampling year, the variability of SOC across the 123 soils (CV = 62–70%) was greatly reduced after grouping soils by ecoregion, with the exception of the ecoregion BT (CV = 82–105%) (Tables 5.8 and 5.9). The variability in soil carbonate content across the 123 soils (CV = 108%), was also strongly reduced after grouping soils by ecoregion, with the exception of the ecoregion MG (CV = 121%) (Table 5.10). Similarly, the variability of SOC and carbonate content across the 123 soil samples were generally reduced after segmenting the samples by slope position, except for SOC in the L slope position (CV = 88–89%) and carbonate content in the U slope position (CV = 133%). Grouping samples by ecoregions or slope position had either no influence, or reduced, the variability of EC (CV = 56–68%), total microbial activity (CV = 61–65%), soil pH (CV = 16% in both years), clay content (CV = 39%), sand content (CV = 38%) and CEC (CV = 42%) that were observed across all 123 soil samples, although there were exceptions (Tables 5.8 to 5.10). For example, regardless of the sampling year, the variability of EC was relatively large in the AP ecoregion (CV = 74–78%) and U slope positions (CV = 67–76%), the variability of total microbial activity was relatively large in U slope positions (CV = 67–81%), and the variability of soil pH was relatively large in

the MMG ecoregion (CV = 19–22%). Also, the variability of total microbial activity was relatively large in the MG ecoregion in 2002 (CV = 77%) (Table 5.8), and the variability of EC was relatively large in the BT region in 2004 (CV = 73%) (Table 5.9). In addition, after grouping soils by ecoregions or slope position, the variability of clay content was relatively large in the BT (CV = 43%) and FG (CV = 53%) ecoregions. In the BT ecoregion, the variability of sand content (CV = 44%) and CEC (CV = 58%) were also increased, relative to the variability of these soil properties across all 123 soil samples (Table 5.10). In 2002, grouping samples by ecoregions or slope position had either no influence, or greatly reduced the variability in *Kd* across the 123 soils (CV = 87%), with relatively low variability in *Kd* in the PL (CV = 47%) and FG (CV = 29%) ecoregions and the L slope positions (CV = 76%). In 2004, grouping soils by ecoregion or slope position also resulted in relatively low variability of *Kd* in the PL (CV = 48%) and FG (CV = 15%) ecoregions and the L slope positions (CV = 76%). However, for the 2004 samples, the BT (CV = 104%) and MG (CV = 105%) ecoregions showed increased variability, relative to the variability of *Kd* across all 123 soil samples (CV = 87%). Regardless of the sampling year, grouping soils by ecoregion strongly reduced the variability of *Koc* associated with all 123 soils (CV = 57–60%) for the PL (CV = 40% in both years), AP (CV = 39–41%) and FG (CV = 28–29%) ecoregions (Tables 5.8 and 5.9). In 2002, the variability of *Koc* was also relatively low in the BT region (CV = 40%). Relative to all soils, grouping samples by slope position had no pronounced effect on the variability of *Koc* (Tables 5.8 and 5.9). In both 2002 and 2004, the variability of total degradation was already low across all 123 soils (CV = 6–7%) and grouping soils by ecoregion or slope position had no influence on this variability except that the FG

ecoregion demonstrated a larger variability in total 2,4-D degradation in 2004 (CV = 14%) (Table 5.9). Relative to the variability of degradation rates (CV = 38–40%) and half-lives (CV = 38–48%) that were observed across all 123 soils, grouping samples by ecoregions had either no influence, or reduced the variability of both parameters except that, in 2004, variations in 2,4-D half-lives were very large for the FG ecoregion (CV = 102%) and the L slope position (CV = 60%) (Tables 5.8 and 5.9).

Segmentation of samples by ecoregion had only small affects on the ability to predict *Kd* relative to the regression model for all samples (Table 5.4). In both 2002 and 2004, grouping samples by ecoregion improved the predictions of *Koc* for the MMG and MG ecoregions, but decreased the predictions of *Koc* for the PL ecoregion (Table 5.5). SOC, soil pH or a combination of the two soils properties were the most significant parameters in regression models predicting *Kd* within ecoregions (Table 5.4). Soil pH was the best predictor of *Koc* (Table 5.5). Clay content, CEC, carbonate content and microbial activity were also significant parameters in some regression equations predicting *Kd* and *Koc*, but not consistently for the two years (Tables 5.4 and 5.5).

Relative to the regression model for all samples, segmentation by slope position did not improve the ability to predict *Kd*, except for a better model for the M slope position in 2004 (Table 5.4). Segmentation by slope position generally improved the ability to predict *Koc*, except for L slope positions in 2004 (Table 5.5). Again, SOC and pH were the most important soil properties predicting *Kd* (Table 5.4), and soil pH for predicting

Koc (Table 5.5). Regression models significant at $P < 0.05$ also included clay content in 2002 and carbonate content, CEC, EC, sand content and microbial activity in 2004.

Regression models predicting 2,4-D degradation parameters within ecoregions or slope positions were generally only significant at $P < 0.05$ (Tables 5.6 and 5.7). In 2002, relative to the regression model for all samples, predictions of 2,4-D degradation parameters were generally as good or better when samples were segmented by ecoregions, with a very strong improvement for BT and FG ecoregions in the ability to predict total degradation (Table 5.6) and degradation rates (Table 5.7). However, no models could describe total degradation for the MG region in 2002, or for the MMG and FG ecoregions in 2004 (Table 5.6). Similarly, no models could describe degradation rate for the AP ecoregion in 2002, or for the MMG ecoregion in either year, as well as that the prediction for MG was relatively poor (Table 5.7). *Kd,* CEC and clay content were generally significant parameters in regression models to predict total 2,4-D degradation in ecoregions (Table 5.6). Carbonate and sand content were the most significant soil properties in models predicting 2,4-D degradation rate (Table 5.7).

In both 2002 and 2004, segmentation by slope position improved the ability to predict degradation rates and total degradation in the L slope position, but not in the other slope positions (Tables 5.6 and 5.7). In 2004, no regression models could be fit for the U slope positions to describe total 2,4-D degradation (Table 5.6) or degradation rate (Table 5.7). Similar to models for the ecoregions, *Kd* and CEC were generally significant parameters in regression models to predict total 2,4-D degradation in landscape positions, while

carbonate content was also an important parameter in the 2002 models (Table 5.6). In both 2002 and 2004, SOC, soil texture and microbial activity were important parameters to predict degradation rate within slope positions (Table 5.7).

5.5 Discussion

The soils in Alberta demonstrated generally larger *Kd* values than those previously documented for 2,4-D in agricultural soils (Mallawatantri and Mulla, 1992; Bekbölet et al., 1998; Farenhorst et al., 2001; Gaultier et al., 2006), with the exception of soils from the MG ecoregion that had low sorption capacity. Values for *Koc* fell within the range reported in the literature for specific soils (Bekbölet et al., 1998; Gaultier et al., 2006) but were much higher than the value of 20 mL g^{-1} reported in a generalized database of pesticide properties (Agriculture Research Service, 2001). Generalized databases of pesticide properties are being used in used for pesticide fate modeling at regional scales (McQueen et al., 2007).

Cumulative degradation curves did not exhibit the lag phase associated with biphasic degradation kinetics sometimes reported for 2,4-D degradation (Soulas, 1993; Veeh et al., 1996; Shaw and Burns, 1998). Therefore, parameters describing 2,4-D degradation were suitably estimated by first-order degradation kinetics (r^2 = 0.95 to 0.99, $P < 0.0001$). Total [carboxy-^{14}C] 2,4-D degradation in this study fell within the range of that observed for the degradation of both 2,4-D and its metabolites combined ([ring-U-^{14}C] 2,4-D) in soils under a range of incubation periods (31 to 240 days), temperatures (20 to 28 °C) and

moisture contents (80 to 100% water holding capacity) (Ou, 1984; Barriuso et al., 1997; Shaw and Burns, 1998; Boivin et al., 2005). The experimental values of total 2,4-D degradation were also in agreement with those for [carboxyl-^{14}C] 2,4-D degradation in soils obtained from agricultural fields in Manitoba, Canada (Chapter 3). Rates of 2,4-D degradation in this study were rapid resulting in some of the lowest observed half-life values for 2,4-D compared to Ou, (1984) and Veeh et al. (1996). The average half life of 2,4-D in the Alberta soils was 2.5 days, much lower than the value of 10 days reported in a generalized database of pesticide properties (Agriculture Research Service, 2001).

Despite the high variability of *Kd* and *Koc* measurements across the soils, 2,4-D sorption varied predictably among soils due to similar variations in SOC and pH. Both the positive relation of SOC and negative relation of soil pH with 2,4-D sorption has been demonstrated previously in both laboratory and field measurements (Bekbölet et al., 1998; Farenhorst et al., 2001; Alam et al., 2002; Coquet and Barriuso, 2002; Spadotto and Hornsby, 2003). Additional soil parameters included in regression models contributed little to the overall prediction of 2,4-D sorption, even though clay content has been included in predictive models at the field scale (Bekbölet et al., 1998; Farenhorst et al., 2001).

Sorption has been shown to limit the bioavailability of pesticides for breakdown, thereby affecting degradation rates (Moyer et al., 1972, Shelton et al., 1998). In this study, sorption of 2,4-D by soil best predicted total 2,4-D degradation, but not necessarily the rate of 2,4-D degradation. Thus, sorption did not limit 2,4-D degradation rates but had a

negative affect on total 2,4-D degradation. Studies have shown that, when herbicide concentrations are sufficiently high, significant amounts of 2,4-D are quickly desorbed into soil solution after being sorbed by soil (Bolan and Baskaran, 1996; Boivin et al., 2005). Also, we expect that immediately after our applications of 2,4-D to soil, the herbicide molecule was only weakly retained by soil, even in the Albertan soils with relatively large amounts of organic matter, thereby not limiting bioavailability and degradation rates. However, as 2,4-D concentrations decrease over time, the strength of 2,4-D sorption by soil increased and desorption rates declined. The decline in 2,4-D degradation was more pronounced in soils with greater SOC because 2,4-D has a large affinity for soil organic matter and is more strongly sorbed in these soils (Hermosin and Cornejo, 1991). Additionally, 2,4-D is eventually incorporated into soil as bound residues that are not available for desorption or degradation (Smith and Aubin, 1991; Barriuso et al., 1997) and bound residue formation increases with increasing SOC (Barriuso et al., 1997). Biovin et al. (2005) found that 2,4-D was readily available to be degraded up to 10 days after application in a range of soils, which may have been the case for this study because cumulative 2,4-D degradation curves only began to plateau after about seven days.

Total 2,4-D degradation and degradation rates were notably influenced by soil texture, likely due to an indirect effect on soil microbial populations (Wardle, 1992) as degradation of 2,4-D occurs predominantly by the action of soil microorganisms (Soulas, 1993). However, although 2,4-D is known to be readily degraded by a range of soil microorganisms (Fulthorpe et al., 1995; Tonso et al., 1995), total microbial activity had

only limited ability to predict 2,4-D degradation parameters. Evidence for the relation between microbial biomass and activity measurements and 2,4-D degradation has been inconclusive; Voos and Groffman (1997) found a strong correlation between the degradation of 2,4-D and microbial biomass and activity, while Willems et al. (1996) found no relation at all. Findings in this study suggest that 2,4-D degradation was weakly related to total microbial activity, as determined by FDA, and that overall, FDA was a poor predictor of degradation parameters.

Measurements of 2,4-D sorption varied significantly between years despite the fact that SOC and pH, the soil properties affecting sorption, did not. However, overall trends and models for the prediction of sorption were similar between years, suggesting that temporal variability of 2,4-D sorption was small. Degradation parameters also varied between sample years but more significantly than sorption as evidenced from the inconsistent ordination of these parameters for the two years. Also, predictions of repeat measurements of 2,4-D degradation parameters between two years were not consistent with specific soil properties and indicate that degradation parameters may need to be measured more often.

Variations in soil pH, carbonate content, CEC and soil texture at the provincial scale in Alberta were similar to variations in these soil properties measured at catchment and regional scales (Brejda et al., 2000; Wirth, 2001; Coquet and Barriuso, 2002) and only slightly higher than variations in these soil properties measured at the field scale (Goderya, 1998; Gaultier et al., 2006). Microbial activity at the provincial scale in

Alberta had similar variability compared with that of soil microbial biomass reported in the literature for the regional scale (Brejda et al., 2000; Wirth, 2001). The variability associated with SOC, however, was much higher for the soils in this study compared with other measurements of the variability of SOC at regional (Brejda et al., 2000; Wirth, 2001; Coquet and Barriuso, 2002) and field scales (Goderya, 1998, Gaultier et al., 2006).

There are limited studies on the spatial variability of pesticide fate parameters at regional and field scales. The variability of 2,4-D sorption by the Alberta soils were twice as great, on average, than those reported for atrazine, isoproturon, metamitron and trifluralin within a catchment (Coquet and Barriuso, 2002) and for atrazine and napropamide within a field (Elabd et al., 1986; Novak et al., 1997). The increased variability of 2,4-D sorption by soils in this study likely reflect the high variability in SOC among soils. The soil organic carbon sorption coefficient is generally preferred as a measure of sorption because *Koc* is accepted to be less variable than *Kd*, as was the case for 2,4-D sorption by the soils at the provincial scale in Alberta. However, *Koc* values still showed considerable variability among soils. Some differences in 2,4-D *Koc* values were caused by differences in soil pH, as indicated by the significance of soil pH in regression models predicting 2,4-D *Koc* values. Variations in 2,4-D *Koc* values may have also resulted from differences in soil organic carbon quality and composition (Ahmad et al., 2001; Farenhorst, 2006) because the sorption of 2,4-D by soil organic carbon is more strongly correlated with aliphatic carbon than with aromatic carbon (Piccolo et al., 1998; Pinheiro-Dicket al., 1999). In contrast with 2,4-D sorption, total 2,4-D degradation among soils showed little spatial variation. The variability of total 2,4-D degradation among soils at

the provincial scale of Alberta were much lower than those for total atrazine, isoproturon and metamitron degradation within a catchment that had coefficient of variation values ranging from 21% to 24% (Charnay et al., 2005). Variability in 2,4-D degradation half-lives was only slightly higher than for other pesticides at the catchment (Charnay et al., 2005) and field scale (Rao and Wagenet, 1985).

Differences in mean soil properties and 2,4-D sorption and degradation existed among ecoregions and slope positions, but significant differences were minimal due to the high degree of spatial variation within ecoregions and slope positions. Lack of significant differences in sorption and degradation of 2,4-D among most of the ecoregions was surprising because ecoregions were delineated based on climate, soils, vegetation and land use factors unique to an area (Ecological Stratification Working Group, 1995). Slope position had even less of an effect on the sorption and degradation of 2,4-D in soil, despite its known effect on these parameters at the field scale (Farenhorst et al., 2001; Gaultier et al., 2006). The limited effect of slope position on 2,4-D fate at the regional scale may have resulted from the fact that soil samples were collected from fields with a slope steepness ranging from 1% to 16%, or from limited sample collection in each slope position. Studies at the field level have demonstrated that 2,4-D sorption and degradation varies within slope positions (Chapters 2 and 3).

Prediction of 2,4-D sorption was only slightly improved when soils were segmented by ecoregion or landscape position. Similar to models for all samples, models predicting 2,4-D sorption within ecoregions were based largely on SOC and pH. As was the case in

Bekbölet et al. (1998) and Farenhorst et al. (2001), inclusion of clay content in regression models slightly improved prediction of 2,4-D sorption in some ecoregions, the negative association reflecting the repulsion between negatively charged clay particles and 2,4-D anions. Inclusion of CEC in some models was likely due to its strong positive relation with SOC (correlation not shown). The effects of carbonate content, EC and microbial activity on sorption were not consistent (both positive and negative effects) and did not greatly improve R^2 values of regression models predicting 2,4-D sorption.

Similar to regression models for all soils, models for ecoregions highlighted the negative relation between 2,4-D sorption and/or CEC and total 2,4-D degradation and relations between 2,4-D sorption, soil texture and degradation rates. The inclusion of carbonate content in regression models predicting 2,4-D degradation rates within ecoregions and total 2,4-D degradation within slope positions improved model R^2, although the relationship between carbonate content and 2,4-D degradation is not understood. The regression models for individual ecoregions and slope positions were able to predict 2,4-D degradation parameters with fewer soil properties as variables compared with models for all samples.

5.6 Conclusions

Results from this study showed a wide range in 2,4-D sorption and degradation parameters across soils at the provincial scale in Alberta, Canada. As such, single value estimates of 2,4-D *Koc* values and soil half-lives at the regional scale may cause large

uncertainties in environmental risk assessments due to the high degree of variability associated with these parameters. However, regardless of large spatial variability of 2,4-D sorption across soils, accurate estimates of 2,4-D sorption coefficients was achieved with models containing SOC and soil pH. Predictions of 2,4-D sorption were not greatly improved for soils segmented according to ecoregion or landscape position. In contrast, predictions of total 2,4-D degradation and degradation rates for the Alberta soils were generally poor and only weakly related with 2,4-D sorption and soil properties. These predictions may be improved by segmenting soils according to ecoregion and slope position. However, large variations among repeated measurements of 2,4-D degradation between two years may further complicate predictions of degradation parameters. Information from more sampling years may improve estimates of 2,4-D degradation parameters as a function of soil properties and 2,4-D sorption data. This should include additional measurements of soil properties and 2,4-D degrading microbial activity that may be more strongly associated with 2,4-D degradation parameters.

Prediction of sorption and degradation of other pesticides, in addition to 2,4-D, at the regional scale are required before the results of this work can be applied more universally. Also, this study only looked at the repeatability of 2,4-D fate measurements between two sampling years. Additional work looking at longer time periods or repeated measures within a season may help determine a time frame for which pesticide database values are valid, thereby limiting uncertainties due to repeatability of measurements.

5.7 References

Adam, G. and Duncan, H. 2001. Development of a sensitive and rapid method for the measurement of microbial activity using fluorescein diacetate (FDA) in a range of soils. Soil Biol. Biochem., **33**: 943–951.

Alam, J.B., Dikshit, A.K. and Bandyophadyay, M. 2002. Effect of different inorganic and organic compounds on sorption of 2,4-D and atrazine. J. Environ. Sci. Health Part B, **B37:** 541–560.

Agricultural Research Service. 2001. Pesticide Properties Database. United States Department of Agriculture. 365 pp. Available online at: www.ars.usda.gov/Services/docs.htm

Ahmad, R., Kookana, R.S., Alston, A.M. and Skjemstad, J.O. 2001. The nature of soil organic matter affects sorption of pesticides. 1. relationships with carbon chemistry as determined by ^{13}C CPMAS NMR spectroscopy. Environ. Sci. Technol., **35:** 878–884.

Ahrens, W.H. (Ed.). 1994. Herbicide Handbook. 7th ed. Weed Science Society of America, Champaign, IL. 352 pp.

Barbash, J.E., Thelin, G.P., Kolpin, D.W. and Gilliom, R.J. 2001. Major herbicides in ground water: results from the National Water-Quality Assessment. J. Environ. Qual., **30:** 831–845.

Barbash, J.E. and Resek, E.A. 1996. Pesticides in ground water : distribution, trends, and governing factors. Ann Arbor Press, Chelsea, MI. 588 pp.

Barriuso, E., Houot, S. and Sierra-Wittling, C., 1997. Influence of compost addition to soil on the behaviour of herbicides. Pestic. Sci., **67:** 211–221.

Beckbölet, M., Yenigen. O. and Yucel, I. 1999. Sorption studies of 2,4-D on selected soils. Water Air Soil Pollut., **111:** 75–88.

Boesten, J.J.T.I. and van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual. **20:** 425–435.

Boivin, A., Amellal, S., Schaivon, M. and van Genuchten, M.T. 2005. 2,4-Dichlorophenoxyacetic acid (2,4-D) sorption and degradation dynamics in three agricultural soils. Environ. Pollut., **138:** 92–99.

Bolan, N.S. and Baskaran, S. 1996. Biodegradation of 2,4-D herbicide as affected by its adsorption-desorption behaviour and microbial activity of soils. Aus. J. Soil Res., **34:** 1041–1053.

Carsel, R.F., Imhoff, J.C., Hummel, P.R., Cheplick, J.M. and Donigan, A.S.J. 1998. PRZM-3. A model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: User manual for release 3.0, National Exposure Research Laboratory, Office of Research and development, U.S. Environmental Protection Agency, Athens, GA., 420 pp.

Cathcart, R.J., Cannon, K.R., Heinz, J.L. 2007. Selection and establishment of the Alberta soil quality benchmark sites. AAFRD Technical report. 31 pp.

Charnay, M.-P., Tuis, S., Coquet, Y. and Barriuso, E. 2005. Spatial variability in ^{14}C-herbicide degradation in surface and subsurface soils. Pest Manag. Sci., **61:** 845–855.

Eason, A., Tim, U.S. and Wang. X. 2004. Integrated modeling environment for statewide assessment of groundwater vulnerability from pesticide use in agriculture. Pest Manag. Sci., **60:** 739–745.

Elabd, H., Jury, W.A. and Cliasth, M.M. 1986. Spatial variability of pesticide adsorption parameters. Environ. Sci. Technol., **20:** 256–260.

Farenhorst, A., Muc, D., Monreal, C. and Florinkski, I. 2001. Sorption of herbicides in relation to soil variability and landscape position. J. Environ. Sci. Health. Part B, **36:** 389–396.

Farenhorst, A. 2006. Importance of soil organic matter fractions in soil-landscape and regional assessments on pesticide sorption and leaching. Soil Sci. Soc. Am. J., **70:** 1005–1012.

Fulthorpe, R.R., McGowan, C., Maltseva, O.V., Holben, W.E. and Tiedje, J.M. 1995. 2,4-Dichlorophenoxyacetic acid-degrading bacteria contain mosaics of catabolic genes. Appl. Environ. Microbiol., **61:** 3274–3281.

Gaultier, J., Farenhorst, A. and Crow, G. 2006. Spatial variability of soil properties and 2,4-D sorption in a hummocky field as affected by landscape position and soil depth. Can. J. Soil Sci., **86:** 89–95.

Gee, G.W. and Bauder, J.W. 1986. Particle-size analysis. *In* Klute, A. (Ed), Methods of soil analysis. Part 1. Physical and mineralogical methods. ASA, SSSA, Madison, WI. pp. 383–412.

Goderya, F.S. 1998. Field scale variations in soil properties for spatially variable control: A review. J. Soil Contam., **7:** 243–264.

Goh, T.B., St. Arnaud, R.J. and Mermut, A.R. 1993. Carbonates. *In* Carter, M.R. (Ed), Soil Sampling and Methods of Analysis. Canadian Society of Soil Science, Lewis Publishers, Boca Raton, FL. pp. 177–186.

Hermosin, M.C. and Cornejo, J. 1991. Soil adsorption of 2,4-D as affected by the clay mineralogy. Toxicol. Environ. Chem., **31/32:** 69–77.

Inskeep, W.P., Wraith, J.M., Wilson, J.P., Snyder, R.D., Macur, R.E. and Gaber, H.M. 1996. Input parameter and model resolution effects on predictions of solute transport. J. Environ. Qual., **25:** 453–462.

Kenkel, N.C., Derksen, D.A., Thomas, A.G. and Watson, P.R. 2002. Multivariate analysis in weed science research. Weed Sci., **50:** 281–292.

Leskiw, L.A., Yarmuch, M.S., Waterman, L.P. and Sansom, J.J. 2000. Baseline soil physical and chemical properties of forty-three soil quality benchmark sites in Alberta. File #99-042, Can-Ag Enterprises Ltd., Edmonton, AB., 175 pp.

Liu, Z., Clay, S.A. and Clay. D.E. 2002. Spatial variability of atrazine and alachlor efficacy and mineralization in an eastern South Dakota field. Weed Sci., **50:** 662–671.

Manitoba Agriculture and Food. 2000. Guide to Crop Protection.

Mallawatantri, A.P. and Mulla, D.J. 1992. Herbicide adsorption and organic carbon contents on adjacent low-input versus conventional farms. J. Environ. Qual., **21:** 546–551.

McKeague, J.A. (Ed.). 1978. Manual on soil sampling and methods of analysis. Canadian Society of Soil Science, Ottawa, ON. 212 pp.

McQueen, R., Farenhorst, A., Allaire, S. and Cessna, A.J. ***In Press.*** Automation and evaluation of three pesticide fate models for a national analysis of leaching risk in Canada. Can. J Soil Sci.

Nelson, D.E. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. *In* Page, A.L. (Ed.), Methods of Soil Analysis. Part 2. Chemical and microbiological properties. ASA, SSSA, Madison, WI. pp. 539–577.

Novak, J.M., Moorman, T.B. and Cambardella, C.A. 1997. Atrazine sorption at the field scale in relation to soils and landscape position. J. Environ. Qual., **26:** 1271–1277.

Oliveira, R.S., Koskinen, W.C., Ferreira, F.A., Khakural, B.R., Mulla, D.J. and Robert. P.J. 1999. Spatial variability of imazethapyr sorption in soil. Weed Sci., **47:** 243–248.

Ou, L.-T. 1984. 2,4-D degradation and 2,4-D degrading microorganisms in soils. Soil Sci., **137:** 100–107.

Piccolo, A., Conte, P., Scheunert, I. and Paci, M. 1998. Atrazine interactions with soil humic substances of different molecular structure. J. Environ. Qual. **27:** 1324–1333.

Pinheiro-Dick, D., Burba, P. and Herzog, H. 1999. Influence of extractant and soil type on molecular characteristics of humic substances from two Brazilian soils. J. Braz. Chem. Soc., **10:** 140–145.

SAS Institute Inc. 2000. SAS system for Windows. Version 8.01. SAS Institute Inc., Cary, NC.

Shaw, L.J. and Burns, R.G. 1998. Biodegradation of 2,4-D in a non-contaminated grassland profile. J. Environ. Qual., **27:** 1464–1471.

Simard, M.J. and Legere, A. 2002. Control of volunteer canola with auxinic herbicides: Does cold hardening or plant size matter? Proc. Canadian Weed Sci. Society National Meeting, Saskatoon, SK.

Smith, A.E. and Aubin, A.J. 1991b. Effects of long-term 2,4-D and MCPA field applications on the soil breakdown of 2,4-D, MCPA, mecoprop, and 2,4,5-T. J. Environ. Qual., **20:** 436–438.

Smith, A.E. and Muir, D.C.G. 1980. Determination of extractable and non-extractable radioactivity from prairie soils treated with carboxyl- and ring-labelled [^{14}C]2,4-D. Weed Res., **20:** 123–129.

Soil Classification Working Group. 1998. The Canadian system of soil classification, 3rd ed. Agriculture and Agri-Food Canada, National Research Council Research Press, Ottawa, ON., pp. 187

Soulas, G. 1993. Evidence for the existence of different physiological groups in the microbial community responsible for 2,4-D mineralization in soil. Soil Biol. Biochem., **25:** 443–449.

Spadotto, C.A. and Hornsby, A.G. 2003. Soil sorption of acidic pesticides: Modeling pH effects. J. Environ. Qual., **32:** 949–956.

Spalding, R.F., Exner, M.E., Snow, D.D., Cassada, D.A., Burbach, M.E. and Monson, S.J. 2003. Herbicides in Ground Water beneath Nebraska's Management Systems Evaluation Area. J. Environ. Qual., **32:** 92–99.

Stewart, I.T. and Loague, K. 1999. A type of transfer function approach for regional-scale pesticide leaching assessments. J. Environ. Qual., **28:** 378–387.

Systat Software Inc., 2000. SigmaPlot 2000 for Windows. Systat Software Inc., Richmond, CA.

ter Braak, C.J.F. and Šmilauer, P. 2002. CANOCO and CanoDraw for Windows, version 4.53. Wageningen University and Research Centre, Wageningen, The Netherlands.

Tonso, N.L., Matheson, V.G. and Holben, W.E. 1995. Polyphasic characterization of a suite of bacterial isolates capable of degrading 2,4-D. Microb. Ecol., **30:** 3–24.

Veeh, R.H., Inskeep, W.P. and Camper, A.K. 1996. Soil depth and temperature effects on microbial degradation of 2,4-D. J. Environ. Qual., **24:** 5–12.

Voos, G. and Groffman, P.M. 1997. Relationships between microbial biomass and dissipation of 2,4-D and dicamba in soil. Biol. Fertil. Soils, **24:** 106–110.

Wagenet, R.J. and Hutson, J.L. 1996. Scale-dependency of solute transport modeling/GIS applications. J. Environ. Qual., **25:** 498–512.

Wardle, D.A. 1992. A comparative assessment of factors which influence microbial biomass carbon and nitrogen levels in soil. Biol. Rev., **67:** 321–358.

Wilson, J.P., Inskeep, W.P., Wraith, J.M. and Snyder, R.D. 1996. GIS-based solute transport modeling applications: Scale effects of soil and climate data input. J. Environ. Qual., **25:** 445–453.

Wood, L.S., Scott, H.D., Marx, D.B. and Lavy. T.L. 1987. Variability in sorption coefficients of metolachlor on a Captina silt loam. J. Environ. Qual., **16:** 251–256.

6. SUMMARY AND CONCLUSIONS

The first component of this study (Chapters 2 and 3) quantified variations in 2,4-D sorption and degradation parameters at the field scale as influenced by soil properties, landscape position (upper slopes, mid slopes, lower slopes and depressions) and soil depth (A, B and C horizons). The second component of this study (Chapter 4 and 5) quantified variations in 2,4-D sorption and degradation parameters at the regional scale in Alberta, Canada as influenced by soil properties, ecoregions (Peace Lowland, Boreal Transition, Mid Boreal Uplands, Aspen Parkland, Moist Mixed Grassland, Fescue Grassland, and Mixed Grassland) and landscape position (upper slopes, mid slopes, lower slopes). Variations among repeated measures of 2,4-D sorption and degradation parameters were also compared at the regional scale between two sampling years (2002 and 2004).

Sorption of 2,4-D varied significantly ($P < 0.05$) with soil depth and among slope positions within the A horizon at the field scale. In contrast, differences in 2,4-D sorption among ecoregions at the regional scale were generally not significant because of large variations in 2,4-D sorption across soils within ecoregions. Differences in 2,4-D sorption across slope positions were more pronounced for the study at the field scale than at the regional scale, possibly because of the greater number of samples taken within slope positions at the field level than at the regional level. Boesten and van der Linden (1991) demonstrated that a change of a factor of 2 in herbicide sorption could result in a 10 times difference in leaching potential within soils. Such differences in 2,4-D sorption occurred

with soil depth, as well as among slope positions in the A horizon at the field scale, suggesting that variations in herbicide sorption with depth and landscape position should be included in simulations of pesticide fate at the field scale. Despite the large variations of 2,4-D sorption in soils within ecoregions, on average, the numerical differences in 2,4-D sorption between some ecoregions exceeded a factor of two, suggesting that in simulations of pesticide fate at the regional scale, the values of herbicide sorption parameters should be based on ecoregions rather than a single value for the entire province of Alberta. Sorption of 2,4-D by soils in lower slope positions was about 1.85 times greater than sorption of 2,4-D by soils in upper slope positions at the regional scale, indicating that landscape position should also be included in larger scale assessments of pesticide leaching risk.

Regardless of scale, soil organic carbon content was the single best predictor of the 2,4-D sorption coefficient, *Kd*, in the Ap horizon. Soil organic carbon content was also the best predictor of 2,4-D sorption in B and C horizons at the field scale that contained low soil organic carbon contents, despite the hypothesis that other soil properties become more important as soil organic carbon content decreases (Reddy and Gambrell, 1987; Green and Karickhoff, 1990). Carbonate content was also a significant factor in regression models predicting *Kd* at the field scale, a relation that had never been previously demonstrated. These findings could suggest that the negative effect of carbonates on 2,4-D sorption was due to an interaction between carbonates and soil organic carbon content that limited sorption, and not due to a pH effect because soil pH had only a weak relation with sorption at the field scale. At the regional scale, however, the effects of soil pH on

2,4-D were important, as indicated by the inclusion of soil pH in regression models predicting 2,4-D sorption by soil. The pH effect may have been more prominent at the regional scale compared with the field scale due to the lower soil pH values of the regional scale soil samples. Similarly, the lack of an effect of carbonates on sorption at the regional scale was likely due to low to no carbonates in soils compared with high carbonate contents in the field scale soils.

The soil organic carbon sorption coefficient, *Koc*, reduced the variability associated with 2,4-D *Kd* values at both field and regional scales. However, *Koc* values were still highly variable among soil depths and slope positions at the field scale and among ecoregions at the regional scale, indicating that a single 2,4-D *Koc* value cannot be considered for pesticide fate modeling purposes. Differences in 2,4-D sorption per unit organic carbon reflect the fact that other soil properties, specifically carbonate content for the field soils and pH for the regional soils, play a significant role in the sorption of 2,4-D in addition to soil organic carbon content. However, predictions of *Koc* based on soil pH at the regional scale were not strong, suggesting that variations in *Koc* were also due to differences in soil organic matter quality and composition (Ahmad et al., 2001; Farenhorst, 2006).

Degradation of 2,4-D in the soils was largely a result of microbial breakdown. In A horizons, 2,4-D degradation followed first-order kinetics at both the field and regional scales. The rapid transformation of 2,4-D in the A horizon was indicative of significant populations of soil microbes able to co-metabolize 2,4-D or of enhanced populations of

specific 2,4-D degraders from previous applications of the herbicide. In contrast, degradation of 2,4-D in B and C horizons was best described by three-half order kinetics because degradation began only after a lag period of 5 to 7 days, possibly the time required for small populations of soil microbes to utilize 2,4-D as a substrate and grow to significant levels for their activity to become measurable.

Unlike sorption, in the A horizon at the field scale, differences in total 2,4-D degradation and degradation rates among slope positions were very small. Similarly, there were generally no significant differences in total 2,4-D degradation and degradation rates among slope positions and ecoregions at the regional scale. However, large differences in total 2,4-D degradation and degradation rates occurred between soil horizons, with much smaller half-lives in the A horizon (on average 6 days) than in the B (on average 42 days) and C (on average 54 days) horizons. Therefore, when using pesticide fate models in predicting 2,4-D fate at the regional scale, it is more important to consider differences in degradation kinetics for different soil depth than for different slope positions or ecoregions.

At both the field and regional scales, the availability of 2,4-D to be degraded in A horizons was limited by 2,4-D sorption by soil. Results of this study indicate that the effect of sorption on 2,4-D degradation in A horizons was more important than variability in total soil microbial activity. In B and C horizons, sorption of 2,4-D had no effect on total 2,4-D degradation or degradation rates, presumably because 2,4-D degradation was limited by microbial activity. Regardless of field or regional scales, or the soil horizon,

the R^2 values of regression models predicting 2,4-D degradation parameters were not as strong as those of regression models predicting 2,4-D sorption coefficients. However, an analysis of 2,4-D degradation in surface soils grouped by soil organic carbon content showed that 2,4-D degradation was significantly greater in soils with less than 1% soil organic carbon content compared with soils with more than 1% soil organic carbon content, due to weaker 2,4-D sorption in soils with lesser soil organic carbon contents. Grouping soils by soil organic carbon content, and adjusting 2,4-D sorption and degradation parameters accordingly, therefore could improve the accuracy of herbicide fate predictions at larger scales.

As expected, spatial variations in soil properties and 2,4-D sorption and degradation were greater among regional soils than for soils within a field. Segmenting A horizons at the field scale by landscape position reduced the variability associated with 2,4-D sorption by soil and improved predictions of *Kd* values by soil properties. In contrast, segmenting soils by landscape position or by ecoregion at a regional scale did not greatly improve predictions of *Kd* by soil properties because of the large variations in 2,4-D sorption within ecoregions and between slope positions across ecoregions. In addition, when data were segmented by ecoregion or by slope positions across ecoregions, also the predictions of 2,4-D degradation parameters were relatively poor.

Variations in the repeatability of 2,4-D sorption measurements were small, and in both 2002 and 2004 variations in herbicide sorption among soils were best explained by soil organic carbon content and soil pH. Using these soil properties in predicting pesticide

sorption parameters resulted in similar and strong (based on R^2 values) equations in both 2002 and 2004. In contrast, total 2,4-D degradation and degradation rates varied significantly among the two sampling years, suggesting that degradation parameters may have to be monitored more often than sorption parameters when determining accurate input parameters in pesticide fate models to predict environmental risk associated with pesticide use. Using the soil properties or 2,4-D sorption to predict 2,4-D degradation parameters resulted in different and weak (based on R^2 values) equations in both 2002 and 2004.

Based on these results, I conclude that when pesticide fate models are used to assess the environmental risk of pesticide use, values of sensitive input parameters such as 2,4-D sorption and degradation parameters should be carefully selected. Instead of the most common approach, obtaining sorption and degradation parameters from a universal database, these parameters are better determined as a function of soil properties. However, determining sorption parameters based on soil properties will be more accurate than determining degradation parameters based on soil properties.

6.1 References

Ahmad, R., Kookana, R.S., Alston, A.M. and Skjemstad, J.O. 2001. The nature of soil organic matter affects sorption of pesticides. 1. relationships with carbon chemistry as determined by ^{13}C CPMAS NMR spectroscopy. Environ. Sci. Technol., **35:** 878–884.

Boesten, J.J.T.I. and van der Linden, A.M.A. 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual. **20:** 425–435.

Farenhorst, A. 2006. Importance of soil organic matter fractions in soil-landscape and regional assessments on pesticide sorption and leaching. Soil Sci. Soc. Am. J., **70:** 1005–1012.

Green, R.E. and Karickhoff, S.W. 1990. Sorption estimates for modeling. *In* Cheng, H.H. (Ed.), Pesticides in the Soil Environment: Processes, Impacts and Modeling. SSSA, Madison, WI. pp. 93–100.

Reddy, K. and Gambrell, R. 1987. Factors affecting the adsorption of 2,4-D and methyl Parathion in soils and sediments. Agric. Ecosyt. Environ. **18:** 231–241.

7. CONTRIBUTION TO KNOWLEDGE

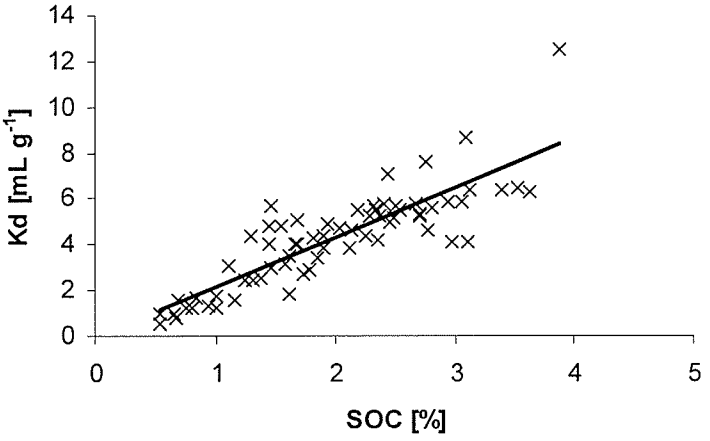
This study was the first to quantify herbicide sorption and degradation for a large number of soils at the regional scale. This is also the first study to measure the repeatability of herbicide sorption and degradation in soils over time. As such, results from this study will have important implications for scientific evaluations regarding pesticide fate modeling at regional scales. Pesticide fate modeling at regional scales is becoming increasingly important to provincial governments in Canada, and federal governments worldwide, to assess the environmental risk associated with pesticide use. Specifically, based on the study results, it is recommended to adjust pesticide sorption and degradation input parameters according to soil organic carbon contents and to account for differences in pesticide sorption and degradation input parameters among soil horizons when simulating pesticide fate at regional scales. Given the study results, it is important to extent this research to other pesticides to define their spatial and temporal differences at field and regional scales. These recommendations are directly applicable the Canadian Indicator of Water Contamination by Pesticides (IROWC-Pest) which is being developed (2004-2009) under the National Agri-Environmental Health Analysis and Reporting Program (NAHARP), Agriculture and Agri-Food Canada. IRWOC-Pest will be used by the federal government of Canada to develop and enact policies aimed at reducing the risk of water contamination by pesticides, and to identify on where the risk is highest. IRWOC-Pest will also provide information on how that risk is changing over time so that policy-makers can measure the effectiveness of their efforts in promoting beneficial management practices that reduce environmental risks associated with pesticide use.

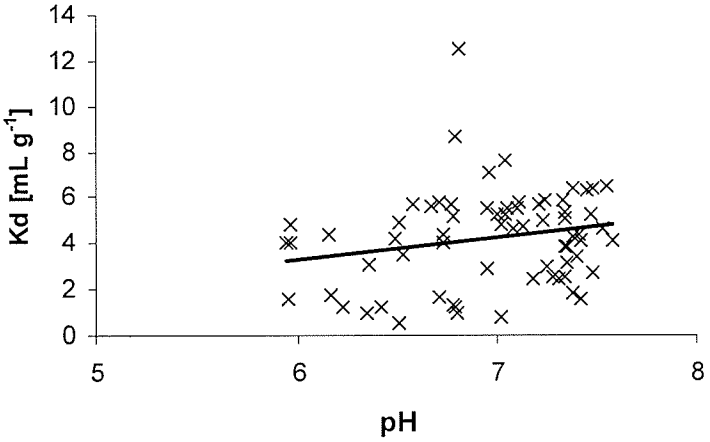
Results of this study also indicated that in calcareous soils, soil carbonates may interact with soil organic carbon reducing amounts of 2,4-D sorbed per unit organic carbon. This relation has not been previously documented for 2,4-D sorption. This finding is of importance because 30 percent of soils worldwide are calcareous worldwide, including soils of the western Canadian prairies.

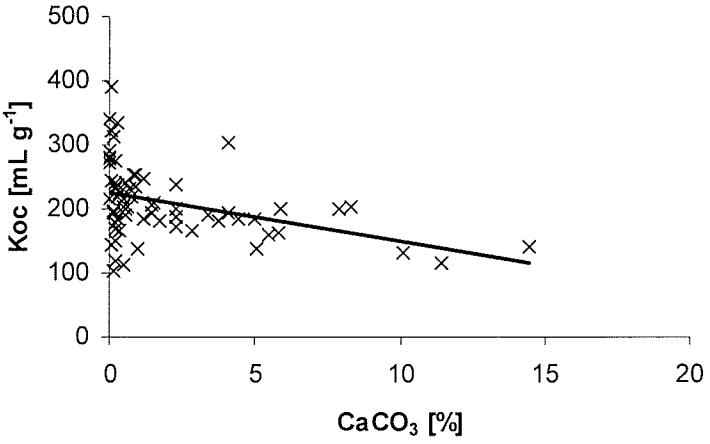
APPENDICES

Appendix A

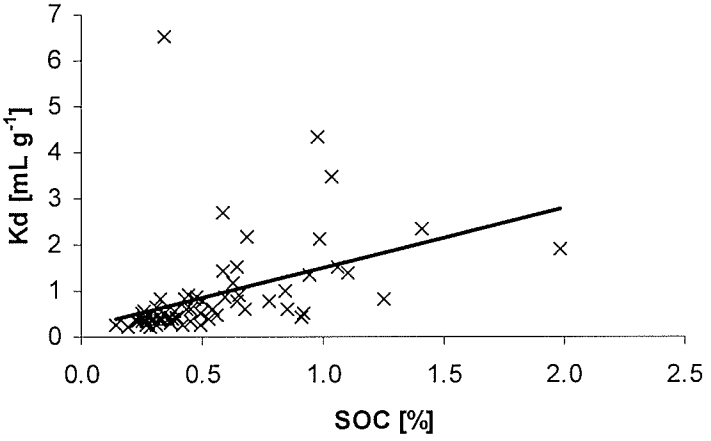
A horizon



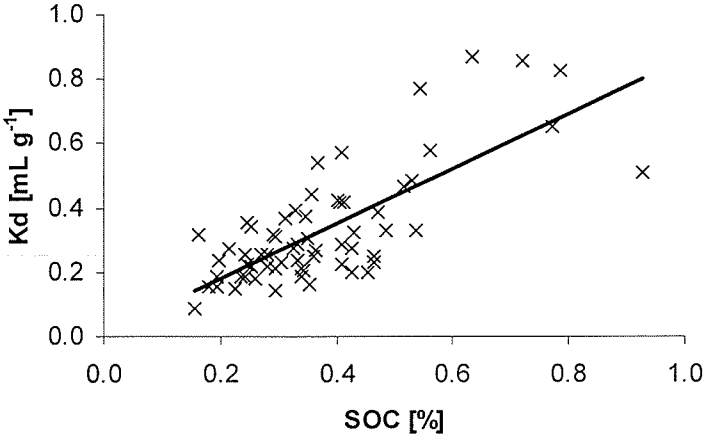


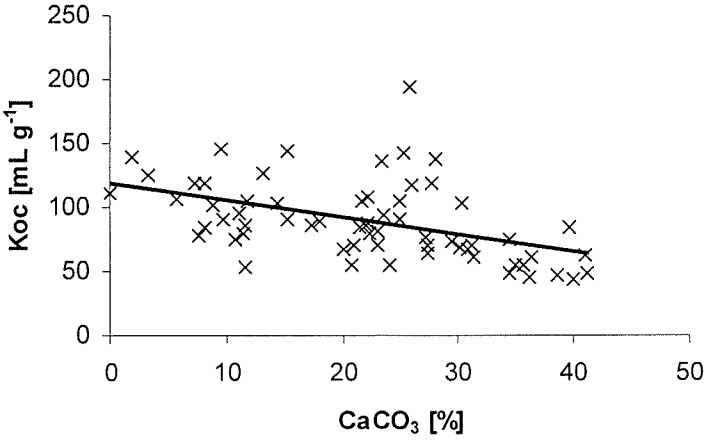


B horizon



C horizon

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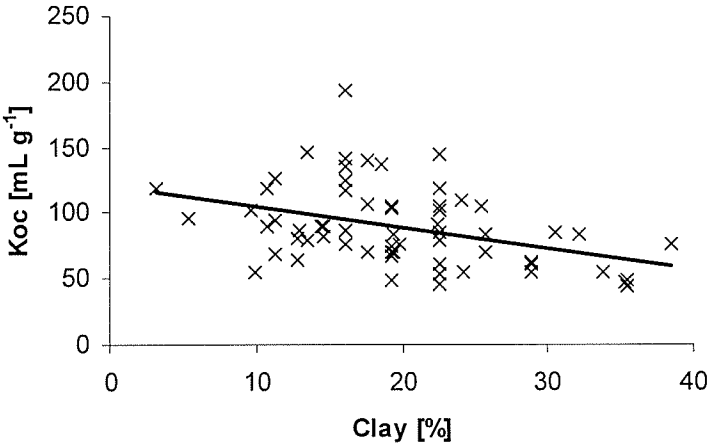
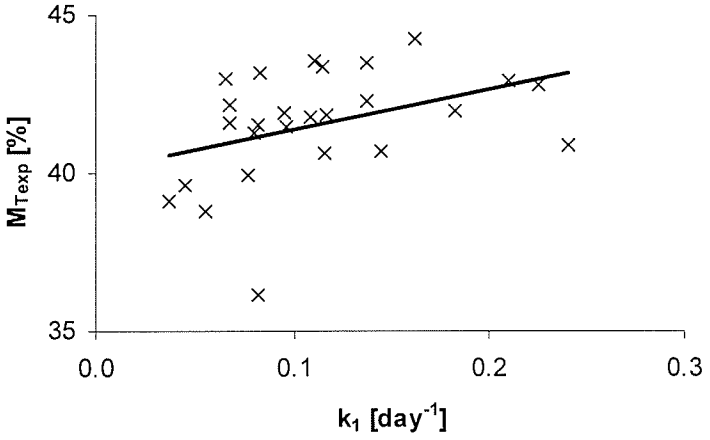
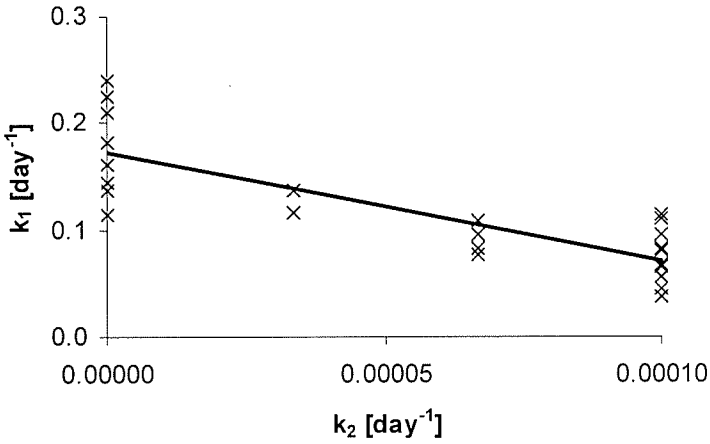
200
150
100
50
0
Koc [mL g-1]
0
10
20
30
40
50
CaCO3 [%]

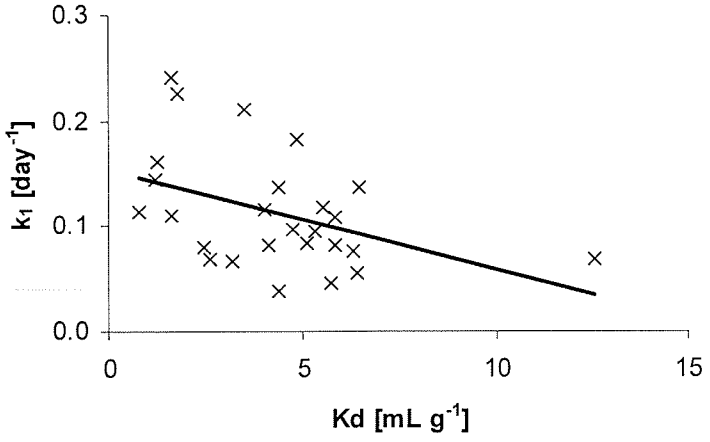

250
200
150
100
50
0
Koc [mL g-1]
0
10
20
30
40
Clay [%]

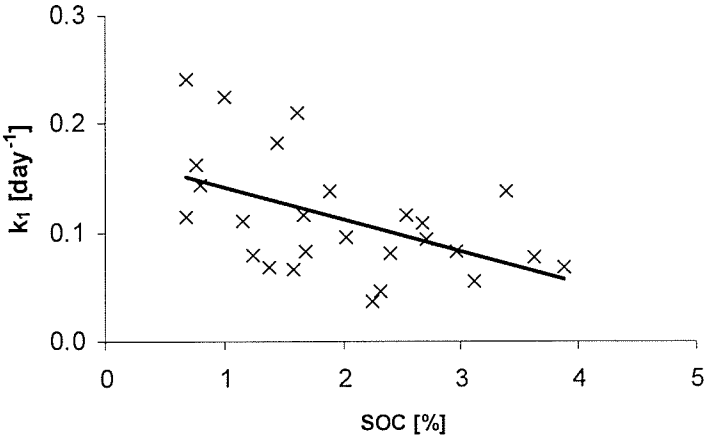
Appendix B

A horizon





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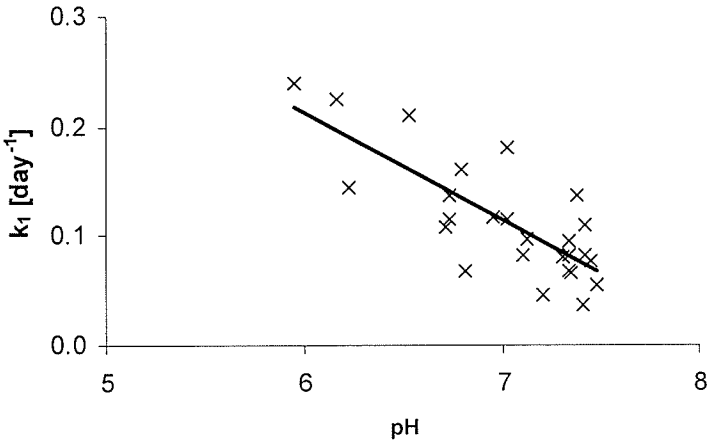
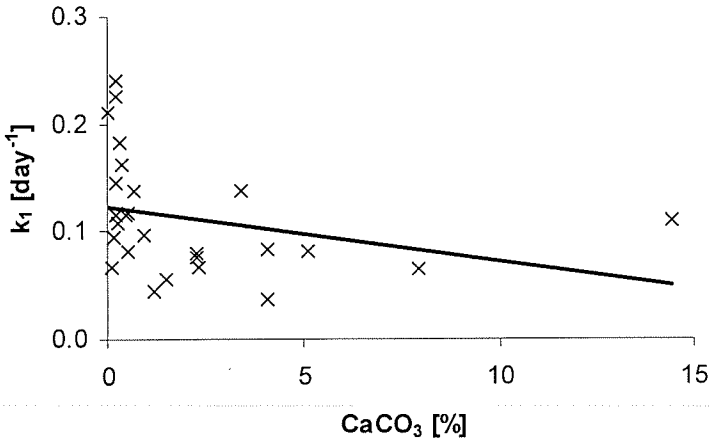
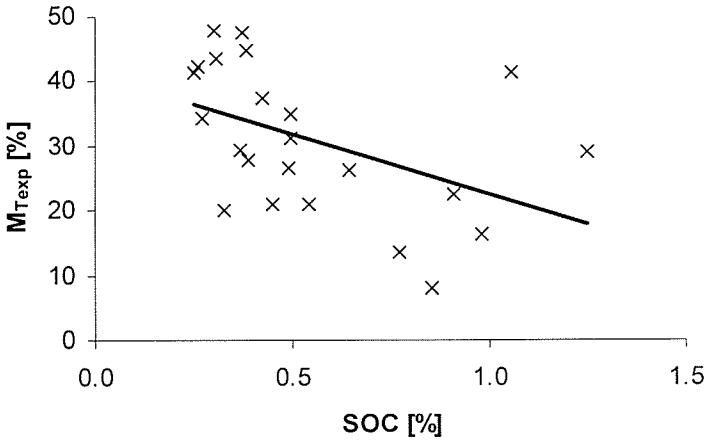
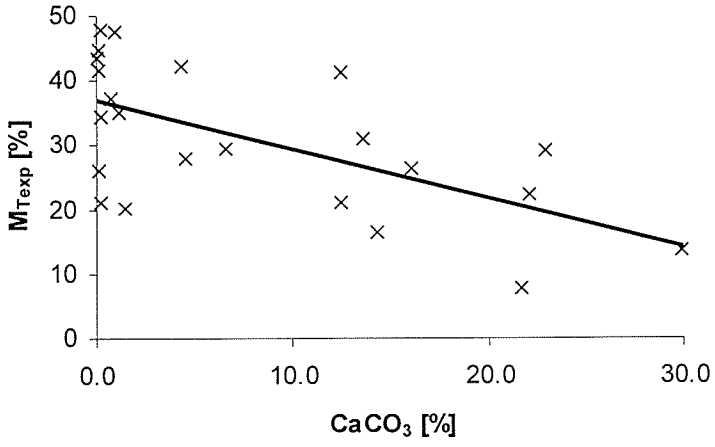
0.2
0.1
0.0
k1 [day-1]
0
1
2
3
4
5
SOC [%]


0.3
0.2
0.1
0.0
k1 [day-1]
5
6
7
8
pH

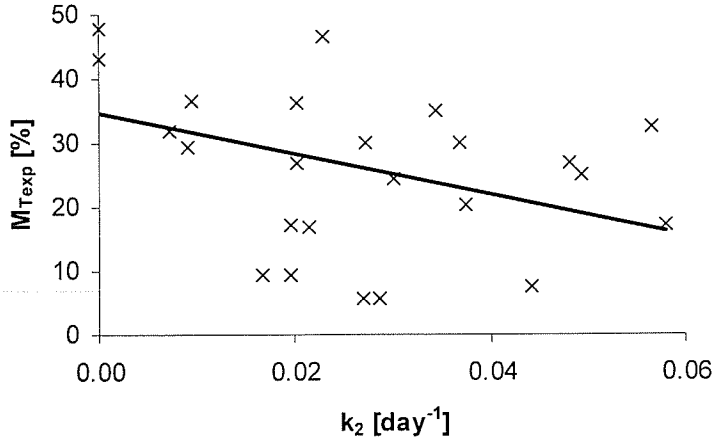

0.3
0.2
0.1
0.0
k1 [day-1]
0
5
10
15
CaCO3 [%]

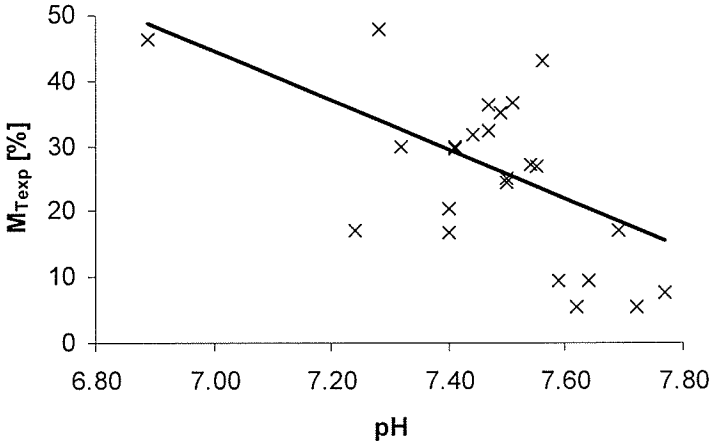
B horizon

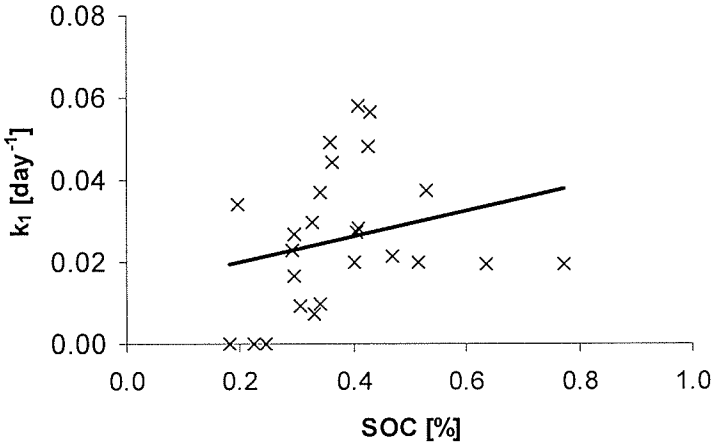




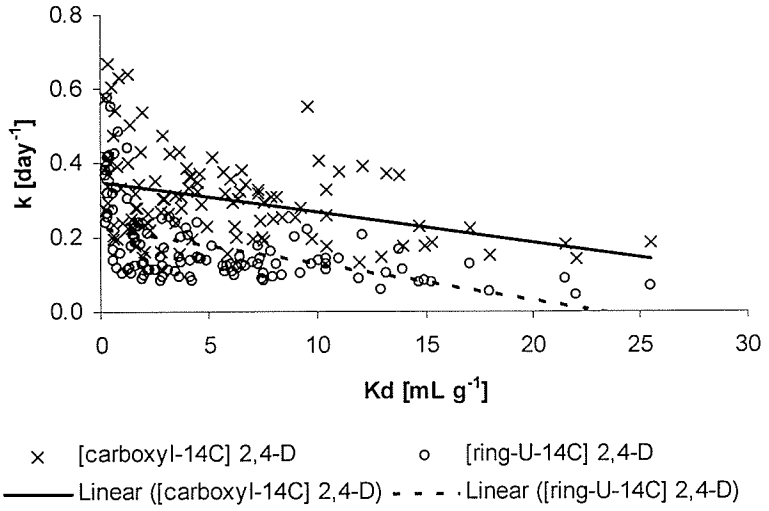
C horizon

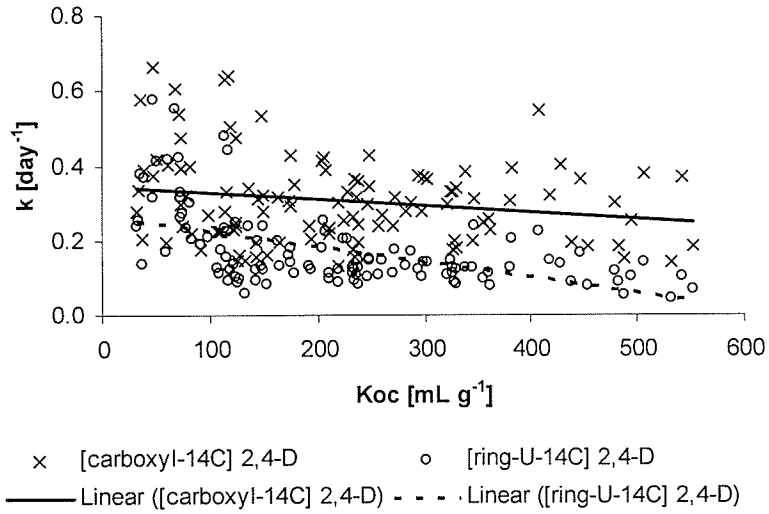


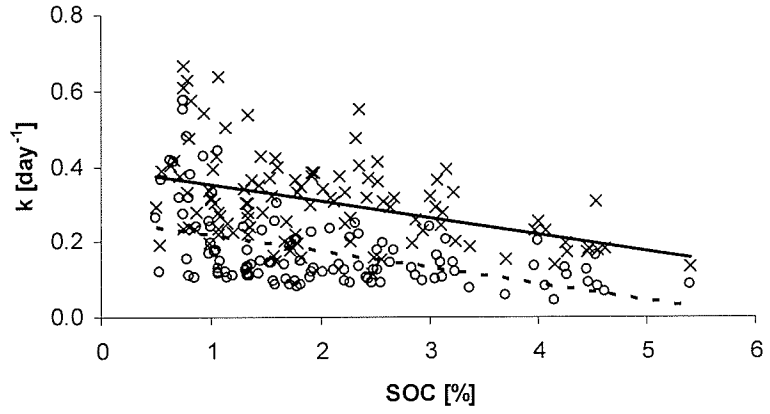

50
40
30
20
10
0
M_{Texp} [%]
6.80
7.00
7.20
7.40
7.60
7.80
pH


0.08
0.06
0.04
0.02
0.00
k_1 [day^{-1}]
0.0
0.2
0.4
0.6
0.8
1.0
SOC [%]

Appendix C

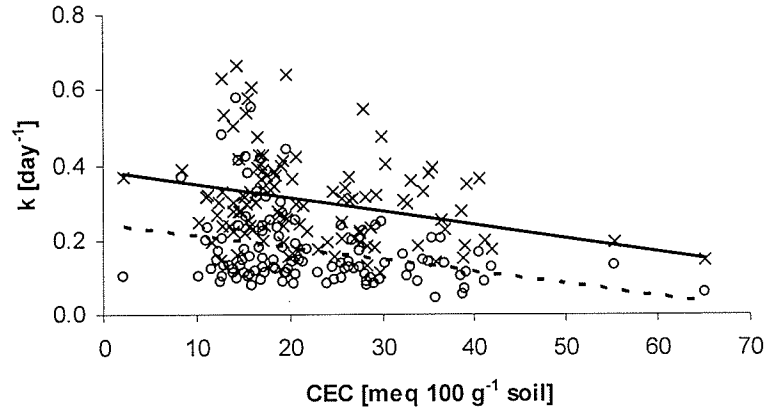

0.8
0.6
0.4
0.2
0.0
k [day-1]
0
5
10
15
20
25
30
Kd [mL g-1]
[carboxyl-14C] 2,4-D
[ring-U-14C] 2,4-D
Linear ([carboxyl-14C] 2,4-D)
Linear ([ring-U-14C] 2,4-D)


0.8
0.6
0.4
0.2
0.0
k [day-1]
0
100
200
300
400
500
600
Koc [mL g-1]
[carboxyl-14C] 2,4-D
[ring-U-14C] 2,4-D
Linear ([carboxyl-14C] 2,4-D)
Linear ([ring-U-14C] 2,4-D)



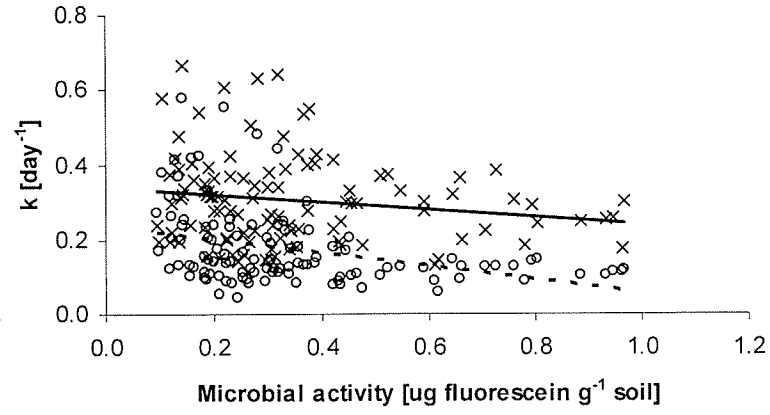
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D

——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)



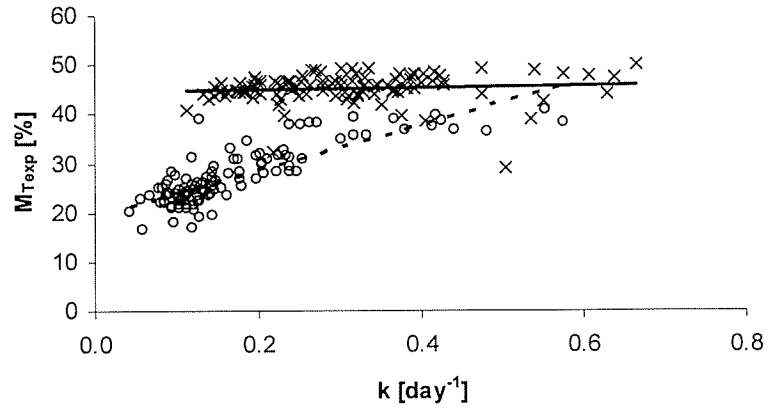
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D

——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)

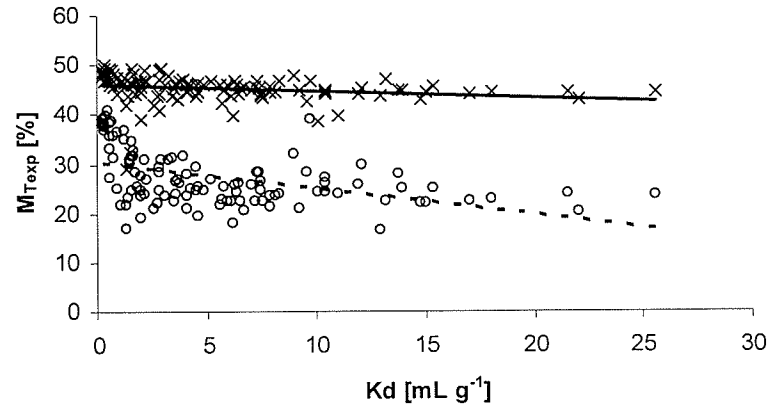


× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D

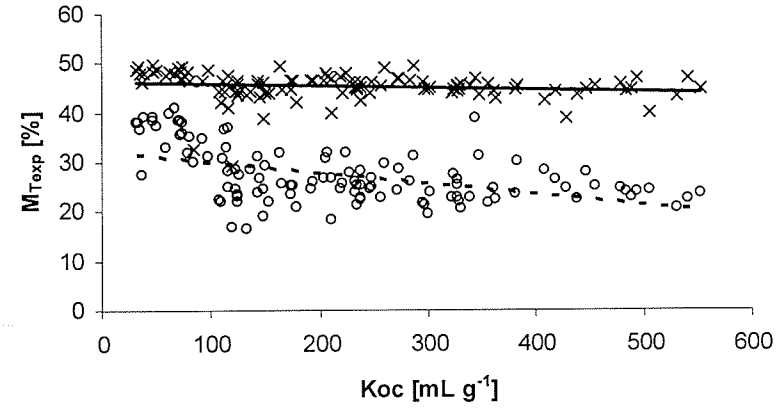
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)



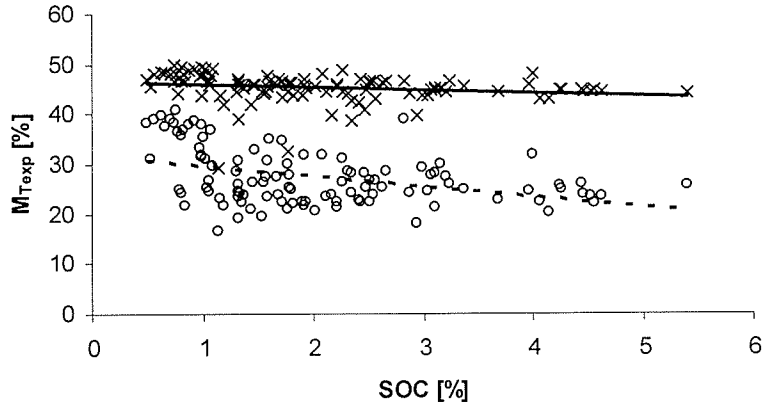
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)



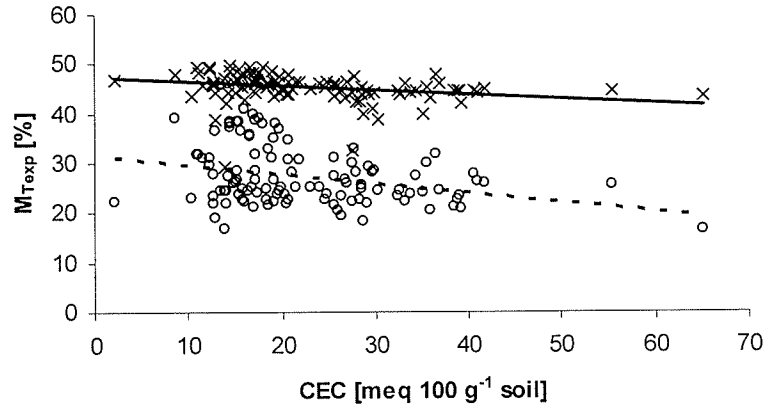
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)



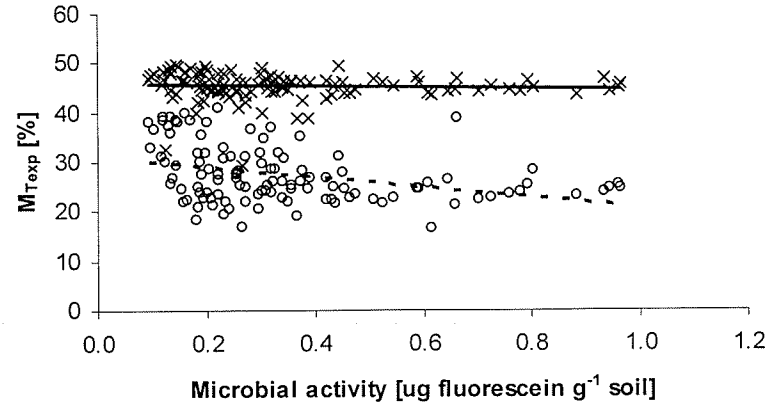
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)



× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)

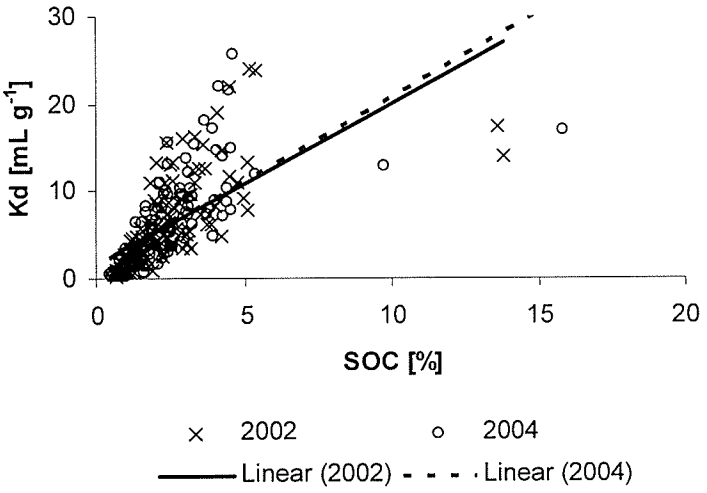


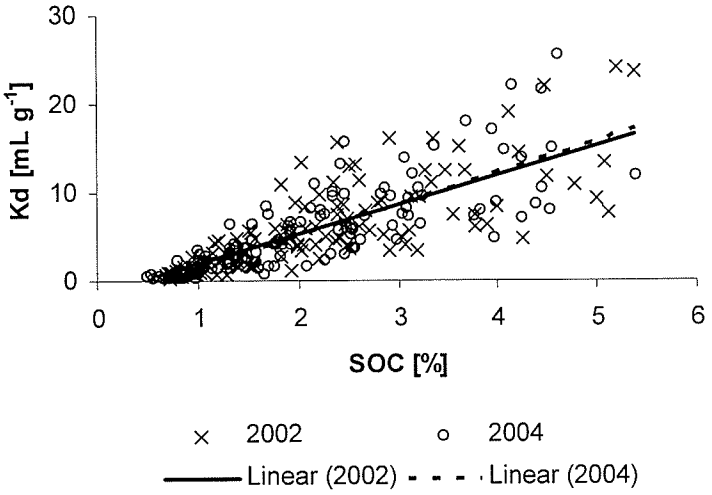
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)



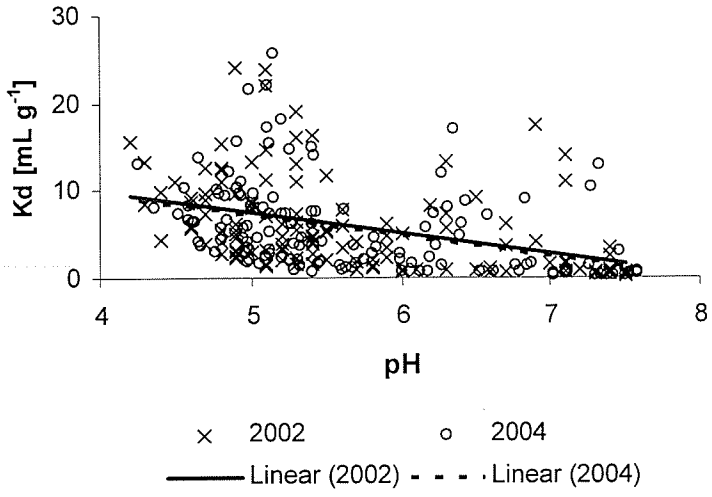
× [carboxyl-14C] 2,4-D ○ [ring-U-14C] 2,4-D
——— Linear ([carboxyl-14C] 2,4-D) - - - Linear ([ring-U-14C] 2,4-D)

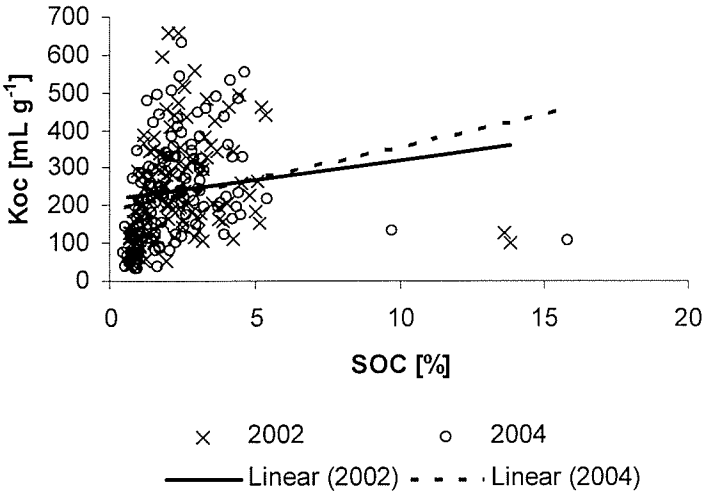
Appendix D

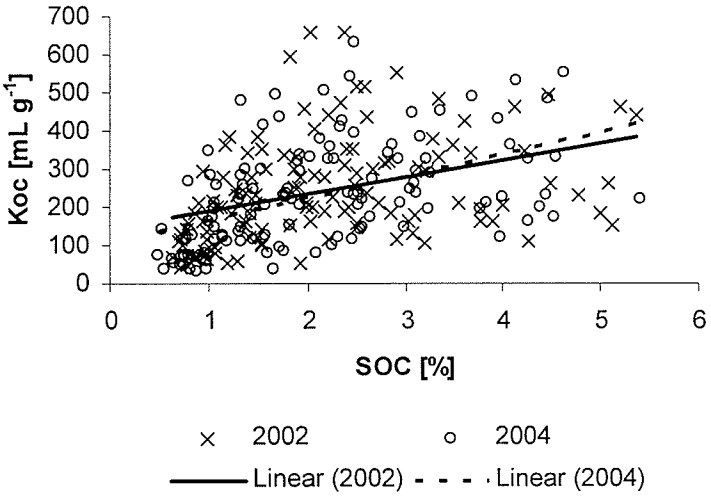




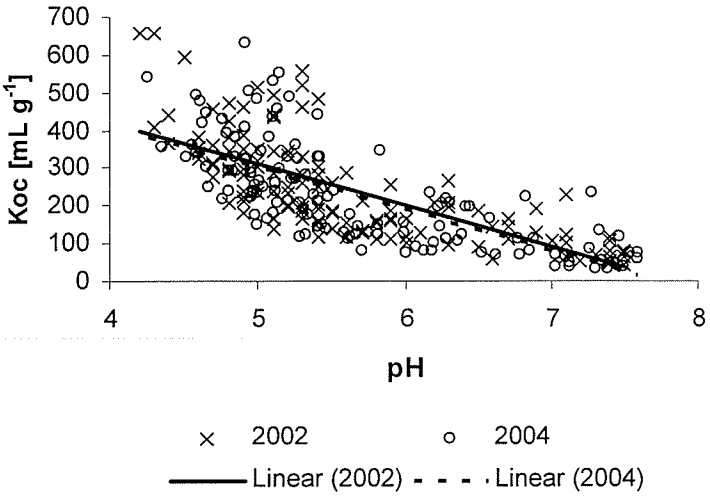
(Without outliers – sites 615L and 703 L)

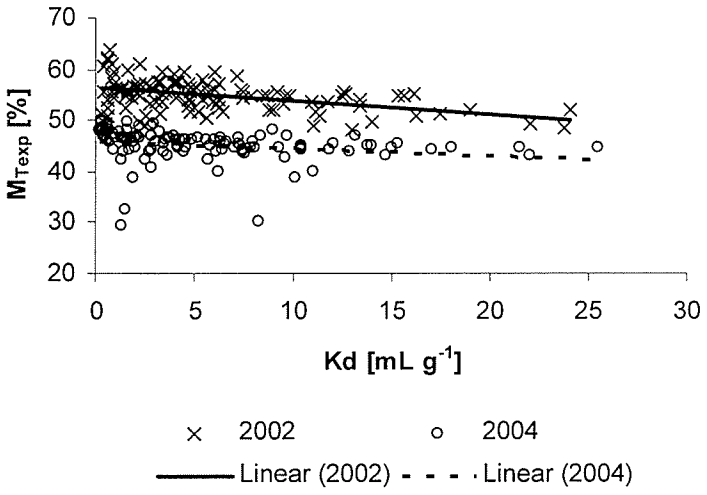


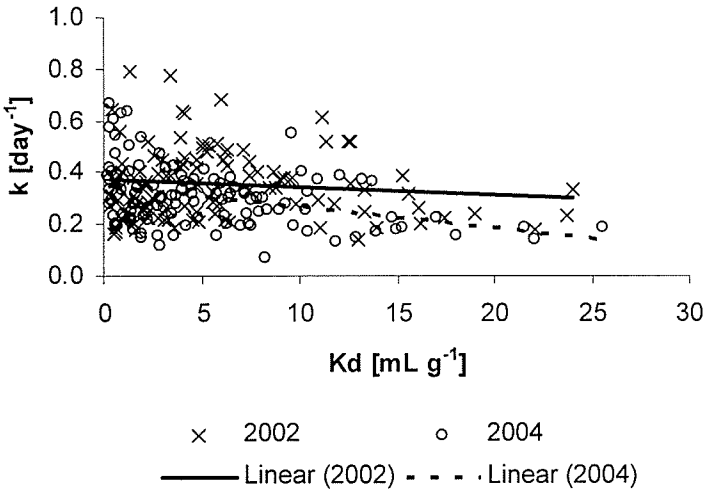




(Without outliers – sites 615L and 703 L)




70
60
50
40
30
20
M_{Texp} [%]
0
5
10
15
20
25
30
Kd [mL g^{-1}]
2002
2004
Linear (2002)
Linear (2004)


1.0
0.8
0.6
0.4
0.2
0.0
k [day^{-1}]
0
5
10
15
20
25
30
Kd [mL g^{-1}]
2002
2004
Linear (2002)
Linear (2004)